CHAPTER 12.20

Lithium

Nicholas J. Welham

Lithium has an atomic number of 3 and occurs in two natural isotopes with atomic masses of 6 and 7; the latter is, by far, the most abundant (92.5%), resulting in an atomic weight of 6.94. Lithium is part of the alkali metal group, along with sodium, potassium, rubidium, and cesium, and occurs naturally as a monovalent cation. It is a soft, silvery metal when pure but rapidly corrodes in moist air to a dull gray. Elemental lithium has a melting point of 181°C (454 K) and a boiling point of 1,330°C (1,603 K). The density at room temperature is 0.534 g/cm^3, the lightest of all metals.

Lithium was first identified in 1817 by Johan August Arfwedson, a Swedish chemist who was unable to identify all components of the mineral petalite. The element was found to have similar properties to sodium and potassium but was discovered from a mineral and initially named "lithion" after *lithos*, the Greek word for *stone*. The same element was also quickly found to be present in spodumene and zinnwaldite. The pure element was first isolated in 1821 by William Thomas Brande, a chemist who electrolyzed lithium oxide. Larger-scale production of lithium was achieved by 1855 when lithium chloride was electrolyzed; this work laid the foundation of modern lithium metal production.

The first industrial-scale production of lithium occurred in Germany in 1923 when a new lead-based antifriction alloy containing 0.04% Li was produced. The alloy was used as bearings in railway trucks by German State Railway until replaced by ball bearings in the 1950s.

PRODUCTION AND USES

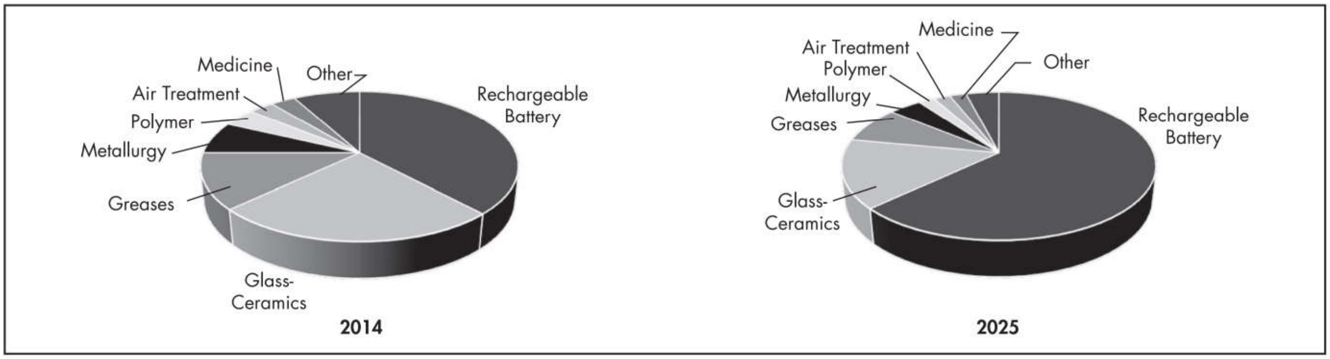
The production of lithium is rapidly expanding because of a major increase in the use of lithium ion batteries, mainly for electric vehicles, with an increasing interest in home solar storage. It is predicted that the quantity of lithium produced in 2015 will need to more than double by 2025 to keep up with demand. A large part of the increase in demand for lithium is driven by the numerous estimates for adoption rates of electric vehicles. The increasing rate of uptake seems to be because of recent governmental and car manufacturer announcements regarding emissions restrictions and even the phasing out of combustion engine vehicles. The predicted growth in batteries is 10%–15% per year, whereas the more traditional uses are expected to grow at 3%–5% per year. Figure 1 shows the estimated sector usage of lithium in 2014 and the predicted use in 2025.

Lithium salts, typically the carbonate, are used as a flux to reduce the melting point and viscosity of silica to make glazes with low thermal expansion for use in ovenware. Lithium hydroxide is heated with fatty acids to produce lithium stearate, which can be used to thicken oils to make high-temperature lubricating greases. Lithium carbonate is also added to fluxes during continuous mold casting to increase fluidity and to aid settling. Lithium fluoride is added to the electrolyte in the Hall–Heroult process for producing aluminum metal. The addition reduces the melting temperature and increases electrical resistance. Lithium metal is also alloyed with aluminum to improve chemical resistance and to refine the grain structure. Alloys of lithium with cadmium, copper, and manganese are used to make high-performance aircraft parts.

The red flame color of lithium, first noted by Arfwedson, is utilized in pyrotechnic compositions. Lithium chloride and bromide are hygroscopic and are used as desiccants for gas streams. Lithium hydroxide and peroxide are used in confined spaces, such as spacecraft and submarines, to absorb carbon dioxide. Both reactions lead to the formation of lithium carbonate; the peroxide also releases oxygen. The lithium salts are preferred over other alkaline hydroxides because of their greater performance per unit weight.

Small quantities of lithium fluoride (LiF) are used in specialized optics for infrared, ultraviolet (UV), and vacuum-UV applications. LiF has one of the lowest refractive indices and the widest transmission range in the deep UV of the most common materials. The nonlinear optical properties of lithium niobate find application in more than 60% of mobile phones as resonant crystals. Organolithium compounds are extensively used in organic syntheses, notably as catalysts/initiators in anionic polymerization of unfunctionalized olefins by promoting carbon–carbon bonds. Other lithium compounds used in chemical synthesis include lithium aluminum hydride, lithium triethylborohydride, n-butyllithium, and tert-butyllithium, all of which are commonly used as extremely strong bases.

Nicholas J. Welham, Principal, Welham Metallurgical Services, Perth, Western Australia, Australia



Source: SignumBox 2014

Figure 1 Uses of lithium by sector in 2014 and predicted use in 2025

Lithium metal and lithium aluminum hydride can be used as high-energy additives for rocket propellants; the latter can also be used directly as a solid fuel.

Figure 1 shows that the major expanding use of lithium is in rechargeable lithium ion batteries, which were first produced commercially in 1991. This type of battery has numerous advantages over other rechargeable batteries, including higher energy density, higher cell voltage, a low discharge rate during storage, low hysteresis, high discharge currents, and high charging currents. The battery consists of a graphite electrode, an oxide electrode, and an organic electrolyte containing lithium salts. There are many variations of battery primarily categorized by the composition of the oxide. The main component of the oxide phase can be lithium cobalt oxide, lithium iron phosphate, or lithium manganese oxide; these main oxide structures can be modified with partial substitution by different metals. During charging, lithium is reduced from monovalent to metal, which is stored by intercalation between the sheets of the graphite electrode. On discharge, the lithium metal oxidizes by reacting with the oxide electrode, releasing energy. It is important to avoid safety problems by preventing ingress of moisture when designing and packaging products containing lithium metal. Because it is necessary to dissipate heat during charging and discharging, especially at high currents, electric vehicles typically use numerous relatively small batteries combined into modules to increase the surface area. For example, the Tesla S (85-kW) battery consists of 7,104 separate batteries connected together, whereas the Tesla Model 3 (50-kW) battery has 2,976 individual cells.

Table 1 Abundance of lithium

Environment	Lithium, ppm
Average earth	17–20
Sedimentary rocks	11.5
Igneous rocks	6
Seawater	0.18
Brines	Up to 1,800

Adapted from Garrett 2004

MINERALOGY

The reactivity of lithium is such that it does not occur in elemental form in nature; instead, it forms largely ionic minerals and occurs in many natural waters, including brine and seawater. The approximate abundance of lithium in assorted natural environments is given in Table 1. The average abundance is similar to that of yttrium, cobalt, niobium, and scandium but higher than lead or tin.

There are ~130 minerals where lithium is considered to be a structural requirement and an additional ~100 where lithium is known to substitute for monovalent cations, notably sodium, but is not essential to the structure (Webmineral 2018). However, the vast majority of these are not found in economic quantities. The major economic deposits are largely composed of the minerals shown in Table 2.

Lithium Ore Bodies

The two commercial sources of lithium are hard rock and brines. U.S. Geological Survey data indicate that the majority

Table 2 Major economic lithium minerals

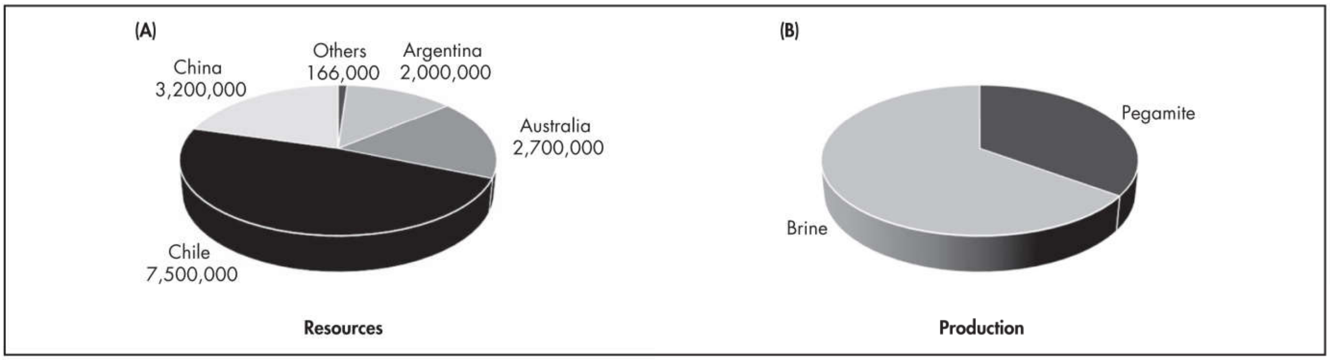
Mineral	Chemical Formula	% Li_2O	Group	Typical % Li_2O in Ore Grade
Spodumene	$LiAlSi_2O_6$	7.99	Pyroxene	1.0–7.7
Petalite	$LiAlSi_4O_{10}$	4.88	Phyllosilicate	3.0–4.7
Amblygonite	$(Li,Na)Al(PO_4)(F,OH)$	7.4–10.2	Phosphate	7.5–9.5
Lepidolite	$K(Li,Al)_3(Si,Al)_4O_{10}(F,OH)_2$	3.0–7.8	Mica	3.0–4.1*
Zinnwaldite†	$KLiFeAl(AlSi_3)O_{10}(F,OH)_2$	4.3–10.7	Mica	2.1–4.3‡
Hectorite	$Na_{0.3}(Mg,Li)_3Si_4O_{10}(OH)_2$	1.17	Clay	0.4–0.7

Adapted from Garrett 2004

*Rb ~0.1%–0.3%; Cs ~0.02%–0.04%.

