

International Symposium on Uranium Raw Material for the Nuclear Fuel Cycle: Exploration, Mining, Production, Supply and Demand, Economics and Environmental Issues (URAM-2018)



Contribution ID: 5

Type: ORAL

A REVIEW OF THE GEOCHEMICAL CONTROLS ON ELEMENTS OF CONCERN IN URANIUM MILL TAILINGS, ATHABASCA BASIN, CANADA

Thursday, 28 June 2018 09:00 (20 minutes)

INTRODUCTION

The Athabasca Basin of northern Saskatchewan (and a small part of Alberta), Canada is a major source of global uranium (U) supplies. Uranium mined from the Basin comprised 22% of the world's supply in 2015, and, as of 2014, there are 235,000 tons of known economically mineable U in reserve in the Basin [1, 2].

There are three U mills currently operating in the Basin (Rabbit Lake, Key Lake, and McClean Lake). Uranium production began at Rabbit Lake in 1975. Key Lake was commissioned in 1983. The McClean Lake mill began operation in 1999. A fourth mill, Cluff Lake, was commissioned in 1980 and decommissioned in 2003 [3]. Conventional U milling processing in the Basin follows the pathways: comminution (crushing and grinding), leaching (using sulfuric acid under oxic conditions and resulting in a solution rich in Fe, Al, Mg, Si, As, Ni, Se, Mo, SO₄, and U (among other elements), solid-liquid separation, purification, precipitation of the dissolved metal(loid)s (as secondary minerals as the solution pH is neutralized to neutral to alkaline pH with slaked lime), and packaging.

Tailings slurries from the mill process can contain elevated concentrations of elements of concern (EOC) including As, Ni, Se, Mo, and ²²⁶Ra. Above ground tailings management facilities (TMF) were first used to store tailings [4]. Subsequently, above ground TMFs were replaced with in-pit TMFs located in mined-out open pits [5]. These in-pit TMFs were engineered to optimize tailings consolidation, and, after decommissioning, minimize groundwater flow through the tailings and ensure EOC transport is dominated by diffusion. The first in-pit TMF was constructed at Rabbit Lake in 1984 (termed the RLITMF) [5]. The second in-pit TMF was constructed at Key Lake in 1996 (termed the DTMF) [6]. The third TMF was constructed at McClean Lake in 1999 (termed the JEB TMF) [7]. All three mills discharge tailings sub-aqueously to the TMFs to prevent transportation of contaminated dust and to spread the tailings more evenly across the TMF [8].

This study summarizes the extensive existing literature on the mineralogical controls on the EOCs in tailings in in-pit TMFs in the Athabasca Basin compiled over that past two decades.

METHODS

Many methods have been used to study the geochemical controls on EOCs in Athabasca Basin tailings. These include solids and aqueous sampling during the neutralization steps at individual mills, analysis of decades-old porewater and solids samples from TMFs, and batch and continuous mode laboratory experiments to generate precipitates of synthetic raffinate solutions. The aqueous and solid phase chemical compositions were measured and used in geochemical models and to study spatial and temporal trends in the tailings. Generally, solid samples were subjected to complementary characterization techniques including sequential extractions, X-ray diffraction (XRD), electron microscopy (EM), and X-ray absorption spectroscopy (XAS).

RESULTS, DISCUSSION AND CONCLUSIONS

Uranium Ores

The U ores in the basin are dominated by uraninite and pitchblende [9]. A strong association of U minerals with sulfide- and arsenide-rich mineralizations including gersdorffite, niccolite, rammelsbergite, pyrite, chalcopyrite, and arsenopyrite exists.

Mineralogy of Tailings

The precipitates in the neutralization processes from the three mills studied are highly dependent on the process pathway, which differs between mills. Different pH setpoints at each stage in each mill affects the saturation state of minerals and influences the final mineralogy of the precipitates. The initial concentrations of the major raffinate elements (which determines the mass of the minerals that precipitates) and the pH setpoints of the neutralization steps determine the solubility controls of EOCs driven by surface complexation or co-precipitation. Secondary minerals constitute 10-20% of the total tailings mass, with the remaining being leach residues. With the exception of gypsum, these precipitates are generally amorphous or nanocrystalline because of the rapid neutralization at high saturation conditions and ambient temperature and pressure inhibiting crystallization [10].

