Mineralogical Controls on Aluminum and Magnesium in Uranium Mill Tailings: Key Lake, Saskatchewan, Canada

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Supporting Information

ABSTRACT: The mineralogy and evolution of Al and Mg in U mill tailings are poorly understood. Elemental analyses (ICP-MS) of both solid and aqueous phases show that precipitation of large masses of secondary Al and Mg mineral phases occurs throughout the raffinate neutralization process (pH 1–11) at the Key Lake U mill, Saskatchewan, Canada. Data from a suite of analytical methods (ICP-MS, EMPA, laboratory- and synchrotron-based XRD, ATR-IR, Raman, TEM, EDX, ED) and equilibrium thermodynamic modeling showed that nanoparticle-sized, spongy, porous, Mg–Al hydrotalcite is the dominant mineralogical control on Al and Mg in the neutralized raffinate (pH ≥ 6.7). The presence of this secondary Mg–Al hydrotalcite in mineral samples of both fresh and 15-year-old tailings indicates that the Mg–Al hydrotalcite is geochemically stable, even after >16 years in the oxic tailings body. Data shows an association between the Mg–Al hydrotalcite and both As and Ni and point to this Mg–Al hydrotalcite exerting a mineralogical control on the solubility of these contaminants.

INTRODUCTION

Mining and milling of uranium (U) ore have generated more than one billion tons of tailings at about 4000 mines worldwide.1 The largest, richest (ore grades of 21 wt %), and most productive (29% of world U production) reserves of U ore in the world are located in the Athabasca Basin, northern Saskatchewan, Canada.2 U mill tailings in this basin typically contain elevated concentrations of potential environmental contaminants, such as As, Ni, Se, and Mo.3–10 Most of these contaminants are solubilized with the U during the leaching stage of the milling process. Once the U is extracted from the acidic solution (pH ~1), the raffinate solution (the acidic aqueous phase remaining after the U is removed) is neutralized in a stepwise manner with slaked lime (Ca(OH)2) up to pH 10.5, after which it is discharged to tailings management facilities (TMFs) as an alkaline oxic slurry. Upon discharge, most of the potential environmental contaminants are removed from the aqueous phase and sequestered in secondary mineral phases.

The mineralogical occurrence of Fe in U tailings and its evolution through the U raffinate neutralization process (from pH 1 to 10.5) is well understood. Ferrihydrite, generated during the neutralization of the raffinate, is a dominant secondary Fe mineral phase and plays a significant role in the sequestration and solubility control of As, Se, Mo, and Ni in mills and associated tailings at U operations such as those at Key Lake and Rabbit Lake, Saskatchewan.8–10 In contrast to Fe, the mineralogical occurrences and evolution of Al and Mg, which are also present in high concentrations in the mill raffinate solution and in low concentrations in the final neutralized raffinate solution, are poorly understood. At the Rabbit Lake mill for example, Al and Mg concentrations in the raffinate (~500 mg/L, pH = 1.0) are of the same order of magnitude as Fe concentrations (860 mg/L) but after neutralization (pH = 10.8) are very low (<1 mg/L). These data indicate that, similar to Fe, the Al and Mg form secondary solid phases in the mill. On the basis of the thermodynamic modeling of the Rabbit Lake mill data, Moldovan and Hendry11 suggested that Al concentrations are controlled by gibbsite (Al(OH)3) and an amorphous aluminum hydroxide (Al(OH)a)3). Unfortunately, they did not conduct a mineralogical investigation and, as such, could not confirm the presence of these phases. Determining the presence of Al, Mg, or Mg–Al hydroxide mineral phases in the mill process and in the associated tailings is important because these non-Fe-based hydroxides can also efficiently remove potential contaminants from tailings systems.12–19

The objectives of the current study were to (1) characterize the evolution of Mg and Al phases from pH 1–11 in an operating U mill and in samples from the associated TMF and (2) comment on the occurrence and sequestration of elements of concern (EOCs; e.g., As, Mo, Ni, Se) in the secondary Mg and Al minerals. For our purposes, EOCs are defined as those elements that are toxic (regulated by WHO, EPA) and have been measured at higher than acceptable concentrations in the aqueous phase of such mill and tailings systems. These objectives were attained by subjecting solid and aqueous...
samples collected through the raffinate neutralization process in a mill and samples of mill tailings to a suite of elemental, molecular, and structural analyses, followed by thermodynamic modeling of the aqueous phase. This research improves upon our limited understanding of the evolution of Al and Mg mineral phases over a broad range in pH values, the geochemical associations between Mg and Al phases in U tailings and potential contaminants, and how these associations may affect the long-term control of contaminants in U tailings pore waters.

