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**Written Submission from
Orano Canada Inc.**

**Mémoire d'
Orano Canada Inc.**

In the matter of

À l'égard d'

Orano Canada Inc.

Application to renew the McClean Lake
Operating Licence for 2-year term

Orano Canada Inc.

Demande pour le renouvellement du
permis d'exploitation de McClean Lake
pour une période de deux ans

**Hearing in writing based on written
submissions**

**Audience par écrit fondée sur des
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Appendix E – Published Papers



Confirmation of the retention of ^{226}Ra in U-mine tailings by barite

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ABSTRACT

Uranium ore from the Athabasca basin in Saskatchewan Canada, particularly from the McClean Lake and Cigar Lake deposits, is extremely rich in uranium (U): 2 to 20–25 % U_3O_8 . The ore is also rich in many elements considered to be Constituents of Potential Concern (COPC) for the environment, including arsenic (As), selenium (Se), nickel (Ni), molybdenum (Mo), lead (Pb), cobalt (Co) and radium-226 (^{226}Ra). Following uranium extraction, residual materials (tailings) containing these elements in partially immobilized forms are placed in the McClean Lake plant Tailings Management Facility (TMF). Uranium tailings are sulfate-rich low-level radioactive waste containing ^{226}Ra , with activities of up to 3000 Bq/g. Barium chloride (BaCl_2) is added to precipitate ^{226}Ra in barite as a solid-solution. Following this neutralisation treatment, ^{226}Ra in the tailings is generally considered as sequestered in barite and sorbed onto ferrihydrite. To assess the subsequent stability of ^{226}Ra in the tailings, an extensive study of its retention potential was performed. Characterisations include assessment of tailings pore water and solids chemistry, tailings mineralogy, cation exchange capacity measurement, scanning electron microscopy and energy-dispersive x-ray spectroscopy (SEM/EDS), and alpha-autoradiography analyses supplemented with thermodynamic modelling. This work confirms that barite is the main ^{226}Ra binding-phase, in agreement with the ^{226}Ra concentration measured in the porewater (6 Bq/L) resulting from a coprecipitation reaction. A $(\text{Ba,Ra})\text{SO}_4$ solid-solution regulates the average ^{226}Ra concentration now and over the long term, through a distribution coefficient which is subject to a gradual shift towards a recrystallisation equilibrium. Recrystallisation causes an increase in the long-term concentration of ^{226}Ra in the tailing water to 10 Bq/L. The work, conducted to assess the management strategy of the tailings, allowed us to ensure that the tailings have no significant effects on the downstream environment over the long term.

1. Introduction

Canada has a long history of uranium (U) mining and is still a major U producer: 8 ktU in 2022, which represents about 15 % of world production. At most there were 27 sites of various sizes of uranium ore production, processing and storage activities, and now five sites are still in operation (the Cigar Lake and McArthur River mines, the production plants at Key Lake and McClean Lake, as well as the Rabbit Lake mine and production plant). At the same time, uranium prospecting remains active, mainly in the Athabasca basin. Thus, the past and present

production of U in Canada has led to the production and current storage of 218 Mt of mine tailings (IAEA and NEA, 2023; Natural Resources Canada, 2021; World Nuclear Association, 2023).

The Athabasca Basin, mined for U since 1975, covers an area of 85,000 km^2 in north-eastern Saskatchewan. The Athabasca U deposits are associated with unconformities between the Athabasca sandstone dating from the Meso-Proterozoic (–1600 to –850 My) and the Archean crystalline basement (Benedicto et al., 2021; Cuney, 2008). The ore is of sandstone composition with mineralisation of up to 25 % U, the highest-grade ore in the world. The mineralisation consists mainly of

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pitchblende and uraninite and is accompanied by high concentrations of arsenic (As), cobalt (Co), copper (Cu), molybdenum (Mo), nickel (Ni), selenium (Se), lead (Pb) and zirconium (Zr) (Fayek et al., 1997; Kaczowka et al., 2021; Mahoney et al., 2007; Situm et al., 2020b; Tourigny et al., 2007) as well as H_2 (Truche et al., 2018).

Uranium was mined at the McClean Lake operation between 1999 and 2010 from five open pits, named JEB, Sue C, Sue A, Sue E and Sue B. The ore was processed in facilities built on the same site near the JEB open pit with an annual production of up to 1500 tU per year. Since 2014, the McClean Lake mill has been processing about 7–8 ktU per year, mostly ore from the Cigar Lake mine (IAEA and NEA, 2023; World Nuclear Association, 2023). The ore is extracted from the underground mine using the jet-boring technique, mixed into a slurry, and trucked to the mill site.

(Fig. 1)

The U-extraction process involves leaching by a sulfuric acid solution with ferric sulfate and hydrogen peroxide. Counter-current decantation and clarifications allow the separation of the uranium-rich solution from the residual solids, with an extraction yield of 98 %. ‘Yellowcake’ is then precipitated from the pregnant aqueous solution. The ‘tailings’ consist of the solid and liquid mill waste from the extraction process.

The McClean Lake mill employs a tailings neutralization process specific to the treatment of high-grade ore and the immobilization of Constituents of Potential Concern (COPC), these being the elements that were present in the ore and remain as wastes after the U is leached U. COPCs include trace metals (As, Se, Ni, Mo, Pb, Co) and radionuclides which are part of the decay chains of U (^{226}Ra). The tailings contain significant concentrations of COPCs and the site must ensure their stability and low concentration in solution (Blanchard et al., 2017; Donahue et al., 2000; Essilfie-Dughan et al., 2013, 2011; Hayes et al., 2014; Mahoney et al., 2007; Shaw et al., 2011; Situm et al., 2020b, 2020a). This treatment increases pH by adding slaked lime (CaO) and promotes oxidizing conditions through the addition of hydrogen peroxide (H_2O_2) and ferric sulfate (FeSO_4). The neutralisation process is based on controlling the chemistry using thermodynamic modelling: key COPCs are fixed in mineral phases by solid-solution formation and sorption: As is precipitated to scorodite ($\text{FeAsO}_4 \cdot 2H_2O$) and Mo to ferrimolybdate $\text{Fe}_2(\text{MoO}_4)_3$ and then powellite (CaMoO_4). ^{226}Ra is treated by adding barium chloride (BaCl_2) to form radiobarite. Other COPCs, such as Ni, are immobilised by the rise in pH leading to the precipitation of metal hydroxides and absorption onto hydrous ferric oxyhydroxide ferrihydrite. The neutralised tailings are then sent to the former JEB open pit which was converted into a tailings management facility (TMF) in 1999.

The JEB TMF has a depth of 120 m and a surface area of 350×450 m. Filters and drains at the bottom of the TMF contribute to the consolidation of the tailings through dewatering and are used to maintain hydraulic containment from the surrounding environment. The TMF currently contains about 1830,000 t of tailings from the treatment

of the McClean Lake ore and 375,000 t of tailings from Cigar Lake ore, maintained under a water cover acting as a radiological barrier. Environmental monitoring ensures the absence of chemical and radiological impacts downstream from the TMF and confirms hydraulic containment. The TMF is a main focus of study to determine the long-term environmental footprint of the McClean Lake operation and is a major element of closure design planning.

Many studies have verified the retention of several COPCs (Blanchard et al., 2017; Donahue et al., 2000; Mahoney et al., 2007; Shaw et al., 2011; Situm et al., 2020b, 2020a) but with little focus on ^{226}Ra : there was no thermodynamic control of the ^{226}Ra concentrations in the residues after the neutralisation process, nor any experimental verification of the ^{226}Ra -carrying phases. ^{226}Ra is considered to be immobilised mainly within barite by coprecipitation, but also by sorption on ferrihydrite (Robertson et al., 2019).

However, among the COPCs, ^{226}Ra requires special attention. Because of its radiogenic origin, ^{226}Ra is initially present in ^{238}U -bearing minerals and is redistributed during the U-leaching process. Radium is an earth-alkaline element which can be incorporated in a mineralogical sample by various retention mechanisms which are common to trace elements. As a cation, Ra^{2+} can sorb onto the surface of many minerals including clay-rich minerals (Ames et al., 1983; Reinoso-Maset and Ly, 2016; Robin et al., 2017a; Yamaguchi et al., 2024), iron oxy-hydroxides (Sajih et al., 2014; Chen and Kocar, 2018), manganese oxides (Dolhańczuk-Śródka et al., 2024; Ivanets et al., 2020; Mott et al., 1993), as well as organic matter (Bordelet et al., 2018) and some silicates including quartz (Beněš et al., 1984; Fabritius et al., 2024). It can also be incorporated in solid solutions, replacing other earth-alkaline elements, making it a good candidate for incorporation in solid-solutions with minerals such as sulfates (Brandt et al., 2020; H.A. Doerner and Hoskins, 1925a; Heberling et al., 2018) and also some carbonates (Curti, 1999; Jones et al., 2011; Langmuir and Reise, 1985a). Because of its chemical similarity to Ba, the most common solid solution to incorporate Ra is barite, forming $(\text{Ba,Ra})\text{SO}_4$, found in both natural and anthropised contexts (Jirásek et al., 2020; Robertson et al., 2019; Sebesta et al., 1981). The addition of BaCl_2 to Ra-rich water is a common process to mitigate aqueous Ra concentrations (Chalupnik and Skubacz, 2005; Chalupnik et al., 2019; Itzkovitch and Ritcey, 1979; Liu and Hendry, 2011; Moffett, 1979; Nirdosh et al., 1984; Rosenberg et al., 2013). Studies have shown radiobarite formation to be the main retention mechanism for ^{226}Ra in some environments, but in competition with sorption processes (Ballini et al., 2020; de Boissezon et al., 2020; Liu and Hendry, 2011; Van Sice et al., 2018).

Because it is an ultra-trace element, ^{226}Ra chemistry is particularly difficult to measure in solid samples. Yet, recent developments both in the knowledge of retention processes for Ra (Brandt et al., 2015; Heberling et al., 2018; Robin et al., 2017b) and in measurement techniques (Angileri et al., 2018; Billon et al., 2024, 2020; Lefevre et al.,

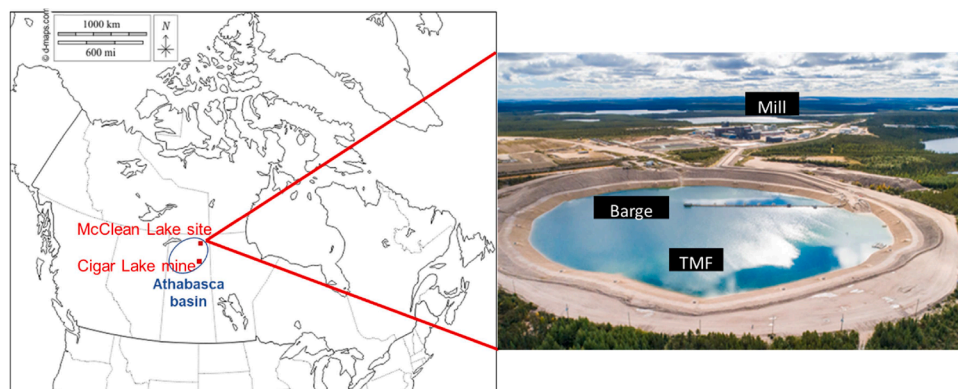


Fig. 1. Site location and aerial view of the JEB TMF at the McClean Lake operation of Orano Canada.

2022; Reymond et al., 2023; Thakur et al., 2021) allow a new insight on the speciation of ^{226}Ra in fine-grained media.

The objective of the present study is to use a novel multidisciplinary approach to characterise the solids and their associated solutions in order to confirm and quantify the retention of ^{226}Ra in the barites and other minerals in McClean Lake tailings. Experimental and non-destructive imagery methods will be used based on the approach developed in Besançon et al. (2022), and by modelling. For the first time to our knowledge for residues but also for geomaterials, the stability of ^{226}Ra retained in barites over the long term is then explored via field measurement and modelling.

The results acquired as part of this study will therefore allow a better understanding of the behaviour of ^{226}Ra following treatment and its retention in the TMF. The work was conducted to assess the management strategy of the tailings and to ensure that the tailings have no significant effects on the downstream environment which remains protected over the long term.

2. Materials and methods

2.1. Tailings sampling

To confirm the mechanical and chemical stability of the tailings in the TMF, a series of sampling campaigns gathered more than 100 tailings samples in 15 to 20 boreholes. Geochemical samples were taken in stainless steel Shelby tubes which were sealed with wax and kept cool until they were processed. For processing the samples were extruded in the on-site laboratory at the McClean Lake operation, sealed with wax and kept cool until they were processed, which occurred as quickly as possible after their initial sampling and porewater was obtained by pressing the samples through titanium pressure filters. The porewater was acidified and filtered on site (as needed) and refrigerated at 4 °C until it was shipped off-site for analysis. Both solid and water samples were analysed for chemistry of their major and trace elements. Grain size measurements were performed on the solids.

This study uses the data from 121 samples from the 2018 campaign, the largest tailings sampling campaign to date, and 34 samples from the 2021 campaign. This body of data enabled the selection of five samples in total representative as best as possible of the two main types of ores (McClean Lake and JEB/Sue pits for samples TMF18–11 SA03, TMF18–06 SA16 and TMF18–01 SA24 and Cigar Lake for samples TMF18–01 SA01 and TMF18–03 SA02) and of different sampling depths. These five samples will be referred to as the TMF samples. Also three samples were taken from the three successive tailings reaction tanks (TRT) at the mill. A diagram of the neutralisation process is available in Figure SI-1. One sample was taken after U extraction and before neutralisation (sample TRT-1), one after $\text{Fe}_2(\text{SO}_4)_3$ and BaCl_2 addition (TRT-2) and one after CaO addition before flocculant (TRT-3). These three samples will be referred to as the TRT samples. Those eight samples were subjected to complementary analyses: spectrometry, x-ray diffraction (XRD), high-resolution (HR) XRD, cation exchange capacity (CEC) measurement, Time-resolved laser-induced fluorescence spectroscopy (TRLFS), EDS and alpha-autoradiography mapping.

2.2. Bulk solid characterisation

Grain size

Grain-size measurements were conducted on the tailings samples in the McClean Lake Metallurgy laboratory for the TMF samples, and at the Centre d'Innovation en Métallurgie Extractive (CIME, ORANO, France) for the mill samples. Both sets of samples were analysed with a Malvern Mastersizer 3000 particle size analyser in water media coupled with a Hydro EV dispersion unit. The aggregated samples were initially slightly dispersed by hand. Comparison of the results from the two labs was made on five TMF tailings samples in order to ensure results duplicability. The minimal particle size detected using this method was 0.3 μm .

Total chemistry

The analytical testing of tailings solids was performed by Saskatchewan Research Council (SRC) Analytical Laboratories in Saskatoon. The total trace metal concentration of the tailings solids was quantified by inductively coupled plasma-mass spectrometry (ICP-MS, Agilent 7900). Gas chromatography with a flame ionisation detector and a mass spectrometry detector was used to detect the concentrations of hydrocarbon species in the solid tailings samples, with the weight percentage of organic carbon content in the tailings determined using a LECO furnace with infrared detection. For sample TRT-1, the total chemistry analysis (XRF and ICP-MS after digestion) was performed by ALS Geochemistry.

The analyses described hereafter were performed on the selection of eight samples representative of the study.

Gamma and alpha spectrometry

Radionuclide characterisation was performed by both gamma spectrometry on the bulk samples and alpha spectrometry on the thin sections. Gamma spectrometry used a DGS NGC 20,195 High-Purity Germanium (HPGe) detector at the L3MR (Laboratoire de Mesures et Modélisation de la Migration des Radionucléides, CEA, France). The reference used was a multigamma source solution provided by the (Laboratoire Etalons d'Activité, Orano, France). The data were analysed using InterWinner 6.0 software and the database from (Bé et al., 2016). ^{226}Ra was identified using the 186.2 keV peak, which was identifiable because of the lower activity of ^{235}U (with a 185.7 keV peak) compared to ^{226}Ra , as the samples are tailings.

Alpha spectrometry was performed by the Department of Chemistry (University of Helsinki, Finland), using a CANBERRA A450 PIPS® detector with a 55 mm chamber. The distance from the section to the sensor was fixed at 8870.2 mm and the number of energy channels was 1024. The data acquisition and analysis were done using MAESTRO 6.05. The energy calibration was performed with a reference sample containing ^{237}Np ($E_\alpha = 4788$ keV, probability = 47 %), ^{241}Am ($E_\alpha = 5486$ keV, probability = 84.5 %) and ^{244}Cm ($E_\alpha = 5805$ keV, probability = 76.4 %). To remove uncertainties of geometry, each thin section was analysed for about 24 h then rotated for another cycle. Alpha-energy reconstruction was done using AASI (Advanced Alpha Spectrometry Simulation) software (Pöllänen et al., 2007; Siiskonen et al., 2008).

Fine fraction separation

The fine fraction gathers most of the minerals involved in the retention of the COECs and its study requires separation as it is in small quantity compared to the major minerals. The wet granulometric separation of the fine fraction (<2 μm) was achieved by using ultrasound on 5 g of air-dried sample in 1000 mL water. After 3 h of sedimentation the supernatant was siphoned out and centrifuged at 10,000 rpm for 20 min.

XRD and HR-XRD

The mineralogical characterisations were performed by XRD using a X'Pert Pro Panalytical with cobalt anode. The fine fraction was analysed in the form of oriented deposits for clay mineral identification. The oriented preparations were then treated with ethylene glycol and heated to 550 °C for 3 h to complete the identification of the phyllosilicates. The XRD measurements were performed at the X-Ray diffraction unit of the Institut de Minéralogie, de Physique des Matériaux et Cosmochimie, Sorbonne Université, France (IMPMC).

The mineralogical characterisations were completed by HR-XRD at the CRISTAL beamline at the SOLEIL synchrotron (Saint-Aubin, France). Polyimide (Kapton) double capillaries (MicroLumen, Oldsmar, USA) of 0.5 mm in diameter were filled with the fine fraction of the sample. The XRD data was collected using a two-circle diffractometer at $\lambda = 0.7270$ Å, with an efficient Mythen 2×9 K detector (Dectris, Switzerland) at 293 K. The goniometer was calibrated, and the LaB_6 standard (NIST, SRM660a) used to refine the wavelength.

Cation exchange capacity (CEC) measurement

Measuring the CEC of a sample allows the determination of the quantity of available sorbents (mostly metal oxy-hydroxides and clay minerals). These sorbents are involved in the retention of COECs. The protocol was adapted from [Wissocq \(2017\)](#). 1.2 g of sample was used with 5 mL of 0.1 M KCl (pH fixed at 9 by a 2 M KOH solution) for one week, then one week in 5 mL of a 0.1 M CsCl solution. During this time, the tubes for the reaction are maintained under multidimensional agitation. The KCl and CsCl solutions were collected using 30 min of 15,000 rpm centrifugation. The supernatant was analysed by inductively coupled plasma optical emission spectroscopy (ICP-OES) at ALIPP6 (Sorbonne-Université, OSU-Ecce Terra, INSU-CNRS). The CEC was calculated using the K concentration measured in the second supernatant. Replicates showed the results were reproducible, and the variation in a sample was low.

Time-resolved laser-induced fluorescence spectroscopy (TRLFS)

TRLFS provided information on the chemical environment of U. The bulk samples in the form of dried powder were placed directly under the excitation laser with a wavelength of 266 nm, and the luminescence emission was collected through a fiber optic cable connected to a monochromator and an intensified CCD camera array. See [Othmane et al. \(2016\)](#), [Sirven et al. \(2023\)](#), [Vercouter et al. \(2017\)](#) for more details of the technique. The analyses were performed at the LANIE (Laboratoire de développement Analytique Nucléaire Isotopique et Élémentaire, CEA, France).

2.3. Water characterisation

Physicochemical parameters

pH, temperature, conductivity, Eh and dissolved-oxygen measurements were collected from the tailings pore water, in the field and during sample preparation. A Barnant 20 digital meter and accompanying pH triode was used to measure porewater pH and temperature, and a platinum electrode with a silver/silver-chloride reference electrode was used to measure its oxidation–reduction potential. Specific conductivity was measured with a Thermo Scientific™ Orion™ 135A conductivity meter. Dissolved oxygen was measured using a Thermo Scientific™ 850 RDO meter.

Chemistry and radionuclides

The analytical testing of tailings porewater was performed by Saskatchewan Research Council (SRC) Analytical Laboratories in Saskatoon. Metal concentrations were measured using ICP-MS (Agilent 7900); sulfate ion concentrations were measured using ICP-OES (Agilent 5100); and the alkalinity by titration with sulfuric acid. For the TRT samples, water characterisation was performed by the LASE (Laboratoire d'Analyse en Soutien aux Exploitants, CEA, France) using ionic chromatography for the anions and inductively-coupled atomic emission spectrometry (ICP-AES) for the cations. Radionuclide analysis was performed by the CIME using ICP-MS and gamma spectrometry. The analysis displayed satisfactory ionic balance (imbalance = $-3 \pm 2\%$, maximum water charge balance error $<10\%$).

2.4. Modelling

Modelling of the speciation and distribution of ^{226}Ra was carried out using PHREEQC software (v. 2.18.00) ([Parkhurst and Appelo, 1999](#)). The PRODATA thermodynamic database, developed for U-mine and related environmental applications ([Reiller and Descostes, 2020](#)), was used for the construction of the geochemical models.

The distribution models included sorption and solid solution mechanisms. They are the main retention mechanisms relevant for this study according to the mineralogical characterisation. The sorption onto ferrihydrite was modelled by using the surface complexation modelling routine within PHREEQC, the sorption constants and the site density

from [Dzombak and Morel \(1990\)](#), to which were added the Ra surface complexation constants and specific surface area from [Sajih et al. \(2014\)](#). The sorption onto clay minerals was modelled by sorption onto illite, using a multi-site ion exchange model according to the Gaines-Thomas convention. The exchange constants for illite originated from [Savoie et al. \(2015\)](#). The constants for Ba and Ra were calculated from the data from [Marques Fernandes et al. \(2023\)](#) for Ra. On [Fig. 2](#) the formalism of the multi-site ion-exchange model was used to fit [Marques Fernandes et al. \(2023\)](#) for Ba and Ra adsorption onto conditioned Na-illite and in 0.02 mol.L⁻¹ NaCl aqueous solution ([Fig. 2](#)). In the presence of Na⁺ as competitor, adsorption of Ba and Ra onto Na-illite can be described with three major sites, previously identified by [Savoie et al. \(2015\)](#) on strontium (Sr), a chemical analogue of Ba and Ra. A nonlinear fitting of the experimental Ba and Ra sorption edges measurement gives an estimation of the selectivity coefficients $K_{2\text{H}/\text{Ba}}$ and $K_{2\text{H}/\text{Ra}}$ associated with the exchange equilibria, shown in [Fig. 2](#). The model for a (Ba,Ra)SO₄ solid solution in PHREEQC is described by the Guggenheim coefficient, which represents the deviation from an ideal solid solution and will be discussed below. The initial value of the partition coefficient a_0 , representing the miscibility of the phases, was chosen at 1.5, the value found by [Brandt et al. \(2015\)](#), [Curti et al. \(2010\)](#) and [Zhang et al. \(2014\)](#) at $23 \pm 2^\circ\text{C}$. This value will be further discussed in this study.

2.5. Imaging techniques to localise ^{226}Ra

Imaging techniques were used on thin sections of the samples to confirm the mineralogical characterisation and also to identify the main ^{226}Ra -bearing minerals using the protocol developed in [Besançon et al. \(2022\)](#). SEM-EDS analyses at the IMPMC were conducted at 15 kV using a 60 µm diaphragm with a Zeiss ULTRA55 SEM equipped with a Bruker QUANTAX EDS Microanalyser. Chemical maps were established using a pixel size of 3 µm. Al, As, Ba, Ca, Fe, K, Mg, Mo, P, Pb, S, Se, Si, titanium (Ti) and U were mapped.

The alpha-autoradiography maps were obtained at the Institut de Chimie des Matériaux et Milieux de Poitiers (IC2MP, University of Poitiers, France). An alpha-autoradiograph is a quantitative map of α emissions without discrimination of the α -emitting radionuclide. The alpha signal was measured using a BeaQuant® alpha-autoradiograph, providing 2D quantitative mapping of the alpha emissions of a thin section. The acquisition lasted 8 h (28,247 s) and 14 h (52,143 s) for four samples respectively sorted by their bulk activity. The resulting maps were post-processed with Beamage® software to obtain a pixel resolution of 50 µm. The BeaQuant®'s intrinsic detection efficiency for counting was determined by measuring a pre-studied uraninite vein ([Sardini et al., 2016](#)).

Wavelength-dispersive spectroscopy (WDS) data complemented the mineralogical characterisation and was acquired at CAMPARIS (Sorbonne-Université, OSU-Ecce Terra, INSU-CNRS, France) using a CAMECA SXFive microprobe. Measurements are related to precise calibrations of reference minerals acquired before each session under the same voltage and amperage conditions. The WDS mapping was conducted at 15 kV, 40 nA, with a 2 µm resolution.

3. Results

Complete chemical and radiological composition, grain size and CEC measurements and TRLFS data are available in Supplementary Information (SI) Table SI-1 with associated porewater characterisations.

3.1. Solid characterisation and determination of potential ^{226}Ra -bearing minerals

Tailings as a whole are quite heterogeneous but individual tailings samples are of homogeneous non-cohesive fine-grained material, with colours ranging from light grey to yellow. Most resemble clayey-silt

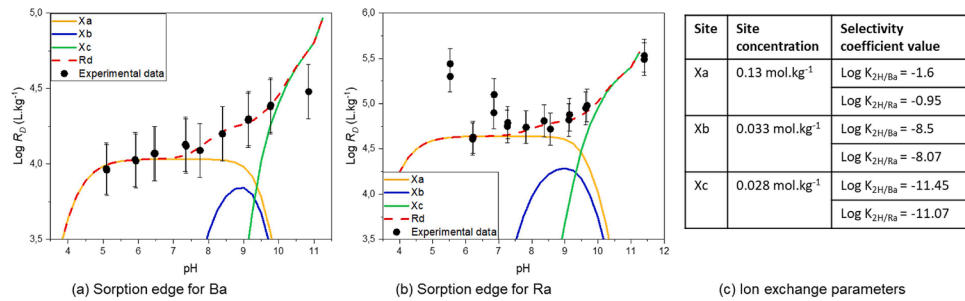


Fig. 2. Concentration of Ba (a) and Ra (b) sorbed onto Na-illite in 0.02 M NaCl as a function of pH. Comparison between experimental results reported by Marques Fernandes et al. (2023) and data calculated from model. (c) Ion exchange parameters for the three ion-exchange sites and log of selectivity coefficients at 25 °C for Ba and Ra relative to proton.

materials with some samples from the bottom of the TMF having more the appearance of greyish sand, including one sample among the eight selected for deeper analysis. This variability is consistent with ore variation, and will be confirmed by mineralogical analysis. Three samples are from the different stages of mill treatment conducted on Cigar Lake ore, and five are from tailings deposited in the TMF. Tailings samples were selected based on their location in the TMF and their chemical composition, to reflect the diversity of the tailings: two samples are from Cigar Lake ore (shallow tailings (2 m deep)), one from a location close to the deposition point and one located further away, and three from JEB/SUE ore (deeper in the TMF (2 to 56 m)). These specifications are detailed in Table SI-1.

Grain size

On the basis of identification (by depth) of the treated ore in the TMF, the grain size allows a first differentiation between the Cigar Lake and the JEB/SUE tailings. Those from Cigar Lake ore have a d_{50} of 20 μm with particles mostly in the range 1–30 μm (Group 1), while JEB/SUE tailings have a higher d_{50} of 60 μm with particles mostly in the range 10–1000 μm (Group 2), so with greater variability. Variations also appear linked to the distance from the deposit point, with finer granulometry ($d_{50} = 40 \mu\text{m}$) for points far from the deposition point while $d_{50} = 60 \mu\text{m}$ for samples close to the deposition point. These groups are represented in Fig. 3. Tailings directly from the treatment plant, which are from Cigar Lake ore, have a very similar dynamic and slightly more diverse granulometry than Group 1 but do have its signature with a d_{50} of 18 μm . Among the samples selected for more detailed analysis are the TRT samples with d_{50} of 10–20 μm , two tailings samples from Cigar Lake

ore with d_{50} of 27 and 21 μm and three samples from JEB/SUE ore with d_{50} of 10, 30 and 160 μm . This highlights the variability of the JEB/SUE tailings.

All these variations of granulometry can be interpreted by changes in mine procedures, the use of flocculent in the tailings neutralisation procedure at the McClean Lake mill and the grain size selection by dynamism in the TMF at the moment of deposition by the barge. Previous work by McClean Lake Operations has shown that the Cigar Lake tailings have a finer particle size than those of previous mines, and that there is a general decrease in particle size with depth, due to the mechanical diagenesis of the mill tailings (AREVA Ressources Canada Inc., 2015).

Chemical analysis

The tailings' composition in major elements shows slight variations but there is great variability in the composition of the trace elements. The tailings samples are composed mostly of silicon (SiO_2) with significant fractions of aluminium (Al_2O_3 : 13 % $\pm$ 5), calcium (CaO : 5 % $\pm$ 5), iron (Fe_2O_3 : 4 % $\pm$ 3), potassium (K_2O : 2 % $\pm$ 1), magnesium (MgO : 1 % $\pm$ 0.5) and small fractions (>0.1 %) of BaO, Cu_2O , Pb_2O_3 , NiO and Pb_2O_5 . Previous work from McClean Lake operations determined that Cigar Lake tailings show smaller proportion of quartz and higher proportion of gypsum, secondary precipitates and clays. This is consistent with the analysis of the major elements of the five selected tailings samples. Significant trace elements (>500 ppm on average) include As (3800 $\pm$ 4200 ppm), Ba (1300 $\pm$ 1800 ppm), Cu (825 $\pm$ 2300 ppm), Pb (2900 $\pm$ 5400 ppm), Ni (2600 $\pm$ 2800 ppm) and vanadium (V) (770 $\pm$ 300 ppm). The detailed chemical analyses of the five tailings samples

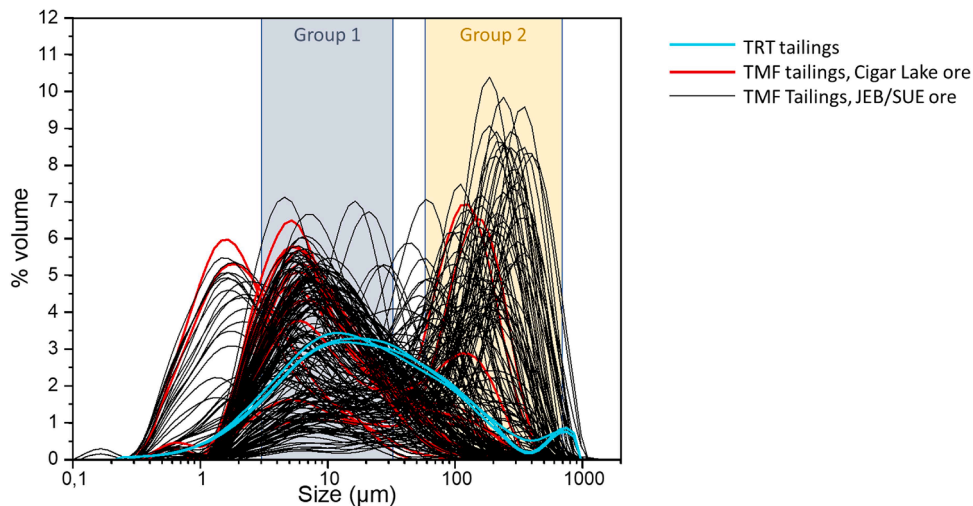


Fig. 3. Grain size distribution of the tailings from the McClean site. TRT = tailings reaction tank, which means the samples were taken directly from the mill before deposition in the TMF and are from Cigar Lake ore.

from the TMF are presented in Table SI-1. The selection of samples demonstrates a representative variability in the range observed in the TMF, especially for the elements relevant to the study of the retention of ^{226}Ra (Al: 3.8–11 %, Fe: 1.34–11.3 %, Ba: 200–10,700 ppm, U: 840–2000 ppm). Sample TMF18–01 SA24 differs from the others by its low Ca (2200 ppm), Ba (200 ppm) and Fe (1.76 %) contents. This sample is among the deepest in the TMF (about 60 m) and is sandier than the other samples: it is probably of JEB ore. As the initial grade in ^{226}Ra is quite low compared to the other samples (81 Bq/g), it is assumed much less BaCl_2 was added. Sample TRT-1, before neutralisation, shows a chemical composition close to the TMF tailings except for Ba (200 ppm, the same as for TMF18–01 SA24) and with very low Ca (10 ppm compared to 0.22–10.2 % for the TMF samples), which confirms that this sample is before any neutralisation addition of CaO and BaCl_2 .

A complete chemical analysis was not performed for samples TRT-2 and TRT-3; these were from Cigar Lake ore tailings, which were identified as quite homogeneous in their major constituents, and have also undergone the BaCl_2 neutralisation process. It is therefore assumed for the following calculations that TRT-2 and –3 have similar compositions to the Cigar Lake tailings in the TMF, with Fe, Ni and As compositions similar to TRT-1 for the TRT-2 sample (Ba had already been added and barite precipitation is less sensitive to pH, so the Ba composition is considered the same as for the Cigar Lake TMF samples).

Radionuclide analysis of the selected samples

^{226}Ra was measured for 50 samples from the 2018 sampling campaign and 37 samples from the 2021 campaign (see Table 1). The samples have an average ^{226}Ra activity of 660 Bq/g. The tailings samples from the Cigar Lake site have a higher activity than those from JEB/SUE ore (1080 Bq/g to 180 Bq/g on average), in agreement with the higher U grade (SUE C deposit has an average grade of 2.6 % U_3O_8 (Tourigny et al., 2007) while Cigar Lake has 8 % (Fayek et al., 1997) and 15 % for the part that has been mined). 25 % of the 2018 tailings samples and 100 % of the 2021 samples were generated from Cigar Lake ore, which explains the difference between the average activity found in the two groups (2018: 410 Bq/g, 2021: 1067 Bq/g).

Eight selected samples were measured by total γ and α spectrometries (the alpha spectra and results are assembled in Figure SI-2 and Table SI-1). These samples have ^{226}Ra activities ranging from 81 to 2920 Bq/g. As expected from tailings samples from ore > 2 My, secular equilibrium is achieved for the ^{228}U chain after ^{226}Ra ($^{226}\text{Ra}/^{210}\text{Pb} = 0.94 \pm 0.02$) but not before ($^{226}\text{Ra}/^{238}\text{U} = 132 \pm 76$). The ^{238}U was of course extracted from the ore at a rate, which can be determined by considering the ore as at secular equilibrium, of 97 ± 5 %. This high theoretical extraction rate is in accordance with the actual extraction rate of the mill. The TRT samples were similar to four of the TMF samples. Sample TMF18–01 SA24 differs from the other tailings samples by its lower ^{226}Ra concentration (81 Bq/g) and U extraction yield of only 85 %. α spectrometry determined that ^{226}Ra contributed to 18 % of the total α signal of the tailings (other α -emitting isotopes are ^{214}Po , ^{218}Po , ^{222}Rn , ^{210}Po , and ^{230}Th).

Elemental correlations

Concentrations of Ba in the solids are clearly correlated with the COPCs ($R_{\text{Ba-Pb}}^2 = 0.88$, $R_{\text{Ba-Mo}}^2 = 0.77$; $R_{\text{Ba-Se}}^2 = 0.88$, $R_{\text{Ba-Ag}}^2 = 0.88$, $R_{\text{Ba-Sn}}^2 = 0.76$, $R_{\text{Ba-U}}^2 = 0.75$) but also with Fe ($R_{\text{Ba-Fe}}^2 = 0.81$). This results from the neutralisation treatment of the tailings, the Cigar Lake ore being more concentrated in U but also in COPCs and therefore treated with a greater addition of slaked lime, $\text{Fe}_2(\text{SO}_4)_3$ and BaCl_2 than JEB/Sue ore.

The addition of BaCl_2 causes the precipitation of barite while the addition of $\text{Fe}_2(\text{SO}_4)_3$ causes the precipitation of scorodite and ferrihydrite (HFO) (the two major secondary phases of Fe in the tailings). Correlations for Ba- ^{226}Ra and Fe- ^{226}Ra , reflecting the occurrence of these ^{226}Ra -carrying phases, are found in the set of samples for which ^{226}Ra was measured ($R_{\text{Ba-}^{226}\text{Ra}}^2 = 0.78$, $R_{\text{Fe-}^{226}\text{Ra}}^2 = 0.69$). Discrimination of the retention phases is not possible by correlation at this scale, justifying the work at the scale of specific samples.

The COECs that are not in inherited minerals are enriched in the fine fraction. This is explained by two phenomena. Firstly, the phases carrying the contaminants, including HFO and barite, are mainly amorphous or poorly crystalline secondary minerals caused by the addition of $\text{Fe}_2(\text{SO}_4)_3$ and BaCl_2 and are therefore of small size. Secondly, Cigar Lake ore has a higher U grade and greater concentrations of COPCs than JEB/Sue ore, and so the preparation of Cigar Lake tailings requires the addition of more $\text{Fe}_2(\text{SO}_4)_3$ and BaCl_2 . In addition, the processing residues from this ore are finer than those from JEB/Sue. The identification of ^{226}Ra -bearing phases must therefore focus on the fine fraction of the residue samples, which justifies a global analysis of the samples. Elementary correlations cannot be used to identify retention phases because they are affected by the neutralisation treatment.

Mineralogical characterisation

Characterisation by XRD confirms the homogeneity of the mineralogy of the studied samples and is in agreement with the minerals described in the literature (Fayek et al., 1997; Mahoney et al., 2007; Tourigny et al., 2007). Diffractograms of the bulk and fine fractions are available in Figures SI-3 and SI-4. The major minerals observed are inherited from the ore rock: quartz is dominant, accompanied by micas, clay minerals, feldspar, hematite, pyroxene with traces of pyrite, galena and hydroxyapatite. Pyrite is a remnant from the ore and is being oxidised into HFO. Also present are minerals formed because of the mill treatment: mostly gypsum, but also traces of scorodite and barite. One sample (TMF18–01 SA24) differs slightly, showing more quartz and less gypsum than the other samples. It is consistent with the previous interpretation as a JEB tailings sample to which less addition was made during the neutralization process, causing less gypsum precipitation.

Extraction of the fine fraction (about 10 % of the mass of the bulk sample) highlights the presence of the clay minerals: chlorite, illite, kaolinite, and muscovite. The fine fraction also shows little quartz, but iron oxy-hydroxides and oxides (ferrihydrite, goethite and hematite), galena, barite, scorodite, feldspar, hydroxyapatite are present. The proportions of the clay minerals vary between samples. The tailings from JEB/SUE ore show a larger occurrence of kaolinite and chlorite.

Barite was barely visible in some samples. To confirm its presence, the fine fraction of three samples was characterised using HR-XRD: one sample from the mill, after addition of BaCl_2 ; one tailings sample from Cigar Lake ore and one tailings sample from JEB/SUE ore (see Fig. 4 and SI-5). HR-XRD analysis confirms the presence of barite in all three samples, as well as sulphides (pyrite, chalcocopyrite, galena), iron oxides and oxy-hydroxides (hematite, goethite, ferrihydrite), calcite, rutile and As-bearing minerals (scorodite, rammelsbergite - NiAs_2).

Elemental and micromorphological observations using SEM/EDS confirmed the results of the XRD characterisation. They highlighted the presence of the Athabasca sandstone primary minerals but also minerals linked to the mill treatment and the diagenesis of the samples. Accessory minerals visible at this scale of observation were barites, rutiles, Mg-clay minerals and kaolinites, zircons, Fe oxides (hematite) and oxy-hydroxides (hematite and ferrihydrite), Al and Pb oxides, gypsum,

Table 1

^{226}Ra concentrations in solids in Bq/g.

Category	All TMF	Cigar Lake ore	JEB/SUE ore	2018 sampling	2021 sampling	TRT samples
Mean	660 ± 720	1080 ± 750	180 ± 200	410 ± 570	1067 ± 764	1540 ± 120
Range	10–2500	13–2500	10–720	10–2230	13–2500	

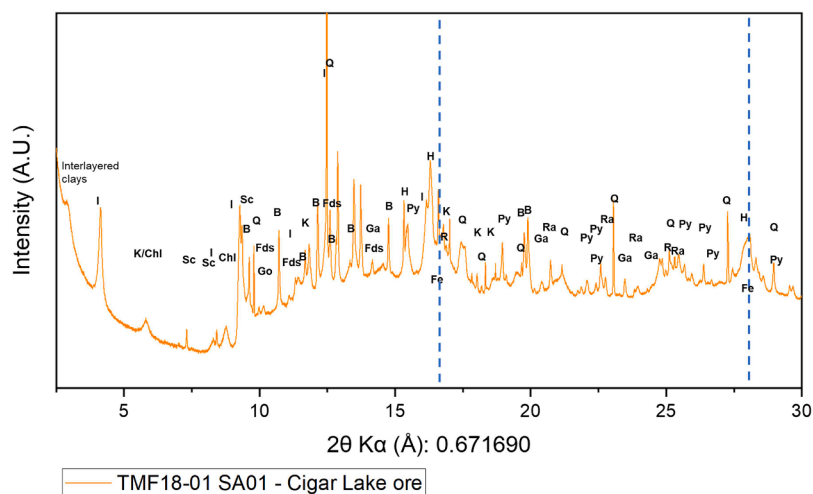


Fig. 4. HR-XRD characterisation of the fine fraction (<2 μm) of TMF tailings sample. Barite (B), chlorite (Chl), feldspar (Fds), galena (G), goethite (Go), hematite (H), hydroxyapatite (Ap), illite (I), kaolinite (K), quartz (Q), pyrite and chalcopyrite (Py), scorodite (Sc), rutile (R), rammelsbergite (Ra), blue dash lines: position of the bulges linked to amorphous ferrihydrite (Fe).

galena, pyrite and chalcopyrite. In one sample, inherited uranium minerals were observed (uraninites and U silicates).

(Fig. 5)

Among the minerals identified, those likely to have an influence on ^{226}Ra are U-minerals by radioactive disintegration, barite by solid-solution formation, and clay minerals and iron oxy-hydroxides by sorption.

Measurement of the CEC

Measuring the CEC of a sample allows the availability of sorption sites of the clay minerals to be confirmed and also provides data for improved sorption modelling. The CEC measured on the eight selected samples averaged 3.9 ± 0.8 meq/100 g (with values ranging from 2.5 to 5.1) for the bulk sample. With the fine fraction representing about 10 % of the bulk sample, these values are consistent with the assemblage of clay minerals identified in the mineralogical characterisation. Illite and chlorite both have CECs of about 10–40 meq/100 g, whereas kaolinite has 5–15 meq/100 g (Morel, 1996).

These CEC measurements give slightly lower values (by 1.5 to 2) than a previous measurement made on ore samples from Cigar Lake that were selected for being rich in clay minerals (Smellie and Karlsson, 1996). The difference can be explained by this selection and by the degradation of clays in the mill treatment. The CEC of sandstone samples is generally lower than 2.5 meq/100 g (Akiba et al., 1989; Kabala and Jedrzejewski, 2024; Pandey et al., 2014).

TRLFS: U-bearing minerals

As uranium-bearing mineral phases are of major importance for understanding ^{226}Ra mineral bearing phases, and were only seen by SEM in one sample, the presence of uranium sorbed onto the surface of the clay minerals was investigated by TRLFS, a technique that can only detect the environments of U(VI). The superposition of the experimental spectra from the tailings samples with those acquired from the reference minerals confirmed the presence of U also sorbed onto the surface of clay minerals and also as schoepite (spectra in Figure SI-6). Schoepite is a hydrated form of U(VI) oxide. Uranium also has a high affinity for ferric oxy-hydroxides. However, these phases cannot be investigated by TRLFS because iron is known to inhibit U(VI) fluorescence (Sirven et al., 2023).

3.2. Water characterisation and estimation of the distribution of ^{226}Ra in the solid by the modelling of mineral-water interactions

Porewater chemistry and radiology

The tailings pore water was generally neutral ($\text{pH} = 7.5 \pm 0.4$), oxidising ($E_h = 230 \pm 85$ mV/SHE) and with high conductivity (3600 ± 700 μS/cm). These extractions demonstrated high calcium-sulfate facies ($[\text{Ca}]_{\text{tot}} = 450$ mg/L, $[\text{SO}_4]_{\text{tot}} = 1950$ mg/L). Mg, Na, K, HCO_3 , Cl, NH_3 were present in concentrations higher than 10 mg/L. The concentration of ^{226}Ra was 6 ± 4 Bq/L. The total concentrations for the eight selected samples are presented in Table SI-1.

Waters from the TRT samples represent different stages in the

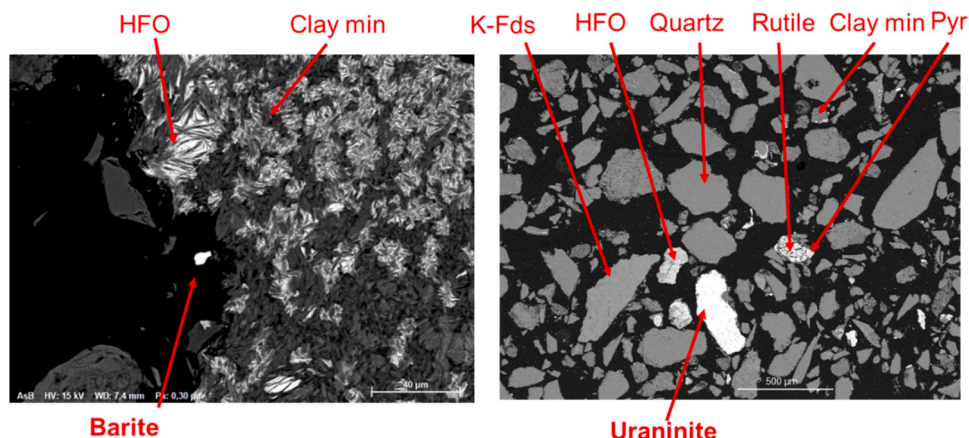


Fig. 5. SEM observations of tailings sample TMF18-01 SA24. Fds-K: K-feldspar, HFO: iron oxy-hydroxides, Pyr: pyrite.

tailings neutralization process and therefore have notably different geochemical properties. Samples are acidic (pH = 2.5) (TRT-1 and TRT-2) and neutral (TRT-3), with sulfate and calcium as major ions ($[Ca]_{\text{tot}}=500$ mg/L, $[SO_4]_{\text{tot}}=4650$ mg/L). TRT-1 and TRT-2 pore waters were also rich in Fe (140 mg/L, compared with 0.1 mg/L for TRT-3) and Ni (250 mg/L, 0.5 mg/L for TRT-3). These observations are in agreement with the observations of similar solid composition between the TRT and TMF samples, while differences are explained by the location of each sample in the tailings neutralization process: as the process moves from low ($\sim$ pH 1) to neutral pH a percentage of COPCs are yet to precipitate in the first two TRT samples. TRT-2 sampled in the tank after BaCl₂ addition: the ^{226}Ra concentration in TRT-2 porewater is already close to the TMF samples (<20 Bq/L) so barite has already precipitated, in contrast with sample TRT-1 ($^{226}\text{Ra} = 129$ Bq/L)

Modelling of the ^{226}Ra distribution

As a first step to understanding the ^{226}Ra -bearing minerals, the stability of the minerals that can play a role in the retention of ^{226}Ra was assessed using PHREEQC modelling of the 122 tailings porewater samples (including Cigar Lake and Jeb/Sue ore sources). All were considered to be in equilibrium with the solubility of barite ($SI_{\text{BaSO}_4(\text{cr})} = 0.3 \pm 0.2$) and to a lesser extent with the solubility of ferrihydrite ($SI_{\text{ferrihydrite}} = 1.5 \pm 0.8$). Calcite was also considered to be in equilibrium ($SI_{\text{calcite}} = 0.3 \pm 0.5$), as was gypsum ($SI_{\text{gypsum}} = -0.2 \pm 0.2$). Mn oxides were not observed in the mineral characterisation and are all undersaturated. Pyrite was highly under-saturated ($SI_{\text{pyrite}} = -100$), confirming that the pyrites are inherited from the ore and unstable in the TMF conditions:

pyrites are passivated by iron oxy-hydroxides or being oxidized with the natural diagenesis of the tailings. Barite and ferrihydrite are therefore considered to be in equilibrium in all samples, with a slight oversaturation. The SI from the eight samples selected for detailed analysis are given in Table SI-1.

Chemical equilibrium modelling was performed to investigate the distribution of ^{226}Ra in the eight selected tailings samples. The minerals considered for the retention of ^{226}Ra are barite forming a (Ba,Ra)SO₄ solid solution, ferrihydrite and clays (solely illite because of its higher sorption capacity compared to kaolinite) as sorption surfaces, and residual U-minerals. These minerals, the amount of which was measured by total U in the tailings, were considered to be in secular equilibrium with ^{226}Ra . The amount of barite, ferrihydrite and illite were calculated using total Ba, Fe and Mg in the tailings respectively. Apart from the fraction in secular equilibrium within the U-minerals, the ^{226}Ra in the solid is assumed initially to be in the (Ba,Ra)SO₄ solid solution and is redistributed until equilibrium with the solution. The partition coefficient for the (Ba,Ra)SO₄ solid solution was tested to achieve solid and solution activities in ^{226}Ra close to the measured activities.

The number of sorption sites determined using the bulk Fe and Mg concentrations correlated well with the measured CEC ($R^2=0.95$) but is about 10 times higher, which indicates that a significant part of Fe and Mg are in different minerals for HFOs and clays (scorodite, pyrite and chlorite for example) and that the sorption processes are maximised by such an approach.

The optimal Guggenheim coefficient found when considering all eight samples was 1.1. The modelled ^{226}Ra concentrations were totally

Table 2

^{226}Ra measurement in the solid ($[^{226}\text{Ra}]_{\text{sol.}}$) and in porewater ($[^{226}\text{Ra}]_{\text{aq.}}$), compared to modelled ^{226}Ra distribution and retention by the minerals as calculated using global imagery analysis. Column 14 ("reduced sorption") uses the sorption corresponding to the CEC of each sample as detailed in part 3.1. The partition coefficient (D) is also given. ■ Barite ; ■ HFO ; ■ Clay min. ; ■ U-min.

	Bulk measurements			Modelled			Imagery: global analysis						
	$[^{226}\text{Ra}]_{\text{sol.}}$	$[^{226}\text{Ra}]_{\text{aq.}}$	D	$[^{226}\text{Ra}]_{\text{sol.}}$	$[^{226}\text{Ra}]_{\text{aq.}}$	Mineral retention of ^{226}Ra with $a_0=1.1$	Mineral	Mass activity for the mineral	Mineral mass	Mineral retention of ^{226}Ra	Total ^{226}Ra activity for sample (bulk y measurement)	Column 14: Mineral retention of ^{226}Ra for reduced sorption (see 4.1)	Total ^{226}Ra activity for sample for reduced sorption
	Bq/g	Bq/L		Bq/g	Bq/L			Bq/g	g/g		Bq/g		Bq/g
TRT-1	1630	129	3±1	1664	107		1	Barite 1.80x10 ⁵	3.40 x10 ⁻⁴		1281 (0.8)		770 (0.5)
TRT-2	1590	18	0.2±0.3	1580	18		1.9	Barite 3.30x10 ⁵	4.480x10 ⁻³		1703 (1.1)		1536 (1.0)
TRT-3	1400	13	0.9±0.4	1416	13		1.6	Barite 2.00x10 ⁵	5.71 x10 ⁻³		1346 (1.0)		1190 (0.9)
TMF18-01 SA01	1780	11	1.1±0.3	1795	7		1.2	Barite 7.35x10 ⁵	5.71 x10 ⁻³		5175 (2.9)		4408 (2.5)
TMF18-03 SA02	1370	5.7	2.2±0.6	1375	9		0.3	Barite 1.90x10 ⁵	3.52x10 ⁻³		891 (0.7)		735 (0.5)
TMF18-11 SA03	2920	5.6	0.3±0.1	2949	6		0.7	Barite 3.10x10 ⁵	1.82 x10 ⁻²		5485 (1.9)		5485 (1.9)
TMF18-06 SA16	228	12	0.5±0.1	241	4		1.9	Barite 1.50x10 ⁵	1.72 x10 ⁻³		334 (1.5)		293 (1.3)
TMF18-01 SA24	81	4	2.9±0.7	86	5		0.5	Barite 2.20x10 ⁵	3.40 x10 ⁻⁴		101 (1.2)		101 (1.2)

in accordance with the concentrations measured in the solid (error of $2\% \pm 2$) and in solution ($-4\% \pm 50\%$). Better correlation was obtained by adjusting the partition coefficient for each sample: the optimal Guggenheim coefficients for each sample were thus between 0.3 and 1.9. The results for ^{226}Ra concentrations in the solid modelled with the mean and optimal Guggenheim coefficients are gathered in Figure SI-7. The results of the distribution of ^{226}Ra are presented in Table 2. The results of the modelling confirm that barite holds the majority of the ^{226}Ra in the solid (85–100 %), the rest of it being on the inherited U-minerals. The sorption processes make a minimal contribution ($<1\%$).

3.3. Experimental determination of the distribution of ^{226}Ra using imaging techniques

Alpha-autoradiography

The TRT and TMF samples have a similar homogeneous distribution of α activity over the whole surface of the sample. The main difference in the appearance of the α maps is linked to the texture of the samples: the TRT samples are not compacted, while the TMF samples form coherent aggregates due to their compaction and diagenesis in the TMF. Sample TMF18-01 SA24 is an exception: the activity is gathered in small (100–450 μm), high- activity (up to 130 counts/250 $\mu\text{m}^2/\text{j}$) hot-spots. The alpha maps, all shown in Figure SI-8, show activities consistent with the measured activities of the tailings samples. The appearance of the maps confirms the samples as fine-grained, as was observed during grain-size analysis.

EDS and WDS maps

One area per thin section was chosen on the basis of the alpha maps to perform an SEM-EDS mapping. The objective was to choose elements that would easily target the minerals that were identified by the mineral characterisation as potentially ^{226}Ra -bearing: inherited U-minerals, barites, iron oxy-hydroxides and clay minerals.

The EDS maps were then superimposed on the alpha maps, and the areas with high activity were also analysed by WDS to confirm the identification of the minerals and the quantification shown by the EDS maps. As shown in Fig. 6, WDS associated high alpha activity with the presence of iron oxy-hydroxides, clay minerals and barite, but no U-minerals, in the TMF samples. The barites are small ($<10\ \mu\text{m}$) and distributed in all aggregates but are locally concentrated. In the TMF sample where alpha activity was concentrated into hot-spots, that

activity was associated with uraninite, also bearing As (about 20 % of the mass) and small grains of galena. In the same area, pyrites and HFO were associated with about 2 % barite.

Alpha-autoradiograph and EDS map superposition

The previous observations of the distributions of the alpha activity and of the mineralogy of the tailings confirmed that the ^{226}Ra -bearing minerals are small ($<50\ \mu\text{m}$ pixel size from the alpha-autoradiograph) and homogeneously mixed, except for sample TMF18-01 SA24. Apart from that sample, where some of the alpha activity was directly associated with the presence of uraninites causing alpha hotspots, such geometry prevents a direct correlation between mineralogy and alpha activity. A global analysis of the maps is necessary to consider the entirety of the signal. Comparison of the alpha activity and elemental maps enables a correlation to be established between alpha activity and the chemical composition and identification of the main ^{226}Ra -bearing mineral of the sample, from which an estimation of the contribution of each mineral to the total activity can be made (Besançon et al., 2022). This methodology makes it possible to link mineralogy and occurrence of ^{226}Ra at the scale of the mineral (tens of μm). The alpha and EDS maps were divided into ‘regions of interest’ (ROI) of 4.8 mm² and analysed using the global approach. The contribution of ^{226}Ra to the global alpha signal measured by alpha autoradiography was determined using the alpha spectrometry results. Mg, Fe and U elemental mapping were used to easily identify clay minerals, iron oxy-hydroxides and U-minerals respectively in the EDS maps. Ba could not be directly used for barite mapping, because rutile was seen during mineralogical characterisation and Ti’s K α ray is very close to that of Ba (4.508 and 4.465 keV respectively) (JEOL, 2019), leading to interference when mapping. The elemental map of Ba intersected with S was therefore used to map barite. These maps are shown in Fig. 7.

Details of the correlations between ^{226}Ra activity measured by alpha-autoradiography and mineral occurrence determined by EDS, and on optimal mass activities obtained for the minerals are described in Table 2 (the correction factors for processing the signal are detailed in Table SI-1). These activities are then associated with the mineral masses within the samples using the total bulk chemistry analysis (Ba, Fe, Mg and U) and reported in Table 2.

These results confirm that the samples which have passed through the BaCl₂ neutralisation process at the McClean Lake mill (all samples except TRT-1 and TMF18-01 SA24) have more than 75 % of ^{226}Ra

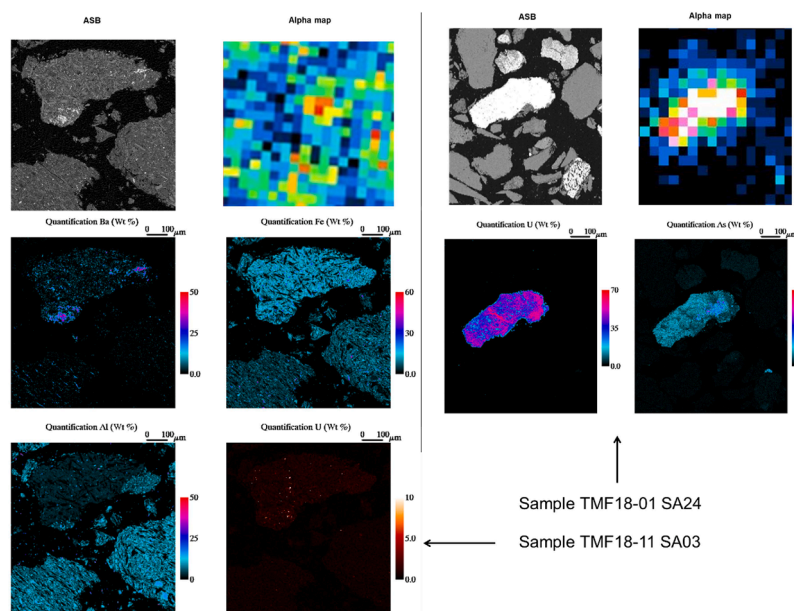


Fig. 6. ASB image, alpha map and WDS elemental maps for ROI of tailings samples where alpha activity was detected.

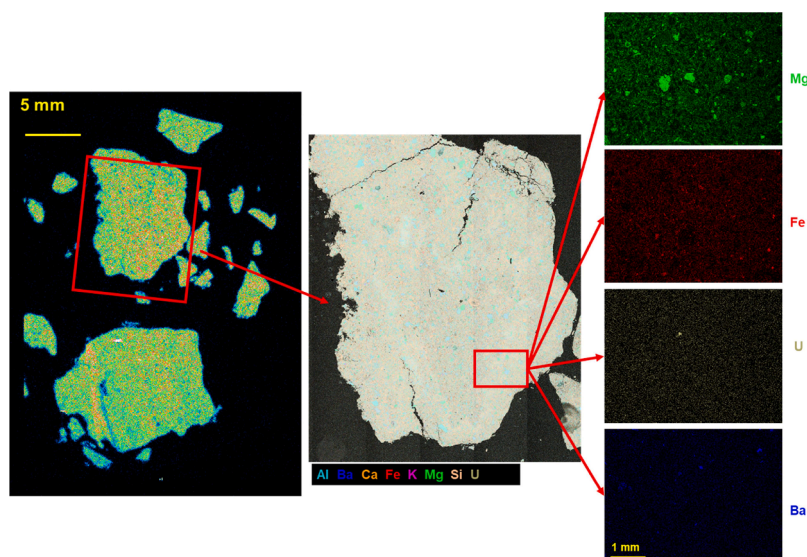


Fig. 7. Left: alpha autoradiograph for sample TMF18-01 SA01. Center: EDS image of part of the same thin section. Right: extractions of the qualitative EDS maps for Mg, Fe, U and Ba.

trapped in barite. The relatively low fraction of ^{226}Ra borne by U-minerals (0–7 %) is consistent with the high extraction yield of the mill. In the case of sample TMF18-01 SA24, the fraction of ^{226}Ra in the U-minerals is higher because of the lower extraction percentage of U. Sample TRT-1 precedes BaCl_2 neutralisation; in this sample a large part of ^{226}Ra is borne by sorption, a less effective retention mechanism than a solid solution. This underlines the efficiency of the BaCl_2 neutralisation step: the change of retention from sorption to solid solution by the precipitation of barites allows the mill to decrease the ^{226}Ra activities in solution from 130 before neutralisation to 5 Bq/L after the process.

4. Discussion

4.1. Remarks considering the methodology: using a global imaging approach

Contribution of this method for fine-grained samples

The method proposed in this study is based on a full set of complementary analyses. The modelling and experimental data acquisitions provide different information, all relevant for the understanding of the dynamics of the retention of trace metals in tailings. To understand the results from both approaches (modelling and experimental), a complete characterisation of the studied material is needed. The study of mine mill tailings sheds additional light on the importance of developing a global approach to the analysis of imaging data, which is an essential methodological development for the study of fine materials. It also renders interpretation possible in the case of materials even finer than the resolution of the acquisition technique, here the 50 μm resolution of the alpha autoradiograph.

The average particle size of a sample is not the only parameter which makes a global approach relevant. The precipitation of secondary mineral phases in the tailings preparation process reduces the average particle size compared with the inherited minerals. As for gypsum or ferrihydrite, the BaCl_2 treatment creates an excess of a newly-formed carrier phase, barite, with a much finer particle size than the average particle size of the sample. The activity is distributed mainly on these small secondary minerals dispersed in the sample and is impossible to study by means of hotspots. The global approach allows for sample-scale quantification and identification of all carrier phases beyond those exhibiting the greatest volumetric alpha activity.

Calculations for ^{226}Ra distribution: verifiability and improvements

The method of systematic alpha-autoradiography and EDS map superposition attributed activities in ^{226}Ra of 0.5 ± 0.5 MBq/g (0.15–1.8 MBq/g) to the barite grains and $1.6 \pm 0.5 \times 10^4$ Bq/g ($1.0\text{--}2.4 \times 10^4$ Bq/g) to the uraninite grains for all samples. The activity of a uraninite grain is 1.09×10^4 Bq/g ^{238}U , with equal activity in ^{226}Ra if the grain is considered to be in secular equilibrium as is the case for such old deposits. The slight overestimation by this method is linked to the number of alpha-emitters borne by uraninite grains. As most of the samples are not at equilibrium overall, 18 % of the total alpha emission of the sample was attributed to ^{226}Ra . However, at secular equilibrium with ^{238}U , only 12 % of the total alpha emission of the uraninite grains are linked to ^{226}Ra . This leads to a small overestimation of the ^{226}Ra in the uraninite grains. ^{226}Ra -rich barites were measured with activities in the range of 0.02–0.5 MBq/g for recrystallised barites by (Heberling et al., 2018) and in the range of 0.1–3 MBq/g for co-precipitated barites by (Billon et al., 2024). As will be discussed below, the barites of the McClean tailings samples are a mixture of co-precipitated and recrystallised barites which correspond well to the activities measured.

The ^{226}Ra activity calculated on the thin sections by the systematic alpha-autoradiography and EDS map superposition method reached values 1.4 ± 0.7 times the activity of the bulk sample measured by gamma spectrometry. Considering the very different representative volumes between these two techniques, the results are close. Some refinements to the technique might help achieve a better correlation.

The complex mineralogy of these tailings has only been considered through the elemental mapping of a small number of marker elements of the minerals identified in the ^{226}Ra retention. To complete a prior mineralogical analysis, it would be possible to process the data acquired by SEM/EDS using mineralogical identification software such as QEMSCAN®. This treatment would allow the mineralogy of the samples to be taken into account more precisely, for example the diversity of clay minerals. However, the data processing time would be extended because the addition of this identification is more difficult to automate.

The approach chosen here to simplify mineralogical quantifications was to use the bulk total chemistry with elements which are part of the signature of the minerals of interest (Ba for barite, Fe for HFO, Mg for clay minerals), but not exclusively. This leads to an overestimation of the amount of such phases, especially for HFO. Characterisation of the tailings helps the uncertainty around this approach to be better understood. The retention modelled by calculating the retention sites corresponding to the bulk-mineralogy approach is 4 ± 1 times higher

than the CEC measured for the tailings samples (available in Table SI-1). Retention by sorption processes is therefore only one fourth, approximately, of what was detected. The retention by sorption was lowered by this ratio in Table 2, the ^{226}Ra activities calculated are then 1.2 ± 0.7 the activities measured by gamma spectrometry.

The global analysis used is an approximate calculation of the contribution of ^{226}Ra to the alpha activity measured on the sample. This calculation is done by measuring the ^{226}Ra on the bulk sample by alpha spectrometry and is then applied to all the pixels of the alpha maps. This reduces the influence of phases carrying ^{226}Ra exclusively (such as barite) and overestimates the importance of phases carrying several radionuclides or alpha-emitting radionuclides other than ^{226}Ra , such as U phosphates, iron oxy-hydroxides and primary minerals of U. There are possible ways to improve this calculation.

A first option would consist of initially using elementary mapping to associate a ^{226}Ra contribution factor, which will depend on the mineralogy, with each alpha map pixel. As each mineral retains a different number of alpha emitters (uraninite would have all eight alpha emitters of the ^{238}U decay chain at secular equilibrium, while neoformed barite would retain only ^{226}Ra and the first elements of its decay chain, so four alpha emitters in this case), this would allow better precision about the activity of each mineral to be achieved.

A second solution would consist of exploiting the spectrum obtained by alpha autoradiography in order to determine the spatial contribution of each alpha emitter and the number of emitters per pixel (Lefevre et al., 2022).

4.2. Assessing the stability of barite as a trap for ^{226}Ra in the McClean tailings

The formation of a solid solution is often more thermodynamically stable than the physical mixing of the two crystalline poles: the Gibbs free energy is reduced by the increase in entropy of the crystal lattices in solid solution (Grandia et al., 2008; Prieto et al., 2013). This allows ^{226}Ra , which would normally remain soluble at these concentrations, to be incorporated in a (Ba,Ra) SO_4 solid solution.

Description of the solid solution model

By studying the incorporation of ^{226}Ra into barite, H.A. Doerner and Hoskins (1925) made the distinction for the first time between two formations of solid solutions: “coprecipitation”, and “replacement” (or recrystallisation). Coprecipitation occurs during the precipitation of a new solid phase from a solution. The mineral forming is in equilibrium with the solution while major and trace elements of the solid solution are subtracted from the solution at the same time. Recrystallisation occurs by the change (or rearrangement) of a pre-existing phase being saturated in the aqueous solution. Only the surface of the mineral is in equilibrium with the solution. The chemical composition of the initial mineral is modified by exchange between the substituted element and the substituting element with the solution (Curti, 1997; H.A. Doerner and Hoskins, 1925b; Zhang et al., 2014). It should be noted that this distinction is macroscopic. At the nanometric scale, the distinction between coprecipitation and recrystallisation is more tenuous, with incorporation into the solid solution occurring through microporosities (Weber, 2017) and microcrystallites on the surface of the minerals.

A thermodynamic description: results of modelling and short-term equilibrium

The thermodynamic equilibrium of a solid solution is defined by the mass action equations from which Guggenheim (1937) wrote the Gibbs equation of the excess free energy of formation for a solid solution according to Eq. (1):

$$G^E = x(1-x)RT(a_0 + a_1((1-x)-x) + a_2((1-x)-x)^2 + \dots) \quad (1)$$

with R the ideal gas constant, T the temperature and a_i the dimensionless

parameters (Guggenheim coefficients of excess free energy). In an ideal solid solution, $a_0 = a_1 = 0$. The Guggenheim coefficient is used in PHREEQC to define solid solutions (Glynn and Reardon, 1990). In the case of radiobarite (Ba,Ra) SO_4 , values in the literature for a_0 vary between 0 and 2.5 (Brandt et al., 2015; Curti et al., 2010; H.A. Doerner and Hoskins, 1925b; Heberling et al., 2018; Vinograd et al., 2013). The value of 1.1, which here minimises the difference between modelled and measured ^{226}Ra concentrations for all samples, is within that range and shows the deviation from ideality of the solid solution.

To obtain more precision, the Guggenheim coefficients, which most accurately reproduce the concentrations measured, are adjusted specifically for each sample. Their values are reported in Table 2 and are in the range of 0.3–1.9. All these values fit within the range of reported values in the literature and confirm that a (Ba,Ra) SO_4 solid solution can properly fit these concentrations of ^{226}Ra in the solid and in solution.

An empirical description: diagenesis in the TMF, variation of the distribution coefficient

Solid solutions are generally described by partition law models. These are empirical laws established during coprecipitation and recrystallisation experiments, being first established by H.A. Doerner and Hoskins (1925) for the partition coefficient D expressed in Eq. (2):

$$D = \frac{X_{\text{RaSO}_4(s)}}{X_{\text{BaSO}_4(s)}}, \quad (2)$$

where $X_{\text{RaSO}_4(s)}$ et $X_{\text{BaSO}_4(s)}$ are the molar fractions of solid phases RaSO_4 (s) et BaSO_4 (s) of the solid solution, and $[\text{Ra}^{2+}]$ et $[\text{Ba}^{2+}]$ the total aqueous concentrations of the substituent/substituted ions (Glynn and Reardon, 1990). In an ideal solid solution, $D_{\text{ideal}} = 1.95$ (Heberling et al., 2018). Experimental data enables the identification of a different partition coefficient between coprecipitation ($D = 1.6 \pm 0.3$) (H.A. Doerner and Hoskins, 1925b; Gordon and Rowley, 1957; Langmuir and Reise, 1985b; Marques, 1934; Zhang et al., 2014) and recrystallisation ($D = 1.0 \pm 0.6$) (Brandt et al., 2020, 2015; Curti et al., 2010; Heberling et al., 2018; Rosenberg et al., 2011; Vinograd et al., 2013) for the (Ba,Ra) SO_4 solid-solution.

The partition coefficient is calculated for the tailings samples using total ^{226}Ra and Ba in the solid and $[\text{Ra}^{2+}]$ and $[\text{Ba}^{2+}]$ concentrations in the porewater. This calculation was made on 50 samples from the 2018 sampling campaign and 34 samples from the 2021 sampling campaign. The results for the partition coefficients are presented in Fig. 8 and in Table 2 for the selected eight samples.

For all samples, the computed partition coefficient is consistent with the solid solution being the main retention mechanism rather than sorption. Among the selected samples, two values of partition coefficient are higher than those reported in the literature: 3.0 for sample TRT-1 and 2.9 for sample TMF18-01 SA24. Sample TRT-1 precedes the BaCl_2 treatment and so the value of the partition coefficient implies that a significant part of the ^{226}Ra is retained by a phase other than the barite, as shown by the global study of α and EDS maps: the barites present in this sample are inherited from the ore. A partition coefficient of recrystallisation of the solid solution (Ba,Ra) SO_4 ($D = 1$) can be achieved for this sample if 33 % of ^{226}Ra of the sample is borne by the solid solution. This value agrees with that of 27 % obtained by the overall study of the sample. For sample TMF18-01 SA24, barite cannot be the only carrier phase. The results of the overall analysis confirm that only 75 % of the ^{226}Ra in the solid is carried by the barite, identifying the remaining ^{226}Ra as carried by U-minerals. The results from the global analysis approach using imaging techniques are therefore confirmed by the calculation of the equilibrium of the (Ba,Ra) SO_4 solid solution.

Within the JEB TMF, it is observed that the overall partition coefficient decreases with the depth of the tailing and therefore with its age. This is very clear when considering only one origin of tailings, such as the Cigar Lake tailings in Fig. 8 (right) or the entirety of the tailings

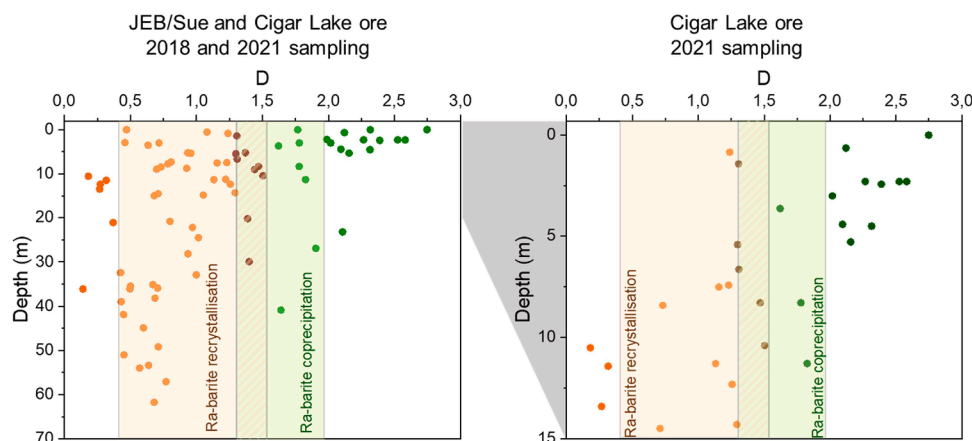


Fig. 8. Variation of the partition coefficient of the (Ra,Ba)SO₄ solid solution within the JEB TMF.

samples (left). The partition coefficient changes from being typical of the coprecipitation mechanism to being typical of the recrystallisation mechanism. No sample from deeper than 30 m has a partition coefficient high enough for the coprecipitation mechanism.

The neutralisation treatment causes conditions of high supersaturation of barite in a solution rich in ²²⁶Ra: at the end of this treatment, the coprecipitation of the solid solution (Ba,Ra)SO₄ is predominant until equilibrium of the barite with the solution has been reached ($D > 1$ for recently deposited residues). The progressive precipitation of barite continues between the mill site and the TMF: the mass of barite increases, which causes an increase in the quantity of Ra in the solid and a reduction of $[^{226}\text{Ra}]_{\text{aq}}$, considering that the mole fraction $\frac{X_{\text{RaSO}_4(s)}}{X_{\text{BaSO}_4(s)}}$ expressed in Eq. (2) is a constant. At the tailings thickener underflow the average concentration of $[^{226}\text{Ra}]_{\text{aq}}$ is 10 Bq/L and it is around 5 Bq/L in recently deposited tailings. Once equilibrium has been reached, precipitation stops. The solid solution can then tend towards a recrystallisation equilibrium ($D < 1$) with the interstitial solution. This change in reaction mechanism has taken place very quickly since the tailings have only been produced since 1999. Looking at the Cigar Lake tailings from the 2021 sampling campaign, the transition from coprecipitation to recrystallisation was made in less than six years. In the long term, the ²²⁶Ra from the tailings will therefore be trapped by the barite via a recrystallisation equilibrium. Understanding this change in partition coefficient values, from $D \sim 2.5$ in recent tailings to $D \sim 0.5$ in older tailings during the diagenesis of tailings, is essential for the long-term management of tailings and their stability, because it modifies the ²²⁶Ra concentration in the porewater.

Long term stability with equilibrium of recrystallisation

According to the definition of the partition coefficient, a reduction in the value of D with fixed $X_{\text{BaSO}_4(s)}$ and (Ba^{2+}) (there is no precipitation or dissolution of barite, which is at equilibrium in the tailings) corresponds to a re-dissolution of part of the ²²⁶Ra in the solid solution $X_{\text{RaSO}_4(s)}$ and therefore an increase in (Ra^{2+}) . Long-term concentrations in the TMF will therefore be higher (around 10 Bq/L) than those observed in recently deposited tailings (around 5 Bq/L). The concentrations already observed in the oldest tailings (sample TMF18–06 SA16 for example) will remain stable over time because the recrystallisation equilibrium of the solid solution (Ba,Ra)SO₄ has been reached.

The saturation indices of the minerals for all tailings samples show that the barite remains stable; and it is a mineral known for being very insoluble. Therefore, the retention of ²²⁶Ra in barite will also remain stable for the long term.

5. Conclusion

The BaCl₂ treatment process is essential for tailings neutralisation, as it allows ²²⁶Ra concentration in the tailings porewater to decrease from >100 Bq/L at the end of U leaching in the mill process to about 5 Bq/L in the tailings placed in the Tailings Management Facility. This study shows that ²²⁶Ra is trapped within a matrix of barite, forming a (Ra,Ba)SO₄ solid solution, confirmed both by thermodynamical modelling and by imaging techniques. This is the first case of the implementation of a novel approach using imaging techniques on mine tailings samples. A global statistical treatment of the signal allows the identification of radionuclide-bearing minerals even in the very fine-grained materials. Using barite for ²²⁶Ra retention was also identified as very stable in the long term: barite was confirmed as the retention phase for the majority of ²²⁶Ra, even for the oldest tailings that were studied. The slight increase in the concentration of ²²⁶Ra in the tailings porewater with depth was interpreted as short-term diagenesis of the tailings within the TMF. The radical changes of the chemistry of the tailings during the neutralisation process require time to reach equilibrium. In particular, it was identified that the (Ra,Ba)SO₄ solid-solution is mostly formed via a coprecipitation process and changes slowly towards a recrystallisation equilibrium. This process was observed in tailings which are less than 30 years old. This work allows the long-term state of ²²⁶Ra in the tailings to be identified more accurately so that they can be modeled by a simplified model using the characteristics of a recrystallised solid-solution in equilibrium with the porewater measured in the deep tailings.

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CRediT authorship contribution statement

C. Besançon: Writing – original draft, Methodology, Investigation, Data curation, Conceptualization. **M. Gérard:** Writing – review & editing, Supervision, Resources, Project administration, Methodology. **F. Lahrouch:** Writing – review & editing, Investigation. **K. Hughes:** Writing – review & editing, Resources. **P. Sardini:** Writing – review & editing, Supervision, Resources, Methodology, Conceptualization. **S. Savoye:** Writing – review & editing, Supervision, Resources, Methodology. **M. Descostes:** Writing – review & editing, Supervision, Resources, Project administration, Methodology, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

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Data availability

Data will be made available on request.

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Supporting Information for
Investigating the geochemical model for molybdenum mineralization in the JEB Tailings
Management Facility at McClean Lake, Saskatchewan: A X-ray absorption spectroscopy

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Tables

Table S1. Molybdenum pore water concentrations, as determined by ICP-MS, in the tailings samples collected during the 2013 and 2008 sampling campaign of the TMF. Errors in the Mo pore water concentrations are estimated to be 15% for concentrations greater than 1 mg/L. Errors are shown in brackets.

2013 sampling campaign			2008 sampling campaign		
Sample	Sample Elevation (mASL ^a)	Mo Pore Water Concentration (mg/L)	Samples	Sample Elevation (mASL ^a)	Mo Pore Water Concentration (mg/L)
TMF13-01-SA01	423.49	15(2)			
TMF13-01-SA03	420.47	22(3)			
TMF13-01-SA04	417.78	16(2)			
TMF13-01-SA06	411.68	15(2)	TMF08-01-SA04	411.06	22(3)
TMF13-01-SA11	399.46	16(2)			
TMF13-01-SA12	398.85	20(3)	TMF08-01-SA09	398.23	11(2)
TMF13-01-SA14	395.47	8(1)			
TMF13-01-SA19	383.59	5(1)			
TMF13-01-SA20	379.68	12(2)			
TMF13-01-SA21	377.49	10(1)			
TMF13-01-SA22	374.47	10(1)			
TMF13-01-SA23	371.37	6(1)			
TMF13-01-SA24	367.46	6(1)	TMF08-01-SA19	366.86	5(1)
TMF13-01-SA25	365.27	1.3(2)			
TMF13-03-SA02	416.89	8(1)			
TMF13-03-SA04	414.37	8(1)			
TMF13-03-SA06	411.37	31(5)	TMF08-03-SA02	411.97	33(5)
TMF13-03-SA07	409.77	37(6)			
TMF13-03-SA11	401.37	44(7)			
TMF13-03-SA12	398.37	30(4)	TMF08-03-SA08	397.04	13(2)
TMF13-03-SA14	392.20	4(1)			
TMF13-03-SA15	388.46	7(1)			
TMF13-03-SA19	379.40	1.6(2)			
TMF13-03-SA21	373.60	1.02(2)			
TMF13-03-SA22	371.09	2.7(4)	TMF08-03-SA16	370.52	5(1)

^a mASL = meters Above Sea Level

Table S2. The concentration of select elements in the JEB TMF tailings solids as determined by ICP-MS.

Samples	Al (µg/g)	As (µg/g)	Ba (µg/g)	Cr (µg/g)	Co (µg/g)	Cu (µg/g)	Fe (µg/g)	Pb (µg/g)	Mo (µg/g)	Ni (µg/g)	Se (µg/g)	U (µg/g)
TMF13-01-SA01	30900	7700	480	170	110	88	22500	670	190	5800	7.2	206
TMF13-01-SA03	33300	3370	280	260	26	44	15600	310	167	2360	2.8	176
TMF13-01-SA04	29800	921	47	220	12	17	10800	240	32	720	2.1	136
TMF13-01-SA06	23400	477	29	230	15	26	9800	120	25	386	0.4	45
TMF13-01-SA11	31500	229	120	230	8.6	18	8800	500	118	189	5.1	620
TMF13-01-SA12	43000	306	270	200	13	25	10900	770	194	263	7.8	326
TMF13-01-SA14	24300	124	41	200	5	13	7500	270	47	111	3.1	344
TMF13-01-SA19	37100	320	58	190	11	23	10400	490	87	253	8.4	306
TMF13-01-SA20	39200	284	87	220	12	21	19600	450	88	201	4.8	348
TMF13-01-SA21	15500	288	46	82	12	18	10000	520	57	361	13	252
TMF13-01-SA22	35700	1070	160	180	30	67	15200	1200	133	985	14	496
TMF13-01-SA23	41700	1060	220	210	36	110	14900	1000	84	987	25	483
TMF13-01-SA24	27500	62	65	210	3.9	8.1	7400	480	40	55	3.6	267
TMF13-01-SA25	53300	7300	1560	150	160	250	37900	1800	108	4140	37	675
TMF13-03-SA02	39000	11800	730	240	230	210	35700	760	218	8100	7.5	187
TMF13-03-SA04	66200	16900	1340	140	280	180	44600	760	345	11800	9.8	258
TMF13-03-SA06	44800	2410	160	140	19	21	15600	560	143	2450	5	92
TMF13-03-SA07	79500	4940	630	170	28	28	23800	500	198	3180	4.9	214
TMF13-03-SA11	60400	490	130	290	100	11	7700	110	36	307	1.2	125
TMF13-03-SA12	61100	218	200	290	7	12	7500	160	37	176	1.6	196
TMF13-03-SA14	84700	725	1000	240	21	42	12900	2000	424	549	13	348
TMF13-03-SA15	64500	130	110	280	7.1	13	8300	360	82	131	4.6	148
TMF13-03-SA19	89100	1340	1010	110	36	77	18300	2200	295	950	18	330
TMF13-03-SA21	84800	1670	1650	80	50	140	26200	6800	505	1130	29	382
TMF13-03-SA22	62100	3500	6900	80	82	200	28000	6100	435	1870	34	545

Table S3. A comparison of R-factors and χ^2 values for the fittings of the Mo K-edge XANES spectra of the 2013 tailings samples fitted to three and four components. Note the significant improvements in R-factors and χ^2 values when fitting the spectra to four components.

Sample	Sample Elevation (mASL ^a)	3 component fits ^a		4 component fits ^b	
		R-factor	χ^2	R-factor	χ^2
TMF13-01-SA01	423.49	0.00665	0.136	0.00276	0.0592
TMF13-01-SA03	420.47	0.00742	0.183	0.00306	0.0790
TMF13-01-SA04	417.78	0.0181	0.453	0.00400	0.0932
TMF13-01-SA06	411.68	0.00544	0.156	0.00415	0.115
TMF13-01-SA11	399.46	0.0113	0.293	0.00181	0.0470
TMF13-01-SA12	398.85	0.00813	0.211	0.00230	0.0519
TMF13-01-SA14	395.47	0.0123	0.321	0.00304	0.0747
TMF13-01-SA19	383.59	0.00910	0.229	0.00185	0.0466
TMF13-01-SA20	379.68	0.00745	0.192	0.00400	0.102
TMF13-01-SA21	377.49	0.0294	0.741	0.00450	0.113
TMF13-01-SA22	374.47	0.0244	0.608	0.00196	0.0489
TMF13-01-SA23	371.37	0.0231	0.579	0.00306	0.0778
TMF13-01-SA24	367.46	0.00976	0.261	0.00319	0.0855
TMF13-01-SA25	365.27	0.00973	0.239	0.00417	0.102
TMF13-03-SA02	416.89	0.00459	0.121	0.00281	0.0742
TMF13-03-SA04	414.37	0.00685	0.171	0.00391	0.0974
TMF13-03-SA06	411.37	0.00376	0.0980	0.00195	0.0508
TMF13-03-SA07	409.77	0.00209	0.0519	0.000993	0.0247
TMF13-03-SA11	401.37	0.0146	0.400	0.00871	0.239
TMF13-03-SA12	398.37	0.00431	0.117	0.00269	0.0732
TMF13-03-SA14	392.20	0.00774	0.200	0.00335	0.0866
TMF13-03-SA15	388.46	0.00849	0.213	0.00282	0.0709
TMF13-03-SA19	379.40	0.00353	0.0935	0.00214	0.0565
TMF13-03-SA21	373.60	0.0101	0.259	0.00406	0.103
TMF13-03-SA22	371.09	0.00469	0.121	0.00286	0.0750

^aSpectra were fitted to CaMoO_4 , $\text{Fe}(\text{OH})_3 - \text{MoO}_4$, and $\text{Fe}_2(\text{MoO}_4)_3 \cdot 8\text{H}_2\text{O}$.

^bSpectra were fitted to CaMoO_4 , $\text{Fe}(\text{OH})_3 - \text{MoO}_4$, $\text{Fe}_2(\text{MoO}_4)_3 \cdot 8\text{H}_2\text{O}$, and MoS_2 .

Figures

Figure S1

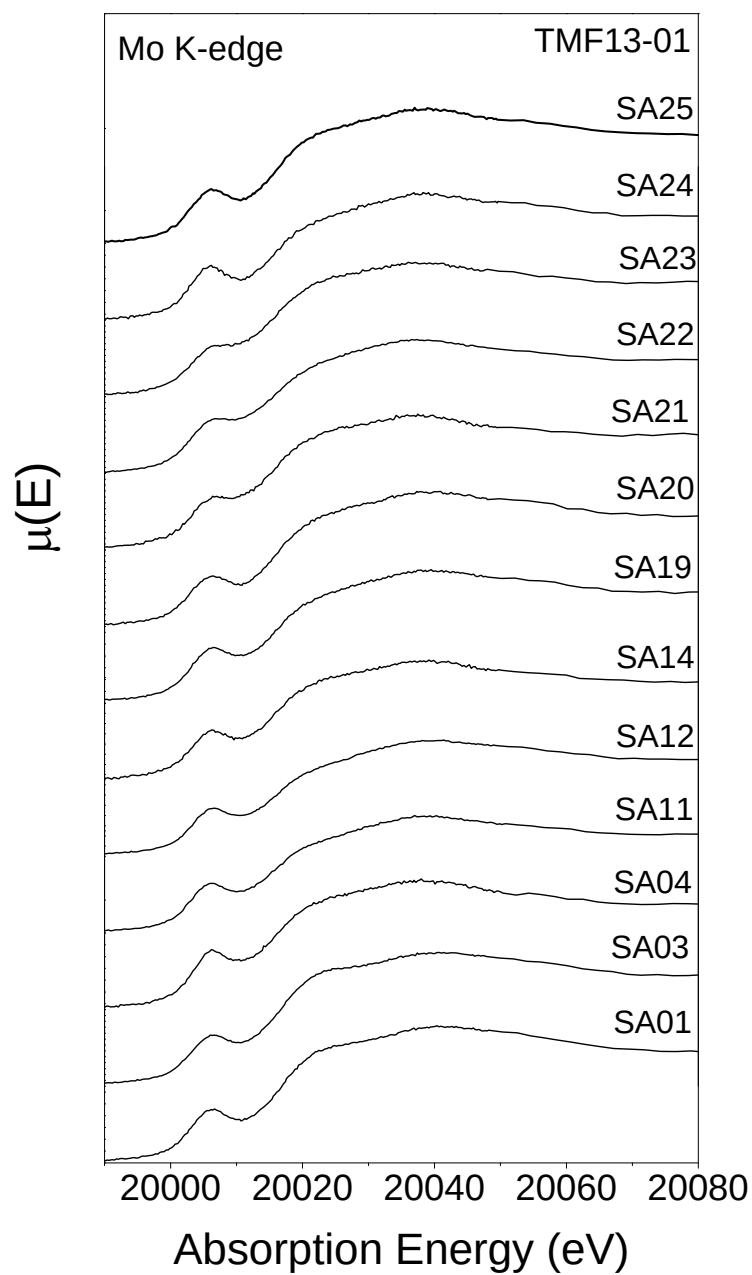


Figure S1. The Mo K-edge XANES spectra of tailings samples collected from the central (TMF13-01) bore-hole.

Figure S2

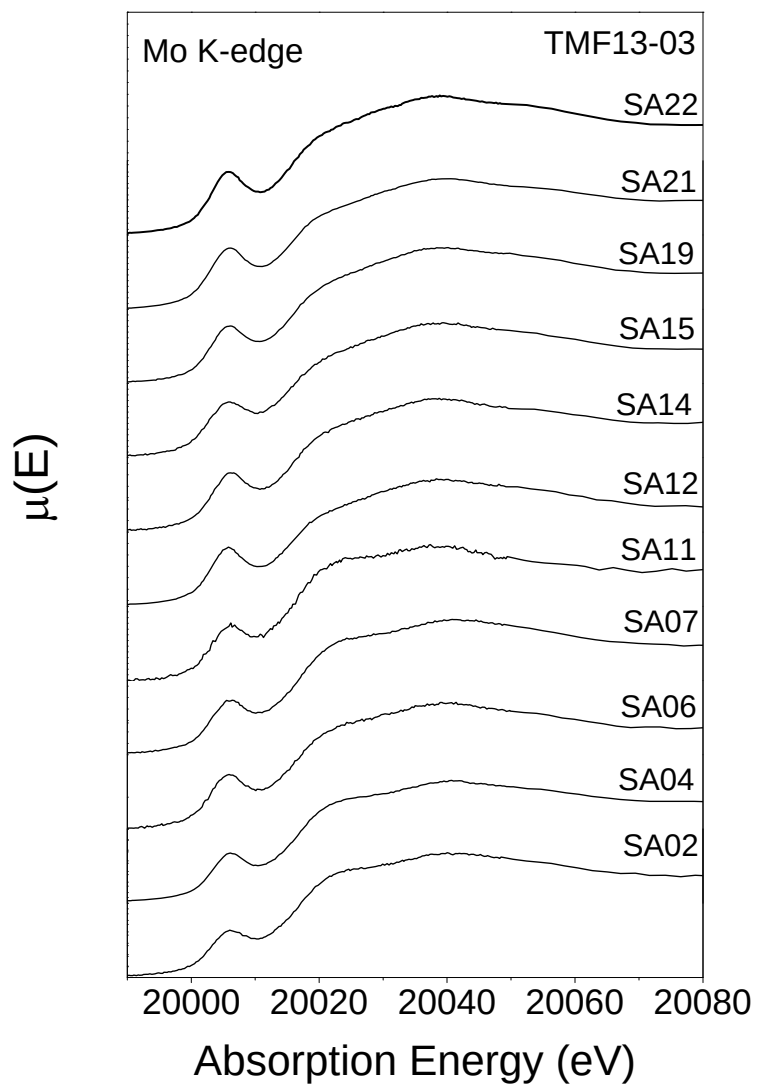


Figure S2. The Mo K-edge XANES spectra of tailings samples collected from the peripheral bore-hole.. (TMF13-03)

Figure S3

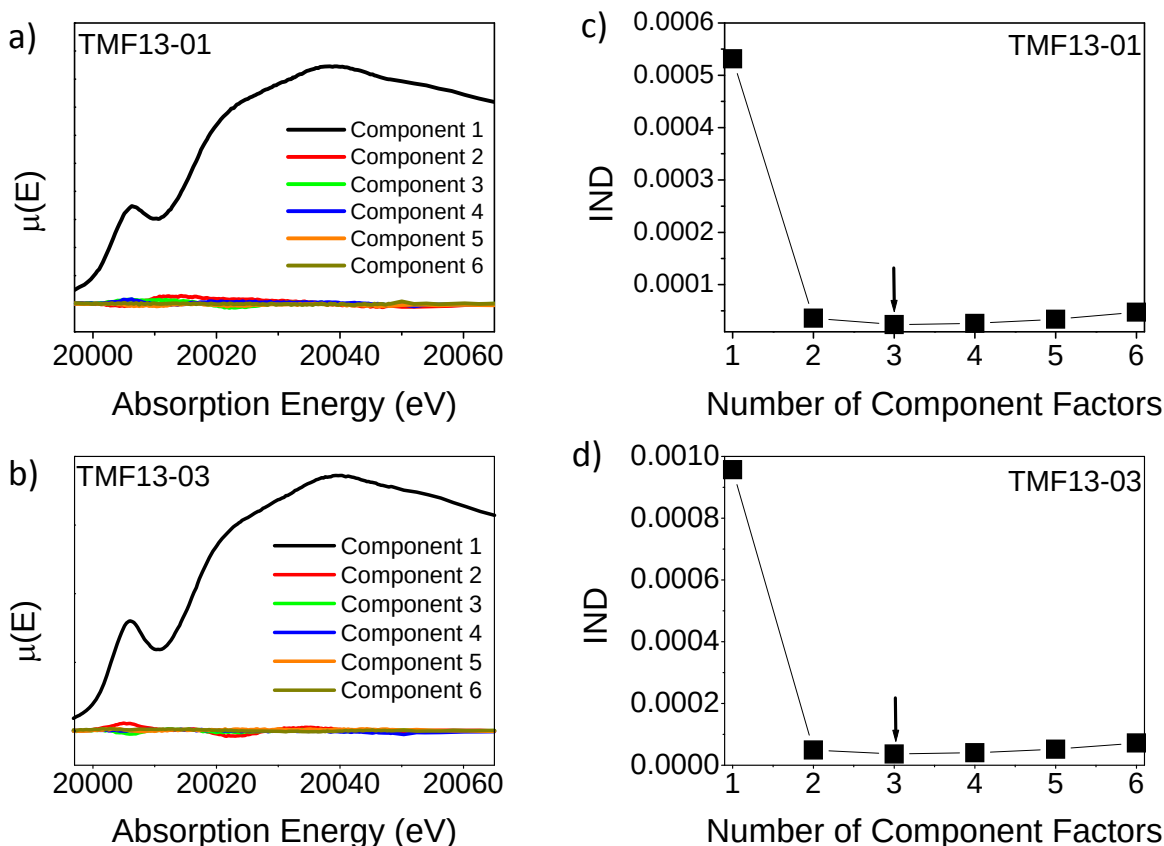


Figure S3. The principle components calculated from the PCA analysis of tailings samples from the a) central and b) peripheral bore-holes. For clarity, only components 1-6 are shown. Component 1 generally has the strongest intensity, accounting for >98 % of the variances. Components 2-4 have similar intensity. The IND functions were calculated and plotted against the number of components calculated for the c) central and d) peripheral bore-holes. The IND function approaches a minimum when the number of component factors is three in both bore-holes. However, The IND values calculated for components 2-4 are similar, possibly indicating each spectrum contains two to four components.

Figure S4

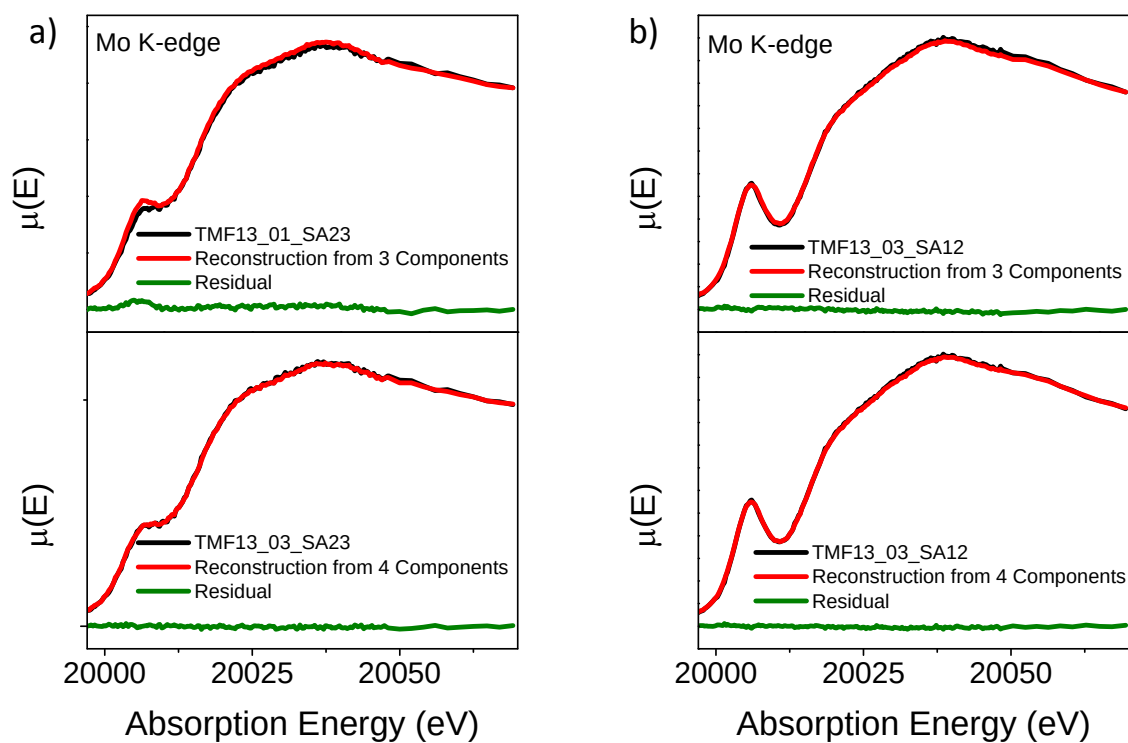


Figure S4. The reconstructed Mo K-edge XANES spectra of a) TMF13-01-SA23 and b) TMF13-03-SA12 using either three (top) or four (bottom) components.

Figure S5

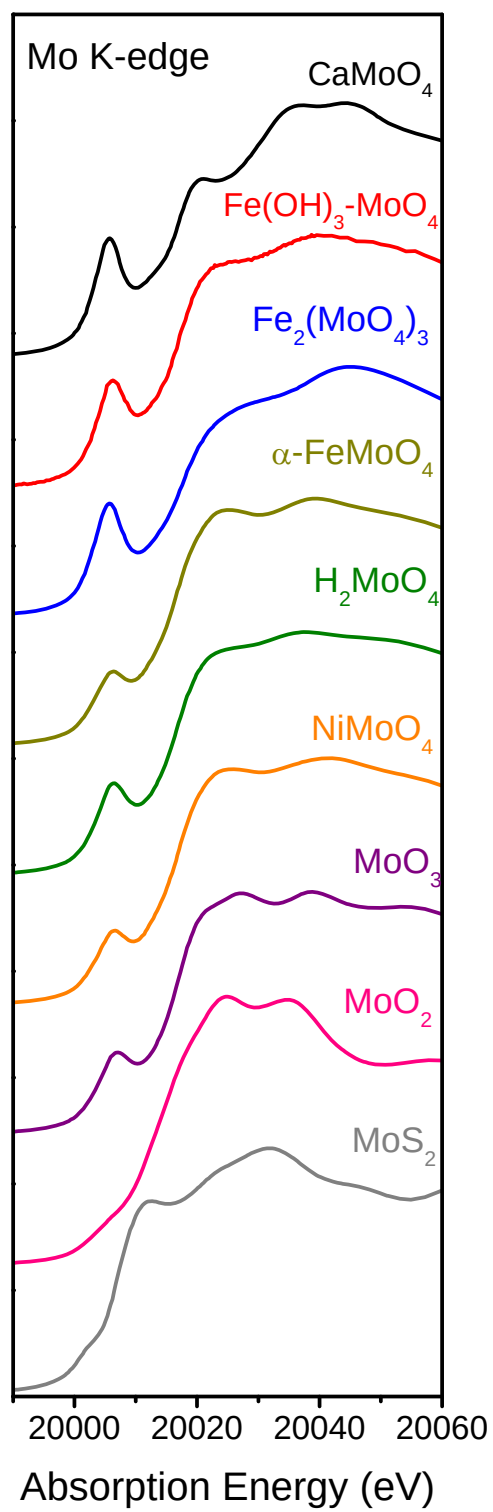


Figure S5. The Mo K-edge XANES spectra of various Mo^{4+} and Mo^{6+} standards. Spectra were first reported in ref. 6.

Figure S6

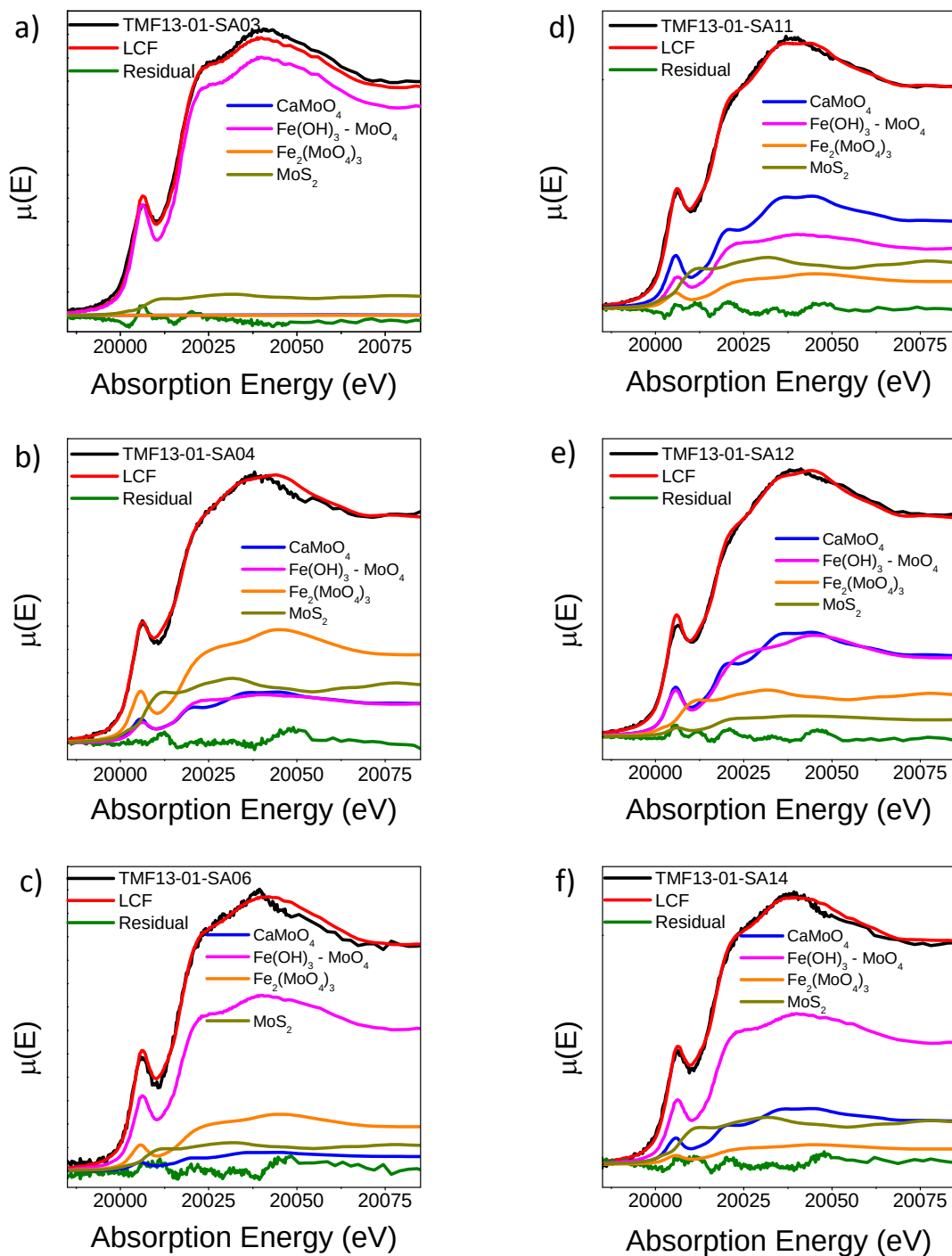


Figure S6. The fitted Mo K-edge XANES spectra of a) TMF13-01-SA03, b) TMF13-01-SA04, c) TMF13-01-SA06, d) TMF13-01-SA11, e) TMF13-01-SA12, and f) TMF13-01-SA14. Linear combination fit of the spectrum is shown in red and the residual is shown in green. The weighted spectra of the standards used to the fit the spectra are also shown.

Figure S7

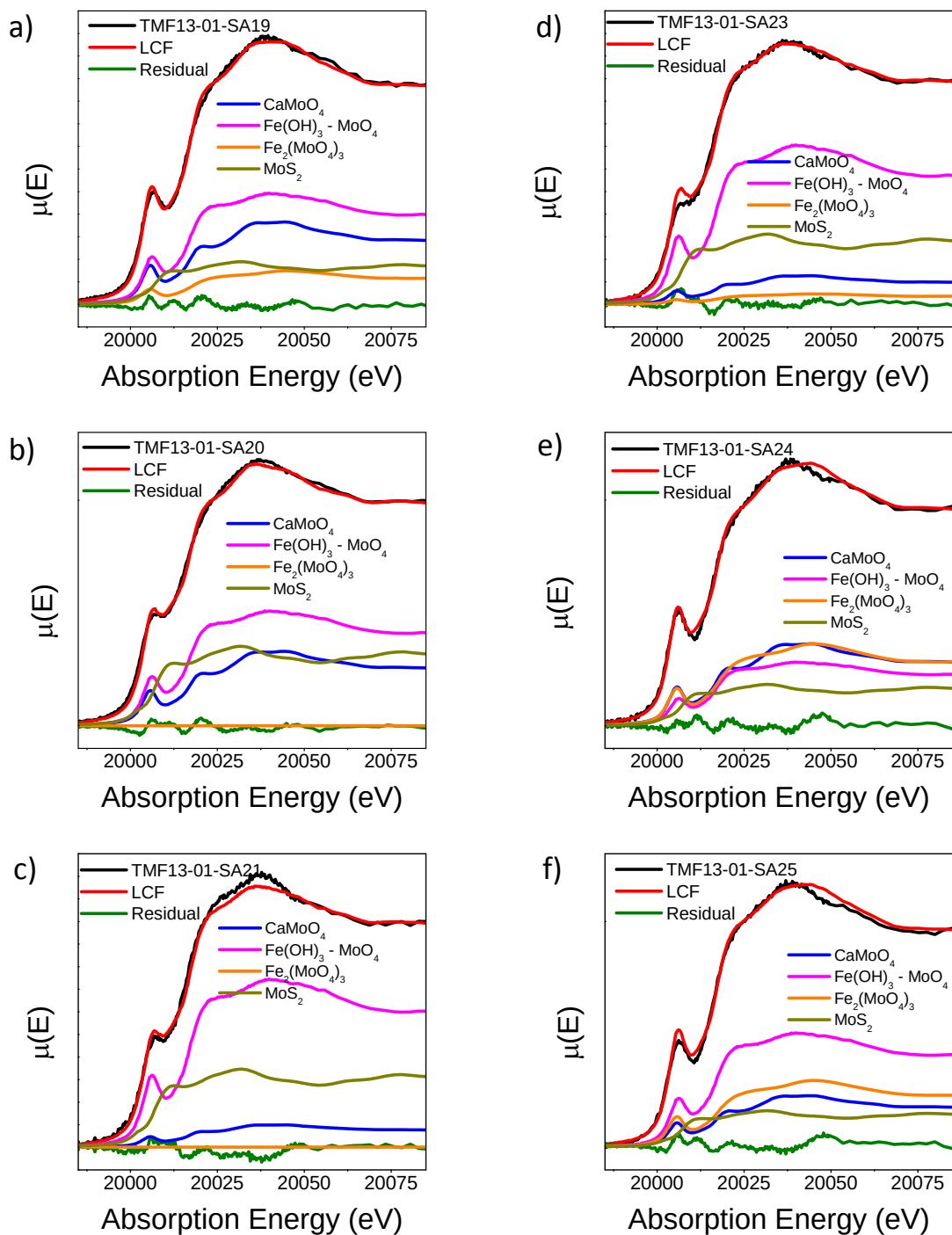


Figure S7. The fitted Mo K-edge XANES spectra of a) TMF13-01-SA19, b) TMF13-01-SA20, c) TMF13-01-SA21, d) TMF13-01-SA23, e) TMF13-01-SA24, and f) TMF13-01-SA25. The linear combination fit of the spectrum is shown in red and the residual is shown in green. The weighted spectra of the standards used to the fit the spectra are also shown.

Figure S8

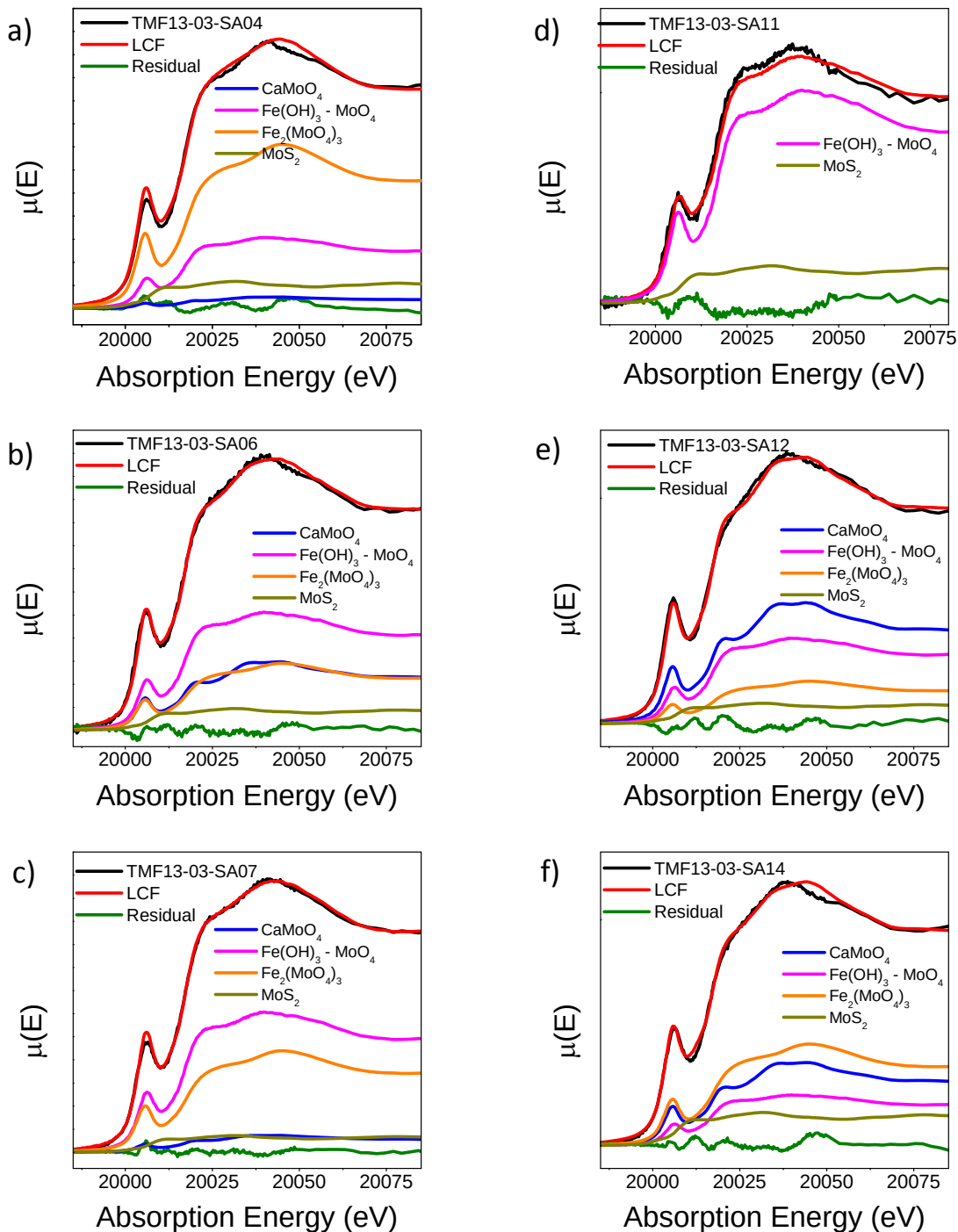


Figure S8. The fitted Mo K-edge XANES spectra of a) TMF13-03-SA04, b) TMF13-03-SA06, c) TMF13-03-SA07, d) TMF13-03-SA11, e) TMF13-03-SA12, and f) TMF13-03-SA14. The linear combination fit of the spectrum is shown in red and the residual is shown in green. The weighted spectra of the standards used to the fit the spectra are also shown.

Figure S9

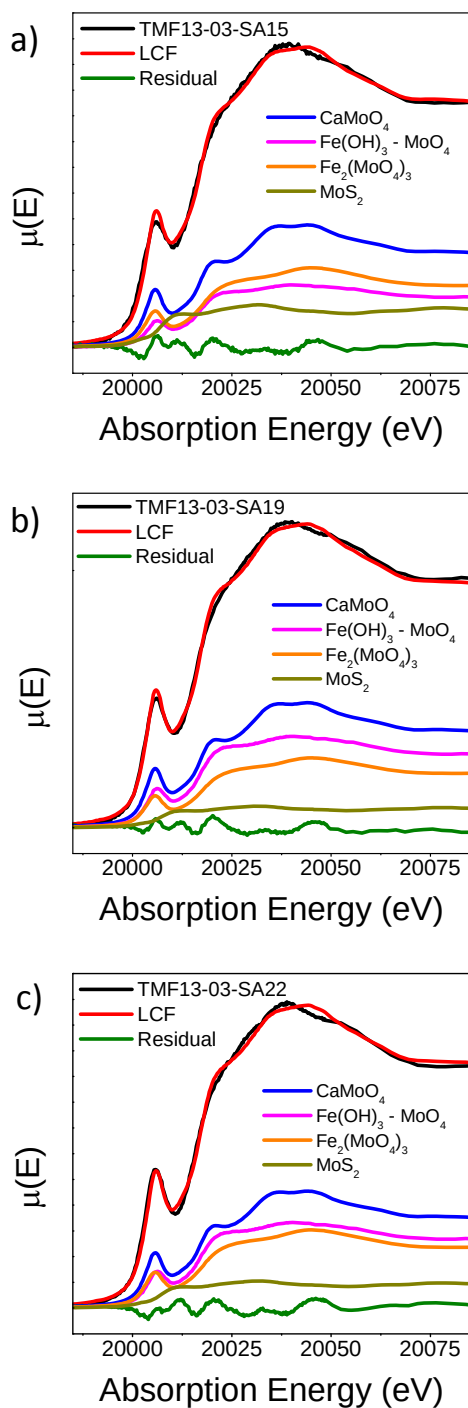


Figure S9. The fitted Mo K-edge XANES spectra of a) TMF13-03-SA15, b) TMF13-03-SA19, and c) TMF13-03-SA22. The linear combination fit of the spectrum is shown in red and the residual is shown in green. The weighted spectra of the standards used to the fit the spectra are also shown.

Figure S10

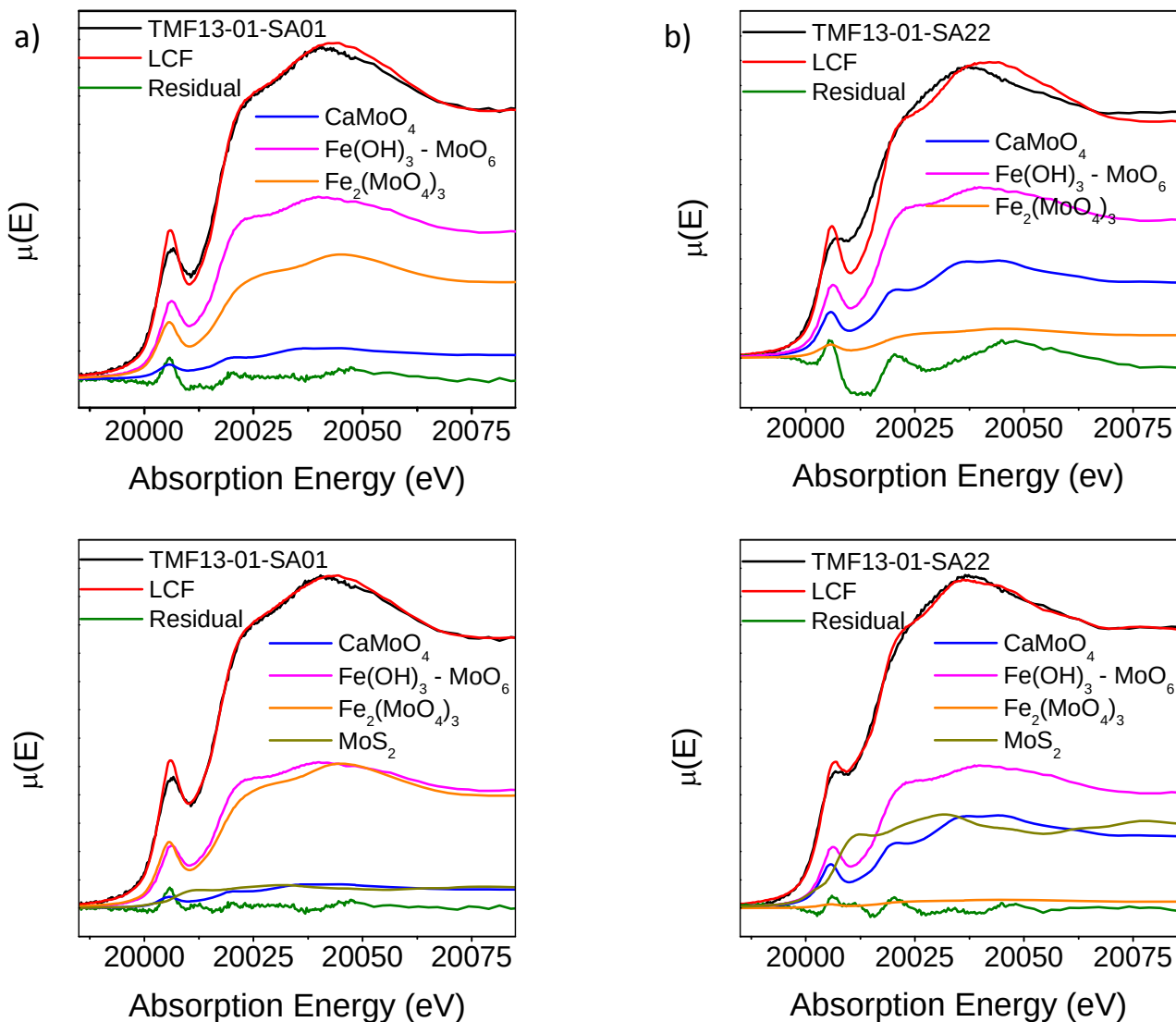


Figure S10. The fitted Mo K-edge XANES spectra of tailing samples a) TMF13-01-SA01 (7 at% molybdenite) and b) TMF13-01-SA22 (28 at% molybdenite) fitted to three (top) and four (bottom) components. Improvements to the fits were obtained when the spectra were fitted with molybdenite as the fourth component.

Figure S11

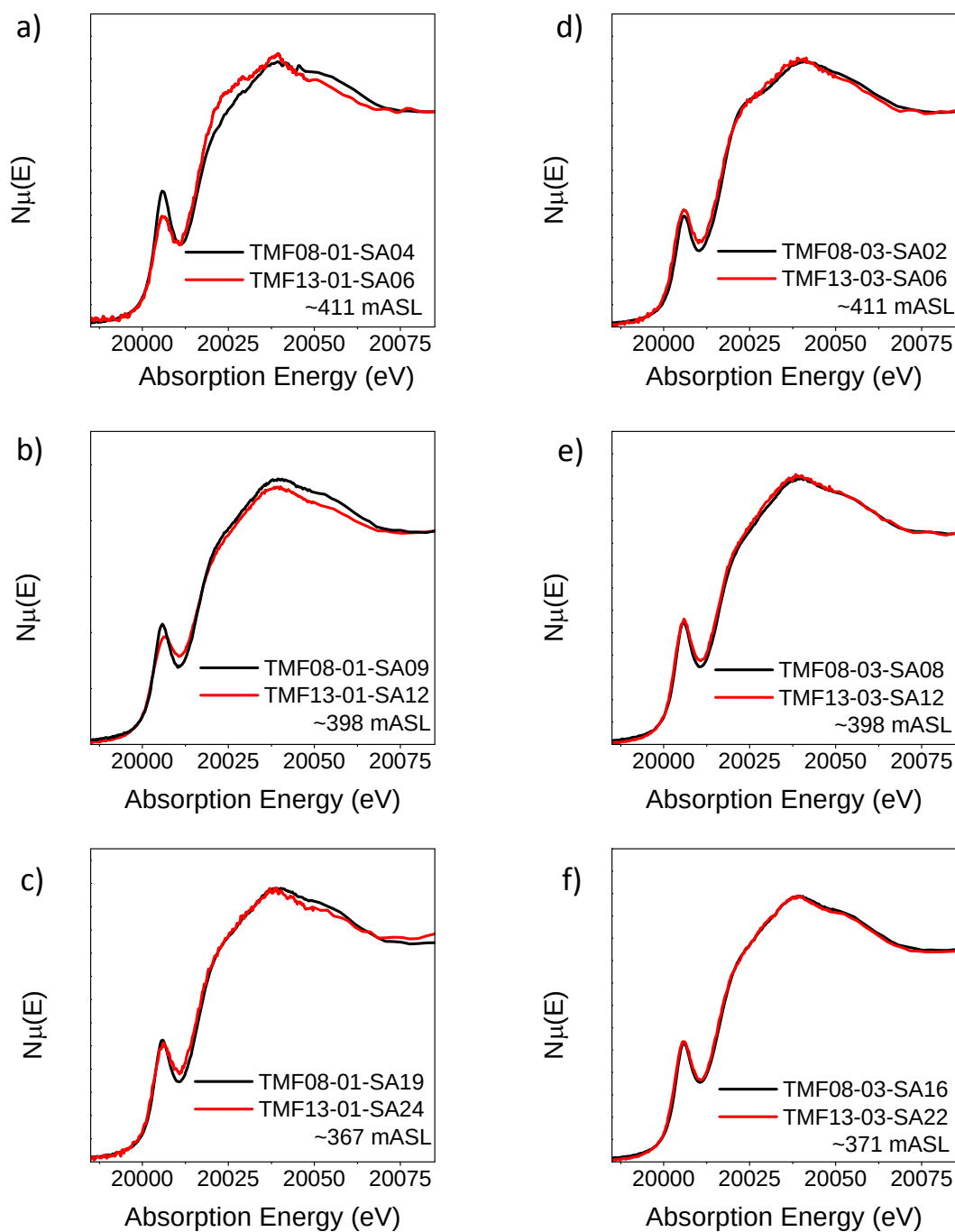


Figure S11. A comparison of Mo K-edge XANES spectra of tailings samples in the (a,b,c) central and (d,e,g) peripheral bore-holes collected during the 2008 (TMF08) and 2013 (TMF13) sampling campaigns.



