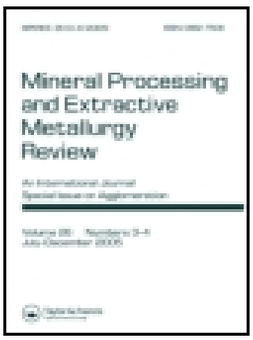

Taylor & Francis
Taylor & Francis Group

Mineral Processing and Extractive Metallurgy Review
An International Journal

ISSN: (Print) (Online) Journal homepage: https://www.tandfonline.com/loi/gmpr20

Lithium Extraction from Spodumene by the Traditional Sulfuric Acid Process: A Review

Javier Rioyo , Sergio Tuset & Ramón Grau

To cite this article: Javier Rioyo , Sergio Tuset & Ramón Grau (2020): Lithium Extraction from Spodumene by the Traditional Sulfuric Acid Process: A Review, Mineral Processing and Extractive Metallurgy Review, DOI: 10.1080/08827508.2020.1798234

To link to this article: https://doi.org/10.1080/08827508.2020.1798234

Published online: 12 Aug 2020.

Submit your article to this journal

Article views: 13

View related articles

View Crossmark data

Full Terms & Conditions of access and use can be found at
https://www.tandfonline.com/action/journalInformation?journalCode=gmpr20

MINERAL PROCESSING AND EXTRACTIVE METALLURGY REVIEW
https://doi.org/10.1080/08827508.2020.1798234

Taylor & Francis
Taylor & Francis Group

Check for updates

Lithium Extraction from Spodumene by the Traditional Sulfuric Acid Process: A Review

Javier Rioyo, Sergio Tuset, and Ramón Grau

Environmental Engineering, Condorchem Envitech, Barcelona, Spain

ABSTRACT

The sulfuric acid process is the dominant technology for lithium extraction from spodumene. However, this process generates huge quantities of waste residue and needs high-temperature pretreatment. The process can be optimized if other high-value elements are found in spodumene deposits, residual lithium can be recycled during mining and processing, and energy savings can be achieved. This paper evaluates the sulfuric acid process for lithium extraction from spodumene from an operational, economic, and environmental perspective. The integration of evaporators and crystallizers during lithium extraction and processing is also reviewed. Finally, further research opportunities for making the process more cost-effective are identified.

KEYWORDS

Lithium; sulfuric acid process; evaporator; crystallizer; spodumene

1. Introduction

The world's demand for lithium extraction has increased in recent years due to lithium use in electric cars and other consumer electronic battery technologies (Braga et al. 2019). This demand has also been boosted by government subsidies and new fuel emissions legislation adopted in various countries to encourage a cleaner environment and reduced dependence on fossil fuels (Champion 2019). Chile holds about 48% of world lithium resources. In 2018, Australia was the world's largest lithium producer, followed by Chile, China, and Argentina (Barrera 2019; Champion 2019). In Australia, six new lithium mines have opened since 2017, and many large lithium extraction projects are being developed worldwide (Umar 2020).

Lithium can be found in the market in different forms such as lithium carbonate, lithium chloride, lithium hydroxide or lithium metal (Champion 2019). For comparison purposes, the lithium content is often expressed in terms of lithium carbonate equivalent (LCE). Lithium is defined as a highly reactive alkali metal and a good conductor of heat and electricity (Samco 2018). The literature regarding the current uses of lithium has already been reviewed (Hu 2012). Lithium can be found in batteries, both non-rechargeable and rechargeable. It is also very useful for the production of glass and ceramics (Champion 2019), these being the main applications up to 2005 (Dessemond et al. 2019). It is also applied for other applications such as the manufacture of high temperature lubricants, pharmaceuticals, and different chemicals (Champion 2019). It is also widely used in the production of psychopharmacological agents for the treatment of bipolar disorder and related illnesses (El Balkhi et al. 2009; Nguyen and Bohle 2004).

Pure elemental lithium cannot be found in nature due to its high reactivity. It is found as a constituent of salts and other compounds (Samco 2018). Lithium is the lightest of all solid elements (Dessemond et al. 2019). It is also the strongest reducing agent. This property gives batteries high gravimetric and volumetric energy densities (Talens Peiró, Villalba and Ayres 2013). The physicochemical characteristics of lithium are shown in Table 1.

A number of authors have extensively reviewed the various lithium extraction and recycling methods (Cheminfo Services Inc 2012; Dessemond et al. 2019; Liu et al. 2019; Liu, Zhao and Ghahreman 2019; Meng et al. 2019; Meshram, Pandey and Mankhand 2014; Mishra and Majumdar 2017; Salakjani, Singh and Nikoloski 2019b; Talens Peiró, Villalba and Ayres 2013). To date, lithium has been extracted from two main sources: (a) 'salars' (dried salt lakes), and (b) pegmatites (mainly spodumene) (Mishra and Majumdar 2017). Currently, about 50% of the production is extracted from mineral ore deposits (Dessemond et al. 2019). Although lithium concentrations in brine are lower than those found in hard rock, the cost of lithium production from ore is generally higher than when produced from brines. This is due to the amount of energy consumption and materials required when lithium is produced from mineral ore (Terence 2020). The process can be more cost-effective if other high value elements are found in spodumene deposits along with lithium, residual lithium is recycled during mining and processing, and energy savings are achieved during the extraction process.

Lithium production from ore is very similar to other types of mining. The nature of pollutants and effluents released to the environment depends upon the host mineral (Cheminfo Services Inc 2012). Lithium extraction from mineral ore generates eight times more solid waste than lithium produced from brine (Talens Peiró, Villalba and Ayres 2013).

The integration of evaporation and crystallization technologies to facilitate effluent compliance with environmental standards and by-product recovery is a common practice in the mining industry (Condorchem Envitech 2020a). The market

CONTACT Javier Rioyo javier.rioyo@condorchem.com Condorchem Envitech, Barcelona, Spain
© 2020 Taylor & Francis Group, LLC

Table 1. Lithium. Physicochemical characteristics.

Parameter	Units	Value
Atomic number		3
Atomic weight		6.941
Melting point	°C	180.5
Boiling point	°C	1336
Density at 20°C	g/cm^3	0.53
Thermal conductivity	cal/(s.cm.°C)	0.17
Specific heat (250°C)	cal/g	0.849
Heat of fusion	cal/g	103.2
Electronegativity	Linus Pauling units	1.0

also provides different solutions to concentrate, crystallize and increase purity standards of lithium salts by a combination of evaporation, crystallization and solids handling technologies. For instance, evaporators are used to concentrate lithium brines. In addition, the use of forced circulation (FC) crystallizers is a common practice to precipitate impurities and to produce high-purity lithium salts. As a result, it is essential to have a good understanding of multi-component systems, aqueous systems, crystallization growth kinetics and equipment requirements to guarantee final product quality standards. In this scenario, bench-scale and laboratory-scale testing is crucial for any project.