**MATERIALS AND METHODS**

**Location of the Mill and Milling Process.** The Key Lake U mill (57°13′N, 105°38′W) and the Deilmann Tailings Management Facility (DTMF) into which its tailings are discharged were selected for study due to the presence of ferrihydrite in the mill and tailings being well documented and thought to control the solubility of EOCs. The mill started operations in 1983 and, based on known reserves, is expected to continue operating to 2040. As of October 2009, the mill had produced more than ~170 million kg of U₂O₅. The production at the mill currently accounts for 16% of the world’s annual U production and is currently the world’s largest high-grade U-milling operation.²,²²⁻²⁴

**Deilmann Tailings Management Facility.** Tailings generated in the mill have been deposited in the DTMF, a mined out pit, since 1996. Between 1996 and 1999, the mill feed was derived entirely from the polymetallic U–Ni–Co–As–S minerals. Since 1999, ore from the McArthur River mine, located 80 km north of the Key Lake mill, has been the primary source of ore for the mill.²³,²⁴

**Sample Collection and Preparation.** Composite samples of secondary precipitates generated in the raffinate neutralization process were collected in August 2011 to compare the mineral phases present in the neutralized raffinate to those in the tailings. Slurries from the pachucas and thickeners were collected along the neutralization process at pH 1.4 (unbuffered raffinate), 4.3, 4.4, 6.5, and 10.1 (Supporting Information Figure S0, Table 2). These were termed 11-KL-01 to 11-KL-05, respectively (note the 11-KL-01 sample contained only an aqueous phase).

Samples were also collected from the underflows from the Se–Mo thickener and the lamella thickener (see sampling points A and B; Supporting Information Figure S0). These samples were mixed at a 1:1 volume ratio to replicate the composite discharge from the mill. The composite sample was amended with slaked lime (to a terminal pH of 11) and barium chloride (sample 11-CS-Ba). A second composite sample without barium chloride addition (11-CS-OO) was collected in September 2011 in the same manner as described above; because of the similarity between the 11-CS-OO and 11-CS-Ba data sets, only data for 11-CS-Ba are presented.

In addition to the neutralized samples from the underflows from the Se–Mo thickener and the lamella thickener, three tailings samples were collected for analysis. The first tailings sample, generated from McArthur River ore (11-McTail-01), was collected in September 2011 from the final tailings mix tank in the mill before discharge to the DTMF (Point C; Supporting Information Figure S0). Two samples of Deilmann tailings (09-E2-GC13 and 09-E2-GC22) were collected from the DTMF at elevations of 395.5 ± 0.5 and 377.8 masl (meters above sea level) in 2009 using a sonic track mounted drill.⁶

Because all solids samples were collected in slurry form (solids and liquids), solid phases were separated via pressure filtration (Hazardous Waste Pressure Filter System, Millipore) with a 0.2 μm pore size filter (EMD Millipore Corp.) and N₂ used to pressurize the filter system. After the aqueous phase was separated and saved for aqueous elemental analysis, the remaining solids were dried at room temperature for 24 h before storage in airtight bags at 4 °C for geochemical analysis. This procedure was applied to all process samples.

**Analytical Methods.** In most cases, solids samples (composite raffinate, process samples, tailings samples) are dominated by gypsum that precipitates during the neutralization process due to the addition of lime (Ca source) and the presence of H₂SO₄ in the solution raffinate. Because this gypsum interferes with the detection of other mineral phases (data not presented), gypsum was removed by leaching with deionized water (Ω = 18 ohms) obtained from an ultrapure water Millipore filtration system. After removal of gypsum, the washed solids samples were dried at room temperature for 24 h, then gently ground with an agitator mortar and pestle. The filtrates of the washed solids were analyzed by inductively coupled plasma-mass spectrometry (ICP-MS) to confirm that no EOCs were leached into solution during the gypsum washing procedure (data not shown). X-ray diffraction (XRD), Raman spectroscopic, and IR spectroscopic analyses were also conducted on samples before and after the washing procedure to confirm no mineralogical phase change occurred (data not shown). Unless stated otherwise, all data for solids samples refer to the gypsum washed, barium-containing samples from the mill process, the final neutralized raffinate, and the tailings.