Identifying calcium-containing mineral species in the JEB Tailings Management Facility at McClean Lake, Saskatchewan



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ABSTRACT

The JEB Tailings Management Facility (TMF) is central to reducing the environmental impact of the McClean Lake uranium mill facility that is operated by AREVA Resources Canada. This facility has been designed around the idea that elements of concern (e.g., U, As, Ni, Se, Mo) will be controlled through equilibrium with precipitants. Confirming the presence of calcium-containing carbonates in the JEB TMF is the first step in determining if gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) controls the concentration of HCO_3^- (aq), limiting the formation of soluble uranyl bicarbonate complexes. A combination of X-ray diffraction (XRD), X-ray absorption near-edge spectroscopy (XANES), and microprobe X-ray fluorescence (XRF) mapping was used to analyze a series of tailings samples from the JEB TMF. Calcium carbonate in the form of calcite (CaCO_3), aragonite (CaCO_3), and dolomite ($\text{CaMg}(\text{CO}_3)_2$) were identified by analysing Ca K-edge μ -XANES spectra coupled with microprobe XRF mapping. This is the first observation of these phases in the JEB TMF. The combination of μ -XANES and XRF mapping provided a greater sensitivity to low concentration calcium species compared to the other techniques used, which were only sensitive to the major species present (e.g., gypsum).

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1. Introduction

AREVA Resources Canada (AREVA) operates the JEB Tailings Management Facility (TMF) to manage and dispose of elements of concern generated in the U ore milling operations located at McClean Lake, Saskatchewan. A location map showing the JEB mill and TMF, as well as some of the ore bodies that feed the mill is presented in Fig. S1 in the Supporting Information (SI). The JEB TMF is designed to reduce the migration of water-soluble elements that co-mineralize with U ore (i.e., As, Ni, Mo, and Se) by promoting the formation of water-insoluble mineral species, effectively “trapping” these elements of concern (AREVA, 2015). The concentration of the solutes are out of equilibrium with the desired mineral phases when initially added to the TMF and may require a long period of time to reach a stable mineralogical end-point. Mineralogical evolution is limited by low temperatures ($+6^\circ\text{C}$), low hydraulic conductivity, and low liquid/solid ratios that reduces mass transport

(AREVA, 2015). A table that identifies a selection of the primary and secondary minerals present in the tailings before being placed in the TMF can be found in the SI (Table S1).

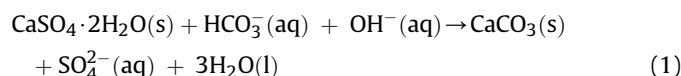
AREVA has been investigating the long-term formation of solid phases containing several elements of concern in the TMF (e.g., As, Ni, Mo) (Langmuir et al., 2006; Mahoney et al., 2007; Chen et al., 2009; Hayes et al., 2014; Blanchard et al., 2015). However, there is little known about the behaviour of U in the JEB TMF. The process of separating yellow cake ($\text{U}_3\text{O}_8(\text{s})$) from the ore consumes small amounts of hydrocarbon material. The largest sources of hydrocarbons used in the mill are organic flocculent (polyacrylamide) and kerosene. Small amounts of kerosene are lost to the raffinate solution that reports to the tailings preparation process. This hydrocarbon material adsorbs onto the surface of the tailings solids and is subsequently deposited in the TMF. Hydrocarbons in the tailings are gradually converted to soluble HCO_3^- (aq) (bicarbonate) in the tailings pore water, which is facilitated by the presence of bacterial communities. Under the oxic conditions of the TMF ($E_h \sim +290\text{ mV}$; $\text{pH} \sim 7$), U oxide (e.g., UO_2 , U_3O_8 , $\text{U}(\text{SiO}_4)_{1-x}(\text{OH})_{4x}$) in the tailings may react with bicarbonate to form an undesirable water-soluble uranyl-carbonate complex. Dissolved bicarbonate

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can be removed from the TMF pore water by co-precipitating with dissolved $\text{Ca}^{2+}(\text{aq})$ as calcium carbonate ($\text{CaCO}_3(\text{s})$). The concentration of dissolved $\text{Ca}^{2+}(\text{aq})$ is relatively high in the TMF (~550 mg/L), as the TMF is saturated with gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}(\text{s})$) that forms from the addition of sulfuric acid and lime during the leaching and tailings preparation stages, respectively. Overall, the conversion of gypsum to calcium carbonate (calcite or aragonite) can be written as (AREVA, 2015):



Although there is some indirect evidence of calcium carbonate precipitation as observed by the decrease in concentration of $\text{Ca}^{2+}(\text{aq})$ in the pore water collected at lower elevations (i.e., deeper depths) of the TMF (AREVA, 2015), calcium carbonate has not been directly observed. Identifying calcium-containing carbonate is an essential first step to understanding how the $\text{HCO}_3^-(\text{aq})$ concentration is controlled in the TMF. Our recent X-ray diffraction (XRD), X-ray absorption near-edge spectroscopy (XANES), and X-ray fluorescence (XRF) microprobe studies have proven useful in identifying Mo-bearing mineral species in the TMF, particularly at low concentrations (Hayes et al., 2014; Blanchard et al., 2015). In the current study, the calcium mineralization in the JEB TMF has been investigated using a combination of these techniques. Detailed micro powder XRD and bulk XANES analyses indicated that the major Ca-containing mineral species in the TMF are gypsum and possibly anhydrite (CaSO_4). Micro XANES (μ -XANES) analysis was able to identify several minor calcium-containing mineral species, including calcite, aragonite, and dolomite ($\text{CaMg}(\text{CO}_3)_2$). Overall, this investigation has demonstrated that μ -XANES coupled with XRF mapping is the most effective way to identify low concentration calcium species in the TMF.

2. Experimental

2.1. Tailings sample description

The samples studied were collected during the 2013 sampling campaign of the JEB TMF. Samples were collected from two bore-hole locations in the TMF. A total of six samples were provided for this study, with three samples collected from the central borehole (TMF13-01-SA12, TMF13-01-SA19, TMF13-01-SA22) and three samples from a periphery borehole (TMF13-03-SA12, TMF13-03-SA15, TMF13-03-SA19) located approximately 55 m from the centre. A figure showing a schematic of the TMF and the location of the bore-holes in plan view is shown in Fig. S2 in the SI. The tailings are placed in the TMF using a floating barge and tremie piping system in a way that minimizes particle size segregation at the point of placement; however, it does not eliminate it. As a consequence, the particle size distribution of the tailings solids is not homogenous in the TMF with the central bore hole possessing a coarser particle size distribution than bore holes located at the periphery of the TMF. More information on the sampling of the tailings can be found in the SI.

2.2. Micro powder XRD

Micro powder X-ray diffraction (μ -XRD) patterns of the tailings samples were collected to determine which crystalline phases are present in the bulk material. Measurements were performed using a PANalytical Empyrean powder X-ray diffractometer equipped with a $\text{Cu K}\alpha_{1,2}$ X-ray source, and powder XRD patterns were analyzed using the PowderCell software package (Kraus and Nolze, 1996). Unground grains from each tailings sample was measured

instead of finely ground powder in an attempt to increase the possibility of detecting minor phases by μ -XRD. More information on these experiments can be found in the SI.

2.3. Bulk XANES

2.3.1. Bulk Ca K-edge XANES

Bulk Ca K-edge XANES measurements were collected on the Soft X-ray Microcharacterization Beamline (SXRMB; 06B1-1) at the CLS (Hu et al., 2010). Finely powdered (i.e., homogenized) tailings samples and standards were lightly dusted onto carbon tape mounted onto a multi-sample holder. A single layer of Kapton foil covered the tailings samples. More details on the experimental setup can be found in the SI. All XANES spectra were analyzed using the Athena software program (Ravel and Newville, 2005). A quantitative analysis of the XANES spectra was performed using principle component analysis (PCA) followed by linear combination fitting (LCF) using the spectra from the standards. The energy range used for PCA and LCF analysis was -20 and $+40$ eV relative to the

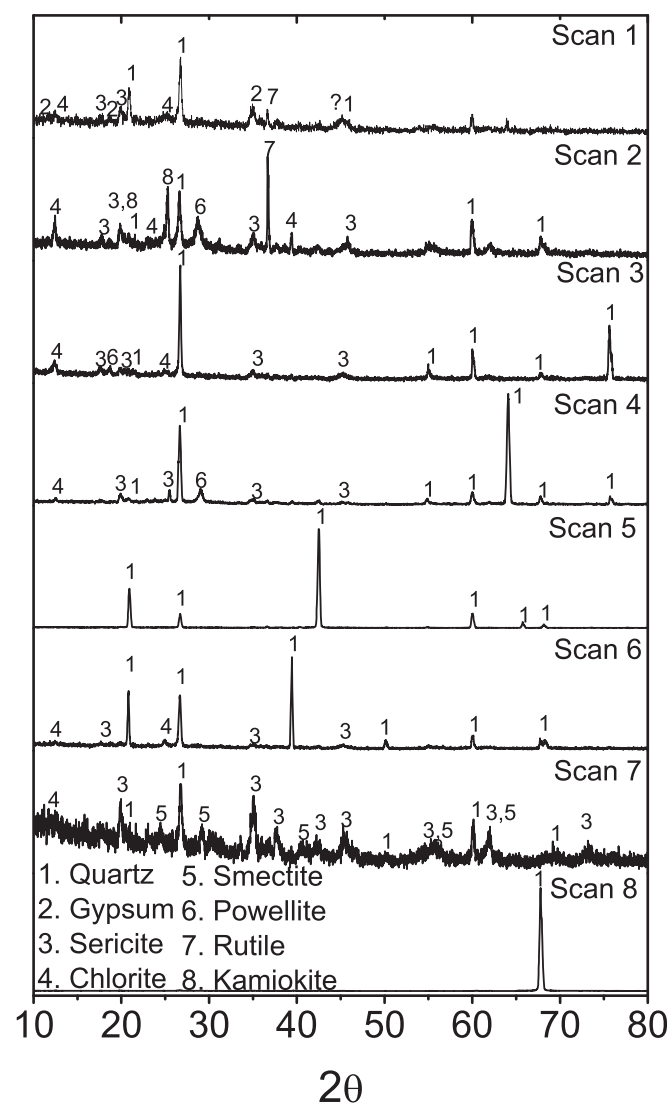


Fig. 1. μ -XRD patterns collected from tailings sample TMF13-01-SA19. Evidence of gypsum is highlighted in scan 1 while evidence of powellite is highlighted in scan 3. The high 2θ diffraction peaks corresponding to quartz shown in the diffraction patterns collected in scans 4 and 8 are so intense due to preferred orientation effects.

Ca K-edge absorption edge energy.

2.3.2. Bulk Ca $L_{2,3}$ -edge and C K-edge XANES

Bulk Ca $L_{2,3}$ -edge and C K-edge XANES spectra from the tailings samples and standards were collected on the Spherical Grating Monochromator (SGM; 11ID-1) beamline at the Canadian Light Source (Regier et al., 2007). Finely ground tailing samples and standards (powders and liquids) were either dusted on carbon tape (Ca $L_{2,3}$ -edge) or drop-coated on a gold-plated silicon wafer (C K-edge). More details on the experimental set-up can be found in the SI. A quantitative analysis of the Ca $L_{2,3}$ -edge XANES spectra was performed using PCA followed by LCF. The energy range used for this analysis was -1 and $+5$ eV relative to the Ca L_3 -edge absorption edge energy. Quantitative analysis could not be performed on the C K-edge due to overlap of the K $L_{2,3}$ -edge.

2.4. Microprobe XRF mapping and Ca K-edge μ -XANES

Microprobe X-ray fluorescence (XRF) maps and Ca K-edge micro XANES (μ -XANES) spectra were collected using the SXRMB beamline (Hu et al., 2010). Unground tailings samples were placed onto carbon tape on a multi-sample holder and covered by Kapton foil. As will be observed during the discussion of the bulk Ca K-edge XANES spectra, collecting spectra from finely powdered tailings samples only resulted in the dominant phases being detected. In the case of the XRF/ μ -XANES experiments, unground grains of the tailings were studied so as to increase the possibility of identifying minor Ca-containing phases. A $10\ \mu\text{m}$ spot size was used to collect the XRF maps and μ -XANES spectra. XRF maps were collected by rastering a $500\ \mu\text{m} \times 500\ \mu\text{m}$ or $1000\ \mu\text{m} \times 1000\ \mu\text{m}$ area using a $10\ \mu\text{m}$ step size with a 1 s dwell time at a monochromatic X-ray energy of 4100 eV. The Ca K-edge μ -XANES spectra were collected using similar parameters used to collect the bulk Ca K-edge spectra. XRF maps were created and analyzed using the SMAK software program and μ -XANES spectra were analyzed using the Athena software program (Ravel and Newville, 2005; Webb, 2011).

2.5. Electron microprobe

Electron microprobe analysis of the tailings samples was carried out using a Japan Electron Optics Laboratory (JEOL) 8600 Superprobe electron microprobe at an accelerating voltage of 15 keV. Tailings samples were mounted in an epoxy resin and the surface was polished using diamond paste. Backscattered electron images and WDS (wavelength dispersive X-ray spectroscopy) maps were collected from each C-coated sample at a magnification of 120X.

3. Results and discussion

3.1. Powder micro X-ray diffraction

Powder μ -XRD patterns were collected from several (unground) grains of each sample. The μ -XRD patterns collected from tailings sample TMF13-01-SA19 are shown in Fig. 1. Patterns collected from the other tailings samples are shown in the SI (Figs. S3–S7). Analysis of the μ -XRD patterns highlights the heterogeneous nature of the tailings samples. μ -XRD diffraction patterns only represent the composition of a few individual grains at most given the small spot size used during the μ -XRD experiments and the large grain size of the tailings (up to hundreds of micrometers in diameter). The width and intensity of the diffraction peaks were observed to vary from spot to spot, which is due to variations in crystallinity and preferred orientation effects. The most common calcium-containing mineral species identified in the μ -XRD pattern was gypsum (cf., Scan 1 in Fig. 1). Several patterns provided support for the presence of powellite (CaMoO_4 ; cf., Scans 2, 3 and 4 in Fig. 1), which has been confirmed to be present in the JEB TMF in previous XANES studies (Hayes et al., 2014; Blanchard et al., 2015). A few peaks are marked as “?” in the μ -XRD patterns (Fig. 1 and Figs. S3, S6, and S7 in SI) as they remain unidentified.

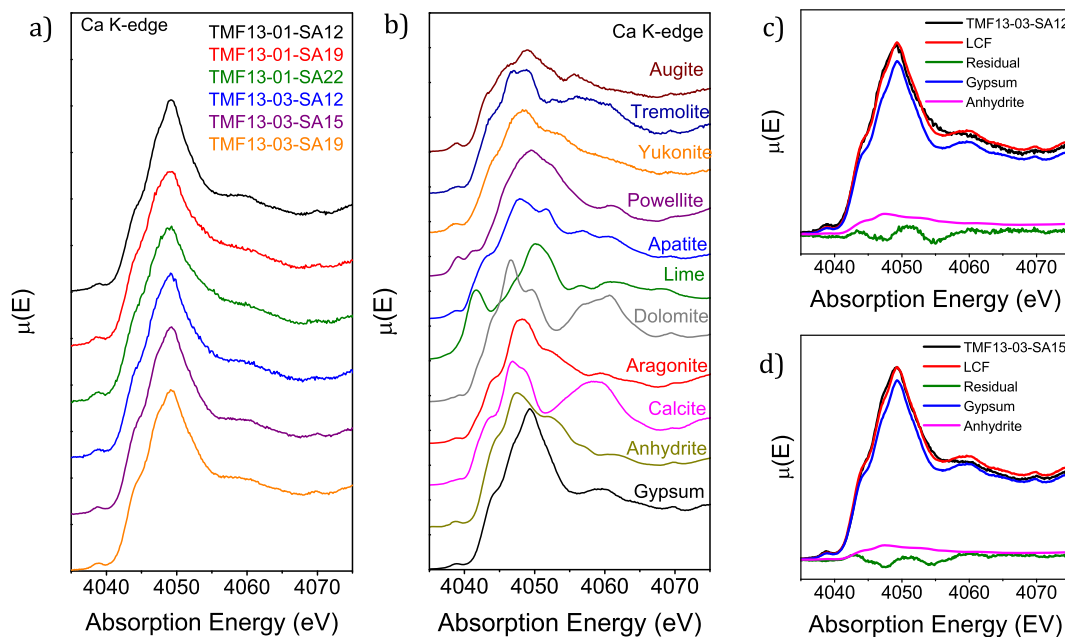


Fig. 2. The Ca K-edge XANES spectra from the tailings and calcium-containing standards are shown in a) and b), respectively. The spectra from the tailings samples were all observed to have similar lineshapes. The fitted bulk Ca K-edge XANES spectra from TMF13-03-SA12 and TMF13-03-SA15 are shown in c) and d), respectively. The linear combination fitting of each spectrum is shown in red and the residual is shown in green. The weighted spectra from the standards used to fit the spectra from the tailings are also shown. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 1

Results of the LCF fitting of the bulk Ca K-edge XANES spectra from the tailings samples. Calculated errors are in brackets.

Sample	Gypsum (at.%)	Anhydrite (at.%)	R-factor	χ^2
TMF13-01-SA12	98(2)	2(2)	0.00581	0.409
TMF13-01-SA19	76(3)	24(3)	0.00627	0.506
TMF13-01-SA22	84(3)	16(3)	0.00674	0.535
TMF13-03-SA12	89(2)	11(2)	0.00487	0.330
TMF13-03-SA15	92(2)	8(2)	0.00451	0.323
TMF13-03-SA19	93(2)	7(2)	0.00312	0.226

3.2. Bulk XANES

Diffraction analysis identified quartz, gypsum, and various clay minerals as the major crystalline materials in the TMF (Hayes et al., 2014). The μ -XRD patterns also indicated that other calcium-containing mineral species might be present in the tailings samples, such as powellite. The presence of highly crystalline phases, particularly quartz, in the tailings likely impedes the ability of this technique to identify minor or poorly crystalline mineral species that may be present in the TMF. Our previous studies of Mo precipitation in the TMF have demonstrated that XANES is capable of detecting mineral species at low concentrations (i.e., ppm) in heterogeneous samples (Hayes et al., 2014; Blanchard et al., 2015). Bulk Ca K-edge and $L_{2,3}$ -edge, and C K-edge XANES spectra of the tailings samples were collected from homogenized samples (i.e., finely ground) using a large (mm size) X-ray spot size.

3.2.1. Bulk Ca K-edge XANES

The bulk Ca K-edge XANES spectra of the tailings samples are shown in Fig. 2a. The spectra from the tailings samples were compared to spectra from several calcium-containing standards, which are shown in Fig. 2b. The Ca K-edge corresponds to a dipole-allowed transition of a 1s electron into unoccupied 4p states. The lineshape of the bulk Ca K-edge XANES spectrum is heavily dependent on the local coordination environment and is often analyzed to identify specific Ca-containing species present in a mixture (Sowrey et al., 2004; Takahashi et al., 2008; Liu et al., 2013).

The bulk Ca K-edge XANES spectra from the tailings samples have similar lineshapes, suggesting that they consist of similar Ca-containing mineral species.

The PCA was used to determine the number of major calcium-containing mineral species present. Assuming a XANES spectrum consists of a linear combination of individual components of a mixture, a PCA calculation decomposes a series of spectra into a set of components (eigenvectors) and weightings (eigenvalues) that describe the variation in the data set (Fernández-García et al., 1995; Beauchemin et al., 2002). Although these components are mathematical constructs with no simple relationship to the chemical species that make up the spectra, it has been assumed here that the minimum number of components that describe the variation in the data set is equivalent to the minimum number of chemical species that make up a XANES spectrum (Fernández-García et al., 1995; Beauchemin et al., 2002). An indicator function (IND) was developed by Malinowski to determine the minimum number of components required to describe a series of spectra (Malinowski, 1977, 2002). It is generally accepted that the minimum number of components is given when the IND function is minimized (Malinowski, 1977, 2002). The number of components predicted by the IND function can be tested by reconstructing the set of spectra using the components calculated in the PCA.

The PCA was performed on the six tailings samples, and the results are shown in Fig. S8a in the SI. The first component calculated for each set of spectra accounts for >99% of the total variances, which is common in PCA of XANES spectra (Cassinelli et al., 2014). The second component is the only other component with an observable intensity, suggesting that two components are required to describe the variation in the set of spectra studied. This was confirmed by calculating the IND value (see Fig. S8b), which is at a minimum when the number of components equals two. Reconstructions of the spectrum of tailings sample TMF13-03-SA12 (Fig. S9 in the SI) shows no visible improvements when reproducing the spectrum with two or three components.

The LCF analysis was used to identify the calcium-containing mineral species in the tailings samples. Each normalized bulk Ca K-edge spectrum was fitted by a linear combination of weighted

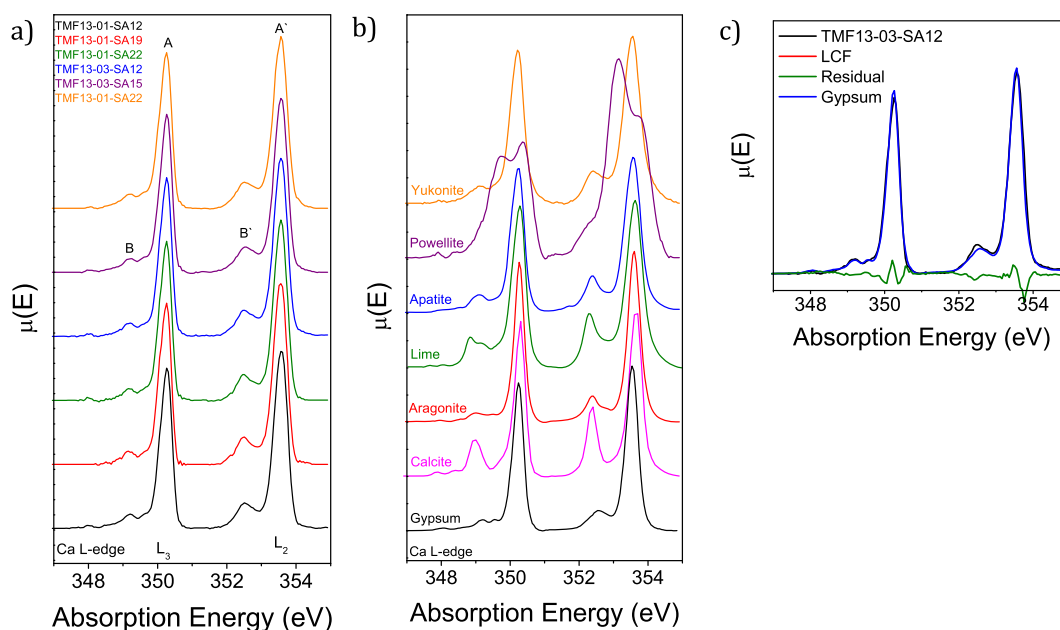


Fig. 3. The bulk Ca $L_{2,3}$ -edge XANES spectra from the a) tailings samples and b) calcium-containing standards are shown. Features A (A') and B (B') are discussed in the text. A comparison between the spectra from tailings sample TMF13-03-SA12 and gypsum is presented in c).

standard spectra. The coefficients calculated in the LCF correspond to the concentration of each Ca species present. Based on the PCA calculations, the number of components used in the fittings was initially restricted to two. Best fits were determined by comparing the χ^2 value. The smaller the χ^2 value, the better the fit. Results of the best fits are tabulated in Table 1 and the fitted bulk Ca K-edge XANES spectra are shown in Fig. 2c–d and Fig. S10 in the SI. The best fits were obtained when fitting the spectra with two different forms of calcium sulfate: gypsum and anhydrite. The majority of calcium in the tailings samples was gypsum, with concentrations ranging from 76 to 98 at.%, while the concentration of anhydrite ranged from 2 to 24 at.% (Table 1). The identification of anhydrite in the tailings might be due to local heating of the sample by the X-ray beam, resulting in dehydration of gypsum to anhydrite. This

being said, the comparison of multiple spectra collected from the same spot did not show any appreciable differences, which is supportive of the finding of anhydrite in the tailings. Further, the spectrum from the gypsum standard did not change during data collection.

Misfits of the spectra are noticeable at higher absorption energies (4055–4070 eV). This region of a XANES spectrum is known to have contributions from multiple scattering resonances (MSR), a low-energy extended X-ray absorption fine structure (EXAFS) phenomenon that is highly dependent on the crystal structure and crystallinity (Rehr, 2000). The fittings in this region of the Ca K-edge suggests that the calcium-containing mineral species in the tailings may be of a lower crystallinity than the standards used in the LCF.

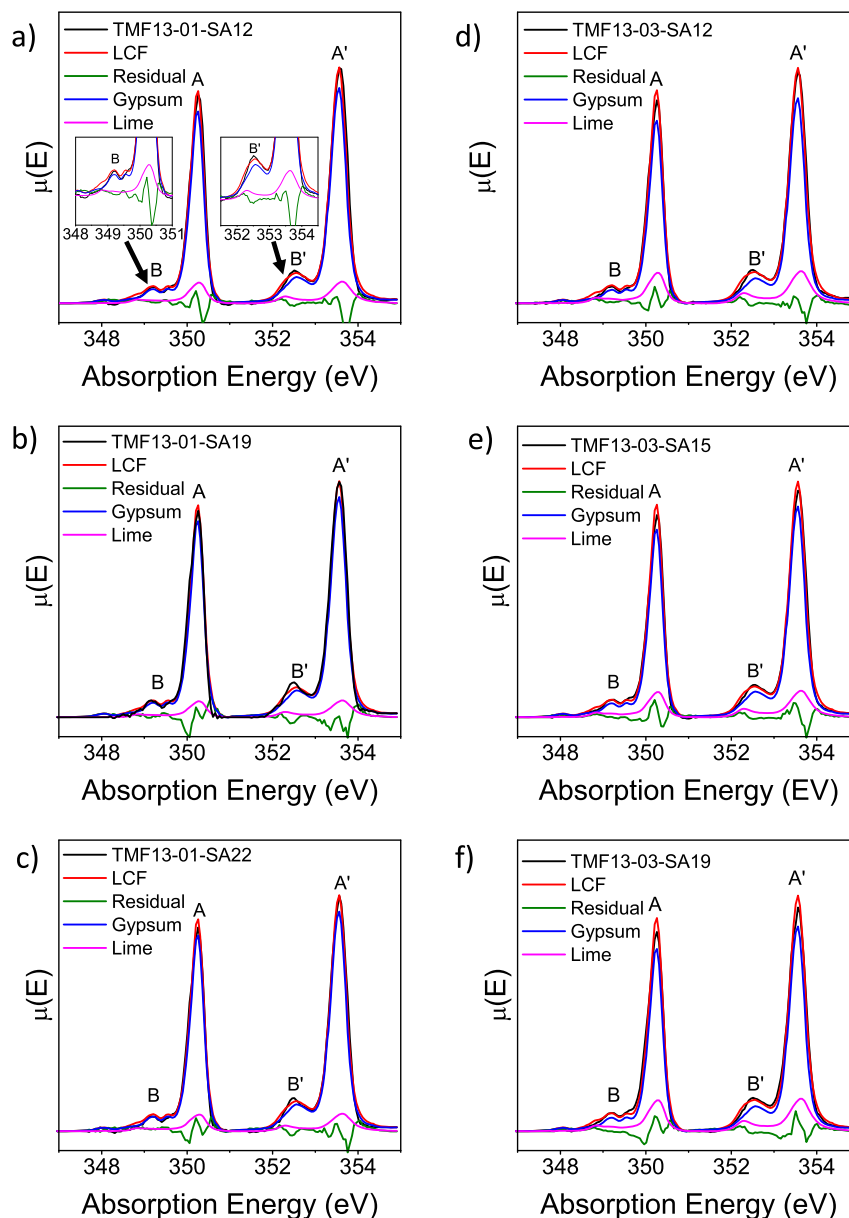


Fig. 4. The fitted bulk Ca L_{2,3}-edge XANES spectra from a) TMF13-01-SA12, b) TMF13-01-SA19, c) TMF13-01-SA22, d) TMF13-03-SA12, e) TMF13-03-SA15, and f) TMF13-03-SA19. The linear combination fitting of each spectrum is shown in red and the residual is shown in green. The weighted spectra from the gypsum and lime are also shown. Note that similar fits were obtained when fitting the spectra to gypsum and other calcium-containing mineral species (see Fig. S12). The inset of Fig. 4(a) shows the intensity differences of features B and B' when comparing the tailings samples to gypsum. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 2

LCF results for the fitting of the bulk Ca $L_{2,3}$ -edge XANES spectra from the tailings samples. Calculated errors are in brackets.

Sample	Gypsum (at.%)	Lime ^a (at.%)	R-factor	χ^2
TMF13-01-SA12	91(2)	9(3)	0.00832	264
TMF13-01-SA19	93(2)	7(6)	0.00962	299
TMF13-01-SA22	93(2)	7(6)	0.00652	194
TMF13-03-SA12	89(3)	11(2)	0.00521	153
TMF13-03-SA15	87(2)	13(3)	0.00685	192
TMF13-03-SA19	87(2)	13(2)	0.00701	193

^a Similar results were obtained when fitting the spectra of the tailings samples to calcite, aragonite, powellite, or yukonite.

3.2.2. Bulk Ca $L_{2,3}$ -edge XANES

Information on the major Ca-containing mineral species can also be obtained from the Ca $L_{2,3}$ -edge XANES spectra collected from homogenized tailings samples using a large X-ray spot size, and are shown in Fig. 3a. The Ca L-edge splits by spin-orbit coupling, resulting in two features corresponding to dipole-allowed $2p_{3/2} \rightarrow 3d$ (L_{3} -edge) and $2p_{1/2} \rightarrow 3d$ (L_{2} -edge) transitions. The L_{3} - and L_{2} -edge further splits into two major peaks; labelled A and B for the L_{3} -edge and A' and B' for the L_{2} -edge. This splitting is characteristic of Ca^{2+} and loosely corresponds to the crystal field splitting of the Ca 3d states (Himpfel et al., 1991; Politi et al., 2005). The relative intensity and energy difference of features A (A') and B (B') depends on the local coordination environment of the Ca^{2+} cation. Several low intensity features are observed below 349 eV and are attributed to core-hole effects (De Groot et al., 1990). As can be observed by comparing the spectra from the tailings to the spectra from the standards in Fig. 3b, the spectra from the tailings all have a similar lineshape to that of gypsum (cf. Fig. 3c). This observation is consistent with the bulk Ca K-edge XANES analysis presented above. Note that feature B (B') in the bulk Ca $L_{3}(L_{2})$ -edge spectra (see Figs. 3c and 4) is more intense in the tailings samples than gypsum, possibly indicating the presence of other calcium-containing minerals.

The PCA analysis indicated that two components are required to explain the variation in the bulk Ca $L_{2,3}$ -edge XANES spectra of the tailings samples (see Fig. S11 in the SI). The LCF analysis of the Ca $L_{2,3}$ -edge was then performed to determine the major calcium-containing mineral species in the tailings. Results of the LCF

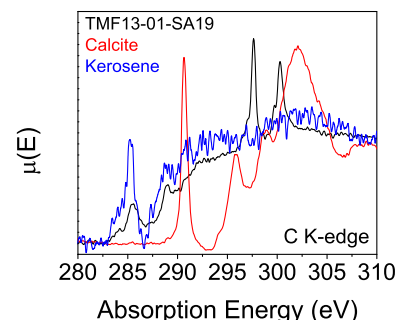


Fig. 6. A comparison of the C K-edge XANES spectra from tailings sample TMF13-01-SA19 (black), carbonate (red), and kerosene (blue). Features in the C K-edge XANES spectrum from the tailings sample are more similar to those observed in organic C compounds than those observed in inorganic C compounds. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

analysis are shown in Table 2 and the fitted bulk Ca $L_{2,3}$ -edge XANES spectra are shown in Fig. 4 when both gypsum and lime were used as the components. The LCF analysis indicated that gypsum was the major calcium-containing mineral species in the tailings samples with the samples containing between 87% and 91% gypsum; however, it was not obvious from the LCF what minor calcium-containing minerals were present in the tailings samples. Fittings having similar R-factors and χ^2 values were obtained when fitting the spectra to gypsum and other calcium-containing standards, including lime, powellite, aragonite, calcite, and yukonite (cf. Fig. 4 and Fig. S12 in the SI). It is possible that crystallinity may affect the lineshape of the Ca $L_{2,3}$ -edge, which would influence the results of the LCF.

3.2.3. Bulk C K-edge XANES

The bulk Ca K/ $L_{2,3}$ -edge XANES analyses indicated that gypsum and possibly anhydrite are the most abundant calcium-containing mineral species in the JEB TMF. If present, the concentration of calcium carbonate is likely significantly lower than that of gypsum and would not be expected to contribute significantly to the line-shapes of the bulk Ca K/ $L_{2,3}$ -edge spectra. The C content of the TMF

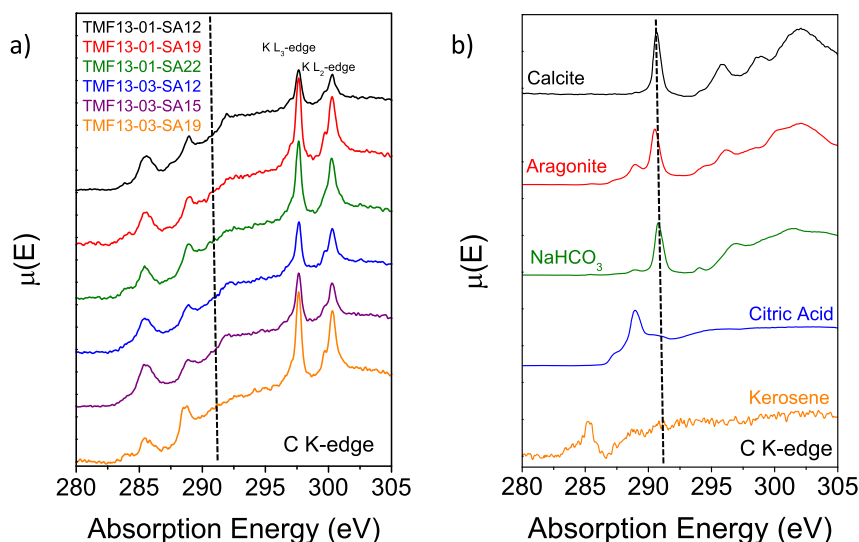


Fig. 5. The bulk C K-edge XANES spectra from the a) tailings samples and b) carbon standards are shown. Peaks corresponding to the K $L_{2,3}$ -edge were observed in the tailings samples due to the presence of K-containing clay minerals. The vertical dashed lines mark the location of the most distinguishable feature in C K-edge spectra from inorganic C species.

is relatively small, with organic and inorganic C accounting for less than 2.1 wt% and 0.4 wt%, respectively, of the total solid content of the tailings samples (see Table S2 in the SI). Therefore, calcium carbonate may be more observable in the bulk C K-edge spectra if it is present in the TMF at all. The bulk C K-edge XANES spectra of the tailings samples and some C-containing standards are shown in Fig. 5. The standards presented were chosen to show the differences between C K-edge XANES spectra collected from organic vs. inorganic C species. The C K-edge corresponds to a dipole-allowed transition of a 1s electron to 2p states. Features corresponding to the K L_{2,3}-edge (~298 eV and ~300.5 eV) were also observed in the spectra as K is found in several of the clay minerals (i.e., sericite, smectite) present in the tailings (Ahmed et al., 2012). Two major features are present in the C K-edge XANES spectra (see Fig. S13). The first feature corresponds to a C 1s → π^* transition (Cooney and Urquhart, 2004; Yabuta et al., 2014). This feature is observed at higher energies in carbonates (i.e., calcite; 290.4 eV) compared to hydrocarbon standards (i.e., kerosene; 284.9 eV). The shift in energy is due to the higher electronegativity of O compared to C (Allred and Rochow, 1958; Solomon et al., 2005). The second feature in the C K-edge corresponds to a C 1s → σ^* transition (>288 eV). Multiple peaks are observed in this region of the C K-edge of carbonate species due to the interaction of carbon σ^* states with next-nearest neighbour states (i.e., Ca 4p states). Broadening of this region in the C K-edge spectrum from kerosene may be due to multiple overlapping σ^* transitions (i.e., C–C, C–H) as kerosene consists of a mixture of multiple hydrocarbon species (Cody et al., 1995).

As shown in Fig. 6, the bulk C K-edge spectra from the tailings samples appear to have a similar lineshape to that of kerosene. The most significant conclusion from this analysis is that the characteristic feature of carbonates (i.e. the C=O π^* transition) was not observed in the spectra from the tailings samples, indicating that carbonates are not the major C-containing species in the TMF.

3.3. X-ray microprobe XRF mapping and Ca K-edge μ -XANES

The bulk XANES analyses indicated that the major Ca and C species in the TMF were gypsum and organic carbon, respectively, with no specific evidence of Ca-containing carbonate minerals being present in the TMF. If calcium carbonates are present in the tailings, the concentrations may be below the detection limits of the bulk XANES spectra collected from finely powdered samples using a large X-ray spot size. As evident from the μ -XRD study, a smaller X-ray beam size (i.e., μ m-size) focused on specific regions of individual grains of the samples can identify minor mineral species. Coupling μ -XANES with element-specific microprobe XRF maps was hypothesized to provide greater sensitivity to minor Ca-containing mineral species compared to both XRD and bulk XANES. Microprobe XRF maps and μ -XANES spectra were collected from three tailings samples (TMF13-01-SA19, TMF13-01-SA22, and TMF13-03-SA22) using a 10 μ m X-ray beam size. The XRF maps collected from sample TMF13-01-SA19 are shown in Fig. 7. All other XRF maps are shown in the SI (Figs. S14–S16). Two sets of XRF maps were collected from tailings sample TMF13-01-SA19 of different sizes; 500 × 500 μ m and 1000 × 1000 μ m. There is generally a strong correlation between Ca and S in all three tailings samples, consistent with the presence of calcium sulfate minerals (i.e., gypsum and anhydrite). A few Ca-rich regions with no correlating S-rich regions were observed in the XRF maps collected from tailings sample TMF13-01-SA19 (see Fig. 7 and Fig. S14 in the SI).

Ca K-edge μ -XANES spectra were collected from various locations of the XRF maps and are shown in Figs. 8 and 9. The locations

of where the spectra were collected from are marked on the calcium XRF maps (see Fig. 7 and Figs. S14–S16 in the SI). Compared to the bulk Ca K-edge XANES spectra, there is a greater degree of lineshape variation in the μ -XANES spectra (see Fig. S17 in the SI), with some having lineshapes that are considerably different from that of gypsum or anhydrite. Several spectra collected from tailings sample TMF13-01-SA19 have lineshapes that are similar to calcite and dolomite (see Figs. 2b, 8, and 9), suggesting that calcium carbonate minerals are present in the tailings.

A LCF analysis was performed on the μ -XANES spectra and the results of the LCF are shown in Table 3 and Table 4. Representative fitted Ca K-edge μ -XANES spectra are shown in Fig. 10. All other

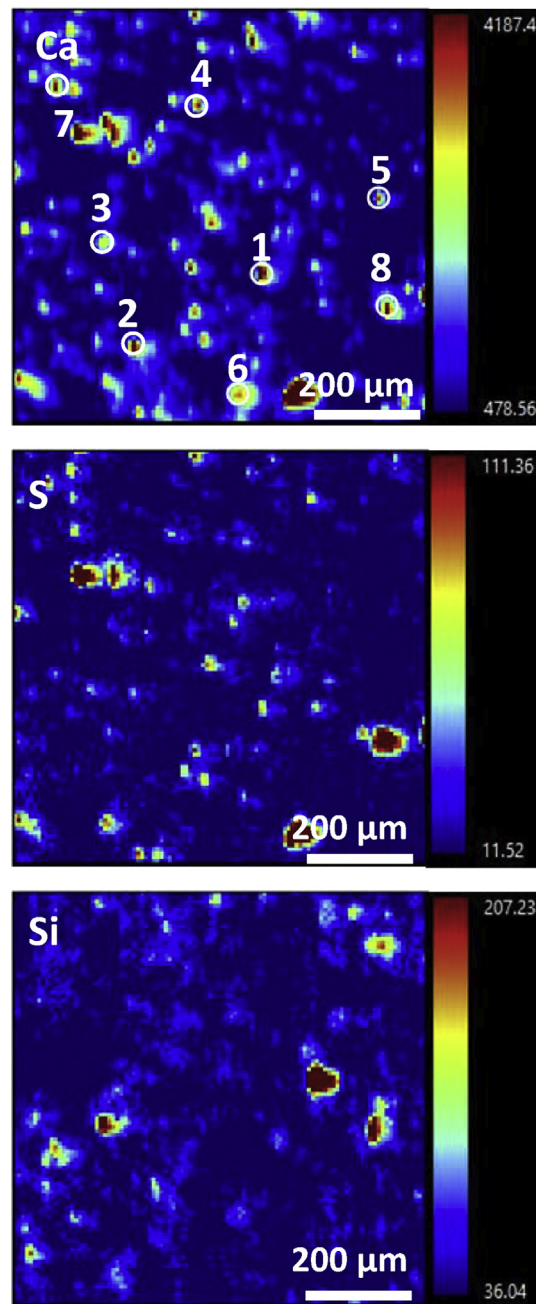


Fig. 7. XRF maps showing the distribution of calcium (top), sulfur (middle), and silicon (bottom) collected from tailings sample TMF13-01-SA19. The size of the map was 1000 μ m × 1000 μ m. Locations where Ca K-edge μ -XANES spectra were collected are marked on the Ca XRF map.

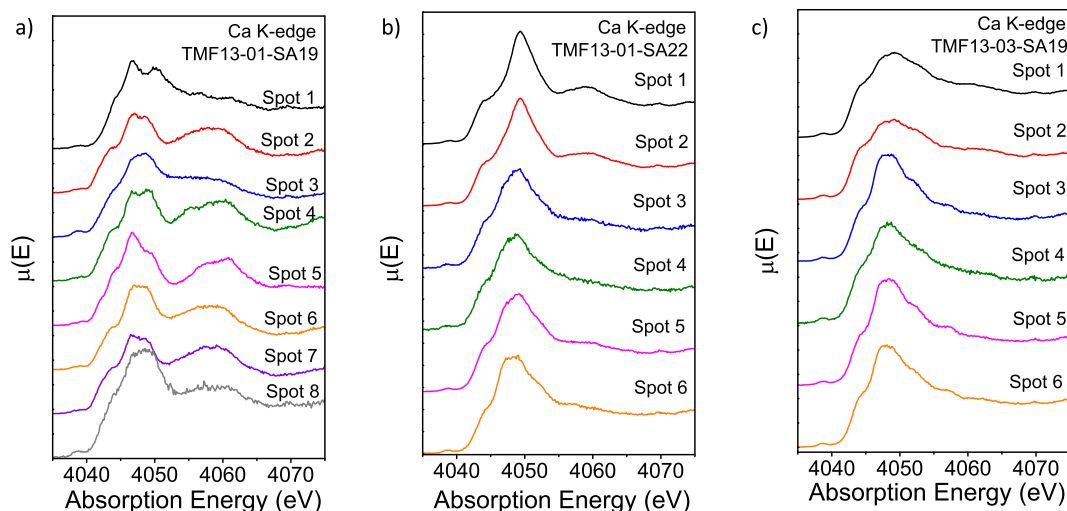


Fig. 8. The Ca K-edge μ -XANES spectra collected from tailings samples a) TMF13-01-SA19, b) TMF13-01-SA22, and c) TMF13-03-SA19. Spectra were collected from the locations marked on the Ca XRF maps shown in Fig. 7 (TMF13-01-SA19), Fig. S15 (TMF13-01-SA22), and Fig. S16 (TMF13-03-SA19).

fitted Ca K-edge μ -XANES spectra are shown in the SI (Figs. S18–S21). Only the fits having the lowest R-factor and χ^2 values are presented. In general, the Ca K-edge μ -XANES spectra were best fitted to one or two components. Most fitted μ -XANES spectra were found to contain gypsum and/or anhydrite, which is consistent with the bulk Ca K-edge XANES analysis. However, several other Ca-containing mineral species were also identified. Specifically, several μ -XANES spectra collected from the tailings samples were fitted to calcite, aragonite, or dolomite (see Fig. 10 and Figs. S18–S19 in the SI). Tremolite ($\text{Ca}_2\text{Mg}_{4.5}\text{Fe}_{0.5}\text{Si}_6\text{O}_{22}(\text{OH})_2$) was also identified in several μ -XANES spectra (see Figs. S18a,d–S19c in the SI), suggesting that calcium magnesium silicate minerals are also present in the tailings. These mineral species appear to be present in the TMF at low concentrations because they were not identified by analysis of the bulk XANES spectra. The wide distribution of the species identified in the tailings, and the concentrations of these species listed in Tables 3 and 4, highlight the heterogeneous nature of the tailings and the considerable variability in composition between tailings samples collected at different locations in the TMF.

It should be noted that the region in the Ca K-edge between 4045 and 4050 eV could not be fitted in some of the Ca K-edge μ -XANES spectra (see Figs. S20d and S21c,e,f in the SI for examples). Also, the Ca K-edge μ -XANES spectrum collected from spot 1 from sample TMF13-01-SA19 (see Fig. 8a) could not be fitted to any Ca-containing standards used in this analysis. This suggests that unknown calcium-containing mineral species may be present in the tailings, which further highlights the complexity of this system.

It is important to note that there are minor misfits in the near-edge region (i.e., 4040–4055 eV) of the Ca K-edge μ -XANES spectra fitted to dolomite (see Fig. 10c,d and Fig. S19a in the SI for examples). Attempts to include a second component in these fittings were unsuccessful. Ideally, Ca^{2+} and Mg^{2+} cations are ordered in the dolomite structure with the $\text{Ca}^{2+}:\text{Mg}^{2+}$ ratio close to 1:1 (i.e., $\text{CaMg}(\text{CO}_3)_2$) (Althoff, 1977). However, there is a small solid solution range in the dolomite structure (i.e., $\text{Ca}_{1-x}\text{Mg}_x(\text{CO}_3)_2$). Misfits in the near-edge region may be due to variations in the composition of dolomite forming in the TMF compared to the composition of the standard used in the LCF analysis. The LCF analysis of the μ -XANES spectra provides the first experimental evidence of the presence of calcium carbonates in the JEB TMF.

3.4. Electron microprobe

Although several Ca K-edge μ -XANES spectra collected were fitted to dolomite, it was not possible to confirm if Mg was present in the tailings solids from the microprobe analysis because the Mg K α X-ray fluorescence energy (1253 eV) was below the detection limit of the detector used. Electron microprobe analysis was performed on several tailings samples to confirm the presence of Mg in the tailings. Backscattered electron (BSE) images and WDS maps (Ca, Mg, S, Si) collected from the tailings samples are shown in Figs. S22–S24 in the SI. Bright spots in the BSE images correspond to regions of the tailings samples consisting of heavier elements. The WDS maps showed a strong correlation between Ca and S and between Mg and Si; however, multiple regions of the tailings were also observed to contain both Mg and Ca.

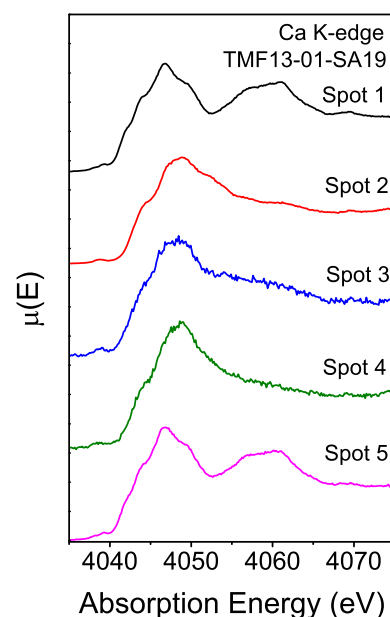


Fig. 9. Ca K-edge μ -XANES spectra collected from tailings sample TMF13-01-SA19. Spectra were collected from specific positions that are marked on the Ca XRF map shown in Fig. S14.

Table 3LCF results for the fittings of the Ca K-edge μ -XANES spectra of the tailings samples. Calculated errors are in brackets.

Sample	Spot	Gypsum (at.%)	Anhydrite (at.%)	Calcite (at.%)	Aragonite (at.%)	Dolomite (at.%)	Tremolite (at.%)	R-factor	χ^2
TMF13-01-SA19 ^a	1 ^b								
	2			100				0.00711	0.779
	3	18(3)					82(5)	0.00550	0.397
	4	22(2)		78(3)				0.00614	0.433
	5					100		0.00604	0.479
	6			100				0.0165	1.21
	7			100				0.00525	0.391
	8	44(3)					56(5)	0.0163	1.124

^a Spectra were collected from locations marked on the calcium XRF map shown in Fig. 7.^b Spectrum could not be fitted to any of the calcium-containing standards used in this analysis.**Table 4**LCF results for the fittings of the Ca K-edge μ -XANES spectra of the tailings samples. Calculated errors are in brackets.

Sample	Spot	Gypsum (at.%)	Anhydrite (at.%)	Calcite (at.%)	Aragonite (at.%)	Dolomite (at.%)	Tremolite (at.%)	R-factor	χ^2
TMF13-01-SA19 ^a	1					100		0.0124	1.07
	2	42(2)	58(3)					0.00362	0.307
	3	22(2)					78(2)	0.00991	0.740
	4	51(3)			49(3)			0.00789	0.759
	5					100		0.0105	0.975
TMF13-01-SA22 ^b	1	100						0.0324	2.43
	2	100						0.0105	1.01
	3	89(3)			11(3)			0.00528	0.485
	4	39(2)			61(2)			0.00400	0.354
	5	91(3)			9(3)			0.00563	0.452
TMF13-03-SA19 ^c	6	100						0.0225	2.282
	1	32(3)	68(3)					0.00448	0.390
	2	28(2)	82(2)					0.00461	0.375
	3	51(5)	49(4)					0.0142	1.46
	4	37(1)			63(2)			0.00292	0.264
	5	53(4)	48(3)					0.0117	1.24
	6	41(3)	59(3)					0.00858	0.890

^a Spectra were collected from locations marked on the calcium XRF map shown in Fig. S14.^b Spectra were collected from locations marked on the calcium XRF map shown in Fig. S15.^c Spectra were collected from locations marked on the calcium XRF map shown in Fig. S16.

3.5. The formation of calcium-containing carbonate in the TMF

Calcite, aragonite, and dolomite were found to be present at low concentrations in samples collected from the TMF. Although calcite is the most thermodynamically stable form of calcium carbonate (Anderson and Crerar, 1993), the stability of different forms of CaCO_3 is influenced by a number of factors such as temperature, pH, and dissolved salt content (Walter, 1986; Burton and Walter, 1990; Cooke and Kepkay, 1980; Berner, 1975). However, pH and dissolved salt concentrations are the most likely factors influencing the formation of calcite and aragonite because the low temperature of the TMF ($\sim 6^\circ\text{C}$) will support the precipitation of both species (Mayer, 1984). Aragonite stabilizes at a pH greater than 7 whereas a lower pH supports the stabilization of calcite (Berner, 1975). Likewise, the presence of dissolved ions, such as SO_4^{2-} , Mg^{2+} , Mn^{2+} , and Fe^{2+} can inhibit the formation of calcite (Walter, 1986; Berner, 1975; Mayer, 1984; Dromgoole and Walter, 1990). Larger cations, such as Sr^{2+} , Ba^{2+} , and Pb^{2+} , can also stabilize aragonite because the larger unit cell of this mineral compared to calcite favours the incorporation of larger cations (Wray and Daniels, 1957). As shown in Table S3 in the SI, the pH of the pore water and the concentrations of many of the ions mentioned above vary throughout the TMF, which would be expected to influence the stability of calcite and aragonite.

The presence of dolomite in the TMF is surprising as hydration of Mg and dissolved salts prevents the ordering of Ca and Mg within the dolomite structure (Althoff, 1977; Folk and Land, 1975). However, dolomite is known to form in the marine environment due to

the substitution of dissolved Mg^{2+} into the calcite structure, forming a disordered magnesium calcite (Folk and Land, 1975; Katz and Matthews, 1977). The ordering of Ca and Mg cations in the calcite structure, particularly at elevated pressures, leads to the formation of dolomite (Althoff, 1977). Although the Mg^{2+} pore water concentration is significantly lower than that of Ca^{2+} (see Table S3), dolomite could form from the ordering of magnesium calcite containing less than 10 at.% of Mg^{2+} (Katz and Matthews, 1977).

4. Conclusions

Tailings samples collected from the JEB TMF in 2013 were analyzed using X-ray diffraction and spectroscopy to determine if calcium-containing carbonates are present. This study demonstrated that μ -XANES analysis coupled with microprobe XRF mapping is the optimum technique for analysing low concentration calcium carbonates in the TMF. This combination of techniques identified several minor calcium-containing mineral species in the TMF, specifically the carbonate minerals of calcite, aragonite, and dolomite.

Current models of the geochemistry of the JEB TMF suggest that the precipitation of Ca-bearing carbonates by the reaction of aqueous bicarbonate and gypsum will control the concentration of aqueous bicarbonate in the tailings, and, as a result, will also control the concentration of soluble uranium carbonate complexes in the TMF. The precipitation of carbonate minerals should limit the ability of U to be exposed to the environment

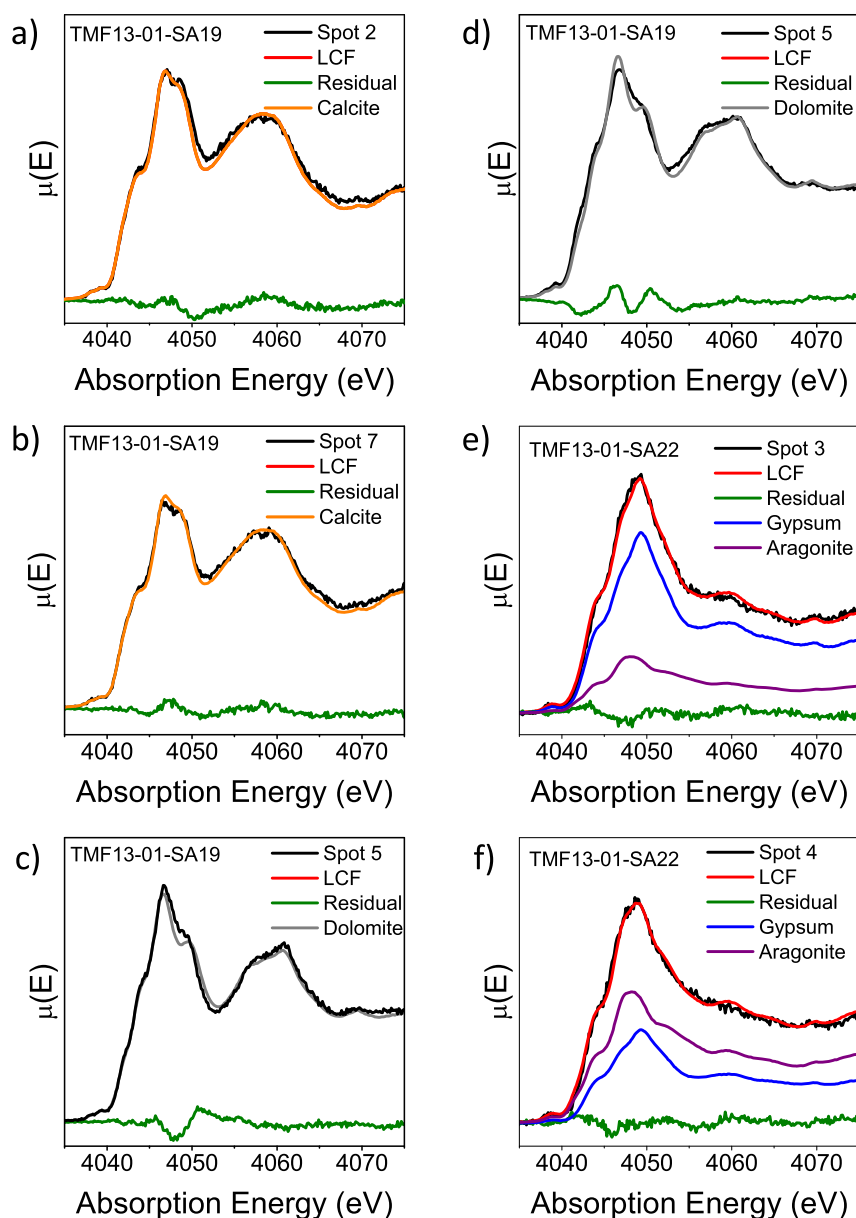


Fig. 10. The fitted Ca K-edge μ -XANES spectra from a) TMF13-01-SA19 (collected from Spot 2 in Fig. 5), b) TMF13-01-SA19 (collected from Spot 7 in Fig. 5), c) TMF13-01-SA19 (collected from Spot 5 in Fig. 7), d) TMF13-01-SA19 (collected from Spot 5 in Fig. S14), e) TMF13-01-SA22 (collected from Spot 3 in Fig. S15), and f) TMF13-01-SA22 (collected from Spot 4 in Fig. S15) are shown. Note that μ -XANES spectra were collected from two different XRF maps of tailings sample TMF13-01-SA19. The linear combination fitting of each spectrum is shown in red and the residual is shown in green. The weighted standard spectra used to fit the spectra are also shown. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

external to the TMF. The identification of calcite, aragonite, and dolomite in the tailings in this study has provided validity to this model, although further studies of how the concentration of Ca-bearing carbonates and U oxides in the TMF change with age will need to be completed before this model can be confirmed.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.apgeochem.2016.08.001>.

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Investigating the Geochemical Model for Molybdenum Mineralization in the JEB Tailings Management Facility at McClean Lake, Saskatchewan: An X-ray Absorption Spectroscopy Study

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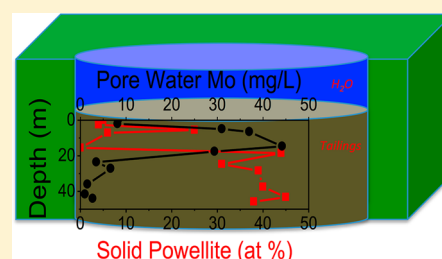
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S Supporting Information

ABSTRACT: The geochemical model for Mo mineralization in the JEB Tailings Management Facility (JEB TMF), operated by AREVA Resources Canada at McClean Lake, Saskatchewan, was investigated using X-ray Absorption Near-Edge Spectroscopy (XANES), an elemental-specific technique that is sensitive to low elemental concentrations. Twenty five samples collected during the 2013 sampling campaign from various locations and depths in the TMF were analyzed by XANES. Mo K-edge XANES analysis indicated that the tailings consisted primarily of Mo^{6+} species: powellite (CaMoO_4), ferrimolybdate ($\text{Fe}_2(\text{MoO}_4)_3 \cdot 8\text{H}_2\text{O}$), and molybdate adsorbed on ferrihydrite ($\text{Fe}(\text{OH})_3 - \text{MoO}_4$). A minor concentration of a Mo^{4+} species in the form of molybdenite (MoS_2) was also present. Changes in the Mo mineralization over time were inferred by comparing the relative amounts of the Mo species in the tailings to the independently measured aqueous Mo pore water concentration. It was found that ferrimolybdate and molybdate adsorbed on ferrihydrite initially dissolves in the TMF and precipitates as powellite.



INTRODUCTION

The JEB Tailings Management Facility (JEB TMF) plays a central role in reducing the environmental impact of AREVA Resources Canada's (AREVA) uranium ore mining operations in Northern Saskatchewan. The geochemistry of the tailings management system is designed to reduce the migration of water-soluble elements that comineralize with U ore (i.e., As, Ni, Mo, and Se) by promoting the formation of mineral species.¹ However, when initially added to the tailings, the concentration of the solutes are generally out of equilibrium with the desired minerals, requiring a long period of time to reach their respective mineralogical end-point.¹ As such, predicting and controlling the long-term mineralization in the TMF is essential to prevent pollutant elements from contaminating the surrounding environment.

AREVA has been investigating the long-term mineralization of elements such as As and Ni in the TMF for many years.^{2–4} $\text{As}^{5+}_{(\text{aq})}$ concentrations are well controlled (<1 mg/L) by the coprecipitation of $\text{Fe}^{3+}_{(\text{aq})}$ and $\text{As}^{5+}_{(\text{aq})}$ as poorly crystalline scorodite ($\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$) because of the excess Fe in the TMF.^{2–4} Likewise, $\text{Ni}^{2+}_{(\text{aq})}$ concentrations are controlled by the adsorption of $\text{Ni}^{2+}_{(\text{aq})}$ on ferrihydrite ($\text{Fe}(\text{OH})_3$).³ There has been comparatively fewer studies of how Mo mineralization in the TMF. The primary Mo-bearing mineral in the ore is molybdenite (MoS_2),⁵ which is oxidized to water-soluble molybdate ($[\text{MoO}_4]^{2-}_{(\text{aq})}$) when leaching (pH ~ 1) the

uranium ore at the JEB uranium mill.⁶ During the tailings preparation process, the waste solid and solution are mixed with ferric sulfate ($\text{Fe}_2(\text{SO}_4)_3$). Although intended to control the release of arsenic in the TMF, $\text{Fe}^{3+}_{(\text{aq})}$ will also coprecipitate with $[\text{MoO}_4]^{2-}_{(\text{aq})}$ to form ferrimolybdate ($\text{Fe}_2(\text{MoO}_4)_3 \cdot 8\text{H}_2\text{O}$) and molybdate adsorbed on ferrihydrite ($\text{Fe}(\text{OH})_3 - \text{MoO}_4$) as the pH is raised to 4.^{1,6} The pH is then raised to 7–8 prior to adding the tailings slurry to the TMF. $[\text{MoO}_4]^{2-}_{(\text{aq})}$ is predicted to be present in the TMF because ferrimolybdate and molybdate adsorbed on ferrihydrite are soluble under the near-neutral conditions of the TMF. Coincidentally, the TMF is saturated with gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) because of the addition of sulfuric acid (H_2SO_4) and lime (CaO) during the milling process, resulting in high concentrations of $\text{Ca}^{2+}_{(\text{aq})}$ (500 mg/L) and $[\text{SO}_4]^{2-}_{(\text{aq})}$ (2800 mg/L) throughout the pore water of the TMF. Thermodynamic calculations predict that the strongly oxidizing conditions of the TMF, with an Eh of +290 mV and a dissolved O^{2-} concentration of 5–7 mg/L, would promote the coprecipitation of $\text{Ca}^{2+}_{(\text{aq})}$ and $[\text{MoO}_4]^{2-}_{(\text{aq})}$ as powellite (CaMoO_4).⁶ The overall geo-

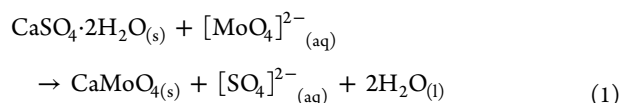
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chemical model for the formation of powellite can be described by the following reaction:



X-ray absorption near-edge spectroscopy (XANES) and X-ray diffraction (XRD) analysis of tailings samples from the JEB TMF collected during the 2008 sampling campaign confirmed the presence of powellite in the TMF.⁷ However, it was not possible to determine if the predicted mineralogical end-point of powellite is correct as only six samples were analyzed. Powellite was also observed in a related XANES study on the Mo speciation in the Deilmann Tailings Management Facility (DTMF) operated by the Cameco Corporation.⁵ Given the environmental implications, it is important to confirm that the geochemical model for controlling the release of Mo in the JEB TMF is correct. XANES was used to identify and quantify the concentrations of the various Mo species in the TMF by analyzing tailings samples collected during the 2013 sampling campaign. XANES is a powerful analytical technique for studying environmental samples because it can be used to identify low concentrations of chemical species present in heterogeneous samples. Twenty five samples were studied, representative of the total depth of the tailings from two bore holes in the TMF. The sampling depth itself correlates with the age of the tailings due to the settled nature of the TMF. Therefore, the mineralization of Mo in the TMF can be inferred by comparing the concentration of the various Mo species in the tailings solids to the concentration of aqueous Mo in the tailings pore water. This study verified the existing geochemical model and confirmed that powellite controls the aqueous Mo pore water concentration in the TMF.

■ EXPERIMENTAL SECTION

Tailings Sample Description and Analysis. The 25 samples analyzed in this study were collected from two bore hole locations during the 2013 sampling campaign of the JEB TMF. Fourteen of the samples were collected from a bore hole located at the center of the TMF (TMF13-01) while 11 of the samples were collected from a periphery bore hole (TMF13-03) located 55 m from the central bore hole. The tailings are placed in the TMF using a floating barge and tremie piping system. While the design minimizes particle size segregation at the point of placement, it does not eliminate it. Consequently, with respect to particle size distribution, the tailings solids in the TMF are not homogeneous. The central bore hole possesses a significantly coarser particle size distribution than the peripheral bore hole. Tailings solids from the central bore hole can contain large grains of primary Mo mineralization (molybdenite; MoS_2) that were too large to be fully oxidized in the uranium mill process.

The samples were collected in approximately 3 m intervals using a Gregory-type piston sampler by engineers from AREVA Resources Canada's Safety, Health, Environment, and Quality (SHEQ) department. Material at the end of the sampler was discarded due to exposure to air. The pore water was collected by hydraulically pressing the samples and analyzed using inductively coupled plasma-mass spectrometry (ICP-MS) analysis to determine the aqueous Mo pore water concentration. The Mo pore water concentration was found to vary from 1.25–44.20 mg/L. Solid tailings samples were nitrogen-

purged, vacuumed-sealed, and stored in a freezer ($\sim 5^\circ\text{C}$) to prevent oxidation. Once transported to the University of Saskatchewan, samples were stored in a N_2 -filled glovebox. Samples were not exposed to air until the XANES measurements were performed, which was approximately one year after the samples were collected from the TMF. A complete sample list, including sample elevation and aqueous Mo pore water concentration, is found in Supporting Information Table S1. The concentrations of select elements in the tailings solids, as determined by ICP-MS, are also found in Supporting Information Table S2.

Mo K-Edge XANES. All Mo K-edge XANES measurements were performed using the Hard X-ray MicroAnalysis (HXMA) beamline (06ID-1) at the Canadian Light Source.⁸ Samples were packed into 2.33 mm thick rectangular Teflon holders, which were sealed with two layers of Kapton tape. Samples were positioned in front of the X-ray beam at a 45° angle. Spectra were collected from 19 800–20 650 eV with a step size of 0.3 eV near the Mo K-edge. The energy range was selected using a silicon (220) crystal monochromator that provided a monochromatic flux on the order of 10^{12} photons/sec with a resolution of 2 eV at 20 keV, which is less than the natural line width of the Mo K-edge (4.52 eV).⁹ All spectra were measured in partial fluorescence yield (PFY) mode using a 32 element Ge detector and calibrated against Mo metal, with the maximum of the first derivative of the Mo K-edge set to 20,000 eV.¹⁰ Multiple scans were collected for each spectrum. The samples were observed to not undergo any X-ray beam-induced reduction as there was no change in the spectra between successive scans.

All XANES spectra were analyzed using the Athena software program.¹⁰ A quantitative analysis of the spectra was conducted by performing a principal component analysis (PCA) followed by a linear combination fitting (LCF) of the spectra. The energy range used for the PCA and LCF analysis was 19990–20075 eV. The standards used in the LCF analysis (MoS_2 , MoO_2 , MoO_3 , H_2MoO_4 , CaMoO_4 , $\alpha\text{-NiMoO}_4$, $\alpha\text{-FeMoO}_4$, $\text{Fe}_2(\text{MoO}_4)_3 \cdot 8\text{H}_2\text{O}$, $\text{Fe}(\text{OH})_3 - \text{MoO}_4$) were the same as those used in our previous Mo K-edge XANES study.⁷ An energy shift was not applied during the LCF as the standards were calibrated against the same reference (Mo metal) as the tailings samples.

■ RESULTS AND DISCUSSION

Mo K-Edge XANES Spectra. The Mo K-edge XANES spectra of representative tailings samples from the central and peripheral bore holes are shown in Figure 1. The complete set of Mo K-edge XANES spectra from the tailings samples studied

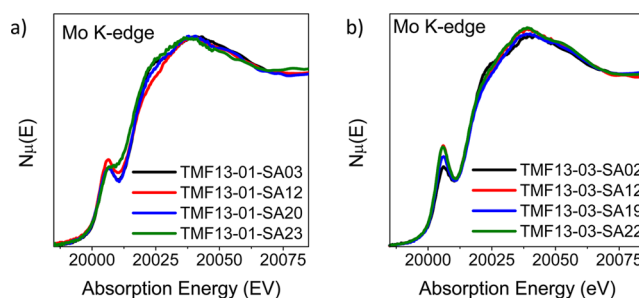


Figure 1. Representative Mo K-edge XANES spectra of tailings samples collected from the (a) central (TMF13-01) and (b) peripheral (TMF13-03) bore holes.

can be found in the Supporting Information Figures S1–S2. The Mo K-edge corresponds to the dipole-allowed ($\Delta l = \pm 1$) transition of the 1s electron into unoccupied Mo 5p states. In general, the absorption-edge energy is sensitive to the oxidation state of Mo, as well as bond covalency.^{7,11} A low intensity pre-edge feature (19 990–20 010 eV) is also observed in the Mo K-edge, which corresponds to a dipole-forbidden ($\Delta l = \pm 2$) transition of a 1s electron into unoccupied Mo 4d states. The intensity of the pre-edge is influenced by the local coordination environment of the absorbing Mo atom.¹¹

The majority of the Mo K-edge XANES spectra from the tailings samples have similar lineshapes. The Mo K-edge absorption-edge energy (and general line shape) of the tailings samples were more similar to that of MoO₃ (Mo⁶⁺) than MoO₂ or MoS₂ (Mo⁴⁺), as shown in Figure 2. The Mo K-edge line

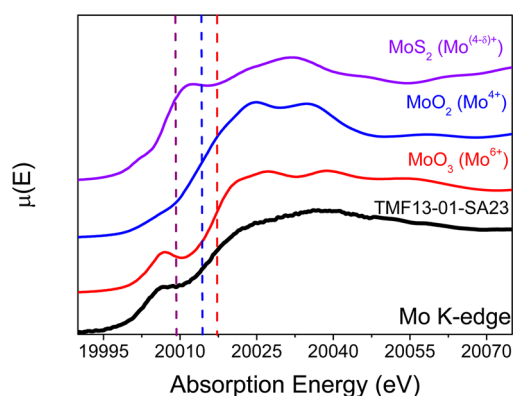


Figure 2. Mo K-edge XANES spectrum of tailings sample TMF13-01-SA23. The absorption-edge energy is similar to that of MoO₃, suggesting a large concentration of Mo⁶⁺.

shape of the tailings samples are also different than that of tetrathiomolybdate ([MoS₄]²⁻; Mo⁶⁺),¹² indicating that the tailings samples consist mostly of Mo⁶⁺ oxides, which is in agreement with a previous report.⁷ Broadening of the near-edge region of spectra from samples collected from the central bore hole (Figure 1a) was observed, which may be due to the presence of Mo⁴⁺.^{13,14}

Principle Component Analysis. Visual inspection of the Mo K-edge XANES spectra suggests the tailings consist of multiple Mo species. Advanced analysis techniques are required to identify and quantify the Mo-bearing species in the TMF. Principle component analysis (PCA) was first used to determine the number of Mo species present in the 2013 tailings samples. The PCA calculation decomposes a series of spectra into a set of components that describes the variation in the data set.^{15,16} Full details of the PCA analysis can be found elsewhere.⁷ Results of the PCA analysis for samples from each bore hole can be found in the Supporting Information Figure S3. The IND function, an empirical function used to differentiate between major and minor components in a PCA, was calculated for each bore hole to determine the minimum number of components in each series.^{17,18} It is generally accepted that the minimum number of components is given when the IND function is minimized.^{17,18} The IND values are generally small after the first component, which may be due to variations in the number of species present in each sample. The similar IND values obtained for 2–4 components suggests a maximum of four components are present in the tailings samples. This can be observed when reconstructing the spectra from tailings samples TMF13-01-SA23 (see Figure S4 in the Supporting Information), where a slight improvement is

Table 1. Results of the LCF Analysis of the Mo K-Edge XANES Spectra from the Tailings Samples^a

sample	CaMoO ₄ (at%)	Fe(OH) ₃ -MoO ₄ (at%)	Fe ₂ (MoO ₄) ₃ (at%)	MoS ₂ (at%)	R-factor	χ ²
TMF13-01-SA01	8(3)	43(2)	43(3)	7(5)	0.00276	0.0592
TMF13-01-SA03	0(3)	55(3)	36(3)	9(5)	0.00306	0.0790
TMF13-01-SA04	18(3)	17(3)	41(4)	24(6)	0.00400	0.0932
TMF13-01-SA06	7(4)	63(3)	20(4)	10(6)	0.00415	0.115
TMF13-01-SA11	41(2)	30(2)	11(3)	19(4)	0.00181	0.0470
TMF13-01-SA12	38(2)	37(2)	17.4(6)	8(4)	0.00230	0.0519
TMF13-01-SA14	20(3)	55(2)	7(3)	17(5)	0.00304	0.0747
TMF13-01-SA19	30(2)	41(2)	13(3)	16(4)	0.00185	0.0466
TMF13-01-SA20	16(3)	45(3)	28(4)	11(6)	0.00400	0.102
TMF13-01-SA21	12(4)	54(5)	5(3)	29.7(9)	0.00450	0.113
TMF13-01-SA22	27(2)	42(2)	3(3)	28(4)	0.00196	0.0489
TMF13-01-SA23	10(3)	59(3)	4(3)	27(5)	0.00306	0.0778
TMF13-01-SA24	30(3)	24(3)	31(3)	16(5)	0.00319	0.0855
TMF13-01-SA25	19(3)	42(3)	25(4)	14(6)	0.00417	0.102
TMF13-03-SA02	5(3)	51(3)	36(3)	8(5)	0.00281	0.0742
TMF13-03-SA04	4(3)	26(3)	60(4)	10(6)	0.00391	0.0974
TMF13-03-SA06	25(2)	43(2)	25(3)	9(4)	0.00195	0.0508
TMF13-03-SA07	6(1)	51(1)	37(2)	6(3)	0.000993	0.0247
TMF13-03-SA11		85(4)		15(9)	0.00871	0.239
TMF13-03-SA12	44(3)	32(3)	16(3)	8(5)	0.00269	0.0732
TMF13-03-SA14	31(3)	19(3)	38(3)	13(5)	0.00335	0.0866
TMF13-03-SA15	39(3)	20(2)	26(3)	14(5)	0.00282	0.0709
TMF13-03-SA19	40(3)	30(2)	23(3)	7(4)	0.00214	0.0565
TMF13-03-SA21	45(3)	19(3)	22(4)	15(6)	0.00406	0.103
TMF13-03-SA22	38(3)	28(3)	26(3)	9(5)	0.00286	0.0750

^aCalculated errors are shown in brackets.

observed (particularly in the pre-edge region) when reconstructing the spectrum with four components.

Linear Combination Fitting Analysis. Linear combination fitting (LCF) analysis was employed to identify the Mo species present in the tailings samples. Each normalized Mo K-edge spectrum was fitted to the linear combination of weighted standard spectra. The Mo K-edge XANES spectra from the Mo-bearing standards used in the LCF analysis are plotted in Figure S5 in the Supporting Information. All of the Mo^{6+} standards consist of MoO_4 tetrahedral units; however, the Mo K-edge line shape of these standards are quite different in the near-edge region (20 010–20 040 eV) due to effects from the presence of different next-nearest neighbors (i.e., Ca, Fe, etc.). The coefficients calculated in the LCF, which correspond to the concentration of each Mo species relative to the total amount of Mo in the tailings, were allowed to vary between 0 and 1 with the total sum of the coefficients constrained to 1. Several different fitting models using different combinations of standards were tested. Best fits were determined by calculating the goodness-of-fit parameters (R -value and χ^2). Generally, the fit with the smallest R -value and χ^2 value was considered the best. Decreasing the fitting range from 19 990–20 075 eV to 19 990–20 040 eV had no effect on the calculated concentrations, indicating that there are sufficient details in the pre- and near-edge regions to distinguish between the different Mo species in the tailings samples. Results of the best fits are tabulated in Table 1 and representative fitted spectra are shown in Figure 3. The fitted spectra from all other tailings samples are presented in Figures S6–S9 in the Supporting Information.

The best fits were obtained when fitting the spectra to ferrimolybdate ($\text{Fe}_2(\text{MoO}_4)_3 \cdot 8\text{H}_2\text{O}$), powellite (CaMoO_4), molybdate adsorbed on ferrihydrite ($\text{Fe}(\text{OH})_3 - \text{MoO}_4$), and molybdenite (MoS_2). The concentration of molybdenite is small in most tailings samples (less than 10 at%). However, including molybdenite significantly improves the fitting of the

near-edge region and the goodness-of-fit (see Figure S10 and Table S3 in the Supporting Information). This suggests that molybdenite is an essential component in the fittings. Because of the oxic conditions of the TMF, the likely source of molybdenite is unprocessed ore that was not fully oxidized during the uranium milling process. Although molybdenite was not found in our previous XANES study of samples collected in 2008, it does not mean that molybdenite was not present in the TMF during this period.⁷

It should be noted that slightly better fits were obtained when using molybdic acid (H_2MoO_4) rather than powellite. However, molybdic acid is soluble at the pH of the TMF (~ 7 – 8).¹⁹ As such, molybdic acid was excluded from the fittings. The overfitting of the broad peak near 20040–20060 eV is likely due to multiple scattering resonance (MSR) peaks contributing to the intensity of this feature. MSR is a low-energy extended X-ray absorption fine structure (EXAFS) phenomenon that is highly dependent on crystal structure and crystallinity.²⁰ The intensity of MSR contributions decreases with decreasing crystallinity, and the overfitting observed in this region is indicative of the poor crystallinity of these materials. This observation is consistent with our previous study of the 2008 tailings samples.⁷

Comparison of the Mo Speciation in the 2008 and 2013 Tailings Samples. The Mo K-edge XANES spectra of the 2008 and 2013 tailings samples collected at the same depth were noticeably different (see Figure S11 in the Supporting Information). This suggests that changes in the Mo speciation in the tailings have occurred over the five year period between sampling campaigns. Comparing the relative amounts of Mo^{6+} species in tailings samples collected at different dates from the same elevation and bore hole can provide some indication as to which Mo^{6+} species are stable in the TMF over long periods of time. In 2008: the tailings deposited at approximately 411 mASL (meters above sea level) were less than 1 year old; at 398 mASL the tailings were approximately 5 years old; and at 371 mASL the tailings were approximately 10 years old. It follows for the 2013 samples that the tailings sampled at 411, 398, and 371 mASL are approximately 5, 10, and 15 years old, respectively. Figure 4 compares the distribution of Mo^{6+} species from the peripheral bore hole in 2008 and 2013. Near the surface of the TMF (~ 411 mASL), the relative amount of powellite increased from 10 at% (2008 tailings sample) to 25 at% (2013 tailings sample). In contrast, the relative amounts of ferrimolybdate and molybdate adsorbed on

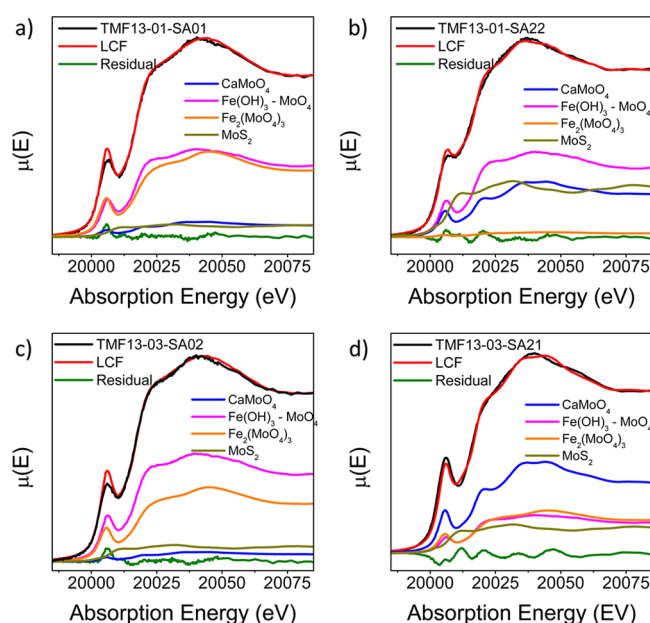


Figure 3. Fitted Mo K-edge XANES spectra of tailings samples (a) TMF13-01-SA01, (b) TMF13-01-SA22, (c) TMF13-03-SA02, and (d) TMF13-03-SA21. The linear combination fit of the spectrum is shown in red and the residual is shown in green. The weighted spectra of the standards used to fit the spectra are also shown.

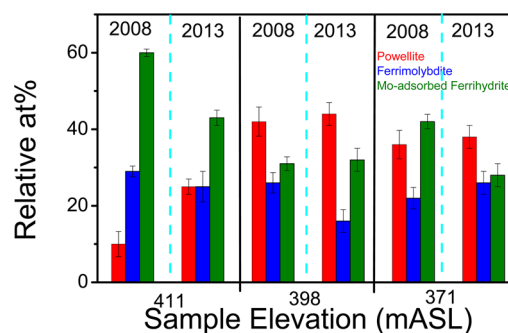


Figure 4. A comparison of the distribution of Mo^{6+} species (powellite, ferrimolybdate, and molybdate adsorbed on ferrihydrite) from tailings samples collected from the peripheral bore hole in 2008 and 2013. Note that a larger amount of powellite was observed in the 2013 tailings samples, particularly at lower elevations.

ferrihydrite decreased over the same five year period, suggesting that powellite is more stable in the TMF over time. Smaller changes in the amount of powellite present were observed at lower elevations. It is apparent that relatively rapid changes in the Mo mineralogy occurs within the first five years of placement in the TMF. Following this, the precipitation of powellite appears to slow.

Depth Analysis of the TMF. Powellite precipitates over time in the TMF, which is consistent with the predicted geochemical model (eq 1). This can be confirmed by comparing the relative amounts of solid Mo species in the TMF to the aqueous Mo pore water concentration. The aqueous Mo pore water concentration is plotted against the sample elevation for the central and peripheral bore holes in Figure 5. In general, higher aqueous Mo pore water concentrations are observed at elevations above 400 mASL (i.e., closer to the surface of the TMF) and sharply decrease at lower elevations. This suggests that, within the older tailings, a solid Mo mineral phase forms that results in a decrease of the

aqueous Mo pore water concentration. It should be noted that this effect is more evident in the peripheral bore hole compared to the central bore hole.

As shown in Figure 5a, a sharp increase in the relative amount of powellite in the tailings is observed at elevations below ~400 mASL, particularly in the peripheral bore hole. The aqueous Mo pore water concentration remains low in tailings containing relatively high powellite content. The increase in the relative amount of powellite at lower elevations confirms that aqueous Mo precipitates to form powellite over time. The opposite trend is observed in the combined relative amounts of ferrimolybdate and molybdate adsorbed on ferrihydrite (Figure 5b). Elevated concentrations of Mo in the pore water of the upper tailings are consistent with the dissolution of ferrimolybdate and molybdate adsorbed on ferrihydrite. The dissolution and reprecipitation of Mo as powellite confirms that the existing Mo geochemical model of the TMF is correct, and that powellite controls the long-term stability of Mo in the pore water.

The effects of particle size of the tailings can be observed by comparing Mo speciation of the tailings from the central bore hole compared to the peripheral bore hole. A larger amount of molybdenite (~30 at%) is observed in three samples (TMF13-01-SA21, TMF13-01-SA22, TMF13-01-SA23) collected from the central bore hole at 370–380 mASL. As shown in Figure 6a, the increase in molybdenite content correlates with a small

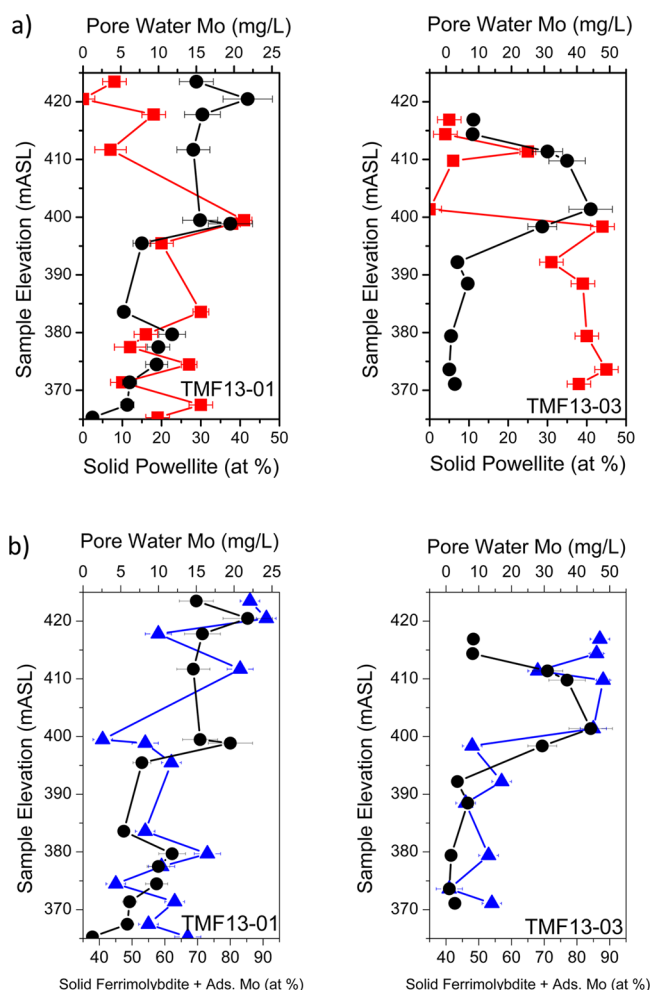


Figure 5. Aqueous Mo pore water concentration (black line) compared to the relative amounts of solid a) powellite (red line) and b) ferrimolybdate and molybdate adsorbed on ferrihydrite (blue line) plotted against the sample depth of the central bore hole (left side) and peripheral bore hole (right side). Errors in the Mo pore water concentrations are estimated to be 15% for concentrations greater than 1 mg/L. Where not apparent, the error bars are smaller than the symbols.

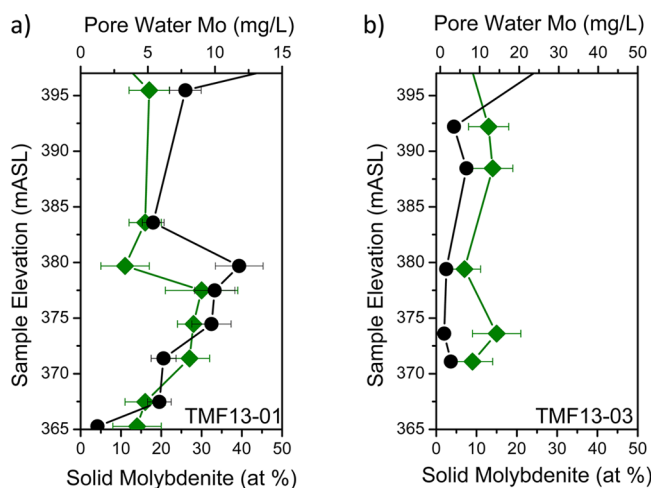


Figure 6. Aqueous Mo pore water concentration (black line) compared to the relative amount of solid molybdenite (green line) plotted against the sample depth of the a) central bore hole (TMF13-01) and b) peripheral bore hole (TMF13-03). The plots highlight the changes in the aqueous Mo pore water concentration and sediment molybdenite at elevations below 400 m (i.e., older tailing samples). Errors in the Mo pore water concentrations are estimated to be 15% for concentrations greater than 1 mg/L. Where not apparent, the error bars are smaller than the symbols.

increase in the aqueous Mo pore water concentration at roughly the same elevation in the central bore hole. There is no significant change in the amount of molybdenite or aqueous Mo pore water concentration of the peripheral bore hole with increasing depth (Figure 6b). Under the conditions of the TMF, molybdenite should oxidize. Therefore, the aqueous Mo pore water concentration should be higher in regions of the TMF containing large (~30 at%) amounts of molybdenite, as is illustrated in Figure 6a. Note that there was no correlation

between the aqueous Mo pore water concentration and the amount of molybdenite at elevations above 400 mASL. This is likely due to the dissolution of ferrimolybdate and molybdate adsorbed on ferrihydrite at higher elevations, increasing the levels of Mo in the pore water and masking this more minor effect.

Overall, these results show that the aqueous Mo pore water concentration decreases as a direct result of the precipitation of powellite.

■ ASSOCIATED CONTENT

■ Supporting Information

Additional details of the Mo content of the tailings samples, results of the PCA of the tailings samples, fitted Mo K-edge spectra from additional tailings samples, and Mo K-edge XANES spectra comparing the 2008 and 2013 tailings samples are reported. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.5b00528.

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Notes

The authors declare no competing financial interest.

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Structural characterization of poorly-crystalline scorodite, iron(III)–arsenate co-precipitates and uranium mill neutralized raffinate solids using X-ray absorption fine structure spectroscopy

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Abstract

X-ray absorption fine structure (XAFS) is used to characterize the mineralogy of the iron(III)–arsenate(V) precipitates produced during the raffinate (aqueous effluent) neutralization process at the McClean Lake uranium mill in northern Saskatchewan, Canada. To facilitate the structural characterization of the precipitated solids derived from the neutralized raffinate, a set of reference compounds were synthesized and analyzed. The reference compounds include crystalline scorodite, poorly-crystalline scorodite, iron(III)–arsenate co-precipitates obtained under different pH conditions, and arsenate-adsorbed on goethite. The poorly-crystalline scorodite (prepared at pH 4 with Fe/As = 1) has similar As local structure as that of crystalline scorodite. Both As and Fe *K*-edge XAFS of poorly-crystalline scorodite yield consistent results on As–Fe (or Fe–As) shell. From As *K*-edge analysis the As–Fe shell has an inter-atomic distance of 3.33 ± 0.02 Å and coordination number of 3.2; while from Fe *K*-edge analysis the Fe–As distance and coordination number are 3.31 ± 0.02 Å and 3.8, respectively. These are in contrast with the typical arsenate adsorption on bidentate binuclear sites on goethite surfaces, where the As–Fe distance is 3.26 ± 0.03 Å and coordination number is close to 2. A similar local structure identified in the poorly-crystalline scorodite is also found in co-precipitation solids (Fe(III)/As(V) = 3) when precipitated at the same pH (pH = 4): As–Fe distance 3.30 ± 0.03 Å and coordination number 3.9; while at pH = 8 the co-precipitate has As–Fe distance of 3.27 ± 0.03 Å and coordination number about 2, resembling more closely the adsorption case. The As local structure in the two neutralized raffinate solid series (precipitated at pH values up to 7) closely resembles that in the poorly-crystalline scorodite. All of the raffinate solids have the same As–Fe inter-atomic distance as that in the poorly-crystalline scorodite, and a systematic decrease in the As–Fe coordination is observed when pH is progressively increased; the basic poorly-crystalline scorodite structural feature remains in the raffinate solid up to pH 7.

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1. INTRODUCTION

Arsenic has drawn world-wide attention in recent years because of environmental and health concerns (e.g., Korte and Fernando, 1991; Bates et al., 1992; Das et al., 1995;

Mandal et al., 1996; Bhattacharya et al., 1997). Arsenic levels in the aquatic environment can be elevated by geological processes such as mineral weathering and dissolution, or more importantly by anthropogenic activities, especially by mining and smelting activities (e.g., Riveros et al., 2001; Moldovan et al., 2003; Paktunc et al., 2003, 2004). This makes the investigation of arsenic-bearing phases with respect to their concentrations, distribution, speciation, mobility and stability important.

The mining of the high-grade uranium deposits located in the Athabasca Basin, northern Saskatchewan, Canada, accounts for approximately one-third of the world's total uranium production (Langmuir et al., 1999). Along with uranium, arsenic co-mineralization is present and the amounts are significant in the ore from some deposits. In a typical acid leach uranium ore processing facility, most of this arsenic is leached into solution. Following uranium removal by solvent extraction and precipitation processes, the arsenic remains in an acidic sulfate waste solution referred to as raffinate. The raffinate generally reports to a lime neutralization process where arsenic is removed by precipitation with ferric iron, thereby producing low solubility iron(III)–arsenates (Riveros et al., 2001). After neutralization, the tailings are placed in a tailings disposal facility. A potential constituent of concern in the pore water of the final placed tailings is soluble arsenic originating from the neutralized raffinate solids.

The mineral scorodite, $\text{FeAsO}_4 \cdot 2(\text{H}_2\text{O})$, possesses the lowest aqueous solubility among the arsenic disposal compounds generated by the metallurgical industry, as determined by the United States EPA Toxicity Characteristic Leach Procedure (TCLP) test (Anonymous, 1992). Scorodite is the preferred precipitate for several reasons, including lower iron content required, high arsenic content, and greater stability (Riveros et al., 2001; Demopoulos, 2005). The tailings neutralization process utilized by AREVA's McClean Lake Operation has been optimized for the production of scorodite (Langmuir et al., 1999, 2006). Ferric sulfate is added to the acidic raffinates at pH 1.5 to assure that the Fe(III)/As molar ratio is maintained at 3 or higher prior to neutralization. Tailings slurries are then neutralized with slaked lime to pH 4, and subsequently to pH 7.5. This procedure will typically reduce arsenic concentrations to values less than 1 mg/L in the neutralized solution. A very small fraction, 0.2% of the total arsenic available, has been determined to be releasable to the tailings pore water (Mahoney et al., 2005).

Previous laboratory studies (Waychunas et al., 1993) and field experiences (Moldovan et al., 2003) indicate that co-precipitation processes resulted in formation of arsenate-adsorbed ferrihydrites. A common feature for these reported co-precipitation processes is that they were all conducted at an elevated pH of 8 or higher. Previous X-ray absorption near edge structure (XANES) work on the McClean Lake neutralized tailing materials (Cutler et al., 2001) indicated that the dominant arsenic species was arsenate, but the local structure beyond the first coordination shell in the arsenate species remains unknown. This is the main question to be addressed in this paper.

The disordered nature of the precipitated raffinate solids in industrial McClean Lake Operation tailings poses a major challenge to their structural characterization. Conventional tools such as X-ray diffraction are still widely applicable in the sense of finger-printing the sample phases. However, the effectiveness of X-ray diffraction to identify the structural features of the low concentration constituents (a few percent or less), such as arsenic existing in the uranium mill tailings, is rather limited. X-ray absorption fine structure (XAFS) (also referred to as extended X-ray absorption fine structure or EXAFS) (Koningsberger and Prins, 1988) is an ideal tool in this situation, as it provides both the element specificity and the local structural information.

In this study, As and Fe *K*-edge XAFS are used to characterize the local structure of the so-called amorphous scorodite (Jia et al., 2003, 2006, 2007), hereafter it will be referred as poorly-crystalline scorodite to reflect its defined arsenic local structure, and later this system will be used as a model for the raffinate solids. The poorly-crystalline scorodite (an iron(III)–arsenate co-precipitate with Fe/As = 1) possesses an XRD spectrum with two broad lines similar to that of two-line ferrihydrite (Eggleton and Fitzpatrick, 1988). The first peak of the poorly-crystalline scorodite XRD pattern is centered at around $29^\circ 2\theta$ (X-ray wavelength $\lambda = 1.54 \text{ \AA}$) corresponding to one of the main peaks of crystalline scorodite at the same position, whereas the second peak is much broader and markedly lower in intensity corresponding to crystalline scorodite's peaks lying in the range of $55\text{--}59^\circ 2\theta$. The corresponding peaks of the 2-line ferrihydrite are respectively at $35^\circ 2\theta$ and $62^\circ 2\theta$ for the same X-ray wavelength. The occurrence of the two peaks of poorly-crystalline scorodite has been observed before (Rancourt et al., 2001) in an "As-rich hydrous ferric oxide co-precipitate" but that was attributed to ferrihydrite and the shift assumed to be due to differences in their crystallite size.

The reference data from crystalline scorodite were used for constraining some of the global parameters used throughout this study. Wherever possible, both As *K*-edge XAFS data were used in the analysis. This is the case for crystalline scorodite and the poorly-crystalline scorodite, both have 1:1 Fe/As molar ratio. The complementary Fe *K*-edge data not only allow more stringent controls over the structural results obtained, but also are a useful probe for Fe–Fe inter-atomic scattering, providing differentiation of the local Fe structure for scorodite and ferrihydrite. Secondly, As *K*-edge XAFS data on solids from co-precipitated systems are compared with the data for poorly-crystalline scorodite to demonstrate the structural consequence of the terminal preparation pH values used during co-precipitation. This is important because the scorodite precipitation–dissolution process is strongly pH dependent (Dove and Rimstidt, 1985; Robins, 1987, 1990; Krause and Ettel, 1988; Zhu and Merkel, 2001; Langmuir et al., 2006; Bluteau and Demopoulos, 2007). Finally, the XAFS results from the neutralized raffinate solids prepared over a range of pH values from 2 to 7 are compared with those of poorly-crystalline scorodite and the typical arsenate-adsorbed systems such as arsenate on goethite.

2. METHODS AND MATERIALS

Whole tailings discharged at a mine site usually have complex compositions as they are produced by physically mixing the neutralized raffinate solids with the leach residue solids in the tailings neutralization process. Therefore in whole tailings there initially exist several As chemical oxidation states (Cutler et al., 2001). Here, only the arsenic species precipitated from the raffinate are of interest. In order to focus on the essential chemistry of As precipitation from the raffinate, an uranium mill raffinate solution without residual solids was neutralized under laboratory conditions to a range of terminal pH values from 2 to 7 (Rowson and Tremblay, 2003). Details are given in the next paragraph.

Two sets of neutralized raffinate solid samples were supplied by AREVA Resources Inc. They were precipitated from a raffinate solution from the McClean Lake Operation (Athabasca Basin, Saskatchewan) uranium ore processing facility (Mahoney et al., 2007). The solid samples represent different terminal pH values as the raffinate is neutralized from an initial pH of 1.0 to various higher pH values. The experimental design permitted the accumulation of solids throughout the neutralization process. The solid samples from the neutralized raffinate experiments were prepared using a mill derived raffinate that was spiked with additional arsenic and nickel. In accordance with the tailings neutralization process in the plant, the Fe/As molar ratio was adjusted to 4.0 by addition of ferric sulfate [$\text{Fe}_2(\text{SO}_4)_3$] prior to neutralization. Ratios greater than 3 have been shown to reduce arsenic concentration in the neutralized solution to 1 mg/L (Langmuir et al., 1999). The arsenic concentration in the spiked raffinate was 732 mg/L, total iron was 2400 mg/L, and initial pH was 1.5. The raffinate also contained Ni at 560 mg/L, sulfate at 14,000 mg/L, and calcium at 760 mg/L, with lesser amounts of aluminum, silica, magnesium and sodium. In some cases up to seven beakers (2 L capacity) were filled with the raffinate. These beakers were placed on a jar tester and stirred continuously while neutralizing agent, either slaked lime ($\text{Ca}(\text{OH})_2$) for set #1, or caustic (NaOH) for set #2, was added in small amounts. The use of lime in set #1 resulted in saturation of the neutralized solution with gypsum hence bringing down the sulfate content of the solution to 1400 mg/L corresponding to gypsum solubility. In set #2 the sulfate content of the solution remained practically unchanged during neutralization with NaOH. Throughout the process the pH was monitored. Additional neutralizing agent was added until the specified pH was reached. The samples from set #1 that were used in this study were prepared at pH of 2.18 (#1–1), 3.15 (#1–2), 4.04 (#1–3), and 6.09 (#1–4), respectively. The colors of these samples change from a pale yellow (#1–1), to yellowish brown (#1–2), to brownish yellow (#1–3), and to brownish green (#1–4), respectively. The samples from set #2 were prepared at pH values of 2.01 and 7.08 (dark brownish green color), respectively. Upon reaching the specified pH, the beaker was removed, and the neutralized raffinate was pressure filtered. The reaction time for precipitation was 1.0–2.5 h depending upon the terminal pH. The solutions were analyzed and the solids collected in the filter

cake were air dried at room temperature. The changes in raffinate solution composition as a function of pH and geochemical modeling for the raffinate neutralization process have been reported elsewhere (Mahoney et al., 2007), and in this work we focus on the speciation of the arsenic in the raffinate solids. The precipitated solids resulted in a very fine powder product with arsenic concentrations of 4–7%.

Synthetic model compounds including crystalline scorodite ($\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$ —Singhania et al., 2005), iron(III)–arsenate co-precipitates and poorly-crystalline scorodite (Jia et al., 2003) were employed. The latter compound with a nominal Fe/As molar ratio equal to one is a co-precipitation product with the following stoichiometry: $\text{FeAs}_{0.976} \cdot 2.39\text{H}_2\text{O}$. A list of the various solids synthesized along with some features of their production procedure is given in Table 1.

The crystalline scorodite material was prepared following the procedure by Singhania et al. (2005). Briefly this involved heating an As(V)– $\text{Fe}_2(\text{SO}_4)_3$ – H_2SO_4 solution (with initial pH 1 at room temperature and Fe/As molar ratio equal to 1) to 95 °C, adjusting the pH to 0.9 with MgO, seeding the solution with a small mass of scorodite crystals and stirring for 2–2.5 h. Via this procedure the arsenic and iron precipitated on the surface of the seed crystals as scorodite. At the end of the precipitation test, the entire suspension was filtered and the solids were washed and dried. The poorly-crystalline scorodite was prepared by raising the pH of a solution of Na_2HAsO_4 (0.1 M As(V)) and $\text{Fe}_2(\text{SO}_4)_3$ (0.1 M Fe(III)) from 1.2 to 4 with MgO. The mixture was stirred for 2 h at room temperature and then filtered to obtain the solid sample. The synthesis of iron(III)–arsenate co-precipitates involved the preparation of an Fe(III)/As(V) solution (75 mM Fe, 18.8 mM As, Fe/As = 4) by dissolving $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$ and $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ in de-ionized water and acidified to pH 1.0–1.5 with HNO_3 . The pH of the solution was raised to 4 and 8, respectively, using NaOH solution with the mixture mechanically stirred vigorously and maintained constant for 24 h. The solid samples (light yellow and brownish yellow in color for the solids of pH 4 and 8, respectively) were separated by filtration and stored as wet cakes for XAFS analysis.

Crystalline goethite was synthesized following O'Reilly et al. (2001). The measured powder X-ray diffraction pattern of the goethite prepared is in good agreement with that for goethite published by the International Center for Diffraction Data (ICDD), the Mineral Powder Diffraction File databook (1993). Using a scanning electron microscope (JEOL 840 A), the morphology of the synthesized goethite powder was observed to consist of randomly oriented prismatic crystals $\sim 1 \mu\text{m}$ in length (along the crystallographic *c* axis) and with a diameter of 0.1–0.2 μm .

Adsorption of arsenate onto the surface of crystalline goethite was performed following the procedure of O'Reilly et al. (2001). Sodium nitrate stock solution (0.1 M) was prepared from pure laboratory standards (NaNO_3 , Merck KGaA, CAS #7631-99-4), pre-equilibrated to pH 6, and stabilized overnight at room temperature before usage. Sodium arsenate stock solution (28 mM) was prepared by adding the required amount of the laboratory standard

Table 1
Summary of sample preparation conditions.

Sample	Initial As	Initial Fe	Final As/Fe molar ratio	Initial pH	Final pH	Acid or base used	Counter anion (final conc.)	Comments
Crystalline scorodite	10 g/L (0.133 M)	7.5 g/L (0.133 M)	1	<0.7	0.9	MgO	Sulfate (~19,000 mg/L)	Slow neutralization for 2 h at 95 °C in the presence of seed
Poorly-crystalline scorodite	7.5 g/L(0.1 M)	5.6 g/L(0.1 M)	0.98	1.2	4	MgO	Sulfate(~14,400 mg/L)	Fast neutralization and stirring at room temperature for 2 h
α -FeOOH—preparation	—	0.2 M		—	12	KOH	Nitrate	Prepared at 65 °C by stirring for 24 h; filter washed and air dried
As on α FeOOH (Sorption step) (Fe/As = 4/1)	0.028 M	10 g/L FeOOH(0.11 M)	—	6	6	HNO ₃	0.1 M NaNO ₃	15 days contact time
As on α FeOOH (Sorption step) (Fe/As = 10/1)	0.011 M	10 g/L FeOOH(0.11 M)	—	6	6	HNO ₃	0.1 M NaNO ₃	14 days contact time
Co-precipitate (CPT-2) pH 4	1.4 g/L (0.019 M)	4 g/L(0.075 M)	—	1	4	NaOH	Sulfate(10,800 mg/L)	Fast neutralization and stirring at room temperature for 24 h
Co-precipitate (CPT-4) pH 8	1.4 g/L (0.019 M)	4 g/L (0.075 M)	—	1	8	NaOH	Sulfate(10,800 mg/L)	Fast neutralization and stirring for 4 h
<i>Neutralized raffinate solids set #1</i>								
1–1	732 mg/L	2400 mg/L	0.92	1.5	2.18	CaO slaked	Sulfate(~1400 mg/L)	1–3 h preparation time, filtered, air dried at room temperature
1–2	L(0.01 M)	L(0.043 M)	0.49		3.15			
1–3			0.44		4.04			
1–4			0.35		6.09			
<i>Neutralized raffinate solids set #2</i>								
2–1	732 mg/L	2400 mg/L	—	1.5	2. 01	NaOH	Sulfate(14,000 mg/L)	1–3 h preparation time, filtered, air dried at room temperature
2–6	L(0.01 M)	L(0.043 M)	—		7.08			

—, information not applicable.

($\text{NaH}_2\text{AsO}_4 \cdot 7\text{H}_2\text{O}$, Sigma Chemical Co., #10048-95-0) to the stabilized sodium nitrate stock solution. The prepared solution was equilibrated overnight at room temperature. Then the stabilized sodium arsenate stock solutions were titrated to pH 6 with nitric acid (HNO_3) and stabilized overnight. A required amount of crystalline goethite powder was added to the titrated sodium arsenate stock solutions resulting in Fe/As molar ratios of 10/1 and 4/1, respectively. The solutions were kept in capped Teflon™ bottles and set on a stirring plate and stirred at 400 rpm. The pH was monitored during the reaction process and at the end of each experiment. Afterwards the samples were centrifuged and kept wet in capped glass vials.

Most of the XAFS measurements were carried out using beamline 20-BM at the Advanced Photon Source (APS). Si(1 1 1) monochromator crystals were used with an entrance slit set at 0.5 mm vertical width. The photon energy was calibrated at the Au L_3 -edge energy (11919.7 eV) using gold foil and tracked with a Haidenhein rotary encoder (ROD 8000) attached to the monochromator main rotation axis. The scan step-sizes used were 2.0 eV/step, 0.3 eV/step, and 0.05 Å⁻¹/step for pre-edge, XANES and XAFS regions, respectively. The As K -edge XANES data clearly indicate that the dominating oxidation state of the arsenic species in the neutralized raffinate solids is As⁵⁺, consistent with previous studies (Moldovan et al., 2003). Both As and Fe K -edge data were collected for crystalline and poorly-crystalline scorodite, and only As K -edge data were collected for the neutralized raffinate samples as there the Fe is present in more than one local structure. Data acquired in transmission mode were used in this work for the reference compounds and in fluorescence mode for the neutralized raffinate samples. The XAFS data for the two iron(III)-arsenate co-precipitate samples, CPT-2 and CPT-4 (Table 1), were collected at beamline X10C in transmission mode, National Synchrotron Light Source (NSLS). Here, Si(2 2 0) monochromator crystals were used with the monochromator entrance slits opened to 1 mm vertically. The data reduction and analysis were performed using WINXAS version 2.3 (Ressler, 1997), as described previously (Jiang, 2002). Briefly, the edge inflection point was defined as the experimental E_0 , the post-absorption edge background was estimated by cubic spline fits. The theoretical scattering amplitudes and phases calculated using FEFF7.02 (Rehr and Albers, 2000) were used in the XAFS data analysis. To estimate the impact of the different arsenic local environments on the FEFF calculated scattering amplitudes and phases, two different model structures were used in the FEFF7 calculation for the scattering amplitudes and phases, namely the crystalline scorodite (Kitahama et al., 1975) and an arsenate tetrahedron adsorbed on a bidentate binuclear site on the (0 0 1) surface of crystalline goethite (α -FeOOH, Szytula et al., 1968). The reason that goethite was used in the latter case was to focus on the predominantly occurring bidentate binuclear adsorption of arsenate on this material (Sherman and Randall, 2003). This provides a simplified representation for the more complicated situation of ferrihydrites for which a consensus on its crystal structure is lacking (Michel et al., 2007). Program ATOM (Ravel, 2001) was used to generate the FEFF7 in-

put files. In the adsorption case, without prior knowledge of the actual configuration of the arsenate tetrahedron an undistorted tetrahedron was used in the modeling. The tetrahedron edge length was assumed to be that of the averaged arsenate tetrahedron edge length in the crystalline scorodite. The scattering amplitudes and phases for the single As–O and As–Fe paths obtained from these two models were essentially the same. Curve-fitting analysis was first performed for the crystalline scorodite. The resultant parameters were used as guiding values and fitting constraints in the analysis for poorly-crystalline scorodite and the neutralized raffinate samples.

Fitting residuals were used to evaluate the magnitude of the resultant uncertainty of the determined inter-atomic distances. This was done following the 1988 recommendation of the XAFS society (Lytle et al., 1989) by progressively increasing the value for R at fixed values different from the best fit value for R while leaving all other fitting parameters float, and repeating the fit until the residual equaled twice that of their starting values. This process led to an uncertainty range of ± 0.02 – 0.03 Å for the second (As–Fe) coordination shells depending on data quality obtained on different samples. The uncertainty estimated by this procedure is conservative (Lytle et al., 1989).

3. RESULTS

The measured XAFS $k^3 \cdot \chi(k)$ and corresponding Fourier transform magnitude of all the samples in this study are shown in Fig. 1. In the k -space, the spectral features of the first XAFS oscillation between 4 and 6 Å⁻¹ can be used to qualitatively group the samples into two speciation types: scorodite (Fig. 1a traces 1 to 3 and traces 7 to 12), and bidentate binuclear adsorption type (Fig. 1a traces 4 to 6). For the scorodite type, the spectrum in this k -space region has an asymmetrically split peak; while for the adsorption type this XAFS oscillation has a flattened top. This kind of qualitative characterizations for the scorodite and adsorption species have been discussed previously (Waychunas et al., 1993; Moldovan et al., 2003), and it was also noted that this is the region in the k -space where the multiple scattering effect could be observed (Foster et al., 1998). In the following, the results on crystalline scorodite and arsenic-adsorbed goethite are discussed first, then the discussion turns to the poorly-crystalline scorodite and As/Fe co-precipitate samples. These reference samples are analyzed to establish the structural reference (characteristic inter-atomic distances and coordination number) up to the As–Fe shell for As K -edge data, and Fe–As shell for Fe K -edge data. In all of these samples only As(V) is present, the nearest neighbors for As are four oxygen atoms forming an arsenate tetrahedron (Fig. 2a). As it has been noted previously (Waychunas et al., 1993; Moldovan et al., 2003), the structural difference between scorodite and an adsorption case, e.g., arsenate adsorption on crystalline goethite (α -FeOOH), lies in the inter-atomic distance of the second shell (between the arsenic at the tetrahedron center and the iron at the octahedron center), and the number of iron octahedrons coordinated to the central arsenate tetrahedron (Fig. 2e). To provide consistent modeling of this sec-

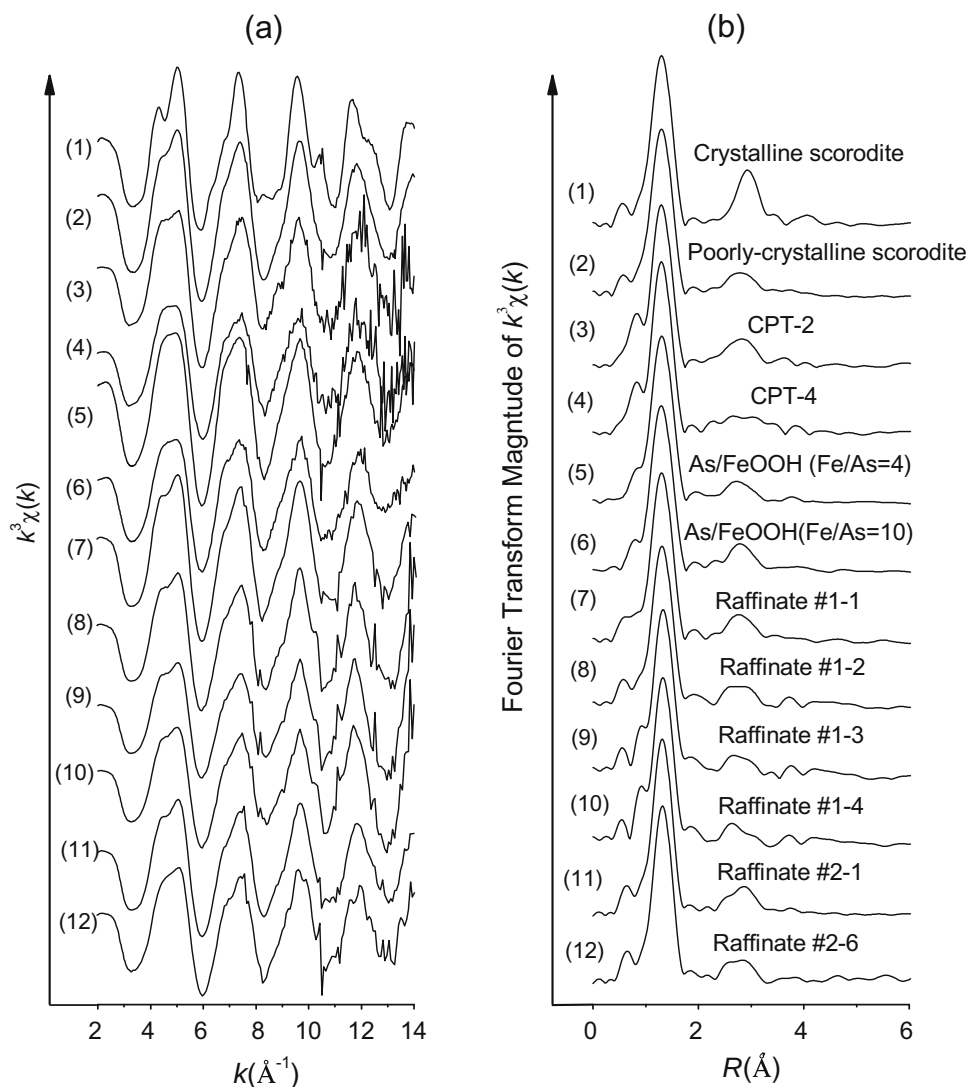


Fig. 1. Arsenic K -edge data used in this study: (a) XAFS $k^3 \cdot \chi(k)$ spectra; (b) Fourier transform of the $k^3 \cdot \chi(k)$, with the transform k interval of 2.7–13.6 $\text{\AA}^{-1}$ and a 30% Gaussian window. The first major peak is from the nearest neighbor As–O shell and the second major peak is mainly from the As–Fe shell. The Fourier transformed spectra have not been corrected for phase shift. The data in (a) and (b) correspond to samples of (1) crystalline scorodite; (2) poorly-crystalline scorodite; (3) iron arsenic co-precipitates CPT-2 with Fe/As = 4 and pH of 4; (4) CPT-4 with Fe/As = 4 and pH of 8; (5) arsenate-adsorbed goethite with Fe/As = 4; (6) arsenate-adsorbed goethite with Fe/As = 10; (7) neutralized raffinate set #1 prepared at pH 2.18; (8) pH 3.15; (9) pH 4.04; and (10) pH 6.09; (11) neutralized raffinate set #2 prepared at pH 2.01 and (12) at pH 7.08, respectively.

ond shell through all the samples in this study, we include in the analysis the multiple scattering (MS) paths within the arsenate tetrahedron as shown in Fig. 2c and d. In the disordered systems such as the poorly-crystalline scorodite and other precipitation systems, the scattering by these nearest neighbor multiple scattering paths could have a comparable intensity as those by the As–Fe paths of interest (see below).

The analysis of the reference samples was carried out first for the well-understood crystalline scorodite (Waychunas et al., 1993; Foster et al., 1998; Jiang, 2002; Sherman and Randall, 2003) for establishing some commonly used parameters such as the XAFS ΔE_0 shift (between the FEFF7 defined energy threshold and the experimentally defined threshold), the many body effect parameter, S_o^2 (Jiang,

2002; Moldovan et al., 2003), and the guiding values for σ^2 of various paths in the structure. Next, the analysis proceeded to the adsorption samples, which represents the other extreme arsenic removal mechanism, to establish the characteristic structural parameter differences between the two models. Arsenate adsorption on goethite was used to focus on the arsenate uptake on the bidentate binuclear sites (Waychunas et al., 1993), which is the most energetically favorable surface complexation configuration of arsenic(V) to iron(III) (hydroxides) (Sherman and Randall, 2003). The study was then focused on poorly-crystalline scorodite and the co-precipitated samples, to establish their structural parameters and the influence of terminal preparation pH. Finally, the neutralized raffinate solid samples

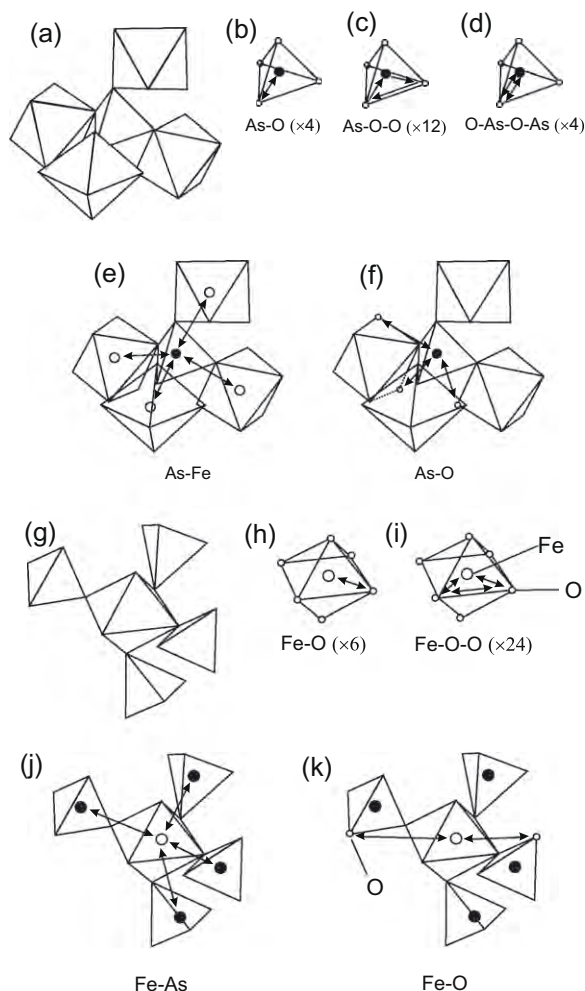


Fig. 2. Local structure environment as well as single and multiple scattering paths in mineral scorodite. (a) Arsenate tetrahedron with iron(III) octahedron neighbors; (b) As–O single scattering paths, with an averaged As–O distance of 1.68 Å (Kitahama et al., 1975); (c) As–O–O multiple scattering paths; (d) As–O–As–O multiple scattering paths; (e) As–Fe single scattering paths; with an averaged inter-atomic distance of 3.36 Å (Kitahama et al., 1975); (f) second nearest neighbor As–O single scattering paths (3 equiv. paths assumed, arrows for illustrative purpose only, see text for detail); (g) Fe local structure; (h) Fe–O single scattering paths, with an averaged Fe–O distance of 2.02 Å (Kitahama et al., 1975); (i) Fe–O–O multiple scattering paths; (j) Fe–As single scattering paths; and (k) second nearest neighbor Fe–O single scattering paths (2 equiv. paths assumed, arrows for illustrative purpose only). The numbers in parentheses represent the total number of the equivalent scattering paths.

from different termination pH values were analyzed based on the results of the reference model compounds.

