

Effectiveness of Arsenic Co-Precipitation with Fe-Al Hydroxides for Treatment of Contaminated Water

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ABSTRACT: Wastewater treatment is a challenging problem faced by the mining industry, especially when mine effluents include acid mine drainage with elevated arsenic levels. Iron (hydr)oxides are known to be effective in removal of As from wastewater, and although the resulting compounds are relatively unstable, the presence of structural Al enhances their stability, particularly under reducing conditions. The purpose of this study was to assess the effectiveness of Al-Fe (hydr)oxide co-precipitates for the removal of As from wastewater and to assess the chemical stability of the products. Different Al-Fe (hydr)oxides were synthesized at room temperature from ferrous and aluminum salts using three different Fe:Al molar ratios (1:0.0, 1:0.3, and 1:0.7) and aged for 90 days (sulfate experiments) or 120 days (chloride experiments) in the presence of arsenic. At the end of the aging periods, the precipitated sludges were dried and characterized in order to evaluate their stability and therefore potential As mobility. All treatments were effective in reducing As levels in the water to below 10 µg L⁻¹, but the presence of Al impaired the effectiveness of the treatment. Aluminum decreased the chemical stability of the precipitated sludge and hence its ability to retain As under natural environmental conditions.

Keywords: wastewater, decontamination, sludge stability, magnetite, goethite.

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INTRODUCTION

One of the most critical and challenging problems faced by the mining industry is the treatment of wastewater before its release into the environment. Mine effluents generated during base metal processing may contain high concentrations of potentially harmful elements, such as arsenic (As). Wastewater treatment is critical in areas where acid mine drainage (AMD) is observed as sulfide-bearing ores undergo oxidation when exposed to atmospheric conditions, producing acid waters with high pollution potential. To comply with environmental legislation, contaminants present in the AMD must be removed, neutralized, or reduced to values lower than an established threshold.

Exposure of sulfides to atmospheric conditions, followed by generation of AMD, has been well-documented in gold (Au) and uranium (U) mines in the state of Minas Gerais, Brazil (Mello et al., 2006). Arsenic and gold are so closely correlated that methods for geochemical prospecting use As as a tracer for Au deposits (Boyle and Jonnasson, 1973). Arsenic, however, has little or no commercial value and is not recovered during mineral processing; thus, mine effluents may become contaminated with As.

The most common strategy to mitigate the environmental impact of AMD water is addition of lime to neutralize its acidity (pH increase) and to precipitate metals. In general, Fe is the dominant free cation in AMD, and at high pH, it precipitates as Fe (hydr)oxides that can co-precipitate or adsorb other trace elements present in solution. The formation of a protective Fe (hydr)oxide layer, termed geochemical barrier (GB), is also possible in waste rock piles. This layer may prevent further oxidation of the sulfide and may also immobilize toxic elements associated with them, and it is often used as a management and remediation tool.

Processes involving precipitation of Fe (hydr)oxides have been widely studied as a mechanism to remove As from mine wastewaters (Makris et al., 2007). Schwertmannite, ferrihydrite, and goethite are the main Fe phases observed in AMD systems as products of Fe sulfide oxidation (Carlson et al., 2002; Fukushi et al., 2003). Arsenic may be incorporated in the structure of poorly crystalline Fe arsenate ($\text{FeAsO}_4 \cdot x\text{H}_2\text{O}$) or crystalline scorodite; however, these As-rich Fe (hydr)oxides are unstable at pH >2 and at an As/Fe molar ratio higher than 0.5 (Carlson et al., 2002).

Nanominerals of Al and Fe (hydr)oxides are ubiquitous in the natural environment and play a crucial role in the biogeochemical mobility of some trace elements. The solubility and stability of Al and Fe (hydr)oxides are governed by pH and redox conditions of the surrounding media. Although it is well known that Al hydroxides are less efficient than Fe (hydr)oxides in retaining inorganic pollutants, Al-substitution of Fe enhances the adsorption capacity of Fe (hydr)oxides and their chemical stability under reducing conditions (Torrent et al., 1987; Silva et al., 2010). Bousserhine et al. (1999) also demonstrated that biological reduction of Al-, Cr-, Mn-, and Co-substituted goethites decreased as Fe-substitution increased, and that Al-goethite was more resistant to reductive dissolution than other substituted goethites. Therefore, understanding of these Fe-substitution reactions may provide additional insights into the AMD water treatment process, thus allowing development of remediation strategies under different geochemical and climatic conditions.

The purpose of this study was to evaluate the effectiveness of co-precipitating Al-Fe (hydr)oxides for removal of As from mining wastewater. The stability of the precipitated phases under different concentrations of Al was also evaluated, as well as the environmental conditions that can be expected in mining areas in tropical and sub-tropical climates. Two different sets of salts (chlorides and sulfates) were used for synthesis of the Al-Fe (hydr)oxides to evaluate their influence on wastewater composition. The experiment was designed to simulate the precipitation of the Al-Fe (hydr)oxides under the alkaline conditions typically encountered in AMD treated after mineral processing. The synthesis using sulfates and chlorides simulates the conditions typically found in gold and base metal deposits, as well as in saline liquors, produced during mineral and coal processing, respectively.

MATERIALS AND METHODS

Experiments were designed and performed to co-precipitate Al-Fe (hydr)oxides in the presence of As. The procedure followed for synthesis of the Fe oxides was an adaptation of the method described in Schwertmann and Cornell (2000), and also used and described in Silva et al. (2010). However, in the present experiments, As was added to the solution along with Fe and Al salts, not after precipitation of the Fe-Al (hydr)oxides. The Al-Fe (hydr)oxides were synthesized from ferrous and aluminum salts (chlorides and sulfates) using three different Fe:Al ratios (Table 1). Precipitation was achieved by adding 5 M potassium hydroxide solution at pH 11.7, as recommended by Schwertmann and Cornell (2000), and the precipitates were aged in plastic bottles for 3 to 4 months at ambient temperature (around 25 °C). Slow oxidation of Fe²⁺ to Fe³⁺ and incorporation of Al³⁺ in the Fe (hydr)oxide structure was achieved by opening the bottles daily and stirring the suspension for five minutes. All treatments were conducted in duplicate.

