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# LITHIUM FROM CLAY VERSUS LITHIUM FROM SPODUMENE

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# ABSTRACT

Interest in lithium for lithium-ion batteries for electric vehicles and other applications continues to drive interest in the extraction of lithium from various sources. Two sources already commercially exploited are lithium-bearing brines and hard rock deposits containing spodumene. A third source of lithium is lithium bearing clays.

This paper presents a comparison of the extraction of lithium from clay against the extraction of lithium from spodumene. The chemistry is examined and process modelling is used to calculate reagent and utility consumption and costs for the two routes.

The finding of this study is that the reagent/utility costs are very similar for the two routes.

Keywords: Lithium, clay, spodumene, sulphate, processing, variable costs

## INTRODUCTION

Currently, the dominant battery technology for electric vehicles and grid storage is based on lithiumion technology. Global lithium production closely matches the current demand, and the projected growth in the energy storage space has spurred great interest in the recovery of lithium from various sources.

Lithium occurs in saline brines, hard-rock minerals such as spodumene, and in lithium-bearing clays and mica. Recovery of lithium from brines and hard rock deposits has been discussed previously<sup>(1,2)</sup>. This paper presents a comparison between the recovery of lithium from a lithium-bearing clay and from spodumene. Published information on the Lithium Americas Thacker Pass Project in Nevada, USA<sup>(3)</sup> and the Quebec Lithium Project<sup>(4)</sup> in Quebec, Canada, was used to define the circuits.

## **CLAY LEACH CHEMISTRY**

Starkey<sup>(5)</sup> discusses the role of clays in fixing lithium. Clays containing lithium are kaolinites, micas, illites, smectites and fibrous clays, with trioctahedral smectites containing the largest amounts of lithium. The clay on which the exercise presented here is based is a mixture of mainly smectite and illite<sup>(3)</sup>. To model the leaching of this clay, the feed analysis must be translated into a plausible suite of minerals that:

- back-calculates to the measured elemental assays;
- accounts for 100 percent of the dry mass of the clay.

Leach stoichiometry and an extent of dissolution must then be assigned to each of the minerals in the suite, such that the measured leach results are replicated as closely as possible. Table 1 lists the analysis of the clay, as assayed and as reconstructed from the minerals listed in Table 4. Data obtained from leaching this clay with sulphuric acid<sup>(3)</sup> and the recoveries back-calculated from the mineral dissolution reactions in Table 3 and the fraction of each mineral leached, as listed in Table 4, are listed in Table 2.

| Element | Assay | Model | Element | Assay | Model  |
|---------|-------|-------|---------|-------|--------|
| Al      | 35713 | 35713 | Мо      | 150   | 150    |
| Ва      | 239   | 239   | Na      | 11907 | 11907  |
| Ca      | 41541 | 41541 | Р       | 46    | 46     |
| Cs      | 205   | 205   | Rb      | 632   | 632    |
| Fe      | 17041 | 17041 | S       | 13954 | 13954  |
| К       | 35785 | 35785 | Sr      | 273   | 273    |
| Li      | 3227  | 3227  | Ti      | 1803  | 1803   |
| Mg      | 56109 | 56109 | Zr      | 181   | 181    |
| Mn      | 551   | 551   | Si      |       | 254634 |

Table 1 – Feed clay, ppm

Table 2 – Measured leach data, as fractional extractions

| Element | Data  | Model |
|---------|-------|-------|
| Li      | 0.961 | 0.961 |
| Al      | 0.197 | 0.197 |
| Ca      | 0.023 | 0.023 |
| Fe      | 0.077 | 0.077 |
| К       | 0.347 | 0.347 |
| Mg      | 0.934 | 0.934 |
| Na      | 0.226 | 0.226 |

One way of calculating these numbers is via the definition of an overall squared error between the data and the corresponding model predictions, then using a search engine to find values for the model parameters that minimise the overall squared error. In this exercise the error function was set up as the total of the squared differences between:

- the measured assays in Table 1 and the assays based on the minerals shown in Table 4;
- the extractions shown in Table 2 and the corresponding extractions calculated by the model.