3.1. Arsenic and iron local structure in crystalline scorodite and modeling considerations

Within the scorodite crystal structure (Kitahama et al., 1975), the arsenate tetrahedron is coordinated with four ferri iron octahedra (Fig. 2a). The initial scattering path

amplitudes are estimated using FEFF7. The major paths considered have their individual scattering amplitude being 5% or more of the strongest neighbor path. These paths are shown in Fig. 2b–f. In *R*-space these paths correspond to the XAFS spectral features under the two prominent peaks extending up to about 3 Å (phase-uncorrected distance) in the Fourier transforms (Fig. 1b, trace 1).

The nearest neighbor peak below 2 Å in Fig. 1b is due to the As–O path inside the arsenate tetrahedron and it is found to have the same average bond length and coordination through all the samples in this work. It should be noted that in crystalline scorodite, the tetrahedron is slightly distorted (Kitahama et al., 1975) with an As–O distance spread of 0.016 Å. In the analysis here, this As–O distance variance has been included in an averaged Debye–Waller factor and the four As–O paths are represented by a single broadened shell. Similarly, the iron octahedron is also distorted in the scorodite structure, with a Fe–O bond length spread of 0.167 Å. Again, a single shell is used to represent the average bond length and a large Debye–Waller factor resulted due to the static distortion from a regular octahedron.

The second nearest neighbor peak around the apparent distance 3 Å in the Fourier transforms (Fig. 1b, trace 1) is mainly due to the single scattering by the As–Fe paths (Fig. 2e). The As–Fe shell is the focus of this analysis as it would differentiate between alternate models for connecting As(V) tetrahedra with Fe(III) polygons (Waychunas et al., 1993; Foster et al., 1998; Moldovan et al., 2003). The FEFF7 calculations indicate that above the 5% threshold the As–Fe shell region also contains contributions from the MS paths inside the arsenate tetrahedron (Fig. 2c–d) and the second nearest neighbor As–O paths (Fig. 2f). Experimentally the spectral features in this second nearest neighbor region can be rather complex: for most raffinate samples (Fig. 1b, traces 8 to 12) there is a double-peak feature between 2.25 and 3.25 Å (phase-uncorrected distance). For these raffinate samples a single As–Fe shell would not be adequate to interpret the data in this region. We attribute the double-peak feature to the spectral manifestation of the MS path contributions (Fig. 2c–d). In *R*-space these MS paths become more observable when the As–Fe shell intensity is reduced to a certain level in these raffinate systems.

For the crystalline scorodite measured at the As *K*-edge, scattering paths up to 3.49 Å from the absorbing arsenic were considered in the fitting analysis to encompass the second nearest neighbor As–Fe shell (Fig. 1b, trace 1). In this region 13 scattering paths were used for modeling the experimental data. These paths are illustrated in Fig. 2: 4 of the nearest neighbor As–O single scattering path (Fig. 2b); 12 of the As–O–O triangular MS path (Fig. 2c); 4 of the As–O–As–O MS path (Fig. 2d); 4 of the As–Fe single scattering path (Fig. 2e); and 3 of the As–O single scattering path outside the arsenate tetrahedron (Fig. 2f). Within the distance range considered, there are 5 of the longer As–O paths (Fig. 2f) that satisfy the amplitude criterion. However, 2 of the 5 lying on the shorter distance side of the As–Fe shell destructively interfere with each other, and were therefore ignored in our analysis. Similar scattering

path enumeration was carried out for the crystalline scorodite measured at the Fe *K*-edge. The paths resulting from the FEFF7 calculation are shown in Fig. 2h–k. For the convenience of discussion, the above identified paths, other than the nearest neighbor As–O and the second nearest neighbor As–Fe, will be collectively referred to as secondary paths.

The number of floating structural parameters (N_{var}) used in the curve-fitting refinement is reduced to typically half of the maximum independent variables in a data set (Jiang, 2002), i.e., the number of free parameters in our curve-fitting is about half of $N_{idp} \approx \frac{2\Delta k \Delta R}{\pi}$ (Lytle et al., 1989). This was done mainly through correlating the related parameters, e.g., the distance and Debye–Waller parameters of all the MS paths were correlated to those of the constituent single scattering paths (Ressler, 2004), and a common ΔE_0 value was used for all the paths. The *R*-space curve-fitting results of crystalline scorodite are shown in Fig. 3a and b

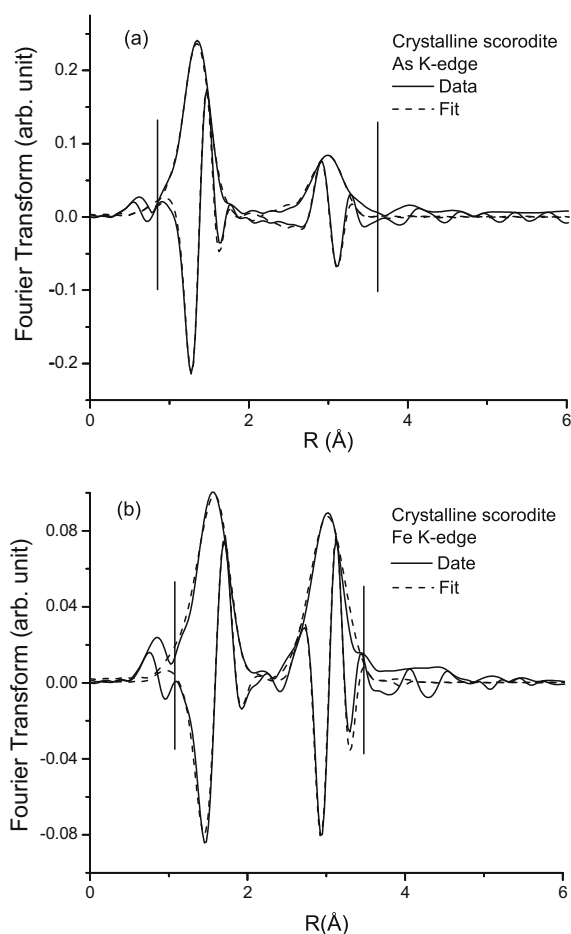


Fig. 3. Curve-fitting of crystalline scorodite in *R*-space: (a) arsenic *K*-edge and (b) iron *K*-edge. The Fourier transforms of $k^3 \cdot \chi(k)$ are with *k* intervals 2.7–17.4 and 2.3–16.4 Å^{−1} for As and Fe data, respectively, and 20% Gaussian windows. The *R*-space fitting ranges are of 0.8–3.5 and 1.1–3.3 Å, correspondingly, indicated by the two vertical lines. Solid and dashed lines are for the data and the fit, respectively. Both the magnitude (positive envelopes) and the imaginary part (oscillating curves) of the Fourier transform are shown.

for the As *K*-edge and Fe *K*-edge, respectively. For the As *K*-edge, the FEFF7 input parameters and the results after the curve-fitting refinement are tabulated in Table 2. Table 2 also lists the parameters for two raffinate systems of low and high terminal preparation pH values, respectively, for comparing the fitting results. Since the nearest neighbor As–O bond length remains virtually the same among all the samples in this study, the resulting lengths of the related MS paths also remains essentially unchanged from crystalline scorodite values calculated from FEFF7 (Table 2). The As–O paths shown in Fig. 2f are at a slightly longer distance than the main As–Fe shell. Inclusion of these three As–O paths is intended to avoid overestimating the As–Fe scattering in this *R*-space region, where other MS and single scattering paths were ignored in the analysis.

Before proceeding further, we examine the usefulness of including the secondary paths (Fig. 2c, d and f). First, we compare the fittings in *k*-space with and without these secondary paths. These comparisons are shown in Fig. 4, where the fitting is to the raw data to avoid any filtering artefacts. The same constraint condition on the MS paths used in *R*-space fitting were applied in the *k*-space, i.e., the MS path lengths were correlated to that of the constituent single paths. In both kinds of *k*-space fits the resulting structural parameters remain in a physically meaningful range, where the As–Fe distances were virtually the same. However, when comparing to the raw data (Fig. 4a and b), the fits with the secondary paths show noticeable improvements near 5 Å^{−1}. The *k*-space raw data are dominated by the single scattering paths As–O and As–Fe, so the impact of the secondary paths is not easy to detect. In *R*-space the spectral features of these secondary paths can be separated from that of the major As–O and As–Fe shells. Fig. 5 shows a focused comparison of the As–Fe shell region of the raffinate set #1 (Fig. 1b, traces 7 to 10). It can be seen that the main spectral feature between 2.25 and 3.25 Å (phase-uncorrected distance) consists of two peak components. In Fig. 5, the peak marked as MS remains relatively constant among the samples, while the peak marked as As–Fe varies systematically in magnitude. Both of these features are clearly above the data noise level and the data were processed in strictly the same manner (same transform range, same *k*-space weighting and same window function). Therefore a single As–Fe shell model would not be sufficient to interpret the data in this region. We attribute the constant magnitude component (marked as MS in Fig. 5) to the contribution from the multiple scattering paths As–O–O (Fig. 2c) and As–O–As–O (Fig. 2d), while the varying magnitude component (marked as As–Fe in Fig. 5) mainly reflects the As–Fe shell. As shown in Table 2, the fitting with the secondary paths provides a rather constant MS contribution through all the samples, which accounts for the MS feature in Fig. 5. However, if the contribution from the secondary paths was not included, the MS spectral feature in Fig. 5 would have not been accounted for in the fits.

Because of the 1:1 Fe/As stoichiometry in scorodite, the As–Fe distance and coordination viewed from a ferric iron should be exactly the same as that from an arsenate. Therefore, the Fe *K*-edge data acquired on the same sample provide a stringent consistency check in the analysis. The

Table 2

Details of calculated and refined fitting parameters. Bold and italic fonts indicate the floating parameters which are free and restrained by parameter correlations (see text), respectively; other parameter constraints are labeled using superscriptions.

			Path	FEFF calculation		Curve fit results			
				<i>N</i>	<i>R</i> (Å)	<i>N</i>	<i>R</i> (Å)	σ^2 (Å ²)	ΔE_0 (eV)
(a) For samples with scorodite type of arsenic local structure									
Crystalline scorodite	Scattering within AsO ₄	As–O	4.0	1.67	4.0 ^a	1.68	0.0016	2.7 ^a	
		As–O–O	2.0	3.02	2.0 ^a	3.02	0.0024	2.7 ^a	
			2.0	3.04	2.0 ^a	3.04	0.0024	2.7 ^a	
			2.0	3.05	2.0 ^a	3.05	0.0024	2.7 ^a	
			2.0	3.05	2.0 ^a	3.05	0.0024	2.7 ^a	
			2.0	3.06	2.0 ^a	3.06	0.0024	2.7 ^a	
			2.0	3.07	2.0 ^a	3.07	0.0024	2.7 ^a	
		As–O–As–O	1.0	3.34	1.0 ^a	3.34	0.0032	2.7 ^a	
			1.0	3.35	1.0 ^a	3.35	0.0032	2.7 ^a	
			1.0	3.37	1.0 ^a	3.37	0.0032	2.7 ^a	
			1.0	3.37	1.0 ^a	3.37	0.0032	2.7 ^a	
		Scattering outside AsO ₄	As–Fe	4.0	3.36	4.0 ^a	3.36	0.0053	2.7 ^a
			As–O	3.0	3.47	3.0 ^a	3.52^b	0.0070	2.7 ^a
		Raffinate #1–1	Scattering within AsO ₄	As–O	4.0	1.67	4.0 ^a	1.69	0.0020
As–O–O	2.0			3.02	2.0 ^a	3.04	0.0030	2.7 ^a	
	2.0			3.04	2.0 ^a	3.04	0.0030	2.7 ^a	
	2.0			3.05	2.0 ^a	3.05	0.0030	2.7 ^a	
	2.0			3.05	2.0 ^a	3.05	0.0030	2.7 ^a	
	2.0			3.06	2.0 ^a	3.07	0.0030	2.7 ^a	
	2.0			3.07	2.0 ^a	3.08	0.0030	2.7 ^a	
As–O–As–O	1.0			3.34	1.0 ^a	3.34	0.0041	2.7 ^a	
	1.0			3.35	1.0 ^a	3.35	0.0041	2.7 ^a	
	1.0			3.37	1.0 ^a	3.37	0.0041	2.7 ^a	
	1.0			3.37	1.0 ^a	3.37	0.0041	2.7 ^a	
Scattering outside AsO ₄	As–Fe			4.0	3.36	3.3	3.31	0.0107	2.7 ^a
	As–O			3.0	3.47	3.0 ^a	3.51^b	0.0068^c	2.7 ^a
Raffinate #1–4	Scattering within AsO ₄			As–O	4.0	1.67	4.0 ^a	1.68	0.0017
		As–O–O	2.0	3.02	2.0 ^a	3.03	0.0025	2.7 ^a	
			2.0	3.04	2.0 ^a	3.04	0.0025	2.7 ^a	
			2.0	3.05	2.0 ^a	3.05	0.0025	2.7 ^a	
			2.0	3.05	2.0 ^a	3.05	0.0025	2.7 ^a	
			2.0	3.06	2.0 ^a	3.06	0.0025	2.7 ^a	
			2.0	3.07	2.0 ^a	3.08	0.0025	2.7 ^a	
		As–O–As–O	1.0	3.34	1.0 ^a	3.34	0.0034	2.7 ^a	
			1.0	3.35	1.0 ^a	3.35	0.0034	2.7 ^a	
			1.0	3.37	1.0 ^a	3.37	0.0034	2.7 ^a	
			1.0	3.37	1.0 ^a	3.37	0.0034	2.7 ^a	
		Scattering outside AsO ₄	As–Fe	4.0	3.36	2.7	3.30	0.0110^d	2.7 ^a
			As–O	3.0	3.47	3.0 ^a	3.49^b	0.0084	2.7 ^a
		(b) For samples with adsorption type of arsenic local structure							
As on αFeOOH (Fe/As = 4/1)	Scattering within AsO ₄	As–O	4.0	1.68	4.0 ^a	1.69	0.0017	2.7 ^a	
		As–O–O	12.0	3.05	12.0 ^a	3.07	0.0026	2.7 ^a	
		As–O–As–O	4.0	3.36	4.0 ^a	3.36	0.0035	2.7 ^a	
	Scattering outside AsO ₄	As–Fe	2.0	3.25	1.7	3.26	0.0089	2.7 ^a	
		As–O	2.0	3.66	2.0 ^a	3.66 ^a	0.0225	2.7 ^a	
Co-precipitate (CPT-4) pH 8	Scattering within AsO ₄	As–O	4.0	1.68	4.0 ^a	1.69	0.0015	2.7 ^a	
		As–O–O	12.0	3.05	12.0 ^a	3.07	0.0022	2.7 ^a	
		As–O–As–O	4.0	3.36	4.0 ^a	3.36	0.0030	2.7 ^a	
	Scattering outside AsO ₄	As–Fe	2.0	3.25	1.6	3.27	0.0097	2.7 ^a	
		As–O	2.0	3.66	2.0 ^a	3.66 ^a	0.0092	2.7 ^a	

^a Fixed.

^b Constrain between 3.40 and 3.52.

^c Low constrain limit reached.

^d High constrain limit reached.

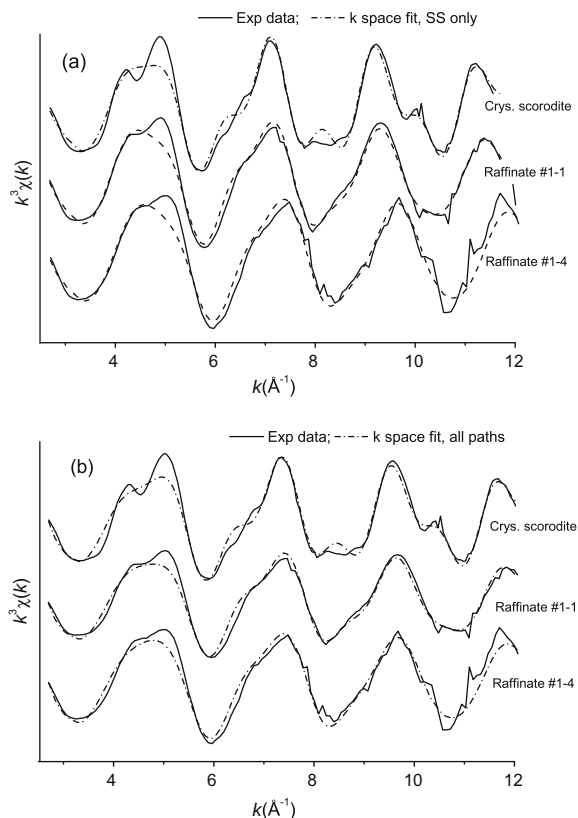


Fig. 4. Representative k -space curve-fittings to the raw (unfiltered) experimental $k^3 \cdot \chi(k)$ for crystalline scorodite, raffinate #1-1 and #1-4, respectively. (a) Using only single scattering (SS) paths of the nearest neighbor As–O and the second nearest neighbor As–Fe shells; (b) Adding to the SS paths the other secondary paths shown in Fig. 2 (see text for more detail).

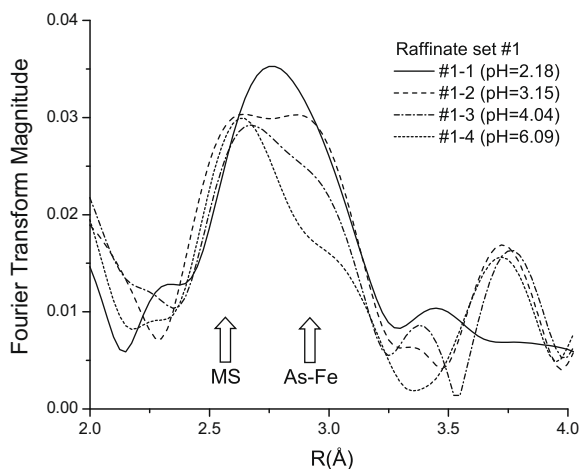


Fig. 5. Comparison of the Fourier transform magnitude in the region of As–Fe shell for the neutralized raffinate set #1. The Fourier transform of $k^3 \cdot \chi(k)$ for each sample is processed identically over k interval $2.7\text{--}13.6 \text{ \AA}^{-1}$ with 30% Gaussian window. Two components under the main feature, i.e., the multiple scattering (MS) and As–Fe scattering, are marked to indicate their approximate locations (see text for detail). The intensity of the As–Fe shell changes systematically with the increase of the sample pH values.

comparison of the analysis for the As K -edge and the Fe K -edge of scorodite is summarized in the first two rows in Table 3. The results from both K -edges of As and Fe are indeed consistent with each other in terms of As–Fe (Fe–As) distance and As–Fe (Fe–As) shell Debye–Waller factor (with the corresponding coordination fixed at the same value, see Table 3). In the R -space fitting for As or Fe K -edge data, the coordination of the first As–O or the first Fe–O shell has been fixed to that of an As tetrahedron or an Fe octahedron. The Fe–O bond in the ferric iron octahedron has a significantly larger σ^2 than the As–O in arsenate tetrahedron, indicating a less satisfactory approximation of equalizing the six Fe–O bonds in the former case. All the R -space fits have been carried out separately for k^2 and k^3 weighted $\chi(k)$'s and the results are consistent. This practice of consistency checks using different k weighting has been implemented throughout the curve-fitting in this study.

3.2. Arsenic adsorbed on the surface of crystalline goethite

For the FEFF7 calculation, the inner-sphere bidentate bi-nuclei adsorption mechanism (Waychunas et al., 1993) was used to build the model structure for the adsorbed samples. Experimentally the Fourier transform of the nearest neighbor As–O shell in these adsorbed systems appears to be virtually the same as that in the crystalline scorodite. Therefore we assumed in the FEFF7 calculation that a rigid arsenate tetrahedron with equal edge length of that averaged from crystalline scorodite is adsorbed on the goethite surface. In the model to connect such a tetrahedron on the goethite surface, the distance between the two vertex oxygens on the neighboring FeO_6 octahedra was reduced from 2.97 to 2.74 Å. The specificity of the model would not lead to significant difference in the amplitude and phase for the single scattering paths, but the intra-arsenate MS paths become more degenerate because of the assumption of the undistorted arsenate tetrahedron. The same number and type of the MS paths as that in the crystalline scorodite were used in the analysis. Table 2b shows the detail modeling parameters for the adsorption case with Fe/As = 4/1. Summary of curve-fitting results for these two samples are shown in Table 3 (row 5 and 6). An averaged $3.26 \pm 0.03 \text{ \AA}$ is found to be the As–Fe distance, consistent with the previous results found for arsenate-adsorbed on two-line ferrihydrites and aged uranium tailings (Moldovan et al., 2003) and other (laboratory prepared) arsenate-adsorbed ferrihydrites (Waychunas et al., 1993; Sherman and Randall, 2003). The determined coordination numbers are significantly lower than those in Table 2a of scorodite type samples, consistent with a typical bidentate adsorption case where the As–Fe coordination should be two.

Compared with crystalline scorodite, there is in the adsorbed case a larger difference between the σ^2 's of the first and second shell. This could be related to the tilting freedom of the arsenate tetrahedron with respect to the tetrahedron bidentate edge at the bidentate, bi-nuclei adsorption site. As the coordination number in this case is known to be two, the σ^2 's obtained provide a reference for the

Table 3

Arsenic and iron *K*-edge XAFS fitting results for reference compounds (n.n. = nearest neighbor).

Sample	Data type	n.n. As–O/Fe–O shell			2nd n.n. As–Fe/Fe–As shell			
		<i>N</i>	<i>R</i> (Å)	σ^2 (Å ²)	<i>N</i>	<i>R</i> (Å)	σ^2 (Å ²)	ΔE_0^b (eV)
Crystalline scorodite	As	4.0 ^a	1.68	0.0016	4.0 ^a	3.36	0.0053	2.7
	Fe	6.0 ^a	1.99	0.0074	4.0 ^a	3.36	0.0056	–2.7
Poorly-crystalline scorodite (Fe/As = 1, pH = 4)	As	4.0 ^a	1.68	0.0018	3.2	3.33	0.0102	2.7
	Fe	6.0 ^a	1.98	0.0092	3.8	3.31	0.0104	–2.7
As/ α FeOOH (Fe/As = 4/1, pH = 6)	As	4.0 ^a	1.69	0.0017	1.7	3.26	0.0089	2.7
As/ α FeOOH (Fe/As = 10/1, pH = 6)	As	4.0 ^a	1.69	0.0018	2.2	3.26	0.0068	2.7
CPT-2 (Fe/As = 4/1, pH = 4)	As	4.0 ^a	1.68	0.0012	3.9	3.30	0.0108	2.7
CPT-4 (Fe/As = 4/1, pH = 8)	As	4.0 ^a	1.69	0.0015	1.6	3.27	0.0097	2.7

^a Fixed.^b ΔE_0 fixed for both shells to 2.7 eV for As data and to –2.7 eV for Fe data, respectively.

Debye–Waller coefficient at the same temperature and similar chemical environments of those for the poorly-crystalline scorodite and other precipitates including the neutralized raffinate solid to be discussed. The σ^2 's for the As–Fe shell of the adsorbed samples could be the lower boundary of that for this latter group of poorly-crystalline samples, considering the shorter As–Fe distance and relatively simpler arsenate coordination environment in the adsorption case than that in the poorly-crystalline cases.

3.3. Arsenic and iron local structure in poorly-crystalline scorodite

FEFF amplitudes and phases calculated based on scorodite were used for poorly-crystalline scorodite characterization. ΔE_0 and S_0^2 from the crystalline scorodite fits are transferred to the poorly-crystalline scorodite case, and the σ^2 's of arsenate-adsorbed on goethite are used as the lower boundaries for that in the poorly-crystalline scorodite. As previously described, the Fe/As molar ratio in the poorly-crystalline scorodite was 0.976 (Jia et al., 2003), which is virtually equal to that in crystalline scorodite. As a result, Fe *K*-edge analyses were also carried out, and the structural results were found consistent with the As *K*-edge counter parts.

For the poorly-crystalline scorodite the first As–O shell from As *K*-edge data, or the first Fe–O shell from Fe *K*-edge data closely resemble those from the crystalline scorodite (Table 3 and Fig. 6a and b). The As–Fe inter-atomic distance is found to be at 3.32 ± 0.02 Å, with a coordination number higher than 3. This As–Fe distance is significantly longer than that in a bidentate bi-nuclei adsorption mechanism (Waychunas et al., 1993; Moldovan et al., 2003), which should have been around 3.25 Å. It is also noted here that this is shorter than the 3.36 Å of As–Fe distance in crystalline scorodite (Table 3). This averaged As–Fe distance, and the much higher coordination number than that for a bidentate bi-nuclei case, indicate a local structural environment in the poorly-crystalline scorodite which is distinctly different from the typical arsenate-adsorbed ferrihydrites, but similar to that of the crystalline scorodite structure. These quantitative results echo the pre-

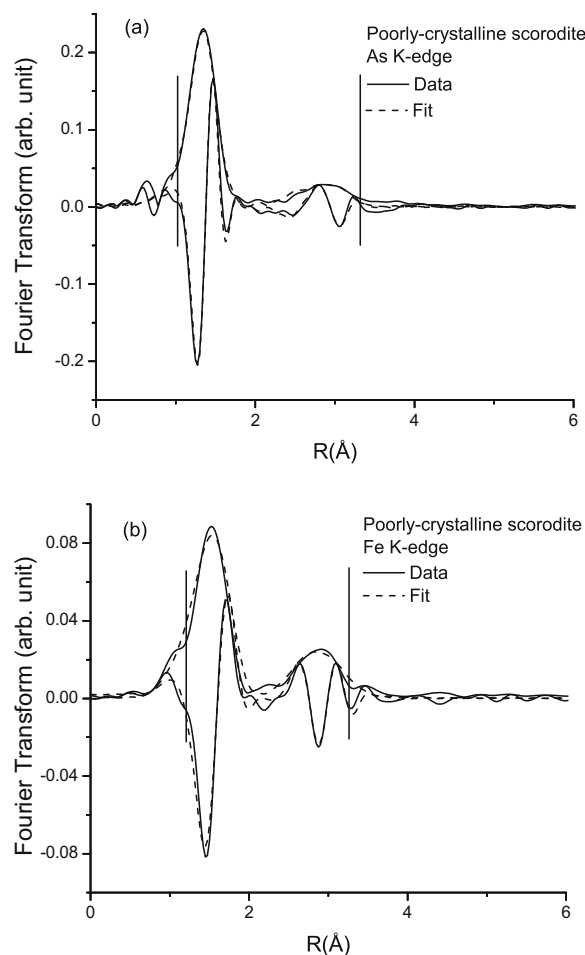


Fig. 6. *R*-space curve-fitting of poorly-crystalline scorodite: (a) arsenic *K*-edge and (b) iron *K*-edge. The Fourier transform of $k^3 \cdot \chi(k)$ are with *k*-space ranges of 2.7–17.5 and 2.4–13.7 Å^{–1} for the As and Fe data, respectively, and 20% Gaussian windows. The *R*-space fitting ranges are of 1.0–3.4 and 1.3–3.3 Å^{–1}, correspondingly, indicated by the two vertical lines. Solid and dashed lines are for the data and the fit, respectively. Both the magnitude (positive envelopes) and the imaginary (oscillating parts) of the Fourier transform are shown.

viously qualitative observation on the raw data in k -space, where the similarity between the poorly-crystalline scorodite and the crystalline scorodite is indicated by the shape of the first XAFS oscillation (Section 2).

3.4. Arsenic local structure in iron(III)–arsenate co-precipitates

The summarized fitting results for As K -edge XAFS of the two co-precipitated samples are shown in Table 3 and Fig. 7a and b. For the sample CPT-4 at pH 8 the details of the fit are shown in Table 2b. The two samples clearly have very different local structures in terms of the As–Fe distance and the Fe to As coordination. The structural difference between these two samples is in fact directly observable from the Fourier transform magnitudes (Fig. 1b, trace 3 to 4) in addition to the difference in k -space dis-

cussed in Section 2, where the sample at pH 4 has a well-defined As–Fe peak similar to that of the poorly-crystalline scorodite (Fig. 1b, trace 2), while the sample at pH 8 has a broadened As–Fe shell distribution with much weaker intensity. Based on the spectral features from the As–Fe shell in both R - and k -space, the sample at pH 4 was fitted with starting parameters of the scorodite model while the sample at pH 8 was fitted with those of the bidentate bi-nuclei model. It should be noted that when the starting parameters were switched between these fits the end results remained the same, i.e., the subtle differences between these models (i.e., whether the arsenate tetrahedron is distorted or not) are not significant. The curve-fitting of the pH 4 co-precipitation sample resulted in the As–Fe inter-atomic distance and coordination number close to those of poorly-crystalline scorodite, namely 3.30 ± 0.03 Å and 3.9, respectively (Table 3). The identical

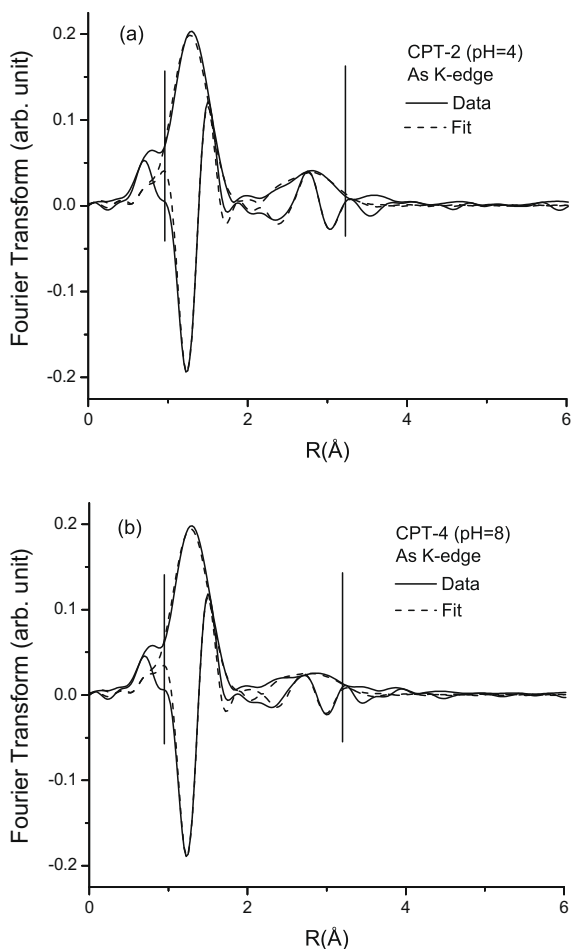


Fig. 7. R -space curve-fitting of arsenic K -edge data for iron arsenic co-precipitates: (a) CPT-2 with Fe/As = 4 and pH of 4; and (b) CPT-4 with Fe/As = 4 and pH of 8. The Fourier transforms of $k^3 \cdot \chi(k)$ (20% Gaussian window) are with the same k -space range 2.7–12.6 Å^{−1} for both of the CPT samples; and the two R -space fits are with the same range of 1.0–3.3 Å, indicated by the two vertical lines. Solid and dashed lines are for the data and the fit, respectively. Both the magnitude (positive envelopes) and the imaginary (oscillating parts) of the Fourier transform are shown.

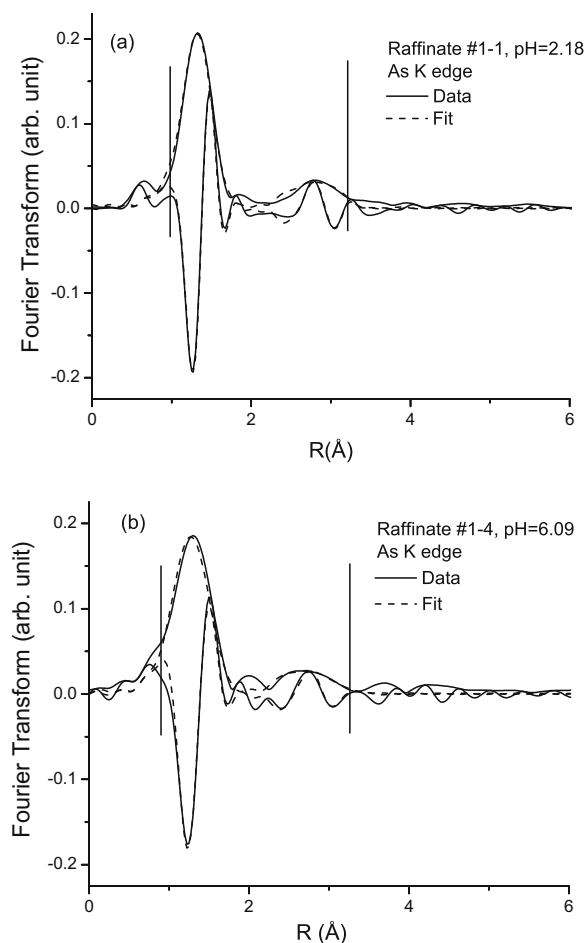


Fig. 8. R -space curve-fitting of arsenic K -edge data for neutralized raffinate set #1 samples: (a) #1-1 and (b) #1-4. The Fourier transforms of $k^3 \cdot \chi(k)$ are with k -space ranges of 2.7–15.5 Å^{−1} for #1-1 and 2.7–12.3 Å^{−1} for #1-4, respectively, and 20% Gaussian windows. Both of the R -space fits are with the data range of 0.9–3.2 Å, indicated by the two vertical lines. Solid and dashed lines are for the data and the fit, respectively. Both the magnitude (positive envelopes) and the imaginary (oscillating parts) of the Fourier transform are shown.

Table 4

Arsenic *K*-edge XAFS fitting results for the neutralized raffinate solid from McClean Lake operation (n.n. = nearest neighbor).

Raffinate solid samples	pH	n.n. As–O shell			2nd n.n. As–Fe shell			
		<i>N</i>	<i>R</i> (Å)	σ^2 (Å ²)	<i>N</i>	<i>R</i> (Å)	σ^2 (Å ²)	ΔE_0^b (eV)
#1–1	2.18	4.0 ^a	1.69	0.0020	3.3	3.31	0.0107	2.7
#1–2	3.15	4.0 ^a	1.69	0.0016	3.2	3.31	0.0107	2.7
#1–3	4.04	4.0 ^a	1.68	0.0017	3.0	3.31	0.0110 ^c	2.7
#1–4	6.09	4.0 ^a	1.68	0.0017	2.7	3.30	0.0110 ^c	2.7
#2–1	2.01	4.0 ^a	1.68	0.0021	3.7	3.31	0.0106	2.7
#2–6	7.08	4.0 ^a	1.68	0.0021	3.1	3.30	0.0110	2.7

^a Fixed.^b ΔE_0 fixed to 2.7 eV for both shells.^c Upper limits of parameter constrains.

parameter correlations for the secondary paths (MS and distant As–O) were applied, and virtually the same results have been obtained for these paths as those shown in Table 2a for the other scorodite type of samples. Conversely, the results for the pH 8 co-precipitation sample are much closer to that of the arsenate-adsorbed goethite, with an As–Fe distance at 3.27 ± 0.03 Å and a coordination number 1.6.

3.5. Arsenic local structure in neutralized raffinate solid samples

The fitting results of all neutralized raffinate solids are summarized in Table 4 and selectively shown in Figs. 8 and 9 for the two sets of tests. The details of the fits are illustrated in Table 2a where the results for the secondary paths are virtually identical to those in the crystalline scorodite (Section 3.1). These solids typically have a Fe/As molar ratio as 1:1, 2:1, 2.3:1 and 2.8:1 for the pH at 2, 3, 4 and 6, respectively (Mahoney et al., 2007). Several observations can be made from the results (Table 4). First, the As–Fe distance at 3.31 ± 0.02 Å closely resembles that of the poorly-crystalline scorodite, as are the As–Fe coordination numbers at all pH values except sample #1–4. Therefore the raffinates prepared up to pH 7 have basically the same local structure as that of the poorly-crystalline scorodite. These results confirm the qualitative observation about the shape of the first XAFS oscillation in the *k*-space (Section 2). Second, there is a discernable trend in the As–Fe coordination number as a function of the pH at which these samples were prepared. With increasing pH values, the As–Fe coordination number decreases, as is shown in the set #1 neutralized raffinate solid samples (Table 4 and Fig. 5). As it has been discussed previously (Section 3.1) the second nearest neighbor peak just below 3 Å in the Fourier transform starts to split into two components (Fig. 5), with the MS component remains relatively constant while the As–Fe shell decreases in intensity with increasing pH values. The MS feature appears stable within the entire pH range, whereas the longer distance feature due to the actual As–Fe coordination shell scattering is losing its intensity with increasing pH. These intensity losses are likely attributable to a combination of increasing disorder or lower coordination, or both. Similar

results are observed in set #2 samples (Fig. 9c and Table 4).

4. DISCUSSION

The results in Tables 3 and 4 indicate that basically all iron(III)–arsenate precipitation products prepared at pH 7 or lower have a local As structure similar to that of poorly-crystalline scorodite. Given, therefore, the significance of this phase it is worthwhile to refine its molecular structural description by further discussing the XAFS results. The overall larger σ^2 's for the As–Fe shell in the poorly-crystalline scorodite compared to that of the crystalline scorodite (Table 3) manifest the higher structural disorder of the sample, consistent with the XRD results (Jia et al., 2003). When the results of As and Fe *K*-edges of poorly-crystalline scorodite are compared with those in the crystalline scorodite, it is evident from the first shell As–O and Fe–O results that the internal structures of the arsenate tetrahedron and ferric iron octahedron are not significantly different from their counterparts in the crystalline scorodite. Therefore structural difference appears to be in the arrangement of these tetrahedra and octahedra in the two cases. The question now is what kind of structure for the poorly-crystalline scorodite would be consistent with the averaged As–Fe distance of 3.32 Å and an As–Fe coordination of 3.5. The large deviation of the As–Fe distance (3.32 Å) in the poorly-crystalline scorodite from that in a bidentate bi-nuclei adsorption model (ca 3.25 Å) strongly disfavors the adsorption model. This is in clear contrast with previously studied co-precipitation systems prepared under higher pH conditions (pH = 8.0; Waychunas et al., 1993; pH = 9 or higher; Moldovan et al., 2003; and pH = 8.5 or higher; Paktunc et al., 2004), and also in contrast with the high pH co-precipitate sample CPT-4 (Table 3). Clearly these results indicate that formation of the scorodite-like precipitates from co-precipitation requires a favorable pH condition. The longer As–Fe distance combined with the high As–Fe coordination in the poorly-crystalline scorodite (3.5 in average), suggests a structure with a higher level of intermixing between the As(V) tetrahedrons and Fe(III) octahedrons—a situation similar to the connectivity of these tetrahedra and octahedra in crystalline scorodite. If it is assumed here that the poorly-crystalline

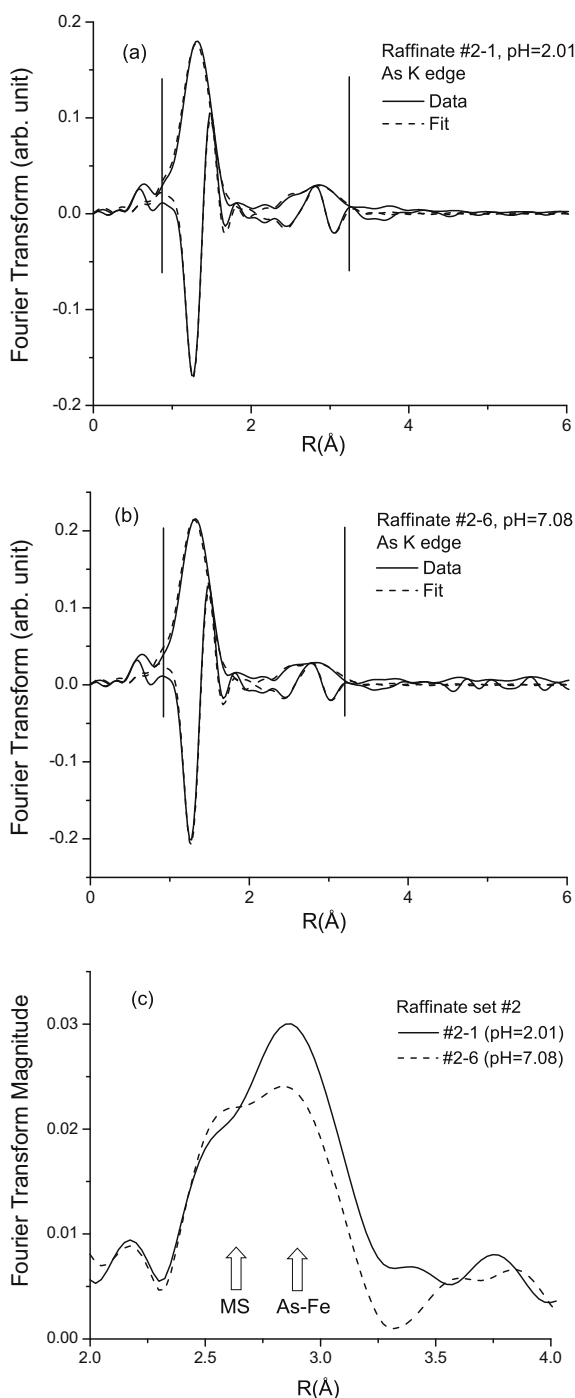


Fig. 9. Neutralized raffinate set #2 samples: R -space curve fits, (a) #2-1 and (b) #2-6. The identical Fourier transform k -space range $2.7\text{--}14.8\text{ \AA}^{-1}$, 20% Gaussian windows, and R -space fitting range $0.9\text{--}3.2\text{ \AA}$ (indicated by the two vertical lines) are applied to both of the two samples shown in (a) and (b). Solid and dashed lines are for the data and the fit, respectively. Both the magnitude (positive envelopes) and the imaginary (oscillating parts) of the Fourier transform are shown. Panel (c) illustrates the As–Fe shell region of Fourier transform magnitude for the neutralized raffinate set #2, showing a similar trend as that of set #1.

scorodite has a structure based on an adsorption mechanism, then the 0.976 As/Fe molar ratio of the poorly-crystalline scorodite would require the existence of a vast majority of single Fe(III) octahedral units to accommodate the arsenate. This would imply that the Fe(III) octahedra are not directly coordinated to each other, but separated by As tetrahedra. It can be concluded, therefore, that in this case the observed structure may be described as the onset of scorodite domain formation. In other words in terms of the local As structure, the poorly-crystalline scorodite is more similar to that of the crystalline scorodite than to arsenate-adsorbed on ferrihydrite. The structural parameter differences, mainly the shorter As–Fe distance in the poorly-crystalline scorodite and the lower Fe coordination, may be related to the very small size of the nucleated scorodite crystallites, resulting in a high composition ratio of surface to bulk species with a shorter As–Fe distance and lower average coordination number. To maintain an Fe/As ratio of 1:1, the nucleated scorodite domains would need to have a random surface termination with either arsenate tetrahedra or Fe(III) octahedra.

Another apparent explanation for the structural difference between the poorly-crystalline scorodite and the crystalline scorodite (Table 3) is that the poorly-crystalline scorodite may simply consist of a mixture of crystalline scorodite and some arsenate-adsorption species, as the latter has a significantly shorter As–Fe distance, which would reduce the average distance. This mixing model is plausible for the other co-precipitated systems with Fe/As ratio significantly larger than one. But for the poorly-crystalline scorodite sample presented here, the existence of the adsorption species is not likely to be significant. Any ferrihydrite formation in the sample would lead to adjacent Fe(III) octahedra, which will introduce Fe–Fe shell components in the Fe K -edge XAFS of the sample. Curve-fitting tests have been carried out to investigate this possibility in two aspects. First, analysis was done by assuming the XAFS data of poorly-crystalline scorodite to correspond to a mixture of crystalline scorodite and of arsenate-adsorbed on ferrihydrite (or goethite in the present work). The results indicate that in order to have the As–Fe distances of the poorly-crystalline scorodite shown in Table 3, a mixture of 30% crystalline scorodite and 70% adsorption species is required. This amount of adsorption species would require much more Fe content in the sample and would contradict the known Fe/As molar ratio in this sample. However, there have been reports on extremely high arsenate loading capacity co-precipitates with As/Fe = 0.7, which have been explained on the basis of the adsorption model involving “depolymerised” ferrihydrite units (Fuller et al., 1993; Waychunas et al., 1993, 1996). To evaluate the possibility of this model for the poorly-crystalline scorodite, test fits were carried out for the second shell in the Fe K -edge data, to see if significant Fe–Fe scattering could be identified by comparing with the spectral intensity of the Fe–As shell. The results did not indicate any significant existence of the Fe bi-octahedron chain in the sample. Therefore, it is not likely that the bi-octahedron moieties of Fe(III) would be playing a dominant role in this sample. In other words, if there is a significant amount of

adsorption species, one would expect a significantly higher degree of ordering along the Fe bi-octahedron.

As shown in *Tables 3 and 4*, all the iron(III)–arsenate precipitation samples (synthetic co-precipitates in *Table 3* and industrial neutralized raffinate solids in *Table 4*), with the exception of the synthetic co-precipitate of pH = 8, have an arsenic local structure resembling that of the poorly-crystalline scorodite, albeit with some subtle differences. This observation is rather general for the pH range 2–7 independent of the starting stock solution (synthetic or industrial process raffinate) and the neutralization base used (lime or NaOH). Furthermore as described earlier it appears that the poorly-crystalline scorodite constituency in these co-precipitated samples possesses a more ordered local arsenic structure when prepared at a lower pH value. As the termination pH increases the As–Fe shell signal intensity clearly decreases (*Tables 3 and 4*). Eventually at high enough terminal pH values (pH 8 or higher), the arsenate-adsorbed ferrihydrite species start to be dominating (e.g., CPT-4 in *Table 3*). This is the first concrete mineralogical evidence (beyond the earlier XRD evidence of *Jia et al., 2003*) of the occurrence of a scorodite-like (amorphous) phase in iron(III)–arsenate co-precipitates produced by neutralization of synthetic or industrial acidic sulfate (with Fe(III)/As(V) molar ratio >1) solutions. This finding is in agreement with *Carlson et al. (2002)* who reported the occurrence of a poorly-crystalline iron(III) hydroxy arsenate (“FeOHAs”) when the Fe/As mole ratio is less than 6.6.

It is conceivable that to some extent these co-precipitation samples (from either synthetic or industrial solution) with a higher Fe/As molar ratio (>1) may consist of multiple As species phases, with poorly-crystalline scorodite as one end member and an arsenate-adsorbed ferric oxyhydroxide phase as the other end member. The poorly-crystalline scorodite features appear to persist until a high pH limit is reached, beyond which the structure favors the arsenate-adsorbed ferric oxyhydroxide phase. From the samples investigated in this study (samples #1–4, #2–6—*Table 4* and sample CPT-4—*Table 3*), this limiting pH value seems to lie between 7 and 8, which coincides with the upper region of scorodite stability in the Fe–As–H₂O Eh–pH diagram published by *Langmuir et al. (1999)*. It should be pointed out that all the precipitation samples in this study were prepared in an oxidized condition therefore the influence of the redox potential to the precipitation species was not investigated.

5. CONCLUDING REMARKS

A systematic XAFS structural study was performed on the iron(III)–arsenate precipitates obtained by the neutralization of an uranium mill process effluent (raffinate). An integral part of this study was the synthesis and structural characterization of a set of reference compounds in order to yield the necessary controlling structural parameters for the XAFS analysis of the neutralized raffinate tailings solids at different terminal pH values.

Based on the XAFS results at As *K*-edge and Fe *K*-edge for the poorly-crystalline scorodite, it is concluded that this

ferric arsenate precipitate possesses an arsenic local structure similar to that in the crystalline scorodite, i.e., there is an extended scorodite-type arrangement of Fe(III) octahedra connected to As(V) tetrahedra. In particular, the second coordination shell from arsenic (As–Fe) is found at 3.33 ± 0.02 Å with a ferric iron coordination above 3 in the poorly-crystalline scorodite, which is close to that of 3.36 ± 0.02 Å with the iron coordination of 4 in crystalline scorodite but significantly different from that of the arsenic bidentate bi-nuclei adsorption species on a ferric oxyhydroxide (ca 3.26 ± 0.03 Å and iron coordination of 2). The structural difference between the poorly-crystalline scorodite and crystalline scorodite is mainly attributed to the non-crystalline nature of the former.

The primary XAFS signature of the poorly-crystalline scorodite, i.e., the significantly longer As–Fe coordination shell distance and an averaged coordination number above 3, has been found as a common structural characteristic for the iron(III)–arsenate precipitates from the neutralized raffinate of the McClean Lake Operation’s uranium mill (Fe/As ratio at 4 or higher) at all neutralization pH levels up to at least 7. It appears that the poorly-crystalline scorodite constituency in these precipitates possesses a more ordered local arsenic structure when neutralization is terminated at a lower pH value. The poorly-crystalline scorodite structure appears to characterize the bulk of arsenic speciation in these precipitates up to a limiting pH somewhere between 7 and 8. At pH 8 or higher the arsenate-adsorbed ferrihydrite structure previously reported by others seems to dominate.

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IDENTIFICATION OF POORLY CRYSTALLINE SCORODITE IN URANIUM MILL TAILINGS

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ABSTRACT

The McClean Lake mill, located in northern Saskatchewan, processes a variety of uranium ore bodies to produce yellowcake. A by-product of this process is an acidic waste solution enriched in arsenic, referred to as raffinate. The raffinate waste stream is treated in the tailings preparation circuit, where arsenic is precipitated as a poorly crystalline scorodite phase. Raffinate neutralization studies have successfully identified poorly crystalline scorodite using XRD, SEM, EM, XANES and EXAFS methods, but to date, scorodite has not been successfully identified within the whole tailing solids. During the summer of 2008, a drilling program sampled the *in situ* tailings within the McClean Lake tailings management facility. Samples from this drilling campaign were sent to the Canadian Light Source Inc. for EXAFS analysis. The sample spectra positively identify a poorly crystalline scorodite phase within the McClean tailings management facility.

INTRODUCTION

The McClean Lake uranium mill, owned by AREVA Resources Canada Ltd, was envisaged to process a variety of ore bodies, including the McClean, Midwest, Cigar Lake and SUE ore deposits. A wide range of arsenic concentrations, from approximately 250 ug/g to 100,000 ug/g, are encompassed by these ore bodies. During the processing of these ores, a substantial amount of arsenic is liberated. During the design phase of the McClean Lake tailings preparation circuit, the mitigation of aqueous arsenic in mill solutions was a driving factor in the process conception. The tailings preparation process required an effective arsenic removal process that produced chemically stable tailings of sufficiently low solubility to be protective of the environment for the long term.

The necessity of such a process was due to the permanent disposal of tailings within the tailings management facility (TMF). The TMF is a previously mined out open pit that has been engineered to control arsenic release to surrounding ground and surface waters. Under current operating conditions, hydraulic containment is achieved by active processes, including de-watering and reclaim wells. Upon completion of milling activities and decommissioning of the TMF, passive controls for maintaining containment have been engineered. An inherent component of that design is that deposited tailings pore waters will have arsenic concentrations of less than 5 mg/L. With this as a primary consideration, a process was designed to ensure arsenic was removed as a chemical precipitate, and the subsequent precipitate would be thermodynamically stable for the long term under the present conditions in the McClean Lake TMF.

At the time the McClean Lake mill was conceived, conventional tailings treatment involved the liming of tailings solutions to increase the solution pH above 10. This process removes metal cations, however arsenite (AsO_3^{-3}) and arsenate (AsO_4^{-3}) tend to de-sorb from specific solids surfaces at elevated pH (Stumm & Morgan, 1996).

Laboratory tests and geochemical modelling performed by Langmuir et al. (1999) examined processes to reduce arsenic and nickel concentrations in TMF pore waters, so as to minimize release from deposited tailings. These large scale laboratory tests were completed to optimize the primary tailings preparation control parameters of ferric sulphate addition rate and terminal pH.

Tailings solids prepared during the laboratory scale tests were then used in aging tests. These tests were meant to simulate the long term conditions in the TMF. Of the nominal pH values used, pH 7 had unacceptably high nickel concentrations in the pore water, whereas pH 9 resulted in high arsenic concentrations. Further research then focused on nominal pH values in the range of 7.5 to 8 (Langmuir et al., 1999).

After completion of laboratory studies, samples were submitted for X-ray diffraction (XRD) analysis, scanning electron microscopy (SEM), electron microprobe (EM) and petrographic work. The XRD and optical results indicated that there were two mineral modes: crystallized major and minor phases comprised of both primary and secondary minerals, and poorly crystalline or amorphous mineral analogues precipitated as secondary minerals (Langmuir et al., 1999).

Further analysis found that arsenate was predominantly associated with iron, in an equal molar relationship (Langmuir et al., 1999). The EM analysis and XRD patterns suggested three possible ferric arsenate phases; scorodite, kankite and an amorphous phase (Krause & Ettel, 1988), possibly a composition between kankite and scorodite. Conclusions drawn at the time, based on XRD analysis, suggested the presence of a relatively amorphous scorodite-like phase (Langmuir et al., 1999).

Tailings derived from the nominal pH of 8 were used to predict arsenic concentrations in tailings pore water after 10,000 years. Using a TMF temperature of 4°C, it was concluded that arsenic concentrations in tailings pore water were not expected to exceed 2 mg/L over a 10,000 year span (Langmuir et al., 1999).

Following the start up of the McClean Lake mill, extensive studies on actual mill raffinate solutions were initiated. It was confirmed that dissolved arsenic could be minimized in treated tailings pore waters if prior to treatment, raffinate solutions had a ferric iron to arsenic molar ratio greater than three (Mahoney et al., 2007). Following this preparation procedure, the final concentration of arsenic in tailings pore water was generally less than 1 mg/L.

Mineralogical examination of prepared tailings samples continued to further elucidate the mineral structure of the iron-arsenic precipitate. This characterization involved XRD analysis of powdered samples, SEM with energy dispersive analysis and qualitative EM and XM scans at Argonne National Laboratory's Advanced Photon Source. Quantitative mineralogical analysis of all samples were performed using the proprietary computer model QMAS (Slaughter, 1985, 1990), which combines the XRD, EM and XM results and sample chemistry using linear programming. This analysis determined that the arsenic in the raffinate precipitated with ferric iron as a poorly crystalline scorodite phase (Mahoney et al., 2007).

Chen et al (2009) conducted extensive Extended X-ray Absorption Fine Structure (EXAFS) studies of the solids produced by Mahoney et al. (2007). The arsenic and iron K-edge spectra were used to characterize the chemical structure of the neutralized tailings solid samples. The arsenic was determined to be bound to iron in a molar ratio of 1: 1 (Chen et al., 2009). The comprehensive analysis of the EXAFS spectra was compared to synthetic model compounds, including crystalline scorodite, $\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$ (Singhania et al, 2005), iron (III)-arsenate co-precipitates (Jia et al., 2003), and poorly crystalline scorodite (Jia et al., 2003). It was concluded that the observed spectra, obtained from the laboratory neutralized raffinate solutions, identified a poorly crystalline scorodite mineral phase (Chen et al., 2009).

In 2008, an *in situ* sampling program for the McClean Lake TMF was undertaken. A drilling rig was used to sample representative regions of the tailings facility. Samples obtained from this program were processed to collect pore waters and solid tailings samples. Solid samples were sent to the Canadian Light Source Inc. (CLSI) for analysis by synchrotron based X-ray absorption techniques.

Tailings Preparation Process

The McClean Lake milling process employs sulphuric acid, as a lixiviant, and hydrogen peroxide, as an oxidant, to liberate uranium from ores. In addition to uranium, this process liberates approximately 80% of the arsenic in the ore. Upon completion of the leaching process, uranium is separated from the acidic leach solution through contacting an organic matrix in the solvent extraction process. The residual arsenic remains in the acidic waste solution, referred to as raffinate. The raffinate reports to the tailings preparation circuit for precipitation of elements of concern and pH adjustment. All process waste streams, both solid and liquid, are treated concurrently by the McClean Lake mill tailings preparation process.

The tailings preparation circuit employs a pre-treatment stage and a two stage neutralization process. The pre-treatment involves the addition of ferric iron to the raffinate waste stream to achieve a molar ratio greater than or equal to 3 parts ferric iron to 1 part arsenic ($\text{Fe (III)} / \text{As molar ratio} \geq 3$). A barium chloride solution is also added to remove radium from the tailings solution. During vigorous mixing, washed residual solids from the leach circuit are added to the raffinate and ferric iron solution, now referred to as tailings feed solution. The tailings feed solution is then directed to the primary reaction tank, where slaked lime addition increases the solution pH from 1 to 4. The Stage 1 process has a residency time of 90 minutes. Upon completion of Stage 1, the tailings slurry is transferred from the primary to the secondary reaction vessel. During Stage 2, slaked lime addition increases the pH from 4 to a terminal pH of 7.5, within a residency time of 90 minutes. The tailings slurry is then pumped to a high rate thickener, where the slurry is settled and subsequently deposited in the TMF. This preparation process reduces aqueous arsenic concentrations to less than 2 mg/L (Rowson and Tremblay, 2003). Figure 1 provides a representation of the tailings preparation process.

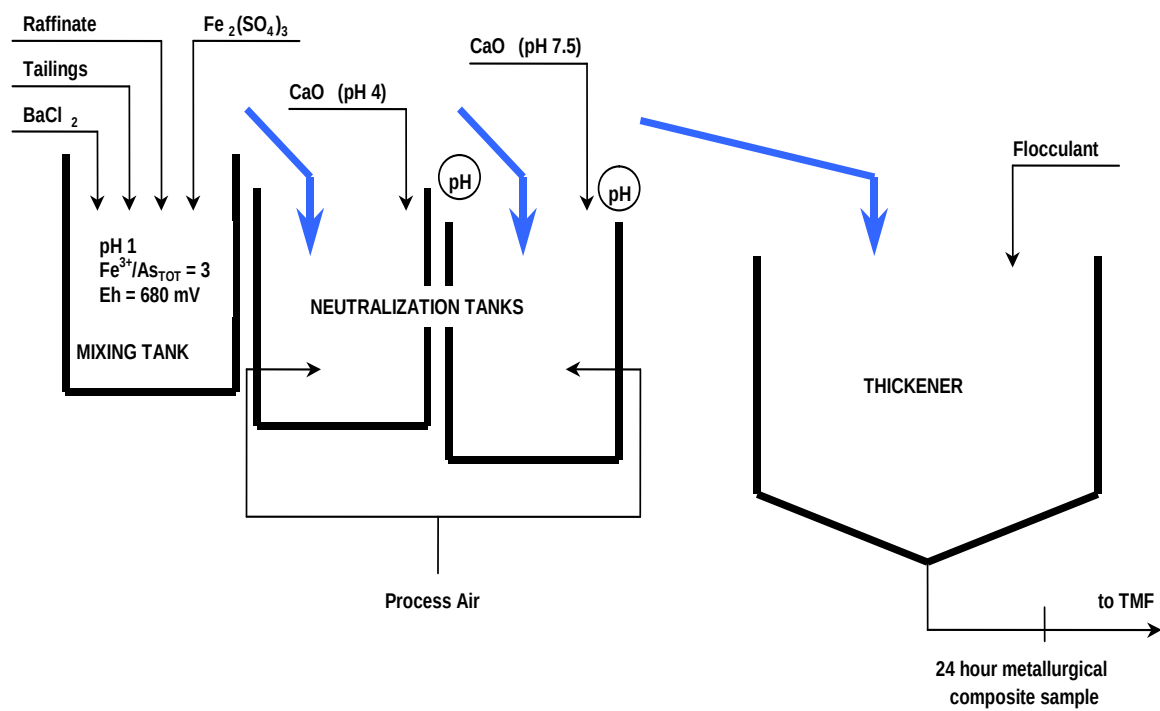


Figure 1 - McClean Lake tailings preparation process

EXPERIMENTAL

TMF Sample Collection

The 2008 McClean Lake TMF *in situ* sampling program collected both geotechnical and geochemical samples. The geochemical samples were collected from 4 locations in the TMF, consistent with previous annual sampling programs.

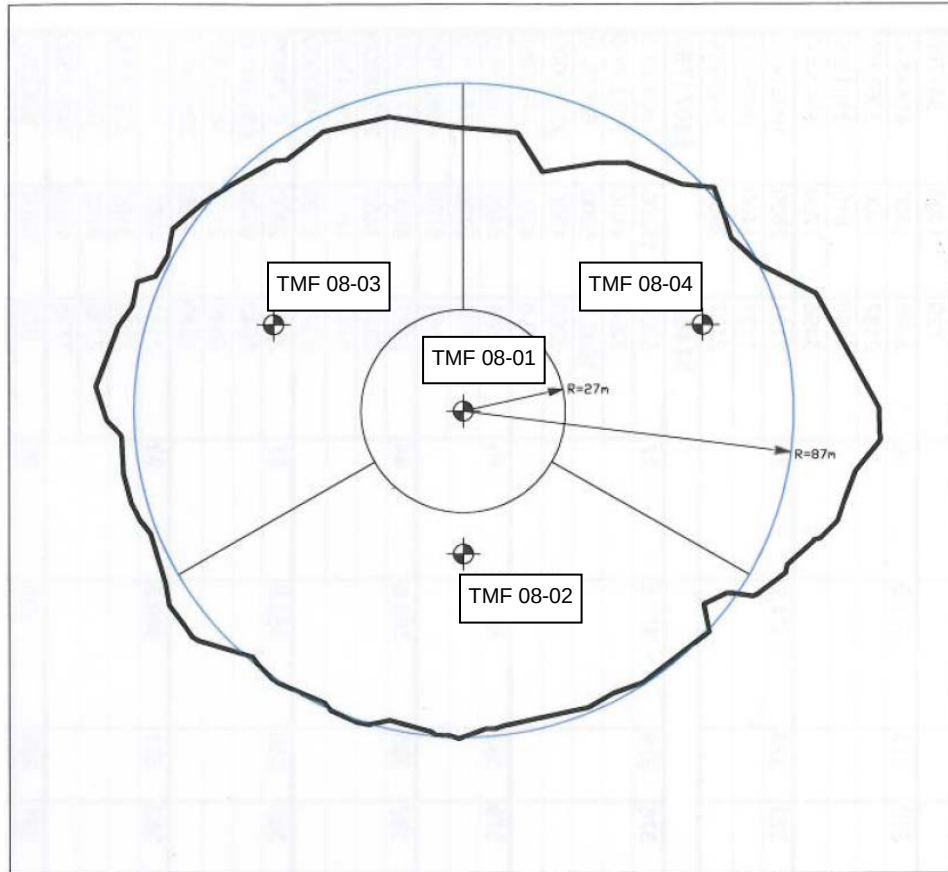


Figure 2 - McClean Lake TMF *in situ* sampling program – Geochemical borehole locations

Samples were collected by positioning a drilling rig, mounted on a floating barge, above the co-ordinates from previous intrusive sampling programs. Every effort was made during the sampling program to place the bore holes in the same co-ordinate locations and to sample at the same elevations as in past drill sampling campaigns so that aging of the tailings sediments and pore water can be monitored.

The drilling program obtained samples in 3 meter intervals from the base of the TMF (364 masl), corresponding to tailings places in July 1999, to tailings recently placed in June 2008 (420 masl) at the surface of the tailings mass. Refer to Figure 3 for tailings placement and elevation during the operations to date of the McClean Lake mill.

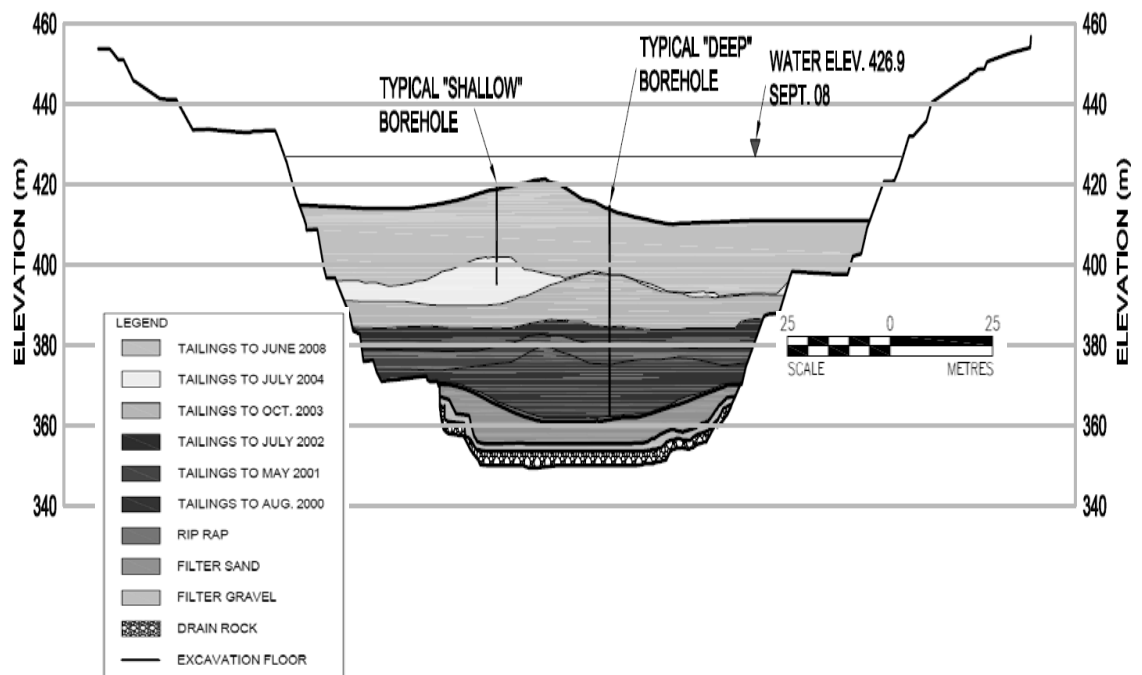


Figure 3 - Tailings placement within the McClean Lake TMF – June 2008

The collected samples were sealed and stored sub-aqueously to minimize oxidation. An extraction device was used to collect pore waters from the core samples. Solid samples were then extruded and vacuumed sealed to preserve the sediment samples from oxidation. Figure 4 provides a schematic diagram of the tailings pore water extraction device. Figure 5 is a picture of an extruded core sample.

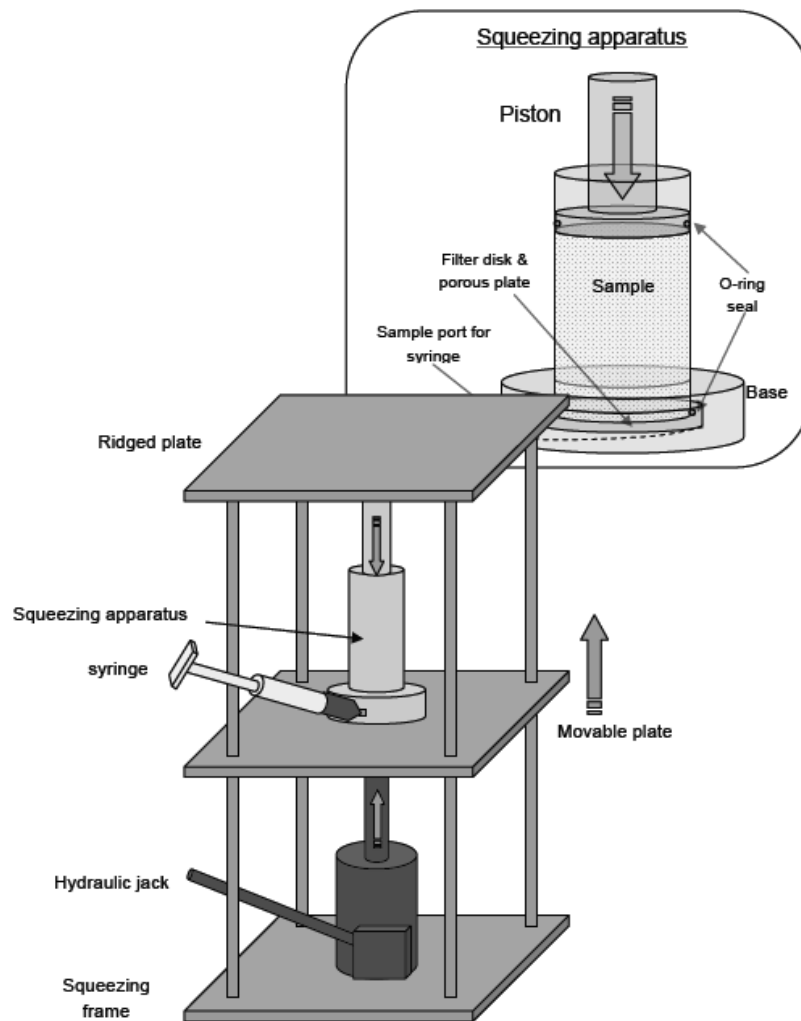


Figure 4 - McClean Lake TMF *in situ* sampling program - Pore water collection apparatus

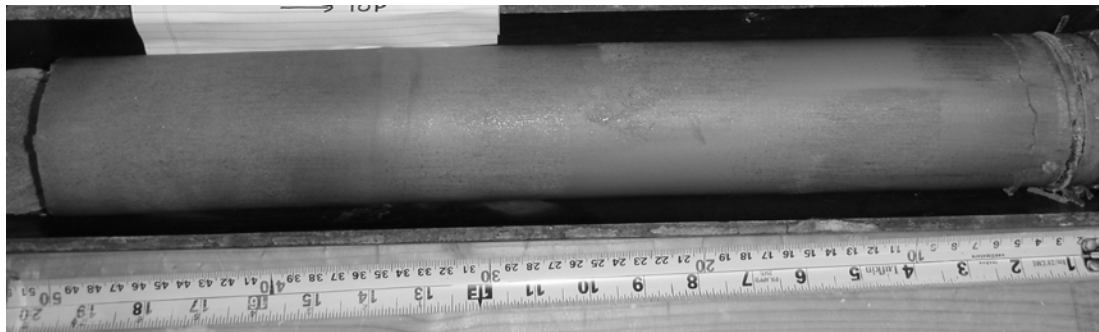


Figure 5 - McClean Lake TMF *in situ* sampling program – Extruded core sample

EXAFS Measurements at CLSI

Extruded tailings solid samples were sent to the CLSI for an initial screening by X-ray Absorption Near Edge Structure (XANES) analysis. Based on the XANES results, samples containing 100% As(V) species were selected for EXAFS analysis. The results from the tailings samples detailed apparent scorodite features in all the initial EXAFS spectra. These preliminary results allowed the selection of two samples for extended EXAFS exposure time and detailed fitting.

The detailed EXAFS measurements were collected on beamline 6ID2, Hard X-ray Micro Analysis (HXMA) at the CLSI. The HXMA beamline uses a superconducting wiggler operating at 1.9 T as a source magnet and a double crystal monochromator for wavelength selection, equipped with Si(111) crystals for measurements. Entrance slits defined the beam size at 1.0 mm vertical height for all samples. The incident beam was detuned 50% to limit the harmonic content at the As K-edge (11867 eV). Sample spectra were collected in fluorescence mode and reference compound spectra were collected using transmission geometry.

All k^3 -weighted samples were Fourier transformed over the k -space range 2-12.7 $\text{\AA}^{-1}$ using a Hanning window function. Fits in R -space extended from 1 – 3.5 $\text{\AA}$ (uncorrected for phase). EXAFS parameters ΔE_0 and S_0^2 were obtained from a fit to scorodite and used as global parameters. Debye-Waller factors, σ^2 , for multiple scattering paths within the arsenate tetrahedron were constrained to keep the number of variable EXAFS parameters to half the total number of independent points (N_{idp} , Lytle et al., 1989). EXAFS analysis was performed using the program Artemis (Ravel and Newville, 2004).

DISCUSSION

Samples TMF 08-01 SA05 and TMF 08-01 SA07 were selected for extended exposure and detailed fitting at the CLSI. Sample TMF 08-01 SA05 was collected from the central geochemical borehole in the TMF, at a depth of 408 meters above sea level (masl). Tailings were deposited at the SA05 location during the late fall of 2004. Sample TMF 08-01 SA07 was also collected from the central geochemical borehole in the TMF, at a depth of 402 masl. Tailings deposited at the SA07 location occurred during the summer of 2004. TMF 08-01 SA05 and SA07 contained arsenic in concentrations of 583 $\mu\text{g/g}$, and 294 $\mu\text{g/g}$ respectively.

As K-edge spectra were collected for TMF 08-01 SA05 and TMF 08-01 SA07. Samples were processed with neutralized raffinate data collected previously (Chen et al., 2009) in order to establish the peak position of arsenic-iron single scattering in the pseudo radial distribution plot of arsenic in samples collected from the TMF.

Of the two samples sent to the CLSI, initial analytical efforts concentrated on the samples of greater arsenic content. As such, this discussion focuses on the results from sample TMF 08-01 SA05. The Fourier transform of the k -space data are presented in Figure 6. For comparison, the transformed data from two selected samples, labelled as pH 7.08 and 6.09, from the laboratory prepared tailings experiment (Mahoney et al., 2007) are included. These laboratory samples were generated following the McClean Lake mill tailings preparation process, but with different terminal pH values. They were the subject of extensive EXAFS analysis and have been previously reported (Chen et al., 2009). The similarities in R -space for all the sets of data are evident. The first major peak at approximately 1.3 $\text{\AA}$ is due to scattering from the nearest As-O shell within the arsenic-oxygen tetrahedron. A second peak of interest, between 2.5 to 3.0 $\text{\AA}$, consists of several components but a significant contribution is the result of scattering from the As-Fe shell in a scorodite structure.

Figure 7 provides a comparison of the Fourier transform magnitude in the region of the As-Fe shell for the laboratory produced tailings and actual tailings from the McClean Lake TMF. Two principal components are present under the main feature; the multiple scattering (MS) from the oxygen atoms in the arsenic-oxygen tetrahedron, and the As-Fe scattering from the scorodite orientation. These are marked with heavy arrows to indicate their approximate locations. From Figure 7, it is readily apparent that a

significant contribution to the main EXAFS feature is due to an orientation of iron around arsenic, as described by the scorodite structure.

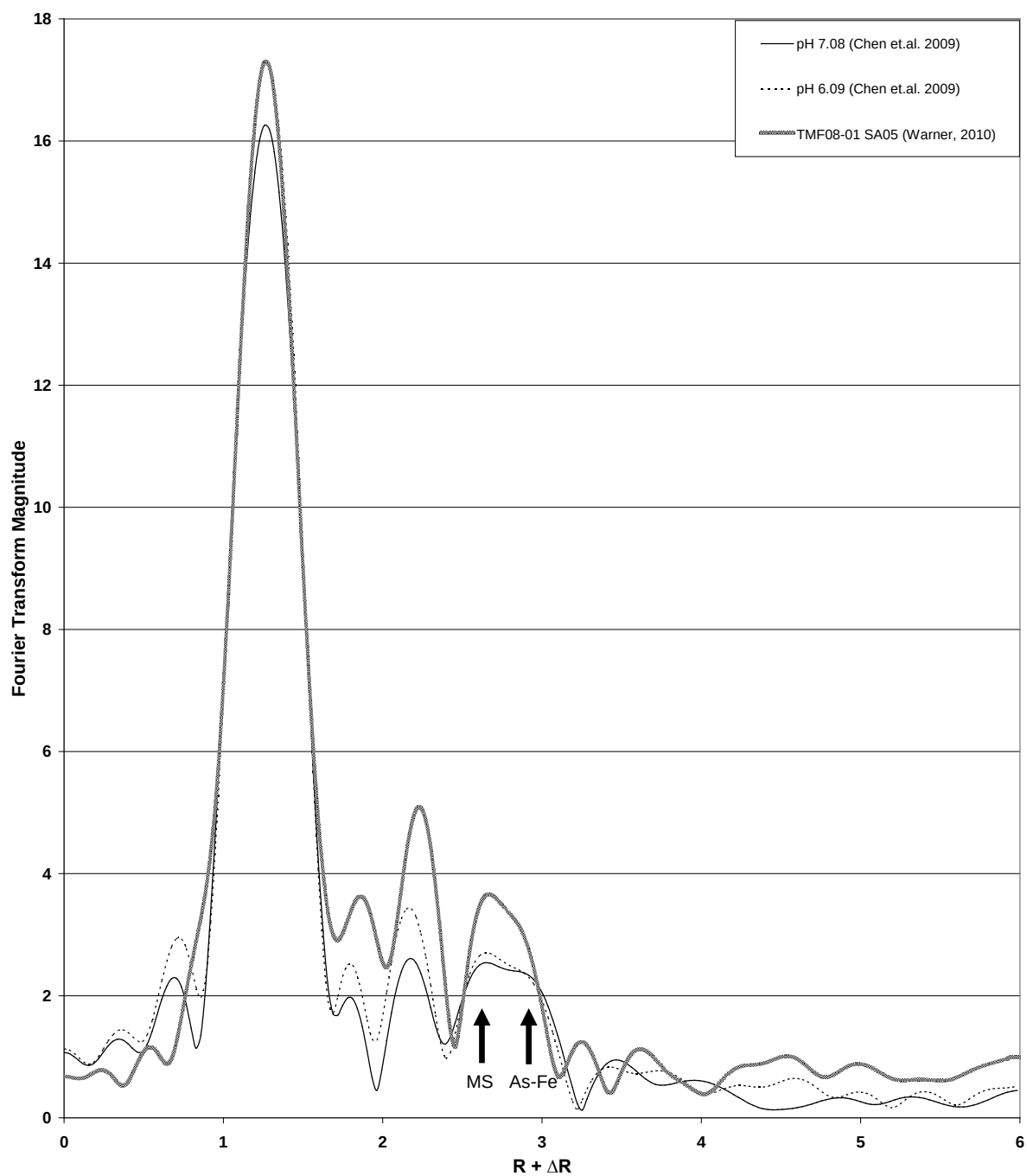


Figure 6 - Detailed EXAFS expanded plot of laboratory prepared tailings solids and TMF *in situ* tailings solid sample TMF 08-01 SA05

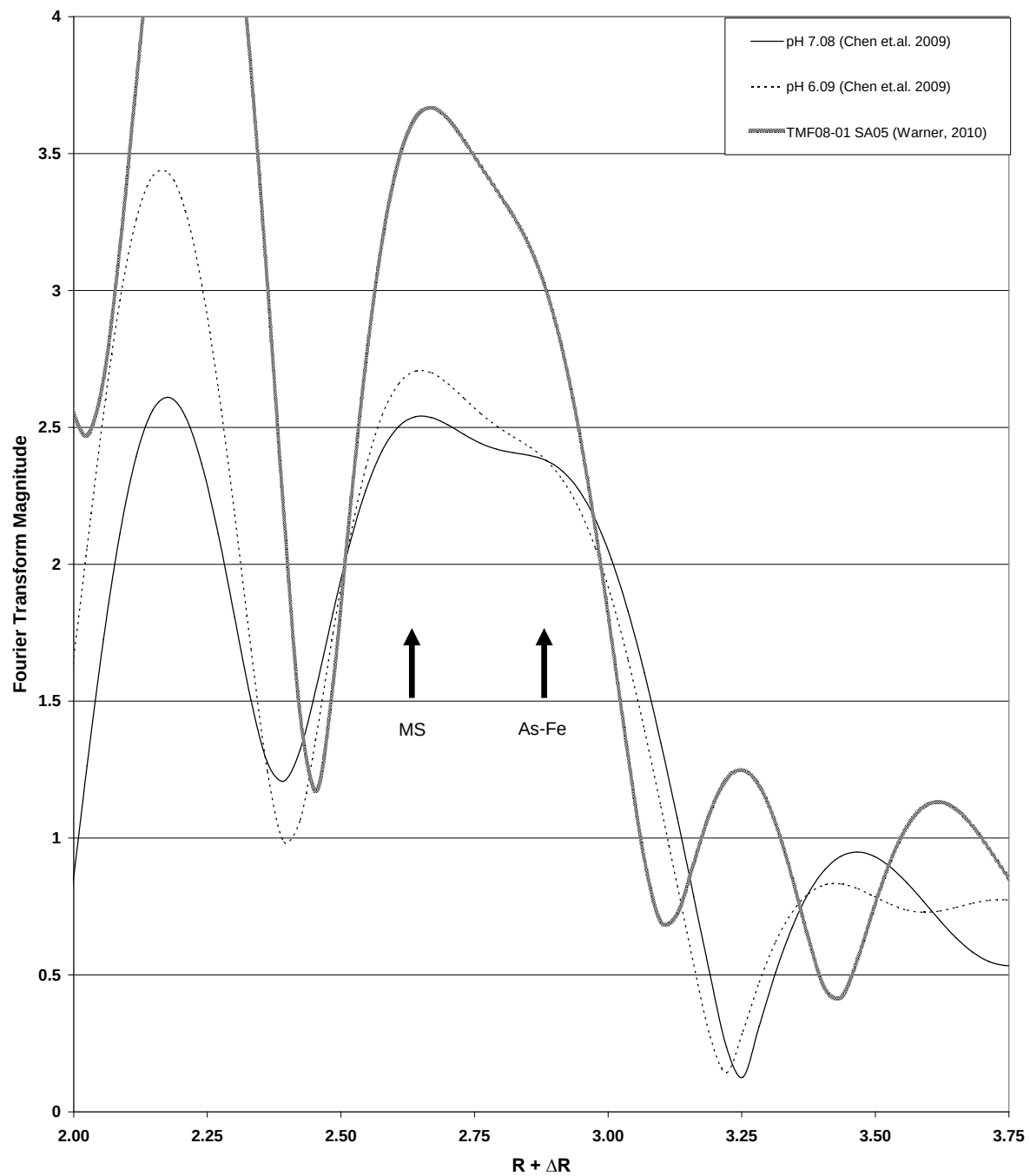


Figure 7 – Comparison of the Fourier transform magnitude in the region of the As-Fe shell for laboratory produced tailings and actual tailings from the McClean Lake TMF.

CONCLUSIONS

After the start up of the McClean Lake mill, raffinate solutions were processed on a laboratory scale. These experiments, using mill raffinate solutions, produced ferric arsenate precipitated solids by simulating the McClean Lake tailings preparation process. These solid samples were then subjected to synchrotron based EXAFS analysis. Further detailed fitting was conducted by Chen et al. Based on the results from the EXAFS As K-edge spectra, it was concluded that the chemical phase of the ferric arsenate precipitate was that of a poorly crystalline scorodite (Chen et al., 2009). Sample TMF 08-01 SA05, collected during the 2008 TMF *in situ* sampling program, exhibits identical EXAFS features with respect to scattering from the As-Fe shell, as reported by Chen et al. (2009) for the laboratory prepared tailings. It is concluded that arsenic in the McClean Lake TMF is present in a poorly crystalline form of the mineral scorodite. Based on laboratory test work, this structure was observed and predicted to exist within the TMF sediments. This presentation reports the first direct evidence of a “scorodite like” structure within the TMF tailings sediments.

ACKNOWLEDGMENTS

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Analysis of the Mo Speciation in the JEB Tailings Management Facility at McClean Lake, Saskatchewan

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S Supporting Information

ABSTRACT: The JEB Tailings Management Facility (TMF) is central to reducing the environmental impact of the uranium ore processing operation located at the McClean Lake facility and operated by AREVA Resources Canada (AREVA). The geochemical controls of this facility are largely designed around the idea that elements of concern, such as Mo, will be controlled in the very long term through equilibrium with supporting minerals. However, these systems are far from equilibrium when the tailings are first placed in the TMF, and it can take years, decades, or centuries to reach equilibrium. Therefore, it is necessary to understand how these reactions evolve toward an equilibrium state to understand the very long-term behavior of the TMF and to ensure that the elements of concern will be adequately contained. To this end, the Mo speciation in a series of samples taken from the JEB TMF during the 2008 sampling campaign has been analyzed. This analysis was performed using powder X-ray diffraction (XRD), X-ray fluorescence mapping (μ -XRF), and X-ray absorption near-edge spectroscopy (XANES). These results show that only XANES was effective in speciating Mo in the tailings samples, because it was both element-specific and sensitive enough to detect the low concentrations of Mo present. These results show that the predominant Mo-bearing phases present in the TMF are powellite, ferrimolybdate, and molybdate adsorbed on ferrihydrite.



1. INTRODUCTION

The JEB Tailings Management Facility (TMF) is central to reducing the environmental impact of AREVA Resources Canada's (AREVA) uranium ore processing operations at the McClean Lake facility in northern Saskatchewan, Canada. Ultimately, geochemical control of solute concentrations in the JEB TMF, like many other TMFs around the world, will be provided over the long term through equilibrium with supporting minerals. The placed tailings are generally heterogeneous, and at the time of deposition into the TMF, the initial solute concentrations are generally out of equilibrium with their respective solids. Once the tailings are placed in the TMF, the solutes and mineralogy will gradually evolve toward a stable mineralogical end point. This evolution is slow (i.e., years, decades, or centuries) and generally limited by low hydraulic conductivity, low temperature ($\sim 6^\circ\text{C}$), and low liquid/solid ratios that limit mass transport.¹ As part of its operating license issued by the Canadian Nuclear Safety Commission, it is incumbent upon AREVA to determine the minerals controlling the long-term pore water concentration of several elements of concern. These elements of concern are often co-mineralized with U in the ore body and include As, Ni, Mo, and Se in addition to U and ²²⁶Ra. Mineralogical investigations by AREVA concerning several of these elements have been in progress for over a decade.^{2–6} However, little

work has been performed to determine the Mo-bearing minerals present.¹ In concordance with AREVA's operating requirements, it is prudent to ascertain what Mo-bearing phases are currently present in the TMF and how these phases evolve over time.

During the tailings preparation process, Mo is precipitated out of the solution component of the tailings slurry at a pH of 4 as ferrimolybdate [$\text{Fe}_2(\text{MoO}_4)_3 \cdot 8\text{H}_2\text{O}$] and molybdate adsorbed on ferrihydrite [$\text{Fe}(\text{OH})_3\text{--MoO}_4$]. However, under the near-neutral TMF conditions unique to the JEB TMF (pH 7.3), these species are not stable and should dissolve, resulting in the formation of a new, relatively insoluble Mo-bearing phase. The geochemical models of the JEB TMF, which were based on thermodynamic calculations, predict that powellite (CaMoO_4) should precipitate in the TMF and control the Mo pore water concentration.⁷ This is in contrast to another northern Saskatchewan TMF, which is operated at a higher pH, where NiMoO_4 or molybdate adsorbed on ferrihydrite have been identified as the prominent Mo species currently present.⁸ It is necessary to experimentally determine if powellite is

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currently present in the JEB TMF to help verify the geochemical model. Further, it is also necessary to establish what other Mo-bearing phases are in the TMF and to understand how the Mo mineralogy in the TMF evolves over time. Such a study will help establish how the solubility of Mo will change over the very long term in a TMF with near-neutral pH.

To this end, the Mo speciation in several tailings samples from the 2008 sampling campaign was analyzed. AREVA conducts a sampling campaign of the TMF once every 5 years, and each campaign acts as a snapshot in time. The collective results will allow for an understanding of how these various equilibria processes evolve over time.¹ The Mo concentrations in the samples studied here range from 20 to 409 ppm (see Table S1 of the Supporting Information). Powder X-ray diffraction (XRD), X-ray fluorescence mapping (μ -XRF), and X-ray absorption near-edge spectroscopy (XANES) were used to analyze the Mo species present in the tailings. On the basis of this study, it can be concluded that powellite is present in the TMF and that it currently accounts for 10–40% of the Mo species in the JEB TMF. This result will aid future modeling of the JEB TMF as well as other TMFs. This study also found that the balance of the Mo was present as ferrimolybdate [$\text{Fe}_2(\text{MoO}_4)_3 \cdot 8\text{H}_2\text{O}$] and molybdate adsorbed on ferrihydrite [$\text{Fe}(\text{OH})_3\text{--MoO}_4$]. Additionally, the effectiveness of several common techniques used in speciating low-concentration elements is also discussed. This investigation showed that only XANES was effective in determining the Mo species present because of the low Mo concentration and highly complex nature of the tailings samples.

2. EXPERIMENTAL SECTION

2.1. Mine Tailing Sample Selection. The samples used in this study were collected during the 2008 sampling of the JEB TMF. In these studies, drilling was conducted at four different locations around the TMF, and samples were collected at 3 m vertical intervals. The samples studied here were collected from two drilling positions, TMF08-01 (N 112.00°, E 52.89°), which is in the center of the TMF, and TMF08-03 (N 112.22°, E 52.39°), which is located at the periphery of the TMF. Three samples from each position were analyzed, and these are labeled as TMF08-01 SA04, TMF08-01 SA09, TMF08-01 SA19, TMF08-03 SA02, TMF08-03 SA08, and TMF08-03 SA16, where increasing SA numbers indicate deeper sampling depths. The depths of the samples used in this study are reported in Table S1 of the Supporting Information. In general, because of the deposition process of tailings within the TMF, coarser particles were expected to be found near the center of the TMF and finer particles were expected to be found at the periphery. Because of the settled nature of the TMF, the depth of the core sample can be correlated to the sample age, allowing for an analysis of the aging process of the tailings.

2.2. Preparation of Standard Materials. A series of Mo-bearing standards were either prepared or purchased to allow for analysis of the Mo speciation via Mo K-edge XANES experiments. These standards were chosen on the basis of a previous study of the Mo content of the DTMF operated by the Cameco Corporation.⁸ The purchased standards were MoO_3 (Acrös Organics, 99+%), MoS_2 (Aldrich), MoO_2 (Alpha Aesar, 99%), and H_2MoO_4 (Sigma Aldrich, >85%). The synthesized standards were powellite (CaMoO_4), α - NiMoO_4 , α - FeMoO_4 , ferrimolybdate [$\text{Fe}_2(\text{MoO}_4)_3$], and MoO_4^{2-} adsorbed on ferrihydrite [$\text{Fe}(\text{OH})_3\text{--MoO}_4$]. The details of

the synthetic methods used are presented in the Supporting Information.^{8–13} The phase purity of all of the synthesized standards was checked by XRD using the instrument described in section 2.3.

2.3. Powder XRD. Powder XRD patterns from the tailings samples were collected to make an initial assessment of the phases present in these materials. Measurements were collected using a PANalytical Empyrean X-ray diffractometer equipped with a $\text{Cu K}\alpha_{1,2}$ X-ray source. The μ -XRD diffraction patterns were collected using a 200 μm diameter spot size. The details of the sample preparation and experimental setup are outlined in the Supporting Information. All powder XRD patterns were analyzed using the X'Pert HighScore Plus and PowderCell software packages.¹⁴

2.4. X-ray Fluorescence Imaging and Laue Diffraction. X-ray fluorescence (XRF) maps and Laue XRD patterns from three of the tailings samples were collected using the VESPERs beamline at the Canadian Light Source (CLS). (μ -XRD experiments were also attempted using multiple incident energies, but the collected signal was not high enough to produce a usable diffraction pattern.) Details of the sample preparation and experimental setup are presented in the Supporting Information. Fluorescence (elemental) maps were created and analyzed using the SMAK program, and the Laue diffraction patterns were analyzed using the XMAS program.^{15,16}

2.5. XANES. Mo K-edge XANES measurements were carried out using the HXMA beamline at the CLS.^{17,18} The details of the sample preparation and experimental setup are presented in the Supporting Information. In all cases, multiple scans of each sample were collected at a single spot. These scans did not change in any systematic way, indicating that no beam damage occurred during the measurements. The spectra were fitted from 25 eV below the absorption edge to 55 eV above the absorption edge when performing the principle component analysis (PCA) and linear combination fitting (LCF). The absorption edge of a spectrum was defined as the most intense, lowest energy peak in the first derivative of the spectrum. The Athena software program was used to normalize the spectra and perform all of the PCA and LCF analyses.¹⁹

3. RESULTS AND DISCUSSION

3.1. Powder XRD. Powder XRD patterns from the bulk tailings samples were collected to provide an initial characterization of the tailings materials (see Figure S1 of the Supporting Information). The dominant crystalline phases observed in these samples were quartz and gypsum. In general, the patterns from the central bore-hole samples (TMF08-01 SA04, TMF08-01 SA09, and TMF08-01 SA19; see Figure S1a of the Supporting Information) have a flatter background than the patterns from the periphery bore-hole samples (TMF08-03 SA02, TMF08-03 SA08, and TMF08-03 SA16; see Figure S1b of the Supporting Information), which contain a broad peak spanning $\sim 15\text{--}30^\circ$. This indicates that the samples from the central bore hole are more crystalline than the samples from the periphery bore hole.²⁰ This is consistent with the design of the TMF, because coarser particles are expected to congregate near the center of the TMF, while finer particles are expected to be found toward the edge of the TMF. Finally, the powder patterns show that none of the expected crystalline Mo-bearing phases (i.e., α - FeMoO_4 , α - NiMoO_4 , and powellite) could be detected using bulk powder XRD. This result was expected given the low concentrations of Mo in these samples (see Table

S1 of the Supporting Information) but does not preclude the presence of these phases in the tailings samples.

Given the limitations of a standard powder XRD experiment, these studies were followed by performing μ -XRD experiments. The X-ray beam was focused to a 200 μm spot size in these studies, and diffraction patterns were gathered from multiple aliquots of each sample. The results from sample TMF08-03 SA08 are presented in Figure 1 (the μ -XRD patterns from the

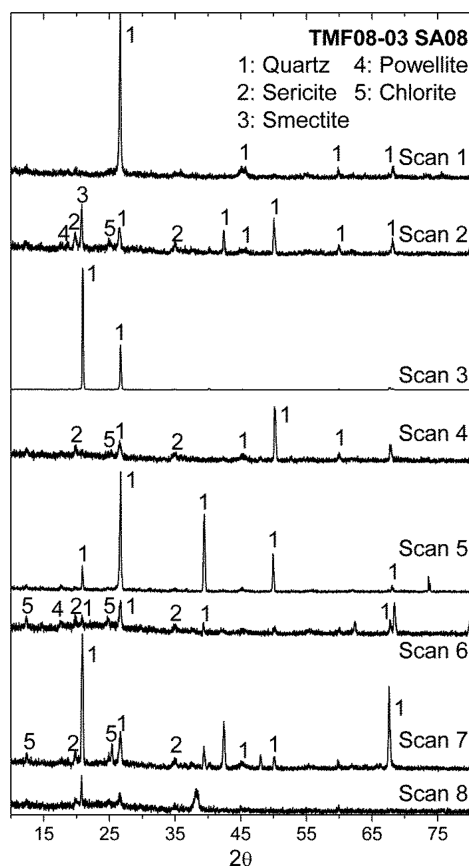


Figure 1. μ -XRD patterns collected from aliquots of the TMF08-03 SA08 tailings sample. The diameter of the beam spot was 200 μm . In some scans, the intensities of the identified peaks do not match the calculated intensity from the reference pattern. This is most notably seen for the quartz peaks in scans 3 and 7 and is likely caused by graininess of the crystallites. A peak consistent with the presence of powellite is found in scans 2 and 6.

other tailings samples are presented in Figures S2–S6 of the Supporting Information). The significant variations in the diffraction patterns observed indicate that the tailings samples are heterogeneous, which was also confirmed by visual inspection (photographs of two of the tailings samples are presented in Figure S7 of the Supporting Information). Additionally, the peak widths of the μ -XRD patterns vary, indicating that the crystallinity of the tailings is not uniform. Here, diffraction patterns with sharper peaks indicate a more crystalline sample. In general, the peaks can be assigned to phases previously reported to be found in the samples.¹ Interestingly, the intensities of peaks from highly crystalline phases varied significantly between samples (cf. scans 3 and 5 in Figure 1). These intensities also deviated significantly from the reported standard diffraction pattern. It is likely that these variations occur because of poor crystallite statistics (“graini-

ness”), in which the crystallites are sufficiently large that too few grains are illuminated to obtain a statistically representative distribution of grain orientations, resulting in a random distortion of the diffraction peak intensities.²¹ This seems likely given the large grain sizes (the samples were not ground) and the small X-ray spot size. These patterns provide some possible evidence for the presence of β -FeMoO₄ and powellite phases. However, for powellite, the predominant peak observed is not the most intense peak in the reported reference pattern, suggesting that graininess is likely an issue here as well. Overall, these results show that a more sophisticated approach is required to determine the Mo speciation in these tailings samples.

3.2. XRF Imaging and Laue Diffraction. **3.2.1. XRF Imaging.** XRF experiments were performed to map the elemental distribution within the tailings samples. In these experiments, the samples were illuminated with a highly focused X-ray pink beam, which had a spot size of 5 μm . The samples were then rastered using 10 μm steps, and the resulting fluorescence at each spot was measured, allowing for a map to be generated. The results of this experiment for the TMF08-03 SA08 sample are shown in Figure 2. Two other tailings samples were also mapped (see Figures S8 and S9 of the Supporting Information), but Mo could not be detected in the regions studied.

A Mo-rich region was observed near the bottom left-hand corner of the map, as outlined by the red rectangle in Figure 2. Relatively intense fluorescence signals from U, As, Ni, and Fe were also observed in this region. The size and shape of these hotspots were similar, suggesting that these elements are intimately mixed with Mo. There was little overlap between the Ca- and Mo-rich regions, although some small, isolated Ca hotspots were observed to overlap with the main Mo hotspot. A strong correlation between the U and Mo signals was observed, which may indicate that U and Mo are present in a single phase. However, it is more likely that this result is an artifact of the relatively poor resolution of the fluorescence detector. The Mo K α emission line has an energy of 17 480 eV, and the U L β emission line has an energy of 17 220 eV. It is possible that the overlap between signal channels resulted in this correlation.¹⁸ In general, these results may indicate that Ni and Mo are intimately mixed, consistent with the presence of a NiMoO₄ phase, but it is more likely that this observation was a result of the co-mineralization of Ni- and Mo-bearing phases from the original ore. Overall, no conclusive results about the Mo speciation could be drawn from this experiment.

3.2.2. Laue Diffraction. Laue diffraction patterns were collected at different sample positions based on the results of the XRF mapping experiments. The positions at which patterns were collected are labeled in Figure 2 and Figures S8 and S9 of the Supporting Information, on the As fluorescence maps. The samples were illuminated using an X-ray pink beam with a spot size of 5 μm in these experiments. Representative examples of the patterns collected are presented in Figure 3.

The spot size used (5 $\times$ 5 μm) was on the order of the size of the crystallites, and the resulting diffraction patterns collected generally resemble single-crystal diffraction patterns. This is observed best in the pattern presented in Figure 3b, in which small, well-defined diffraction spots are observed. However, the significant penetration depth of the X-rays can also result in several crystallites being illuminated simultaneously, resulting in large, non-circular diffraction spots (see panels a and c of Figure 3).

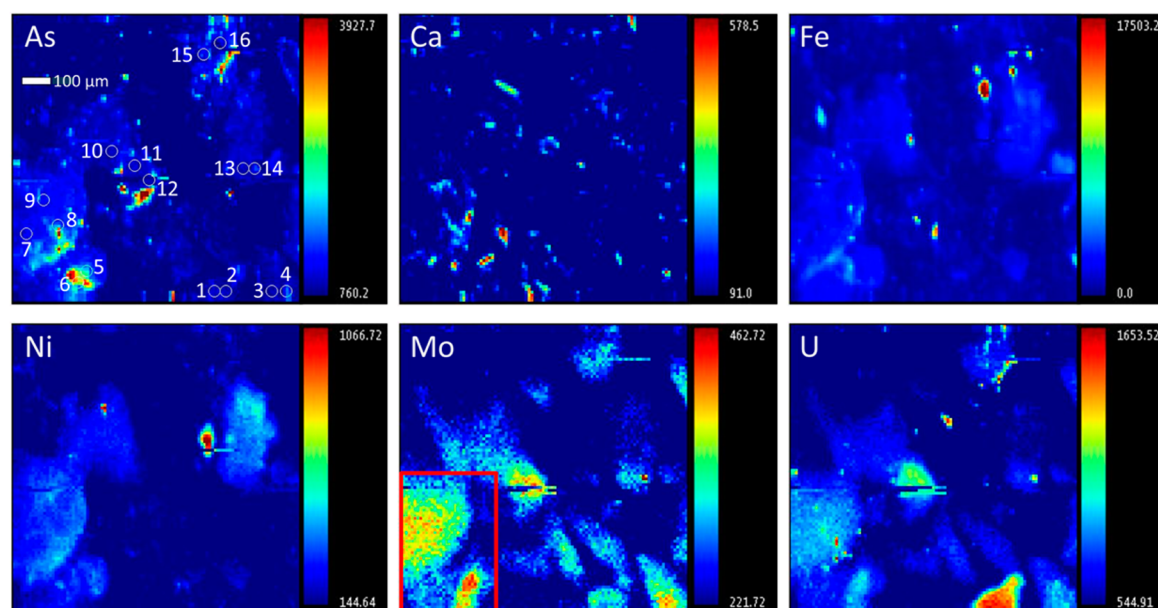


Figure 2. Fluorescence maps collected from the TMF08-03 SA08 sample. The spot size of the beam was $5 \times 5 \mu\text{m}$, and the map was collected using $10 \mu\text{m}$ steps. The spots where Laue diffraction patterns were collected are labeled according to their scan number in the As map. A large Mo concentration hotspot was found in the lower left-hand corner of the Mo map, as outlined by the red rectangle. Fe, Ni, As, and U fluorescence signals were also observed in this region, indicating that these elements were likely intimately mixed.

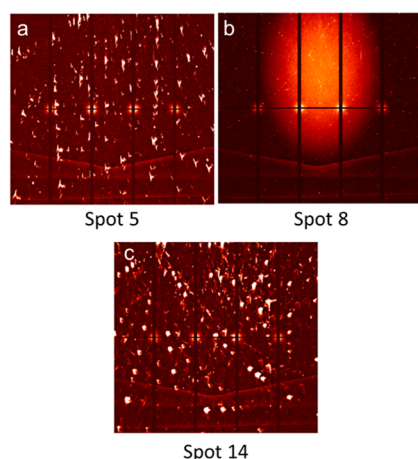


Figure 3. Laue diffraction patterns collected at (a) spot 5, (b) spot 8, and (c) spot 13 from the TMF08-03 SA08 tailings sample. The spot size of the beam was $5 \times 5 \mu\text{m}$. The “V shape” present in the bottom half of the patterns is the result of shadowing from the sample holder. The diffraction patterns collected at spots 5 and 14 are broad and non-circular, indicating that multiple crystallites were illuminated. The diffraction pattern collected at spot 8 is small and circular, indicating that only one crystallite was illuminated.

These patterns were analyzed using the crystal structure of known standards to index the diffraction spots. If the number of diffraction spots indexed was close to the number of diffraction spots observed, it is likely that the phase indexed is present.²² Here, the phases indexed were those reported by AREVA to be in the tailings. The results of these fitting attempts are summarized in Table 1 and Tables S2 and S3 of the Supporting Information (note that some spots did not produce usable diffraction patterns). In general, none of the phases indexed resulted in a definitive fit. However, for TMF08-03 SA08, spot 8 may have been indexed by powellite and the diffraction pattern of spot 6 was modeled fairly well by gypsum.

Ultimately, the complexity of the tailings samples did not allow for any conclusions to be drawn.

3.3. XANES. Mo K-edge XANES spectra from the tailings samples and a series of Mo-bearing standards were collected and are presented in Figure 4. The spectra were analyzed to determine the speciation of Mo in the tailings samples. The results of this analysis are discussed below.

3.3.1. Analysis of the Mo Oxidation State in the Tailings.

The Mo K-edge XANES spectra were first analyzed to determine the oxidation state of Mo in the tailings species. This analysis was performed by comparing the absorption edge energies of spectra from the tailings samples to spectra from samples with known Mo oxidation states (Figure 5). The absorption edge energy is sensitive to the oxidation state of the metal center, and the absorption edge shifts to higher energy with increasing oxidation state. Increasing the oxidation state decreases the amount of screening of the nuclear charge that the core-electron experiences, leading to a more tightly bound ground state.^{23,24} The edge energy is also sensitive to the chemical environment around the metal center, because changes in the electronegativity of the surrounding anions can change the bond covalency. In general, as the surrounding ions become less electronegative (i.e., the bonds become more covalent), the charge of the Mo center decreases and the absorption edge energy shifts to lower energy.^{23,24} This is best observed by comparing the edge energies of MoO_3 (Mo^{6+}), MoO_2 (Mo^{4+}), and MoS_2 (Mo^{4+}) in Figure 5; as the Mo oxidation state decreases, the edge energy also decreases. Examination of Figure 6 shows that the absorption edge energies from the tailings samples are similar to the absorption edge energy from MoO_3 . It can be concluded that Mo adopts a 6+ oxidation state in the tailings samples and is likely surrounded by O anions. This is consistent with the processing of the tailings, in which a large amount of Fe^{3+} is added to the mixture, because it is well-known that the $\text{Fe}^{3+}/\text{Mo}^{4+/5+}$ redox couple strongly favors the formation of Fe^{2+} and Mo^{6+} under a wide variety of conditions.^{25,26}

Table 1. Summary of Laue Fitting Results, TMF08-03 SA08

image ^b	number of peaks indexed ^a						
	powellite	quartz	illite–smectite	chlorite	gypsum	kamiokite	β -FeMoO ₄
1	34	43	42	49	46	29	126
2	47	49	36	43	46	45	147
6	19	12	15	15	29	18	48
8	56	56	48	54	58	54	175
11	55	43	43	27	39	43	149
13	43	31	28	27	41	27	97
14	35	40	31	42	45	40	131
15	35	42	41	60	40	41	156
16	43	67	42	49	52	40	162

^aLarger numbers of peaks indexed usually indicate a higher quality fit.²² ^bNumbering refers to where on the sample the diffraction pattern was collected. Please refer to Figure 2 for image locations.

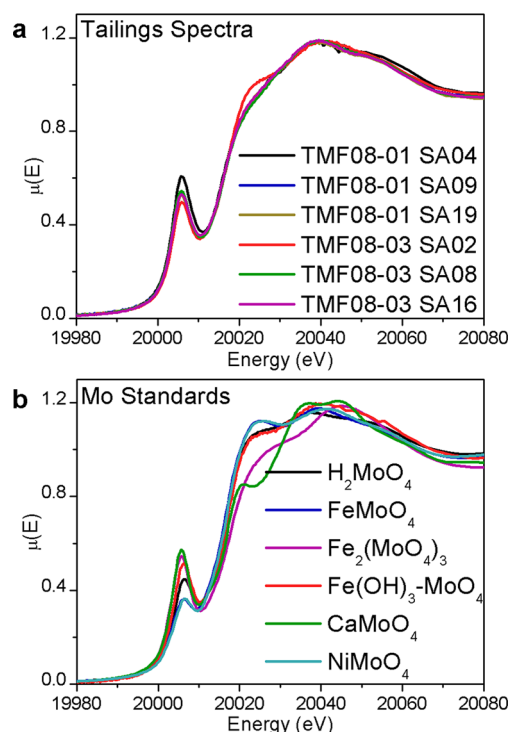


Figure 4. (a) Mo K-edge XANES spectra from the tailings samples. All spectra were fairly similar, with the exception of the spectrum collected from the TMF08-03 SA02 sample. (b) Mo K-edge XANES spectra from the Mo standards used for the linear combination fitting.

3.3.2. PCA. Beyond information on the oxidation state and the local coordination environment around the metal center, XANES can also provide information about the number of species present in a mixture and the identity of those species. Such information is achieved through the use of advanced data processing techniques, such as PCA. In this context, the term “component” and the term “factor” are interchangeable. To avoid the confusion of trying to refer to both chemical and mathematical components, the term “factor” will be used when describing PCA components. The basic principle of PCA (in the context of XANES) is grounded in the fact that a XANES spectrum from a mixture can be constructed from a linear combination of the spectra from each of the individual components in that mixture.²⁷ Because of this property, the spectra from a series of mixtures bearing similar individual components can be decomposed into q principle factors, which can be used to reconstruct the original data.²⁸ PCA has been

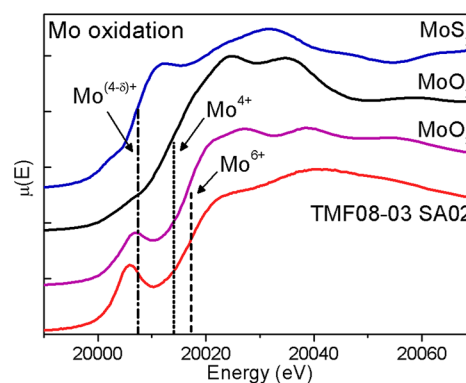


Figure 5. Absorption edge energy of the TMF08-03 SA02 sample is compared to Mo standards with different oxidation states. The absorption edge energy is similar to that from MoO₃, which has a 6+ oxidation state, indicating that Mo likely adopts a 6+ oxidation state and is surrounded by O²⁻ anions in the tailings samples.

performed on the set of tailings spectra investigated here, and the results of this analysis are plotted in Figure S10 of the Supporting Information. It is important to note that, despite their appearance, the principle factors derived from the data are mathematical constructs and do not have physical meaning. The analysis of the spectra reported here is similar to the analysis used to determine the Mo species present in the DTMF, which is a U-milling TMF also located in northern Saskatchewan.⁸

Given a perfect data set with no experimental error, the number of principle factors would be equal to the number of components within the set of mixtures. However, the number of principle factors derived is always greater than the number of components in the set of mixtures because of experimental error.²⁸ In this case, the excess principle factors describe the contributions of experimental error to the data. The principle factors attributable to the components within the set of mixtures are referred to as primary factors, while principle factors attributable to experimental error are referred to as secondary factors. Malinowski has developed the empirical IND function to differentiate between the primary and secondary factors, and the number of primary factors is given when the IND function output is minimized.^{28,29} The values of the IND function have been evaluated and are plotted in Figure S11 of the Supporting Information. The IND function reached a minimum value when the number of principle factors was 3. It was concluded from this analysis that there are three Mo-bearing species in the tailings. This conclusion is confirmed by

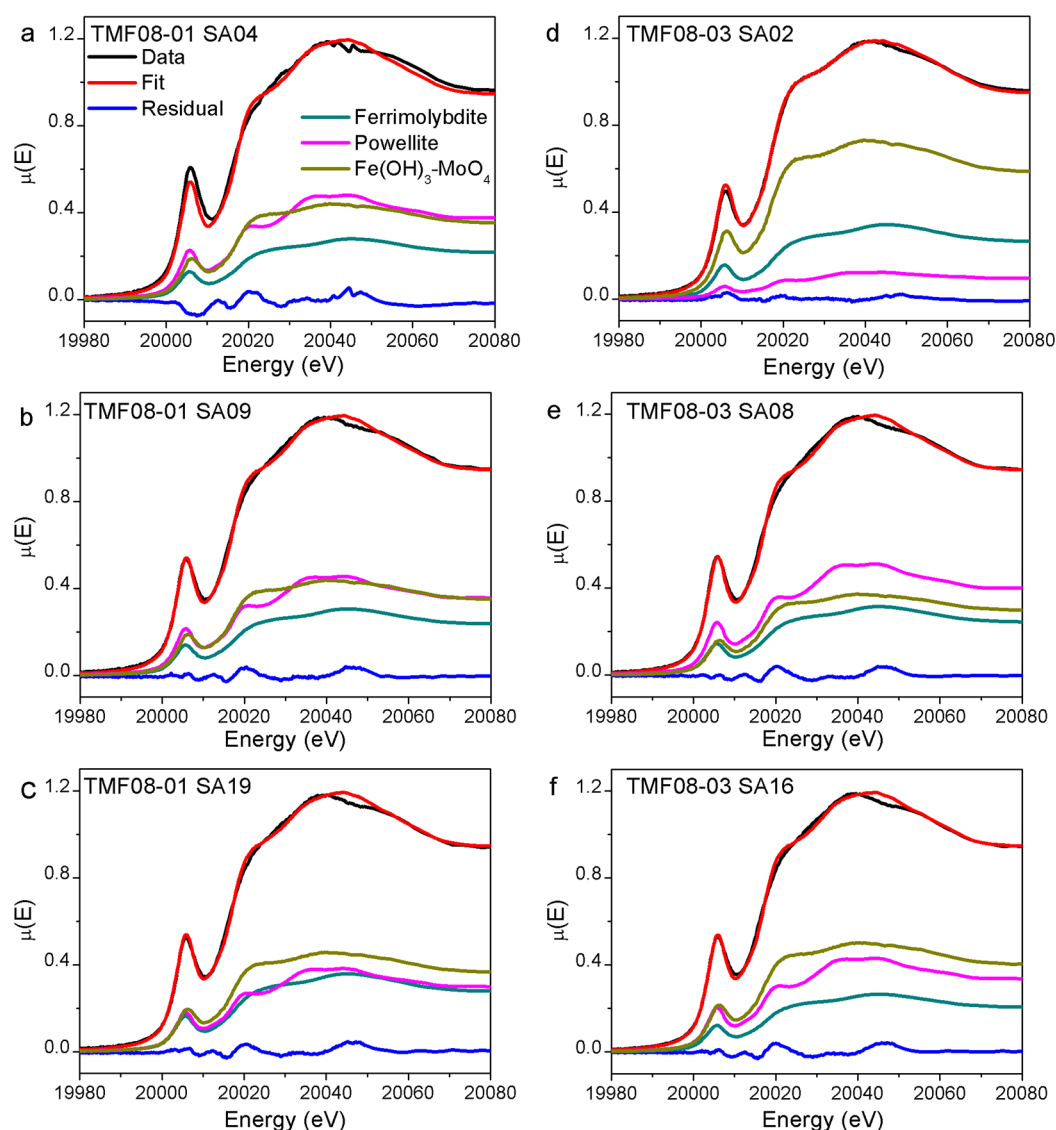


Figure 6. Mo K-edge XANES spectra from (a) TMF08-01 SA04, (b) TMF08-01 SA09, (c) TMF08-01 SA19, (d) TMF08-03 SA02, (e) TMF08-03 SA08, and (f) TMF08-03 SA16 are presented along with results of the linear combination fit. The weighted spectra from the fitted standards are also plotted.

Table 2. Summary of LCA Fits^a

sample	powellite		ferrimolybdate		Fe(OH) ₃ -MoO ₄		R factor	χ^2
	concentration	error	concentration	error	concentration	error		
TMF08-01 SA04	0.40	0.040	0.24	0.071	0.37	0.029	0.00466	0.16064
TMF08-01 SA09	0.38	0.022	0.26	0.038	0.36	0.017	0.00155	0.05318
TMF08-01 SA19	0.37	0.042	0.30	0.027	0.38	0.018	0.00178	0.06292
TMF08-03 SA02	0.10	0.033	0.29	0.014	0.600	0.0097	0.00052	0.01788
TMF08-03 SA08	0.42	0.038	0.26	0.027	0.31	0.018	0.00175	0.06185
TMF08-03 SA16	0.36	0.037	0.22	0.028	0.42	0.019	0.00191	0.06674

^aResults of the linear combination fittings of the Mo K-edge spectra from the tailings samples. The best fits using powellite, ferrimolybdate, and Fe(OH)₃-MoO₄ are reported.

the reconstructions of the tailings spectra (see Figure S12 of the Supporting Information). It can be clearly seen in Figure S12 of the Supporting Information that no significant improvements are observed when reproducing the spectra with four versus three components, indicating that only three factors are necessary to describe the data.

3.3.3. Quantitative Analysis of Mo Speciation. The Mo K-edge spectra collected from the tailings samples can be compared to the Mo K-edge spectra from Mo-bearing standards to determine the speciation of Mo in the tailings samples. The standards used to fit the Mo K-edge spectra were H₂MoO₄, α -FeMoO₄, α -NiMoO₄, molybdate adsorbed on ferrhydrite [Fe(OH)₃-MoO₄], ferrimolybdate, and powellite.

The Mo K-edge spectra from these standards are presented in Figure 4b (the anhydrous ferrimolybdate standard used was an appropriate model system for hydrated ferrimolybdate given the local structural similarities around the Mo center in the two systems).

The tailings spectra were fitted by linear combinations of the XANES spectra from the standards using the linear combination fit function in the Athena software program.¹⁹ Each tailings spectrum was fitted by all combinations of three or fewer standards, and the best fit was determined by the χ^2 value from these fittings. The coefficients of the linear combination fit were normalized and represent the concentrations of each species present as a function of total percent Mo. The best fits to the spectra are summarized in Table 2, and the fitted spectra are plotted in Figure 6.

In all cases, the spectra were fitted best using ferrimolybdate, powellite, and either H_2MoO_4 or $\text{Fe}(\text{OH})_3\text{-MoO}_4$. The linear combination fits using either H_2MoO_4 or $\text{Fe}(\text{OH})_3\text{-MoO}_4$ were generally of equal quality, likely because of the strong similarities between the spectra from H_2MoO_4 and $\text{Fe}(\text{OH})_3\text{-MoO}_4$ (Figure 4b). Therefore, it is not possible to determine which of these species [H_2MoO_4 or $\text{Fe}(\text{OH})_3\text{-MoO}_4$] is present by analysis of the XANES spectra alone. However, H_2MoO_4 is known to be highly soluble at the pH of the pore water present in the TMF (pH 7.3), and it therefore does not seem likely that this phase would be found as a solid in the JEB TMF.³⁰ This leads to the conclusion that the third component in these samples is $\text{Fe}(\text{OH})_3\text{-MoO}_4$.

In general, the resulting fits accurately reproduce the collected spectra from the tailings samples, with the exception of the region between 20 040 and 20 050 eV, where the fitted spectra are consistently more intense than the experimental data. It is likely that multi-scattering resonances (MSRs) contribute significantly to the intensity of the features found in this region of the spectra.³¹ In a MSR process, the core electron is excited to a continuum state and scatters multiple times off neighboring atoms, resulting in constructive and destructive interference of the photoelectron wave.³² As such, these structures are highly dependent upon the crystal structure of the materials, and the intensity of MSR features will decrease as the crystallinity of the material decreases.³³ The XRD patterns show that the crystallinity of the phases present in the tailings samples vary widely and exhibit a high degree of disorder (cf. Figure 1 and Figure S1 of the Supporting Information). Therefore, it is highly likely that the Mo phases have only a low degree of crystallinity in the tailings samples, which would result in a muted MSR feature compared to the MSR feature observed in the Mo K-edge XANES spectra from the crystalline standards.

The interpretation reported here relies heavily on the assumption that the standards used in this analysis account for all of the Mo-bearing species in the sample. For example, the $\beta\text{-NiMoO}_4$ phase, which could not be successfully synthesized, represents a possible Mo species that was not included in the standards measured. In this species, Mo occupies a tetrahedral site, which would increase the intensity of the XANES spectrum in the pre-edge region (i.e., the ~20 000–20 010 eV energy range) compared to the pre-edge region from $\alpha\text{-NiMoO}_4$, in which Mo occupies a six-coordinate site.³⁴ When fitting the spectra using $\alpha\text{-NiMoO}_4$ as a component, the pre-edge was consistently under fitted, while the main edge was accurately reproduced. The statistics of these fits were poor compared to the statistics reported in Table 2,

which lead to the conclusion that $\alpha\text{-NiMoO}_4$ was not a component in the tailings samples. However, on the basis of the XRF results, which showed some correlation between the Ni and Mo signals, and the conditions under which the tailings are treated, which are similar to the reported $\beta\text{-NiMoO}_4$ synthetic conditions, it seems possible that $\beta\text{-NiMoO}_4$ could be present.^{1,35,36} Notwithstanding, all fits that included $\alpha\text{-NiMoO}_4$ also required a significant contribution from the powellite spectrum to reproduce the data. Therefore, on the basis of these fits, the conclusions regarding the presence of powellite remain valid.

These results show that powellite is present as a major component in the JEB TMF. They also show that ferrimolybdate and $\text{Fe}(\text{OH})_3\text{-MoO}_4$ likely account for significant amounts of the Mo species present in the TMF. The conclusions of this study are consistent with the long-term geochemical models of the TMF, which predict that powellite will be the predominant Mo-bearing phase when the TMF reaches equilibrium.⁷

■ ASSOCIATED CONTENT

● Supporting Information

Details of the synthetic procedures used, $\mu\text{-XRD}$ patterns, XRF maps, and results of the Laue diffraction indexing of the tailings samples studied and the principle factors calculated from the PCA and reconstructions of the measured Mo K-edge spectra from the tailings using the factors computed from the PCA. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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**Analysis of the Mo-speciation in the JEB Tailings Management Facility at McClean Lake,
Saskatchewan**

Supporting Information

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Includes:

17 pages

3 tables

12 figures

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Preparation of Powellite, α -FeMoO₄, α -NiMoO₄:

Powellite was prepared by mixing stoichiometric amounts of CaCO₃ and MoO₃.⁹ This mixture was heated at 700 °C for 1.5 days to decompose CaCO₃ to CaO. The powder was air quenched, reground, and then heated at 1200 °C for 3 days. α -NiMoO₄ and α -FeMoO₄ were also prepared via a solid-state synthesis reaction.¹⁰ Stoichiometric amounts of NiO and MoO₃ or Fe, Fe₂O₃ and MoO₃ were mixed and sealed in evacuated fused silica ampules. The samples were then heated at 950 °C for 1.5 d. The α -FeMoO₄ sample was quenched in liquid nitrogen to prevent the formation of β -phase impurities, and the α -NiMoO₄ sample was also quenched in air.¹⁰

Preparation of anhydrous ferrimolybdate (Fe₂(MoO₄)₃):

An anhydrous ferrimolybdate standard (Fe₂(MoO₄)₃) was prepared using a co-precipitation synthesis route.¹¹ Stoichiometric amounts of H₂MoO₄ and Fe(NO₃)₃·9H₂O were dissolved separately in ~50 mL of distilled water. A small amount of concentrated ammonia was added to the H₂MoO₄ solution to aid the dissolution of H₂MoO₄. The two solutions were then mixed and stirred, resulting in the formation of a bright yellow precipitate. After stirring, the solution was placed in an oven at 110 °C and left to dry overnight. The resulting light-brown powder was then collected, ground, and calcined at 400 °C for 4 h.