†Zinnwaldite is no longer recognized as a specific mineral. It is considered to be within a solid solution series between siderophyllite $KFe_2Al(Al_2Si_2)O_{10}(F,OH)_2$ and polylithionite $KLi_2AlSi_4O_{10}(F,OH)_2$.

‡Up to ~0.9% Rb.



Source: USGS 2018

Figure 2 (A) Location of lithium reserves and (B) reserve type

of reserves (i.e., economically extractable lithium) are in South America (Figure 2A) and that the vast majority of those are brine based (Figure 2B; USGS 2018). Many other potentially significant resources are not considered to be reserves (e.g., Salar de Unuyi in Bolivia, the world's largest salt flat), given the absence of sufficient data. The considerable interest in lithium is also expanding the hard rock resource base around the world.

Figure 3 shows the grade and size of major reported brine and hard rock deposits (in million metric tons [Mt]), the primary difference being much lower lithium grade in the brines.

Brine Deposits

Brine deposits are formed by the ongoing evaporation of water from an enclosed basin into which salty water flows. The inflow of salty water needs to be lower than the outflow of water in order to build up the concentration of salt. Over time, the concentration of salt in the water increases until crystallization of the least-soluble salts occurs, forming a crust on the surface up to several meters in thickness. The lithium salts, being among the most soluble, do not typically crystallize but remain in a concentrated brine solution. The natural processes that formed the lake will have resulted in the deposition of loosely bound sediments ranging in size from gravel to clays. The salty brine occupies the pore space between the particles.

The conditions required to form brine deposits are unusual and occur in only a few places around the world. The host basin needs minimal outflow, the inflow water needs to have a consistent supply of salt, the outflow needs to be extremely low, and the evaporation rate has to be very high.

The highly concentrated brine solution has K^+, Na^+, Li^+, Ca^{2+}, and Mg^{2+} as the main cations and Cl^- and SO_4^{2-} as the main anions. In addition to these, also present will be lower levels of other cations and anions, such as NO_3^-, Br^-, and I^-. The composition of the brine varies across the surface of the lake and with depth.

Table 3 shows the average composition of brines from different salars. The range of elemental concentrations is broad, and deposits are often defined by the theoretical composition based on the relative concentrations of the ions. For extraction purposes, it is the ratios of the elements, especially the (Mg+Ca) to lithium, that are of major importance. Deposits where the (Mg+Ca):Li ratio is greater than 15:1 are harder to process by solar evaporation, as some of the lithium will co-crystallize with the calcium and magnesium salts. The presence of <400 ppm of lithium is also unfavorable for solar evaporation because of the higher volumes of water needing to evaporate to achieve the required lithium concentration for final processing.

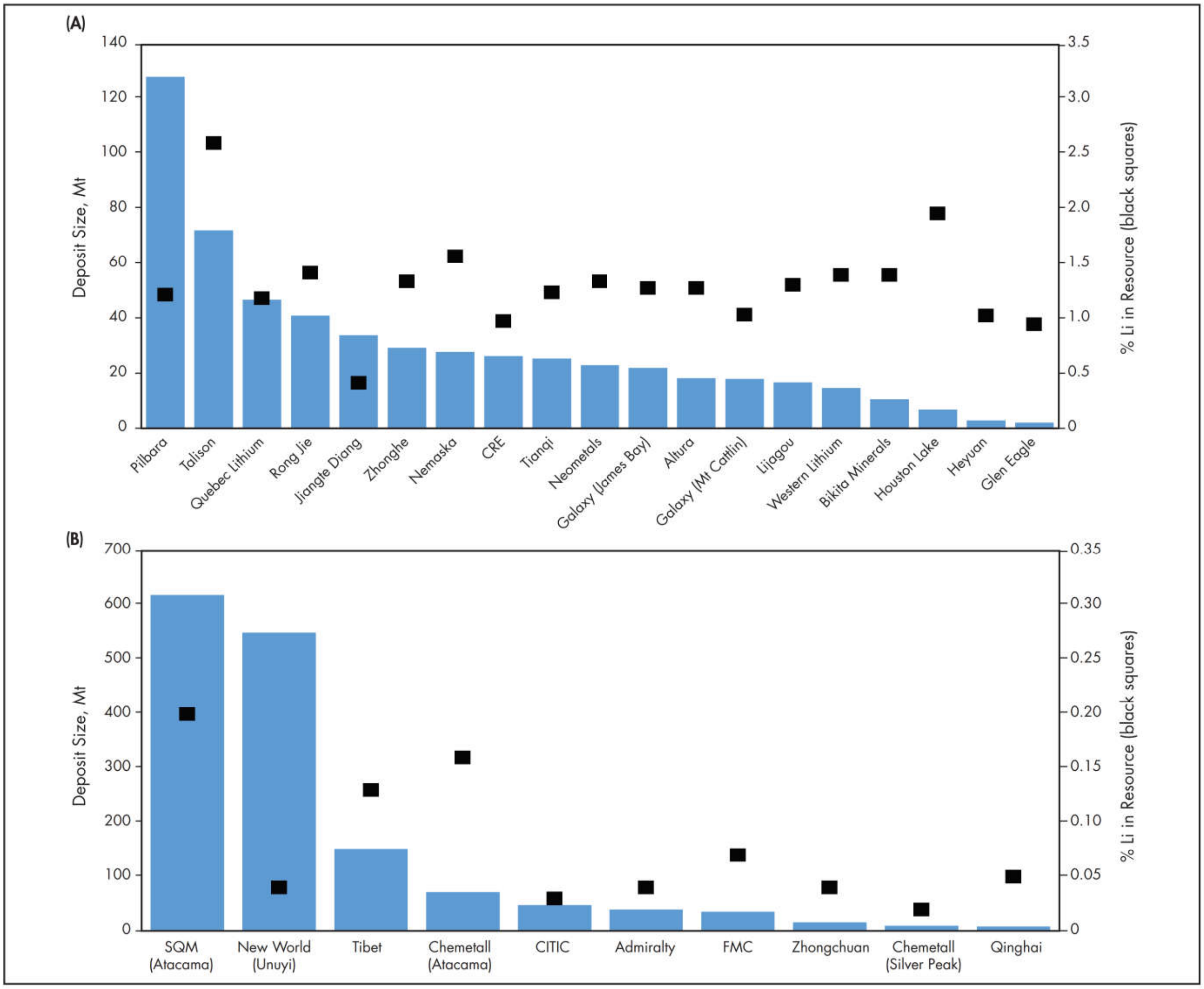
Extraction from brine deposits is very different from classical mining methods, being more similar to oil than to ore. The brine solution is extracted from wells, pits, or trenches cut into the brine-loaded sediment layers. The slower the flow of the brine into the collector, the larger the required area. Ultimately, the extraction of the brine is governed by the permeability of the host sediments; a low permeability will result in much lower extraction rates. Thus, when assessing a project, it is critical to determine the maximum pumping rate, as this ultimately determines the production rate. The replenishment rate of the brine within the sediments is also an important factor and can only be assessed by determining the reduction in volume pumped over time. When the permeability and/or the replenishment rate is low, more bores or longer trenches will be required in order to provide the brine flow rate required for production.

Taking all of the factors into account, the level of extraction from brine deposits is significantly lower than from more classical ore deposits, and the method for definition of the resource/reserves is notably different. The CIM Definition Standards for Mineral Resources and Mineral Reserves (Hains 2012) allows for a maximum 33% recovery from brine deposits. This is before a range of different reduction factors are taken into account. In reality, an extraction of 10%–15% is likely to be the realistic maximum for most deposits.

Hard Rock Deposits

The hard rock deposits are composed of granitic pegmatites in which zonation has occurred. The core of the pegmatite is generally barren, while the periphery is lithium rich due to the lower melting point of lithium-rich fluids. Many of the pegmatites also contain other exotic metals, including tantalum/niobium, rubidium/cesium, and tin in separate zones. The occurrence of tin and lithium has led to a new lease on life for mines that were historically exploited for their tin content but now have an inventory of surficial tailings containing lithium and mine workings that have ore-grade lithium remaining from the tin-mining days.

Figure 4 shows the zoning of the pegmatite at the Greenbushes deposit in Western Australia. The main minerals present in the deposits are quartz, feldspar, and mica. Also commonly present in the lithium-rich zones is tourmaline, which presents a minor processing challenge for high-grade



Source: Jephcott 2016

Figure 3 Data for the size and grade of (A) hard rock resources and (B) brine

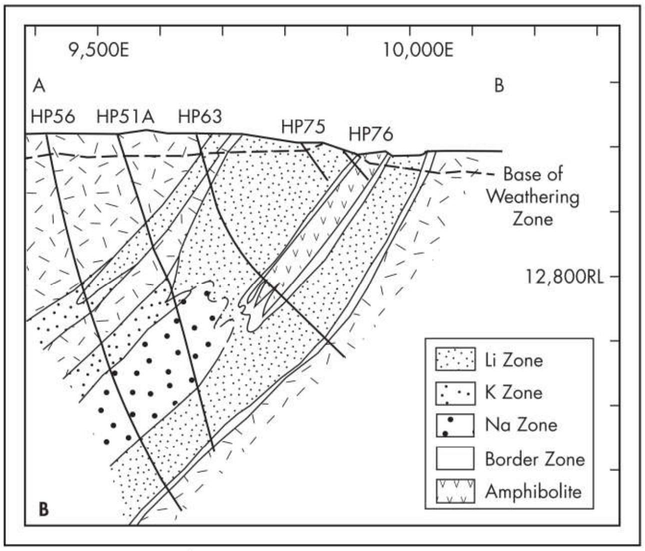
Table 3 Composition of a range of global brine resources*

Deposit	Type	Li	K	Mg	Ca	SO4	Mg/Li	SO_4/Li	Ca/Li	SO_4/K
Salar de Atacama, Chile	$MgSO_4$-Li_2SO_4-LiCl-$CaCl_2$	1,835	22,626	11,741	379	20,180	6	11	0.2	0.9
Salar de Cauchari, Argentina	Na_2SO_4-K_2SO_4-Li_2SO_4	618	5,127	1,770	476	19,110	3	31	0.8	3.7
Salar de Hombre Muerto, Argentina	Na_2SO_4-K_2SO_4-Li_2SO_4	744	7,404	1,020	636	10,236	1	14	0.9	1.4
Salar de Maricunga, Chile	KCl-LiCl-$CaCl_2$	1,036	8,869	8,247	11,919	1,095	8	1	11.5	0.1
Salar de Olaroz, Argentina	Na_2SO_4-K_2SO_4-Li_2SO_4	774	6,227	2,005	416	18,630	3	24	0.5	3.0
Salar de Rincon, Argentina	$MgSO_4$-Li_2SO_4	397	7,513	3,419	494	12,209	9	31	1.2	1.6
Salar de Unuyi, Bolivia	$MgSO_4$-Li_2SO_4	424	8,719	7,872	557	10,342	19	24	1.3	1.2
Silver Peak, USA	Na_2SO_4-K_2SO_4-Li_2SO_4	245	5,655	352	213	7,576	1	31	0.9	1.3
West Taijinaier, China	$MgSO_4$-Li_2SO_4	256	8,444	15,737	NS†	35,315	61	138	NS	4.2
Zhabuye Salt Lake, China	Li_2CO_3-Na_2SO_4	1,217	17,083	17	NS	38,917	0	32	NS	2.3

Source: Desormeaux 2015

*Elemental concentrations are in parts per million.