To date, there is a lack of technical papers reviewing the integration of evaporation and crystallization technologies during lithium extraction from spodumene by the traditional sulfuric acid process. This paper aims to (a) critically review the sulfuric acid process for lithium extraction from spodumene from an operational, economic, and environmental point of view, (b) evaluate the feasible integration of evaporation and crystallization techniques at different stages during lithium extraction and processing, and (c) disclose further research opportunities.

2. Lithium extraction from spodumene. The traditional process

2.1 Resources of lithium minerals

Lithium can be found in more than 145 different minerals (Talens Peiró, Villalba and Ayres 2013). Important resources of lithium minerals are available in Australia, Canada, and China (Champion 2019). It is found in pegmatites which are considered texturally complex igneous rocks (London 2018). Pegmatites are formed by the crystallization of magma at depth in the Earth's crust (Talens Peiró, Villalba and Ayres 2013). There are two types of pegmatite: (a) granitic and (b) non-granitic, with spodumene a granitic pegmatite (Dessemond et al. 2019). Spodumene mineral is mostly mined for lithium production although other minerals such as lepidolite, petalite, amblygonite, and eucryptite can be used (Talens Peiró, Villalba and Ayres 2013). Australia chiefly produces lithium from spodumene mineral. Average grades from 1% to 3% LiO_2 are common in mineral deposits and nearly all economically viable Australian sources of lithium can be found in Western Australia (Champion 2019).

2.2 Initial concentration process

Following crushing, a flotation process is commonly applied to separate the mineral and produce a spodumene concentrate from mineral ores. This process involves the use of heavy medium separation. Dense nonaqueous liquids can be used in a froth flotation process. As a result, lithium ores are concentrated with respect to lithium oxide from 1% to 3% Li_2O to 4–6% Li_2O (Mishra and Majumdar 2017).

2.3 Sulfuric acid process for lithium carbonate production (the traditional process)

The sulfuric acid process is also referred as the traditional process (Dessemond et al. 2019) or acid baking (Salakjani, Singh and Nikoloski 2019b). The world's first continuous plant using this method was commissioned in 2012 in China (Meshram, Pandey and Mankhand 2014).

The process begins with a heating step in a rotary kiln at 1,100°C. In this step, α-spodumene is converted to β-spodumene, which is a form more amenable to chemical attack (Talens Peiró, Villalba and Ayres 2013). This initial step is called decrepitation and a direct-fired kiln is commonly used. This kind of kiln provides direct contact between process gas and the material to thermally process the ore. The kiln has to be set at a small angle. This allows gravity to assist in moving material through the rotating drum. During this heating treatment, the spodumene crystal structure expands by about 30% (Ebbens and Carlson 2020). Figure 1 a) and 1 b) show images of α-spodumene and β-spodumene. Table 2 provides the main differences between α-spodumene and β-spodumene.

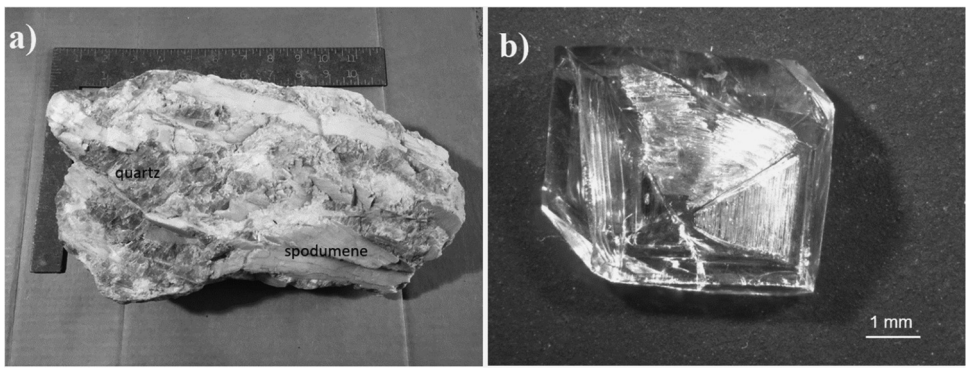

Figure 1. A) Quartz-spodumene-α assemblage from pegmatite and b) Synthetic β-spodumene grown from flux.

Table 2. Differences between α-spodumene and β-spodumene.

	Natural α-spodumene	β-spodumene	Reference
System	natural monoclinic α-form	tetragonal β-form	(Peltosaari et al. 2015)
Leaching properties	Refractory to acid leaching	More reactive form	(Salakjani, Singh and Nikoloski 2019a)
Specific gravity (g/cm^3)	3.1	2.4	(SGS 2013)
Macroscopic level	Appears as a hard-rock	Dusty material Low resistance to grinding	(Dessemond et al. 2019)
Microscopic level	Compact material	Presents cracks on its structure Larger surface area. Porous material	(Dessemond et al. 2019) (Peltosaari et al. 2015)

Next is a cooling step at 65°C, and β-spodumene is grounded (<149 μm) and mixed (Talens Peiró, Villalba and Ayres 2013). β-spodumene is then roasted in a second kiln with an excess of concentrated H_2SO_4 at 200–250°C (Mishra and Majumdar 2017). This process can take from 10 minutes to 1 h. At least 30–40% excess acid is required to guarantee that enough protons are available after reaction with the existing impurities (Salakjani, Singh and Nikoloski 2019b). The overall purpose of acid roasting is to facilitate lithium extraction from the mixture as water-soluble lithium sulfate. This process is carried out in an indirect kiln, often referred to as a calciner. This kind of indirectly fired kiln is heated externally and guarantees that beta-phase spodumene is not exposed to the products of combustion (Ebbens and Carlson 2020). At this stage, Li_2SO_4 is generated, which is soluble in water (SGS 2013) and an insoluble ore residue according to the following reaction (Mishra and Majumdar 2017):

$$Li_2O.Al_2O_3.4SiO_2 + H_2SO_4 \rightarrow H_2O.Al_2O_3.4SiO_2 + Li_2SO_4 \quad (1)$$