Preparation of molybdate absorbed on ferrimolybdate

Fresh ferrihydrite (Fe(OH)₃) was prepared within 2 weeks of beamtime using a previously reported procedure.^{8,12} Briefly, 8.0769 g of Fe(NO₃)₃·9H₂O was dissolved in 100 mL of distilled water, and the pH of the solution was then raised from 1.38 to 7.43 through the addition of 14.81 mL of 4M NaOH solution. A dark brown precipitate was formed during this process. This precipitate was collected via vacuum filtration, washed six times, and dried in air for 24 h. MoO₄²⁻ was adsorbed to the ferrihydrite by mixing a 0.3 M solution of H₂MoO₄ with a slurry containing 0.3000 g of ferrihydrite.^{8,13} The pH was then adjusted to 8.89 by adding 4 M NaOH and this mixture was covered and stirred for 24 h. The solid product was then collected via vacuum filtration and left to dry in air overnight.

Powder X-ray diffraction experimental details

Bulk powder diffraction patterns were collected by grinding the tailings samples and mounting the resulting powder on glass slides using ethanol. A spinning sample stage was employed during these measurements to prevent preferred orientation. Following these measurements, the Cu X-ray tube was mounted in the “Point Focus” position and the diffractometer was equipped with a mono-capillary attachment that reduced the X-ray spot size to a 200 μm diameter to collect micro powder X-ray diffraction ($\mu\text{-XRD}$) patterns. Samples were prepared by mounting unground sample on a glass slide using ethanol, and 10 slides per tailings sample were prepared. The samples were mounted on the diffractometer using a stationary sample holder during the $\mu\text{-XRD}$ measurements.

X-ray Fluorescence imaging and Laue diffraction experimental details

The $\mu\text{-XRF}$ and Laue diffraction data were collected using the VESPERS beamline at the CLS. Samples were prepared by sealing a thin layer of the unground tailings sample between two layers of Kapton tape. The samples were mounted perpendicular to the beamline and at an angle of 45° from the horizontal axis. X-ray fluorescence emissions were collected using a single element Vortex silicon drift detector (SDD) and the diffraction patterns were imaged using a Pilatus CCD located directly above the sample. All fluorescence spectra and diffraction patterns were collected using the “Pink Beam” mode, which includes all X-ray energies from 5-30 keV. Note that a significant drop off in flux occurs for energies above 20 keV. For all measurements, a 5 μm spot size was used. Fluorescence spectra were collected by rastering over a 1000 μm x 1000 μm area using 10 μm steps and a 1 s dwell time per step.

X-ray absorption near-edge spectroscopy experimental details

Mo K-edge XANES measurements were carried out using the HXMA beamline at the CLS. The flux was on the order of 10^{12} photons/s, and the maximum achievable resolution was better than 2 eV at 20 keV using the Si (220) monochromator.¹⁶ Tailings samples were prepared by packing the as-provided material in 2.38 mm thick Teflon sample holders which were then sealed between two layers of Kapton tape. Spectra were collected using a 0.3 eV step through the absorption edge, and the spectra were measured in partial fluorescence yield mode using a 32-element Canberra Ge detector. To prepare the Mo-bearing standards, the materials were finely ground and

mounted on a strip of Kapton tape which was then folded multiple times. The Mo K-edge spectra from the standards were collected in transmission mode using ionization chambers filled with $N_{2(g)}$. All spectra were calibrated using the Mo K-edge spectra from a Mo metal reference foil collected in-line with the sample, which has a known absorption-edge energy of 20,000 eV.¹⁷

Table S1 Concentration of selected elements in the JEB-TMF tailings samples as determined by ICP-MS

Bore-hole		Central (TMF08-01)			Periphery (TMF08-03)		
Sample		SA-04	SA-09	SA-19	SA-02	SA-08	SA-16
Sample Elevation (mASL ^a)		411	398	366	411	397	370
Analyte	units						
Al	ug/g	50100	51500	82600	82500	76000	95000
Sb	ug/g	<0.2	<0.2	0.6	0.2	<0.2	0.4
As	ug/g	227	433	7000	5100	5700	5600
Ba	ug/g	46	150	270	150	110	330
Be	ug/g	2.3	4.1	7	4.0	4.2	8.1
B	ug/g	100	140	240	430	290	450
Cd	ug/g	<0.1	<0.1	0.2	<0.1	<0.1	0.2
Cr	ug/g	4.6	28	33	15	26	25
Co	ug/g	5.7	8.2	110	23	30	82
Cu	ug/g	5.1	18	260	34	30	170
Fe	ug/g	7700	10100	13700	11200	10400	21000
Pb	ug/g	41	478	889	409	134	2200
Mn	ug/g	40	76	300	120	160	460
Mo	ug/g	20	92	97	143	185	409
Ni	ug/g	194	311	4200	3100	3700	3500
Se	ug/g	0.5	5.7	30	7.0	5.5	22
Ag	ug/g	0.1	1	6	1.5	1.2	6.0
Sr	ug/g	180	170	280	380	420	370
Tl	ug/g	0.2	0.3	0.8	0.5	0.5	1.4
Sb	ug/g	0.2	0.3	0.7	0.6	0.7	1.0
Ti	ug/g	120	210	170	400	280	470
U	ug/g	40	219	649	208	554	504
V	ug/g	262	570	745	628	781	1000
Zn	ug/g	9.8	23	54	44	12	64

^ameters above sea level

Table S2 Results of Laue diffraction fitting for TMF08-01 SA19

Image	Number of Peaks Indexed ^b						
	Powellite	Quartz	Illite-Smectite	Chlorite	Gypsum	Kamiokite	β-FeMoO ₄
1	47	82	55	49	40	58	160
5	47	62	45	44	47	58	167
8	49	264	48	48	60	69	169
10	55	59	57	48	49	50	168

^aNumbering refers to where on the sample the diffraction pattern was collected. Please refer to Figure S8 for image locations.

^bA larger numbers of peaks indexed usually indicates a higher quality fit.

Table S3 Results of Laue diffraction fitting for TMF08-03 SA16

Image ^a	Number of Peaks Indexed ^b						
	Powellite	Quartz	Illite-Smectite	Chlorite	Gypsum	Kamiokite	β-FeMoO ₄
1	92	14	89	82	81	86	314
6	66	86	65	75	71	75	243
7	86	104	78	86	93	108	308
8	77	92	72	78	68	76	253

^aNumbering refers to where on the sample the diffraction pattern was collected. Please refer to Figure S9 for image locations.

^bA larger numbers of peaks indexed usually indicates a higher quality fit.

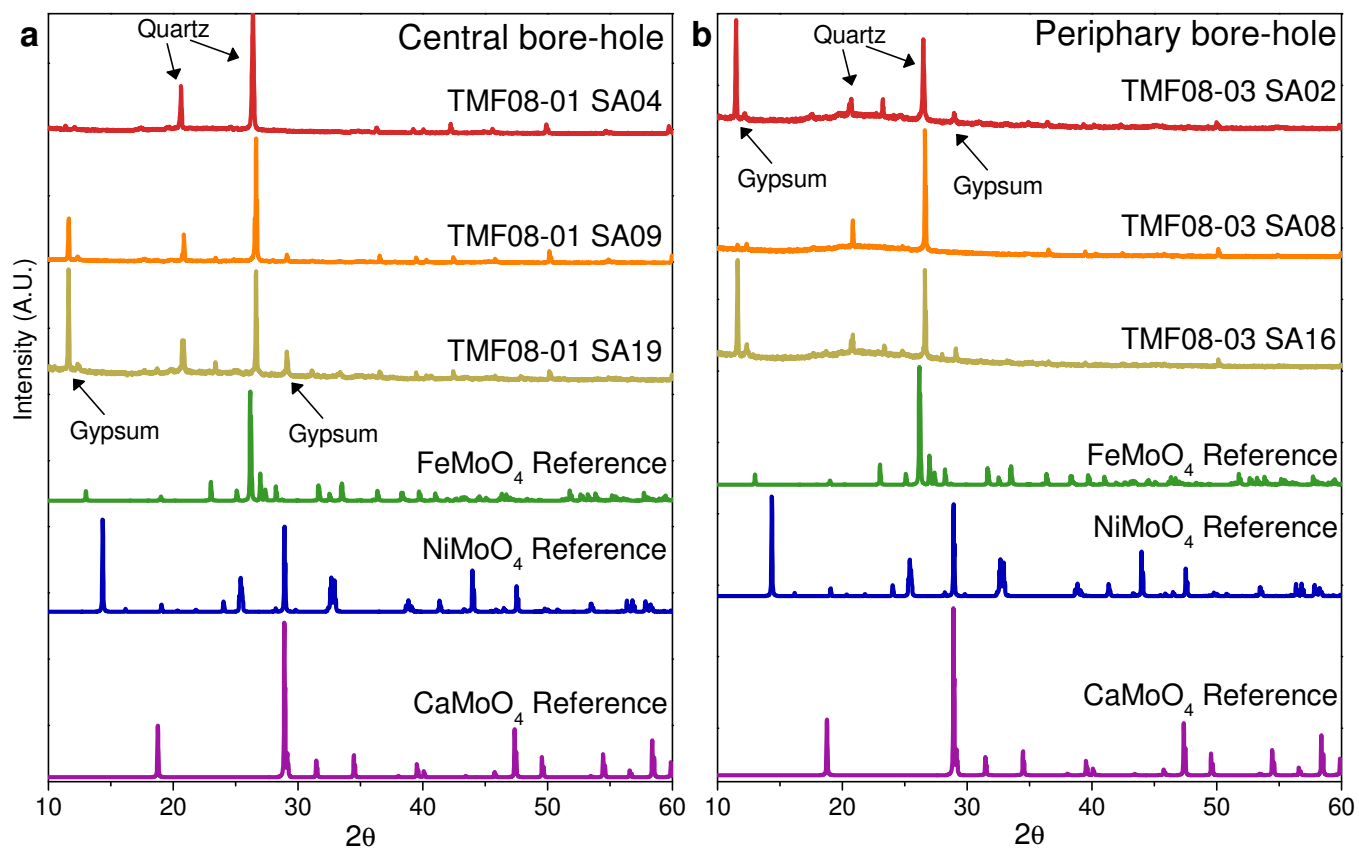


Figure S1: Bulk powder XRD patterns from the (a) central bore-hole and (b) periphery bore-hole tailings samples are compared to reference patterns from Mo-bearing standards. The predominant crystalline phases in the tailings samples are gypsum and quartz. No evidence of Mo-bearing species was observed.

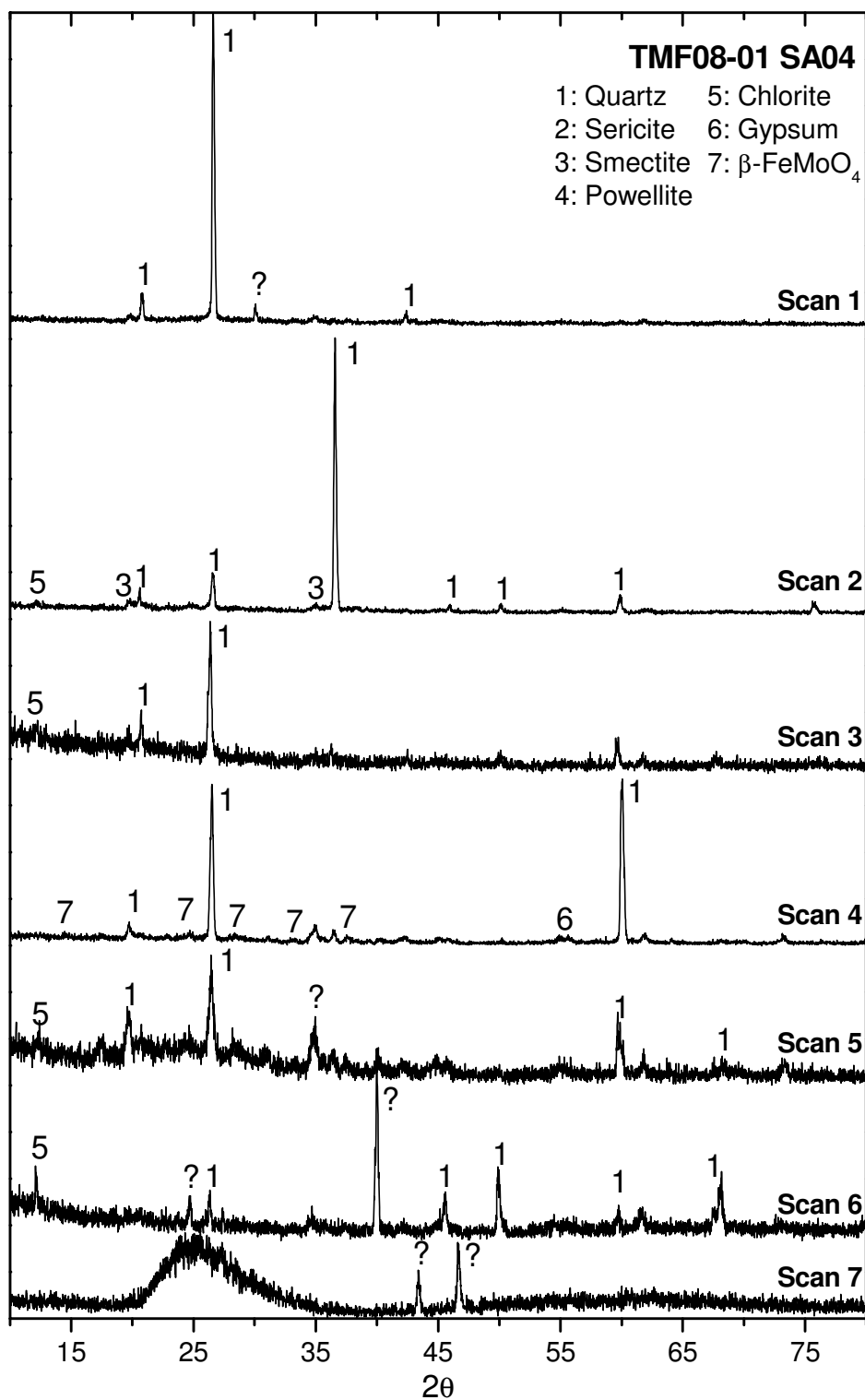


Figure S2: The μ XRD results from the TMF08-01 SA04 sample are presented. Possible evidence of a β -FeMoO₄ phase was observed in Scan 4. Peaks that could not be identified are labeled with a “?”.

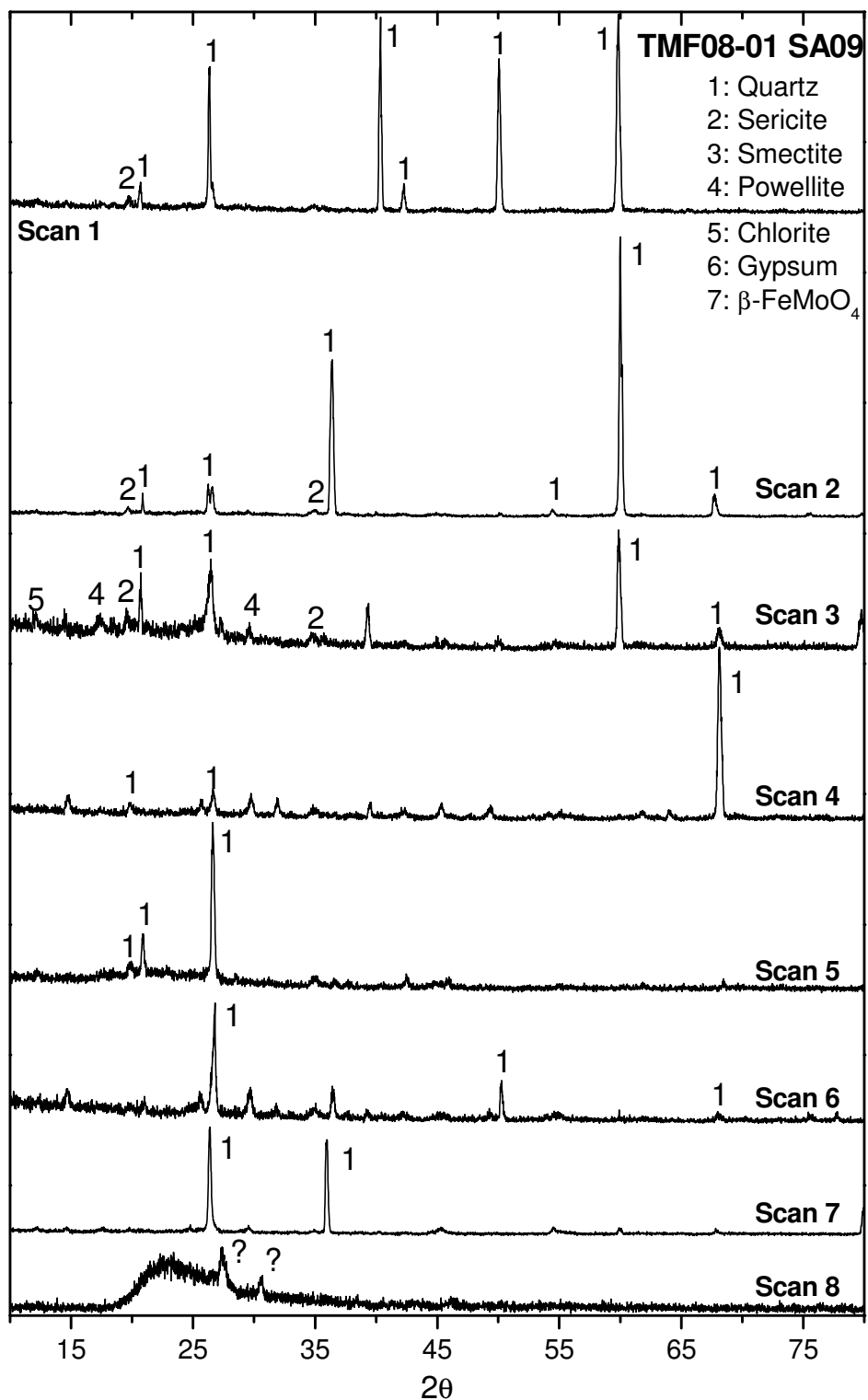


Figure S3: The μ XRD results from the TMF08-01 SA09 sample are presented. Peaks associated with the powellite phase were observed in Scan 3. Peaks that could not be identified are labeled with a “?”.

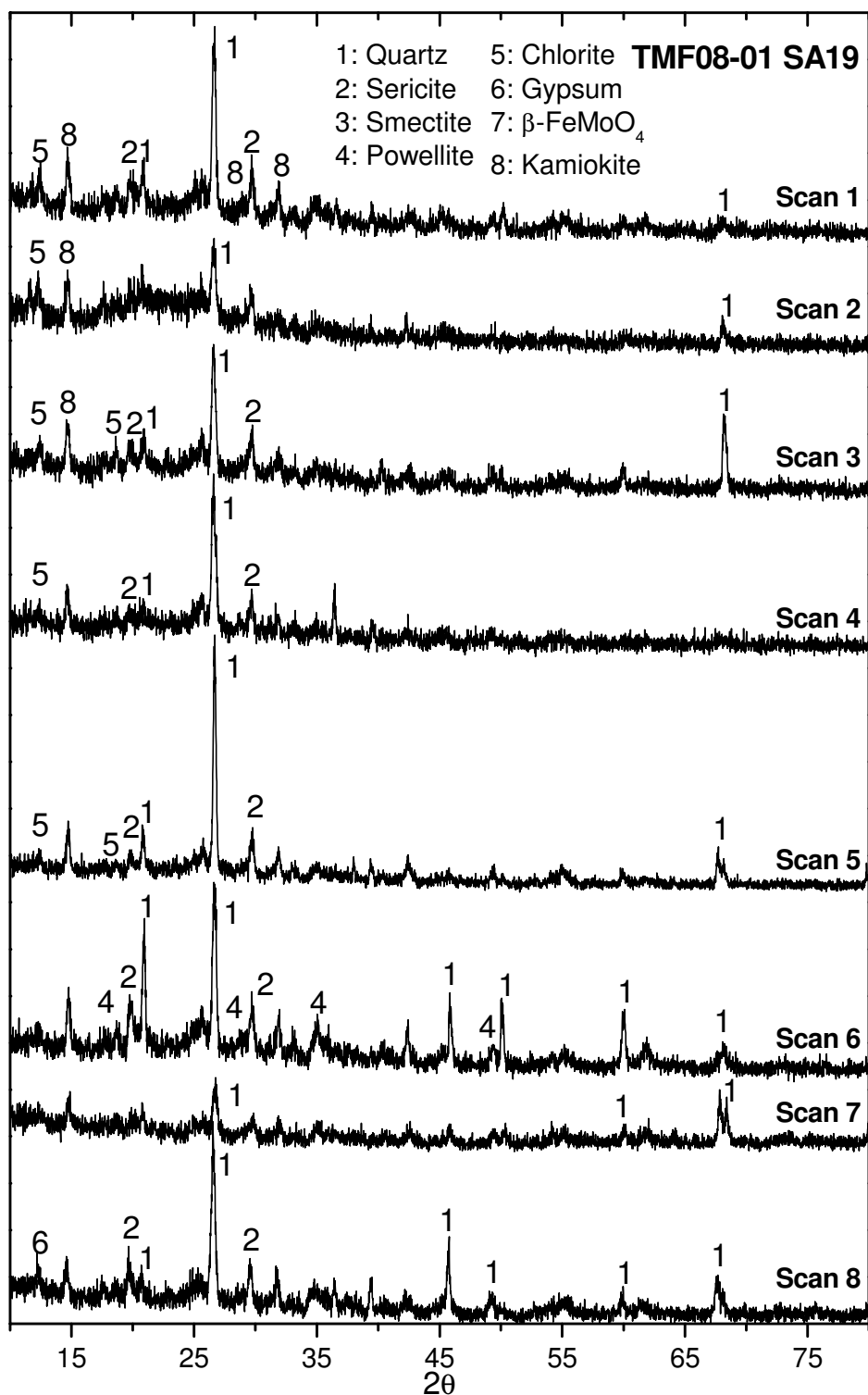


Figure S4: The μ XRD results from the TMF08-01 SA19 sample are presented. Possible peaks from a kamiokite phase were observed in Scans 1-3.

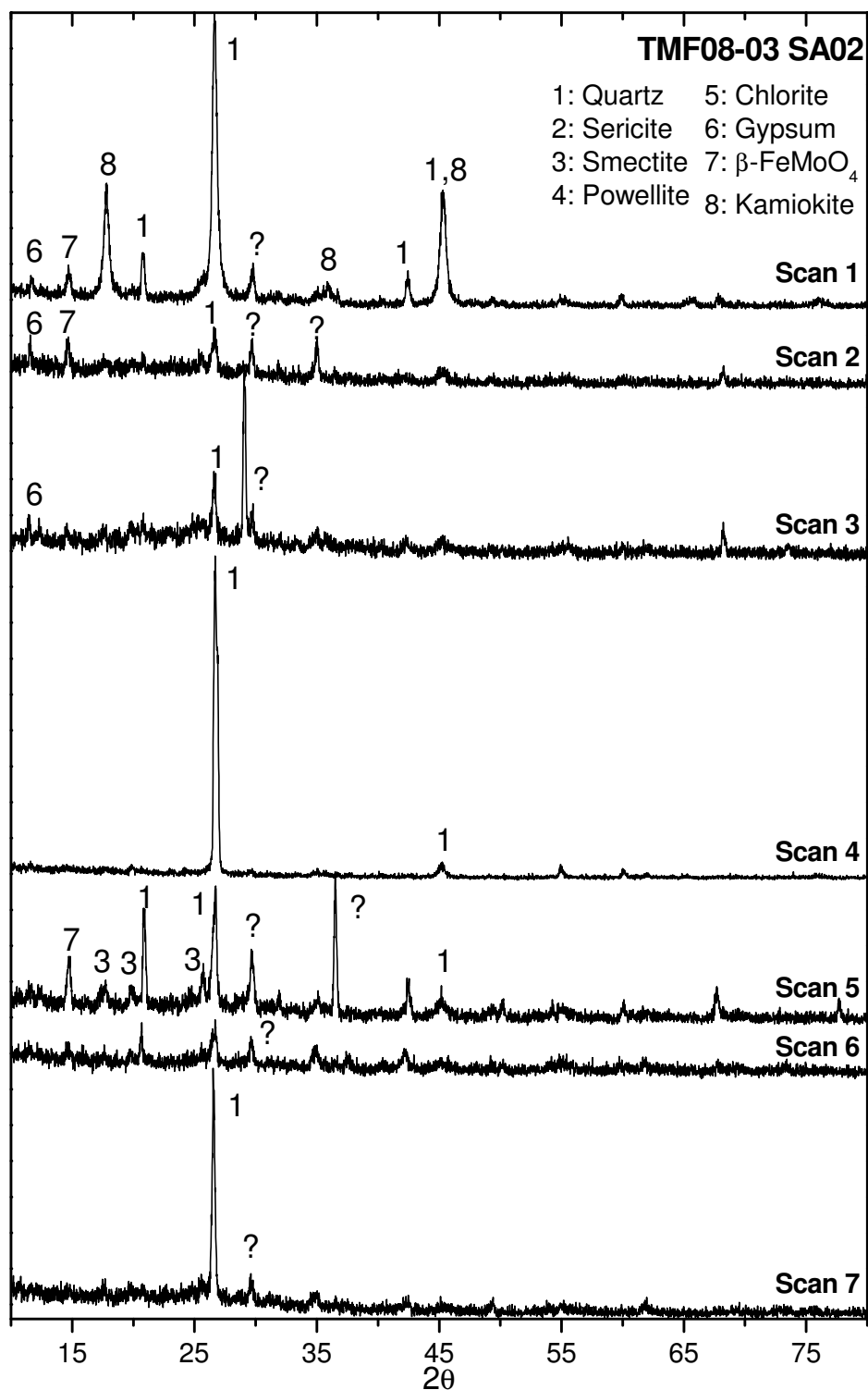


Figure S5: The μ XRD results from the TMF08-03 SA02 sample are presented. Possible evidence of a β -FeMoO₄ phase was observed in Scans 1, 2, and 5. Peaks that could not be identified are labeled with a “?”.

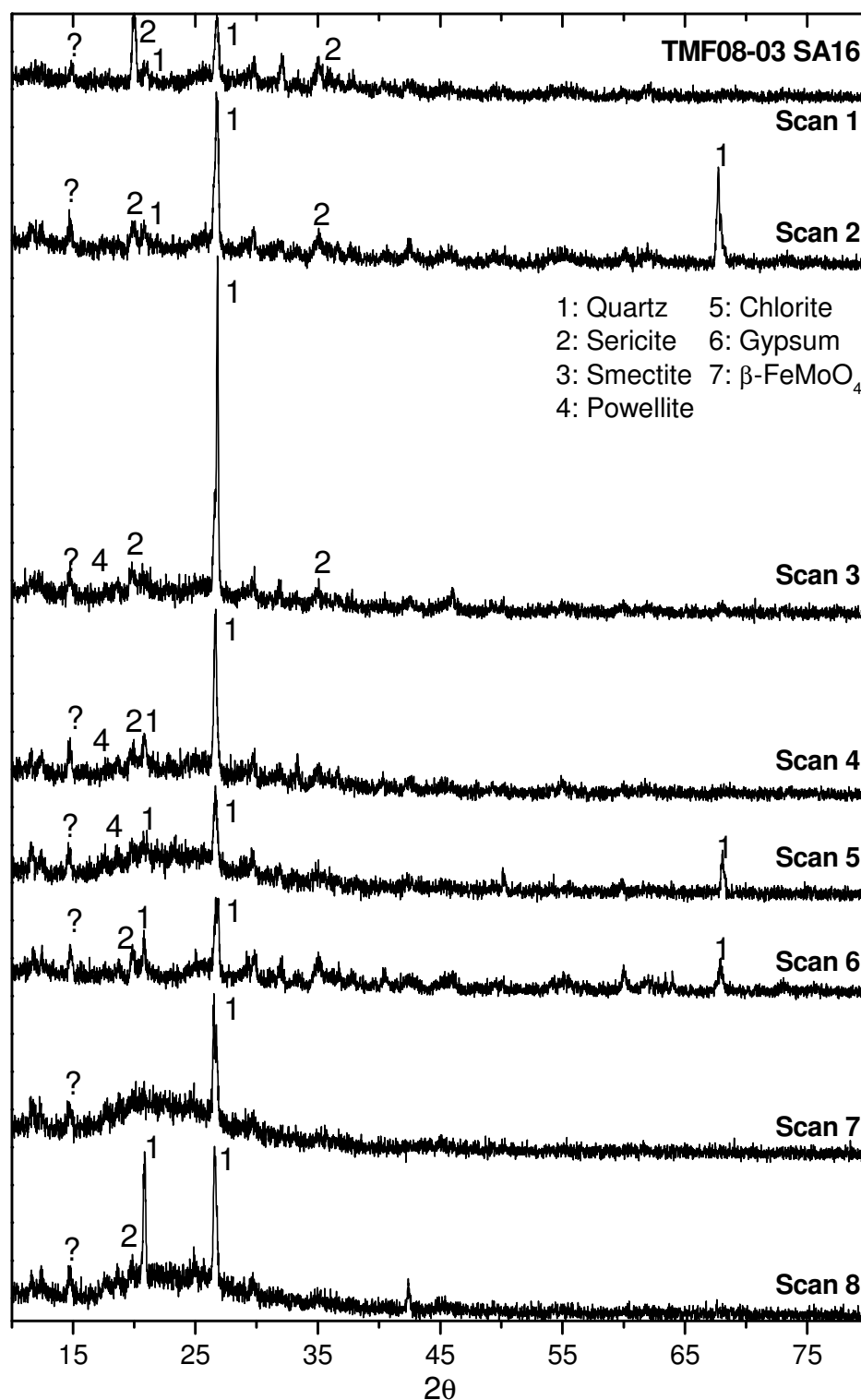


Figure S6: The μ XRD results from the TMF08-03 SA16 sample are presented. Peaks associated with the powellite phase were observed in Scans 3-5. Peaks that could not be identified are labeled with a “?”.

a)



b)



Figure S7: Photographs of the tailings samples from a) TMF08-01 SA09 and b) TMF08-03 SA16. The ruler markings indicate 1 mm intervals. These pictures provide a visual confirmation that the tailings samples are heterogeneous. The photographs also show that the heterogeneity of the samples varied widely. In general, the μ -XRD patterns from the highly heterogeneous samples (i.e. TMF08-01 SA09, cf. Figure S3) varied more than the less heterogeneous samples (i.e., TMF08-03 SA16, cf. Figure S6).

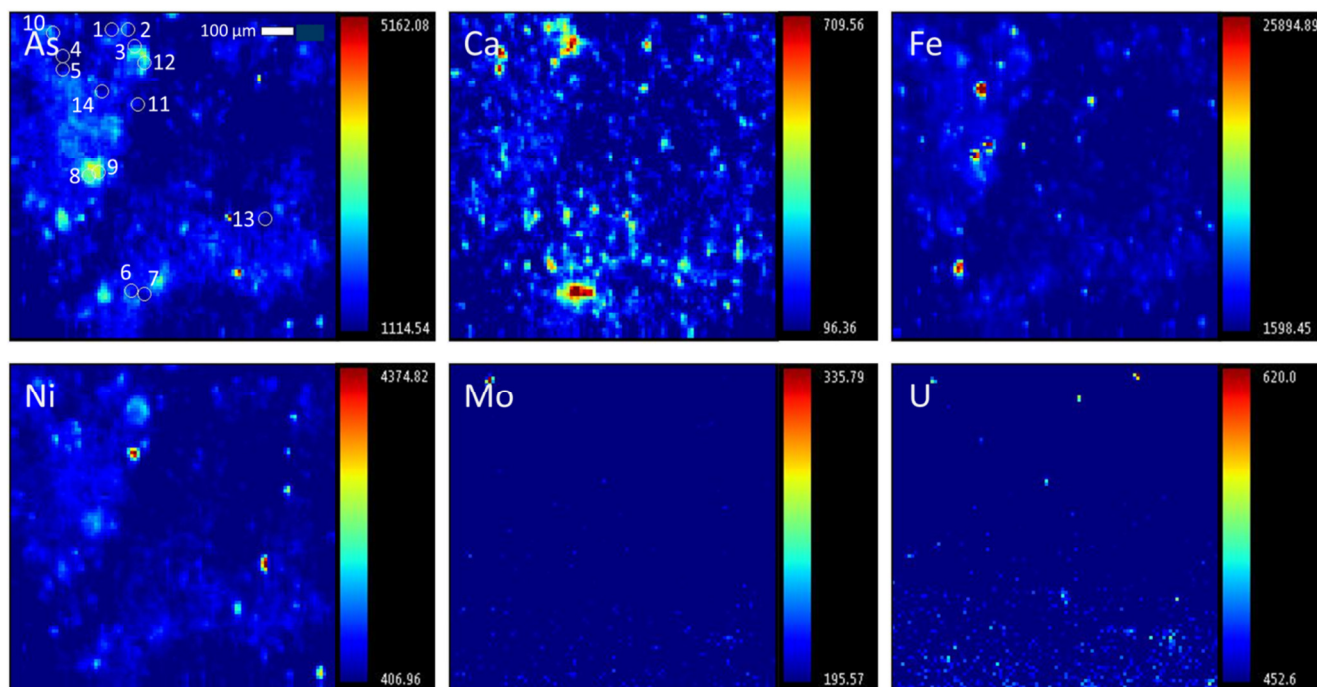


Figure S8: Fluorescence maps collected from the TMF08-01 SA19 sample. The spots where Laue diffraction patterns were collected are labeled according to their Scan number in the As map. No fluorescence signals from Mo or U were observed.

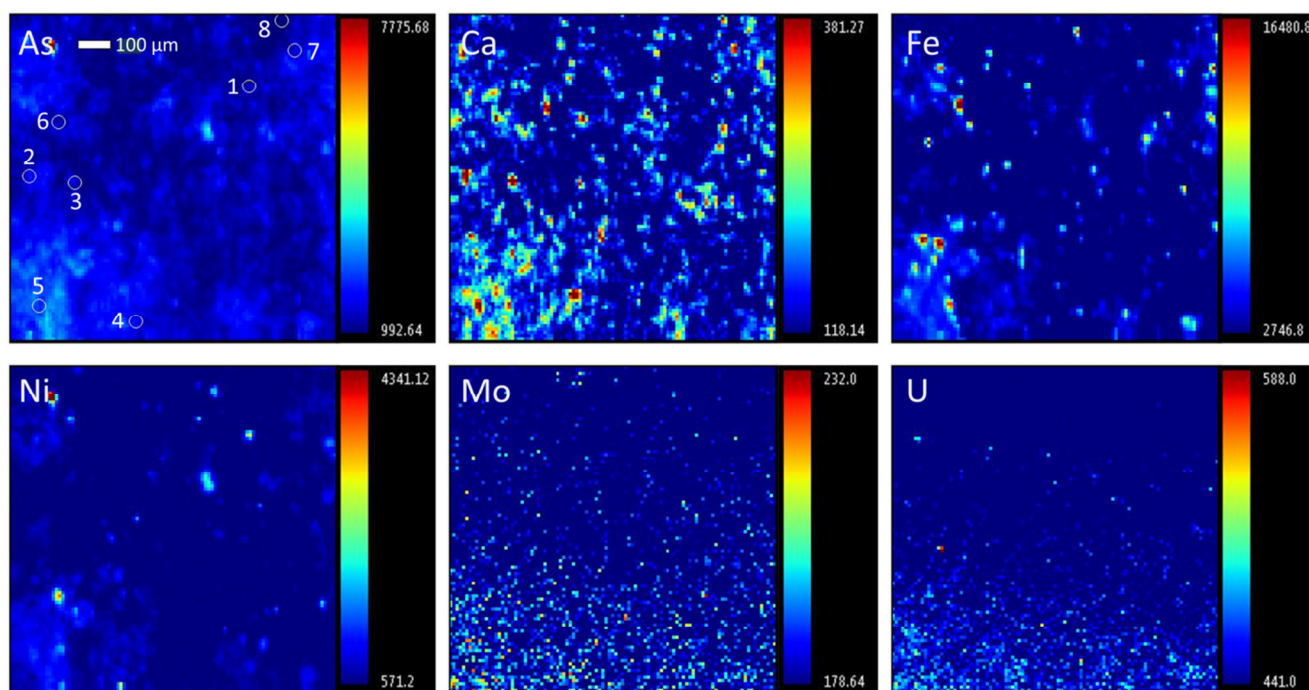


Figure S9: Fluorescence maps collected from the TMF08-03 SA16 sample. The spots where Laue diffraction patterns were collected are labeled according to their Scan number in the As map. No fluorescence signals from Mo or U were observed.

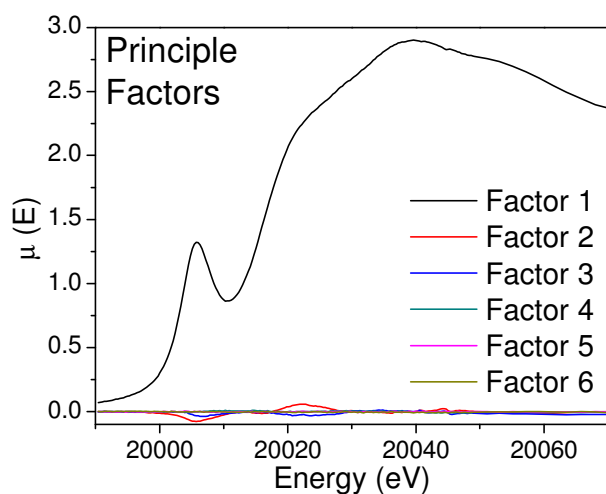


Figure S10: The principle factors calculated from the set of Mo K-edge XANES spectra from the tailings samples are presented. Only factors 1-3 appear to have significant amplitudes. It should be noted that, despite their appearance, the principle factors are only mathematical constructs and do not have physical meaning.

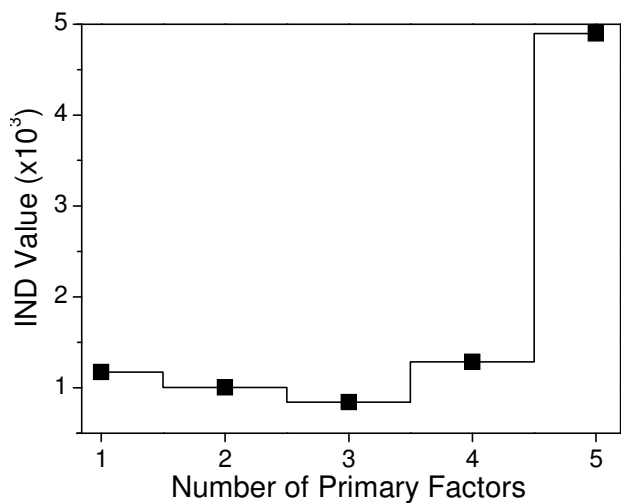


Figure S11: A plot of the calculated IND values as a function of the number of primary factors. The connecting lines are meant as a guide to the eye only. The IND value is minimized when the number of primary factors is 3, indicating that there are at most 3 Mo-bearing species in the tailings samples.

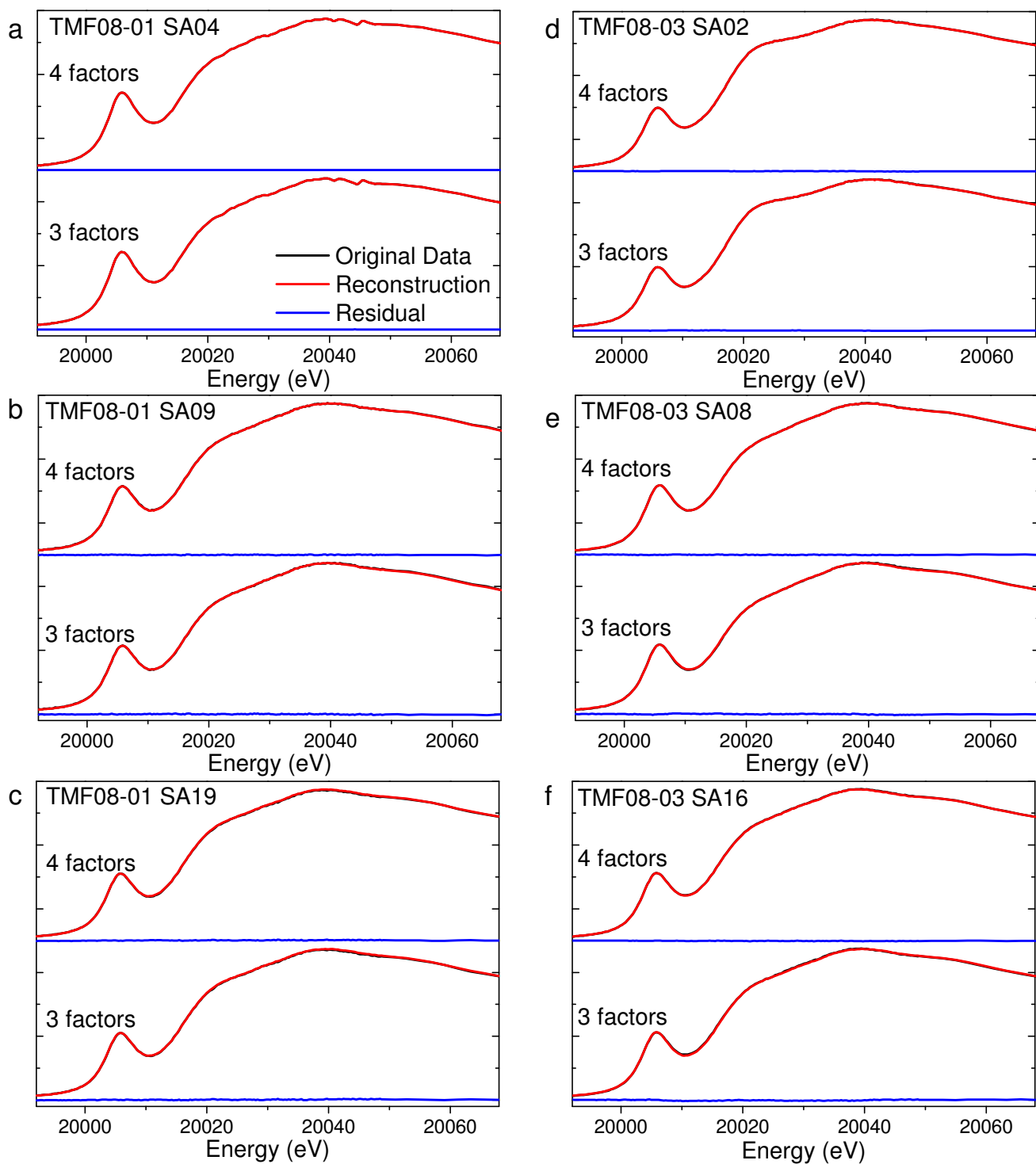


Figure S12: Reconstructions of the Mo K-edge spectra from (a) TMF08-01 SA04, (b) TMF08-01 SA09, (c) TMF08-01 SA19, (d) TMF08-03 SA02, (e) TMF08-03 SA08, and (f) TMF08-03 SA16 using either 3 or 4 factors. In all cases, no significant improvements were observed in the quality of the reconstructions when using more than 3 factors.

THE FATE OF ENTRAINED HYDROCARBON MATERIALS IN THE MCCLEAN LAKE OPERATION MILL TAILINGS

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ABSTRACT

Under the oxidizing conditions of the McClean Lake Tailings Management Facility (TMF) hydrocarbons entrained on the surface of tailings material from mill processes are gradually converted to soluble bicarbonate ion. This has been observed to be a process occurring over approximately three years likely encouraged by the presence of a microbiological community within the tailings mass and in the water column. A recent tailings sampling campaign has provided evidence that bicarbonate ion is participating in the conversion of gypsum to calcite. In older tailings, equilibrium with calcite appears to be controlling the terminal bicarbonate ion concentration.

INTRODUCTION

The McClean Lake Operation is an uranium mine and mill facility operated by AREVA Resources Canada Inc. It is located 700 km north of Saskatoon on the eastern edge of the Athabasca Basin. At McClean Lake, the JEB mill has been in operation since 1999.

The JEB mill is composed of a number of circuits that extract uranium from ore and produce a packaged product commonly referred to as yellowcake. Leaching is the hydrometallurgical process of dissolving uranium and other metals into solution from the ore by the addition of appropriate chemicals. In the leach circuit, the JEB mill employs both sulphuric acid, as a lixiviant, and hydrogen peroxide, as an oxidant, to liberate uranium from the ore. The leach discharge is cycled through the counter current decantation circuit which is responsible for washing the solids of soluble uranium. Flocculent is added in the circuit to segregate the solids. The uranium is then removed from the acidic leach solution through contacting an organic matrix in the solvent extraction process. Dissolved metals remain in the acidic sulphate waste solution, referred to as raffinate.

All process waste streams, both solid wastes and liquid raffinate, are treated concurrently by the tailings preparation circuit. The tailings preparation circuit employs a pre-treatment stage and a two stage neutralization process (Figure 1). The pre-treatment involves the addition of ferric iron and barium chloride to precipitate dissolved metals and peroxide to oxidize the slurry. During vigorous mixing, washed residual solids from the leach circuit are added to the raffinate and ferric iron solution, now referred to as tailings feed solution. The tails feed solution is then directed to the primary reaction tank, where slaked lime addition increases the solution pH from approximately 1 to 4. The stage 1 neutralization tank has a residency time of 90 minutes. The slurry from the primary tank is then transferred to the secondary reaction vessel. The secondary tank again uses slaked lime addition to increase the pH from 4 to a terminal pH of 7.5. The secondary neutralization tank also has a residency time of 90 minutes.

The neutralized slurry is then pumped to a high rate thickener, where the slurry reaches a density of 35% solids and is subsequently deposited in the tailings management facility (TMF) for long term disposal. Tailings lines from the mill run down the TMF ramp onto a floating walkway leading to the placement barge. The discharge pipe is suspended below the barge and the tailings are placed within a fluidized bed of tailings using a shallow injection tremie method. The deposited tailings flow in a laminar motion outwards from the deposition point to the outer edges of the TMF. As a result of the tailings preparation process, the deposited tailings are highly oxidized ($E_h = 200 \text{ mV}$ to 500 mV) and have a neutral pH of approximately 7.4.

Deposited tailings consist of three general components: ground host rock, clays and neutralized raffinate solids. The ground host rock is composed of relatively large grains of silica quartz with a mean particle size of approximately $110 \mu\text{m}$. Illites are the most abundant clay mineral, followed by kaolinite and chlorite. Included with the quartz or clay minerals may be occluded, partly occluded or large remnants of primary minerals that were not fully leached during the mill process and remained as a solid in the leach residue fraction of the tailings. Identified neutralized solids include monoclinic gypsum minerals and iron rich precipitates. Organic carbon material is adsorbed onto the surface of tailings solids. The organic material consists of residual amounts of synthetic flocculant (long chain polyacrylimides) and petroleum based hydrocarbons (kerosene, tricaprylamine and isodecanol) derived from the mill processing.

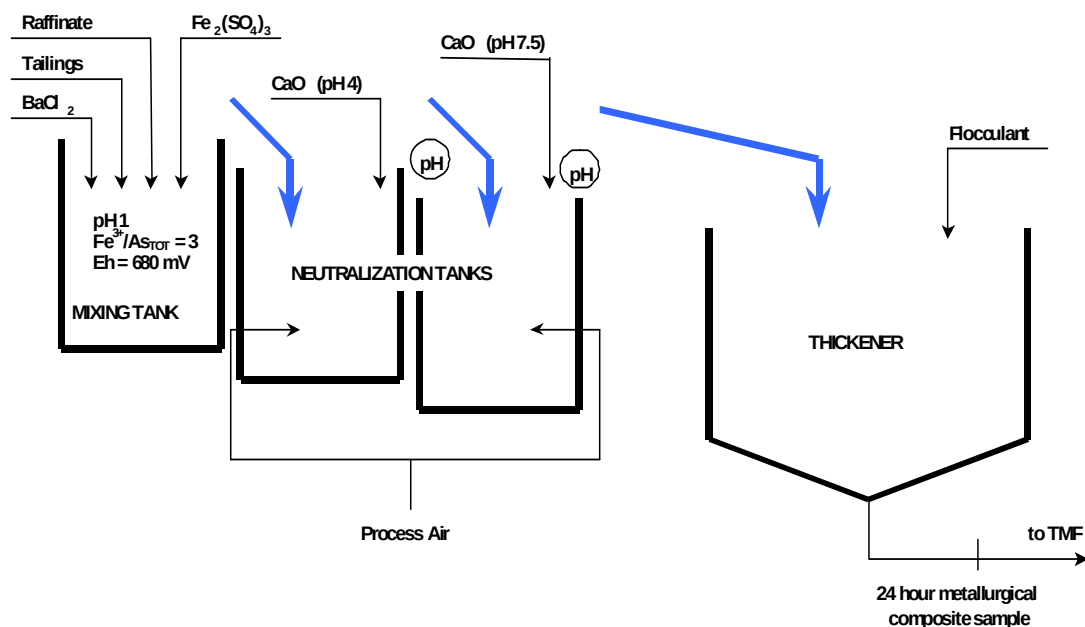


Figure 1 – Schematic diagram of tailings preparation process

METHODOLOGY

At the McClean Lake Operation, a comprehensive tailings research and monitoring program, known as the Tailings Optimization and Validation Program (TOVP) has been under way since 1999. Mill tailings have been continuously deposited in the TMF since July 1999. A component of the TOVP consists of tailings sampling campaigns where deposited tailings sediment and pore water are sampled for complete chemical analysis. Pore water chemistry analyses from the TMF sampling campaigns are used to evaluate the long-term behaviour of tailings pore water. Four deep bore holes were sampled on five separate occasions (2001, 2002, 2003, 2004 and 2008). These four boreholes were located at approximately the same coordinates for each sampling campaign. Tailings sediments and pore water were sampled at the same elevations for each of the bore holes. This methodology has facilitated the observation of aging characteristics of the tailings pore water and sediment.

RESULTS AND DISCUSSION

Evidence for the oxidation of organic carbon to bicarbonate

An increase in bicarbonate concentration over consecutive sampling campaigns has been observed in the TMF pore waters. Figure 3 compares the average concentration of bicarbonate from N11222; E5239 with sample elevation from 2001 to 2008. The bicarbonate concentrations have increased at each elevation as the sediment ages. The increase in soluble bicarbonate ions is facilitated by the presence of bacteria in the tailings which use the organic carbon as an electron source causing the oxidation of organic carbon to bicarbonate to occur.

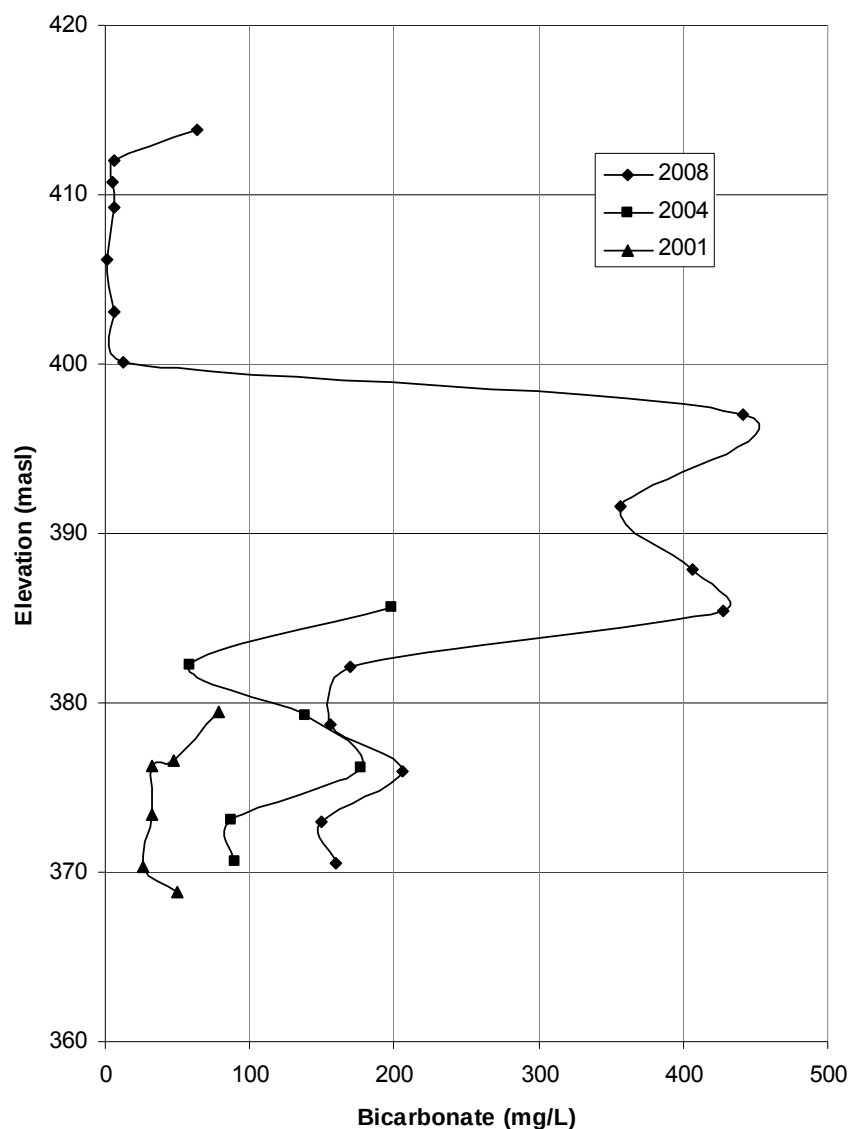


Figure 3 – Concentration of bicarbonate in tailings pore water from consecutive TMF sampling campaigns

Sources of organic carbon available for oxidation in the TMF include hydrocarbons (HC) entrained on the surface of tailings material from mill processes. Due to the specialized nature required, organic analyses have not been routinely conducted on the tailings sediment samples. However, hexane extractions followed by gas chromatography and infrared spectrometry were completed on five sediment samples from the 2001 TMF sampling campaign. The available organic analyses in these sediments are presented in Table 1.

A relatively small amount of hydrocarbon materials are lost to the mill process and adsorbed onto the surface of tailings solids. All samples but one showed extractable petroleum hydrocarbons with carbon numbers of 11 to 20. This would include kerosene and isodecanol. The hydrocarbon content of three of the samples ranged between 500 and 1100 $\mu\text{g/g}$. These are representative of expected values from organic

solvent loss for normal mill operation. The laboratory technician processing the sediment cores noticed a thin (<1 cm) dark layer in the sediment core and selected a sample at that elevation. That sample returned 32,000 µg/g extractable organic as listed in the table. This concentration of organic carbon is not representative of normal operation but does indicate the potential for the occurrence of thin localized seams of organically enriched sediments.

The quantity of four specific aromatic hydrocarbons was determined: benzene, ethylbenzene, toluene and xylene. The first three are commonly found in lighter petroleum distillates, such as gasoline, and none were present above the detection limit in the tailings sediments. Xylene is the heaviest aromatic carbon compound listed and is typically found in kerosene. Its presence in small quantities is indicative of a kerosene foot print in the TMF sediments.

Table 1 - Total petroleum hydrocarbon analyses in tailings sediments

Analysis	Location and Elevation				
	N11200	N11222	N11233	N11210	N11224
	E5289	E5239	E5345	E5264	E5358
	364.4 masl	376.4 masl	373.3 masl	369.0 masl	371.8 masl
extractable HC,C ₁₁ -C ₂₀ (µg/g)	610	590	32,000	<10	1100
extractable HC,C ₂₁ -C ₃₆ (µg /g)	<10	<10	<10	<10	<10
purgeable HC,C ₆ -C ₁₀ (µg /g)	<1	<1	<1	<1	<1
total Petroleum HC (µg /g)	610	590	32,000	<10	1100
benzene (µg /g)	<0.01	<0.01	<0.01	<0.01	<0.01
ethylbenzene (µg /g)	<0.01	<0.01	<0.01	<0.01	<0.01
toluene (µg /g)	<0.01	<0.01	<0.01	<0.01	<0.01
xylene (µg /g)	2.2	<0.01	2.3	<0.01	2.6

Figure 2 compares the extractable hydrocarbon content of two samples from Table 1 with the available bicarbonate concentrations from consecutive sampling campaigns at the same sample location. For these locations, by 2004 the accumulated bicarbonate concentrations reflect the quantity of extractable petroleum hydrocarbons measured in 2001. Oxidation appears to be complete within approximately 1000 days.

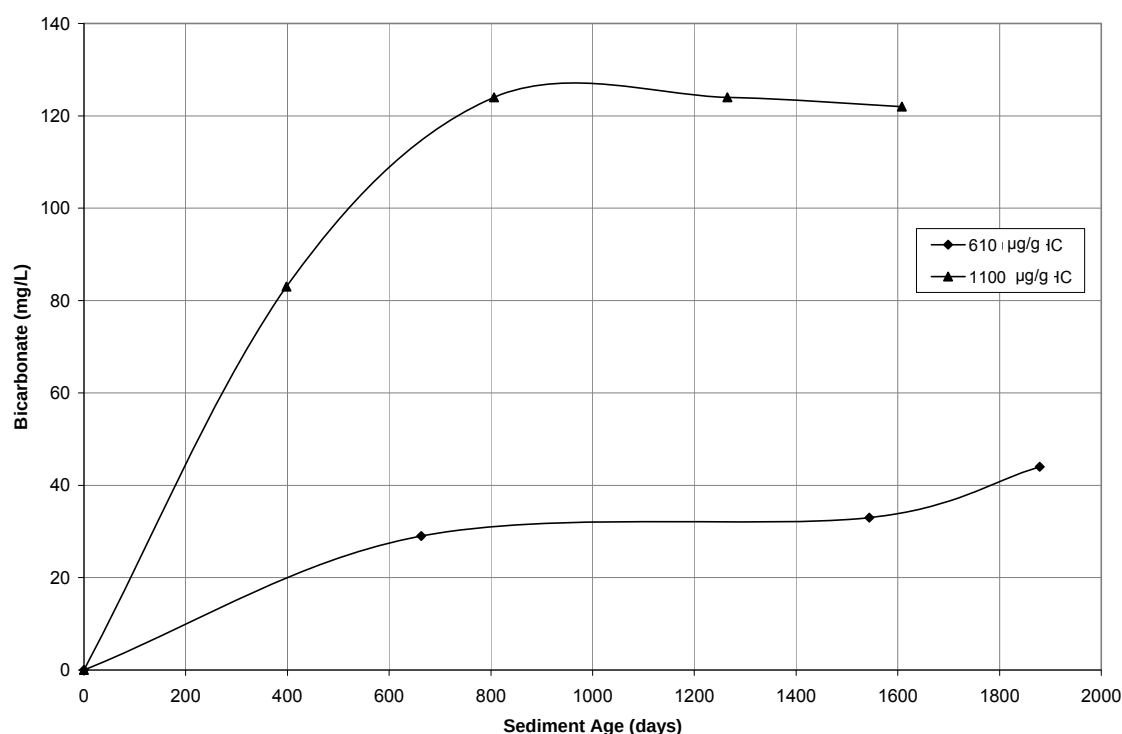


Figure 2 - Extractable hydrocarbon content and sediment age

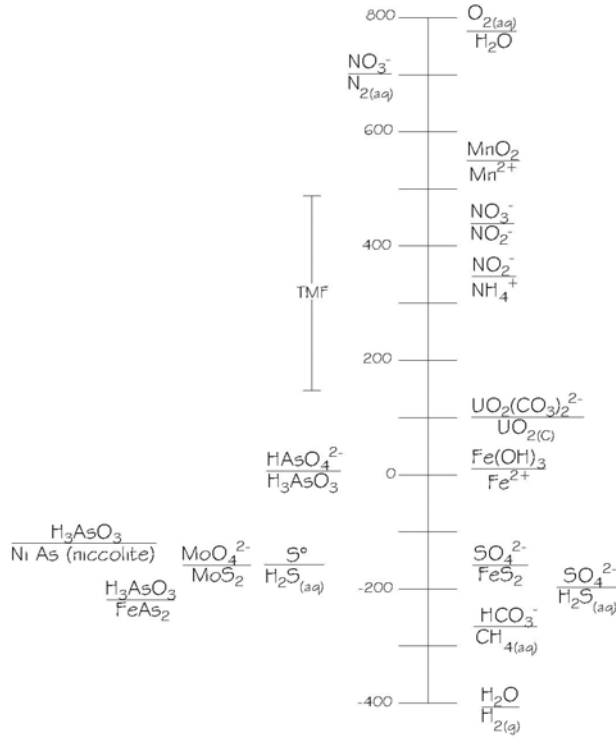
A secondary source of organic carbon is thought to be derived from phytoplankton and algae communities flourishing within the TMF surface waters although the amount of organic carbon from this source has not been quantified.

Chemical analyses of the TMF sediments and pore water included a number of minerals and dissolved species whose concentrations are directly or indirectly affected by oxidation reduction reactions. Knowledge of redox conditions is important for interpretation of the entire system. The redox conditions in the TMF have been defined by using different methods. The redox potential of the TMF pore water has been electrochemically measured with a platinum electrode, dissolved oxygen concentrations are measured and redox sensitive species such as arsenic (As^{3+} vs. As^{5+} , Fe^{2+} vs. Fe^{3+}) have been quantified. These results have shown that oxidizing conditions are prevalent throughout the TMF.

A redox ladder diagram, Figure 4 [2], shows the Eh values at pH 7 that correspond to different oxidation reduction reactions at chemical equilibrium. The range of Eh measurements completed to date for TMF pore waters is indicated in this Figure (+200 mV to +500 mV). Between these Eh values, species found in the pore water that have a range of stability include NO_3^- , NO_2^- , NH_4^+ , $[\text{UO}_2(\text{CO}_3)_2]^{2-}$, Mn^{2+} , MoO_4^{2-} , AsO_4^{3-} , Fe^{3+} , SO_4^{2-} , and HCO_3^- .

However in the TMF, minor concentrations of reduced hydrocarbon species have been observed as shown in Table 1. In Figure 4, the stability of organic carbon plots below the $\text{H}_2\text{O}/\text{H}_2(\text{g})$ boundary which indicates that reduced hydrocarbon species (generalized as organic carbon CH_2O) are not thermodynamically stable within the more oxidizing Eh range measured in TMF pore waters. Over time, redox sensitive species, such as organic carbon (represented as CH_2O), are evolving to more stable forms,

such as bicarbonate (represented by HCO_3^-) within the TMF sediments. The pore water therefore contains a mixture of thermodynamically stable and unstable redox-sensitive species. Redox processes may have very slow kinetics and it is unlikely that a system is in complete thermodynamic equilibrium with respect to measured oxidation potentials [1].



The theoretical Eh (mV) of some important oxidation reduction couples at equal molar ion concentrations except as indicated below at pH 7 and 25 °C. Other conditions are: $\text{NO}_3^-/\text{N}_2(\text{aq})$ at $\text{N}_2(\text{aq}) = 14 \text{ mg/L}$, $\text{NO}_3^- = 62 \text{ mg/L}$; MnO_2 (pyrolusite)/ Mn^{2+} at $\text{Mn}^{2+} = 1 \text{ mg/L}$; $\text{UO}_2(\text{CO}_3)_2^{2-}/\text{UO}_2$ (uraninite) at 10^{-8} mol/L dissolve U(VI) and $\text{P}_{\text{CO}_2} = 10^{-2} \text{ bar}$; $\text{Fe}(\text{OH})_3/\text{Fe}^{2+}$ at $\text{Fe}^{2+} = 1 \text{ mg/L}$ assuming K_{sp} for $\text{Fe}(\text{OH})_3 = 10^{-38.5}$; $\text{SO}_4^{2-}/\text{FeS}_2$ (pyrite) at $\text{Fe}^{2+} = 1 \text{ mg/L}$ and $\text{SO}_4^{2-} = 96 \text{ mg/L}$; $\text{MoO}_4^{2-}/\text{MoS}_2$ at $\text{MoO}_4^{2-} = 10^{-6} \text{ mol/L}$ and total S = $10^{-3.7} \text{ mol/L}$; and S^0 (native sulphur)/ $\text{H}_2\text{S}(\text{aq})$ at $\text{H}_2\text{S}(\text{aq}) = 108 \text{ mg/L}$ (10-1.5 mol/L). Modified after [2]. Arsenic solids data from [5]. Data for FeS_2 from [2]. Data for niccolite (NiAs) from [3, 4].

Figure 4 – Eh ladder diagram for important redox sensitive species in TMF pore waters

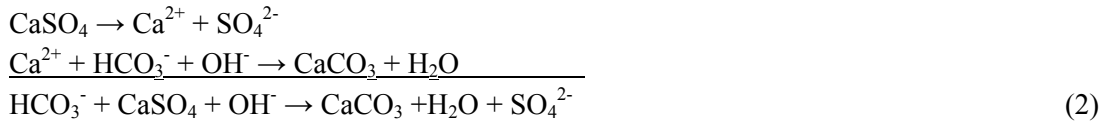
Conversion of Gypsum to Calcite

Due to the oxidation of organic carbon, bicarbonate concentrations have been shown to increase with tailings age, finally reaching an average plateau value of 168 mg/L. Increases in the concentrations of bicarbonate from sources other than the dissolution of calcite may supersaturate water with respect to calcite, causing it to precipitate [2]. It is apparent that calcite and gypsum equilibrium conditions are responsible for the final concentration of bicarbonate in the tailings pore water.

The oxidation of organic carbon facilitated by bacterial action:



causes the concentration of bicarbonate in the near neutral pH tailings pore water to increase. This increase causes common-ion driven calcite precipitation:



where there is a gradual equilibrium conversion of gypsum (CaSO_4) to calcite (CaCO_3). Calcium from gypsum dissolution, which is more soluble than calcite, derives the common ion effect reaction. Due to the highly consolidated nature, low temperature and lack of mixing in the lower tailings, this reaction proceeds slowly, first allowing bicarbonate to accumulate before it is consumed in the precipitation of calcite. This results in an initial rise in bicarbonate followed by a gradual decline to its equilibrium concentration. Both reactions produce increasing amounts of bicarbonate ion with depth.

This explanation is supported by observed concentration trends of sodium, calcium, sulphate and bicarbonate in the lower tailings pore water as shown in Figure 5. Calcium, sulphate and bicarbonate are direct products and reactants from Equation (2). Sodium participates by balancing the accumulation of anions in solution. The source of sodium is thought to be sodium adsorbed onto the ion exchange sites of clay minerals. Below 384 masl, the dissolution of gypsum has caused sulphate concentration to increase. Calcite precipitation has caused calcium and bicarbonate concentrations to decrease. At the same time, adsorbed sodium ions are released from adsorption sites to charge balance the solution.

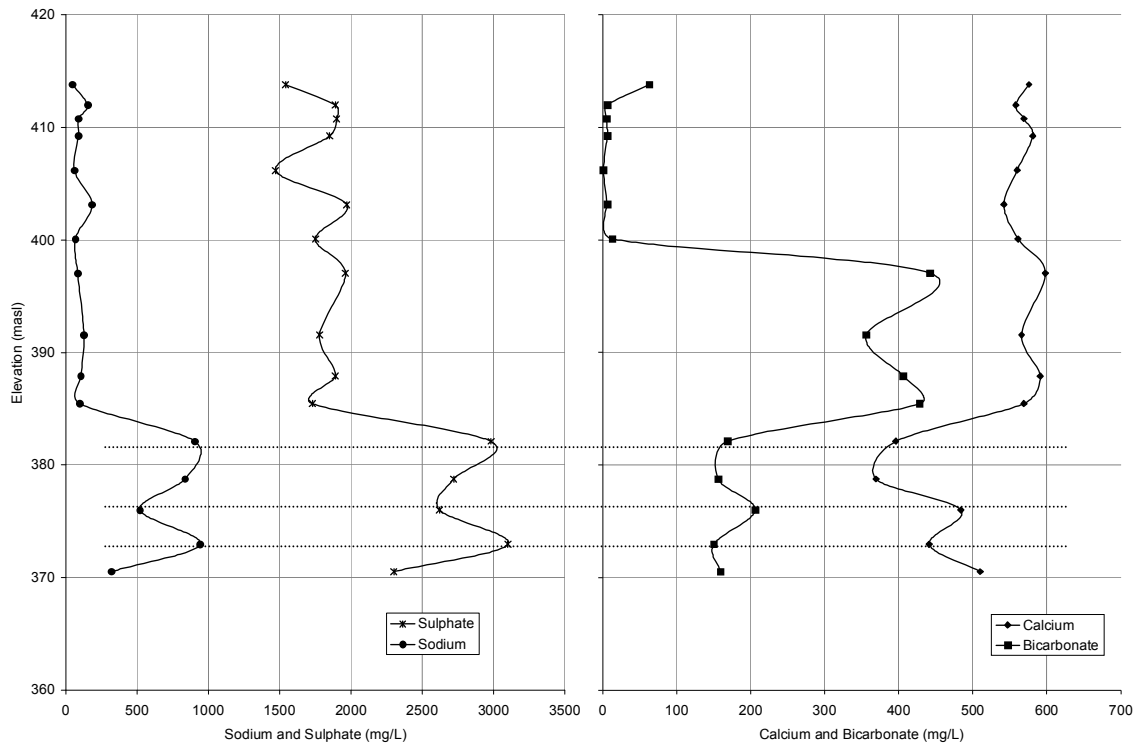


Figure 5 – Major ion concentrations in tailings pore water from 2008 sample location N11222; E5239

Modeling Equilibrium Bicarbonate Concentrations

To estimate the equilibrium concentration of bicarbonate in the tailings pore water the geochemical calculation program, PHREEQC [6] was used. The PHREEQC input included the complete pore water chemical analysis for each sample. The solution was allowed to equilibrate with excess gypsum while calcite was specified to precipitate by setting the saturation index to 0. No additional organic carbon was added to the simulation. The results of the equilibrium model are compared to actual TMF samples in Figure 7. Fixing the pH at 7.5 resulted in a modeled average equilibrium concentration of 92 mg/L from samples below 384 masl. It was found that the actual tailings bicarbonate concentrations were more closely modeled by allowing the pH to float while the solution was equilibrating. The modeled average equilibrium concentration with a floating pH below 384 masl was 158 mg/L.

The equilibrium concentration of bicarbonate in the TMF pore waters was determined by averaging the equilibrium concentration from each sample in location N11222, E5239 below a depth of 384 masl. Below this depth, it was assumed that the redox reaction of oxidation of organic matter and calcite precipitation reactions was approaching equilibrium. Equilibrium modelling of Equation (2) with PHREEQC supports a final bicarbonate concentration of approximately 168 mg/L.

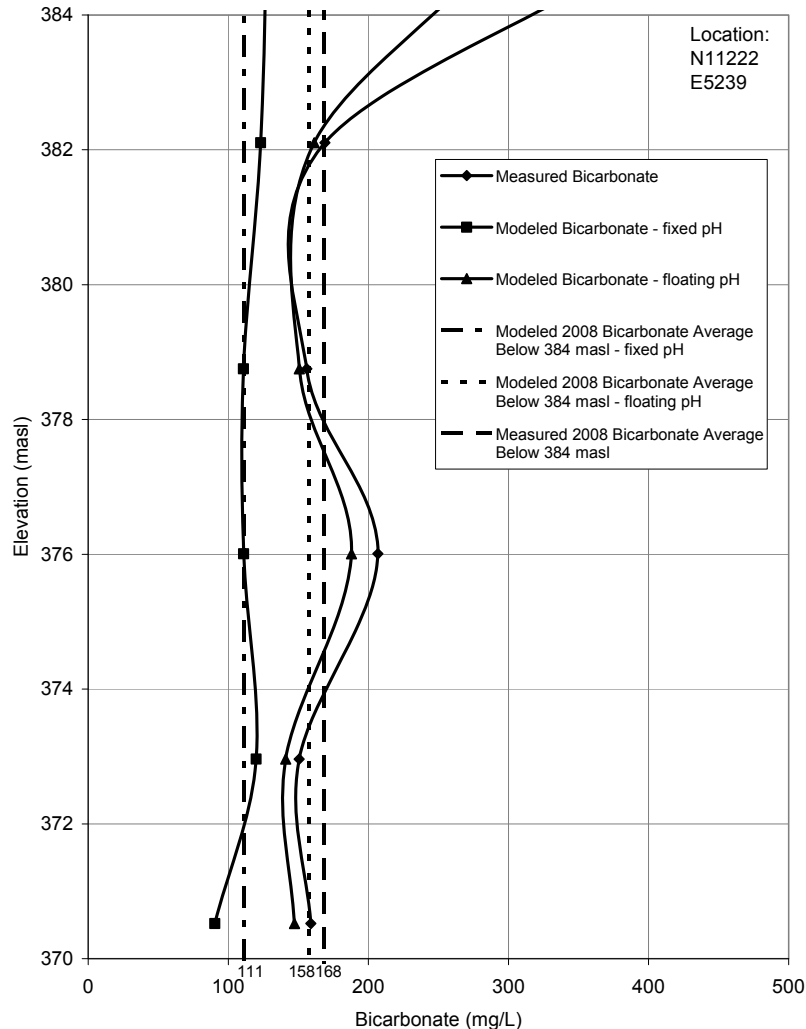


Figure 7 – Bicarbonate equilibrium modeling compared to measured TMF pore water concentrations

CONCLUSIONS

An increase in tailings pore water bicarbonate concentration has been observed over time through consecutive TMF sampling campaigns. This increase is due to the highly oxidized nature of deposited tailings which oxidizes organic carbon to bicarbonate which is thermodynamically stable at the neutral pH range of the TMF. Sources of organic carbon are mainly derived from the mill process and a secondary source is thought to be from the phytoplankton and algae communities flourishing in the TMF.

An upper bound on bicarbonate concentrations is established in older tailings. This equilibrium concentration is established by the dissolution of gypsum due to increasing bicarbonate concentrations and the subsequent precipitation of calcite. This reaction was modeled with PHREEQC to confirm a bicarbonate equilibrium concentration of 168 mg/L in the tailings pore water.

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Solubility products of amorphous ferric arsenate and crystalline scorodite ($\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$) and their application to arsenic behavior in buried mine tailings

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Abstract

Published solubility data for amorphous ferric arsenate and scorodite have been reevaluated using the geochemical code PHREEQC with a modified thermodynamic database for the arsenic species. Solubility product calculations have emphasized measurements obtained under conditions of congruent dissolution of ferric arsenate ($\text{pH} < 3$), and have taken into account ion activity coefficients, and ferric hydroxide, ferric sulfate, and ferric arsenate complexes which have association constants of $10^{4.04}$ ($\text{FeH}_2\text{AsO}_4^{2+}$), $10^{9.86}$ (FeHAsO_4^+), and $10^{18.9}$ (FeAsO_4). Derived solubility products of amorphous ferric arsenate and crystalline scorodite (as $\log K_{\text{sp}}$) are -23.0 ± 0.3 and -25.83 ± 0.07 , respectively, at 25°C and 1 bar pressure. In an application of the solubility results, acid raffinate solutions (molar $\text{Fe}/\text{As} = 3.6$) from the JEB uranium mill at McClean Lake in northern Saskatchewan were neutralized with lime to pH 2–8. Poorly crystalline scorodite precipitated below pH 3, removing perhaps 98% of the $\text{As}(\text{V})$ from solution, with ferric oxyhydroxide (FO) phases precipitated starting between pH 2 and 3. Between pH 2.18 and 7.37, the apparent $\log K_{\text{sp}}$ of ferric arsenate decreased from -22.80 to -24.67 , while that of FO (as $\text{Fe}(\text{OH})_3$) increased from -39.49 to -33.5 . Adsorption of $\text{As}(\text{V})$ by FO can also explain the decrease in the small amounts of $\text{As}(\text{V})(\text{aq})$ that remain in solution above pH 2–3. The same general $\text{As}(\text{V})$ behavior is observed in the pore waters of neutralized tailings buried for 5 yr at depths of up to 32 m in the JEB tailings management facility (TMF), where arsenic in the pore water decreases to 1–2 mg/L with increasing age and depth. In the TMF, average apparent $\log K_{\text{sp}}$ values for ferric arsenate and ferric hydroxide are -25.74 ± 0.88 and -37.03 ± 0.58 , respectively. In the laboratory tests and in the TMF, the increasing crystallinity of scorodite and the amorphous character of the coexisting FO phase increases the stability field of scorodite relative to that of the FO to near-neutral pH values. The kinetic inability of amorphous FO to crystallize probably results from the presence of high concentrations of sulfate and arsenate.

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1. Introduction

Scorodite is the least soluble arsenate phase in many mine tailings systems, and as such understanding and controlling its solubility is of special relevance in efforts to limit arsenic releases to tailings pore waters and to the environment. Published solubility products for amorphous and crystalline scorodite have generally been computed from

solubility measurements without properly taking into account the chemical composition and thermodynamic properties of the solutions at equilibrium. Also, the solubility of both crystalline and amorphous scorodite has usually been measured in solutions where equilibrium was approached from undersaturation only.

Published solubility data for amorphous ferric arsenate (AFA) to crystalline scorodite (scorodite(cr)) measured in starting solutions without dissolved Fe or As, are plotted versus pH in Fig. 1. The solubility data of Chukhlantsev (1956), Makhmetov et al. (1981), Dove and Rimstidt

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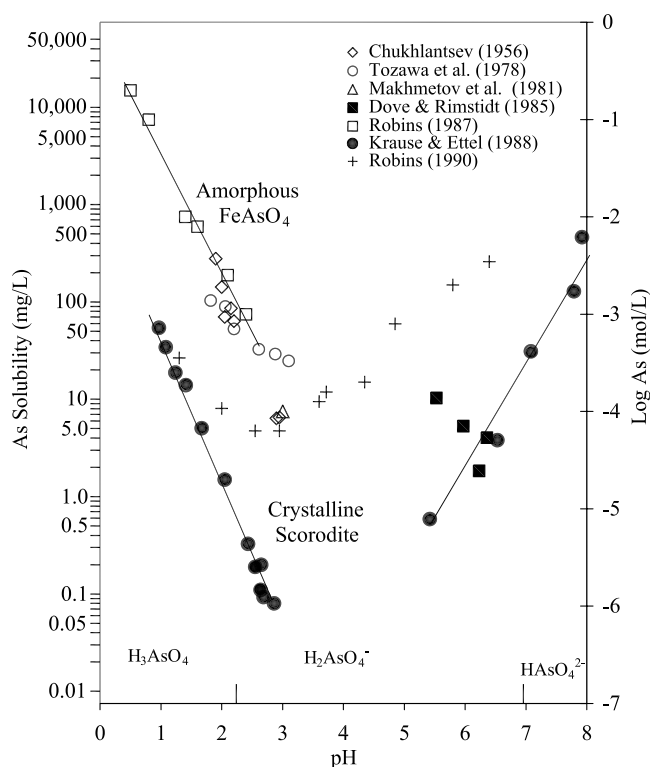


Fig. 1. Solubility of amorphous ferric arsenate and crystalline scorodite ($\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$) as reported by various observers. Only solubility experiments in which the initial Fe/As molar ratio was near unity are shown. The solubility data of Robins (1990) is for a partially crystalline scorodite. See text.

(1985), and Robins (1987), are given in Table 1. The data from Tozawa et al. (1978), Krause and Ettel (1988), and Robins (1990) are listed in Table 2. Lines drawn through the data points in Fig. 1, which show the general behavior of AFA and scorodite(cr) as a function of pH, have no theoretical or statistical significance. As discussed below, the solubility data of Robins (1990), which lies between that for AFA and scorodite(cr) is apparently for a scorodite phase of intermediate crystallinity.

In their calculation of solubility products, Chukhlantsev (1956) and Krause and Ettel (1988) ignored ion activity coefficients. Chukhlantsev (1956) also did not consider important ferric hydroxide and ferric sulfate complexes. Except for Zhu and Merkel (2001), most researchers have also ignored ferric and other metal arsenate complexes. Dove and Rimstidt (1985) neglected ferric arsenate complexes and made their four solubility measurements from pH 5.53 to 6.36, where scorodite dissolves incongruently with precipitation of a ferric oxyhydroxide phase (cf. Nordstrom and Parks, 1987; Robins, 1987). The incongruity of their experiments is evident from the molar Fe/As ratios of their final solutions which are given in Table 1. We have chosen not to use solubility measurements obtained under incongruent conditions in our determination of the solubility product of scorodite.

A somewhat similar reevaluation of published ferric arsenate/scorodite solubility data to ours was performed by Zhu and Merkel (2001). However, these authors

Table 1

Experimental data measured at 20–25 °C and PHREEQC model-computed ion activity products of ferric arsenate and ferric hydroxide for the ferric arsenate/scorodite solubility results of Chukhlantsev (1956), Makhmetov et al. (1981), Dove and Rimstidt (1985) and Robins (1987)

pH	As (mg/L)	Fe (mg/L)	Fe/As molar	Ferric arsenate log IAP	Ferric hydroxide log IAP
Chukhlantsev (1956)					
1.90	280	209	1.00	−22.45	−41.27
2.00	144	107	1.00	−22.64	−41.14
2.05	70	52	1.00	−22.72	−40.57
2.15	86	64	1.00	−22.68	−40.85
2.20	64	48	1.00	−22.61	−40.25
2.95	6.6	4.9	1.00	−23.24	−39.47
Makhmetov et al. (1981)					
3.0	7.5	6.1	1.10	−23.08	−38.68
Dove and Rimstidt (1985)					
5.53	10.3	1.14	0.15	−23.59	−37.65
5.97	5.3	0.81	0.21	−23.75	−37.02
6.23	1.8	1.76	1.28	−23.56	−35.21
6.36	4.0	2.68	0.89	−23.27	−35.38
Robins (1987)					
0.5	15370	11457	1.00	−22.69	−42.74
0.8	7631	5688	1.00	−23.12	−43.34
1.4	754	562	1.00	−22.93	−42.02
1.6	599	446	1.00	−22.59	−41.47
2.1	189	141	1.00	−22.31	−40.32
2.4	75	56	1.00	−22.41	−39.73

The data of Robins (1987) was read from a graph by Krause and Ettel (1988), assuming congruent dissolution of ferric arsenate, which was also assumed by Chukhlantsev (1956). All results are from dissolution experiments.

Table 2

Experimental data and PHREEQC model-computed ion activity products of ferric arsenate and ferric hydroxide for the ferric arsenate and scorodite solubility results of Tozawa et al. (1978), Krause and Ettel (1988), Robins (1990), and Nishimura and Robins (1996)

pH	As (mg/L)	Fe (mg/L)	SO ₄ (mg/L)	Na (mg/L)	Fe/As molar	Ferric arsenate log IAP	Ferric hydroxide log IAP	pH	As (mg/L)	Fe (mg/L)	Na (mg/L)	NO ₃ (mg/L)	SO ₄ (mg/L)	Fe/As molar	Ferric arsenate log IAP	Ferric hydroxide log IAP
Tozawa et al. (1978)								Robins (1990)								
1.82	130	73	1230		0.753	−23.11	−41.36	1.30	26.6	18.94	0.0	842		0.954	−24.78	−42.50
2.06	91	20	577		0.295	−23.18	−41.24	2.00	8.04	2.08	0.0	154		0.346	−24.30	−41.33
2.20	53	10	390		0.253	−23.33	−41.09	2.55	4.74	0.255	0.0	41.2		0.0723	−24.60	−41.17
2.61	33	2.3	123		0.094	−23.57	−40.93	2.95	4.74	0.075	0.0	15.6		0.0213	−24.93	−41.22
2.88	29	0.41	54.1		0.019	−24.19	−41.32	3.60	9.45	0.053	0.0	1.9		0.0075	−24.96	−40.97
3.10	25	0.17	26.4		0.009	−24.52	−41.40	3.72	11.9	0.029	0.0	0.6		0.0033	−25.21	−41.21
2.03	79	41	679		0.696	−23.01	−40.92	4.35	15.0	0.022	3.5	0.0		0.002	−25.31	−40.79
2.32	45	12	287		0.358	−23.11	−40.69	4.85	59.6	0.028	18.1	0.0		0.0006	−25.20	−40.77
2.68	37	2.2	97.8		0.080	−23.54	−40.91	5.80	150	0.885	49.0	0.0		0.0079	−23.70	−38.68
3.08	36	0.75	22.6		0.028	−23.87	−40.93	6.40	260	1.40	99.8	0.0		0.0072	−23.50	−38.01
Nishimura and Robins (1996)								Krause and Ettel (1988)								
1.48	17,500	1.00		67.5	7.67E-05	−24.97	−45.57	0.97	54	58.6	0		10,900	1.44	−26.22	−44.34
1.50	16,800	0.990		104	7.91E-05	−24.95	−45.52	1.08	34.2	41.3	0		8130	1.62	−26.17	−44.08
1.53	15,000	0.500		105	4.47E-05	−25.20	−45.72	1.24	19.1	21.1	0		5280	1.48	−26.15	−43.79
1.56	12,600	0.530		53.9	5.64E-05	−25.13	−45.57	1.41	14	13	0		3330	1.25	−25.90	−43.38
1.60	11,300	0.300		89.1	3.56E-05	−25.33	−45.70	1.67	5.1	5.31	0		1640	1.39	−25.83	−42.82
1.66	9440	0.340		119	4.83E-05	−25.19	−45.48	2.05	1.50	0.951	0		583	0.85	−25.84	−42.17
1.68	9090	0.340		143	5.02E-05	−25.17	−45.43	2.43	0.33	0.26	0		215	1.06	−25.89	−41.36
1.74	7680	0.070		168	1.22E-05	−25.78	−45.96	2.55	0.19	0.043	0		158	0.30	−26.54	−41.71
1.81	5710	0.050		129	1.17E-05	−25.84	−45.87	2.64	0.11	0.053	0		126	0.65	−26.45	−41.31
1.83	6370	0.070		230	1.47E-05	−25.68	−45.74	2.65	0.2	0.058	0		123	0.39	−26.15	−41.26
1.94	3990	0.040		154	1.34E-05	−25.80	−45.63	2.69	0.093	0.035	0		111	0.50	−26.57	−41.33
1.96	4250	0.035		211	1.10E-05	−25.84	−45.69	2.86	0.08	0.04	0		73.2	0.67	−26.21	−40.76
2.05	3670	0.034		253	1.24E-05	−25.77	−45.51	5.42	0.59	0.013	0.093		0	0.03	−25.59	−38.55
2.17	2170	0.030		155	1.85E-05	−25.71	−45.18	6.53	3.8	1.5	0.714		0	0.53	−23.50	−35.77
2.18	2410	0.025		200	1.39E-05	−25.79	−45.29	7.08	31	7.8	10.1		0	0.34	−22.78	−35.26
2.20	2660	0.025		256	1.26E-05	−25.77	−45.31	7.79	129	12	65.9		0	0.12	−22.60	−34.51
2.34	2010	0.020		247	1.33E-05	−25.77	−45.11	7.92	463	52.1	234		0	0.15	−21.96	−34.07
2.52	1570	0.013		253	1.11E-05	−25.84	−44.97									
2.64	1270	0.010		230	1.06E-05	−25.89	−44.85									
2.68	1110	0.010		205	1.21E-05	−25.88	−44.74									
2.79	934	0.010		188	1.44E-05	−25.83	−44.54									
3.29	704	0.030		187	5.72E-05	−25.24	−43.39									

Also given are concentrations of Na, NO₃, and/or SO₄ adjusted to attain charge balance in the modeling calculations. All the solubility data in the table are for dissolution experiments except for four precipitation experiments of Tozawa et al. (1978) for which the results have been italicized.

discounted the data of Krause and Ettel (1988) for crystalline scorodite, and did not consider the solubility studies of Robins (1990) or Nishimura and Robins (1996).

In this study (see also Langmuir et al., 1999; Mahoney and Langmuir, 2002) we have focused on the solubilities of the most and least soluble ferric arsenate phases, amorphous ferric arsenate (AFA), and well-crystallized scorodite (scorodite(cr)), respectively. Published solubility data has been reevaluated using the geochemical code PHREEQC (Parkhurst and Appelo, 1999), and considering all of the above corrections, with a modified thermodynamic data base for aqueous arsenic species discussed in this paper, and separately for comparison using revised arsenic acid constants proposed by Nordstrom and Archer (2003). We also show the application of the solubility results to scorodite precipitation during the laboratory neutralization of arsenic-rich acid mill tailings raffinates, and to measured arsenic concentra-

tions in the pore waters of buried uranium mill tailings at the JEB tailings management facility at McClean Lake in northern Saskatchewan, Canada.

2. Scorodite solubility

2.1. Auxiliary thermodynamic data

Equilibrium constants for arsenic and arsenous acids and stability constants for metal arsenate complexes used in the PHREEQC calculations of chemical equilibria are given in Table 3. Discussion of the selection and derivation of these constants is presented in Appendix A.

2.2. Studies considered in the revaluation

Because of the difficulty of making accurate activity coefficient corrections in solutions at ionic strengths above

Table 3

Equilibrium constants for As(III) and As(V) aqueous species and their reaction enthalpies used in PHREEQC calculations

Equilibrium constants for As(III) and As(V) aqueous species and their reaction enthalpies used in PHREEQC calculations					
Aqueous species	Reaction	Log <i>K</i>	Δ _r H° (kJ · mol ⁻¹)	Source ^b	
H ₂ AsO ₄ ⁻	H ₃ AsO ₄ = H ₂ AsO ₄ ⁻ + H ⁺	-2.24(-2.30) ^a	-7.11(-7.97)	(1)	
HAsO ₄ ⁻²	H ₃ AsO ₄ = HAsO ₄ ⁻² + 2H ⁺	-9.20(-9.29)	-3.77(-4.95)	(1)	
AsO ₄ ⁻³	H ₃ AsO ₄ = AsO ₄ ⁻³ + 3H ⁺	-20.70(-21.09)	14.35(13.25)	(1)(3)	
As(V)/As(III)	H ₃ AsO ₄ + 2H ⁺ + 2e ⁻ = H ₃ AsO ₃ + H ₂ O	18.90(19.35)	-125.6(-124.74)	(5)(2)	
H ₂ AsO ₃ ⁻	H ₃ AsO ₃ = H ₂ AsO ₃ ⁻ + H ⁺	-9.23(-9.17)	27.45(27.62)	(4)	
HAsO ₃ ⁻²	H ₃ AsO ₃ = HAsO ₃ ⁻² + 2H ⁺	-21.33(-23.27?)	59.4	(5)(6)	
AsO ₃ ⁻³	H ₃ AsO ₃ = AsO ₃ ⁻³ + 3H ⁺	-34.74(-38.27?)	85.8	(5)(6)	
H ₄ AsO ₃ ⁺	H ₃ AsO ₃ + H ⁺ = H ₄ AsO ₃ ⁺	-0.29		(4)	
$M^n + H_3AsO_4 = MH_mAsO_4^{(n+m-3)} + (3-m)H^+$ $n = 2, 3; m = 0-2$					
Aqueous species	Log <i>K</i>	Source ^b	Aqueous species	Log <i>K</i>	Source ^b
CaH ₂ AsO ₄ ⁺	-1.18(-1.24)	(7)	MnAsO ₄ ⁻	-14.57(-14.96)	(7)
CaHAsO ₄ [°]	-6.51(-6.60)	(7)	NiH ₂ AsO ₄ ⁺	-0.72(-0.78)	(7)
CaAsO ₄ ⁻	-14.48(-14.87)	(7)	NiHAsO ₄ [°]	-6.30(-6.39)	(7)
MgH ₂ AsO ₄ ⁺	-0.72(-0.78)	(7)	NiAsO ₄ ⁻	-14.36(-14.75)	(7)
MgHAsO ₄ [°]	-6.34(-6.43)	(7)	CuHAsO ₄ [°]	-5.52(-5.61)	(7)
MgAsO ₄ ⁻	-14.36(-14.75)	(7)	ZnHAsO ₄ [°]	-5.99(-6.08)	(7)
FeH ₂ AsO ₄ ⁺²	1.8(1.74)	(8)	CdHAsO ₄ [°]	-5.49(-5.58)	(7)
FeHAsO ₄ ⁺	0.66(0.57)	(8)	PbH ₂ AsO ₄ ⁺	-0.71(-0.77)	(7)
FeAsO ₄ [°]	-1.8(-2.19)	(8)	PbHAsO ₄ [°]	-6.16(-6.25)	(7)
FeH ₂ AsO ₄ ⁺	0.44(0.38)	(7)	AlH ₂ AsO ₄ ⁺²	0.83(0.77)	(7)
FeHAsO ₄ [°]	-5.66(-5.75)	(7)	AlHAsO ₄ ⁺	-1.91(-2.00)	(7)
FeAsO ₄ ⁻	-13.64(-14.03)	(7)	AlAsO ₄ ⁻	-6.6(-6.99)	(7)
MnHAsO ₄	-5.45(-5.54)	(7)			

^a Parenthetic log *K* and $\Delta_r H^\circ$ values for the arsenic and arsenous acid dissociation reactions are from Nordstrom and Archer (2003). Parenthetic values for metal arsenate complexes have been computed using the listed arsenic acid values from Nordstrom and Archer (2003). Question marks indicate estimates.

^b Sources: (1) Smith and Martell (1976), Baes and Mesmer p. 370 (1976); (2) Bard et al. (1985); (3) Barin (1995); (4) Wagman et al. (1982); (5) Parkhurst (1995); (6) Naumov et al. (1974); (7) Whiting (1992); (8) Robins (1990).

0.1 M, we reviewed only solubility studies performed at lower ionic strengths. In our analysis, we also emphasized studies in which the pH, total dissolved As(V) and Fe(III) concentrations were known, ligand or charge balancing cation concentrations were known or could be estimated, and the studies made measurements either under conditions of congruent dissolution (pH < 3) or conditions that could be extrapolated to conditions of congruent dissolution of AFA or scorodite. Results of the solubility studies of Tozawa et al. (1978), Krause and Ettel (1988), Robins (1990), and Nishimura and Robins (1996) which satisfied these requirements are given in Table 2. Although we modeled the solubility data for AFA reported by Chukhlantsev (1956), Makhmetov et al. (1981), and Robins (1987), which were presumably obtained under congruent conditions, for several reasons these studies were not emphasized in the selection of a log *K*_{sp} value for AFA. Chukhlantsev (1956) only measured the Fe concentration in their equilibrium solutions, and assumed that dissolved mAs = mFe, which is usually not the case as noted below. The data of Robins (1987) was read by Krause and Ettel (1988) from a graph published by Robins (1987), and it was also assumed that mAs = mFe. Only a single solubility result measured at pH 3 was reported by Makhmetov et al. (1981), and the details of their experiments are unknown.

Among the studies we have chosen for detailed consideration, Tozawa et al. (1978) prepared amorphous ferric arse-

nate (AFA) by mixing 0.1 M Fe₂(SO₄)₃ and 0.2 M Na₂HAsO₄ solutions, and adding 0.5 M NaOH solution to maintain the pH at 1.7. The Fe/As ratio of the precipitate was 1.02. Dissolution experiments involved suspending 0.2 g of the AFA in 25 ml of water, with the pH adjusted with H₂SO₄ or NaOH solutions. Runs were kept at 25 °C, and were shaken for 24 h before filtration and analysis of the filtrate for pH, and Fe and As concentrations. Precipitation experiments, which involved the mixing of 0.005 M Na₂HAsO₄ and 0.0025 M Fe₂(SO₄)₃ solutions, were run for 1 h before filtration and solution analysis.

Robins (1990) precipitated AFA by refluxing a mixture of 0.1 M Fe₂(SO₄)₃ and 0.1 M H₃AsO₄ solutions at pH 1 for several days at low temperature. He rolled a slurry of the solid in deionized water for two years with the pH adjusted by adding either HNO₃ or NaOH before measuring equilibrium. TEM micrographs at equilibrium showed that the amorphous phase had formed crystals of scorodite. XRD measurements were not made to confirm the general extent of crystallinity. The solubility results discussed below indicate that the equilibrium phase was a partially crystalline scorodite.

The scorodite used in the experiments of Krause and Ettel (1988) was precipitated material that had been heated in an autoclave at 160 °C for 24 h. The XRD pattern gave sharp peaks indicating well-crystallized scorodite (scorodite(cr)). In the solubility experiments, which were run

between pH 0.97 and 7.92, 5 g of scorodite(cr) was added to 50 mL of H_2SO_4 , or to NaOH solution to increase the pH above 3. The slurry was stirred continuously for 14 days at $23 \pm 1^\circ\text{C}$ to attain equilibrium.

Nishimura and Robins (1996) mixed 0.1 M $\text{Fe}_2(\text{SO}_4)_3$ and 0.2 M H_3AsO_4 solutions at 25°C and pH 2 to precipitate ferric arsenate. The precipitate was washed until no sulfate was detected. The vacuum-dried precipitate had a molar Fe/As ratio of 1.01. Dissolution experiments involved adding precipitates to 100 mL bottles containing 25 mL of arsenic acid of variable concentrations. The bottles were shaken for 1–3 months at 25°C to attain equilibrium. X-ray diffraction and SEM analyses of the solids at equilibrium indicated they had become well-crystallized scorodite.

2.3. Formation of well-crystallized scorodite: the role of temperature and solution Fe/As ratio

In systems where the Fe/As molar ratio equals or exceeds unity, scorodite formed at ambient temperatures is more soluble (more amorphous) than that formed or aged at or above 100°C (cf. Welham et al., 2000). In their experiments, Dutrizac and Jambor (1988) found that completely crystalline scorodite was only formed at temperatures above 105°C . At lower temperatures some residual amorphous material remained which increased the apparent solubility of the scorodite. In the study of Demopoulos et al. (1995) the Fe/As molar ratio ranged from 1 to 4. By seeding their solutions with scorodite in a solution at low supersaturation, Demopoulos et al. (1995) precipitated crystalline scorodite at temperatures as low as 80°C . Such precipitation occurred in the absence of a seed only at or above 95°C .

In contrast, working in arsenic acid solutions with a molar Fe/As ratio ranging from 1×10^{-5} to 8×10^{-5} ($\text{Fe/As} \ll 1$), Nishimura and Robins (1996) formed well-crystallized scorodite at 25°C by shaking a ferric arsenate precipitate for 1–3 months in the continued presence of arsenic acid. X-ray diffraction showed that after that time the initially amorphous material had become scorodite(cr). The solubility results of Nishimura and Robins (1996) discussed below confirm that their scorodite was well-crystallized.

2.4. Incongruent dissolution: The Fe/As ratio

There is general agreement that the solubility product of scorodite should be computed from measurements at a pH low enough so that scorodite dissolution is congruent (i.e., no Fe(III) oxyhydroxide is precipitated). Incongruent dissolution of scorodite can take place at any pH, with the pH of incongruity depending on Fe and As concentrations, complexing, and the Fe/As ratio of the solution.

The empirical solubility data and modeled results in Table 2 indicate that with increasing pH, there are four possible solubility regions with respect to ferric arsenate and ferric oxyhydroxide (FO) solids. With increasing pH, starting in acid ferric arsenate solutions in which the molar

Fe/As ratio is initially equal to unity, these solubility regions are:

1. Undersaturated with respect to a ferric arsenate phase if that phase has completely dissolved before the solution can attain saturation.
2. At equilibrium with respect to a ferric arsenate phase which has a fixed K_{sp} . As and Fe concentrations decrease with increasing pH.
3. At equilibrium with respect to an FO phase which has a fixed K_{sp} , and with a ferric arsenate phase of decreasing then increasing apparent solubility.
4. In apparent equilibrium with a ferric arsenate phase and an increasingly amorphous FO phase. The solubilities and apparent K_{sp} values of both phases increase with increasing pH.

Of particular interest has been the pH of incongruent dissolution, which is the pH value that separates solubility regions 2 and 3. In solubility studies in which scorodite(cr) or AFA are dissolved in solutions that lack initial Fe(III) or As(V) concentrations, this pH is the pH above which the solution attains saturation with and begins to precipitate an FO phase and the Fe/As ratio of the solution drops below unity. Krause and Ettel (1988) assumed that congruent dissolution of crystalline scorodite took place in their experiments at pH 2.43 and below. Robins (1990), and Zhu and Merkel (2001) based on a literature survey, concluded that AFA dissolution is incongruent above about pH 2. Dove and Rimstidt (1985) argued that their four scorodite(cr) solubility measurements made between pH 5.53 and 6.36 were congruent. However, as shown in Table 1, the molar Fe/As ratios of their final solutions did not equal unity, and their solutions were generally supersaturated with respect to an amorphous FO phase, indicating that their solubility experiments were incongruent.

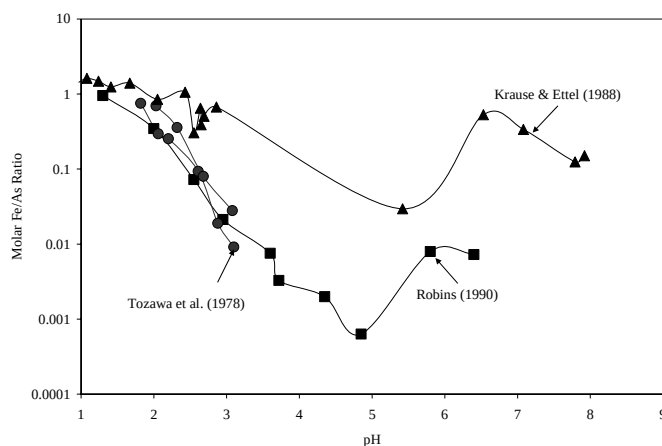


Fig. 2. Molar Fe/As(aq) ratio as a function of pH during dissolution/precipitation of ferric arsenate/scorodite in solutions initially free of dissolved As(V) and Fe(III) species. Data of Tozawa et al. (1978), Krause and Ettel (1988), and Robins (1990) are shown as solid circles, triangles, and squares, respectively.

Only Tozawa et al. (1978), Krause and Ettel (1988), and Robins (1990) (see Table 2) dissolved ferric arsenate or scorodite(cr) in solutions free of initial Fe(III) or As(V) species as a function of pH, and measured the aqueous concentrations of both Fe(III) and As(V) at equilibrium under conditions where a congruent solubility could be determined or estimated. Fig. 2 and Table 2 show that in the Tozawa et al. (1978) study of AFA solubility the Fe/As (aq) ratio decreases from 0.75 at pH 1.82 to 0.03 and below at pH 3.1 indicating incongruent dissolution throughout. Regression of their Fe/As versus pH data indicates that congruent dissolution of AFA in solutions without initial Fe(III) or As(V) (region 2) takes place below pH 1.82.

The ferric arsenate considered by Robins (1990) was partially crystalline. Table 2 and the Fe/As plot in Fig. 2 show that at his lowest pH of 1.30, Fe/As(aq) = 0.95, and the ratio decreased with increasing pH indicating incongruent dissolution.

In the dissolution experiments of Krause and Ettel (1988), the Fe/As ratio ranges from 1.25 to 1.62 between pH 0.97 and pH 1.67. The ratio drops to 1.06 and below 1.00 at pH 2.05 and above. Clearly, the authors' assertion that dissolution of scorodite was congruent for all runs between pH 0.97 and pH 2.43 is questionable. Based on their reported solubility, only about 0.3% or less of the scorodite in their runs would have been dissolved at equilibrium. The molar Fe/As ratio of their synthetic scorodite was 1.073 and dropped during dissolution, indicating the initial presence of an excess of dissolved Fe(III), which decreased with dissolution. This may explain why aqueous Fe/As ratios in their lowest pH runs exceeded unity.

Nishimura and Robins (1996) studied scorodite solubility in arsenic acid solutions in which the Fe/As ratio was near 10^{-5} . The plot of their Fe/As ratio versus pH in Fig. 3 shows rapidly decreasing ratios with pH below pH 1.74, constant ratios from pH 1.74 to 2.79, and an increased ratio at pH 3.29. Probable reasons for this behavior are discussed in Section 2.6.

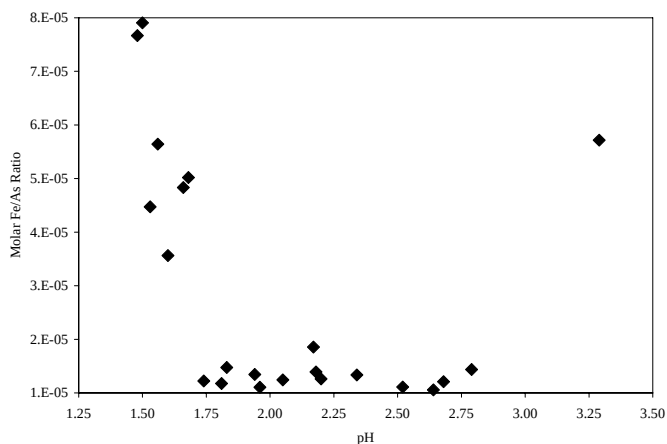


Fig. 3. Molar Fe/As(aq) ratio as a function of pH during the scorodite(cr) dissolution experiments of Nishimura and Robins (1996).

2.5. Stability of ferric oxyhydroxide phases

The ion activity product (IAP) of $[\text{Fe}^{3+}][\text{OH}^-]^3$ computed from the ferric arsenate/scorodite solubility runs of Tozawa et al. (1978), Krause and Ettel (1988), Robins (1990), and Nishimura and Robins (1996), is given in Table 2 and plotted versus pH in Fig. 4. At the lowest pH values of Krause and Ettel (1988) and Robins (1990) and in all of the experiments of Nishimura and Robins (1996), log IAP increases with increasing pH indicating undersaturated conditions with respect to FO.

At intermediate pHs, log IAP values for FO computed from the results of Tozawa et al. (1978), Robins (1990) and Krause and Ettel (1988) are relatively independent of pH. Thus, the average log IAP is -41.15 ± 0.25 for 22 experiments, which include the six dissolution and four precipitation experiments of Tozawa et al. (1978) between pH 1.82 and 3.08, the seven dissolution experiments of Robins (1990) between pH 2.00 and 4.85, and the five dissolution experiments of Krause and Ettel (1988) between pH 2.43 to 2.69. This average value is plotted as a dashed horizontal line in Fig. 4. It indicates that the FO phase precipitated between about pH 1.8 and 4.74 by incongruent dissolution of ferric arsenate solids is partially crystalline.

Above roughly pH 4.7 (the start of region 4), log IAP values for FO computed from the solubility data of Robins (1990) and Krause and Ettel (1988) lie on a line of decreasing stability (increasing solubility) with increasing pH in Fig. 4. According to Langmuir (1997) and others the log IAP of amorphous FO in systems low in arsenic (and sulfate) is -37 . Larger values than this, which occur above pH 6 in Fig. 4, indicate supersaturated conditions with respect to amorphous FO. The precipitation of an FO phase under these conditions has probably been kinetically inhibited by the abundance of arsenate and/or sulfate in the experiments (Swash and Monhemius, 1994; Langmuir et al., 1999).

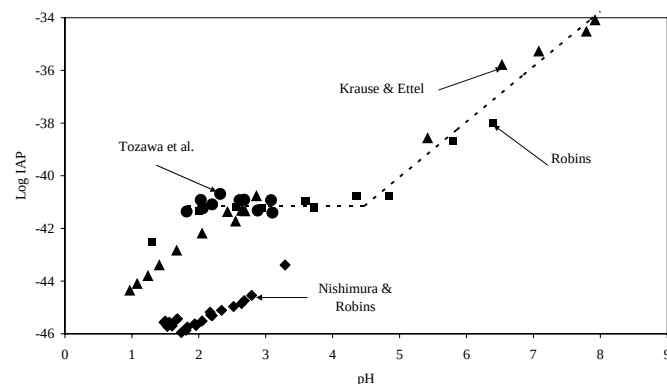


Fig. 4. Log IAP of ferric hydroxide in ferric arsenate/scorodite solubility studies of Tozawa et al. (1978)(circles), Krause and Ettel (1988)(triangles), Robins (1990)(squares), and Nishimura and Robins (1996) (diamonds). The dashed horizontal line is drawn at the average log IAP value of -41.2 between pH 1.8 and 4.7. The dashed sloping line is a linear regression of the 8 values at and above pH 4.7. See text.

2.6. Solubility of amorphous ferric arsenate and crystalline scorodite

If we wish to define the pH values that bound scorodite solubility regions 1–4, studying changes in the Fe/As (aq) ratio by itself is not as effective as also examining concurrent changes in the ion activity products of ferric hydroxide and ferric arsenate as a function of pH. Shown in Fig. 5 are log IAP values for $[\text{Fe}^{3+}][\text{AsO}_4^{3-}]$ plotted versus pH computed from the study results of Krause and Ettel (1988), Tozawa et al. (1978), and Robins (1990), along with vertical lines defining the four solubility regions introduced in section 2.4. The trend in log IAP values computed from the results of Krause and Ettel (1988) suggests that the three solubility runs between pH 0.97 and 1.24 were undersaturated with respect to crystalline scorodite and so are in region 1. The greater and constant log IAP values obtained between pH 1.41 and 2.43 represent equilibrium with respect to scorodite(cr) (region 2). The average and standard deviation of these four values is $\log \text{IAP} = -25.86 \pm 0.03$. When results of the same four runs are modeled using the stability constants for arsenic acid species and complexes based on Nordstrom and Archer (2003), the result for scorodite(cr) is $\log \text{IAP} = -26.22 \pm 0.03$. From pH 1.41 to 2.43 the dominant arsenate complex is H_2AsO_4^- , which comprises 93–96% of total arsenic. The dominant ferric complexes are $\text{Fe}(\text{SO}_4)_2^-$ and FeHAsO_4^+ , which comprise from 41–89% and 7–56% of total iron, respectively.

In region 3 of the study of Krause and Ettel (1988), the log IAP values for ferric arsenate are more negative than the average value in region 2, while the log IAP value for FO rises from -41.7 at pH 2.55 to -40.8 at pH 2.86, consistent with precipitation of increasingly amorphous FO in this pH range. Above pH ~ 4.7 (see Fig. 4) As(V) and Fe(III) concentrations rise, indicating increasing solubilities of scorodite and FO.

Log IAP values for ferric arsenate computed from the results of Tozawa et al. (1978) and Robins (1990), are also shown in Fig. 5, along with the suggested limits of the four

solubility regions for each study. In the amorphous ferric arsenate (AFA) dissolution experiments of Tozawa et al. (1978), which were all run in solubility region 3, the log IAP for FO averages -41.08 ± 0.24 , and the molar Fe/As(aq) ratio decreases from 0.75 to 0.009 between pH 1.82 and pH 3.1, respectively, indicating incongruent dissolution. In the same pH range, log IAP values for ferric arsenate decrease from -23.11 to -24.52 . In four precipitation experiments from pH 2.03 to pH 3.08, these authors found Fe/As dropped from 0.70 to 0.03, and the ferric arsenate log IAP from -23.01 to -23.87 , respectively. Assuming conditions for congruent dissolution exist below pH 1.82, where Fe/As = 1, and that only for such conditions can a reliable log K_{sp} value for AFA be obtained, we conclude that log $K_{\text{sp}}(\text{AFA})$ is greater than -23.01 . In the absence of reliable solubility measurements for AFA, we will assume, somewhat arbitrarily, that the log K_{sp} for AFA is -23.0 ± 0.3 (-23.3 ± 0.3 if we assume the arsenic acid constants of Nordstrom and Archer, 2003). This compares favorably with average log K_{sp} values in Table 1 computed from the less reliable data of Chukhlantsev (1956), Robins (1987) and Makhmetov et al. (1981), which are -22.62 ± 0.10 , -22.67 ± 0.31 , and -23.08 , respectively. In the runs of Tozawa et al. (1978), the dominant aqueous complexes were H_2AsO_4^- , and secondarily FeHAsO_4^+ , which together comprised 84% or more of the iron and arsenic species in solution. FeSO_4^+ , equaled about 16% or less of the dissolved Fe(III) concentration.

The plot of log IAP values in Fig. 5 computed from the results of Robins (1990), shows that the log IAP of ferric arsenate increases from -24.8 at pH 1.30, where Fe/As = 0.95, to -24.3 at pH 2.00, where Fe/As = 0.35. Over the same pH range the log IAP for FO increases from -42.5 to -41.3 . These values probably indicate undersaturated conditions with respect to ferric arsenate at pH 1.30 (region 1), and incongruent dissolution of ferric arsenate at pH 2.00 (region 3). If congruent dissolution of ferric arsenate was possible in these experiments, it would occur only in a narrow pH range near but above pH 1.3 and below pH 2.0. Assuming this assumption is correct, the log IAP (log K_{sp}) value of the ferric arsenate studied by Robins (1990) is between -24.3 and -24.8 , suggesting that the phase is a partially crystalline scorodite. From pH 2.00 to pH 4.35 (in region 3) the log IAP value for ferric arsenate decreases from -24.3 to -25.3 , respectively. Its value further increases at higher pH in region 4.

Nishimura and Robins (1996) measured the solubility of scorodite in 22 experiments between pH 1.48 and 3.29. Concentrations of dissolved As(V) greatly exceeded those of Fe(III) at equilibrium, with an Fe/As ratio in solution near 10^{-5} . The solubility data (including pH, and total dissolved As(V) and Fe(III) concentrations) were input into PHREEQC, using the arsenic acid constants of Smith and Martell (1976), and the stability constants for arsenate complexes consistent with these acid constants from Table 3. It was found that all solutions were deficient in cations, with an average charge balance error of -32% . The IAP for

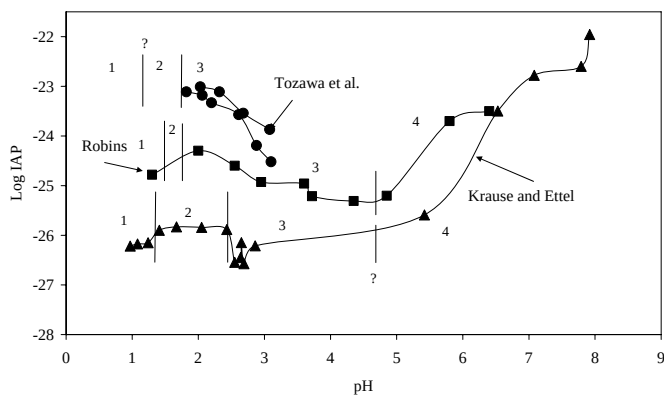


Fig. 5. Log IAP of ferric arsenate based on the solubility data of Tozawa et al. (1978), Krause and Ettel (1988), and Robins (1990). The lines have no statistical significance. Regions 1, 2, 3, and 4 for each data set are described in the text.

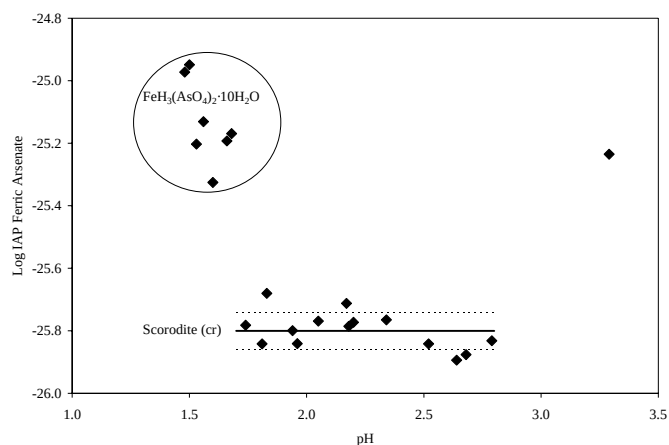


Fig. 6. Log IAP for ferric arsenate computed from the scorodite(cr) dissolution results of Nishimura and Robins (1996). Horizontal lines are drawn to show the average and ± 1 standard deviation of the average log IAP value for the 14 measurements of scorodite(cr) solubility. Circled points at low pH probably represent the solubility of $\text{FeH}_3(\text{AsO}_4)_2 \cdot 10\text{H}_2\text{O}$.

scorodite ($[\text{Fe}^{3+}][\text{AsO}_4^{3-}]$) was computed both ignoring this charge balance error, and introducing Na^+ to adjust the charge balance to zero. The log IAP computed with the corrected charge balance is plotted versus pH in Fig. 6. The figure shows relatively constant log IAP values for the 14 runs between pH 1.74 and 2.79, and larger log IAP values for runs below pH 1.74, and a run above pH 2.79. The higher solubility observed below pH 1.74 probably reflects equilibration with $\text{FeH}_3(\text{AsO}_4)_2 \cdot 10\text{H}_2\text{O}$, a phase identified by Nishimura and Robins (1996) in their experiments at slightly lower pHs. The increased log IAP value computed from the data at pH 3.29 corresponds to a further reduction in dissolved arsenic and an increase in iron concentrations with a resultant log IAP for FO of -43.4 which may indicate the precipitation of a relatively crystalline FO phase.

For the 14 data points between pH 1.74 and 2.79, which appear to be at equilibrium with respect to scorodite(cr), we obtain an average of $\log \text{IAP} = -25.80 \pm 0.06$ and $\log \text{IAP} = -25.79 \pm 0.06$, correcting and not correcting for the charge balance error, respectively. The low standard deviation of these averages provides confidence in the result. The same calculation performed using the arsenic acid constants of Nordstrom and Archer (2003) gives an average log IAP of -26.02 ± 0.05 for scorodite(cr) corrected for

charge balance. Solution speciation calculations indicate that in the 14 runs more than 99% of dissolved As(V) is present as $\text{H}_2\text{AsO}_4^{-1}$, and more than 99% of dissolved Fe(III) occurs as the FeHAsO_4^+ and $\text{FeH}_2\text{AsO}_4^{+2}$ complexes. This log K_{sp} value for crystalline scorodite is in excellent agreement with $\log K_{\text{sp}} = -25.86 \pm 0.03$ obtained from our analysis of the data of Krause and Ettel (1988). The average of these values, which we adopt for crystalline scorodite, is $\log K_{\text{sp}} = -25.83 \pm 0.07$. If we use the arsenic acid constants of Nordstrom and Archer (2003), the average value for crystalline scorodite is instead -26.12 ± 0.06 . The recommended solubility products for ferric arsenate and scorodite determined in this study are listed in Table 4.

2.7. Phase relations of ferric arsenate and FO phases in $\text{Fe}/\text{As} \sim 1$ systems

The relative thermodynamic stability of ferric arsenate and ferric hydroxide (FO) is obviously complicated by the fact that these phases vary widely in stability. Following discussion only applies to solubility studies in which the system Fe/As ratio is near unity, and focuses on explaining the data for scorodite(cr) as reported by Krause and Ettel (1988). The solid curves in Fig. 7 define As and Fe concentrations at equilibrium with scorodite(cr) and FO, computed with PHREEQC when we fix their $-\log K_{\text{sp}}$ values at 25.83 and 41.2, respectively. Also plotted are measured As and Fe concentrations from Krause and Ettel (1988) (Table 2), and the pH ranges of regions 1–4.

As discussed above, scorodite solubility region 1 occupies a low pH range where the solution is undersaturated with respect to scorodite(cr). In region 2, the solution is at equilibrium with scorodite(cr). Regions 1 and 2 define pH conditions where scorodite(cr) should dissolve congruently.

If scorodite(cr) and the FO phase behaved as if they had the fixed solubilities assigned to them in Fig. 7, scorodite(cr) would dissolve incongruently above $\text{pH} \sim 2.5$ (above point B). Both phases would then coexist, but arsenic values would rise along the scorodite(cr) curve, while $\text{Fe}(\text{aq})$ values declined along the FO solubility curve. Although declining $\text{Fe}(\text{aq})$ values roughly follow the FO solubility curve drawn for a constant $-\log K_{\text{sp}}$ of 41.2, this is obviously not how the arsenic behaves. Above pH 2.5 in region 3, the solubility data of Krause and Ettel (1988) and

Table 4

Recommended solubility products of amorphous ferric arsenate, a partially crystalline scorodite, and scorodite(cr) computed assuming thermodynamic data for arsenic acid species and arsenate complexes based on this study, and based on Nordstrom and Archer (2003)

Phase	$\log K_{\text{sp}}$		Source of $\log K_{\text{sp}}$ value
	This study	Nordstrom and Archer	
Amorphous ferric arsenate	-23.0 ± 0.3	-23.3 ± 0.3	Extrapolated from the measurements of Tozawa et al. (1978)
Partially crystalline scorodite	-24.3 to -24.8	-24.6 to -25.1	Interpolated from the measurements of Robins (1990)
Crystalline scorodite	-25.83 ± 0.07	-26.12 ± 0.06	Average of average values computed from studies of Krause and Ettel (1988) and Nishimura and Robins (1996)

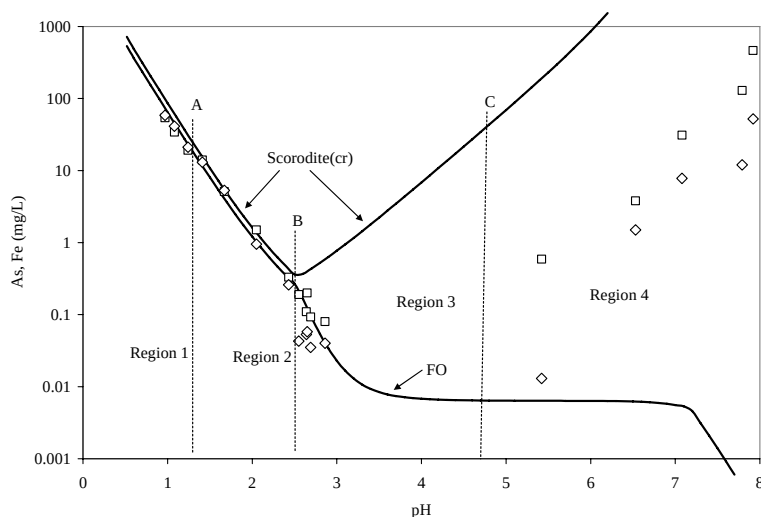


Fig. 7. The solubility of scorodite(cr) and FO in terms of As (upper solid line) and Fe (lower solid line) in the solutions of Krause and Ettel (1988) as computed by PHREEQC, assuming $-\log K_{sp}$ values of 25.83 and 41.2 for scorodite(cr) and FO, respectively. Also plotted is the solubility of scorodite(cr) as reported by Krause and Ettel (1988) with dissolved As and Fe concentrations shown as open squares and diamonds, respectively. Solubility regions and their boundaries are defined in the text.

