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Geochemistry of uranium mill tailings in the Athabasca Basin, Saskatchewan, Canada: A review

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ABSTRACT
The Athabasca Basin, located in northern Saskatchewan, Canada, is a major source of global U and an important economic driver for the province and country. Athabasca Basin U deposits consist of uraninite and pitchblende dominated by quartz and aluminosilicates and varying amounts of sulfide and arsenide minerals associated with varying concentrations of As, Se, Mo, Ni, and 226Ra (elements of concern; EOCs). Processing these U ores results in tailings that are often enriched in EOCs. Mill treatment processes are designed to generate tailings that minimize the long-term environmental impact of U tailings, although many challenges exist in reaching this goal. Many studies have contributed to our understanding of the geochemistry of these tailings and EOCs and their potential impact on the surrounding hydrosphere. Using nearly two decades of data from tailings samples, mill sampling campaigns, and laboratory experiments, this review provides a comprehensive analysis of the geochemistry and long-term behavior of U tailings in the Athabasca Basin and develops a geochemical model of the tailings. Results of this review are applicable to tailings generated from other milling operations with comparable acid leaching hydrometallurgical processes. This holistic review also highlights the limitations to our current understanding of U tailings geochemistry.

1. Introduction
The Athabasca Basin covers approximately 85,000 km² of northern Saskatchewan, Canada (Figure 1) and is a major source of global uranium (U) resources. Uranium mined from the basin comprised 22% (or 13,325 t U) of the world’s supply in 2015, and, as of 2016, 225,000 t of known economically mineable U remained in the basin (Saskatchewan Mining Association, 2016; World Nuclear Association, 2016a). Over 11% of the world’s electricity was generated by nuclear power plants in 2016 (World
Nuclear Association, 2016b). As such, the region is an important source of U for nuclear power plants and global efforts to reduce carbon-based fuel consumption (World Nuclear Association, 2016b). The U mined and milled in the basin is also economically important to Canada and the Province of Saskatchewan. Uranium exported from the basin was valued at $1.2 billion CAD in 2015 (Canadian Nuclear Association, 2017). The U not exported supplied 16.6% of Canada’s electricity in 2016 (Canadian Nuclear Association, 2017).

The Athabasca Basin contains some of the richest U deposits in the world, with average grades ranging from 0.5 to 25% U₃O₈ by mass (Bharadwaj & Moldovan, 2005; World Nuclear Association, 2016c). Uranium production in the basin began at Rabbit Lake in 1975. Mining and milling activities increased with the commissioning of the Cluff Lake (decommissioned in 2003) and Key Lake operations in 1980 and 1983, respectively (World Nuclear Association, 2016c). The McClean Lake mill is the newest mill in the Athabasca Basin and began operating in 1999. The discovery and development of high-grade U ore deposits in the new millennium resulted in the Key Lake and McClean Lake mills processing ore grades up to 20 to 25% U₃O₈ (Bharadwaj & Moldovan, 2005; Cameco Corporation, 2012; World Nuclear Association, 2016c). Figure 1 shows the locations of current and historic U mills and mines in the basin. Earlier U mining operations (1950s) on the northern shore of Lake Athabasca near Uranium City (Figure 1) are not considered part of Athabasca Basin mining operations because they are not part of the same geological group; these ores were often rich in carbonate minerals and processed using alkaline leach processes (Merritt, 1971).

![Figure 1](image_url)
With the ongoing expansion of U mining in the basin, mine waste is continually being generated and methods of waste management are being refined as the understanding of the geochemistry of these wastes improves. These mine wastes can include overburden waste rock and mill tailings, the latter of which is a focus of this review. Tailings slurries are a large component of this waste and include residual gangue minerals separated from the processed ore and neutralized secondary precipitates containing elevated concentrations of elements of concern (EOCs), including As, Ni, Mo, Se and $^{226}$Ra which can reach concentrations of 10%, 5%, 0.1%, 50 $\mu$g/g, 320 Bq/g, respectively in the tailings solids (Blanchard et al., 2015; Donahue, Hendry, & Landine, 2000; Heinrich, Kyser, Chipley, & Lam, 2010; Shaw, Hendry, Wellschläger, Kotzer, & Essilfie-Dughan, 2011). If not properly handled, these tailings slurries can pose a risk to local groundwaters. In legacy U mining environments around the world, inadequate disposal and containment of U tailings has caused contamination of soils, surface water, and groundwater (Abdelouas, 2006). The globally accumulated costs of decommissioning and remediation of old U mine sites numbers in the tens of billions of dollars (Abdelouas, 2006). These remediation costs of legacy sites will no doubt grow, and most often at the expense of the tax-payer. It is therefore imperative that operational and future mining projects improve their waste management strategies while being held accountable by society.

The U mining operations in the Athabasca Basin have taken steps to develop robust tailings management strategies. Above-ground tailings management facilities (TMF) were the first method of tailings storage when U mining and milling in the basin began in the 1970s (Donahue, 2000). These TMFs were constructed with engineered berms and long-term dedicated collection systems for recycling tailings seepage and surficial supernatants back to mill neutralization circuits. These facilities confined the tailings above the water table to minimize transport of contaminants present in the tailings porewater and were constructed at the Cluff Lake, Rabbit Lake, and Key Lake mine sites. Above-ground TMFs were replaced a decade later with in-pit TMFs that use the open pits of mined-out surface deposits for tailings storage. In-pit TMFs are engineered to optimize tailings consolidation and minimize EOC transport to the surrounding groundwater both before and after decommissioning. The first in-pit TMF was constructed at Rabbit Lake in 1984 and is called the Rabbit Lake In-Pit Tailings Management Facility (RLITMF) (Donahue et al., 2000). The second in-pit TMF in the basin was the Deilmann Tailings Management Facility (DTMF) constructed at Key Lake in 1996 in the mined out Deilmann pit (Figure 2a shows a cross section of the Key Lake DTMF) (Shaw et al., 2011). The third and most recent TMF was constructed at McClean Lake in 1999 (Mahoney, Langmuir, Gosselin, & Rowson, 2005).
and is called the JEB TMF (Figure 2b shows a cross section of the JEB TMF). The Key Lake and McClean Lake operations discharge tailings subaqueously to the TMFs to maintain saturated conditions, prevent the transport of contaminated dust and more evenly spread the tailings around the TMFs (IAEA, 2004).

The development of the TMFs in the Athabasca Basin has been accompanied by research programs to better understand the fate of the U tailings. The geochemistry of these in-pit TMFs has been studied for the past two decades, with the primary focus of many of these studies being the geochemistry of EOCs. The EOCs originate from the U ore and are solubilized during oxidative leaching processes in the mill. Neutralization processes in the mill treat process water to precipitate and adsorb the suite of EOCs and other dissolved metals within secondary minerals before discharging these precipitates into TMFs. The stability of these newly formed secondary
minerals and the unreacted primary minerals has been the subject of numerous studies of U tailings in the basin. A key driver for these studies is the extensive federal and provincial regulatory oversight of the tailings mass. Regulatory agencies (e.g., Canadian Nuclear Safety Commission) require long-term containment of EOCs from mine and mill tailings (Mahoney, Slaughter, Langmuir, & Rowson, 2007; Moldovan, Hendry, & Harrington, 2008), including minimizing EOC transport to the regional groundwater and meeting water quality objectives. Geochemical studies of the tailings bodies define the potential short- and long-term environmental impacts of EOCs on the hydrosphere and biosphere to determine if regulatory requirements can be met with current best practices. The development of the research programs for Athabasca Basin TMFs are an example of proactive steps towards minimizing the environmental impact from mining activities.

With the overall goal of improving our understanding of U tailings geochemistry to minimize environmental impacts, the objectives of this review are to: (1) integrate the existing literature of U tailings geochemistry into a single document and critically review the current understanding of mineralogical controls on EOCs in U tailings; (2) define the long-term environmental impacts of EOCs in U tailings generated in the Athabasca Basin; and (3) identify potential limitations in our understanding of U tailings geochemistry.

This review article is arranged into six sections. First, the mineralogy of the U ore deposits is characterized, followed by discussion of the U milling process, the fate of non-U minerals in the milling process (§2). The general geochemistry of the tailings bodies is then evaluated to summarize the current and future states of U tailings in the basin (§3). Next, a detailed analysis of the secondary minerals that form during effluent treatment and the mineralogical controls exerted on EOCs in these processes is provided (§4). The results of the review are then integrated into a conceptual geochemical model of the neutralization and tailings systems to summarize our understanding of the complete tailings geochemistry (§5). These results are used to identify gaps in the understanding of U tailings geochemistry and suggest areas for future studies (§6). Because the extent of mineralogical and EOC characterization undertaken at U mills and tailings bodies is much greater than for any other acid-leaching milling processes of metals and resultant tailings bodies, our findings are then related to mineralogical controls on EOCs in other tailings bodies (§7).

2. Uranium mining and milling in the Athabasca Basin

2.1. Mineralogy of uranium deposits and ore

The Athabasca Basin hosts unconformity-type U ores comprised of uraninite and pitchblende (UO$_{2+x}$), with occurrences of coffinite (U(SiO$_4$)$_1$-
\((x\text{OH})_4\) intergrown with silicate and clay gangue minerals (Hossain, 2014; Jefferson et al., 2007) at grades of 0.5 to 25% \(\text{U}_3\text{O}_8\) (Bharadwaj & Moldovan, 2005; World Nuclear Association, 2016c). Ores at Rabbit Lake are typically lower-grade and range from 0.8 to 2.1% \(\text{U}_3\text{O}_8\). Early ores at McClean Lake were mined from the JEB, Sue A, Sue B, Sue C, and Sue E deposits and averaged 2.4% \(\text{U}_3\text{O}_8\) (World Nuclear Association, 2016c). In 2014, the McClean Lake mill began processing high-grade ore averaging 20.7% \(\text{U}_3\text{O}_8\) from the Cigar Lake deposit (World Nuclear Association, 2016c). The Key Lake mill currently processes ore from the McArthur River deposit (averaging 25% \(\text{U}_3\text{O}_8\)) and production is expected to continue until 2034 (Bharadwaj & Moldovan, 2005; Cameco Corporation, 2012).

The type of deposit being milled has a strong influence on the mineralogy and composition of the resulting tailings. A broad range of mineralization occurs in the U deposits of the Athabasca Basin. The bulk mineralogy generally contains quartz (\(\text{SiO}_2\)) and phyllosilicates, such as illite \(((K,\text{H}_3\text{O})(\text{Al,Mg,Fe})_2(\text{Si,Al})_4\text{O}_{10}((\text{OH})_2,(\text{H}_2\text{O}))\)), Mg-chlorite \((\text{Mg}_5\text{Al}(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH,F})_2)\), kaolinite \((\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4)\), muscovite \((\text{KAl}_2(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH,F})_2)\), clinochlore \(((\text{Mg,Fe})_5\text{Al}(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_8))\), and tourmaline \((\text{NaMg}_3\text{Al}_6(\text{BO}_3)_3\text{Si}_6\text{O}_{18}(\text{OH})_3\text{F})\) (Carl, von Pechmann, Hohndorf, & Ruhrmann, 1992; Delaney, Hockley, Chapman, & Holl, 1998).

The unconformity deposits range from high organic matter content deposits rich with lignite or bitumen in the southwest region of the basin (Alexandre & Kyser, 2006) to low organic matter content deposits from sandstone- and basement-hosted mineralizations with graphite as the primary source of organic matter in the eastern region of the basin (Alexandre, Kyser, Thomas, Polito, & Marlat, 2009). The deposits utilized by the three major mills in the Athabasca Basin are of the latter type and do not contain significant amounts of organic matter (Wilson, Stasiuk, & Fowler, 2002). Only traces of organic matter are reported in McArthur Rive ore (Wilson et al., 2002), while the average organic carbon concentration from Cigar Lake ore samples is 0.3% (Kaczowka, 2017).

Of more relevance to this review, however, is the association of the U minerals with sulfide- and arsenide-rich mineralizations. Table 1 summarizes the mineralogy of the major deposits in the basin. These deposits can be divided into two types: monometallic and polymetallic. Monometallic U ores contain only trace amounts of other metals (with the exception of Cu and Fe). Polymetallic U ores are associated with sulfide and arsenide minerals that are rich in Ni, Co, Cu, Pb, Zn, Mo, and Se. For example, the Key Lake, Deilmann, Gaertner, and Cigar ore bodies contain(ed) elevated amounts of Ni- and Co-bearing arsenide/sulfide minerals (e.g., gersdorffite, niccolite (NiAs), and cobaltite (CoAsS)) (Kaczowka, 2017; von Pechmann, 1981). Likewise, the ore milled at McClean Lake and Rabbit Lake is
concentrated with up to 10% As and 5% Ni as arsenide/sulfide minerals (rammelsbergite (NiAs₂), niccolite, and gersdorffite) (Donahue et al., 2000; Langmuir, Mahoney, Rowson, & MacDonald, 1999; Rinas, Rowson, Frey, & Hughes, 2010). In Cigar Lake ores, Se often occurs within sulf(arsen)ide minerals through substitution of Se²⁻ with S²⁻ with Se concentrations reaching 2%, while Mo occurs as molybdenite and within uraninite at concentrations up to 4% (Kaczowka, 2017). The monometallic McArthur River ore currently milled at Key Lake contains lower concentrations of sulfide and arsenide minerals compared to other deposits, although waste rock from polymetallic deposits is blended with McArthur River ore for dilution purposes and contributes a large portion of the metals that report to the tailings. Trace metals in the McArthur River ore are associated with pyrite, chalcopyrite (CuFeS₂), covellite (CuS), and arsenopyrite (FeAsS) (Delaney et al., 1998; Jamieson & Frost, 1997). Analyses of the McArthur River ore by Heinrich et al. (2010) show Se and Mo are present in phyllosilicates, uraninite, and, to a lesser extent, sulfides and arsenides. A characterization study of the McArthur River ore by Hossain (2014) showed As and Ni were most frequently associated with cobaltite, gersdorffite, molybdenite, galena (PbS), pyrite, and chalcopyrite.

### 2.3. The uranium milling process

The U milling process (which is dependent on the ore mineralogy) defines the geochemistry of U tailings. The major characteristics of the Rabbit Lake, Key Lake, and McClean Lake mills are summarized in Table 2. The conventional U milling process (Figure 3) follows a pathway featuring comminution, leaching, solid-liquid separation, purification (frequently solvent extraction), U precipitation, and product packaging. The first four steps of this process impact the tailings geochemistry, with the U precipitation step also impacting the geochemistry in some mills.