The excess H_2SO_4 can be neutralized with $CaCO_3$ to a pH 6 to 6.5. The kiln is then leached with water for 60 minutes (Salakjani, Singh and Nikoloski 2019b). Following filtration of the resulting slurry, a concentrated Ca_2SO_4 solution free of aluminum and iron is achieved. Lime can then be used to precipitate magnesium and soda ash to precipitate residual calcium. After filtration and pH adjustment with H_2SO_4, the lithium solution can be concentrated in a multiple-effect (MEF) evaporator (Talens Peiró, Villalba and Ayres 2013). A high concentrated lithium-containing solution is required to achieve a high lithium recovery rate (Zhao et al. 2019). Eventually, lithium is precipitated as Li_2CO_3 through soda ash addition at 90–100°C (Talens Peiró, Villalba and Ayres 2013). To guarantee maximum lithium precipitation, an excess of about 5% soda ash is added according to the following reaction (SME 2019):

$$Li_2SO_4 + Na_2CO_3 \rightarrow Li_2CO_3 + Na_2SO_4 \quad (2)$$

Following crystallization, the resulting solution is centrifuged. Then, Li_2CO_3 precipitates are washed and dried (Talens Peiró, Villalba and Ayres 2013). Technical grade lithium carbonate is produced with about 95% purity (SME 2019). Overall, lithium extraction from spodumene could be considered a mature technology. Figure 2 shows a feasible layout.

Battery grade lithium carbonate requires 99.5 purity and a d_{90} of between 9 and 15 μm. d_{90} means the diameter of 90% particles (Peng et al. 2019). A number of lithium carbonate purification methods are in use (Chen, Lee and Ho 2018). When extra lithium carbonate purification is required, this could be achieved using the following procedure: (1) slurry the impure lithium carbonate in clean water, (2) inject carbon dioxide to reduce pH below 8.5 and to dissolve $LiHCO_3$, (3) heat the resulting solution to precipitate lithium carbonate

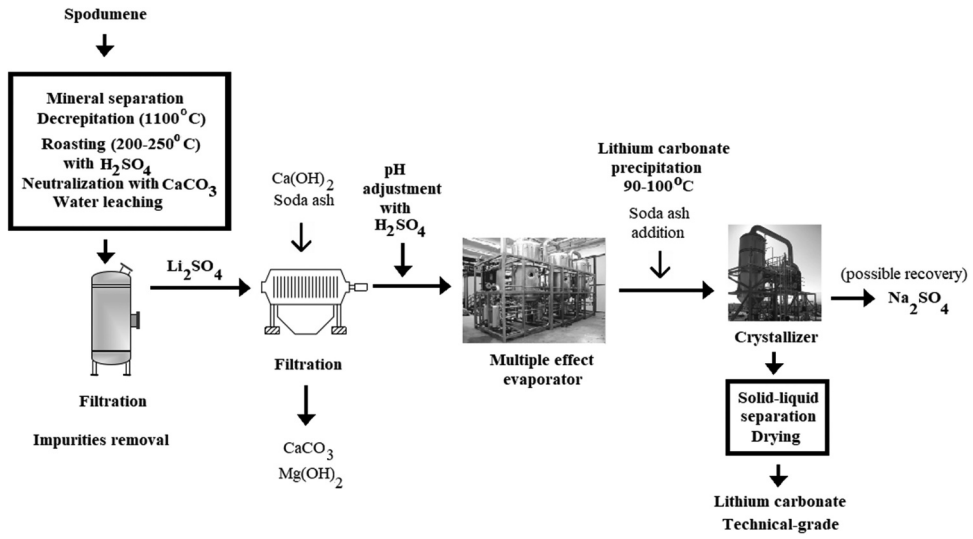

Figure 2. Technical-grade lithium carbonate production layout.

while keeping soluble impurities in the solution, (4) apply a high-intensity magnetic treatment to remove impurities, (5) filtrate and (6) dry the lithium carbonate in a rotary kiln. At this stage, the more soluble impurities remain in the solution (SME 2019). A similar process was reported by Chunlong et al. for Li_2CO_3 preparation using the carbonation decomposition method (Chunlong et al. 2018).

The sulfuric acid process for Li_2CO_3 production has been used for more than 50 years. One handicap of this traditional approach is that it can introduce impurities into the leaching solution. Consequently, additional purification stages may be required (Salakjani, Singh and Nikoloski 2019b). Another disadvantage of the sulfuric acid process is that it generates huge quantities of waste residue and requires a high-temperature pretreatment (Xing et al. 2019) which is energy intensive. It has been reported that the energy requirements necessary to produce one ton of Li_2CO_3 are 1.66 GJ and 1.01 GJ of natural gas and electricity, respectively. The production process also requires the following materials: 1.34 tons of Spodumene, 0.48 tons of H_2SO_4, 0.52 tons of Na_2CO_3, and 24 tons of H_2O (Talens Peiró, Villalba and Ayres 2013).

A recent study reported that the cost of Li_2CO_3 carbonate production was above U$2,000/ton. This study was performed starting with ore at a nominal 3% lithium oxide content. Eventually, further purification to battery grade lithium carbonate can be required (Seddon 2016).

2.4 Production of different lithium salts

2.4.1 LiOH production by reaction of Li_2CO_3 with lime

LiOH is used in batteries (Gea 2020b). When LiOH production is targeted instead of Li_2CO_3, two different processes are available: (a) reaction of Li_2CO_3 with lime according to reaction 3 (SME 2019), or (b) membrane electrolysis (ME) from Li_2SO_4 liquor (Anzaplan 2020):

$$Li_2CO_3 + Ca(OH)_2 \rightarrow 2LiOH + CaCO_3 \quad (3)$$

In the first case (reaction with lime), the generated LiOH liquor can have a 50% lower concentration than in the second case. Therefore, much higher energy is required during the crystallization step (Anzaplan 2020).

Following reaction with lime, a monohydrate LiOH can be obtained by evaporation of the liquor (Anzaplan 2020). The process involves the following steps: (1) heat a lithium carbonate slurry of approximately 210 g/L to about its boiling point, (2) add $Ca(OH)_2$, (3) stir and (4) filtrate to separate LiOH from the precipitated $CaCO_3$. A 5% excess of $Ca(OH)_2$ is generally added and a 48 g/L LiOH solution is eventually achieved. The LiOH solution is then treated by evaporation to crystallize a lithium hydroxide monohydrate that can be recovered by centrifugation (SME 2019). A previous study also reported the recovery of LiOH through the reaction of lime with spent Li_2CO_3 used as an absorbent for CO_2 in breathing apparatus (Kim 2008).