Bulk elemental analyses were conducted on subsamples using a Perkin-Elmer NexION 300D ICP-MS with a relative standard deviation (RSD) of ±10%. To analyze the aqueous samples, 1 mL of the solution of interest was diluted accordingly in aqueous HNO₃ to fit within a three-point calibration curve. All solids were digested in an acidic media (HF-HNO₃) then left overnight to dissolve. Samples were diluted for analysis of Fe, Al, Mg, and the EOCs Ni, Se, As, and Mo.²⁵,²⁶

Powdered subsampled wafer specimens were mounted on the rotating disk transmission holders and bulk X-ray diffractograms measured with an Empyrean Pro PANalytical diffractometer equipped with a cobalt target (Co Kα, radiation, λ = 1.7902 Å), a crystal graphite monochromator, and a scintillation detector. The diffractometer used 40 kV and 45 mA. The scans were measured from 10° to 100° 2θ with a 0.01° step and a scan step time of 85 s. High-resolution synchrotron powder diffraction data for higher sensitivity phase analysis was also collected using beamline 11-BM at the Advanced Photon Source (APS; Argonne, IL) using a wavelength of 0.4857(2) Å.²⁷ phase identification and semiqualitative Rietveld refinement for phase analysis was conducted with XpertHighScore Plus software using the PAN-Inorganic and Mineral Crystal Structure Database, version 1.5 as well as previous works on similar materials.²⁸

Subsamples were placed in cylindrical plugs (5 mm diameter), filled with epoxy, and allowed to harden at room temperature. The surfaces of the plugs were then polished for electron microprobe microanalysis (EMPA) using a JEOL JXA-8900L operating at 15 kV and 20 mA, with a beam size of 2 μm and counting time of 20 s. Two distinct 60 × 60 μm areas were analyzed and mapped for Fe, As, Mo, Se, Ni, Al, and Mg in each plug to obtain a representative mapping of the phase(s) of interest.
Transmission electron microscopy (TEM) imaging and analysis were conducted on selected particles in the subsamples via energy dispersive X-ray analysis (EDX) and electron diffraction (ED) using a Philips CM-200 microscope. Nano-mapping of elements was done in STEM mode using a JEOL 2000 FS microscope. Both microscopes were operated at 200 kV. Subsamples were prepared by dropping dilute solutions of the particles in ethanol onto 400-mesh carbon-coated copper grids and evaporating the solvent to dryness before inserting them into the sample holder and chamber.

Raman spectra were collected on subsamples with a Renishaw InVia Raman microscope in confocal mode using a laser operating at 785 nm with a spot size of approximately \( \leq 5 \) \( \mu m \) in diameter using the 50X short distance objective. Data presented represent the average of five scans collected from 1400 to 150 cm\(^{-1}\) with an energy resolution of 4 cm\(^{-1}\). Scans were collected at 30 s per scan using 10% of the laser output at the microscope exit to avoid radiation damage to the ferrihydrite particles.\(^{29}\) Infrared spectra were obtained on powdered subsamples using a Perkin-Elmer Fourier transform infrared (FTIR) (Spectrum BX model) spectrometer with a Miracle single bounce diamond attenuated total reflectance (ATR) cell from PIKE Technologies. Spectra over the 4000–550 cm\(^{-1}\) range were obtained by the coaddition of 200 scans with a resolution of 4 cm\(^{-1}\).

**Thermodynamic Modeling.** Thermodynamic modeling was used to simulate the precipitation of secondary mineral phases of Mg, Al, and Fe in the mill during a stepwise neutralization of the raffinate solution (pH 1 to the terminal pH of 10.5 at 0.5 pH steps) with slaked lime. All modeling calculations were performed using PHREEQC, version 2.18.3.5570.\(^{30}\) The Lawrence Livermore National Laboratory (LLNL) thermodynamic database (included with PHREEQC) was modified with additional thermodynamic data (see previous similar computations\(^{6,9}\)), as well as hydrotalcite thermodynamic data from the HATCHES (HARwell/Nirex Thermodynamic Database for ChEmical Equilibrium Studies) Database, version NEA19 (i.e., reaction \( \text{Mg}_2\text{Al}_5\text{O}_8\text{H}_{10} + 14\text{H}^+ = 2\text{Al}^{2+} + 17\text{H}_2\text{O} + 4\text{Mg}^{2+}; \log k = 75.34 \)).\(^{31}\)

### RESULTS AND DISCUSSION

**Solid and Aqueous Chemistry of Neutralized Raffinate.** The pH and concentration of Al, Mg, Fe, and EOCs (As, Mo, Ni, and Se) in aqueous and solid phase samples collected at various steps in the Key Lake mill neutralization process are presented in Tables 1 and 2. The concentrations of Al, Mg, and Fe exceeded 1 g/L with the concentration of Al > Fe > Mg in the unneutralized raffinate (11-KL-01; pH 1.4).\(^{32}\) The Lawrence Livermore National Laboratory (LLNL) thermodynamic database (included with PHREEQC) was modified with additional thermodynamic data (see previous similar computations\(^{6,9}\)), as well as hydrotalcite thermodynamic data from the HATCHES (HARwell/Nirex Thermodynamic Database for ChEmical Equilibrium Studies) Database, version NEA19 (i.e., reaction \( \text{Mg}_2\text{Al}_5\text{O}_8\text{H}_{10} + 14\text{H}^+ = 2\text{Al}^{2+} + 17\text{H}_2\text{O} + 4\text{Mg}^{2+}; \log k = 75.34 \)).\(^{31}\)