Two different sets of experiments were carried out: one with sulfates and another with chlorides. Both experiments started with the addition of a 10,000 mg L⁻¹ of As Merck standard solution to 2 L of deionized water in 5 L plastic containers, in order to obtain three different final concentrations of As (Table 1). Such concentrations were considered in a range from weak to moderate arsenic contamination of wastewater. Ferrous (1 mol L⁻¹ FeSO₄·7H₂O or FeCl₂·4H₂O) and Al salts [0.5 mol L⁻¹ Al₂(SO₄)₃·18H₂O or 1 mol L⁻¹ AlCl₃] were then added to the plastic bottles in order to achieve different Fe:Al molar ratios. The volume was made up to 3 L with deionized water, and the pH was buffered at 11.7 by adding a 5 mol L⁻¹ potassium hydroxide solution. The containers were then filled to 4 L with deionized water and aged for 90 days (sulfate experiments) or 120 days (chloride experiments). The experiments with chloride salts were aged longer to further assess the stability of precipitated phases.

Aliquots of the supernatant solutions were collected at different aging times: immediately after precipitation (3 h) and after 1, 7, 14, and 60 days (sulfate experiments) or 1, 15, 30, 60, and 120 days (chloride experiments). Potentiometric determinations of pH and Eh were performed in supernatants at each collection time, and the pH values were kept >11 by adding KOH if necessary. Immediately after sampling, the aliquots were filtered using 0.45 µm mixed cellulose ester filters, acidified using ultra-pure HNO₃, and kept in a refrigerator at around + 4 °C until analysis. The concentrations of soluble As, Al, Fe, K, and S in equilibrium with the precipitates were then measured in the aliquots by inductively coupled plasma optical emission spectroscopy (ICP-OES Perkin-Elmer 8300) in the geochemistry laboratory of The University of Queensland. The soluble As concentrations in the sulfate experiments were also measured by atomic fluorescence spectrometry AFS (PS Analytical Myllemium System) in the trace elements laboratory of

Table 1. Experimental conditions for sulfate and chloride experiments

Treatment	Fe:Al molar ratio	Initial As concentration mg L ⁻¹
1	1:0.7	5.00
2	1:0.3	5.00
3	1:0.0	5.00
4	1:0.7	1.00
5	1:0.3	1.00
6	1:0.0	1.00
7	1:0.7	0.20
8	1:0.3	0.20
9	1:0.0	0.20

the Federal University of Viçosa (Brazil). Analytical quality was monitored by analysis of internationally certified reference materials (CRM) SLRS-4 (river water) and SLEW-3 (estuarine water) as well as synthetic solutions, and analytical blanks and replicates were processed together with the samples. All results were within 95 % of certified values. Relative standard deviation (RSD) of duplicate samples (two different aliquots of the same sample) was lower than 2 % for all elements. Detection limits for each element and set of analyses are indicated in the relevant tables. It should be noted that all samples required significant dilution prior to analysis to minimize the effects of the high salinity due to the presence of sulfates or chlorides, and high concentrations of K used for pH buffering. Therefore, measured counts were often only slightly higher than detection limits, hence the large errors in terms of standard deviation of replicate analyses.

At the end of the aging periods, the supernatants were discharged by siphoning and then air dried. The remaining suspensions were recovered and homogenized to characterize the precipitates. An aliquot of each suspension was dialyzed using 30 mL G2 dialysis cassettes (3.5 kD membrane molecular weight cutoff) and then freeze dried. The resulting powder precipitates were characterized by scanning electron microscopy (SEM) (JEOL JSM 6460) and X-ray diffraction (XRD) (Bruker D8 Advance) analysis. Operating conditions for the XRD analyses were Co source, 35 kV, 40 mA, step size 0.02 degrees two theta, and counting time 2 sec/step. The XRD peaks were matched to mineral phases using the Diffraction software (Diffraction, 2013). Another aliquot of each suspension was oven dried at 50 ± 2 °C and then characterized using Toxicity Characteristic Leaching Procedure (TCLP) tests and the European Union BCR-701 extraction procedure (Rauret et al., 1999). Arsenic associated with Al compounds and specifically adsorbed phases were also analyzed in these samples.

Toxicity Characteristic Leaching Procedure analyses were performed in oven-dried samples as described in EPA method 1311 (Usepa, 1990). Bureau Communautaire de Reference analyses were also performed in oven-dried samples, but using discrete extractions with the recommended BCR solutions instead of the sequential procedure. The discrete extraction procedure was evaluated by Baig et al. (2009) and was adopted here to minimize the error caused by sample loss during washing between sequential extractions. Initially, the samples (4 g) were washed two times with 40 mL and then one more time with 20 mL of Milli-Q water in 50 mL centrifuge tubes. After shaking for 2 h at 35 rpm, the suspensions were centrifuged at 3000 rpm for 5 minutes and filtered through 0.45 µm micropore filters. The three aliquots of supernatants were combined and analyzed for As, Fe, Al, and K concentrations by ICP-OES. These washed samples were dried again, and a 0.5 g aliquot was used for BCR extractions. According to the BCR-701 protocol, the phases leached in each extraction are (1) acid leachable with 0.11 mol L⁻¹ acetic acid; (2) easily reducible with 0.1 mol L⁻¹ hydroxylammonium chloride at pH 2.0, and reducible with 0.5 mol L⁻¹ hydroxylammonium chloride at pH 2.0; and (3) oxidizable with 8.8 mol L⁻¹ hydrogen peroxide in a water bath at 85 °C, followed by washing with 1 mol L⁻¹ ammonium acetate. The solid:solution ratio was 1:40, as described by Larios et al. (2012). The BCR 701 is the only reference material certified for sequential leaching analysis; however, this CRM is not certified for As. Therefore, the BCR 701 values for Cd, Cr, Cu, Pb, and Zn were used as a quality check for the acid leachable fraction, whereas the quality of the reducible and oxidizable extractions was checked against Cd and Zn (Table 2).

Arsenic associated with Al (hydr)oxides was extracted from the washed samples using 0.5 mol L⁻¹ NH₄F at pH 8.2 in a 1:60 solid to solution ratio, and the specifically adsorbed As was extracted with 0.5 mol L⁻¹ K₂HPO₄ at pH 8.0 in a 1:80 solid to solution ratio, as described by Larios et al. (2012). These extractions were performed in 50 mL centrifuge Falcon tubes, shaken at 35 rpm for 8 h (specifically adsorbed) or 15 h (associated with Al), centrifuged at 5000 rpm for 15 minutes, and filtered using 0.45 µm micropore filters. Solutions were then prepared for As, Fe, Al, and K analysis by ICP-OES.

