Sequestration of As and Mo in uranium mill precipitates (pH 1.5–9.2): An XAS study

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Article info

Article history:
Received 1 November 2015
Received in revised form 15 June 2016
Accepted 22 June 2016
Available online 23 June 2016

Keywords:
Uranium milling
Precipitates
Arsenic
Molybdenum
Tailings
XAS

Abstract

As- and Mo-bearing secondary mineral phases formed during the neutralization of uranium mill wastes require characterization. Previous studies indicate that ferrihydrite and scorodite are the dominant controls in the tailings materials. A lab-scale plant was employed to characterize secondary precipitates from a variety of ore blends. Through total elemental analysis of precipitates and As and Mo K-edge X-ray absorption spectroscopy, different ratios of contributing phases were determined for each pH stage (4.2, 6.5, and 9.2) of the neutralization process. Overall, arsenate adsorbed to ferrihydrite was the dominant As mineral phase regardless of pH or sample blend (53–77%), with fractional contribution from ferric arsenates, and adsorption to aluminum phases. Molybdate adsorbed to ferrihydrite was the dominant Mo mineral phase, with fractional contribution decreasing with increasing pH (100–69%). The characterization of these phases in the secondary precipitates provides further understanding of the contributing mineral species in tailing facilities.

1. Introduction

Arsenic (As) and molybdenum (Mo) are naturally occurring elements. However, when present at elevated concentrations in groundwater and surface waters, both can be hazardous to human health. As a result, regulatory limits and guidelines have been established for drinking water (Mo = 70 µg/L, As = 10 µg/L; WHO, 1993a, 1993b), the protection of aquatic life in freshwater (Mo = 73 µg/L, As = 5 µg/L; CCME, 1997, 1999a, 1999b, 2007), and freshwater quality (chronic As = 150 µg/L, acute As = 340 µg/L; US EPA, 1995). Natural water quality criteria have not been published for Mo by the US EPA due to rare occurrences of elevated concentrations, though a groundwater standard for inactive uranium sites has been proposed (Mo = 100 µg/L; US EPA, 1987).

A significant anthropogenic source of As and Mo contamination in surface and ground waters is tailings generated by mining (Donahue et al., 2000; Cutler et al., 2003; Paktunc et al., 2003, 2004; Wang and Mulligan, 2006; Heinrich et al., 2010; Shaw et al., 2011; Adra et al., 2013; Blanchard et al., 2015). Uranium (U) ores mined in northern Saskatchewan, Canada from deposits such as Cigar Lake, McClean Lake, Rabbit Lake, McArthur River, and Key Lake often contain elevated concentrations of As and Mo (Langmuir et al., 1999, 2006; Cutler et al., 2003; Mahoney et al., 2005, 2007; Jia et al., 2005, 2006; Chen et al., 2009). Arsenate (As\(^{3+}\)) adsorbed to ferrihydrite controls As in the solid phase when co-precipitated in a four stage (pH 4.2, 6.5, 9.2, and 11) rapid and continuous bulk neutralization circuit at high Fe/As ratios (Fe/As > 5) with shorter settling
times (<30 min) (Pichler et al., 2001; Moldovan et al., 2003, 2008; Moldovan and Hendry, 2005; Essilfie-Dughan et al., 2012). Important distinguishing characteristics between these two As sequestration mechanisms include the Fe/As molar ratio, pH, and retention times (Moldovan et al., 2003; Twidwell et al., 2005; Jia et al., 2007; Mahoney et al., 2007). Though neutralization techniques are similar, the differences in sequestration mechanisms may account for the variety of As-bearing mineral phases formed. Ferric arsenate forms at acidic pH values (pH 2–4). It has been reported as surface precipitates on ferrihydrite (Jia et al., 2006, 2007; Moldovan and Hendry, 2005) and have been postulated to be a small polymer of single chains of corner-sharing Fe(OH)₆ octahedra with bridging arsenate tetrahedral alternating along the chains (Paktunc et al., 2008). In contrast, scorodite is characterized by a highly symmetrical local structure made of four Fe³⁺ octahedrally coordinated around an arsenate tetrahedron (Foster, 2003; Chen et al., 2009; Essilfie-Dughan et al., 2013). For Fe/As ratios about 3–4 and pH 3–5, mixtures of poorly crystalline ferric arsenate and ferrihydrite are reported to co-exist. As the molar ratios increase above 4, however, the major phase becomes ferrihydrite with arsenate adsorbed to the surface (Jia et al., 2006; Paktunc et al., 2008). In continuous synthesis experiments, Paktunc et al. (2008) observed variable mixtures of Fe₃(AsO₄)₂(PO₄)·(OH)₄. Ferric arsenate formed with the proportion of ferrihydrite increasing with either time or increased Fe/As ratio and at the expense of ferric arsenate. Ferrihydrite begins to form above pH 3 with the optimal pH range for arsenate adsorption between pH 4 and 6; this is most effective at Fe/As molar ratios ≥ 4–7 (Dixit and Hering, 2003; Moldovan and Hendry, 2005; Twidwell et al., 2005). Ferric arsenate is reported to dissolve in the same pH range (>pH 4.5) releasing FeO₆ octahedra that will rapidly polymerize to form ferrihydrite (Paktunc et al., 2008). The local structure of arsenate adsorbed on ferrihydrite is described as bidentate binuclear bridging, where the arsenate tetrahedron is connected to edge sharing Fe⁶⁺ octahedra (Waychunas et al., 1993; Foster, 2003; Moldovan et al., 2003; Chen et al., 2009; Essilfie-Dughan et al., 2013). Co-precipitated anions that adsorb to the surface (AsO₄³⁻, MoO₄²⁻, Al(OH)₄⁻) may disrupt the growth of ferrihydrite into more extended structures such as goethite and hematite (Waychunas et al., 1993; Ford, 2002; Twidwell et al., 2005; Jia et al., 2007).

Because of the strong absorption of As by iron oxyhydroxides (e.g. ferrihydrite, hematite, and goethite) in most environmental systems, many studies have characterized these arsenic-iron phases under various environmental conditions (Willie and Hering, 1996; Ford, 2002; Dixit and Hering, 2003; Twidwell et al., 2005; Waychunas et al., 2005; Fukushima and Sverjensky, 2007; Fritzsche et al., 2011; Gomez et al., 2013b; Das et al., 2014a, 2014b). In the U mining industry, X-ray absorption spectroscopy (XAS) studies of As in tailings from the Key Lake Deilmann tailings management facility (DTMF) and the Rabbit Lake in-pit tailings management facility (RLITMF) at Cameco’s northern Saskatchewan mining operations show that the As is predominantly adsorbed to ferrihydrite through inner-sphere bidentate linkages (Moldovan et al., 2003; Essilfie-Dughan et al., 2013). Results from sequential extraction experiments performed on DTMF samples in conjunction with thermodynamic modeling support conclusions that ferrihydrite is the dominant solubility control on aqueous As concentrations (Shaw et al., 2011). Similar studies on tailings at the McClean Lake tailings management facility observed As associated as a mixture of amorphous ferric arsenates and arsenates adsorbed onto ferrihydrite (Cutler et al., 2003; Mahoney et al., 2007). The apparent differences in literature led to the current study’s objectives to identify mineral phases formed during the neutralization of mill wastes, before combination into final tailings. Many factors may account for this difference, such as ore materials, reagents or kinetic factors (time, temperature, settling times). Additionally, both ferric arsenate and arsenate adsorbed to ferrihydrite may be contributing to the tailings material in a heterogeneous mixture, as described by Paktunc et al. (2008) in continuous neutralization experiments.

