

ALUMINUM AND MAGNESIUM MINERALOGICAL CONTROLS OF ELEMENTS OF CONCERN IN BULK NEUTRALIZED URANIUM MILL TAILINGS

J. Robertson^{1,2}, M.J. Hendry¹ and J. Essilfie-Dughan¹

¹ University of Saskatchewan, Saskatoon, Saskatchewan, Canada

² Cameco Corporation, 2121-11th Street West, Saskatoon, SK, S7M 1J3, Canada

jared.robertson@usask.ca, jim.hendry@usask.ca, joe377@mail.usask.ca

Abstract

The Deilmann Tailings Management Facility (DTMF) is located at Cameco Corporation's Key Lake U mill in northern Saskatchewan, Canada. A large portion of the deposited tailings are comprised of secondary mineral phases that precipitate during bulk neutralization of raffinate - an acidic, U-barren waste solution. The tailings discharged from the mill into the DTMF contain elevated concentrations of elements of concern (EOC) including As, Ni, Se, and Mo that originate from the U ore. Past studies established that secondary Fe mineral phases (e.g., ferrihydrite) act as a primary control on the solubility of these EOC. However, the identification of the presence of large quantities of uncharacterized secondary Al and Mg mineral phases in the tailings suggested that these phases may provide additional geochemical controls on EOC. A lab-scale continuous model of the Key Lake bulk neutralization circuit was constructed to study the mineralogy and evolution of the secondary phases that precipitate during raffinate neutralization and discharge as part of the tailings. Characterization of these phases showed amorphous AlOHSO_4 and Al-substituted ferrihydrite as prominent precipitates in the pH 4.0 slurries, and amorphous $\text{Al}(\text{OH})_3$ and MgAlSO_4 -type hydrotalcite in the pH 9.5 slurries. X-ray elemental mapping showed As, Se, and Mo associated with amorphous AlOHSO_4 , $\text{Al}(\text{OH})_3$, and Al-substituted ferrihydrite, while Ni was associated with hydrotalcite. Extended X-ray absorption fine structure (EXAFS) spectroscopy indicated that As was bonded to multiple phases (amorphous $\text{Al}(\text{OH})_3$, ferrihydrite, and hydrotalcite). Analysis of reference compounds suggested As is chemically bonded to these phases through bidentate-binuclear linkages. These results show that the EOC present in raffinate can be sequestered by both Fe and Al/Mg phases. The results of the study also show that, even in the absence of secondary Fe mineral phases, EOC can be effectively sequestered from raffinate, thereby demonstrating that multiple EOC controls exist in the final tailings.

1. Introduction

The process of milling U involves leaching of the U ore in an acidic, oxidizing solution, resulting in the dissolution of many minerals containing elements such as Al, Mg, Fe, As, Se, Mo, and Ni from the ore. Following separation of U from the other elements, an acidic (pH 1.0-1.5) waste stream called raffinate remains that contains elevated concentrations of the impurities dissolved from the ore. At the Key Lake U mill in northern Saskatchewan, Canada, raffinate is treated in

the bulk neutralization circuit to precipitate the impurities prior to releasing the effluent to the environment. Precipitation of the dissolved metal(oids) is facilitated by adding slaked lime to raise the pH of the raffinate in a stepwise manner (Fig. 1). The resulting slurries are mixed with the insoluble host rock residue from leaching and sent to the Deilmann Tailings Management Facility (DTMF) at pH 10.5 for long-term disposal.

The mineralogical characteristics of the bulk neutralization slurries have been studied in detail to better understand how environmental elements of concern (EOC) including As, Se, Mo, and Ni are precipitated during neutralization and the long-term stability of these precipitates in the DTMF. Many studies show that secondary Fe minerals are major contributors to EOC sequestration. Ferrihydrite, an amorphous Fe-hydroxide mineral phase that precipitates at pH > 3.5, exhibits strong solubility controls on EOC through surface complexation [1-3]. Poorly crystalline scorodite ($\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$ or ferric arsenate) has also been shown to control As concentrations in similar neutralization processes [4].