#### Table 3 – Leach stoichiometry

$$\begin{split} & \mathsf{KFe}^{3+}\mathsf{Al}_2\mathsf{Si}_3\mathsf{O}_{10}(\mathsf{OH})_2{}^{\bullet}\mathsf{2}\mathsf{H}_2\mathsf{O} + 10\mathsf{H}_3\mathsf{O}^+ \to \mathsf{K}^+ + \mathsf{Fe}^{3+} + 2\mathsf{Al}^{3+} + 3\mathsf{SiO}_2 + 18\mathsf{H}_2\mathsf{O} \\ & \mathsf{KMn}^{3+}\mathsf{Al}_2\mathsf{Si}_3\mathsf{O}_{10}(\mathsf{OH})_2{}^{\bullet}\mathsf{2}\mathsf{H}_2\mathsf{O} + 10\mathsf{H}_3\mathsf{O}^+ \to \mathsf{K}^+ + \mathsf{Mn}^{3+} + 2\mathsf{Al}^{3+} + 3\mathsf{SiO}_2 + 18\mathsf{H}_2\mathsf{O} \\ & \mathsf{CsMgAl}_2\mathsf{Si}_4\mathsf{O}_{10}(\mathsf{OH})_5{}^{\bullet}\mathsf{2}\mathsf{H}_2\mathsf{O} + 9\mathsf{H}_3\mathsf{O}^+ \to \mathsf{Cs}^+ + \mathsf{Mg}^{2+} + 2\mathsf{Al}^{3+} + 4\mathsf{SiO}_2 + 18\mathsf{H}_2\mathsf{O} \\ & \mathsf{RbMgAl}_2\mathsf{Si}_4\mathsf{O}_{10}(\mathsf{OH})_5{}^{\bullet}\mathsf{2}\mathsf{H}_2\mathsf{O} + 9\mathsf{H}_3\mathsf{O}^+ \to \mathsf{RbCs}^+ + \mathsf{Mg}^{2+} + 2\mathsf{Al}^{3+} + 4\mathsf{SiO}_2 + 18\mathsf{H}_2\mathsf{O} \\ & \mathsf{Na}_{33}\mathsf{Al}_{167}\mathsf{Mg}_{33}\mathsf{Si}_{400}\mathsf{O}_{1000}(\mathsf{OH})_{200}{}^{\bullet}\mathsf{200\mathsf{H}_2\mathsf{O}} + 6\mathsf{B00\mathsf{H}_3\mathsf{O}^+} \to 33\mathsf{Na}^+ + 167\mathsf{Al}^{3+} + 3\mathsf{Mg}^{2+} + 400\mathsf{SiO}_2 + 1200\mathsf{H}_2\mathsf{O} \\ & \mathsf{Li}_2\mathsf{Mg}_3\mathsf{Si}_4\mathsf{O}_{10}(\mathsf{OH})_4{}^{\bullet}\mathsf{5}\mathsf{H}_2\mathsf{O} + 8\mathsf{H}_3\mathsf{O}^+ \to 2\mathsf{Li}^+ + 3\mathsf{Mg}^{2+} + 4\mathsf{SiO}_2 + 19\mathsf{H}_2\mathsf{O} \\ & \mathsf{Li}_2\mathsf{Mg}_3\mathsf{Si}_4\mathsf{O}_{10}(\mathsf{OH})_4{}^{\bullet}\mathsf{5}\mathsf{H}_2\mathsf{O} + 8\mathsf{H}_3\mathsf{O}^+ \to 2\mathsf{Li}^+ + 3\mathsf{Mg}^{2+} + 4\mathsf{SiO}_2 + 19\mathsf{H}_2\mathsf{O} \\ & \mathsf{Li}_2\mathsf{Mg}_3\mathsf{Si}_4\mathsf{O}_{10}(\mathsf{OH})_4{}^{\bullet}\mathsf{5}\mathsf{H}_2\mathsf{O} + 8\mathsf{H}_3\mathsf{O}^+ \to 2\mathsf{Li}^+ + 3\mathsf{Mg}^{2+} + 4\mathsf{SiO}_2 + 19\mathsf{H}_2\mathsf{O} \\ & \mathsf{Fe}_2\mathsf{O}_3{}^{\bullet}\mathsf{H}_2\mathsf{O}^+ + 6\mathsf{H}_3\mathsf{O}^+ \to 2\mathsf{Fe}^{3+} + 10\mathsf{H}_2\mathsf{O} \\ & \mathsf{CaSO}_4{}^{\bullet}\mathsf{2}\mathsf{H}_2\mathsf{O} \to \mathsf{Ca}^{2+} + \mathsf{SiO}_2 + 3\mathsf{H}_2\mathsf{O} \\ & \mathsf{MgSiO}_3 + 2\mathsf{H}_3\mathsf{O}^+ \to \mathsf{Mg}^{2+} + \mathsf{SiO}_2 + 3\mathsf{H}_2\mathsf{O} \\ & \mathsf{Na}_2\mathsf{SiO}_3 + 2\mathsf{H}_3\mathsf{O}^+ \to 2\mathsf{Na}^+ + \mathsf{SiO}_2 + 3\mathsf{H}_2\mathsf{O} \\ & \mathsf{CaSi}_2\mathsf{O}_5{}^{\bullet}\mathsf{2}\mathsf{H}_2\mathsf{O} + 2\mathsf{H}_3\mathsf{O}^+ \to \mathsf{Ca}^{2+} + 2\mathsf{SiO}_2 + 5\mathsf{H}_2\mathsf{O} \\ & \mathsf{Ca}_{10}(\mathsf{PO}_4)_6(\mathsf{OH})_2 + 2\mathsf{H}_3\mathsf{O}^+ \to \mathsf{Ca}^{2+} + \mathsf{6PO}_4{}^{3-} + 4\mathsf{H}_2\mathsf{O} \\ & \mathsf{Ca}_{10}(\mathsf{PO}_4)_6(\mathsf{OH})_2 + 2\mathsf{H}_3\mathsf{O}^+ \to \mathsf{Ca}^{2+} + \mathsf{TiO}_2 + \mathsf{SiO}_2 + 3\mathsf{H}_2\mathsf{O} \\ \\ & \mathsf{Ca}_{10}\mathsf{SiO}_5 + 2\mathsf{H}_3\mathsf{O}^+ \to \mathsf{Ca}^{2+} + \mathsf{TiO}_2 + \mathsf{SiO}_2 + 3\mathsf{H}_2\mathsf{O} \\ \\ & \mathsf{Ca}_{10}\mathsf{I}\mathsf{O}^+ \mathsf{O}^+ \mathsf{O}^+ \mathsf{O}^+ \mathsf{O}^+ \mathsf{O}^{2+} + \mathsf{IO}_2 + \mathsf{O}^{2+} + \mathsf{I}^{2}\mathsf{O}_2 \\ \\ & \mathsf{Ca}_{10}\mathsf{O}^+ \mathsf{O}^+ \mathsf{O}^+ \mathsf{O}^+ \mathsf{O}^+ \mathsf{O}^{2+} + \mathsf{IO}_2 + \mathsf{O}^{2+} \mathsf{O}_2 \\ \\ & \mathsf{Ca}$$