RESULTS AND DISCUSSION

Soluble As in equilibrium with precipitates during incubation

Concentrations of soluble As in equilibrium with precipitates synthesized from sulfate salts of Fe and Al decreased drastically in the first day after precipitation (Table 3). In general, all treatments were effective in removing As from the solution, as concentrations were lower than the World Health Organization (WHO) recommended limit of $10 \mu\text{g L}^{-1}$ for drinking water, and even lower than the AFS detection limits ($0.5 \mu\text{g L}^{-1}$). The lower the initial concentration of As in solution was, the faster the decrease to below the $10 \mu\text{g L}^{-1}$ WHO threshold. As little as 24 hours were enough for treatments with the lowest As concentration ($200 \mu\text{g L}^{-1}$), but treatments with the highest As concentration ($5,000 \mu\text{g L}^{-1}$) took more than a week to reach that limit.

In general, the presence of Al decreased the efficiency of the treatment. In contrast, As concentrations in the treatments containing only Fe dropped below the detection limit in less than 24 hours, regardless of the initial As concentration. These results are

Table 2. Quality control for BCR sequential analysis

	As	Cd	Cr	Cu	Pb	Zn
Step 1 - Acid-leaching fraction (0.11 mol L^{-1} acetic acid)						
BCR 701	2.99	7.03	2.31	48.97	2.72	194.95
DL	1.50	0.04	0.05	0.15	0.94	0.04
Certified Value	-	7.30	2.26	49.3	3.18	205
Recovery (%)	-	96.3	102.2	99.3	85.5	95.1
Step 2 - Reducible fraction (0.5 mol L^{-1} hydroxylammonium chloride, pH 2.0)						
BCR 701s	13.41	3.29	nd	nd	nd	98.50
DL (mg kg^{-1})	0.38	0.005	nd	nd	nd	0.03
Certified Value	-	3.77	45.7	124	126	114
Recovery (%)	-	87.3	nd ⁽¹⁾	nd	nd	86.4
Step 3 - Oxidizable fraction (8.8 mol L^{-1} hydrogen peroxide)						
BCR 701s	< DL ⁽²⁾	0.31	nd	nd	nd	43.28
DL (mg kg^{-1})	0.95	0.05	nd	nd	nd	4.89
Certified Value	-	0.27	143	55	9.30	46.00
Recovery (%)	-	114.8	nd	nd	nd	94.1

⁽¹⁾ Not determined. ⁽²⁾ Detection limit of the analytical method.

Table 3. Concentration of As in supernatant solutions in equilibrium with precipitates synthesized from sulfate salts after different aging periods (As measured by AFS)

Fe:Al ratio	Initial As mg L^{-1}	Aging time				
		24 hours	7 days	14 days	21 days	90 days
		$\mu\text{g L}^{-1}$				
1:0.7	5.0	45.94 (7.81) ⁽¹⁾	36.48 (5.16)	<0.5	0.92 (0.33)	<0.5
1:0.3	5.0	88.27 (2.93)	1.66 (0.38)	11.61 (4.63)	<0.5	<0.5
1:0.0	5.0	<0.5 ⁽²⁾	<0.5	6.05 (0.83)	<0.5	<0.5
1:0.7	1.0	6.52 (0.45)	12.52 (2.37)	1.65 (0.76)	<0.5	<0.5
1:0.3	1.0	12.03 (4.77)	0.48 (0.16)	0.97 (0.27)	<0.5	<0.5
1:0.0	1.0	<0.5	<0.5	<0.5	<0.5	<0.5
1:0.7	0.2	1.27 (0.37)	0.97 (0.10)	<0.5	<0.5	<0.5
1:0.3	0.2	3.10 (1.06)	<0.5	<0.5	<0.5	<0.5
1:0.0	0.2	<0.5	<0.5	<0.5	<0.5	<0.5

⁽¹⁾ Numbers between brackets are the two-sigma standard deviation of replicates. ⁽²⁾ The number after the symbol < means the detection limit of the analytical method.

in agreement with previous findings that show that Al is less effective than Fe for the treatment of As-contaminated water (Gulledge and O'Connor, 1973; Scott et al., 1995; Usepa, 2000). Data from Silva et al. (2012) further suggest a weaker As-Al association than the As-Fe association. Treatments with intermediate amounts of Al (Fe:Al ratio of 1:0.3) showed higher As concentrations than the treatments with higher amounts of Al (1:0.7 ratio) 24 hours after precipitation, but this trend was reversed after one week.

Results for the chloride treatments showed the same pattern observed in the sulfate treatments. Regardless of the Fe:Al ratio, the As concentrations decreased to below the detection limit, however, only after 1 month (Table 4). Thus, Fe-Al (hydr)oxides precipitated from chloride salts were also effective in removing As from the solutions. As in sulfate salts, the WHO threshold was also achieved sooner for treatments with lower Al concentrations.

The delay in achieving the WHO As threshold in the presence of Al is ascribed to the relative importance and effectiveness of the adsorption and co-precipitation processes. Considering the formation of bayerite (or gibbsite, in the natural environment) and Al-substituted goethite in the treatment with Fe:Al = 1:0.7, and only Al-substituted goethite in the Fe:Al = 1:0.3 treatment, it appears that the presence of Al initially hinders the incorporation of As in the Fe-(hydr)oxide structure and, therefore, As co-precipitation. However, the As remaining in solution is slowly adsorbed to the surface of the Al-substituted Fe-(hydr)oxides and Al-hydroxides after their formation. Segregation of Al to form a separate Al-rich phase is suggested by SEM elemental mapping (Figure 1) and confirmed by detection of bayerite following X-ray diffraction analysis (Figure 2). Irrespective of the mechanisms and timing of As co-precipitation or adsorption, experimental results show that only magnetite is formed from the precipitation of ferrous salts (both sulfates and chlorides) at high pH in the absence of Al, and that precipitation of magnetite is the most efficient process for rapid removal of As from the solution. In a recent study, Freitas et al. (2016) showed that larger amounts of As are incorporated into Al-magnetite than into Al-goethite. These authors also proposed a mechanism of As entrapment in mesocrystals following its adsorption onto primary nanoparticles. Up to a certain point, the presence of Al would favor this oriented attachment of nanoparticles to immobilize As in Fe(hydr)oxide mesocrystals.