Ferrihydrite has also been shown to also play a significant role in controlling the solubility of other EOCs such as Mo, Se and Ni in the DTMF (Shaw et al., 2011; Essilfie-Dughan et al., 2012; Gomez et al., 2013a) due to its high sorption capacities for metal and anion contaminants (Stipp et al., 2002; Waychunas et al., 2005). However, a XAS study of Mo in the DTMF identified NiMoO₄ and powellite (CaMoO₄) in addition to Mo adsorbed onto ferrihydrite as phases responsible for solubility control of Mo in the tailings (Essilfie-Dughan et al., 2011). Another recent XAS study of Mo in uranium tailings at McClean Lake found ferrimolybdate (Fe₂(MoO₄)₃·8H₂O) in addition to CaMoO₄ and Mo adsorbed to ferrihydrite to be the major Mo-bearing phases in the tailings management facility (Hayes et al., 2014).

Recently, adsorption to amorphous aluminum hydroxides and hydrotalcite-like layered double hydroxides (HT-LDHs) has been identified as solubility controls on anions (such as AsO₄³⁻ and MoO₄²⁻) in solution (Arai et al., 2001; Goldberg, 2002; Paikaray et al., 2013) with possible applications to U mill wastes (Gomez et al., 2013a; Robertson et al., 2016a). Greater uptake affinities have been reported for As than Mo when precipitated with both MgFe₂SO₄·Mo₄Al₂CO₃·hydrotalcites (HTLCs) over the pH range 6–8 (Paikaray and Hendry, 2013; Paikaray et al., 2013). Amorphous aluminum hydroxides which precipitate over a pH range of 5–9 adsors oxyanions such as arsenates beginning at pH 5; with maximum loading reported to occur between pH 7 and 8 (Arai et al., 2001; Goldberg, 2002; Moldovan and Hendry, 2005). Thus, these Al phases would have the greatest impact on the sequestration EOCs at high pH values (pH 6–10).

Although the occurrence of EOCs (As and Mo) in the DTMF are well characterized (Shaw et al., 2011; Essilfie-Dughan et al., 2011, 2013; Gomez et al., 2013a), the evolution of secondary mineral phases which controls the solubility of the EOCs during the progressive neutralization of raffinate wastes remains poorly understood. To date, studies by Robertson et al. (2014, 2016a), De Klerk et al. (2012), and De Klerk (2008) have characterized the evolution of As and Mo within lab-scale U mill neutralization circuits. Robertson et al. (2014, 2016a) used synthetic raffinate in a continuous flow lab-scale model of the Key Lake process to show that ferrihydrite precipitated in the mill process contains AI and may best be described as aluminous ferrihydrite. Robertson et al. (2016a) also utilized extraction experiments to show that the As and Mo were associated with both the AI-doped ferrihydrite and Mg–Al and Mg–Al–Fe HTLCs. De Klerk et al. (2012) compared batch versus bench-scale continuous circuit lime neutralization to determine the role of process and chemical parameters on the removal of As with ferric ions between one, two, and three stage neutralization systems. They concluded that the lowest residual arsenate concentrations were obtained using a two stage (pH 4 and 8) co-precipitation circuit, where co-precipitates consisted of a mixture of gypsum, poorly crystalline ferric arsenate, and (arsenate-bearing) ferrihydrite (De Klerk, 2008; De Klerk et al., 2012). Aluminum was also found to be a suitable equimolar substitute for a portion of the ferric ion in this study.

Overall, the As- and Mo-bearing secondary mineral phases formed during the bulk neutralization of uranium mill wastes, before combination with leach residues to form final tailings, remain largely uncharacterized. As such, the objectives of the current study were to: (i) characterize the As- and Mo-bearing secondary mineral phases that precipitate during raffinate neutralization (pH 1.5 to 9.2) and (ii) determine what effect different mill feed materials (ore blends) have on the formation of
the secondary mineral phases that serve to control the solubility of the EOCs in the tailings. Characterizing these secondary mineral phases in the precipitates of the neutralized mill wastest will aid in predicting source terms for As and Mo in the tailings facilities and in understanding the impact of future ore sources on the long-term stability of the precipitated secondary mineral phases in the tailings facilities.

The study was conducted using a unique laboratory-scale model of the Key Lake mill using current and future ore blends. In all cases, samples of solids precipitated over various incremental pH ranges during the neutralization process in the mill model were analyzed using inductively coupled plasma-mass spectrometry (ICP-MS), X-ray diffraction (XRD), scanning electron microscope (SEM) and X-ray absorption spectroscopy (XAS) to characterize the precipitates formed and ultimately determine the evolution of the As- and Mo-bearing secondary mineral phases. This is, to the authors’ knowledge, the first time a continuous flow lab-scale model of a U mill bulk neutralization circuit has been used to characterize the precipitated mineral phases containing As and Mo from actual ore blends intended for U mill production.

2. Materials and methods

2.1. Site description and bulk neutralization process

The Key Lake mill is located in northern Saskatchewan, Canada (57°11’N, 105°34’W) and is currently one of the largest U mills in the world, producing 7.37 M kg U in 2015 (cameco.com). This mill processes the McArthur River deposit that contains high grade U ore (average concentration 15.8% U3O8 by weight) and must be blended with low-grade uranium-bearing ore (<0.5% U3O8) to achieve acceptable target mill grades (feed grade of 4% U3O8) prior to milling (Hossain, 2014; Bissonnette, 2015). The low grade ore sources contribute most of the As and Mo concentrations found in the tailings (Hossain, 2014). The historical development of the Key Lake mill and a description of previously mined reserves up to 25% U3O8 by weight are presented in detail elsewhere (Bharadwaj and Moldovan, 2005).

The Key Lake mill uses H2SO4 (94% vol/vol), oxygen (93% vol/vol), and steam (target temperature 60 °C) to leach U from the crushed ore slurry. This acidic leachate (free acid = 40 g/L) reports to the counter current decantation process, where the U-bearing solution is separated from leach residues (Bharadwaj and Moldovan, 2005; Lieu et al., 2010). The U-bearing solution containing dissolved As and Mo reports to solvent extraction where tertiary amines are used to purify and concentrate the U in solution. The U-bearing solution containing As and Mo reports to the counter current decantation process, where the U-Bearing solution is separated from leach residues (Bharadwaj and Moldovan, 2005; Lieu et al., 2010). The U-bearing solution containing dissolved As and Mo reports to solvent extraction where tertiary amines are used to purify and concentrate the U in solution. The purified U solution continues on to the yellowcake precipitation process, while the U-barren waste solution (raffinate) containing As and Mo (As ~ 200 mg/L, Mo ~ 2 mg/L) reports to the mill effluent treatment process called bulk neutralization (BN).

