

15th Water-Rock Interaction International Symposium, WRI-15

## Role of Arsenic during the Aging of Acid Mine Drainage Precipitates

Pablo Cruz-Hernández<sup>a,1</sup>, Rafael Pérez-López<sup>a</sup> and José Miguel Nieto<sup>a</sup><sup>a</sup>*Department of Geology, University of Huelva, Campus 'El Carmen' s/n, 21071, Huelva, Spain*

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### Abstract

Iron-rich sediments cover the riverbeds affected by acid mine drainage (AMD) resulting from sulfide mineral oxidation. Precipitates are mainly composed of schwertmannite, which is a poorly-crystalline Fe-oxyhydroxysulfate that recrystallizes over a short-time period to goethite. Schwertmannite precipitation has a strong capacity for removal of some toxic elements like As. This study examines the influence of the initial As(V) concentration on the kinetics of precipitation and transformation of schwertmannite by means of batch experiments. A set of schwertmannites were synthesized with different As concentrations, and solid-solution interactions were allowed at 60°C during different time periods (from 1 h to 75 d). The increase of the initial As concentration notably the precipitation of schwertmannite and its transformation to goethite. Moreover, the transformation of schwertmannite into goethite entails the release of sulfate and, at a longer time scale, of part of the previously retained As. Thus, As acts as a retardant for schwertmannite transformation; however, this toxic element is released from the precipitates once the schwertmannite is transformed, which is *per se* an environmental paradox. Furthermore, schwertmannite precipitation also plays an important role in the AMD treatment systems; hence, the long-term behavior of these precipitates should be considered for the solid waste management.

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Peer-review under responsibility of the organizing committee of WRI-15

**Keywords:** acid mine drainage; arsenic; schwertmannite; goethite

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\* Corresponding author. Tel.: +34-959-239-682; fax: +34-959-219-810.

E-mail address: [Pablo.cruz@dgeo.uhu.es](mailto:Pablo.cruz@dgeo.uhu.es)

## 1. Introduction

Arsenic is one of the elements considered as more harmful for the environment and human beings. This toxin is often associated with the metallic sulfide ore bodies. Sulfide oxidation under meteoric conditions leads to acidification of waters and release of high concentrations of sulfates and metal(oid)s such as Fe, As, Cd, Cu, Zn, and Pb. The oxidative leaching of sulfide-rich mining wastes is known as acid mine drainage (AMD). Under these conditions, a poorly-crystalline oxyhydroxysulfate, schwertmannite  $[\text{Fe}_8\text{O}_8(\text{OH})_x(\text{SO}_4)_y \cdot n\text{H}_2\text{O}]$ ,  $x=8-2y$ ,  $1 < y < 1.75$ , spontaneously precipitates on AMD-affected riverbeds<sup>1,2</sup>. Schwertmannite is considered as an efficient scavenger of trace elements from the solution, showing predilection for As<sup>3,4</sup>. However, this phase is metastable and transforms, under natural conditions, into goethite ( $\text{FeOOH}$ ) in some weeks. During this short-term maturation, most of As remains linked to the solid phase<sup>5</sup>. Following the observations of Ford<sup>6</sup> for ferrihydrite ( $\text{Fe}_2\text{O}_3 \cdot 0.5\text{H}_2\text{O}$ ), it is expected that precipitation and transformation of schwertmannite can be also affected by As concentration in solution; although no information on this point has been found in the literature. Throughout this study, reaction rates of precipitation and transformation of schwertmannite were calculated in the laboratory using different As(V) concentrations in solution and heat to accelerate the transformation process.

## 2. Methodology

### 2.1. Sample preparation

The precursor phase, schwertmannite, was synthesized following the protocol of<sup>7</sup> but in the presence of different As(V) concentrations and at 60°C. Thus, batch experiments were carried out by previously heating deionized water and adding 2 g L<sup>-1</sup> of pre-dehydrated  $\text{Fe}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$  and different concentrations of  $\text{Na}_2\text{HAsO}_4 \cdot x\text{H}_2\text{O}$  (0, 0.05, 0.0125, 0.25, 0.5 and 1 mM of As(V)). The solutions remained in the oven for variable time periods, ranging from 1 hour to 75 days. After experiments, solutions were filtered through 0.45 µm nylon syringe filters, acidified with suprapure  $\text{HNO}_3$  and stored at 4°C until analysis. Solid samples were recovered by filtering solutions using cellulose nitrate membrane filters in a vacuum system coupled to a Büchner flask. These solids were rinsed twice with deionized water and dried at room temperature in presence of silica gel in order to avoid further mineral transformation.

### 2.2. Sample analysis

Concentrations of dissolved As, Fe, S, and Na in the solutions were analyzed by inductively coupled plasma atomic emission spectrometry (ICP-AES; Jobin-Yvon Ultima2). The analytical errors were estimated to be below 5%. To check the accuracy of the results, the analysis sequence consisted of laboratory standards, quality control solutions analyzed as blind samples, blanks and duplicates. For solid characterization, bulk powder x-Ray diffraction (XRD) was performed by using a Bruker D8 advance diffractometer with  $\text{CuK}\alpha$  radiation. Diffractometer was fitted at 40kV, 30 mA, and with a scan range of 2-65° 2θ, 0.05 °2θ step size, and 20 s time per step. All analyses were performed in the laboratories of the University of Huelva.