Despite the analytical limitations from the extreme salinity of the solutions, the data clearly show that the concentrations of soluble As decreased to below the detection

Table 4. Concentration of As in supernatant solutions in equilibrium with precipitates synthesized from chloride salts after different aging periods (As measured by ICP-OES)

Fe:Al ratio	Initial As mg L ⁻¹	Aging time					
		03 hours	24 hours	15 days	30 days	60 days	120 days
1:0.7	5.0	52.4 (11.4) ⁽¹⁾	45.4 (3.4)	71.4 (52.6)	111.4 (58.2)	<11.6	<11.6
1:0.3	5.0	<11.6 ⁽²⁾	37.8 (19.4)	<11.6	37.8 (5.2)	<11.6	<11.6
1:0.0	5.0	<11.6	<11.6	<11.6	<11.6	<11.6	<11.6
1:0.7	1.0	28.2 (9.0)	25.6 (0.8)	<11.6	<11.6	<11.6	<11.6
1:0.3	1.0	<11.6	<11.6	<11.6	<11.6	<11.6	<11.6
1:0.0	1.0	<11.6	<11.6	<11.6	<11.6	<11.6	<11.6
1:0.7	0.2	<11.6	<11.6	<11.6	<11.6	<11.6	<11.6
1:0.3	0.2	<11.6	<11.6	<11.6	<11.6	<11.6	<11.6
1:0.0	0.2	<11.6	<11.6	<11.6	<11.6	<11.6	<11.6

⁽¹⁾ Numbers between brackets are the two-sigma standard deviation of replicates. ⁽²⁾ The number after the symbol < means the detection limit of the analytical method.

limit after one month. The experiment with chlorides was kept for a longer time in order to evaluate the stability of the precipitated solids. These apparently remained stable even after 4 months, as the soluble As concentration in solution remained lower than the ICP-OES detection limit (Table 4). In terms of compliance with drinking water regulations, the ICP-OES results are inconclusive because their detection limit is slightly higher than the interim value of $10 \mu\text{g L}^{-1}$ set by WHO (2004). The AFS results for sulfates, however, were fully compliant with WHO drinking water guidelines ($<0.5 \mu\text{g L}^{-1}$).

TCLP test of the precipitates

The precipitated material was dried at $50 \text{ }^\circ\text{C}$ after siphoning, and the soluble phases remaining in solution after siphoning precipitated as the solution was drying out. This procedure is equivalent to the process commonly used to dry out the solid sludge in water treatment plants. The sludge can be classified as a waste and its toxicity can be evaluated using TCLP EPA Method 1311. Although the initial pH of the suspensions was high ($\text{pH} \approx 11$), the solution used for the extraction was glacial acetic acid ($\text{pH} 4.98$) as that pH was not buffered and had dropped to below 5.0 after addition of 1 mol L^{-1} HCl.

Results show that the leached As was below the ICP-OES detection limit (Table 5), and all the precipitates can thus be considered as “non-toxic” regardless of the initial concentration of As and the Fe:Al ratio. Iron concentrations were higher in the treatments with no added Al. Considering that only magnetite was formed in the treatment without Al (Figure 2), this result can be ascribed to the higher solubility of magnetite compared to goethite. Equilibrium constants for dissolution reactions of Fe-(hydr)oxides predict higher Fe activities in solutions in equilibrium with magnetite compared to goethite (Lindsay, 1979), and this is consistent with the results presented in table 5. As was noted for As, the leaching of Fe and Al does not pose any environmental concerns as the concentrations for both in the TCLP tests were in the parts per billion range.

Concentrations of K and S in the TCLP leachates were higher than those of Fe and Al, suggesting the precipitation of soluble K and S salts as the suspensions were drying out. The concentrations of both K and S seemed to decrease with increasing Fe:Al ratios, but this is likely a consequence of larger amounts of water remaining in the suspensions richer in Al after siphoning, due to the higher density of magnetite compared to goethite. It probably has no meaning in terms of mineralogy of the precipitates. High concentrations of K and S soluble salts can be problematic and may require treatment to be released in the environment.

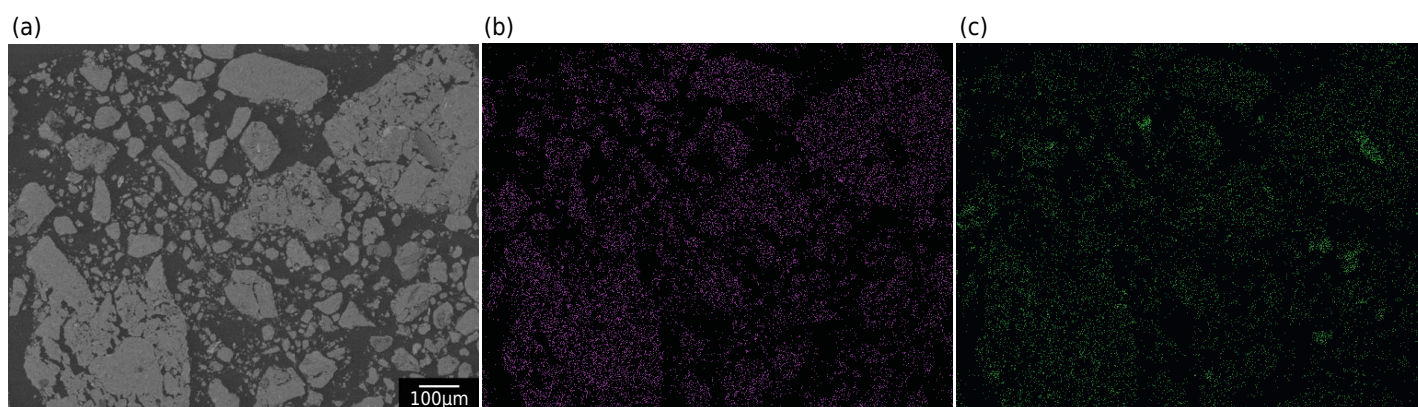


Figure 1. Scanning electron microscopy images of minerals synthesized from treatment 1 (Table 1) using sulfate salts. (a) backscattered electron image, showing aggregates of goethite (light gray) with a small number of Al-rich aggregates (dark gray), interpreted as bayerite $[\text{Al}(\text{OH})_3]$; (b) Fe elemental map; and (c) Al elemental map of the backscattered image shown in (a). Note the homogeneous distribution of Al across the goethite aggregates