**Table 1. Solids Chemistry of the Mill Generated and Tailings Samples Analyzed in This Study**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Solid Raffinate and Tailings Samples</th>
<th>Solid Tailings Samples from DTMF</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Key Lake Mill</td>
<td>DTMF</td>
</tr>
<tr>
<td>Mg</td>
<td>34500</td>
<td>1900</td>
</tr>
<tr>
<td>Al</td>
<td>25200</td>
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<td>Fe</td>
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<td>8400</td>
</tr>
<tr>
<td>As</td>
<td>136</td>
<td>8500</td>
</tr>
<tr>
<td>Se</td>
<td>1.3</td>
<td>29</td>
</tr>
<tr>
<td>Mo</td>
<td>43</td>
<td>95</td>
</tr>
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</table>

Unwashed neutralized raffinate sample collected in August 2011. Sample is a composite of sample points A and B (see Figure 1). Fresh, unwashed McArthur River tailings sample collected September 2011 (see Figure 1 point C). Solids samples collected during 2009 drilling campaigns at the DTMF site.\(^{6}\)

Complementary elemental analyses of the solids at each step of the process (Table 2) support the observed solution precipitation efficiencies. At pH 10, however, the Al and Fe solids contents were lower than at pH 6.4, reflecting the greater mass of precipitates formed at lower pH stages. These results demonstrate that precipitation of Al, Mg, and Fe secondary mineral phases occur throughout the neutralization process.

The solids in the combined and neutralized underflows from the Se–Mo thickener and the lamella thickener (11-Cs-Ba) and McArthur (11-McTail-01) and Deilmann tailings (09-E2-GC13 and 09-E2-GC22) samples (Table 1) also had elevated concentrations of Al, Mg, and Fe, consistent with neutralized raffinate samples (Table 2). Further, the mean concentrations in solids and aqueous tailings samples collected from the DTMF and presented in Shaw et al.\(^{16}\) support these findings. Tailings solids samples resulting from McArthur and Deilmann ores had elevated concentrations of Al, Mg, and Fe, with concentrations of Al > Mg > Fe; the mean concentrations of the associated aqueous samples were <3 mg/L. Notably, however, tailings samples also contained phyllosilicates such as muscovite \( \{\text{KAl}_2\text{Si}_4\text{O}_{10}(\text{OH},\text{F})_2\}\), kaolinite \( \{\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4\}\), and clinochlore \( \{\text{Mg(Al)}_2\text{AlSi}_3\text{O}_{10}(\text{OH})_2\}\), as well as unreacted primary minerals such as pyrite \( \{\text{FeS}_2\}\), chalcopyrite \( \{\text{CuFeS}_2\}\), gersdorffite \( \{\text{NiAsS}\}\), and nicoelite \( \{\text{NiAs}\}\).\(^{6,10}\) As such, direct comparisons cannot be made between the elemental concentrations belonging solely to one phase of any of the given element (e.g., Fe, Al, Mg) in the tailings samples (primary + secondary minerals) and neutralized raffinate samples (secondary minerals).

In summary, precipitation of Al, Mg, and Fe mineral phases takes place throughout the Key Lake mill neutralization process and masses of Al and Mg in the secondary mineral phases of the final neutralized raffinate and tailings are large, regardless of which ore (McArthur or Deilmann) was milled. Further, because the solids Al and Mg concentrations are similar to or exceed that of Fe, the Al and Mg secondary minerals are as prevalent, if not more so, in the tailings than the secondary precipitates of Fe (ferrihydrite).

**Mineralogy and Characteristics of Precipitates in Neutralized Raffinates.** EMPA mapping of the final neutralized raffinate (11-Cs-Ba) shows all observable elements of interest are homogeneously distributed at the microscale between Mg and Al (Figure 1). Iron exhibits some spatial
correlation (at the microscale) with Mg and Al. Low concentrations prevented the observation of As, Mo, Se, and Ni using our lab-based EMPA.