†NS = Not stated.



Source: Partington et al. 1995

Figure 4 Cross section of the Greenbushes deposit in Western Australia showing the zonation typical of such pegmatites

products. Extraction of the pegmatites is either via open pit, for those deposits that are close to the surface or at low dip angles, or underground mining for deeper and more steeply dipping deposits.

RECOVERY OF LITHIUM FROM BRINE DEPOSITS

The recovery of lithium from brine deposits is a relatively simple process dominated by the use of solar energy (Garrett 2004). The low initial lithium concentration, high competing ion concentrations, and comparative lack of reactivity of the lithium ion effectively prevent direct recovery of lithium from the brines. Lithium can be solvent extracted from brines as the LiCl neutral ion (Epstein et al. 1981), and further development of this concept may well lead to a commercially viable process. The most recent of these developments has shown promise in the laboratory using a Bateman pulsed column (Lipp 2014).

However, as in many of the new or proposed processes to selectively extract lithium from brine, it is necessary to remove most, if not all, of the calcium and magnesium prior to solvent extraction (SX). In these, the high capital cost of solar evaporation ponds is offset by the increased operational cost of removing calcium and magnesium prior to the lithium.

The low level of lithium is addressed by using solar evaporation to reduce the volume of water, thereby concentrating the lithium and other elements. The ponds cover a large area but are relatively shallow to maximize the surface area to volume ratio to enhance evaporation and therefore have a very high footprint (1,700 ha [SQM 2018]). The ponds need to be leak resistant, and plastic liners similar to those used in heap leaching are employed. The preparation of the ponds is one of the major capital costs.

The significantly higher concentrations of other elements lead to the crystallization of the least-soluble salts in the system as the volume decreases. There is also some variation in phases precipitated due to annual seasonal changes in local atmospheric conditions (Vergara-Edwards and Parada-Frederick 1983). The formation of brine lakes occurs in places that are also excellent for promoting the evaporation of water by a combination of high altitude, low humidity, low rainfall, wind strength, high evaporation rates, and high solar energy density.

The identity and sequence of salts crystallized will vary between deposits and even between brine sources within a single deposit due to the variability in composition outlined in Table 3. Through management of the volume evaporated, the different salts crystallized can be largely separated by allowing the volume to decrease and then transferring the brine to a smaller pond. The sequence for SQM at the Salar de Atacama in Chile is sodium chloride (NaCl), potassium chloride (KCl), and $KMgCl_3 \cdot 6H_2O$ (SQM 2017). The NaCl is discarded, and the KCl and $KMgCl_3 \cdot 6H_2O$ are further processed to pure KCl for sale. As time goes on, the brine becomes increasingly concentrated in lithium until it is ready to transfer to a more intensive recovery process. The solar evaporation process relies on considerable operational experience in knowing when to move the brine onto the next pond to prevent contamination of the product. The typical time required from initial brine to final stages is approximately 18–24 months. This can be considerably longer if there is an unexpectedly high rainfall event onto the ponds.

Solar evaporation is used until it has concentrated the brine to the point where lithium will start to precipitate with other salts. For brines where the (Mg + Ca):lithium ratio is higher than 15, the precipitation of Li + Ca/Mg salts (e.g., $LiMgCl_3 \cdot 7H_2O$) occurs significantly earlier in the evaporation process than for brines where the ratio is lower. Only recently have such high-ratio brines been considered as potential resources due to the increased complexity of lithium extraction compared to the low-ratio brines.

The concentrated brine solution is initially treated to remove boron. This is commonly performed by SX using branched aliphatic alcohols, such as 2-ethylhexanol and 2-butyl-1-n-octanol as extractants. The brine is reduced in pH to <2.5 where the boron is present as neutral boric acid, H_3BO_3, and this is extracted by the alcohol. Recovery of the boron is by contacting with water, after which the solution is evaporated to form crystals of boric acid that can be sold.

Calcium and magnesium are then removed by adding Na_2CO_3 to form insoluble carbonates that are filtered and disposed of. Care needs to be taken to prevent excessive precipitation of Li_2CO_3 by careful monitoring of the solution. Further soda ash is then added to precipitate the lithium carbonate, which is filtered, washed, and dried. The filtrate contains a mixture of sodium and potassium salts that are crystallized, and flotation is used to separate the NaCl and KCl into separate products. The overall flow sheet is shown in Figure 5.

RECOVERY OF LITHIUM FROM HARD ROCK LITHIUM DEPOSITS

The flow sheet for the processing of hard rock lithium ores is largely determined by two factors:

1. **Ore texture.** If the mineral particle is coarse or there is a clear differentiation between particles at crush sizes of >1–2 mm, then physical separation methods can be used to upgrade the lithium minerals. Ore sorting is not presently in use for lithium ores but early test work has indicated that it is possible to upgrade some spodumene

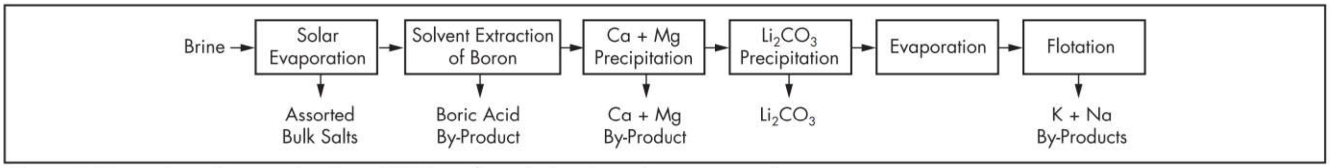


Figure 5 Flow sheet for production of lithium from brine by solar evaporation

ores; mica ores are generally somewhat finer grained and do not separate well at coarse particle sizes. The most common method of physical separation in use is dense medium separation. If the mineral is finely divided, then flotation is the only viable method.

2. **Ore mineralogy.** There is a significant difference between spodumene and mica ores. Spodumene ores are typically coarser and higher grade than mica ores. The higher density of spodumene allows gravity separation to be used, whereas micas are almost exclusively processed by flotation.

Importantly, many pegmatite deposits contain both spodumene and lithium micas in association. The relative ratio of the two will largely determine the processing route, as the subsequent concentrate conversion process will operate on spodumene or, less commonly, mica. The presence of mica in the spodumene concentrate results in a financial penalty, because it increases the operational complexity of the conversion process, most notably due to problems within the initial calcination stage. Lithium from spodumene that is present in a mica ore will not be recovered during the conversion process and is typically not considered when determining the head grade. Ore deposits where the lithium is present at >10% of the minority phase are more economically challenging because of the lower “real” head grade once the unwanted component is eliminated.

Comminution

Crushing is ordinarily undertaken with open-circuit primary and closed-circuit secondary crushing. Tertiary and quaternary crushers are used for ores that are to undergo physical separation. Undersize particles are either discarded, stockpiled for future exploitation, or fed into a grinding circuit in preparation for flotation. Flow sheets that do not use gravity separation and go directly to flotation may use primary crushing followed by semiautogenous milling.

The softness of the micas compared to the other minerals present results in preferential sliming of the micas. For ores where the main lithium mineral is a mica, this can result in high losses when desliming prior to flotation. Unlike most grinding circuits prior to flotation, it is best to avoid using cyclones to size the ground product. The platy mica particles tend to behave according to the largest dimension and report preferentially to the oversize for regrinding. As a consequence, there can be a noticeable concentration of lithium mica in the slimes compared to the flotation feed (e.g., 0.8% Li_2O in the feed and 1.1% Li_2O in the slimes, with >25% loss of Li_2O to slimes). In such situations, an upflow classifier is a more appropriate choice of sizer, as this takes advantage of the platy nature of the mica to separate the particles. To reduce overgrinding of the lithium mica, the classifier is placed prior to the grinding mill. The undersize from the classifier can be passed over Derrick, or similar, screens to remove the slimes prior to flotation.

Table 4 Densities of the major minerals present in pegmatite deposits

Mineral	Density, g/cm^3	Mineral	Density, g/cm^3
Spodumene	3.1–3.2	Quartz	2.65
Feldspar	2.55–2.76	Mica	2.8–3.4
Petalite	2.4	Zinnwaldite	2.9–3.1
Lepidolite	2.8–3.0	Columbite/tantalite	6.3–8.2

Physical Separation

The densities of the major minerals present are given in Table 4. The ranges given depend on the chemical composition of the mineral, which is deposit specific. In order to be separable by simple gravity methods, there needs to be a difference in density > 0.2. This is the case for spodumene and quartz, but the remaining lithium minerals are too close to the gangue to give an effective separation. Thus, gravity methods are only viable for spodumene ores.

