

# A Triple Closed-Loop Chemical Technology for Producing Lithium Carbonate, High-Purity Alumina, and High-Quality Metallurgical-Grade Silicon from a Spodumene Concentrate

James G. (Jim) Blencoe, Ph.D.<sup>1</sup>

CTO, Medaro Mining Corp.

June 30, 2023

To whom it may concern:

Global Lithium Extraction Technologies, Inc. (“GLET”) and Medaro Mining Corp. (“Medaro”) have developed a special chemical technology (the “Technology”) for industrial production of high-purity lithium carbonate ( $\text{Li}_2\text{CO}_3$ ) from the spodumene ( $\sim\text{LiAlSi}_2\text{O}_6$ ) present in a spodumene concentrate. High-purity alumina ( $\text{Al}_2\text{O}_3$ ) and high-quality Grade 3 metallurgical-grade silicon (MG-Si) are optional saleable byproducts. The text below describes the Technology, as well as some of the work that’s been done to prove its commercial viability.

**Modularity and scalability.** The Technology is completely modular and highly scalable, and therefore, amenable to implementation in both central and remote geographic locations.

**Integration with spodumene concentrate production.** Plant operations can be integrated with spodumene concentrate production at a mine site, a key benefit of this being avoidance of expenses that would otherwise be incurred from land shipment of the concentrate.

**Highly continuous chemical processing.** The Technology is continuous in most of its unit operations.

**High Li, Al and Si recovery levels.** Literature data, and results obtained from GLET-Medaro bench-scale laboratory tests, indicate that Li, Al and Si recovery levels >95% will be possible in all commercial applications of the Technology.

**Feedstock materials.** Only three feedstock materials are required for chemical processing: (i) a spodumene concentrate; (ii) high-purity  $\text{CO}_2$ , which is consumed in forming  $\text{Li}_2\text{CO}_3$ ; and (iii) high-purity  $\text{H}_2\text{O}$ , which is consumed if  $\text{LiOH}\cdot\text{H}_2\text{O}$  is manufactured.

**Avoidance of problematic chemical substances.** The chemical steps in the Technology are sulfur-, sodium-, fluorine- and hydrocarbon-free, and they use only Earth-abundant materials.

**Proven chemical reactions.** The lithium solvent (nitric acid) regeneration reaction has already been proven at commercial scale; all remaining chemical reactions in the Technology have been proven at bench scale.

**Mild temperatures and pressures of processing.** With the exception of spodumene concentrate calcination at  $\sim 1,050\text{ }^\circ\text{C}$  to convert  $\alpha$ -spodumene to  $\beta$ -spodumene, and production of lithium metal at  $450\text{-}500\text{ }^\circ\text{C}$  (see below), all chemical reactions in the Technology occur at temperatures  $\leq 200\text{ }^\circ\text{C}$  and at pressures between 1 and 10 atm.

---

<sup>1</sup>Work address: 13 Vintage Way, #1334, Fernandina Beach, FL 32034. Telephone (cell): (865) 384-2251. Email: jimblencoe@orionlaboratories.com

**Near-zero net consumption of process reagents.** Internal closed-loop recycling of chemical materials reduces their irrecoverable losses to make-up amounts. This key attribute of the Technology *very significantly* lowers total product manufacturing costs.

**A third-party validation.** The technical viability of the GLET-Medaro method for producing  $\text{Li}_2\text{CO}_3$  was confirmed by a process engineer at Process Engineering International, LLC.

**Lower cost of producing lithium carbonate.** Due to the favorable characteristics of the GLET-Medaro method for producing  $\text{Li}_2\text{CO}_3$ , its total cost in commercial implementations will be 30 to 50% lower than current industrial methods.

**Byproducts.** The revenue potential of the Technology is enhanced by optional co-production of high-purity alumina and Grade 3 MG-Si. *To date, no company that manufactures spodumene-sourced  $\text{Li}_2\text{CO}_3$  and/or  $\text{LiOH}\cdot\text{H}_2\text{O}$  has succeeded in forming these valuable byproducts.*

**Lithium hydroxide monohydrate manufacturing.** The Technology uses an electrolytic process to convert  $\text{Li}_2\text{CO}_3$  to aqueous LiOH, and thereafter a crystallizer to convert the aqueous LiOH to granular  $\text{LiOH}\cdot\text{H}_2\text{O}$ .

