The Role of Secondary Iron Phases in Acid Mine Drainage: Implications for Contaminant Mobilization

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Abstract

This study investigates the role of secondary Fe phases in controlling arsenate retention under conditions of acid mine drainage (AMD). Natural samples collected from the Valdarcas mine and laboratory-synthesized goethite and schwertmannite were compared to evaluate the arsenate adsorption capacity. Mineralogical and chemical characterization was performed using XRD, SEM, TEM, and ICP-MS, followed by batch adsorption experiments at pH 3, 5, and 7. Natural goethite showed high arsenate removal (>98%), whereas synthetic goethite showed lower efficiency (36–41%). Natural and synthetic schwertmannite exhibited moderate adsorption (50–57%). Results indicate that schwertmannite acts as a short-term arsenate reservoir, while goethite promotes long-term immobilization in AMD-affected environments.

Keywords: Goethite, schwertmannite, adsorption, arsenate, Valdarcas mine

Introduction

Acid mine drainage (AMD) is a global environmental problem associated with mining activities, particularly in areas where sulfide-rich ores are exposed to atmospheric conditions. The oxidation of sulfide minerals, such as pyrite, releases acidity, sulfate and dissolved metal(loid)s into surrounding waters (Jönsson *et al.*, 2006; Valente *et al.*, 2012). As Fe(II) released during sulfide oxidation is further oxidized to Fe(III), secondary iron minerals precipitate, forming characteristic ferruginous coatings and sediments in AMD-affected environments (Jönsson *et al.*, 2006; Valente & Gomes, 2009).

The composition and stability of these secondary Fe(III) precipitates are strongly controlled by environmental factors such as pH, sulfate concentration and redox conditions. Under highly acidic conditions ($pH < 3$), minerals such as jarosite may precipitate, whereas at slightly higher pH values schwertmannite and ferrihydrite are commonly observed. With increasing pH and time, more crystalline and thermodynamically stable phases such as goethite may develop (Jönsson *et al.*, 2006; Antelo *et al.*, 2012). In several AMD-systems these precipitates occur as mixtures of poorly crystalline and more stable phases due to ongoing mineral transformations and geochemical variations.

Secondary Fe-minerals play a key role in controlling the mobility of metal(loid)s in AMD environments. Due to their high specific surface area and reactive sites, these minerals can remove contaminants from solution through adsorption, coprecipitation or surface complexation processes (Antelo *et al.*, 2012). Among these contaminants, arsenic is of environmental concern due to its toxicity and common association with sulfide mineral deposits. Several studies have shown that schwertmannite can efficiently retain arsenate under acidic conditions (Regenspurg, and Peiffer, 2005; Song *et al.*, 2015; Lee et a., 2023), while more crystalline iron oxides such as goethite also exhibit moderate sorption capacities for oxyanions (Antelo *et al.*, 2021). However, the stability and transformation of these phases may affect the long-term mobility of contaminants in AMD-systems, highlighting the importance of understanding their mineralogical proprieties and adsorption behavior.

The present study focuses on the Valdarcas mine, a former tungsten and tin mine hosted in a skarn-type deposit with abundant pyrrhotite (Valente and Gomes, 2009). Although the site was rehabilitated in 2007, AMD persists due to the presence of residual sulfide-rich wastes in the drainage system (Alves *et al.*, 2011; Barroso *et al.*, 2023). The aim of this study is to investigate the mineralogical characteristics and arsenate adsorption behavior of secondary Fe-precipitates collected from this AMD-affected mining area. Natural Fe-precipitates were characterized using mineralogical, microscopic and wet chemical techniques and compared with synthetic schwertmannite and goethite. Adsorption experiments were conducted to evaluate the role of these phases in arsenic retention.

Methods

Two natural samples of secondary Fe-phases were collected from Valdarcas mine (Covas, in Northern Portugal NW Portugal), a rehabilitated site affected by AMD, where the precipitation of Fe-oxyhydroxides and hydroxysulfates is commonly observed. The samples correspond to ferruginous precipitates and iridescent films formed in AMD environments. After field collection, the samples were transported to the laboratory, dried at room temperature, and carefully examined under a binocular microscope to obtain subsamples composed of a reduced number of mineral phases suitable for mineralogical and chemical characterization. A set of complementary analytical techniques was used to identify the mineral phases and assess their physicochemical properties. Mineralogical identification was performed by X-ray diffraction (XRD). Particle size and morphology characteristics were investigated by scanning electron microscopy (SEM) and transmission electron microscopy (TEM), whereas the chemical composition, including major and trace elements, was determined by inductively coupled plasma mass spectrometry (ICP-MS) following total digestion. These analyses were performed at Activation Laboratories (Actlabs, Canada). Quality assurance and quality control (QA/QC) protocols included the systematic analysis of procedural blanks, laboratory duplicates, internal standards, and certified reference materials. All QC results strictly met the laboratory acceptance criteria, with duplicates yielding a relative percent difference (RPD) of ≤5% for major elements and ≤10% for trace elements.