Historically, spirals have been used in spodumene plants with some success. Modern plants only use spirals to separate the tantalite from other minerals, as the tantalite may prove to be a significant revenue source in some deposits. Modern lithium plants almost exclusively use dense medium separation (DMS) using cyclones for gravity separation. The required separation density is only achievable using ferrosilicon media. The particle feed size is greater than 0.5 mm, but greater than 2 mm gives a more effective separation. Figure 6 shows a typical single-stage DMS circuit with the ancillary equipment required to recover and make up the ferrosilicon to the required density.

Figure 7 shows two DMS circuit designs. Figure 7A shows a two-stage circuit in which there are primary and secondary dense medium cyclones (DMCs) acting as rougher and cleaner stages. Figure 7B is a three-stage circuit that produces an intermediate density product that is ground and floated.

The inherent complexity of DMS plants precludes the operation of cyclones at different medium densities in order to produce multiple products. The DMS tails may be either sent to tailings, stockpiled, or, more commonly, combined with the screen undersize and ground in preparation for flotation.

DMS is capable of producing a 6% Li_2O concentrate from spodumene ores at good recoveries. This concentration is the current benchmark for conversion to lithium salts. As a consequence, plants may be developed in two stages. Initially, only DMS is used to produce the 6.0% concentrate from higher-quality ore to generate cash flow. The second stage is the installation of grinding and flotation to re-treat the DMS floats and allow higher recoveries at the required grade from lower-quality ores.

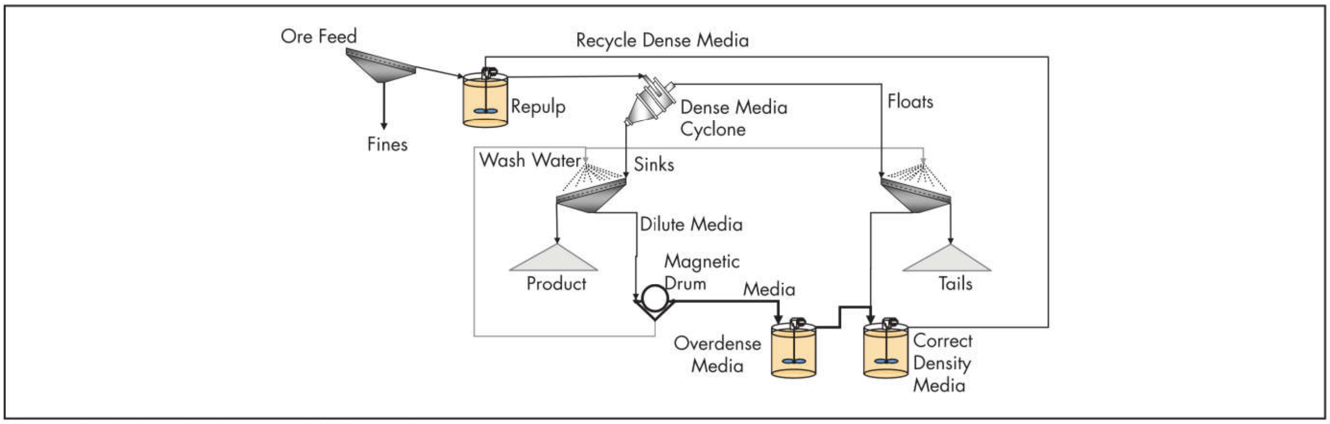


Figure 6 Typical single-stage DMS circuit

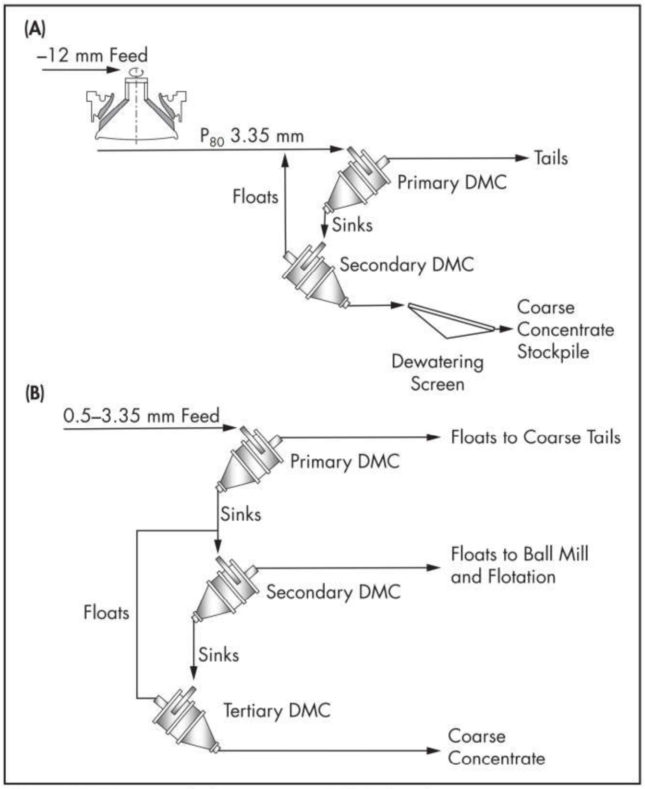


Figure 7 Two- and three-stage DMS circuits

Other Methods

Magnetic Separation

Zinnwaldite is amenable to magnetic separation because of its weakly magnetic nature. Separation from other weakly magnetic minerals, including muscovite, is likely to prove challenging for such deposits. However, no commercial plant currently operates such a process.

Ore Sorting

There is good potential to use ore sorting in upgrading lithium-bearing ores. The potential is greater for spodumene than micas because of the coarser particle size typically present. However, the strong violet/pink color of lepidolite ores can be used to produce a high-grade concentrate from some ores.

Flotation

Spodumene Flotation

The flotation of lithium ores has been a relatively minor market until recently. The classic flotation process using oleic acid as collector has been used since the 1950s and remains the major process used today. The more recent expansion of interest in lithium has led to the development of specialized collectors by manufacturers, though at this stage there is no known plant using reagents other than oleic acid. The flotation of lithium micas is a more recent development, and the typical mica collectors, notably amines, are commonly used. The operating conditions for the process depend on the associated gangue minerals.

Oleic acid is a long-chain fatty acid derived from olive oil. The chemical formula is $CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$. It has a density when pure of 895 kg/m^3 and is pale yellow or brownish yellow with a lard-like odor. It melts at 13°–14°C and boils at 360°C. Oleic acid is insoluble in water, forming an immiscible layer on top of the water. To increase the solubility of the oleic acid, it is saponified with soda ash (Na_2CO_3) or sodium hydroxide (NaOH) to form water-soluble sodium oleate. The reaction is slow and necessitates a comparatively long conditioning time of 10–30 minutes. The reaction is accelerated by operation at elevated temperature. Typically 500–700 g/t of oleic acid are added in the conditioning stage.

Conditioning is undertaken at 60% slurry density for 10–30 minutes with the addition of 0.5–1.0 kg NaOH/t. The NaOH increases the pH to aid saponification and to help chemically clean the mineral surface. The long conditioning time results in particle attrition. This has two effects: cleaning of the mineral surfaces, which aids adsorption of the collector, and production of slimes, which have to be removed prior to flotation.

The conditioned ore is deslimed and the slimes discarded to tailings. The slurry is diluted to 30%–40% and fed into a bank of rougher cells. The flotation pH is adjusted using sulfuric acid to 6.6–6.9, although ores with more complex mineralogy may use pH 8.0–8.2 to help depress flotation of impurities. No frother is generally required, as the oleic acid also acts as a frother; for low-grade ores, a commercial frother may be added to the second bank of roughers (or scavengers) to ensure recovery.

A typical flow sheet for a flotation plant is shown in Figure 8. The feed is the screen undersize from a previous DMS operation, such as that shown in Figure 7B; the middlings

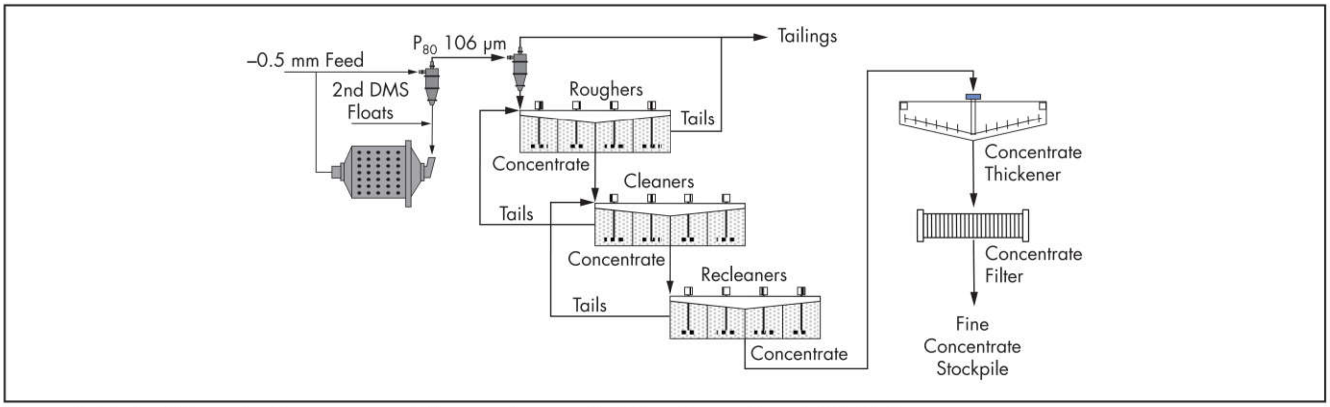


Figure 8 Typical flow-sheet arrangement for spodumene flotation to produce 6.0% Li_2O

from the multistage DMS are also fed into the mill. The ore is ground to a P_{80} of 106 µm in closed circuit with a cyclone; the undersize is deslimed in smaller cyclones and fed into a conditioning tank and rougher bank. The concentrate is diluted to a lower slurry density, cleaned and recleaned to produce a 6.0% Li_2O concentrate; the tails from the cleaners are recycled to the previous stage. The rougher tails may be either scavenged or sent to tailings. The final cleaned concentrate is thickened and filtered to produce a fine concentrate for shipping.

There is a smaller market for higher-grade concentrates than the 6.0% Li_2O destined for conversion to lithium carbonate or hydroxide. To produce grades of up to 7.7% Li_2O, the ore is ground more finely and additional cleaning stages are required. The slurry density in the stages reduces from 35%–40% solids in the roughers to 30%–35% in the cleaners and 25%–30% in the recleaners. The reduced slurry density improves separation primarily by greatly reducing entrainment and increasing flotation time. The froth depth down the bank is adjusted using moveable weirs, with the depth being lowest in the last cells where there is the least floatable material.

