



Selectivity assessment of an arsenic sequential extraction procedure for evaluating mobility in mine wastes



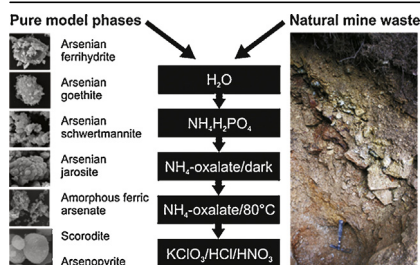
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HIGHLIGHTS

- Extraction efficiency and selectivity of phosphate and oxalate were tested.
- Pure As-bearing mineral phases and mine wastes were used.
- The reagents were found to be specific and selective for most major forms of As.
- An optimized sequential extraction scheme for mine wastes has been developed.
- It has been tested over a model mineral mixtures and natural mine waste materials.

GRAPHICAL ABSTRACT



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ABSTRACT

An optimized sequential extraction (SE) scheme for mine waste materials has been developed and tested for As partitioning over a range of pure As-bearing mineral phases, their model mixtures, and natural mine waste materials. This optimized SE procedure employs five extraction steps: (1) nitrogen-purged deionized water, 10 h; (2) 0.01 M $\text{NH}_4\text{H}_2\text{PO}_4$, 16 h; (3) 0.2 M NH_4 -oxalate in the dark, pH 3, 2 h; (4) 0.2 M NH_4 -oxalate, pH 3/80 °C, 4 h; (5) $\text{KClO}_3/\text{HCl}/\text{HNO}_3$ digestion. Selectivity and specificity tests on natural mine wastes and major pure As-bearing mineral phases showed that these As fractions appear to be primarily associated with: (1) readily soluble; (2) adsorbed; (3) amorphous and poorly-crystalline arsenates, oxides and hydroxosulfates of Fe; (4) well-crystalline arsenates, oxides, and hydroxosulfates of Fe; as well as (5) sulfides and arsenides. The specificity and selectivity of extractants, and the reproducibility of the optimized SE procedure were further verified by artificial model mineral mixtures and different natural mine waste materials. Partitioning data for extraction steps 3, 4, and 5 showed good agreement with those calculated in the model mineral mixtures (<15% difference), as well as that expected in different natural mine waste materials. The sum of the As recovered in the different extractant pools was not significantly different (89–112%) than the results for acid digestion. This suggests that the optimized SE scheme can reliably be employed for As partitioning in mine waste materials.

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1. Introduction

Mine wastes are well known and substantial local sources of arsenic on the Earth's surface. At hundreds of sites of active or abandoned mines around the globe, waste is stored in piles, tailing impoundments, and slag heaps; further, these can contain up to

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several wt% of As [1–5]. Assessing the species and mobility of As associated with these wastes is crucial for determining whether As is being released from these wastes, and whether the concentrations and forms of As are the cause for human and ecological health concerns. Accurate assessment of both the species and mobility of As contained in the mine waste is necessary for determining the need for and types of remediation that should be taken.

Sequential extraction (SE) procedures are frequently used to assess operationally defined pools of trace elements on the basis of the dissolution behavior of the target binding phases in different solid constituents [6,7]. Nowadays, SE schemes are usually adapted for the corresponding needs, but they are often criticized for their well-known weaknesses such as the lack of selectivity of extractants, possible re-adsorption, re-precipitation processes during extraction, and the lack of quality control [6–8]. Despite these drawbacks, Bacon and Davidson [7] in their review “Is there a future for sequential extraction?” concluded that SE methods will still be useful in the 21st century, but that their results should be interpreted with the full awareness of their limitations.

Several SE procedures have been carefully designed by previous research to fractionate As in soils and sediments [9–14], and several procedures were proposed to leach As sequentially in highly contaminated mine wastes [5,15,16]. All of these methods have been applied at numerous contaminated sites, including mining environments, to study the complex processes of sulfide oxidation and the retention of mobilized As by secondary phases via precipitation and sorption processes [17–22]. However, none of these schemes have been evaluated for their suitability for As-rich mine wastes, often with their high arsenate mineral content and characteristic As-bearing mineral suites. Greatly fluctuating geochemical conditions (e.g., in pH; redox; and proportions of Fe, As, and S in the waste system) and the stage of the progressive oxidation of the mine waste (i.e., the age of the mine waste) are key features of these systems; creating a situation where unique As mineral assemblages form [23,24]. Accordingly, it would be unwise to adopt the current SE procedures without a systematic examination of their specificity for As-bearing mineral phases typical for mine wastes.