To compare the adsorption behavior of the natural samples with that of pure mineral phases, synthetic schwertmannite and goethite were prepared in the laboratory. Schwertmannite was synthesized following the hydrogen peroxide oxidation method described by Regenspurg *et al.* (2004), in which $FeSO_4$ dissolved in distilled water reacts with H_2O_2 to produce a red-orange precipitate under acidic conditions. After approximately 24 h, the precipitated material was separated by filtration and freeze-dried. Goethite was prepared following a procedure analogous to that described by Schwertmann and Cornell (2008), by adding a NaOH solution dropwise to a $Fe(NO_3)_3{\cdot}9H_2O$ solution under continuous stirring and N_2 bubbling to prevent contamination by atmospheric CO_2. The resulted precipitate was aged at 60 °C for 72 h, dialyzed against double-distilled water, and finally oven-dried at 50 °C for two days to obtain a dry powder.

Batch experiments were conducted to evaluate the arsenate adsorption capacity of both natural and synthetic samples of goethite and schwertmannite. Arsenate solutions were prepared from KH_2AsO_4 and added to the mineral suspensions at a concentration of 400 µM AsO_4^{3-}, for goethite and 1200 µM for shwertmannite. Immediately after arsenate addition, the pH of the suspensions was adjusted using standard HNO_3 or KOH solutions within the range of pH 3–7, and all experiments were conducted under constant ionic strength conditions (0.1 M KNO_3). For goethite samples, the suspensions were agitated for 24 h, with pH adjustments performed every 2 h to maintain stable experimental conditions. In the case of schwertmannite, adsorption experiments lasted 72 h, with pH adjustments carried out every 6 h. After equilibration, the suspensions were filtered through 0.45 µm Millipore membrane filters, and the filtrates were stored at 4 °C until analysis. The concentration of arsenic remaining in solution was subsequently determined by ICP-MS.

Reagents used in the experiments were of analytical grade; arsenic reagents were purchased as potassium salts from Sigma-Aldrich, whereas all other chemicals were obtained from Merck. All experiments were performed using double-distilled, CO_2-free water at 25 ± 1 °C. Polycarbonate materials were used throughout the preparation of stock solutions, synthesis procedures, and adsorption experiments to avoid contamination by dissolved silica, and all laboratory equipment was previously washed with 10% HNO_3 and thoroughly rinsed with ultrapure water.

Results and discussion

Field observations revealed two distinct types of Fe-precipitates associated with acidic drainage water in the rehabilitated mining area (Figure 1). One sample corresponds to iridescent films precipitate at acidic surface water, which, after drying, develop fragile orange-brown crusts. The other sample occurs as powdery to crusty ferruginous precipitates accumulated in drainage channels constructed during the mine rehabilitation process.

The XRD patterns of the samples confirm the presence of two main mineral phases with markedly different degrees of crystallinity. The sample corresponding to the iridescent precipitates exhibits broad and poorly defined reflections at approximately 3.39 Å, 2.55 Å, 2.28 Å, 1.95 Å, 1.66 Å, and 1.52 Å, which are characteristic of schwertmannite (Figure 2 a). In contrast, the second sample shows well-defined and intense diffraction peaks at 4.18 Å, 2.68 Å, 2.44 Å, 2.18 Å, 1.71 Å, and 1.55 Å, consistent with the presence of goethite (Figure 2b). The sharpness and intensity of these reflections indicate a more crystalline and structurally ordered mineral phase. Microscopic observations further support these mineralogical differences. SEM and TEM analyses reveal that schwertmannite occurs as aggregates of spheroidal particles with diameters ranging from approximately 350 nm to 1.3 µm. These aggregates display rough surfaces and radial acicular projections, producing the characteristic "hedgehog-like" morphology frequently described for schwertmannite (Cornell and Schwertmann, 2003) (Figure 2c). In contrast, the goethite

Figure 1 Images of the sampling sites of the two samples studied. Each panel shows a field photograph of the material, together with a binocular microscope image of the sample.