Major elemental constituents of the precipitated secondary minerals, however, have gone mostly unstudied. For example, dissolved Al and Mg in the raffinate are present in concentrations similar to Fe (>1 g/L), suggesting a large portion of the tailings mineralogy is uncharacterized. The objective of this study was to: (i) characterize the Al and Mg minerals precipitating during bulk neutralization, (ii) evaluate the potential EOC controls of these Al and Mg minerals, and (iii) determine how these minerals impact the established model of Fe mineralogical controls on EOC. The results of this study are presented in greater detail by Robertson et al. [5-7].

2. Method

A continuous mode lab-scale model of the Key Lake bulk neutralization process was constructed to perform controlled experiments (Fig. 1). A validation study was performed with the model and it was determined that the aqueous and major mineralogical characteristics of the Key Lake bulk neutralization process are recreated well with the model [7]. The precipitation trends throughout the process are modeled accurately, with the exception of the Fe(II)/Fe(III) redox couple which is difficult to control at the lab scale. Raffinates with controlled compositions were neutralized and the resulting precipitates were analyzed to determine their mineralogical characteristics. Scenarios without Fe in the raffinate were studied to observe the Al and Mg precipitates without being masked by Fe precipitates, while scenarios with Fe in the raffinate were studied to observe the Al and Mg precipitates in an environment representative of the mill. Slurry samples from the Se-Mo thickener (pH 4.0) and Lamella thickener (pH 9.5) were collected for characterization. These two slurries were also combined in equal volumes and the pH was raised to 10.5 to simulate the final precipitates discharged to the DTMF. The precipitates were characterized using X-ray diffraction (XRD), transmission electron microscopy (TEM), and X-ray absorption spectroscopy (XAS) coupled with linear combination fitting (LCF).

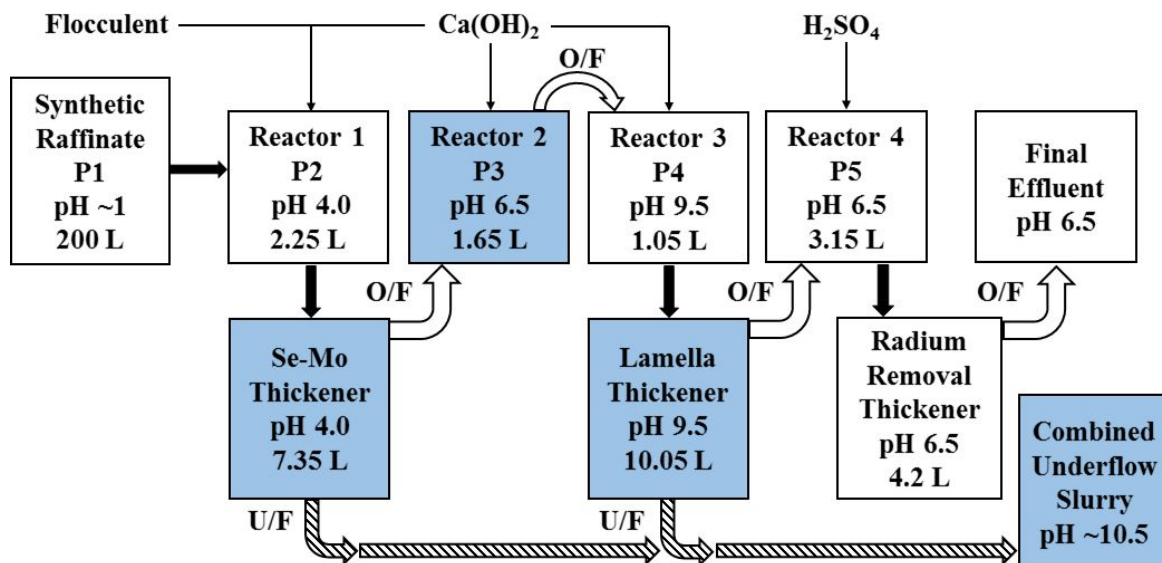


Figure 1. Process flow diagram of the lab scale model of the Key Lake bulk neutralization circuit. Coloured blocks indicate locations of aqueous and solid sampling points and white blocks indicate aqueous sampling only. Overflow and underflow of thickeners are indicated by O/F and U/F, respectively (from [6]).

