



Stability of arsenate-bearing Fe(III)/Al(III) co-precipitates in the presence of sulfide as reducing agent under anoxic conditions



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H I G H L I G H T S

- Fe(III)/Al(III) co-precipitates are very stable under anoxic conditions.
- The presence of S^{2-} as reducing agent resulted in up to 1% As release.
- Up to 45% of ferric is reduced to ferrous.
- Al has a stabilizing effect in absence or presence of sulfide ions.
- Sulfide did not reduce arsenate to arsenite.

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Currently, the co-precipitation of arsenate with ferric iron at molar ratios $Fe(III)/As(V) \geq 3$ by lime neutralization produces tailings solids that are stable under oxic conditions. However not much is known about the stability of these hazardous co-precipitates under anoxic conditions. These can develop in tailings storage sites by the action of co-discharged reactive sulfides, organic reagent residuals or bacterial activity. The ferric matrix can then undergo reductive dissolution reactions, which could release arsenic into the pore water. Co-ions like aluminum could provide a redox-immune sink to scavenge any mobilized arsenic as a result of reduction of ferric. As such, in this work $Fe(III)/As(V) = 4$ and aluminum substituted $Fe(III)/Al(III)/As(V) = 2/2/1$ co-precipitates were produced in a mini continuous co-precipitation process circuit and subjected to excess sulfide addition under inert gas to evaluate their stability. It was found that the ferric-arsenate co-precipitate could retain up to 99% (30 mg/L in solution) of its arsenic content despite the high pH (10.5) and extremely reducing ($E_h < -200$ mV) environment. There was no significant reduction of arsenate and only 45% of ferric iron was reduced. Partial aluminum substitution was found to cut the amount of mobilized arsenic by 50% (down to 15 mg/L) hence mixed $Fe(III)/Al(III)$ -arsenate co-precipitates may offer better resistance to reductive destabilization over the long term than all iron co-precipitates.

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1. Introduction

Mine tailings have to be stable for thousands of years after the mining operation ceases. This requires the discharged tailings to be stable under a variety of storage conditions. For arsenic the stabilizing phases, produced by co-precipitation with lime neutralization, are ferric arsenate ($FeAsO_4 \cdot xH_2O$) and arsenate adsorbed ferrihydrite ($FeOOH \cdot 0.5H_2O$) (Chen et al., 2009; Langmuir et al.,

2006; Le Berre et al., 2007) Several studies have investigated their stability in oxic conditions in terms of pH and $Fe(III)/As(V)$ molar ratio (Krause and Ettel, 1989; Papassiopi et al., 1996; Robins et al., 1988) as well as neutralization medium and concluded the co-precipitates to be stable under oxic conditions (De Klerk et al., 2012; Jia and Demopoulos, 2008). However, organic matter acting as complexing or reducing agent (McCreadie et al., 2000; Wang and Mulligan, 2009) or inorganic or biologically-generated reducing species like sulfides can cause the destabilization of the iron(III)-arsenate containing tailings solids. Although solidification/stabilization technologies (Singh and Pant, 2006) are available for arsenical hazardous wastes, they are not suitable for voluminous

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mine tailings such as those generated by uranium mines in Northern Saskatchewan, Canada (Moldovan et al., 2003).

McCreadie et al. (2000) found high arsenic concentrations in old mine tailings pore-waters at the Campbell Mine in Balmertown, Canada, where according to the authors residual organics caused the destabilization of iron(III)-arsenate containing solids via reduction of ferric and arsenate to ferrous and arsenite respectively. The concurrent sulfate reduction resulted in the release of protons and therefore a drop in pH (McCreadie et al., 2000). Harris in a review paper (Harris, 2003) raised the possibility of reductive destabilization of ferric arsenate tailings, like the ones considered by McCreadie et al. (2000), by co-deposited reactive sulfides such as pyrrhotite. So far it appears that mainly the reduction of ferrihydrite and ferrihydrite loaded with arsenic has attracted research attention. Arsenical ferrihydrite, for example, has been shown to reductively dissolve by chemical reducing agents such as hydroquinone (Erbs et al., 2010). Co-precipitated arsenate and ferrihydrite were shown to release less arsenate compared to arsenate-adsorbed on pre-prepared ferrihydrite. Ferrihydrite has been further shown to be reductively dissolved by bacteria at high pH (9.5) (Zavarzina et al., 2011) and neutral pH (7.1) (Tufano et al., 2008). Bacterial sulfate reduction was also shown to lead to formation of ferrous sulfide. Arsenate, however, was not released from the solids in the process. The authors suggest reduction to arsenite being a crucial step for arsenic release into solution (Saalfield and Bostick, 2009).