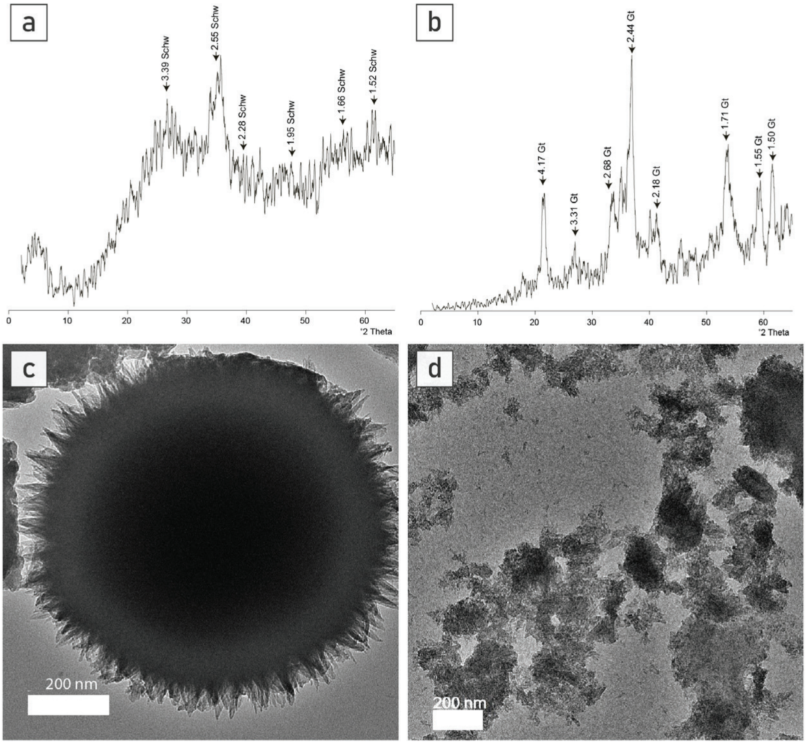

***Figure 2** XRD patterns of schwertmannite (a) and goethite (b), and TEM images showing the morphology of schwertmannite (c) and goethite (d).*

sample is composed of elongated and acicular aggregated particles (Figure 2d).

The chemical composition determined by ICP-MS reveals clear differences between the goethite and schwertmannite natural samples (Figure 3). Iron is the dominant element in both phases, as expected for secondary precipitates formed in AMD environments. However, the relative abundance of the remaining elements differs between the two samples, reflecting distinct mineralogical compositions. The schwertmannite sample is characterized by comparatively higher proportions of Al and several trace elements, particularly Mn, Ni, Zn, and Pb, suggesting a greater capacity to incorporate or retain these elements during precipitation under acidic conditions. In contrast, the goethite sample shows a composition strongly dominated by Fe and relatively higher proportions of Cu and Sb when compared with the schwertmannite. Cr and Co occur in both samples in comparable proportions, whereas Cd is only present at very low levels. Arsenic was detected in both mineral phases, confirming that these secondary iron precipitates can act as relevant sinks for this metalloid in AMD-affected environments. Overall, the chemical data indicate that, although both phases are Fe dominated, they differ in their minor and trace element signatures, which is consistent with their distinct crystal chemistry, formation pathways and environmental behavior.

The arsenate adsorption experiments revealed differences in adsorption behavior between natural and synthetic samples (Figure 4). Schwertmannite exhibited intermediate adsorption efficiencies. The natural schwertmannite sample (V4W_Sch) removed approximately 54–56% of arsenate, whereas the synthetic sample showed slightly lower values, around 50–52%. In both cases, adsorption was only weakly affected by

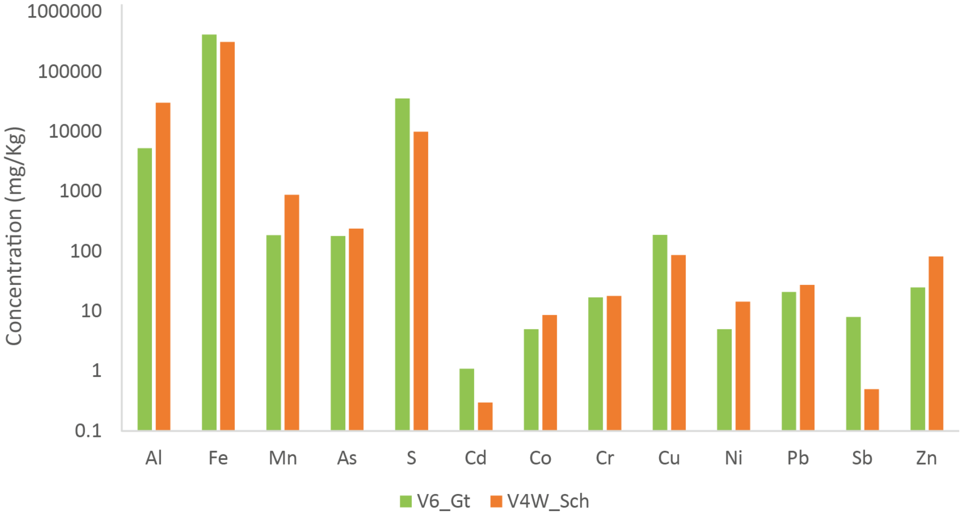

Figure 3 *Relative distribution of metal(loid)s in the natural goethite (V6_Gt) and schwertmannite (V4W_Schw) natural samples determined by ICP-MS. Values are plotted on a logarithmic scale.*