The BN circuit (Fig. 1) treats multiple mill process-based waste streams (e.g., raffinate and contaminated water streams from the site’s tailings management activities). The raffinate flows through four reaction vessels (Pachucas). In the series of Pachucas (labeled A, B, D, and E), slaked lime (Ca(OH)2) is added to increase the pH from 1.5 to 4.2 to 6.5 to 9.2 and precipitate As- and Mo-bearing mineral phases from solution. In addition to slaked lime, BaCl2 is added at points B, E, and F to remove Ba-226 from the effluent. Two thickeners are located at strategic process locations to allow solids to settle with addition of flocculant at pH 4.2 (C; SeMo thickener) and pH 9.2 (F; Lamella thickener).

2.2. Sampling the lab-scale plant mill

To replicate the current Key Lake tailings production process at the laboratory scale, three U-feed blends were created from an ore deposit currently being mined (McA) and a potential ore deposit, Millennium (MLM), being considered for future milling. The purpose of using a variety of ore blends was to determine if the sinks for As and Mo would remain the same, regardless of starting material. The first was created from 100% McA ore (scenario one: S1), a second that combined 75% McA ore and 25% representative core material from the MLM (scenario two: S2), and the third from 100% MLM ore (scenario three; S3) (Table S1). The ore blends were processed through a unique continuous-flow lab-scale model of the Key Lake mill that was validated to replicate the Key Lake milling process by comparison to mill performance targets and effluent quality (Bissonnette, 2015).

The lab-scale BN circuit was constructed at 1/311,600 scale of the Key Lake mill (Fig. 1). Slurry samples were collected from each thickener in the lab-scale plant (LSP), C (SeMo thickener; pH 4.2), and F (Lamella thickener; pH 9.2), as well as the reaction vessel D (Pachuca 3; pH 6.5). The Key Lake BN circuit was also sampled from actual process slurries in the same locations to provide a baseline for comparison to the LSP study. Four sets of slurry samples (n = 12) were vacuum filtered through commercially available 6 μm filter paper at standard temperature and pressure. Filtered solids were dried at ambient conditions then stored at 4 °C until analysis.

2.3. ICP-MS

ICP-MS was used for bulk elemental analysis of both solution and solid phases. Solution samples were preserved with 0.5% HNO3 before analysis. Solid samples were digested in a four acid leach (HCl, HNO3, HClO4, HF) (Donallson, 1981) in the Key Lake chemistry laboratory as well as in the Aqueous and Environmental Laboratory (AEL), Department of Geological Sciences, University of Saskatchewan using a two acid leach (HNO3, HF) for comparison (Longerich et al., 1990; Stefanova et al., 2003). Bulk elemental analysis on all samples was performed using Agilent 7500cx and 7700 instruments equipped with an ASX-500 series sample changer (RSD ±10%) at the Key Lake chemistry laboratory and a Perkin-Elmer NexION 300D instrument (RSD ±10%) at the University of Saskatchewan.

2.4. XRD

X-ray diffraction (XRD) analysis were conducted on washed solid samples (n = 12) using a PANalytical Empyrean X-ray diffractometer equipped with a Spellman generator and Co target (λ Co Kα = 1.7902 Å), operating at 40 kV and 45 mA. The samples were mounted on glass substrates as methanol slurries, and scanned in continuous mode using a spinning reflection/transmission stage. Spectra were acquired from 8 to 80° 2θ with a step size of 0.017° and a scan speed of 1.2°/min. Detection limits for phases defined by lab-based XRD are reported as 1–5 wt% (Bish and Chipera, 1995; Gomez et al., 2014).

2.5. SEM

Scanning electron microscopy (SEM) imaging was performed using a JEOL JSM 840A. Samples washed to remove gypsum (n = 4) were dry mounted, one particle thick, on double sided adhesive tape and coated with approximately 200 Å of gold using an Edwards S150B sputter coater. Images were acquired at ×1,000, ×25,000 and ×50,000 magnifications.

2.6. XAS

X-ray absorption spectroscopy (XAS) analysis was conducted...
using the Hard X-ray Microanalysis beamline (HXMA-06ID-1) at the Canadian Light Source (CLS), a third generation synchrotron facility operating at an electron energy of 2.9 GeV and injection current of 250 mA. Approximately 200 mg of dried sample was loaded onto Teflon® holders contained by triple layers of Kapton tape due to the radioactive nature of the samples. Two-line ferrihydrite was prepared from FeCl₃ (J.T. Baker) at the University of Saskatchewan according to the methods of Schwertmann and Cornell (1991) with slight modifications as per Jia et al. (2007) and Das et al. (2014b) and confirmed using X-ray diffraction (XRD) and BET surface area analyses. As and Mo adsorbed to 2-line ferrihydrite (As(III), ferrihydrite, As(III), ferrihydrite, and Mo_ferrihydrite) were prepared using 0.1 M NaCl as the electrolyte at three different pH values to achieve target molar ratios using known methods (Dixit and Hering, 2003; Raven et al., 1998). Commercially purchased reference compounds Ca₃(AsO₄)₂ (Alfa AESAR), NaAsO₂, As₂O₃, MoO₂, NiMoO₄, CaMoO₄, and FeMoO₄ (Sigma Aldrich) were diluted with boron nitride and loaded onto same holders, while synthesized sorption standards were prepared in the same way as samples. Previously characterized scorodite, amorphous ferric arsenate (am-FeAsO₄), and yukonite were prepared in the same way as purchased compounds (Essilfie-Dughan et al., 2013; Moldovan et al., 2003). Spectra from previously characterized arsenate adsorbed to aluminum phases (hydratolcitae, Al(OH)₃ and AlOHSO₄) were used for comparison (Paikaray and Hendry, 2014; Robertson et al., 2016a). All standards and samples were stored at ~17 °C following preparation and immediately cooled with liquid nitrogen before analysis to prevent changes in oxidation state. Arsenic K-edge XAS spectra were collected in a cryostat from 200 to +800 eV of the edge (11,867 eV) using gold (Au) foil for simultaneous calibration measurement. Molybdenum K-edge XAS spectra were collected from 200 to +200 eV the adsorption edge (20,000 eV) using Mo foil for simultaneous calibration measurement. Cryostat equipment under liquid helium was monitored to ensure the temperature remained below ~20 K for all standards and samples. XAS data for reference compounds were collected in transmission mode, whereas the samples and sorption standards were collected in fluorescence mode using a Canberra 32-element detector. X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) analyses were carried out together for As samples; only XANES data were collected for Mo samples due to low concentrations and time constraints.

Data was analyzed using IFFEFIT, with data reduction, principal component analysis (PCA) and linear combination fitting (LCF) analysis performed using ATHENA whereas EXAFS analysis was performed using ARTEMIS (Newville, 2001; Ravel and Newville, 2005). Data reduction included the standard procedures of energy calibration, multiple scan averaging, background and spline subtraction, normalization, and extraction of EXAFS. The PCA followed by target transform analysis with reference compounds was used to identify the reference compounds most likely to make up the complex precipitates in the samples tested. Based on the results of the PCA and target transform, LCF analysis was applied to determine the fraction of each Mo species present by fitting reference compounds best matched to sample spectra using normalized μ(E) data in the energy range from ~20 to ~30 eV. LCF with As K-edge spectra best matched by target transforms were performed from 2 to 12 Å⁻¹ in k² weighted χ(k) space. The residuals (R-factor) and the total values represent the goodness of fit. Smaller values for R-factors provide a measure of best fit for each calculation and the totals when unconstrained can provide a measure of the goodness of fit by fractional amounts summing to 1.00.