If required, produced lithium hydroxide can be treated for impurity removal. The impure monohydrate is dissolved in fresh boiling water. The impurities are then removed by soda ash, lime and activated carbon addition. After filtration and evaporation/re-crystallization $LiOH.H_2O$ is produced. Finally, the product is centrifuged, washed, dried, and bagged (SME 2019). Figure 3 illustrates the LiOH production process by reaction with lime and subsequent purification process to achieve battery-grade lithium hydroxide.

2.4.2 LiOH production by ME of a Li_2SO_4 liquor

Selection of the appropriate reagent for pH adjustment and impurity removal during the extraction process with sulfuric acid is a key issue if ME is the option of choice for LiOH production. If ME technology is applied, a mixture of NaOH and LiOH could eventually be produced in the cathode. To avoid this outcome, CaO or $Ca(OH)_2$ would be more suitable reagents than NaOH for pH adjustment and impurity removal

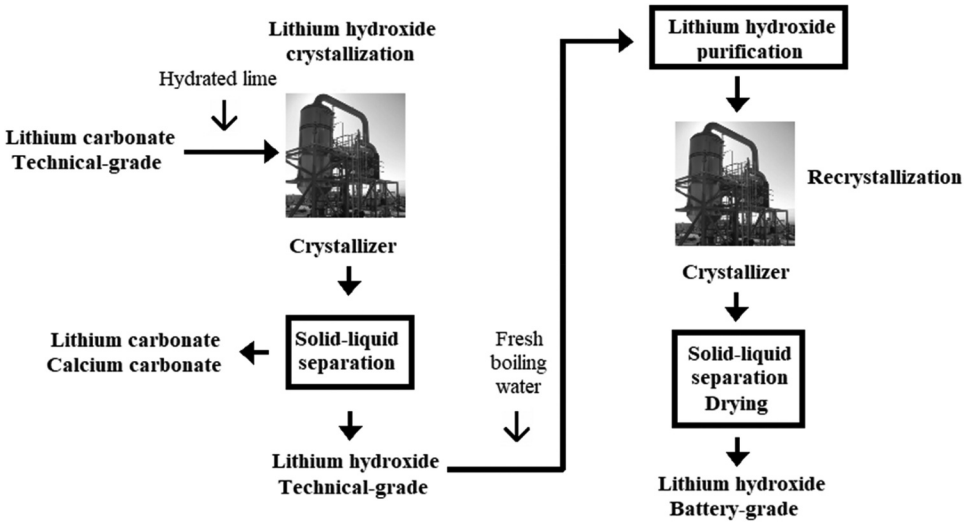

Figure 3. Production of LiOH by reaction of Li_2CO_3 with lime.

during the extraction process if ME technology is selected. Hydrated lime reacts with sulfates to form gypsum according to reaction 3 (Anzaplan 2020):

$$H_2SO_4 + Ca(OH)_2 \rightarrow 2H_2O + CaSO_4 \quad (4)$$

Calcium could be then separated by precipitation or IX technology. At this stage other nuisance pollutants are also removed. Therefore, a liquor suitable for ME treatment is guaranteed. A three-chamber set-up is the common ME configuration where Li_2SO_4 liquor is fed through the central chamber. During the ME treatment, the cathode chamber is enriched with LiOH while the anode one is enriched in H_2SO_4 according to the following reaction (Anzaplan 2020):

$$2SO_4^{2-} + 2H_2O \rightarrow 2H_2SO_4 + O_2 + 4e^- \quad (5)$$

However, other alkali metals like sodium and potassium could also be enriched in the cathode chamber. This could be solved by implementing a crystallization process following ME. NaOH and KOH solubilities are 10 times higher than LiOH solubility. NaOH, KOH, and LiOH solubilities are 1,090, 1,120, and 128 g/L, respectively. Therefore, it is feasible to precipitate most LiOH while keeping NaOH and KOH in the solution. This alternative for direct production of LiOH (without intermediate precipitation of Li_2CO_3) can be worthwhile when working with spodumene and petalite minerals (Anzaplan 2020).

2.4.3 LiOH production by reaction of Li_2SO_4 with caustic soda

An alternative lithium hydroxide production method could be by reaction of purified lithium sulfate with sodium hydroxide. An excess of NaOH addition is required to increase solution pH and promote conversion (SME 2019):

$$Li_2SO_4 + 2NaOH \rightarrow 2LiOH + Na_2SO_4 \quad (6)$$

Subsequent cooling is undertaken to about −3 to −5°C for about 12 hours for Glauber's salts precipitation and removal by centrifugation (SME 2019). Sodium sulfate decahydrate is known as Glauber's salt (Levy and Lisensky 1978). The remaining solution is treated by evaporation/crystallization to produce monohydrate lithium hydroxide crystals which are centrifuged and washed for impurities removal. Further stages of dissolution/crystallization would have to be undertaken to increase purity of the final product (SME 2019).

2.4.4 LiCl production by reaction of Li_2CO_3 with HCl

High-purity lithium carbonate can react with hydrochloric acid to form lithium chloride according to the following reaction (Seetharaman et al. 2014):

$$Li_2CO_3 + 2HCl \rightarrow 2LiCl + H_2CO_3 \quad (7)$$

Lithium chloride can then be used for the production of lithium metal as explained in the following section.

2.5 Li metal production

Metallic lithium is produced by molten salt electrolysis. The process requires a melt comprising of an equal mixture of LiCl and KCl to produce a molten eutectic electrolyte (Mishra and Majumdar 2017). KCl is added with two purposes: (1) increase the conductivity of the lithium and (2) lower the fusion temperature (Terence 2020). The cell is operated at a temperature ranging from 400°C to 420°C. The cell is provided with a steel cathode with cast iron collectors and a graphite anode (Mishra and Majumdar 2017). During the process, chlorine gas is released. In addition, molten lithium rises to the surface (Terence 2020) and is recovered in a collector. Eventually, electrolytic lithium could be refined by re-melting, achieving a purified lithium with less than 100 mg/L of potassium (Mishra and Majumdar 2017). The electrode reactions are calculated by the following (Seetharaman et al. 2014):

$$Cathode: Li^+ + e^- = Li(l) \quad (8)$$

$$Anode: Cl^- = \frac{1}{2}Cl_2(g) + e^- \quad (9)$$

$$Overall: LiCl(l) = Li(l) + \frac{1}{2}Cl_2(g) \quad (10)$$

It has been estimated that the cost for lithium metal production starting from mineral ore (3% Li_2O content) can reach U$22,000/ton. The whole process involves the following subprocesses: initial lithium carbonate production by the sulfuric acid process, lithium carbonate transformation to lithium chloride and final lithium metal production by electrolysis. However, further purification and metal casting can be required to produce a battery grade material (Seddon 2016).