| Minoral             | Formula  | Composition, ppm |         | Fraction |
|---------------------|--|------------------|---------|----------|
| Willera             |  | Feed             | Residue | leached  |
|                     | $KFe^{3+}Al_2Si_3O_{10}(OH)_2 + 2H_2O$   | 125541           | 114950  | 0.0844   |
| Illite              | $KMn^{3+}Al_2Si_3O_{10}(OH)_2\bullet 2H_2O$  | 4639             | 2525    | 0.4556   |
| linte               | $CsMgAl_2Si_4O_{10}(OH)_5$ •2 $H_2O$   | 934              | 856     | 0.0831   |
|                     | $RbMgAl_2Si_4O_{10}(OH)_5$ •2 $H_2O$   | 4117             | 3775    | 0.0831   |
| Smootito            | Na <sub>33</sub> Al <sub>167</sub> Mg <sub>33</sub> Si <sub>400</sub> O <sub>1000</sub> (OH) <sub>200</sub> •200H <sub>2</sub> O | 179468           | 130299  | 0.2740   |
| Sillectite          | $Li_2Mg_3Si_4O_{10}(OH)_4$ •5 $H_2O$   | 120237           | 4665    | 0.9612   |
| Goethite            | Fe <sub>2</sub> O <sub>3</sub> •H <sub>2</sub> O   | 3031             | 2980    | 0.0167   |
| Gypsum              | CaSO <sub>4</sub> •2H <sub>2</sub> O   | 74384            | 72651   | 0.0233   |
| Celestine           | SrSO <sub>4</sub>  | 572              | 572     | 0.0000   |
| Mg metasilicate     | MgSiO₃   | 146094           | 1060    | 0.9927   |
| Na metasilicate     | Na <sub>2</sub> SiO <sub>3</sub>   | 22642            | 17942   | 0.2076   |
| K metasilicate      | K <sub>2</sub> SiO <sub>3</sub>  | 48922            | 26570   | 0.4569   |
| Ca silicate hydrate | CaSi <sub>2</sub> O <sub>5</sub> •2H <sub>2</sub> O  | 119460           | 116676  | 0.0233   |
| Hydroxyapatite      | $Ca_{10}(PO_4)_6(OH)_2$  | 251              | 245     | 0.0233   |
| Ca molybdate        | CaMoO <sub>4</sub>   | 314              | 314     | 0.0000   |
| Ba silicate         | BaSi <sub>2</sub> O <sub>5</sub>   | 476              | 476     | 0.0000   |
| Sphene              | CaTiSiO₅   | 7382             | 7210    | 0.0233   |
| Zircon              | ZrSiO <sub>4</sub>   | 364              | 114950  | 0        |
| Quartz              | SiO <sub>2</sub>   | 141173           | 2525    | 0        |

| Table 4 – Minera | logy represent | tina the feed ( | clay and leached | 1 residue |
|------------------|----------------|-----------------|------------------|-----------|
|                  |                |                 | 0.01 0.100       |           |

The search engine was initialized by assigning initial guesses for the individual minerals and fractions leached. A multivariate search was then run to adjust the mineral contents and fractions leached to minimize overall squared-error function. The search engine used was Analytic Solver<sup>(6)</sup>. The model

parameter values found by the search engine closely reproduce the measured elemental extractions and the assay data for the feed clay. It could well be that different minerals and stoichiometry would give equally good results. Those found here were used in this exercise, the argument being that if the model reproduces the available data, the model can be used.