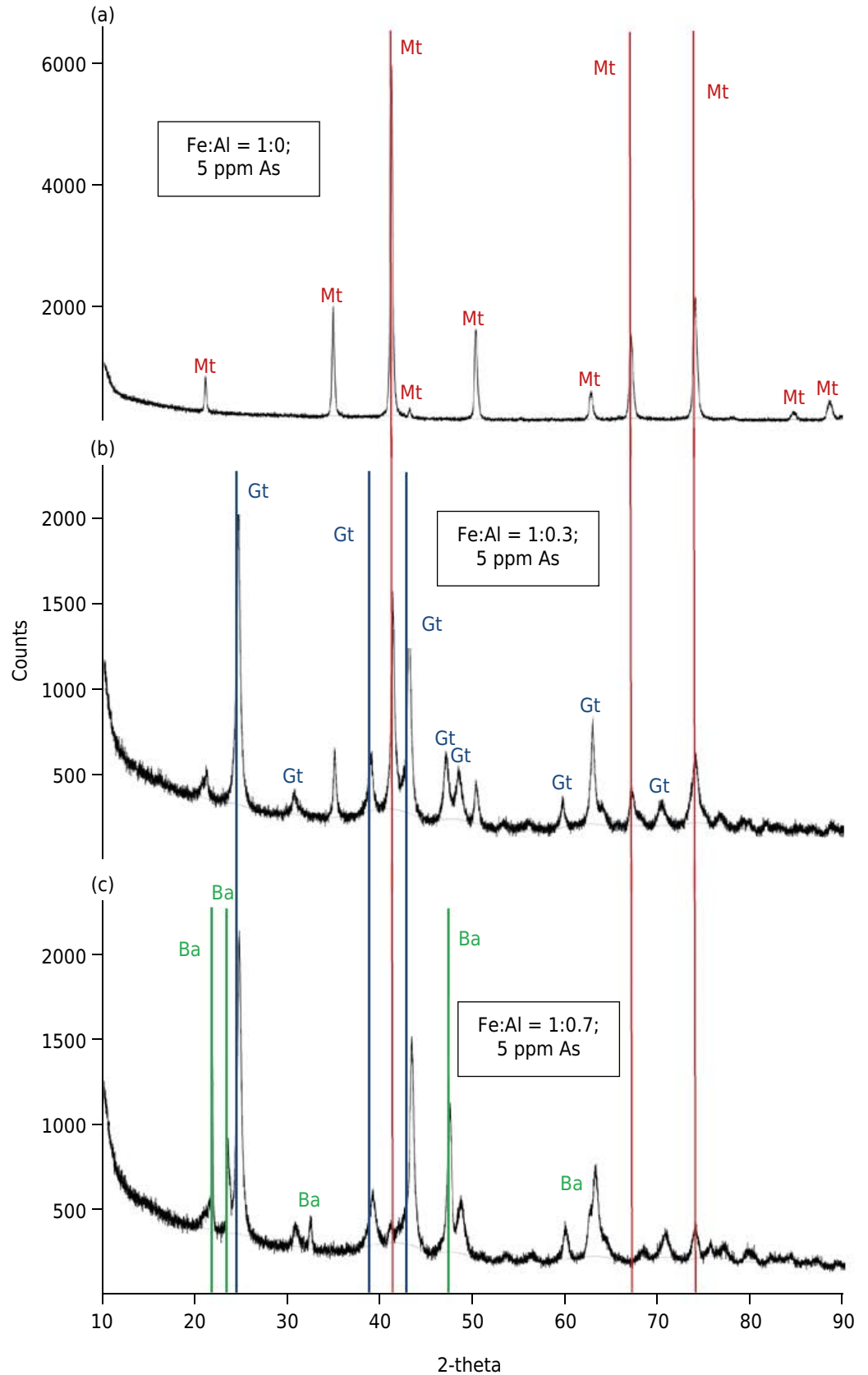


Figure 2. X-ray diffractograms of samples synthesized from sulfate salts with (a) Fe:Al = 1:0 and 5 ppm As (magnetite only); (b) Fe:Al = 1:0.3 and 5 ppm As (goethite and magnetite); and (c) Fe:Al = 1:0.7 and 5 ppm As (goethite and bayerite with traces of magnetite). Mt = magnetite; Gt = goethite; Ba = bayerite. The three strongest lines for each mineral have been marked with a continuous line. Note the slight shift in the goethite spectra relative to “pure” goethite, which is attributed to the presence of Al in the goethite structure

Table 5. Concentrations of As, Al, Fe, K, and S leached by the acetic acid solution after the TCLP test, quantified by ICP-OES

Fe:Al ratio	Initial [As]	As	Al	Fe	K	S
	mg L ⁻¹	µg L ⁻¹			mg L ⁻¹	
Experiments with sulfates						
1:0.7	5.0	<14.5 ⁽¹⁾	35.3 (18.9) ⁽²⁾	56.7 (28.5)	6990 (1825)	1937 (660)
1:0.3	5.0	<14.5	22.2 (5.4)	43.7 (14.1)	5380 (700)	1422 (165)
1:0.0	5.0	<14.5	<5.6	75.3 (70.4)	1633 (315)	439 (140)
1:0.7	1.0	<14.5	29.8 (9.8)	63.3 (15.5)	6079 (320)	1615 (224)
1:0.3	1.0	<14.5	32.3 (0.1)	66.1 (9.3)	3902 (639)	1194 (305)
1:0.0	1.0	<14.5	<5.6	219.4 (15.3)	731 (125)	221 (1.4)
1:0.7	0.2	<14.5	31.5 (24.3)	69.2 (51.8)	5228 (424)	1412 (93)
1:0.3	0.2	<14.5	44.1 (19.4)	47.9 (6.8)	4420 (404)	1387 (174)
1:0.0	0.2	<14.5	<5.6	110.0 (113.1)	2456 (1657)	623 (346)
Experiments with chlorides						
1:0.7	5.0	<14.5	22.6 (4.0)	28.5 (10.8)	2700 (478)	<4.0
1:0.3	5.0	<14.5	32.7 (6.1)	53.1 (13.8)	2779 (250)	<4.0
1:0.0	5.0	<14.5	<5.6	60.7 (10.6)	1797 (3.5)	<4.0
1:0.7	1.0	<14.5	31.9 (3.4)	51.2 (4.7)	2923 (74)	<4.0
1:0.3	1.0	<14.5	27.3 (11.5)	55.2 (28.2)	2008 (1107)	<4.0
1:0.0	1.0	15.0 (0.7)	<5.6	58.5 (9.0)	2068 (40)	<4.0
1:0.7	0.2	<14.5	22.3 (2.2)	39.1 (3.6)	2919 (1003)	<4.0
1:0.3	0.2	<14.5	25.9 (13.6)	52.8 (42.8)	2602 (7.8)	<4.0
1:0.0	0.2	<14.5	<5.6	56.4 (2.5)	2112 (179)	<4.0

⁽¹⁾ The number after the symbol < means the detection limit of the analytical method. ⁽²⁾ Numbers between brackets are the two-sigma standard deviation of replicates.

BCR analysis of the precipitates

The results for the wash solutions prior to BCR extraction were consistent with those obtained in the TCLP procedure. Arsenic was not detected in this fraction, but Al and Fe were detected in very low concentrations (Table 6), and S was present in relatively high concentrations only in the experiment with sulfates (data not shown). Potassium contents are not reported, but K was also present in high concentrations, reflecting the high salinity of the precipitates, as previously reported.