TEM imaging and TEM-EDX analyses show the presence of two distinct types of widely distributed nanoparticle phases in the neutralized raffinate samples: a spongy porous Al–Mg phase, composed of Mg–Al–O, and a globular Fe-rich phase (Figure 2a). ED analysis of the spongy Al–Mg rich nanoparticles shows them to be polycrystalline in nature with diffraction planes at 2.17 and 1.52 Å, corresponding to the (015) and (110) planes consistent with the hydrotalcite phase (JCPDS 98-000-6182 and 98-004-0925) and in agreement with literature works.\(^{15,32-35}\) The particle morphology of the Mg–Al–O phase was also consistent with a hydrotalcite phase.\(^ {32}\) Moreover, EDX spectra of the Mg–Al hydrotalcite particles (Figure 2b) show this Mg–Al–O phase is also associated with some Mo and Si.

Electron diffraction and EDX data indicate the globular particles are amorphous and iron rich, respectively, making them consistent with the expected ferrihydrite (Figure 2a and 2b).\(^ {4,11,28}\) EDX analyses on the ferrihydrite particles demonstrate the presence of some Al, Mg, Si, and Mo. Notably, Al and Si can exist as impurities in ferrihydrite.\(^ {36,37}\) Analysis of the higher resolution TEM images of the neutralized raffinate sample (11-Cs-Ba) show that some of the nanoparticle-sized Mg–Al hydrotalcite exists in association with the Fe-rich globular ferrihydrite (Figure 2c). This close association (observed in washed and unwashed samples) is discussed below in relation to the Key Lake process and tailings samples.

Representative results of lab-based XRD analyses of the final neutralized raffinate (11-CS-Ba) (Supporting Information Figure S1) show the bulk structure consists of a semicrystalline phase unlike that expected from 2-line ferrihydrite.\(^ {28}\) Solids analyses indicate that the majority of the components in the

<p>| Table 2. Chemical Analysis of the Solutions and Solids at Various Steps in the Key Lake Mill Neutralization Process Using the McArthur Ore As the Source(^ {2,6}) |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|</p>
<table>
<thead>
<tr>
<th>McArthur ore</th>
<th>pH</th>
<th>Al</th>
<th>Mg</th>
<th>Fe</th>
<th>Ni</th>
<th>As</th>
<th>Se</th>
<th>Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>11-KL-01-Raffinate</td>
<td>solid (μg/g)</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td></td>
<td>aqueous (mg/L)</td>
<td>1.4</td>
<td>1635</td>
<td>1044</td>
<td>1428</td>
<td>23.3</td>
<td>27.8</td>
<td>0.4</td>
</tr>
<tr>
<td>11-KL-02-Pachuca 2 underflow</td>
<td>solid (μg/g)</td>
<td>116</td>
<td>604</td>
<td>396</td>
<td>10.3</td>
<td>0.45</td>
<td>0.16</td>
<td>0.14</td>
</tr>
<tr>
<td></td>
<td>aqueous (mg/L)</td>
<td>4.3</td>
<td>34521</td>
<td>2553</td>
<td>19576</td>
<td>138</td>
<td>409</td>
<td>1.01</td>
</tr>
<tr>
<td>11-KL-03-SeMo thickener</td>
<td>solid (μg/g)</td>
<td>32694</td>
<td>2231</td>
<td>2078</td>
<td>116</td>
<td>447</td>
<td>nd*</td>
<td>81.9</td>
</tr>
<tr>
<td></td>
<td>aqueous (mg/L)</td>
<td>4.4</td>
<td>62.8</td>
<td>649</td>
<td>445</td>
<td>12.7</td>
<td>0.32</td>
<td>0.21</td>
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<tr>
<td>11-KL-04-Pachuca 3 underflow</td>
<td>solid (μg/g)</td>
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<td>4101</td>
<td>84418</td>
<td>1499</td>
<td>69.77</td>
<td>4.47</td>
<td>32.6</td>
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<td></td>
<td>aqueous (mg/L)</td>
<td>6.4</td>
<td>0.07</td>
<td>602</td>
<td>8.51</td>
<td>4.38</td>
<td>0.01</td>
<td>0.02</td>
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<tr>
<td>11-KL-05-Lamellar thickener</td>
<td>solid (μg/g)</td>
<td>18245</td>
<td>55243</td>
<td>35278</td>
<td>981</td>
<td>25.4</td>
<td>nd*</td>
<td>11.8</td>
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<tr>
<td></td>
<td>aqueous (mg/L)</td>
<td>10.1</td>
<td>0.49</td>
<td>2.38</td>
<td>0.06</td>
<td>0.03</td>
<td>0.01</td>
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*nd*: Not detected.