For the highest-grade products, the flotation concentrate is thickened and agitated in a tank with sulfuric acid; this reverses the oleic acid saponification reaction, leading to desorption of collector from the mineral surface. The acid also removes small amounts of surficial iron and any acid-soluble minerals (such as apatite), if present. The concentrate undergoes low-intensity magnetic separation to remove strongly magnetic materials and then wet high-intensity magnetic separation to remove weakly magnetic materials, including tourmaline. The final product is belt filtered and then thermally dried before bagging to customer requirements.

Mica Flotation

Flotation of lithium-bearing mica is a relatively new technology and there are no operational plants at present. The standard mica collectors are largely effective, and some newer variations are being marketed as collectors for lithium mica. Performance is strongly dependent on the composition of the lithium mica and the gangue mineralogy. Rubidium-bearing lepidolite is less effectively floated than low-rubidium lepidolite under identical conditions (Bulatovic 2014). The large variation in mica compositions and gangue mineralogy between and within deposits makes ongoing optimization of flotation conditions a challenge for any lithium mica flotation operations.

Among the reagents reported to act as collectors are dodecylamine at pH 2.5–12; hexadecyl amine acetate at pH 3.5; and octadecylamine, which requires sodium silicate and Li_2SO_4 as lepidolite activators. Another effective collector for lepidolite (0.7% Li_2O) from quartz, albite, and calcite is stearyl trimethyl ammonium chloride (STAC) $(CH_3)_3CH_3(CH_2)_{16}NCl$ (Choi et al. 2015). A rougher Li_2O recovery of 95% was reported when using 100 g/t of STAC at pH 9.0. Calcite was removed by lowering the pH to 6.3 and adding 20 g/t of frother; quartz and albite were removed by further reducing the pH to 2, giving a final lithium grade of 2.76% Li_2O at 76.0% recovery. A flow sheet for mica beneficiation is shown in Figure 9.

Flotation of Other Lithium Minerals

The rarity of, and small market for, lithium has limited the amount of work on the flotation of lithium minerals. Petalite has been floated using dodecylamine collector with recovery being possible at pH 2.0–11.0. However, in the presence of a complex pegmatite ore containing feldspar, lepidolite, mica, and albite, selectivity was very poor at pH 2.0–8.0. A somewhat more complex process was patented for an ore containing spodumene, petalite, feldspar, and mica (Jessup and Bulatovic 2000). The mica floated at pH 2 using a cationic amine, and after pH adjustment to 8.5–10, spodumene was floated using oleic acid. The flotation medium was changed to a 10% brine by adding NaCl and KCl, which depressed the feldspar. The brine was reduced to pH 2–3 using a mixture of hydrofluoric acid (HF) and sulfuric acid (H_2SO_4), which cleaned the surface of the petalite, allowing a quaternary ammonium salt to be added at 250–400 g/t as collector. After a 4–10-minute flotation time, a final Li_2O grade of 4.7%–4.8% was achieved, with the concentrate being 96%–98% petalite. A modification of this process is proposed for the Separation Rapids project in Kenora, Ontario, Canada (Aiken et al. 2016).

For ores where there is limited separation possible by flotation of the lithium mineral due to fine particle size or excessive sliming at fine grind sizes, it is possible to undertake reverse flotation and remove the gangue minerals, potentially at a somewhat coarser grind size. This method has been proposed for the removal of calcite from lithium clay deposits to reduce the acid consumption during leaching.

Commercial Aspects

The current lithium market is dominated by the production of the SC6.0 grade with 6.0% Li_2O as this is the most

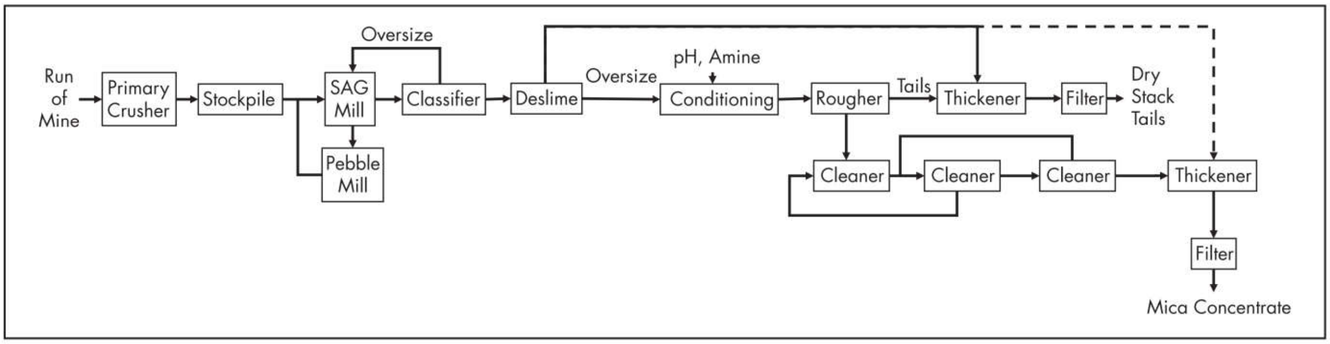


Figure 9 Flow sheet for mica beneficiation

Table 5 Elemental composition of spodumene concentrates

Element	Talison SC6.0	Talison SC7.5	Kings Mountain	Mount Cattlin	Pilgangoora	Pure Spodumene
Li_2O	6.05	7.60	6.00	5.50	6.68	8.03
SiO_2	66.30	64.50	63.00	64.00	64.43	64.57
Fe_2O_3	0.70	0.07	1.90	1.60	1.46	
CaO	0.40	0.05	Not stated	0.84	0.12	
K_2O	0.65	0.015	1.01	1.00	0.47	
Na_2O	0.55	0.08	0.61	0.90	0.39	
Al_2O_3	23.70	26.50	25.40	26.60	24.50	27.40
Totals	98.35	98.92	97.92	100.44	98.05	100.00

Note: Analyses of P_2O_5, TiO_2, MgO, and MnO are also important, especially for the highest Li_2O concentrates.

common feed to conversion plants that make lithium carbonate or hydroxide. Although higher grades are possible, up to 7.7% Li_2O, the end-user market is much smaller and necessitates greater capital expenditures and operating expenditures to achieve. It further needs to be borne in mind that the SC6.0 grade only contains around 75% spodumene—the remaining 25% is an assortment of gangue minerals that are strongly dependent on the ore body being mined.

Table 5 shows the reported composition of a range of different spodumene concentrates and that of pure spodumene. In addition to the elements listed, P_2O_5, TiO_2, MgO, and MnO are also important, especially for the highest Li_2O concentrates. The level of Fe in the Talison products is very noticeably lower than all others; this is due to the unusually low level of impurity minerals in the Greenbushes ore body, leading to a cleaner concentrate.

The only major specification of SC6.0 appears to be a minimum Li_2O content of 6.0%—there do not appear to be any restrictions on the levels of other elements. Such a minimum Li_2O content is only realistically possible for spodumene, because the maximum concentration possible is dictated by the mineralogy, with mica deposits struggling to get >1.5% Li_2O at high recoveries.

Table 6 Mass of starting material at given Li_2O grade required to produce 1 t of product at 100% recovery

Product	Formula	6.0%	3.0%	1.5%
Metal	Li	35.7	71.3	142.6
Carbonate	Li_2CO_3	6.7	13.4	26.8
Oxide	Li_2O	16.6	33.1	66.3
Hydroxide	LiOH	10.3	20.7	41.3
Chloride	LiCl	5.8	11.7	23.3
Bromide	LiBr	2.8	5.7	11.4
Butyl lithium	C_4H_9Li	3.9	7.7	15.5

One consequence of this is that transportation becomes a significant limiting factor in the value of the concentrate. Table 6 shows the mass of concentrate required to produce 1 t (metric ton) of a range of different lithium products. The table assumes 100% Li recovery during the conversion process. Clearly, a minimum of 6.7 t of SC6.0 spodumene concentrate is required to produce 1 t of Li_2CO_3; for a mica concentrate of ~1.5%, more than 26 t of concentrate are required. As the feed grade of concentrate decreases, the mass required increases significantly, making it economically harder to separate concentrator and conversion plant. It should also be borne in mind that only Li_2O is recovered from the concentrate in the conversion plant, resulting in the vast majority of the mass of the feed reporting to tailings.

Where concentrators use both DMS and flotation, the concentrate will be in the form of a mixture of coarse and fine particles. Conversion plants are typically set up to treat either DMS or flotation products, as the particle size difference changes material handling and affects several areas of the conversion process.

Concentrate Conversion

Spodumene Conversion

Spodumene is not readily soluble in acids unless there are sufficient fluoride ions present to form the stable hexafluorosilicate anion, SiF_6^{2-}. Neither baking with concentrated sulfuric acid at 250°C nor boiling in azeotropic hydrochloric acid (HCl) results in any significant dissolution. To overcome this refractoriness, the spodumene is heated to about 1,050°C for two to three hours. During heating, the spodumene changes crystal form from monoclinic α-spodumene to tetragonal β-spodumene and undergoes a density decrease from 3.1 to 2.4 g/cm^3. The large volume change results in the production of friable particles.

The heating process is generally carried out in a direct-fired rotary kiln, which is designed to give the required residence time for a particular feed particle size range. Blending of the coarse DMS and fine flotation concentrates leads to several process issues. The larger particles are slower to heat up and require a longer residence time but are also more rapidly transported down the kiln by rolling. This necessitates a larger kiln, or installation of lifters and weirs to increase residence time. The finer particles are more readily blown out of the kiln and

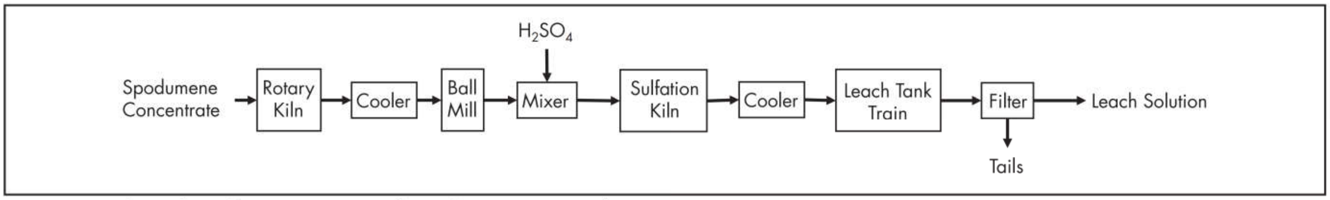


Figure 10 Flow sheet for conversion of spodumene into solution

need to be recovered in a baghouse and returned to the kiln to achieve the required residence time. Typically, 95%–97% of the spodumene is converted into the acid-leachable form in this process.