---

**Table 1. Summary of the typical mineralogy of each major uranium deposit mined and milled at the reviewed sites.**

<table>
<thead>
<tr>
<th>Rabbit Lake</th>
<th>Key Lake</th>
<th>McClean Lake</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Rabbit Lake (P)</strong> - Niccolite, carollite, pyrite, chalcopyrite, bornite</td>
<td><strong>Key Lake, Deilmann, Gaertner (P)</strong> - Gersdorffite, niccolite, cobaltite</td>
<td><strong>JE, Sue A, Sue B, Sue C, Sue E</strong> - Gersdorffite, nibolite, maucherite, brav-oite, violarite, polydimite, safflor-ite, millerite, tennantite, pyrite, chalcopyrite, bornite, hematite</td>
</tr>
<tr>
<td><strong>B-zone (P)</strong> - Niccolite, gersdorffite, rammelsbergite, safflorite, molybdenite</td>
<td><strong>McArthur River (M)</strong> - Pyrite, chalcopyrite, covellite, arsenopyrite, gersdorffite, cobaltite, molybdenite, galena</td>
<td><strong>Cigar Lake (P)</strong> - Gersdorffite, niccolite, rammelsbergite, galena, chalcopyrite, jarosite, pyrite, rutile, molybdenite, cobaltite, bornite, chalcocite, sphalerite, pyrrhotite</td>
</tr>
<tr>
<td><strong>A-zone &amp; D-zone (P)</strong> - Niccolite, gersdorffite, rammelsbergite, para-rammelsbergite, hematite</td>
<td><strong>Eagle Point (M)</strong> - Brav-oite, chalco-pyrite, bornite, marcasite</td>
<td></td>
</tr>
</tbody>
</table>

*Note: P, polymetallic; M, monometallic. All deposits contain major amounts of quartz, illite, chlorite, and kaolinite.*
The U ores are brought to the mill as slurries or solid rock that is mixed with variable amounts of waste rock and sized through comminution (particle size distribution of $30 - 40\% < 75$ $\mu m$) to optimize the exposure of $U$ minerals in the downstream leaching process (Merritt, 1971). Next, the ore is fed to the leaching process as a slurry (ore mixed with water). The lixiviant used during leaching is dependent on the host rock mineralization. Athabasca Basin U mills use a strong acid leach process to dissolve $U$ minerals because the ores occur with clay and silicate minerals. Sulfuric acid is used in combination with $O_2$, $HClO_4$, or $H_2O_2$ to convert insoluble $U(IV)$ to soluble $U(VI)$ at temperatures between 50 and 60 °C and an $Eh \geq 600$ mV. The leaching of $U$ can be described by the dissolution-redox series:

$$2Fe^{2+} + \frac{1}{2}O_2 + 2H^+ \rightarrow 2Fe^{3+} + H_2O,$$

Table 2. Major characteristics of each mill in the scope of the review that affect tailings geochemistry.

<table>
<thead>
<tr>
<th></th>
<th>Rabbit Lake Mill</th>
<th>Key Lake Mill</th>
<th>McClean Lake Mill</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Host rock characteristics</strong></td>
<td>Monometallic and polymetallic</td>
<td>Monometallic (current) and polymetallic (past)</td>
<td>Polymetallic</td>
</tr>
<tr>
<td><strong>Ore mineralogy</strong></td>
<td>Uraninite, pitchblende</td>
<td>Uraninite, pitchblende, coffinite</td>
<td>Uraninite, pitchblende, coffinite</td>
</tr>
<tr>
<td><strong>Leach process reagents</strong></td>
<td>$H_2SO_4$, $NaClO_4$</td>
<td>$H_2SO_4$, $O_2$</td>
<td>$H_2SO_4$, $H_2O_2$, $Fe_2(SO_4)_3$, $O_2$</td>
</tr>
<tr>
<td><strong>Initial raffinate $Fe/As^a$</strong></td>
<td>1–4</td>
<td>15–70</td>
<td>1–4</td>
</tr>
<tr>
<td><strong>Neutralization reagents</strong></td>
<td>$CaO$, $BaCl_2$, $Fe_2(SO_4)_3$</td>
<td>$CaO$, $BaCl_2$, $H_2O_2$</td>
<td>$CaO$, $BaCl_2$, $Fe_2(SO_4)_3$</td>
</tr>
<tr>
<td><strong>Leach residue</strong></td>
<td>Mixed with neutralized raffinate slurry</td>
<td>Mixed with neutralized raffinate slurry</td>
<td>Mixed with raffinate before neutralization</td>
</tr>
<tr>
<td><strong>Neutralization steps</strong></td>
<td>3</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td><strong>Tailings discharge pH</strong></td>
<td>10–11</td>
<td>10–11</td>
<td>7–8</td>
</tr>
<tr>
<td><strong>Tailings discharge control</strong></td>
<td>Injection, subaerial, or submerged discharge</td>
<td>Submerged discharge</td>
<td>Placement by tremie pipe</td>
</tr>
</tbody>
</table>

*Ranges estimated based on published raffinate compositions.

Figure 3. Generalized process flow diagram of the tailings stream of the U milling processes used in the Athabasca Basin.

The U ores are brought to the mill as slurries or solid rock that is mixed with variable amounts of waste rock and sized through comminution (particle size distribution of $30–40\% < 75$ $\mu m$) to optimize the exposure of $U$ minerals in the downstream leaching process (Merritt, 1971). Next, the ore is fed to the leaching process as a slurry (ore mixed with water). The lixiviant used during leaching is dependent on the host rock mineralization. Athabasca Basin U mills use a strong acid leach process to dissolve $U$ minerals because the ores occur with clay and silicate minerals. Sulfuric acid is used in combination with $O_2$, $HClO_4$, or $H_2O_2$ to convert insoluble $U(IV)$ to soluble $U(VI)$ at temperatures between 50 and 60 °C and an $Eh \geq 600$ mV. The leaching of $U$ can be described by the dissolution-redox series:

$$2Fe^{2+} + \frac{1}{2}O_2 + 2H^+ \rightarrow 2Fe^{3+} + H_2O,$$
Iron(II) is generated by the dissolution of Fe-containing minerals and from oxidation of elemental Fe resulting from mechanical abrasion of equipment in the grinding circuits (Merritt, 1971). At McClean Lake, Fe$_2$(SO$_4$)$_3$ is added (if there is insufficient Fe in the ore) to ensure U(IV) is oxidized to maximize U recovery. The acidic and oxic conditions of the process dissolve and oxidize other silicate, arsenide, and sulfide minerals present in the host rock, resulting in a solution rich in Fe, Al, Mg, Si, As, Ni, Se, Mo, SO$_4$, and U (among other elements). These reactions are enhanced due to the increased surface area after comminution. The oxidation of gersdorffite (NiAsS) is an example of the concomitant dissolution of As and Ni with U, where

$$2\text{NiAsS} + 3\text{H}_2\text{O} + \frac{13}{2}\text{O}_2 \rightarrow 2\text{SO}_4^{2-} + 2\text{AsO}_3^{3-} + 2\text{Ni}^{2+} + 6\text{H}^+$$  \hspace{1cm} (3)

Uranium recoveries during leaching are > 95%; however, a large fraction of the host rock (refractory silicates and clay minerals) and minor amounts of sulfide and arsenide minerals survive the leaching process. These minerals are separated from the U-rich leachate (pregnant leach solution) using clarifiers that form a thickened slurry called the leach residue.

The purification step separates the U from the other dissolved metals and metalloids. Solvent extraction is used in the milling processes, although ion-exchange techniques are also used as an alternate purification step. An organic solution selectively extracts U from the pregnant leach solution. The resulting aqueous solution, termed raffinate, diverges from the U-bearing organic solution at this point in the process. The U is stripped from the organic solution using either H$_2$SO$_4$ or NH$_4$(SO$_4$)$_2$ solutions and is subsequently precipitated using reagents such as H$_2$O$_2$ or NH$_3$. The final ‘U ore concentrates’ vary from mill to mill but are generally packaged and shipped to a conversion facility that produces the U fuel.

The raffinate from the purification step is sent to a neutralization process. Raffinate is acidic (∼pH 1–2) and rich in major elements (Mg, Si), metal(loid)s (Al, As, Co, Cu, Fe, Mo, Ni, Se), and SO$_4$. The raffinate is the primary carrier of EOCs through the milling process and is treated by the neutralization process to increase the pH and remove EOCs from the aqueous phase via precipitation reactions (not to be confused with the U precipitation process). At McClean Lake, the leach residue is also added to the neutralization process to sequester EOCs that are still present in sulfide and arsenide minerals. The neutralization processes used by the mills in the Athabasca Basin follow the same chemical concepts. Raffinate is neutralized to neutral to basic pH with slaked lime (hydrated CaO), resulting in the
precipitation of gypsum and dissolved metal(loid)s as secondary minerals. The precipitates are separated from the aqueous solution using thickeners or clarifiers. After further site-specific treatment processes, the neutralized aqueous solution is analyzed and, if the concentrations of metal(loid)s meet regulatory requirements, discharged to the environment. The thickened precipitates are pumped as a slurry to a TMF for final disposal. Depending on the mill, the leach residue from the leaching circuit is either neutralized with the raffinate or neutralized raffinate slurry prior to disposal in the TMF. The environmental conditions of the TMFs are discussed in §3.2.

2.4. The fate of primary gangue minerals in the mill and tailings

The oxic-acid leaching of U ores dissolves the U minerals and select gangue silicate, arsenide, and sulfide minerals. The elements that compose the host rock minerals are transferred to the leaching solution and precipitate downstream as secondary minerals during raffinate neutralization. Hossain (2014) quantified the minerals that dissolve during acid leaching using mineral liberation analysis (Table 3). Leaching tests of McArthur River ore show that kaolinite, quartz, and illite are the most acid-resistant minerals in the ore with only 2, 6, and 7% of these phases dissolving, respectively. The persistence of these same minerals is observed in McClean Lake and Rabbit Lake leach residues as well (Langmuir et al., 1999; Mahoney et al., 2005; Pichler, Hendry, & Hall, 2001). Unlike kaolinite and illite, the other phyllosilicates (muscovite and chlorite) are less resistant to acid leaching. These minerals are a major source of the soluble Al, Mg, and Fe(II)/Fe(III) precipitated downstream during raffinate neutralization. Phyllosilicate dissolution, especially chlorite (Eq. 4) (Lowson, Comarmond, Rajaratnam, & Brown, 2005), contributes a large number of major cations to the resulting raffinate on a mass basis, as reflected by

\[
(Mg, Fe, Al)_6(AlSi_3O_{10})(OH)_8 + 16H^+ \rightarrow [6(Mg, Fe, Al)]^{13+} + Al^{3+} + 3H_4SiO_4 + 6H_2O
\]

Sulfides are slightly resistant to dissolution in the oxic leaching process, although the observed resistance could be explained by kinetic limitations. A major portion of the dissolved Fe likely originates from the oxidative dissolution of pyrite and chalcopyrite, although uncharacterized Fe-oxides also contribute to the total soluble Fe. Pyrite is oxidatively dissolved as shown in Eq. 5, in addition to a cascading oxidation couple for pyrite as shown in Eqs. 6–7:

\[
2FeS_2 + 7O_2 + 2H_2O \rightarrow 2Fe^{2+} + 4SO_4^{2-} + 4H^+.
\]
Other sulfides such as gersdorffite dissolve by a similar mechanism. The release of As and Ni is demonstrated by

\[
4\text{NiAsS} + 6\text{H}_2\text{O} + 13\text{O}_2 \rightarrow 4\text{SO}_4^{2-} + 4\text{AsO}_4^{3-} + 4\text{Ni}^{2+} + 12\text{H}^+.
\]  

(8)
Warner, and Kotzer (2012, Essilfie-Dughan, Hendry, Warner, & Kotzer, 2013) characterize Fe and As in the DTMF tailings and observe chalcopyrite, pyrite, and gersdorffite as the major primary Fe, As, and Ni minerals. About 10–30% of the total Fe in the DTMF is in pyrite and chalcopyrite regardless of ore type, while 12% of the total As in the McArthur River ore section of the DTMF is in gersdorffite (Essilfie-Dughan et al., 2013). Pichler et al. (2001) report similar findings for As in Rabbit Lake tailings, where 20% of the total As is associated with sulfide minerals. Arsenide oxidation occurs in the JEB TMF and is observed as increasing As(III) concentrations in tailings porewater (Rinas et al., 2010). Molybdenum and Se are evenly distributed in the bulk and clay size fractions in McArthur River leach residue (Hossain, 2014). Molybdenite exists as a discrete Mo phase in both the JEB TMF and DTMF (Blanchard et al., 2015; Hossain, 2014). The presence of primary sulfide and arsenide minerals in the tailings presents a potential risk of EOC mobilization through oxidation.

3. Geochemistry of the tailings bodies

3.1. Hydrogeology of in-Pit tailings management facilities

The three active U TMFs in the Athabasca Basin are mined-out pits repurposed to control the hydrogeology around the tailings body. The RLITMF uses a pervious surround design; high hydraulic conductivity (K) coarse grained rock and sand-filter walls line the outer boundary of the TMF, allowing groundwater to preferentially flow around the tailings through the high K zones (Figure 4) (Donahue et al., 2000). Water from the TMF migrates through the pervious surround to a dewatering drainage system. This method decreases the K of the tailings and creates a ‘plug’ in the hydrogeological system to ensure long-term transport of EOCs in the tailings is controlled by diffusion (Langmuir et al., 1999; Moldovan et al., 2008). Diffusion cell testing and reactive transport modeling of the RLITMF suggest the source term of As is controlled by diffusion and adsorption processes, resulting in a 40–70% decrease of aqueous As relative to the initial tailings over a 10,000 year period. This model suggests that As concentrations in groundwater 50 m downgradient of the tailings should remain at background levels (0.001 mg/L) (Moldovan et al., 2008). The DTMF uses a similar concept with the exception that the pervious surround is a natural formation of outwash sand (Bharadwaj & Moldovan, 2005). Tailings porewater is recycled to the mill through underdrains located at the bottom of the DTMF (Figure 2a), further dewatering the tailings. The JEB TMF uses a similar tailings management method with tailings water drawn through drainage rock placed below the tailings (Figure 2b) and recirculated back to the mill (Rinas et al., 2010).
3.2. Aqueous and solids geochemistry of the tailings