**Figure 1.** EMP maps of elements of interest in the neutralized raffinate product 11-Cs-Ba. The presence of Al and Mg is homogeneously distributed and correlated throughout the sample and exhibits some spatial correlation with Fe. Note that the concentrations of the EOCs As, Ni, Mo, and Se are not presented because they were too low to be observed with the EMP. Scale bar = 100 μm.
Figure 2. (a and b) TEM, ED, and EDX of typical particles observed in the final neutralized raffinate (11-Cs-Ba), showing the two types of particles commonly observed throughout the sample. The first is a globular, iron-rich particle showing no diffraction pattern indicative of ferrihydrite (FH). The second is a spongy Mg-Al rich oxide that shows a distinct diffraction pattern and has a channel-like structure often observed in hydrotalcite (HTLC)-like structures. (c) TEM images of final neutralized raffinate (11-Cs-Ba) showing the close association between the globular (ferrihydrite, FH) and spongy (Mg-Al hydrotalcite) particles. The scale bars on the larger images are all 100 nm, while the scale on the inset images of the EDX data are 50 nm.

The final neutralized raffinate sample are Mg-Al hydrotalcite, ferrihydrite, and minor amounts of barite and gypsum. Higher sensitivity synchrotron-based XRD verified the presence of characteristic Mg-Al hydrotalcite (003), (009), (110), and...
planes that were less pronounced in the lab-based analyses (Supporting Information Figure S1). These data confirm that Mg and Al are present as Mg−Al hydrotalcite, not as individual hydroxides (e.g., gibbsite, brucite) as suggested by Moldovan and Hendry.11

To further characterize the Mg−Al mineral phase, the molecular makeup and environment of these assemblages were investigated using ATR-IR and Raman vibrational spectroscopy. Representative vibrational spectra of the final neutralized raffinate (11-Cs-Ba) (Supporting Information Figure S2) in general suggest the presence of a sulfate hydroxyl-hydrated carbonate-containing phase. Comparison with a synthetic Mg−Al hydrotalcite sample and spectra from the literature33,38−40 indicates that the molecular environment of the groups and vibrational signature are consistent with hydrotalcite and unlike that of barite, gypsum, Mg, and Al (hydr)oxides (brucite or gibbsite), or sulfate/arsenate containing ferrihydrite (band locations labeled in Supporting Information Figure S2).41−49 This vibrational phase analysis provides evidence beyond that from EMPA, TEM-EDX, and XRD analyses with respect to the presence of Mg−Al hydrotalcite in the final neutralized raffinates of the Key Lake mill process at the bulk (macro-) and nanoscale.

The mineralogy of the solids along the neutralization process (Supporting Information Figure S0) determined using XRD, Raman spectroscopy, and ATR-FTIR spectroscopy is summarized in Supporting Information Figure S3. Solid-phase precipitation commences between pH 1.4 and 4.4 and results in precipitation of the majority of the Fe and Al and most of the Mg (Table 2). Mineralogical analyses of the solids (12-KL-02 and 12-KL-03) precipitated at pH 4.3 and 4.4 show them to be in an X-ray amorphous metal-containing sulfate hydrated-hydroxy phase (i.e., ferrihydrite and ALOHSO₄). At pH 6.4 (12-KL-04), data from XRD, Raman spectroscopy, and ATR-FTIR spectroscopy indicate the presence of ferrihydrite and, for the first time, Mg−Al hydrotalcite. Because it contained the first observed occurrence of the Mg−Al hydrotalcite, the precipitate collected at pH 6.4 (11-KL-04) was investigated further using TEM-EDX. Inspection of the particles reveals the typical Mg−Al−O components of Mg−Al hydrotalcite and the presence of Al in the ferrihydrite samples (Al-doped FH), in some cases occurring as separate individual components or appearing to be derived from the same particle source (Supporting Information Figure S4). The presence of the Mg−Al hydrodrotalcite is also evident in the XRD, ATR-FTIR spectroscopic, and Raman spectroscopic data from pH 10.1 (12-KL-05). The solids elemental data presented in Table 2 show that the Mg/Al molar ratio (~3) in these solids formed at pH 10.1 is ideal for stoichiometric Mg−Al hydrotalcite.