3. Application of evaporation and crystallization techniques during lithium extraction from spodumene by the traditional sulfuric acid process

3.1 Process applications

Evaporation and crystallization technologies are incorporated in different subprocesses during lithium extraction and processing. For instance, these technologies can be applied for (a) lithium brine concentration, (b) lithium salts crystallization, (c) lithium salts purification by re-crystallization, (d) by-products recovery from lithium processing, and (e) water contaminated treatment. Table 3 provides some examples.

Table 3. Possible applications of evaporation and crystallization technologies during lithium extraction and processing.

Sub-process	Technology
Concentration of lithium sulfate solution & crystallization of technical grade lithium carbonate	Evaporator + Crystallizer
Purification of lithium carbonate	Crystallizer
Recovery of sodium sulfate as a byproduct during lithium carbonate production	Crystallizer
Lithium chloride production	Crystallizer
Lithium hydroxide production	Crystallizer
Water contaminated (tailings) treatment	Evaporator + Crystallizer

Condensate water produced during evaporation/crystallization treatment can be recycled into the process. As shown in Section 2.3, 24 tons of water are spent to produce one ton of lithium carbonate from spodumene.

3.2 Evaporation technology

3.2.1 Evaporation concepts

Every single liquid exerts a vapor pressure which depends on its volatility. High vapor pressure liquids evaporate easily while low pressure vapor liquids evaporate slowly. Boiling occurs when a liquid is heated to a temperature at which its vapor pressure equals the atmospheric pressure. Then, rapid evaporation occurs. On the other hand, if the external pressure decreases (under vacuum), water can boil at a lower temperature (Kemmer 1988).

Different solutions generated during the lithium extraction process can be concentrated in an evaporator. The process can involve a reduction of the interior pressure of the evaporation chamber below atmospheric pressure (1013.25 mbar). As a consequence, the boiling point of the liquid to be evaporated and energy consumption are reduced (Condorchem Envitech 2020b). During the concentration process, the evaporation rate decreases as water salinity increases. This increase in the boiling point can be explained because of the reduction in the water vapor pressure due to the increased soluble salts concentration in the solution. For effective performance of an evaporation unit, scheduled chemical treatment is required to maintain clean heat transfer surfaces (Kemmer 1988).

3.2.2 Types of evaporators

MEF and mechanical vapor recompression (MVR) evaporators are common in the mining industry. MEF are powered by hot water, steam or diathermic oil. One of the main advantages of this kind of evaporator is that the use of heat residual streams is possible (Condorchem Envitech 2020b). Units in MEF evaporators can be 1, 2, 3 or more, staged and heat transferred to the evaporated product (first effect) is fully recycled during the following stages (Degrémont 2007; Kemmer 1988). Generally, the condensate produced in the first effect is more pure (Kemmer 1988). There are also different configurations. MEF evaporators can incorporate an external heat exchanger and FC, or a submerged tube exchanger (Condorchem Envitech 2020b). The number of effects depends on the ratio of operating cost to capital investment. This is also limited by the evaporation capacity and boiling point elevation of the solution (Gea 2020a).

MVR evaporators can facilitate low energy consumption. These units can incorporate a preheating system of the brine to be concentrated using vapor or electrical resistors installed inside the boiler. Following preheating, a root-pump is used to compress the vapor which is evaporated from the brine to increase its temperature and pressure. Therefore, it can be used as a heating source to evaporate the raw brine again. There are different configurations such as (a) FC and (b) falling film (FF) evaporators. In FC evaporators, energy consumption can be about 50 kwh/m^3 produced distillate. In FF evaporators, energy consumption can range from 36 to 100 kwh/m^3 produced distillate (Condorchem Envitech 2020b).

In the FC configuration, a forced water circulation is applied to optimize the heat exchange process and energy consumption. There are different possibilities but working temperature can be set to around 60°C and vacuum can be maintained about 200 mbar. In the FF set-up, the recirculation pump continuously feeds brine from the bottom of the evaporator to the top of a falling-film evaporator. From this point, a film of brine flows-down the tube walls and evaporates. The vapor, compressed by the root pump, condenses on the outside of the tubes, transferring heat to the evaporating solution on the inside of the tubes. The working temperature can be set to around 90°C and vacuum can be maintained about 700 mbar. (Figure 4a,b) illustrate both configurations (Condorchem Envitech 2020b).

Overall, selection of MEF or MVR technology depends upon the relative cost and availability of natural gas and power, or residual heat streams on-site. This has to be carefully evaluated for each site.

3.3 Crystallization process

3.3.1 Crystallization concepts

Salt crystallization requires supersaturation. The metastable region is defined as the area over normal solubility, in which a solution can be supersaturated (Myerson and Ginde 2002). This can be achieved by: (a) evaporation, (b) cooling and (c) chemical precipitation reaction. The last path involves rapid crystallization and the process can often be controlled to only a small extent (Mersmann 2001). There is an "induction period" between the achievement of supersaturation and the initial appearance of crystals. This can depend on different factors such as: (a) the level of supersaturation (ΔC), (b) agitation, (c) presence of impurities and (d) viscosity (Mullin 2001).

When the solubility of a solute is mostly independent to temperature, evaporative crystallization is recommended (Mersmann 2001). However, when solubility of the salt to be precipitated strongly depends on temperature, vacuum cooling crystallization could be an interesting alternative to consider. In this second set-up, no cooling surface is required, and incrustation is prevented (Gea 2020a). Overall, selected crystallizer for any single application depends on the type of supersaturation produced and has to meet final product specifications in terms of purity, particle size and operating time.