EXAFS fitting was performed using theoretical phase and amplitude functions generated from the computer code FEFF version 6 in the IFFEFIT package (Rehr, 1995; Newville, 2001) and the reported structure for scorodite (Ravel, 2001). Fits were performed in R-space (k-range: 2.6–3 to 12–12.5 Å⁻¹) with the amplitude reduction factor (Sₘ₀) constrained to 0.95. Coordination numbers (CN) were fixed, while the Debye-Waller parameter (σ²) and interatomic distance (R) were allowed to float during the fitting process. Threshold energy (Eₜ) was allowed to float but constrained to the first shell value for successive shells in the radial distribution function. Multiple scattering (MS) paths were used where inclusion improved the fit, by considering all 3-leg and 4-leg multiple scattering for the arsenite tetrahedron (Foster et al., 2003; Chen et al., 2009). The fits reported in Table 3 are all from k² weighted, background-subtracted, normalized EXAFS spectra.

3. Results and discussion

3.1. Characterization of BN precipitates

The evolution of the As, Mo, Fe, Mg, and Al concentrations was evaluated for all three scenarios in the LSP mill and for the Key Lake BN mill (Fig. 2). Most of the elements were removed from solution.
early in the BN process. Average removals by precipitation for As, Mo, Fe, and Al were 99.9, 98.0, 91.1, and 91.5%, respectively, by pH 4.2 (SeMo thickener); precipitation of Fe and Al were near complete (99.6 and 99.4%, respectively) by pH of 6.5 (Pachuca 3). The precipitation of Mg was notable different, with only 80.8% removed from solution by pH 6.5 (Pachuca 3) but 98.8% by pH 9.2 (Lamella thickener). These observations are consistent with a previous study that reports complete As removal (99.9–100%) and near complete Mo removal (95.5–99.6%) from the solution phase in a similar U mill bulk neutralization circuit by pH 4 (Robertson et al., 2014). The mill is designed to sequester the majority of As- and Mo-bearing minerals at the low pH stage of the circuit in the first thickener (C; SeMo Thickener) where the initial formation of phases including ferricyanide, FeAsO₄, and CaMoO₄ complexes begin (Lieu et al., 2010; Parkhurst and Appelo, 2013). The full suite of elemental analysis can be found in Supplementary Material (Table S2 – S5).

Results of the elemental analysis of the precipitates with increasing pH are consistent with the elemental mass lost from the raffinate during neutralization. As and Mo concentrations in the solid phase were highest in the first stage of the neutralization circuit (1951 to 3014 μg/g and 146–331 μg/g, respectively) where neutralized slurries were allowed to settle in the SeMo thickener (pH set point 4.2; Table 1). The presence of lower As and Mo concentrations (81.6–556 and 11.8–25.6 μg/g respectively) at the high pH stage (pH set point 9.2) indicate precipitation of As- and Mo-bearing mineral phases continues to occur but their contribution to the total in the final tailings is minimal (<2%). Though the pH targets were achieved for all scenarios during the experiments, some measured pH values drifted from the set point in certain samples (Table 1). The slaked lime addition for the LSP’s smaller reaction vessels was more challenging than in the mill due to suspended lime particulates that dissolve slowly and continue to increase above the pH set points over time. The pH for the Key Lake samples did not drift as noticeably above or below set points, though it is known to occur in the mill as well. The pH drifting may be the result of undissolved lime entering the thickeners and dissolving during settling or from lime collecting on sides of the reaction vessels and dislodging in larger quantities than intended to be added by the pH controlled pumps in the LSP scenarios. The experiments were monitored continuously, and dilute HCl added when pH values drifted upward, but due to the reactive nature of slaked lime particles, addition may not have been continuous for the entire experiment and dilute acid may have contributed to lower final pH values after solids had settled from solutions. Despite these minor inconsistencies in pH, all three scenarios were comparable to the Key Lake results based on an examination of final concentrations of EOCs in regulatory compliant effluent (Bissonnette, 2015).

The Fe/As and Fe/Mo molar ratios for all samples were greater than those reported in U tailings studies where molybdate and arsenate adsorbed to ferricyanide were the dominant mineral phases (Langmuir et al., 1999; Moldovan et al., 2003; De Klerk, 2008; Chen et al., 2009; Essilfie-Dughan et al., 2011). The solids elemental data presented in Table 1 show the Mg/Fe molar ratios (1.64–2.87) favor the formation of Mg–Al–Fe HTLCs over Mg–Al HTLCs (Mg/Al ratios: 0.46 to 1.39) and indicate Mg–Al–Fe HTLCs are most likely to exist at pH 9.2 (Gomez et al., 2014; Paikaray and Hendry, 2014; Robertson et al., 2014).

The results of the XRD and SEM analysis (Fig. S1 – S2) indicates the presence of amorphous Fe and Al phases (ferricyanide, amorphous ferric arsenate, and aluminum hydroxides) in the SeMo thickener (pH 4.2) solids and the presence of HTLCs in the lamella thickener (pH 9.2) solids. The crystalline phase observed in both SeMo and Lamella solids is attributed to calcite (Fig. S1c) and remains of gypsum removed during washing of the solids. Gypsum precipitation is well documented in the neutralization of acidic raffinate solutions (Donahue et al., 2000; Moldovan et al., 2003; Mahoney et al., 2007; Shaw et al., 2011; Gomez et al., 2013a; Robertson et al., 2014, 2016a) and washing to remove this phase was justified based on previous studies using similar techniques (Gomez et al., 2013a; Robertson et al., 2014; Bissonnette, 2015). The formation of calcite can be attributed to Ca from lime addition and the dissolution of atmospheric CO₂ (Table S2-S5). The SeMo solids also contained broad bands suggestive of an amorphous phase (Fig. S1a). These may be attributed to the presence of 2-line

![Fig. 2](image-url) Raffinate concentrations of As, Mo, Fe, Al, Mg, and Ca before neutralization and % precipitation with respect to solution pH of a) As, b) Mo, c) Fe, d) Mg, and e) Al for Key Lake (KL) and scenario 1 (S1), scenario 2 (S2), and scenario 3 (S3) samples.
ferrihydrite which have broad band peaks at approximately 34° and 76° 2θ (Figure S1c), though it cannot be confirmed by this technique alone. Adsorption of anions to the surface of ferrihydrite and the presence of ferric arsenates are reported to shift these bands to lower angles of diffraction (~29° and 59° 2θ) and may account for the shift observed in these samples (Ford, 2002; Jia et al., 2006; Paktunc et al., 2008). The amorphous solids may also include contributions from an Al mineral phases (AlOHSO 4 and/or Al(OH) 3 ) or Al-doped ferrihydrite as have been previously described (Gomez et al., 2013a; Robertson et al., 2014, 2016a). Comparison of the XRD spectra of the Lamella thickener solids to that of reference compounds (ferrihydrite and MgAlFe-HTLC) and KL mill samples (SeMo and Lamella) (Fig. S2) contain a HTLC phase in addition to calcite. Contributions from amorphous phases such as ferrihydrite and Al(OH) 3 were not resolved (i.e. suppressed) in the XRD spectra of the lamella sample due to the more intense peaks of the HTLC. The type of HTLC phase could not be identified by the XRD analyses and may have contributions from Mg, Al, Fe as well as either CO 3 or SO 4 (Paktunc et al., 2016a).