Mineralogy of Tailings Samples. XRD phase analyses (via Xpert highscore software) of both the younger McArthur River (11-McTail-01) and older Deilmann (09-E2-GC22 and 09-E2-GC13) tailings from the DTMF indicated the presence of the expected quartz, ferrihydrite, gypsum, barite, and,

Figure 3. Thermodynamic modeling results (a−c) and analytical results for Fe, Al, and Mg in solution (d) through the raffinate neutralization process (pH 1.0 to 10.5). For the modeling, panel a presents the mineral phases precipitated, panel b presents the mineral phases precipitated without gypsum, and panel c presents calculated Fe, Al, and Mg concentrations in solution.
interestingly, Mg–Al hydrotalcite (Supporting Information Figure S5). Electron microscopic and nanoelemental mapping analyses (TEM and EMPA) confirmed the presence of Mg–Al hydrotalcite throughout these samples (Supporting Information Figures S6–S10), while TEM and EDX analyses show the presence of both individual globular Fe-rich particles (ferrihydrite) and spongy Mg–Al hydrotalcite particles (Supporting Information Figure S7). Higher resolution TEM images also show that these Mg–Al hydrotalcite particles are in close association with ferrihydrite (Supporting Information Figures S4 and S11). These observations are consistent with measurements made on the neutralized raffinate samples discussed above and show that, upon mixing of the neutralized raffinate with the leach residue to produce the final product (neutralized tailing; 11-McTail-01), both the ferrihydrite and Mg–Al hydrotalcite phases remain unaltered with respect to their mineralogy. The presence of ferrihydrite and Mg–Al hydrotalcite phases in the Deilmann tailings samples indicates that these minerals likewise remain unaltered even after >16 years in the DTMF. The presence of Mg–Al hydrotalcite in fresh raffinate and in old tailings derived from two distinct ore bodies (McArthur and Dielmann) indicates that our results are not only applicable to the U ores bodies found in Saskatchewan, Canada (which contain large amounts of Al and Mg), but also to other ore bodies in which similar hydrometallurgical sulfate acid leaching processes are used to liberate soluble elements (e.g., Mg, Al) followed by neutralization to treat the waste solutions. Notably, if the ore body is Al-rich or Mg-rich, then the occurrence of Mg–Al hydrotalcite will vary or may be absent (e.g., if 98% Al-rich and 2% Mg-rich, only gibbsite will likely form).

**Thermodynamic Modeling.** The phase evolution of the precipitates of Mg and Al, as well as Fe, Ca, and SO₄ during the neutralization process at the Key Lake mill was thermodynamically modeled to provide additional evidence for the formation of Mg and Al mineral phases. Modeling was conducted using the analytical data from the samples collected throughout the Key Lake mill process (samples 12-KL-1 to 12-KL-5) (Supporting Information Figure S0 and Table 2), using the complete aqueous chemistry data for 12-KL-1 (pH = 1.4) as the initial solution chemistry.

The dominant mineral phases controlling Ca, S, Al, Fe, Mg, and Ni over the pH range 1 to 10.5 and that could possibly precipitate were predicted after review of the calculated saturation indices (SI) for aqueous samples 12-KL-1 to 12-KL-5. In this simulation, no equilibrium phases were specified and minerals with SI values >0.0 were considered potential secondary minerals in the neutralizing raffinate. This analysis suggests the dominant secondary precipitates are gypsum, amorphous Al(OH)₃, gibbsite, AlOHSO₄, ferrihydrite, goethite, hemaitte, brucite, and Mg–Al hydrotalcite. As the experimental data from our analysis indicate gypsum, ferrihydrite, and an Mg–Al iron containing hydrotalcite are dominant secondary mineral phases in the final neutralized raffinate, the equilibrium mineral phases specified in the model simulations were refined to include these as well as AlOHSO₄ and amorphous Al(OH)₃ (to account for the decrease in solution concentration of Al at pH 2 and 6.7).

Reaction path modeling was conducted by stepwise (every 0.5 pH unit) addition of slaked lime (Ca(OH)₂) to the raffinate solution (to pH 10.5), starting with sample 12-KL-1 at a pH of 1.4. Results of the modeling (Figure 3a) show that the addition of the slaked lime results in the precipitation of a considerable mass of gypsum between pH 1 and 10.5, with most precipitating from pH 1 to 3.3. The model also shows that Fe precipitates as ferrihydrite, starting at pH ~3, reaching a maximum at pH ~6.2, and continuing to the terminal pH of 10.5 (Figure 3b). The precipitation of gypsum and ferrihydrite in the neutralization process is consistent with results from Moldovan and Hendry¹¹ and Essilfie-Dughañ et al.⁹,¹⁰ Model results for Al suggest that AlOHSO₄ precipitates between pH 2 and 6, then redissolves by pH 6.3 as the formation of amorphous Al(OH)₃ and the more stable Mg–Al hydrotalcite at pH ≥ 6.7 is favored (Figure 3b). Notably, although 60% of the Mg remained in solution at the pH 6.4 step in the process, the presence of Mg–Al hydrotalcite is clear from our phase analysis (Supporting Information Figure S3 and S4); the origin (e.g., amorphous gibbsite or brucite) and exact mechanism of formation of this Mg–Al hydrotalcite phase remains to be determined. Mg remains mostly in solution until it precipitates with Al as Mg–Al hydrotalcite at pH ≥ 6.7 (Figure 3b).