The mineral suite, leach stoichiometry and individual extents of reaction fitted to the feed assay and leach extraction data also enable calculation of the theoretical amount of acid consumed in the leach. Table 5 lists the calculated and measured<sup>(3)</sup> acid values relative to the lithium extracted, expressing the lithium as lithium carbonate equivalents (LCE). The measured acid requirement is, as would be expected, greater than the theoretical amount. Adding only the amount theoretically required would give zero residual acid, at which stage the final dissolution rate would also be zero and the maximum possible extraction would not be reached.

#### Table 5 – Acid required for lithium extraction from clay, kg H<sub>2</sub>SO<sub>4</sub> per kg LCE

| Theoretical      | 18 |
|------------------|----|
| Average measured | 23 |

#### SPODUMENE LEACH CHEMISTRY

Spodumene (LiAlSi<sub>2</sub>O<sub>6</sub>) is a pyroxene mineral found in lithium-bearing pegmatites, along with other minerals such as quartz, feldspar and mica<sup>(7)</sup>. Spodumene is separated from the ore by physical separation methods, typically flotation. In nature it occurs as  $\alpha$ -spodumene that is refractory to sulphuric acid. Heating  $\alpha$ -spodumene to above 900°C converts it to  $\beta$ -spodumene, which is amenable to acid attack, which is normally done as an acid bake, mixing the spodumene with concentrated sulphuric acid and heating the mix to 200°C. The stoichiometry of the acid bake step is:

$$2\text{LiAlSi}_2\text{O}_6 + \text{H}_2\text{SO}_4 \rightarrow 2\text{HAlSi}_2\text{O}_6 + \text{Li}_2\text{SO}_4$$

Testing by SGS in Canada<sup>(7)</sup> found a 30 percent excess of sulphuric acid, as per this stoichiometry, to give 97% conversion of the lithium in the spodumene tested to dissolved lithium, in a water leach following the thermal conversion and acid bake. The analysis of the solution obtained is listed in Table 6.

| Al <sup>3+</sup> | 4.3  | Mg <sup>2+</sup>                    | 0.02 |
|------------------|------|-------------------------------------|------|
| Fe <sup>3+</sup> | 0.1  | Mn <sup>2+</sup>                    | 0.3  |
| K⁺               | 0.1  | Na⁺                                 | 1.6  |
| Li <sup>+</sup>  | 23.6 | Free H <sub>2</sub> SO <sub>4</sub> | 21.4 |
| Ca <sup>2+</sup> | 0.3  |                                     |      |

Table 6 - Water leach solution, g/L

The stoichiometry of the acid attack on  $\beta$ -spodumene, with the 30 percent excess acid and 97 percent conversion, translates to an acid requirement of 1.8 kg per kg LCE, which is much lower than the acid requirement for the clay. However,  $\beta$ -spodumene is a thermally processed concentrate, while the lithium-bearing clay is essentially as-mined. The  $\beta$ -spodumene tested by SGS was produced from a flotation concentrate of  $\alpha$ -spodumene analysing 6.37 percent Li<sub>2</sub>O that was in turn produced from a sample of ore containing 1.61 percent Li<sub>2</sub>O, at a lithium recovery of 88 percent. That translates to 4.5 kg of ore milled per kg of flotation concentrate produced. A technical report<sup>(4)</sup> on the Quebec Lithium Project, for which this testing was done, lists the cost of mining as \$16.73/t milled (\$1.02/kg LCE) and the cost of crushing, grinding and flotation as \$8.52/t milled (\$0.52/kg LCE). Converting  $\alpha$ -spodumene to  $\beta$ -spodumene consumes 80.2 GJ of heat, typically from fuel, per tonne of Li in the spodumene, and a further 1.1 MWh of electricity per tonne of Li for the kiln itself and the subsequent re-milling of the  $\beta$ -spodumene<sup>(8)</sup>.

Comparing costs for clay and spodumene, per kg LCE from ore to dissolved lithium sulphate, requires the price of sulphuric acid. The quantity of acid used for a typical lithium operation from spodumene would normally not justify a dedicated sulphuric acid plant, and would thus require the purchase of sulphuric acid from the market. The higher acid demand of a clay-based operation allows for the economic construction of a sulphuric acid plant that produces acid and steam from elemental sulphur,

the steam being available for either the generation of electricity or for supplying thermal energy to evaporation in the downstream processing of the lithium solution ex the leach. This somewhat blurs the comparison between the extraction of lithium from clay and from spodumene, because while the spodumene option would have to purchase sulphuric acid, the clay option could assign the costs for making acid such that the transfer price of the acid to the leach is much lower than the market price of sulphuric acid.