Robins (1990) (Table 2 and Fig. 5), indicate that As(aq) and Fe(aq) concentrations continue to drop up to about pH 3 and pH 4.7, respectively.

The drop in As(aq) values to less than 0.1 mg/L near pH 3 corresponds to a decrease in the log IAP of scorodite (Table 2), but may partly reflect As(aq) adsorption by or co-precipitation with the FO phase. Above pH 4.7 (in region 4), As(aq) and Fe(aq) concentrations and $-\log$ IAP values for scorodite and FO decrease with pH. The $-\log$ IAP values for FO are as high as 34.07 at pH 7.92. That these values greatly exceed saturation with respect to amorphous FO which has a $-\log K_{sp}$ value of about 37 (Langmuir, 1997; Macalady et al., 1990) indicates that FO precipitation

was kinetically inhibited during the experiments of Krause and Ettel (1988), probably by the arsenic in the system.

Fig. 8 shows PHREEQC-computed solubility curves for coexisting ferric arsenate and ferric hydroxide and attempts to explain scorodite behavior in region 4. The plot indicates that when ferric arsenate and coexisting FO become more soluble with increasing pH (Table 2), the stability field of scorodite expands relative to that of FO from point B to successively higher pH values at points B', in good agreement with the As and Fe solubility data reported by Krause and Ettel (1988).

The pH value above which scorodite should dissolve incongruently and equilibrate with a precipitating FO

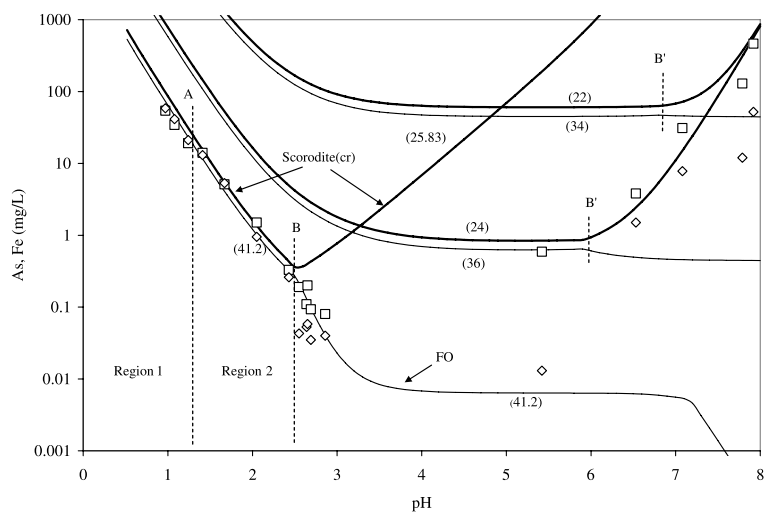


Fig. 8. The solubility of scorodite and FO in terms of As (heavy solid lines) and Fe (light solid lines) in the solutions of Krause and Ettel (1988) as computed by PHREEQC, assuming paired $-\log K_{sp}$ values of 25.83 and 41.2, 24.0 and 36.0, and 22.0 and 34.0, for scorodite and FO, respectively. Also plotted is the solubility of scorodite(cr) as reported by Krause and Ettel (1988) with dissolved As and Fe concentrations shown as open squares and diamonds, respectively. Solubility regions; and their boundaries are defined in the text.

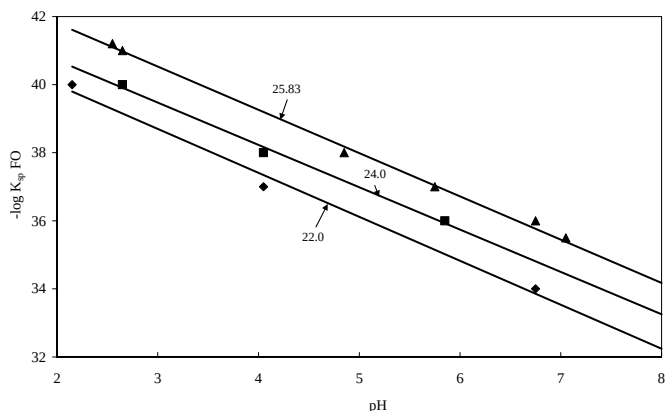


Fig. 9. The dependence of the pH at which ferric arsenate dissolves to precipitate an FO phase (points B and B' in Fig. 8) on the $-\log K_{sp}$ value of the FO phase, for ferric arsenate $-\log K_{sp}$ values of 22.0, 24.0, and 25.83.

phase (the pH of points B and B') is plotted in Fig. 9 as a function of the $-\log K_{sp}$ values for coexisting scorodite and FO. The figure shows that in the experimental solutions of Krause and Ettel (1988) scorodite coexists with an increasingly soluble FO phase at pH values that range from as low as 2.5 in acid solutions, to as high as 7 in near-neutral solutions where precipitation of the highly supersaturated FO phase is kinetically inhibited.

3. Application to arsenic behavior in buried mill tailings

3.1. Decrease in the apparent $\log K_{sp}$ ($\log IAP$) of ferric arsenates with increasing pH and increasing Fe/As ratio

In systems in which the Fe/As ratio equals 1, the apparent (computed) solubility product ($IAP = K_{sp}$) of the ferric arsenates decrease with pH up to pH 4–5 in Fig. 5. That the solubility product decreases and scorodite crystallinity increases may reflect a slowing rate of scorodite precipitation in the presence of lower concentrations of dissolved Fe(III) and As(V). Also, with increasing pH, relatively amorphous scorodite becomes undersaturated and would be expected to preferentially dissolve, leaving a more crystalline fraction behind. Any released arsenic may then reprecipitate as a more crystalline scorodite. It has been argued that the apparent decrease in the solubility of scorodite with increasing pH results from arsenate adsorption by the FO, however, insufficient iron is present in systems with Fe/As ~ 1 to explain the observed effect.

Numerous studies have shown that arsenic concentrations and the apparent $\log K_{sp}$ of scorodite (i.e., the $\log IAP$ of ferric arsenate) also decrease when the Fe/As ratio of the acid solution being neutralized is increased (cf. Fig. 10). For example, Vircikova et al. (1995) measured the solubility of ferric arsenate/FO mixtures as a function of the Fe/As ratio of the system. Our modeling of their solubility data at pH 2 shows that the apparent $\log K_{sp}$ for ferric arsenate is -23.89 for Fe/As = 1.6, -24.80 for Fe/As = 5.9, and -24.97 for Fe/As = 14.4.

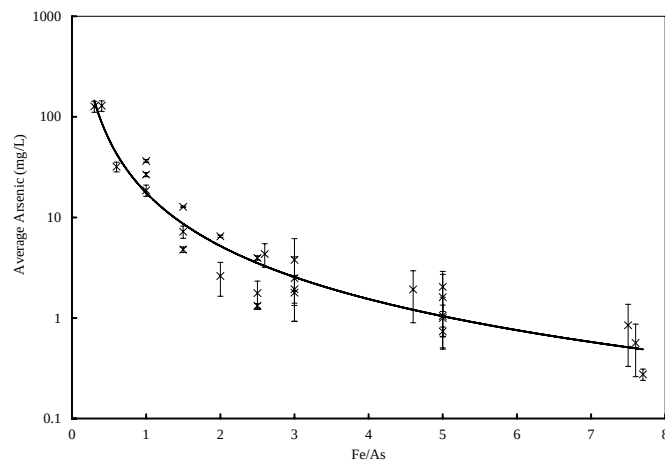


Fig. 10. Average arsenic concentrations in neutralized tailings solutions between pH 7–8 after 72 to 144 h aging tests at 25 °C as a function of the molar Fe/As ratio of the acid raffinate solutions before neutralization. From Langmuir et al. (1999).

3.2. Scorodite in raffinate neutralization experiments at the JEB Mill at McClean Lake

Neutralization of acid raffinates of uranium mill tailings produced at the JEB mill at McClean Lake in northern Saskatchewan, has been studied in laboratory experiments. In these experiments and in the mill, in a two-stage process, slaked lime [$\text{Ca}(\text{OH})_2$] is added to the acid raffinate which has a Fe/As molar ratio of ≥ 3 . When the pH is held at pH 2–3 for a sufficient time during lime addition (~ 90 min. in the mill), poorly crystalline scorodite is formed. The pH is subsequently increased to a final pH of 7–8. The scorodite produced by this procedure has been identified by XRD, SEM, EM, and EXAFS analyses of the solids (cf. Langmuir et al., 1999; Jia et al., 2003; Cutler et al., 2003; and Jianget al., 2004). Precipitates contain both poorly crystalline scorodite and a relatively amorphous FO phase in which small amounts of the arsenic are adsorbed or co-precipitated.

In example neutralization experiments, mill-produced acid raffinate solution with Fe/As = 3.6 was placed in six two-liter beakers on a multi-jar tester. Lime in increasing amounts was added to successive beakers while stirring, so that each beaker attained a predetermined pH value ranging from 2 to 8. All beakers were in the pH 2–4 range for 1 h or more during neutralization as in the mill, facilitating scorodite precipitation. After the beakers reached their target pH values, the slurries were filtered and the solutions and slurries analyzed. Chemical analyses of the acid raffinate solution and two neutralized solutions are given in Table 5.

Arsenic concentrations in the batch experiments as a function of pH are shown in Fig. 11. The plot indicates that As(aq) decreases from 686 mg/L in the raffinate to less than 1 mg/L after neutralization above pH 6. Fig. 12 gives $\log IAP$ values for ferric arsenate and ferric hydroxide as a function of pH computed with PHREEQC. Not shown are IAP values for the raffinate at pH 0.97, which are undersaturated

Table 5
Chemical analyses of the raffinate solution used in the batch neutralization tests and example neutralized raffinate solutions

Species or parameter	Raffinate	Neutralized sample pH 2.18	Neutralized sample pH 7.32
$T^{\circ}\text{C}$	25	25	25
pH	0.97	2.18	7.32
Pe	11.32	10.88	−3.19
As(3)	447	100	0.199
As(5)	221	48	0.17
Fe(2)	685	540	26
Fe(3)	1169	881	6.7
Al	200	803	0.01
Ca	589	512	612
Cl	13	16	18
Cu	19	16	0.01
K	357	394	477
Mg	229	1086	749
Na	23	83	59
Ni	515	502	13.1
Si	190	582	8
SO ₄	21,430	10,150	3020

Concentrations are in mg/L unless otherwise noted. Higher concentrations in neutralized samples than in the raffinate may result from concentrating solutions because of removal of water by the precipitation of gypsum [$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$], or contaminants added in the lime used for neutralization.

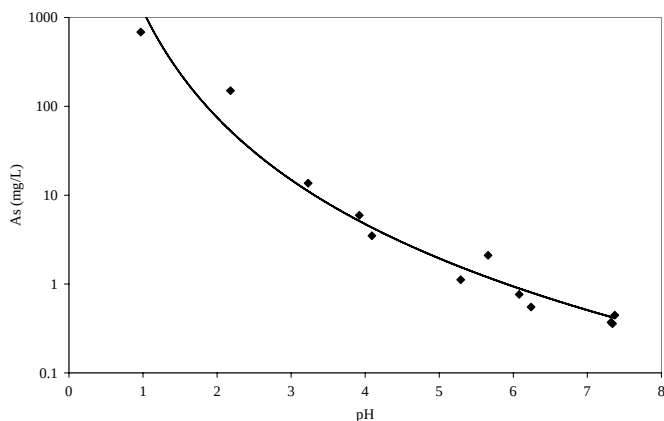


Fig. 11. Arsenic concentrations as a function of pH during batch neutralization of acid raffinate solution.

with respect to both solids. Log IAP values for ferric arsenate in Fig. 12 decrease from −22.80 at pH 2.18 indicating an AFA precipitate, to −24.67 at pH 7.37 indicating a more crystalline scorodite may be present at higher pH values.

Over the same pH range, the log IAP of FO increases from −39.49 to near −33.5. Log IAP values greater than −37, which is the log K_{sp} value for amorphous FO (Macalady et al., 1990; Langmuir, 1997) indicate a system in which the precipitation of a ferric hydroxide phase is kinetically inhibited, probably by the elevated arsenic and sulfate concentrations present (Langmuir et al., 1999). The high apparent solubility of the FO increases the stability field of scorodite to higher pH values relative to the stability field of the FO phase. The low solubility of scorodite at pH 7.37 is evident

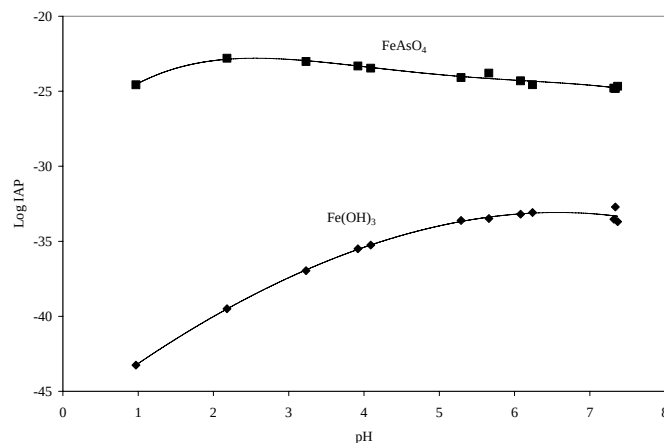
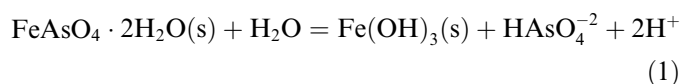


Fig. 12. Log IAP values for ferric arsenate and ferric hydroxide as a function of pH in the batch raffinate neutralization tests. Calculations made using measured Fe(III) and As(V) concentrations.

from calculations involving the ferric arsenate/ferric hydroxide equilibrium reaction, which may be written:



Assuming the apparent (computed) log K_{sp} values of −24.67 and −33.5 for ferric arsenate and ferric hydroxide respectively, the equilibrium constant of this reaction is:

$$K_{\text{eq}} = 10^{-21.67} = [\text{HAsO}_4^{-2}][\text{H}^+]^2 \quad (2)$$

which gives an equilibrium HAsO_4^{-2} activity of 1.2×10^{-7} mol/L or 0.009 mg/L As at pH 7.37. This is less than the measured total As(aq) concentration of 0.45 mg/L because we have neglected activity coefficient corrections and other complexes in our simplified calculation. The result shows that at pH 7.37, ferric arsenate is more stable than the FO phase if As(aq) concentrations exceed this value, and that Reaction 1 should buffer As(aq) concentrations below 1 mg/L at pH 7.37.

Between pH 1 and 2, the ferric arsenate precipitated during lime neutralization removes more than 90% of As(aq) in the raffinate. Additional As(aq) removal with further pH increases in this system can be attributed to the apparent increase in scorodite crystallinity (decrease in the log IAP of ferric arsenate), or to arsenic adsorption and/or co-precipitation.

A simple modeling calculation suggests that As(V) adsorption by FO alone can explain the drop in arsenic concentrations with lime neutralization above pH 2–3. In this calculation, we use the diffuse layer model and parameters for As(V) sorption by FO from Dzombak and Morel (1990) given in PHREEQC, and assume a one-step adsorption process starting at pH 2.18 with As(V) adsorption to pH 7.37. Further assumptions include no back reaction of precipitated ferric arsenate, an initial As(V) concentration of 54.5 mg/L at pH 2.18, and 1440 mg/L of dissolved Fe at pH 2.18 which is precipitated as FO (as ‘FeOOH’ in the model), at pH 7.37. Sorbent FeOOH has an assigned

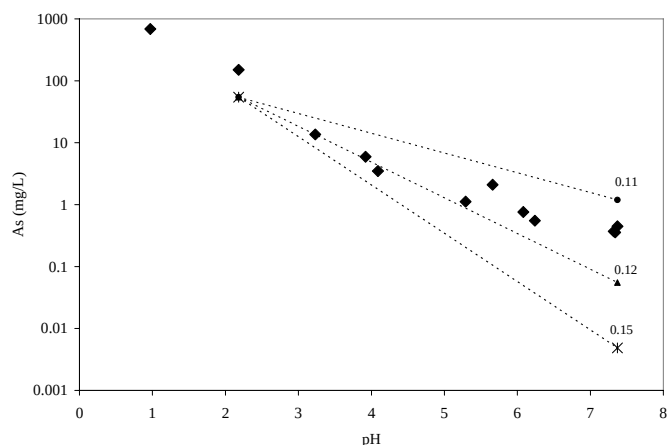


Fig. 13. Arsenic concentrations (solid diamonds) plotted as a function of pH during the batch neutralization tests. The dotted lines show trends in As(V) adsorption, predicted using the diffuse layer model (Dzombak and Morel, 1990), on ferrihydrite precipitated in a single step between pH 2.18 and 7.37. The model assumes initial precipitation of scorodite at pH 2.18. All remaining arsenic is then adsorbed by ferrihydrite. The dotted lines show As concentrations at a final pH of 7.37, assuming sorption site (Hfo_wOH) densities of 0.11, 0.12, and 0.15 mol of sites per mole of ferrihydrite precipitated. See text for further modeling details.

surface area of $600 \text{ m}^2/\text{g}$. Modeling results plotted in Fig. 13 show that a sorption density of 0.11 to 0.12 moles of As per mole of Fe in $FeOOH$ can explain the reduction in arsenic concentrations to less than 1 mg/L at pH 7.37.

There are important problems with this modeling exercise. Most importantly, the model assumes reversible As(V) adsorption by the FO precipitated from the raffinate, which is not observed. Mahoney et al. (2005) found that the As(V) readily released from neutralized tailings and raffinates to pore waters was only 0.2% of the total As present in the tailings. Whether precipitated as ferric arsenate, co-precipitated with an FO phase (cf. Waychunas et al., 1993) or adsorbed, most of the As(V) held by solids following neutralization to pH values near 7 is held irreversibly. This irreversibility apparently increases as the Fe/As ratio of raffinates is increased (cf. Harris and Krause, 1993).

3.3. Scorodite in the JEB tailings management facility

Starting in 1999, neutralized tailings slurry from the JEB mill at McClean Lake has been emplaced below the water table in the JEB open pit, or tailings management facility (TMF). In 2004, pore waters in the TMF were sampled from depths above mean sea level ranging from 364 m (oldest tailings) to 396 m (youngest tailings). Three example analyses of pore waters obtained from different depths are given in Table 6. Redox speciation of dissolved Fe and As in the pore waters was computed with PHREEQC from measured pH and Eh values and total Fe and As concentrations.

The average pore water pH is 7.76 ± 0.24 . There is no significant correlation between pH and pore water elevation. However, arsenic concentrations vary with elevation.

Table 6

Chemical analyses of some pore waters sampled at three different depths from the JEB tailings management facility in 2004

Parameter/analyte	Sample elevation (meters above mean sea level)		
	397.8	378.9	364.3
$T^\circ\text{C}$ (field)	12.2	NR ^a	10.7
pH (field)	7.54	7.45	7.70
Eh (mV) (field)	450	369	390
Specific Conductance (mS/Cm)	2460	2440	2480
DO (field)	6.8	8.2	9.0
Na	120	150	34
K	25	18	22
Mg	34	79	120
Ca	510	440	562
Sr	0.62	0.64	0.27
Ba	0.052	0.062	0.019
Mn (total)	1.75	5.97	1.6
Fe (total)	0.008	0.27	0.004
Ni	0.46	0.77	0.53
Al	<0.005	<0.005	<0.02
U	2.3	3.1	0.41
Cl	29	48	58
Si	4.1	9.3	4.6
SO_4	1600	1500	1900
HCO_3	55	179	44
$NH_3 + NH_4^+$ as N	7.3	10	NR
$NO_3^- + NO_2^-$ as N	<0.01	0.23	0.07
COD	6	29	NR
As(III)	0.053	3.13	0.096
As(V)	0.257	1.17	0.384
Mo	7.22	7.14	4

Concentrations are in mg/L unless otherwise noted.

^a NR denotes not reported.

The average total As concentration at all depths is $4.1 \pm 3.6 \text{ mg/L}$, with the highest values occurring at intermediate depths (between 375 and 392 m). Above and below these depths As concentrations in the youngest and oldest buried tailings, are less than $1\text{--}2 \text{ mg/L}$. The increase in total As values at intermediate depths is as As(III)(aq), probably derived from the oxidation and dissolution of unreacted arsenide minerals in the residual tailings and As(III) desorption from tailings solids. This As(III)(aq) is subsequently oxidized to As(V) and precipitated in scorodite or adsorbed by FO solids in tailings at depths below 370 m.

There is no statistically significant trend in the log IAP values for ferric arsenate or ferric hydroxide with sample elevation. As in the laboratory study, computed log IAP values for ferric arsenate decrease with pH, while those for FO increase with pH. For the 35 pore waters between pH 7.18 and pH 8.28 $\log IAP(\text{ferric arsenate}) = -25.74 \pm 0.88$ and $\log IAP(\text{FO}) = -37.03 \pm 0.58$. This suggests that arsenic and iron concentrations in the TMF are limited by the solubility of a relatively crystalline scorodite phase and an amorphous FO phase, respectively. The apparent crystallinity of the scorodite and the amorphous character of the associated FO phase stabilizes scorodite relative to FO in the TMF. Both the neutralized

raffinates and TMF pore waters are at saturation with gypsum. The amorphous FO phase in the neutralization experiments and in the TMF is apparently prevented from crystallizing by the high amounts of arsenate and sulfate present in both of these systems.

X-ray diffraction analysis of core solids from the TMF was performed in 2001. Results suggested that scorodite averaged 0.7 ± 0.8 weight percent of the tailings in seven samples obtained over a depth range of 17 m. Detailed characterization of the scorodite was impossible because of its small relative amount in the tailings.

4. Conclusions

Published solubility data for amorphous ferric arsenate and for crystalline scorodite, was reevaluated using the geochemical code PHREEQC (Parkhurst and Appelo, 1999), taking into account ionic strength and ferric and arsenate aqueous complexes, and only considering studies where some measurements were made in acid solutions where congruent dissolution of the arsenate was possible, and the measured pH and concentrations of total As and Fe were reported. Computer modeling of the solubility data indicates that $\log K_{sp} = -23.0 \pm 0.3$ and -25.83 ± 0.07 for amorphous ferric arsenate and crystalline scorodite, respectively, at 1 bar pressure and 25 °C.

Laboratory experiments were performed in which arsenic-rich acid raffinate solutions from the JEB uranium mill at McClean Lake in northern Saskatchewan were neutralized to pH 2–8 with added $\text{Ca}(\text{OH})_2$. Poorly crystalline scorodite precipitated around pH 2, and relatively amorphous ferric oxyhydroxides (FO) began to precipitate between pH 2 and 3. Arsenic concentrations dropped from 686 mg/L at pH 0.97 to less than 1 mg/L at pH 7.37. At pH 7.37 the scorodite had an apparent $\log K_{sp}$ of -24.67 and so was partially crystalline, whereas the FO was highly amorphous and kinetically inhibited from precipitation. Arsenic removal during neutralization could also be explained by assuming precipitation of 90–98% of the As(V) in scorodite up to pH 2–3, and adsorption of the remaining As(V) by a precipitated FO phase between pH 2.18 and 7.37. Whatever the As(V) removal mechanism, it is largely irreversible.

A slurry of neutralized uranium mill tailings has been emplaced continuously in the JEB tailings management facility (TMF) at McClean Lake for five years, and as of 2004 occupied a thickness of about 32 m in the TMF. Pore waters sampled from the TMF in 2004 had an average pH of 7.76 and an As(aq) concentration of 4.1 mg/L which decreased to 1–2 mg/L or less in the oldest tailings. The average $\log \text{IAP}$ values for ferric arsenate and FO were -25.74 and -37.03 , respectively, indicating that well-crystallized scorodite and amorphous FO may control arsenic and ferric iron concentrations in TMF pore waters at near-neutral pH values.

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Associate editor: Liane G. Benning

Appendix A. Auxiliary thermodynamic data

A.1. Arsenic and arsenous acids

Cumulative dissociation constants for arsenic and arsenous acids used in the solubility modeling are given in Table 3. Of particular concern in this study, which involves oxidizing conditions, are the arsenic acid constants. In previous studies, Whiting (1992) and the authors (cf. Langmuir et al., 1999) have used the critically selected arsenic acid constants suggested by Smith and Martell (1976) and Baes and Mesmer (1976). More recently Nordstrom and Archer (2003) have reevaluated these constants and recommended the significantly different values given in Table 3. The consequences of using both sets on the stability of scorodite are considered in this study.

A.2. Metal arsenate complexes

Also important in the solubility calculations is consideration of metal arsenate complexes, which have been neglected by most previous researchers. Robins (1990) reported free energy values for the ferric arsenate complexes which have been used to compute the stability constants of these species listed in Table 3.

Lacking published stabilities of other metal arsenate complexes, Whiting (1992) estimated their stabilities. His approach involved using the Electronicity Principle of Brown and Sylva (1987a,b) (the BSEP model), and graphical methods. In both approaches a comparison is made between the measured and modeled association constants (K_{assoc} values) of metal phosphate complexes and corresponding arsenate complexes. This of course means that the accuracy of the association constant that we predict for a given metal arsenate complex will be limited by the accuracy with which we know the constant for the corresponding phosphate complex used in the prediction.

The BSEP model considers such factors as the hard and soft acid and base properties of the cation and ligand forming the complex, the charge and radius of the cation, whether the cation is a transition metal species, and the degree of ionicity or covalency of bonding in the complex. In his BSEP modeling effort, Whiting (1992) first compared the measured association constants of 23 metal phosphate complexes reported in the literature to values predicted using the BSEP model. The ratio $[\log K_{\text{assoc}}(\text{measured})/\log K_{\text{assoc}}(\text{predicted})]$ (the ‘correction factor’) was then computed for each complex. The aver-

age of the correction factors for all 23 phosphate complexes was 0.96 ± 0.33 , showing generally good agreement between measured and predicted values. The BSEP model was then used to predict the stabilities of the metal arsenate complexes. Assuming correction factors for the metal arsenate complexes would be the same as for the corresponding metal phosphate complexes, the predicted $\log K_{\text{assoc}}$ value for each metal arsenate complex was multiplied by the corresponding phosphate-derived correction factor. Some confidence in the results of this approach can be gained by comparing the BSEP model predicted and measured $\log K_{\text{assoc}}$ values for the $\text{FeH}_2\text{AsO}_4^{2+}$, FeHAsO_4^+ , and FeAsO_4 complexes. The predicted values are 4.06, 9.76, and 18.85, compared to the values measured by Robins (1990), which are 4.04, 9.86, and 18.9, respectively.

The stability of the metal arsenate complexes was also estimated graphically. This involved plotting measured $\log K_{\text{assoc}}$ values for arsenate complexes against measured values for corresponding phosphate complexes. The only published arsenate stability constants available for such plots are those for the arsenic acid species and the ferric arsenate complexes (Table 3).

A third point for each figure was obtained as follows. A plot of $\log K_{\text{assoc}}$ values for metal HPO_4^{2-} and H_2PO_4^- phosphate complexes versus the electronegativity (EN) of the metal cations in the complexes (see Fig. A1, Whiting, 1992, and Langmuir, 1997, p. 102) shows that as the EN of metal cations decreases, cation bonding with phosphate ligands (and presumably also with corresponding arsenate ligands) becomes more purely electrostatic, and $\log K_{\text{assoc}}$ values asymptotically approach constant values. These $\log K_{\text{assoc}}$ values should be equal for the same metal phosphate and arsenate complexes. For the metal $(\text{M}^{+2})\text{-H}_2\text{PO}_4^+$ and HPO_4^{2-} complexes the asymptotic $\log K_{\text{assoc}}$ values are 1.0 and 2.3, respectively. (See Fig. A1). The same extrapolation approach for the metal PO_4^{3-} complexes suggests an asymptotic $\log K_{\text{assoc}}$ value of about 5.2 for cation EN values below 0.4 (Whiting,

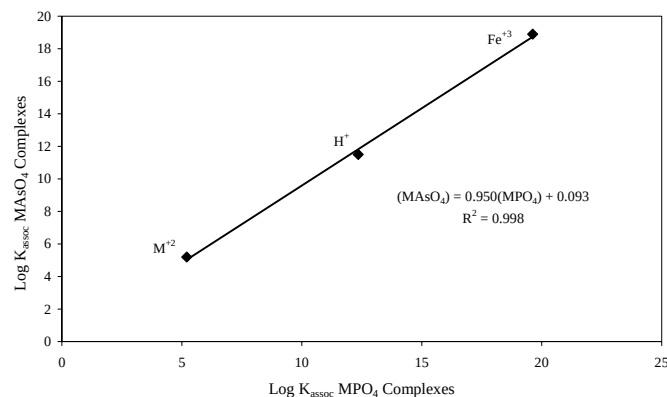


Fig. A2. Comparison of $\log K_{\text{assoc}}$ values of phosphate and corresponding arsenate complexes. Parentheses in the equation enclose the $\log K$ values of the association constants for the cation arsenate and phosphate complexes.

1992). That these are unrealistically low $\log K_{\text{assoc}}$ and EN values does not significantly affect the resultant equation of the line in Fig. A2, which is relatively insensitive to the value we choose for the third and lowest point on the plot where $\log K_{\text{assoc}}(\text{MPO}_4^-) = \log K_{\text{assoc}}(\text{MAsO}_4^-)$.

Regression of the three data points in each plot gives the equations:

$$(\text{MH}_2\text{AsO}_4) = 0.955(\text{MH}_2\text{PO}_4) + 0.10, \text{ with } R^2 = 0.998;$$

$$(\text{MHAsO}_4) = 0.987(\text{MHPO}_4) - 0.15, \text{ with } R^2 = 0.999; \text{ and}$$

$$(\text{MAsO}_4^-) = 0.950(\text{MPO}_4^-) + 0.10, \text{ with } R^2 = 0.998.$$

In these equations the parenthetic terms represent the $\log K_{\text{assoc}}$ values for the metal complex (M) with the specified ligand. Agreement between $\log K_{\text{assoc}}$ values predicted for the arsenate complexes using the corrected BSEP model and the graphic approach are excellent. Thus the average ratio of these two values is 1.01 ± 0.02 . Association constants for the metal arsenate complexes given in Table 3 are averages of the values obtained with the corrected BSEP model and using the graphic approach.

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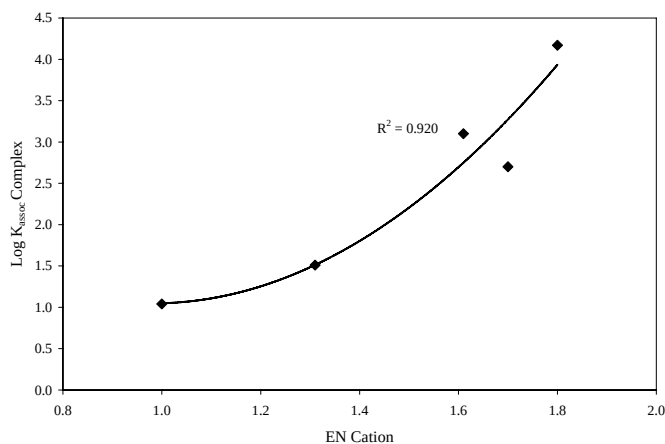


Fig. A1. Association constants of metal- H_2PO_4^- complexes plotted against the electronegativity of the metal cation.

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Arsenic readily released to pore waters from buried mill tailings

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Abstract

At the McClean Lake Operation in the Athabasca Basin of northern Saskatchewan, the untreated acid raffinate solutions associated with U mill tailings contain up to 700 mg/L dissolved As. To reduce the concentration of As and other contaminants in acid tailing slurries at the JEB mill at McClean Lake, ferric sulfate may be added to the acid raffinates to assure that their molar Fe/As ratio equals or exceeds 3. Tailings slurries are then neutralized with lime to pH 4, and subsequently to pH 7–8. The neutralized tailings contain minerals from the original ore, which are chiefly quartz, illite, kaolinite and chlorite, and precipitated (secondary) minerals that include gypsum, scorodite, annabergite, hydrobasaluminite and ferrihydrite. Most of the As is associated with the secondary arsenate minerals, scorodite and annabergite. However, a few percent is adsorbed and/or co-precipitated, mainly by ferrihydrite. Of major concern to provincial and federal regulators is the risk that significant amounts of As might be released from the tailings to pore waters after their subaqueous disposal in the tailings management facility. A laboratory study was performed to address this issue, measuring readily desorbed As using a method known as equilibrium partitioning in closed systems (EPICS). The EPICS method was selected because it employs a leaching solution that, except for its As concentration, is identical in composition to the neutralized raffinate in contact with the tailings. Laboratory experiments and modeling results demonstrated that the As that could be readily released to pore waters is about 0.2% of the total As in the tailings. Long-term, such releases may contribute no more than a few mg/L of dissolved As to tailings pore waters.

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1. Introduction

Predicting the mobility in ground water of contaminants such as As has become increasingly important as risk assessment plays a greater role in the licensing and permitting of waste disposal facilities. In the Athabasca Basin of northern Saskatchewan, elevated concentra-

tions of As in the U ore (up to 10% by weight) have required that detailed studies be conducted to assist in designing methods to reduce pore water concentrations of As in the neutralized tailings that are disposed of in contact with ground water in a tailings management facility or TMF (cf. Langmuir et al., 1999a,b).

At the JEB mill at McClean Lake, U is extracted from the ore using H₂SO₄. The leach residue from the ore consists chiefly of unreacted quartz and illite, with lesser amounts of kaolinite and chlorite. After U extraction, the leach residue solids are mixed with the barren

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leach solution (raffinate), which commonly has a pH below 2.0. To reduce dissolved As concentrations, which often reach 700 mg/L in the acid raffinate, the raffinate has its molar Fe/As ratio increased to 3/1, if necessary, by the addition of ferric sulfate. The combined raffinate and leach residue slurry is then neutralized by lime addition to about pH 4 and subsequently to pH 7–8. After neutralization, As concentrations in slurry pore waters in the mill are typically less than 1–2 mg/L. Neutralization causes the precipitation of non-As bearing phases that include gypsum [$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$], hydrobasaluminite [$\text{Al}_4\text{SO}_4(\text{OH})_{10} \cdot n\text{H}_2\text{O}$, $n = 2\text{--}3$], ferrihydrite [α Fe(III) hydroxide] and theophrastrite [$\text{Ni}(\text{OH})_2$]. Precipitated phases that contain important amounts of As include the poorly crystalline arsenate minerals. In the tailings these phases are non-stoichiometric solid solutions that also contain Al (scorodite: $\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$) and Mg and Fe(II) (annabergite: $(\text{Ni}_3\text{AsO}_4)_2 \cdot 2\text{H}_2\text{O}$), an oxyhydroxide coprecipitate with a variable Fe/As ratio, and As that may be surface precipitated or adsorbed onto ferrihydrite and other mineral surfaces (cf. Li and Stanforth, 2000; Ler and Stanforth, 2003). Preceding formulas are for the pure, end-member mineral phases.

Solids in the neutralized tailings slurry are typically comprised of 50–70% leach residue minerals with the remainder as precipitated solids. The tailings slurry is pumped into the JEB Tailings Management Facility (TMF) for final disposal using a subaqueous emplacement process. Underdrains allow for the removal of the pore water expelled by settling and compaction of the tailings, which is pumped to a water treatment facility.

At the McClean Lake Operation, a comprehensive research program, known as the Tailings Optimization and Validation Program (TOVP) has been under way since 1997. The TOVP has consisted of a series of studies designed to: (1) understand reaction controls on As behavior in the tailings neutralization process in the McClean Lake mill; (2) examine, and optimize the tailings neutralization process in order to reduce As concentrations in JEB TMF pore waters and (3) to evaluate the long-term behavior of As in the TMF.

Several TOVP studies have demonstrated the importance of arsenate mineral dissolution/precipitation reactions as the chief control on As concentrations in tailings pore waters in the TMF. Based on laboratory experiments and modeling, Langmuir et al. (1999a,b) predicted that As concentrations in TMF pore waters over the long-term (thousands of years) would not exceed 1–2 mg/L. This conclusion has been supported by further laboratory tests involving the neutralization of mill raffinates and tailings with Fe/As = 3 (Mahoney et al., 2005), which indicate that pore water As concentrations are less than 1 mg/L in neutralized raffinates. Mill tailings have been continuously emplaced in the TMF since July 1999, and tailings pore waters have been

sampled for chemical analysis each year since then (COGEMA, 2002, 2003). Measurements show that As concentrations in TMF pore waters have decreased from a high of about 5–7 to 1–2 mg/L after 2–3 a of burial (COGEMA, 2003). A substantial amount of work has been performed to assess the distribution of As species in the tailings and pore waters. Redox conditions in the tailings are oxidizing, with E_h values in the TMF typically around 350 to 400 mV (COGEMA, 2002). Additional details about changes in redox related species will be provided in Mahoney et al. (2005). Geochemical modeling of the laboratory and TMF results using PHREEQC (Parkhurst and Appelo, 1999) show that As concentrations are close to chemical equilibrium with respect to a poorly crystalline aluminous scorodite phase ($\text{Fe}_{0.9}\text{Al}_{0.1}\text{AsO}_4 \cdot 2\text{H}_2\text{O}$) (Log K_{sp} for this aluminous scorodite is -25.69), which has been identified in both the experimental studies (Mahoney et al., 2005) and the TMF (COGEMA, 2003). This suggests that over the long-term, the solubility product of scorodite influences the maximum As concentrations in tailings pore waters.

Canadian federal and provincial regulators have expressed concern that significant concentrations of adsorbed As might be released with time from the tailings to TMF pore waters. This study, which was a part of the TOVP, was performed to determine the amount of As that could be readily released from the tailings to pore waters in the TMF.

2. Predicting arsenic releases to TMF pore waters

Published studies and work performed as part of the TOVP indicate that As releases to pore water could be derived from: (1) dissolution of arsenate minerals which in general contain more than 95% of the total As in the tailings; (2) dissolution of Fe/As oxyhydroxide coprecipitates; (3) dissolution of surface precipitated As and (4) desorption of As, probably chiefly associated with ferrihydrite or hydrous ferric oxides (HFO).

In principle, there are two fundamental approaches one could take to estimate or predict As releases to TMF pore waters from potential sources (1) through (4). The first approach, which may be described as the in-depth basic science approach, is to thoroughly characterize the aqueous phase and all of the solid phases in the tailings, and to predict As releases based on an understanding of all reactions and processes in the tailings that potentially affect As concentrations. Theoretically, this approach would allow one to both extrapolate and interpolate from known data using models to predict As releases from any complex tailings, soil or sediment system to pore waters.

The second approach, which is used in this paper, is to measure As releases from solids under conditions as

similar as possible to those observed in the disposal site. The results of such a study will only be applicable to the site and system being investigated.

The in-depth basic science approach requires a full characterization of the solids and solutions involved in reactions that affect As. Solid characterization in complex systems containing As can involve detailed chemical analysis, X-ray diffraction, scanning electron microscopy, electron microprobe, and petrography (cf. Langmuir et al., 1999a), X-ray absorption spectroscopy (XAS) and extended X-ray absorption fine structure (EXAFS) spectroscopy (cf. Waychunas et al., 1996; Manning et al., 1998; Sherman and Randall, 2003; Paktunc et al., 2003, 2004; Cutler et al., 2003). Selective or sequential chemical extractions have also been employed to determine the nature and extent of As associations with different solids in complex systems (cf. Gruebel et al., 1988; Shiwatana et al., 2001; Kim et al., 2003).

3. Determination of adsorbed and desorbed arsenic

3.1. Adsorbed arsenic determination via selective extraction methods

Selective or sequential extraction techniques have been used to distinguish amounts of the different forms of As in complex materials such as soils and tailings (cf. Gruebel et al., 1988; Shiwatana et al., 2001; Linge and Oldham, 2003; Kim et al., 2003). However, there is no consensus on which methods to use for different purposes. For example, Shiwatana et al. (2001) leached soils with 0.5 M NaHCO_3 to desorb surface adsorbed As. In contrast, Kim et al. (2003) treated mine tailings with 0.1 M Na_2HPO_4 solution at pH 8 to release adsorbed As (see also Tokunaga et al., 1991). Although not specific to As, Loux et al. (1989) used hydroxylamine hydrochloride to dissolve amorphous $\text{Fe}(\text{OH})_3$ in soils. The adsorbed metals were believed to report to the leachate solution. The use of a leaching agent demonstrates a problem inherent to all of the methods that employ reagents. Mainly, that to some degree these methods tend to dissolve amorphous phases, which can cause an artificial increase in the amount of so-called readily releasable As.

3.2. Direct measurement of arsenate desorption

Several studies have measured arsenate desorption. Darland and Inskeep (1997) report adsorption and desorption rate constants for arsenate onto poorly crystalline $\text{Fe}(\text{III})$ oxides at pH 4.0–4.5. Their rate constant for desorption is 30 times larger than the constant for adsorption, indicating hysteresis in the desorption process. O'Reilly et al. (2001) and Fuller et al. (1988) measured arsenate desorption resulting from the addition

of phosphate, from goethite and from precipitated HFO, respectively. O'Reilly et al. (2001) found that about 35% of adsorbed arsenate was desorbed from goethite in 24 h, but that further desorption after longer times was relatively minor. In their study of adsorption by HFO, Fuller et al. (1988) reported that after times ranging from 144 to 188 h, the amount of arsenate desorbed ranged from 0.01% to 13% of adsorbed arsenate. In separate experiments in which SO_4 was added to cause arsenate desorption from goethite, O'Reilly et al. (2001), found that only 2.5% of adsorbed arsenate was desorbed after 5 months.

There is no consensus explanation for the observation that arsenate desorption is usually a small fraction of total adsorbed As. In their study of phosphate adsorption by goethite, Strauss et al. (1997) proposed that the initial, rapid adsorption is onto goethite surfaces, with subsequent uptake through diffusion into the goethite particles. Darland and Inskeep (1997) proposed that slow sorption and desorption rates of arsenate by HFO are controlled by slow intra-particle and film diffusion rates. It seems possible that stronger arsenate–Fe surface bonds are formed with time following arsenate adsorption (e.g., bidentate bonds formed from monodentate bonds), accounting for both slower desorption rates and the incompleteness of arsenate desorption.

In a study relevant to the present one, Paktunc et al. (2003) examined As mobilization from Au mine tailings. They employed column leaching tests, mineralogical characterization and EXAFS spectral analysis. Unfortunately, the composition of their leaching solutions was not reported. Paktunc et al. concluded that As in the tailings (about 4% by weight) was present in $\text{Fe}(\text{III})$ and Ca–Fe arsenates (43–76%), and bonded to Fe oxyhydroxides (24–50%). In experiments involving tailings and standing water at pH 6.5–7 (roughly comparable to conditions in the JEB TMF), they measured As concentrations of between 0.3 and 2.6 mg/L. No explanation is given for these concentrations, which may have resulted chiefly from the breakdown of the Ca-bearing arsenate phases, as these phases are only stable under alkaline conditions (Bothe and Brown, 1999). Because the authors do not report final solution compositions, it is not possible to determine the state of saturation of those solutions with respect to scorodite or other arsenate phases. Thus, insufficient information is provided to distinguish As concentrations that might have been desorbed from the tailings from those that might have resulted from arsenate mineral dissolution. A notable difference in the present study and that of Paktunc et al. (2003) is that the tailings solids contain abundant gypsum, whereas those of Paktunc et al. (2003) lacked gypsum. The gypsum buffers high pore-water SO_4 concentrations, which stabilize HFO. This prevents the HFO from crystallizing with age and releasing its adsorbed As (Langmuir et al., 1999a).

4. EPICS method and model

4.1. General approach

The studies of Fuller et al. (1988) and Darland and Inskeep (1997) among others, suggest that readily desorbable As is a small fraction of total adsorbed As, and that most adsorbed As is strongly bound to mineral surfaces. In this study, the As that could be readily desorbed from tailings solids has been measured using a method that involves the successive addition, to the neutralized raffinate and tailings, of aliquots of the same raffinate, but free of As, and measuring the As released to solution following each addition. This method of measuring desorbable As is obviously less aggressive than those suggested by Shiowatana et al. (2001) and Kim et al. (2003), and probably avoids significant dissolution of abundant, relatively amorphous arsenate phases and the release of their associated As. In this study it is assumed that desorbable As does not include As from the dissolution of arsenate minerals, or from the dissolution of Fe/As oxyhydroxide precipitates or As surface precipitates.

4.2. Mathematical derivation

To quantify the readily desorbable As in the tailings, a series of laboratory measurements were performed using a procedure based upon a methodology described by Gossett (1987), which he called equilibrium partitioning in a closed system (EPICS). Conceptually, the method is simple. By changing the liquid to solid ratio in a water and solid (tailings) mixture, while keeping the amount of desorbable As plus dissolved As constant, and the total solids constant, the total amount of initially desorbable As can be calculated based upon changes in the dissolved As concentration.

The following example explains the method. A sample consisting of 1 L of solution with a concentration of 1.0 mg/L of dissolved As is diluted to 2 L. The As concentration is thus reduced to 0.5 mg/L. If, however, a supply of releasable As is available to the solution, some of it will be released and dissolved As concentrations will exceed 0.5 mg/L. When the system undergoes further dilution, dissolved As concentrations will not decrease in accordance with a simple dilution process, but rather additional releasable As will transfer from the solids to the solution. As infinite dilution is approached, the amount of potentially releasable As approaches zero, all the As is in the solution, but the dissolved As concentrations become too low to measure. For this reason, in this study the authors extrapolate from measurable concentrations to infinite dilution.

In the following derivation, As that occurs in precipitated forms in the neutralized tailings slurry (as arsenate minerals such as scorodite and annabergite, Fe/As oxyhydroxide precipitates or surface precipitates)

is defined as $As_{(ppt)}$. Adsorbed As that is not readily desorbed is also considered part of $As_{(ppt)}$. Desorbable As is termed $As_{(desorb)}$. Sorbent phases include ferrihydrite, hydroxysulfate minerals, clays and possibly precipitated gypsum. The third form of As is that dissolved in the solution ($As_{(aq)}$). These 3 forms make up the total As ($As_{(total)}$).

$$As_{(total)} = As_{(ppt)} + As_{(desorb)} + As_{(aq)} \quad (1)$$

Total and aqueous As concentrations can be readily determined using standard analytical methods. The desorbable As plus dissolved As in Eq. (1) may be defined as the readily released As ($As_{(rr)}$),

$$As_{(rr)} = As_{(desorb)} + As_{(aq)} \quad (2)$$

Desorbable As responds rapidly to slight changes in conditions such as temperature, pH or liquid to solid ratio. Arsenic in precipitated form, or irreversibly bound to surfaces, will respond to such changes at a much slower rate or not at all.

There are several mathematically equivalent approaches to estimate the amount of readily released As in the tailings. The most straightforward is based upon the EPICS method (Gossett, 1987). In Gossett's work, the EPICS methodology was used to measure Henry's law constants for volatile organic compounds. The authors use a similar approach here to measure the distribution coefficient for readily released As (K_d^{rr}).

For a fixed mass of slurry ($M_{(solid)}$), the readily released As ($As_{(rr)}$) is operationally defined by Eq. (3):

$$As_{(rr)} = As_{(desorb)}M_{(solid)} + As_{(aq)}V_{(aq)} \quad (3)$$

Where $As_{(desorb)}$ is the desorbable As concentration associated with slurry solids, and $As_{(aq)}$ and $V_{(aq)}$ are the aqueous As concentration and volume of the aqueous phase.

The distribution coefficient for readily released As is defined as:

$$K_d^{rr} = \frac{As_{(desorb)}}{As_{(aq)}} \quad (4)$$

The superscript rr distinguishes this distribution coefficient from the total distribution coefficient, K_d^{total} , which is defined by

$$K_d^{total} = [As_{(ppt)} + As_{(desorb)}] / As_{(aq)} \quad (5)$$

Substituting Eq. (4) into Eq. (3)

$$As_{(rr)} = As_{(aq)}[V_{(aq)} + K_d^{rr}M_{(solid)}] \quad (6)$$

If samples 1 and 2, prepared with different volumes of liquid, both contain the same total amount of readily releasable As and mass of solid, then

$$\begin{aligned} As_{(aq1)}[V_{(aq1)} + K_d^{rr}M_{(solid)}] \\ = As_{(aq2)}[V_{(aq2)} + K_d^{rr}M_{(solid)}] = As_{(rr)}, \end{aligned} \quad (7)$$

where the subscripts 1 and 2 represent the As concentrations and volumes at specified steps. Solving for K_d^{rr} gives:

$$K_d^{rr} = \frac{As_{(aq1)}V_{(aq1)} - As_{(aq2)}V_{(aq2)}}{[As_{(aq2)} - As_{(aq1)}]M_{(solid)}}. \quad (8)$$

This equation shows that K_d^{rr} can be determined by experimentally changing the proportions of water to solid in a system in which $As_{(rr)}$ and $M_{(solid)}$ are fixed.

The simplest method of computing K_d^{rr} from such experimental data, is to plot the inverse of the As concentrations ($1/As_{(aq)}$) vs. the volume of solution for two or more experiments. As shown by the derivation given in Appendix A, K_d^{rr} then equals the intercept (b) of the line connecting the data, divided by the slope (m) of that line times the mass of solid, or

$$K_d^{rr} = b/[mM_{(solid)}]. \quad (9)$$

The most direct method to estimate the amount of readily released As is to first calculate $F_{(desorb)}$, the fraction of As that is readily desorbed. This is defined by,

$$F_{(desorb)} = \frac{As_{(desorb)}M_{(solid)}}{As_{(desorb)}M_{(solid)} + As_{(aq)}V_{(aq)}}. \quad (10)$$

Introducing K_d^{rr} , and rearranging Eq. (10) becomes:

$$F_{(desorb)} = \frac{\left[\frac{K_d^{rr}}{V_{(aq)}/M_{(solid)}} \right]}{\left[1 + \frac{K_d^{rr}}{V_{(aq)}/M_{(solid)}} \right]}. \quad (11)$$

The desorbable concentration can be calculated with the equation:

$$As_{(desorb)} = \frac{F_{(desorb)}(As_{(aq)}V_{(aq)})}{(1 - F_{(desorb)})M_{(solid)}}. \quad (12)$$

The total amount of readily released As ($As_{(rr)}$) can then be calculated by summing the As mass in the liquid phase [$As_{(aq)}V_{(aq)}$] and $As_{(desorb)}$. The total readily released As can also be calculated using the equation:

$$As_{(rr)} = \frac{[As_{(aq)}V_{(aq)}]}{[1 - F_{(desorb)}]} \quad (13)$$

4.3. Model simulations

The EPICS methodology was originally designed to measure concentrations in simple systems where the distribution coefficient behaves in a linear fashion. A series of model simulations were performed here to verify that the assumptions and the computational method could be applied to the more complicated system of As desorption from ferrihydrite.

The desorption reactions were modeled using the program PHREEQC (Parkhurst and Appelo, 1999), and the diffuse layer model (Dzombak and Morel, 1990). Table 1 lists the species and surface complexes used in the modeling. The PHREEQC model was used because the distribution of the different forms of As can be readily determined at each modeling step. Therefore, the amount of readily released As measured using

Table 1
Summary of data used in PHREEQC simulations for As aqueous species and diffuse layer adsorption reactions^a

Aqueous species	Reaction	Log K
$H_2AsO_4^-$	$H_3AsO_4 = H_2AsO_4^- + H^+$	-2.24
$HAsO_4^{2-}$	$H_3AsO_4 = HAsO_4^{2-} + 2H^+$	-9.2
AsO_4^{3-}	$H_3AsO_4 = AsO_4^{3-} + 3H^+$	-20.7
$CaHAsO_4^0$	$Ca^{+2} + H_3AsO_4 = CaHAsO_4 + 2H^+$	-6.51
$CaAsO_4^-$	$Ca^{+2} + H_3AsO_4 = CaAsO_4^- + 3H^+$	-14.48
$CaH_2AsO_4^+$	$Ca^{+2} + H_3AsO_4 = CaH_2AsO_4^+ + H^+$	-1.18
$MgAsO_4^-$	$Mg^{+2} + H_3AsO_4 = MgAsO_4^- + 3H^+$	-14.36
$MgHAsO_4^0$	$Mg^{+2} + H_3AsO_4 = MgHAsO_4 + 2H^+$	-6.34
$MgH_2AsO_4^+$	$Mg^{+2} + H_3AsO_4 = MgH_2AsO_4^+ + 1H^+$	-0.72
Surface complex		
$Hfo_wOH_2^+$	$Hfo_wOH + H^+ = Hfo_wOH_2^+$	7.29
Hfo_wO^-	$Hfo_wOH = Hfo_wO^- + H^+$	-8.93
$Hfo_wH_2AsO_4$	$Hfo_wOH + AsO_4^{3-} + 3H^+ = Hfo_wH_2AsO_4 + H_2O$	29.31
$Hfo_wHAsO_4^-$	$Hfo_wOH + AsO_4^{3-} + 2H^+ = Hfo_wHAsO_4^- + H_2O$	23.51
$Hfo_wOHAsO_4^{2-}$	$Hfo_wOH + AsO_4^{3-} = Hfo_wOHAsO_4^{2-}$	10.58
Hfo_wOCa^+	$Hfo_wOH + Ca^{+2} = Hfo_wOCa^+ + H^+$	-5.85
Hfo_wOMg^+	$Hfo_wOH + Mg^{+2} = Hfo_wOMg^+ + H^+$	-4.6
$Hfo_wOHSO_4^-$	$Hfo_wOH + SO_4^{2-} = Hfo_wOHSO_4^-$	0.79
$Hfo_wSO_4^-$	$Hfo_wOH + SO_4^{2-} + H^+ = Hfo_wSO_4^- + H_2O$	7.78

^a Data for arsenic solution species from Langmuir et al. (1999a). Data for surface complexation reactions from Dzombak and Morel (1990).

the EPICS calculation could be directly compared to the amount estimated using PHREEQC. A potential problem was expected if the distribution coefficients did not follow linear isotherms as assumed in the EPICS model. A non-linear isotherm could be expected if the surface charge of sorbing solids were to change during the experiments, which would change the surface potential.

Although the units for K_d^{tr} as shown in Eq. (8) are volume/mass (V/M), the modeling calculations do not require that K_d^{tr} be reported in V/M units. This is because the sorbed concentration is expressed in terms of a concentration of adsorbed As/L. In the diffuse layer model in PHREEQC, surface sorption sites have no mass. The substrate, which is typically HFO, has a mass, but the model does not require that the adsorption sites have a mass. In the model, the units for K_d^{tr} in this application are (moles/L of As_{sorbed})/(moles/L of As_{in solution}). In the experiments the mass of the sorbent is not required, because all concentrations are referenced to the aqueous phase. The authors calculate a dimensionless distribution coefficient in the same fashion that a dimensionless Henry's law constant is calculated. In the experimental measurements that use actual tailings, the mass of solid is a constant for each test, so that likewise it is eliminated from subsequent calculations.

For the primary leaching solution, which was As-free, the assumed major ion concentrations were 400 mg/L Ca, 230 mg/L Na, 243 mg/L Mg and 2400 mg/L SO₄. Arsenic was added to the primary solution in various initial concentrations to produce the starting solution for each model. One liter of the primary solution was allowed to react with the adsorption sites. To further simplify the calculations, only one type of adsorption site was used. The weak sites (Hfo_wOH), as defined by Dzombak and Morel (1990) were assumed at a concentration of 0.001 mol/L, for all of the simulations.

To obtain the data required for the EPICS calculation, additional leach solution was added to the initial

1-L system, changing the solution/sorbent ratio. In these simulations the final volumes were 1.2, 1.4, 1.6, 1.8, 2.0, 3.0, 4.0 and 5.0 L. In the PHREEQC models, the leaching solution is added using the MIX keyword, which mixes two or more solutions. The increase in volume as the solutions are added together is included as part of the MIX keyword calculations. This makes the PHREEQC program ideally suited to verifying the EPICS method. A portion of a PHREEQC input file is shown in Appendix B. For each step in the process, the 1 L of As bearing solution was mixed with a volume (0.2 to 4.0 L) of the “As-free” leaching solution, and the new mixture equilibrated with the adsorption sites. This is not exactly the same process that occurs in the experimental measurements, but the models do provide data that can be used to verify the computational methods.

The simulations of As adsorption on HFO were run at various As concentrations, and pH values adjusted with Ca(OH)₂. Table 2 summarizes the verification calculations at concentrations of 0.1, 1, and 10 mg/L total As. The amount of readily releasable As is calculated using Eq. (12) to first estimate the EPICS calculated sites and then Eq. (13) to calculate the total amount of readily released As. Table 2 provides a comparison of EPICS and PHREEQC calculated site concentrations. The model, and subsequent calculations, show that readily released As concentrations, calculated using the EPICS methodology, and the total initial values used in PHREEQC are in close agreement. The model simulations demonstrate that the EPICS method is computationally sound.

Fig. 1 shows As concentrations for two PHREEQC simulations. The theoretical dilution lines in Fig. 1 show As concentrations if simple dilution is the only process operating on the system. Departures of model-simulated lines from the dilution lines indicate that a significant solid reservoir of As buffers dissolved As concentrations. The data are replotted in Fig. 2 as inverse concentrations, which linearizes both the data and the dilution

Table 2
Verification of the EPICS procedure by comparison with PHREEQC modeling results

Initial As concentration (mg/L)	pH	As _(aq) (moles/L)	K_d^{tr}	$F_{\text{(desorb)}}$	EPICS Calculated sites (moles)	PHREEQC Calculated sites (moles)	Readily released As (moles/L)		Percent agreement EPICS vs. PHREEQC
							EPICS	PHREEQC	
0.1	6	1.22×10^{-8}	155	0.99	1.32×10^{-6}	1.33×10^{-6}	1.35×10^{-6}	1.34×10^{-6}	100.6
	7	9.14×10^{-10}	5725	1.00	1.34×10^{-6}	1.34×10^{-6}	1.34×10^{-6}	1.34×10^{-6}	100
	8	8.64×10^{-11}	506	0.99	1.33×10^{-6}	1.34×10^{-6}	1.33×10^{-6}	1.34×10^{-6}	99.4
1	6	1.31×10^{-7}	469	0.98	1.32×10^{-5}	1.33×10^{-5}	1.35×10^{-5}	1.34×10^{-5}	100
	7	1.03×10^{-8}	123	0.99	1.34×10^{-5}	1.34×10^{-5}	1.34×10^{-5}	1.34×10^{-5}	100
	8	9.61×10^{-10}	448	0.99	1.33×10^{-5}	1.34×10^{-5}	1.33×10^{-5}	1.34×10^{-5}	99.3
10	6	2.69×10^{-6}	28.4	0.93	1.25×10^{-4}	1.31×10^{-4}	1.30×10^{-4}	1.34×10^{-4}	97.3
	7	6.45×10^{-7}	53.5	0.96	1.29×10^{-4}	1.33×10^{-4}	1.30×10^{-4}	1.34×10^{-4}	97.4
	8	4.87×10^{-8}	130	0.98	1.31×10^{-4}	1.34×10^{-4}	1.31×10^{-4}	1.34×10^{-4}	98.2

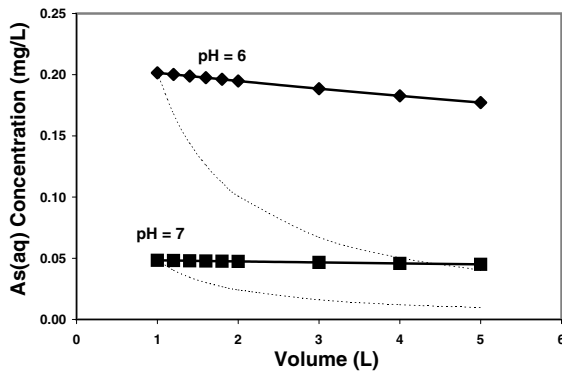


Fig. 1. Model derived $As_{(aq)}$ values computed from PHREEQC simulation of the EPICS procedure at pH 6 and 7, assuming As adsorption on ferrihydrite (HFO), and total readily released As = 10 mg/L. Theoretical dilution lines are dashed.

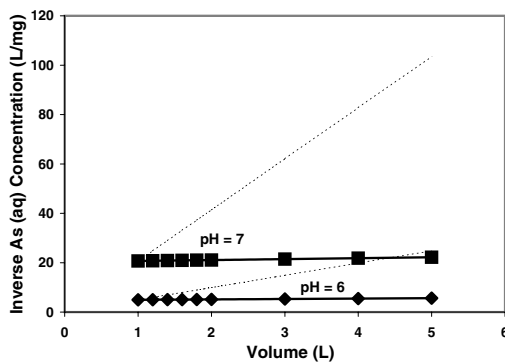


Fig. 2. Inverse concentrations of model derived $As_{(aq)}$ values computed from PHREEQC simulation of the EPICS procedure at pH 6 and 7, assuming As adsorption on HFO, and total readily released As = 10 mg/L. Theoretical dilution lines are dashed.

lines. By definition, the dilution lines correspond to a K_d^{tr} of 0.0. As shown by Fig. 2 these lines have an intercept of zero, and a slope that equals the inverse concentration at the first data point.

For the pH 7.0 data, a regression calculation gives a slope of 0.38, an intercept of 20.3, and a K_d^{tr} of 53. Similar calculations for the pH 6.0 data lead to $K_d^{tr} = 28$. The K_d^{tr} for the pH 7.0 data is greater than that for pH 6.0 because both solutions contain large SO_4 concentrations. Desorption of the SO_4 with increasing pH increases the number of sites available for As adsorption, which increases K_d^{tr} .

5. Experimental methods and measurements with tailings

A pre-weighed container (approximately 7-L size, wide-mouth plastic bucket) was partially filled with approximately 1 L of neutralized tailings slurry. The

pH of the slurry was measured. The mass of the slurry was measured by reweighing the container. The initial volume was defined as V_1 . For most measurements, the slurries contained 400–600 g of solids. The remainder of the slurry consisted of neutralized raffinate. Slurry solids were allowed to settle and an aliquot of supernatant solution was carefully drawn off. This and subsequent aliquot volumes were kept as small as possible, and were always less than 25 mL. The collection of small aliquots was necessary to keep the overall system ‘closed’ with respect to total As. This was also the primary reason for using large initial volumes. The aliquot was filtered (0.45 μ m) and analyzed for total As. After each aliquot was drawn off, the container was reweighed to estimate the mass of solution removed.

The leaching procedure required waters with two different As concentrations. The starting solution was the neutralized and unmodified raffinate, which typically has an As concentration of <1 mg/L. The second water was the ‘As-free’ leaching solution. Approximately 3 to 4 L were required for each desorption experiment.

Earlier verification calculations using PHREEQC demonstrated the need to maintain a constant ferrihydrite surface charge as the two solutions were mixed. Consequently, leaching solutions had to have the same pH and major ion composition as the starting solutions. The ‘As-free’ leaching solution was prepared as follows. A 9% ferric sulfate solution, made up by diluting a stock ferric sulfate solution, was neutralized with added lime to pH 5, yielding a precipitate that consisted primarily of gypsum and an amorphous ferric hydroxide. This precipitate was rinsed and pressure filtered to remove unreacted ferric sulfate solution and unreacted lime. The tailings discharge water was then added to the rinsed filter residue and pressure filtered. The filtrate was collected and analyzed for As and major ions including SO_4 , Ca, Na, Mg and Ni. This produced an ‘As-free’ water with an As concentration of less than 0.01 mg/L. The composition of the leaching solution was compared to the composition of the starting solution to assure that As removal did not change the major ion concentrations. If the dissolved As concentration in the leaching solution was less than 1.0% of its value in the neutralized raffinate/tailings slurry, and if concentrations of the other major species were within 15 relative percent difference (RPD) of their values in the neutralized raffinate, then that composition was considered suitable for use as the leaching solution. Because the usual concentration of As in the tailings thickener underflow water is approximately 1 mg/L, the maximum acceptable As in the leaching solution was less than 0.01 mg/L. Table 3 shows the As and other species concentrations in the starting solution, leaching solution and final solution from a typical set of desorption measurements. The results indicate RPDs of less than 10% for SO_4 , 12% or less for Ca, and zero for Mg and Na.

Table 3
Summary of analytical results for a typical desorption experiment

Solution	pH	As	Ca	Mg	Na	SO ₄	Fe	Ni
Starting solution	7.67	0.98	590	100	100	2100	0.24	0.87
Leaching solution	7.14	0.004	670	100	100	2310	0.02	0.59
Final solution	7.7	0.32	650	100	100	2260	0.1	1.04

All concentrations are in mg/L.

Because of the large volumes required by the experimental procedure, the amounts of solution and masses of solids in the mixtures were measured gravimetrically. To start the experimental procedure, approximately 1 L of “As-free” leaching solution was added to a liter of the tailings slurry. The total volume added was determined after reweighing the container and correcting for the density of the leachate solution. The new volume was defined as V_2 . The slurry was mixed for approximately 10 min and the pH was measured. If the pH had changed by more than 0.1 pH units, it was adjusted by adding either $\text{Ca}(\text{OH})_2$ or concentrated H_2SO_4 . The reaction bottle was mixed again and the solids allowed to settle. In most experiments settling times were limited to approximately 1 h. The pH was rechecked, and if it had not changed by more than 0.1 units from the starting solution value, a sample was withdrawn for chemical analysis. Because dissolved As concentrations are a strong function of pH, the pH was kept constant throughout all the dilution steps.

The process of adding leaching solution, measuring the weight and volume of solution after the addition, adjusting pH, and extracting an aliquot for chemical analysis was repeated two more times (V_3 and V_4). Finally, the remaining water in the slurry was removed by filtration and the solids weighed. The filtered solution and solids were then analyzed for their As concentrations. For the liquid aliquots, total As was measured using inductively coupled Ar plasma spectrometry.

6. Results and discussion

Series 1 desorption experiments were run with 1 h between extractions (Table 4). Results of 4 of these experi-

ments, plotted as inverse concentrations, along with theoretical dilution lines are shown in Figs. 3(a) and (b). Table 4 also gives the ratio V_4/V_1 , which represents the overall dilution during the tests. Values for K_d^{tr} were estimated using the linear regression derived slopes and intercepts from the inverse concentration data. Compared to the dimensionless K_d^{total} values, which range from 600 to 1400 for the experiments, the values for K_d^{tr} are relatively small and range from 0.44 to 2.77 (Table 4). With the exception of the first set of measurements (Set 1.1), correlation coefficients (R^2) range from 0.92 to nearly 1.0. Table 4 also includes the initial and final pH values measured for each step during the process. In spite of an up to 5-fold dilution in some experiments, only slight changes in pH were noted during the tests and so corrections to the pH of the slurries were not required. It is believed that the solids helped buffer the pH.

The results of the first series of tests indicated that little As was released from the solids. In the Series 1 tests extraction times were limited to approximately 1 h. The complete procedure for the 3 steps took less than 4 h. A short time for the extractions was originally used because of concerns that other processes such as mineral dissolution could release additional As into the solution. The generally low amounts of As released from the Series 1 measurements demonstrated that releases from other phases were not an issue. To determine if a slow release process needed to be considered, additional tests were run using a longer time between dilutions. Table 5 summarizes the measurement results for the Series 2 tests. The first test was run as a control with the usual 1 h between measurements. The second two tests were run with 12 h between measurements. During these tests, samples were gently mixed every 2 h.

Table 4
Summary of As desorption measurement results for Test 1 experiments, with 1 h between extractions

Test number	Initial pH	Final pH	Initial As _(aq) (mg/L) (C_1)	Final As _(aq) (mg/L) (C_4)	V_4/V_1	Inverse slope	Inverse intercept	R^2	K_d^{tr}
1.1	7.65	7.68	0.62	0.14	5.8	2.01	0.89	0.64	0.44
1.2	7.7	7.67	0.32	0.12	4.4	1.83	1.1	0.95	0.6
1.3	8.1	8.04	0.81	0.31	4.5	0.63	0.79	0.96	1.25
1.4	8.03	7.94	0.95	0.49	4.2	0.31	0.86	0.92	2.77
1.5	7.57	7.7	0.98	0.32	5.1	0.68	0.6	0.99	0.88

V_4/V_1 is the overall dilution for the tests.

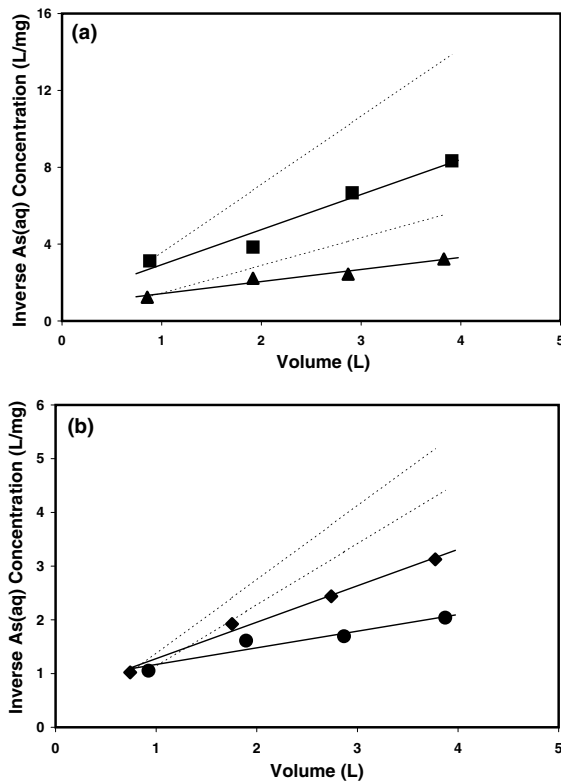


Fig. 3. (a) Test 1 (1 h between extractions): inverse concentrations of EPICS experimental results (Sets 1.2 (filled squares) and 1.3 (filled triangles)) showing experimental data (symbols), linear regressions of the data (solid lines), and theoretical dilution lines (dashed). (b) Test 1 (1 h between extractions): inverse concentrations of EPICS experimental results (Sets 1.4 (filled circles) and 1.5 (filled diamonds)) showing experimental data (symbols), linear regressions of the data (solid lines), and theoretical dilution lines (dashed).

Fig. 4 demonstrates that there was no difference between the Series 2 experiments that used 12 h between leaching/sampling times and the experiment with 1 h between leaching steps. The similarity of results supports the assumption that readily released As is rapidly desorbed in response to changes in the dissolved As concentration. The fact that additional As was not released over time also demonstrates that the remaining As (most

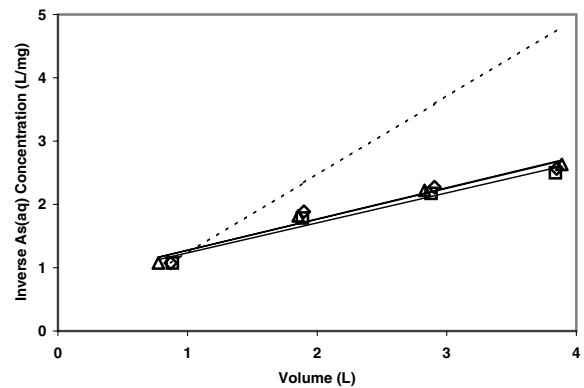


Fig. 4. Test 2 inverse concentrations of EPICS experimental results showing experimental data (Test 2.1, 1 h, open triangle; Test 2.2, 12 h, open diamond; Test 2.3, 12 h, open square), linear regressions of the data (solid lines), and a single theoretical dilution line (dashed).

of the As) associated with the solid phases is practically immobile.

The results in Fig. 4 show little scatter in the calculated concentrations of readily released As. This demonstrates that the method has a high degree of precision. Unlike the Series 1 tests, which were performed separately over several weeks using different feeds from the tailings neutralization circuit, the slurry used in the Series 2 tests was collected and composited over a few hours. The slight variability of K_d^{rr} values for the Series 1 tests in Table 4 probably results from either variations in the composition of the raffinate and leach residue sent to the tailings neutralization circuit, or from variations within the tailings neutralization circuit during several weeks of mill operation.

Table 6 summarizes results of subsequent EPICS calculations, including the values of K_d^{rr} and $F_{(desorb)}$. The table compares initial $As_{(aq)}$ concentrations to the concentration of desorbed As, and to the total amount of readily released As. In these tests, initial As concentrations constitute from 38% to 70% of the total readily released As in the slurry.

The percentage of readily released As in the tailings slurry is compared to the total As content of the slurry in Table 7. Clearly, only a very small % of the total As

Table 5
Summary of As desorption measurement results for Test 2 experiments with 12 h between extractions

Test number	Initial pH	Final pH	Initial concentration of As (C_1) (mg/L)	Final concentration of As (C_4) (mg/L)	V_4/V_1	Inverse slope	Inverse intercept	R^2	K_d^{exch}
2.1–1 h	7.82	7.76	0.93	0.38	5.0	0.49	0.79	0.98	1.6
2.2–12 h	7.89	7.88	0.93	0.39	4.4	0.49	0.78	0.95	1.6
2.3–12 h	7.89	7.88	0.93	0.4	4.3	0.47	0.76	0.97	1.6

V_4/V_1 is the overall dilution for the tests.

Table 6

Calculation of readily released As in JEB mill tailings using the EPICS method

Test	K_d^{rr}	$F_{(desorb)}$	Initial As _(aq) (mg/L)	As desorbed (mg/L)	Readily released As (mg/L)
1.1	0.44	0.31	0.62	0.27	0.89
1.2	0.6	0.38	0.32	0.19	0.51
1.3	1.25	0.56	0.81	1.01	1.82
1.4	2.77	0.73	0.95	2.63	3.58
1.5	0.88	0.47	0.98	0.86	1.84
2.1–1 h	1.6	0.62	0.93	1.49	2.42
2.2–12 h	1.6	0.62	0.93	1.49	2.42
2.3–12 h	1.6	0.62	0.93	1.49	2.42

Table 7

Percentage of readily released As in mill tailings

Test	Initial volume of solution (L)	Readily released As (moles)	Mass solids (g)	% As in solids	Total As in solids (g)	Total As in solids (moles)	Total As in solution (moles)	Readily released As %
1.1	1.07	1.28E-05	464.7	0.158	0.734	0.010	8.85E-06	0.130
1.2	0.88	6.01E-06	298.2	0.126	0.376	0.005	3.76E-06	0.120
1.3	0.85	2.07E-05	277.9	0.149	0.414	0.006	9.19E-06	0.374
1.4	0.92	4.40E-05	470.46	0.25	1.176	0.016	1.17E-05	0.280
1.5	0.74	1.82E-05	337.8	0.26	0.878	0.012	9.68E-06	0.155
2.1–1 h	0.78	2.52E-05	575.4	0.177	1.018	0.014	9.68E-06	0.185
2.2–12 h	0.87	2.81E-05	575.1	0.167	0.960	0.013	1.08E-05	0.219
2.3–12 h	0.88	2.84E-05	561.7	0.199	1.118	0.015	1.09E-05	0.190
Average								0.21
SD								0.08

is dissolved in solution or readily desorbed from the solids. An average of only $0.21 \pm 0.08\%$ of the total As is readily released. The low percentage of readily released As in the neutralized tailings slurry, demonstrates that processing of the acid tailings slurry in the JEB mill to immobilize As has been optimized. However, this only applies to the tailings slurry before it is discharged into the JEB TMF. The discharged slurry typically contains 200 to 400 g/L of solids. In the TMF the tailings are dewatered and become compacted so that the ratio of solids to liquids increases. This suggests all other factors remaining constant, that the percent of total As present in the tailings as readily released As may decrease further with compaction of the tailings.

7. Conclusions

Of major concern to Canadian provincial and federal regulators has been the possibility that As releases from buried U mill tailings in the JEB TMF at McClean Lake, Saskatchewan, might significantly contaminate adjacent ground waters and surface waters. The authors developed and tested a method to address this issue, which included laboratory measurement and modeling of As desorption from neutralized mill tailings slurries. Based on the EPICS method of Gossett (1987), experi-

ments involved the addition of successive volumes of an As-free leaching solution to the neutralized tailings slurry. This resulted in As desorption from the slurry. Both the slurry solution and the leaching solution were chemically identical, except for their dissolved As content, which was about 1 mg/L in the initial slurry solution. In the experiments and modeling, readily released As was defined as the sum of the As initially dissolved in the neutralized slurry plus the As desorbed to solution following addition of the As-free leaching solution. The EPICS approach for measuring As desorption was selected: (1) because it is relatively gentle and avoids the leaching of As associated with poorly crystalline arsenate solids and strongly adsorbed by hydrous Fe(III) oxides and (2) because it closely matches the conditions in JEB TMF pore waters. Prior to performing the desorption experiments, the validity of the mathematical derivation of the EPICS method was checked by comparing EPICS-predicted desorption results to the same results predicted using the diffuse layer adsorption model (Dzombak and Morel, 1990) in the geochemical code PHREEQC (Parkhurst and Appelo, 1999). Excellent agreement between the modeling results demonstrated that the EPICS method was computationally sound.

The experimental results indicated that the amount of As readily released from the tailings is small. In all cases, the As desorbed by dilution was less than 3

mg/L. Distribution coefficients for readily released As ranged from 0.44 to 2.77. With K_d^{rr} values this small, the total amount of desorbed As was similar in magnitude to the concentration of As in the initial tailings solution. In fact, the initial slurry concentration of As comprised from 38% to 70% of the total readily releasable As.

Total As comprised from 0.13% to 0.26% of the total weight of tailings solids. Previous work (Langmuir et al., 1999a,b) indicates that the vast majority of the As in the tailings is strongly bound in solids, either as arsenate mineral precipitates or as specifically adsorbed arsenate on ferrihydrite. Of this total amount, the readily releasable As averaged only $0.21 \pm 0.08\%$. That 99.8% of the total As in the tailings is fixed and not readily desorbed supports the efficacy of the procedures being used for As immobilization in the JEB mill and tailings management facility. These involve the addition of ferric sulfate, if necessary to produce a molar Fe/As ratio of 3 or more in acid tailings raffinates, followed by the addition of lime to pH 4 to optimize precipitation of scorodite. The slurry is retained in the pH 4 tank for approximately 90 min and then transferred to another tank for further liming to pH 7–8 before tailings disposal in the JEB TMF.

Separately, this study shows that distribution coefficients for the desorption of contaminants from complex solids can be determined using the EPICS method when dilution effects are the chief cause of desorption as expected in the JEB TMF. The method is applicable to desorption measurements not only from tailings, but also from other complex solids including soils and sediments.

Appendix A. Derivation of the relationship between inverse concentration slope and intercept with K_d^{rr}

For solutions 1 and 2, the slope m equals

$$m = \frac{\frac{1}{As_{(aq2)}} - \frac{1}{As_{(aq1)}}}{V_{(aq2)} - V_{(aq1)}}. \quad (A.1)$$

Rearranging gives

$$m = \frac{As_{(aq1)} - As_{(aq2)}}{As_{(aq1)}As_{(aq2)}[V_{(aq2)} - V_{(aq1)}]}. \quad (A.2)$$

The intercept b can be estimated from

$$\frac{\frac{1}{As_{(aq2)}} - b}{V_{(aq2)} - 0} = \frac{As_{(aq1)} - As_{(aq2)}}{As_{(aq1)}As_{(aq2)}[V_{(aq2)} - V_{(aq1)}]}. \quad (A.3)$$

Solving for b , this becomes

$$b = \frac{1}{As_{(aq2)}} - \frac{[As_{(aq1)} - As_{(aq2)}]V_{(aq2)}}{As_{(aq1)}As_{(aq2)}[V_{(aq2)} - V_{(aq1)}]}. \quad (A.4)$$

Combining terms produces

$$b = \frac{As_{(aq1)}[V_{(aq2)} - V_{(aq1)}] - [As_{(aq1)} - As_{(aq2)}]V_{(aq2)}}{As_{(aq1)}As_{(aq2)}[V_{(aq2)} - V_{(aq1)}]} \quad (A.5)$$

which is equivalent to

$$b = \frac{As_{(aq2)}V_{(aq2)} - As_{(aq1)}V_{(aq1)}}{As_{(aq1)}As_{(aq2)}[V_{(aq2)} - V_{(aq1)}]}. \quad (A.6)$$

The intercept divided by the slope is

$$b/m = \frac{[As_{(aq2)}V_{(aq2)} - As_{(aq1)}V_{(aq1)}]}{As_{(aq1)}As_{(aq2)}[V_{(aq2)} - V_{(aq1)}]} \times \frac{As_{(aq1)}As_{(aq2)}[V_{(aq2)} - V_{(aq1)}]}{[As_{(aq1)} - As_{(aq2)}]}. \quad (A.7)$$

The $As_{(aq1)}As_{(aq2)}[V_{(aq2)} - V_{(aq1)}]$ terms cancel to give

$$b/m = \frac{As_{(aq2)}V_{(aq2)} - As_{(aq1)}V_{(aq1)}}{[As_{(aq1)} - As_{(aq2)}]}. \quad (A.8)$$

Multiplying both the top and bottom by -1 produces

$$b/m = \frac{As_{(aq1)}V_{(aq1)} - As_{(aq2)}V_{(aq2)}}{[As_{(aq2)} - As_{(aq1)}]}. \quad (A.9)$$

This equation is similar in form to Eq. (8). Dividing by the mass of solid ($M_{(solid)}$) gives K_d^{rr} .

$$K_d^{rr} = \frac{As_{(aq1)}V_{(aq1)} - As_{(aq2)}V_{(aq2)}}{[As_{(aq2)} - As_{(aq1)}]M_{(solid)}}. \quad (A.10)$$

Accordingly, the slope and intercept can be obtained from a linear regression of the inverse concentration data.

Appendix B. Portions of a PHREEQC input file used in testing EPICS calculations

TITLE: MODEL OF As ADSORPTION FOR EPICS CALCULATIONS 1 mg/L pH 7.0

SOLUTION 1 Raffinate for first experiments

pH	7.0
temp	25
units	mg/L
As	1.0
Ca	400
Na	230
S	2400
Mg	243.0

SAVE solution 1

PHASES

Fix_H+

H+ = H+

log_k 0.0

(continued on next page)

Appendix B (continued)**SELECTED_OUTPUT**

```
-file EPICS sorb one ppm As.sel
      -reset true
      -totals As
      -molalities Hfo_wOHAsO4-3
      Hfo_wHAsO4- Hfo_wH2AsO4
```

END

USE Solution 1

EQUILIBRIUM_PHASES 2

```
O2(g)      -30.0
Fix_H+      -7.0 Ca(OH)2 10.0
```

SAVE Solution 2

END

SOLUTION 3

```
pH          7.0
temp        25
units       mg/L
Ca          400
Na          230
S           2400
Mg          243.0
```

END

EQUILIBRIUM_PHASES

```
O2(g)      -30.0
Fix_0H+     -7.0 Ca(OH)2 10.0
```

USE SOLUTION 2

SURFACE 1

```
      Hfo_wOH 1.e-3 600. .52
# surface site density 0.2 moles/mole
```

END

MIX

```
2      1
3      .2
```

EQUILIBRIUM_PHASES

```
O2(g)      -30.0
Fix_H+      -7.0 Ca(OH)2 10.0
```

SURFACE 1

```
      Hfo_wOH 1.e-3 600. .52
# surface site density 0.2 moles/mole
```

END

MIX

```
2      1
3      .4
```

EQUILIBRIUM_PHASES

```
O2(g)      -30.0
```

Appendix B (continued)

```
Fix_H+      -7.0 Ca(OH)2 10.0
```

SURFACE 1

```
      Hfo_wOH 1.e-3 600. .52
```

END

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Control of As and Ni releases from a uranium mill tailings neutralization circuit: Solution chemistry, mineralogy and geochemical modeling of laboratory study results

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Abstract

Processing U ores in the JEB Mill of the McClean Lake Operation in northern Saskatchewan produces spent leaching solutions (raffinates) with $\text{pH} \leq 1.5$, and As and Ni concentrations up to 6800 and 5200 mg L^{-1} , respectively. Bench-scale neutralization experiments ($\text{pH} 2\text{--}8$) were performed to help optimize the design of mill processes for reducing As and Ni concentrations in tailings and raffinates to $\leq 1 \text{ mg L}^{-1}$ prior to their disposal. Precipitate mineralogy determined by chemical analysis, XRD, SEM, EM, XM and EXAFS methods, included gypsum (the dominant precipitate), poorly crystalline scorodite (precipitated esp. from $\text{pH} 2\text{--}4$), annabergite, hydrobasaluminite, ferrihydrite, green rust II and theophrastite. The As was mostly in scorodite with smaller amounts in annabergite and trace As adsorbed and/or co-precipitated, probably by ferrihydrite. Geochemical modeling indicated that above $\text{pH} 2$, the ion activity product (IAP) of scorodite lies between the solubility products of amorphous and crystalline phases ($\log K_{\text{sp}} = -23.0$ and -25.83 , respectively). The IAP decreases with increasing pH , suggesting that the crystallinity of the scorodite increases with pH . Forward geochemical models support the assumption that during neutralization, particles of added base produce sharp local pH gradients and disequilibrium with bulk solutions, facilitating annabergite and theophrastite precipitation.

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1. Introduction

Predicting and controlling the mobility of contaminants such as As in groundwater becomes

increasingly important as risk assessment plays a greater role in the licensing and permitting of waste disposal facilities. Uranium ore from the Athabasca Basin of Northern Saskatchewan contains up to 10% As and 5% Ni by weight (Bourayne et al., 1999), and as a result of the extraction processes used to recover U, significant concentrations of As and Ni dissolve in the raffinate. In the JEB

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Mill, U is extracted from the ore using H_2SO_4 . After U extraction, the leach residue solids are mixed with raffinate, commonly having $\text{pH} < 1.5$. Arsenic and Ni concentrations up to 6800 mg L^{-1} and 5200 mg L^{-1} have been quantified in some raffinates. Following neutralization, solids in the tailings slurry typically consist of 50–70% leach residue minerals with the remainder as precipitated phases. The leach residue contains unreacted quartz and illite, with lesser kaolinite and chlorite. Minor As and Ni also are present in residual niccolite (NiAs) and gersdorffite (NiAsS). The tailings slurry is pumped into the JEB Tailings Management Facility (TMF) for permanent disposal below the water table, using subaqueous emplacement (Bourayne et al., 1999). For facilities licensed by the Canadian Nuclear Safety Commission, federal and provincial Canadian regulators require that environmental effects of U mill tailings disposal on receiving waters remain acceptable over the very long term (greater than 10 ka). Based upon site-specific conditions, As concentrations of less than 5 mg/L for placed tailings pore waters were determined to be acceptable.

A goal of this study was to guide the design and operation of the tailings/raffinate neutralization circuit at the JEB Mill so as to minimize dissolved As and Ni concentrations in treated tailings before their disposal in the TMF. Laboratory studies conducted since 1997 (Langmuir et al., 1999a,b, 2006; Mahoney et al., 2005) show that As and Ni concentrations in neutralized raffinate can be minimized by implementing the following procedures. Prior to neutralization, the molar Fe/As ratio of the raffinate

is increased to ≥ 3 , (if necessary) by the addition of ferric sulfate in a flash mixing tank (Fig. 1). Previous studies have shown that As in neutralized solutions can be reduced to $1\text{--}2 \text{ mg L}^{-1}$ or less if, prior to neutralization, the molar Fe/As ratio is adjusted to ≥ 3 (Krause and Ettel, 1985; Harris and Monette, 1988; Harris and Krause, 1993; Langmuir et al., 1999a,b; Riveros et al., 2001). In the JEB Mill, after adjusting the Fe/As ratio, the combined raffinate and leach residue slurry is neutralized with lime to $\text{pH} 4$ in the first neutralization tank, and to $\text{pH} 7.0\text{--}7.5$, in the second neutralization tank (Fig. 1). Residence times in each tank are approximately 90 min. Laboratory work conducted prior to startup demonstrated that; (1) neutralization to $\text{pH} 4$ and a 90 min holding time in the first tank optimized the precipitation of As(V) in scorodite, and (2) a final $\text{pH} 7\text{--}8$ in the second tank reduced both Ni and As concentrations to 1 mg L^{-1} or less (Langmuir et al., 1999a,b).

A number of researchers have studied the mineralogy of arsenical mine tailings (cf. Foster et al., 1998; Roussel et al., 2000; Pichler et al., 2001; Paktunc et al., 1998, 2003, 2004; Moldovan et al., 2003; Moldovan and Hendry, 2005). Only Moldovan and Hendry (2005) considered the mineralogy of As in tailings during raffinate neutralization. However, in their mill-scale study of Rabbit Lake U mill tailings, their identification of scorodite and ferrihydrite was inferred from geochemical modeling calculations, not proven by mineralogical analysis. Based on modeling calculations they concluded that scorodite was precipitated between $\text{pH} 2.4$ and 3.1 , while from $\text{pH} 3.2$ to 11 , the scorodite presumably

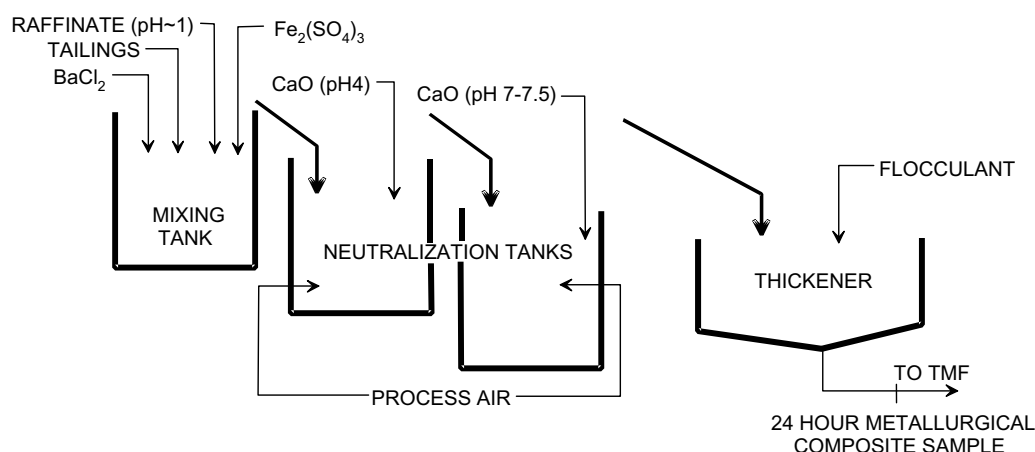


Fig. 1. Schematic diagram of the tailings neutralization circuit at the JEB Mill. The redox potential (Eh) in the mixing tank is approximately 660 mV.

dissolved and arsenate concentrations were controlled by its adsorption onto ferrihydrite. In the Rabbit Lake mill and in the tailings neutralization study of Moldovan and Hendry (2005), the pH is raised rapidly and continuously from pH 1–11 by the addition of lime ($\text{Ca}(\text{OH})_2$). As discussed below, this procedure does not favor the precipitation and crystallization or persistence of scorodite.

In this study, batch neutralization tests were performed from pH 2–8 using raffinate produced by the JEB U mill. The goals, most of which were original to this study, included to

- (1) evaluate the consequences of neutralizing the acid raffinates with NaOH versus with $\text{Ca}(\text{OH})_2$;
- (2) determine detailed changes in solution composition and mineralogy of precipitated solids as a function of increasing pH;
- (3) precipitate As and Ni-rich phases for quantitative mineralogical identification and characterization, using total chemical analysis, x-ray diffraction (XRD), scanning electron microscopy (SEM), electron microprobe (EM), x-ray microprobe (XM) and extended x-ray absorption fine structure (EXAFS) techniques;
- (4) determine the importance of As(III) and As(V) species in the neutralization process;
- (5) establish if the presence or absence of primary tailings solids (leach residue) from the leach circuit affects concentrations of As and Ni and the composition of solutions and secondary solids precipitated during neutralization and
- (6) develop a geochemical model that explains the changes in solution chemistry and secondary mineralogy as neutralization of the raffinate proceeds, including the precipitation and persistence of metastable phases, such as annabergite.

2. Experimental methods

2.1. Batch tests

In the first set of batch tests, approximately 60 L of Raffinate 1 (Table 1) was collected and spiked with As, Ni and Fe(III). A second set of tests utilized ~20 L of Raffinate 2, primarily to assess redox reactions. In both sets, the raffinate was spiked with

additional As as As_2O_5 (anhydrous), and Ni as $\text{NiSO}_4 \cdot 5\text{H}_2\text{O}$. Increasing the amounts of As- and Ni-bearing phases in the precipitated solids improved the reliability of their identification and characterization. Ferric sulfate (Triron[®] solution) was added to the raffinates to increase the Fe/As ratio.

Batch test experiments evaluated As and Ni behavior from pH 2 to ~8. Neutralizing agents included NaOH pellets, dry $\text{Ca}(\text{OH})_2$, and slaked lime ($\text{Ca}(\text{OH})_2 \cdot n\text{H}_2\text{O}$) slurry. Most tests used 2-L beakers as reaction vessels. Up to six 2-L beakers occupied a multi-jar tester (Fig. 2), with a 7th beaker, if needed, stirred separately. In the procedure, a neutralizing agent was added to all the beakers, while continuously stirring and monitoring pH. Larger amounts of base were added to successive beakers, so that each beaker attained its predetermined terminal pH, ranging from 2 to 8. After target pH values were reached, the slurries were filtered and the supernatant solutions analyzed.

2.2. Single-beaker test

To further concentrate As-bearing phases for mineralogical analysis, one experiment was performed in a container with ~5 L of spiked Raffinate 2. The neutralization procedure was similar to that used in the batch experiments, except that when the neutralized raffinate was filtered, the solution was returned to the beaker for additional neutralization and subsequent filtration. This procedure separated different solids as the pH increased by removing previously precipitated solids. Most significant was the removal of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) accompanied by lesser amounts of scorodite ($\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$), precipitated at about pH 2. For the samples collected at pH > 2.2, aliquots of the raffinate were collected for laboratory analysis. Removal of solution for analysis reduced the total amount of raffinate available for subsequent neutralization. Samples of solids were collected at pH values of 2.17, 3.92, 5.66 and 7.34. Filtered samples of solution were taken at pH values of 3.92, 5.66 and 7.34. To increase the amount of solution and solids available during neutralization, a sample was not collected at pH 2.17, because an aliquot from the batch experiments taken at this pH (Sample 9-27-1, pH 2.18) was previously analyzed.

Table 1
Raffinate compositions and summary of Raffinate 2 slaked lime neutralization experimental results (concentrations in mg L⁻¹)

Parameter	Raffinates		Batch tests						Duplicates		Single beaker tests		
	Raffinate 1 Spiked	Raffinate 2 Spiked	9-27-1	9-27-2	9-27-3	9-27-4	9-27-5	9-27-6	9-28-A (duplicate of 9-27-5)	9-28-B (duplicate of 9-27-6)	SB-2	SB-3	SB-4
pH	1.5	0.97	2.18	3.23	4.09	5.29	6.24	7.32	6.08	7.37	3.92	5.66	7.34
Eh (mv)		670	640	590	460	280	140	-190	170	1.0	480	250	-200
Total As	732	690	150	14	3.6	1.15	0.56	0.39	0.76	0.45	6.04	2.1	0.34
As(III)		450	100	7	1.4	0.65	0.40	0.20	0.47	0.20	3.0	1.2	0.25
As(V)		220	48	7	2.0	0.46	0.16	0.17	0.29	0.24	2.9	0.92	0.10
Total Fe	2400	1850	1400	810	695	600	417	33	406	24	705	560	320
Fe(II)		685	540	460	460	390	330	26	320	20	450	440	280
Al	420	200	800	435	440	0.7	0.03	0.01	0.06	0.01	448	1.0	0.06
Ca	760	590	510	520	500	510	530	612	500	540	660	900	1000
Cl	14	13	16	18	19	20	17	18	19	22	16	19	19
Cu		19	16	15	15	1.2	0.03	0.01	0.01	0.11	15	1.3	0.07
K	210	360	390	640	745	570	403	477	160	210	200	260	240
Mg	260	230	1100	490	1010	50	380	750	340	310	340	440	640
Na	48	23	80	43	90	38	24	59	30	32	52	47	45
Si	260	190	580	330	240	62	20	8	19	4	180	58	26
Sulfate	14,100	21,400	10,200	7800	6500	4750	4400	3000	4000	3100	6900	5700	4900
Ni	560	515	500	480	460	370	240	13	230	13	470	380	230
Initial Fe/As	4.4	3.6											
Initial Fe/Ni	4.5	3.8											



Fig. 2. Experimental setup in the batch tests at near final pH values for Raffinate 1 neutralized with slaked lime. The pH values in beakers 1–5 from right to left were 2.18, 3.15, 4.04, 6.09 and 7.38.

3. Methods of chemical and mineralogical analysis

3.1. Solution analyses

Total concentrations of As, Fe and Ni were analyzed using a Perkin Elmer Optima Inductively Coupled Plasma (ICP) Optical Emission Spectrometer (OES). Spectral interference and background correction was accomplished by constructing a multicomponent spectral fitting model using Perkin Elmer software. For Al, Ca, K, Mg, Na and Si the samples were treated with 5% HNO_3 and analyzed directly using a sample injection system consisting of a Gem Cone Nebulizer, a Cyclonic Spray Chamber and a Lumina Injector. Ferrous iron was determined using a HACH Colorimetric Spectrophotometer with 1,10-phenanthroline as the colorimetric reagent. For the measurements involving Raffinate 2, an Amberlite IRA-900 anion exchange resin separated As(III) from As(V). Arsenic(III) and As(V) were individually analyzed by an ion chromatographic method (Tan and Dutrizac, 1985). Sulfate was measured gravimetrically using BaCl_2 .

All pH readings were obtained with a Fisher Accumet Model 15 meter with an Accumet glass body single-junction Ag/AgCl combination electrode (4 m KCl). Redox potential (Eh) was measured during the Raffinate 2 batch tests using a Fisher Accumet Model 10 meter with a combination platinum Ag/AgCl reference electrode (4 m KCl). Calibration of pH was performed daily using pH 4.01 and 7.00 buffers. Redox electrodes were checked daily using quinhydrone in buffered solutions at pH values of 4.01 and 7.00. Eh values were corrected for reference electrode potentials. Chemical analyses of the raffinate solutions used in the batch and single bea-

ker tests, and the experimental results of the tests are given in Table 1.

3.2. Mineralogical analyses

Chemical analyses of solids, except for S, organic C and water, were done by the University of Colorado Mineral Analysis Laboratory using ICP emission spectrometry following HCl and HNO_3 digestion. Sulfur was analyzed using a Leco Sulfur Analyzer (model S144DR) by ASTM method D4239. Organic C was analyzed using a Leco Carbon Analyzer (model CR12) by ASTM method D5373 (American Society for Testing and Materials, 2005), concentrations were commonly on the order of 0.01% or less for organic C. Water was determined by weight loss on heating. H_2O^- was measured as water loss at 70 °C. H_2O^+ was determined as water loss above 70 °C at 100 °C intervals to 900 °C to insure that there was no weight gain due to oxidation of iron. Iron(II) analyses were conducted using a hot digestion in HF and H_2SO_4 , followed by a dissolving solution of boric and phosphoric acids, and a potassium dichromate titration using Na diphenylamine sulfonate as an indicator. Analyses were done in triplicate and averaged. For the Raffinate 2 solids, Fe(II) analyses were performed on the damp samples immediately after filtration to avoid Fe oxidation.

Mineralogical testing included X-ray diffraction (XRD) of powdered samples using a Scintag diffractometer employing Cu $\text{K}\alpha$ radiation. Each sample was scanned at 2°/min from 2° 2θ to 70° 2θ . In the analysis of diffraction patterns, scans were presented with a maximum intensity of 200 counts s^{-1} , to eliminate the upper portions of gypsum diffractions and to emphasize weak diffractions of the

always minor amounts of poorly crystalline phases precipitated from the raffinate. Scanning electron microscopy (SEM) with energy dispersive analysis was performed on select samples using a JEOL Electron Microscope, and analyzed for As, Ni, Fe, S, Al, Si, Mg and Ca. Sample powders were mounted on standard (Au-coated) EM cylinders. Qualitative EM and XM scans at Argonne National Laboratory's Advanced Photon Source supplemented the SEM analyses. The XM slides were mounted dry on glass slides.

Quantitative mineralogical analyses of all samples were performed using the computer model QMAS (Slaughter, 1985, 1990), which combines the XRD, EM and XM results and sample chemistry using linear programming. In the QMAS model, sets of linear inequalities optimize linear “objective functions” to determine approximate mineral compositions and mineral amounts. The inequalities are of either $\geq$ or $\leq$ kinds. One may specify an objective function and inequalities for each type of analysis, whether by x-ray diffraction, optical, infrared, chemical and/or other method. Mineral Gibbs free energies of formation may also be used in the

inequalities, with specified ranges of mineral compositions. The objective functions and sets of inequalities may be combined. The QMAS method determines approximate chemical compositions of selected minerals including scorodite, annabergite ($\text{Ni}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$), ferrihydrite ($\text{Fe}_2\text{O}_3 \cdot 0.5\text{H}_2\text{O}$), theophrastite ($\gamma\text{-Ni}(\text{OH})_2$) and basaluminite ($\text{Al}_4\text{SO}_4(\text{OH})_{10} \cdot n\text{H}_2\text{O}$; $n = 2$ to 13).

4. Results and discussion

4.1. Mineralogical results

Mineralogical analyses of Raffinate 2 batch and single beaker test precipitates are summarized in Tables 2 and 3 as quantified by the QMAS program. Table 2 shows the dominance of gypsum and the later “dilution” of phases such as early forming scorodite, as other phases (mainly ferrihydrite and basaluminite) precipitate with increasing pH. The basaluminite has a composition between hydrobasaluminite (36 H_2O) and basaluminite (10 H_2O). The mineralogical analyses provided both qualitative and quantitative evidence of changes in the

Table 2
Mineral composition (wt%) of solids from slaked lime neutralization of Raffinate 2 in batch tests

Sample no.	9-27-1	9-27-2	9-27-2 (duplicate)	9-27-3	9-27-4	9-27-5	9-27-6	9-28-A	9-28-B
pH	2.18	3.23	3.23	4.09	5.29	6.24	7.32	6.08	7.34
Amorphous Silica	0.06	0.2	0.2	0.81	1.3	1.52	1.53	1.51	1.46
Rutile	0.09	0.08	0.08	0.07	0.06	0.06	0.05	0.07	0.05
Basaluminite	0.03	0.07	0.06	1.6	5.3	4.7	4.4	5.8	4.4
Ferrihydrite	0	0	0	0	2.4	2.6	3.7	3.9	2.9
Goethite	0	2.8	2.6	2	0.34	0	0	0	0
Gypsum	83	80	77	77	76	75	74	68	71
$\text{Ca}(\text{OH})_2$	2.2	1.7	3.0	1.6	0.07	0.23	0.34	1.8	1.9
Theophrastite	0	0	0	0	0.3	1.2	2.3	1.2	2.4
Jarosite	0.04	1.1	1.1	2.2	1	0.9	0.85	1.1	0.9
Annabergite	0	0	0.04	0.17	0.58	0.47	0.29	0.63	0.31
Scorodite	6.5	6.8	7.2	5.7	5.0	4.6	4.4	7.9	6.2
Strengite	1.9	2.0	2.3	1.8	1.6	1.6	1.4	1.8	1.5
Quenstedtite	6.1	5.5	5.9	6.8	6.3	6.8	7.0	7.1	7.2
Total (wt%)	99.98	99.98	99.96	99.95	99.98	99.97	99.95	99.97	99.99
Normalized concentrations (wt%) without gypsum, $\text{Ca}(\text{OH})_2$ or quenstedtite									
Amorphous Silica	0.7	1.8	1.4	5.6	7.3	8.6	8.0	6.5	7.3
Rutile	1.04	0.61	0.59	0.48	0.34	0.34	0.26	0.30	0.25
Basaluminite	0.4	0.5	0.4	11	29	26	23	25	22
Ferrihydrite	0	0	0	0	13.	15	20	12.9	15
Goethite	0.00	21	19	14	1.9	0	0	0	0
Theophrastite	0.00	0.00	0.00	0.00	1.9	6.7	12.	5.5	12
Jarosite	0.46	8.4	8.2	15	5.6	5.2	4.5	4.9	4.3
Annabergite	0.00	0.00	0.29	1.2	3.2	2.7	1.5	2.7	1.6
Scorodite	76	52	53	40	28	26	23	34	31
Strengite	22	16	17	13	9.1	8.9	7.5	8.0	7.3

composition and mineralogy of the solids formed during neutralization. These changes are visually apparent in Fig. 2, which shows slaked lime neutralized Raffinate 1 suspensions near their final pH values.

In the neutralization of Raffinate 2, an olive green color was present in the higher pH samples (Fig. 2). High Fe(II) concentrations were found in the samples collected at pH > 7. X-ray diffraction of precipitates from Raffinate 2 batch test samples 9-27-6 and 9-28-B (Table 2) gave a diffraction peak at 8.7° 2θ, suggesting a phase intermediate between green rust II and ferrihydrite. This peak is a shift from the 8.1° 2θ (001) diffraction of green rust II. Single beaker sample SB#4 collected at pH 7.34 (Table 3) shows diffractions of green rust II shifting to an intermediate phase, then becoming true ferrihydrite. Upon drying, the intermediate phase has an orange brown color, although not all the Fe(II) has oxidized. The mineral fougérite $[(\text{Fe}^{2+}, \text{Mg})_6\text{Fe}_2^{3+}(\text{OH})_{18} \cdot 4\text{H}_2\text{O}]$ is noted in one single beaker sample. Its presence is due in part to

the availability of substituent Fe(II). Fougérite occurs in the same pH range as goethite and “iron oxide hydrate” (JCPDS #13-92 (JCPDS, 2005)). Fougérite is an oxyhydroxide with a hydration state slightly greater than one, with diffractions near those of ferrihydrite, but suggestive of incipient “green rust II”.

Goethite ($\alpha\text{-FeOOH}$), also precipitates beginning at pH ~ 2.5 to 3, where it is identified by X-ray diffraction. The goethite forms coatings on lime particles that are most obvious when dry $\text{Ca}(\text{OH})_2$ is used as the base, but they are also noted when slaked lime slurry is used. As the pH increases, the goethite visibly dissolves from the beakers and is replaced by ferrihydrite and “green rust II” as indicated by the diffraction data. The raffinate solids suspended in solution at pH 7.4 (Fig. 2) have a deep olive green color, and a lighter olive green color at pH 6.09 consistent with the presence of “green rust II”. The deep olive green color suggests that Fe(II) partially substitutes for Fe(III). In the experiments with Raffinate 1, the solids were allowed to air dry before analysis. This resulted in additional Fe(II) oxidation. Ferrihydrite was the dominant solid in all samples formed at pH > 6, in which FeO was still present in the ferrihydrite, as evidenced by chemical analysis, the green color, and shifted high angle diffractions. Jarosite ($\text{KFe}_3^{3+}(\text{SO}_4)_2(\text{OH})_6$) occurs in most samples with Na partially substituting for K. The jarosite usually precipitates with goethite at low pH, with maximum precipitation around pH 4 to 4.5. Some phases, most notably quenstedtite ($\text{Fe}_2(\text{SO}_4)_3 \cdot 11\text{H}_2\text{O}$), were found in the experiments, but are not present in the tailings at the JEB TMF. Quenstedtite is an evaporation product that formed because the filter cakes could not be thoroughly washed after filtration.

Fig. 3 shows the mineralogical composition of the As, Ni and Fe bearing phases in the single beaker tests, normalized after removal of gypsum, quenstedtite and unreacted $\text{Ca}(\text{OH})_2$. The figure shows that scorodite is the dominant As-bearing precipitate at pH 2.17. At pH 3.9, scorodite precipitation is completed and Fe-bearing phases (dominantly fougérite but probably including ferrihydrite) start to form. Sample SB-3 (pH 5.66) shows increasingly smaller proportions of the Fe-bearing minerals because of their dilution by precipitating basaluminite (Table 3; not shown on the figure) and initial formation of theophrastrite. Ferrihydrite and theophrastrite dominate the composition of the final sample (SB-4) at pH = 7.34.

Table 3

Mineral composition (wt%) of solids from slaked lime neutralization of Raffinate 2 in Single beaker tests

Sample no.	SB#1	SB#2	SB#3	SB#4
pH	2.17	3.92	5.66	7.34
Amorphous Silica	0.14	1.3	3.10	3.10
Rutile	0.08	0.05	0	0.01
Basaluminite	0.05	8.3	29.	0.91
Ferrihydrite	0	0	0.16	47
Fougérite	0	18.1	0	0
Gypsum	77	25	478	11.
$\text{Ca}(\text{OH})_2$	0.66	3.8	3.0	1.61
Theophrastrite	0	0	3.4	35
Jarosite	0.19	13	0.09	0.02
Annabergite	0.13	3.3	0.18	0.64
Scorodite	10	7.6	0.07	0.14
Strengite	2.1	3.2	0.07	0.06
Quenstedtite	9.3	16	13	0.76
Total (wt. %)	100	99.79	99.95	99.98

Normalized concentrations (wt%) without gypsum, $\text{Ca}(\text{OH})_2$ or quenstedtite

Amorphous Silica	1.1	2.3	8.6	3.6
Rutile	0.63	0.09	0	0.01
Basaluminite	0.39	15	80	1.0
Ferrihydrite	0	0	0.44	54
Fougérite	0	33	0	0
Theophrastrite	0	0	9.3	40.3
Jarosite	1.5	24	0.25	0.02
Annabergite	1.0	6.0	0.49	0.74
Scorodite	79	14	0.19	0.16
Strengite	16	5.9	0.19	0.07

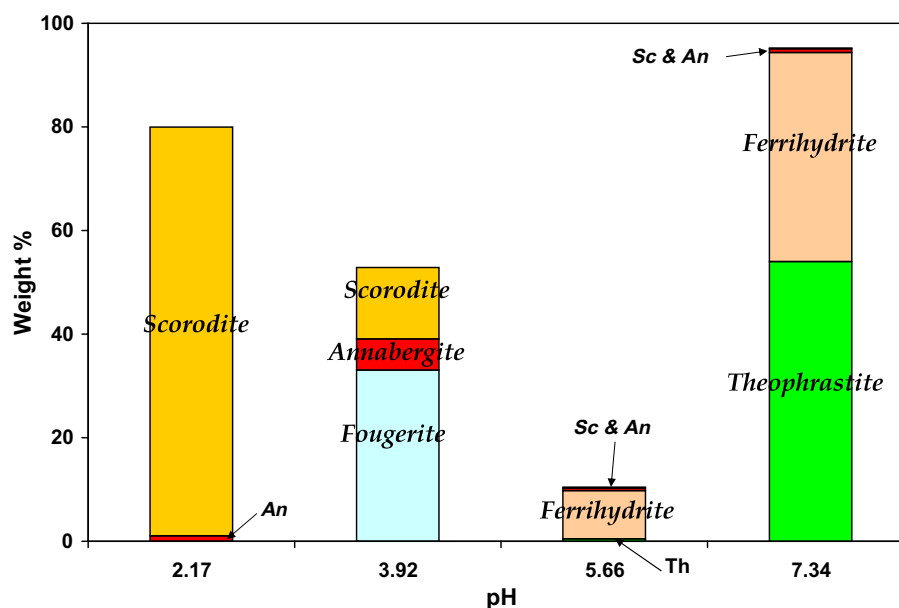


Fig. 3. Relative weight percent values of minerals precipitated in the single beaker tests using lime and Raffinate 2 with final pH values of 2.17, 3.92, 5.66 and 7.34. Weight percent values have been normalized by subtracting the amounts of gypsum, quenstedtite and unreacted $\text{Ca}(\text{OH})_2$. Abbreviations are annabergite, An; scorodite, Sc; and theophrastite, Th. See Table 3.

No significant increase in As concentrations is observed with increasing pH, suggesting that precipitated scorodite remains insoluble as the pH increases to at least 7.4. The scorodite contains Ni^{2+} and Fe(II) substituting for Fe(III). With increasing pH, Ni(II) substitution for Fe(III) increases, while Fe(II) substitution decreases. SEM, EM and XM elemental scans show Ni intimately integrated in the scorodite phases from samples collected at $\text{pH} < 4$, but especially in the pH 2.17 sample. An exhaustive EXAFS study (Chen, 2006) concluded that the As in scorodite, which is normally 4-fold oxygen coordinated, has a coordination number slightly less than 4 in these samples. Substitution of Ni(II) and Fe(II) for Fe(III) most likely has reduced the domain size, effectively reducing the As coordination number. A broad scorodite diffraction peak at $28\text{--}29^\circ 2\theta$ and a second characteristic scorodite diffraction peak at $19.8\text{--}19.9^\circ 2\theta$ persisted and did not change with changing pH or with time. Analysis of aged samples from the mill that had undergone acid dissolution to selectively remove gypsum showed that the acid did not completely remove Ni, demonstrating that Ni is present in an acid insoluble phase (i.e. in scorodite). Aluminum, limited to 2 mole % of Fe(III) in the scorodite, occupies octahedral sites. A separate study of solids from the TMF, as well as solids stored as part of a series of laboratory aging tests (nominal pH of 7 to

7.5, room temperature) indicated that the scorodite persists and remains poorly crystalline for at least several years.

During the initial neutralization of the raffinate, Ni precipitates mainly as a substituent in scorodite or other Fe-bearing phases. Some annabergite also forms as a result of the pH gradients between the bulk raffinate solution and particles of added $\text{Ca}(\text{OH})_2$. With increasing pH, Ni precipitates as a highly disordered Ni–Mg hydroxide, resembling poorly crystalline theophrastite with substituent Mg.

4.2. Arsenic, nickel and iron concentrations

Concentrations of total As versus pH in all of the neutralization experiments are shown in Fig. 4. Results for the different experiments are generally similar. However, experiments that used Raffinate 2 show higher As concentrations in the higher pH ranges, probably resulting from the smaller Fe/As ratio in Raffinate 2 (Table 1). Fig. 4 includes data sets using slaked lime or NaOH as neutralizing agents. The presence of leach residue and the choice of neutralizing agent evidently have no effect on final As concentrations. The continuously decreasing As concentrations, and the similarity of the As concentrations between the Raffinate 2 batch

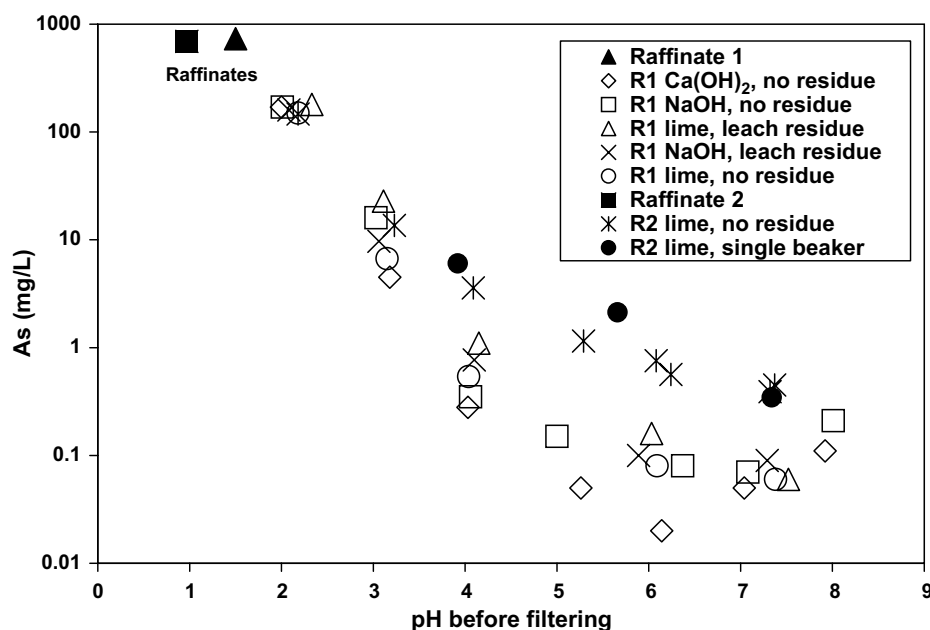


Fig. 4. Total As concentrations as a function of pH in all of the raffinate neutralization experiments. Raffinate 1 (R1) and Raffinate 2 (R2) are shown as a solid triangle and solid square, respectively. Experiments were performed with and without mineral leach residues, and used lime (CaO), slaked lime (Ca(OH)₂), or NaOH as added bases.

measurements, which contained accumulated secondary solids, and the single-beaker measurements, in which solids were removed as precipitation proceeded, indicates that once precipitated, the solids that contain As do not react (re-equilibrate) further with the solutions.

Fig. 5 shows Ni concentrations as a function of pH, and indicates that the choice of neutralizing agents does not influence Ni concentrations in the batch tests. Unlike the effect of the Fe/As ratio on As concentrations, differences in the Fe/Ni ratio do not significantly affect Ni concentrations at near

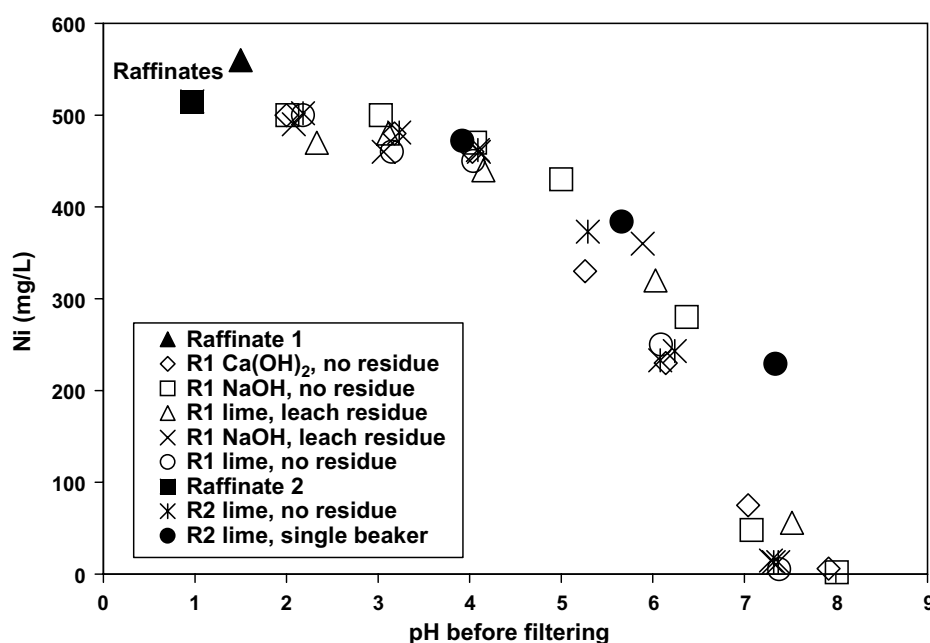


Fig. 5. Nickel concentrations as a function of pH in all of the raffinate neutralization experiments. Raffinate 1 (R1) and Raffinate 2 (R2) are shown as a solid triangle and solid square, respectively. Experiments were performed with and without mineral leach residues, and used lime (CaO), slaked lime (Ca(OH)₂), or NaOH as added bases.

terminal pH values. However, the 3 samples from the single-beaker experiment have greater Ni concentrations than were found in the batch tests, particularly at higher pH values. Fig. 6 shows total As, total Fe, Fe(II) and Ni concentrations during Raffinate 2 neutralization, and demonstrates a correlation between Ni and Fe(II). At comparable pH values, Ni and Fe(II) concentrations tend to be greater in the single-beaker tests than in the batch tests. Removal of previously precipitated solids capable of adsorbing Ni may explain the greater Ni concentrations in the single-beaker tests.

Fig. 7 shows moles of As, total Fe, Ni and Fe(II) removed from solution as neutralization proceeds in the Raffinate 2 batch tests. The molar amounts shown at pH of 2.18 represent the change in composition from the un-neutralized raffinate at pH 0.97. Precipitated amounts in Fig. 7 are cumulative changes. Thus, the data shown at pH 5.29, for example, represent changes from pH 0.97 to pH 5.29. At pH 7.32, essentially all of the Fe and As and most of the Ni have been removed. The amount

removed roughly equals the composition of the original raffinate. Iron and As are removed in a 1/1 ratio up to pH 2.18; strong evidence for scorodite precipitation under these conditions. Continued removal of As in scorodite beyond pH 2.18 is supported by mineralogical analyses of the single-beaker precipitates. As the pH increases to 3.23 most of the remaining As is removed, probably still as scorodite. Approximately 98% of the total As and a significant amount of the Fe is in the solids by pH 3.23.

At low pH, small amounts of Ni are precipitated in annabergite. This is because of strong pH gradients and local pH values that exceed 10 near added particles of slaked lime. Coupled with the abundance of As and Ni, this allows the formation of annabergite. Nevertheless, saturation index (SI) calculations indicate that annabergite is substantially undersaturated in the bulk solution. The SEM, EM and XM work described above, indicate that some Ni is incorporated in rapidly precipitating scorodite. With increasing pH (pH > 5) following complete removal of the As, the remaining Ni precipitates in theophorite.