The presence of impurities in the concentrate (a 6.0% Li_2O concentrate is ~75% spodumene and 25% impurities) becomes a factor in the process at this point. Table 5 shows the composition of a range of different spodumene concentrates. Despite similar Li_2O concentrations, the remaining elements are somewhat different because of the differences in the ore-body mineralogy and processing route.

The impurities have variable behavior during the heating stage. Quartz and feldspar remain largely inert while phases containing iron, phosphorus, potassium, and sodium can melt or form low-melting-point phases by reaction. The formation of liquid phases will bind the particles of spodumene and form larger particles, which will affect the residence time. As it cools, a glassy phase will be somewhat sticky and potentially form barriers within the kiln, leading to blockages and increased downtime for cleaning. The cooled glass-bound spodumene particles will be harder to leach, with <75% Li recovery reported from such particles. Any mica that is present in the concentrate will melt and form glassy phases; thus there is a typical maximum limit to the quantity of mica permissible in the spodumene concentrate.

This heating stage is highly endothermic, requiring a minimum of 4.2 MW·h/t for pure spodumene, and represents the majority of energy costs in the conversion process. The absence of this extremely energy-intensive step is the major reason why brine producers are able to produce Li_2CO_3 at a lower cost.

After conversion to β-spodumene, the solid is cooled in a water-sprayed rotary cooler. After dry grinding to 150 µm, the calcine is mixed with 105%–130% of the stoichiometric amount of concentrated sulfuric acid and heated again to about 250°C. The stoichiometric excess is to ensure complete recovery of lithium and overcome acid consumption by undesirable reactions with the gangue minerals. The main reaction can be summarized as follows:

$$2LiAlSi_2O_6 + H_2SO_4 = Li_2SO_4 + H_2O + Al_2O_3 + 4SiO_2$$

This reaction is highly exothermic and self-heats by ~200°C from the starting temperature, thereby improving the kinetics. After the reaction is complete, the mixture is water-leached at about 50°C, dissolving about 98% of the lithium and other impurities as sulfates, the residue being composed primarily of poorly crystalline phases. The leaching time is kept short to give an initial separation of the fast-dissolving lithium from the slower-dissolving impurities.

It is also possible to leach the β-spodumene directly in hydrochloric acid. The leach requires 6–12 hours of leaching at ~106°C in azeotropic HCl. The resultant solution has higher impurities than the sulfate route, as there is much more time for the impurities to dissolve and chlorides tend to be more soluble than sulfates.

The aluminosilicate residue from the acid leaching is filtered and washed to reduce the level of SO_4^{2-} or Cl^- present. There is potential to use this material as an additive to cement or as a feedstock to other processes, as it is largely amorphous, has a high surface area, and is relatively reactive. A typical flow sheet for solubilization of spodumene is shown in Figure 10.

Of the other lithium minerals, lepidolite and zinnwaldite are directly soluble in sulfuric acid but are often calcined before leaching; petalite is processed similarly to β-spodumene, being heated with H_2SO_4 at 300°C, giving >95% Li extraction; and amblygonite is directly soluble in sulfuric acid.

Mica Conversion

The lithium micas are considerably less refractory than spodumene and require less energy-intensive processes to solubilize the lithium. The lower energy cost is offset by the increased complexity of the process due to the presence of a larger number of impurities. In addition to the impurities in the spodumene process (iron, aluminum, sodium, potassium, cesium, and magnesium), the micas also contain some uncommon impurities such as rubidium, cesium, fluorine, and chlorine, which have to be removed to achieve the required purity.

Several different processes have been proposed for the recovery of lithium from micas; however, only two seem to have been put into large-scale operation. The first mixes ground mica concentrate with concentrated sulfuric acid and heats it to 250°C; the second combines the mica concentrate with potassium sulfate (K_2SO_4) and heats it to 850°C. The result from both routes is much the same: conversion of the lithium into a water-soluble sulfate. However, many impurities also form soluble sulfates, giving high levels of impurities in solution after leaching.

When the mica is roasted with K_2SO_4, there is an additional step to remove K_2SO_4 from solution. This is carried out after the step to precipitate calcium and magnesium using carbonate. The solution is heated and evaporated to the point where it is almost saturated with Li_2SO_4 (35–40 g/L Li), by which time a large proportion of the K_2SO_4 will have crystallized out and can be separated for recycle to the sulfation kiln. A general flow sheet for the processing of mica using K_2SO_4 roasting is shown in Figure 11.

It is also possible to leach lepidolite directly in sulfuric acid using 50 g/L of free acid at 120°C for 12 hours. The final solution is close to Li_2SO_4 saturation with >95% dissolution. The slurry is filtered and the largely amorphous silica residue is either disposed of or re-leached in NaOH to form sodium silicate as a by-product.

The solution at this stage is processed largely the same as that from sulfuric acid leaching of spodumene. The major difference is the presence of ions of rubidium, cesium, and fluorine.

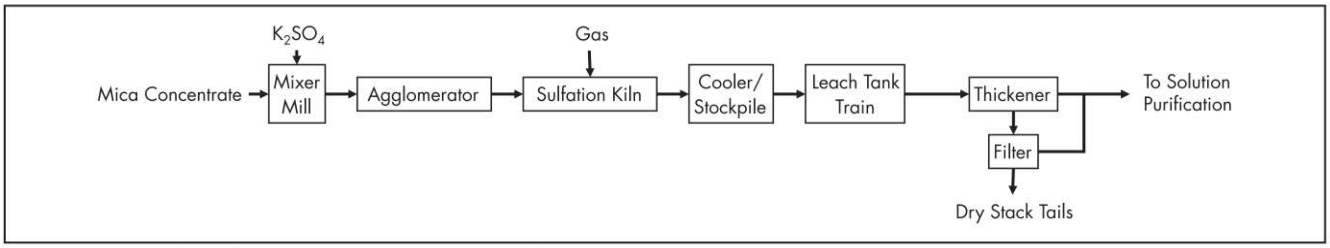


Figure 11 Flow sheet for mica processing using sulfation roasting

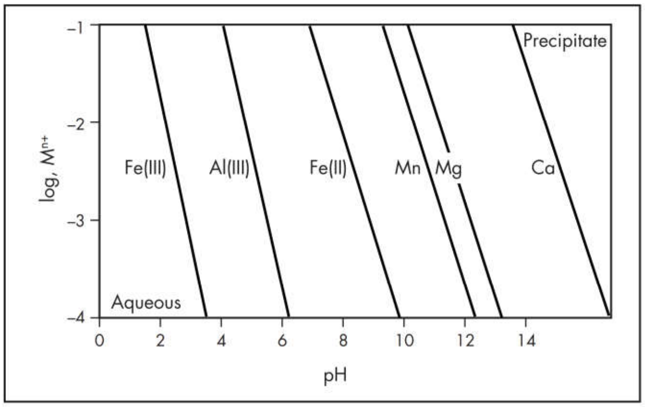


Figure 12 Solubility as a function of pH for metals present in lithium leach solutions

Solution Purification

For all minerals and concentrates, the major ions present in the solution will be highly dependent upon the impurities present in the concentrate. Typically these will include lithium, sodium, potassium, magnesium, calcium, iron, aluminum, and sulfate; lesser amounts of phosphate, fluorine, rubidium, cesium, and SiO_2 may also be present. The solutions from mica leaching will be notably higher in rubidium, cesium, and fluorine than spodumene leach solutions, as these elements are within the mica structure.

Ideally, the lithium ions would be directly and selectively extracted from the other ions. However, lithium is not amenable to standard hydrometallurgical separation processes such as solvent extraction (SX) and ion exchange (IX). Lithium also forms very few highly insoluble salts that are not also equally insoluble for the other metals present, so selective precipitation is not possible. The comparative inertness of the lithium ion is therefore exploited and, instead of selectively removing Li, the other metals are removed.

The principal method is to precipitate the impurities by increasing the solution pH by the addition of bases. Figure 12 shows the solubility of relevant metals as a function of pH. As the pH increases, the solubility of the assorted metals decreases until it reaches the point at which precipitation will occur.

In the purification process for sulfuric acid leaching, the pH increase occurs in three stages. The initial stage, which removes iron and aluminum, uses lime to increase the pH to ~6; this reduces their concentration to <5 ppm. The addition of calcium ions leads to the precipitation of gypsum, which can cause other problems, such as scaling within the circuit and increased tailings volume. Sodium hydroxide can also be used for removing the iron and aluminum, but it adds sodium ions, making the solution predominantly Na_2SO_4. If the plant produces lithium hydroxide (LiOH), that could be used as the alkalizing agent to reduce the levels of impurities, but an ongoing bleed to remove chloride and sulfate would still be required. The precipitate is filtered or centrifuged and washed to reduce lithium losses to around 1%. If some of the iron is present as ferrous ions, hydrogen peroxide can be added to convert it to the less soluble ferric form.

The second step uses sodium carbonate to precipitate magnesium and calcium carbonates, leaving <5 ppm Ca+Mg and a more concentrated Na_2SO_4 solution. This step requires careful process control to prevent substantial losses of lithium as Li_2CO_3. The best control will result in only 1%–2% loss of lithium in this stage. The quantity of lithium in the Mg+Ca carbonate precipitate is insufficient to warrant further treatment to recover the lithium and it is disposed of. If a higher purity of Li_2CO_3 or LiOH is required, the low levels of iron, aluminum, magnesium, and calcium remaining after precipitation can be removed using IX. This is not usually the case for the standard 99.5% Li_2CO_3 battery-grade product. It is also possible to add ethylenediaminetetraacetic acid (EDTA) to complex with the magnesium and calcium ions, preventing them from precipitating during the lithium precipitation. However, the EDTA complexes build up over time, necessitating a bleed that needs to be treated to recover the lithium.