The exact size and shape of the particles observed by SEM analysis were difficult to determine due to their aggregated nature, as has been previously reported (Das and Hendry, 2014). However, similarities in morphology between model compounds (ferrihydrite and MgAlFe-HTLC) and KL mill samples (SeMo and Lamella thickener, respectively) were evident between pH set point 4.2 and 9.2, respectively) stages (Fig. S2). The morphologies of ferrihydrite in Fig. S2(a) and (b) resemble those of the SeMo thickener (KL-C, pH set point 4.2, samples in Fig. S2(e) and (f) with an approximate particle size of 200–500 nm. Ferric arsenate has been reported to occur similarly as particles aggregated into clusters with rounded outlines measuring 10–100 nm (Paktunc et al., 2008; Paktunc and Bruggeman, 2010), decreasing in particle size with increase Fe/As ratio (Paktunc et al., 2008) and may also be contributing to this phase. The MgAlFe-HTLC in Fig. S2(c) and (d) resemble the solids from the Lamella thickener (KL-L, pH set point 9.2) samples in Fig. S2 (g) and (h) with an average particle size approximately 100–200 nm (Fig. S2). The optimal pH for MgAlFe-HTLC formation is approximately pH 10 with crystal sizes reported from 12.1 to 88.5 nm, increasing with increased cation ratios (Paikaray and Hendry, 2014). The SEM results support this statement and agrees with analysis of XRD spectra. Thus, the variety of possible mineral phases identified by both XRD and SEM were used to guide the selection of reference compounds to be included in XAS analysis.

3.2. XANES and EXAFS analysis of As K-edge spectra

Generally, the energy position of for As K-edge shifts to higher energy with increased oxidation state over a 10 eV interval starting at the As 3+ absorption edge at approximately 11,867 eV. Comparison of the As 3+ and As 5+ reference compound XANES spectra to that of the samples indicate that arsenate (As 5+) was the dominant form of arsenic in the BN precipitates, regardless of pH or sample blend (Fig. S3). This finding agrees with results obtained from comparison of XANES spectra of reference standards to that of tailings samples from the DTMF and RLTMF as well as geochemical modeling of mill waste neutralization by Moldovan et al. (2003) and Essiflie-Dughan et al. (2013).

Principal component analysis (PCA) and linear combination fitting (LCF) analysis of the XAS data were used to determine the fraction of various As and Mo-bearing phases in the BN precipitates samples. A similar approach has been successfully used in previous studies, to determine As-, Fe- and Mo-bearing mineral phases in uranium tailings samples from the DTMF (Essiflie-Dughan et al., 2013, 2011). The PCA results of As K-edge EXAFS of the samples (n = 9) indicated that the spectra was comprised of contributions from three components (Fig. S4). Subsequent target transform analyses involving a range of reference compounds (arsenate adsorbed to aluminum hydroxide sulfate (AsAl(OH) 4 ), ammonium aluminum hydroxide (AsAl(OH) 3 ), hydrotalcite (AsHTLC), ferrihydrite (AsFerr), scorodite, ferric arsenate (FeAsO 4 ), CaSO 4·2H 2 O, yukonite, and NaAsO 2 ) (Fig. S5) suggested that the possible reference compounds present in the samples were AsFerr, FeAsO 4 , and AsAl(OH) 4 at pH set point 4.2, AsFerr, FeAsO 4 , and AsAl(OH) 4 at pH set point 6.5, and AsFerr, AsAl(OH) 3 and AsHTLC at pH set point 9.2 (data not shown). Because crystalline phases (such as scorodite) were not identified by XRD or SEM, and the thermodynamic requirements for crystallization were not met by the LSP mill conditions (Moldovan and Hendry, 2005; Langmuir et al., 2006; Chen et al., 2009), they were not included in the subsequent LCF analysis. Results of the LCF of scenario 1 SeMo thickener (pH 3.9) sample is shown with spectra denoting the fractional contributions of the components used to generated the fitted spectrum (Fig. 3a) and the LCF for each pH set point for scenario 1 (Fig. 3b).

LCF analysis results indicated that samples contained highest contributions (53–76%) from arsenate adsorbed to ferrihydrite (AsFerr) for all samples regardless of pH or sample blend, with minor contributions from ferric arsenate (FeAsO 4 ) and arsenate adsorbed to aluminum hydroxide sulfate (AsAl(OH) 4 ), aluminum

<table>
<thead>
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<th>Sample</th>
<th>Target pH</th>
<th>Actual pH</th>
<th>As (µg/g)</th>
<th>Mo (µg/g)</th>
<th>Fe (µg/g)</th>
<th>Mg (µg/g)</th>
<th>Al (µg/g)</th>
<th>Fe/As (M)</th>
<th>Fe/Mo (M)</th>
<th>Mg/Al (M)</th>
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<tr>
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<td>152</td>
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<td>668</td>
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hydroxide (As$_{\text{Al(OH)3}}$) and hydroxyltalcite phases (As$_{\text{HTLC}}$) (Table 2). This can be explained by the solubility profiles of these mineral phases (Moldovan et al., 2003; Langmuir et al., 2006; Paktunc and Bruggeman, 2010; Chen et al., 2009; Paikaray et al., 2013; Robertson et al., 2016a). Solubility factors suggest FeAsO$_4$ will control As solely at the pH of the SeMo thickener (pH 4.2) and LCF results indicate it makes up 23–26% of the As in the solids at this pH (Table 2). The results also indicate that 3–4% of the As occur as As$_{\text{Al(OH)3}}$ at the pH of 4.2 as suggested by documented solubility profiles (Robertson et al., 2014, 2016a). Given that the <5% As$_{\text{Al(OH)3}}$ occurrence may be considered not significant (Adra et al., 2013), these values are included to ensure goodness of fit values (R-factor) and total of As species (100%) were satisfactory. The observed presence of As$_{\text{Al(OH)3}}$ in the SeMo samples is further supported by the results of a recent study by Robertson et al. (2016b) that found As$_{\text{Al(OH)3}}$ as one of the As-bearing mineral phases present in the precipitates of neutralized simulated raffinate at a similar pH range. In the middle pH stage (Pachuca 3, pH 6.5), the results indicate that As$_{\text{Ferr}}$ remained the dominant mineral phase (66–77%) with minor contributions from FeAsO$_4$ (<1–8%) and As$_{\text{Al(OH)3}}$ (15–34%). Although the formation of HTLC and Al(OH)$_3$ is more thermodynamically favourable at the pH of 9.2 (Lamella thickener) (Paikaray and Hendry, 2014; Robertson et al., 2014, 2016a) the LCF results indicate that As$_{\text{HTLC}}$ and As$_{\text{Al(OH)3}}$ occur as minor As-bearing phases (<1–24%) and (17–47%) respectively, and As$_{\text{Ferr}}$ remained the dominant phase (53–74%) in the Lamella thickener (Table 2).