Figure 1 shows US prices for sulphuric acid (left) and elemental sulphur(right), adjusted for inflation and going back almost three decades<sup>(9,10,11)</sup>. Over that period the average price for sulphuric acid (2018 currency), was US\$ 180/t. The corresponding average price for elemental sulphur was \$89/t. The upper and lower dotted lines mark the average price plus or minus one standard deviation over the period shown. For the past three decades, whenever the price of sulphuric acid or elemental sulphur went more than one standard deviation away from the long-term average, it reverted back towards the average relatively quickly. Any lithium operation built today would run for at least two decades, so it is illogical to base calculations of the project economics on short term price fluctuations; the long-term average is a better prediction for a project that will span two or more decades<sup>(12)</sup>.



Figure 1 – Average prices for H<sub>2</sub>SO<sub>4</sub> and elemental S (2018 \$)

Accepting the argument that an operation extracting lithium from clay can justify its own sulphuric acid plant while a spodumene operation cannot, and using the long-term average prices of sulphuric acid and elemental sulphur as the input costs for the acid consumed in the leach, leads to the numbers listed in Table 7 for lithium extraction from spodumene and from clay, from ore to dissolved lithium sulphate ex the leach. This is, of course, an incomplete comparison, not least because it does not take the capital cost of the acid plant into account. Operating costs in the acid plant, other than for the incoming sulphur, are about 0.25 per kg LCE<sup>(3)</sup>.

| Starting from spodumene ore   | Amount  | Unit cost  | \$/kg LCE |
|---|---------|------------|-----------|
| Spodumene concentrate (mining, milling, flotation)  | 6.35 kg | \$0.244/kg | 1.54      |
| Kiln energy for the transition $\alpha$ -LiAl <sub>2</sub> O <sub>6</sub> $\rightarrow$ $\beta$ -LiAl <sub>2</sub> O <sub>6</sub> | 15 MJ   | \$0.011/MJ | 0.16      |
| Milling the $\beta$ -LiAl <sub>2</sub> O <sub>6</sub>   | 0.7 MJ  | \$0.019/MJ | 0.01      |
| Sulphuric acid to acid bake, as H <sub>2</sub> SO <sub>4</sub>  | 1.78 kg | \$180/t    | 0.32      |
|   |         | Sub-total  | 2.03      |
| Starting from lithium-bearing clay  | Amount  | Unit cost  | \$/kg LCE |
| Clay to leaching (0.7% Li₂O)  | 61 kg   | \$5/t      | 0.31      |
| Sulphur for making sulphuric acid, as S   | 7.5 kg  | \$89/t     | 0.67      |
| Operating costs other than incoming sulphur   |         |            | 0.25      |
|   |         | Sub-total  | 1.23      |

| Tahlo 7 _ C | lost from oro | to dissolvo | d lithium cu | Inhato haso    | d on 1 ka I CE |
|-------------|---------------|-------------|--------------|----------------|----------------|
|             |               |             | u nunum su   | inpliate, base |                |

#### CHEMISTRY OF PURIFICATION AND RECOVERY

The recovery of lithium from the sulphate solutions ex the leaching of clay or acid-baked  $\beta$ -spodumene exploits the solubilities of the relevant sulphate and carbonate salts. The battery industry requires very specific product purity and composition stability to produce reliable, active cell components. The lithium sulfate solution from either hard-rock (spodumene) or clay-based resources must be purified to an acceptable level before production of the finished lithium chemical. The path chosen for purification depends on the specific composition of the solution ex leach, and the costs of the relevant reagents and utilities at the location of the operation concerned. A previous paper(2) presents a discussion of the chemistry. Figure 2 shows the solubilities of sodium, potassium, lithium, magnesium and calcium carbonates in water. The vertical axis is logarithmic.



Figure 2 – Solubility of carbonates in water

The standard approach is to use CaCO<sub>3</sub> (limestone), which is cheaper than Ca(OH)<sub>2</sub> (slaked lime) to raise the pH enough to precipitate the trivalent cations, then Ca(OH)<sub>2</sub> to raise the pH further and precipitate the divalent cations (e.g.  $Mg^{2+}$ ,  $Mn^{2+}$ ) other than calcium, and finally sodium hydroxide and sodium carbonate to precipitate the calcium, leaving the monovalent cations (Na<sup>+</sup>, K<sup>+</sup>, Li<sup>+</sup>) in solution. Figure 3 (top left) shows the results of calculations using software commercially known as OLI Studio<sup>(13)</sup> to simulate the addition of limestone to the solution from the clay leach and (top right) adding lime to the solution remaining after the addition of limestone. The left and right vertical axes are concentration and pH, respectively. The horizontal axes are the amount of limestone or lime added, in kg per kg LCE in the leach solution.

