Geochemical and Mineralogical Study of Lithologies and Tailings from the Whabouchi Lithium Mine Site, Québec, Canada

Tomy Roy[1], Benoît Plante[1], Mostafa Benzaazoua[1], Isabelle Demers[1], Isabelle Petit[2]

[1]University of Québec in Abitibi-Témiscamingue, 445 boulevard de l'Université, Rouyn-Noranda (QC) J9X 5E4, Canada, Tomy.Roy@uqat.ca, Benoit.Plante@uqat.ca, Mostafa.Benzaazoua@uqat.ca, Isabelle.Demers@uqat.ca

[2]Nemaska Lithium, 101 avenue Chahoon, Shawinigan (QC) G9T 7J1, Canada, isabelle.petit@nemaskalithium.com

Abstract

From growth in demand for lithium, especially for electric batteries, arises renewed interest in lithium mining from hard-rock deposits such as spodumene pegmatites. However, water quality from lithium mine tailings remains a poorly studied subject. Six samples of rock lithologies and tailings coming from various ore beneficiation steps at the Whabouchi spodumene mine site were studied in laboratory and on-site. Results show that pegmatite tailings produce neutral leachates, with spodumene responsible for Li leaching up to a few milligrams per liter. Laboratory and field results were consistent and, overall, similar.

Keywords: lithium, pegmatite, water quality prediction, geochemistry, mineralogy

Introduction

In the past few years, worldwide demand for lithium (Li) increased continuously, driven by the growing market of batteries for electric vehicles (Eftekhari et al. 2019). Although brine deposits in South America account for roughly two-thirds of all known Li resources, other types of deposits are also attracting renewed interest (Grosjean et al. 2012). Spodumene (LiAlSi2O6), a pyroxene mineral, was in 2019 the main source of Li (U.S. Geological Survey 2019) and remains a prime exploration target due notably to its presence on all continents and its century-long history of production and processing (Grosjean et al. 2012). It is found in rare-metal pegmatites and can be accompanied by a wide range of minerals with economic relevance, e.g. beryl and tantalite.

Despite a decades-long mining history, only a few studies have been conducted specifically about the environmental challenges associated with spodumene extraction from pegmatites, and thus the geochemical behavior of Li-pegmatite mine wastes is still poorly understood to date (Bradley et al. 2017). Karavaiko et al. (1979) reported concentrations between 4 and 8 mg/L Li2O (1.9 to 3.8 mg/L Li) in the pit lake and along rock walls of an open pit spodumene mine. No more details were given about mine water geochemistry in this context. Similarly, Rahn et al. (1996) reported circumneutral (8-9) pH and low (10-130 µS/cm) electric conductivity for pit water of abandoned spodumene mines in the Black Hills (U.S.A.), but without giving any more details. Li concentrations up to 15 mg/L have also been reported from "tailings dams of lithium mineral beneficiation plants" (Aral and Vecchio-Sadus 2011). Substantial amounts of unrecovered spodumene in tailings have been observed at different historic Li mining operations such as Foote Minerals' Kings Mountain, U.S.A. (0,44% Li2O) (Browning et al. 1964) and Transbaikal Mining-and-Processing Integrated Works, Russia (0.26% Li_2O) (Yusupov et al. 2015), for example. Besides challenges associated with industrial extraction of Li from spodumene, this mineral has been known for a long time to readily alter under meteoric conditions, losing primarily its Li content (Ginzburg 1959; Singh and Gilkes 1993).

Although it is not the only process that can occur in pegmatitic mine tailings exposed to meteoric conditions, Li release from residual (unrecovered) spodumene is the main focus of this paper. It is part of a broader research project aimed at better understanding the geochemistry of tailings and wastes produced at a spodumene mining site. Results of laboratory and field tests (the latter conducted over a 2-year time period) are presented, along with some mineralogical characterizations, in order to compare how different materials produced throughout Li ore processing behave geochemically at different scales.

Materials and Methods

Site Description and Sampling

Nemaska Lithium's Whabouchi lithium mine is currently being developed approximately 30 km southeast of the Cree community of Nemaska, northern Québec, Canada. A total of 36.7 Mt ore with an average grade of 1.30% Li2O will be extracted during the mine's life (Nemaska Lithium, 2020). The site has a subarctic climate, with a snow-free period ranging from June to October. Geologically, the orebody consists of a poorly zoned albite-spodumene pegmatite being approximately 1.3 km long, 60 to 330 m wide and more than 500 m deep. Simpler spodumene-depleted ("barren") pegmatites are also encountered in association with the orebody. Enclosing rocks consist of metamorphised amphibolites, but they are not the subject of this paper.