Tailings in the three TMFs are neutral to basic in pH, oxic, and at low temperatures (0–12 °C) (Donahue & Hendry, 2003; Langmuir, Mahoney, & Rowson, 2006; Shaw et al., 2011). The mean pH of porewater from tailings samples collected in 1997 from the RLITMF was 9.9 (range 6.6 to 13.0) and the mean Eh of the porewater was 174 mV (range −400 to 400 mV, indicating reducing zones are present in the RLITMF) (Donahue & Hendry, 2003). A similar study collected continuous cores deposited in the DTMF between 2004 and 2009, with samples containing tailings representing both the Deilmann and McArthur River orebodies. The measured mean porewater pH was 9.6 in both tailings types (range 7.6 to 10.7) (Shaw et al., 2011). The mean Eh in the Deilmann and McArthur orebody tailings was 189 mV, and the range in Eh (−64 to 472 mV) shows a primarily oxic geochemical system (Shaw et al., 2011). Tailings samples collected from the JEB TMF in 2002 had a mean pH of 7.8 (range 6.5 to 8.9) and a mean Eh of 350 mV (range 156 to 484 mV) (COGEMA, 2003). In 2013, JEB TMF tailings samples had a mean pH of 6.9 (range 6.3 to 7.7) (Blanchard et al., 2017). The large range of porewater pH and Eh measurements from all three sites could result from several causes. The simplest answer is a loss of process control (e.g., excess or insufficient slaked lime addition) resulting in discharge pH above or below operational targets in certain regions. In situ reactions such as sulfide oxidation or microbial activity could influence localized acidic or reducing conditions. The heterogeneous nature of the tailings makes these localized zones possible, although localized reducing conditions are only directly observed in the RLITMF and DTMF.
Depth profiles of porewater concentrations of EOCs in the three TMFs are presented in Figures 5–7 and often show depth-dependent trends. These trends are primarily attributed to differences in the mineralogy of the ore being processed at the time of tailings deposition (COGEMA, 2003; Donahue & Hendry, 2003; Moldovan, 2006; Shaw et al., 2011). In the DTMF, a geochemical boundary separates the Deilmann and McArthur River orebody tailings (Figure 5). Deilmann-derived tailings feature elevated concentrations of solid phase As, Fe, Mo, Ni, and Se and a low Fe/As ratio (∼4), while McArthur River tailings feature lower concentrations of the same elements and a greater Fe/As ratio (∼30), which is a key parameter for controlling EOC concentrations (Shaw et al., 2011). The porewater concentrations of As and Mo are negatively correlated with the solid phase Fe/As and Fe/Mo ratios. The greater ratios in the McArthur River tailings favor the formation of As and Mo surface complexes on ferrihydrite during tailings neutralization without oversaturating ferrihydrite surface sites, resulting in lower As and Mo porewater concentrations. Porewater concentrations could also be influenced by redox conditions. In the 430 to 440 masl depths (Figure 5), a spike in aqueous Fe concentrations occurred in 2005 samples and could indicate an event of solid Fe(III) reduction to Fe(II). This potentially had the effect of releasing adsorbed EOCs as...
Figure 6. Solid phase (top) and porewater (bottom) concentrations from one core profile from the RLITMF in 1999 (data from Moldovan, 2006).

Figure 7. Solid phase (top) and porewater (bottom) depth averaged concentrations of tailings core samples from five locations collected one year apart at the JEB TMF in 2001 and 2002 (data from COGEMA, 2003).
suggested by increases in aqueous As and Se. Depth profiles of Eh are not available to confirm this speculation, although Eh values as low as −64.0 mV were measured in the McArthur River tailings and could support localized Fe(III) reduction.

Boundaries between tailings from different orebodies in the RLITMF are not well defined because multiple deposits were often processed in a single year. However, As porewater concentrations are < 1 mg/L in tailings from raffinates with Fe/As > 10 but can exceed 40 mg/L in tailings from raffinates with Fe/As < 4 (Figure 6) (Donahue & Hendry, 2003; Moldovan, 2006). This correlation is consistent with the relationship between the Fe/As ratio and As porewater concentrations in the DTMF. Aqueous and solid phase As and Ni concentrations are strongly correlated in polymetallic ore tailings in the RLITMF due to large amounts of gersdorffite and niccolite (Figure 6) (Donahue, 2000). The same correlation between As and Ni occurs in the JEB TMF at McClean Lake; evidence of in situ oxidation of arsenide minerals from the polymetallic ores is also indicated by the increasing As porewater concentrations (Figure 7).

The aqueous speciation of an EOC influences its mobility, reactivity, and toxicity in the tailings. In porewater samples collected from the RLITMF in 1999, As(V) comprised 88% of the total aqueous As, with the remainder as As(III) (Moldovan et al., 2008). Up to 18% of solid phase As in RLITMF tailings from 1997 was associated with sulfide minerals (Pichler et al., 2001). In the DTMF, Shaw et al. (2011) demonstrate that As(V) is the dominant oxidation state of solid phase As (~96%); the residual As is associated with gersdorffite and other sulfide minerals (Essilfie-Dughan et al., 2013). Minor amounts of solid phase As(III) occur as ferrihydrite adsorption complexes, while aqueous As(III) is not detected (Essilfie-Dughan et al., 2012; Shaw et al., 2011). Aqueous arsenic is either present as As(V) (86%) or a monomethyl- and monothiol-As(V) (Shaw et al., 2011). The presence of monomethyl-As(V) is explained by abiotic methylation of As with entrained organic compounds from the solvent extraction process, while monothio-As(V) potentially forms through abiotic reactions of As(III) with sulfide minerals (Shaw et al., 2011). Monothio-As(V) is only observed at depths corresponding to Deilmann ore tailings (i.e., polymetallic ore with elevated sulfide and As concentrations). A mixture of aqueous As(V) and As(III) has been observed over the lifetime of the JEB TMF. Solid phase As occurs in three oxidation states in JEB TMF tailings: As(V), As(III), and As(-I). A trend of increasing solid phase As(V) and variable As(III) with time is attributed to oxidation reactions of arsenide minerals (discussed in §3.2) (Blanchard et al., 2017; Rinas et al., 2010; Warner & Rowson, 2007).
Speciation of Se and Mo in the tailings is not well defined. Stability field diagrams for Se and Mo in the DTMF using tailings porewater pH and Eh data (Shaw et al., 2011) suggest \( \text{SeO}_3^{2-} \) (Se(IV)) and \( \text{MoO}_4^{2-} \) (Mo(VI)) are the dominant equilibrium aqueous species. The measured aqueous Se speciation, however, is approximately 65% Se(VI), suggesting the aqueous geochemistry of Se is not at equilibrium (Shaw et al., 2011). The cause of this disequilibrium is not clear, but slow Se(VI) reduction rates can be speculated to be due to a lack of readily available electron donors for Se(VI) reduction (either biotic or abiotic) and the diffusion-dominated nature of the tailings porewater. Selenium(VI) has higher mobility than Se(IV) (Das, Hendry, & Essilfie-Dughan, 2013); thus, the equilibrium speciation of Se in the tailings will influence the long-term Se porewater concentrations in the TMFs.

Ferrihydrite, amorphous Al(OH)_3, and layered double hydroxides are present in the tailings and provide surface complexation sites for As, Se, Mo, Ni, and ^226^Ra (Bissonnette, Essilfie-Dughan, Moldovan, & Hendry, 2016; Essilfie-Dughan, Pickering, Hendry, George, & Kotzer, 2011; Lieu et al., 2010; Liu & Hendry, 2011; Moldovan, Jiang, & Hendry, 2003; Robertson, Essilfie-Dughan, Lin, & Hendry, 2017). Secondary minerals such as ferric arsenate (which crystallizes to scorodite), NiMoO_4, (Ba,^226^Ra)SO_4, and powellite are important EOC-bearing phases in the tailings as well (Blanchard et al., 2015, Blanchard et al., 2017; Essilfie-Dughan et al., 2011; Liu & Hendry, 2011; Mahoney et al., 2007). The porewater concentrations of EOCs in the tailings are controlled by these pH-dependent surface complexation reactions as well as the precipitation of secondary minerals in the neutralization process (discussed in detail in §4.3). The terminal pH of tailings is historically set at pH > 10 to ensure Ni remains precipitated. However, increased re-dissolution of certain As phases (e.g., ferric arsenate) occurs at increasingly basic pH (Langmuir et al., 2006). Furthermore, electrostatically-controlled outer-sphere surface complexation of oxyanions such as \( \text{MoO}_4^{2-} \) and \( \text{SeO}_4^{2-} \) decreases as the pH increases (Dzombak & Morel, 1990). This was a contributing factor in setting the JEB TMF terminal pH to 7, because the McClean Lake mill was anticipating processing As-rich ore (Langmuir et al., 1999).

Mineral saturation indices in tailings porewater can be used to infer the presence and stability of specific mineral phases at equilibrium. Ferrihydrite is theoretically slightly undersaturated in the DTMF porewater while hematite and goethite are supersaturated, suggesting ferrihydrite could crystallize to these phases over time (Shaw et al., 2011). However, surface complexes (e.g., adsorbed AsO_4^{3-}) stabilize ferrihydrite and should inhibit or prevent ferrihydrite transformation (Das, Hendry, & Essilfie-Dughan, 2011). Scorodite and ferric arsenate are undersaturated in the DTMF and
RLITMF because of the basic pH, while scorodite is saturated at the neutral pH of the JEB TMF (Blanchard et al., 2017; Donahue & Hendry, 2003; Shaw et al., 2011). Observations of scorodite in the JEB TMF support crystallization of ferric arsenate over time (Blanchard et al., 2017). The lack of scorodite in the DTMF and RLITMF suggests that ferric arsenate only crystallizes to scorodite at pH $\leq 7$. As such, ferric arsenate likely dissolves and re-precipitates as As-adsorbed ferrihydrite. Powellite is saturated in each TMF and is physically observed in the DTMF and JEB TMF (Blanchard et al., 2015; Essilfie-Dughan et al., 2011). Powellite concentrations in the JEB TMF are increasing over time (Blanchard et al., 2015), which is evidence of tailings still moving towards an equilibrium. Tailings porewater is saturated with respect to Ca-arsenate minerals yet there is minimal evidence of Ca-arsenates in the tailings (Donahue & Hendry, 2003). Ca-arsenate precipitation might be rate-limited, similar to powellite, and will precipitate as equilibrium is reached.

### 3.3. Organic materials and microbiological processes

As previously discussed in §2.1, organic matter is present in many regions of the Athabasca Basin, but minimal organic matter is observed in U ore actively mined in mills being reviewed. In addition, any organic matter is likely to be oxidized in the strongly oxidizing conditions of the acid-leach processes in the mills and suggests that the primary organic matter content in the tailings is low. However, non-ore sources of organic carbon are added throughout the U milling and neutralization processes. An organic solution composed of kerosene, isodecanol, and a tertiary-amine is used in the solvent extraction process; small amounts of this organic solution remains entrained in the raffinate and reports to the TMFs (Donahue et al., 2000; Hughes, Rinas, Frey, & Rowson, 2010). Polyacrylamide flocculants are used at multiple points in the mills and adsorb to tailings surfaces (Blanchard, Grosvenor, Rowson, Hughes, & Brown, 2016; Hughes et al., 2010). These organic compounds are potential sources of organic carbon for micro-organisms.

Microbiological studies of RLITMF and DTMF tailings samples have provided a baseline for the microbial communities present in these oxic and basic environments. In both the RLITMF and DTMF, the bacterial community is diverse with a composition that changes with depth due to ore composition variability (Bondici et al., 2013; Wolfaardt, Hendry, & Korber, 2008). Iron and sulfate reducing bacteria are commonly observed in tailings samples from the DTMF (Bondici et al., 2016, 2014; Khan et al., 2013), suggesting that despite the prevailing oxic conditions of the TMFs, reducing microenvironments likely exist. Biofilms containing these reducing
bacteria have been cultured from tailings samples and generate elevated amounts of reduced Fe (Bondici et al., 2016, Bondici et al., 2014). These reducing environments may have implications for metal mobility (§3.4). Direct microbial studies have not been conducted on JEB TMF tailings; however, carbon cycling is observed and may be a result of microbial activity. Observed increases in HCO$_3^-$ concentrations in JEB TMF porewaters with depth and time are suggested to be a result of microbially-mediated organic carbon oxidation (Blanchard et al., 2016; Hughes et al., 2010). This results in temporary accumulation of HCO$_3^-$ before carbonate minerals eventually precipitate (Hughes et al., 2010). Conversely, direct biogeochemical processes have not been observed at the RLITMF and DTMF. The observations of diverse microbial communities in these tailings, along with observations of carbon cycling at the JEB TMF suggest that biogeochemical processes should be occurring in all three TMFs. More biogeochemical studies are needed to better understand these processes in the TMFs.

3.4. Geochemical stability

Tailings discharged to the TMFs are not at geochemical equilibrium (Hayes et al., 2014). Fresh tailings are a mixture of newly precipitated solids and primary minerals from the leach residue that were pulverized and exposed to acid. Geochemical reactions will occur in this mixture as the tailings move towards equilibrium, and are evident in changes of the tailings porewater chemistry over time. Temporal studies of As speciation in JEB TMF porewater show total As concentrations increasing after deposition. Arsenide minerals are oxidizing, releasing As(III) to solution; the subsequent oxidation of As(III) to As(V) is the rate-limiting step and causes temporary accumulation of As(III) in the porewater (Rinas et al., 2010; Warner & Rowson, 2007). This mechanism is not explicitly observed in the RLITMF or DTMF. Due to changes in the proportions of polymetallic waste rock, ore mill feeds, and milling of different ore bodies over time, arsenides and sulfides occur at varying concentrations within the tailings in the DTMF and RLITMF. As a result, in situ oxidation of arsenides and sulfides could mobilize As in the future (Moldovan et al., 2008; Pichler et al., 2001; Shaw et al., 2011). In the DTMF, As(III) adsorbs to ferrihydrite and its origin is hypothesized to be primary mineral oxidation (Essilfie-Dughan et al., 2012). However, As(V) is the dominant As oxidation state (~96%) in the DTMF solids, remaining constant between 1998 and 2013 (Essilfie-Dughan et al., 2013). Arsenide oxidation suggests that sulfide minerals (e.g., pyrite, chalcopyrite, and molybdenite) are also oxidized in the tailings, thereby generating acid and releasing associated metal(loid)s. Ultimately,
the presence of sulfides in any tailings system must be considered as a potential long-term source of As and other EOCs.

The stability of secondary arsenate phases is an important consideration for tailings preparation and process design. Ferric arsenate crystallizes to scorodite at pH ≤ 7; however, ferric arsenate dissolves at a rate proportional to increasing pH (>8) and decreasing Fe/As ratio (Langmuir et al., 1999). The equilibrium As concentration is 1 mg/L at pH 8 and an Fe/As ratio of 3.0 (Langmuir et al., 1999). Scorodite is thermodynamically stable under the geochemical conditions in the JEB TMF, although would destabilize with any pH increase (Blanchard et al., 2017). This emphasizes the need to maintain a neutral pH at the JEB TMF. Ferric arsenate likely dissolves in the DTMF and RLITMF due to the basic pH. If available, excess amorphous metal hydroxides and LDHs should sequester this As released from ferric arsenate dissolution. Arsenic(V)-adsorbed ferrihydrite inhibits ferrihydrite transformation to goethite or hematite at pH 10. Extrapolation of transformation rates of As(V)-adsorbed ferrihydrite suggests these complexes should remain stable for several tens of thousands of years under the geochemical conditions of the DTMF (Das et al., 2011).