The solution ex the clay leach contains a fairly high level of magnesium. Allowing the solution after the addition of limestone to cool (Figure 3, bottom left) causes about a third of the magnesium to crystallise as magnesium sulphate, reducing the amount of lime required (Figure 3, bottom right) to remove the remaining magnesium.

Once most of the impurities have been removed, the next step is to concentrate the lithium in the solution to slightly short of the point at which lithium sulphate begins to crystallise. Figure 4 shows the calculated concentration of lithium (left) and the amounts of magnesium and calcium remaining (right) as the evaporative concentration of lithium proceeds. Crystallisation of  $Li_2SO_4 \bullet H_2O$  begins at about 81 percent volume reduction, by which stage a considerable fraction of the residual Ca<sup>2+</sup> and Mg<sup>2+</sup> have been precipitated and the concentration of Li<sup>+</sup> has been increased from 7 to 34 g/L.



Figure 3 – Solution purification with limestone and lime, solution from clay



Figure 4 – Evaporation after liming, solution from clay

The penultimate step is to add enough sodium carbonate to the concentrated solution to precipitate as much of the residual calcium as possible, without losing lithium. Figure 5 shows the results of OLI calculations for adding sodium carbonate to the solution ex the lime addition step, precipitating calcium carbonate at 40°C (red line) and at 95°C (blue line). The two vertical lines mark the points at which lithium carbonate begins to precipitate (red 40°C, blue 95°C). Doing this step at the higher temperature removes slightly more calcium than at the lower temperature, but the gap between the maximum calcium removal and the onset of lithium loss is much smaller at the higher temperature than at the lower temperature.

Finally, lithium carbonate can be precipitated from the purified solution. Figure 6 shows the results calculated by OLI for this step, from solution purified at 40°C (top) and at 95°C (bottom). The upper curves in the two plots on the left are the calculated purity of the lithium carbonate. The only significant impurity is calcium carbonate, and the final purity of the lithium carbonate is very much the same for the two purification temperatures ahead of the precipitation of lithium carbonate, although the impurity profiles versus  $Na_2CO_3$  addition are different.



Figure 5 – Calcium and lithium precipitation with sodium carbonate, clay



Figure 6 – Precipitation of Li<sub>2</sub>CO<sub>3</sub> from purified solution, clay

Figure 7 shows the results of the corresponding OLI calculations for the solution ex the water-leach of acid-baked  $\beta$ -spodumene. In this case the concentration of lithium ex the water leach is high enough for evaporation in the purification sequence to be unnecessary. Starting from spodumene, the purity of the final lithium carbonate is about 99.9 percent, which is very similar to the case starting from clay.

Table 8 lists the calculated percentages of  $Li_2CO_3$  and Ca in the final precipitate of lithium carbonate, alongside the Albemarle specification for battery-grade lithium carbonate<sup>(14)</sup>. The OLI calculations predict that while the lithium carbonate from clay and from spodumene will meet the specification for  $Li_2CO_3$  content, neither meets the specification for calcium, thus both would need further purification. Such further purification might take the form of an ion exchange step ahead of the precipitation of lithium carbonate (not re-dissolving the calcium carbonate), filtration and re-precipitation of purified lithium carbonate. Since this step would be common to both the clay and the spodumene circuits, it was left out of this exercise because it would "cancel out" as far as the comparison between the two circuits is concerned.



Figure 7 – Purification and lithium precipitation, solution, spodumene

| Component | Albemarle spec. | Spodumene | Clay |
|-----------|-----------------|-----------|------|
| Li₂CO₃    | >99.8           | 99.9      | 99.9 |
| Ca        | <0.016          | 0.06      | 0.04 |

Table 8 – Purity of the lithium carbonate, mass %

## PROCESS COMPARISON

To compare the recovery of lithium from clay and from spodumene more fully, two process models (numerically rigorous mass-energy balances) were built using Aspen Plus<sup>®</sup> process simulation software. The Lithium Americas Thacker Pass Project<sup>(3)</sup> and the Quebec Lithium Project<sup>(4)</sup> were picked as templates for the two circuits modelled.