The batch and single beaker tests show that a variety of secondary As, Fe and Ni phases precipitate during the neutralization of acid raffinate solutions. With increasing pH these include scorodite, ferrihydrite and theophorite. Among the metastable phases, goethite and fougurite disappear with increasing pH, whereas annabergite persists at pH values above 7. A raffinate Fe/As ratio of ≥ 3 reduces the As concentrations resulting from neutralization to less than 1 mg/L and apparently stabilizes scorodite up to pH values above 7 (cf. Mahoney et al., 2005).

4.3. Redox concepts

There are several ways to assess oxidation–reduction conditions during neutralization, although they generally give different answers. One of the simplest methods is to measure the Eh of the system with a Pt or other indicator electrode and a reference electrode (Macalady et al., 1990). However, in a system such as the raffinate, the measured Eh is a total voltage resulting from the combined effect of multiple electron transfer reactions, many of which are poorly reversible. These involve the redox pairs As(V)/As(III), Fe(III)/Fe(II), and the redox sensitive elements Mn, C, S and N, among others. Because the measured Eh is the sum of potentials generated by

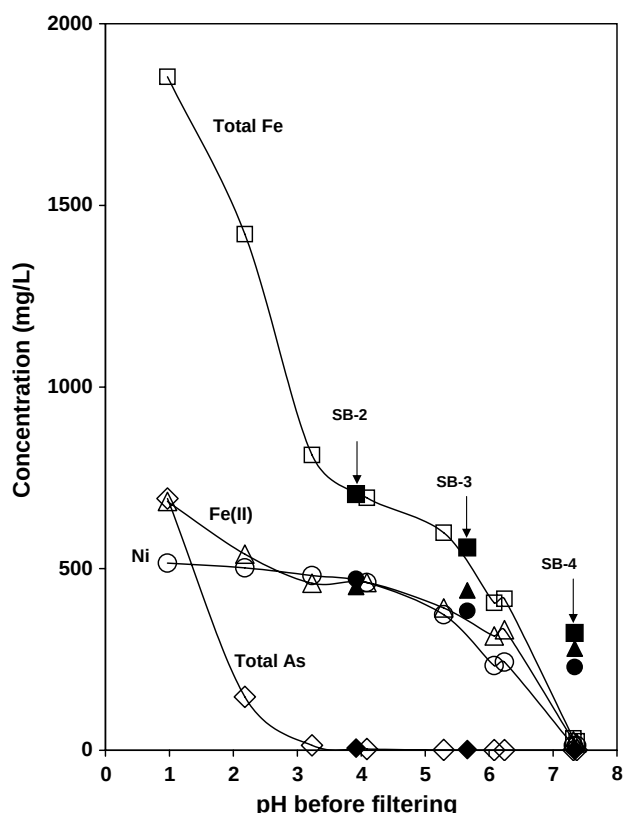


Fig. 6. Arsenic, Ni, total Fe and Fe(II) concentrations during slaked-lime neutralization of Raffinate 2. Squares denote total Fe, diamonds As, circles Ni, and triangles Fe(II) concentrations. Filled symbols are single beaker (SB) results. Solid curves connect results of the 9–27 batch experiments. See Table 1.

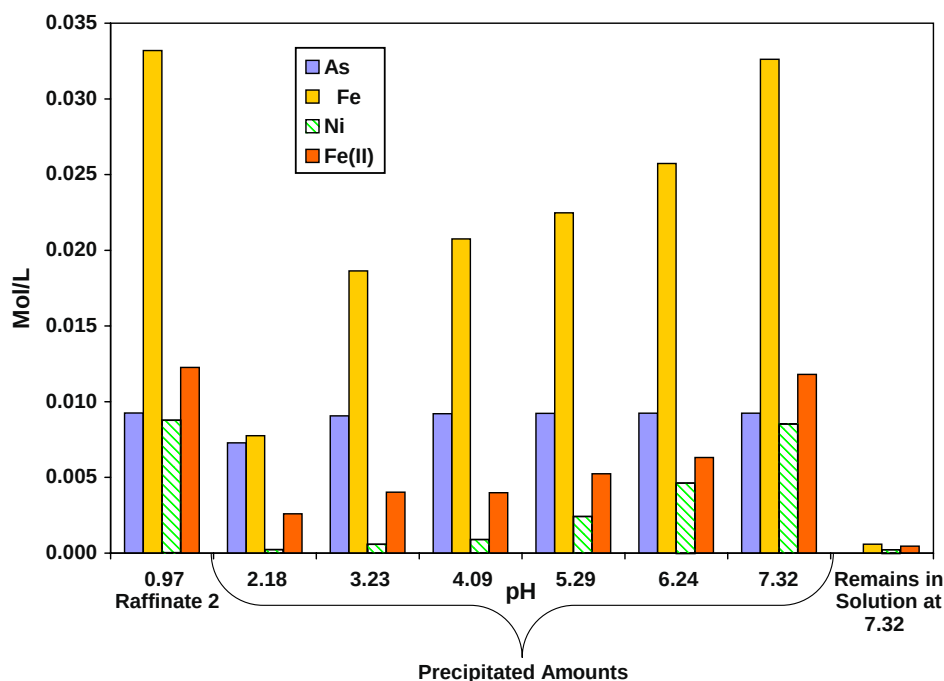


Fig. 7. Molar concentrations in the Raffinate 2 batch neutralization experiments involving added slaked lime. Shown are dissolved molar concentrations in the raffinate, molar amounts precipitated in experiments from pH 2.18 to 7.32, and molar amounts remaining in solution at pH 7.32. Precipitated amounts are based on differences in concentrations in the raffinate and in respective neutralized solutions.

more than one redox reaction, and these reactions are usually not in equilibrium with each other, it is termed a mixed potential (Stumm and Morgan, 1996). Given the probability that the measured Eh is a mixed potential, it is important also to compute apparent Eh values from the measured concentrations of the species in individual redox couples.

4.4. Redox conditions

In the experiments, three types of redox determinations were made. First, nearly continuous Eh measurements were obtained using a Pt indicator electrode and a reference electrode. Samples also were analyzed for total As, and separately for their As(III) and As(V) concentrations. Total Fe and Fe(II) concentrations also were measured, with Fe(III) calculated by difference. Fig. 8 is a plot of the measured Eh, as well as Eh values computed separately from the concentrations of Fe and As species using PHREEQC (Parkhurst and Appelo, 1999). Measured Eh values are generally less than the values computed from the Fe pair, and greater than the values computed from the As pair, possibly indicating that the measured Eh is a mixed potential. Given the general disagreement between Eh values computed from concentrations of Fe and As redox pairs

and the measured Eh, calculations of As(V) speciation and the saturation state of arsenate and Fe(III) minerals were performed using measured concentrations of total As(V) and Fe(III), and not the Eh. Table 1 shows that concentrations of the reduced As and Fe species are comparable to those of the oxidized species, regardless of pH. Although this is true in this study and in mill processing, evidence from laboratory aging tests and from the pore waters of buried tailings in the TMF after 5a of aging indicates that ultimately the system becomes fully oxidized with As(V) and Fe(III) species dominating in the pore water and in the solids.

4.5. Arsenate speciation

Arsenate speciation as a function of pH was computed with PHREEQC for the Raffinate 2 data (Table 1) using measured total Fe(III) and As(V) concentrations. Fig. 9 shows that with increasing pH the dominant arsenate species are H_3AsO_4 , FeHAsO_4^+ , and FeAsO_4 .

4.6. Eh–pH relations

Fig. 10 shows the theoretical stability fields of aqueous Fe species and $\text{Fe}(\text{OH})_3(\text{s})$ in the system

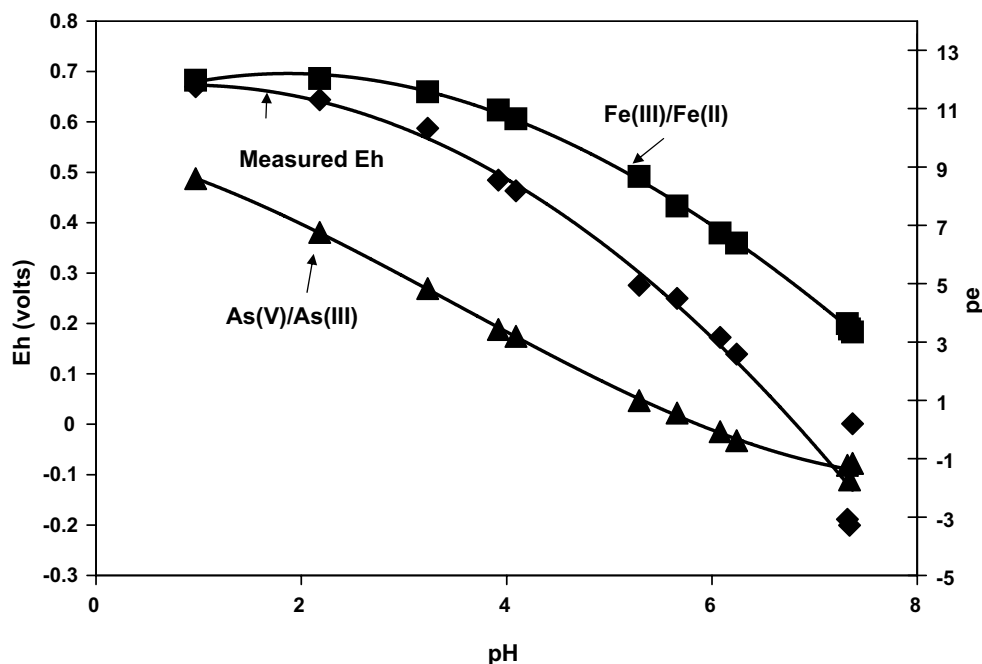


Fig. 8. Measured Eh values and Eh values computed from the concentrations of Fe and As redox species measured during neutralization of Raffinate 2 with slaked lime.

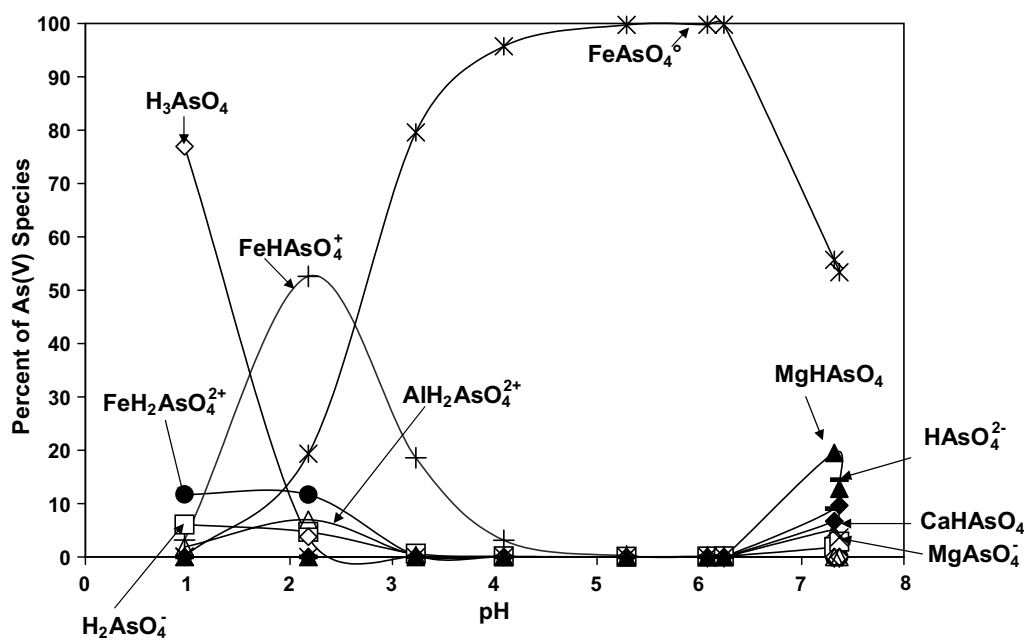


Fig. 9. Percent distribution of As(V) aqueous complexes in batch experiments during neutralization of Raffinate 2 with slaked lime. The figure is computed with PHREEQC, based on the chemical analytical data in Table 1. The Fe and As concentrations used in the calculations are the Fe(III) and As(V) chemical analyses from Table 1.

Fe–H–O–CO₂–S at concentrations typical of the raffinate neutralization experiments and the mill neutralization circuit. Also shown are Eh values computed from measured Fe concentrations, which decrease generally during neutralization particularly

above pH 4. The Eh values, which are based on the activities of free Fe²⁺ and Fe³⁺ ions, were calculated with PHREEQC from the Fe(II) and Fe(III) concentrations. The high SO₄²⁻ concentration (0.1 mol L⁻¹), which is a typical value for the

raffinates, lowers the activity of free Fe^{3+} ion to about 0.1% of the total Fe(III) concentration, and preferentially complexes Fe^{3+} over Fe^{2+} . This reduces the Eh boundary for the $\text{Fe}^{3+} + \text{e}^- = \text{Fe}^{2+}$ reaction from 0.77 V to 0.69 V, so that the first 5 data points plot on the boundary between the Fe(III) and Fe(II) species fields in Fig. 10.

5. Geochemical modeling

5.1. Overview

Geochemical modeling using PHREEQC (Parkhurst and Appelo, 1999) was used to confirm the reactions that control As and Ni behavior during slaked lime neutralization of Raffinate 2. Modeling calculations used an updated thermodynamic data base for metal arsenate complexes and amorphous and crystalline scorodite (Langmuir et al., 2006), the primary source of the database was the WATEQ4F.DAT file provided with the program.

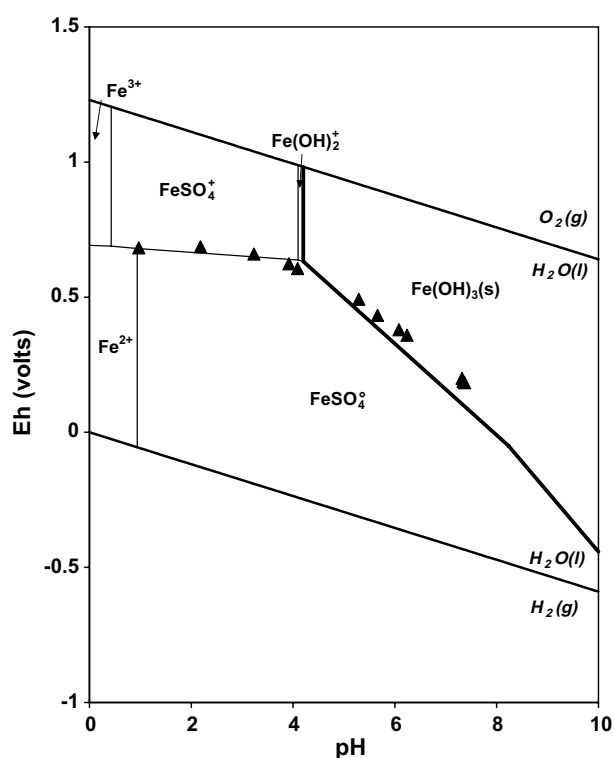


Fig. 10. Theoretical Eh–pH diagram for the system Fe–O–H–S–CO₂ neglecting sulfide aqueous species and solids. Triangles denote Eh values computed with PHREEQC from measured Fe(III) and Fe(II) concentrations. The $\text{Fe}(\text{OH})_3(\text{s})/\text{solution}$ boundary is drawn (in bold) for a dissolved Fe concentration of $10^{-5} \text{ mol L}^{-1}$. The solution contains $\text{SO}_4^{2-} = 0.1 \text{ mol L}^{-1}$ and $\text{HCO}_3^- = 10^{-2.7} \text{ mol L}^{-1}$.

Pertinent reactions can be reviewed in the supplementary information available from the publisher's website. Redox conditions were defined by Eh measurements, and separately by the Eh values computed using PHREEQC from measured concentrations of Fe(III) and Fe(II), and As(V) and As(III) species. A forward geochemical model was also developed to explain the precipitation of metastable annabergite and theophrastite from low-pH solutions.

5.2. Saturation Index Calculations

PHREEQC (Parkhurst and Appelo, 1999) was used to calculate saturation indices (SI values), which are defined as

$$\text{SI} = \log \frac{(\text{IAP})}{(K_{\text{sp}})}$$

where IAP is the ion activity product of the mineral, and K_{sp} is the solubility product constant. At a saturation index of 0.0, the IAP equals the K_{sp} and the mineral is at equilibrium with the solution. Positive values mean that the solution is supersaturated with respect to the mineral. Barring kinetic constraints, the mineral should then precipitate and concentrations in solution should decrease. Negative SI values mean that the solution is undersaturated and the mineral, if present, should dissolve.

Saturation indices of minerals containing Fe(III) and As(V) were computed using the measured concentrations of these species (Table 1). Fig. 11 shows PHREEQC-computed SI values for amorphous ferric arsenate and crystalline scorodite, ferrihydrite, theophrastite and annabergite. Based on the SI calculations, gypsum (not shown) is at equilibrium with the solution at all pH values, with an average SI value of 0.05 ± 0.13 . Saturation with respect to gypsum has been a consistent condition in all solutions including in pore water samples collected from the TMF, and has thus been used as a confirmation that Ca and SO_4 chemical analyses and gypsum SI calculations are correct. As pH values increased, ionic strengths decreased from 0.3 to approximately 0.1 molal. PHREEQC uses the Davies Equation to calculate ion activity coefficients, which for this range of ionic strengths is an appropriate choice.

Fig. 11 shows that during neutralization the SI of scorodite(cr) decreases from highly supersaturated values ($\text{SI} \sim +2$ to $+3$) between pH 1.5 to 3, to $\text{SI} \sim +1$ at pH 7.4. Saturation indices for ferric

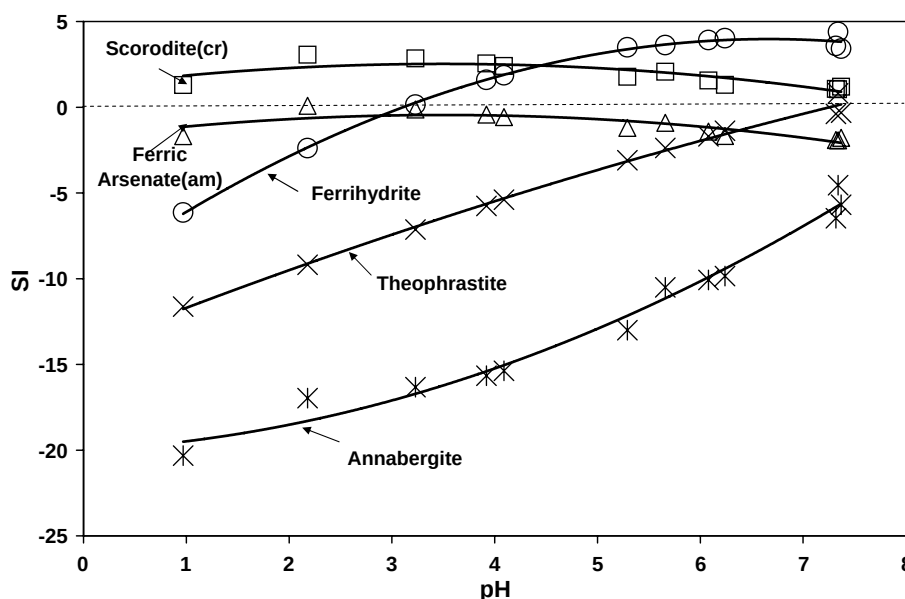


Fig. 11. Saturation indices of some important minerals as a function of pH during neutralization of acid raffinate with slaked lime in batch experiments. The Fe and As concentrations input into the PHREEQC model are the measured concentrations of Fe(III) and As(V) from Table 1.

arsenate(am) indicate that it is near equilibrium with the solution up to $\text{pH} \sim 3$, but becomes progressively undersaturated at higher pH values. Such behavior is consistent with an amorphous ferric arsenate (or poorly crystalline scorodite) being replaced by more crystalline scorodite (less soluble) material as the pH increases to 7.4. This trend suggests that the solubility product of precipitated scorodite decreases with increasing pH. There is a logical reason for such behavior (Langmuir, 1997). Because of decreasing concentrations of dissolved Fe(III) and As(V) with increasing pH, the rate of precipitation of scorodite must decrease. This should produce a more crystalline (ordered) phase. Also, with increasing pH, relatively amorphous scorodite becomes undersaturated and should preferentially dissolve, leaving the more crystalline fraction behind. Any released As is then reprecipitated in more crystalline scorodite. This may be a result of Ostwald ripening (Langmuir, 1997).

The SI of ferrihydrite (HFO) as $\text{Fe}(\text{OH})_3$ ($\text{p}K_{\text{sp}} = 37.1$) in Fig. 11 increases from undersaturated values below pH 3–5, to substantially supersaturated values above this pH. The supersaturated values for HFO probably reflect the slow kinetics of its precipitation and crystallization, because of the elevated sulfate and arsenate concentrations in these solutions (Langmuir et al., 2006). SI values for theophrastite show that it is generally undersaturated, but attains saturation at

pH 7.4. Annabergite is always undersaturated in the neutralization experiments.

5.3. Forward geochemical modeling

Forward geochemical models were developed to simulate the processes that take place during neutralization. It was found that different models can produce similar results. Most importantly the models help explain the precipitation of minerals that cannot be explained by equilibrium-based geochemical modeling. The models were designed primarily to explain changes in As, Ni and Fe concentrations, with an emphasis on As and Ni behavior. First, a geochemical model that assumed equilibrium with the bulk solution was developed to reproduce the precipitation of gypsum, scorodite and theophrastite. Calcium and SO_4 were assumed to be controlled by gypsum precipitation, consistent with its abundance and near-zero saturation indices. Aluminum was assigned to basaluminite. The decrease in Ni concentrations with increasing pH required inclusion of a modeling step to precipitate increasing amounts of annabergite, in spite of the fact that annabergite remains undersaturated in the bulk solutions. Accordingly, the modeling addressed localized precipitation of the Ni arsenates by assuming locally higher pH values out of equilibrium with the bulk solution, such that annabergite could precipitate. Model assumptions were tested by

matching computed and measured concentrations of As, Ni, SO_4 , Al and Fe to the experimental results.

5.4. Modeling Details

Initial modeling simulations assumed equilibrium conditions. In the initial models, $\text{Ca}(\text{OH})_2(\text{s})$ was added to the raffinate at pH 0.97 to raise its pH in single steps to 2.18, 3.23, 4.09 and 5.29, respectively. At each final pH, minerals that had become supersaturated were allowed to precipitate.

To improve the fit between measured and modeled As concentrations, increasingly negative $\log K_{\text{sp}}$ values for poorly crystalline scorodite were assumed with increasing pH, as suggested by the foregoing discussion (Fig. 11, Table 4). Redox conditions were based upon the Eh measurements. The Eh values were included because the model required a mechanism to oxidize the As(III) to As(V). PHREEQC cannot use separate redox conditions for Fe and As, so measured Eh values provided a reasonable compromise. With adjustments to the K_{sp} for scorodite, the simple equilibrium model did an excellent job of matching measured As and Fe concentrations. However, this model did not reproduce Ni concentrations, particularly at low pH.

To match observed Ni concentrations, a non-equilibrium step was added, in which a portion of the raffinate is neutralized to pH 7 without allowing scorodite to precipitate. This step reflects the disequilibrium conditions that must surround particles of incompletely reacted base, causing minerals to precipitate that are not stable in the low-pH bulk solution. A flow chart of the models is given Fig. 12. In the models, a portion of the raffinate is brought to pH 7 and annabergite and ferrihydrite are allowed to precipitate. These solids are then removed from the pH 7 solution (defined as Solution 11 in Fig. 12), which lowers the As, Ni and

Fe concentrations for this solution. The same solution, less the precipitated solids, is then mixed back with the original raffinate.

The proportions of raffinate and the pH 7 solution were estimated from measured changes in Ni concentrations in the bulk solution with increasing pH. For example, Raffinate 2 (pH 0.97) had an initial Ni concentration of 530 mg L^{-1} . At pH 2.18, the Ni concentration was 510 mg L^{-1} , indicating a loss of approximately 4% of Ni between pH 0.97 and 2.18. These differences are considered to be significant, as decreases in Ni concentration were consistently seen among all of the different experimental setups, and Ni was found in the precipitated solids derived from the low pH measurements. A mixture of 96% raffinate and 4% Solution 11 produces a Ni concentration of approximately 510 mg L^{-1} . This was considered an acceptable model fit. Redox conditions were not explicitly defined in these intermediate steps, rather the program estimated a pe value, which was between -0.55 to -0.76 .

To model the pH 3.23 solution, a mixture of 87% raffinate and 13% of the pH 7 solution was assumed. In general, as the pH increased the proportion of neutralized solution increased. These initial steps were used for all the models (Table 4). The proportions of neutralized solution were similarly increased to model the pH 4.09 and 5.29 solutions. The pH 5.29 solution required 60% raffinate and 40% of the pH 7 solution (Fig. 12). The pH 5.29 solution was the starting solution for modeling the solutions at pH 6.24 and 7.32. To model the pH 6.24 solution the pH 5.29 solution was neutralized to pH 6.24. Scorodite, gypsum, basaluminite and ferrihydrite precipitated at this pH. The pH 6.24 solution was then used as the starting composition for the final simulation. At pH 7.32, the model predicted that gypsum, theophorite and ferrihydrite would precipitate. Excellent agreement is observed

Table 4
Parameters used in the geochemical model and modeling results

Solution Number	pH	pe	$-\log K_{\text{sp}}$ Scorodite	Proportions: Raffinate/ High pH Solution	Measured As (mg/L)	Modeled As (mg/L)	Measured Ni (mg/L)	Modeled Ni (mg/L)
1	0.97	11.3	Undersaturated		690		530	
2	2.18	10.9	22.36	0.96/0.04	150	180	510	510
3	3.23	9.93	22.79	0.87/0.13	13	13	490	490
4	4.09	7.83	23.50	0.82/0.18	3.5	3.1	470	470
5	5.29	4.66	24.39	0.60/0.40	1.1	1	380	390
6	6.24	2.36	25.55	No Mix	0.56	0.55	240	390
7	7.32	0.0	25.55	No Mix	0.37	0.55	13	29

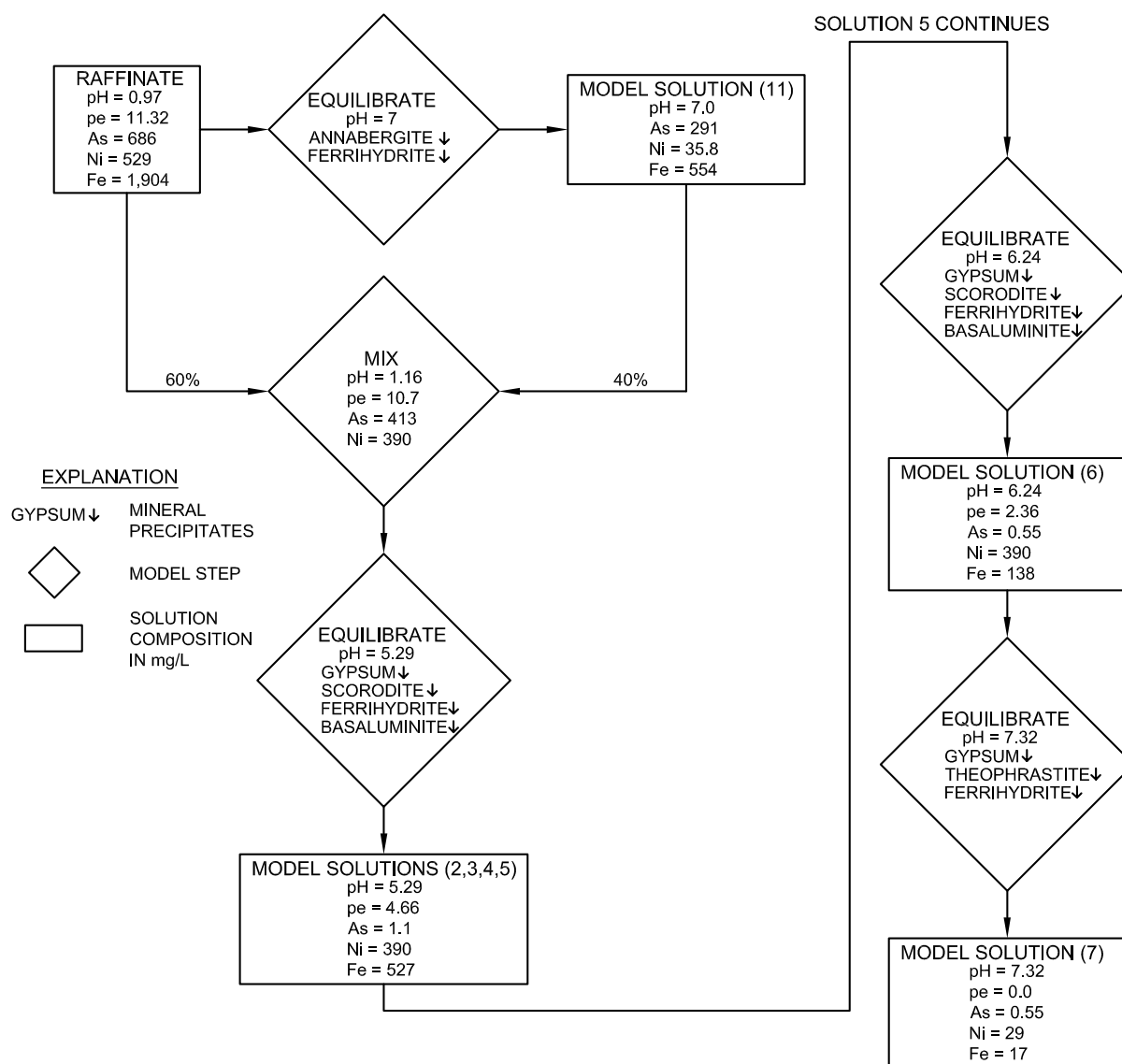


Fig. 12. Flow chart showing steps used in the geochemical model. The figure shows the conditions and resulting compositions needed to produce the final three solutions (numbers 5, 6 and 7). The pH 5.29 solution (Solution 5) is saved and provides the starting composition for Solutions 6 and 7.

between actual and modeled concentrations (Fig. 13).

Successful modeling of the raffinate neutralization process required that both equilibrium and non-equilibrium reactions be considered. To model the non-equilibrium reactions certain modeling steps and conditions were explicitly defined. Alternative model assumptions could have been chosen to produce the same final concentrations. For example, the pH for the disequilibrium step could have been set at pH 9 instead of 7. More Ni would have been removed and smaller proportions of the pH 9 solution would have been required in subsequent mixing steps. It is likely that theophrastrite rather

than annabergite precipitates in response to the pH gradients, particularly in the mid pH ranges where most of the As already has been removed. Because of its non-unique nature, the model at best provides a qualitative understanding of neutralization processes.

The model does not include any surface complexation modeling. There are several reasons why surface complexation modeling was not included. Phase rule requirements are violated if it is assumed that simultaneous equilibrium involving a precipitated phase and a “surface complexed phase” will result in an As concentration that is lower than the solubility of the precipitated phase. For such

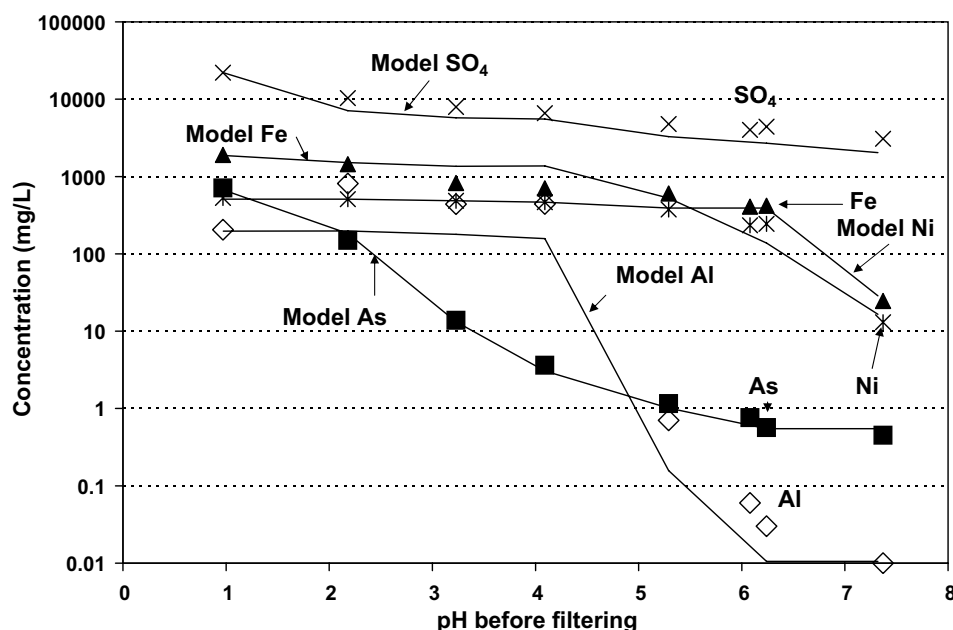


Fig. 13. Model fits (lines) of the concentration data (points) measured during neutralization of raffinate with slaked lime. Modeling assumptions and results are summarized in Table 4. Symbols: SO_4 = X, Fe = triangle, As = square, Ni = lined X, Al = diamond.

conditions the phase (or reaction) that equilibrates with the highest activity of As will control its concentration in solution. For example, any As released from scorodite dissolution should adsorb until the sorption capacity of the ferrihydrite is reached, and the remaining scorodite would still define the activity of dissolved As. Accordingly, for precipitation and adsorption both to apply requires that the two processes not be coupled in the same model step. Simulations that separate the processes often produce unrealistically low final concentrations.

Interaction with secondary solids does, however, play a role in the behavior of Ni. Concentrations in solution are lower than a mineral precipitation equilibrium model would predict, even when a stable $\text{Ni}(\text{OH})_2$ phase is used in the model. The difference between Ni concentrations observed in the bulk experiments and the single beaker experiments suggests that the secondary solids, such as ferrihydrite, influence Ni concentrations. Adsorption reactions may exert an influence on the final Ni concentrations in these experiments, but for reasons outlined above adsorption of Ni was not included in the model.

6. Conclusions

Previous studies have shown that elevated As and Ni concentrations in acid raffinates can be reduced to $1\text{--}2\text{ mg L}^{-1}$ or less if the molar Fe/As ratio of

the raffinate is adjusted to ≥ 3 prior to neutralization (cf. Krause and Ettel, 1985; Langmuir et al., 1999a,b). After Fe/As ratio adjustment, the raffinate/tailings slurry in the JEB mill at McClean Lake is neutralized with lime to pH 4, and then to pH 7.0–7.5 in successive neutralization tanks with residence times in each tank of about 90 min. The result is final As and Ni concentrations of 1 mg L^{-1} or less in neutralized raffinate/tailings slurries prior to their sub-aqueous disposal in a tailings management facility.

This study was designed to understand changes in the solution chemistry and mineralogy of the raffinate/tailings during neutralization in the JEB mill, with a focus on the behavior of As and Ni. Mill-produced raffinates from U ore processing were neutralized from pH 2 to 7.5 in laboratory batch tests. Study results led to the following conclusions. Neither the use of NaOH or $\text{Ca}(\text{OH})_2$ as the base, or whether primary tailings solids (leach residue) were present or absent during neutralization affected final As nor Ni concentrations. Precipitate mineralogy was determined by chemical analysis, XRD, SEM, EM, XM and EXAFS methods. Among the minerals precipitated, gypsum constituted from 71 to 83% of the total, and was at saturation ($\text{SI} = 0.05 \pm 0.13$) at all pH's.

Arsenic(III) which apparently exceeded As(V) in the raffinate, was rapidly oxidized during neu-

tralization. Annual sampling programs conducted at the JEB TMF have shown that with time As(III) is completely oxidized to As(V) in the buried tailings. Other researchers have demonstrated that the oxidation of As(III) to As(V) is facilitated through hydrated Fe(III) oxide particles (Greenleaf et al., 2003). Arsenic in the raffinate was precipitated chiefly in poorly crystalline scorodite, with smaller amounts in annabergite, and trace amounts coprecipitated or adsorbed, probably by ferrihydrite. Geochemical modeling indicated that the scorodite, most of which was precipitated between pH 2–4, decreases in solubility (increases in crystallinity) with increasing pH. Other precipitated phases included hydrobasaluminite, “green rust II”, strengite, jarosite and theophrastite. Nickel was removed from the raffinate by precipitation in scorodite, annabergite and theophrastite. Forward geochemical modeling supports the conclusion that the annabergite, which is always undersaturated in the bulk solutions, and some theophrastite, which only equilibrates above pH 7, were precipitated at lower bulk solution pHs in the vicinity of particles of unreacted base where local pH values may be as high as 10–12.

Acknowledgement

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AGING OF REDUCED ARSENIC MINERALS IN URANIUM MILL TAILINGS AT THE MCCLEAN LAKE OPERATION

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ABSTRACT

The primary arsenic minerals in the uranium ore processed at the McClean Lake Operation are rammelsbergite, niccolite and gersdorffite. During processing, a large fraction, typically (80 - 95%), of these reduced minerals is oxidized and dissolves primarily as As^{5+} in the leachate solution. In the tailings preparation circuit the dissolved As^{5+} is precipitated as a poorly crystalline form of the mineral scorodite. Following subaqueous deposition in the tailings management facility, a temporal rise and fall in arsenic pore water concentrations has been observed. This is due to the oxidation of the residual quantities of reduced arsenic minerals initially present in the tailings sediment. The XANES (x-ray absorption near edge spectrometry) technique has shown that As^{1-} is gradually oxidized to As^{3+} and then finally to As^{5+} in the tailings sediment. This oxidation process results in a temporary accumulation of As^{3+} in solution and is the source of the rise and fall in arsenic concentration observed.

INTRODUCTION

The McClean Lake Operation is an uranium mine and mill facility operated by AREVA Resources Canada Inc. It is located 700 km north of Saskatoon on the eastern edge of the Athabasca Basin. At McClean Lake, the JEB mill has been in operation since 1999. It was designed to process ore from various uranium deposits in the region. Co-mineralized arsenic is commonly associated with uranium deposits in the region [9] and the arsenic content of the ore can range from 0.025% to 4%. Therefore, the mill process had to be capable of treating waste solutions with a wide range of arsenic concentrations. The tailings produced from the mill are ultimately disposed of in the JEB Tailings Management Facility (TMF). This permanent, below grade, subaqueous disposal of a large volume of tailings presents technical challenges because the potential for constituent release from this facility to affect water quality in nearby lakes and streams over the long term exists.

To control long term release of potential constituents of concern to the surrounding groundwater flow system, the JEB TMF is dependent on two principal design parameters. The first principal design parameter is a fine-grained tailings material that, when consolidated, has a hydraulic conductivity at least two orders of magnitude less than the surrounding sandstone. Under these conditions for the long term, the consolidated tailings represent a low-permeability zone and groundwater is expected to preferentially flow around the tailings mass through the surrounding host rock as illustrated in Figure 1.

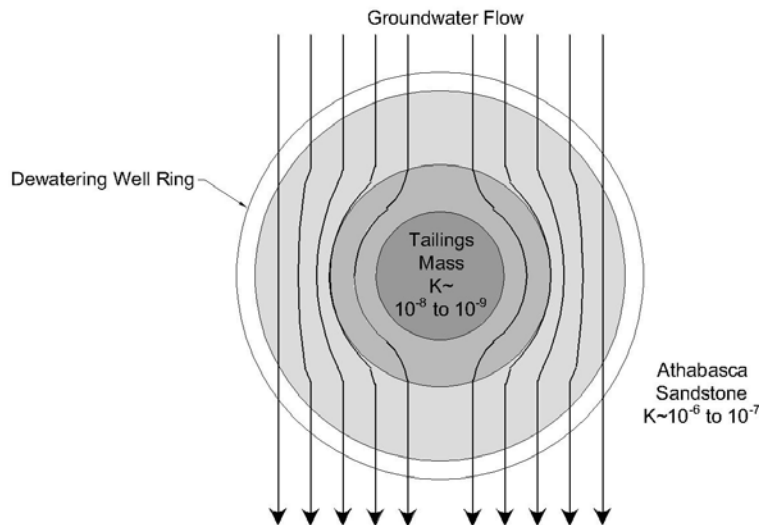


Figure 1 - Plan view depicting the principle physical containment control of the JEB TMF

The second principal design parameter is an engineered tailings geochemistry concept, which is designed to maintain the concentrations of constituents of concern in the tailings pore water at such low levels that releases over the long term are environmentally acceptable. Arsenic must be primarily contained in solid form within the TMF and the arsenic containing solids must be stable in an oxidized environment over the very long term. Arsenic solubility of the solids has to be sufficiently low to provide long-term protection of the receiving environment. Understanding the chemical structure of constituents of concern, such as arsenic, contained in these waste solids and the mineral forms that may evolve into the future are required to predict the long term environmental effects.

DESIGN OF THE TAILINGS PREPARATION CIRCUIT

The preliminary design of the tailings preparation circuit began with a comprehensive literature review and initial scoping tests where fixation of arsenic by ferric iron was selected as the most promising option for consistent treatment of tailings and raffinates. This was followed by larger scale test work conducted at AREVA's pilot plant facility by Service d'Etudes de Procédés et Analyses or SEPA. SEPA Protocol 1 was developed to optimize the impact of iron and lime additions on dissolved arsenic concentrations in tailings raffinate and SEPA Protocol 2 applied an accelerated aging test to estimate the long term arsenic pore water concentration within tailings placed in the TMF. A summary of the SEPA protocols is provided, while the details can be found in Langmuir et al. [4].

The SEPA Protocol 1 was designed to define optimum conditions for removal of arsenic from the raffinates during processing of the tailings by adjusting the Fe/As ratio of tailings raffinates and adjusting the final pH due to slaked lime addition. The procedure simulated the reactions that take place in the mill tailings preparation circuit. Representative tailings were produced in a pilot plant from all ores intended to be processed through the JEB mill. Varying amounts of ferric sulphate and slaked lime were added to reaction vessels that contained 1 kg of tailings and 6.0 L of raffinate solution. These tests were performed in contact with atmospheric oxygen for three hours duration, the expected residence time of the tailings during processing.

The results of the SEPA Protocol 1 tests indicated that by adding ferric sulphate and slaked lime in the tailings preparation circuit to give a raffinate Fe/As molar ratio of at least three and a nominal pH of 7.5, arsenic concentrations of 2 mg/L or less were consistently achieved.

Mineralogical analyses of the laboratory processed tailings concluded that tailings solids include largely unaltered mineral phases from the original ore and a roughly equal amount of solids precipitated by neutralization of the acid raffinate solutions. The majority of the arsenic was precipitated as a poorly crystalline form of the mineral scorodite as the pH was increased by lime addition. All arsenic present in the solids was in the As^{5+} oxidation state.

The accelerated aging portion of the SEPA tests (Protocol 2) were designed to help predict long term arsenic concentrations in TMF pore water after disposal. The tests used the reaction products from the Protocol 1 tailings preparation tests as initial starting materials. The tests were carried out in sealed vessels and continued for 5-6 days to maximum of 49 days, under anaerobic conditions at three different temperatures: 50 °C, 25 °C, and 4 °C. The reactions were accelerated by agitating the vessels on a shaker table.

Predictions from the accelerated aging tests gave consistent results and showed that arsenic concentration in pore waters was unlikely to exceed 2 mg/L in the long term for all ores expected to be processed by the JEB mill.

Overview of Milling Process

The JEB mill employs both sulphuric acid, as a lixiviant, and hydrogen peroxide, as an oxidant, to liberate uranium from ores mined in the Athabasca Basin. This same process liberates approximately 80%

of the arsenic in the ore. The uranium is then removed from the acidic leach solution through contacting an organic matrix in the solvent extraction process. The arsenic remains in the acidic sulphate waste solution, referred to as raffinate.

The raffinate reports to the tailings preparation circuit for precipitation of elements of concern and pH adjustment. All process waste streams, both solid and liquid, are treated concurrently by the JEB mill tailings preparation process. After neutralization, the tailings are placed in the JEB tailings management facility.

The results of the SEPA tests defined the parameters to be used in the tailings preparation portion of the mill process. The preparation circuit employs a pre-treatment stage and a two stage neutralization process (Figure 2). The pre-treatment involves the addition of ferric iron to the raffinate waste stream to achieve a molar ratio greater than or equal to three parts ferric iron to one part arsenic. (Fe/As molar ratio ≥ 3). During vigorous mixing, washed residual solids from the leach circuit are added to the raffinate and ferric iron solution, now referred to as tailings feed solution. The tails feed solution is then directed to the primary reaction tank, where slaked lime addition increases the solution pH from 1 to 4. The stage 1 neutralization tank has a residency time of 90 minutes where slaked lime addition increases the solution pH to 7.5. The slurry from the primary tank is then transferred to the secondary reaction vessel. The secondary neutralization tank also has a residency time of 90 minutes. The arsenic is precipitated with ferric iron as a poorly crystalline form of the mineral scorodite – $\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$ as identified by XRD, SEM, EM, and EXAFS analyses of the solids [1, 5].

The neutralized slurry is then pumped to a high rate thickener, where the slurry is settled and subsequently deposited in the tailings management facility (TMF) for long term disposal. Tailings lines from the mill run down the TMF ramp onto a floating walkway leading to the placement barge. The discharge pipe is suspended below the barge and the tailings are placed within a fluidized bed of tailings using a shallow injection tremie method. The deposited tailings flow in a laminar motion outwards from the deposition point to the outer edges of the TMF.

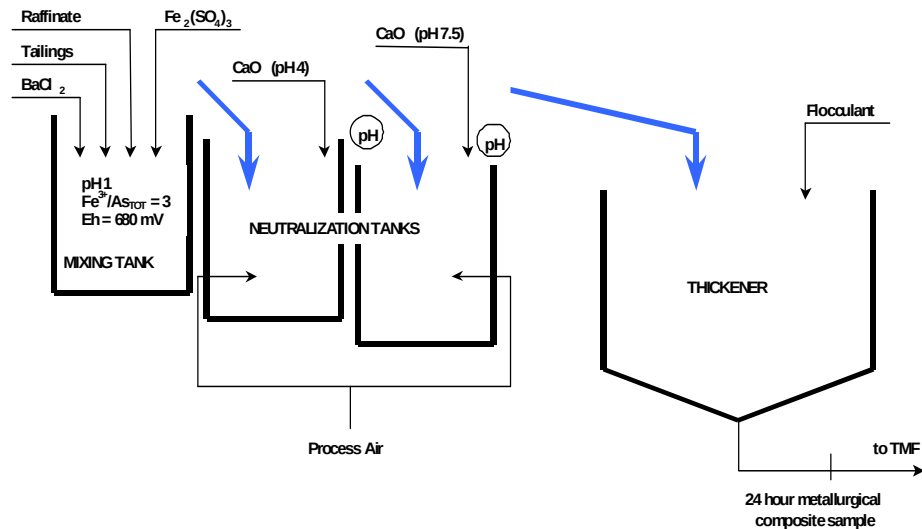


Figure 2 - Schematic diagram of tailings preparation process

PERFORMANCE OF TAILINGS PREPARATION CIRCUIT

When actual production tailings became available, the Tailings Optimization and Validation Program or TOVP aging tests were developed and carried out to validate the performance of the tailings preparation circuit. Initial TOVP aging tests used relatively high arsenic JEB ore which contained about 0.5 to 0.8 wt % arsenic. The Fe/As molar ratio of the acid raffinates was approximately 4. The acid raffinates held about 1100 mg/L arsenic and 1200 mg/L iron. Tailings and raffinates were neutralized with lime in two stages; to pH 4 and 7.5. Samples for the aging tests were obtained by sampling the tailings thickener underflow over a 24 hr period. The samples were split into separate 1 L sample containers for storage at 4 °C, 20 °C, and 50 °C for successive time periods ranging up to 320 days. Sample containers including solids and neutralized raffinate were stored at temperature without mixing until sampled for chemical and mineralogical analysis.

The results of the TOVP aging tests exhibited a temporary rise and fall of arsenic concentration in the pore water, which was not evident in the SEPA aging tests. The arsenic concentration increased immediately after tailings preparation and then decreased over time to the original concentration as shown in Figure 3. The time to reach an equilibrium concentration was dependent on temperature, with the lower temperature series taking the longest time and the higher temperature series taking less time.

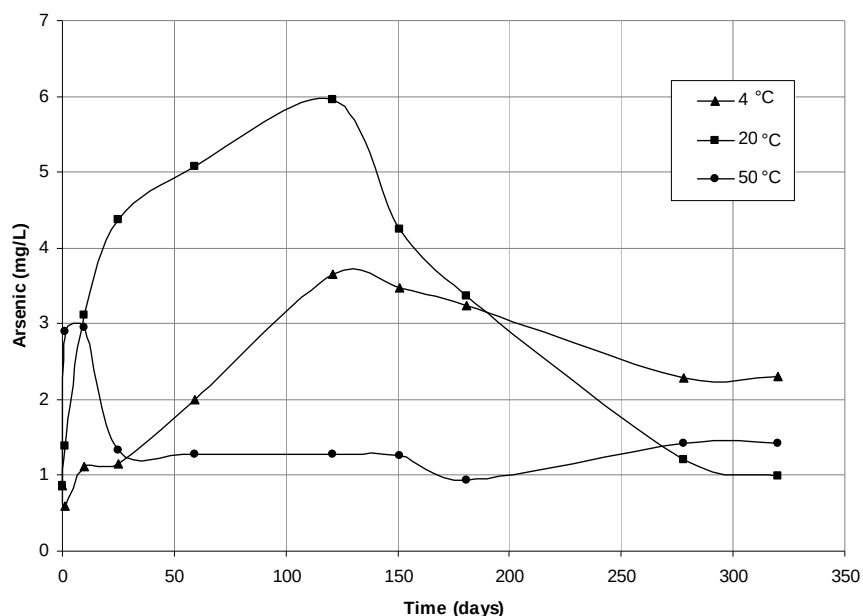


Figure 3 - JEB ore TOVP aging test results - arsenic concentration in tailings pore water

Figure 4 provides a comparison of arsenic pore water concentrations generated by the two techniques. For the SEPA aging technique, the arsenic pore water concentration reach its terminal value within the first day of aging and remained at the same value for the 63 day aging period. Arsenic concentrations in the TOVP test case gradually rose for about seven days and then declined slightly for 14 days. After 21 days, until the end of the aging period, both tests produced very similar results.

There is a significant difference between the SEPA and TOVP aging test techniques with respect to reaction kinetics. The SEPA tests were continuously agitated on a shaker table, while the TOVP aging

tests were static in the sample container, only being vigorously agitated upon final sampling. By agitating the samples the reaction kinetics were increased in the SEPA tests, while diffusion controlled kinetics dominated the TOVP aging tests.

It was suspected that the rise and decline of arsenic concentration was caused by the release of arsenic to solution from an unstable or metastable solid, followed by incorporation of the arsenic in a more stable solid with time. Arsenic was allowed to accumulate in the pore water before precipitating due to the slow reaction kinetics of a diffusion dominated system. Additional TOVP aging tests were conducted to confirm and further investigate this theory.

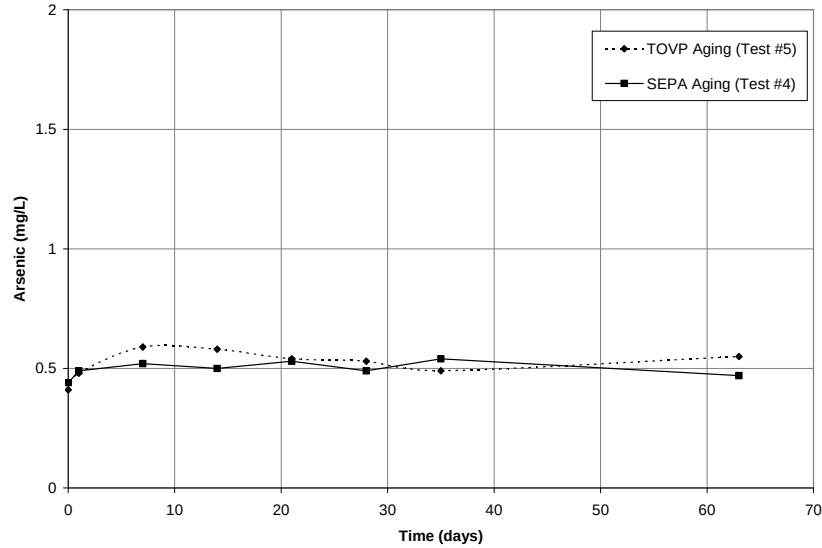


Figure 4 - Comparison of arsenic pore water concentration generated by SEPA and TOVP aging techniques.

The additional TOVP aging tests compared the effects of different raffinate preparations. TOVP test #6 included a preliminary oxidation of the raffinate to achieve a As^{5+}/As_{TOT} ratio of 100% compared to TOVP test #8 which had a As^{5+}/As_{TOT} ratio of 62%. Figure 5 compares the pore water arsenic concentrations for TOVP tests #6 and #8. In pore water generated from fully oxidized raffinate, the arsenic concentration climbed slowly for approximately seven days and remained relatively constant until the termination of aging. In contrast, for the partly oxidized experiment, the arsenic concentration rose sharply to about three times the terminal value in two to three days, and then reduced to the terminal value within 21 days. Thereafter, until the end of aging, the pore water arsenic concentrations were similar for both tests #6 and #8.

For the partially oxidized arsenic tests, a small quantity of soluble As^{3+} is present at the start of aging. Within seven days of aging, As^{3+} is no longer detectable in the sample. This implies that during the early stage of aging with partially oxidized tailings, the small amount of As^{3+} entering the pore water is oxidized to As^{5+} by Fe^{3+} and precipitates. In summary, the additional TOVP tests identified As^{3+} in the initial raffinate as responsible for the transient arsenic concentration observed in the TOVP aging tests.

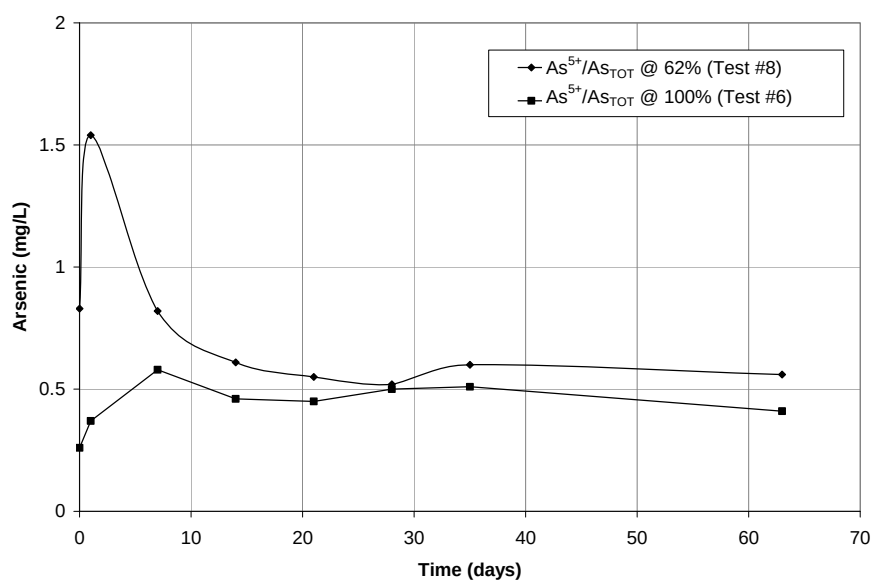


Figure 5 - Effect of arsenic oxidation state in initial raffinate on arsenic concentration during TOVP aging tests

Recent TOVP aging tests completed on Sue A tailings produces similar results to previous TOVP aging tests (Figure 6). In this case, arsenic concentrations reached a maximum of approximately 13 mg/L before declining to 2 mg/L. The arsenic concentration reaches equilibrium after approximately 350 days.

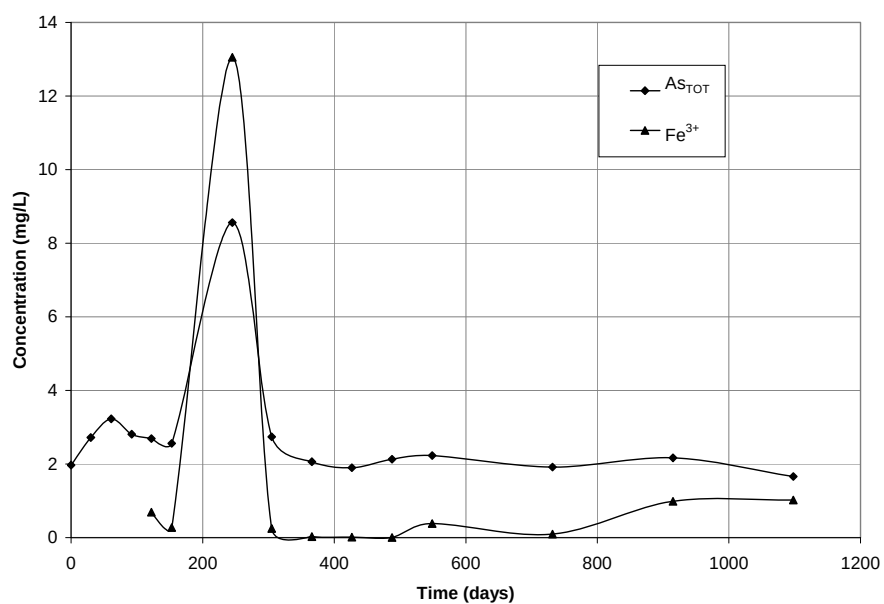
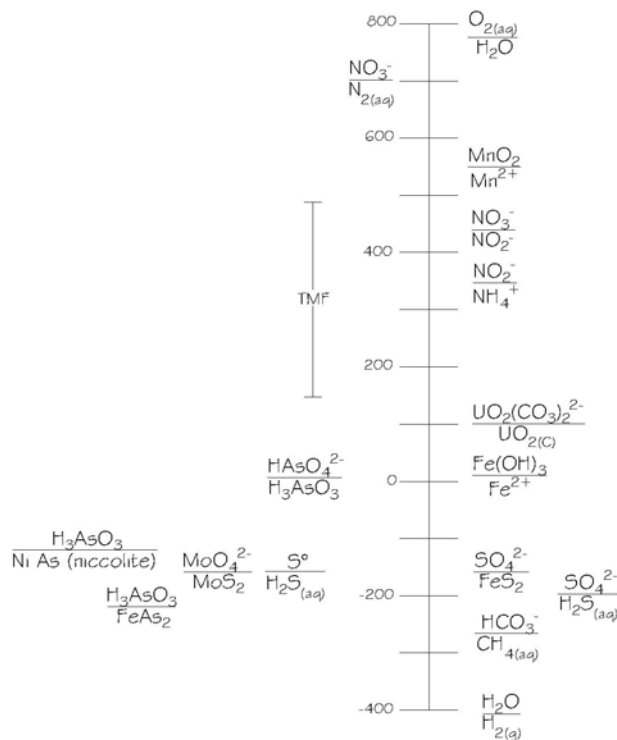


Figure 6 - TOVP aging test of tailings and raffinate produced from milling of Sue A ore

To help understand the oxidation of As^{3+} to As^{5+} in the tailings pore water, a redox ladder diagram from Langmuir [3] shows the Eh values at pH 7 that correspond to different oxidation reduction reactions at chemical equilibrium (Figure 7). The range of Eh measurements completed to date for TMF pore waters is indicated in this Figure (+200 mV to +500 mV). Between these Eh values, species found in the pore water that have a range of stability include NO_3^- , NO_2^- , NH_4^+ , $[\text{UO}_2(\text{CO}_3)_2]^{2-}$, Mn^{2+} , MoO_4^{2-} , AsO_4^{3-} , Fe^{3+} , SO_4^{2-} , and HCO_3^- .

However in the TMF, minor concentrations of reduced species such as As^{3+} and residual amounts of initial arsenic minerals such as rammelsbergite and niccolite have been observed. These latter minerals were not dissolved during leaching and arsenic is present in the As^{1-} oxidation state. Figure 7 indicates that none of the latter species are thermodynamically stable within the more oxidizing Eh range measured in TMF pore waters. Over time, redox sensitive species are evolving to more stable forms within the TMF sediments. This evolution takes a long time because redox processes have very slow kinetics [2]. The pore water therefore contains a mixture of thermodynamically stable and unstable redox-sensitive species. Several redox environments are physically distributed in the TMF due to varying tailings characteristics. Within the pore water analytical data, evidence exists that these reduced species are being oxidized with time.



The theoretical Eh (mV) of some important oxidation reduction couples at equal molar ion concentrations except as indicated below at pH 7 and 25 °C. Other conditions are: $\text{NO}_3^-/\text{N}_2(\text{aq})$ at $\text{N}_2(\text{aq}) = 14 \text{ mg/L}$, $\text{NO}_3^- = 62 \text{ mg/L}$; MnO_2 (pyrolusite)/ Mn^{2+} at $\text{Mn}^{2+} = 1 \text{ mg/L}$; $\text{UO}_2(\text{CO}_3)_2^{2-}/\text{UO}_2$ (uraninite) at 10^{-8} mol/L dissolve U(VI) and $\text{P}_{\text{CO}_2} = 10^{-2} \text{ bar}$; $\text{Fe}(\text{OH})_3/\text{Fe}^{2+}$ at $\text{Fe}^{2+} = 1 \text{ mg/L}$ assuming K_{sp} for $\text{Fe}(\text{OH})_3 = 10^{-38.5}$; $\text{SO}_4^{2-}/\text{FeS}_2$ (pyrite) at $\text{Fe}^{2+} = 1 \text{ mg/L}$ and $\text{SO}_4^{2-} = 96 \text{ mg/L}$; $\text{MoO}_4^{2-}/\text{MoS}_2$ at $\text{MoO}_4^{2-} = 10^{-6} \text{ mol/L}$ and total S = $10^{-3.7} \text{ mol/L}$; and S^0 (native sulphur)/ $\text{H}_2\text{S}(\text{aq})$ at $\text{H}_2\text{S}(\text{aq}) = 108 \text{ mg/L}$ (10-1.5 mol/L). Modified after [3]. Arsenic solids data from [7]. Data for FeS_2 from [3]. Data for niccolite (NiAs) from [6,8].

Figure 7 - Eh ladder diagram for important redox sensitive species in TMF pore waters

Laboratory testing has shown that small residual quantities of arsenic bearing minerals originally in the ore prior to processing, such as rammelsbergite, niccolite and gersdorffite, are present in the leach residue component of the tailings sediment.

Over a period of time, the As^{1-} is gradually oxidized in two steps from As^{1-} to As^{3+} and then finally to As^{5+} in the tailings sediment. The first oxidation step from As^{1-} to As^{3+} occurs more quickly and readily than the second step from As^{3+} to As^{5+} . This oxidation process results in a temporal accumulation of As^{3+} in solution until the As^{1-} source material has been depleted.

All laboratory aging tests to date concludes that the long term pore water concentration for arsenic will remain at 2 mg/L or less for tailings made from all ore bodies expected to be processed in the JEB mill.

TMF Sediment and Pore Water Sampling

Pore water and sediment analytical results from the annual TMF sampling campaigns are being used to confirm that the laboratory aging test work predictions have provided a reliable basis for long term performance of deposited tailings. Four deep bore holes were sampled on five separate occasions. These four boreholes were located at approximately the same coordinates for each sampling campaign. Tailings sediments and pore water were sampled at the same elevations for each of the bore holes. This methodology has facilitated the observation of aging characteristics of the tailings sediment.

The XANES technique was used to analyze the sediment samples from the TMF sampling campaigns. XANES analytical data from the center bore hole with coordinates N11200; E5289 was plotted against sediment age in Figure 8. Measurable quantities of As^{1-} are found in the young sediments which appear to deplete to zero after about 700 days of aging in the TMF. The As^{1-} state is initially oxidized to As^{3+} . The As^{3+} content in the sediments is then observed, over a longer time frame, to deplete and become As^{5+} by a second oxidation step. Within 1,500 days of aging, the relative As^{5+} content has risen from 66% to 91%. This trend authenticates that the long term stable state for arsenic in the TMF sediments is As^{5+} .

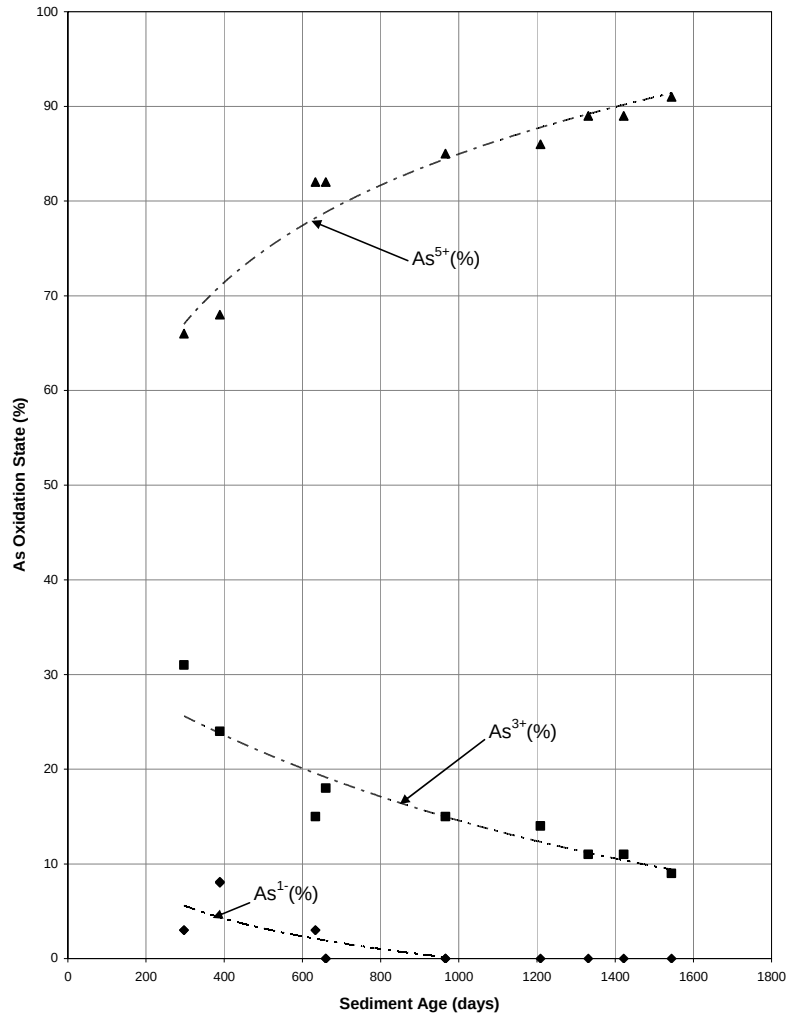


Figure 8 - Relative arsenic oxidation state versus tailings sediment age bore hole coordinates N11200; E5289

Pore water analytical results from the annual TMF sampling campaigns are used to confirm that the laboratory aging test work predictions have provided a reliable basis for long term performance of in situ tailings. The comparison is made in Figure 9. In Figure 9, Case Study #1 presents the arsenic pore water concentrations observed by sampling the same location in the TMF by the annual consecutive TMF sampling campaigns. Clearly, analytical testing results indicate that placed tailings within the JEB TMF have achieved the same end point as both the SEPA and TOVP aging techniques, at approximately 2 mg/L arsenic in tailings pore water. At this point, tailings pore water concentrations appear to be at saturation equilibrium with a poorly crystalline scorodite.

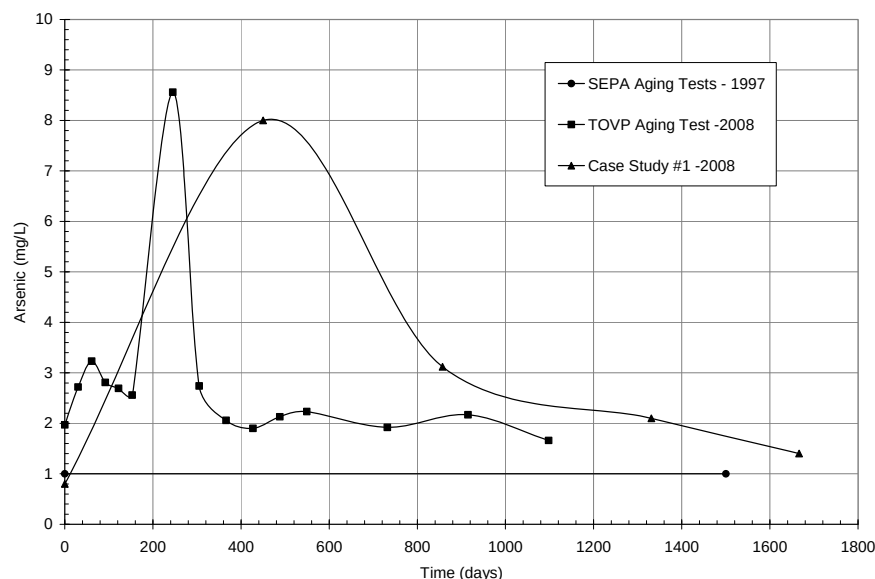


Figure 9 - Arsenic pore water concentration comparison between SEPA aging tests, TOVP aging tests and TMF samples

CONCLUSION

To protect the receiving environment, the JEB TMF at the McClean Lake Operation is dependent on physical as well as geochemical properties of tailings placed within it. The tailings are geochemically designed to maintain low concentrations of constituents of concern. Arsenic must be primarily contained in solid form within the TMF and the arsenic containing solids must be stable in an oxidized environment over the very long term.

Laboratory testing and TMF pore water and sediment sampling has confirmed the long term concentration of arsenic in the TMF pore waters to be 2 mg/L or less. The neutralized raffinate solids of the tailings sediment contain small amounts of arsenic in the As^{1-} and As^{3+} oxidation states. The As^{1-} state represents arsenic in the form of primary minerals of rammelsbergite and niccolite found in the initial ore. Partially oxidized remnants of these minerals are disclosed by the presence of the As^{3+} oxidation state in the leach residue solids. With reference to the Eh ladder diagram, Figure 7, neither of these oxidation states are thermodynamically stable within the more oxidizing Eh range in TMF pore waters. Over a period of several years, the As^{1-} is gradually oxidized by a two step process to As^{3+} and then finally to As^{5+} in the tailings sediments. The first oxidation step from As^{1-} to As^{3+} occurs more quickly and readily than the second step from As^{3+} to As^{5+} . If only As^{3+} were present, anticipated effects on arsenic pore water concentrations would be predicted to be minimal as the rate at which As^{3+} would go into solution would be governed by the rate at which As^{3+} can be oxidized to As^{5+} and removed from solution. However, the oxidation of As^{1-} generates an additional source of As^{3+} to the pore water at a rate faster than it can be oxidized to As^{5+} and removed from solution. This accumulation of As^{3+} in the pore water would be expected to exist until the source material had been depleted. The two stage arsenic oxidation process thus gives rise to the temporal rise and fall in As^{3+} concentrations predicted by the laboratory aging tests and observed in the TMF.

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**An X-ray Spectromicroscopy Study of the Calcium Mineralization in the JEB Tailings Management
Facility at McClean Lake, Saskatchewan**

Supporting Information

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Table S1. The sample depth, pH and porewater concentrations of select elements in the TMF tailings samples as measured during the 2013 sampling campaign.

Sample name	Depth (mASL) ^a	pH	[HCO ₃ ⁻] (mg/L)	[CO ₃ ²⁻] (mg/L)	[SO ₄ ²⁻] (mg/L)	[Ca ²⁺] (mg/L)
Borehole 1						
TMF13-01-SA05	414.68	6.279	146	1	2400	520
TMF13-01-SA12	398.85	6.658	212	1	2100	560
TMF13-01-SA14	395.47	6.910	251	1	1800	550
TMF13-01-SA16	388.77	6.826	188	1	1700	570
TMF13-01-SA17	386.66	6.918	204	1	1700	570
TMF13-01-SA19	383.59	6.905	143	1	1500	510
TMF13-01-SA20	379.68	6.883	155	1	1800	540
TMF13-01-SA22	374.47	7.035	250	1	2100	560
TMF13-01-SA23	367.46	6.623	157	1	1800	550
TMF13-01-SA25	365.27	6.746	102	1	2100	550
Borehole 3						
TMF13-03-SA14	392.20	7.186	421	1	1880	626
TMF13-03-SA16	386.08	7.353	388	1	2000	638
TMF13-03-SA18	381.17	7.286	351	1	2120	656
TMF13-03-SA22	371.09	7.198	179	1	2390	589
Borehole 6						
TMF13-06-SA16	383.69	7.137	195	1	1900	620

Meters above sea level (mASL)

Table S2. The sample depth (meters above sea level), and pore water concentrations of select elements in the TMF tailings samples as measured during the 2008 sampling campaign.

Sample name	Depth (mASL)	pH	[HCO ₃ ⁻] (mg/L)	[CO ₃ ²⁻] (mg/L)	[SO ₄ ²⁻] (mg/L)	[Ca ²⁺] (mg/L)
	Borehole 1					
TMF08-01-SA02	414.11	7.54	71	1	1800	500
TMF08-01-SA08	398.26	7.23	345	1	1900	570
TMF08-01-SA09	394.91	7.47	444	1	1700	570
TMF08-01-SA11	388.20	7.44	259	1	2000	520
TMF08-01-SA12	386.07	7.20	300	1	1700	520
TMF08-01-SA13	383.02	7.36	273	1	1800	540
TMF08-01-SA14	379.06	7.00	586	1	2000	620
TMF08-01-SA16	373.88	7.29	190	1	2100	460
TMF08-01-SA17	370.83	7.22	249	1	2000	520
TMF08-01-SA19	364.73	6.79	110	1	2100	560
	Borehole 3					
TMF08-03-SA09	391.55	7.96	356	1	1780	566
TMF08-03-SA11	385.46	7.65	428	1	1730	569
TMF08-03-SA13	378.75	N/R	N/R	1	2720	369
TMF08-03-SA16	370.52	7.31	159	1	2300	510

Analysis for borehole 6 is unavailable, N/R = no result available

Table S3. The sample depth (meters above sea level), and pore water concentrations of select elements in the TMF tailings samples as measured during the 2013 sampling campaign.

Sample name	Depth (mASL)	[Mg ²⁺] (mg/L)	[Fe] (mg/L)	[As] (µg/L)	[U] (µg/L)	[Ba] (mg/L)
	Borehole 1					
TMF13-01-SA05	414.68	120	0.31	1080	650	0.016
TMF13-01-SA12	398.85	120	10.9	21500	13400	0.02
TMF13-01-SA14	395.47	87	0.86	5830	24200	0.024
TMF13-01-SA16	388.77	82	1.2	15400	8520	0.026
TMF13-01-SA17	386.66	87	0.22	11300	9660	0.034
TMF13-01-SA19	383.59	67	0.021	14600	2620	0.043
TMF13-01-SA20	379.68	92	0.64	11100	3560	0.026
TMF13-01-SA22	374.47	210	0.98	19700	6920	0.026
TMF13-01-SA23	367.46	160	0.6	9320	5510	0.032
TMF13-01-SA25	365.27	180	0.13	1020	1160	0.023
	Borehole 3					
TMF13-03-SA14	392.20	106	0.81	7030	34200	0.021
TMF13-03-SA16	386.08	109	0.15	5790	53300	0.028
TMF13-03-SA18	381.17	167	1.1	11300	18600	0.031
TMF13-03-SA22	371.09	210	0.0092	1980	4530	0.045
	Borehole 6					
TMF13-06-SA16	383.69	130	2.8	6120	8910	0.029

Table S4. The sample depth (meters above sea level), and pore water concentrations of select elements in the TMF tailings samples as measured during the 2008 sampling campaign.

Sample name	Depth (mASL)	[Mg ²⁺] (mg/L)	[Fe] (mg/L)	[As] (µg/L)	[U] (µg/L)	[Ba] (mg/L)
Borehole 1						
TMF08-01-SA02	414.11	40	0.007	1620	500	0.022
TMF08-01-SA08	398.26	120	4	2490	40500	0.015
TMF08-01-SA09	394.91	77	0.84	3010	18700	0.028
TMF08-01-SA11	388.20	92	0.02	6110	38700	0.026
TMF08-01-SA12	386.07	79	0.38	7590	13500	0.049
TMF08-01-SA13	383.02	120	0.5	8210	10200	0.017
TMF08-01-SA14	379.06	180	0.037	4740	12600	0.031
TMF08-01-SA16	373.88	120	0.12	7970	3000	0.035
TMF08-01-SA17	370.83	190	0.5	4550	2590	0.012
TMF08-01-SA19	364.73	180	0.008	950	1290	0.021
Borehole 3						
TMF08-03-SA09	391.55	102	0.54	5720	28600	0.039
TMF08-03-SA11	385.46	110	<0.005	4440	38600	0.052
TMF08-03-SA13	378.75	56	0.006	1020	2510	0.049
TMF08-03-SA16	370.52	117	0.71	1250	3310	0.024

Analysis for borehole 6 is unavailable

Table S5. The concentrations of various C species in the TMF tailings samples as measured during the 2013 sampling campaign.

Sample	Carbon, Inorganic (wt%)	Carbon, Organic (wt%)	Hydrocarbons, (C10-C16) (ppm)	Hydrocarbons, (C16-C34) (ppm)	Hydrocarbons, (C34-C50) (ppm)	Kerosene (ppm)
TMF13-01-SA05	0.03	0.25	3.5	5	5	86
TMF13-01-SA12	0.04	2.09	3.5	5	5	11
TMF13-01-SA14	0.03	0.41	3.5	5	5	10
TMF13-01-SA16	0.01	0.77	3.5	5	5	10
TMF13-01-SA17	0.02	0.66	3.5	5	5	10
TMF13-01-SA19	0.11	0.38	3.5	5	5	10
TMF13-01-SA20	0.08	0.36	3.5	5	5	10
TMF13-01-SA22	0.06	0.41	3.5	5	5	10
TMF13-01-SA23	0.23	1.32	3.5	5	5	10
TMF13-01-SA25	0.06	0.29	3.5	5	5	490
TMF13-03-SA14	0.02	0.59	3.5	5	5	10
TMF13-03-SA16	0.06	3.13	3.5	5	5	10
TMF13-03-SA18	0.02	0.63	3.5	5	5	100
TMF13-03-SA22	0.01	0.64	3.5	5	5	180

Analysis of C speciation for TMF13-06-18 is unavailable

Table S6. The concentrations of various C species in the TMF tailings samples as measured during the 2008 sampling campaign.

Sample	Hydrocarbons, (C11-C20) (ppm)
TMF08-01-SA02	<10
TMF08-01-SA08	<10
TMF08-01-SA09	<10
TMF08-01-SA11	130
TMF08-01-SA12	<10
TMF08-01-SA13	<10
TMF08-01-SA14	<10
TMF08-01-SA16	<10
TMF08-01-SA17	<10
TMF08-01-SA19	46
TMF08-03-SA09	<10
TMF08-03-SA11	100
TMF08-03-SA13	95
TMF08-03-SA16	130

Analysis of C speciation for borehole 6 is unavailable

Table S7. List of Ca containing mineral standards for which Ca K-edge XANES spectra was collected and used in LCF of Ca K-edge μ -XANES spectra collected from tailings. Group 1 and group 2 refer to the groups described in Section 2.4 of this study.

Group 1	Group 2
Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$)	Quicklime (CaO)
Bassanite ($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$)	Yukonite ($((\text{Ca}_7\text{Fe}_{12}(\text{AsO}_4)_{10}(\text{OH})_{20} \cdot 15\text{H}_2\text{O}))$)
Anhydrite (CaSO_4)	Montmorillonite 1 ($(\text{Na,Ca})_{0.33}(\text{Al,Mg})_2(\text{Si}_4\text{O}_{10})(\text{OH})_2 \cdot n\text{H}_2\text{O}$)
Calcite (CaCO_3)	Montmorillonite 2 ($(\text{Na,Ca})_{0.33}(\text{Al,Mg})_2(\text{Si}_4\text{O}_{10})(\text{OH})_2 \cdot n\text{H}_2\text{O}$)
Aragonite (CaCO_3)	Apatite (brown) ($\text{Ca}_5(\text{PO}_4)_3(\text{F,Cl,OH})$)
Dolomite ($\text{CaMg}(\text{CO}_3)_2$)	Apatite (yellow) ($\text{Ca}_5(\text{PO}_4)_3(\text{F,Cl,OH})$)
Amorphous calcium carbonate (CaCO_3)	Labradorite ($(\text{Ca, Na})(\text{Al, Si})_4\text{O}_8$)
Rapidcreekite ($\text{Ca}_2(\text{SO}_4)(\text{CO}_3) \cdot 4\text{H}_2\text{O}$)	Anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$)
Barytocalcite ($\text{BaCa}(\text{CO}_3)_2$)	Oligoclase ($(\text{Ca, Na})(\text{Al, Si})_4\text{O}_8$)
Thaumasite ($\text{Ca}_3\text{Si}(\text{OH})_6(\text{CO}_3)(\text{SO}_4) \cdot 12\text{H}_2\text{O}$)	Hornblende ($\text{Ca}_2(\text{Mg,Fe,Al})_5(\text{Si,Al})_8\text{O}_{22}(\text{OH})_2$)
Kutnohorite ($\text{CaMn}(\text{CO}_3)_2$)	Angite ($\text{Ca}(\text{Mg,Fe})\text{Si}_2\text{O}_6$)
Powellite (CaMoO_4)	Amphibolite ($(\text{Na,K,Ca,Pb})(\text{Li,Na,Mg,Fe,Mn,Ca})_2(\text{Li,Na,Mg,Fe,Mn,Zn,Co,Ni,Al,Fe,Cr,Mn,V,Ti,Zr})_5(\text{Si,Al,Ti})_8\text{O}_{22}(\text{OH,F,Cl,O})_2$)
Tremolite ($\text{Ca}_2(\text{Mg,Fe})_5\text{Si}_8\text{O}_{22}(\text{OH})_2$)	Uranophane ($\text{Ca}(\text{UO}_2)_2\text{SiO}_3(\text{OH})_2 \cdot 5(\text{H}_2\text{O})$)
Augite ($(\text{Ca,Na})(\text{Mg,Fe,Al})(\text{Al,Si})_2\text{O}_6$)	Calcium chloride (CaCl_2)
Glauberite ($\text{Na}_2\text{Ca}(\text{SO}_4)_2$)	Calcium hydroxide ($\text{Ca}(\text{OH})_2$)
Collinsite ($\text{Ca}_2(\text{Mg,Fe})(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$)	Monetite (CaHPO_4)
Whitlockite ($\text{Ca}_9(\text{Mg,Fe})(\text{PO}_4)_6(\text{PO}_3\text{OH})$)	Calcium pyrophosphate ($\text{Ca}_2\text{O}_7\text{P}_2$)

Table S8. Summary of all Ca K-edge μ -XANES LCF performed in this study. All values stated for calcium containing standards are in atomic %.

Sample and spot	χ^2	Depth (mASL)	Gypsum	Rapidcreekite	Bassanite	Anhydrite	Powellite	Dolomite	Monite	Collinsite	Glauberite	AlC	Glauberite	Lime	Calcium pyrophosphate	Calcite	Augite	Montmorillonite 1	Whitlockite	Aragonite	Tremolite	Calcium hydroxide	Thamaseite	Montmorillonite 2
TMF13-01-SA05 Spot 1	0.11	414.68	22	58		20																		
TMF13-01-SA05 Spot 2	0.33	414.68	67		22		10																	
TMF13-01-SA05 Spot 3	0.14	414.68	64		33			3																
TMF13-01-SA05 Spot 4	0.37	414.68		57					43															
TMF13-01-SA05 Spot 5	0.19	414.68		32					14	54														
TMF13-01-SA12 Spot 1	1.85	398.85	66				34																	
TMF13-01-SA12 Spot 2	0.25	398.85		42	35						23													
TMF13-01-SA12 Spot 3	0.37	398.85				28						38	34											
TMF13-01-SA12 Spot 4	0.23	398.85		36	34				30															

Sample and spot	χ^2	Depth (mASL)	Gypsum	Rapiclaesite	Bassanite	Anhydrite	Powellite	Dolomite	Monetite	Collinsite	Glauberite	ACC	Glauberite	Line	Calcium pyrophosphate	Calcite	Augite	Montmorillonite 1	Whitlockite	Aragonite	Tremolite	Calcium hydroxide	Thamaseite	Montmorillonite 2
TMF13-01-SA12 Spot 5	0.19	398.85		28	33						39													
TMF13-01-SA12 Spot 6	0.36	398.85		42	46							12												
TMF13-01-SA12 Spot 7	0.34	398.85		47	32						22													
TMF13-01-SA12 Spot 8	0.25	398.85		24	33						42													
TMF13-01-SA12 Spot 9	1.51	398.85	10	35	55																			
TMF13-01-SA12 Spot 10	2.92	398.85		58		30								12										
TMF13-01-SA12 Spot 11	0.74	398.85		16					56		28													
TMF13-01-SA14 Spot 1	0.28	395.47				38								17	45									
TMF13-01-SA14 Spot 2	0.13	395.47				26								15	59									
TMF13-01-SA14 Spot 3	0.08	395.47		20	28											51								

Sample and spot	χ^2	Depth (mASL)	Gypsum	Rapicreekite	Bassanite	Anhydrite	Powellite	Dolomite	Monetite	Collinsite	Glauberite	ACC	Glauberite	Lime	Calcium pyrophosphate	Calcite	Augite	Montmorillonite 1	Whitlockite	Alagonite	Trenolite	Calcium hydroxide	Thamaseite	Montmorillonite 2
TMF13-01-SA14 Spot 4	0.68	395.47	77		23																			
TMF13-01-SA14 Spot 5	0.04	395.47		18	19											62								
TMF13-01-SA17 Spot 1	1.20	386.66		67		2											31							
TMF13-01-SA17 Spot 2	0.20	386.66			20					58								22						
TMF13-01-SA17 Spot 3	0.09	386.66			34					34								32						
TMF13-01-SA17 Spot 4	0.05	386.66			48	30													22					
TMF13-01-SA19 Spot 1	0.31	383.59	27																	27	46			
TMF13-01-SA19 Spot 2	0.26	383.59				60			25													15		
TMF13-01-SA19 Spot 3	0.27	383.59	24		31												45							
TMF13-01-SA19 Spot 4	0.26	383.59	43		37													20						

Sample and spot	χ^2	Depth (mASL)	Gypsum	Rapicreekite	Bassanite	Anhydrite	Powellite	Dolomite	Monelite	Collinsite	Glauberite	ACC	Glauberite	Ume	Calcium pyrophosphate	Calcite	Augite	Montmorillonite 1	Whitlockite	Avogonite	Tremolite	Calcium hydroxide	Thamaseite	Montmorillonite 2
TMF13-01-SA19 Spot 5	0.34	383.59	28								36							35						
TMF13-01-SA19 Spot 6	0.53	383.59		37	28																			35
TMF13-01-SA19 Spot 7	0.51	383.59									40									46				15
TMF13-01-SA19 Spot 8	0.10	383.59	61	17									23											
TMF13-01-SA19 Spot 9	0.25	383.59													45			16		39				
TMF13-01-SA19 Spot 10	0.22	383.59	9		61													30						
TMF13-01-SA19 Spot 11	0.15	383.59	34		45													21						
TMF13-01-SA19 Spot 12	0.16	383.59	30		50													20						
TMF13-01-SA19 Spot 13	0.22	383.59	31		30												39							
TMF13-01-SA19 Spot 14	0.20	383.59			35												51							14

Sample and spot	χ^2	Depth (mASL)	Gypsum	Rapicreekite	Bassanite	Anhydrite	Powellite	Dolomite	Monelite	Collinsite	Glauberite	ACC	Glauberite	Ume	Calcium pyrophosphate	Calcite	Augite	Montmorillonite 1	Whitlockite	Aragonite	Tremolite	Calcium hydroxide	Thamaseite	Montmorillonite 2
TMF13-01-SA20 Spot 1	0.22	379.68	42					23		35														
TMF13-01-SA20 Spot 2	0.18	379.68	34					22		44														
TMF13-01-SA20 Spot 3	0.04	379.68	55	23											22									
TMF13-01-SA20 Spot 4	0.10	379.68	39												18					42				
TMF13-01-SA20 Spot 5	0.24	379.68		56				7	37															
TMF13-01-SA22 Spot 1	0.94	374.47	64	30			6																	
TMF13-01-SA22 Spot 2	1.63	374.47	95				5																	
TMF13-01-SA22 Spot 3	0.93	374.47	70	18			11																	
TMF13-01-SA22 Spot 4	0.01	374.47	84				14																	
TMF13-01-SA22 Spot 5	0.45	374.47	56	22			22																	

Sample and spot	χ^2	Depth (mASL)	Gypsum	Rapidcreekite	Bassanite	Anhydrite	Powellite	Dolomite	Monelite	Collinsite	Glauberite	ACC	Glauberite	Ume	Calcium pyrophosphate	Calcite	Augite	Montmorillonite 1	Whitlockite	Aragonite	Tremolite	Calcium hydroxide	Thamaseite	Montmorillonite 2
TMF13-01-SA22 Spot 6	0.42	374.47		60	28		12																	
TMF13-01-SA22 Spot 7	0.39	374.47	22	39	39																			
TMF13-01-SA22 Spot 8	0.54	374.47		55	31		14																	
TMF13-01-SA22 Spot 9	0.80	374.47		57	36		7																	
TMF13-01-SA22 Spot 10	4.33	374.47	88															12						
TMF13-01-SA22 Spot 11	0.30	374.47		34			25				42													
TMF13-01-SA22 Spot 12	0.59	374.47		59	41																			
TMF13-01-SA22 Spot 13	0.22	374.47		49	41						9													
TMF13-01-SA23 Spot 1	0.27	371.37	35			48																18		
TMF13-01-SA23 Spot 2	0.65	371.37	83							12				5										

Sample and spot	χ^2	Depth (mASL)	Gypsum	Rapicreekite	Bassanite	Anhydrite	Powellite	Dobsonite	Monelite	Collinsite	Glauberite	ACC	Glauberite	Ume	Calcium pyrophosphate	Calcite	Augite	Montmorillonite 1	Whitlockite	Aragonite	Tremolite	Calcium hydroxide	Thamaseite	Montmorillonite 2
TMF13-01-SA23 Spot 3	0.39	371.37	49		36													16						
TMF13-01-SA23 Spot 4	2.17	371.37	83		17																			
TMF13-01-SA25 Spot 1	2.13	365.27	89	8			3																	
TMF13-01-SA25 Spot 2	1.33	365.27	43	52			5																	
TMF13-01-SA25 Spot 3	2.81	365.27	74	25	1																			
TMF13-01-SA25 Spot 4	0.45	365.27	43	52			4																	
TMF13-01-SA25 Spot 5	1.92	365.27	70	16	13																			
TMF13-01-SA25 Spot 6	0.71	365.27	49	32			19																	
TMF13-01-SA25 Spot 7	0.53	365.27	37	46	17																			
TMF13-01-SA25 Spot 8	0.39	365.27	19	50	31																			

Sample and spot	χ^2	Depth (mASL)	Gypsum	Rapidcreekite	Bassanite	Anhydrite	Powellite	Dolomite	Monelite	Collinsite	Glauberite	ACC	Glauberite	Ume	Calcium pyrophosphate	Calcite	Augite	Montmorillonite 1	Whitlockite	Avogonite	Tremolite	Calcium hydroxide	Thamaseite	Montmorillonite 2
TMF13-01-SA25 Spot 9	0.51	365.27		32		11			57															
TMF13-01-SA25 Spot 10	0.57	365.27	67		5		28																	
TMF13-01-SA25 Spot 11	0.22	365.27		56	38		7																	
TMF13-03-SA14 Spot 1	0.22	392.2				34				34													32	
TMF13-03-SA14 Spot 2	0.19	392.2			24	32			44															
TMF13-03-SA14 Spot 3	0.09	392.2	5	35	60																			
TMF13-03-SA14 Spot 4	0.69	392.2	19		81																			
TMF13-03-SA16 Spot 1	0.19	386.08	32		36										32									
TMF13-03-SA16 Spot 2	0.09	386.08		37	33				30															
TMF13-03-SA16 Spot 3	0.19	386.08		21	55										24									

Sample and spot	χ^2	Depth (mASL)	Gypsum	Rapicreekite	Bassanite	Anhydrite	Powellite	Dobsonite	Monelite	Collinsite	Glauberite	ACC	Glauberite	Ume	Calcium pyrophosphate	Calcite	Augite	Montmorillonite 1	Whitlockite	Aragonite	Tremolite	Calcium hydroxide	Thamaseite	Montmorillonite 2
TMF13-03-SA16 Spot 4	0.25	386.08							70	24	6													
TMF13-03-SA18 Spot 1	0.27	381.17	88							8								4						
TMF13-03-SA18 Spot 2	0.32	381.17	75		15			9																
TMF13-03-SA18 Spot 3	0.44	381.17	74			15								10										
TMF13-03-SA18 Spot 4	0.14	381.17	64			28								7										
TMF13-03-SA18 Spot 5	0.12	381.17		32		35			33															
TMF13-03-SA22 Spot 1	0.12	371.09		48		18									34									
TMF13-03-SA22 Spot 2	0.97	371.09	79		20																			
TMF13-03-SA22 Spot 3	0.27	371.09	51		30													19						
TMF13-03-SA22 Spot 4	0.23	371.09	39							49								12						

Sample and spot	χ^2	Depth (mASL)	Gypsum	Rapicreekite	Bassanite	Anhydrite	Powellite	Dobsonite	Monelite	Collinsite	Glauberite	ACC	Glauberite	Lime	Calcium pyrophosphate	Calcite	Augite	Montmorillonite 1	Whitlockite	Aragonite	Tremolite	Calcium hydroxide	Thamaseite	Montmorillonite 2
TMF13-06-SA16 Spot 1	0.29	383.69											35		54			11						
TMF13-06-SA16 Spot 2	0.07	383.69						23			11	67												
TMF13-06-SA16 Spot 3	0.19	383.69				24						60									16			
TMF13-06-SA16 Spot 4	0.75	383.69	63															4		33				
TMF13-06-SA16 Spot 5	0.51	383.69		51	33															16				

Figure S1.

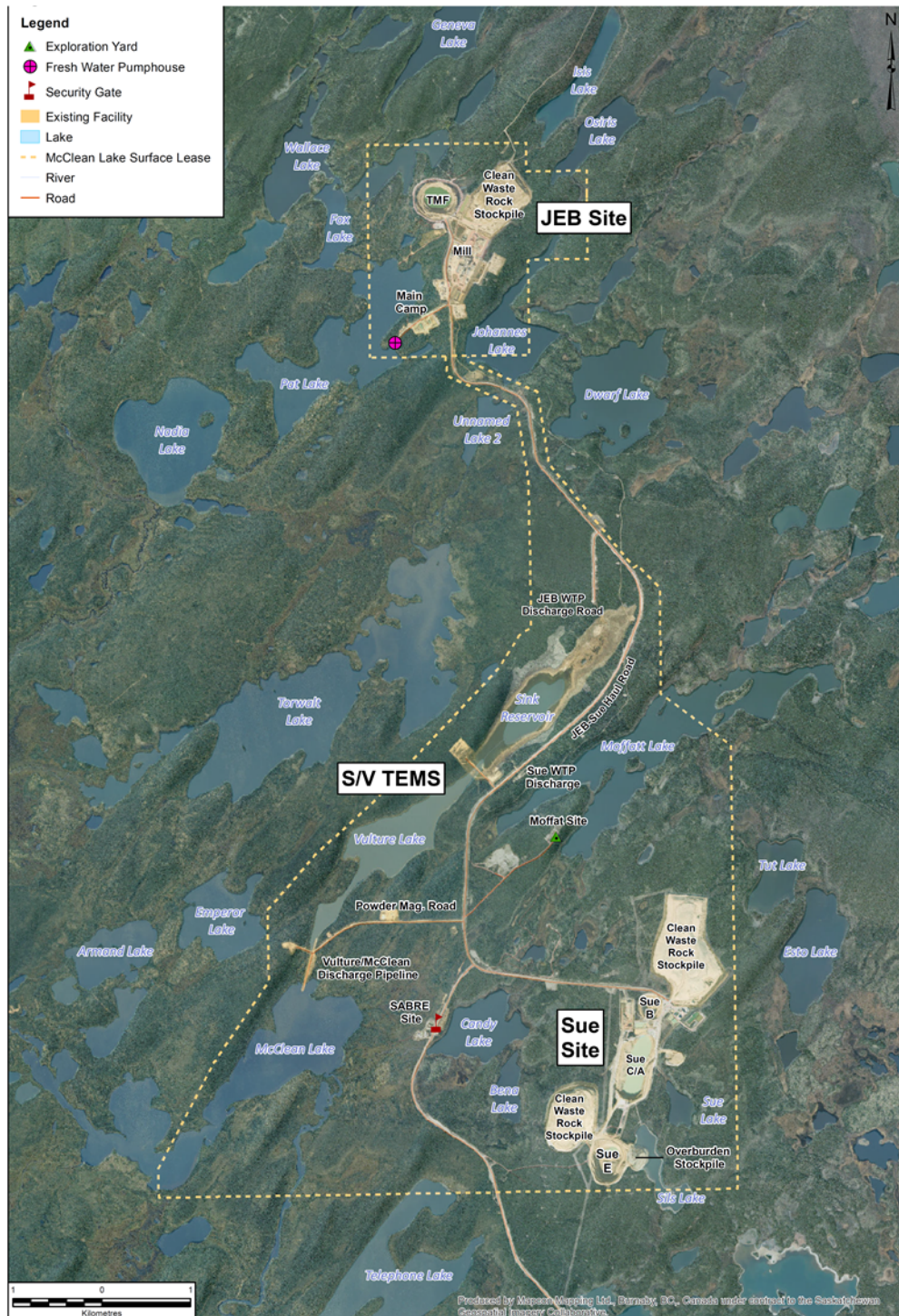


Figure S1. A location map showing the location of the JEB mill and TMF at McClean Lake, Saskatchewan as well as the location of some of the ore bodies that have been mined are shown. Six ore bodies have been milled by the McClean Lake facility to date, with four deposits being sandstone hosted and two ore bodies being partially basement hosted.

Figure S2.

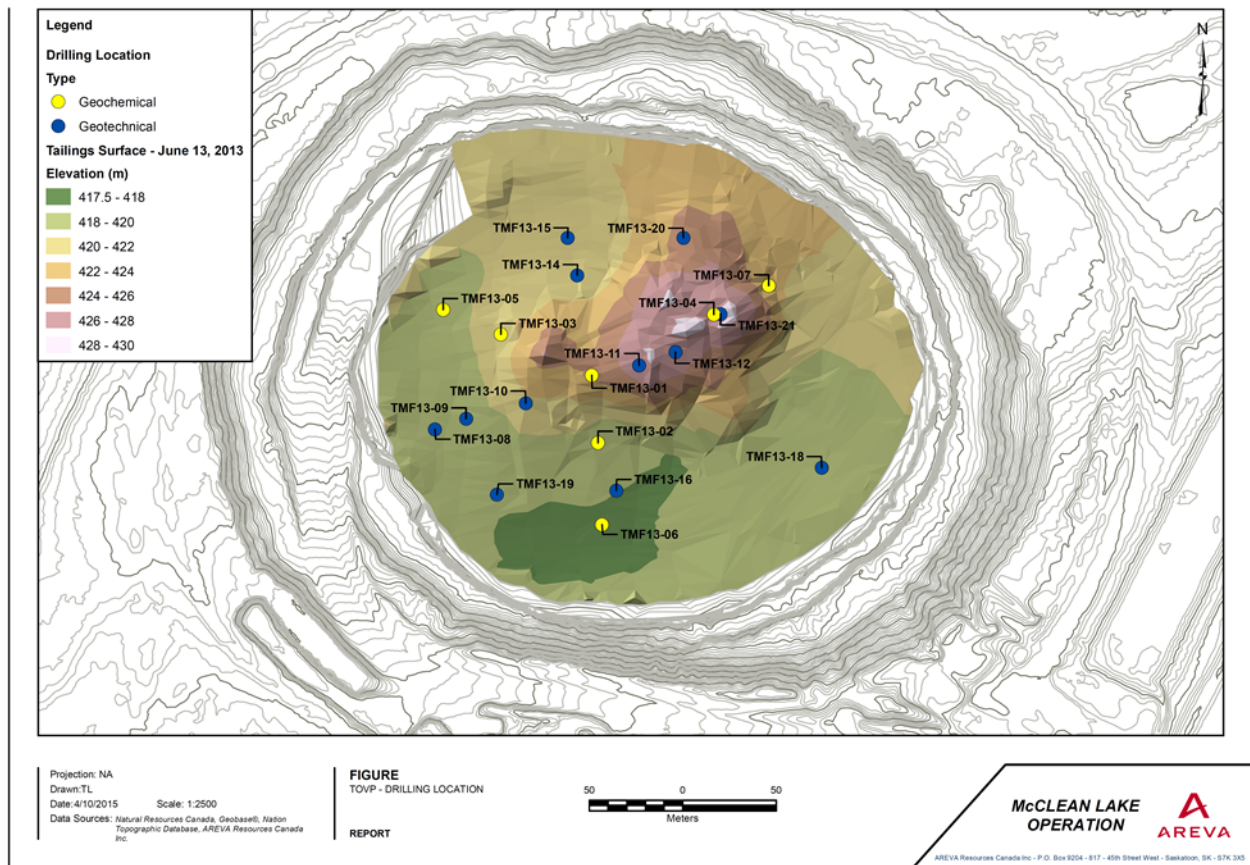


Figure S2. A plan-view diagram of the JEB TMF is shown. The locations of the bore-holes where samples were taken from are indicated on the figure. The samples investigated in this study were taken from TMF13-01, TMF13-03, and TMF13-06.

Figure S3.

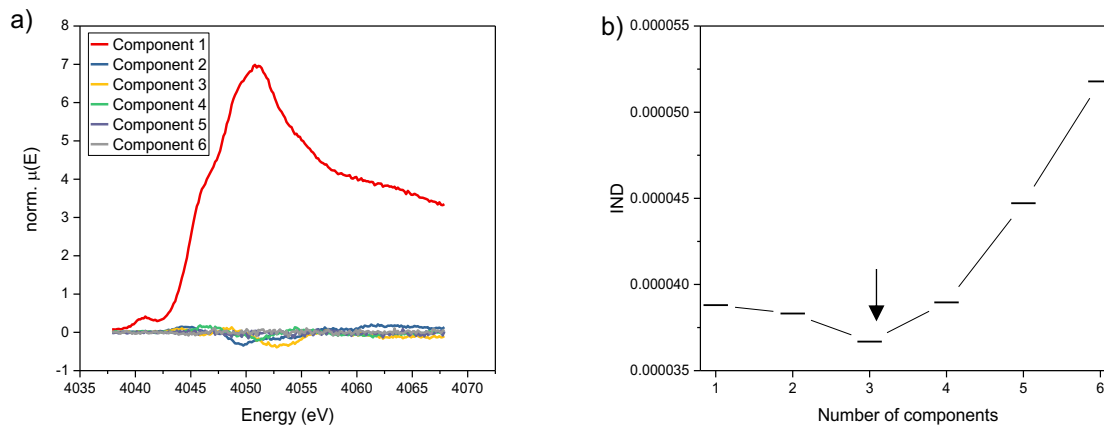


Figure S3. a) Principle components calculated from the PCA of the Ca K-edge μ -XANES spectra collected from TMF13-01-SA19. b) The IND function was calculated and plotted versus the number of components. The IND function approaches a minimum when the number of components is three. The number of components shown was restricted to 6 for clarity.

Figure S4.

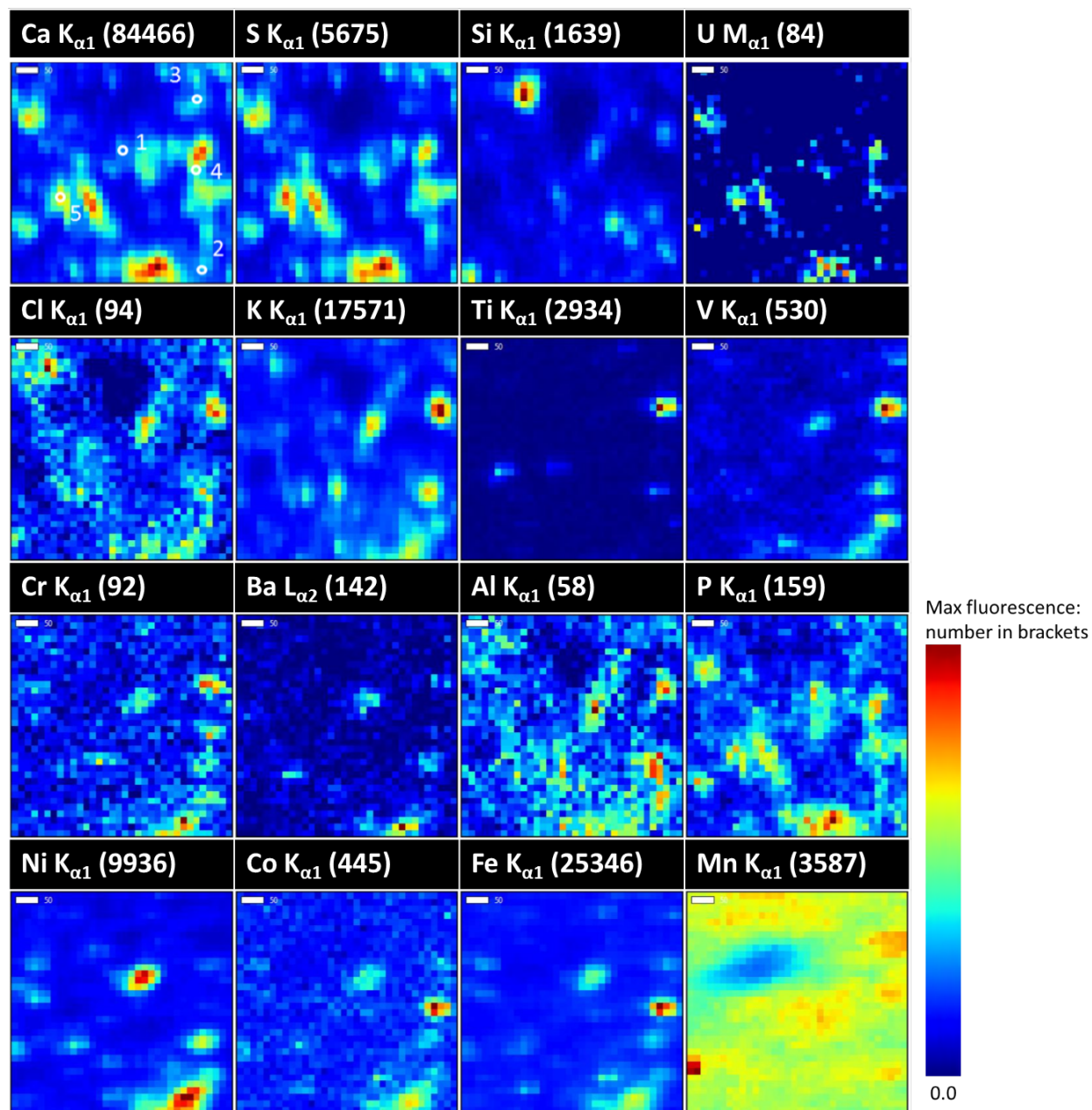


Figure S4. XRF maps showing the distribution of Ca, S, Si, U, Al, P, Cl, K, Ti, V, Ba, Ni, Co, Fe, Mn, and Cr collected from tailings sample TMF13-01-SA05. The size of the maps was 500 μm x 500 μm . Spots where Ca K-edge μ -XANES spectra were collected are marked on the Ca K_{α1} XRF map. The number in the brackets denotes the maximum counts observed from each element's XRF map. All scale bars are 50 μm in length.

Figure S5.

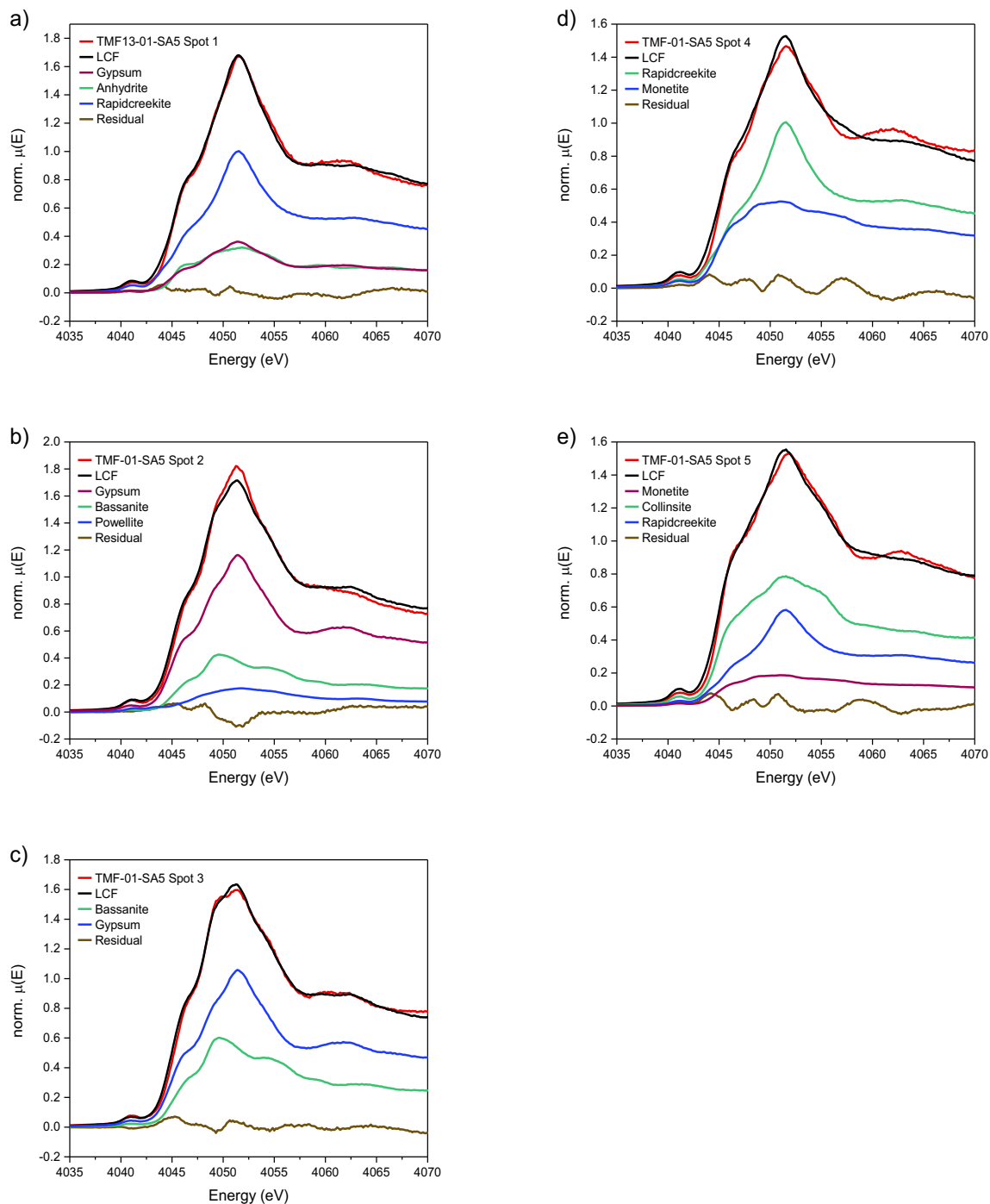


Figure S5. The fitted Ca K-edge μ -XANES spectra from TMF13-01-SA05 at spots marked 1 to 5 on Figure S4 are shown in a) to e), respectively. Only Ca K-edge μ -XANES spectra fits with a χ^2 below 0.5 are shown.

Figure S6.

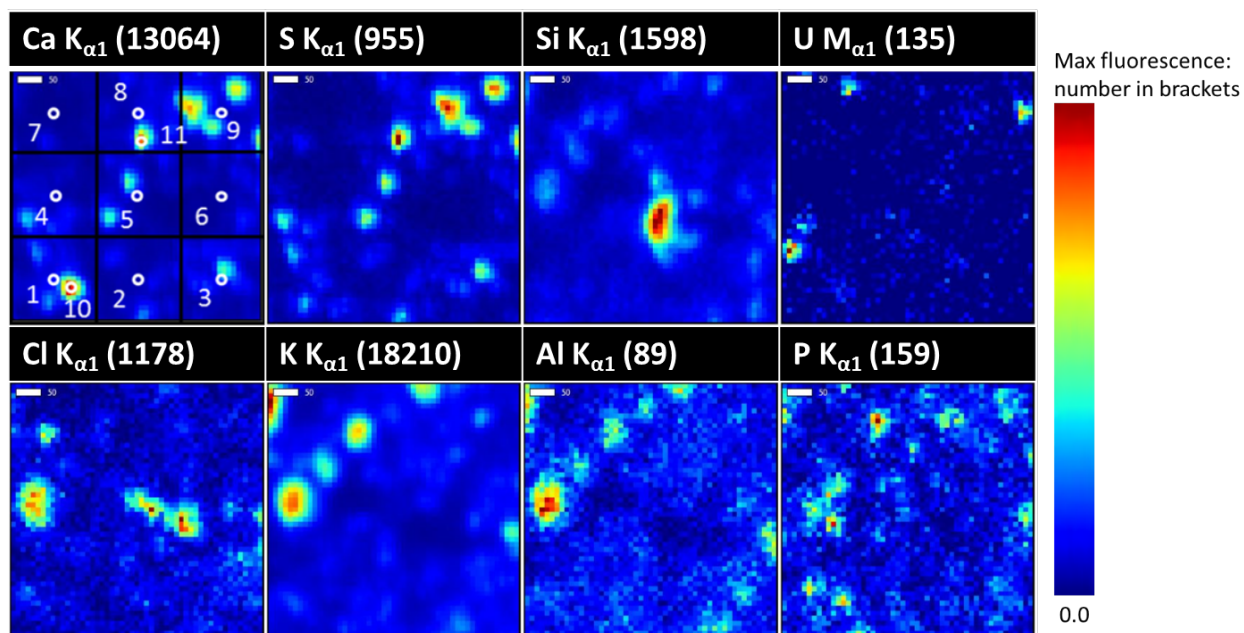


Figure S7. XRF maps showing the distribution of Ca, S, Si, U, Al, P, Cl, and K collected from tailings sample TMF13-01-SA012. The size of the maps was 500 $\mu\text{m} \times 500 \mu\text{m}$. Spots where Ca K-edge μ -XANES spectra were collected are marked on the Ca $K_{\alpha 1}$ XRF map. The number in the brackets denotes the maximum counts observed from each element's XRF map. All scale bars are 50 μm in length.

Figure S7.

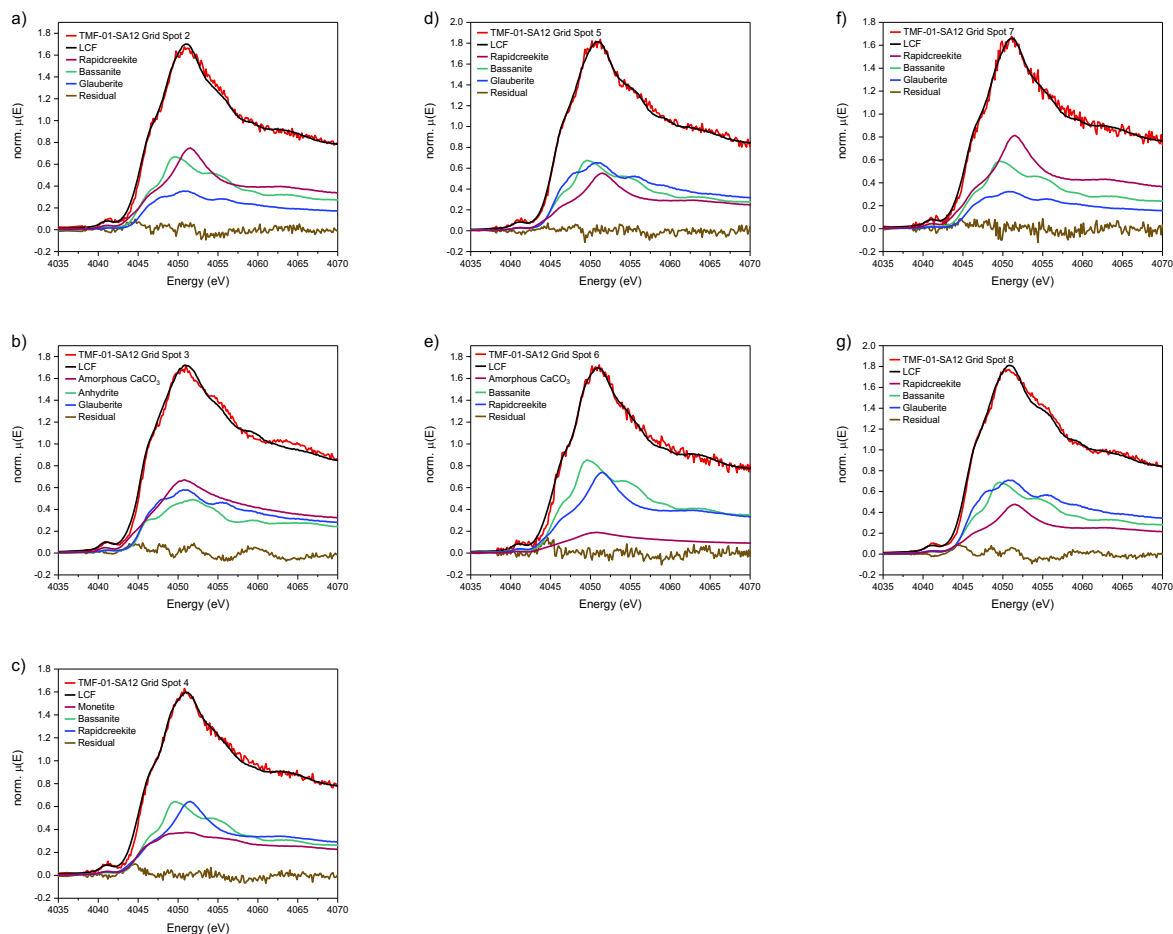


Figure S7. The fitted Ca K-edge μ -XANES spectra from TMF13-01-SA12 at spots marked on the Ca $K_{\alpha 1}$ XRF map Figure S6 are shown in a) to g), respectively. Only Ca K-edge μ -XANES spectra fits with a χ^2 below 0.5 are shown.

Figure S8.

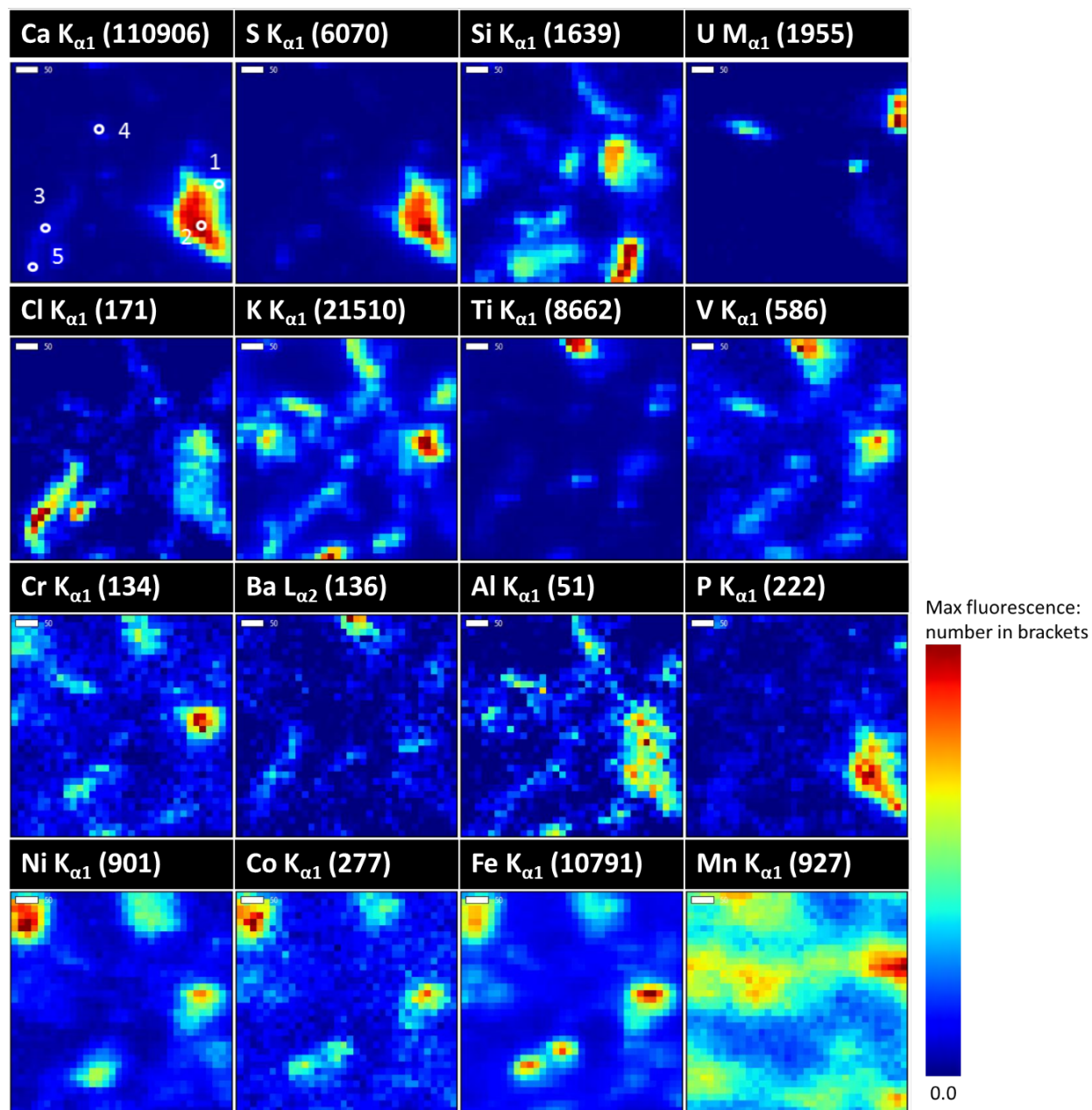


Figure S8. XRF maps showing the distribution of Ca, S, Si, U, Al, P, Cl, K, Ti, V, Ba, Ni, Co, Fe, Mn, and Cr collected from tailings sample TMF13-01-SA14. The size of the maps was 500 $\mu\text{m} \times 500 \mu\text{m}$. Spots where Ca K-edge μ -XANES spectra were collected are marked on the Ca $K_{\alpha 1}$ XRF map. The number in the brackets denotes the maximum counts observed from each element's XRF map. All scale bars are 50 μm in length.