The As k$^2$-weighted χ(k) space spectra and the corresponding Fourier transformed (FT) EXAFS using the Hanning window (k-range = 3–12.5, with phase correction) are shown in Fig. 4. In the k-space spectra, the region indicated by arrows was observed to broaden and flatten out with increasing pH (Fig. 4a). The feature appears as a split peak in samples from the SeMo thickener (C, pH set point 4.2), begins to broaden in samples from Pachuca 3 (D, pH set point 4.2), and then completely plateaus in samples from the Lamella thickener (F, pH set point 9.2). The same feature is present in the scorodite reference standard, begins to broaden in ferric arsenate (FeAsO$_4$), and then completely plateaus for arsenate adsorbed to ferrihydrite (As$_{\text{Ferr}}$), consistent with previously published EXAFS studies on these As-bearing mineral phases (Moldovan et al., 2003; Paktunc et al., 2004, 2008; Chen et al., 2009; Das et al., 2014b). Moldovan et al. (2003) attributes these fine structure differences between scorodite and As$_{\text{Ferr}}$ to backscattering from second neighbour Fe ions in a mono- or bi-dentate arsenate complex on the ferrihydrite surface. The double hump feature is similar to that identified by Paktunc et al. (2008) in continuously synthesized precipitates with Fe/As = 1. In their study, the feature became less prominent as the Fe/As ratio increased, indicating a simultaneous increase and decrease in the formation of As$_{\text{Ferr}}$ and FeAsO$_4$ respectively with increase Fe/As ratio. This may explain the observed decrease (Table 2) in the fraction of FeAsO$_4$ which forms as Fe/As ratio increase (Table 1) with increasing pH during neutralization of the raffinate. Feature contributions from the EXAFS spectra of arsenate adsorbed to aluminum hydroxide sulfate (As$_{\text{Al(OH)3}}$), aluminum hydroxide (As$_{\text{Al(OH)3}}$) and hydroxyltalcites (As$_{\text{HTLC}}$) reference standards were not obvious in the spectra of the samples due to the low contribution of these phases to the bulk samples (<4, 47, and 24% respectively in Table 2), as well as the similar interatomic distances in As–Fe and As–Al backscattering paths (Robertson et al., 2016b).

The results of the EXAFS fit analysis of the As K-edge EXAFS spectra of scorodite, ferric arsenate, and arsenate adsorbed to ferrihydrite (Table 3) indicated CNs and bond lengths were consistent with previous reports (Fuller et al., 1993; Moldovan et al., 2003; Jia et al., 2005, 2006; Paktunc et al., 2008; Das et al., 2014a, 2014b). The EXAFS fit results for the spectra of samples from pH set point 4.2 (SeMo thickener, C) and 6.5 (Pachuca 3, D) are shown for comparison (Table 3). All the EXAFS fits (k range 2.6–3 to 12–12.5 Å$^{-1}$) involved the initial fitting of the first peak, below 2 Å in the Fourier Transform (FT) corresponding to the As–O shell, followed by fitting of successive shells in the radial distribution function. Phase correction was included during the fit to eliminate R-shifts and asymmetric peaks typical of transform peaks where phase correction is neglected (Cotelesage et al., 2012). Because of the positive correlation between the coordination number (CN) and Debye-Waller parameter ($\sigma^2$) (Foster et al., 2003), as well as the direct

Fig. 3. Experimental and linear combination fits (solid lines represent data, dotted red lines optimal fit and dash-dot blue lines represent calculated residual) for a) sample S1-C (SeMo thickener) along with spectra denoting fraction contributions of components used to generate the fit and b) samples from each pH set point in scenario 1 with pH values as shown in Table 1 and sample locations in Fig. 1. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
correlation between amplitude reduction factors ($S_0^2$) and CN (Ravel and Newville, 2005), fixed CN were used as indicated in Table 3. To reduce the error associated with the number of floating parameters, typically held to half the maximum independent variables (Chen et al., 2009), we ensured the number of variables were held to 7 mainly by correlating related parameters, such as the Debye-Waller factors for MS paths, and by constraining the $E_0$ value for all paths to that of the first path. The results for the first shell (As–O), with CNs of 4–4.4 and bond lengths of 1.68–1.69 ± 0.01 Å, indicates an arsenate tetrahedron (AsO$_4$) and are the same for standards and samples. The consistent interatomic distances indicate that the AsO$_4$ tetrahedron remains relatively rigid (i.e. not distorted) in all the reference compounds as well as the samples. The second peak in the FT at an apparent distance between 2 to 3 Å (corrected for phase shift) corresponds to single scattering of the As–Fe shell as well as contributions from multiple scattering effects. Multiple scattering (MS) paths were therefore included in all the fits. This was justified due to the complexity of spectral features from second nearest neighbors characterized by a double-peak observed in Fig. 4b (Paktunc et al., 2004; Chen et al., 2009). Various MS paths from the FEFF calculation results for the arsenate tetrahedron in scorodite were tested sequentially during the fit with floated parameters (Debye-Waller factors and bond length) constrained to equal paths from the same shell. The double scattering path labeled MS(1) with CN from 4 to 4.5 and the obtuse angle of the As–O scattering path in the arsenate tetrahedron, labeled MS(2) with CN 12 to 16, were included due to marked improvements for all fits. The maximum double scattering allowed for the MS path of As–O in a tetrahedral anion is 12 (Paktunc et al., 2003; Chen et al., 2009; Essilfie-Dughan et al., 2013), though larger coordination numbers have been reported and attributed to excess amplitude of As-MS shell than accounted for by modeling calculations (Paktunc et al., 2003; Paktunc and Dutrizac, 2005). This could explain the improved fits in our study with...
the arsenate in the samples tested is predominantly adsorbed onto ±3.34 atomic distances of the As

for the samples at pH set point 4.2 and 6.5 indicate that the inter-

actions within the arsenate tetrahedron did not improve

2016b). Multiple scattering paths corresponding to As

Paktunc and Dutrizac, 2003; Chen et al., 2009; Robertson et al.,

CN > 12. The bond lengths of MS(1) and (2) agree with those reported in literature when errors are included (Paktunc et al., 2003; Paktunc and Dutrizac, 2003; Chen et al., 2009; Robertson et al., 2016b). Multiple scattering paths corresponding to As–O–As–O interactions within the arsenate tetrahedron did not improve fits, and was neglected.