3. Results

The first neutralization step at pH 4.0 serves to precipitate the Fe- and Al-hydroxides with an emphasis on As, Se, and Mo removal. In the absence of Fe, amorphous AlOHSO_4 (a precursor to hydrobasaluminite) precipitated as the major Al phase at pH 4.0 as determined by geochemical modeling, XRD, and Al K-edge XANES combined with LCF. Fitting of amorphous $\text{Al}(\text{OH})_3$ was attempted for the pH 4.0 precipitates; however, a poor fit was obtained. In the presence of Fe, ferrihydrite precipitated at pH 4.0 and was observed with Al^{3+} substituted at Fe^{3+} sites (Al-ferrihydrite); no discrete AlOHSO_4 phase was observed with Fe present. The second stage of neutralization serves to precipitate the remaining Al and Ni. A mixture of amorphous $\text{Al}(\text{OH})_3$ and a MgAl-type hydrotalcite ($\text{Mg}_2\text{Al}(\text{SO}_4)(\text{CO}_3)(\text{OH}) \cdot x\text{H}_2\text{O}$) precipitated at pH 9.5 in both the Fe-free and Fe-containing experiments. The precipitates from the low pH and high pH stages are combined and neutralized further to pH 10.5 before being discharged to the DTMF. Upon combining the slurries, AlOHSO_4 was not observed, suggesting the phase had transformed or dissolved/re-precipitated as amorphous $\text{Al}(\text{OH})_3$ and hydrotalcite. The final combined tailings slurries were determined to be a complex mixture of Al-ferrihydrite (approximately 20 - 30 mol% $\text{Al}/(\text{Al} + \text{Fe})$), amorphous $\text{Al}(\text{OH})_3$, and hydrotalcite. The concentrations of Mg, Al, and Fe in the final combined precipitates were 21.3, 23.8, and 16.2 mg/g, respectively.

When Fe was present, aqueous concentrations of As, Se, and Mo decreased >98.2% at pH 4.0 and Ni decreased by 99.9% at pH 9.5. During the neutralization of an Fe-free raffinate, the concentrations of As, Se, and Mo decreased (97.6%, 93.0%, and 43.7% removed) at pH 4.0 and Ni decreased (99.9% removed) at pH 9.5, indicating that Al and/or Mg mineral phases play a role

in sequestering these EOC. X-ray mapping at the nanoscale showed As, Se, Mo, and Ni associated with $\text{Al}(\text{OH})_3$ particles at pH 4.0 in the absence of Fe. With Fe present, the same EOC were associated to the Al-ferrihydrite at pH 4.0 (Fig. 2). In experiments with and without Fe, the pH 9.5 precipitates (amorphous $\text{Al}(\text{OH})_3$ and hydrotalcite) showed a strong association with Ni (Fig. 3). The combined slurries contained the characteristics of their constituent slurries. Most of the As, Se, and Mo was partitioned to Al-ferrihydrite/amorphous $\text{Al}(\text{OH})_3$ from the pH 4.0 step and most of the Ni was partitioned to hydrotalcite from the pH 9.5 step.

