

Arsenic distribution and mobilization from abandoned mine wastes

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INTRODUCTION

Arsenic (As) is present in diverse metal ores, especially in those including sulfide mineralization. The exploitation of such ores for the elements of economic interest has generated large amounts of wastes exposed to atmospheric conditions, thus provoking sulfide oxidation with the concomitant risk of acid production and release of potentially toxic elements such as As. The main objective of this study was to assess the As distribution in abandoned mine wastes and the risk of further As mobilization to surrounding environment under different environmental conditions.

MATERIALS AND METHODS

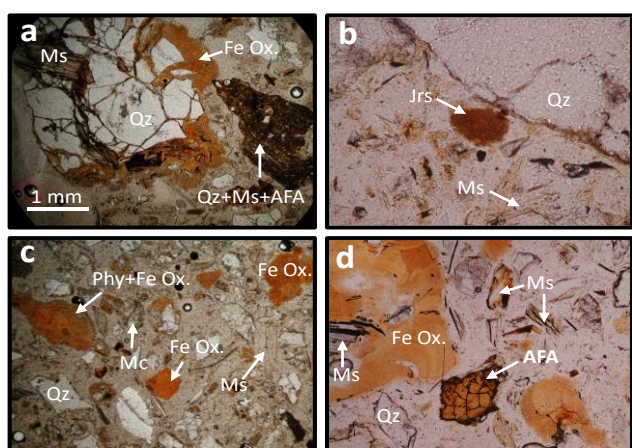
Mine wastes were sampled from a former dump of the Barruecopardo mine, which was the main tungsten deposit in Spain. This dump accumulates small-sized mine-waste particles (< 10 mm). Samples were collected from the surface of this mine dump (0-20 cm) at different places, mixed, and homogenized to generate a composite sample, being subjected to mineralogical, chemical, and environmental characterization. X-ray powder diffraction (XRD), polarized light microscopy (transmitted and reflected light), and electron microprobe were employed to perform the chemical and mineralogical characterization. The following properties were determined in the environmental characterization: pH by the water-saturated paste method, net neutralization potential (NNP) estimated as the difference between the neutralization potential (NP) (method of Sobek et al., 1978) and the acid potential (AP), chemical fractionation following the modified BCR protocol established by Rauret et al. (1999), and leaching behavior using batch [European leaching test EN-12457-4 (2002)] and column studies. Column studies were performed in glass columns (2.95 x 15 cm) packed with 100 g of mine wastes, being leached under saturated flow regime with 6 L of deionized water at a flow rate of 60 mL/h. This water volume is approximately equivalent to 10-year rainfall in the study area (10 years x 900 mm/year). Mine wastes derived from the column leaching studies were also analyzed for their mineralogical characterization as described before.

RESULTS AND DISCUSSION

According to the XRD analyses, the minerals present in mine wastes were quartz, muscovite, microcline, albite, and kaolinite. These minerals were also observed in the microscopic study in transmitted light together with scarce biotite and chlorite, Fe (oxyhydr) oxides (dispersed and covering quartz, mica, and feldspar), jarosite (in small sphere aggregates), and amorphous hydrated ferric arsenates (AFAs) (in grains and as a cementing phase of quartz, feldspar and mica), showing brown, orange, or reddish-brown colors, a cracked appearance, and an isotropic character (Fig. 1). Also, scarce finely disseminated opaque phases were detected, likely corresponding to sulfides, as observed in reflected light microscopy. The spot chemical analyses show that As was mainly found in AFAs (As₂O₅: 32.95-42.61%, Fe₂O₃: 35.62-48.71%, SO₃: 1.74-18.43%), Fe (oxyhydr)oxides (Fe₂O₃: 79.21-81.90%, As₂O₅: 3.01-4.46%, SO₃: 0.12-0.24%), and jarosite (Fe₂O₃: 41.20-45.45%, SO₃: 29.83-35.24%, K₂O, Na₂O and Al₂O₃: <1%, As₂O₅: 0.19-3.98%). In jarosite, the SO₃ content decreased with the increasing As₂O₅, pointing out the structural incorporation of As.

Mine wastes had a pH (3.7) in the range for acid-producing materials (pH < 4) and a negative NNP value (- 1.73 kg CaCO₃/t), theoretically characteristic of acid-producing materials. Nevertheless, materials with intermediate NNP values (from -20 to 20 kg CaCO₃/t) have uncertain acid generation potential. According to the European standard

EN 12457-4 (2002), the leachable As content of mine wastes (0.73 mg/kg) was below the limit value (2 mg/kg) established for the acceptance in landfills of non-hazardous waste (Council Decision 2003/33/EC). The chemical fractionation study showed that As was mostly partitioned in the reducible fraction (55.4%), an important distribution level was also found in the residual fraction (36.9%), while its partitioning in the oxidizable (7.20%) and weak acid-soluble (0.43%) fractions were quite moderate and low, respectively. This As distribution highlights the important role played by amorphous/low crystalline Fe (oxyhydr)oxides to attenuate the As spreading from the mine dump. Nevertheless, there is a great risk of As mobilization if reducing conditions are established. Under these circumstances such phases are dissolved, releasing the As retained by them. The cumulative concentrations of As, Fe, and S leached during the percolation of a water volume equivalent to 10-year rainfall in the study area (Fig. 2) reached values of 4.76, 1.38, and 148 mg/kg, respectively. These leached concentrations, the shape of the leaching curves, and the microscopic study (Fig. 1) showed that the dissolution of jarosite occurred releasing sulfate, iron, and the As retained by this mineral. Also, the partial dissolution of other phases such as AFAs and sulfides should have contributed to the release of such elements. Sulfate remained in solution, whereas iron precipitated, leading to the neoformation of Fe (oxyhydr)oxides, immobilizing only partially the As released from the phase dissolution occurring along the leaching process.



AFA: amorphous ferric arsenates, Fe Ox.: Fe (oxyhydr)oxides, Jrs: jarosite, Mc: microcline, Ms: muscovite, Phy: phyllosilicates, Qz: quartz.

Fig 1. Microscopic images of original (a, b) and leached (c, d) samples.

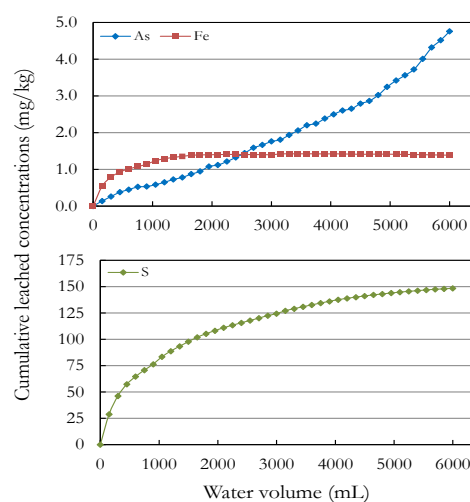


Fig 2. Cumulative concentrations leached from mine wastes.

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