Figure 8 illustrates the clay-based circuit, which is based on the Thacker Pass Project. The main process sections are:

- Comminution of the incoming clay (the model assumes a mill for simplicity);
- Leaching the comminuted clay with fresh and recycled sulphuric acid, separating the leach residue by thickening and washing the underflow with water in a three-stage counter-current decantation train, the overflow from first thickener of the counter-current decantation train being recycled to the leach via the acid make-up step;
- Cooling the supernatant from the leach thickener to crystallize out part of the magnesium sulphate, capturing the crystallized salt by centrifugation, the salt exiting the circuit, and recycling part of the centrate to the leach to build up the lithium concentration;
- Oxidation and neutralization of the balance of the centrate with air and limestone, using live steam injection to raise the temperature, precipitating iron and aluminium, the

resulting hydroxide solids being captured by filtration, washed with water and exiting the circuit;

- Evaporation of the filtrate and crystallization of magnesium sulphate, the crystallized magnesium sulphate being captured by centrifugation and exiting the circuit;
- Addition of slaked lime to the centrate to raise the pH sufficiently to precipitate most of the remaining magnesium, then addition of sodium hydroxide and sodium carbonate to precipitate calcium and any remaining magnesium (also any other divalent cations) to very low levels, followed by filtration, washing of the precipitate with water and recycling it to the iron/aluminium precipitation section;
- Precipitation of lithium carbonate from the purified solution via the addition of sodium carbonate, the precipitated lithium carbonate being recovered by filtration and washed with water, the wash filtrate used to prepare the solution of sodium carbonate added to precipitate the lithium carbonate and the washed lithium carbonate exiting the circuit as the product;
- Addition of acid to the primary filtrate from the filtration of lithium carbonate to destroy
  residual carbonate, the CO<sub>2</sub> evolved being vented, part of the resulting solution recycled
  to the lime slaker ahead of the liming step and the balance going through vacuum
  degassing to remove residual carbon dioxide;
- Two stages of evaporation using mechanical vapor recompression to first crystallize a mixed sodium-potassium sulphate, then sodium sulphate (the crystallized sulphates exit the circuit), recycling the lithium in the remaining solution via the lime slaker.

Figure 9 illustrates the spodumene-based circuit. This process model excludes the ore preparation and pyrometallurgical parts of the overall circuit. The main sections modelled are:

- Leaching the acid-baked β-spodumene with water, filtration and washing the filter cake with water, the washed residue leaving the circuit;
- Oxidation and neutralization of the water-leach filtrate, using live steam injection to raise the temperature, precipitating iron and aluminium, the resulting hydroxide solids being captured by filtration, washed with water and exiting the circuit;
- Addition of slaked lime to raise the pH sufficiently to precipitate most of the remaining magnesium, then addition of sodium hydroxide and sodium carbonate to precipitate calcium (any remaining divalent cations are also precipitated) to very low levels, followed by filtration, washing of the precipitate with water and recycling the washed precipitate to the iron/aluminium precipitation section;
- Precipitation of lithium carbonate from the purified solution via the addition of sodium carbonate, the precipitated lithium carbonate being recovered by filtration and washed with water, some of the lithium carbonate re-dissolving in the wash water; the wash filtrate used to prepare the solution of sodium carbonate added to precipitate the lithium carbonate and the washed lithium carbonate exiting the circuit as the product;
- Addition of acid to the primary filtrate to destroy residual carbonate, the CO<sub>2</sub> evolved being vented, part of the resulting solution recycled to the lime slaker ahead of the liming step and the balance going through vacuum degassing to remove residual carbonate;
- Evaporation using mechanical vapor recompression, crystallization of sodium-potassium sulphate (that exits the circuit), recycling the lithium in the remaining solution via the lime slaker.







Figure 9 – Process model, spodumene-based circuit

The process models were used to calculate the amounts of reagents and utilities required, and thence to calculate reagent/utility costs for each circuit. Table 9 lists the reagents and amounts consumed. Table 10 is a breakout of the water usage and Table 11 lists the calculated electricity requirements. The clay circuit produces surplus water because the ROM clay contains water, at 25% by mass<sup>(3)</sup>.

| Table 9 – Reagent | consumption, | kg p | er kg | LCE |
|-------------------|--------------|------|-------|-----|
|-------------------|--------------|------|-------|-----|

| Circuit   | Clay | Spodumene |
|---|------|-----------|
| Sulphuric acid, as 100% H <sub>2</sub> SO <sub>4</sub>    | 19.7 | 4.2       |
| Limestone, as 100% CaCO <sub>3</sub>                      | 2.1  | 2.1       |
| Lime, as 100% CaO   | 4.0  | 0.01      |
| Sodium hydroxide, as 100% NaOH                            | 0.02 | 0.01      |
| Sodium carbonate, as 100% Na <sub>2</sub> CO <sub>3</sub> | 2.3  | 2.1       |

| Circuit                           | Clay  | Spodumene |  |
|-----------------------------------|-------|-----------|--|
| Water in the incoming feed        | 22    | 0         |  |
| Water in incoming sulphuric acid  | 1.0   | 0.03      |  |
| Steam to oxidation/neutralisation | 2.9   | 1.7       |  |
| Water to solids washing           | 9.7   | 1.3       |  |
| Water to reagent make-up          | 5.2   | 4.7       |  |
| Total fresh water input           | 34.7  | 16.1      |  |
| Condensate from evaporation       | -46.0 | 12.3      |  |
| Total fresh water requirement     | -12.1 | 3.8       |  |