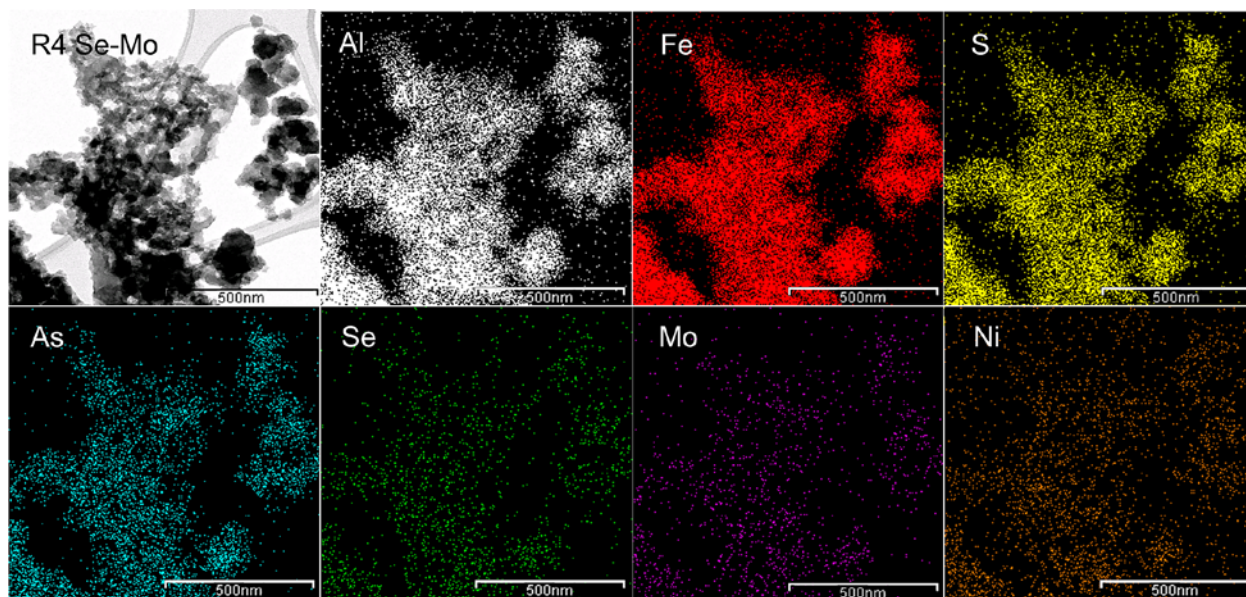


Figure 2. Transmission electron microscope image (top left) of a sample collected from the Se-Mo underflow (pH 4.0) from the Fe-containing experiment. The remaining images are element specific X-ray maps (from [6]).

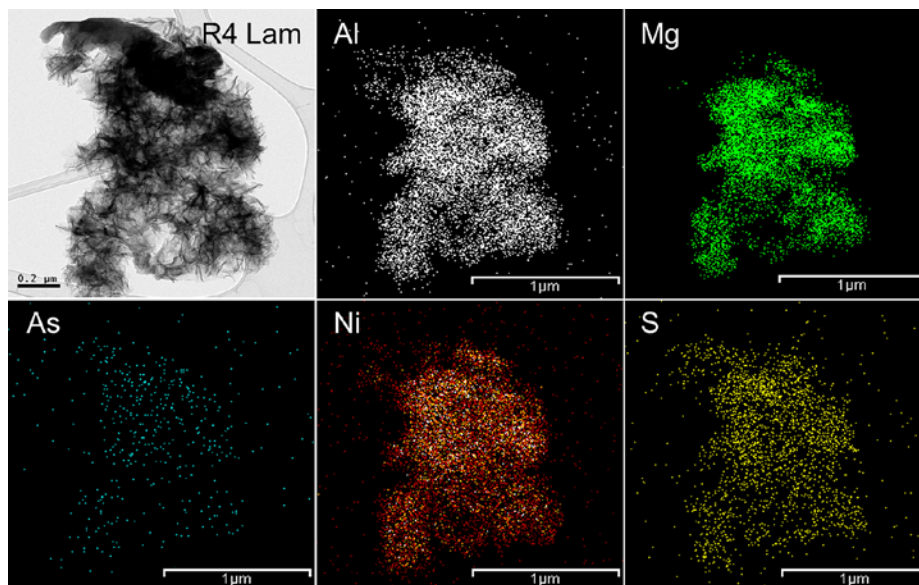


Figure 3. Transmission electron microscope image (top left) of a sample collected from the Lamella underflow (pH 9.5) from the Fe-containing experiment. The remaining images are element specific X-ray maps (from [6]).