**Lithium metal manufacturing.** At present, the Technology employs a conventional method to produce metallic lithium, it involving: first, dissolving  $\text{Li}_2\text{CO}_3$  in hydrochloric acid (HCl) to form lithium chloride (LiCl); second, adding potassium chloride (KCl) to the LiCl, and then dehydrating the mixture prior to heating it to 450-500 °C to create a nearly binary LiCl-KCl molten salt; and finally, electrolyzing the molten salt to produce molten Li metal, which is subsequently solidified, and then, optionally, purified by vacuum distillation. It should be recognized, however, that this method of Li metal manufacturing is very energy intensive and co-produces large amounts of unwanted chlorine gas, and for these two reasons in particular, GLET-Medaro is actively investigating alternative means for converting  $\text{Li}_2\text{CO}_3$  to metallic Li.

**Lithium product selectivity.** The Technology permits  $\text{Li}_2\text{CO}_3$ ,  $\text{LiOH}\cdot\text{H}_2\text{O}$  and metallic Li to be produced in any desired proportion.

**Minimal production of chemical waste.** First, by highly effective and energy-efficient closed-loop chemical recycling of the materials involved in recovering Li, Al and Si from  $\text{LiAlSi}_2\text{O}_6$ , and second, by converting the Al and Si to byproducts that can be sold at a profit, the amount of chemical waste produced by the Technology is extremely small.

**Green electrification.** The Technology can be powered entirely by green electricity!

**Submission of patent applications.** Two *provisional* patent applications describing the Technology have been submitted to the U.S.P.T.O., and both filings will soon be converted into corresponding *nonprovisional* patent applications.

**Potential applicability to processing lithium-enriched claystones.** Many of the chemical steps in the Technology are adaptable to production of  $\text{Li}_2\text{CO}_3$ , high-purity  $\text{Al}_2\text{O}_3$ , and high-quality Grade 3 MG-Si from claystones.

**Money invested to develop the Technology over the past ~2 years.** To date, close to US\$860,000 has been spent to bring the Technology to its current advanced state. A significant portion of that money was used to pay the costs of more than 50 benchtop laboratory experiments and more than 100 chemical and powder XRD analyses. It is also noteworthy that US\$60,000 has been spent to buy equipment for a pilot plant. Now, GLET-Medaro is seeking funds to finish building the plant.

**Results of recent, highly successful benchtop laboratory tests.** Recently, a new round of GLET-Medaro benchtop laboratory tests produced extremely positive results, among them being much-better-than-expected amounts of lithium extracted from small granular samples of high-purity  $\beta$ -spodumene. A parental mass of the latter was created by processing a small piece of a large single crystal of  $\alpha$ -spodumene excavated from a mine in the Black Hills of South Dakota. Tables 1 and 2 below list the percents of lithium and aluminum extracted from the starting granular  $\beta$ -spodumene via contact with 40 wt. % nitric acid for ~2 hours at ~120 °C and ambient pressure (undoubtedly very close to one atmosphere), with some material agitation to promote reaction.<sup>2</sup> It can be seen in Table 1 that the percent values for “Calculated Li leached” are *extremely high*, and thus bolster

Table 1. Lithium Extraction Results for a High-Purity $\beta$ -Spodumene				
Subsample	ppm Li in subsample	Subsample pair	ppm Li in subsample pair	Observed Li leached
Subsample 1, unleached	36,400	{Subsample 1, unleached Subsample 1, leached}	36,400 ppm and 1,470 ppm	96.3%
Subsample 2, unleached	35,700	{Subsample 1, unleached Subsample 2, leached}	36,400 ppm and 1,050 ppm	97.3%
Subsample 1, leached	1,470	{Subsample 2, unleached Subsample 1, leached}	35,700 ppm and 1,470 ppm	96.2%
Subsample 2, leached	1,050	{Subsample 2, unleached Subsample 2, leached}	35,700 ppm and 1,050 ppm	97.3%