The results of the fit analysis for the As–Fe shell for scorodite indicate an As–Fe bond distance of 3.38 ± 0.03 Å with CN of 4.2, consistent with results from previous studies (Moldovan et al., 2003; Chen et al., 2009; Essilfie-Dughan et al., 2013). The fit result for As–Fe shell for ferric arsenate indicates a bond distance of 3.35 ± 0.03 Å and a CN of 3.4. Similar bond distance and CN have been reported by Chen et al. (2009) for poorly crystalline scorodite. However, the arsenate adsorbed to ferrihydrite has a shorter As–Fe bond distance of 3.29 ± 0.03 Å and a smaller CN of 2.1. The result agrees with previous published results which described the local structure of arsenate adsorption to ferrihydrite as being through a bidentate binuclear bridging complex to an edge sharing Fe3 octahedra (Moldovan et al., 2003; Waychunas et al., 1993; Chen et al., 2009; Essilfie-Dughan et al., 2013). The fit analysis results for the samples at pH set point 4.2 and 6.5 indicate that the interatomic distances of the As–Fe shell range from 3.29 to 3.34 ± 0.01–0.04 Å with CNs between 1.5 and 3.2 and suggests that the arsenate in the samples tested is predominantly adsorbed onto ferrihydrite. Although, LCF results for some of the samples such as S1-D indicated the contributions from FeAsO₄ (8%) and As₂(OH)₃ (15%), (Table 2), the As–Fe bond length (3.30 ± 0.04 Å) and coordination number (1.5) agreed well with those reported for arsenate adsorbed to ferrihydrite in bidentate-binuclear coordination (Fuller et al., 1993; Waychunas et al., 1993; Moldovan et al., 2003; Jia et al., 2005; Das et al., 2014b). The As–Fe peak of S1-D (Pachuca 3, pH 4.4) and S1-C (SeMo thickener, pH 3.9) are shown in Fig. 5 with reference compounds for comparison. In all the results, within error, compare well with those reported for As in neutralized raffinate samples from the Rabbit Lake uranium mill (Moldovan et al., 2003) which also indicated that arsenate precipitated predominantly as arsenate adsorbed on ferrihydrite. However, the relatively longer As–Fe bond distances (3.31–3.34 Å) for some of the samples, compared to the bond distance for an ideal arsenate adsorbed to ferrihydrite bidentate coordination at 3.28 Å (Waychunas et al., 1993), could be attributed to contribution from amorphous ferric arsenate and/or Al substitution in the ferrihydrite structure (Adra et al., 2013). Paktunc et al. (2008) reported similar As–Fe bond lengths for the compound postulated to be a heterogeneous mixture of both ferric arsenate and arsenate adsorbed on ferrihydrite. Given results from LCF and the longer As–Fe bond lengths of the samples, ferric arsenate is a significant arsenic phase together with predominant arsenate adsorbed on ferrihydrite, especially at the
pH 4.2 set point. However, at the pH 6.5 set point, the LCF results indicate that As$_{Al(OH)}$ replaces ferric arsenate as the significant As-bearing minor phase. As previously discussed, in As-rich natural systems, hydrous ferric oxide precipitates having Fe/As ratios <4 may contain heterogeneous materials composed of ferric arsenate and arsenical ferricydrite, and may in fact occur in synthetic arsenic-bearing ferricydrites such as in our study (Paktunc et al., 2008). Although in this study, Fe/As ratios were >4 and LCF results indicated that both As-bearing phases were present in the precipitates, especially at the pH 4.2 set point.

From the results of the LCF analysis and the EXAFS fit results we determined that arsenate adsorbed on ferricydrite is the predominant As-bearing mineral which forms during the bulk neutralization of the raffinate, regardless of pH or sample blend considered in this study. This finding is important because when co-precipitated, adsorption of arsenate to ferricydrite have been shown to slow the transformation of this iron oxide to more crystalline forms, such as goethite and hematite, thus stabilizing the ferricydrite from phase transformation (Ford, 2002; Das et al., 2011, 2014a, 2014b). Previous studies have assessed the stability of scorodite, ferric arsenates and arsenic adsorbed to ferricydrite with respect to U mill wastes (Moldovan et al., 2003, 2008; Moldovan and Hendry, 2005; Langmuir et al., 2006; Mahoney et al., 2007; Paktunc et al., 2008, Paktunc and Bruggeman, 2010). In these studies, geochemical modeling showed As precipitated as ferric arsenate will decrease in solubility with increasing pH (Mahoney et al., 2007) and the kinetics of scorodite transformation from ferric arsenate are strongly controlled by pH (Paktunc et al., 2008). Other models predict ferric arsenate will dissolve above pH 3 with concurrent ferricydrite content increasing at the expense of ferric arsenate (Moldovan and Hendry, 2005; Paktunc et al., 2008). Even in precipitates that transformed from 2-line ferricydrite to 6-line ferricydrite as has been reported for Fe/As ratios >5 (Paktunc et al., 2008), the ferricydrite would control the As concentration in solution by providing additional sites for arsenic adsorption as ferric arsenate dissolution progressed. Additionally, the As in minor phases such as ferric arsenate and adsorbed to aluminum hydroxides maybe taken up by hydrotalcites at higher pH values, providing an efficient process for minimizing As release to the tailings porewater. Though there is not an abundance of literature regarding the long-term stability of hydrotalcites in high sulfate matrices, Gomez et al. (2013a) reported phases identified in freshly precipitated neutralized raffinates were identical to those deposited >15 years earlier in the Key Lake DTMF. Because As concentrations are not observed to increase in the tailings pore water (Bissonnette, 2015) these minor phases are either stabilized by the high sulfate media (SO$_4$ > 1500 mg/L, Shaw et al., 2011) or released As is being re-adsorbed by ferricydrite and hydrotalcites precipitated at higher pH values (>6.5).

### 3.3. XANES analysis of Mo K-edge spectra

Comparison of the edge positions of the Mo K-edge XANES spectra of the reference compounds to that of the samples showed that molybdate (Mo$^{6+}$) is the dominant form of Mo in the samples, regardless of pH or sample blend (Fig. S6). This finding was supported by results from geochemical modeling of the mill waste neutralization process (using PHREEQC: data not presented) as well as pH/Eh diagrams generated using the aqueous concentrations of Mo (Takeno, 2005; Parkhurst and Appelo, 2013). The pre-edge feature in the spectra of the Mo$^{6+}$ compounds (e.g. NiMoO$_4$) as well as the samples at approximately 19,995 eV, but absent in the Mo$^{4+}$ reference compound (MoO$_2$) provides a strong indication of oxidation state of Mo in the samples (Fig. S6). The pre-edge peak observed in the XANES spectra of NiMoO$_4$ is attributed to dipole forbidden 1s → 4d transitions that gain intensity due to admixing of the 4d levels with p orbitals in Mo environments without a centre of symmetry (Essilfie-Dughan et al., 2011; Wharton et al., 2003).