The stability of LDHs and their controls on EOC concentrations have not been explicitly studied in Athabasca Basin TMFs. However, LDHs are present in 15-year-old DTMF samples, suggesting they are stable, at least over a short time period (Gomez, Hendry, Koshinsky, et al., 2013). Structural metals of layered double hydroxides (e.g., Mg$^{2+}$) dissolve as the pH decreases towards circumneutral conditions (Goh, Lim, & Dong, 2008). In a laboratory study, As(V)-adsorbed LDHs equilibrated at pH 10 released < 1.0% of the total As (Palmer & Frost, 2011). Additionally, adsorbed oxyanions are shown to stabilize LDHs (Morimoto, Anraku, Hoshino, Yoneda, & Sato, 2012). These data suggest the basic conditions of the DTMF and RLITMF are favorable for the stability of layered double hydroxides and their EOC controls.

The presence of active microbial communities in the TMFs could influence the geochemical stability of primary and secondary minerals and the mobility of EOCs. The greatest risk of instability is reductive dissolution of Fe-(hydr)oxide minerals by Fe-reducing bacteria and subsequently releasing adsorbed or co-precipitated EOCs (Khan et al., 2013; Wolfaardt et al., 2008). Ferrihydrite reduction by bacteria cultured from tailings samples was observed via accumulation of Fe(II) and magnetite (Bondici et al., 2016) and is a potential mechanism for EOC mobility. Conversely, certain cultures from the DTMF reduced molybdate and oxidized arsenite (Bondici et al., 2013) which suggests the potential for bioremediation to less toxic species. Sulfate-reducing bacteria present in the tailings (Bondici et al., 2013) could also reductively dissolve abundant sulfate minerals such as...
barite and gypsum (Campbell, Gallegos, & Landa, 2015). Dissolution of barite would be concerning as it is an important mineral for $^{226}$Ra sequestration. However, the risk of microbially-mediated instability is uncertain because of a lack of in situ data studying the biogeochemistry of the TMFs. It can be argued that this risk is low due to the cold temperatures, limiting availability of organic carbon and essential nutrients (e.g., phosphate and nitrate), and exposure to often toxic elements (e.g., As, Ni, and Cu).

The low temperature (0 to 12 °C) and permeability of the TMFs largely inhibit porewater-mineral interactions and thereby promote mineralogical stability of the tailings (Donahue & Hendry, 2003; Hayes et al., 2014; Moldovan et al., 2008; Shaw et al., 2011). The combination of these characteristics suggests that U tailings in the basin should be more geochemically stable than comparable acid-leached hydrometallurgical mill tailings in warmer climates or tailings disposed of by methods that are less controlled than the in-pit method with engineered hydrogeological surrounds.

4. Uranium mill raffinate neutralization and secondary mineral precipitation

4.1. Neutralization processes

All water brought into U mills is discharged as tailings slurry or eventually treated and discharged as clean effluent. The water stream requiring the most treatment is raffinate, because it contains the highest EOC concentrations and acidity (pH $\lessapprox 1$) compared to the other streams. Accordingly, the majority of the literature (including this review) addresses raffinate neutralization because it has the greatest impact on the tailings’ chemical composition. Each mill in the basin neutralizes raffinate slightly differently, but the neutralization processes all operate using the same principles: add a neutralizing agent to the raffinate to precipitate the dissolved constituents, separate the precipitates from the water, and discharge the precipitates to the TMF. The specific flow paths of the neutralization processes used in the three Athabasca Basin mills are summarized in Figure 8.

Each neutralization process starts with an initial mixing step that combines the specific streams to be neutralized. The first neutralization step increases the pH to $\approx 4$, with trivalent metals precipitating and anionic EOC species being complexed or co-precipitated. Intermediate pH ($\approx 7$) and high pH ($\approx 10$) neutralization steps precipitate the remaining dissolved species, primarily divalent metals and cationic EOC species. At varying points in each mill, the precipitated solids are separated from solution in vessels called thickeners and clarifiers. The thickened neutralized precipitates are pumped to their respective TMFs at specific pH set points, which vary from mill to mill (pH 10–11 at Rabbit Lake, pH 10.5 at Key Lake, and
pH 7 at McClean Lake) (Gomez et al., 2013; Mahoney et al., 2007; Moldovan et al., 2003) and strongly influence the equilibrium mineralogy and geochemistry of the tailings. At Rabbit Lake and Key Lake, the aqueous solution leaving the high pH thickener is amended with H₂SO₄ and BaCl₂ to bring the solution to pH 6.0 and precipitate residual ²²⁶Ra. This solution is discharged to the environment after chemical analysis of the water confirms it meets environmental regulations. At McClean Lake, the aqueous solution leaving the final thickener reports to the JEB TMF. The water from the JEB TMF is further treated in a water treatment plant prior to being discharged to the environment.

4.2. Aqueous chemistry of raffinate

The initial aqueous chemistry of the raffinate strongly influences the secondary precipitate mineralogy and the resulting solubility controls on
EOCs (e.g., surface complexation or co-precipitation). Raffinates are acidic (pH 1–2) and oxic (Eh = 400–750 mV) due to the addition of H₂SO₄ and oxidant in the leaching process. The addition of slaked lime to the raffinate supersaturates and precipitates metal-hydroxides at multiple pH steps. The most important factor influencing the resulting secondary precipitate mineralogy is the concentrations of metal(loid)s in the raffinate. Table 4 presents a summary of raffinate compositions from the three U mills in the basin. Raffinate composition varies between mills and between samples collected from the same mill at different times. These variations reflect the milling of different ore deposits and the heterogeneity of ores from the same deposit. Generalizing about the secondary mineralogy across the three mills is difficult due to this variability although general trends exist (discussed further in §4.3.1 to §4.3.7). As such, mill samples represent a snapshot in time rather than a representative sample of steady state operations.

As discussed above, the McArthur River ore processed at Key Lake is from a monometallic deposit while ores processed at McClean Lake and Rabbit Lake primarily originate from polymetallic deposits. Monometallic ores are more aluminosilicate rich (Table 1) and their effect on raffinate composition is indicated by the elevated concentrations of Al and Mg (Table 4). In contrast, Al and Mg concentrations are generally lower in raffinates from polymetallic ores (milled at Rabbit Lake and McClean Lake). Tailings from McArthur River ore are therefore enriched in secondary Al/Mg precipitates and can possess a different set of EOC mineralogical controls compared to tailings from polymetallic deposits. Iron(III) is the dominant species of Fe in mill raffinates (Table 4) due to the oxic conditions, although Fe(II) is also present. Concentrations of EOCs in raffinates from monometallic deposits are generally lower than those from polymetallic deposits. Key Lake, however, blends legacy polymetallic waste rock with monometallic ore, resulting in raffinate concentrations of As and Ni similar to those observed in McClean Lake and Rabbit Lake raffinates.

The speciation and oxidation state of EOCs in raffinate also influence the resulting EOC mineralogical controls (discussed in detail in §4.3). Minimal in situ oxidation state data are available, although laboratory-generated raffinates at McClean Lake contain As(V)/As(III) ratios between 2.5 and 5.3 (Langmuir et al., 1999). In lieu of in situ raffinate data, stability field diagrams can estimate equilibrium speciation and oxidation states for As, Mo, Se, and Ni during the neutralization process (Figure 9a–d). Such diagrams show EOCs generally remain in the same oxidation state throughout neutralization (As(V), Mo(VI), Se(IV), and Ni(II)) and the dominant aqueous species is pH dependent.
Table 4. Compositional data of uranium mill raffinates from the Athabasca Basin.

<table>
<thead>
<tr>
<th>Study</th>
<th>Site</th>
<th>Ore</th>
<th>pH</th>
<th>Eh (mV)</th>
<th>Al</th>
<th>As</th>
<th>As(III)</th>
<th>As(V)</th>
<th>Fe</th>
<th>Fe(II)</th>
<th>Mg</th>
<th>Mo</th>
<th>Ni</th>
<th>226Ra</th>
<th>Se</th>
<th>Si</th>
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<tr>
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<td>—</td>
<td>—</td>
<td>2429</td>
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<td>—</td>
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</tr>
<tr>
<td>1</td>
<td>KL</td>
<td>Millenium</td>
<td>1.46</td>
<td>629</td>
<td>1108</td>
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<td>—</td>
<td>—</td>
<td>1311</td>
<td>—</td>
<td>553</td>
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<td>63.6</td>
<td>—</td>
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<tr>
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<td>JEB</td>
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<td>400</td>
<td>434</td>
<td>366</td>
<td>72</td>
<td>294</td>
<td>430</td>
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<tr>
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<td>271</td>
<td>52.9</td>
<td>218</td>
<td>517</td>
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<td>43</td>
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<tr>
<td>6</td>
<td>ML</td>
<td>Sue C</td>
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<td>632</td>
<td>708</td>
<td>141</td>
<td>29</td>
<td>112</td>
<td>811</td>
<td>633</td>
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<td>ML</td>
<td>0.75</td>
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<td>393</td>
<td>275</td>
<td>52.5</td>
<td>222</td>
<td>950</td>
<td>419</td>
<td>61.7</td>
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<td>164</td>
<td>1.18</td>
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<tr>
<td>6</td>
<td>ML</td>
<td>Sue A + B</td>
<td>0.3</td>
<td>491</td>
<td>1690</td>
<td>2430</td>
<td>493</td>
<td>1937</td>
<td>1080</td>
<td>821</td>
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<td>26.7</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>6</td>
<td>ML</td>
<td>Cigar</td>
<td>0.4</td>
<td>588</td>
<td>4280</td>
<td>580</td>
<td>126</td>
<td>454</td>
<td>3260</td>
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<td>—</td>
</tr>
<tr>
<td>6</td>
<td>ML</td>
<td>Sue C + Cigar</td>
<td>0.34</td>
<td>—</td>
<td>1601</td>
<td>251</td>
<td>53</td>
<td>198</td>
<td>1423</td>
<td>1142</td>
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<td>—</td>
</tr>
<tr>
<td>6</td>
<td>ML</td>
<td>Midwest + Sue A + Sue B + Cigar</td>
<td>0.99</td>
<td>—</td>
<td>2491</td>
<td>6807</td>
<td>1080</td>
<td>5727</td>
<td>1492</td>
<td>1240</td>
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<td>27</td>
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<td>—</td>
</tr>
<tr>
<td>6</td>
<td>ML</td>
<td>Midwest + Sue A + Sue B</td>
<td>0.99</td>
<td>—</td>
<td>538</td>
<td>2940</td>
<td>9100</td>
<td>2620</td>
<td>6480</td>
<td>2870</td>
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<td>752</td>
<td>—</td>
<td>6990</td>
<td>5.86</td>
<td>—</td>
</tr>
</tbody>
</table>

Notes: KL, Key Lake; ML, McClean Lake; RL, Rabbit Lake. Dashes indicates the corresponding data were not available.

Study 1: Bissonnette et al., 2016; Study 2: Gomez et al., 2013; Study 3: Liu & Hendry, 2011; Study 4: Mahoney et al., 2007; Study 5: Moldovan & Hendry, 2005; Study 6: Langmuir et al., 1999.

aLaboratory generated samples are raffinates generated from laboratory-scale leaching experiments of the corresponding ore.

bThe concentration of these analytes were spiked to enable easier characterization of subsequent precipitates.
4.3. Secondary mineral precipitation

Secondary minerals constitute 10–20% of the total solid tailings mass, with the remaining mass comprised of leach residues. With the exception of gypsum, these precipitates are generally amorphous (i.e., no long-range order) or nanocrystalline because the rapid neutralization at high saturation conditions and ambient temperature and pressure inhibits crystallization (Demopoulos, 2009). This section describes the precipitation pathways characteristic of the major secondary precipitates and their respective controls on EOCs. The mineralogical controls on As, Se, Mo, Ni, and $^{226}$Ra during raffinate neutralization detailed in the proceeding section are summarized in Table 5.

4.3.1. Iron precipitation

Iron comprises 1–4% of the secondary precipitates by mass (Robertson et al., 2014, Robertson, Hendry, Essilfie-Dughan, & Chen, 2016). The
precipitation trend of Fe through the neutralization process is shown in Figure 10a. The speciation of Fe precipitates strongly depends on the molar ratio of Fe/As in the raffinate. The initial Fe/As ratio in raffinates from polymetallic deposits (McCLean Lake and Rabbit Lake) is frequently low (≈1–4), with the solution amended with Fe₂(SO₄)₃ to maintain Fe/As ratios > 3 (Langmuir et al., 1999; Mahoney et al., 2007; Moldovan & Hendry, 2005). The Fe/As ratios in raffinates from monometallic deposits (Key Lake) are frequently high (≈15–70) (Bissonnette et al., 2016; De Klerk, Jia, Daenzer, Gomez, & Demopoulos, 2012). At low Fe/As ratios, the ferric arsenate mineral system controls Fe concentrations beginning at ≈ pH 2 (De Klerk et al., 2012; Mahoney et al., 2007). Notably, the nomenclature of the ferric arsenate system in the literature is frequently ambiguous and poorly defined. Scorodite, poorly crystalline scorodite, and amorphous ferric arsenate have all been used to describe low-pH raffinate precipitates with minimal crystallinity and Fe/As ratios ≈ 1. Scorodite is a crystallized equilibrium endmember and does not precipitate directly in the neutralization process. The term poorly crystalline scorodite is a misnomer that adds to the confusion. This section uses the term ferric arsenate to describe these initial precipitates with Fe/As ratios ≈ 1 and poor crystallinity and uses scorodite to describe the crystalline mineral. As the Fe/As ratio approaches 8 (see more detailed discussion on the Fe-As system in §4.3.2), the dominant Fe phase shifts to ferrihydrite (Chen et al., 2009; Jia, Xu, Fang, & Demopoulos, 2006). Geochemical modeling shows 2-line ferrihydrite (effectively amorphous Fe(OH)₃) rapidly precipitates between pH 3.1 and 3.4 (Essilfie-Dughan et al., 2012; Moldovan & Hendry, 2005). XAS analyses

Table 5. Reported mineralogical controls of elements of concern in raffinate neutralization processes at the reviewed sites.