Overall, the formation sequence of mineral phases suggested by the model results is consistent with the experimentally observed mineralogical solids chemistry neutralization process and the changes in solution chemistry of Al, Fe, and Mg during neutralization (Figure 3c). However, the mineralogy and thermodynamic modeling data are inconsistent with earlier studies that suggest the secondary minerals of Al and Mg in the tailings and neutralized raffinate at the Rabbit and Key Lake operations are dominated by aluminum nickel hydroxide, aluminum oxide, magnesium oxide, magnesium hydroxide, or aluminum hydroxide.⁶,⁷,⁹,¹¹,²₈

Environmental Implications of Mg–Al Hydrotalcite in Tailings. Low concentrations of the EOCs As, Se, Mo, and Ni in the McArthur River sample (11-McTail-01) and the Deilmann tailings samples (09-E2-GC22 and 09-E2-GC13) prevented their observation via lab based EMP analysis. However, some As was spatially correlated with both the Fe and the Mg and Al (Supporting Information Figures S6 and S7) at the macro- and nanoscale, suggesting it is associated with both ferrhydrite and Mg–Al hydrotalcite. Data from TEM-EDX analyses of the McArthur River and Deilmann tailings samples not only confirm the association of As with Mg–Al hydrotalcite particles (and the ferrihydrite) but show a similar association with Ni (Supporting Information Figure S7). Nano elemental mapping images of the higher concentration Dielmann samples also showed this was the case (Supporting Information Figure S9–S10). The association of As and Ni with ferrihydrite in these tailings is well documented²⁹,¹¹,²₈ but the association with Mg–Al hydrotalcite in the tailings has not been observed to date in a U mill and aged tailings of such a large-scale operational site as Key Lake, Saskatchewan. This association is consistent with literature that demonstrates that synthetic and natural hydrotalcite-like layered double hydroxides exhibit anion exchange properties (e.g., 3.1–4.4 mequiv/g)²⁷ and, as such, can function as an efficient sink for contaminants.¹₄,₁₆,₅₀–₅₂ The presence of both ferrhydrite and Mg–Al hydrotalcite requires an understanding of how these types of materials (composed of two powerful toxic element control phases) will behave together. However, no literature reports how combined toxic element control phases react in situ in laboratory studies let alone at the industrial scale as demonstrated here. The observation that EOCs are associated with Mg–Al hydrotalcite in our products (particularly the final neutralized mill raffinate) suggests that hydrotalcite should also play a role in controlling the solubility of EOCs in the tailings.
For example, we can postulate that (a) the primary Fe control removes the majority of the EOCs, with the remaining EOCs swept up by the Mg–Al hydrotalcite throughout the mill neutralization treatment process (Dual Phase Toxic Element Control), and (b) this mechanism could control the solubility of EOCs if the tailings become reducing in the future, in which case ferrihydrite might transform to other more stable phases (e.g., lepidocrocite, goethite)\textsuperscript{58,59} and release the associated adsorbed EOCs.\textsuperscript{55} The potential for EOC solubility control by Mg–Al hydrotalcite in the presence of ferrihydrite (as found in these systems) warrants investigation as no studies have considered how the presence of a dual toxic element control phase systems will behave, especially under reducing conditions.

The coassociation in element composition and phase between ferrihydrite and the Mg–Al hydrotalcite observed in some of the solids samples (e.g., Figures 2c, Supporting Information S4 and S6–S10) also warrants investigation with respect to how it will affect the overall behavior-reactivity of U mill raffinates and tailings products. Although the association can be attributed to the precipitation of hydrotalcite on existing secondary ferrihydrite, as suggested by thermodynamic modeling, its presence as a hybrid-like ferrihydrite–Mg-Al-hydrotalcite phase cannot be ruled out based on the data presented. Notably, while solid solution dual phase morphism (two different mineral phases nucleating from the same source) is common in multicomponent systems,\textsuperscript{58,59} it has not been reported in the case of ferrihydrite and other non-Fe phases (e.g., hematite, lepidocrocite, goethite).

## ASSOCIATED CONTENT

### Supporting Information
Additional details regarding materials collection, sampling, and analytical methods and additional EMPA, XRD, ATR-IR, and Raman data. This material is available free of charge via the Internet at http://pubs.acs.org.

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**Notes**

The authors declare no competing financial interest.

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