Using an approach similar to the one employed for the determination of As speciation using As K-edge EXAFS, results of the PCA of Mo K-edge spectra of the samples (n = 9), illustrated by the plots of the calculated Eigenvectors (Fig. S7), showed that the samples consisted of four components. Target transform analysis of PCA results with the Mo reference compounds (Fig. S8) indicated the
best matches were molybdate adsorbed to ferrihydrite (Mo_Ferr), NiMoO₄, CaMoO₄, and Fe₂(MoO₄)₃ (data not included). LCF analysis was subsequently used to fit the spectra of the four reference standards to each of sample spectra over the energy range of 20 to 30 eV to determine fractional occurrence of the Mo reference compounds in each sample. LCF analysis of Mo K-edge spectra has previously been used successfully in the determination of Mo speciation in uranium mine tailings (Essilfie-Dughan et al., 2011; Hayes et al., 2014). Results of the LCF analysis indicate that the occurrence of Mo as NiMoO₄ increases, whereas the occurrence of Mo_Ferr decreases with increasing pH for all scenarios. This is consistent with predictions based on thermodynamic modeling as well as previous studies on Mo speciation in the tailings from the DTMF (Essilfie-Dughan et al., 2011; Parkhurst and Appelo, 2013). In summary, the interpretation of XANES analyses indicates the dominant mineral phase controlling Mo in the secondary precipitates was Mo_Ferr, with minor contributions from NiMoO₄ and Fe₂(MoO₄)₃.

### Table 4

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<th>R-factor</th>
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<td>NiMoO₄</td>
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<td>0.00 (0.04)</td>
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<tr>
<td>C (pH 4.2)</td>
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<td>0.21 (0.13)</td>
<td>0.00 (0.14)</td>
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</tbody>
</table>

| a Fit using the choice of reference compounds: molybdate adsorbed to ferrihydrite (Mo_Ferr), Fe₂(MoO₄)₃, NiMoO₄, CaMoO₄, and FeMoO₄. Phases were included at pH range most thermodynamically favourable to form and where inclusion improved the R-factors (goodness of fit). |
| b < 5% are not considered significant but were included to ensure satisfactory R-factors. |
The results above indicate that adsorption to ferrihydrite is the dominant phase of both As and Mo in the precipitated neutralized raffinate and together with minor mineral phases observed at high pH (As\(_{\text{Al(OH3)}}\), As\(_{\text{HTLC}}\), and NiMoO\(_4\)) are expected to remain stable when deposited as tailings into the DTMF. Previous studies (Shaw et al., 2011; Essilfie-Dughan et al., 2011, 2013) have shown that with the current oxidized environment in the DTMF (average pH 9.7, Eh +200 mV, temperature 1–2 °C) arsenic exists predominantly as As\(_{\text{V}}\) and molybdenum as Mo\(_{\text{VI}}\). The documented high affinity of ferrihydrite for oxyanions such as AsO\(_4^{\text{3-}}\) and MoO\(_4^{\text{2-}}\) and its characteristic high surface area make ferrihydrite a major solubility control for As and Mo in the tailings (Ford, 2002; Moldovan et al., 2003; Essilfie-Dughan et al., 2011, 2013). As such, under the current environmental conditions in the DTMF and the adsorption of anions onto the ferrihydrite surface, ferrihydrite is not expected to transform to more crystalline phases such as goethite and hematite (Ford, 2002; Das et al., 2011, 2014a, 2014b). The observed occurrence of Mo as molybdate adsorbed to ferrihydrite together with minor Mo phases such as Fe\(_2\)(MoO\(_4\)) and NiMoO\(_4\), the concentration in the tailings porewater will be stable and remain at the average level at which it is discharged (Shaw et al., 2011). Blanchard et al. (2015) found ferrimolybdate and molybdate adsorbed on ferrihydrite initially dissolves in the TMF and precipitates as powellite, adding additional controls on Mo solubility in the tailings porewater. Further work using Fe XAS analysis is recommended to confirm the dominance of ferrihydrite as a solubility control for both As and Mo. A previous study using reactive transport modeling, predicted the adsorption of As to the surface of ferrihydrite would limit transport of EOCs for >10,000 years (Moldovan et al., 2008). Confirmation of these findings in addition to aging tests would be beneficial for making predictions about the long-term stability of the As- and Mo- bearing phases identified.

4. Conclusion

Arsenic and molybdenum concentrations in uranium mine wastes have the potential to adversely impact local groundwater and surface water quality after tailings facilities have been decommissioned. Characterization of the As- and Mo-bearing mineral phases formed during the bulk neutralization of mill wastes is critical to determining the long-term chemical stability of elements of concern in the tailings. The first stage in the bulk neutralization process of the raffinate (pH 4.2) accounts for 99.9 and 98.0% removal of As and Mo, respectively, from solution through precipitation as secondary mineral phases. XAS analyses indicate arsenic occurs predominantly as arsenite (As\(_{\text{III}}\)) adsorbed to ferrihydrite, whereas molybdenum exists predominantly as molybdate (Mo\(_{\text{VI}}\)) adsorbed to ferrihydrite in the precipitates of the first stage (pH 4.2) in the bulk neutralization process. Other minor secondary mineral phases of As and Mo observed in the precipitates from the various pH set points (pH 4.2, 6.5, 9.2) during bulk neutralization include ferric arsenate; arsenate adsorbed to aluminum hydroxide sulfate, amorphous aluminum hydroxide and hydrotalcite; nickel molybdate, and ferrous molybdate. The occurrence of the As- and Mo-bearing mineral phases were pH dependent: ferric arsenates, arsenate adsorbed to ferrihydrite and aluminum hydroxide sulfate, and ferrous molybdate were observed at low pH (4.2–6.5) and arsenate adsorbed to ferrihydrite, amorphous aluminum hydroxide and hydrotalcite at high pH (9.2). Molybdate adsorbed to ferrihydrite had a decreasing contribution and nickel molybdate an increasing contribution with increasing pH. EXAFS analysis results indicate that the arsenite is adsorbed to ferrihydrite via inner sphere bidentate linkages, regardless of pH or sample blend. The differences in ores tested (sample blend) exhibited no measurable effect on secondary mineral formation. These findings are in keeping with previously published studies on the occurrence of As and Mo in U mill tailings facilities. Adsorption of anions to the surface of ferrihydrite is important for As and Mo sequestration because it will inhibit conversion to more crystalline forms of iron oxides and the subsequent release of these anions. Given the current environmental conditions in the DTMF and the incorporation of anions onto the surface of ferrihydrite, and the documented stability of these mineral phases, the identified precipitates are expected to exhibit long-term geochemical control on arsenic and molybdenum levels in the tailings pore water, well below regulatory levels.

Acknowledgment

Financial support was provided by Cameco Corporation and the Natural Sciences and Engineering Research Council of Canada (NSERC) through a Senior Industrial Research Chair (grant 184573) to MJH. Assistance received from F. Nelson, J. Fan, E. Schmeling, T. Bonli, and B. Novakowski (Geological Sciences, University of Saskatchewan), N. Chen, W. Chen, and J. Lin (Canadian Light Source staff), and J. Robertson, M. Cleavely, K. Lutz, S. Bwaya, and A. Lieu (students, University of Saskatchewan) are kindly acknowledged.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.apgeochem.2016.06.007.

Abbreviations

BN bulk neutralization
DTMF Deilmann tailings management facility
EXAFS extended X-ray absorption fine structure
HTLC hydrotalcites
ICP-MS inductively coupled plasma mass spectrometry
LCF linear combination fitting
LSP lab-scale plant
PCA principle component analysis
RLITMF Rabbit Lake in-pit tailings management facility
SEM scanning electron microscope
XANES X-ray absorption near edge spectra
XRD X-ray diffraction

References