Figure S9.

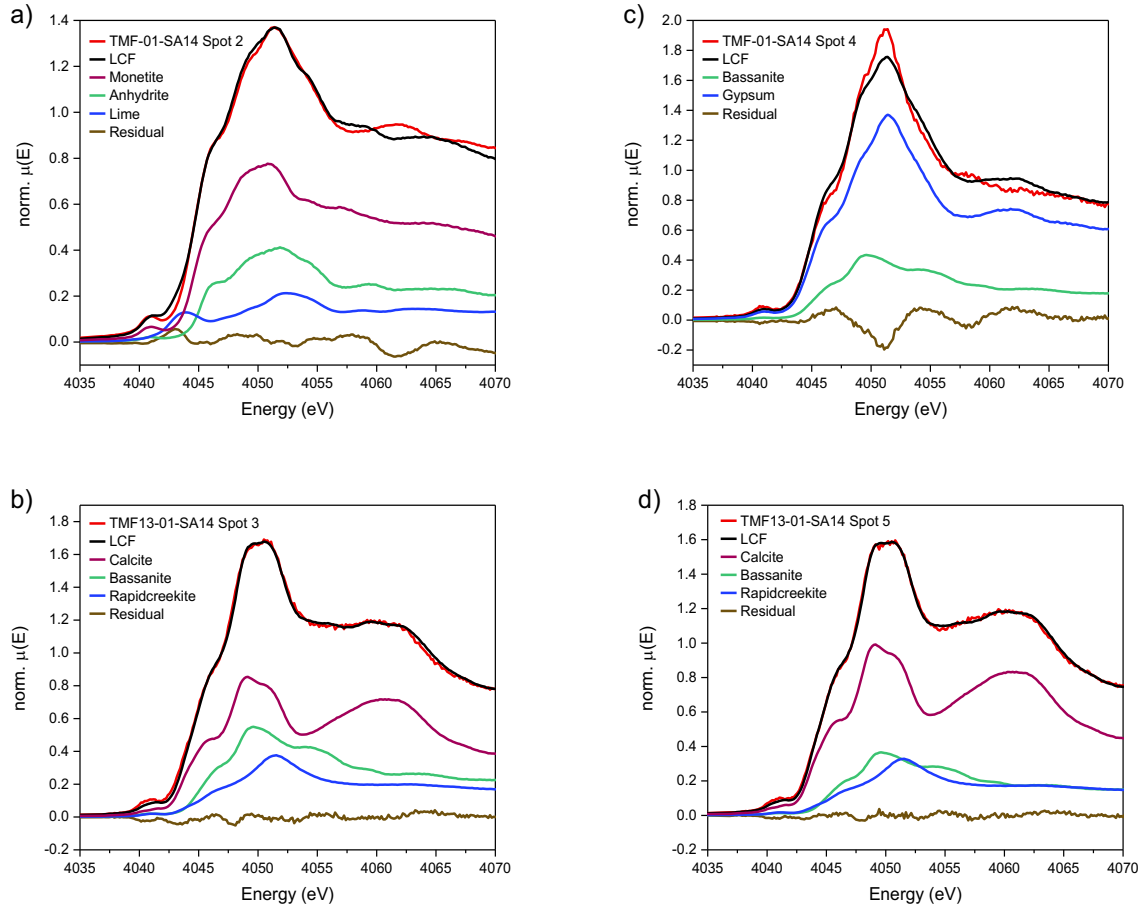


Figure S9. The fitted Ca K-edge μ -XANES spectra from TMF13-01-SA014 at spots marked on Figure S8 are shown in a) to d), respectively. Only Ca K-edge μ -XANES spectra fits with a χ^2 below 0.5 are shown.

Figure S10.

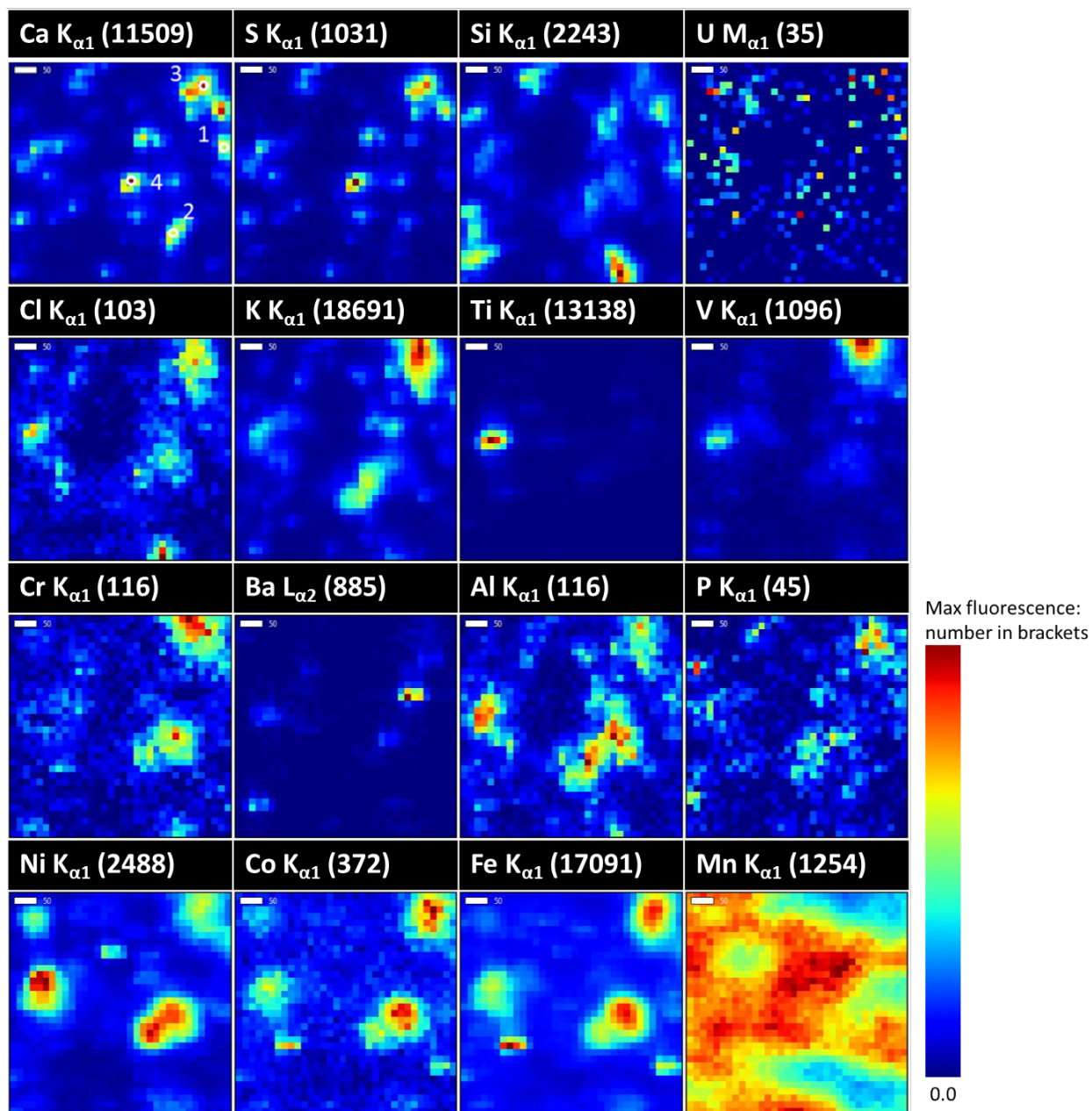


Figure S10. XRF maps showing the distribution of Ca, S, Si, U, Al, P, Cl, K, Ti, V, Ba, Ni, Co, Fe, Mn, and Cr collected from tailings sample TMF13-01-SA17. The size of the maps was 500 μm x 500 μm. Spots where Ca K-edge μ-XANES spectra were collected are marked on the Ca K_{α1} XRF map. The number in the brackets denotes the maximum counts observed from each element's XRF map. All scale bars are 50 μm in length.

Figure S11.

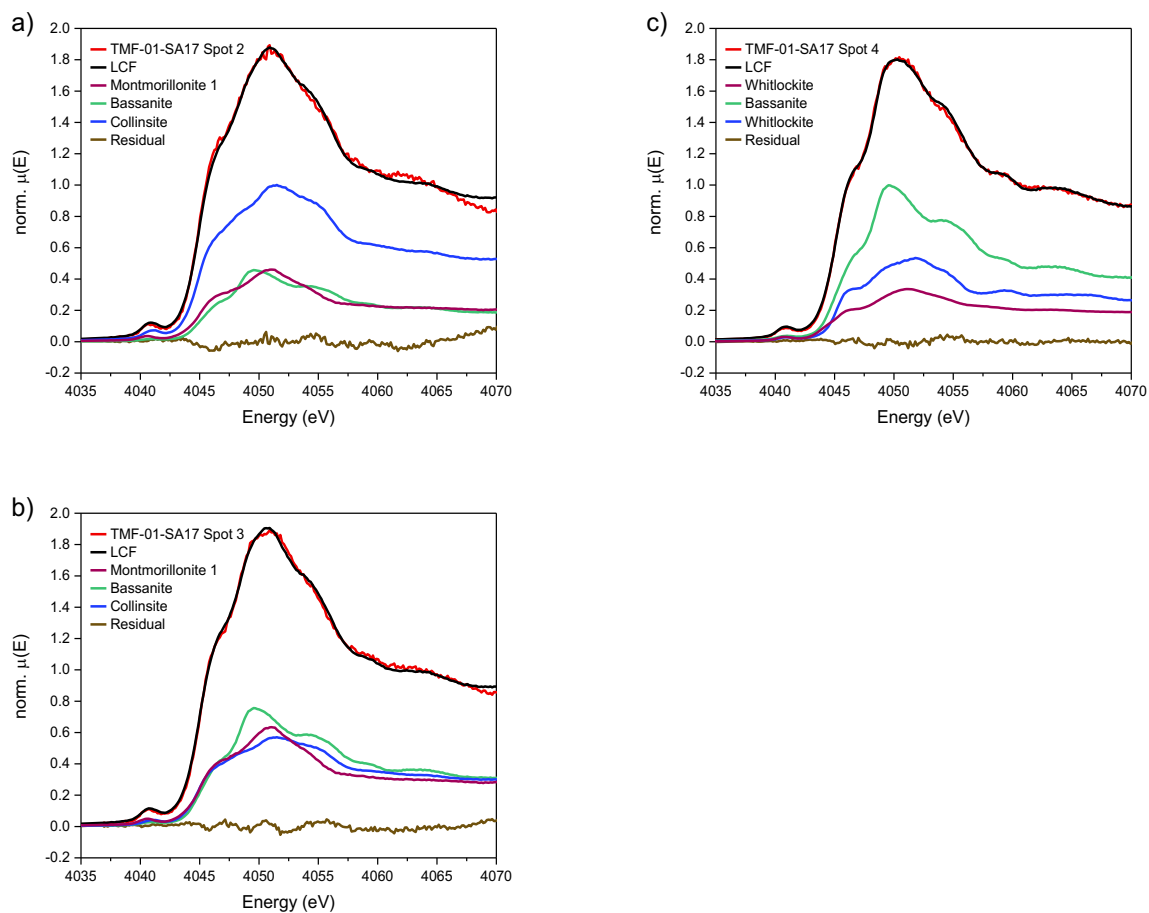


Figure S11. The fitted Ca K-edge μ -XANES spectra from TMF13-01-SA017 at spots marked on Figure S10 are shown in a) to c), respectively. Only Ca K-edge μ -XANES spectra fits with a χ^2 below 0.5 are shown.

Figure S12.

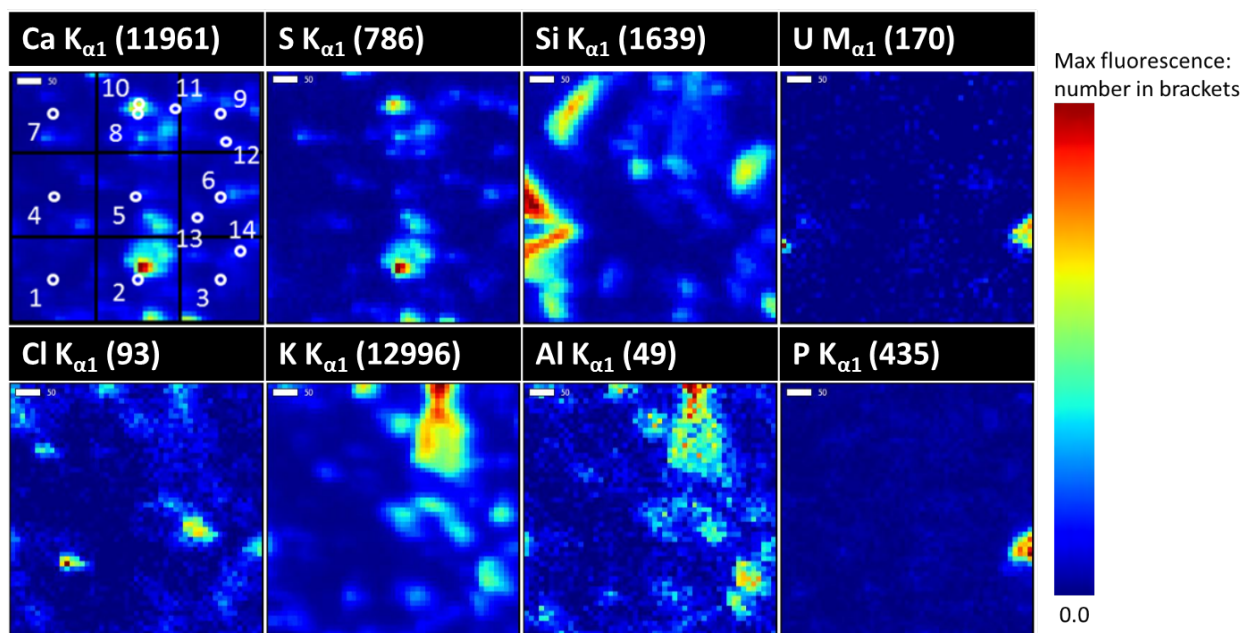


Figure S12. XRF maps showing the distribution of Ca, S, Si, U, Al, P, Cl, and K collected from tailings sample TMF13-01-SA19. The size of the maps was 500 μ m x 500 μ m. Spots where Ca K-edge μ -XANES spectra were collected are marked on the Ca $K_{\alpha 1}$ XRF map. The number in the brackets denotes the maximum counts observed from each element's XRF map. All scale bars are 50 μ m in length.

Figure S13.

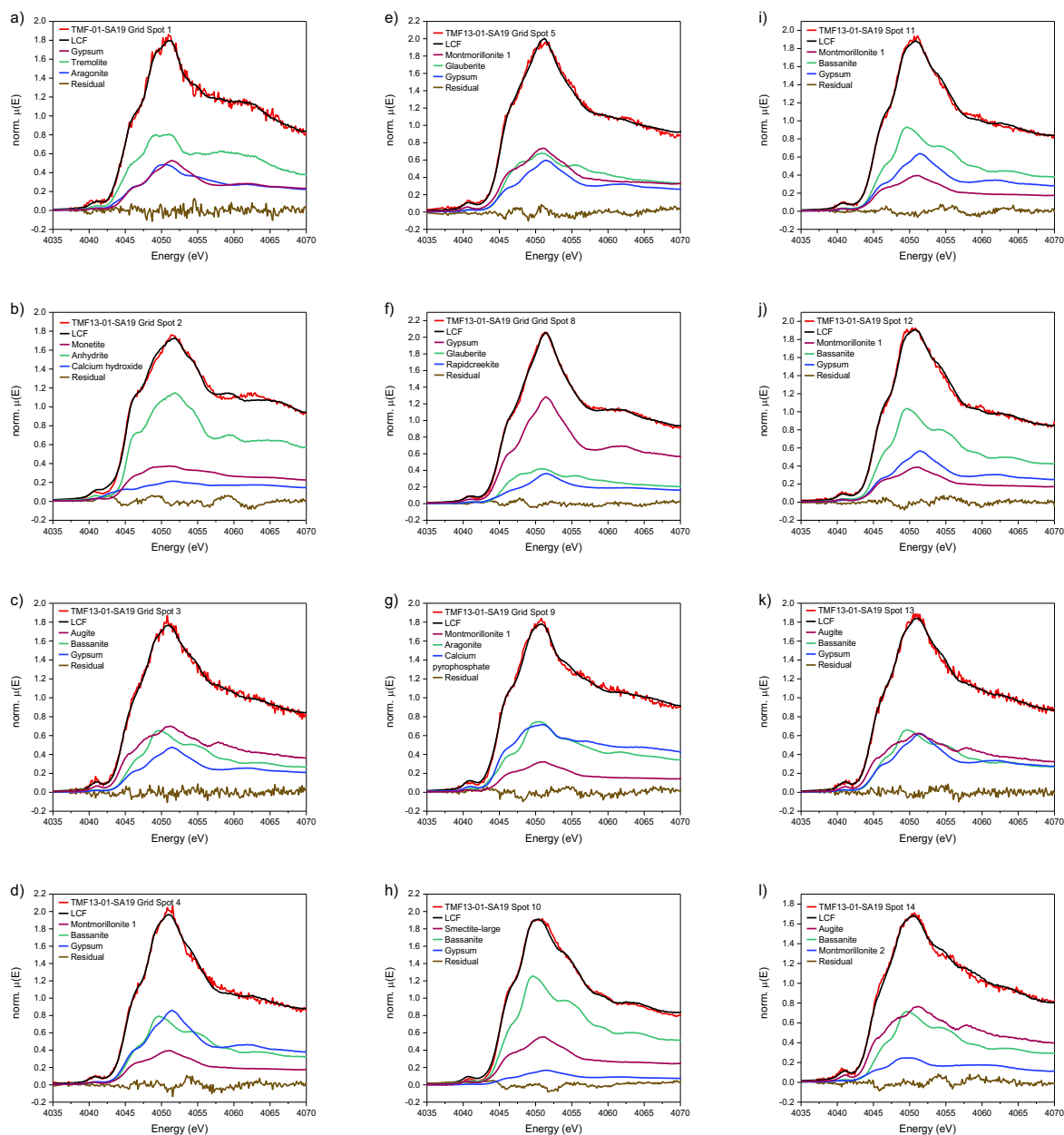


Figure S13. The fitted Ca K-edge μ -XANES spectra from TMF13-01-SA19 at spots marked on the Ca $K_{\alpha 1}$ XRF map Figure S12 are shown in a) to l), respectively. Only Ca K-edge μ -XANES spectra fits with a χ^2 below 0.5 are shown.

Figure S14.

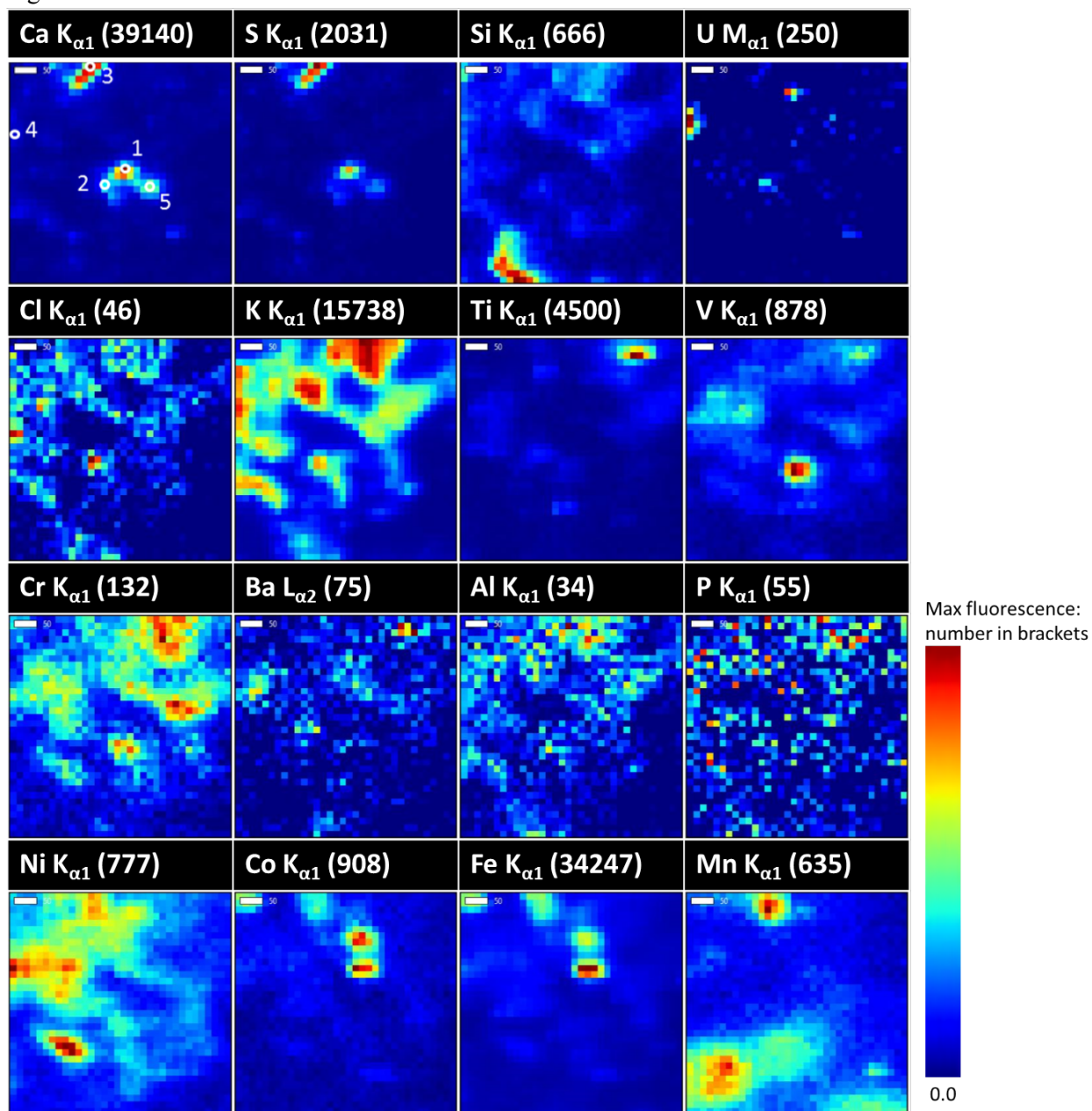


Figure S14. XRF maps showing the distribution of Ca, S, Si, U, Al, P, Cl, K, Ti, V, Ba, Ni, Co, Fe, Mn, and Cr collected from tailings sample TMF13-01-SA20. The size of the maps was 500 μm x 500 μm. Spots where Ca K-edge μ-XANES spectra were collected are marked on the Ca K_{α1} XRF map. The number in the brackets denotes the maximum counts observed from each element's XRF map. All scale bars are 50 μm in length.

Figure S15.

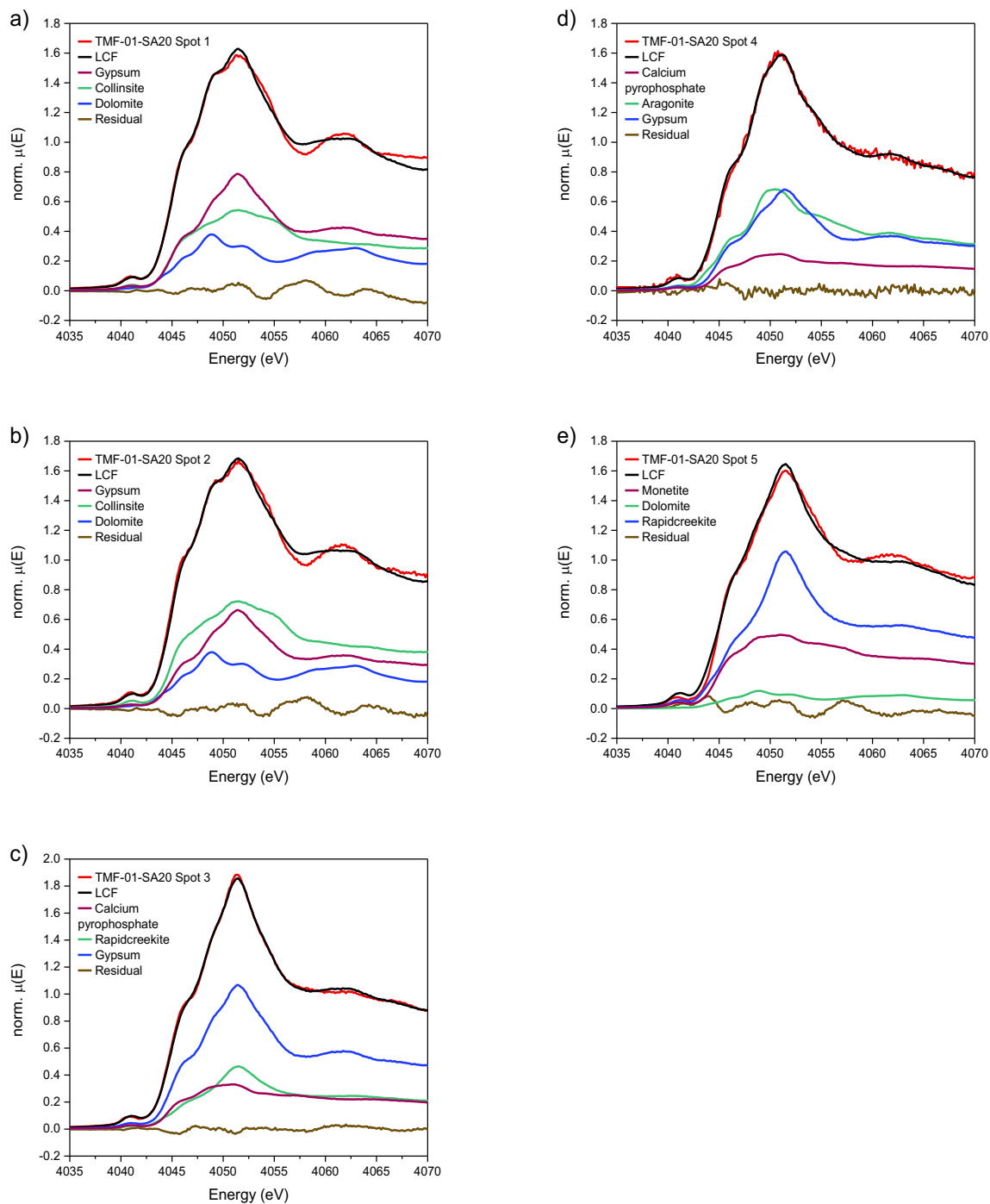


Figure S15. The fitted Ca K-edge μ -XANES spectra from TMF13-01-SA020 at spots marked on Figure S14 are shown in a) to e), respectively. Only Ca K-edge μ -XANES spectra fits with a χ^2 below 0.5 are shown.

Figure S16.

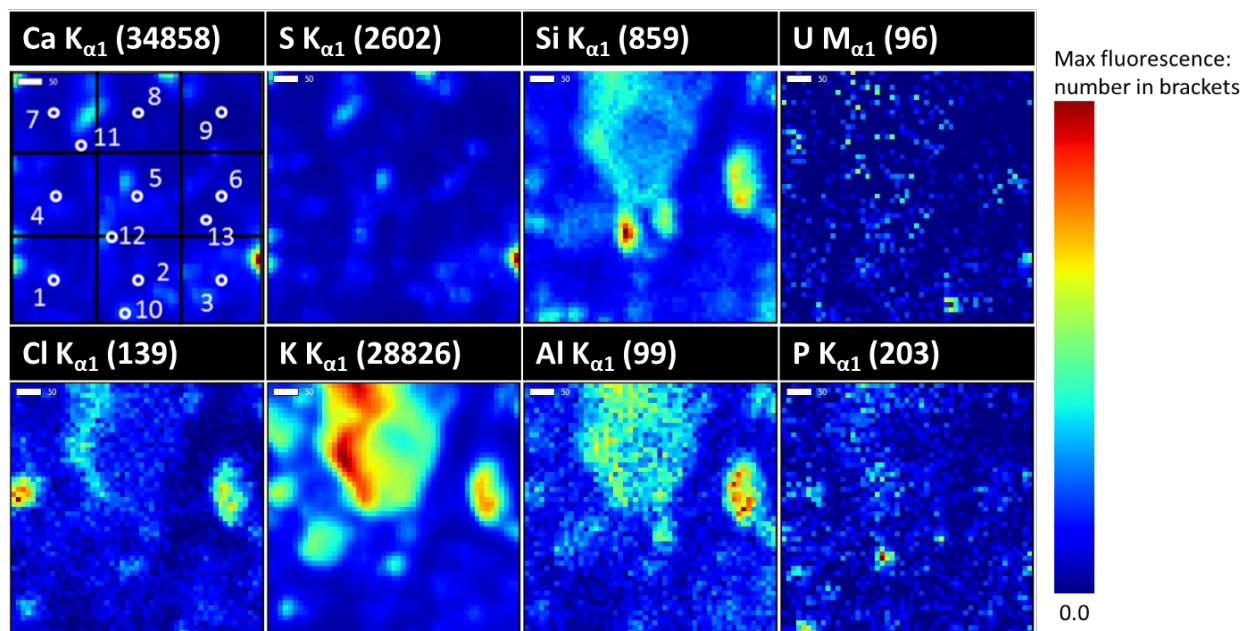


Figure S16. XRF maps showing the distribution of Ca, S, Si, U, Al, P, Cl, and K collected from tailings sample TMF13-01-SA22. The size of the maps was 500 μ m x 500 μ m. Spots where Ca K-edge μ -XANES spectra were collected are marked on the Ca $K_{\alpha 1}$ XRF map. The number in the brackets denotes the maximum counts observed from each element's XRF map. All scale bars are 50 μ m in length.

Figure S17.

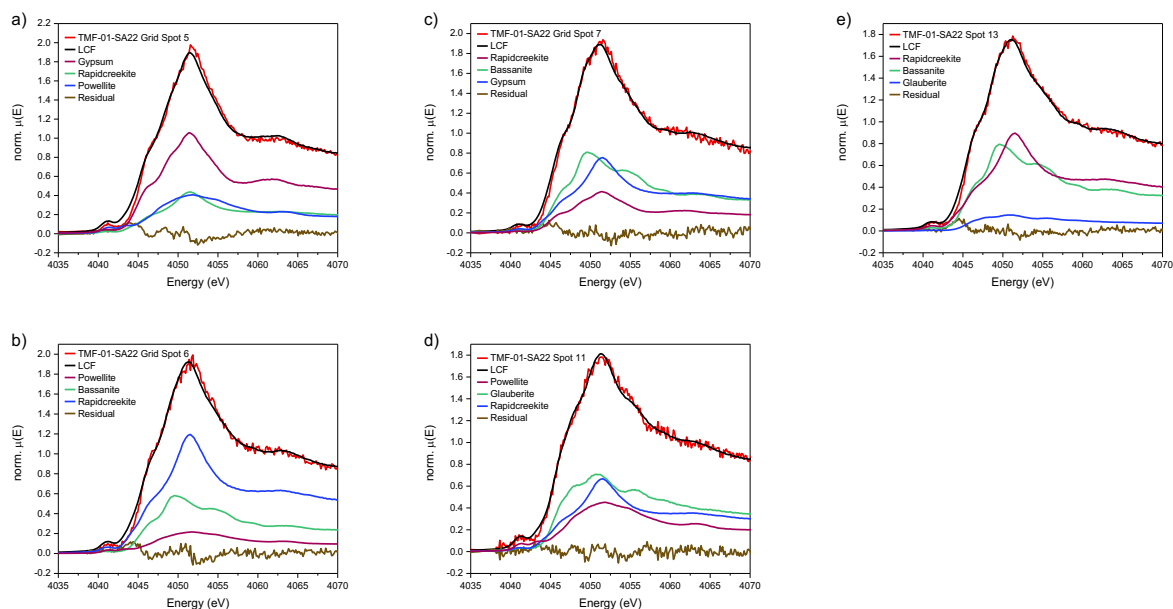


Figure S17. The fitted Ca K-edge μ -XANES spectra from TMF13-01-SA22 at spots marked on the Ca $K_{\alpha 1}$ XRF map Figure S16 are shown in a) to e), respectively. Only Ca K-edge μ -XANES spectra fits with a χ^2 below 0.5 are shown.

Figure S18.

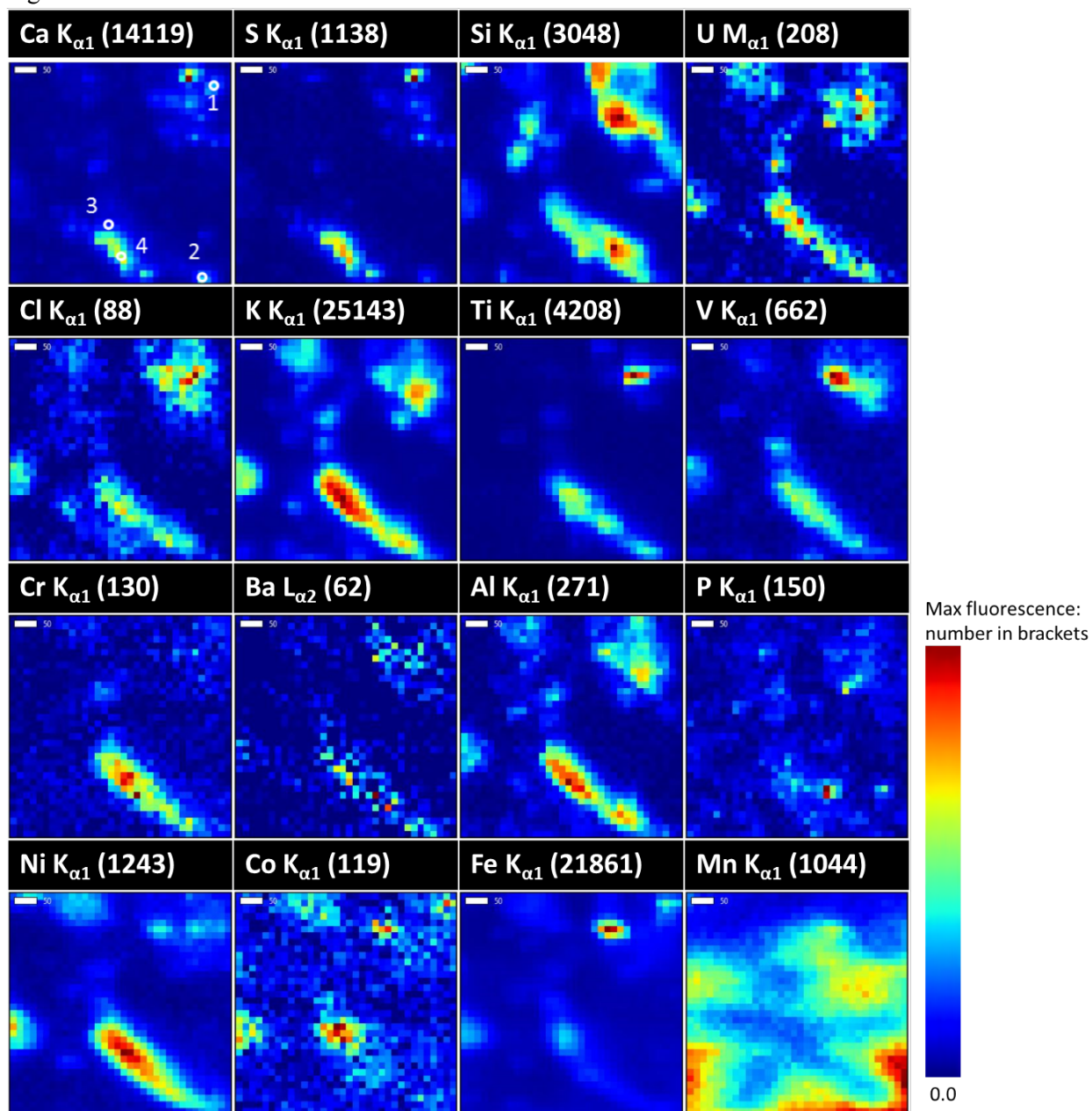


Figure S18. XRF maps showing the distribution of Ca, S, Si, U, Al, P, Cl, K, Ti, V, Ba, Ni, Co, Fe, Mn, and Cr collected from tailings sample TMF13-01-SA23. The size of the maps was 500 μm x 500 μm. Spots where Ca K-edge μ-XANES spectra were collected are marked on the Ca K_{α1} XRF map. The number in the brackets denotes the maximum counts observed from each element's XRF map. All scale bars are 50 μm in length.

Figure S19.

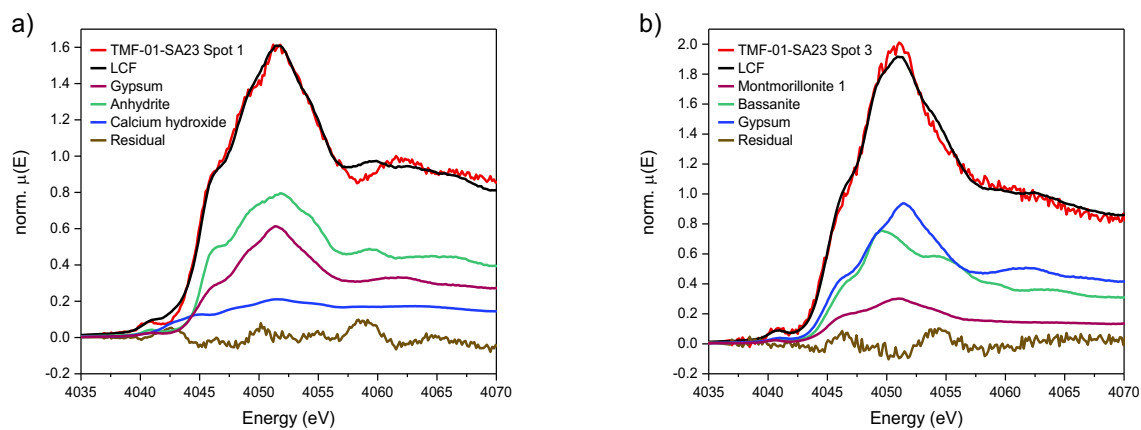


Figure S19. The fitted Ca K-edge μ -XANES spectra from TMF13-01-SA23 at spots marked on Figure S18 are shown in a) and b), respectively. Only Ca K-edge μ -XANES spectra fits with a χ^2 below 0.5 are shown.

Figure S20.

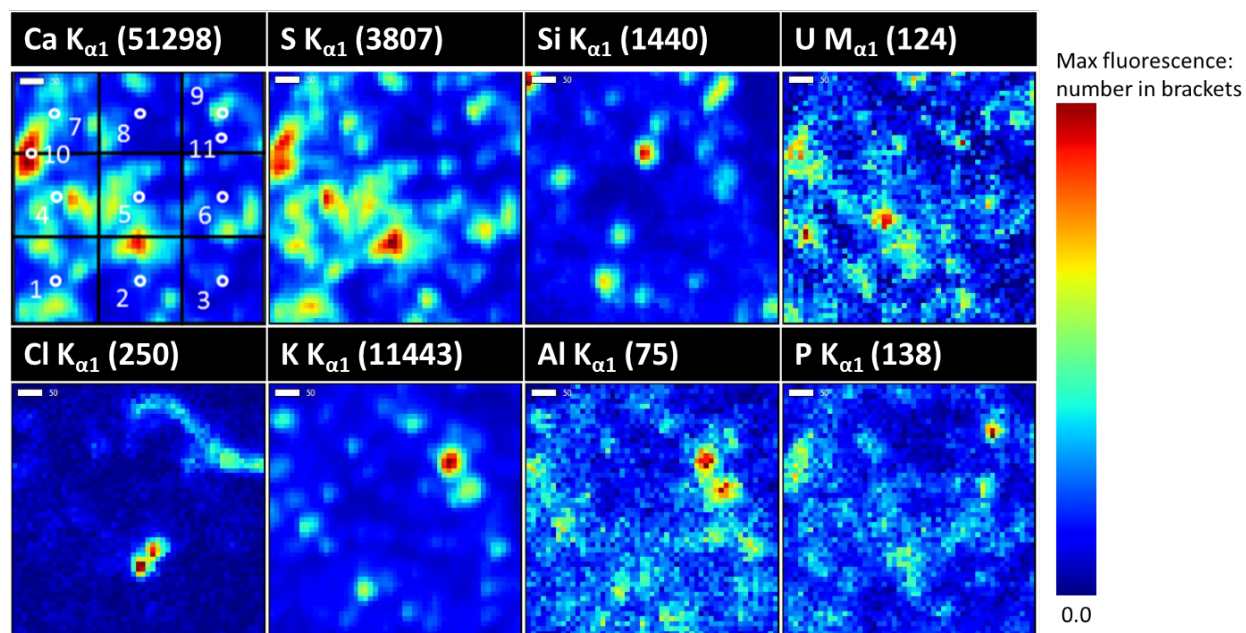


Figure S20. XRF maps showing the distribution of Ca, S, Si, U, Al, P, Cl, and K collected from tailings sample TMF13-01-SA25. The size of the maps was 500 μm x 500 μm. Spots where Ca K-edge μ -XANES spectra were collected are marked on the Ca $K_{\alpha 1}$ XRF map. The number in the brackets denotes the maximum counts observed from each element's XRF map. All scale bars are 50 μm in length.

Figure S21.

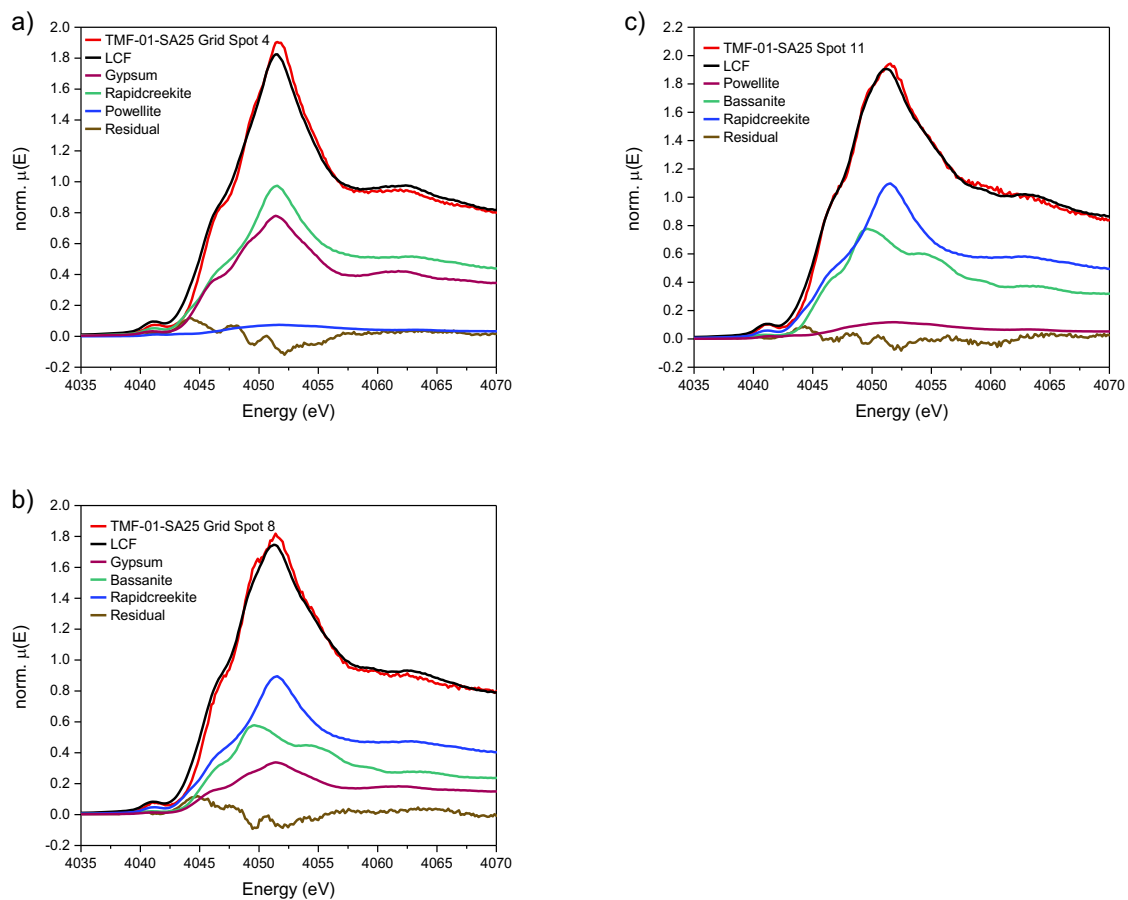


Figure S21. The fitted Ca K-edge μ -XANES spectra from TMF13-01-SA25 at spots marked on the Ca $K_{\alpha 1}$ XRF map Figure S20 are shown in a) to c), respectively. Only Ca K-edge μ -XANES spectra fits with a χ^2 below 0.5 are shown.

Figure S22.

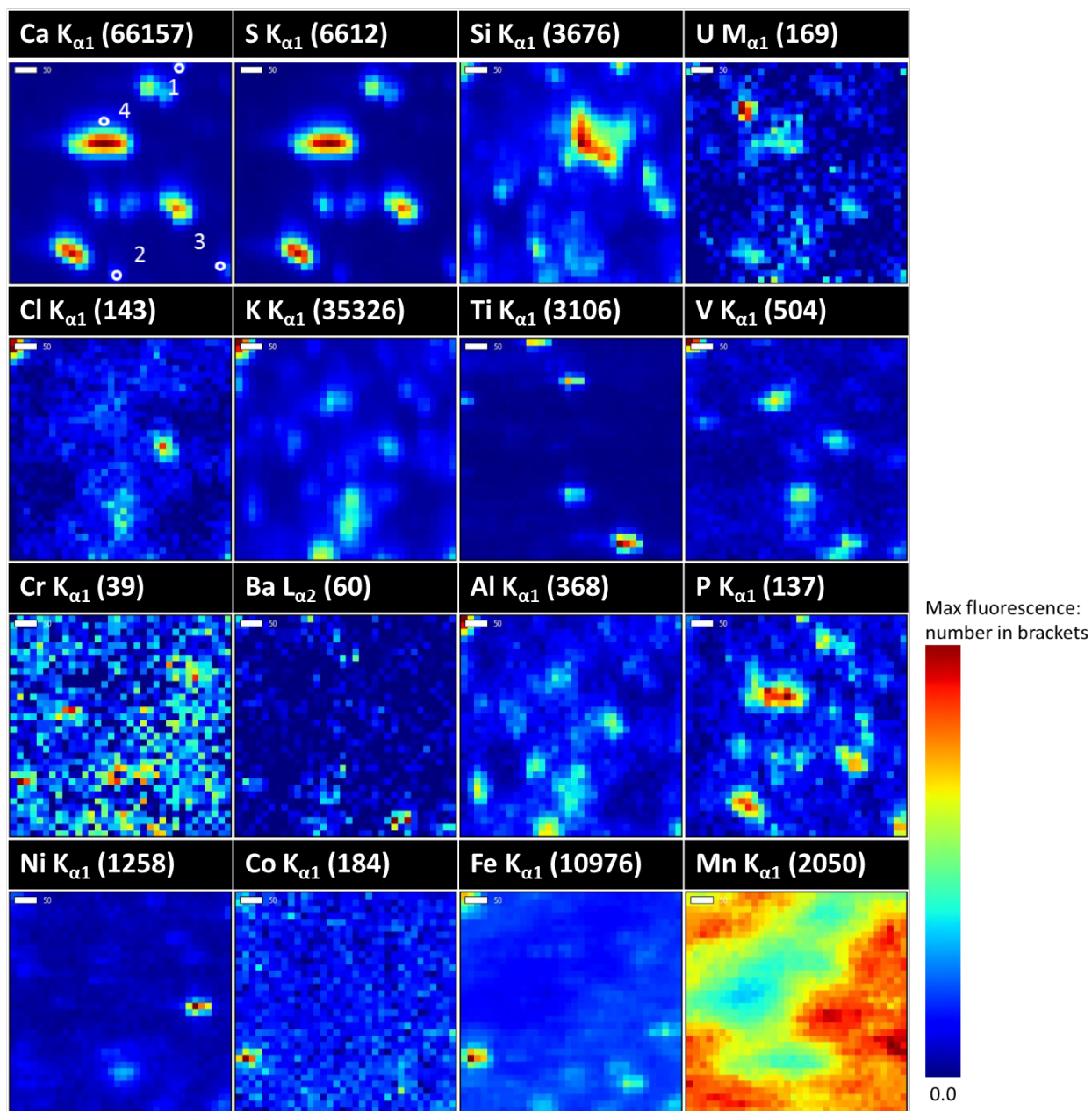


Figure S22. XRF maps showing the distribution of Ca, S, Si, U, Al, P, Cl, K, Ti, V, Ba, Ni, Co, Fe, Mn, and Cr collected from tailings sample TMF13-03-SA14. The size of the maps was 500 μm x 500 μm. Spots where Ca K-edge μ-XANES spectra were collected are marked on the Ca K_{α1} XRF map. The number in the brackets denotes the maximum counts observed from each element's XRF map. All scale bars are 50 μm in length.

Figure S23.

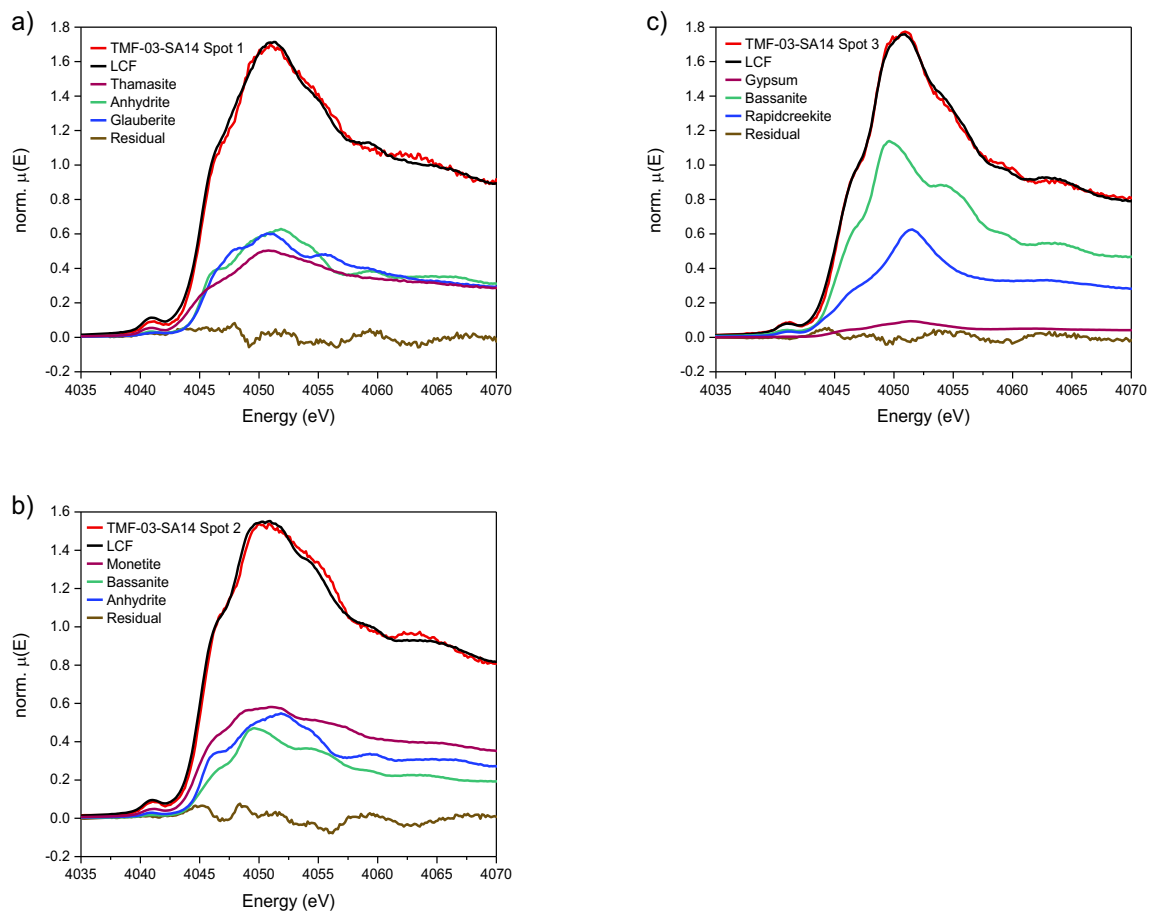


Figure S23. The fitted Ca K-edge μ -XANES spectra from TMF13-03-SA14 at spots marked on Figure S22 are shown in a) to c), respectively. Only Ca K-edge μ -XANES spectra fits with a χ^2 below 0.5 are shown.

Figure S24.

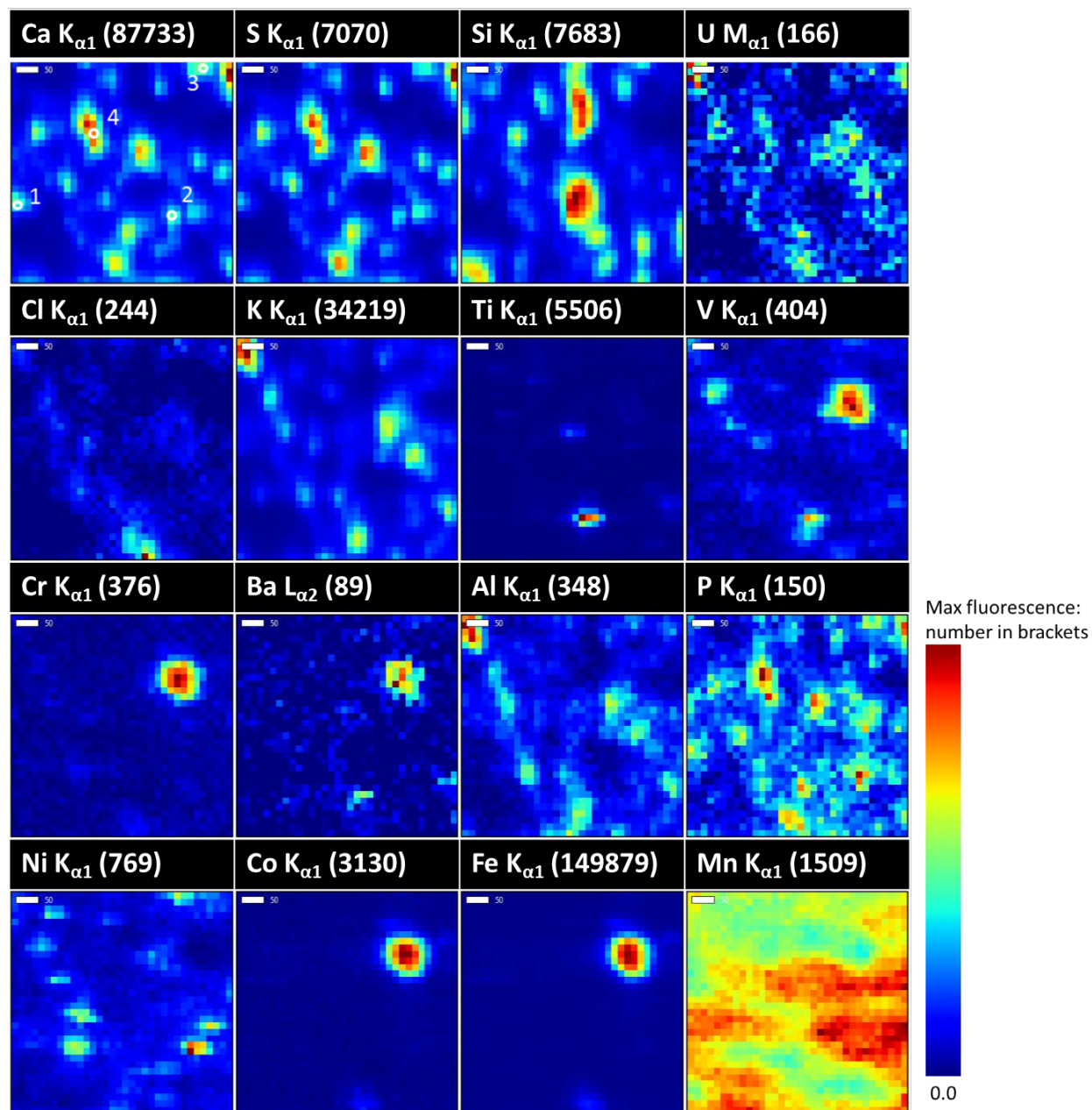


Figure S24. XRF maps showing the distribution of Ca, S, Si, U, Al, P, Cl, K, Ti, V, Ba, Ni, Co, Fe, Mn, and Cr collected from tailings sample TMF13-03-SA16. The size of the maps was 500 μm x 500 μm. Spots where Ca K-edge μ-XANES spectra were collected are marked on the Ca K_{α1} XRF map. The number in the brackets denotes the maximum counts observed from each element's XRF map. All scale bars are 50 μm in length.

Figure S25.

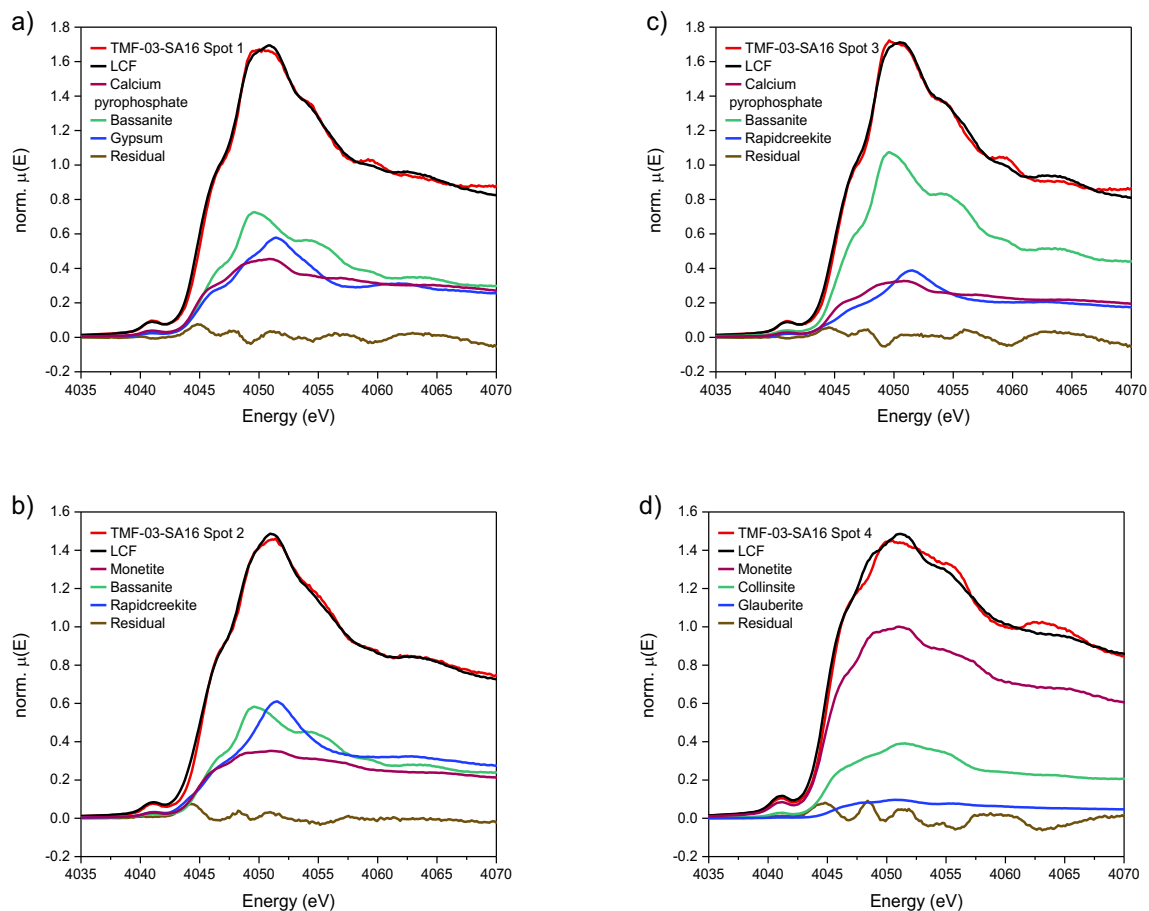


Figure S25. The fitted Ca K-edge μ -XANES spectra from TMF13-03-SA16 at spots marked 1 to 4 on Figure S24 are shown in a) to d), respectively. Only Ca K-edge μ -XANES spectra fits with a χ^2 below 0.5 are shown.

Figure S26.

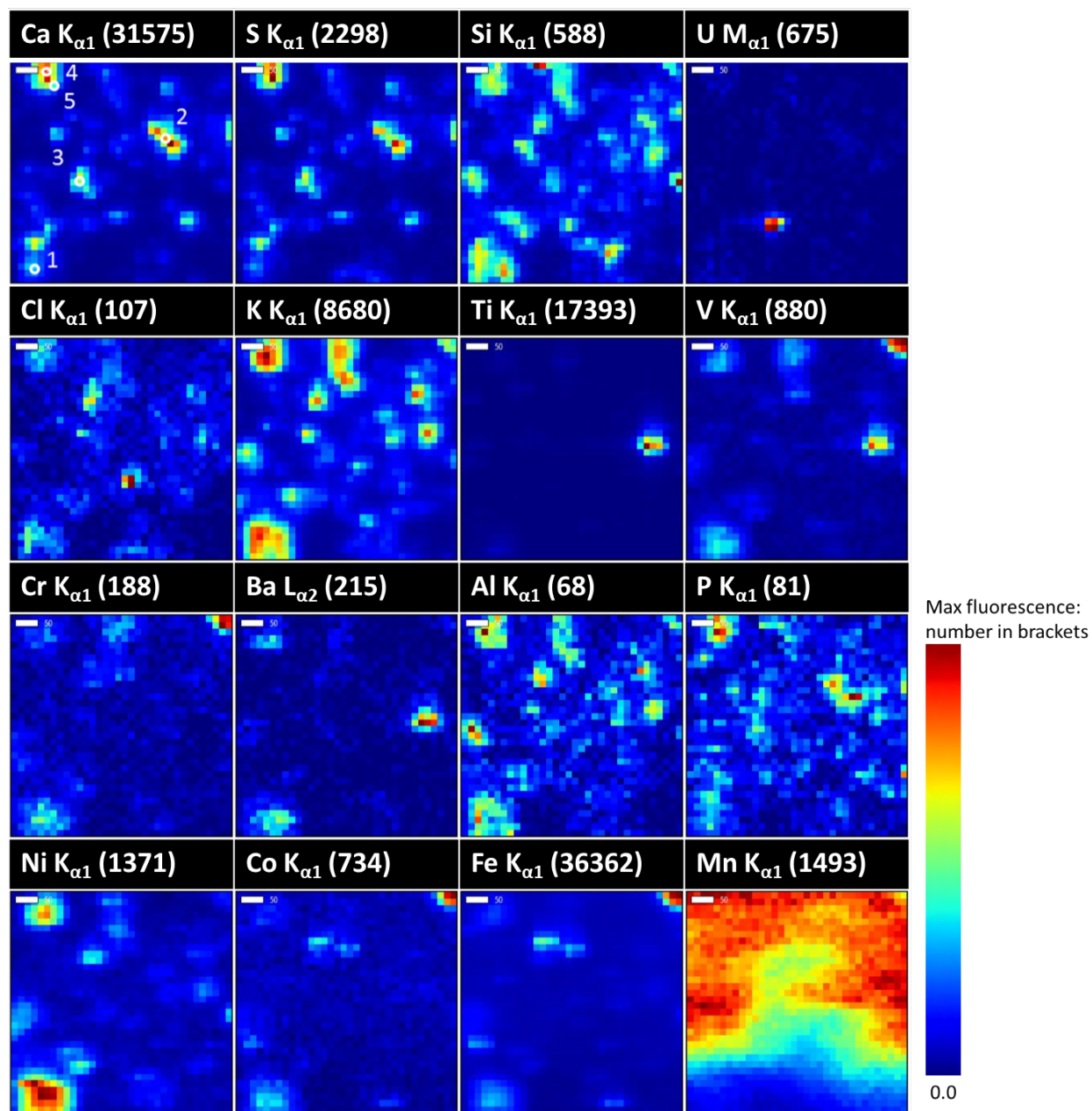


Figure S26. XRF maps showing the distribution of Ca, S, Si, U, Al, P, Cl, K, Ti, V, Ba, Ni, Co, Fe, Mn, and Cr collected from tailings sample TMF13-03-SA18. The size of the maps was 500 µm x 500 µm. Spots where Ca K-edge µ-XANES spectra were collected are marked on the Ca K_{α1} XRF map. The number in the brackets denotes the maximum counts observed from each element's XRF map. All scale bars are 50 µm in length.

Figure S27.

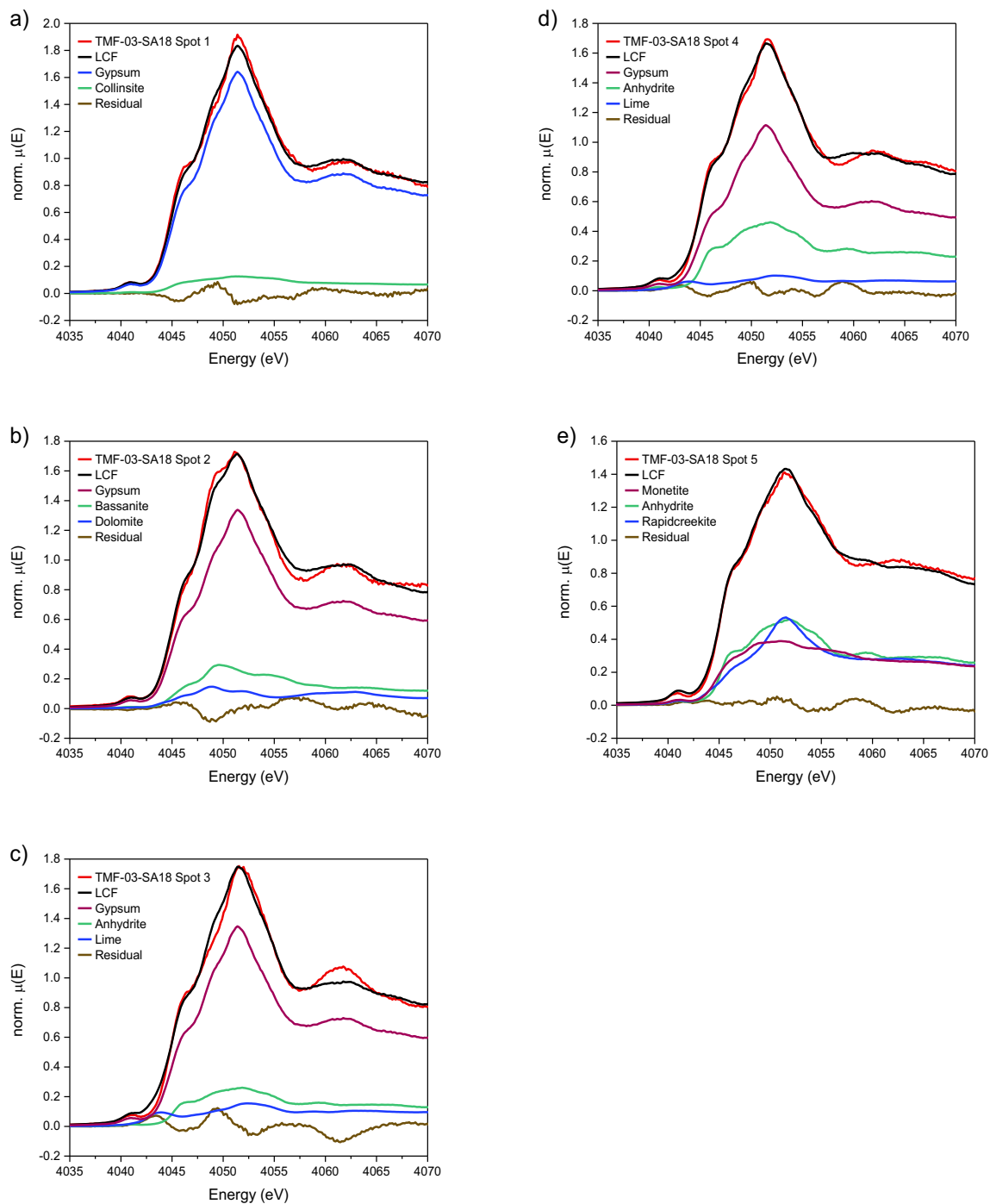


Figure S27. The fitted Ca K-edge μ -XANES spectra from TMF13-03-SA18 at spots marked 1 to 5 on Figure S26 are shown in a) to e), respectively. Only Ca K-edge μ -XANES spectra fits with a χ^2 below 0.5 are shown.

Figure S28.

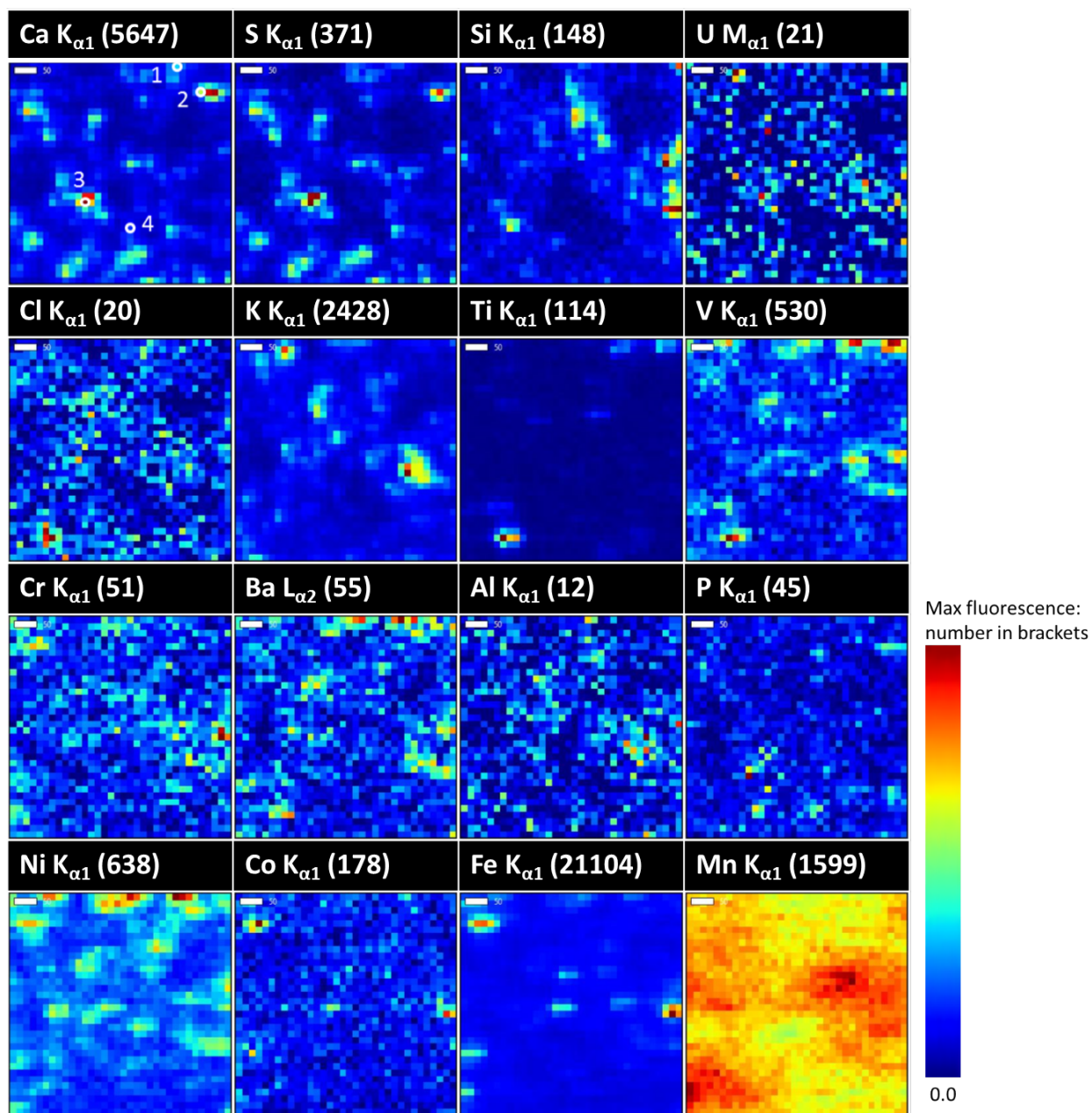


Figure S28. XRF maps showing the distribution of Ca, S, Si, U, Al, P, Cl, K, Ti, V, Ba, Ni, Co, Fe, Mn, and Cr collected from tailings sample TMF13-03-SA22. The size of the maps was 500 μm x 500 μm. Spots where Ca K-edge μ-XANES spectra were collected are marked on the Ca K_{α1} XRF map. The number in the brackets denotes the maximum counts observed from each element's XRF map. All scale bars are 50 μm in length.

Figure S29.

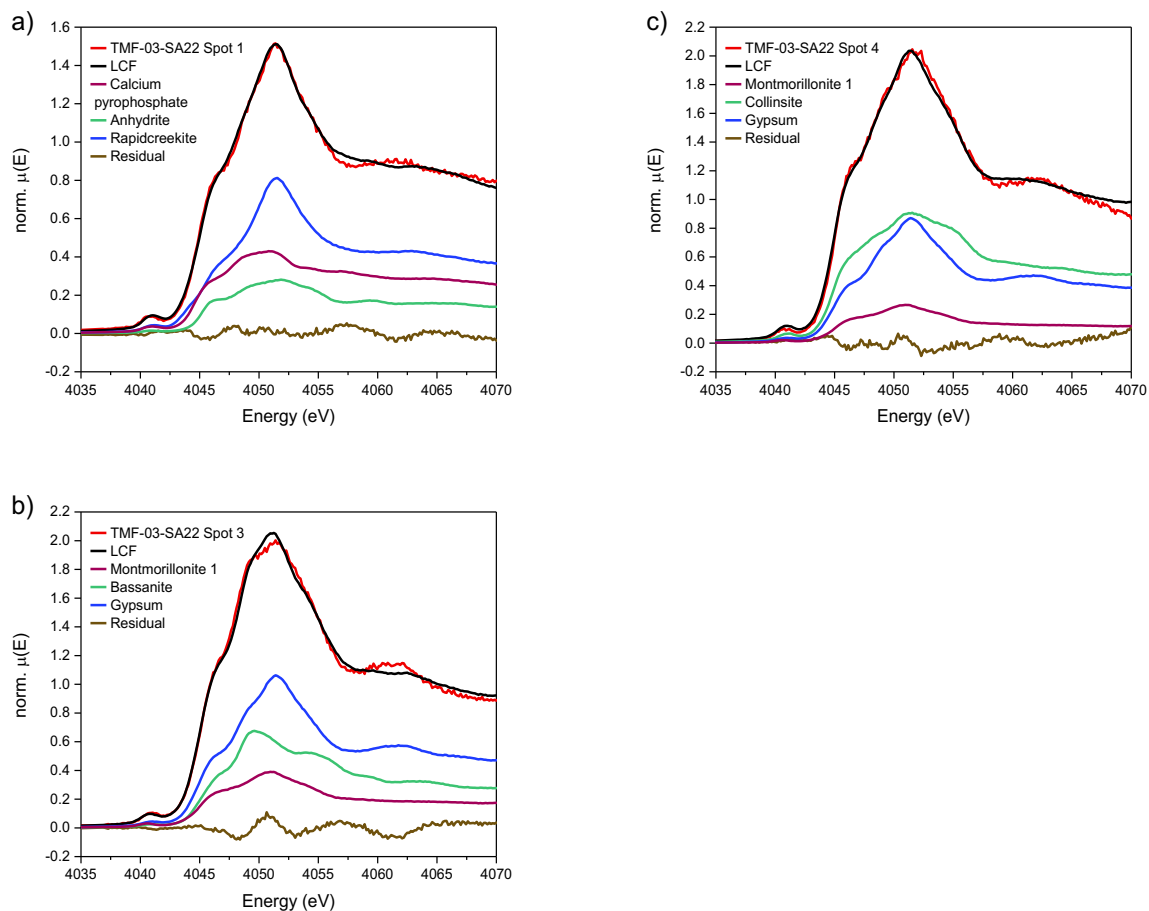


Figure S29. The fitted Ca K-edge μ -XANES spectra from TMF13-03-SA22 at spots marked on Figure S28 are shown in a) to c), respectively. Only Ca K-edge μ -XANES spectra fits with a χ^2 below 0.5 are shown.

Figure S30.

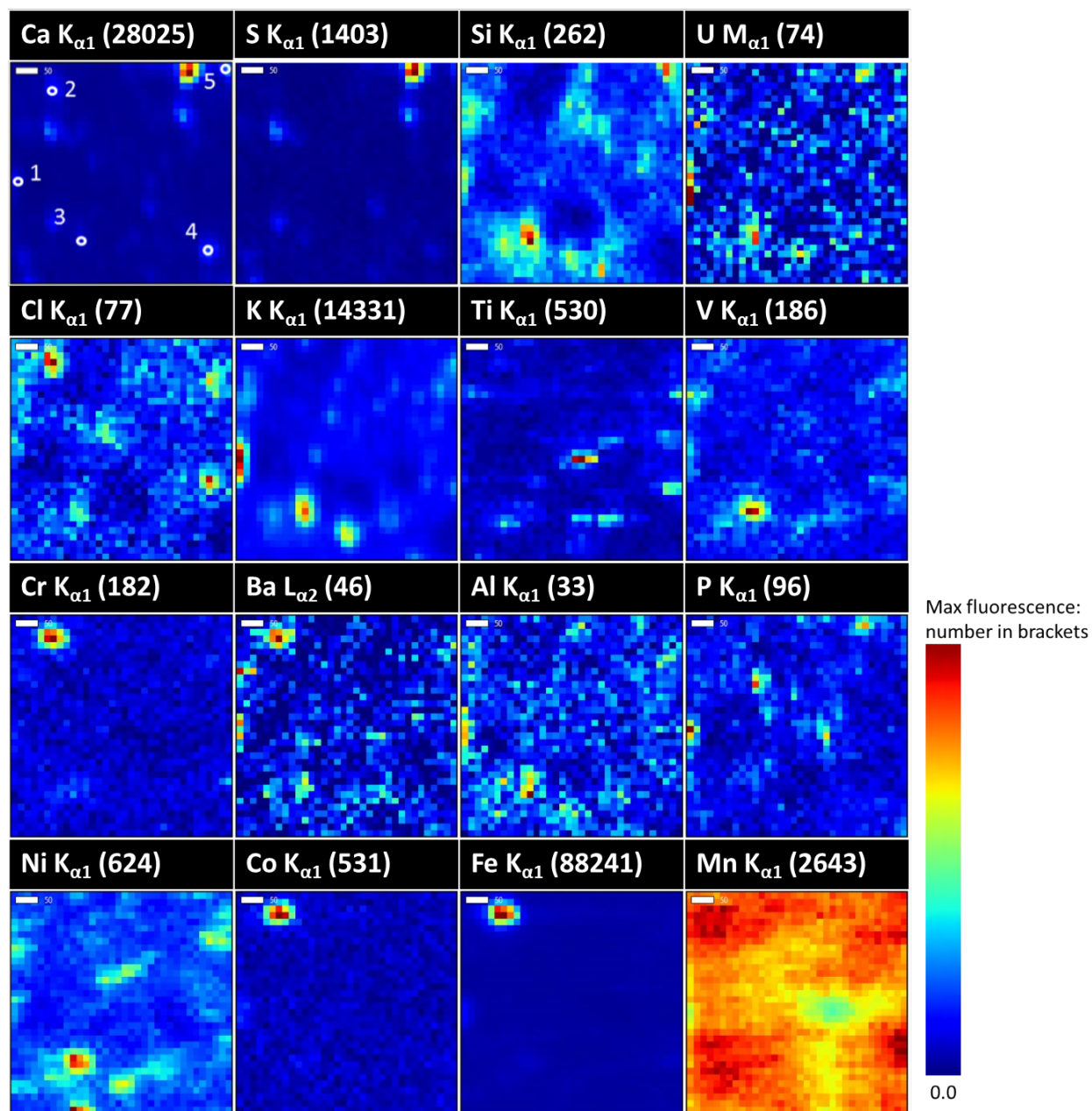


Figure S30. XRF maps showing the distribution of Ca, S, Si, U, Al, P, Cl, K, Ti, V, Ba, Ni, Co, Fe, Mn, and Cr collected from tailings sample TMF13-06-SA16. The size of the maps was 500 µm x 500 µm. Spots where Ca K-edge µ-XANES spectra were collected are marked on the Ca K_{α1} XRF map. The number in the brackets denotes the maximum counts observed from each element's XRF map. All scale bars are 50 µm in length.

Figure S31.

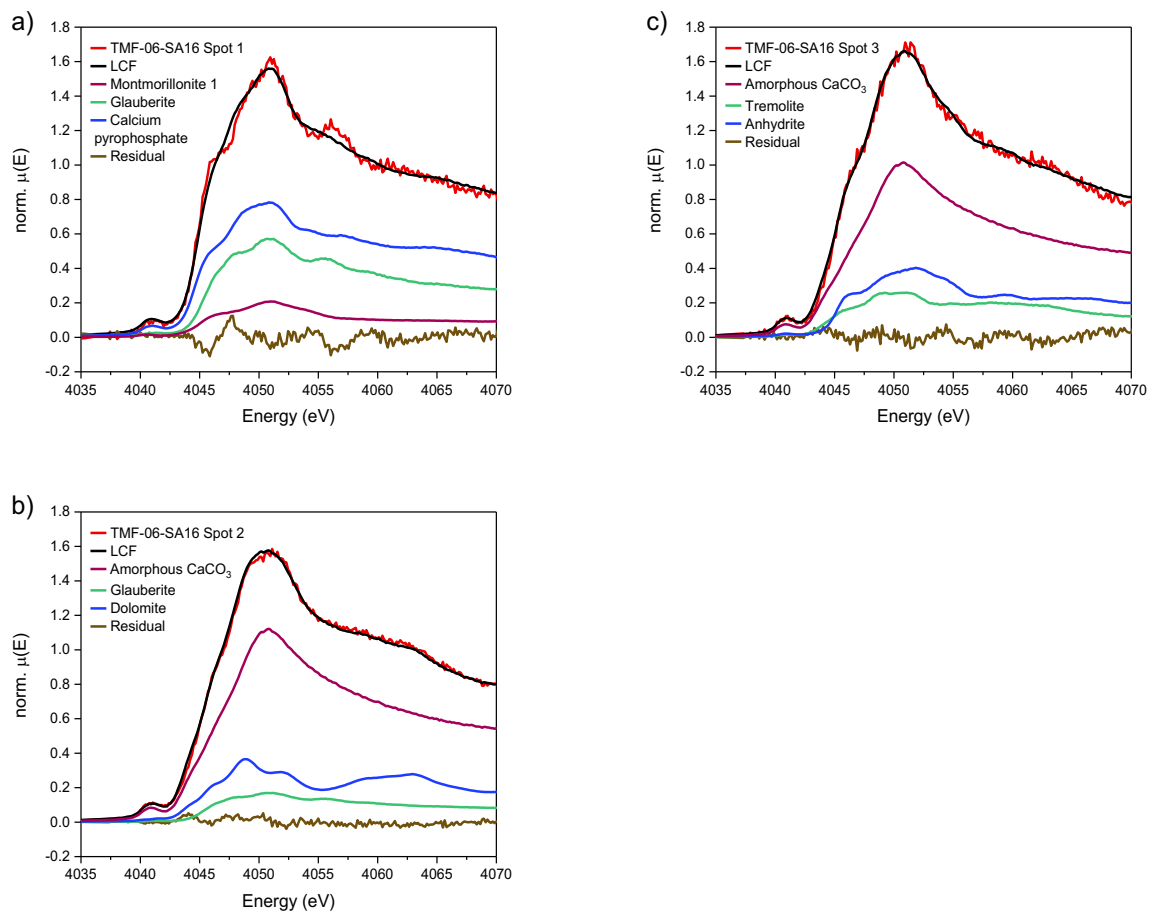


Figure S31. The fitted Ca K-edge μ -XANES spectra from TMF13-06-SA016 at spots marked on Figure S30 are shown in a) to c), respectively. Only Ca K-edge μ -XANES spectra fits with a χ^2 below 0.5 are shown.

Figure 32.

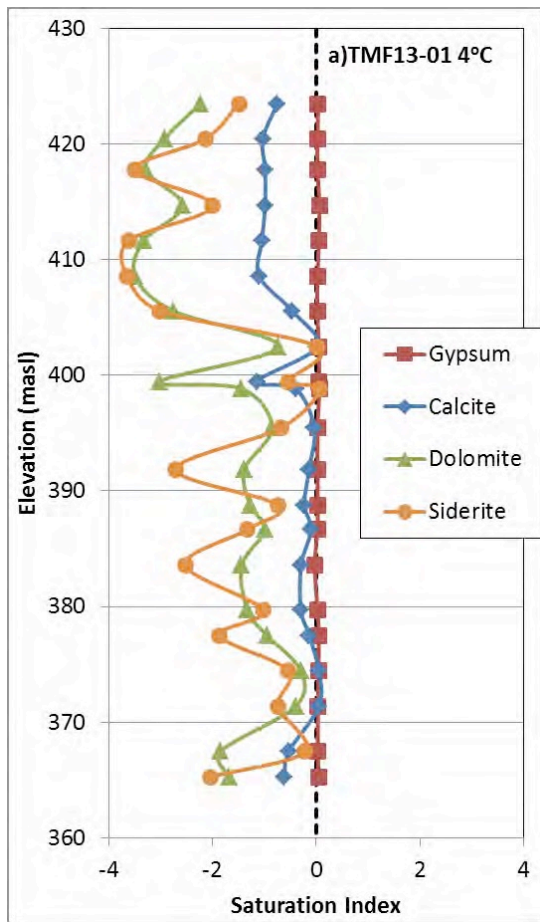


Figure S32. Sample depth vs. saturation index of dolomite, siderite (FeCO_3), calcite, and gypsum for the central borehole (TMF13-01).

Figure S33.

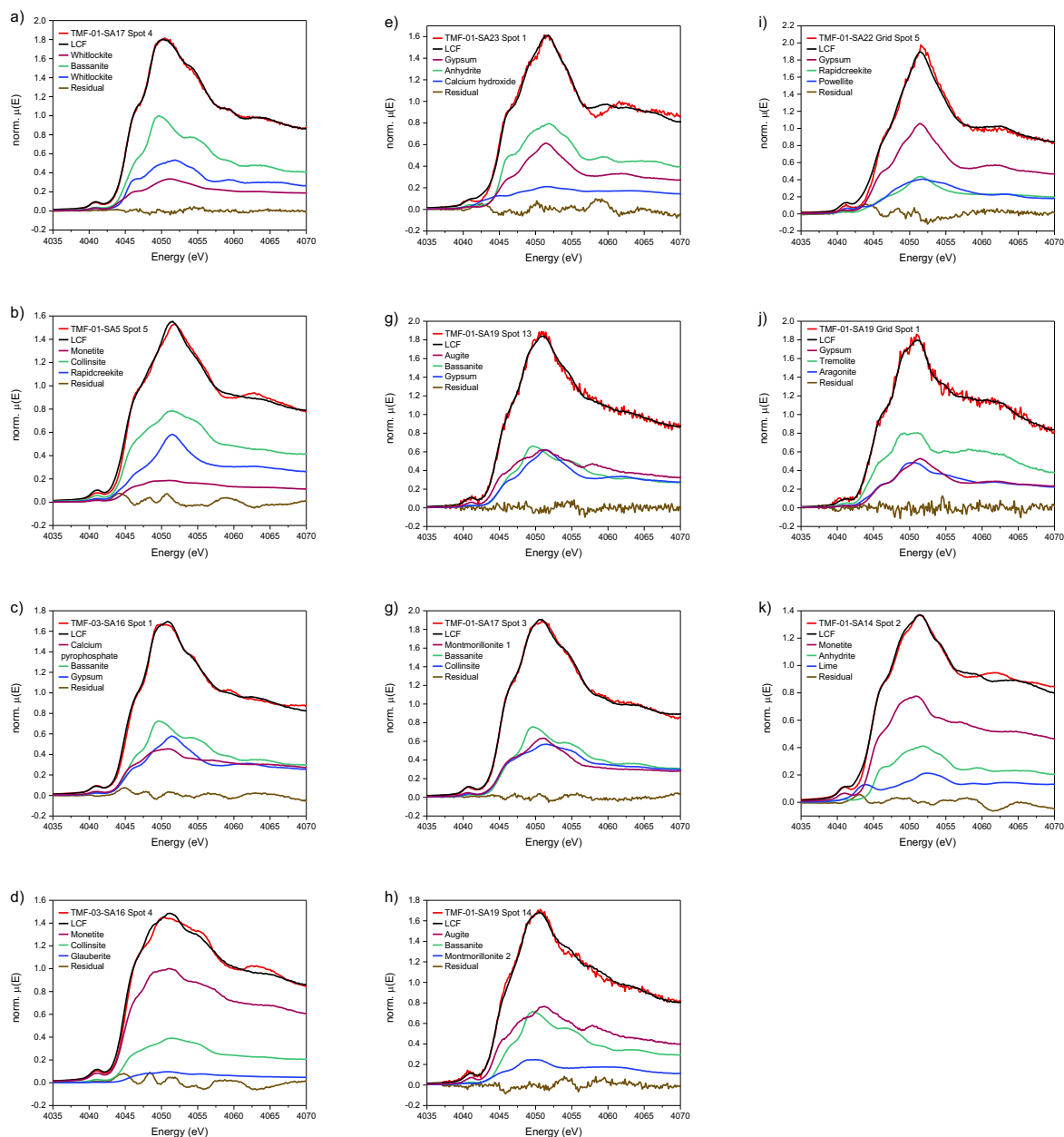


Figure S33. The fitted Ca K-edge μ -XANES spectra a) from TMF13-01-SA17 (collected from spot 4 in Figure S10), b) from TMF13-01-SA5 (collected from spot 5 in Figure S4), c) from TMF13-03-SA16 (collected from spot 1 in Figure S24), d) from TMF13-03-SA16 (collected from spot 4 in Figure S24), e) from TMF13-01-SA23 (collected from spot 1 in Figure S18), f) from TMF13-01-SA19 (collected from spot 13 in Figure S12), g) from TMF13-01-SA17 (collected from spot 3 in Figure S10), h) from TMF13-01-SA19 (collected from spot 14 in Figure S12), i) from TMF13-01-SA22 (collected from spot 5 in Figure S16), j) from TMF13-01-SA19 (collected from spot 1 in Figure S12), and k) from TMF13-01-SA14 (collected from spot 2 in Figure S8).

Figure S34.

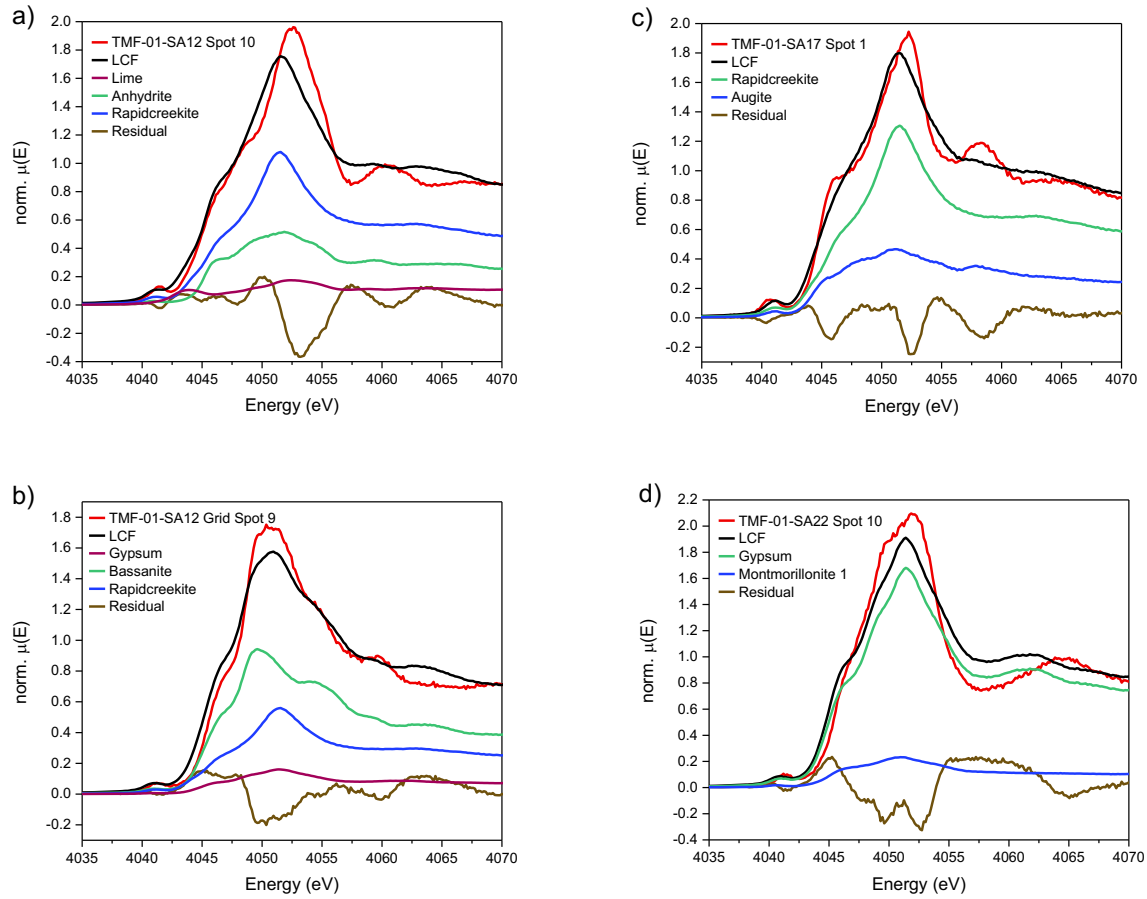


Figure S34. The fitted Ca K-edge μ -XANES spectra from TMF13-01-SA12 (collected from a) spot 10 and b) spot 9 in Figure S6), c) from TMF13-06-SA17 (collected from spot 1 in Figure S10), and d) from TMF13-01-SA22 (collected from spot 10 in Figure S16).

Figure S35.

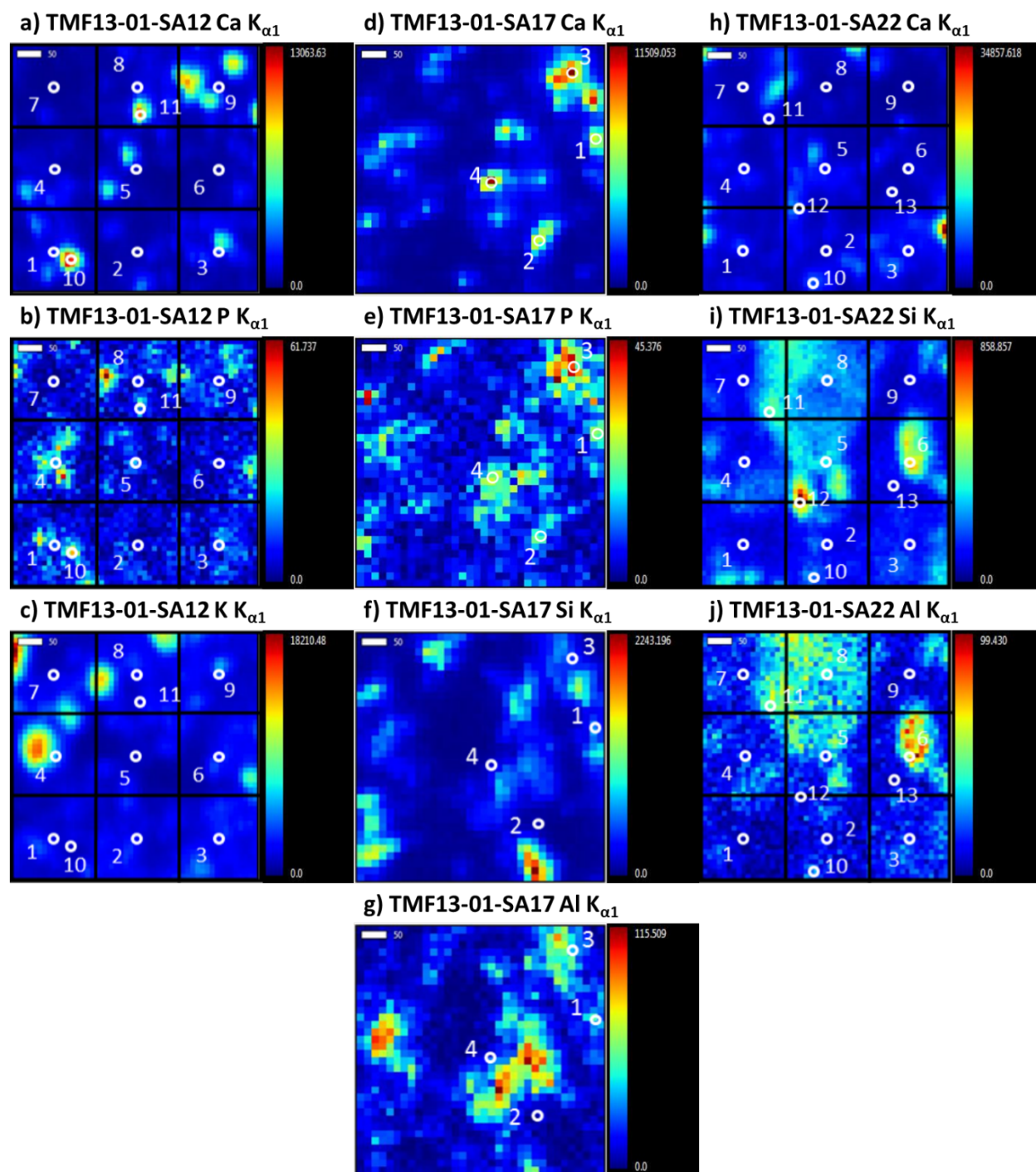


Figure S35. XRF maps showing the distribution of a) Ca, b) P, and c) K collected from tailings sample TMF13-01-SA12, d) Ca, e) P, f) Si, and g) Al collected from tailings sample TMF13-01-SA17, and h) Ca, i) Si, and j) Al collected from tailings sample TMF13-01-SA22. The size of the maps was 500 μm x 500 μm. Spots where Ca K-edge μ-XANES spectra were collected are marked on all XRF maps. All scale bars are 50 μm in length.

Figure S36.

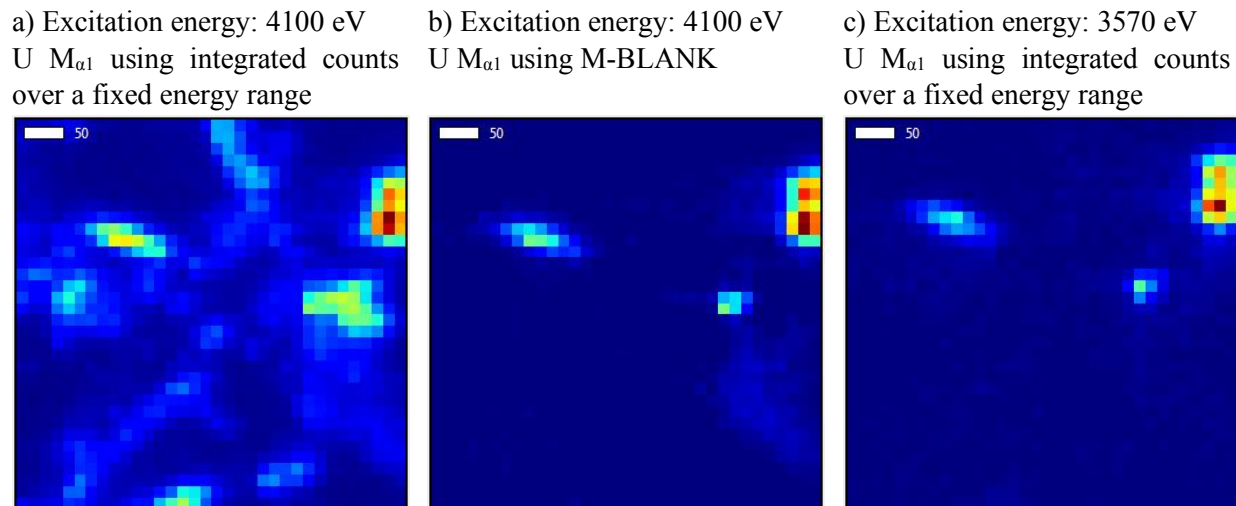


Figure S36. U $M_{\alpha 1}$ XRF maps collected from TMF13-01-SA14 using an: a) excitation energy of 4100 eV and integrated counts over a fixed energy range, b) excitation energy of 4100 eV and M-BLANK for deconvolution of emission spectra, and c) excitation energy of 3570 eV and integrated counts over a fixed energy range. All scale bars are 50 μm in length.

Figure S37.

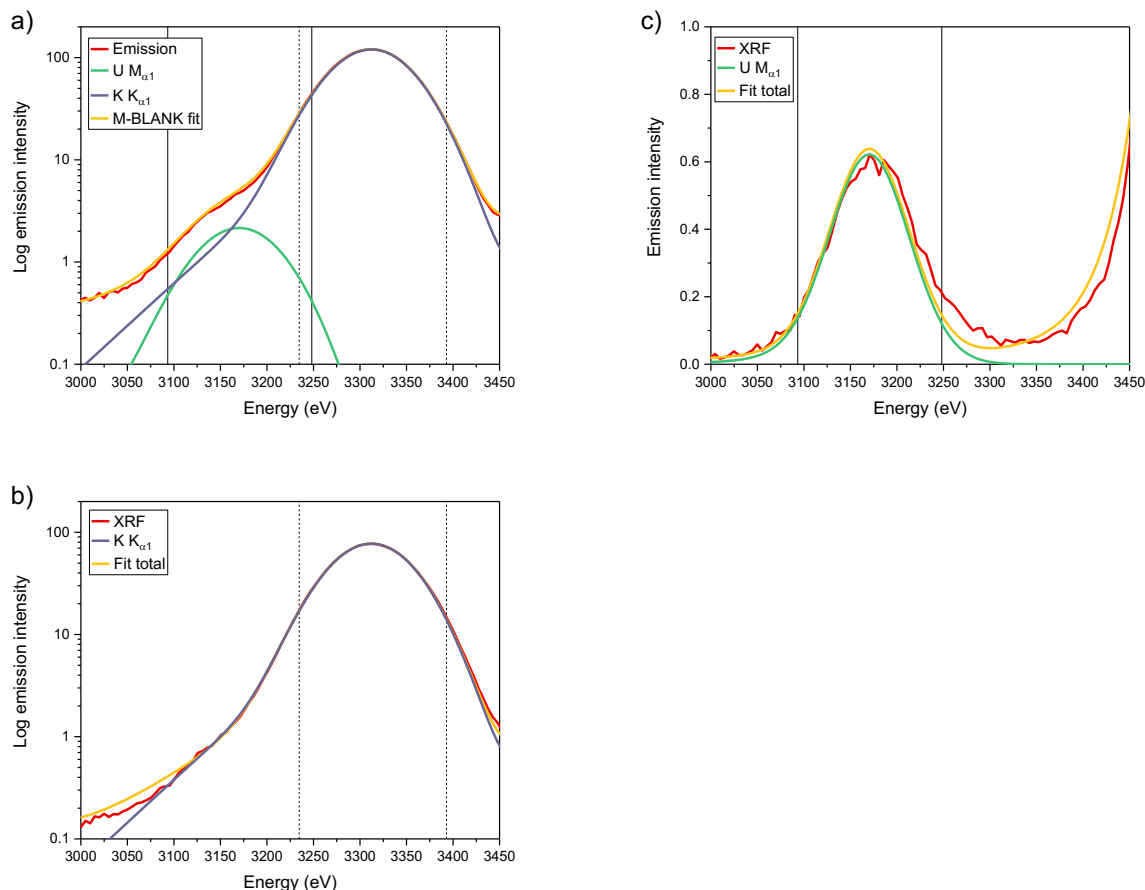


Figure S37. K $K_{\alpha 1}$ and U $M_{\alpha 1}$ emission spectra showing the energy fixed energy range used in integration and the modified Gaussians calculated using M-BLANK for the emission locations. a) emission spectra collected using an excitation energy of 4100 eV from TMF13-01-SA14 that contains a relatively high concentration of U, generated using an excitation energy of 4100 eV (corresponding with the XRF maps shown in Figure S36 a) and b)). b) emission spectra collected using an excitation energy of 4100 eV from TMF13-01-SA17 that contains a relatively low concentration of U, generated using an excitation energy of 4100 eV (corresponding with the XRF maps shown in Figure S10). c) emission spectra collected using an excitation energy of 3570 eV from TMF13-01-SA14 that contains a relatively high concentration of U generated using an excitation energy of 4100 eV (corresponding with the XRF maps shown in Figure S36 c)). In all cases, the solid lines correspond with the energy fixed energy range used in integration of U $M_{\alpha 1}$ counts, while the dashed lines correspond with the energy fixed energy range used in integration of K $K_{\alpha 1}$ counts.



An X-ray spectromicroscopy study of the calcium mineralization in the JEB tailings management facility at McClean Lake, Saskatchewan

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ABSTRACT

Solid mine/mill waste, known as tailings, often contain trace chemical species of interest that cannot be easily identified using bulk analysis methods. Existing methodologies for the identification of trace chemical species within heterogeneous materials, such as the identification of trace Ca-containing carbonates within the gypsum saturated McClean Lake uranium mill tailings, are limited. One methodology previously used in the study of the aforementioned tailings is the combination of X-ray fluorescence (XRF) mapping and Ca K-edge micro X-ray absorption near edge spectroscopy (μ -XANES). This work expands this methodology: Firstly, through use of a fitting procedure that allows a library of 34 XANES spectra collected from Ca-containing standards to be applied to each μ -XANES spectrum collected from the tailings. Secondly, by deeper interrogation of analyte concentrations measured in tailing porewater to rationalize the presence of trace Ca-containing carbonates of interest. It has also been demonstrated in this study that the comparison of the elemental distribution in the tailings determined by XRF mapping to the fitting results of the μ -XANES spectra can be used to help validate the results of the fittings of the μ -XANES spectra.

1. Introduction

A tailings management facility (TMF) is a facility designed to contain the ground-up rock and effluent produced in mining operations. These facilities often contain trace chemical species of interest such as those that affect the mobility of elements of environmental concern within the porewater. These trace chemical species are often not easily studied using bulk analysis techniques because the existence of other high-concentration chemical species with a similar composition dominates the results obtained from these bulk analysis techniques. Additionally, the formation of these species may take place years after the tailings have been deposited into the TMF, necessitating the study of tailings extracted from boreholes over a long-term period.

In recent years, the combination of two techniques – X-ray absorption near edge spectroscopy using a micro X-ray beam (μ -XANES) and X-ray fluorescence (XRF) mapping – has emerged as an effective approach to studying trace chemical species within tailings. In this approach, XRF is used to collect elemental maps which are then used to identify areas

that may contain trace chemical species of interest. These areas are subsequently analyzed with μ -XANES to obtain chemical information from the area of interest, including the chemical information from trace species that would otherwise be undetectable if bulk XANES were used. The purpose of this study is to improve the use of μ -XANES and XRF mapping via modifications to the data collection and analysis procedures. These improvements are demonstrated through an analysis of the Ca chemistry of the U mill tailings from the JEB tailings management facility (TMF) operated by Orano Canada (formerly AREVA Resources Canada) at McClean Lake, Saskatchewan.

The JEB TMF (herein referred to as “the TMF”) is designed to mitigate the migration of water-soluble species containing elements of environmental concern, such as U, by promoting the formation of water-insoluble mineral species; a summary of mineral phases present in the tailings prior to being deposited in the TMF is shown in Table 1 (AREVA ARCL, 2015). In the specific case of U within the TMF, uranyl ions (UO_2^{2+}), formed in the tailings as a result of the oxic conditions of the TMF ($E_h \sim +290 \text{ mV/SHE}$; $\text{pH} \sim 7$), may react with bicarbonate to

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Table 1

A summary of mineral phases present in the tailings prior to being deposited in the TMF.

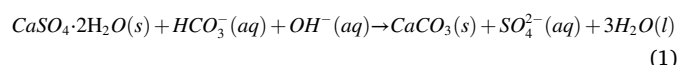
Mineral type	Major	Minor/Trace
Primary	Quartz (SiO ₂), Amorphous silica (SiO ₂), Chlorite ((Fe,Mg,Mn,Ni, Zn,Al,Li,Ti) ₄₋₆), (Si,Al) ₄ O ₁₀ (OH) ₈ , Illite ((K,H ₃ O)(Al,Mg, Fe) ₂ (Si,Al) ₄ O ₁₀ [(OH) ₂ (H ₂ O)]), Kaolinite (Al ₂ Si ₂ O ₅ (OH) ₄), Uraninite (UO ₂)	Molybdenite (MoS ₂), Goethite (FeO(OH)), Pyrite (FeS ₂), Chalcopyrite (CuFeS ₂), Galena (PbS), Rutile (TiO ₂), Coffinite (U (SiO ₄) _{1-x} (OH) _{4x}), Niccolite (NiAs), Rammelsbergite (NiAs ₂), Gersdorffite (CoAsS)
	Major and minor/trace	
Secondary	Gypsum (CaSO ₄ ·2H ₂ O), Hydrobasaluminite (Al ₄ (SO ₄)(OH) ₁₀ · 12–36H ₂ O), Scorodite (FeAsO ₄ ·2H ₂ O), Cabrerite (Ni ₃ (AsO ₄) ₂ · 8H ₂ O), Jarosite (KFe ₃ (OH) ₆ (SO ₄) ₂), Ferrihydrite (Fe(OH) ₃) Ferrimolybdate (Fe ₂ (MoO ₄) ₃ ·nH ₂ O), Annabergite (Ni ₃ (AsO ₄) ₂ · 8H ₂ O), Theophrasite (Ni(OH) ₂)	

*Note: This should not be considered an extensive list of the primary and secondary mineralogy.

form soluble uranyl-carbonate complexes as shown in Fig. 1 a). In an iron oxy(hydroxide) rich geo-environmental system such as the JEB TMF tailings, some of the uranyl-carbonate complexes may adsorb onto the iron oxy(hydroxide) mineral surfaces (Bargar et al., 1999, 2000). In the presence of an elevated concentration of dissolved calcium, as it occurs in the TMF tailings, ternary U-Ca-CO₃ complexes may also form, as shown in Fig. 1 b). The formation of ternary U-Ca-CO₃ complexes such as Ca₂UO₂(CO₃)₃ and CaUO₂(CO₃)₃²⁻ may reduce the activity of Ca²⁺ and HCO₃²⁻ in the tailings porewater and therefore limit the precipitation of calcium carbonate mineral phases such as calcite in the tailings. The formation of these soluble U complexes in the tailings porewater also increases the potential source term of U that could possibly be mobilized from the tailings after the TMF is decommissioned. It is therefore important to understand mechanisms through which the solubilization of uranium can be controlled or mitigated.

Bicarbonate is formed in the TMF from organic matter deposited into the TMF as a result of the consumption of small amounts of kerosene (used in the solvent extraction process) and polyacrylamide (used a

flocculent) in the milling process. Kerosene is gradually converted to soluble bicarbonate (HCO₃⁻(aq)), which is facilitated by the presence of bacterial communities (Blanchard et al., 2016). Bicarbonate can be limited in its reactions with uranyl ions through reactions with Ca²⁺(aq) dissolved from gypsum (CaSO₄·2H₂O) within the TMF to precipitate calcium carbonate (CaCO₃(s)). The precipitation of carbonate minerals is proposed to limit the concentration of aqueous bicarbonate in the TMF that is able to form soluble uranyl-carbonate complexes ((AREVA) ARCL, 2015). Gypsum is produced in the tailings preparation stage as a result of the addition of sulfuric acid (used in the leaching circuit) and lime (CaO) (added to control pH in the tailings preparation process). The tailings are saturated with gypsum resulting in a high Ca²⁺(aq) concentration (~550 mg/L) ((AREVA) ARCL, 2015). The overall reaction of bicarbonate with gypsum that has been proposed by Orano to form calcium carbonate in the TMF is shown in Equation (1) ((AREVA) ARCL, 2015; Blanchard et al., 2016):



The model shown in Equation (1) shows bicarbonate rather than carbonate reacting with gypsum to form calcium carbonate as bicarbonate is the dominant species at the near neutral conditions of the TMF ((AREVA) ARCL, 2015). However, this reaction can also take place with carbonate, with the only difference being that a hydroxide ion is not needed to react with the proton given off by bicarbonate ((AREVA) ARCL, 2015).

Since the commissioning of the TMF, a number of studies have been conducted that examined the chemistry of the tailings ((AREVA) ARCL, 2015; Blanchard et al., 2016; Blanchard et al., 2015; Hayes et al., 2014; Blanchard et al., 2017). A specific study, conducted by Blanchard et al., investigated whether calcium-containing carbonate compounds were present within the TMF through a series of analysis techniques, including XRF mapping and Ca K-edge μ -XANES (Blanchard et al., 2016). The combination of these two techniques was the only methodology able to detect the trace amounts of calcium carbonate present in the tailings (Blanchard et al., 2016). Although the previous study identified the use of XRF mapping and Ca K-edge μ -XANES as the best approach to study the speciation of Ca in the TMF, significant improvements are available for the XRF mapping and Ca K-edge μ -XANES methodology that are used to study these heterogeneous materials (Blanchard et al., 2016). This study sets out to demonstrate various improvements to this methodology through modified data collection and analysis procedures.

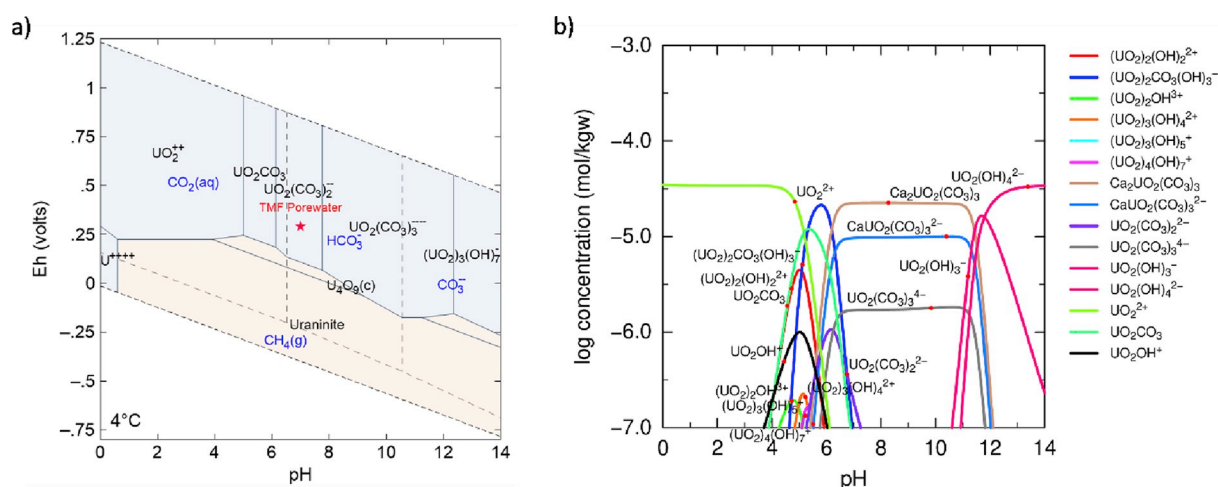


Fig. 1. a) Eh-pH diagram for the U-CO₃-H₂O system at 4 °C showing carbonate as well as soluble uranyl-carbonate complexes. The average Eh and pH the porewater of the tailings in the TMF are shown as the red star. b) Distribution of soluble species for the U-Ca-HCO₃-H₂O system at 4 °C with pH showing soluble uranyl-carbonate as well as U-Ca-CO₃ ternary complexes. The figures were generated using porewater concentrations from the TMF ([U] = 8.3 mg/L; [HCO₃⁻] = 168.0 mg/L; [Ca] = 550 mg/L). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article).

2. Experimental

2.1. Tailings sample description

A location map showing the JEB mill and TMF, as well as some of the ore bodies that feed the mill, is presented in Fig. S1 in the Supporting Information (SI). The tailing samples studied were collected from the TMF during the 2013 sampling campaign. Samples were collected from three borehole locations in the TMF. A total of sixteen samples were provided for this study. Nine samples collected from the central borehole (TMF13-01), four samples were collected from a borehole located approximately halfway from the center and edge of the tailings facility (TMF13-03), and one sample was collected from the lowest depths of a periphery borehole (TMF13-06). Fig. S2 shows a schematic of the TMF and the location of the bore-holes in plan-view. The tailings were deposited in the TMF using a floating barge and tremie piping system. Particle size segregation is known to occur resulting in the central borehole possessing coarser particles than boreholes located at the periphery of the TMF. Samples were collected at different depths from the boreholes at ~3 m intervals and were hydraulically pressed to extract porewater with the solid tailings then being nitrogen-purged and vacuumed-sealed.

2.2. TMF porewater analysis

Analysis of porewater concentrations of various elements in the TMF was performed by the Saskatchewan Research Council (SRC). Metal concentrations were measured using inductively coupled plasma – mass spectrometry (Agilent 7900, ICP-MS); sulfate ion concentrations were measured using inductively coupled plasma – optical emission spectroscopy (Agilent 5100, ICP-OES); and the concentrations of carbonate and bicarbonate were measured by determining the alkalinity of the porewater samples by titration with sulfuric acid. The concentrations of SO_4^{2-} , HCO_3^- , and Ca^{2+} in the porewater and the pH and sample depth are listed in Table S1 for all samples discussed in this study (concentrations as of 2008 are shown in Table S2). The porewater concentrations for other select elements and ions for all samples discussed in this study are listed in Table S3 (concentrations as of 2008 are shown in Table S4). Gas chromatography with a flame ionization detector and a mass spectrometry detector was used to detect the concentrations of hydrocarbon species in the solid tailings samples, with the weight percent of organic and inorganic carbon content in the tailings determined using a LECO furnace with IR detection. Carbon content results are shown in Table S5 for all samples included in this study (concentrations as of 2008 are shown in Table S6).

2.3. X-ray spectromicroscopy measurements

All XRF maps and Ca K-edge μ -XANES spectra were collected with the Soft X-Ray Microcharacterization Beamline (SXRMB) located at the Canadian Light Source (CLS) using a Si (111) crystal monochromator (Hu et al., 2010). Double-sided carbon tape was used to hold unground tailings samples on sample plates which were covered by Kapton foil. The purpose of using unground tailings was to increase the possibility of identifying minor Ca-containing phases. A 10 μm spot size was used during the collection of XRF maps and μ -XANES spectra. The XRF maps were collected by rastering a 500 $\times$ 500 μm^2 area using a 15 μm step size with a 1 s dwell time using an excitation energy of 4100 eV or 8350 eV, with the former used to collect Al, Si, P, S, Cl, K, and Ca $K_{\alpha 1}$ maps and U $M_{\alpha 1}$ maps while the latter was used to collect Ti, V, Cr, Mn, Fe, Co, and Ni $K_{\alpha 1}$ maps and Ba $L_{\alpha 2}$ maps. Additionally, an excitation energy of 3570 eV was used to collect U $M_{\alpha 1}$ XRF maps from several samples, as this energy lies between the U $M_{5\text{-edge}}$ (3552 eV) and the K K-edge (3608 eV); this, in turn, was used to generate U $M_{\alpha 1}$ XRF maps without contributions from the overlapping K $K_{\alpha 1}$ signal.

The selection of spots on the XRF maps where Ca K-edge μ -XANES

spectra were collected were chosen using one of two approaches: nine fixed spots on the XRF map based on a 3 $\times$ 3 grid, or selection of locations based on points of interest on the XRF map. The grid-based approach was utilized for four tailings samples extracted from borehole 1 that were analyzed in this study and are listed in Table S1 (TMF13-01-SA12, TMF13-01-SA19, TMF13-01-SA22, and TMF13-01-SA25). The rationale for this approach was to select spots for Ca K-edge μ -XANES collection without bias to quantify trace Ca phases within the tailings that may not appear notable based on the XRF maps alone. The approach of selecting spots based on points of interest was utilized in all tailing samples analyzed in this study. This approach involved a comparison of multi-element XRF maps to select spots likely to possess Ca phases that did not contain sulfate ions. As was discussed by Blanchard et al., most of the Ca in the TMF is in the form of gypsum ((AREVA) ARCL, 2015; Blanchard et al., 2016). Spots that were determined to be points of interest were identified by comparing XRF maps and identifying locations that had high Ca concentrations and low S concentrations as these locations were more likely to possess Ca phases other than gypsum (Blanchard et al., 2016). Ca K-edge XANES spectra were collected using a 0.15 eV step through the Ca K-edge. All spectra were measured in partial fluorescence yield (PFY) mode using a Bruker fluorescence detector. The Ca K-edge XANES spectra were calibrated using the Ti K-edge XANES spectrum from elemental Ti powder with the maximum of the first derivative of the Ti K-edge XANES spectrum set to 4966 eV (Thompson et al., 2009).