The SE procedure evaluated here is designed for mine wastes in terms of geochemical partitioning of As. The scheme seeks to partition As into: deionized water (water-soluble sulfates and As oxides), $\text{NH}_4\text{H}_2\text{PO}_4$ (adsorbed As), 0.2 M NH_4 -oxalate in the dark (As incorporated in amorphous and poorly-crystalline oxides and arsenates), 0.2 M NH_4 -oxalate at 80 °C (As incorporated in well-crystallized oxides and arsenates), and concentrated KClO_3/HCl followed by boiling 4 M HNO_3 (As associated with sulfides and organics). This extraction scheme is a hybrid of two well-established and popular SE procedures developed by Wenzel et al. [10] and Dold [25] that were designed to remove As from oxidized soils and mine wastes, respectively. The majority of extractants, and the extraction order chosen for this work, are described therein. However, we inferred that the mine wastes used herein would be abundant in different As-bearing mineral phases; therefore, a modified SE procedure was designed on the basis of preliminary tests of extraction efficiency and selectivity for the pure As-bearing mineral phases and natural samples. Next, the optimized SE procedure was validated using model mineral mixtures and five natural As-rich mine wastes that had been previously characterized for As speciation.

2. Experimental design

2.1. Mine waste sampling and characterization

To test our extraction procedure, representative samples of oxidized mine wastes were collected from historic mining sites in

the Czech Republic contaminated by As. They included mining waste dump from: (i) Šafary (Kaňk-S), and (ii) Kuntery (Kaňk-K) (both (i) and (ii) are medieval Ag–Pb–Zn mines, approx. 500 years old, located in the Kaňk ore district); (iii) Dlouhá Ves Ag–Pb–Zn mine (approx. 50 years old, now closed, located in the Havlíčkův Brod ore district); (iv) Giftkies As mine (250–400 years old from the Jáchymov ore district); and (v) cyanidation tailings located in the Roudný ore district (approx. 100 years old).

The mine waste samples were freeze-dried, passed through a clean 2 mm stainless steel sieve, and stored in a freezer until analyses. Particle size analysis (sand, silt, clay) of the fraction (<2 mm) was carried out by a density method [26]. Mine waste pH_{KCl} was measured in a 1 M KCl suspension after 1 h of agitation, using a combined pH electrode and WTW multimeter. An aliquot sample was milled to analytical fineness in an agate mortar and used for determination of the bulk mine waste chemistry. Total organic carbon (TOC), total inorganic carbon (TIC) and total sulfur (S_{Tot}) were determined using combustion and/or H_3PO_4 decomposition with infrared detection on an Eltra CS 530 analyzer (Eltra). “Total” As and Fe were analyzed using an X-ray fluorescence spectrometer (XRF, ARL 9400 XP⁺). The As “pseudototal” was determined after extraction in concentrated KClO_3/HCl , followed by gentle boiling with 4 M HNO_3 [27]. Despite the lower recoveries of As in the pseudototal digests (82–94% compared to total As), these values have been shown to correlate well ($R^2=0.999$, $p < 0.001$) with total As analyzed by XRF. This finding may imply an incomplete dissolution of As mineral phases by the mixture of $\text{KClO}_3/\text{HCl}/\text{HNO}_3$; however, this could also be due to the inaccessibility of As phases enclosed within resistant silicate minerals.

The X-ray diffraction analyses (XRD) of the bulk mine waste samples and selected particles were employed to identify the principal and potential As-bearing phases in the mine waste samples. XRD analyses were performed using a PANalytical X'Pert Pro diffractometer (settings Cu $K\alpha$ radiation, 40 kV and 30 mA, 2θ range 3–80°, step 0.02, counting time of 400 s using an X'Celerator multichannel detector). The qualitative analysis of the XRD patterns was performed using PANalytical X'Pert HighScore software (version 3.0e) and the ICDD PDF-2 database [28]. The polished thin sections of the untreated samples were examined by electron microprobe analysis (Cameca SX 100).

The pore-water was collected from the mine dumps and tailings using Rhizon[®] samplers (Eijkelkamp). Values of pH and Eh were immediately recorded using WTW multimeters. Fe, As, and SO_4^{2-} in the filtered samples (<0.2 μm) were determined using ICP-MS (ThermoScientific Xseries^{II}) and Dionex ICS-2000 ion chromatography systems with 8% accuracy range for SO_4^{2-} . The accuracy of the trace element determinations was checked by measurement of NIST 1940 standard reference materials, and was <6% of the relative standard deviation for As and Fe.

2.2. Preparation of As-bearing phases

Selection of the As-bearing phases for the dissolution tests was based on a mineralogical study of the mine waste samples (see Section 3.1), as well as a thorough review of Majzlan et al. [24], which lists the most abundant and environmentally important As-bearing phases in mine wastes.

Synthetic 2-line ferrihydrite [$5(\text{Fe}_2\text{O}_3)\cdot 9(\text{H}_2\text{O})$] and poorly crystalline goethite ($\alpha\text{-FeOOH}$) were synthesized in the presence of As(V), following the procedures in Schwertmann and Cornell [29] with minor modifications [30]. Schwertmannite [$\text{Fe}_8\text{O}_8(\text{OH})_6\text{SO}_4$] and jarosite [$\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$] were prepared in the presence of As(V), following the methods of Regenspurg et al. [31] and Baron and Palmer [32], respectively. The synthesis of beudantite [$\text{PbFe}_3(\text{AsO}_4)(\text{SO}_4)(\text{OH})_6$] was loosely based around

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