Salt crystallization is a two-step process. The first step is nucleation (birth of new crystals), and the second is crystal growth. Nucleation is divided in primary nucleation (no crystals initially present) and secondary nucleation (crystals already present in the solution) (Mullin 2001). In industry, primary homogeneous nucleation rarely happens due to the low ΔC employed and the presence of impurities which induces heterogeneous nucleation (Myerson and Ginde 2002). Primary nucleation happens at the commencement of crystallization, when concentration of the solvent surpasses the metastable region. The secondary nucleation (induced by crystals) occurs in the metastable region and is due to direct contact between a crystal and another surface such as: (a) another crystal, (b) the walls or (c) the impeller (Gea 2012). Crystal-agitator contacts are the most effective source for secondary nuclei production (Mullin 2001). Although the process is not

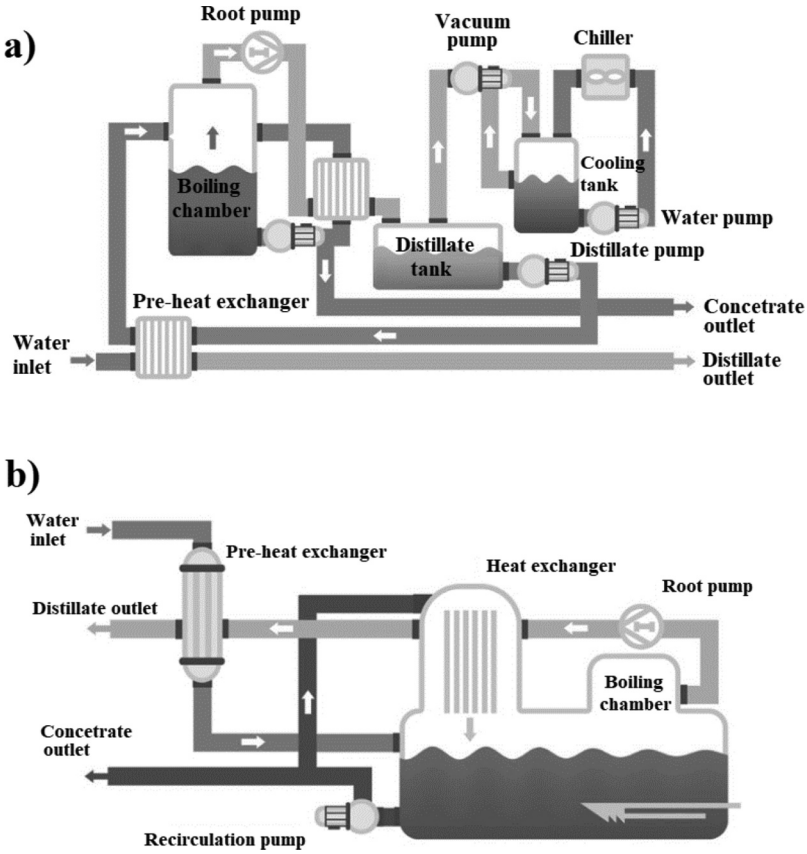

Figure 4. MVR evaporator lay-out: a) Forced circulation and b) Falling film (Condorchem Envitech 2020b).

clearly understood (Myerson and Ginde 2002), secondary nucleation (*Bo*) depends on the dissipated mixing energy (ε), ΔC and suspension density (m) as shown in the following equation (Gea 2012):

$$B_0 = k_N{}^{*}\varepsilon^{r*}m_T^{i,*}\Delta C^{n} \tag{11}$$

The crystal growth rate measures how fast a crystal grows in a crystallizer (Mullin 2001). It is a complex process (Mersmann 2001). Both, the crystal growth rate and the nucleation rate depend on ΔC, although the second is affected to a higher extent. Therefore, larger crystals are formed at low nucleation rates. To achieve this, it must: (a) limit ΔC in the crystallizer so that is does not exceed the metastable region, (b) set a ΔC where growth rate is maximized and (c) optimize the mixing energy to control ΔC and minimize secondary nucleation (Gea 2012). Finally, the presence of impurities has a dramatic effect on crystal growth, morphology, and nucleation (Meenan, Anderson and Klug 2002).

3.3.2 Types of crystallizers

FC crystallizers provide high rates of evaporation and are suitable for salts that grow readily and can be employed for lithium carbonate, lithium hydroxide and sodium sulfate crystallization (Jordproxa 2018). FC crystallizers are provided with: (a) an evaporation (boiling) chamber, (b) a recirculation pump which provides the mixing energy and (c) an external heat-exchanger as illustrated in Figure 5 (Condorchem Envitech 2020b). Centrifugal pumps are commonly used to circulate the slurry (Mersmann 2001). The circulation rate must be appropriate to maintain the crystals in suspension.

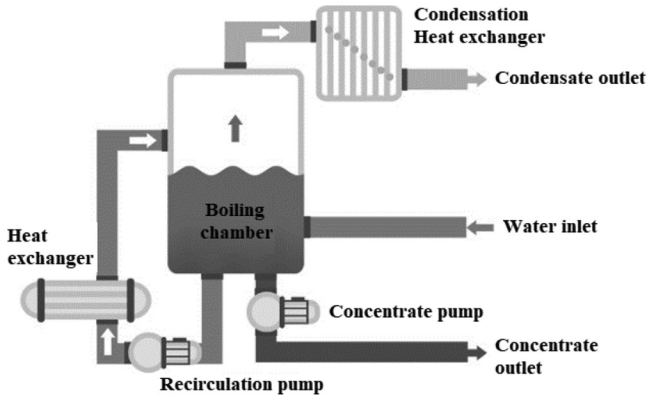

Figure 5. FC crystallizer (Condorchem Envitech 2020b).

FC crystallizers can operate: (a) under vacuum or (b) at low super-atmospheric pressure (Gea 2012). A particle size lower that 0.5 mm is achievable using FC crystallizers (Mullin 2001). During the crystallization step, the crystals must be separated from the mother liquor. This can be achieved with a pusher centrifuge, if the crystal size is big enough, following pre-concentration in a thickener. Different brands specialize in providing centrifuges for this purpose (Andritz 2020; Riera Nadeu 2018).

Other types of crystallizers available in the market are: (a) draft tube baffled crystallizers, (b) Oslo crystallizers, (c) vacuum crystallizers, (d) reactive crystallizers, (e) adiabatic flash crystallizers and (f) calandria crystallizers. Draft tube baffled crystallizers and Oslo crystallizers can produce crystals of higher particle size than FC crystallizers.

3.4 Waste energy recovery

As discussed in Section 2.3, the traditional process of extracting lithium from spodumene is energy intensive. To cut costs, waste heat could be recovered from the high-temperature pretreatment to provide both steam and electricity. An energy-mass-balance must first be prepared to model energy uses on site. Steam could be generated by passing the waste gases of the kiln (decrepitation process at 1100°C) through boilers. Then, the steam drives a turbine-generator powering the downstream physical and chemical separation units of the extraction process including evaporators and crystallizers. The initial investment costs can be high, so calculating the payback period is necessary.