In the context of co-precipitation and stability of arsenic with iron(III), it is also important to consider the possible role of aluminum that is a common cation in ore leaching operations and which upon hydrolysis can provide reduction-immune co-precipitates. Thus arsenate adsorbed on aluminum-substituted ferrihydrite has been shown to release minimal amounts of arsenic as arsenite, when exposed to arsenate reducing bacteria, but in that study, a rather large excess of Fe and Al was used, namely $(\text{Fe} + \text{Al})/\text{As} = 100$ and $\text{pH} = 7.3$ (Babechuk et al., 2009), therefore it has yet to be proven if this scenario holds true in metallurgical tailings with significantly smaller $(\text{Fe} + \text{Al})/\text{As}$ ratios. Aluminum hydroxide alone was not a sufficient arsenic sink (Babechuk et al., 2009), but arsenate reduction on the surface of $\text{Al}(\text{OH})_3$ does not seem to result in quick arsenite release (Zhang et al., 2012). Recently Jia et al. reported the batch co-precipitation of arsenate in a 2-step process with ferric (first step from pH 1 to 4 at $\text{Fe(III)/As(V)} = 2$ and aluminum (second step from pH 4 to 8 at $\text{Al/As} = 2$) (Jia et al., 2012). It was found that aluminum increases arsenic retention in oxic, sulfide reducing and bacterial reducing conditions.

In this study, continuous two-stage co-precipitation of $\text{Fe(III)/Al(III)/As(V)}$ was conducted and the produced solids were exposed to excess sulfide reducing agent under inert gas (ensuring a complete anoxic environment) to evaluate the stability of the solids. The slurry samples were placed on a shaker table to keep the solids in suspension and thereby accelerate the tailings aging process and the attainment of pseudo-equilibrium/long-term trends.

2. Materials and methods

2.1. Production of co-precipitates and sample preparation

The production of solids was achieved by continuous co-precipitation by lime neutralization using a two-reactor circuit, reported in detail elsewhere (De Klerk et al., 2012). Two types of co-precipitates were produced: the standard one with a molar ratio of $\text{Fe(III)/As(V)} = 4$ (labeled “CD4c”) and the alternative mixed $\text{Fe(III)/Al(III)/As(V)} = 2/2/1$ system (labeled “CD5”). The feed solutions were prepared by dissolving the required amounts of ferric and aluminum sulfate salts along arsenic pentoxide to give 1.4 g/L As(V) ,

$[\text{Fe} + \text{Al}]/[\text{As}] = 4$ and $\text{pH} = 1.5$. The exact feed compositions for both co-precipitation experiments can be found in Table 1. The mean retention time for each reactor was 1 h and the circuit was operated for 9.5 h; steady-state operation was achieved after 6.5 h.

The slurries were used in stability testing as obtained from the co-precipitation process (steady-state produced co-precipitates only), except the solid/liquid ratio was doubled by decanting an appropriate amount of water. Sulfide was used as the reducing agent (0.33/0.66 M, $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$). The two co-precipitates ($\text{Fe(III)/As(V)} = 4$ and $\text{Fe(III)/Al(III)/As(V)} = 2/2/1$) were exposed to one equivalent of sulfide per mole of iron. The slurry samples were placed (all handling was done in a glove-box) in inert gas-filled septum bottles secured on a shaker table that was set to 180 oscillations per minute to keep the slurries fully mixed and the solids in suspension. The bottles were continuously shaken for different times up to a maximum of 4 weeks. Each bottle represented one sample, i.e. a simple sampling point thus avoiding potential risk of air infiltration because of excessive handling.

2.2. Stability testing

Solids produced in the co-precipitation experiments were exposed to stability testing under two conditions: (1) in the presence of sulfide ions (labeled “sulfide series”) and (2) in the absence of sulfide ions (labeled “Drift series”) for comparison purposes. Details of the two type of stability tests are given below.

2.2.1. Stability of sulfide samples

80 mL of $\text{Fe(III)/As(V)} = 4$ (CD4c) or $\text{Fe(III)/Al(III)/As(V)} = 2/2/1$ (CD5) co-precipitate slurry was filled in 125 mL tinted septum bottles. 30 mL of a 0.33 M/0.66 M sulfide solution was added to obtain $\text{S}^{2-}/\text{Fe(III)} = 1$. The sulfide solution was adjusted to $\text{pH} = 8$ with 50% concentrated H_2SO_4 just prior to addition to the co-precipitate slurry. Ten samples per co-precipitate series were generated in this manner to be sampled every third day. Used samples were discarded. They were evacuated right after sulfide addition and the atmosphere replaced with nitrogen in a glovebox.

2.2.2. Stability of drift samples

Four “Drift” samples per series were produced without the addition of reducing agent but put under a nitrogen atmosphere to act as reference. These were sampled every six days.

2.3. Methods of analysis

Fe(II) was analyzed by a modified dichromate titration method. For total Fe(II) a 1 mL slurry sample was digested in 5 mL concentrated HCl. Since elemental sulfur is not soluble in concentrated HCl the slurry was filtered with a 0.2 μm filter and the solids washed with an addition 5 mL DI water. The solutions were then combined and diluted with 25 mL $\text{H}_2\text{SO}_4\text{-H}_3\text{PO}_4$ buffer and 50 mL DI water. 3 drops of a 0.001 N diphenylamine sulfonate indicator were added and titrated with 0.01 N $\text{Cr}_2\text{O}_7^{2-}$ until the color changed to purple. Filtrate samples were first diluted with 50 mL DI water, then buffer and concentrated HCl were added. Arsenite, sulfite and sulfide solutions were titrated to see if these ions interfere with the

Table 1
Feed composition for all CCPTN experiments.

Name	Concentration [mg/L]			Molar ratio	
	Fe(III)	As(V)	Al(III)	Fe(III)/As(V)	Al(III)/As(V)
CD4c	3905	1495	–	3.5	–
CD5	1966	1504	1132	1.8	2.1

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