To better understand the partitioning of As and Ni to the Al and Mg precipitates, extended X-ray absorption fine structure spectroscopy (EXAFS) was performed on synthesized reference compounds that were identified in the previous mineralogical characterization. Arsenic reference compounds consisted of ferric arsenate, scorodite, and As adsorbed -ferrihydrite, -amorphous $\text{Al}(\text{OH})_3$, $-\text{AlOHSO}_4$, and $-\text{MgAlFe}$ -hydrotalcite. Nickel reference compounds consisted of β - $\text{Ni}(\text{OH})_2$, amorphous $\text{Ni}(\text{OH})_2$, and Ni adsorbed -ferrihydrite, -amorphous $\text{Al}(\text{OH})_3$, and $-\text{MgAlFe}$ -hydrotalcite. Due to the chemical complexity of the samples (which did not allow for EXAFS analysis), the structural characteristics of the reference compounds were characterized by EXAFS instead. This allowed the coordination nature of As and Ni in the samples to be inferred by determining the abundance of the reference compounds in the samples via LCF.

Results from the Fe-free samples at pH 4.0 showed that As was adsorbed to AlOHSO_4 via bidentate-binuclear linkages (inferred from EXAFS results of the actual As adsorbed AlOHSO_4 reference compound). When Fe was present at pH 4.0, As complexed to ferrihydrite (bidentate-binuclear; not necessarily in the form of Al-ferrihydrite as an As-adsorbed Al-ferrihydrite standard was not prepared), ferric arsenate, and AlOHSO_4 . Linear combination fitting of the precipitates showed that 60% ($\pm 3\%$) of the As was associated to ferrihydrite, 25% ($\pm 6\%$) to ferric arsenate, and 15% ($\pm 5\%$) AlOHSO_4 suggesting that Fe precipitates are the primary sequestration mechanism of As at low pH.

Arsenic in the pH 9.5 precipitates were mostly adsorbed to hydrotalcite (86% ($\pm 6\%$) in the Fe-free experiment and 88% ($\pm 7\%$) in the Fe-containing experiment) with the remaining As adsorbed to amorphous $\text{Al}(\text{OH})_3$ (14% ($\pm 6\%$) and 12% ($\pm 7\%$) in the Fe-free and Fe-containing experiments, respectively). Both $\text{Al}(\text{OH})_3$ and hydrotalcite adsorption mechanisms are bidentate complexes. Nickel was shown to form both a Ni-Al layered double hydroxide surface precipitate on MgAl -hydrotalcite (39% ($\pm 3\%$) and 42% ($\pm 3\%$) for Fe-free and Fe-containing experiments) and an adsorption complex with amorphous $\text{Al}(\text{OH})_3$ (61% ($\pm 3\%$) and 58% ($\pm 3\%$) Fe-free vs. Fe-containing) at pH 9.5. These results suggest that Al and Mg precipitates are the primary sequestration mechanism at high pH neutralization steps.

The characteristics of the final combined slurry (pH 10.5) reflected those of its solids constituents (i.e, those from pH 4.0 and 9.5). While the pH 4.0 precipitates with Fe indicated that As was coordinated with AlOHSO_4 and ferric arsenate as previously mentioned, these phases were not observed in the combined precipitates at pH 10.5. Instead, an increased mass of As was coordinated with amorphous $\text{Al}(\text{OH})_3$. Without Fe in the precipitates, 58% ($\pm 3\%$) of the As was associated to amorphous $\text{Al}(\text{OH})_3$ and 42% ($\pm 3\%$) was associated with hydrotalcite. With Fe in the precipitates, 54% ($\pm 3\%$) of the As was associated with ferrihydrite, 42% ($\pm 4\%$) with amorphous $\text{Al}(\text{OH})_3$. The LCF results also suggested a minor presence of As adsorbed hydrotalcite (4% ($\pm 3\%$)), but this is beyond the sensitivity of the technique. There was also an overall increase of As associated to Al phases relative to the As in the pH 4.0 precipitates upon raising the pH to 10.5 (42% As associated to Al phases at pH 10.5 versus 15% at pH 4.0),

suggesting that a portion of the As transfers from the dissolution of ferric arsenate at increased pH to $\text{Al}(\text{OH})_3$ and potentially hydrotalcite. Since very little Ni was sequestered in the pH 4.0 precipitates, the characteristics of Ni in the combined slurry was similar to the pH 9.5 precipitates in that Ni-Al layered double hydroxide (51% ($\pm 6\%$) and 34% ($\pm 3\%$) Fe-free vs. Fe-containing) and Ni-adsorbed amorphous $\text{Al}(\text{OH})_3$ (49% ($\pm 7\%$) and 66% ($\pm 3\%$) Fe-free vs. Fe-containing) were the primary mechanisms of Ni control. Nickel was not observed to be associated to any Fe precipitates in these samples. The identification of Al and Mg mineral phases exerting solubility controls at the terminal neutralization step shows that multiple phases are active in EOC sequestration at the DTMF and could provide further long-term security for the surrounding environment.