Alternatively, steam or hot water can be readily used as a power supply in MEF evaporators to generate water vapor that leaves the first evaporator and is used as the heating medium in the second evaporator, and so on. In MVR evaporators, steam can also be used in the pre-heating system. Finally, FC crystallizers can also be powered by hot water or steam (Condorchem Envitech 2020b).

3.5 Opportunities for future research

The increasing demand for lithium products promotes the development of new lithium extraction methods and the improvement of the existing methods (Salakjani, Singh and Nikoloski 2019b). Even the recycling of spent lithium-ion batteries has been seriously suggested to alleviate resource shortage (Liu et al. 2019).

There are many opportunities for future research. For instance, lithium recovery and recycling can occur during mining and processing (Talens Peiró, Villalba and Ayres 2013). Residual Li_2CO_3 can be recycled from washing solutions. Lithium concentrations up to 1,500 mg/L have been measured in washing waters. A feasible solution, can be to pump them back to the water leach step following impurity removal. Alternatively, precipitation as phosphate can be possible following hardness removal (SME 2019).

In addition, research could be conducted for tailings minimization/concentration using a combination of membrane and evaporation-based concentration technologies. Bench-scale or pilot plant testing could provide the accurate prediction of achievable results. The main advantage of evaporative-crystallization over traditional membrane filtration technologies is its theoretical potential to minimize the volume of concentrated saline wastewater to zero, as well as the possibility of recovering solid residues such as pure salts or mixtures. The evaporated water is recovered by the condensation of generated steam. These technologies can also be used to treat high salinity waters obtained from RO or nanofiltration (NF) treatment processes. It would also be interesting to evaluate the heat residual streams available on site. These types of thermal-evaporation processes can be profitable if residual heat or a cheap fuel source is available in the installation. Energy consumption varies with design, flow-rate, and salinity. In arid areas or areas with few water resources, the cyclical use of process water is increasingly important. Overall, the trend to ZLD (zero liquid discharge) becomes a key goal. Finally, it would be interesting to evaluate the use of solar energy in the process to cut costs further, and avoid/minimize gas emissions.

Membrane distillation (MD) is another promising technology that has been tested for concentration/minimization of different kinds of brines and RO concentrates (Pérez-González et al. 2012; Rioyo, Aravinthan and Bundschuh 2019; Rioyo et al. 2017). Membrane distillation coupled with crystallization has also been proposed in the scientific literature as an alternative to conventional crystallizers (Ruiz Salmón and Luis 2018). The application of MD technology for lithium recovery from brines has been reported in some research papers (Park et al. 2020; Quist-Jensen et al. 2016). High capital and operating costs of membrane technologies can be a handicap (Li et al. 2019). Overall, the possible integration of MD technology with the traditional lithium extraction process from spodumene requires further research.

4. Conclusions

The "traditional" sulfuric acid process is the dominant technology for lithium extraction from spodumene in Australia and worldwide. However, this process generates huge quantities of waste residue and requires high-temperature pretreatment. In addition, the process can introduce impurities into the leaching solution requiring additional purification stages. The extraction process can be optimized if other high-value elements are found in spodumene deposits along with lithium, residual lithium can be recycled during mining and processing, and energy savings can be achieved.

The integration of evaporation and crystallization technologies is very common in the mining industry for facilitating effluent compliance with environmental standards and by-product recovery. Evaporators and crystallizers can be incorporated in different steps during the lithium extraction and processing such as brine concentration, salt crystallization and purification, by-product recovery, impurity removal and effluent treatment. Overall, it is essential to have a good understanding of crystallization growth kinetics and equipment requirements to guarantee final product quality standards. The accurate prediction of achievable results can be facilitated by preliminary bench-scale and pilot-scale testing. The utilization of heat residual streams available on-site can facilitate energy savings during evaporation and crystallization steps. For instance, waste heat generated during decrepitation and acid roasting pretreatment could be recycled in the process.

Further research could be required for tailings minimization/concentration using a combination of membrane and evaporation-based concentration technologies. Tailings represent a major environmental problem and often require massive amounts of land for storage and contain metals-contaminated water. Generally speaking, the trend to ZLD is becoming a key issue, especially in arid or semi-arid areas facing a lack of fresh water. In addition, it would be interesting to evaluate the possible options for the integration of MD technology with the traditional lithium extraction process from spodumene. Finally, the use of solar energy in different steps of the extraction process to further cut costs and avoid/minimize gas emissions seems to be interesting.

Acknowledgments

The authors would like to thank Natural Resources Canada for providing Figure 1a,b.

Disclosure statement

No potential conflict of interest was reported by the author(s).

References

Andritz. 2020. www.andritz.com/products-en/group/separation/filter-centrifuges/krauss-maffei-sz-pusher-centrifuge.

Anzaplan. 2020. www.anzaplan.com/minerals/lithium.

Barrera, P. 2019. www.investingnews.com/daily/resource-investing/battery-metals-investing/lithium-investing/lithium-producing-countries.

Braga, P., S. Franca, R. Neumann, M. Rodriguez, and G. Rosales, 2019, Alkaline process for extracting lithium from spodumene. Paper presented at the Hydroprocess 2019. 11th International Seminar on Process Hydrometallurgy, Santiago, Chile.

Champion, D. 2019. *Australian Resource Reviews: Lithium 2018*. Geoscience Australia: Camberra: https://d28rz98at9flks.cloudfront.net/126759/ARR_Lithium_2018.pdf.

Cheminfo Services Inc. 2012. http://reviewboard.ca/upload/project_document/EA1011-001_Review_of_the_Rare_Earth_Elements_and_Lithium_Mining_Sectors.PDF.

Chen, W.-S., C.-H. Lee, and H.-J. Ho. 2018. Purification of lithium carbonate from sulphate solutions through hydrogenation using the dowex G26 resin. *Applied Sciences* 8:2252.

Chunlong, Z., Z. H. I. Sun, Z. Hong, W. Gao, and Y. Zhang. 2018. Research progress of lithium carbonate preparation and purification process. *Guocheng Gongcheng Xuebao/The Chinese Journal of Process Engineering* 18:20–28.

Condorchem Envitech. 2020a. www.condorchem.com/en.

Condorchem Envitech. 2020b. www.condorchem.com/en/evaporators.

Degrémont. 2007. *Water treatment handbook*. Rueil-Malmaison: Degrémont.

Dessemond, C., F. Lajoie-Leroux, G. Soucy, N. Laroche, and J.-F. Magnan. 2019. Spodumene: The lithium market, resources and processes. *Minerals* 9:334.

