

Arsenic solid speciation in tailings of the abandoned Pan de Azúcar mine, Northwestern Argentina

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ABSTRACT: In the Argentina Puna region there are several metal sulfide mines that ceased their activity twenty years ago without a proper closure plan. The exposure of the waste rocks and tailing impoundments to weathering led to sulfide oxidation and generation of highly acid solutions rich in metal(oid)s, that react with the unaltered waste rocks, partitioning into different solid phases. The As speciation along a 120 cm depth oxidation profile described in the Pan de Azucar mine tailings was studied by standardized sequential extraction procedures. Results show that the highest As concentration remain in the bottom unaltered layer mainly associated with primary and secondary sulfides. In the upper layers, the total As concentrations are ~40 to 70% lower than that of the bottom layer, and most As is associated with amorphous and crystalline oxides. More bioavailable forms of As (exchangeable and soluble) account for less than 1.5% of the total As concentration.

1. INTRODUCTION

The exposure of metal sulphide mine wastes to the atmosphere, the hydrosphere and the action of microorganisms generates drainage that may be acid and rich in dissolved metal(oid)s and sulfate (Jamieson, 2011; Nordstrom and Alpers, 1999). During weathering, the physical and chemical characteristics of the sediments change over long periods of time. The main process involves the transformation of the original parent sulphide into secondary minerals such as sulphates, oxides, oxihydroxi-sulphates, etc., and thus releasing potentially toxic elements to water (Lottermoser, 2010). Many of these minerals are fine-grained and have a high capacity for adsorption of potentially toxic metal(oid)s, and therefore can limit the aqueous concentration.

Arsenic is one of the most hazardous contaminants associated with acid mine drainage (AMD). In solution, arsenic occurs as the As (V) species H_2AsO_4^- and HAsO_4^{2-} and the uncharged As (III) species H_3AsO_3^0 . These species may be partitioned between different phases present in the sediments, such as organic matter, Fe/Al/Mn oxyhydroxides, phyllosilicate minerals, carbonates and sulfides, by different mechanisms (ion exchange, adsorption, precipitation or co-precipitation).

The abandoned Pan de Azúcar district, located in the Argentina Puna ($22^\circ32' \text{ S}$, $66^\circ01' \text{ W}$ – $22^\circ38' \text{ S}$, $66^\circ08' \text{ W}$; 3700 m a.s.l) was active until 1990 (Figure 1). Pb, Ag, Zn and Sb were extracted from sphalerite and galena ores present in a mineralised hydrothermal vein developed in dacitic rocks and dacitic breccia. Some minority arsenopyrite, bournonite and chalcopyrite are also present. Gangue minerals consist of quartz, pyrite and marcasite, as well as some scarce calcite.

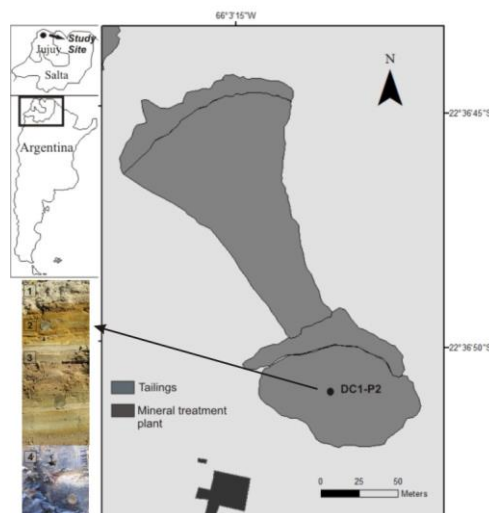


Figure 1. Location of the study area. DC1-P2: profile sampling point.

The solid mine wastes were stored in piles and tailings impoundments near the mine and abandoned without a proper closure plan. Nowadays the area show evidences of advanced acid mine drainage generation and metal release (Kirschbaum et al., 2012 a,b).

