Water Rock Interaction [WRI 14]

Morphology and solubility products of calcium arsenates found in arsenic contaminated soils in an abandoned smelter

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Abstract

The dissolution of calcium arsenates in residues released on the premises of an inactive smelter has caused high levels of arsenic pollution in the adjacent down-gradient 6 km of a perched aquifer, reaching up to 158 mg/L of dissolved arsenic, and releasing a total of 7.5 tons of arsenic in a year. We characterized the morphology of the calcium arsenates responsible of this pollution and determined their thermodynamic solubility products by (1) following the dissolution of arsenic from soil samples in batch reactors until equilibrium was reached and (2) modeling dissolution data using the geochemical code PHREEQC. Solubility product calculations took into account soil solution chemistry. Our results provide critical thermodynamic data to better understand interactions between water and arsenic containing minerals in the environment.

Keywords: arsenic dissolution; thermodynamic solubility product; arsenic dissolution kinetics.

1. Introduction

Arsenic is a major contaminant in aqueous effluents and smelter gases in the metallurgical industry. A common stabilization practice involves the addition of lime to form calcium arsenate salts and/or other Ca-As compounds [1-3]. Although calcium arsenate salts are able to remove high concentrations of arsenic from the environment [4-5], information on their morphology, kinetics, and solubility is very

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limited. In the present work we characterized the morphology of calcium arsenates in soil samples and determined the thermodynamic solubility product carrying out dissolution tests and using the geochemical code PHREEQC.

2. Materials and Methods

Arsenic contaminated soil samples collected nearby an inactive smelter were used in this study. Location and geographical positions are detailed in Martínez-Villegas, et al. [4] and correspond to sampling points one, fifteen, and sixteen, for surface soil (0-5 cm) and deep (5-30 cm) soil, each. Scanning electron microscopy analyses were done on a FEI Quanta 200 SEM coupled to an EDAX energy dispersive system in soil samples to determine the morphology of arsenic containing particles. Arsenic dissolution tests were carried out by mixing 1 g of soil with 100 mL of deionized water in a polypropylene container for 4, 8, 20, 64, 128, 252, and 500 h at 25°C in an orbital shaker. After equilibration, the suspension was decanted and the supernatant filtered through a 0.45 µm-pore membrane. Redox potential and pH were measured in an aliquot of each supernatant using a multiparameter WE50050 from YSI. The remaining supernatant was divided in two subsamples. One subsample was acidified to pH<2 with HNO_3 and stored until analysis of mayor cations, trace elements and arsenic by inductively coupled plasma optical emission spectroscopy (ICP-OES). Mayor anions were determined in the other subsample by high-performance liquid chromatography (HPLC) and by total dissolved inorganic carbon analysis using a total organic carbon analyzer (TOC). Temperature, pH, pe, major cations and anions, trace metals, and arsenic were fed to the chemical speciation code PHREEQC [6] in order to estimate aqueous solution speciation, ion activity products, and saturation indexes. All model runs were carried out using the wateq4f database for PHREEQC but updating it with recent available literature values of metal arsenate solubility product constants and aqueous species as detailed elsewhere [4].