A spodumene concentrate will be produced on-site. Ore processing begins with crushing and screening at a 850 µm grain size. Coarser (grain size > 850 µm) particles undergo a 2-step dense media separation (DMS), where the lesser dense particles (density < 2.7) are discarded. Coarser particles with a density over 2.96 are considered as spodumene concentrate. Coarser particles with an intermediate density (between 2.7 and 2.96) are milled to a grain size under 850 µm and, along with the screened < 850 µm ore, undergo chemical conditioning (including an attrition step done at pH = 12 by adding caustic soda) prior to spodumene hydroflotation. Fig. 1 summarizes the ore processing to be done at the Whabouchi site and highlights the origin of some of the materials studied.

Sampling of rock lithologies (spodumene pegmatite and barren pegmatite) was achieved by selecting halves of drilling cores in order to have "fresh" samples spatially distributed over all the projected mine pit. Samples from each lithology were then crushed (<2 cm) and homogenised.

Samples of sieved ore, DMS tailings and flotation tailings were randomly collected from materials produced during pilot processing tests (fig. 1). A mix of flotation tailings and screened ore (half-half by weight) was also produced to simulate a "worst case" scenario where spodumene recovery would be low and also to obtain enough material to fill the field test cells (see below).

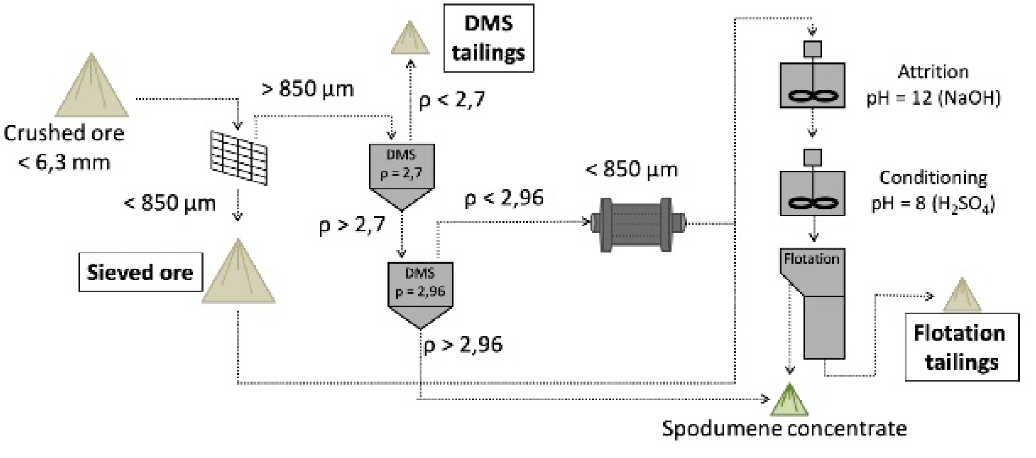

__Figure 1__ Simplified flowsheet of the ore beneficiation process at the Whabouchi mine site highlighting studied materials. Note: ρ is in g/cm^3; DMS = Dense Media Separation.

Mineralogical Characterizations

For each rock lithology, a subsample was further crushed to <2 mm to render more statistically representative results by mass unit and mounted on 2 epoxy polished sections. Mineralogical composition was investigated by scanning electron microscope (SEM) with TIMA (Tescan Integrated Mineral Analyser). Li contents in spodumene and in other possible carrying minerals (chiefly muscovite) were quantified by laser ablation coupled with inductively coupled plasma - mass spectrometry (LA ICP-MS). Mineralogical characterizations for other materials are currently being performed and are not presented in this paper. Nevertheless, as they are all derived from the ore (spodumene-pegmatite), their composition should be related to that of the ore. Sulfur and carbon contents of the 6 materials were determined with an induction furnace (ELTRA CS-2000) coupled with an infrared analyzer.

Column Laboratory Kinetic Tests

Six plastic columns with a 14 cm-inner diameter were set up (one for each material tested) and kept at room temperature (18-25 °C). Each column was filled with approximately 25 kg of material. Once every two weeks (for crushed drill cores) or once every month (for tailings and screened ore), 2 L of deionized water is added to the top of the column and left to percolate during 4 h while the column's bottom valve is closed. Then, the valve is opened and columns are allowed to drain by gravity until leachates stop flowing (but not more than 24 h for drill core columns and 48 h for tailings and screened ore columns to ensure freshness of the leachates). Leachates are then collected and immediately analyzed. Rinse cycles were repeated for 10 to 14 months, until stabilization of the geochemical response.