2.4. Data analysis

The XRF maps were analyzed using the SMAK software program (Webb, 2011). Fitting of XRF data (when necessary) was carried out using the XRF fitting program M-BLANK to deconvolute the overlapping K $K_{\alpha 1}$ and U $M_{\alpha 1}$ emission signals (Crawford et al., 2018). Briefly, the XRF spectrum from each pixel was fitted using a linear least-squares method using a series of modified Gaussians representing the various X-ray fluorescence emissions along with terms governing contributions from the background, Compton scattering, and Raleigh scattering (Crawford et al., 2018).

The collected μ -XANES spectra were analyzed using the Athena software program (Ravel and Newville, 2005). Principle component analysis (PCA) followed by linear combination fitting (LCF) using the spectra from Ca standards was performed to quantitatively analyze the Ca K-edge μ -XANES spectra from the tailings. The energy range used for PCA and LCF analysis was –10 eV and +20 eV relative to the Ca K-edge absorption edge energy (4038 eV) (Thompson et al., 2009). The purpose of performing PCA was to determine the number of Ca-bearing mineral species present in a set of Ca K-edge μ -XANES spectra (Fernandez-Garcia et al., 1995; Beauchemin et al., 2002). PCA works by decomposing a set of XANES spectra into a series of components (eigenvectors) and weightings (eigenvalues) that do not simply relate to the chemical species present in the XANES spectra, but rather describe the variation within the set (Fernandez-Garcia et al., 1995; Beauchemin et al., 2002). The PCA calculation assumes that each XANES spectrum in the set is made up of a linear combination of individual component spectra (Fernandez-Garcia et al., 1995; Beauchemin et al., 2002). Moreover, it is assumed that the minimum number of eigenvectors needed to describe the variation in the set of XANES spectra is equivalent to the minimum number of chemical components that make up a XANES spectrum within the set of XANES spectra (Fernandez-Garcia et al., 1995; Beauchemin et al., 2002). The indicator function (IND) developed by Malinowski was used to find the minimum number of eigenvectors needed to describe the variation in the set of spectra to determine the minimum number of components required to describe a set of spectra (Malinowski, 1977, 2002). The results from PCA and the calculation of the IND function from the μ -XANES spectra that were obtained from the sample identified as TMF13-01-SA19 are shown in Fig. S3. The minimum IND function for TMF13-01-SA19 was found to correspond to three components, with

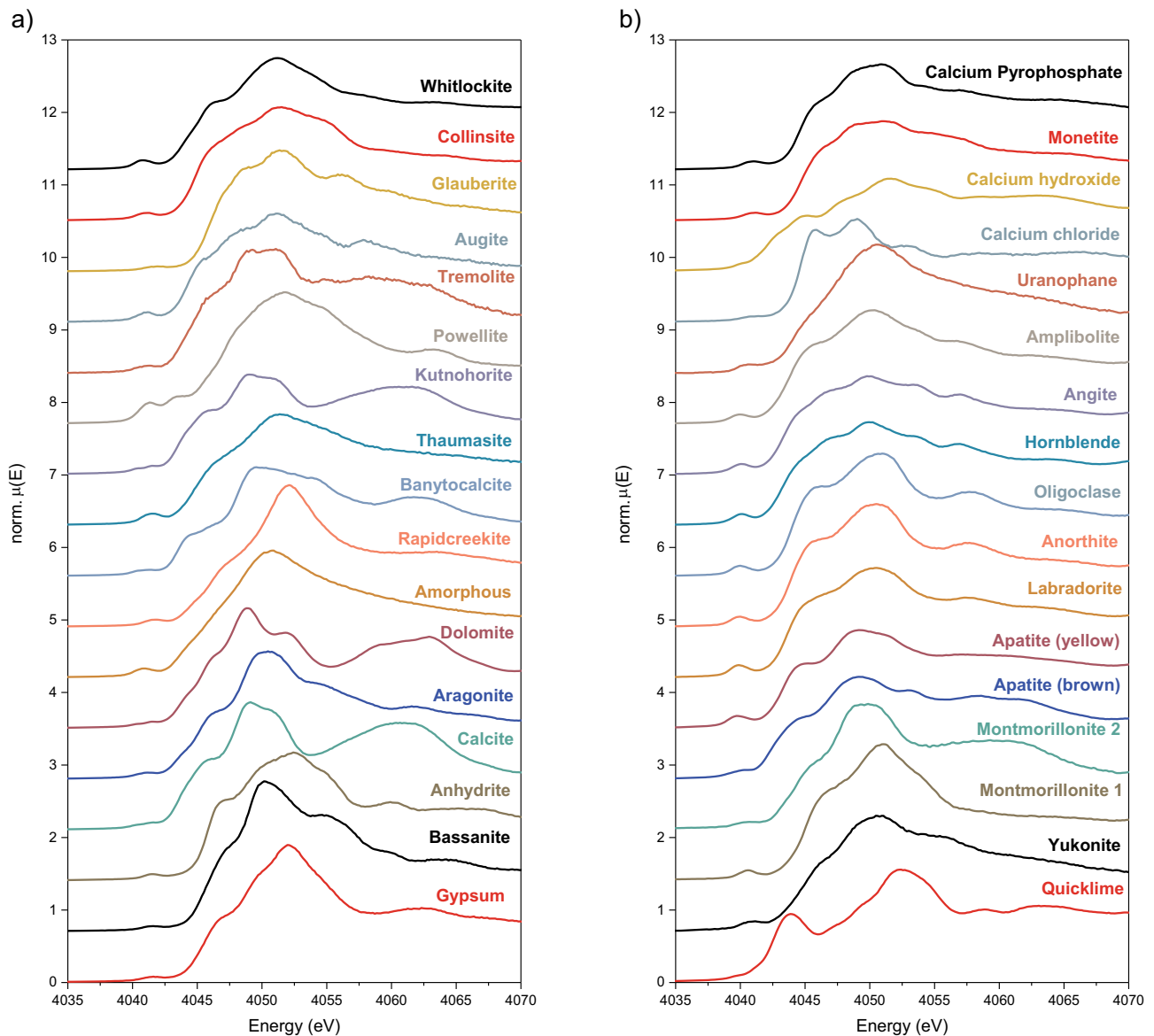


Fig. 2. The Ca K-edge XANES spectra from Ca standards collected in this study, with Ca standards from group 1 and 2 shown in a) and b), respectively.

other samples showing a minimum IND with no more than three components. This indicates that three components were the minimum number of components needed to fit a μ -XANES spectrum from these tailings samples. As a result, each LCF was restricted to three components.

LCF was used in order to identify the Ca-containing mineral species contributing to the Ca K-edge μ -XANES spectra collected from tailings samples. LCF involves fitting each Ca K-edge μ -XANES spectrum with a linear combination of Ca K-edge XANES spectra collected from Ca-containing mineral species known or suspected to be present in the TMF. The best fit was evaluated by comparison of χ^2 values. Due to the diversity in Ca minerals present in the TMF, a large library of Ca K-edge XANES spectra from standard materials (herein referred to as: "spectra from the standards") was generated to be used in the LCF of the Ca K-edge μ -XANES spectra from the tailings (herein referred to as: "spectra from the tailings"). The Ca-containing standards used in this study were procured from a wide range of sources including the Department of Geological Sciences at the University of Saskatchewan, the Royal Ontario Museum, the Smithsonian Museum, Fisher Scientific, and private mineral vendors. It was necessary to develop a methodology for fitting each spectrum collected from the tailings with the spectra

collected from the standards. This fitting methodology was required due to the size of the library of standards (containing 34 Ca K-edge XANES spectra) which would require 6545 individual fits to be computed if each tailings spectrum was fit directly with all standard spectra in the library. In order to avoid this large computing time an LCF methodology was developed that uses a three-stage process. First, the library of spectra from the standards was divided into two groups of 17 spectra (herein referred to as group 1 or group 2). A list of every Ca-containing mineral included in this study sorted into group 1 and group 2 is presented in Table S7. Second, the group 1 and group 2 sets of spectra were individually used to fit each spectrum from the tailings with the maximum number of spectra from the standards included in each fit restricted to three based on the PCA results shown in Fig. S3. Thirdly, for each spectrum collected from the tailings, the top six spectra from the standards from each of group 1 and group 2 were identified by comparison of χ^2 values and used to create a new group of twelve spectra from the standards. The top six standards from each group were chosen based on the order in which they were present within the fits (i.e., the fits possessing the first and second lowest χ^2 values had the standards within them ranked among the top six). In cases where two or more standards were present within the same fitting, the standard with the highest

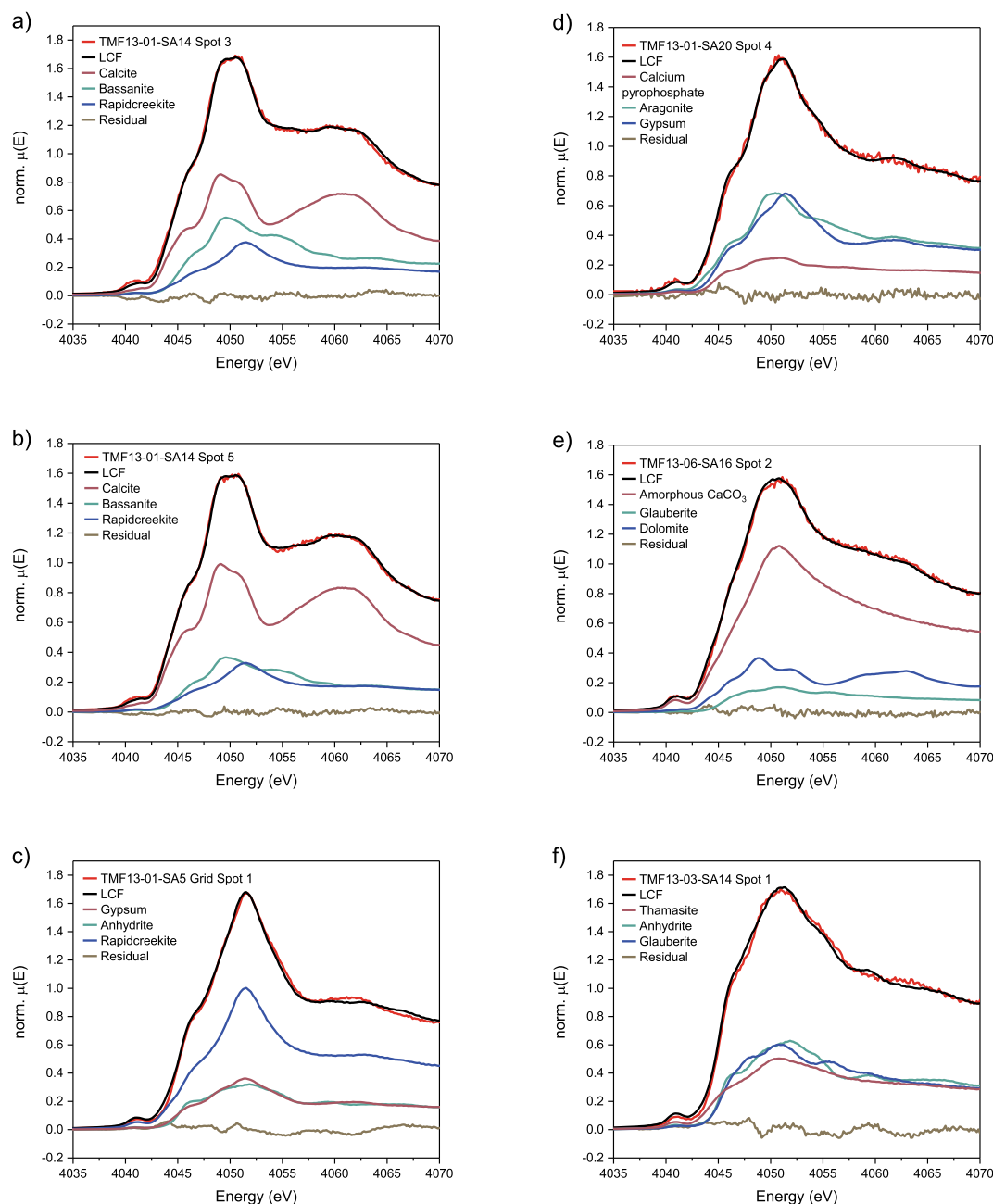


Fig. 3. The fitted Ca K-edge μ -XANES spectra from TMF13-01-SA14 (collected from a) spot 3 and b) spot 5 on Fig. 4), c) from TMF13-01-SA05 (collected from spot 1 in Figs. S4) and d) from TMF13-01-SA20 (collected from spot 4 in Figs. S14) and e) from TMF13-06-SA16 (collected from spot 2 in Figs. S30) and f) from TMF13-06-SA16 (collected from spot 1 in Fig. S22).

contribution to the fit was chosen (i.e., a standard with a 50% contribution would be ranked higher than a standard with only a 5% contribution). This new group of spectra from the standards was then used in the LCF of the spectrum collected from the tailings with the single best fit being reported in this study. The maximum number of spectra from the standards included in each fit was restricted to three based on the PCA results shown in Fig. S3. Additionally, fits were deemed to be acceptable when the χ^2 value was lower than 0.5.

3. Results and discussion

3.1. Ca K-edge XANES spectra from the standards

Ca K-edge XANES spectra were collected from a wide range of Ca-containing minerals that are suspected or known to be present in the tailings and were used in the LCF of the spectra from the tailings. Fig. 2 shows the Ca K-edge XANES spectra that were collected from the standards. As can be observed in Fig. 2, each Ca K-edge XANES spectrum possesses unique spectral features that allow them to act as a

“fingerprint” for the respective Ca-containing mineral. The Ca K-edge spectrum itself is primarily a result of a dipole transition of a 1s electron into unoccupied 4p states, with a minor contribution from the quadrupole transition to 3d states corresponding to a so-called ‘pre-edge’ peak located at approximately 4041 eV (Martin-Diaconescu et al., 2015).

3.2. Identification of Ca-bearing carbonates in the tailings

XRF maps and fitted Ca K-edge μ -XANES spectra for every tailings sample analyzed in this study are shown in Fig. S4 – S31 and are ordered based on borehole number and sample number. The original chemical model (Equation (1)) proposed by Orano Canada to control the formation of water-soluble uranyl carbonate complexes was through the reaction of dissolved calcium with bicarbonate to form calcium carbonates as this would limit the concentration of bicarbonate available to react with uranyl ions ((AREVA) ARCL, 2015). Blanchard et al. identified the presence of several calcium carbonates within the TMF13-01-SA19 sample which suggested that the model proposed by Orano (Equation (1)) was possible (Blanchard et al., 2016). Within this study, the calcium carbonates previously identified by Blanchard et al. were identified (calcite (CaCO_3), aragonite (CaCO_3), and dolomite ($\text{CaMg}(\text{CO}_3)_2$)) in addition to rapidcreekite ($\text{Ca}_2(\text{SO}_4)(\text{CO}_3)\cdot 4\text{H}_2\text{O}$), amorphous CaCO_3 (ACC), and thaumasite ($\text{Ca}_3\text{Si}(\text{OH})_6(\text{CO}_3)(\text{SO}_4)\cdot 12\text{H}_2\text{O}$). Example LCF results showing the presence of each of these compounds are shown in Fig. 3.

3.2.1. Identification of calcite

XRF maps of a series of elements collected from the TMF13-01-SA14

sample are shown in Fig. 4 and the Ca K-edge μ -XANES spectra collected from the spots marked as 3 and 5 on Fig. 4, along with LCF of these spectra, are shown in Fig. 3 a) and b), respectively. Both fits indicated the presence of calcite, one form of calcium carbonate, as the standard with the largest contribution with the concentrations being 48% and 56% for the Ca K-edge μ -XANES spectra collected from spots 3 and 5, respectively. The other two standards present in both fits were bassanite ($\text{CaSO}_4\cdot 0.5\text{H}_2\text{O}$) and rapidcreekite. Furthermore, The Ca and S XRF maps shown in Fig. 4 a) and b) indicate that a relatively low sulfur concentration was present at the locations where calcite was identified (spots 3 and 5 in Fig. 4) compared to the calcium concentrations at these locations. The low sulfur concentration is consistent with XRF mapping and Ca K-edge μ -XANES results reported by Blanchard et al. from the TMF13-01-SA19 sample. That study also reported a high calcium concentration and low sulfur concentration at the locations where calcite was identified (Blanchard et al., 2016).

The TMF13-01-SA14 and TMF13-01-SA19 samples are the only two samples studied where calcite was identified by either Blanchard et al. or within the current study (Blanchard et al., 2016). While an explanation for why calcite was only observed in these particular samples is not apparent from the XRF and Ca K-edge μ -XANES data alone, comparison of these results to the concentration of bicarbonate in the porewater provides a possible rationale. Fig. 5 shows the dissolved bicarbonate porewater concentrations measured in 2008 and 2013 plotted against the depth of each sample location as of 2013. The bicarbonate concentration above which calcite was predicted to form by Orano is also indicated in Fig. 5, and the depth per sample vs saturation index of some carbonate minerals as well as gypsum is shown in Fig. S32 ((AREVA)

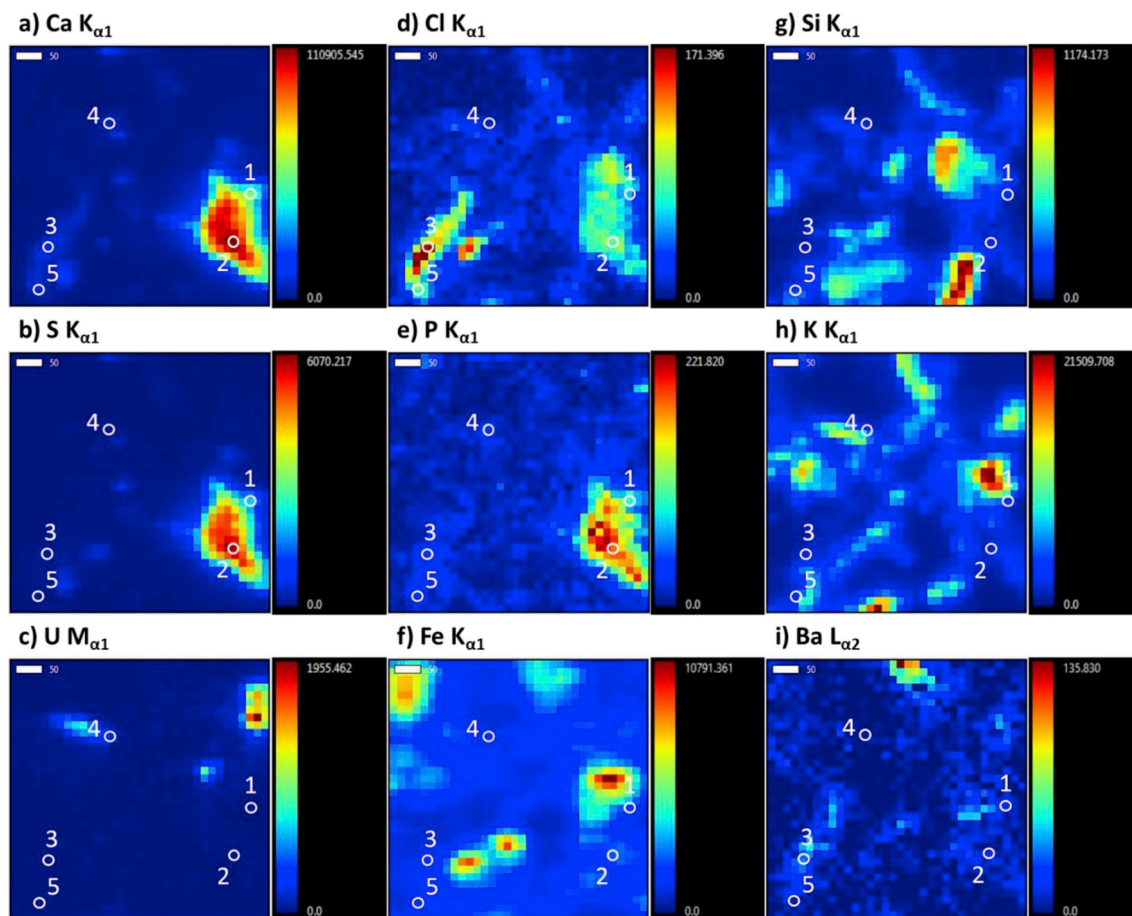


Fig. 4. XRF maps showing the distribution of Ca, S, U, Cl, P, Fe, Si, and K collected from tailings sample TMF13-01-SA14 in a) to i), respectively. The size of the maps was 500 $\mu\text{m} \times 500 \mu\text{m}$. The U map was obtained by deconvolution of the $\text{U M}_{\alpha 1}$ from the $\text{K K}_{\alpha 1}$ emission signals using the M-BLANK program as described in Section 3.4. Spots where Ca K-edge μ -XANES spectra were collected are marked on all XRF maps. All scale bars are 50 μm in length.

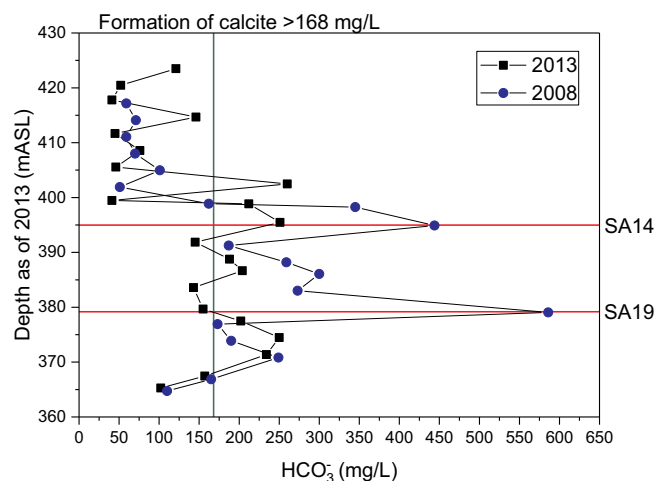


Fig. 5. Dissolved bicarbonate porewater concentration in 2008 (blue line) compared to 2013 (black line) plotted against the sample depth of the central borehole. The concentration of bicarbonate (168 mg/L) above which calcite was predicted by Orano to form is indicated by the vertical green line. The red lines labeled SA14 and SA19 on both plots denote the two samples where calcite was identified in the 2013 tailings samples. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article).

ARCL, 2015). It can be observed from Fig. 5 that the majority of porewater measurements obtained in 2008 from the central borehole below ~400 mASL (meters above sea level) have bicarbonate concentrations above the predicted equilibrium concentration for calcite (~168 mg/L based on a fixed pH and Ca^{2+} concentration) ((AREVA) ARCL, 2015). It can also be observed that the concentrations of bicarbonate measured in 2008 from the depths corresponding to samples TMF13-01-SA14 and TMF13-01-SA19 are significantly higher when compared to the concentrations measured at the other depths from borehole one that were studied (see Fig. 5). Furthermore, it can be observed in Fig. 5 that the concentration of bicarbonate decreased when comparing the 2008 values to the 2013 values at the depths that correspond to samples TMF13-01-SA14 and TMF13-01-SA19, which may be attributed to the formation of a carbonate containing precipitate (e.g., calcite). These results suggest that a higher than predicted bicarbonate concentration of 168 mg/L may be needed in order for calcite to form within the tailings.

3.2.2. Identification of rapidcreekite

The calcium carbonate that was most consistently observed within tailings samples was rapidcreekite ($\text{Ca}_2(\text{SO}_4)(\text{CO}_3)\cdot 4\text{H}_2\text{O}$), which unlike calcite, was observed in all but two samples in borehole 1 and showed no trend with depth or bicarbonate concentration (see Table S8). Dydo et al. investigated the precipitation of calcium sulfates and carbonates in a saturated CaSO_4 solution with varying molar ratios of CO_3^{2-} and SO_4^{2-} (Dydo et al., 2003). This study showed that the formation of rapidcreekite occurred by co-precipitation in the presence of a $\text{CO}_3^{2-}:\text{SO}_4^{2-}$ molar ratio of 4.5×10^{-3} (Dydo et al., 2003). Similarly, Onac et al. studied a natural deposit of rapidcreekite and concluded that rapidcreekite could form following precipitation of gypsum and before the formation of a CaCO_3 species in the presence of a $\text{CO}_3^{2-}:\text{SO}_4^{2-}$ molar ratio of $6 \times 10^{-2} - 4.6 \times 10^{-1}$ and at a pH above 6.4 (Onac Bogdan et al., 2013). The measured porewater concentrations of CO_3^{2-} within the TMF are below the detection limit of the porewater alkalinity measurements that were performed by titration with sulfuric acid (<1 mg/L), which would suggest a $\text{CO}_3^{2-}:\text{SO}_4^{2-}$ ratio much lower than that reported by either Dydo et al. or Onac et al. (9×10^{-9} based on 1 mg/L carbonate) ((AREVA) ARCL, 2015; Dydo et al., 2003; Onac Bogdan et al., 2013). However, Dydo et al. reported that calcite was observed when the $\text{CO}_3^{2-}:\text{SO}_4^{2-}$ ratio was 5×10^{-2} while calcite was not observed as a precipitate

when the $\text{CO}_3^{2-}:\text{SO}_4^{2-}$ ratios were lower than 5×10^{-2} (Dydo et al., 2003). Considering that calcite has been identified within the TMF by both the current study and by Blanchard et al., this suggests that the $\text{CO}_3^{2-}:\text{SO}_4^{2-}$ ratio may vary considerably from the 9×10^{-9} ratio estimated using the porewater concentration data at some locations (see Table 1) ((AREVA) ARCL, 2015; Blanchard et al., 2016). The implication of the detection of calcite is that if the $\text{CO}_3^{2-}:\text{SO}_4^{2-}$ ratio exceeds the value necessary for the formation of calcite (5×10^{-2}), then it is probable that the $\text{CO}_3^{2-}:\text{SO}_4^{2-}$ ratio will exceed the value necessary for the formation of rapidcreekite (4.5×10^{-3}) in some locations (Blanchard et al., 2016; Dydo et al., 2003). These findings, in combination with the LCF shown in Fig. 3 c), support the presence of rapidcreekite within the TMF (Dydo et al., 2003).

3.2.3. Identification of amorphous CaCO_3 , aragonite, thaumasite, and dolomite

Other carbonates have been identified within this study in addition to calcite and rapidcreekite, including amorphous calcium carbonate (ACC), aragonite, and, to a lesser extent, thaumasite and dolomite. Example LCF results showing the presence of each of these compounds are shown in Fig. 3 d), e), and f). The stabilization of ACC by ion impurities such as Mg^{2+} and PO_4^{3-} has been studied by Loste et al. and Kababya et al., respectively (Loste et al., 2003; Kababya et al., 2015). The presence of both ions in the TMF may explain the presence of ACC (see Table S3) ((AREVA) ARCL, 2015). Likewise, the formation of aragonite under near neutral conditions has been shown to be facilitated by the presence of dissolved SO_4^{2-} , Mg^{2+} , Mn^{2+} , and Fe^{2+} as these ions will increase the stability of aragonite (Berner, 1975; Walter and Gautier, 1985; Burton and Walter, 1990; Meyer, 1984). Furthermore, the presence of Sr^{2+} , Ba^{2+} , and Pb^{2+} can lower the stability of calcite (Berner, 1975; Walter and Gautier, 1985; Burton and Walter, 1990; Meyer, 1984). All ions listed above that facilitate the formation of aragonite and lower the stability of calcite have been detected within the TMF (see Table S1 and Table S3) ((AREVA) ARCL, 2015).

3.2.4. Implications of Ca-bearing carbonate results on the proposed model

Based on the model proposed by Orano (Equation (1)) and the low temperature and mobility of the tailings, it would be expected that a higher concentration of calcium carbonates would be found at lower depths of the TMF where the older tailings reside. Although no correlation between the presence of Ca-bearing carbonates and depth (i.e., time) was observed, the identification of several Ca-bearing carbonate minerals in the tailings (see Table S8) indicates that the model proposed by Orano in Equation (1) is plausible.

3.3. Identification of non-carbonate Ca-bearing minerals

In the process of investigating the presence of calcium carbonates within the tailings, several other Ca-bearing species were identified when fitting the Ca K-edge μ -XANES spectra from the tailings samples using the large library of standards used in this study, some of which are shown in Fig. 6. The majority of calcium is bound with sulfate because of the additions of sulfuric acid and lime (CaO) in the mill within the TMF ((AREVA) ARCL, 2015). The most common species containing both calcium and sulfate was gypsum; however, the presence of the other hydration states of calcium sulfate (bassanite ($\text{CaSO}_4\cdot 0.5\text{H}_2\text{O}$) and anhydrite (CaSO_4)) along with and glauberite ($\text{Na}_2\text{Ca}(\text{SO}_4)_2$) have also been identified by the LCF of the spectra from the tailings reported in this study. Examples of the fitted Ca K-edge μ -XANES spectra collected from tailings indicating the presence of the aforementioned calcium sulfate compounds are shown in Fig. 6. Co-mineralization of bassanite and anhydrite with gypsum has been well studied and the presence of these minerals within the gypsum-rich tailings is not surprising (Hardie, 1967).

In general, XRF maps collected from all tailings samples showed a correlation between the locations of Ca and S; however, a correlation

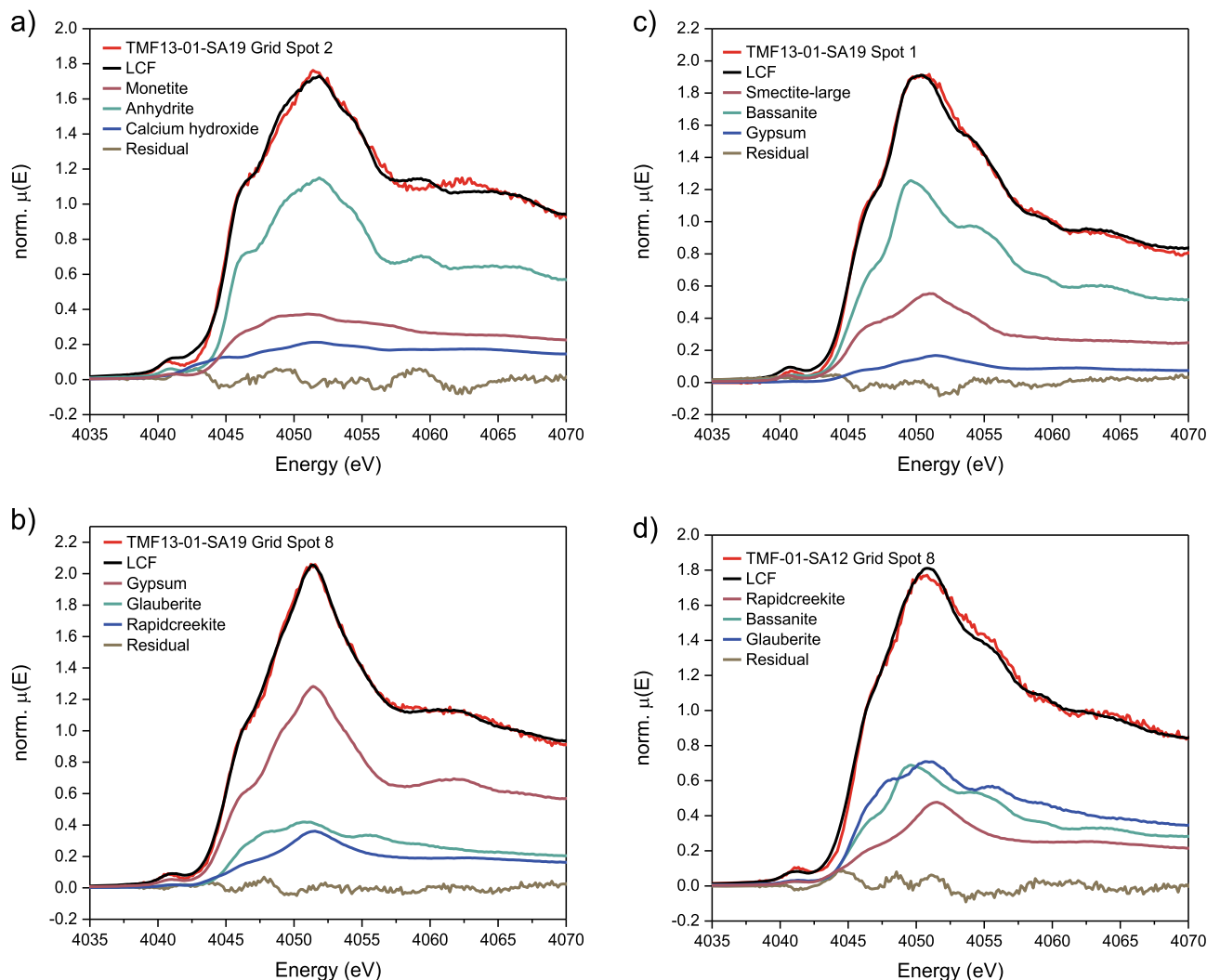


Fig. 6. The fitted Ca K-edge μ -XANES spectra from TMF13-01-SA19 (collected from a) spot 1, b) spot 8, and c) spot 10 in Fig. S8) and from TMF13-01-SA12 (collected from d) spot 8 in Fig. S4).

between the locations of Ca and P was also observed in a number of samples. A good example of this correlation between Ca and P can be observed in the XRF maps shown in Fig. 4 a), b), and e) where high concentrations of Ca, S, and P were observed near spot 2. Ca K-edge XANES spectra from standards containing Ca and P were collected to identify compounds containing both Ca and P in the tailings. As a result, whitlockite ($\text{Ca}_9(\text{Mg,Fe})(\text{PO}_4)_6(\text{PO}_3\text{OH})$), collinsite ($\text{Ca}_2(\text{Mg,Fe})(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$), calcium pyrophosphate ($\text{Ca}_2\text{P}_2\text{O}_7$), and monetite (CaHPO_4) were identified to be present by LCF of the spectra from the tailings (see Fig. S33).

Figure S33 also shows examples of LCF results that support the presence of Ca minerals that do not contain sulfate, carbonate, or phosphate. The LCF results shown in Fig. S33 support the presence of calcium hydroxide ($\text{Ca}(\text{OH})_2$), augite ($(\text{Ca,Na})(\text{Mg,Fe,Al})(\text{Al,Si})_2\text{O}_6$), and two types of montmorillonite ($(\text{Na,Ca})_{0.33}(\text{Al,Mg})_2(\text{Si}_4\text{O}_{10})(\text{OH})_2 \cdot n\text{H}_2\text{O}$), which is a clay, within the tailings. The two montmorillonite clays (referred to as montmorillonite 1 and 2) were observed to have significantly different Ca K-edge XANES spectral line shapes (see Fig. 1 b)). The reason for this difference may be due to the local chemical environment of Ca in the clay minerals, which can be altered by factors such as the number of water groups present in the compound (Hatch et al., 2012). An example of the effect that the addition or removal of water groups may have on the Ca K-edge XANES spectra can be observed when

comparing the Ca K-edge XANES spectra from gypsum, bassanite, and anhydrite (Fig. 1 a)). Finally, the previously identified Ca-containing compounds powellite (CaMoO_4), tremolite ($\text{Ca}_2(\text{Mg,Fe})_5\text{Si}_8\text{O}_{22}(\text{OH})_2$), and lime were also observed to be present in the tailings samples examined in the current study (see Fig. S33) (Blanchard et al., 2016).

Despite the large number of standards used within this study, there still remain some Ca K-edge μ -XANES spectra from the tailings that were unable to be fitted using the current library of standards (cf., Fig. S35). However, even without having spectra from all of the Ca-containing chemical species that contribute to each of these Ca K-edge μ -XANES spectra, the XRF maps are able to provide information on the possible elemental composition of these unidentified Ca-containing species. Fig. S35 shows select XRF maps from the samples where the spectra from the tailings shown in Fig. S34 were collected from. It can be observed from the spots marked as 10 and 9 on the XRF maps in Fig. S35 b) and c) that the spectra from the tailings shown in Fig. S34 a) and b) were collected from locations that possess high P or K concentrations, respectively. Similarly, the spectrum shown in Fig. S34 c) was collected from a location that contained high P, Si, and Al concentrations (See spot 1 on Fig. S35 e), f), and g)). Finally, it can be observed from the location marked as spot 10 on Fig. S35 i) and j) that the spectrum shown in Fig. S34 d) was collected from a location high in Si and Al. This ability to obtain elemental distribution information from XRF maps in tandem

with the μ -XANES spectra may be valuable when trying to ascertain the elements present within unknown species.

3.4. Use of multi-element XRF maps to validate μ -XANES LCF results

The information on the elemental distribution in the tailings provided by the XRF maps can be utilized to help verify LCF fits by screening for false positives in the LCF results. Three instances of false positives were identified using XRF maps within the LCF results reported in this study, the first of which was the identification of the arsenate-containing mineral yukonite ($\text{Ca}_7\text{Fe}_{12}(\text{AsO}_4)_{10}(\text{OH})_{20} \cdot 15\text{H}_2\text{O}$). XRF maps of a series of elements (shown in Fig. 7) were collected from the sample identified as TMF13-06-SA16, and various locations were selected for μ -XANES analysis based on the criteria described in Section 2.3. A Ca K-edge μ -XANES spectrum was collected from the location marked as 3 on Fig. 7 and an LCF of this spectrum was performed using the full library of standards. Shown in Fig. 8 a) and b) are the LCF results with and without yukonite as a standard. The LCF results shown in Fig. 8 a) and b) are almost identical with χ^2 values of 0.186 and 0.177 for the fits with (Fig. 8 a)) and without (Fig. 8 b)) yukonite, respectively. Although the goodness of fit values are similar, the Fe $\text{K}_{\alpha 1}$ XRF map shown in Fig. 7 f) indicates that only a low concentration of Fe was present at the location of spot 3. This low Fe concentration indicates that the LCF fit shown in Fig. 8 a) that contains the Fe rich yukonite species is unlikely to be valid. This determination is also in line with a recent study that reported an investigation of the chemistry of As throughout the TMF by examination of As K-edge XANES spectra with the reported spectra not supporting the presence of yukonite in the TMF (Blanchard et al.,

2017).

A second example of XRF mapping being used to verify LCF fits is with the U containing compound, uranophane ($\text{Ca}(\text{UO}_2)_2\text{SiO}_3(\text{OH})_2 \cdot 5\text{H}_2\text{O}$). Fig. 8 c) and d) shows a Ca K-edge μ -XANES spectrum collected from the spot marked as 3 on the XRF maps shown in Fig. 4. The LCF fits shown in Fig. 8 c) and d) both show the presence of calcite. The fit shown in Fig. 8 c) contains calcite, gypsum, and uranophane while the fit shown in Fig. 8 d) contains calcite, basanite, and rapidcreekite. Although both fits look similar, the fit shown in Fig. 8 c) had a χ^2 value of 0.0736 while the fit shown in Fig. 8 d) had a χ^2 value of 0.0772. The (slightly) lower χ^2 value would indicate that the fitting result shown in Fig. 8 c) is the more probable of the two fits shown in Fig. 8 in the absence of the elemental information provided by XRF maps. However, it can be observed from the U $\text{M}_{\alpha 1}$ XRF map shown in Fig. 4 c) that the location of spot 3 does not have U, thus making the uranophane containing LCF results shown in Fig. 8 c) improbable despite the slightly better goodness of fit.

It should be noted that the U $\text{M}_{\alpha 1}$ XRF map shown in Fig. 4 c) was only obtainable using an excitation energy of 4100 eV because of the deconvolution of the overlapping K $\text{K}_{\alpha 1}$ and U $\text{M}_{\alpha 1}$ fluorescence emissions, as described in Section 2.4. This can be seen in Fig. S36 by comparing the integrated counts over a fixed energy range characteristic of U $\text{M}_{\alpha 1}$ fluorescence emission and fitted XRF spectra from the TMF13-01-SA14 sample collected using an excitation energy of 4100 eV. Overlap of the K $\text{K}_{\alpha 1}$ and U $\text{M}_{\alpha 1}$ emissions results in a U distribution map that is reminiscent of the K distribution map (see Fig. S36). An example of the overlapping K $\text{K}_{\alpha 1}$ and U $\text{M}_{\alpha 1}$ emission signals can be seen in the emission spectrum shown in Fig. S37 a), while Fig. S37 b) shows an

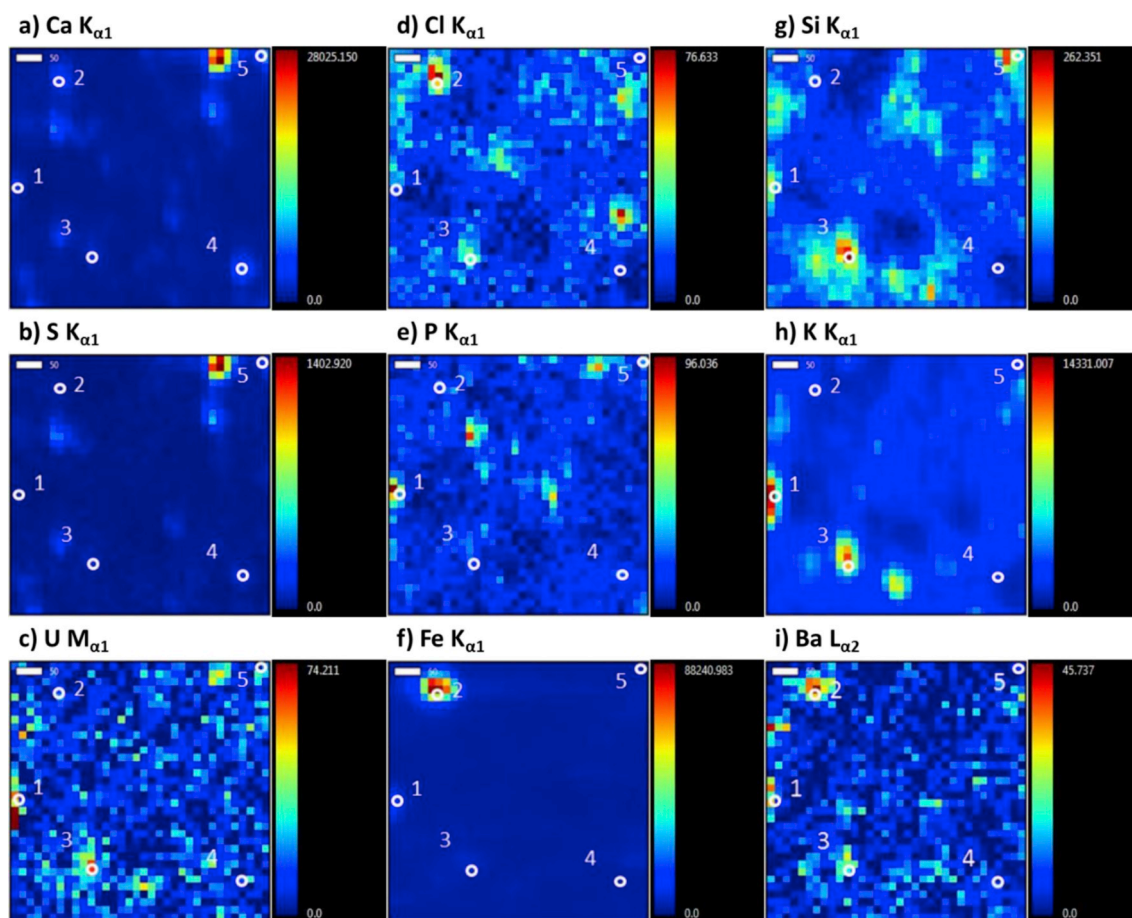


Fig. 7. XRF maps showing the distribution of Ca, S, U, Cl, P, Fe, Si, and K collected from tailings sample TMF13-06-SA16 in a) to h), respectively. The size of the maps was 500 $\mu\text{m} \times 500 \mu\text{m}$. The U map was obtained by deconvolution of the U $\text{M}_{\alpha 1}$ from the K $\text{K}_{\alpha 1}$ emission signal using the M-BLANK program as described in Section 3.4. Spots where Ca K-edge μ -XANES spectra were collected are marked on all XRF maps. All scale bars are 50 μm in length.

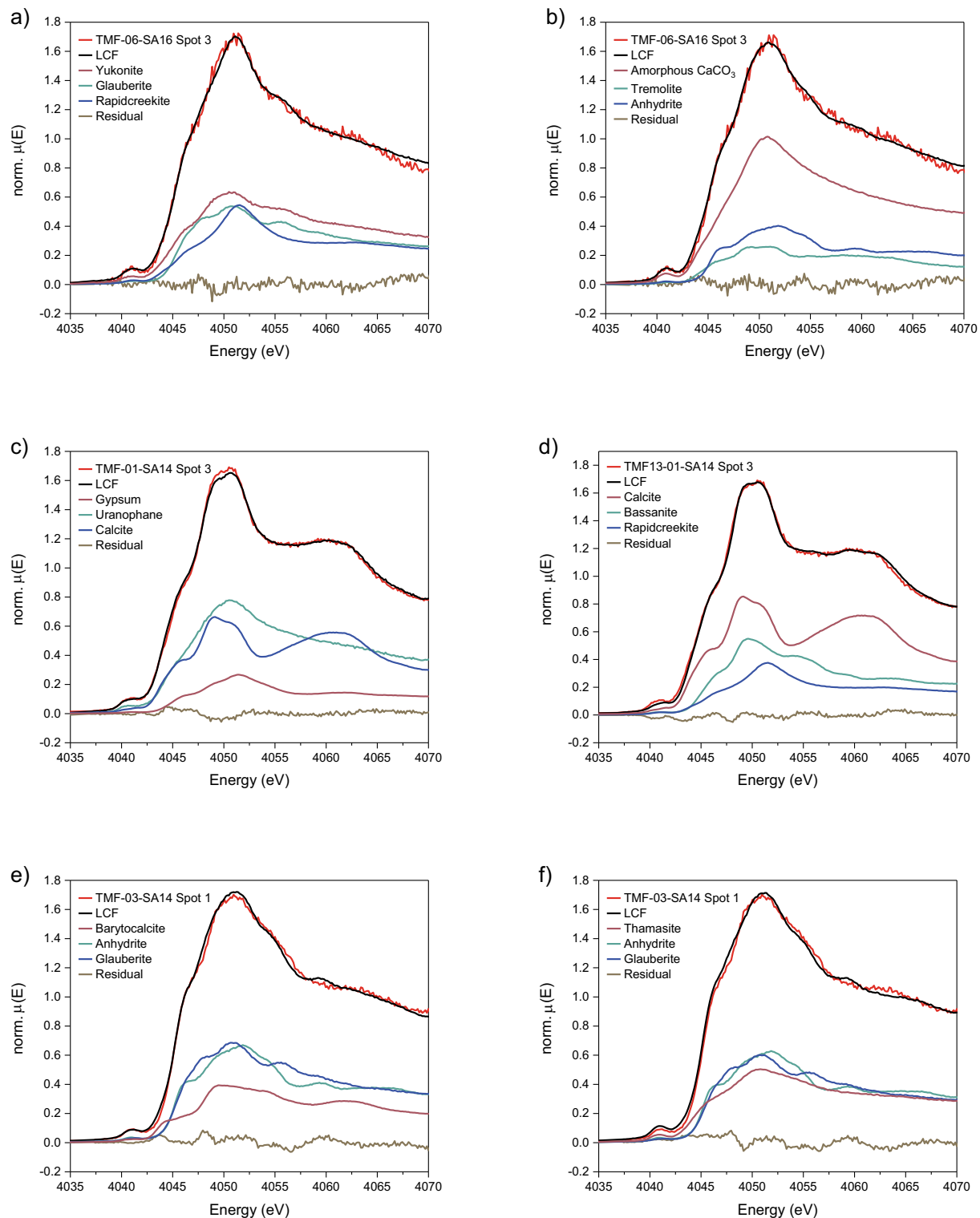


Fig. 8. The fitted Ca K-edge μ -XANES spectra from: TMF13-06-SA16 (collected from spot 3 in Fig. 7) a) with yukonite and b) without yukonite as an LCF standard; TMF13-01-SA14 (collected from spot 3 in Fig. 4) c) with uranophane and d) without uranophane as an LCF standard; and, TMF13-03-SA14 (collected from spot 1 in Fig. 9) e) with barytocalcite and f) without barytocalcite as an LCF standard.

emission spectrum obtained from a tailings sample containing a significantly lower U concentration and thus lacks a $U M_{\alpha 1}$ peak. It is possible to isolate the $U M_{\alpha 1}$ fluorescence signal if an excitation energy below the K absorption edge (e.g., 3570 eV) is used, an example of which is shown in Fig. S35 c) with the corresponding $U M_{\alpha 1}$ XRF map being shown in Fig. S36 c). The maximum $U M_{\alpha 1}$ fluorescence counts using an excitation

energy of 3570 eV from TMF13-01-SA14 was 556 while the maximum counts from TMF13-01-SA17 was 20. These maximum $U M_{\alpha 1}$ fluorescence counts were used to determine that TMF13-01-SA14 has a relatively high U concentration while TMF13-01-SA17 has a relatively low U concentration.

A final example of how LCF fits can be verified using XRF mapping

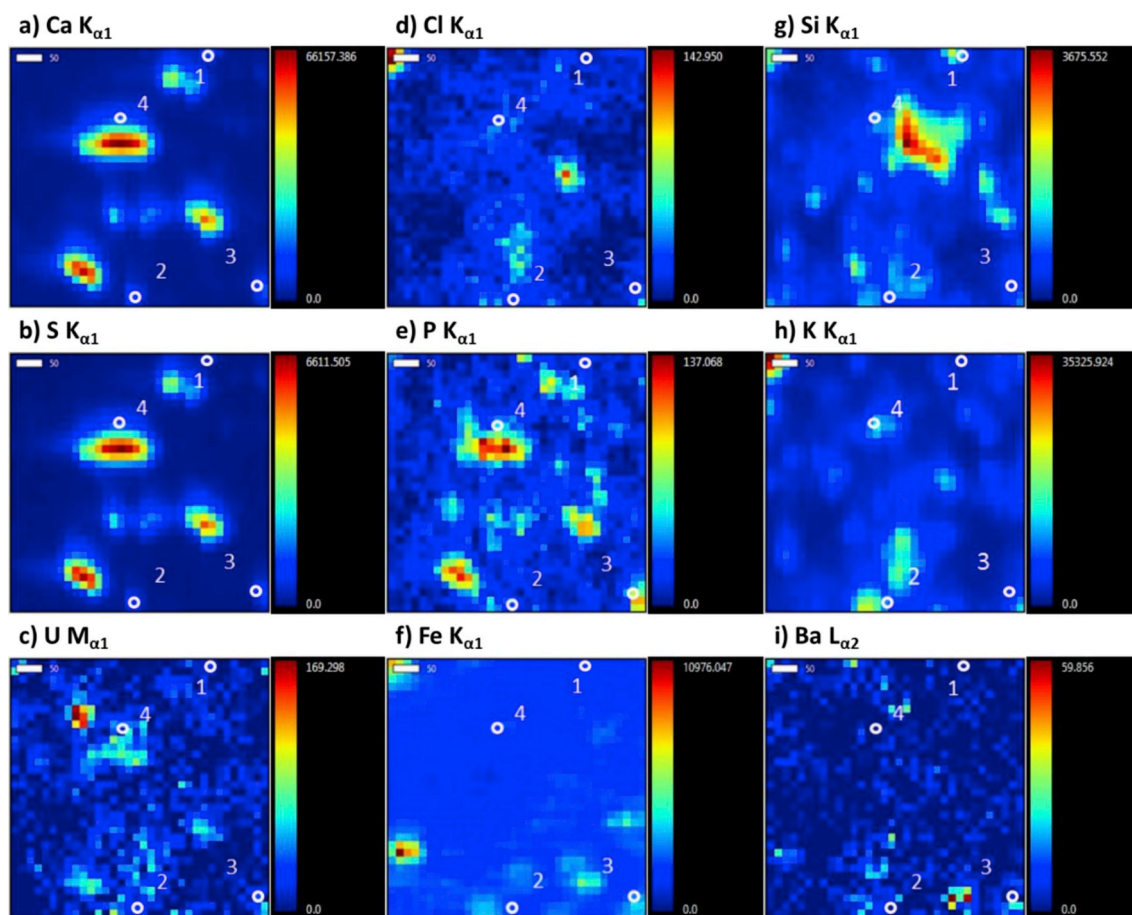


Fig. 9. XRF maps showing the distribution of Ca, S, U, Cl, P, Fe, Si, and Ba collected from tailings sample TMF13-03-SA14 in a) to h), respectively. The size of the maps was $500\ \mu\text{m} \times 500\ \mu\text{m}$. The U map was obtained by deconvolution of the $\text{U M}_{\alpha 1}$ from the $\text{K K}_{\alpha 1}$ emission signal using the M-BLANK program as described in Section 3.4. Spots where Ca K-edge μ -XANES spectra were collected are marked on all XRF maps. All scale bars are $50\ \mu\text{m}$ in length.

involves the Ba-containing compound, barytocalcite ($\text{BaCa}(\text{CO}_3)_2$). Ba is introduced to the tailings as BaCl_2 during the tailings preparation process as a way of controlling the Ra concentration within the tailings porewater ((AREVA) ARCL, 2015). A series of XRF maps collected from the TMF13-03-SA14 sample are shown in Fig. 9. A Ca K-edge μ -XANES spectrum collected from the spot marked as 1 on Fig. 9 that was fitted with and without barytocalcite as a standard is shown in Fig. 8 e) and f). The LCF fit containing barytocalcite (Fig. 8 e) was observed to have a lower χ^2 value (0.192) than the χ^2 value (0.217) for the LCF fit that did not include barytocalcite (Fig. 8 f)). Despite this, the $\text{Ba L}_{\alpha 2}$ XRF map (Fig. 9 i)) indicated that Ba was not present at the location of spot 1, making the LCF fit shown in Fig. 8 e) containing barytocalcite unlikely. These three examples of XRF maps being utilized to validate the LCF fitting of μ -XANES spectra highlights the advantages of pairing the elemental distribution information provided by XRF maps with the chemical speciation information obtained by LCF of μ -XANES spectra.

4. Conclusion

Presented in this study was a detailed investigation of the Ca-containing species within the U mill tailings extracted from various depths and boreholes within the tailings management facility (TMF) located at McClean Lake, Saskatchewan using a combination of multi-element XRF mapping and Ca K-edge μ -XANES. This study expands our knowledge of the Ca-bearing minerals present in the TMF, including the formation of rapidcreekite which contains both carbonate and sulfate ions. Special attention has also been paid to the identification of carbonate minerals in the TMF due to the predicted formation of these

minerals by the geochemical model presented in Equation (1). The identification of carbonate minerals is of particular interest as the precipitation of these minerals has been predicted to limit the bicarbonate concentration within the TMF, and by extension, the formation of soluble uranyl carbonates. It was shown in this study through comparison of porewater concentration data that calcite is only identified in tailings samples that contained bicarbonate concentrations that were significantly higher than the predicted bicarbonate equilibrium concentration of $168\ \text{mg/L}$ at which calcium carbonates would be expected to precipitate. Although no correlation was observed between the presence of Ca-bearing carbonates and depth (i.e., time), the model proposed in Equation (1) that would result in a reduction of the aqueous bicarbonate concentration in the TMF is plausible due to the identification of several Ca-bearing carbonate minerals in the tailings.

This study has improved upon the X-ray spectromicroscopy methodology that has been used previously for the identification of trace species within heterogeneous uranium mill tailings. These improvements have resulted from two distinct advancements. The first advancement is a fitting procedure that allows for a much larger library of XANES standards to be applied to each experimental μ -XANES spectra, thus allowing for μ -XANES spectra collected from the tailings to be screened against a larger set of species possibly present in the tailings. The second advancement is the collection of XRF maps of additional elements to help validate the μ -XANES fittings. This study provides further insight into the chemistry of Ca-bearing minerals in the TMF and demonstrates advancements to the spectromicroscopy method used to obtain this information. Ultimately, the application of this spectromicroscopy method in this and future studies is critical to obtaining a

better understanding of the chemistry within the TMF and, by extension, its impact on the surrounding environment. Moreover, the application of the spectromicroscopy methodology can be generalized to other geochemistry studies that utilize a combination of XRF mapping and μ -XANES.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.apgeochem.2019.104459>.

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Analysis of low concentration U species within U mill tailings using X-ray microprobe

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Abstract

Trace U species (i.e., ppm) found in the solid waste and effluent from uranium milling operations, known as tailings, is of scientific interest as tailings management facilities (TMFs) are designed to keep U species and other potentially harmful substances isolated from the surrounding environment. Use of X-ray microprobe to study U within solid tailings is challenging due to overlapping U $M_{\alpha 1}$, and K $K_{\alpha 1}$ X-ray fluorescence (XRF) signals. This problem of overlapping XRF signals is worsened due to the K concentration in the tailings being much higher than that of U. Reported herein is a methodology for using X-ray microprobe and the U $M_{\alpha 1}$ XRF signal to determine the distribution of U in samples of U mill tailings from the TMF located at McClean Lake, SK. The reported methodology utilizes an excitation energy just above the U M_5 -edge to avoid excitation of the K K -edge or an excitation energy higher than the K K -edge that requires the XRF spectra to be fitted to deconvolute the overlapping U $M_{\alpha 1}$ and K $K_{\alpha 1}$ XRF signals. Also discussed is the use of U M_5 -edge micro X-ray absorption near edge spectroscopy (μ -XANES) to both verify the U X-ray microprobe map collection methodology and to obtain chemical information on the U species present in the tailings.

Keywords: Uranium mining, Tailings, Geochemistry, Synchrotron radiation, X-ray absorption spectroscopy, X-ray microprobe

1. Introduction

Multiple physical and chemical processes are carried out in Orano Canada's U ore mill (McClean Lake, Saskatchewan) to extract the maximum amount of U from the processed ore so that it may be converted into yellowcake (U_3O_8) [1]. The residual uranium that remains in the ground-up rock and effluent (i.e., tailings) when they are deposited into the JEB Tailings management facility (herein referred to as the TMF) will be converted to uranyl ions (UO_2^{2+}) as a result of the TMF's oxidizing environment [1]. The mobility of these uranyl ions within the TMF is predicted to be primarily controlled by sorption and desorption from hydrated ferric oxide [1]. Although the majority of the U is predicted to be present within an insoluble form, the potential for small amounts to form soluble uranyl carbonate complexes has resulted in an interest in studying the chemistry of U within the tailings [1]. Multiple studies have been published on the chemistry of the tailings in the years since the TMF was commissioned, with a focus being placed on the chemistry of As, Ni, Mo, and Ca [2-9]. Conversely, little information is known about the U chemistry within the TMF. This is due to the very low concentration of U within the TMF. To date, the use of X-ray microprobe to identify the distribution of U within the tailings has yet to be attempted. The major barrier impeding such an investigation has been the overlapping U $M_{\alpha 1}$ (3170.8 eV) and K $K_{\alpha 1}$ (3313.8 eV) X-ray fluorescence (XRF) signals; an issue that is exasperated by the large concentration difference between U (~ 400 ppm on average) and K (~ 19,600 ppm on average) in the tailings.

One analysis technique that can take advantage of an U $M_{\alpha 1}$ X-ray microprobe map is micro X-ray absorption near edge spectroscopy (μ -XANES). XANES is an invaluable tool for studying the tailings as it is able to provide information on the chemistry of an element of interest from tailings containing many elements [2-9]. Of the recent studies on the chemistry of

the TMF, a subset have used an X-ray spectromicroscopy approach where a sample of the tailings is mapped using X-ray microprobe followed by collection of μ -XANES spectra [2, 3]. This approach has three distinct advantages over the collection of bulk XANES spectra. The first is the potential to collect high intensity μ -XANES spectra with high signal to noise ratios from specific locations containing the element of interest. The second is that the X-ray microprobe provides information on which elements are present at the location where a μ -XANES spectrum is collected from. The elemental information provided by X-ray microprobe maps can greatly aid in determining the speciation of the element being probed by μ -XANES [2, 3]. The third advantage to this approach is that it can allow for trace species of interest to be identified in heterogeneous samples. The objective of this study was to develop a methodology for determining the elemental distribution of U within the tailings using X-ray microprobe.

2. Experimental

2.1 Tailings sample description

Samples containing a mixture of solid tailings and porewater were extracted from boreholes that were drilled into the tailings in the TMF in 2013. The porewater was extracted from the solid tailings by hydraulic pressing followed by nitrogen-purging and vacuumed-sealing of the solid tailings. The three samples discussed herein are referred to as Samples A, B, and C. The concentrations of K and U in the solid tailings were measured using inductively coupled plasma-mass spectrometry (Agilent 7900, ICP-MS).

2.2 X-ray spectromicroscopy measurements

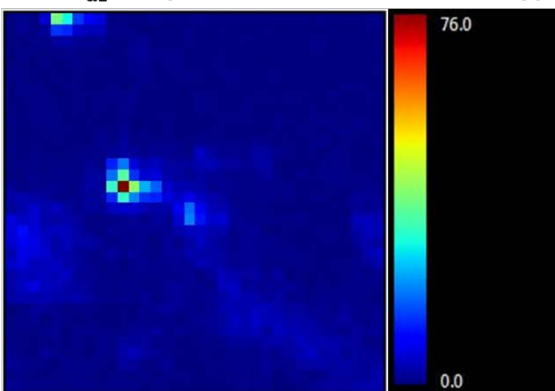
All X-ray microprobe and μ -XANES measurements were carried out using the Soft X-Ray Microcharacterization Beamline (SXRMB) located at the Canadian Light Source (CLS) and a Si (111) crystal monochromator [10]. X-ray microprobe maps and μ -XANES spectra were collected in partial fluorescence yield (PFY) mode using a Bruker fluorescence detector [10]. Solid tailings samples were held onto aluminum sample plates using double-sided carbon tape and covered by Kapton foil to prevent the release of the samples into the surrounding environment. Solid tailings samples were not ground prior to data collection in order to determine the association of elements in individual particles. A beam size of 10 μm was used to collect the X-ray microprobe maps and μ -XANES spectra.

Large area, low resolution (1000 μm x 2000 μm , 50 μm step size, 1s dwell time) U X-ray microprobe maps were collected from three tailings samples (labelled as Samples A, B, and C) using an excitation energy of 3570 eV (see Figures S1, S2, and S3). The purpose of using an excitation energy of 3570 eV was to collect U X-ray microprobe maps that did not contain overlapping U $M_{\alpha 1}$ and K $K_{\alpha 1}$ XRF signals, as this excitation energy lies between the U M_5 -absorption edge (3552 eV) and the K K-absorption edge (3608 eV). The large area U X-ray microprobe maps were used to identify areas containing high U XRF signals from which smaller but higher resolution X-ray microprobe maps (500 μm x 500 μm , 15 μm step size, 1 s dwell time) could be collected. High-resolution X-ray microprobe maps were collected using an excitation energy of 3570 eV or 8350 eV. An excitation energy of 3570 eV was used to collect S and Cl $K_{\alpha 1}$ maps as well as U $M_{\alpha 1}$ maps while an excitation energy of 8350 eV was used to collect S, Cl, and K $K_{\alpha 1}$ maps as well as U $M_{\alpha 1}$ maps. The U $M_{\alpha 1}$ X-ray microprobe maps were collected using excitation energies of 3570 eV and 8350 eV so that they could be compared

while the K $K_{\alpha 1}$ X-ray microprobe maps could only be collected using an excitation energy that was higher than the K K-absorption edge (3608 eV).

The locations from where the X-ray microprobe maps were collected shifted to a minor amount due to the movement of the X-ray beam on the monochromator when the excitation energy was changed from 3570 eV to 8350 eV. The Cl $K_{\alpha 1}$ X-ray microprobe maps collected using an excitation energy of 3570 eV and 8350 eV were compared in order to determine the extent of the shift, with an example of this comparison being shown in Figure 1 for Sample A. The spots on both X-ray microprobe maps in Figure 1 with the highest Cl $K_{\alpha 1}$ signal (colored in dark red) are considered to be in the same location. It can be observed from Figure 1 that the map collected using an excitation energy of 8350 eV (Figure 1 b)) is shifted down and to the right relative to the X-ray microprobe map collected using an excitation energy of 3570 eV (Figure 1 a)). The Cl $K_{\alpha 1}$ X-ray microprobe maps collected using excitation energies of 3570 eV and 8350 eV from Sample B can be found in Figure S4. The S $K_{\alpha 1}$ X-ray microprobe maps collected using excitation energies of 3570 eV and 8350 eV were used for Sample C to identify the shift in the position of the X-ray microprobe maps due to the low XRF signal from Cl (see Figure S5).

a) Cl $K_{\alpha 1}$ using 3570 eV an excitation energy



b) Cl $K_{\alpha 1}$ using 8350 eV an excitation energy

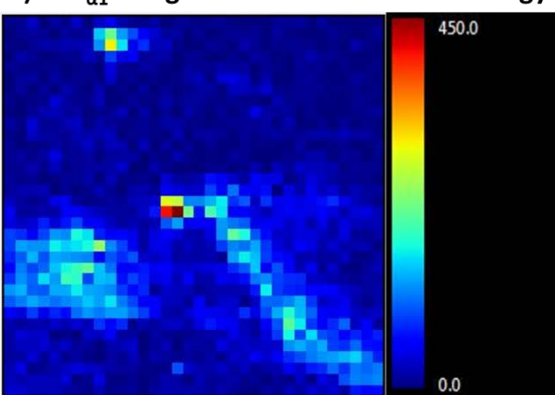


Figure 1. Cl X-ray microprobe maps collected from Sample A using an excitation energy of a) 3570 eV and b) 8350 eV. The dark red locations on both maps are considered to be the same location on the sample and demonstrate the shift in the position of the analysis area experienced when the excitation energy was changed.

U M_5 -edge μ -XANES spectra were collected using a 10 μm x 10 μm sized beam from locations on the X-ray microprobe maps containing different U XRF signal intensities. All U M_5 -edge XANES spectra were collected using a dwell time of 1 second and a step size of 0.15 eV through the absorption edge. A Ag L_{III} -edge (3351 eV) XANES spectrum was collected from Ag metal to calibrate the U M_5 -edge XANES spectra. The maximum of the first derivative of the Ag L_{III} -edge XANES spectrum was set to 3351 eV [11].

U M_5 -edge XANES spectra collected in PFY mode will possess some degree of absorption effects. Transmission and PFY U M_5 -edge XANES spectra were collected from a sample of yellowcake (U_3O_8 ; Orano Canada) in order to determine the extent to which the U M_5 -

edge XANES spectra were affected by absorption effects. Spectra were collected using the ambient end station attached to SXRMB. The sample and ionization chambers were filled with He gas during data collection. The sample was finely ground powder spread between two pieces of Kapton tape.

2.3 Data analysis

Sam's Microprobe Analysis Kit (SMAK) was used to analyze all X-ray microprobe maps [12]. The X-ray microprobe fitting program M-BLANK was used to fit the XRF spectra collected at each pixel to deconvolute overlapping XRF signals (i.e., K $K_{\alpha 1}$ and U $M_{\alpha 1}$) [13]. M-BLANK fits XRF spectra from each pixel of an X-ray microprobe map using a series of modified Gaussians representing the various XRF signals and a linear least-squares method. M-BLANK also incorporates terms representing contributions from Compton and Raleigh scattering as well as the XRF background signal [13]. A detailed comparison of X-ray microprobe maps generated after fitting the XRF spectra vs. X-ray microprobe maps generated simply by integration of the XRF spectra over an energy range associated with each elemental XRF signal is presented in Section 3.1.

The Athena software program was used to analyze all XANES spectra [14]. The U M_5 -edge μ -XANES spectra from the tailing were fitted using a linear combination fitting (LCF) method and U M_5 -edge XANES spectra collected from U mineral standards. LCF analysis was performed using an energy range of -10 to +20 eV relative to the U M_5 -edge energy (3552 eV) and the best fit was determined by analysis of χ^2 values [11]. U mineral standards used in this study were procured from the Smithsonian Museum, Orano Canada, and the University of Alberta. A list of the U mineral standards used in this study is presented in Table 1.

Table 1. List of U containing mineral standards from which U M₅-edge XANES spectra were collected and used in LCF of U M₅-edge μ -XANES spectra collected from tailings. Samples obtained from the Smithsonian have associated sample numbers indicated.

Standard name	Composition
Liebigite (R16951 00)	$\text{Ca}_2(\text{CO}_3)_3 \cdot 11\text{H}_2\text{O}$
Uranophane (120748 00)	$\text{Ca}(\text{UO}_2)_2(\text{SiO}_3\text{OH})_2 \cdot 5\text{H}_2\text{O}$
Yellowcake	U_3O_8
Autunite	$\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 10\text{--}12\text{H}_2\text{O}$
Coffinite (141110 00)	$\text{U}(\text{SiO}_4)_{1-x}(\text{OH})_{4x}$
Rutherfordine (B10751 00)	UO_2CO_3
Wyartite (150757 00)	$\text{CaU}(\text{UO}_2)_2(\text{CO}_3)\text{O}_4(\text{OH}) \cdot 7\text{H}_2\text{O}$

3. Results and Discussion

3.1 Use of X-ray microprobe for mapping the U distribution in the tailings

The concentration of U within the tailings is very low (~400 ppm on average) when compared to K (~19,600 ppm on average). This large difference in concentration presents a problem when studying the U distribution in the tailings using X-ray microprobe as the U M _{α 1} (3170.8 eV) and K K _{α 1} (3313.8 eV) XRF signals overlap. The overlapping XRF signals result in the U M _{α 1} peak appearing as a weak shoulder on the low-energy side of the K K _{α 1} peak, as can be seen in Figure 2 b). The consequence of the proximity of these two XRF signals is that the distribution of U is not able to be reliably mapped using X-ray microprobe when the XRF spectra are integrated across the U M _{α 1} energy range and an excitation energy that is higher than the K K-edge absorption energy (3608 eV) is used [11].

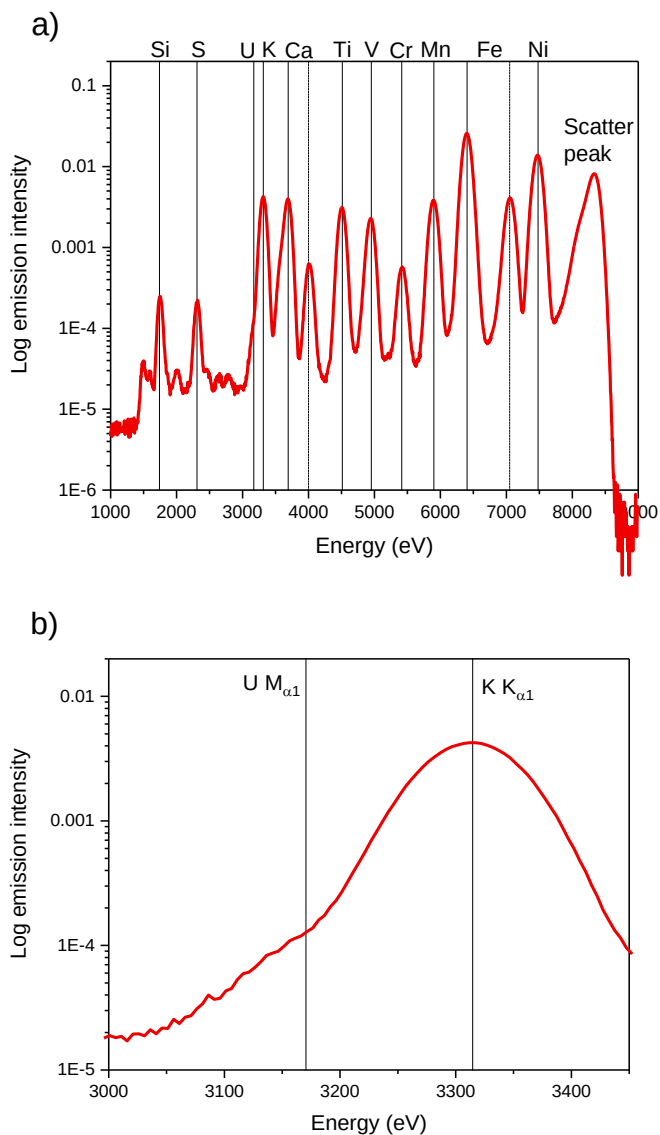


Figure 2. Averaged XRF spectrum collected using an excitation energy of 8350 eV from Sample A with all major emissions labeled. a) shows the averaged XRF spectrum over the entire collected energy range. The energy range over which the XRF spectra was integrated is $\pm \sim 78$ eV relative to all emissions labelled with solid lines. b) shows the averaged XRF spectrum over the energy range associated with the U $M_{\alpha 1}$ and K $K_{\alpha 1}$ XRF signals.

3.1.1 Use of an excitation energy above the K K-absorption edge

The U $M_{\alpha 1}$ and K $K_{\alpha 1}$ signals in the XRF spectra collected from Sample A were deconvoluted by fitting the spectra when an excitation energy above the K K-absorption edge was used (e.g., 8350 eV), as described in Section 2.3. A XRF spectrum that was collected using

an excitation energy of 8350 eV and then fitted to deconvolute the overlapping U and K XRF signals is shown in Figure 3 a). The K and U X-ray microprobe maps that were collected using an excitation energy of 8350 eV and generated by either integrating the XRF signal over a fixed energy range or fitting the XRF spectra are shown in Figure 4 a) to d). As can be seen from Figure 4 a) and c), simply integrating the XRF spectra over a fixed energy range produces K and U X-ray microprobe maps that are nearly identical to each other. This is due to the overlapping nature of the XRF signals as well as the much higher intensity of the K $K_{\alpha 1}$ signal compared to the U $M_{\alpha 1}$ signal. In contrast to this, the K and U X-ray microprobe maps collected using an excitation energy of 8350 eV and produced after fitting the XRF spectra (Figure 4 b) and d), respectively) share far less resemblance to each other. However, there is very little change in the K X-ray microprobe map produced by fitting the XRF spectra compared to the K X-ray microprobe map produced by the integration of the XRF spectra over a fixed energy range (cf. Figure 4 a) and b)). This lack of change between K X-ray microprobe maps is a result of the U $M_{\alpha 1}$ signal being far weaker than the K $K_{\alpha 1}$ signal due to the significantly higher K concentration.

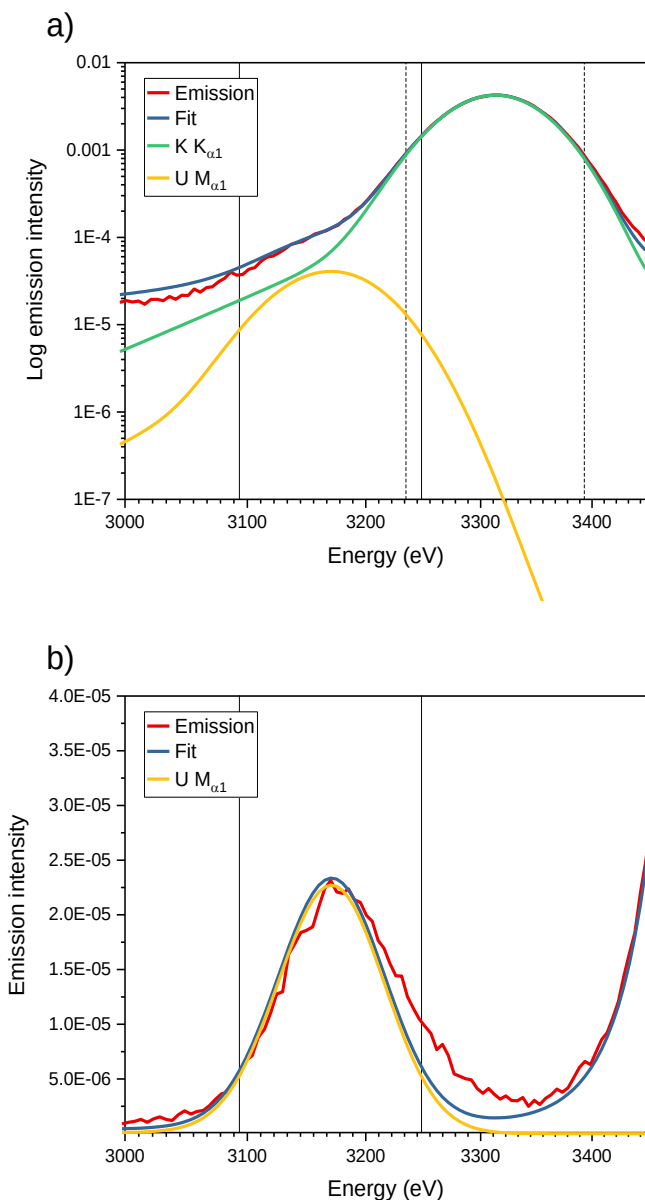


Figure 3. K $K_{\alpha 1}$ and U $M_{\alpha 1}$ XRF spectra showing the fixed energy range used in integration and the modified Gaussians fitted to the XRF spectra to deconvolute the K $K_{\alpha 1}$ and U $M_{\alpha 1}$ XRF signals. a) averaged XRF spectrum collected using an excitation energy of 8350 eV from Sample A (corresponding with the X-ray microprobe maps shown in Figure 4 a) to d)). b) averaged XRF spectrum collected using an excitation energy of 3570 eV from Sample A (corresponding with the X-ray microprobe maps shown in Figure 4 e) and f)). In all cases, the solid lines correspond with the fixed energy range used in the integration of U $M_{\alpha 1}$ peak, while the dashed lines correspond with the fixed energy range used in the integration of K $K_{\alpha 1}$ peak.

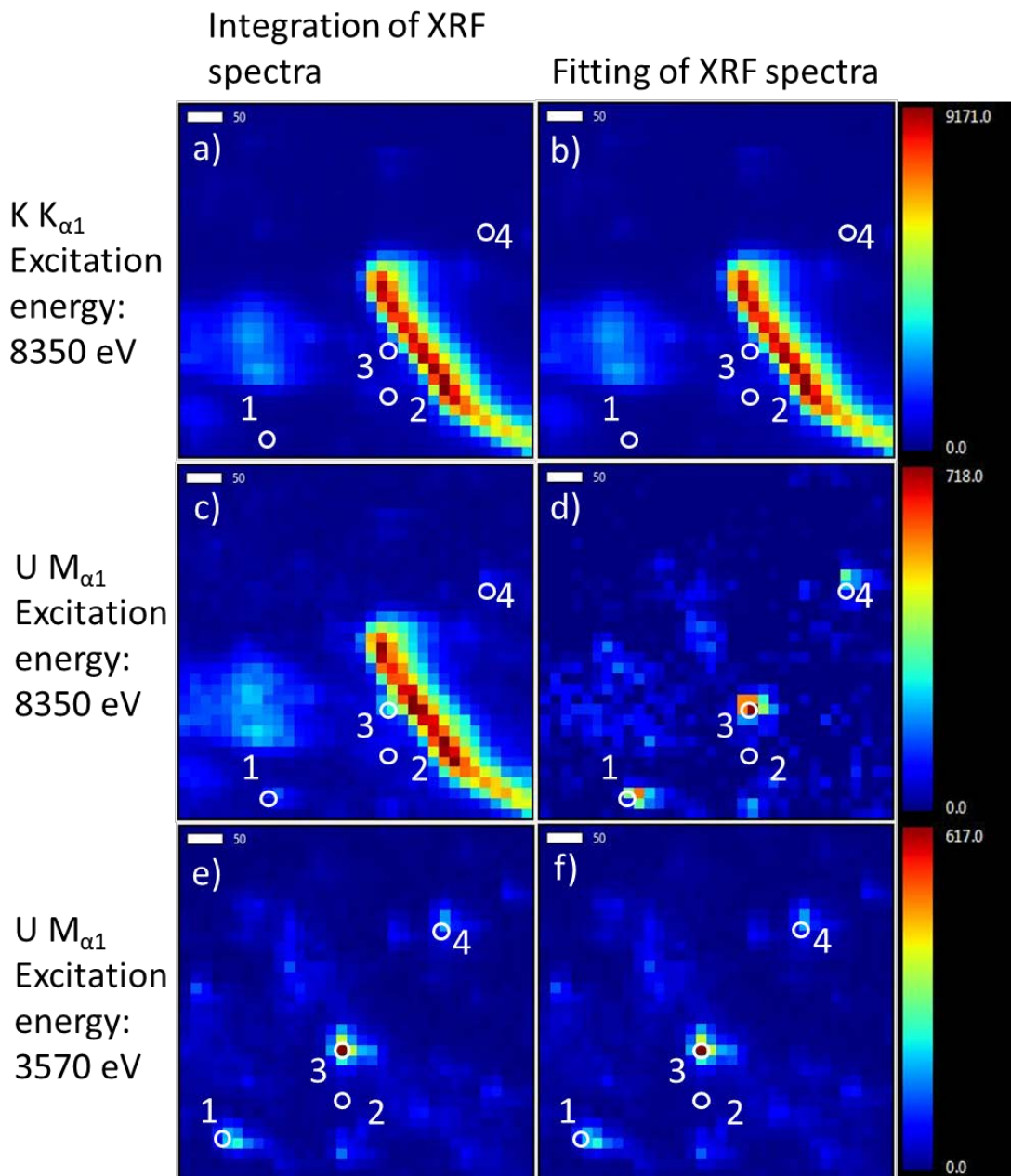


Figure 4. K $K_{\alpha 1}$ X-ray microprobe maps collected from Sample A using an excitation energy of 8350 eV with a) integrated counts over a fixed energy range and b) fitted to deconvolute the XRF spectra. U $M_{\alpha 1}$ X-ray microprobe maps collected from Sample A using an excitation energy of 8350 eV with c) integrated counts over a fixed energy range and d) fitted to deconvolute the XRF spectra. U $M_{\alpha 1}$ X-ray microprobe maps collected from Sample A using an excitation energy of 3570 eV with e) integrated counts over a fixed energy range and f) fitted to deconvolute the XRF spectra. Spots where U M_5 -edge μ -XANES spectra were collected are marked on all X-ray microprobe maps.

3.1.2 Use of an excitation energy between the U M_{5-} and the K K -absorption edges

The use of an excitation energy of 3570 eV which lies between the U M_{5-} -edge (3552 eV) and the K K -edge (3608 eV) produces an XRF spectrum from Sample A that has a U $M_{\alpha 1}$ peak but no K $K_{\alpha 1}$ peak, as can be seen in Figure 3 b) [11]. The resulting X-ray microprobe maps produced from Figure 3 b) by integration of the XRF spectra over a fixed energy range or after fitting the XRF spectra are shown in Figure 4 e) and f), respectively. The U X-ray microprobe maps produced using an excitation energy of 3570 eV are nearly identical to each other (see Figure 4 e) and f)) due to the lack of the K $K_{\alpha 1}$ signal in the XRF spectra.

3.1.3 Comparison between the use of an excitation energy of 3570 eV and 8350 eV

A second set of U and K X-ray microprobe maps were collected from Sample B to further understand how detailed U X-ray microprobe maps can be collected without interference from the K XRF signal. The X-ray microprobe maps are presented in Figure 5 and were collected using excitation energies of 8350 eV and 3570 eV and generated either by integrating the XRF signal over a fixed energy range or fitting the XRF spectra. An important difference between Sample A and Sample B was that the U $M_{\alpha 1}$ XRF signals observed in the spectra from Sample B are significantly lower than was observed for Sample A. The maximum intensity of the U $M_{\alpha 1}$ signal collected from Sample B using an excitation energy of 3570 eV was >5 times lower than that for Sample A (Sample B: 122 counts vs. Sample A: 617 counts). The effect of the relatively lower concentration of U in Sample B is that deconvolution of the U $M_{\alpha 1}$ and K $K_{\alpha 1}$ XRF signals by fitting the XRF spectra is far more challenging. The U X-ray microprobe map collected from Sample B using an excitation energy of 8350 eV and generated by fitting the XRF spectra (Figure 5 d)) possess a strong XRF signal near the center of the map marked by the white oval. Similarly, this strong XRF signal within the white oval is also present in the K X-ray microprobe

maps (Figure 5 a) and b)). In contrast, the U X-ray microprobe map collected from Sample B using an excitation energy of 3570 possesses almost no XRF signal within the white oval (Figure 5 e) and f)). This indicates that the XRF signal originating from within the white oval of the U X-ray microprobe map collected using an excitation energy of 8350 eV (Figure 5 c) and d)) is primarily a result of the K XRF signal that was not deconvoluted from the U XRF signal even when the XRF spectra were fitted (Figure 5 d)).

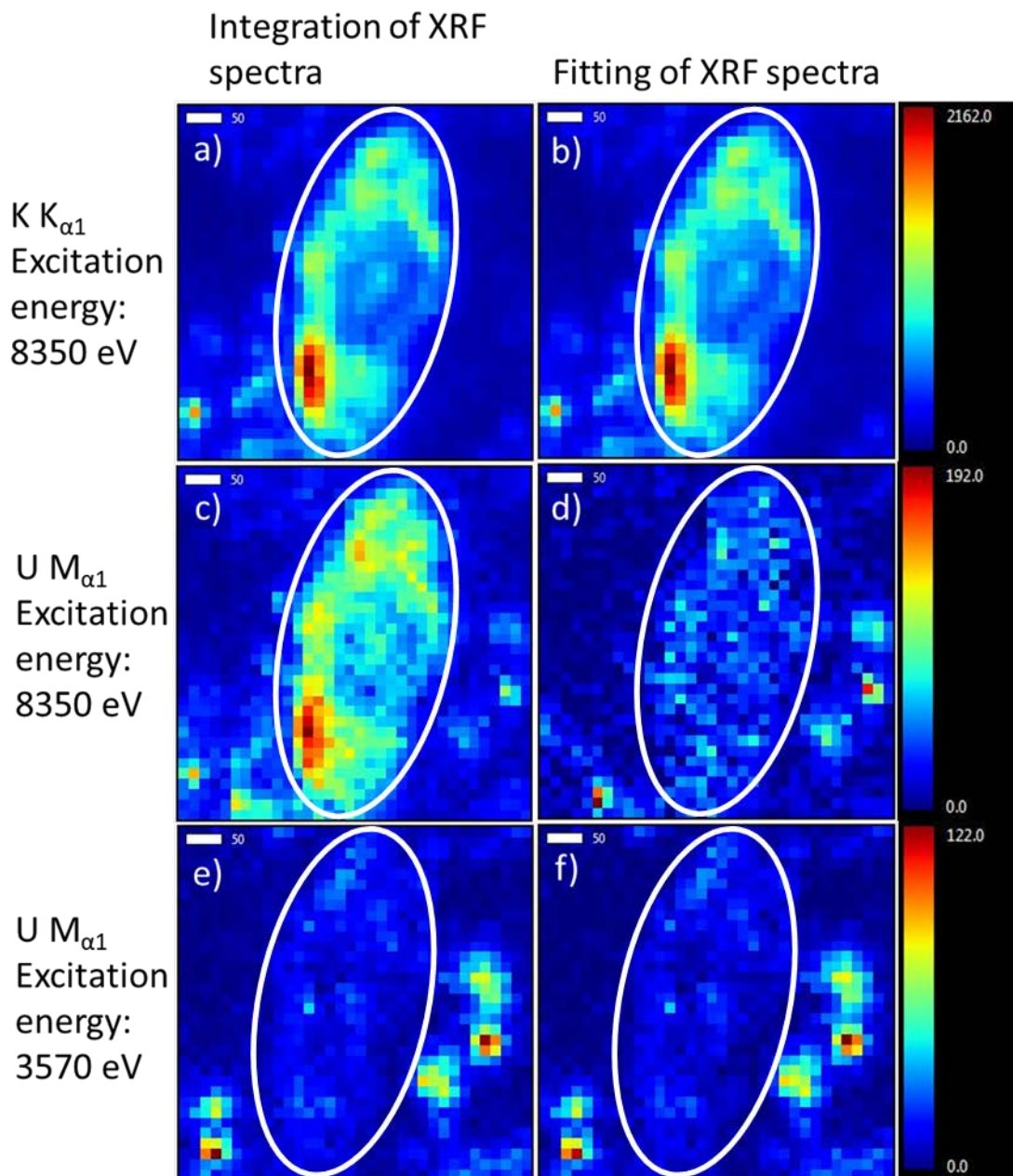


Figure 5. K $K_{\alpha 1}$ X-ray microprobe maps collected from Sample B using an excitation energy of 8350 eV with a) integrated counts over a fixed energy range and b) fitted to deconvolute the XRF spectra. U $M_{\alpha 1}$ X-ray microprobe maps collected from Sample B using an excitation energy of 8350 eV with c) integrated counts over a fixed energy range and d) fitted to deconvolute the XRF spectra. U $M_{\alpha 1}$ X-ray microprobe maps collected from Sample A using an excitation energy of 3570 eV with e) integrated counts over a fixed energy range and f) fitted to deconvolute the XRF spectra. The area on all X-ray microprobe maps where the XRF signal is primarily coming from K $K_{\alpha 1}$ has been marked with a white circle.

Figure 4 and Figure 5 show that the use of an excitation energy of 3570 eV is the most accurate way of determining the distribution of U in a tailings sample by analysis of the U $M_{\alpha 1}$ XRF signal when K is also present. Using an excitation energy of 3570 eV is particularly advantageous for samples with lower concentrations of U and higher concentrations of K, as was the case for Sample B (see Figure 5). However, the analysis of X-ray microprobe maps collected using a higher excitation energy (e.g., 8350 eV) and generated by fitting the XRF spectra may have advantages over maps collected using lower excitation energies. This is because a single excitation energy above the absorption edges of all elements of interest can be used to collect X-ray microprobe maps, which avoids the need to collect XRF maps using different excitation energies.

3.2 Comparison of X-ray microprobe maps and U M_5 -edge μ -XANES spectra

U M_5 -edge μ -XANES spectra were collected to compare the intensities of these spectra to the corresponding U $M_{\alpha 1}$ XRF signals from the locations of the X-ray microprobe map where the XANES spectra were collected. U $M_{4,5}$ -edge XANES spectra correspond to a transition of core 3d electrons to unoccupied 5f states [15]. X-ray microprobe maps of the K and U distributions were collected from Sample A using excitation energies of either 8350 eV or 3570 eV and are shown in Figure 4. The U M_5 -edge μ -XANES spectra were collected from the locations marked on the X-ray microprobe maps shown in Figure 4. It should be noted that U M_4 -edge μ -XANES spectra were not collected due to the high-intensity K K-edge (3608 eV) lying just below the absorption energy of the U M_4 -edge (3728 eV) [11].

Normalized and unnormalized U M_5 -edge μ -XANES spectra collected from the locations indicated on Figure 4 are shown in Figure 6 a) and b), respectively. Comparing the intensities of the unnormalized U M_5 -edge μ -XANES spectra to the XRF signal intensities from the locations

on the microprobe map from where each U M₅-edge μ -XANES spectrum was collected can be used to validate the X-ray microprobe methodology presented in Section 3.1. Figure 6 c) shows a plot of the intensity of each U M₅-edge μ -XANES spectrum collected from Sample A vs. the U M _{α 1} XRF signal collected using an excitation energy of 3570 eV and generated by integrating the XRF spectrum over a fixed energy range. The positive linear relationship observed in Figure 6 c) demonstrates the validity of using an excitation energy of 3570 eV when mapping the U distribution as it shows that the XRF signal corresponds with the relative U concentration measured by the U M₅-edge μ -XANES spectra.

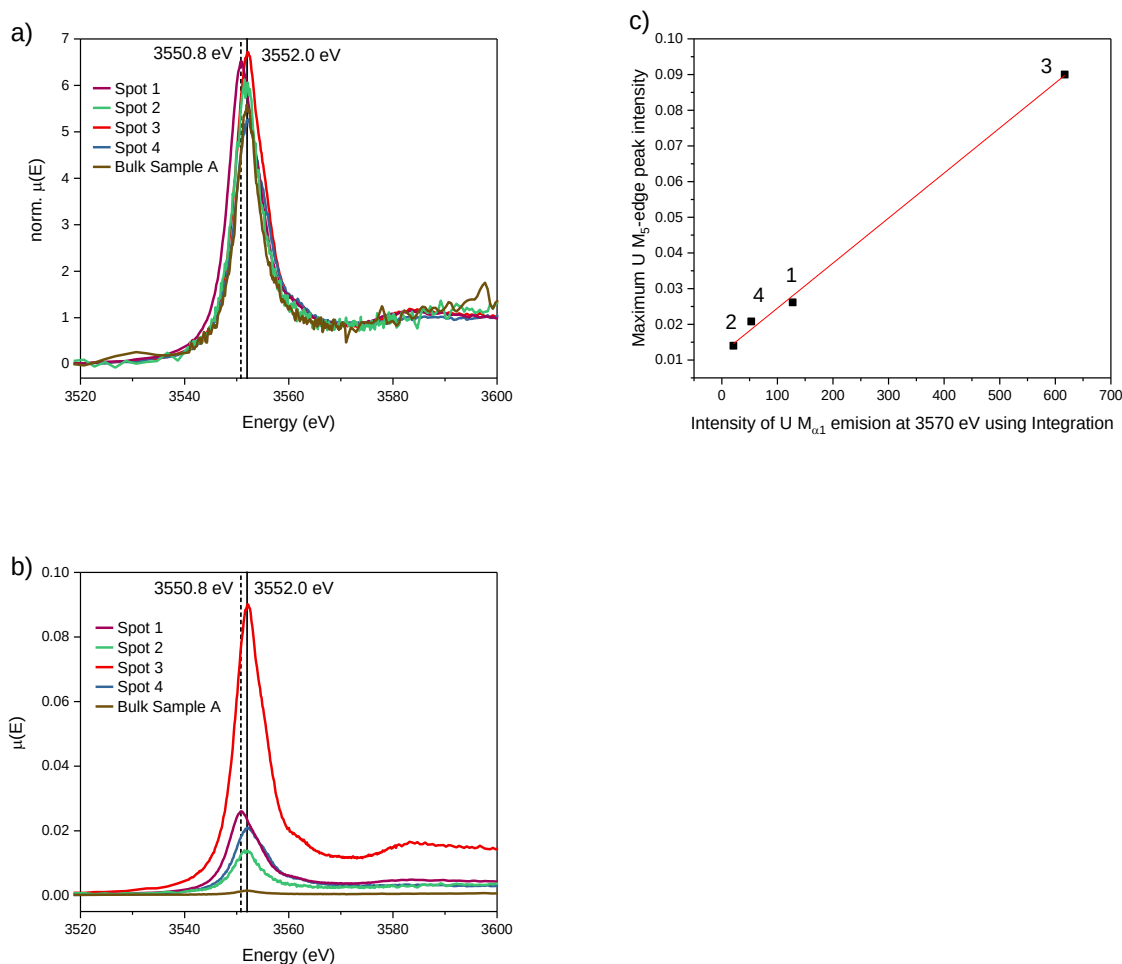


Figure 6. The U M_5 -edge XANES spectrum collected from ground up Sample A and U M_5 -edge μ -XANES spectra collected from Sample A at spots marked 1 to 4 on Figure 4 that are a) normalized and b) unnormalized. c) maximum peak height of unnormalized U M_5 -edge μ -XANES spectra collected from Sample A plotted vs. the U $M_{\alpha 1}$ signal collected using an excitation energy of 3570 eV when the XRF spectra were integrated over a fixed energy range (Figure 4 e)) at each point where a U M_5 -edge μ -XANES spectra was collected.

The primary reason for collecting μ -XANES spectra from locations on the X-ray microprobe maps that were observed to contain high U XRF signals rather than collecting XANES spectra using a larger X-ray beam size was to collect U M_5 -edge XANES spectra that have a high intensity and signal to noise ratio considering the low concentration of U within the tailings. For example, the U within the tailings has an average concentration of 405 ppm and the U M_5 -edge XANES spectrum collected from Sample A after being homogenized and using a

large X-ray beam size ($\sim 1 \text{ cm}^2$) has a very low intensity and signal to noise ratio (cf., Figure 6 b)). In contrast, a U M₅-edge μ -XANES spectrum collected from a grain of Sample A that was identified to have a high U concentration by U X-ray microprobe possessed a high signal intensity as well as a high signal to noise ratio (cf., Figure 6 b)).

Figure 7 shows plots of the intensity of each U M₅-edge μ -XANES spectrum collected from Sample A vs. the U XRF signal intensity from the locations on the X-ray microprobe maps where the spectra were collected. Figure 7 a) and b) plots the U XRF signal intensities from the X-ray microprobe maps that were collected using an excitation energy of 8350 eV and generated by integration of the XRF signal over a fixed energy range or by fitting the XRF spectra. Additionally, Figure 7 c) plots the intensity of each U M₅-edge μ -XANES spectrum collected from Sample A vs. the U XRF signal intensities from the X-ray microprobe map that was collected using an excitation energy of 3570 eV and generated by fitting the XRF spectra. As can be observed from Figure 7 c), a positive linear trend exists between the intensity of each U M₅-edge μ -XANES spectrum and the U XRF signal collected using an excitation energy of 3570 eV when the XRF spectra were fitted. This is in line with the observation that the U X-ray microprobe maps collected using an excitation energy of 3570 eV appear identical regardless of whether the XRF spectra are integrated over a fixed energy range or fitted (see Figure 4 e) and f)). Conversely, when the U XRF spectra are collected using an excitation energy of 8350 eV and fitted to form a microprobe map, it was observed that the resulting plot no longer possessed a linear trend (see Figure 7 b)). This observation is in line with the discussion of Sample B (see Section 3.1.3) where it was clear that fitting of the XRF spectra was only able to give an approximation of the U distribution within a sample if an excitation energy higher than the K K-edge was used (see Figure 5 d)).

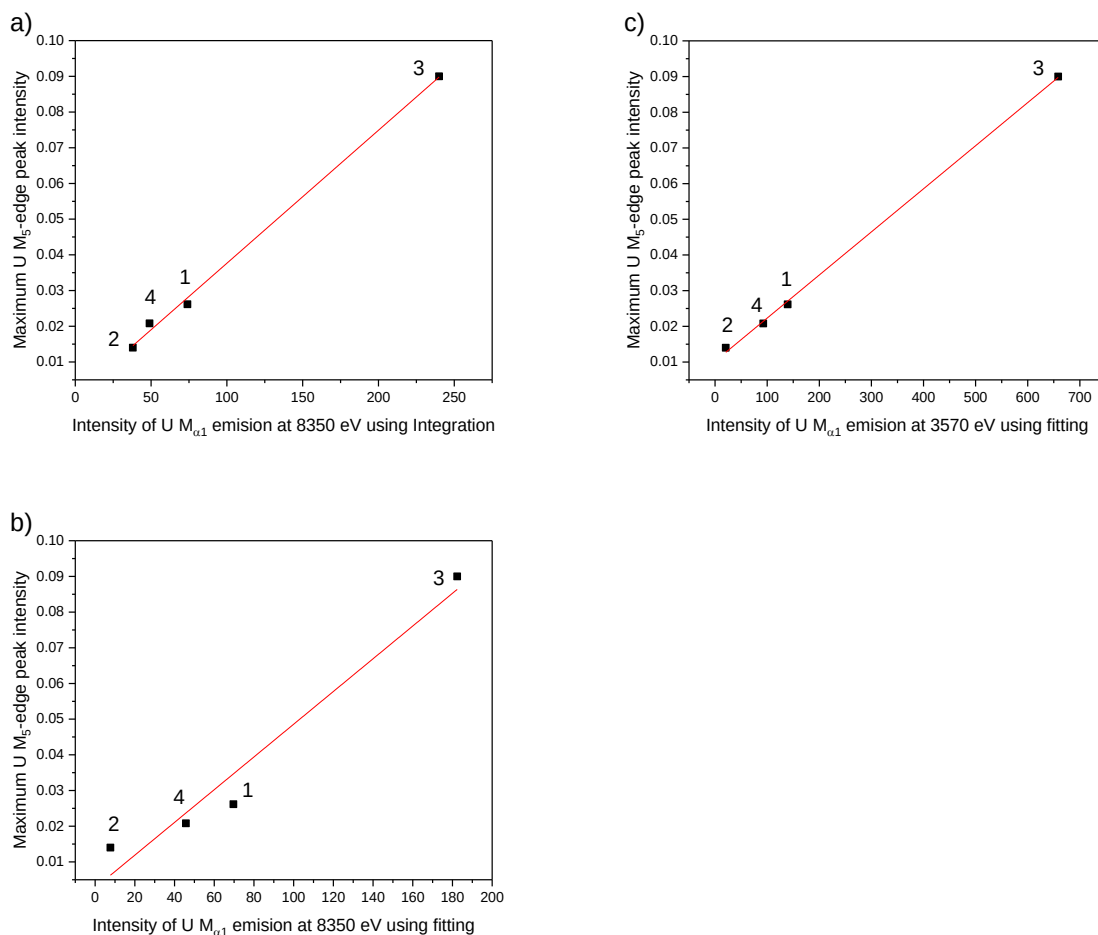


Figure 7. Maximum peak height of unnormalized U M₅-edge μ -XANES spectra collected from Sample A plotted vs. the U M_{α1} signal collected using a) an excitation energy of 8350 eV when the XRF spectra were integrated over a fixed energy range (Figure 4 c)), b) an excitation energy of 8350 eV when the XRF spectra were fitted (Figure 4 d)), and c) an excitation energy of 3570 eV when the XRF spectra were fitted (Figure 4 f)), at each point where a U M₅-edge μ -XANES spectra was collected, respectively.

U and K X-ray microprobe maps were collected from a third sample (Sample C) in order to demonstrate the unreliability of U X-ray microprobe maps collected using an excitation energy of 8350 eV and generated by integrating the XRF signal over a fixed energy range and are shown in Figure 8. Two locations appearing to contain relatively high U XRF signals were observed near the center of the U X-ray microprobe map collected using an excitation energy of 8350 eV (Figure 8 c)). U M₅-edge μ -XANES spectra were collected from these two locations (spots 1 and 2 on Figure 8) and are shown in Figure 9. The U X-ray microprobe map from

Sample C collected using an excitation energy of 8350 eV and generated by integration of the XRF signal over a fixed energy range (Figure 8 c)) indicates that the U $M_{\alpha 1}$ XRF signal intensities at spots 1 and 2 are similar; however, the U M_5 -edge μ -XANES spectra collected from these locations (Figure 9) clearly indicate that the U concentration is higher at spot 1 compared to spot 2. This discrepancy can be rectified when analysing the X-ray microprobe maps collected using an excitation energy of 3570 eV (Figure 8d and 8e). These maps clearly indicate that the U concentration at spot 1 is higher than the U concentration at spot 2, which agrees with the M_5 -edge μ -XANES spectra (Figure 9). The comparison between the X-ray microprobe maps shown in Figure 8 and the U M_5 -edge μ -XANES spectra shown in Figure 9 clearly shows the drawbacks of using an excitation energy higher than the K K-edge when the XRF signal is integrated over a fixed energy range to generate a U X-ray microprobe map (i.e., lack of correlation between XRF signal and U M_5 -edge μ -XANES intensity).

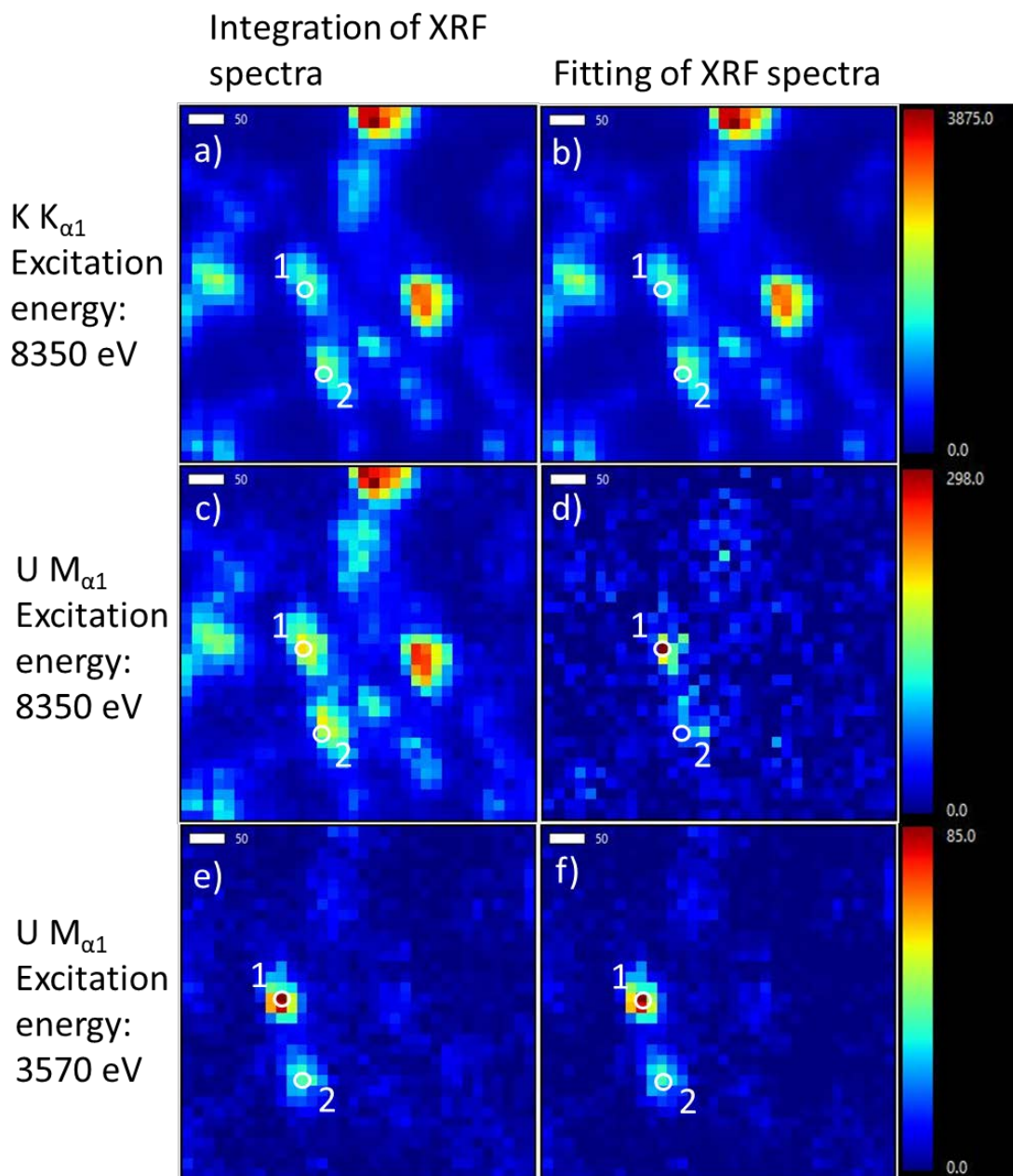


Figure 8. K $K_{\alpha 1}$ X-ray microprobe maps collected from Sample C using an excitation energy of 8350 eV with a) integrated counts over a fixed energy range and b) fitted to deconvolute the XRF spectra. U $M_{\alpha 1}$ X-ray microprobe maps collected from Sample C using an excitation energy of 8350 eV with c) integrated counts over a fixed energy range and d) fitted to deconvolute the XRF spectra. U $M_{\alpha 1}$ X-ray microprobe maps collected from Sample C using an excitation energy of 3570 eV with e) integrated counts over a fixed energy range and f) fitted to deconvolute the XRF spectra. Spots, where U M_{5} -edge μ -XANES spectra were collected, are marked on all X-ray microprobe maps.

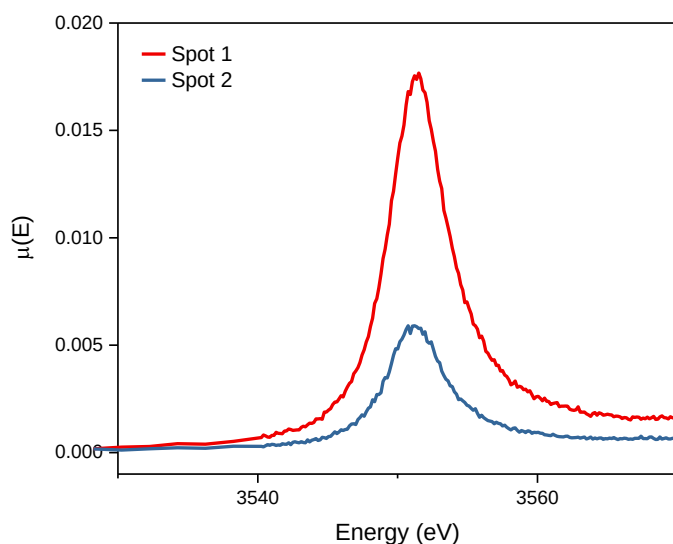


Figure 9. Unnormalized U M₅-edge μ -XANES spectra collected from Sample C from spots marked 1 and 2 on Figure 8.

3.3 Fitting of the U M₅-edge μ -XANES spectra

Fitting μ -XANES spectra using linear combination fitting (LCF) can be used to determine speciation information from specific locations on X-ray microprobe maps [2, 3, 14, 16, 17]. One of the concerns associated with trying to quantify chemical species using a white line spectrum collected in PFY mode (e.g., the U M₅-edge μ -XANES spectra discussed here) is that this type of spectrum is known to be susceptible to absorption effects [18]. An example of these absorption effects is shown in Figure 10 a) by comparing U M₅-edge spectra collected from U₃O₈ in PFY and transmission mode. The absorption effects observed in U M₅-edge μ -XANES spectra collected from the tailings would be expected to be similar to the U M₅-edge XANES spectra collected from mineral standards in PFY mode. LCF was applied to the U M₅-edge μ -XANES spectra collected from the tailings using the U M₅-edge XANES spectra collected from the mineral standards. An example of the potential to use LCF to identify U species in the tailings is presented in Figure 10 b) where a spectrum from the tailings were fitted using spectra

from standard U-bearing minerals (see Figure 10 c)). The example fitting shown in Figure 10 b) demonstrates that the U M₅-edge μ -XANES spectrum collected from spot 4 on Figure 4 can be fitted using a combination of uranophane ($\text{Ca}(\text{UO}_2)_2(\text{SiO}_3\text{OH})_2 \cdot 5\text{H}_2\text{O}$) and rutherfordine

(UO_2CO_3).

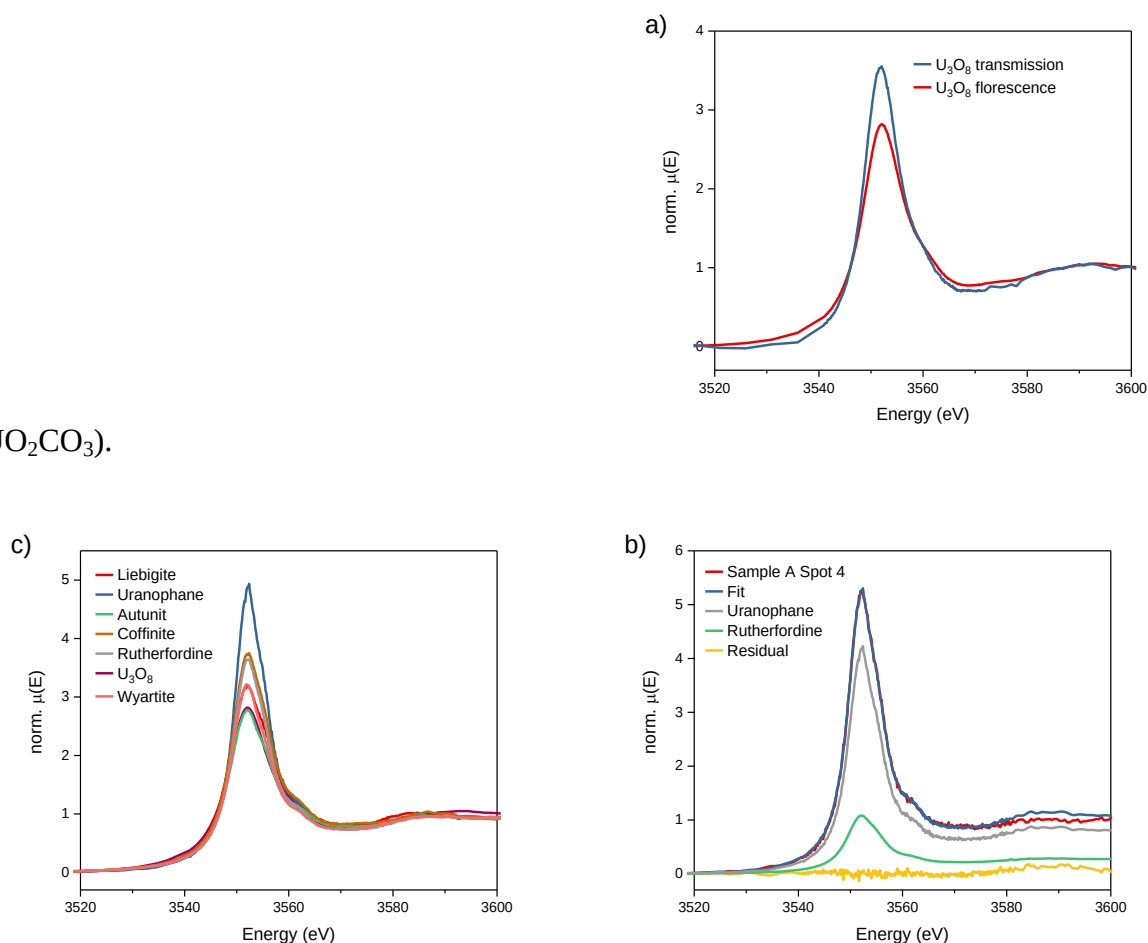


Figure 10. a) U M₅-edge XANES spectra collected from yellowcake using PFY and transmission mode. b) U M₅-edge XANES spectra collected from uranium minerals. c) The fitted U M₅-edge μ -XANES spectrum from Sample A (collected from spot 4 on Figure 4).

Conclusion

This study presents a detailed methodology for the collection of U M _{α 1} X-ray microprobe maps from solid tailings extracted from a U mill TMF. The primary obstacle overcome by this study was the isolation of the U M _{α 1} XRF signal from the much more intense K K _{α 1} XRF signal. This was accomplished through the use of an excitation energy just above the U M₅-absorption edge

(3552 eV) but below the K K-absorption edge (3608 eV) or by using an excitation energy higher than the K K-absorption edge followed by fitting the XRF spectra collected at each pixel to deconvolute the U $M_{\alpha 1}$ and $K_{\alpha 1}$ K XRF signals. It can be beneficial to collect X-ray microprobe maps using a high excitation energy as this can allow for maps to be generated for multiple elements; however, fitting XRF spectra to deconvolute signals that are close in energy can be difficult if there are extreme concentration differences. In this study, it was determined that collection of U X-ray microprobe maps using an excitation energy that lies between the U M_5 -absorption edge and the K K-absorption edge (i.e., 3570 eV) was the preferred approach as this excitation energy was able to isolate the low concentration U $M_{\alpha 1}$ XRF signal from the high concentration K $K_{\alpha 1}$ XRF signal.

Also explored in this study was the use of U M_5 -edge μ -XANES to both validate the X-ray microprobe collection methodology as well as to obtain chemical information on U containing minerals in the tailings. Comparing the U M_5 -edge μ -XANES spectral intensities to the U $M_{\alpha 1}$ XRF signals collected at each pixel in the U X-ray microprobe map confirmed that use of an excitation energy of 3570 eV was ideal for collecting accurate U X-ray microprobe maps. Information on the speciation of U in the tailings was obtained by fitting the U M_5 -edge μ -XANES spectra. Overall, this study demonstrates the potential to use U X-ray microprobe to provide accurate information on the distribution of U within the heterogeneous tailings so that high intensity U M_5 -edge μ -XANES spectra may be collected for the study of the U in the tailings.

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Analysis of low concentration U species within U mill tailings using X-ray microprobe

Supporting Information

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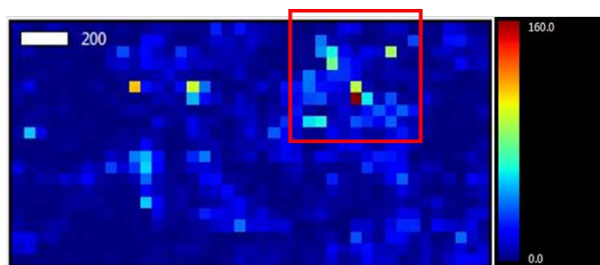


Figure S1. U $M_{\alpha 1}$ X-ray microprobe map collected from Sample A using an excitation energy of 3570 eV and integration over a fixed energy window. The red box represents the area over which additional X-ray microprobe maps were collected.

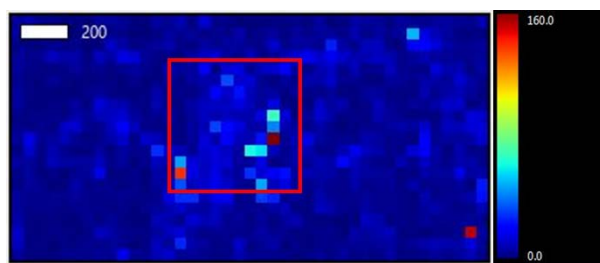


Figure S2. U M α_1 X-ray microprobe map collected from Sample B using an excitation energy of 3570 eV and integration over a fixed energy window. The red box represents the area over which additional X-ray microprobe maps were collected.

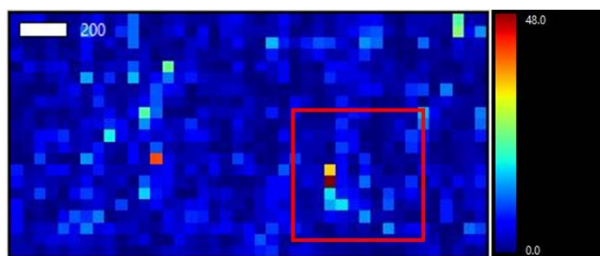
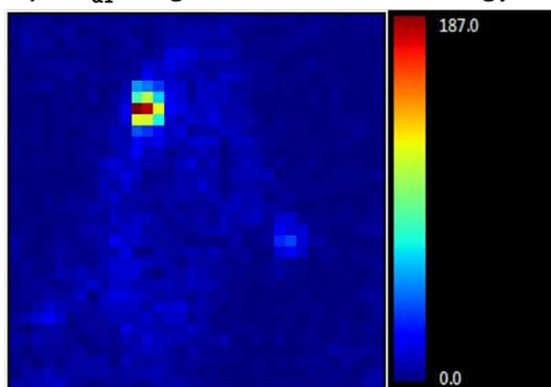


Figure S3. U $M_{\alpha 1}$ X-ray microprobe map collected from Sample C using an excitation energy of 3570 eV and integration over a fixed energy window. The red box represents the area over which additional X-ray microprobe maps were collected.

a) Cl $K_{\alpha 1}$ using 3570 eV excitation energy



b) Cl $K_{\alpha 1}$ using 8350 eV excitation energy

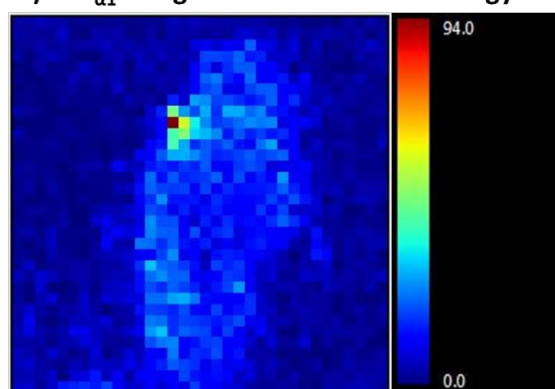
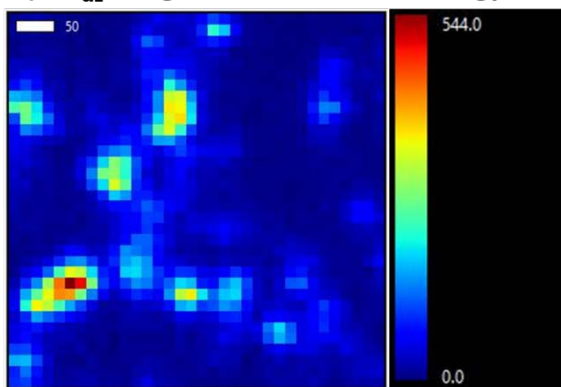


Figure S4. Cl X-ray microprobe maps collected from Sample B using an excitation energy of a) 3570 eV and b) 8350 eV. The dark red locations on both maps are considered to be the same location on the sample.

a) S $K_{\alpha 1}$ using 3570 eV excitation energy



b) S $K_{\alpha 1}$ using 8350 eV excitation energy

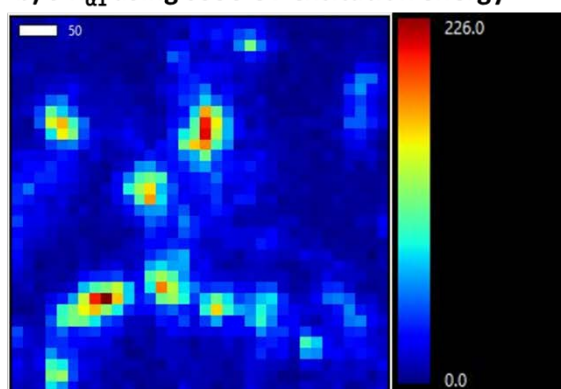


Figure S5. S X-ray microprobe maps collected from Sample C using an excitation energy of a) 3570 eV and b) 8350 eV. The dark red locations on both maps are considered to be the same location on the sample.