## 3. Results

### 3.1. Mineralogical identification

Powder XRD data show that schwertmannite was the only phase precipitated initially in most of the experiments. Only in experiments with the highest As concentration (1 mM) an amorphous phase was initially formed instead of schwertmannite. Secondly, schwertmannite transformed into goethite, which progressively appeared in all the batch experiments. The occurrence time of goethite increased with the initial As concentration; ranging from 48 h in the As-free experiment to 240 h in the experiment with 1 mM of As. This observation is consistent with those previously reported for ferrihydrite by<sup>6</sup>.

### 3.2. Chemical trend of solutions

Iron concentrations in solution reveal three different stages: (1) a sharp decrease, likely due to massive homogeneous nucleation, (2) a slight decrease linked to cluster growth, and (3) a steady-state that denotes equilibrium solution-mineral (Fig. 1). The first stage and part of the second one correspond to the schwertmannite precipitation, which is concomitant with the decrease of  $\text{SO}_4$  concentrations. After that,  $\text{SO}_4$  is released due to the transformation of schwertmannite into goethite. Similar to the behavior of  $\text{SO}_4$ , As is depleted from the solution by schwertmannite precipitation at the onset of the experiment and then it is slightly released to solution during the long-term transformation into goethite. This fact indicates that the affinity of As for more crystalline phases is lower than in their poorly crystalline precursors.

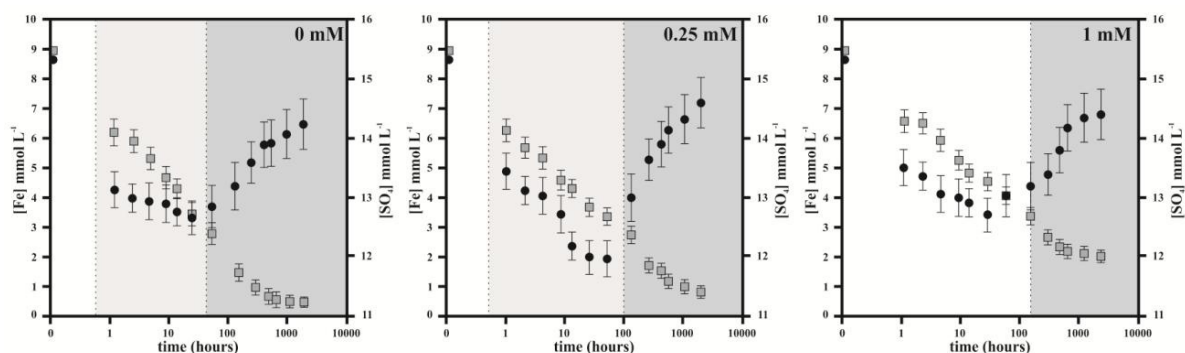


Figure 1: Evolution of (squares) Fe and (circles)  $\text{SO}_4$  concentrations in a representative batch experiment, with As-free solution, 0.25 and 1 mM  $[\text{As}]_{\text{initial}}$ . Graphics are divided into three stages; nucleation, cluster growth and equilibrium (from white to grey).

## 4. Discussion

The spontaneous precipitation rate of schwertmannite can be obtained by linear regression of the change in  $[\text{Fe}]_{\text{precipitated}}$  with time in the first stage. It was observed that the increase of  $[\text{As}]_{\text{initial}}$  in solution decreases the precipitation rate (Fig. 2a). On the other hand, pseudo-first order transformation rates of schwertmannite into goethite can be calculated using the natural logarithm of  $[\text{SO}_4]_{\text{precipitated}}/[\text{SO}_4]_{\text{initial}}$  during the transformation period, as proposed by<sup>6</sup>. Accordingly, it was observed that the increase of  $[\text{As}]_{\text{initial}}$  in solution also decreases the transformation rate of schwertmannite into goethite (Fig. 2b); which is in agreement with the mineralogical observations.

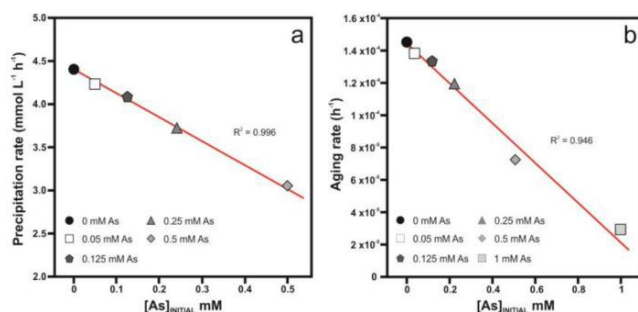


Figure 2: Rates of (a) precipitation of schwertmannite and (b) transformation into goethite vs. the initial As concentration.

## 5. Conclusions

This research has shown the interference of As(V) during schwertmannite transformation into goethite. The remobilization of As during the maturation of the AMD sediments could have important implications in the long-term fate of AMD-related pollutants. In addition, this information must be considered in the management of the wastes obtained in the passive AMD treatments. However, this study plans to be expanded to include the formation of more stable phases such as hematite, to evaluate the behavior of trace elements during the complete transformation of AMD precipitates.

## Acknowledgments

The Spanish Ministry of Economy and Competitiveness financed this research through the project EMPATIA (Ref. CGL2013-48460-C2-1-R). Dr. R. Pérez-López acknowledges the Spanish Ministry of Science and Innovation and the ‘Ramón y Cajal Subprogramme’ (MICINN-RYC 2011). P. Cruz-Hernández was supported by a graduate scholarship from the Spanish Ministry of Economy and Competitiveness (METODICA, CGL2010-21956-C02-02).

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