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Arsenic speciation in cemented paste backfills and synthetic calcium–silicate–hydrates

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ABSTRACT

Arsenic (As) is a major pollutant in many mine tailings resulting from base metal and gold deposits. It can potentially cause environmental risks because of its high toxicity at low concentrations. A new tailings' management technique has become popular in new mines, the cemented paste backfill (CPB). It consists of mixing tailings with water (typically 25%) and a low proportion of hydraulic binder (3–7%) to produce a paste that can be stored in underground mine openings. Even if CPB is mainly used for improving mining techniques and for tailings storage purposes, it could also provide environmental advantages by stabilizing contaminants such as As. In the present study, X-ray absorption fine structure (XAFS) investigations were conducted on CPB samples synthesized in the laboratory and spiked with As. XAFS analysis were also performed on a variety of As-bearing compounds (natural or synthetic), to provide a database of reference XAFS spectra. Among these reference samples, calcium–silicate–hydrates (C–S–H) spiked with various amounts of As through adsorption and co-precipitation were synthesized.

The nature and amounts of the As species in the CPB samples, as well as As valence state were determined by linear combination of the reference spectra, in a least squares fitting procedure. As speciation in C–S–H was determined by extended X-ray absorption fine structure (EXAFS) fitting using theoretical curves from *ab initio* calculations.

The results indicate that the binders promote the oxidation of As(III) to As(V) in the CPB. The As species formed in CPB are composed mainly of calcium arsenates, but other secondary minerals such as ferric arsenate can be present. Moreover, the use of fly ash binder could promote the formation of calcium–iron arsenates. However, CPB samples do not seem to contain arsenical C–S–H, as shown by the fitting results involving the synthetic C–S–H. In these samples, As reacts mainly through sorption mechanisms.

1. Introduction

Cemented paste backfill (CPB) is a technique widely used in metalliferous mines to fill underground openings with a mix of tailings, water and a hydraulic binder. Such a backfilling provides mechanical strength to the mine stopes while ensuring improved ground stability (Belem and Benzaazoua, 2008; Hassani and Archibald, 1998; Hughes et al., 2010; Landriault et al., 1997). The main advantages of this technique are to provide better safety to the mine workers, as well as to enhance the recovery of the remaining ore. It also provides an environmental benefit by reducing surface storage requirements for tailings (Fall and Benzaazoua, 2005). Furthermore, tailings management facilities could be a major environmental concern for tailings containing sulfide minerals. Air oxygen and meteoric waters oxidize sulfide minerals and lead to the release of sulfates, metals, and metalloids to the drainage solutions. This phenomenon is well-known in mining and remains one of the main concerns regarding the mine impacts on the environment. It is called Acid Mine Drainage (AMD) if the pH is acidic, or Contaminated Neutral Drainage (CND, also called Neutral Drainage, ND) if the pH remains circum-neutral (Aubertin et al., 2002; Lowson, 1982; MEND, 2004; Plante, 2010). Previous studies have shown that returning a part of the tailings in CPB reduces the reactivity of tailings, by maintaining a high degree of saturation of water that decreases the diffusion rate of oxygen in the material (Godbout et al., 2004; Ouellet et al., 2006; Verburg, 2002). Other studies have shown that CPB can also be considered as a

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solidification/stabilization technique in reducing the potential of contaminant releases from the tailings (Benzaazoua et al., 2004b, 2005; Coussy et al., 2011; Fried et al., 2007; Picquet, 1995). These studies focused only on the release of contaminants to the effluents, but did not take into account the mechanism of contaminant immobilization from the solid phases. However, an understanding of the speciation of the contaminants in cementitious matrices is the first step to determine the contaminants stability.

Among the contaminants in mine drainage waters, arsenic (As) represents a specific concern because of the high solubility of some As-bearing minerals or compounds in a wide range of pH conditions. Aqueous As species include both pentavalent and trivalent As. Most of the As soluble species are harmful, but trivalent arsenic is the most labile and toxic form (Smedley and Kinniburgh, 2002). The mechanisms of solidification/stabilization of As by cementitious products have been well investigated in previous studies (e.g. Dutré et al., 1998; Vandecasteele et al., 2002). Arsenic immobilization by cementitious products involves generally the precipitation of calcium arsenates or calcium arsenites. The composition of calcium arsenates depends on the pH of the pore water, the Ca/As ratio and the As concentration as function to calcium arsenate solubility products (Bothe and Brown, 1999). Arsenic can also interact with specific cementitious minerals such as ettringite through co-precipitation or adsorption (Mollah et al., 1998; Myneni et al., 1998). Interaction of As with calcium–silicate–hydrates (C–S–H) is also possible (Halim et al., 2004). However, the mechanisms of interaction and the speciation of As in C–S–H are not well known.