Field Test Cells

Experimental field cells were built on the Whabouchi property in late 2017 (fig. 2) as part of a broader research program. Two of them were filled with the mix of screened ore and flotation tailings, but with different configurations. One cell (called Nem-PT for "Nemaska - Pyramidal Tailings") was built with a truncated pyramidal shape using 40 m3 of material and its footprint is impermeabilized with a geomembrane. A bigger cell (called Nem-CD for "Nemaska - Co-Disposal) was built with a flat top using 80 m3 of material, with a 3 m2 impermeabilized lysimeter under its center (see fig. 2). Natural precipitations are allowed to freely drain by gravity. Leachates are collected once every two or three weeks from May to October and

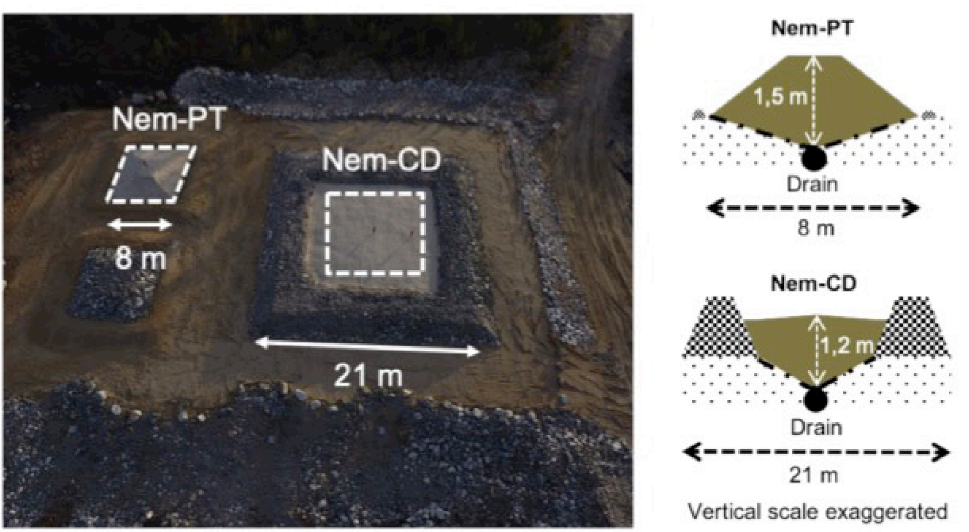

Figure 2 *Aerial view of the field cells built at the Whabouchi site, left (credit: Nemaska Lithium) and schematic cross-sections, right. Note: the lysimeters' surface projections are highlighted by dotted lines.*

immediately sent to a laboratory where they are analysed on the same day.

Leachates Analyses

Leachates are analysed for many physico-chemical parameters, but this paper will focus only on pH, electrical conductivity, sodium (Na) and Li. Cations (including Na and Li) were determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) using a Perkin-Elmer Optima 3100. Samples were previously filtered (0.45 µm) using nylon filters and acidified with environmental-grade nitric acid.

Results and discussion

Mineralogical Characterizations

TIMA mineralogical composition of the rock lithologies (parent material) is presented in table 1. In spodumene-pegmatite, the average Li content in spodumene is 3.82% (w/w), which is slightly higher than the theoretical stoichiometric value (3.73%). It indicates that the spodumene is "fresh" and has not been submitted to prior substantial alteration. Muscovite has an average Li content of 0.14%, corresponding to a negligible part of the sample's total Li content. Quartz and feldspars both make up to 90% of the barren pegmatite and more than three-quarters of the spodumene-pegmatite. In plagioclase feldspars, the sodic end-member (albite) is predominant. Major minerals (quartz, feldspars, spodumene and even muscovite) appear as often pluricentimetric well-shaped crystals that are consequently fairly well liberated when crushed to finer grain sizes as it is the case for tailings.

Carbon and sulfur contents determined by induction furnace were under the detection limits (0.05 and 0.009 wt% respectively for C and S) for all 6 materials. In addition to results shown above, preliminary mineralogical characterizations (not shown) suggest a sometimes elevated (about 5% or more) residual spodumene content in flotation tailings.

Water Quality

The pH of the leachates (fig. 3) remained circumneutral (6.5-8.5) for all tested materials in all settings. The pH of the leachates from field cells showed slightly greater variability, which can be explained by variability of precipitation and temperature under a natural climate. ORP values (not shown) exhibited no clear trend, but remained in the range 200-700 mV for all materials, indicating oxic conditions.