Differences exist in raffinate compositions between mills and between samples collected from the same mill at different times. These differences are attributed to variability of ore deposits and heterogeneity of ores from the same deposit. These variations render it difficult to generalize what secondary minerals will precipitate from the neutralization processes, although general trends exist.

The dominant Fe mineralogy of the final mill precipitates in all three neutralization processes is ferrihydrite. The lower terminal pH at McClean Lake is, however, more favorable for increased concentrations of ferric arsenate. Raffenates processed at Key Lake contain much greater concentrations of Al compared to raffenates processed at McClean Lake and Rabbit Lake due to the ores used. Aluminum and Mg comprise 1-5% of the secondary precipitates by mass in Key Lake tailings [11, 12]. Calcium comprises 10-20% of the final neutralized precipitates and is mostly as gypsum [12, 13].

Mineralogical Controls on Elements of Concern in Mill Tailings

Research shows that Fe and Al secondary minerals provide the dominant mineralogical controls of EOCs in the precipitates from raffenates [7, 14-20]. Most studies of Ca mineralogical controls on As and Mo show that Ca minerals provide a minor control compared to Fe and Al minerals [5, 16 21-24]. Co-precipitation with barite (barium chloride is added to the neutralization processes to precipitate 226Ra) is an important mineralogical control on 226Ra [25, 26]. However, adsorption of 226Ra to ferrihydrite appears to be the dominant sequestration mechanism [26].

Co-precipitation of ferric arsenate and the adsorption of arsenate to ferrihydrite are major mechanisms of As sequestration [14, 17, 19]. Molybdenum is primarily removed from raffinate by outer-sphere complexation with ferrihydrite at low pH neutralization stages [21, 23, 27, 28]. Studies of mineralogical controls of dissolved Ni are less prominent than As and much of the data is only qualitative or semi-quantitative [5, 6, 15, 17, 18, 24, 28, 29]. There is a lack of literature on the removal of Se during the neutralization processes.

Arsenic remaining in solution after the low pH stage forms bidentate adsorption complexes with amorphous Al(OH)₃ and hydrotalcite at pH 9.5. Between 41% and 71% of adsorbed As in pH 9.5 precipitates is associated with these Al phases [13, 29]. In a final tailings slurry samples collected at pH 10.9, 59% of solid phase As was associated to Al phases (amorphous Al(OH)₃ and hydrotalcite) and the remainder associated with Fe phases [29]. This distribution may be attributed 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 the Al phases during the pH adjustment [30]. The dissolution of ferric arsenate could also be a source of As adsorption to Al phases.

Most studies of EOC controls by Al and Mg minerals were determined on Key Lake samples [13, 28, 29]. As an example, Al was measured to control 5-25% of As at low pH stages (pH 4) through adsorption with amorphous Al(OH)₃ (bidentate-binuclear bonds) [13, 28]. In a final tailings slurry sample collected at pH 10.9, 59% of solid phase As was associated to Al phases (amorphous Al(OH)₃ and hydrotalcite) and the remainder with Fe phases [29]. Robertson et al. (2017) determined that Ni is controlled by amorphous Al(OH)₃ and Ni-Al layered double hydroxide surface precipitates on the surface of hydrotalcite. This observation is in contrast to results from other studies of laboratory and in situ tailings that suggest Ni is predominantly controlled by adsorption to ferrihydrite or precipitation of theophorite, annabergite, or cabrerite [15, 17, 18].

Long-term financial support for much of this work was provided by Cameco Corporation and the Natural Sciences and Engineering Research Council of Canada (NSERC) through a Senior Industrial Research Chair to MJH (grant 184573). Numerous individuals from our research group contributed to this body of work over many years. These include (but are not limited to): B. Moldovan, J. Bissonnette, K. Shacklock, R. Frey, S. Das, T. Bonli, J. Fan, J. Chen, R. Donahue, and Fina Nelson. Input from Areva Resources Canada is acknowledged.

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Country or International Organization

Canada

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Session Classification: Tailings and waste management

Track Classification: Track 11. Tailings and waste management