In CPB materials, conditions of hydration are different from conventional solidification/stabilization techniques (Benzaazoua et al., 2004a, 2010). CPB has high water contents (typically 25%) to ensure the transportation of the paste by gravity in a pipe network whereas the amounts of hydraulic binders are low (i.e. 3–7 wt.%). Moreover, the mixing water involved in CPB is often the process water from the ore processing plants. Such mixing water could contain high dissolved amounts of sulfates, especially in gold mines where the SO_2-air process (INCO process) is used to destroy cyanides. These specificities of implementation promote the formation of abundant secondary precipitates containing sulfate, as ettringite, monosulfoaluminates or gypsum, in parallel to normal hydration processes forming typical cementitious minerals such as C–S–H and AFm (Benzaazoua et al., 2004a).

The behavior of As in CPB has been studied by environmental assessment methods (Coussy et al., 2011; Fried et al., 2007), and a preliminary mineralogical characterization has been conducted on synthetically prepared CPB (Coussy, 2011). Scanning electron microscope investigations coupled to energy-dispersive spectrometry (SEM-EDS) have demonstrated that (i) arsenic (under As(V) valence state) is dispersed in the cementitious matrix as localized aggregates of cementitious minerals (C–S–H associated with sulfates); (ii) As is always associated with calcium and iron, and other elements such as phosphorus in other instances. Arsenic can also occur in the form of rare Ca–As–Fe–S compounds measuring 3–5 μm across.

Synchrotron-based X-ray absorption fine structure (XAFS) spectroscopy has been extensively used to elucidate the speciation of heavy metals and metalloids in natural conditions. In particular, As speciation in tailings, determined by XAFS provided useful information about the forms of As carriers and their behavior under various environmental conditions (Morin and Calas, 2006; Paktunc et al., 2004, 2008). Indeed, XAFS spectroscopy is element specific and provides important information on atomic neighborhood of a target element, as well as on its valence state.

In the present study, XAFS spectroscopy was performed for identification and quantification of the dominant As species in CPB. This characterization would enable to predict the stability of the As compounds, and consequently the potential As release at a large scale in the underground mine effluents.

Synthetic CPB samples made of two hydraulic binders and containing various amounts of As with different valence states were studied. Moreover, As adsorption and co-precipitation experiments were conducted on synthetically prepared C–S–H. The speciation of As in various CPB matrices was investigated by linear least-squares fitting of the experimental spectra by reference minerals/compounds. The speciation of As in C–S–H was assessed by fitting experimental EXAFS curves using the ‘shell modeling’ approach with theoretical curves derived from *ab initio* calculations. A comparison of the As speciation in CPB and synthetic C–S–H samples was discussed further.

2. Materials and methods

2.1. Paste backfill preparation

CPB samples were prepared by mixing the hydraulic binders with calibrated silica, to simulate the tailings, and with mixing waters containing As. The details of the paste backfill preparation are given in Coussy et al. (2010) and Coussy et al. (2011).

2.1.1. Synthetic contaminated mine waters

Two synthetic mixing waters were prepared with the purpose to simulate typical tailings pore water containing arsenic. All chemical reagents were provided by Sigma-Aldrich Company and were chosen for their high solubility, particularly sodium arsenate [$Na_2HAsO_4{\cdot}7H_2O$] and sodium arsenite [$NaAsO_2$] as shown in previous studies (Leist et al., 2003; Mollah et al., 1998). The reagents were mixed together, and then sulfuric acid and deionized water were added to obtain three loading levels of synthetic mixing waters (Zagury et al., 2006). Aliquots of these solutions were analyzed by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) on a Jobin Yvon ULTIMA 2 spectrometer, and by ion chromatography (Dionex IC25). Synthetic water compositions are shown in Table 1.

Table 1
Chemical composition of the various synthetic mixing waters.

Component	Mixing water 0 (mg l^{-1})	Mixing water 1 (mg l^{-1})[a]	Mixing water 2 (mg l^{-1})[a]	Mixing water 3 (mg l^{-1})[a]	Source
As_{tot}	0 (<DL)	80	360	3700	$Na_2HAsO_4{\cdot}7H_2O$, $NaAsO_2$
Fe^{2+}	0 (<DL)	1090	4400	2910	$FeSO_4{\cdot}7H_2O$
Cu^{2+}	0 (<DL)	39	260	130	$CuSO_4$
Zn^{2+}	0 (<DL)	44	190	130	$ZnSO_4{\cdot}7H_2O$
Ca^{2+}	0 (<DL)	250	190	290	$CaSO_4{\cdot}2H_2O$
Na^{+}	0 (<DL)	38	160	2630	$Na_2HAsO_4{\cdot}7H_2O$, $NaAsO_2$
SO_4^{2-}	0 (<DL)	3060	13,200	11,470	H_2SO_4 (complement)

<DL: below detection limit.
[a] Uncertainty on these results is ±5%.