Table 2. Aluminum Extraction Results for a High-Purity $\beta$ -Spodumene				
Subsample	ppm Al in subsample	Subsample pair	ppm Al in subsample pair	Observed Al leached
Subsample 1, unleached	146,000	{Subsample 1, unleached Subsample 1, leached}	36,400 ppm and 1,470 ppm	27.8%
Subsample 2, unleached	148,000	{Subsample 1, unleached Subsample 2, leached}	36,400 ppm and 1,050 ppm	25.0%
Subsample 1, leached	114,000	{Subsample 2, unleached Subsample 1, leached}	35,700 ppm and 1,470 ppm	28.9%
Subsample 2, leached	118,000	{Subsample 2, unleached Subsample 2, leached}	35,700 ppm and 1,050 ppm	26.1%

the conclusion that *the GLET-Medaro spodumene processing technology merits intense evaluation as a potential replacement for methods currently used to produce lithium products from spodumene concentrates*. On the other hand, the corresponding percent values for “Calculated Al leached” presented in Table 2 clearly show that nitric acid leaching removed Al to a far lesser extent than Li. For this reason, a magnesiothermic reduction method was devised to permit close to 100% recovery of the Al and Si present in the granular leached spodumene produced by nitric

<sup>2</sup>The ppm values for Li and Al provided in Tables 1 and 2 were measured by Galbraith Laboratories, Inc. (Knoxville, Tennessee, USA), and listed in Galbraith Report 147768 dated 5/9/23.

acid treatment of granular  $\beta$ -spodumene. The technique converts the Al in leached spodumene to high-purity  $\text{Al}_2\text{O}_3$  and the Si to high-quality MG-Si and, significantly, *these two byproducts are formed with essentially no net consumption of Mg.*

### The characteristics and advantages of the Technology vis-à-vis incumbent methods

Data for seven Li leaching technologies appear in Table 3. By comparing the results for the various methods it becomes evident quickly that those for the GLET-Medaro method include some characteristics that are clearly superior to those of the other technologies, the most profound advantages of the GLET-Medaro method being: *milder processing conditions, internal recycling of process intermediates, co-production of valuable Al and Si materials, and generation of much less chemical waste.*

**Table 3. Descriptions of competing methods for spodumene-sourced lithium production**

Technology feature	Li leaching technology						
	Acid roasting	Alkaline roasting	Alkali digestion	Direct acid leaching			
Li leaching agent	$\text{H}_2\text{SO}_4$	$\text{Na}_2\text{CO}_3$	$\text{NaOH}$	$\text{H}_2\text{SO}_4$	$\text{HCl}$	$\text{HNO}_3$	$\text{HNO}_3$ , GLET-Medaro
Industrial usage level	High	High	Low	High	-	-	-
Temperature and pressure during chemical processing	250-300 °C, ~1 atm	200-250 °C, ~1 atm	200-300 °C, ~40 atm	180-250 °C, ~1 atm	80-120 °C, ~1 atm	120-140 °C, 1-15 atm	120-140 °C, 1-10 atm
Initial Li-rich substance produced	$\text{Li}_2\text{SO}_4$	$\text{Li}_2\text{CO}_3$	$\text{LiOH}$	$\text{Li}_2\text{SO}_4$	$\text{LiCl}$	$\text{LiNO}_3$	$\text{LiNO}_3$
Li product(s) sold	In each technology the option exists to manufacture and sell one or more of $\text{Li}_2\text{CO}_3$ , $\text{LiOH}\cdot\text{H}_2\text{O}$ and Li metal.						
Li recovered <sup>1</sup>	90-95%	80-90%	90-95%	70-95%	80-95%	~95%	>96%
Al recovered	~25% as $\text{Al}_2(\text{SO}_4)_3$	0%	0%	~25% as $\text{Al}_2(\text{SO}_4)_3$	~25% as $\text{AlCl}_3$	~25% as $\text{Al}_2\text{O}_3$	>95% as $\text{Al}_2\text{O}_3$
Si recovered	0%	0%	0%	0%	0%	0%	>95% as Si
Reagents consumed in major amounts <sup>2</sup>	$\text{H}_2\text{SO}_4$	$\text{Na}_2\text{CO}_3$	$\text{NaOH}$	$\text{H}_2\text{SO}_4$	$\text{HCl}$	-	-
Amount of chemical waste produced	Relatively large	Relatively large	Relatively large	Relatively large	Relatively large	Small	Small

<sup>1</sup>The percentage figures in this and the next two rows indicate the extent to which each Li leaching technology can recover spodumene-sourced Li, Al and Si for the purposes of manufacturing one or more saleable Li, Al and Si products.

<sup>2</sup>In addition to the materials listed in this row: (i) alkaline roasting excepted,  $\text{CO}_2$  gas is consumed in each technology whenever  $\text{Li}_2\text{CO}_3$  is manufactured and sold; and (ii)  $\text{H}_2\text{O}$  is consumed if  $\text{LiOH}\cdot\text{H}_2\text{O}$  is manufactured and sold.