Analysis following the BCR discrete extractions showed As concentrations below the detection limits (Table 7), implying that the residues are stable under acidic or reducing conditions. The amounts of Al and Fe released in the acid-leaching and reducible fractions were in general lower in the experiments with sulfates than in the experiments with synthesis with chlorides. These results suggest that sulfate salts should preferably be used to obtain a more stable product in water treatment plants. The exceptions to this general trend were the Fe contents in reducible fractions in the absence of Al. In this case, Fe contents trended to be higher in the synthesis with sulfates with the 1:0 Fe:Al ratio. This observation implies that sulfate salts will produce more stable muds when Al is present or added in the treatment of As contaminated water.

It is important to examine the results obtained in this study from a practical perspective for wastewater treatment. Sulfates are always present in AMD water, as they are the direct consequence of sulfide oxidation. As the Fe-(hydr)oxides precipitated from sulfate solutions seem to be more stable in the presence of Al, perhaps the precipitation of Al-free magnetite should be prevented either by the addition of Al or by promoting Fe oxidation before its precipitation in treatment of AMD water. On the other hand, as discussed earlier, Al-magnetites seem to immobilize a larger amount of As than Al-goethites or Al-free magnetite (Freitas et al., 2016), and have the obvious advantages of magnetic properties in separation of As-bearing sludges.

Table 6. Concentrations of soluble As, Al, and Fe in the precipitates prior to BCR extractions, quantified by ICP-OES. Data calculated from values measured in the leached solutions (Milli-Q water) and taking into account the precipitate/solution ratio

Fe:Al ratio	Initial [As] mg L ⁻¹	Experiments with chlorides			Experiments with sulfates		
		As	Al	Fe	As	Al	Fe
1:0.7	5.0	<0.74 ⁽¹⁾	8.25 (3.36) ⁽²⁾	1.20 (0.61)	<0.74	4.70 (0.25)	2.70 (0.50)
1:0.3	5.0	<0.74	7.75 (0.76)	1.75 (0.07)	<0.74	5.10 (0.25)	4.45 (1.75)
1:0.0	5.0	<0.74	1.45 (0.18)	1.15 (0.38)	<0.74	1.45 (0.70)	5.15 (1.92)
1:0.7	1.0	<0.74	8.30 (3.97)	1.85 (0.52)	<0.74	6.80 (0.28)	2.35 (0.11)
1:0.3	1.0	<0.74	4.05 (0.52)	1.75 (0.97)	<0.74	4.05 (2.63)	1.30 (0.62)
1:0.0	1.0	<0.74	1.00 (0.33)	1.40 (0.11)	<0.74	0.25 (0.01)	3.50 (0.69)
1:0.7	0.2	<0.74	6.80 (0.71)	1.50 (0.28)	<0.74	4.85 (1.18)	2.25 (0.84)
1:0.3	0.2	<0.74	7.75 (3.03)	1.30 (0.74)	<0.74	1.95 (0.26)	1.45 (0.15)
1:0.0	0.2	<0.74	1.25 (0.21)	1.65 (0.53)	<0.74	1.65 (0.17)	2.75 (0.71)

⁽¹⁾ The number after the symbol < means the detection limit of the analytical method. ⁽²⁾ Numbers between brackets are the two-sigma standard deviation of replicates.

Some As was detected in the oxidizable fraction, but only in the treatments with Al and for high initial As concentrations (Table 7). In the experiments with sulfates, it could be argued that As may be associated with reduced ferrous compounds or sulfides, due to the use of ferrous sulfates in the synthesis and low redox potentials measured at the beginning of the incubation period (data not shown). This hypothesis, however, does not account for the presence of As also in the experiments with chlorides, and the amounts of Fe extracted from this fraction were very low and not correlated with the extracted As (concentrations of both were very low, and Al was not even detected). Irrespective of the process responsible for detection of As, its concentrations were extremely low and represented only an insignificant amount (less than 0.5 %) of the total As load.

Despite the procedural and analytical uncertainties, the amounts of acid leachable As were very low compared to the total As amounts calculated in the solids based on the experimental conditions (Table 8). The actual concentrations of As extracted could not be measured accurately because all were below detection limits in all experiments and for all initial Fe/Al ratios and As contents in solution (with two exceptions - see Table 7). Even assuming As concentrations as high as detection limits, the acid leachable As ranged from 7.84 % (synthesis with sulfates, 1:0.7 Fe:Al ratio and 0.2 mg L⁻¹ initial As load) to 0.12 % (synthesis with sulfates, 1:0.0 Fe:Al ratio and 5 mg L⁻¹ initial As load). Therefore, the amounts of As potentially mobile under the range of conditions that can reasonably be expected in the natural environment are low, and the precipitates can be considered safe for disposal.

Arsenic associated with Al and specifically adsorbed onto precipitated phases

In spite of extracting considerable amounts of Al, no As was detected in the NH₄F extracts (Table 9). In contrast, K₂HPO₄ extracted significant amounts of As from precipitates containing Al at medium to high As (1 and 5 mg/L initial As, respectively), but virtually no As was detected in precipitates containing only Fe, even with the highest As load. Higher adsorption of As in the presence of Al can be explained by smaller size, and so larger surface area, as suggested by broadening of the Al-goethites peaks relative to well crystalized magnetite in diffractograms (Figure 2). These findings also corroborate those of Silva et al. (2012), who observed that Al-As binding is weaker than Fe-As binding, as phosphate was more efficient in removing As bound to matrices that contain structural Al. This suggests that while most of the As is co-precipitated with pure Fe-(hydr)oxides, small amounts can also be specifically adsorbed onto the Al-Fe-(hydr)oxides (typically less than 4 % of the total As), possibly following the oriented attachment growth process described by Freitas et al. (2015). Results of the NH₄F extracts also indicate that there is no As co-precipitated with Al compounds.