The As speciation and mineralogical composition of mine wastes accumulated in a 120 cm depth oxidation profile in the Pan de Azucar tailings was studied in order to identify the As-bearing minerals along the profile and to evaluate its mobility and geochemical behaviour during weathering.

2. METHODS/EXPERIMENTAL

Sampling and mineralogical characterization

Samples were collected from four oxidation levels described in a 120 cm depth profile (DC1-P2) developed in the tailing impoundment of Pan de Azucar mine (Figure 1). After collection, samples were air-dried and stored in plastic zip-lock bags until analysis. The mineralogy was determined by XR Diffractometry and chalcographic microscopy.

Bulk chemical composition and sequential extraction

The bulk chemical composition was determined by ICP/OES after lithium metaborate/tetraborate fusion. Besides, the 7-steps sequential extraction procedure proposed by Dold (2003) was followed in order to identify the main As-bearing phases. After each extraction, samples were centrifuged at 4000 rpm for 15 min. The obtained supernatants were filtered using 0.22 μm cellulose membranes and the chemical composition was determined by ICP-OES.

3. RESULTS AND DISCUSSION

Mineralogical and chemical composition

The highest total As concentration was determined in the bottom unaltered layer while in the upper layers, the total As concentrations are ~40 to 70% lower.

The bottom layer (87-120 cm) is composed of pyrite, marcasite, sphalerite, galene, arsenopyrite, quartz and albite. Kaolinite and illite are also present as well as some gypsum efflorescences. In the upper layers (0-87 cm), gypsum, jarosite, alunite, and basaluminite were detected. Primary minerals are quartz, albite, and illite. Amorphous Fe-(hydr)oxides are abundant between 13-87 cm depth.

Sequential Extractions

The proportion of different As-bearing phases along the studied profile is shown in Figure 2. In the upper levels, As is mainly associated with amorphous and crystalline Fe oxides, while in the base of the profile, where the rock wastes remain almost unaltered, As is mostly associated with primary and secondary sulphide minerals and organic matter.

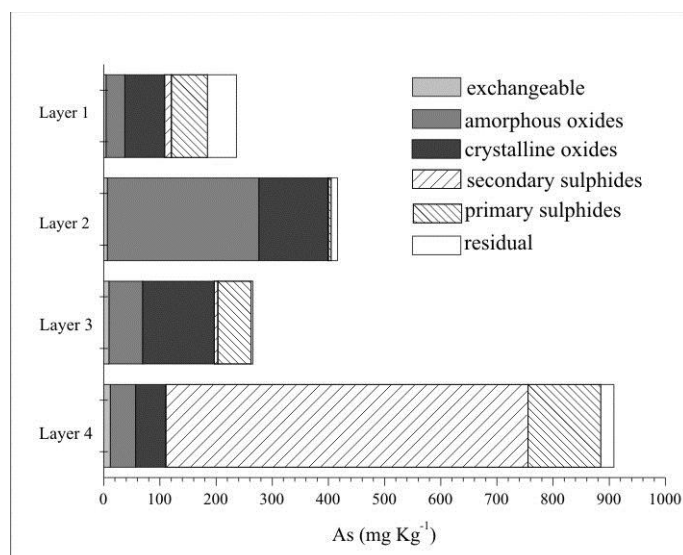


Figure 2. Distribution of As-bearing phases along the studied profile

4. CONCLUSIONS

Arsenic partitioning was consistent with the mineralogy of the rock wastes. The highest As concentration was determined in the bottom unaltered layer, where As is likely included into the lattice of primary and secondary sulfides. In the upper layers, the most relevant association of arsenic occurs with iron oxyhydroxides. The more bioavailable forms of As (i.e., exchangeable and soluble) account for less than 1.5% of the total As concentration. The release of adsorbed As from the upper layers will be favoured under alkaline conditions while structural As in the bottom layer will be released under oxidizing conditions.

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