<table>
<thead>
<tr>
<th>Element</th>
<th>Rabbit Lake</th>
<th>Key Lake</th>
<th>McClean Lake</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
<td>Ferrihydrite (ads)*</td>
<td>Amorphous Al(OH)₃ (ads)</td>
<td>Fe₃(AsO₄)₂·2H₂O</td>
</tr>
<tr>
<td></td>
<td>Ca₄(OH)₂(AsO₄)₂·4H₂O</td>
<td>Ferrihydrite (ads)</td>
<td>Annabergite</td>
</tr>
<tr>
<td>Se</td>
<td>Ferrihydrite (ads)</td>
<td>Amorphous Al(OH)₃ (ads)</td>
<td>Fe₂(MoO₄)₃</td>
</tr>
<tr>
<td></td>
<td>Layered double hydroxide (ads)</td>
<td>CaMoO₄</td>
<td>CaMoO₄</td>
</tr>
<tr>
<td>Mo</td>
<td>Ferrihydrite (ads)</td>
<td>Fe₂(MoO₄)₃</td>
<td>NiMoO₄</td>
</tr>
<tr>
<td></td>
<td>Ni(OH)₂</td>
<td>CaMoO₄</td>
<td>Layered double hydroxide (ads)</td>
</tr>
<tr>
<td></td>
<td>Ni-Al hydroxide</td>
<td>NiMoO₄</td>
<td>Annabergite</td>
</tr>
<tr>
<td>Ni</td>
<td>Ni(OH)₂</td>
<td>Ferrihydrite (ads)</td>
<td>Cabrerite</td>
</tr>
<tr>
<td></td>
<td>Ni-Al hydroxide</td>
<td>Amorphous Al(OH)₃ (ads)</td>
<td>Ni(OH)₂</td>
</tr>
<tr>
<td></td>
<td>NiAl layered double hydroxide</td>
<td>NiMoO₄</td>
<td>NiMoO₄</td>
</tr>
<tr>
<td></td>
<td>Ni(OH)₂</td>
<td>Ferrihydrite</td>
<td>Barite</td>
</tr>
<tr>
<td>Ra</td>
<td>Barite</td>
<td>Barite</td>
<td>Barite</td>
</tr>
</tbody>
</table>

* “ads” denotes the element is controlled by adsorption.
confirm the presence of ferrihydrite in neutralization process samples (pH 3.2–4.2) (Bissonnette et al., 2016; Moldovan et al., 2003; Robertson et al., 2017). Microscale structures of ferrihydrite are also observed as ferrihydrite coatings on gypsum particles (possibly providing a nucleating surface for ferrihydrite) (Essilfie-Dughan et al., 2012). Iron(III) is the main Fe species precipitated at low pH; however, fougerite \([\text{(Fe(II), Mg)}_6\text{Fe(III)}_2\text{(OH)}_{18}\cdot\text{C}_1\text{H}_2\text{O}])\) is identified as a potential Fe(II) mineral phase at pH 3.2 in batch neutralization of McClean Lake raffinate (Mahoney et al., 2007). This study also posited that Fe(II) substitutes for Fe(III) in ferric arsenate in a sample collected at pH 2.2, although it is not clear how this was determined. Neutralization from pH 1 to 4 marks the end point of the low pH stage of the three mill processes although, as previously stated, the precipitates at McClean Lake are not separated from solution at this stage.

At ~ pH 5, <1 mg/L Fe(III) remains in solution and Fe(II) begins precipitating (although data for Fe(II) precipitation during mill raffinate neutralization are limited). At Key Lake, \(\text{H}_2\text{O}_2\) is added after the pH 4 step causing dissolved Fe(II) to oxidize to Fe(III) and precipitate as

![Figure 10. Aqueous precipitation trends of elements during the neutralization process: (a) Fe, (b) Al, (c) Mg, (d) As, (e) Ni, (f) Mo, and (g) Se. Data points were collected from multiple publications. When multiple datasets were available, the dataset name used in the publication is used in the legend. Due to the range in concentrations, values were normalized relative to the raffinate concentration (i.e., C/C_0).](image_url)
additional ferrihydrite. In the absence of an oxidant, Fe(II) might precipitate as an amorphous Fe(OH)$_2$ phase although the presence of this product is only supported by thermodynamic modeling (Robertson et al., 2014). X-ray diffraction (XRD) data of McClean Lake laboratory precipitates suggest a green rust phase initially precipitates at neutral pH (7.34), but then transforms to a ‘true ferrihydrite’ phase (Mahoney et al., 2007). In the same study, multiple solid samples between pH 6.09 and 7.4 that were initially olive green in color (representing Fe(II)) oxidized to Fe(III), although Fe(II) persisted in subsequent measurements (Mahoney et al., 2007). For how long the green rust-containing samples were exposed to oxidizing conditions before the XRD measurements were made is unclear, although it can be inferred that Fe(II) oxidizes over time in the oxic conditions of the TMFs. In Key Lake samples, pH 9.5 precipitates contain higher concentrations of Fe than precipitates that form at pH 4 (Bissonnette et al., 2016; Gomez et al., 2013). Gomez et al. (2013) identify ferrihydrite as the dominant Fe phase in the high pH precipitates. This could result from the pathway discussed above where H$_2$O$_2$ oxidizes Fe(II), resulting in rapid precipitation of Fe(III) as ferrihydrite. Minor amounts of Fe are also identified in Mg-Al hydrotalcite particles in the same samples. Separate analyses by Paikaray, Gomez, Jim Hendry, and Essilfie-Dughan (2014) support the presence of Mg-Al-Fe hydrotalcite precipitates. Conversely, Essilfie-Dughan et al. (2013) identify ferrihydrite as the only secondary Fe precipitate and (primary) pyrite as the only appreciable Fe(II) phase in Key Lake tailings. At Rabbit Lake, Pichler et al. (2001) identify ferrihydrite as the dominant phase at pH 10.5 (after washing gypsum and calcite from the sample), while Moldovan et al. (2003) identify ferrihydrite in pH 8.5 precipitates. Although these results do not exclude the possibility of solid phase Fe(II) secondary precipitates in the TMFs, Fe(II) is not a major species in the final neutralized precipitates.

The Fe mineralogy of the final precipitates is dominated by ferrihydrite in the neutralization process at all three mills. The lower terminal pH and Fe/As ratio at McClean Lake is, however, favorable for increased concentrations of ferric arsenate and eventual scorodite crystallization. Processes with elevated Al and Mg might increase the mass of Fe partitioned to LDHs, as observed at Key Lake. Layered double hydroxide-type precipitates are not explicitly observed in processes with low Al and Mg, suggesting Fe is predominantly ferrihydrite in Rabbit Lake precipitates.

### 4.3.2. Iron mineralogical controls on EOCs

Ferric arsenate precipitation and ferrihydrite adsorption of arsenate are major mechanisms of As sequestration (Essilfie-Dughan et al., 2013;
Distinguishing between the two phases is difficult because ferric arsenate precipitation and ferrihydrite adsorption occur as a continuum dependent on multiple variables (e.g., pH and initial Fe/As) (Paktunc, Dutrizac, & Gertsman, 2008). Acidic solutions with Fe/As ratios of 1–4 that are neutralized to pH 4.5 result in a mixed precipitate of ferric arsenate and As-adsorbed ferrihydrite rather than a single phase. Increasing the pH of ferric arsenate solids (Fe/As = 2) to pH 4.5 results in incongruent dissolution of 85% of the ferric arsenate and polymerization of ferrihydrite, providing additional surface sites for arsenate adsorption. Ferric arsenate is absent from precipitates with Fe/As $\geq 5$ at pH 4.5 (Paktunc et al., 2008). Chen et al. (2009) synthesized ferric arsenate compounds (Fe/As = 4) and show a distinct change in the coordination environment (As-Fe coordination number decreasing from 3.9 to 1.6) as the pH increases from pH 4 to 8. This suggests ferric arsenate transforms to As-adsorbed ferrihydrite, as observed by Paktunc et al. (2008). A two-stage (pH 4 and 8) laboratory neutralization of a solution with an Fe/As ratio of 4 indicated 57% of the solid phase As is associated with ferric arsenate and the remainder adsorbs to ferrihydrite at pH 8 (De Klerk et al., 2012).

Greater than 99% of As in the raffinate is precipitated by pH 3 (Figure 10d). The McClean Lake literature shows As concentrations are predominantly controlled by co-precipitation of Fe(III) and As(V) as ferric arsenate, followed by precipitation of ferrihydrite and subsequent adsorption of As(V) with increasing pH (Chen et al., 2009; Frey, Rowson, Hughes, Rinas, & Warner, 2010; Langmuir et al., 1999; Mahoney et al., 2005, Mahoney et al., 2007). The Fe/As ratio in the raffinate strongly influences the final As concentrations in the tailings porewater and is a primary focus of operations at McClean Lake. An Fe/As ratio $\geq 3$–4 generally results in long-term As concentrations of 1–2 mg/L and is controlled by adding Fe$_2$(SO$_4$)$_3$ to the raffinate solution (Langmuir et al., 1999). In batch neutralizations of various McClean Lake raffinates, ferric arsenate comprises 6.5% of the precipitates at pH 2.2 and 4.4% of the precipitates at pH 7.3 (Mahoney et al., 2007). Ferrihydrite is not detected in these samples until pH 5.3, when it comprises 2.4% of the precipitates. At pH 7.3, the precipitates are 3.7% ferrihydrite (Mahoney et al., 2007). This shows a decrease in ferric arsenate and an increase in ferrihydrite with pH. In a EXAFS study by Chen et al. (2009), the As-Fe coordination number in McClean Lake raffinate precipitates decreases from 3.3 to 2.7 as the pH increases from $\sim$2 to 6 (solid phase Fe/As = 1.1 to 2.9), indicating that an increasing fraction of As adsorbs to ferrihydrite rather than co-precipitating as ferric arsenate. These results can be linked to the batch experiments of Mahoney et al. (2007), in which the ferrihydrite
concentration increases with pH, and suggest at least two Fe phases control As concentrations during raffinate neutralization.

At Key Lake, the As distribution to Fe-phases in two samples collected from the Se-Mo thickener (\(\sim \text{pH} 4\)) is approximately 75% adsorbed to ferrihydrite and 25% ferric arsenate (Bissonnette, 2015; Robertson et al., 2017). The raffinate Fe/As ratios for these samples are 15.1 and 47.1, while the solid phase Fe/As ratios are 13.1 and 28.2, respectively. Synthetic and field samples from Key Lake that contain ferric arsenate at \(\sim \text{pH} 4\) are devoid of ferric arsenate once neutralized to pH 10.5 (Robertson et al., 2017). In situ tailings samples from the DTMF show As-adsorbed ferrihydrite is the dominant Fe sequestration mechanism, even in samples with an Fe/As ratio less than 4 (Essilfie-Dughan et al., 2013). The lack of ferric arsenate in a system where the Fe/As ratio is favorable for its precipitation indicates that ferric arsenate is not stable at increasingly basic pH; rather, the Fe-As system is controlled by ferrihydrite under these conditions. This agrees with the conclusions of Paktunc et al. (2008) discussed earlier.

Pichler et al. (2001) suggest As associates with amorphous Fe-oxyhydroxides at pH 10.5 in the Rabbit Lake neutralization process, with only minor evidence for a ferric arsenate phase. They also characterize three particle types: As-Fe rich, Al-Ni-As-Fe rich, and Ni-As-Fe rich. Subsequent Rabbit Lake samples collected by Moldovan et al. (2003) at pH 3.5 and 8.5 and an Fe/As ratio of 7.4 show As adsorbed to ferrihydrite is the dominant As-bearing phase. Subsequent geochemical modeling of the same system, however, indicates that concentrations of Fe at low pH are affected by precipitation of both ferrihydrite and ferric arsenate (Moldovan & Hendry, 2005). These results are in general agreement with the pH dependence of the Fe-As pathways observed in McClean Lake and Key Lake neutralization processes.

Based on the observations and conclusions from the three mills, we propose a pathway for the Fe-As system during raffinate neutralization that explains differences between the Fe-As systems at McClean Lake and Key/Rabbit Lake. A large range of Fe/As ratios (0.3 to 68.9) are reported for raffinates (Gomez et al., 2013; Langmuir et al., 1999). The mass of ferric arsenate precipitated during the first neutralization step is dependent on the Fe/As ratio of the initial solution. Specifically, a low Fe/As ratio will result in more ferric arsenate relative to As-adsorbed ferrihydrite (as observed at McClean Lake), and vice versa for solutions with high Fe/As ratios (as observed at Key Lake). Raffinate is rapidly neutralized to pH \(\sim 4\) in the first neutralization step. Laboratory and modeling studies of raffinate neutralization show that ferric arsenate precipitation begins at pH 2–3 (Mahoney et al., 2007; Moldovan & Hendry, 2005). Given an arbitrary volume of raffinate that begins mixing with slaked lime, rapid ferric arsenate
co-precipitation occurs during the transient period when the pH of the solution sweeps through pH 2–3. As that volume of solution in the reactor reaches the target pH of 4, ferrihydrite begins precipitating and simultaneously adsorbs As (if aqueous Fe and As are still available). The ferric arsenate that precipitated during the transient pH period remains stable. This specific volume of solution remains at pH 4 for the residence time of the reactor (on the order of 1–3 h depending on flow rates). The presence of ferric arsenate in solutions with high Fe/As ratios is potentially caused by this brief period of disequilibrium as the incoming solution is raised to its target pH. As the low pH slurry (pH 4) is pumped to the next neutralization step (pH 6.5–7.5), ferric arsenate can transform to As-adsorbed ferrihydrite. At McClean Lake, this transformation is halted at the terminal pH of 7, resulting in a mixture of ferric arsenate and As-adsorbed ferrihydrite. At Key Lake and Rabbit Lake, the transformation continues in the next neutralization step as the pH increases to 10.5, resulting in ferrihydrite being the primary Fe control on As in these tailings regardless of the Fe/As ratio.

Essilfie-Dughan et al. (2012) report the nucleation and growth of ferrihydrite coatings on gypsum particles at Key Lake. Their results show EOC controls evolve as the precipitates move through the neutralization process. Gypsum particles rapidly precipitate at the beginning of the process. Gypsum particle surfaces provide a nucleation sites for ferrihydrite, which provides adsorption sites. The ferrihydrite-coated gypsum particles from Essilfie-Dughan et al. (2012) contain elevated concentrations of adsorbed As (and likely Se and Mo) on their inner section, representing initial precipitation at low pH. The ferrihydrite coating grows as the pH increases, but As concentrations decrease in the outer sections of the coating. Coated gypsum particles are not likely to be dominant EOC control mechanisms; however, these structures demonstrate mineralogical controls evolving with pH.

Aluminum substitution into the structure of ferrihydrite and ferric arsenate is observed in neutralized precipitates and influences As solubility (Mahoney et al., 2005; Robertson et al., 2016). Impurities within ferrihydrite are common in natural systems (Adra et al., 2013). Studies of acid mine drainage sites (which are mechanistically similar to these neutralization processes) note As adsorption on Al-ferrihydrite and examine the change in reactivity of impure ferrihydrite (Adra et al., 2013, Adra, Morin, Ona-Nguema, & Brest, 2016). When the Al/Fe ratio of ferrihydrite increases, the As(V) adsorption density increases relative to pure ferrihydrite, suggesting both inner- and outer-sphere As surface complexes form on Al-ferrihydrite (Adra et al., 2016). However, these sorption experiments were conducted at pH 6.5, so whether the additional As outer-sphere
complexes will remain stable in basic TMFs is uncertain. Also unclear is if the number of inner-sphere surface complexes in Al-ferrihydrite decreases; however, the specific surface area of the sorbent decreases, suggesting decreased inner-sphere adsorption capacity (Adra et al., 2016). The adsorption capacity and stability of Al-ferrihydrite in the neutralized raffinate precipitates with respect to EOCs could be an area of future study.