Table 7. Content of As, Al, and Fe in the precipitates leached using the BCR discrete extraction solutions, quantified by ICP-OES. Data calculated from values measured in the leachates and taking into account the precipitate/leachate ratio

Fe:Al ratio	Initial [As] mg L ⁻¹	Experiments with chlorides			Experiments with sulfates		
		As	Al	Fe	As	Al	Fe
mg kg ⁻¹							
Acid leached fraction ⁽¹⁾							
1:0.7	5.0	<1.5 ⁽²⁾	770 (92) ⁽³⁾	9.5 (2.2)	<1.5	264 (16)	24 (1.4)
1:0.3	5.0	<1.5	717 (76)	49 (18)	<1.5	284 (29)	7.6 (2.4)
1:0.0	5.0	<1.5	<2.37	654 (38)	<1.5	<2.37	415 (41)
1:0.7	1.0	<1.5	696 (39)	12 (1.5)	<1.5	257 (5)	2.9 (0.1)
1:0.3	1.0	<1.5	724 (17)	73 (49)	<1.5	330 (12)	8.0 (0.1)
1:0.0	1.0	<1.5	<2.37	711 (60)	<1.5	<2.37	300 (37)
1:0.7	0.2	<1.5	803 (47)	82 (97)	<1.5	235 (5)	2.4 (0.9)
1:0.3	0.2	<1.5	660 (54)	67 (29)	<1.5	460 (109)	9.1 (5.7)
1:0.0	0.2	<1.5	<2.37	671 (110)	<1.5	<2.37	604 (410)
Easily reducible fraction ⁽⁴⁾							
1:0.7	5.0	<0.36	254 (81)	2664 (291)	<0.36	13 (1.6)	880 (7)
1:0.3	5.0	<0.36	250 (79)	3665 (42)	<0.36	24 (11)	1236 (301)
1:0.0	5.0	<0.36	<3.2	6499 (132)	<0.36	<3.2	7186 (106)
1:0.7	1.0	<0.36	196 (96)	2357 (230)	<0.36	11 (1)	827 (47)
1:0.3	1.0	<0.36	367 (114)	3387 (298)	<0.36	26 (9)	1106 (63)
1:0.0	1.0	<0.36	<3.2	5934 (27)	<0.36	<3.2	6883 (34)
1:0.7	0.2	<0.36	179 (39)	2347 (84)	<0.36	16 (4)	856 (43)
1:0.3	0.2	<0.36	327 (186)	3970 (628)	<0.36	82 (75)	1421 (582)
1:0.0	0.2	<0.36	<3.2	6031 (49)	<0.36	34 (47)	6273 (235)
Reducible fraction ⁽⁵⁾							
1:0.7	5.0	<0.38	551 (32)	4773 (316)	<0.38	207 (30)	3278 (324)
1:0.3	5.0	<0.38	511 (26)	5909 (321)	<0.38	203 (23)	3237 (313)
1:0.0	5.0	<0.38	20 (27)	9358 (19)	<0.38	3 (0.56)	9877 (532)
1:0.7	1.0	<0.38	486 (4)	4049 (851)	<0.38	183 (2)	3319 (95)
1:0.3	1.0	<0.38	569 (72)	5629 (326)	<0.38	220 (29)	2942 (55)
1:0.0	1.0	<0.38	<1.92	8306 (347)	<0.38	3 (0.56)	9878 (190)
1:0.7	0.2	<0.38	470 (44)	4511 (278)	<0.38	182 (26)	2851 (28)
1:0.3	0.2	<0.38	534 (118)	6266 (706)	<0.38	380 (215)	3260 (381)
1:0.0	0.2	<0.38	<1.92	8997 (55)	<0.38	3 (0.56)	9177 (932)
Oxidizable fraction ⁽⁶⁾							
1:0.7	5.0	1.77 (0.31)	<0.45	0.28 (0.18)	2.00 (1.06)	<0.45	0.36 (0.07)
1:0.3	5.0	1.12 (0.03)	<0.45	0.53 (0.16)	<0.95	<0.45	0.51 (0.20)
1:0.0	5.0	<0.95	<0.45	0.29 (0.05)	<0.95	<0.45	0.49 (0.13)
1:0.7	1.0	<0.95	<0.45	0.38 (0.02)	1.04 (0.04)	<0.45	0.43 (0.12)
1:0.3	1.0	<0.95	<0.45	0.35 (0.10)	<0.95	<0.45	0.48 (0.04)
1:0.0	1.0	<0.95	<0.45	0.27 (0.04)	<0.95	<0.45	0.57 (0.01)
1:0.7	0.2	<0.95	<0.45	0.40 (0.13)	<0.95	<0.45	0.47 (0.27)
1:0.3	0.2	<0.95	<0.45	0.49 (0.01)	<0.95	<0.45	0.69 (0.07)
1:0.0	0.2	<0.95	<0.45	0.35 (0.12)	<0.95	<0.45	0.61 (0.05)

⁽¹⁾ Extracted by 0.11 mol L⁻¹ acetic acid; solid to solution ratio = 1:40. ⁽²⁾ Numbers between brackets are the two-sigma standard deviation of replicates.

⁽³⁾ The number after the symbol < means the detection limit of the analytical method. ⁽⁴⁾ Extracted by 0.1 mol L⁻¹ hydroxylammonium chloride, pH 2.0; solid to solution ratio = 1:40. ⁽⁵⁾ Extracted by 0.5 mol L⁻¹ hydroxylammonium chloride, pH 2.0; solid to solution ratio = 1:40. ⁽⁶⁾ Extracted by 8.8 mol L⁻¹ hydrogen peroxide digestion.

Table 8. Proportions of As (relative to theoretical total As concentrations in the precipitates) extracted by the different BCR solutions calculated from As detection limits

Fe:Al ratio	Initial [As] mg L ⁻¹	Recovered weight g	Theoretical As content mg kg ⁻¹	Fraction				
				Soluble ⁽¹⁾	Acid leachable ⁽²⁾	Easily reducible ⁽³⁾	Reducible ⁽⁴⁾	Oxidizable ⁽⁵⁾
				% As				
Experiment with sulfates								
1:0.7	5.0	44.51	449.46	0.16	0.33	0.08	0.08	0.21
1:0.3	5.0	30.56	654.66	0.11	0.23	0.05	0.06	0.14
1:0.0	5.0	16.43	1217.52	0.06	0.12	0.03	0.03	0.08
1:0.7	1.0	43.16	92.75	0.80	1.62	0.39	0.41	1.02
1:0.3	1.0	30.32	132.07	0.56	1.14	0.27	0.29	0.72
1:0.0	1.0	16.14	247.84	0.30	0.61	0.14	0.15	0.38
1:0.7	0.2	41.68	19.13	3.86	7.84	1.88	1.99	4.97
1:0.3	0.2	32.86	24.35	3.04	6.16	1.48	1.56	3.90
1:0.0	0.2	18.04	44.63	1.66	3.36	0.81	0.85	2.13
Experiment with chlorides								
1:0.7	5.0	32.91	607.75	0.12	0.25	0.06	0.06	0.16
1:0.3	5.0	25.02	799.42	0.09	0.19	0.04	0.05	0.12
1:0.0	5.0	16.97	1178.90	0.06	0.13	0.03	0.03	0.08
1:0.7	1.0	33.81	118.34	0.63	1.27	0.30	0.32	0.80
1:0.3	1.0	24.19	165.36	0.45	0.91	0.22	0.23	0.57
1:0.0	1.0	17.31	231.10	0.32	0.65	0.16	0.16	0.41
1:0.7	0.2	33.97	23.55	3.14	6.37	1.53	1.61	4.03
1:0.3	0.2	23.61	33.89	2.18	4.43	1.06	1.12	2.80
1:0.0	0.2	16.99	47.11	1.57	3.18	0.76	0.81	2.02