pH, with a slight increase towards neutral conditions for the natural sample. This slight difference in adsorption capacity may be associated with the presence of Al in the natural schwertmannite (V4W_Schw). Previous studies (e.g., Carrero *et al.*, 2022) suggest that Al incorporation can slightly enhance arsenate adsorption. However, this effect is generally moderate, and other factors, such as surface area, structural order, and the presence of impurities, may also play an important role in the observed differences.

On the other hand, the natural goethite sample (V6_Gt) showed the highest adsorption efficiency, with arsenate removal consistently around 98% at all tested pH values (pH 3, 5, and 7). In contrast, the synthetic goethite sample displayed substantially lower adsorption efficiencies, ranging from approximately 36 to 41%. Although the adsorption capacity remained relatively stable with pH, the marked difference relative to the natural sample suggests that the surface properties of the natural goethite are more favorable for arsenate retention. This behavior may reflect the greater mineralogical and structural complexity of the natural material, including the presence of defects, poor crystalline domains, minor element substitutions, or residual associated phases, all of which may increase the number and reactivity of available adsorption sites.

Conclusions

The results obtained in this study highlight the importance of secondary Fe minerals in AMD environments. The combined mineralogical, microscopic, and chemical characterization confirmed the presence of schwertmannite and goethite, two representative Fe phases formed under distinct geochemical conditions.

The adsorption experiments demonstrated that both minerals can retain arsenate, although with different efficiencies. Schwertmannite, both natural (V4W_Schw) and synthetic (Sch_syn), exhibited moderate adsorption capacity, with the natural sample showing slightly higher performance. In contrast, natural goethite (V6_Gt) exhibited a higher adsorption capacity than its synthetic counterpart (Gt_syn).

These distinct behaviors underscore that laboratory-synthesized minerals may not always act as accurate proxies for natural specimens when evaluating geochemical controls. The enhanced performance of the natural samples is driven by mineralogical

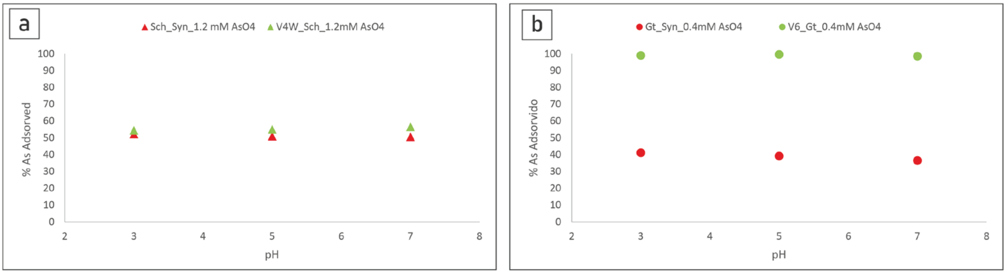

***Figure 4** Arsenate adsorption as a function of pH for natural and synthetic schwertmannite (a) and goethite (b) samples.*

heterogeneity and surface reactivity, features that remain difficult to fully replicate in the lab. Specifically, natural phases possess greater structural and compositional complexity, often including crystal defects, minor-element substitutions, varying crystallinity, and associated minor phases, which can increase the number and reactivity of adsorption sites.

Overall, these findings suggest that secondary iron phases play a key role in controlling arsenic mobility in AMD-affected and rehabilitated mining environments. Consequently, this study suggests that while synthetic phases remain fundamental benchmarks for understanding baseline mechanisms, relying solely on them may not fully capture the complexity of real-world scenarios. This highlights the clear benefit of combining both synthetic and natural materials in environmental assessments. Furthermore, these discrepancies point to the need for a more in-depth mineralogical and structural characterization of these phases, which is essential to better understand how specific chemical and structural differences influence arsenic retention capacities. Therefore, their formation, transformation, and physicochemical properties should be carefully considered when assessing contaminant behavior and predicting the long-term stability of arsenic in these systems.

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