Studies of mineralogical controls of dissolved Ni are less prominent than As and much of the data is only qualitative or semi-quantitative (Donahue et al., 2000; Essilfie-Dughan et al., 2012; Gomez, Hendry, Hossain, Das, & Elouatik, 2013; Langmuir et al., 1999; Mahoney et al., 2007; Pichler et al., 2001; Robertson et al., 2017; Shaw et al., 2011). Nickel precipitation occurs primarily in the neutral to basic pH neutralization stages beginning at pH $\approx 5$, with complete precipitation occurring at pH $> 8$ (Figure 10e) (Essilfie-Dughan et al., 2012; Moldovan & Hendry, 2005). Adsorption of Ni to ferrihydrite occurs above pH 5 (Essilfie-Dughan et al., 2012). However, batch neutralizations of McClean Lake raffinate show the concentration of Ni is independent of the Fe/Ni ratio, suggesting other elements are more important as mineralogical controls for Ni (Mahoney et al., 2007). Distinct Ni-Fe mineralogical controls are not evident in Rabbit Lake precipitates; rather, minor associations of Ni and Fe are overshadowed by Ni-Al associations (Pichler et al., 2001). Similarly, an EXAFS study of Key Lake samples (synthetic and in situ) did not identify Fe controls on Ni. Instead, Al is the dominant mineralogical control of Ni (discussed further in §4.3.4) (Robertson et al., 2017). When Al is not abundant, however, ferrihydrite can adsorb Ni at basic pH provided the surface sites are not already saturated.

Molybdenum is primarily removed from raffinate by outer-sphere complexation with ferrihydrite at low pH neutralization stages (pH 3.5 to 4; Figure 10f) (Bissonnette, 2015; Blanchard et al., 2015; Essilfie-Dughan et al., 2011; Gomez et al., 2013; Hayes et al., 2014). Bissonnette et al. (2016) determined that 84 to 100% of the solid phase Mo is adsorbed to ferrihydrite, and the remainder is ferrimolybdite ($\text{Fe}_2(\text{MoO}_4)_3$). Residual aqueous Mo present after the low pH neutralization step precipitates as NiMoO$_4$ and adsorbs to ferrihydrite, although the actual solid phase concentration of Mo at this stage is minor ($< 0.003\%$) because most Mo precipitates at pH 3.5–4 (Bissonnette et al., 2016). At McClean Lake, the mineralogical controls of Mo have been studied in tailings but not directly in the neutralization process (Blanchard et al., 2015; Hayes et al., 2014). The speciation of solid phase Mo is more variable in McClean Lake tailings samples compared to Key Lake; 17–55\% adsorbs to ferrihydrite and 25–60\% precipitates as ferrimolybdite at a final pH of 7–8. The increase in ferrimolybdite at McClean Lake compared to Key Lake might be due to differences in the
terminal pH at the two mills, much like the transformation of ferric arsenate to As-adsorbed ferrihydrite as the terminal pH increases above 8.

Literature on the removal of Se during the neutralization processes is lacking. Selenium precipitates at low pH (Figure 10g), most likely through inner- and outer-sphere adsorption to ferrihydrite (Bissonnette et al., 2016; Gomez et al., 2013; Lieu et al., 2010; Robertson et al., 2014, Robertson et al., 2016). This is supported by elemental maps from synthetic Key Lake precipitates that show an association of Se to an amorphous Al-Fe(OH)₃ phase (Robertson et al., 2016). The extent of Se adsorption with ferrihydrite depends on the oxidation state of Se; Se(IV) has a stronger affinity to ferrihydrite than Se(VI) (Das et al., 2013; Su & Suarez, 2000). Selenium speciation at low pH neutralization steps has not been reported; however, stability field diagrams suggest Se(IV) is the dominant species at pH 4 (Figure 9c). This agrees with the observation of Se(IV) as the primary Se species in the DTMF, although Se(VI) is also observed (Essilfie-Dughan, Hendry, Pickering, George, & Kotzer, 2010).

Barium chloride is added to the neutralization processes to precipitate ²²⁶Ra (discussed in §4.3.7); however, adsorption of ²²⁶Ra to ferrihydrite is also a major sequestration mechanism (Liu & Hendry, 2011). Sequential extractions show that 73% of solid phase ²²⁶Ra in neutralized precipitates is associated with amorphous Fe(OH)₃ (Liu & Hendry, 2011). In the absence of BaCl₂, ²²⁶Ra activities decrease from 150 Bq/L (pH 1.2) to 1 Bq/L (pH 11) with the majority precipitating after pH 6 (Liu & Hendry, 2011). Radium adsorption by ferrihydrite reaches a maximum at pH 8 and greater (Sajih et al., 2014), and shows the relative importance of Fe in the sequestration of ²²⁶Ra in neutral to basic TMFs. However, ferrihydrite adsorption is not enough to decrease ²²⁶Ra activities below environmental release limits; BaCl₂ addition is required.

A final point to consider is the pH dependence of electrostatically-controlled (outer-sphere) surface complexes with ferrihydrite. Ferrihydrite adsorption of oxyanions and cations is controlled by the point of zero charge of ferrihydrite (pH 7.9–8.2) (Dzombak & Morel, 1990). At low pH, oxyanions are attracted to the positively charged surface: AsO₄³⁻ adsorbs strongly at low pH until pH 9 but adsorption reaches a minimum at pH 13, and SeO₄²⁻ adsorbs strongly at low pH until pH 4 and then adsorption decreases to zero after pH 7.5. Conversely, Ni adsorbs to ferrihydrite at pH 6 and reaches a maximum at pH 8 (Dzombak & Morel, 1990).

### 4.3.3. Aluminum and magnesium precipitation

Both Al and Mg each comprise 1–5% of the secondary precipitates by mass in Key Lake tailings (Robertson et al., 2014, Robertson et al., 2016). Raffinates processed at Key Lake contain much higher concentrations of Al
compared to raffinates processed at McClean Lake and Rabbit Lake due to mineralogical differences in the ores used. Measured Al concentrations in mill samples range from 1,635 to 3,510 mg/L at Key Lake and 200 to 498 mg/L at McClean Lake and Rabbit Lake (Table 4; although laboratory raffinates generated from hypothetical ore blends result in higher Al concentrations). This large difference influences the Al mineralogy in the secondary precipitates.

The majority of Al precipitation occurs between pH 3.5 and 5.0 (Figure 10b). Robertson et al. (2016) characterized the evolution of Al secondary mineral precipitates at Key Lake. Scanning transmission electron microscopy and Al K-edge X-ray absorption near edge structure (XANES) analyses show an amorphous Al phase in pH 4.0 precipitates. The Al and SO$_4$ stoichiometry is consistent with hydrobasaluminite (Al$_4$SO$_4$(OH)$_{10}$·12–36H$_2$O) but is referred to as AlOHSO$_4$. Some debate exists in the acid mine drainage literature regarding AlOHSO$_4$-type phase characterization because thermodynamic models predict Al remains soluble below pH 5 and precipitates as Al(OH)$_3$ otherwise (Nordstrom & Ball, 1986). However, SO$_4^{2-}$-rich media (such as raffinate) might decrease Al solubility, causing AlOHSO$_4$ phases to precipitate before Al(OH)$_3$/gibbsite as predicted by thermodynamic models (Bertsch & Parker, 1996). In addition to AlOHSO$_4$, substitution of Al into the structure of co-precipitated ferrihydrite is observed at pH 4.0 (Robertson et al., 2016). Aluminum that does not precipitate at the low pH stage precipitates at pH 6.5 as a mixture of amorphous Al(OH)$_3$ and AlOHSO$_4$. The solubility of AlOHSO$_4$ increases with pH and could transform to amorphous Al(OH)$_3$ according to (Adams & Rawajfih, 1977)

$$Al_4(OH)_{10}SO_4 + 2OH^-\rightarrow 4Al(OH)_3 + SO_4^{2-}. \quad (9)$$

At pH 9.5, hydrotalcite or, more generally, LDHs are identified as the dominant Al-phase (61–70%), with the remaining Al precipitating as amorphous Al(OH)$_3$. Paikaray et al. (2014) suggest Mg$^{2+}$ substitutes into the existing Al(OH)$_3$ precipitates as the pH increases to pH > 8, transforming Al(OH)$_3$ to LDHs according to

$$Al(OH)_3 + 2Mg^{2+} + 3OH^- + A^{n-} + xH_2O \rightarrow Mg_2Al(OH)_6A \cdot xH_2O, \quad (10)$$

where $A^{n-}$ represents a model anion.

Magnesium precipitation is greatest at pH 8 (Figure 10c) and is evidence of LDH precipitation. Robertson et al. (2016) suggest that residual AlOHSO$_4$ at high pH transforms to LDHs by a similar mechanism, with SO$_4^{2-}$-incorporating into the LDH interlayer. This is consistent with the final mineralogy of the secondary precipitates at pH 10.5, in which LDHs
and amorphous Al(OH)$_3$ are the dominant phases and minimal to no hydrobasaluminite is detected (Robertson et al., 2016).

AlOHSO$_4$ (referred to as a poorly crystalline hydrobasaluminite) is identified in laboratory neutralization experiments of McClean Lake raffinates conducted at pH 3.2–7.3 (Langmuir et al., 1999; Mahoney et al., 2005, Mahoney et al., 2007). Although the Al and Mg concentrations in the initial raffinates in McClean Lake studies are unclear, the data suggest the aqueous concentrations of each element in the raffinate is 200 to 420 mg/L (an order of magnitude lower than concentrations measured at Key Lake) (Mahoney et al., 2007). Because the McClean Lake neutralization process only neutralizes the tailings to pH 7–8 and the raffinate concentrations of Al and Mg are lower than Key Lake, LDHs are likely not as abundant (if present at all) in the JEB TMF as in the DTMF. While LDHs can precipitate at neutral pH, the transformation mechanism of Mg$^{2+}$ substitution into Al(OH)$_3$ is not observed until pH > 8. Rather, a stoichiometric variation of hydrated Al$_4$SO$_4$(OH)$_{10}$ and/or amorphous Al(OH)$_3$ likely persists in the JEB TMF. Mahoney et al. (2005) also observe Al substitution in ferri arsenate at low pH, consistent with the Al substitution in ferrihydrite at Key Lake.

Aluminum precipitation at Rabbit Lake is not well documented. Geochemical modeling by Moldovan and Hendry (2005) suggests amorphous Al(OH)$_3$ and gibbsite are the major Al precipitates, but might not be the only Al phases. Pichler et al. (2001) identify a Ni-Al hydroxide phase low in S content in neutralized precipitates (pH 10.5), suggesting AlOHSO$_4$ might not be present in the final tailings at Rabbit Lake. The Ni-Al hydroxide phase is also possibly an LDH given the Ni(II)/Al(III) ratio is $\simeq$ 1 and the basic pH comparable to the Key Lake tailings. Although Mg was not measured in this sample, it is likely present and might associate with this Ni-Al hydroxide phase to form an LDH, thereby increasing the M(II)/M(III) ratio of the phase to values required for LDH formation. X-ray diffraction patterns of these samples rule out gibbsite precipitation, suggesting any Al(OH)$_3$ present is amorphous.

### 4.3.4. Aluminum and magnesium mineralogical controls on EOCs

The influence of Al and Mg minerals on EOCs in Athabasca Basin tailings was not investigated prior to 2013. However, adsorption properties of amorphous Al(OH)$_3$ are well defined in other fields (Arai, Elzinga, & Sparks, 2001; Foster & Kim, 2014; Goldberg & Johnston, 2001; Kappen & Webb, 2013) and suggest Al could exert mineralogical controls on EOCs in these tailings. Amorphous Al(OH)$_3$ possesses similar adsorptive characteristics to ferrihydrite but is a weaker adsorbent (Goldberg, 2002). Arsenic(V) adsorption with amorphous Al(OH)$_3$ occurs through bidentate-binuclear
corner-sharing linkages (Foster & Kim, 2014). This complex is strongly resistant to phosphate exchange, suggesting it is relatively stable (Burke et al., 2013). Layered double hydroxides can adsorb oxyanions to both surfaces and interlayers (Das, Das, Dash, & Parida, 2002; Frost, Musumeci, Martens, Adebayo, & Bouzaid, 2005; Goh et al., 2008). Unlike the Al-oxyhydroxide surface complex, As adsorbed on LDHs is moderately phosphate-exchangeable, which might indicate a degree of instability if chemical conditions change (Burke et al., 2013).

Most studies of EOC controls by Al and Mg minerals originate from Key Lake (Bissonnette et al., 2016; Gomez et al., 2013; Robertson et al., 2016, Robertson et al., 2017). Aluminum controls 5–25% of the total As at low pH stages (pH 4) through adsorption by amorphous AlOHSO\textsubscript{4} (Bissonnette et al., 2016; Robertson et al., 2017). Arsenic remaining in solution after the low pH stage forms adsorption complexes with amorphous Al(OH)\textsubscript{3} and LDHs at pH 9.5. Between 41 and 71% of the adsorbed As in pH 9.5 precipitates is associated with these Al phases (Bissonnette et al., 2016; Robertson et al., 2017). In a final tailings slurry sample collected at pH 10.9, 59% of solid phase As was associated with Al phases (amorphous Al(OH)\textsubscript{3} and LDHs) and the remainder with Fe phases (Robertson et al., 2017). A possible explanation for this distribution is the higher point of zero charge of Al-hydroxides relative to Fe-hydroxides, resulting in As desorbing from the ferrihydrite surface and re-adsorbing to Al phases during the pH adjustment (Adra et al., 2016). The dissolution of ferric arsenate could also be a source of As adsorbing to Al phases. Robertson et al. (2017) report amorphous Al(OH)\textsubscript{3} and Ni-Al LDH surface precipitates as mineralogical controls of Ni. This differs from the findings of other studies of laboratory and \textit{in situ} tailings that suggest adsorption to ferrihydrite (discussed in §4.3.2) or precipitation of Ni(OH)\textsubscript{2} (theophrastite) and that Ni-arsenates are the dominant controls of Ni (Essilfie-Dughan et al., 2012; Langmuir et al., 1999; Mahoney et al., 2007). We attribute this difference to the elevated concentrations of Al in the Key Lake raffinate, which promotes Al controls on Ni.