⁽¹⁾ Extracted by water. ⁽²⁾ Extracted by 0.11 mol L⁻¹ acetic acid; solid to solution ratio = 1:40. ⁽³⁾ Extracted by 0.1 mol L⁻¹ hydroxylammonium chloride, pH 2.0; solid to solution ratio = 1:40. ⁽⁴⁾ Extracted by 0.5 mol L⁻¹ hydroxylammonium chloride, pH 2.0; solid to solution ratio = 1:40. ⁽⁵⁾ Extracted by 8.8 mol L⁻¹ hydrogen peroxide digestion.

According to Silva et al. (2010), structural Al in Fe(hydr)oxides increases As adsorption capacity and the stability of the adsorbed As under reducing conditions. In contrast, the results of this study indicate that the presence of Al in solution reduces the efficiency of water treatment. It has a negative impact on the chemical stability of the precipitated sludge and on its ability to retain As under natural environmental conditions. These contrasting results may be due to the insufficient time for complete crystal aggregation in the experiments described in this study. The different conclusions may also be due to the fact that As was added to already formed Fe-Al-(hydr)oxides under oxidizing conditions in order to assess adsorption in the experiments carried out by Silva et al. (2010). In contrast, As was co-precipitated with the Fe-Al-(hydr)oxides under reducing conditions in this study. Silva et al. (2010) evaluated the stability of As adsorbed onto the Fe-Al-(hydr)oxides at As loads of about 30,000 mg kg⁻¹, whereas the As concentrations in the Al-goethites synthesized in this study reached a maximum of about 600 mg kg⁻¹. Thus, it is conceivable that the As levels considered in Silva et al. (2010) may have been sufficiently high to cause significant differences between the two studies in the solution chemistry and in the surface properties of the Fe-Al-(hydr)oxides. From a management perspective, however, the As loads and adsorption/co-precipitation processes explored in this study are more realistic for mine sites impacted by As-rich AMD water.

Table 9. Concentrations of As, Al, and Fe extracted from precipitates by potassium phosphate and ammonium fluoride, quantified by ICP-OES. Data calculated from values measured in the leachates and taking into account the precipitate/leachate ratio

Fe:Al ratio	Initial As mg L ⁻¹	Experiments with chlorides			Experiments with sulfates		
		As	Al	Fe	As	Al	Fe
Specifically adsorbed As							
1:0.7	5.0	26.16 (1.69) ⁽¹⁾	15.68 (6.79)	4.41 (1.13)	18.64 (2.72)	4.14 (0.91)	2.99 (0.30)
1:0.3	5.0	15.45 (1.30)	8.59 (7.15)	2.74 (0.29)	2.52 (0.84)	<1.25	2.05 (3.19)
1:0.0	5.0	<0.83 ⁽²⁾	<1.25	<0.12	<0.83	<.25	1.75 (5.50)
1:0.7	1.0	3.00 (0.07)	14.29 (6.30)	6.46 (6.02)	3.15 (0.40)	<1.25	2.09 (2.27)
1:0.3	1.0	<0.83	5.08 (2.72)	1.18 (0.75)	<0.83	<1.25	1.14 (1.82)
1:0.0	1.0	<0.83	<1.25	<0.12	<0.83	<1.25	<0.12
1:0.7	0.2	<0.83	12.41 (4.65)	3.26 (0.26)	<0.83	<1.25	<0.12
1:0.3	0.2	<0.83	16.54 (6.28)	6.47 (4.21)	<0.83	15.09 (25.94)	<0.12
1:0.0	0.2	<0.83	<1.25	<0.12	<0.83	<1.25	<0.12
As associated with Al compounds							
1:0.7	5.0	<0.92	189 (37.4)		<0.92	183 (24.0)	
1:0.3	5.0	<0.92	148 (0.7)		<0.92	183 (11.8)	
1:0.0	5.0	<0.92	<3.85		<0.92	<3.85	
1:0.7	1.0	<0.92	176 (21.0)		<0.92	183 (2.2)	
1:0.3	1.0	<0.92	141 (8.5)		<0.92	137 (6.8)	
1:0.0	1.0	<0.92	<3.85		<0.92	<3.85	
1:0.7	0.2	<0.92	145 (60.3)		<0.92	166 (12.7)	
1:0.3	0.2	<0.92	165 (15.8)		<0.92	163 (12.0)	
1:0.0	0.2	<0.92	<3.85		<0.92	<3.85	

⁽¹⁾ Numbers between brackets are the two-sigma standard deviation of replicates. ⁽²⁾ The number after the symbol < means the detection limit of the analytical method.

CONCLUSIONS

This study demonstrated the role of Fe and Al in treating As residual water by the co-precipitation process. Despite the delay in decreasing the As concentrations to below 10 µg L⁻¹, due to the presence of soluble Al, all treatments were effective in cleaning water contaminated with up to 5 mg L⁻¹ of As by precipitation of Al-Fe (hydr)oxides at high pH. The sludge resulting from this process was classified as “nontoxic” waste according to the TCLP procedure, regardless of the initial As concentration or Fe:Al ratio. In addition, this material was not an environmental concern since the As remained stable under both acidic and reducing conditions according to the BCR procedure.

Bayerite and Al-substituted goethite were detected in precipitates at a higher Fe:Al ratio. Yet, Al-substituted goethite and magnetite were detected at 1:0.3 Fe:Al molar ratio and, in the absence of Al, only magnetite was detected.

In general, there were no noticeable differences in the effectiveness of the treatments using chloride or sulfate salts; however, lower amounts of Al and Fe released in the acid-leaching and reducible fractions suggest that sulfate salts should preferably be used to obtain a more stable product in water treatment plants.

This study also provides useful information for remediation of As-contaminated water. Our data demonstrated that precipitates containing Al hydroxides and Al-substituted goethite act as an effective sink for As, including adsorption, but no specifically adsorbed As was recovered from precipitates containing only magnetite. Furthermore, As did not co-precipitate with Al compounds. These findings imply that the presence of Al in the AMD solution reduces the efficiency of the water treatment; it limits the chemical stability of the precipitated sludge and, hence, limits its ability to retain adsorbed and co-precipitated As under natural conditions.

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