For solutions derived from leaching micas, additional unit operations are required to remove the additional impurities. The rubidium and cesium can be separated by IX, as selectivity for these elements is higher than for potassium, sodium, and lithium—alternatively, it is possible to form insoluble double alums from the leach solution (Jandova et al. 2012). The rubidium is of limited value but the cesium has potential value, if converted into the formate, as a high temperature–high pressure drilling mud in the oil and gas industry. Fluoride is removed using activated alumina, or in higher amounts it will also precipitate as CaF_2 during the initial neutralization of the acid leach solution when using lime or limestone.

The solution at this stage is essentially a mixture of lithium, sodium, and SO_4; the subsequent stages of treatment are dependent upon the required product. A flow sheet for the purification of the leach solution is shown in Figure 13.

Li_2CO_3 Precipitation and Purification

The remaining solution typically contains 35–40 g/L of Li^+, essentially saturated with Li_2SO_4. If the concentration is below 30 g/L, the lithium precipitation efficiency is reduced and the water is generally evaporated to increase the lithium concentration. Figure 14 shows the solubility of lithium as Li_2CO_3 as a function of temperature. From this graph two important points are evident. Li_2CO_3 is unusual in that solubility decreases with increasing temperature, and even the most

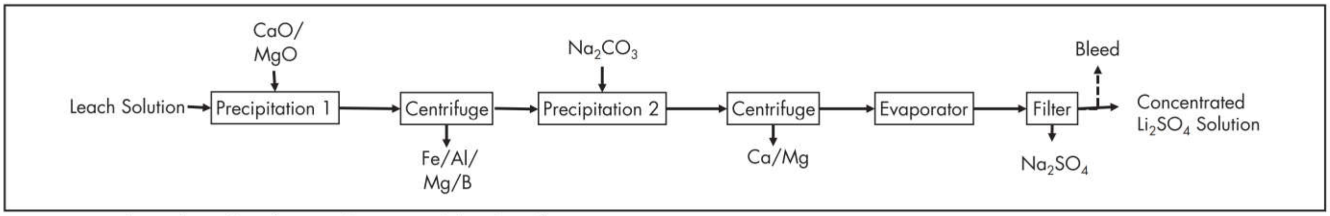


Figure 13 Flow sheet for the purification of leach solutions

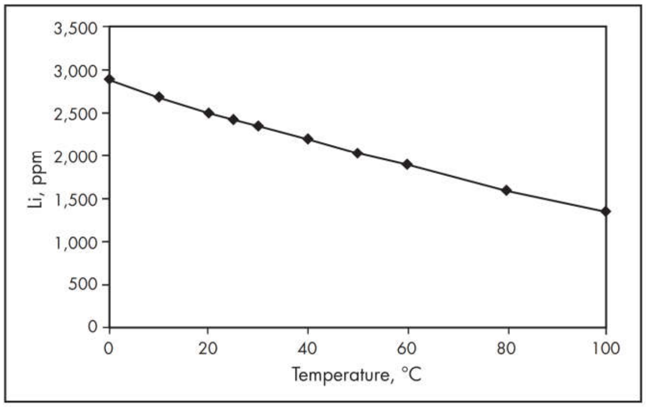


Figure 14 Solubility of lithium in equilibrium with Li_2CO_3 as a function of temperature

efficient precipitation will leave >1.4 g of lithium in solution. The high solubility necessitates recycling of the final solution back into the leaching circuit to minimize lithium losses. In any event, the lithium-bearing solution is heated to 90°C and a solution of Na_2CO_3 mixed in. The precipitation reaction is

$$Li_2SO_4 + Na_2CO_3 \Rightarrow Li_2CO_3 + Na_2SO_4$$

Typically, an excess of around 5% Na_2CO_3 is added to ensure the maximum lithium precipitation.

The Li_2CO_3 product is centrifuged and washed in clean water. At this stage, the major impurities are sodium and SO_4^{2-}, and the overall purity is ~95% Li_2CO_3. To increase the product purity further, a purification stage is undertaken. The impure Li_2CO_3 is slurried in clean water and CO_2 is injected to reduce the solution pH to <8.5, which is sufficient for soluble $LiHCO_3$ to form by the following reaction:

$$Li_2CO_3 + H_2O + CO_2 \Leftrightarrow 2LiHCO_3$$

The reaction is then reversed by heating the solution to precipitate 99.5% Li_2CO_3 with the more soluble impurities remaining in solution. If even higher-purity products are required, the carbonation–decarbonation cycle can be repeated several times. The final solution remains saturated with Li_2CO_3, which can lead to scaling problems and must be recycled within the process to prevent loss of lithium.

The Li_2CO_3 slurry is passed through a high-intensity magnetic separator to remove any magnetic materials present, the majority of which are from the equipment rather than the chemical process. The slurry is filtered, commonly using candle filters, and dried in a rotary kiln prior to micronization and/or bagging to customer requirements. If the product is to be reduced in particle size, a ceramic stirred mill with ceramic media is used to minimize contamination by mill material. Figure 15 shows the flow sheet for the production of lithium carbonate.

LiOH Precipitation and Purification

Direct production of LiOH from the purified solution is based on the following reaction:

$$Li_2SO_4 + 2NaOH \Rightarrow 2LiOH + Na_2SO_4$$

For this process, the solution can be lower in lithium than for carbonate production, with 21–26 g/L Li being typical. A 1.5–1.7-fold excess of NaOH is added to increase the solution pH, which promotes the conversion. The resultant solution is then cooled to –5° to –3°C for around 12 hours, during which time crystals of Glauber's salt, $Na_2SO_4 \cdot 10H_2O$ form and are removed by centrifugation. The crystals are washed and the solution recycled. The salt crystals formed need to be either sold or disposed of. If sold, they are typically converted to anhydrous Na_2SO_4 via additional crystallization steps, centrifuging, and drying.

The remaining solution is then heated to evaporate water until $LiOH \cdot H_2O$ (monohydrate) crystallizes, the evaporation continuing until a 50–60 vol % slurry of $LiOH \cdot H_2O$ is formed. The crystals are centrifuged and washed to remove impurities. The $LiOH \cdot H_2O$ is redissolved at 90°C to give a solution of around 33 g/L Li. The sulfate concentration in this solution should not exceed 15 g/L to prevent it recrystallizing during the next evaporation stage. The evaporation/crystallization of $LiOH \cdot H_2O$ is repeated, with the crystals washed—this time, there is very little sulfate crystallized with the $LiOH \cdot H_2O$ and the product is 99.5% $LiOH \cdot H_2O$. Further stages of dissolution/crystallization can be used to increase purity as required.

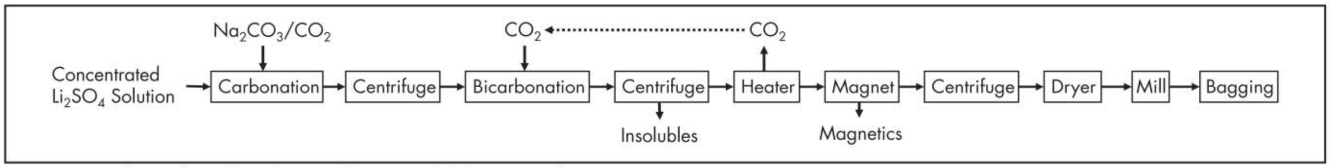


Figure 15 Flow sheet for the production of lithium carbonate

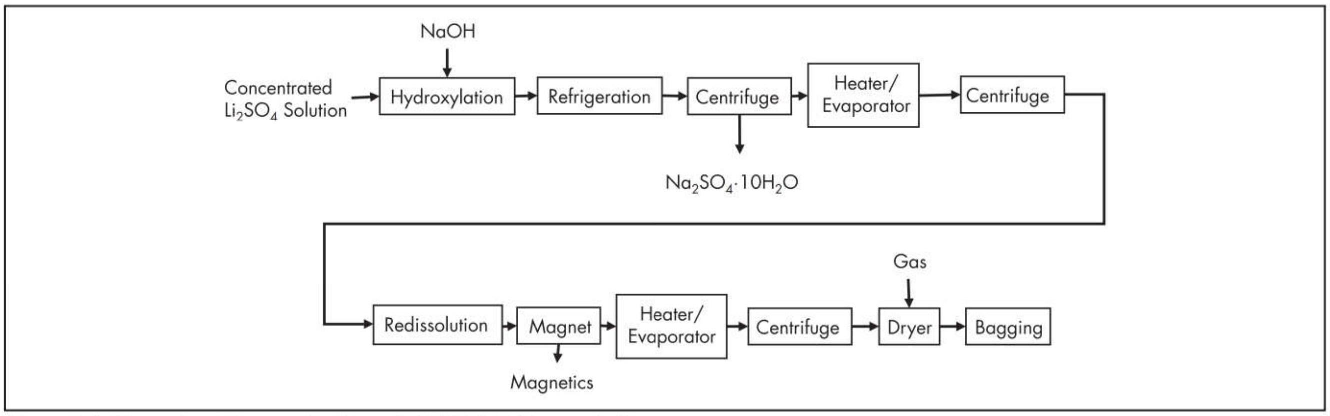


Figure 16 Flow sheet for production of $LiOH{\cdot}H_2O$ from solution

The final product is dried to remove water and bagged. It is possible to dehydrate the monohydrate to LiOH by heating under vacuum at 180°C. However, the anhydrous hydroxide is extremely hygroscopic and the rehydration generates significant heat, presenting significant difficulties with handling and transporting the anhydrous material. In general, the anhydrous LiOH is made on demand. Figure 16 shows the flow sheet for production of $LiOH{\cdot}H_2O$ from purified solution.

Li_2CO_3 Conversion to LiOH

It is also possible to convert the carbonate to hydroxide. This used to be the major process route due to the lower demand for hydroxide than carbonate. However, growth in hydroxide demand is expected to be higher than carbonate, so direct production of hydroxide by the preceding route is increasingly attractive.