3. Results

Calcium arsenate precipitates found in soil samples showed three different morphologies; massive, laminar, and needlelike (Fig. 1), being the latter the most commonly found. Fig. 2 shows the evolution of the concentration of arsenic and calcium during the dissolution tests for a soil sample containing needlelike calcium arsenates (Surface Soil 1). At the very beginning of the experiment, water is obviously free of arsenic and calcium, but as calcium arsenates and other minerals dissolve the concentration of arsenic and calcium increase until reaching equilibrium. A significantly higher concentration of calcium respect to arsenic is attributed to dissolution of gypsum and calcite. At equilibrium, the ion activity product (*IAP*) of any mineral depicting (or even actually controlling) arsenic solubility should approach its solubility product (*K$_{sp}$*) resulting then in a saturation index (*SI*) of zero. Hence, we plotted the saturation indexes of calcium arsenates displayed by PHREEQC and choose the one approaching to zero to get insight on the mineral depicting/controlling arsenic solubility and its solubility product. In the case of soils containing the calcium arsenates with a needlelike morphology, the solubility product was estimated to be $10^{-13.63}$, corresponding to $Ca_5H_2(AsO_4)_4 \cdot xH_2O$. This solubility product is indicative of high dissolution explaining the large mobilization and transport of massive quantities of arsenic in this environment [4]. Our results highlight the importance of strengthening environmental legislation on the disposal of arsenic as calcium arsenates in the environment.
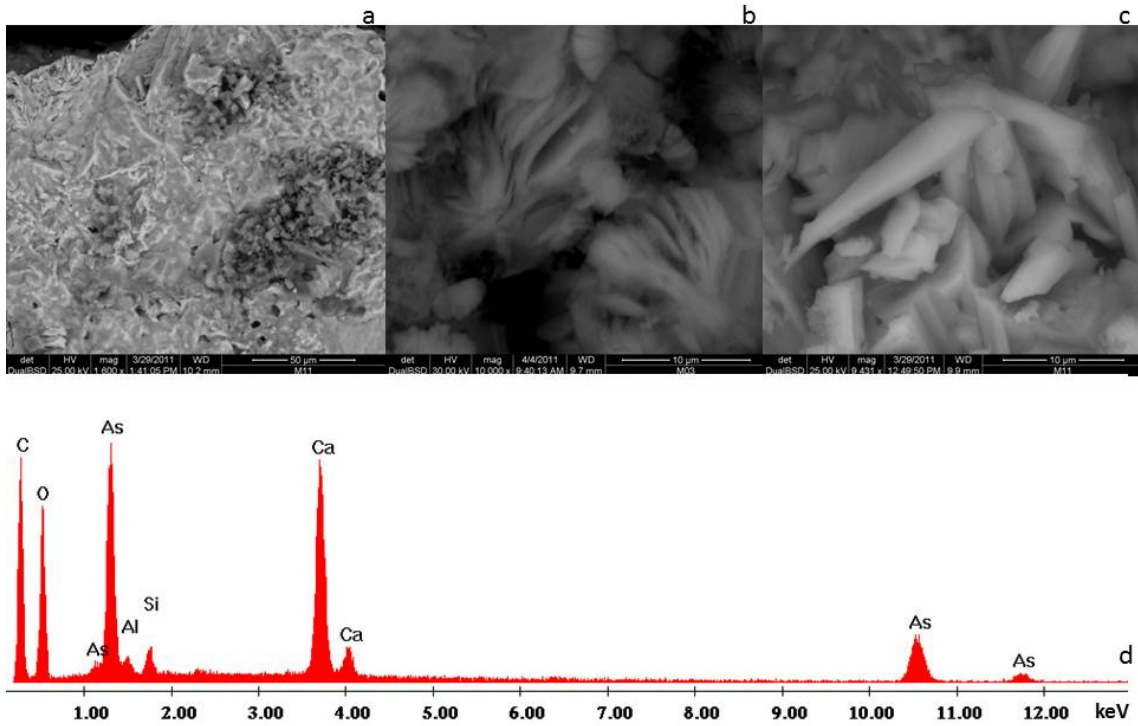
Fig. 1. (a) Massive, (b) laminar and (c) needlelike morphology of calcium arsenate commonly found in contaminated soil samples; (d) Representative EDS spectrum showing the composition of these precipitates, which comprises mainly arsenic, calcium and oxygen.
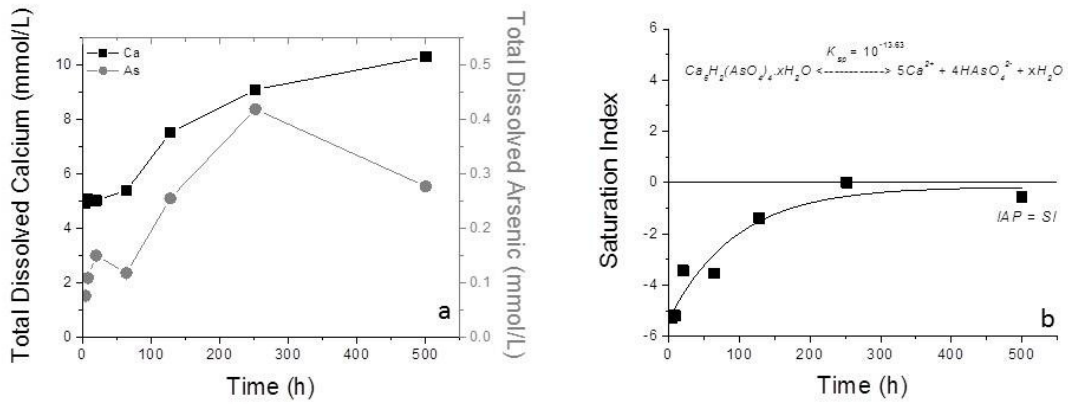

Fig. 2. (a) Total dissolved calcium and arsenic over time, (b) Evolution of the saturation index of the dissolution test for soil containing needlelike calcium arsenates.

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