## Table 10 – Water, kg per kg LCE

## Table 11 – Electricity, kWh per kg LCE

| Circuit                        | Clay  | Spodumene |
|--------------------------------|-------|-----------|
| Milling                        | 0.052 | 5.855     |
| Pumping                        | 0.004 | 0.002     |
| Steam compression, evaporation | 4.533 | 1.593     |

Table 12 lists the reagent/utility costs calculated for the two circuits. The costs calculated for each circuit modelled differ by less than ten percent. At this level of analysis, a difference of this magnitude is insignificant, which implies similar overall variable operating costs for the two routes.

| Circuit  | Clay | Spodumene |
|--|------|-----------|
| Incoming feed (\$7/t)  | 0.61 | 2.04      |
| Sulphur to acid plant, as 100% S (\$89/t)                        | 0.64 | -         |
| Sulphuric acid, as 100% H <sub>2</sub> SO <sub>4</sub> (\$180/t) | -    | 0.06      |
| Limestone, as 100% CaCO <sub>3</sub> (\$60/t)                    | 0.13 | 0.13      |
| Lime, as 100% CaO (\$180/t)                                      | 0.72 | 0.002     |

Sodium hydroxide, as 100% NaOH (\$500/t)

Fresh water (\$5/t)

Electricity (\$0.0632/kWh)

Reagent & utility cost, \$/t LCE

Sodium carbonate, as 100% Na<sub>2</sub>CO<sub>3</sub> (\$300/t)

0.007

0.56

0.04

0.21

3.05

0.01

0.61

-

0.06

2.88

## Table 12 – Operating costs, \$/kg LCE

Were the clay circuit to purchase sulphuric acid instead of having its own acid plant, its reagent/utility cost would be \$6.39/kg LCE. Table 13 lists the capital costs published in 2018 for the Thacker Pass project and Figure 10 shows the results of IRR (internal rate of return) calculations, plotted against the years of plant operation, for having an acid plant versus purchasing sulphuric acid in the clay project, assuming the unit costs in Table 12 for sulphuric acid and elemental sulphur. This IRR exceeds 20 percent after five years of operation, and tends to 34 percent after 10 years, which would certainly justify the extra capital expenditure for the acid plant in the case of the clay circuit.

Table 13 – Published capital costs for Thacker Pass, \$ million (2018)

| Mine                           | 55  |
|--------------------------------|-----|
| Ore Crushing and Handling      | 31  |
| Process Plant                  | 77  |
| Sulphuric Acid Plant           | 135 |
| Tailings Management            | 56  |
| On-Site Infrastructure         | 41  |
| Total                          | 395 |
| Total less mine and acid plant | 205 |



Figure 10 –IRR for the acid plant in the clay circuit

Table 14 lists the capital costs published in 2012 for the Quebec Lithium Project, as published, adjusted to 2018 currency using the Chemical Engineering Plant Cost Index<sup>(15)</sup> and with the capacity adjusted to 30 thousand tonnes per year using the "0.6 rule"<sup>(16)</sup>.

Table 14 Published capital costs for the Quebec Lithium Project

| Voor                       | 2012    | 2018   |         |
|----------------------------|---------|--------|---------|
| rear                       | 20 kt/y | 20kt/y | 30 kt/y |
| Mine                       | 13      | 14     | 17      |
| Tailings management        | 17      | 17     | 22      |
| Electrical substation      | 4       | 5      | 6       |
| Ore Crushing and Handling  | 21      | 22     | 28      |
| Physical separation        | 28      | 29     | 37      |
| Pyrometallurgy             | 13      | 14     | 17      |
| Hydrometallurgy            | 13      | 13     | 17      |
| Buildings                  | 51      | 53     | 67      |
| Reagent & product handling | 6       | 6      | 8       |
| Total                      | 168     | 173    | 221     |
| Total less mine            | 154     | 159    | 203     |

Interestingly, after subtracting the capital cost for the mine from the total capital cost of the Quebec Lithium Project, and subtracting the capital costs of the mine and the acid plant in the Thacker Pass Project, the remaining capital costs are essentially the same for the two projects. That implies that the pyrometallurgy required in the spodumene circuit is balanced, in terms of capital cost, by the extra evaporation and crystallisation required in the clay circuit.

## CONCLUSION

The exercise presented here compares the extraction of lithium from lithium-bearing clay to the extraction of lithium from spodumene. The reagent/utility costs calculated for the two circuits differ by less than ten percent, which is not a significant difference at this level of analysis.

From the numbers published in the technical reports for the two projects used as templates, the spodumene circuit appears to have a lower capital cost than the clay circuit because the clay circuit has a sulphuric acid plant that the spodumene circuit does not. A simple IRR calculation indicates that the acid plant is a highly beneficial addition to the clay circuit.

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