Carbonate conversion is based on the reaction between lime and lithium carbonate, with the insolubility of the $CaCO_3$ being the main chemical driver:

$$Ca(OH)_2 + Li_2CO_3 = 2LiOH + CaCO_3$$

The starting Li_2CO_3 slurry is made up to around 210 g/L and heated to just below its boiling point; a 5% excess of $Ca(OH)_2$ is added. Higher concentrations of carbonate or higher excesses of $Ca(OH)_2$ lead to $CaCO_3$ in the final product. The slurry is stirred and the reaction occurs with Li_2CO_3 dissolving and $CaCO_3$ precipitating, the final solution containing 48 g/L LiOH. The slurry is filtered to separate the LIOH solution from the $CaCO_3$, and the $CaCO_3$ is washed to recover the lithium and either disposed of or calcined back to CaO for recycle. The LiOH solution is evaporated to crystallize the $LiOH{\cdot}H_2O$, which is recovered by centrifugation. The impure monohydrate is redissolved in boiling fresh water and impurities removed by adding Na_2CO_3, CaO, and activated carbon. After filtration to remove the solids, further evaporation results in crystallization of $LiOH{\cdot}H_2O$, which is centrifuged, washed, dried, and bagged.

Conversion of carbonate to hydroxide is a tried and tested process, having been in use for more than 40 years. The hydroxide product is of high quality, mainly because the starting carbonate has already undergone some purification. However, the process is considerably more complex than direct production of hydroxide since both carbonate and hydroxide plants are required.

Residual Li_2CO_3 in Solutions

The constant washing with clean water results in solutions containing an appreciable quantity of lithium as a 1,500-ppm Li solution. In plants there are efforts made to recover this lithium because it may represent a loss of a few percent of total lithium production. The most common method is to recycle the wash waters back through the plant countercurrent to the lithium product and into the water leach step. Ultimately, the constant recycle results in the buildup of impurities above the level where they contaminate the product and a bleed is essential. The bleed can be treated to remove the impurities and the lithium-bearing solution recycled or disposed of; recycling leads to problems with the water balance. There is potential to recover the lithium by precipitation as phosphate, which has a solubility of 0.39 g/L (i.e., 70 ppm Li); however, to achieve this requires the removal of calcium and magnesium, as these also form insoluble phosphates. The phosphate produced can be either dissolved in acid and recycled or, if there is sufficient quantity, sold as an additive for the manufacture of low-expansion enamel glazes (FMC Corporation 2007).

Product Specifications

There are no current international specifications for the purity of lithium salts. A Chinese standard for battery-grade Li_2CO_3 (YS/T582-2013) is the only attempt at codifying the situation. Table 7 shows purity data for a range of different lithium carbonate products from various resources and suppliers. The sample from Olaroz is notably higher in purity than the others, which is indicative of having been through a stage of bicarbonation. The samples from Gangfeng and Tianqi are marketed as being within the specifications of the Chinese standard.

The data in Table 7 show that there is a fairly high variability between products by nominally the same routes. In the absence of an international standard, the acceptable impurity requirements are more likely to be defined by the customer and their requirements. Since the majority of the products are going into battery manufacture, the allowable levels of different impurities will vary between manufacturers because of the different chemistries in use. The rapid development of new battery anodes, cathodes, and electrolytes is likely to see a

Table 7 Reported specifications of battery-grade lithium carbonates

Property	SQM, Chile	FMC Corporation, USA	Orocobre, Australia	Albemarle, USA	Gangfeng, China*	Tianqi, China*	Targray, Canada†
Li_2CO_3, wt %	NS‡	99.5	99.5	99.8	99.57	99.5	99.5
Na, ppm	600	500	100	650	200	250	250
K, ppm	50	NS	10	10	15	10	10
Ca, ppm	100	400	100	160	31	50	50
Zn, ppm	10	5	5	NS	NS	3	10
Mg, ppm	100	NS	60	70	39	80	100
Fe, ppm	10	5	5	10	2	10	20
Ni, ppm	10	6	5	NS	2.9	10	30
Al, ppm	NS	NS	5	NS	22	10	50
Mn, ppm	NS	NS	10	NS	0.9	3	10
Pb, ppm	10	NS	5	NS	1.3	3	10
Cu, ppm	10	5	5	NS	1.2	3	10
Cr, ppm	10	NS	5	NS	NS	NS	NS
B, ppm	NS	NS	10	NS	NS	NS	NS
Si, ppm	NS	NS	10	NS	1	30	50
Cl, ppm	100	100	50	150	17	30	50
SO_4, ppm	300	1,000	300	500	660	800	800
F, ppm	NS	NS	NS	NS	NS	NS	NS
Moisture, wt %	0.2	0.5	0.2	0.35	0.2	0.25	0.4

Adapted from Harman 2018

*The Gangfeng and Tianqi samples are produced from spodumene; the remainder from brines.

†Data from Targray 2011.

‡NS = Not stated.

Table 8 Composition of battery-grade $LiOH{\cdot}H_2O$ (manufacturers' specifications)

Component	FMC Corporation, USA	Leverton, UK	Tianqi, China
LiOH, wt %	56.5	56.5	99.5 $LiOH{\cdot}H_2O$
CO_2, ppm	3,500	2,000	3,000
Cl, ppm	20	30	20
SO_4, ppm	100	300	320
Ca, ppm	15	100	20
Fe, ppm	5	5	7
Na, ppm	20	150	20
Al, ppm	10	NS*	BDL†
Cr, ppm	5	5	NS
Cu, ppm	5	5	BDL
K, ppm	10	100	NS
Ni, ppm	10	NS	BDL
Si, ppm	30	NS	BDL
Zn, ppm	10	5	NS
Heavy metals as Pb, ppm	10	NS	BDL
Acid insolubles, ppm	100	50	20

*NS = Not stated.

†BDL = Below detection limit.

new level of purity being required into the long term to maximize the battery performance.

Table 8 shows the composition of three battery-grade LiOH products. As with the carbonates, there is a wide range of impurity levels within the specifications and different impurities being specified. There is no current standard for this product.

REFERENCES

Aiken, S.R., Gowans, R., Hawton, K.E., Jacobs, C., Pilcher, B., Spooner, J., and Trueman, D.L. 2016. *NI 43-101 Technical Report on the Preliminary Economic Assessment of Lithium Hydroxide Production, Separation Rapids Lithium Project, Kenora, Ontario.* Toronto, ON: Micon International.

Bulatovic, S.M. 2014. *Handbook of Flotation Reagents: Chemistry, Theory and Practice. Vol. 3: Flotation of Industrial Minerals.* Amsterdam: Elsevier.

Choi, J., Hong, J., Park, K., Han, Y., Kim, H., Kim, W., and Kim, S.B. 2015. Lepidolite flotation from low grade ores using a cationic surfactant. SME Preprint No. 15-002. Englewood, CO: SME.

Desormeaux, D. 2015. What to expect from the Chilean lithium industry following the National Commission's advancement plan? Presented at the 7th Lithium Supply and Markets Conference, Shanghai, China, June 16–18.

Epstein, J.A., Feist, E.M., Zmora, J., and Marcus, Y. 1981. Extraction of lithium from the Dead Sea. *Hydrometallurgy* 6(3-4):269–275.

FMC Corporation. 2007. Lithium phosphate data sheet. www.fmclithium.com/Portals/FMCLithium/content/docs/DataSheet/QS-PDS-1038%20r0.pdf. Accessed June 2018.

Garrett, D.G. 2004. *Handbook of Lithium and Natural Calcium Chloride.* Amsterdam: Elsevier Academic Press.

Hains, D.H. 2012. CIM best practice guidelines for resource and reserve estimation for lithium brines. https://mrmr.cim.org/media/1041/best-practice-guidelines-for-reporting-of-lithium-brine-resources-and-reserves.pdf. Accessed June 2018.

Harman, G. 2018. What is battery grade lithium carbonate? Presented at the ALTA Conference, Perth, Australia, May 24–25.

Jandová, J., Dvořák, P., Formánek, J., and Vu, H.N. 2012. Recovery of rubidium and potassium alums from lithium-bearing minerals. *Hydrometallurgy* 119-120:73–76.

Jephcott, B. 2016. *Lithium Industry Analysis 2016.* Beijing: Golden Dragon Capital. www.goldendragoncapital.com/wp-content/uploads/2016/07/Lithium-Industry-Analysis-2016.pdf. Accessed May 2018.

Jessup, T., and Bulatovic, S. 2000. U.S. Patent 6,138,835. Recovery of petalite from ores containing feldspar minerals.

Lipp, J. 2014. LiSX™: A breakthrough in lithium production. Presented at ISEC2014—International Solvent Extraction Conference, Würzburg, Germany, September 7–11.

Partington, G.A., Mcnaughton, N., and Williams, I.S. 1995. Mineralization history of the Li-Sn-Ta Greenbushes pegmatite and granitoids of the southwestern Yilgarn Block, Western Australia. *Econ. Geol. Bull. Soc. Econ. Geol.* 90(3):616–635.

SignumBox. 2014. *Lithium, Batteries and Vehicles—Perspectives and Trends*, 8th ed. Santiago, Chile: SignumBox.

SQM. 2017. SQM Investor Day 2017 [presentation]. Chile: SQM. http://s1.q4cdn.com/793210788/files/doc_news/2017/SQM-Investor-Day-2017_FINAL_Sept6.pdf. Accessed June 2018.

SQM. 2018. Salar brines: Salmueras. Chile: SQM. www.sqm.com/en-us/acercadesqm/recursosnaturales/salmuera.aspx. Accessed June 2018.

Targray. 2011. Product data sheet: Lithium carbonate. https://www.targray.com/content-data/mediafiles/images/documents/pds-lithium-carbonate.pdf. Accessed July 2018.

USGS (U.S. Geological Survey). 2018. Lithium: Statistics and information. In *Mineral Commodity Summaries.* Reston, VA: USGS. pp. 98–99.

Vergara-Edwards, L., and Parada-Frederick, N. 1983. Study of the phase chemistry of the Salar de Atacama brines. In *Proceedings of the Sixth International Symposium on Salt*. Vol. II. Alexandria, VA: Salt Institute. pp. 345–366.

Webmineral. 2018. Mineral species containing lithium (Li). http://webmineral.com/chem/Chem-Li.shtml. Accessed June 2018.

YS/T582-2013. *Nonferrous Metals Industry Standard of the People's Republic of China: Battery Grade Lithium Carbonate.* Beijing: Ministry of Industry and Information Technology of the People's Republic of China.