Electrical conductivity measurements are also presented in figure 3. This parameter is affected by the leachates ionic strenght and can be, at least qualitatively, a proxy for overall reactivity of the materials. In laboratory columns, electrical conductivity quickly settled around a near-constant value after a few rinse cycles. It exhibited few if any variation from the start for DMS tailings, stabilizing around a low value of 50 µS/cm. In field cells, even if it shows some variation that could be attributed to climate (and mostly precipitation) fluctuations, electrical conductivity seems to be on an overall decreasing trend which will be validated with coming seasons. For Nem-CD, the first sample of 2019, which shows unusually low values for many parameters, was heavily diluted due to ongoing snow melting. Also, the effect of the cells' geometry on water infiltration will have to be closely looked upon.

Li concentrations (fig. 3) from the field cells, as well as those obtained during early laboratory rinse cycles, are similar to those reported in the literature for Li mines (2-15 mg/L). In laboratory, Li values tend to settle near or under 1 mg/L. It will be interesting,

Table 1 *TIMA mineralogical composition of the rock lithologies (in wt%).*

Mineral	Chemical Formula	Barren Pegmatite	Spodumene Pegmatite
Quartz	SiO_2	32.7	23.2
Plagioclase	$(Na,Ca)(Si,Al)_4O_8$	49.3	39.6
K-Feldspar	$KAlSi_3O_8$	10.2	14.2
Spodumene	$LiAlSi_2O_6$	3.1	20.6
Muscovite	$KAl2(AlSi_3O_{10})(OH,F)_2$	2.5	1.6
Other*	-	2.2	0.8

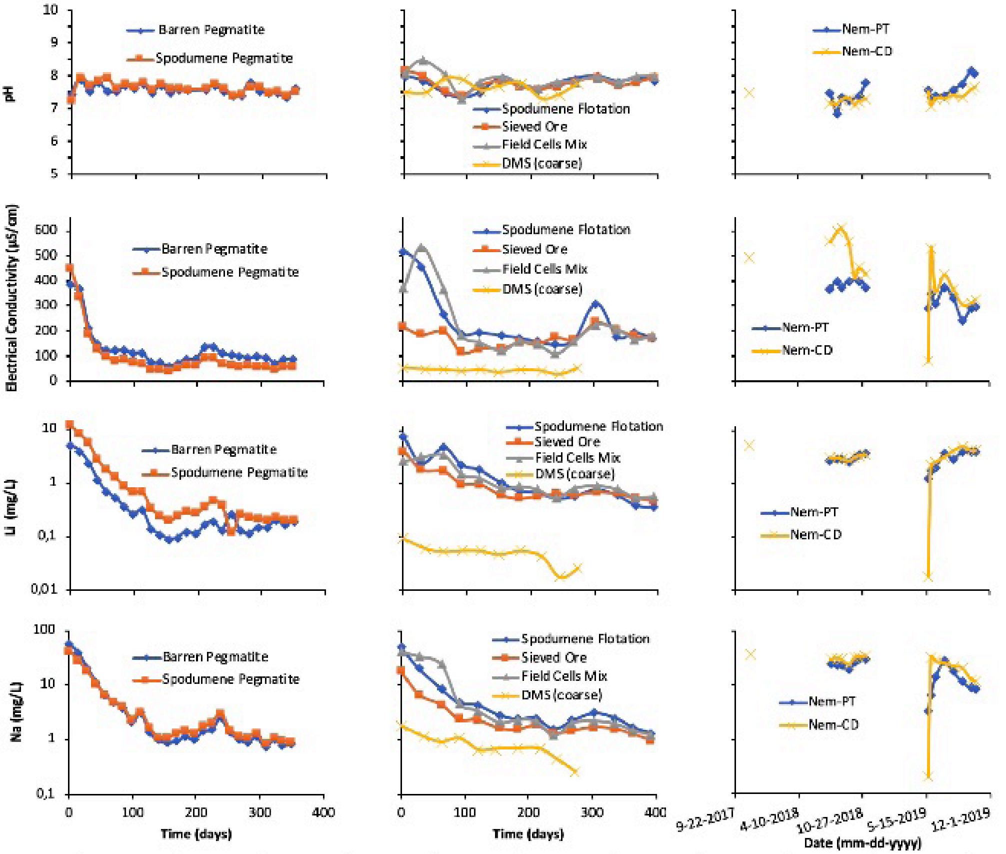

Figure 3 Water quality results (selected parameters) for rock lithologies columns (left), tailings columns (center) and field cells (right).

in the upcoming years of the research project, to see if this is the case as well for field cells, which currently vary around 2-5 mg/L. Na (fig. 3), which is assumed to come mostly from plagioclase dissolution, follows similar patterns as Li in laboratory. On-site, it shows slightly greater variation, with a somewhat decreasing trend in 2019 compared to the previous year.