Robertson et al. (2016) studied the adsorption characteristics of As(V), Mo(VI), and Se(IV) on LDH-rich precipitates at pH 9.6. With each element isolated, the adsorption capacities of the LDH-rich precipitate are 0.91 mmol/g (As(V)), 0.67 mmol/g (Mo(VI)), and 0.62 mmol/g (Se(IV)). These adsorption capacities are the same order of magnitude as those for ferrihydrite. In a competitive system (As, Se, and Mo competing for adsorption sites), the adsorption capacities of each element are 0.73 mmol/g (As(V)), 0.57 mmol/g (Mo(VI)), and 0.16 mmol/g (Se(IV)), representing decreases relative to the isolated experiments. These experiments demonstrate the type of LDH precipitated at Key Lake can adsorb residual EOCs at high
pH and potentially sequester any release of EOCs in the DTMF (e.g., in the event of Fe reduction or sulfide mineral oxidation). However, stability tests of these adsorption controls were not performed and the mechanism of EOC uptake remains unclear.

Pichler et al. (2001) note that a Ni-Al hydroxide precipitate (pH 10.5) at Rabbit Lake is often associated with As-rich ferrihydrite. They identify a particle with equimolar concentrations of Ni and Al, suggesting the presence of a mixed-metal LDH consistent with that observed at Key Lake (Pichler et al., 2001). However, they present no evidence of Al controls on As. Geochemical modeling of Rabbit Lake neutralization by Moldovan and Hendry (2005) includes amorphous Al(OH)$_3$ adsorption of As; ferrihydrite adsorption controls As adsorption with only 0.2% of the As in the model adsorbed by amorphous Al(OH)$_3$.

Laboratory neutralization tests of McClean Lake raffinate by Langmuir et al. (1999) did not explicitly identify Al controls on EOCs; rather, they observe Al associations with ferric arsenate. Amorphous AlOHSO$_4$ phases are also characterized, although EOC controls are not reported. Layered double hydroxides are not observed in McClean Lake tailings, likely due to the terminal pH ($\approx$ 7) being below the pH at which LDHs precipitate (generally pH $>$ 8) (Paikaray et al., 2014). As previously mentioned, several samples examined by XRD indicate Ni and Mg in the form of cabrerite during batch neutralization of potential McClean Lake raffinates (Langmuir et al., 1999). Four major peaks of crystalline cabrerite are identified in all tailings samples considered in this work, but none in any other XRD analyses of in situ tailings from the basin. The formation of cabrerite in these batch samples might be a product of laboratory conditions. Langmuir et al. (1999) suggest cabrerite only precipitates around pH 5 to 6 when concentrations of Fe are low and Ni is abundant. When Fe concentrations are high, more ferric arsenate precipitates, resulting in lower concentrations of AsO$_4^{3-}$ and undersaturated conditions for cabrerite. A subsequent study of laboratory neutralized tailings identified a highly disordered Ni-Mg hydroxide phase at higher pH values (Mahoney et al., 2007).

4.3.5. Calcium precipitation
Calcium comprises 10–20% of the final neutralized precipitates at Key Lake (and likely at the other mills) and is mostly present in gypsum (CaSO$_4$·2H$_2$O) (Bissonnette et al., 2016; Robertson et al., 2014). Mixing SO$_4^{2-}$-rich raffinate with slaked lime precipitates gypsum in the neutralization process (Langmuir et al., 1999). The majority of gypsum precipitates between pH 1.0 and 4.0, and lesser masses continue to precipitate as lime is added to the terminal pH (Essilfie-Dughan et al., 2012). Calcite (CaCO$_3$) precipitates at higher pH stages at Key Lake and Rabbit Lake and is a
minor Ca phase (Pichler et al., 2001; Robertson et al., 2014). Calcite, aragonite, and dolomite were identified at neutral pH in the JEB TMF, where it is hypothesized that gypsum dissolution facilitates carbonate precipitation (Blanchard et al., 2016). Excess aqueous Ca can exert solubility controls on As and Mo, as discussed in §4.3.6.

4.3.6. Calcium mineralogical controls on EOCs

Due to the excess amount of Ca added during raffinate neutralization, calcium minerals are often proposed as mineralogical controls for arsenate and molybdate. Geochemical models predict supersaturation of Ca-arsenates and Ca-molybdates in these neutralization processes; however, direct evidence of Ca mineral phases is limited. Samples from the RLITMF show associations between Ca, As, Ni, and S (Donahue et al., 2000). Tailings samples with Fe/As ratios < 2 indicate evidence of an amorphous Ca-arsenate phase (Donahue & Hendry, 2003). This phase also contains the greatest mass of water soluble As, suggesting a lack of long-term stability. Saturation calculations of pore fluids from the RLITMF and DTMF show Ca-arsenate phases are either over- or under-saturated depending on the thermodynamic data used; however, Ca₄(OH)₂(AsO₄)₂·4H₂O is the most likely phase based on the basic pH (~10) and the Ca/As ratio of the samples (Donahue & Hendry, 2003; Shaw et al., 2011). A parallel study of RLITMF samples (Ca/As ≈ 2.2) hypothesizes the presence of Ca-arsenates; however, Ca-arsenates are not observed in scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy dispersive X-ray spectroscopy (EDX), or XRD analyses of these samples (Pichler et al., 2001). Additionally, XANES studies of fresh precipitates or aged tailings samples from all three TMFs do not indicate Ca-arsenate phases (Bissonnette et al., 2016; Chen et al., 2009; Essilfie-Dughan et al., 2012, Essilfie-Dughan et al., 2013; Moldovan et al., 2003; Robertson et al., 2017; Warner & Rowson, 2007). Calcium arsenate precipitation cannot be ruled out based on these data alone; however, they are not a major mineral phase in the tailings.

Powellite (CaMoO₄) is predicted to precipitate in the TMFs based on thermodynamic calculations (Blanchard et al., 2015; Shaw et al., 2011). A combination of geochemical, Mo K-edge XANES, and XRD data from the JEB TMF confirm the presence of powellite (10 to 40% of Mo-bearing phases) (Blanchard et al., 2015, Blanchard et al., 2016; Hayes et al., 2014). Blanchard et al. (2015) identify increased powellite precipitation over the course of five years; core samples from the same location and depth show an increase in powellite content from 10–25 at% and a corresponding decrease in the aqueous Mo concentrations relative to younger tailings. Powellite precipitation could occur from gradual dissolution of
ferrimolybdite or mobilization of outer-sphere Mo surface complexes in the tailings, although precipitation is rate limited due to the low hydraulic conductivity and low temperature of the TMF (Hayes et al., 2014). Samples from the bottom of the JEB TMF collected at the same position five years apart show minimal change in powellite concentrations, suggesting powellite is stable under the current TMF conditions (Blanchard et al., 2015).

Powellite is observed in the DTMF, although at lower concentrations compared to the JEB TMF. An increasing trend of powellite precipitation with time is not observed in the DTMF; rather, powellite concentrations tend to increase when Fe/Mo and Ni/Mo ratios decrease and Ca and Mo concentrations are high (Essilfie-Dughan et al., 2011). Aqueous Mo concentration profiles with depth in the DTMF determined in sampling campaigns in 2005 and 2009 are relatively consistent; Mo porewater concentrations of young tailings do not deviate with time to the same extent as observed in the JEB TMF (Shaw et al., 2011). The JEB TMF samples contain significantly more Mo (mean = 164 μg/g, median = 118 μg/g) (Blanchard et al., 2015) than DTMF samples (mean = 68 μg/g, median = 77 μg/g) (Essilfie-Dughan et al., 2011), which could partially explain the difference in powellite concentrations. Powellite concentrations are negatively correlated with the Fe/Mo ratio of tailings samples in both the JEB TMF and DTMF (Blanchard et al., 2015; Essilfie-Dughan et al., 2011). These results suggest that both sufficient time and low Fe/Mo ratios are required for powellite to precipitate.

4.3.7. Other mineralogical controls on EOCs

Early studies observed annabergite in low pH precipitates of laboratory raffinates containing high concentrations of Ni and As (Mahoney et al., 2007). Conversely, annabergite supersaturation does not occur at any point during the neutralization process. Bulk XAS studies have not identified annabergite in any tailings sample. In addition, concentrations of Ni in mill neutralization samples at Rabbit Lake indicate Ni precipitates independently from As and does not precipitate until pH > 5, suggesting annabergite precipitation is not a dominant process during neutralization (Moldovan & Hendry, 2005).

Theophrastite precipitation at pH 7 to 8 is a suggested mineralogical control of Ni in multiple studies (Bissonnette, 2015; Essilfie-Dughan et al., 2012; Mahoney et al., 2007; Shaw et al., 2011). The lack of crystalline phases in XRD data of laboratory and field samples, however, precludes the presence of theophrastite despite the relative abundance of Ni in the raffinate (De Klerk et al., 2012). A Ni phase not associated with other metals has been observed in McClean Lake laboratory samples, suggesting an amorphous Ni(OH)₂ phase could precipitate (Mahoney et al., 2007). However, Ni
removal is greater in the presence of other precipitates and Ni(OH)$_2$ precipitation alone cannot explain the decrease in Ni concentrations during raffinate neutralization, suggesting adsorption or precipitation of other Ni phases occurs (Mahoney et al., 2007). Nickel XAS measurements of high pH (~10) samples did not identify pure phase Ni(OH)$_2$; Ni was only associated with Al (Robertson et al., 2017). As such, Ni is likely dominantly coordinated with other metal phases rather than as pure Ni(OH)$_2$.

NiMoO$_4$ is observed in DTMF tailings and is dependent on the ore composition (Essilfie-Dughan et al., 2011). Tailings derived from the Deilmann deposit are elevated in Ni and Mo concentrations and contain higher concentrations of NiMoO$_4$ (~45–95% of the total Mo) versus Mo-adsorbed ferrihydrite; tailings derived from McArthur River contain low concentrations of Ni and Mo relative to Fe and contain higher proportions of Mo-adsorbed ferrihydrite versus NiMoO$_4$ (~26–29% of the total Mo) (Essilfie-Dughan et al., 2011). Bissonnette et al. (2016) note 20% of the Mo precipitates as NiMoO$_4$ in high-pH samples from the Key Lake neutralization process. A similar study could not identify α-NiMoO$_4$ in JEB TMF samples, but suggests β-NiMoO$_4$ could exist instead (Hayes et al., 2014). The same study reports associations of Ni and Mo in μXRF data bit did not determine if the phase is primary or secondary in nature.

Barium chloride is added in all three neutralization processes to co-precipitate $^{226}$Ra with barite (Eq. 11), according to

$$Ba^{2+} + Ra^{2+} + SO_4^{2-} \rightarrow (Ba, Ra)SO_4.$$ (11)

Both Ra and Ba are divalent cations in solution with nearly identical hydrated ionic radii (Liu & Hendry, 2011). Excess SO$_4^{2-}$ in the raffinate ensures Eq. 11 is strongly favored. Storing $^{226}$Ra as a solid solution in barite is desirable because barite is sparingly soluble (log$K_{sp} = -9.97$) and should be stable under the conditions of the tailings (Langmuir & Melchior, 1985). Goulden (1997) analyzed tailings from the decommissioned Cluff Lake mill and concludes that barite is a major solubility control with respect to $^{226}$Ra. Liu and Hendry (2011) titrated raffinate from the Key Lake process (with and without BaCl$_2$) to systematically determine the fate of $^{226}$Ra during raffinate neutralization. The reported activity of $^{226}$Ra in their raffinate sample is 150 Bq/L; activities of $^{226}$Ra in the Key Lake treated effluent range from 0.02 to 0.07 Bq/L, demonstrating the effectiveness of the mineralogical controls of $^{226}$Ra during neutralization. However, Liu and Hendry (2011) determined that only 17% of $^{226}$Ra is associated with barite, while 73% is associated with Fe-oxides (e.g., ferrihydrite), 3.7% with soluble phases (likely gypsum), and the remainder with minor phases. However, $^{226}$Ra adsorption by ferrihydrite is reversible (Sajih et al., 2014) and in the event of ferrihydrite transformation or dissolution,
$^{226}$Ra would be mobilized. The saturated state of the porewater with respect to barite would likely ensure $^{226}$Ra would be quickly sequestered as (Ba,Ra)SO$_4$, suggesting barite is important in regulating the long-term geochemical stability of $^{226}$Ra.

5. Conceptual geochemical model

In this section, we propose a generalized conceptual geochemical model of lime-neutralized U mill tailings. The conceptual model is divided into two parts: a neutralization model (Figure 11) and an in-pit tailings model (Figures 12–13). The neutralization model addresses the kinetically controlled reactions occurring in the raffinate neutralization processes that generate the secondary precipitates deposited in the TMFs. The neutralization model is based on observations and conclusions of the studies reviewed in §4.0. The in-pit tailings model addresses the equilibrium-controlled reactions occurring in the TMFs and has a predictive component based on what is currently known about the tailings, the geochemical setting, and thermodynamics. The biogeochemistry of the tailings is ignored in these models due to the low probability that microbial communities would have a significant impact on the overall tailings chemistry given the challenging growth conditions of the tailings environment. These models aim to describe the complex geochemistry of these tailings systems in an easily digestible form and to give the reader a broad overview of the important mechanisms influencing the evolution of the tailings.

The neutralization model (Figure 11) describes the concentration profile and precipitation mechanisms of key elements during raffinate neutralization. When multiple precipitation or adsorption mechanisms are possible at a specific pH, each mechanism likely occurs simultaneously; however, the dominant mechanism primarily depends on the elemental concentrations in the raffinate. When slaked lime is used as the neutralization agent, gypsum precipitates continuously throughout the process. At pH $\geq 2$, ferric arsenate precipitation begins. Ferrihydrite precipitation starts as the pH approaches 3.2 and occurs simultaneously with ferric arsenate precipitation. Arsenic, Mo, and Se adsorb via inner- and outer-sphere surface complexation with the newly formed ferrihydrite. Ferric arsenate precipitation is likely limited by the availability of As; therefore, ferric arsenate precipitation should cease as As adsorbs to ferrihydrite. Around pH 4, Al begins precipitating as AlOHSO$_4$ and co-precipitates with ferrihydrite to form a mixed amorphous (Al,Fe)(OH)$_3$ phase. Nickel adsorbs to the newly formed AlOHSO$_4$. As the raffinate reaches neutral pH, the remaining Fe and Al in solution precipitate as (Al,Fe)(OH)$_3$ or discrete ferrihydrite and amorphous Al(OH)$_3$ phases, depending on their concentrations after the pH 4 step.
Residual As, Ni, Se, and Mo will also adsorb to these phases. As the neutralization continues to pH 10, a fraction of adsorbed anionic outer-sphere complexes (e.g., SeO$_3^{2-}$ and MoO$_4^{2-}$) desorb unless the precipitates are removed from solution beforehand. The basic pH will result in Mg precipitation and transformation of amorphous Al(OH)$_3$ to LDHs. Residual Ni is also adsorbed or incorporated into the LDH structure. Continued addition of BaCl$_2$ throughout the neutralization process precipitates (Ba,$^{226}$Ra)SO$_4$. The individual neutralization processes in each mill separate the precipitates at various points to strategically prevent dissolution of EOCs in

**Figure 11.** Conceptual neutralization model of a generalized raffinate. Top panel: Concentration profile (arbitrary units) of selected elements during neutralization of an acidic raffinate plotted vs. time (arbitrary units). A change in the background color shading indicates a change in the dominant precipitation mechanism. Bottom panel: The phases precipitated during neutralization plotted vs. time (arbitrary units). White text indicates the dominant phase of a given stage. Solid parallel lines show inner-sphere complexation. Dashed lines show outer-sphere complexation. Stages labeled with ML, KL, and RL (McLean Lake, Key Lake, and Rabbit Lake) indicate processes specific to a given mill.
subsequent neutralization steps, with the ultimate objective of decreasing the concentration of contaminants in the neutralized raffinate to environmentally acceptable levels.