4. Conclusions

This study shows that not only do Al-Mg precipitates comprise an appreciable mass of the precipitates reporting from the Key Lake bulk neutralization process to the DTMF, but they also exert solubility controls on As and Ni. Decreases in Se and Mo concentrations were also observed, suggesting that Al-Mg precipitates effect the solubility of these elements as well. Although Fe precipitates are the primary sequestration mechanisms of EOC, this study demonstrates that Al-Mg also act in concert with the Fe precipitates to control EOC concentrations in the slurries discharged to tailings facilities. Improved characterization of these precipitates allows for a better understanding of the long-term fate of the final tailings of milling activities and will allow for the design of more effective processes for controlling EOC in uranium tailings

5. Acknowledgments

Financial support was provided by Cameco Corporation and the Natural Sciences and Engineering Research Council of Canada (NSERC) through a Senior Industrial Research Chair to MJH and NSERC's CGS-M program. The authors acknowledge the technical assistance of Jianzhong Fan, Jing Chen, Fina Nelson, and Tom Bonli at the University of Saskatchewan. Research described in this work was performed at the Canadian Light Source, which is supported by the NSERC, the National Research Council Canada, the Canadian Institutes of Health Research, the Province of Saskatchewan, Western Economic Diversification Canada, and the University of Saskatchewan. The use of the SGM and HXMA beamlines at the Canadian Light Source and the support received by the beamline staff (T. Regier, J. Dynes, and D. Chevrier at SGM and N. Chen and W. Chen at HXMA) is gratefully acknowledged.

6. References

- [1] Moldovan, B. J., Jiang, D. T., Hendry, M. J., "Mineralogical characterization of arsenic in uranium mine tailings precipitated from iron-rich hydrometallurgical solutions", *Environ. Sci. Technol.*, Vol. 37, 2003, pp. 873-879.

- [2] Essilfie-Dughan, J., Hendry, M. J., Warner, J., Kotzer, T., "Arsenic and iron speciation in uranium mine tailings using X-ray absorption spectroscopy", *Appl. Geochemistry*, Vol. 28, 2013, pp. 11-18.
- [3] Douglas, G. B., Wendling, L. A., Pleysier, R., Trefry, M. G., "Hydrotalcite formation for contaminant removal from Ranger Mine process water", *Mine Water Environ.*, Vol 29, 2010, pp. 108-115.
- [4] Mahoney, J., Slaughter, M., Langmuir, D., Rowson, J., "Control of As and Ni releases from a uranium mill tailings neutralization circuit: Solution chemistry, mineralogy and geochemical modelling of laboratory study results", *Appl. Geochemistry*, Vol. 22, 2007, pp. 2758-2776.
- [5] Robertson, J., Essilfie-Dughan, J., Lin, J., Hendry, M.J., "Coordination of arsenic and nickel to aluminum and magnesium phases in uranium mill raffinate precipitates", *Environ. Sci. Technol.*, In submission, 2016b.
- [6] Robertson, J., Hendry, M.J., Essilfie-Dughan, J., Chen, J., "Precipitation of aluminum and magnesium secondary minerals from uranium mill raffinate (pH 1.0-10.5) and their controls on aqueous contaminants", *Appl. Geochemistry*, Vol. 64, 2016a, pp. 30-42.
- [7] Robertson, J., Shacklock, K., Frey, R., Gomez, M.A., Essilfie-Dughan, J., Hendry, M.J., "Modeling the Key Lake Uranium Mill's Bulk Neutralization Process using a Pilot-Scale Model", *Hydrometallurgy*, Vol. 149, 2014, pp. 210-219.