Flotation tailings are the only tested material to have been exposed to chemical conditioning prior of being submitted to laboratory and field testing. Further physical and mineralogical characterizations will allow to assess potential effects of processing on the materials reactivity, especially in regard to mineral liberation and physical weakening of the particles.

In Québec as in many other jurisdictions, Li is not a regulated parameter (there is no numerical criterion for Li in mining effluents), nor is it regarded as a potential threat for the environment. However, as virtually almost every compound, it is indirectly regulated by toxicity standards (in Québec specifically, for *Daphnia magna* and *Oncorhyncus mykiss*). Thus, a detailed knowledge of the release mechanisms of a metal in water, its mineralogical origin and its typical concentrations under relevant settings can prove valuable to help minimize harmful effects on the receiving environment.

Conclusions

This paper presented water quality results from 6 samples coming from various beneficiation steps of a hard-rock lithium ore. These samples were submitted to laboratory kinetic tests as well as field-scale tests under a natural subarctic climate. Results showed that all these samples produce circumneutral leachates. Spodumene's signature in drainage waters was also evidenced, with Li concentrations up to a dozen mg/L during early testing. In general, laboratory results were very consistent with field results. This research highlights the interdependency between mineralogy, ore processing, tailings storage and water quality. More detailed mineralogical characterization will allow a better understanding of the influence of various parameters (e.g. mineral liberation, associations and textures) on water quality. Furthermore, it will also make possible to assess if minor minerals, which are numerous in spodumene pegmatites and are sometimes very specific to these rocks, play an important role in these materials' geochemical behavior.

Acknowledgements

The authors gratefully thank Simon Thibault, Nathalie Tremblay and Pierre Mercier for their implication during the project's initial years and field logistics. Many thanks to Yvan Poirier, Pierre-Alain Jacques, Joël Beauregard, Joseph Tsopnang, Marc Paquin and Mélinda Gervais for their help with field and laboratory work. TIMA and LA ICP-MS analyses were performed by PMC Process Mineralogical Consulting Ltd. (Maple Ridge, BC, Canada). All other laboratory work was performed at UQAT's *Unité de recherche et de service en technologie minérale* (URSTM). This research is funded by a Collaborative Research and Development Grant from the Natural Sciences and Engineering Research Council of Canada.

References

Aral H, Vecchio-Sadus A (2011) Lithium: Environmental Pollution and Health Effects. In: Nriagu JO (ed) Encyclopedia of Environmental Health. Elsevier, p 499-508

Bradley DC, McCauley AD, Stillings LL (2017) Mineral-deposit model for lithium-cesium-tantalum pegmatites. U.S. Geological Survey Scientific Investigations Report 2010–5070–O, doi:10.3133/sir20105070O

Browning J, McVay T, Bennett P (1964) Continuous flotation of beryl from spodumene mill tailings, Foote Mineral Company, Kings Mountain, NC. US Bureau of Mines Report of Investigations 6466:24

Eftekhari A (2019) Lithium Batteries for Electric Vehicles: From Economy to Research Strategy. ACS Sustain Chem Eng 7:5602-5613, doi:10.1021/acssuschemeng.8b01494

Ginzburg AI (1959) Spodumene and its alteration processes. Works of the Mineralogical museum of the Academy of Sciences of the USSR [trudy mineralogicheskogo muzeya] 9:19-52

Grosjean C, Miranda PH, Perrin M, Poggi P (2012) Assessment of world lithium resources and consequences of their geographic distribution on the expected development of the electric vehicle industry. Renew Sustain Energy Rev 16:1735-1744, doi:10.1016/j.rser.2011.11.023

Karavaiko G, Avakyan Z, Krutsko V et al. (1979) Microbiological investigations on a spodumene deposit. Microbiol 48:393-398

Nemaska Lithium (2020). Lithium Resources & Reserves, available at: https://www.nemaskalithium.com/en/whabouchi/lithium-resources-reserves/ [accessed 23 March 2020].

Rahn P, Davis A, Webb C, Nichols A (1996) Water quality impacts from mining in the Black Hills, South Dakota, USA. Environ Geol 27:38-53

Singh B, Gilkes R (1993) Weathering of spodumene to smectite in a lateritic environment. Clays and Clay Min 41:624-630

U.S. Geological Survey (2019) Mineral commodity summaries 2019. U.S. Geological Survey, https://doi.org/10.3133/70202434

Yusupov TS, Isupov VP, Vladimirov AG et al. (2015) Analysis of material composition and dissociation potential of minerals in mine waste to assess productivity of lithium concentrates. J Min Sci 51:1242-1247