Fates of the primary minerals and secondary precipitates in the TMFs are controlled by equilibrium reactions that define the geochemical end-

Figure 12. Conceptual tailings model of the evolution of individual elements in lime-neutralized uranium mill tailings. Italicized text denotes initial phases. Bold text denotes predicted final phases. Bold and italicized text denotes phases present in the initial and final state of the tailings. Arrows denote a reaction pathway. Parallel solid lines denote inner-sphere surface complexation. Dotted lines denote outer-sphere surface complexation.
point of the tailings. As such, the initial geochemical state of the tailings and the subsequent interdependent equilibrium reactions need to be understood to predict the final geochemical state of the tailings. The conceptual tailings geochemical model presents our current understanding of the geochemical evolution of the individual components of the tailings (Figure 12) and the tailings body as a whole (Figure 13).

Abundant minerals in the tailings include quartz, clay minerals, sulfides, gypsum, and calcite (Figure 12). Quartz and clay minerals are generally unreactive under the geochemical environment of the tailings. Any residual sulfides from the ore should gradually oxidize and release $SO_4^{2-}$, acid, and associated metal(loid)s. The porewater is saturated with respect to gypsum, and any additional $SO_4^{2-}$ will react with $Ca^{2+}$ to precipitate gypsum. Acid generated from sulfide oxidation should be neutralized by excess $OH^-$ or $CO_3^{2-}$ in the tailings. Calcite is supersaturated and should precipitate over time. Ferrihydrite and amorphous $Al(OH)_3$ (likely present as a mixed

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**Figure 13.** Conceptual tailings model of the complete geochemical evolution of lime-neutralized uranium mill tailings. Italicized text denotes initial phases. Bold text denotes predicted final phases. Bold and italicized text denotes phases present in the initial and final state of the tailings. Arrows denote a reaction pathway. Parallel solid lines denote inner-sphere surface complexation. Dotted lines denote outer-sphere surface complexation.
(Fe,Al)(OH)_3 phase) should be stabilized by adsorbed EOCs. Layered double hydroxides are likely stable under basic conditions.

The evolution of As is likely strongly dependent on the terminal pH of the TMF (Figure 12). Deposited ferric arsenate is thermodynamically unstable and likely either crystallizes to scorodite at pH ≤ 7 or dissolves and reprecipitates as ferrihydrite at pH > 7. Released As should then be adsorbed, depending on the surface site availability of ferrihydrite. Alternatively, As can potentially be adsorbed by LDHs if they are present. Similar to sulfides, residual arsenides from the ore should oxidize over time and release As(III) as H₃AsO₃. Although kinetically limited, the oxidizing conditions of the TMFs should convert As(III) to As(V), which should then be sequestered as scorodite (pH ≤ 7) or adsorbed to (Fe, Al)(OH)_3 or LDHs (pH > 7).

The main source of mobile Ni is residual sulfide and arsenides (e.g., gersdorffite, nicollite, etc.) as oxidation of these minerals should gradually release Ni^{2+} (Figure 12). Incorporation of Ni^{2+} into the structure of LDHs, precipitation of NiAl-LDH, or adsorption by (Fe,Al)(OH)_3 are the likely sequestration mechanisms for Ni released by sulfide and arsenide oxidation. Adsorption of Ni is pH dependent and is likely a weaker control in neutral pH TMFs.

Large masses of Se and Mo are likely controlled by outer-sphere complexes on the surface of (Fe,Al)(OH)_3 and LDHs (Figure 12). As more basic conditions develop, less Se and Mo can remain on the increasingly negatively charged surface of ferrihydrite. The long-term fate of Se in the tailings is poorly understood; however, LDHs might adsorb greater amounts of Se at basic pH relative to ferrihydrite and could be a dominant long-term control of Se porewater concentrations (Robertson et al., 2016). While desorbed Mo might also be sequestered in LDHs, powellite precipitation is likely the dominant equilibrium control of Mo porewater concentrations (Blanchard et al., 2016).

Radium is sequestered as a solid solution with barite and adsorption complexes with ferrihydrite. Although the long-term fate of Ra has not been extensively studied, Ra should remain mostly stable in the TMFs as barite is insoluble and supersaturated under the geochemical conditions of the TMF.

Combining the reaction pathways of the key elements highlights the interdependency of these equilibrium reactions (Figure 13). Diffusion-dominated transport in the tailings bodies should kinetically limit the geochemical evolution of the tailings. Once equilibrium is reached, however, the tailings should be comprised of quartz, clay minerals, gypsum, calcite, amorphous (Fe, Al)(OH)_3, LDHs, scorodite, powellite, and NiMoO₄. Aqueous concentrations of EOCs will likely remain at concentrations
similar to current concentrations due to ongoing adsorption and equilibrium phase processes.

6. Future studies

Many aspects of the geochemistry and geochemical evolution of the Athabasca Basin U tailings are well studied. These aspects include the identification of primary and secondary minerals, mineralogical controls of EOCs (although studies are dominated by As), and porewater chemistry. Arguably, this body of literature is more extensive than for any other milling process and tailings characterization worldwide. However, other aspects remain poorly understood. The biogeochemistry of the tailings is understudied relative to the large amount of inorganic studies. Most biogeochemical research on U tailings focuses on bioremediation of U rather than the potential for tailings instability and metal mobilization (Bondici et al., 2014). Beyond the microbial characterization of DTMF and RLITMF tailings samples, there is minimal research on quantifiable effects of bacterial communities in the tailings. A future objective for this body of research should be to quantify the risk of microbially-mediated EOC mobility and the role micro-organisms play in the long-term stability of the tailings.

The mechanism of Se sequestration in the tailings has not been explicitly defined and is only inferred to be controlled by inner- and outer-sphere surface complexation with ferrihydrite. Detailed X-ray absorption spectroscopic studies could be conducted on Se adsorption complexes of Fe- and Al-(hydr)oxides to better constrain Se adsorption mechanisms under TMF-relevant conditions (e.g., pH, Eh, and porewater compositions). The influences of microbial activity on possible SeO$_4^{2-}$ reduction would be of interest as well.

The stability of amorphous Al(OH)$_3$ and LDHs in the tailings is not known and is only speculated upon using studies with controlled chemical conditions that might not represent those in the tailings. As Al(OH)$_3$ and LDHs in the tailings are likely to contain redox-sensitive Fe, a question remains as to whether or not these phases could be affected by abiotic or biotic redox reactions. As such, the stability of EOCs with respect to these phases should be further investigated under environmentally feasible conditions. Laboratory aging tests of simulated and actual tailings that define the stability of amorphous Al(OH)$_3$ and LDHs and their associated EOCs should be conducted under a range of pH and redox conditions and in the presence of representative microbial communities. These studies would improve the confidence of LDHs as stable phases for EOC sequestration in neutral and basic TMFs.
The aforementioned studies could also be conducted in larger scale column studies to better simulate *in situ* conditions. Tailings samples from varying depths and ages could be placed in columns to study the (bio)geochemical changes under a variety of settings such as reducing, oxidizing, and biologically-stimulating conditions. Mobilization and transport of EOCs could also be monitored in the columns. These studies would be more representative of the scale of the tailings and would help inform on the overall stability of the tailings for the future.

The tailings conceptual model presented in §5.0 and Figure 13 is speculative based on what is currently known about the tailings geochemistry and thermodynamic data. Refinement and validation of this model would be valuable to mine operators, regulators, and researchers of similar sites. Methods of validation could involve aging tests of current tailings samples under possible future environments and would address many uncertainties. For example, how would the porewater and mineralogy evolve under reducing conditions, microbial activity, or local sulfide oxidation? How extreme do these conditions need to be before they impact the tailings chemistry on a large scale? Furthermore, additional numerical models of the equilibrium and transport geochemistry of porous media (i.e., saturated tailings) would be beneficial to further refine the understanding of porewater-surface interactions as they relate to EOC mobility and transport.

The geochemical research in the Athabasca Basin is robust; however, assumptions such as the scalability of these studies add uncertainty towards the long-term geochemical model that has gradually developed for these TMFs. Application of the current state of knowledge could greatly inform the direction of these model validation studies to further improve the certainty of the research.

**7. Applicability of uranium tailings research to other mining environments**

**7.1. Other uranium milling facilities**

Uranium tailings geochemistry is strongly influenced by the characteristics of the ore and host rock and subsequent milling conditions. Geochemical studies of Athabasca Basin tailings are highly applicable to other U milling operations that use an oxic acid leach process for similar ores. For example, the Ranger Mine in the Northern Territory, Australia mills U ore rich in chlorite, quartz, and sericite with minor amounts of galena, pyrite, chalcopyrite, dolomite, apatite, rutile, and hematite (Douglas, Wendling, Pleysier, & Trefry, 2010; Sinclair, Taylor, & Paul, 2006). The Ranger process uses an acid leach to dissolve U minerals and a lime neutralization to treat raffinate, with tailings disposal to an in-pit TMF above neutral pH (Sinclair
et al., 2006). Ferrihydrite, hydrobasaluminite, amorphous Al(OH)$_3$, and LDHs are observed as secondary minerals in the resulting tailings, suggesting that mineralogical controls similar to Athabasca Basin mills exist in other facilities (Douglas et al., 2010; Sinclair et al., 2006). Specifically, the conceptual geochemical model developed here (Figures 11–13) should be directly applicable to the Ranger site to further develop tailings management programs. The model should also be relevant with respect to the transport of contaminants from the Schneckenstein U tailings dam in Germany (Merkel, 2006) in understanding how EOCs in seepage water can be attenuated downstream. Understanding the potential mineralogical controls (or lack thereof) on these contaminants could assist in remediation efforts, predicting the future mobility of contaminants and understanding their fate downstream from the dam. Furthermore, the research and design in the Athabasca Basin can be used as a model for tailings management for new U mines and mills in the future. Design of future U process water treatment facilities and TMFs can utilize a combination of the known incoming ore mineralogy, the planned U milling process, and the geochemistry reviewed in this paper to optimize treatment performance and tailings stability. Environmental regulators can also use this research as a benchmark for what is attainable for a U tailings management program.

7.2. General applications

The geochemistry of U tailings is not unique to the geochemistry of other tailings systems, acid mine/rock drainage, or other contaminated sites. The most common process used to remove metals from industrial effluents is chemical precipitation with lime or NaOH (Blais, Djedidi, Cheikh, Tyagi, & Mercier, 2008). The neutralization chemistry of these processes is often similar to the neutralization of U mill raffinate as metal hydrolysis and a complex suite of sorption reactions occur. Other metal processing industries, such as the gold industry, deposit As-rich tailings sub-aqueously (pH 6.2 to 8.0). Arsenic-bearing secondary phases (e.g., Ca-Fe arsenates and As-bearing Fe oxyhydroxides) are abundant in these tailings (Craigen, 2006). Acidic and metalliferous water generated by acid mine drainage is often rich in Fe derived from sulfide oxidation and Al from aluminosilicate dissolution (Blowes, Reardon, Jambor, & Cherry, 1991; Moncur, Ptacek, Blowes, & Jambor, 2005). The Fe- and Al-rich acidic drainage is gradually neutralized by carbonate minerals in the natural environment as it migrates through the soils, resulting in amorphous Fe(OH)$_3$ and Al(OH)$_3$ precipitation (Bigham & Nordstrom, 2000; Cismasu, Michel, Tcaciuc, Tyliszczak, & Brown, 2011; Moncur et al., 2005). These hydrolysis products adsorb metal(loid)s liberated through the acid mine drainage process. The large scale
and controlled environment of U mill tailings are valuable for scientific advances in environmental research. For example, adsorption capacity measurements of metal hydroxides and LDHs can be applied to disciplines interested in using these adsorbents as treatment methods (Robertson et al., 2016). Several EXAFS studies of U tailings have contributed to the understanding of metal(loid) co-precipitation and adsorption with metal hydroxides and LDHs (Bissonnette et al., 2016; Chen et al., 2009; Essilfie-Dughan et al., 2013; Moldovan et al., 2003; Robertson et al., 2017).

The conceptual model from §5 should also be generally applicable to the geochemistry of other industrial and natural sites where acidic water is neutralized as well as the description of primary and secondary minerals in equilibrium with neutral to basic and oxic waters. Other conceptual models of neutralization geochemistry have been developed in other studies (Blowes, 1990; Morin, Cherry, Dave, Lim, & Vivyurka, 1988; Salmon & Malmström, 2004). Morin et al. (1988) present a transport and hydrogeochemical model of U tailings seepage migration from Elliot Lake, Canada wherein acidic tailings seepage is neutralized by mineral precipitation-dissolution reactions and aqueous metal concentrations decrease. The geochemistry of this model is similar to our neutralization model, with the primary difference being active neutralization (lime addition) versus passive neutralization (mineral dissolution). The conceptual model of Morin et al. (1988) was extended to neutralization of acidic water from sulfide mine tailings by Blowes (1990) and column experiments of acid neutralization and metal release in mine tailings by Jurjovec, Ptacek, and Blowes (2002). Other models incorporate different facets of similar geochemical settings; for example, Salmon and Malmström (2004) developed a mathematical model of kinetic and biogeochemical processes in a pyritic tailings deposits. Like the conceptual model presented in this review, other conceptual models are not comprehensive of all the processes occurring in a system; instead, the models focus on specific facets of a system (e.g., neutralization, kinetics, equilibrium, and transport). The availability of multiple conceptual models covering different facets of a certain environment allows for a holistic understanding of how a system may evolve and will further help researchers, industry, and regulators design more sustainable sites. As such, the inclusion of our conceptual model based on our review of decades of research should be a useful addition to the scientific literature. While U tailings represent only a subset of mine-impacted environments, the extensive research in this area shows many similarities to the problems faced by the mining industry. The studies from the Athabasca Basin TMFs represent a strong body of research that can be drawn upon for many applications.
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**Appendix A. Supplementary data**

A compilation of sampling and experimental methods used in studies of Athabasca Basin U tailings is provided as supplementary data. A PHREEQC geochemical model of both a generalized neutralization process and U tailings pit is also provided.