Ebbens, A., and C. Carlson. 2020. The role of the calciner in the extraction of lithium from spodumene. *FEECO International*. https://feeco.com/the-role-of-the-calciner-in-the-extraction-of-lithium-from-spodumene/

El Balkhi, S., B. Megarbane, J. Poupon, F. J. Baud, and M. Galliot-Guilley. 2009. Lithium poisoning: Is determination of the red blood cell lithium concentration useful? *Clinical Toxicology* 47 (1):8–13.

Gea. 2012. *Mass Crystallization from Solutions*. Germany: GEA Group.

Gea. 2020a. *Leading Evaporation & Crystallization*. France: GEA Group.

Gea. 2020b. *Solutions for Lithium Processing*. Germany: GEA Group.

Hu, Q. 2012. Lithium: the literature regarding its uses in chemistry, psychiatry, and the engineering of materials and batteries. *Science & Technology Libraries* 31 (2):190–99.

Jordproxa. 2018. www.jordproxa.com/jordproxa-products/crystallisation.

Kemmer, F. N., Nalco Chemical Company. 1988. *The nalco water handbook*, Second. New York, USA: McGraw Hill Book Co.

Kim, K. J. 2008. Recovery of lithium hydroxide from spent lithium carbonate using crystallizations. *Separation Science and Technology* 43 (2):420–30.

Levy, H. A., and G. C. Lisensky. 1978. Crystal structures of sodium sulfate decahydrate (Glauber's salt) and sodium tetraborate decahydrate (borax). Redetermination by neutron diffraction. *Acta Crystallographica Section B Structural Crystallography and Crystal Chemistry* 34:3502–10.

Li, X., Y. Mo, W. Qing, S. Shao, C. Y. Tang, and J. Li. 2019. Membrane-based technologies for lithium recovery from water lithium resources: A review. *Journal of Membrane Science* 591:117317.

Liu, C., J. Lin, H. Cao, Y. Zhang, and Z. H. I. Sun. 2019. Recycling of spent lithium-ion batteries in view of lithium recovery: A critical review. *Journal of Cleaner Production* 228 (2019):801–13.

Liu, G., Z. Zhao, and A. Ghahreman. 2019. Novel approaches for lithium extraction from salt-lake brines: A review. *Hydrometallurgy* 187:81–100.

London, D. 2018. Ore-forming processes within granitic pegmatites. *Ore Geology Reviews* 101:349–83.

Meenan, P. A., S. R. Anderson, and D. L. Klug. 2002. The influence of impurities and solvents on crystallization. *Handbook of Industrial Crystallization*, 2, 67. Cambridge: Cambridge University Press.

Meng, F., J. McNeice, S. S. Zadeh, and A. Ghahreman. 2019. Review of lithium production and recovery from minerals, brines, and lithium-ion batteries. *Mineral Processing and Extractive Metallurgy Review* 1–19. doi:10.1080/08827508.2019.1668387

Mersmann, A. 2001. *Crystallization Technology Handbook*. New York: Marcel Dekker.

Meshram, P., B. D. Pandey, and T. R. Mankhand. 2014. Extraction of lithium from primary and secondary sources by pre-treatment, leaching and separation: A comprehensive review. *Hydrometallurgy* 150:192–208.

Mishra, B., and G. Majumdar. 2017. Alkali metals production (Li, Na, K), In *Reference module in materials science and materials engineering*, 1–2. Netherlands: Elsevier.

Mullin, J. W. 2001. *Crystallisation*. *4th* ed. Oxford, UK: Butterworth-Heinemann.

Myerson, A. S., and R. Ginde. 2002. Crystals, crystal growth, and nucleation. *Handbook of industrial crystallization*, 2, 33–62. Cambridge: Cambridge University Press.

Nguyen, A. N. H., and D. S. Bohle. 2004. Selectivity and uptake of lithium. *Comments on Inorganic Chemistry* 25 (5–6):129–46.

Park, S. H., J. H. Kim, S. J. Moon, J. T. Jung, H. H. Wang, A. Ali, … Y. M. Lee. 2020. Lithium recovery from artificial brine using energy-efficient membrane distillation and nanofiltration. *Journal of Membrane Science* 598:117683.

Peltosaari, O., P. Tanskanen, E.-P. Heikkinen, and T. Fabritius. 2015. α→γ→β-phase transformation of spodumene with hybrid microwave and conventional furnaces. *Minerals Engineering* 82 (2015):54–60.

Peng, C., F. Liu, Z. Wang, B. P. Wilson, and M. Lundström. 2019. Selective extraction of lithium (Li) and preparation of battery grade lithium carbonate (Li2CO3) from spent Li-ion batteries in nitrate system. *Journal of Power Sources* 415:179–88.

Pérez-González, A., A. M. Urtiaga, R. Ibáñez, and I. Ortiz. 2012. State of the art and review on the treatment technologies of water reverse osmosis concentrates. *Water Research* 46 (2):267–83.

Quist-Jensen, C. A., A. Ali, S. Mondal, F. Macedonio, and E. Drioli. 2016. A study of membrane distillation and crystallization for lithium recovery from high-concentrated aqueous solutions. *Journal of Membrane Science* 505:167–73.

Riera Nadeu. 2018. www.rieranadeu.com/wordpress/en/rina-500.

Rioyo, J., V. Aravinthan, and J. Bundschuh. 2019. The effect of 'High-pH pretreatment' on RO concentrate minimization in a groundwater desalination facility using batch air gap membrane distillation. *Separation and Purification Technology* 227:115699.

Rioyo, J., V. Aravinthan, J. Bundschuh, and M. Lynch. 2017. A review of strategies for RO brine minimization in inland desalination plants. *Desalination and Water Treatment* 90:110–23.

Ruiz Salmón, I., and P. Luis. 2018. Membrane crystallization via membrane distillation. *Chemical Engineering and Processing - Process Intensification* 123:258–71.

Salakjani, N. K., P. Singh, and A. N. Nikoloski. 2019a. Production of lithium – A literature review part 1: Pretreatment of spodumene. *Mineral Processing and Extractive Metallurgy Review* 41 (5):1–14.

Salakjani, N. K., P. Singh, and A. N. Nikoloski. 2019b. Production of lithium –A literature review. Part 2. Extraction from spodumene. *Mineral Processing and Extractive Metallurgy Review* 1–16. doi:10.1080/08827508.2019.1700984

Samco. 2018. www.samcotech.com/what-is-lithium-extraction-and-how-does-it-work.
Seddon, D. 2016. Lithium production. Technology and economics. *Chemistry in Australia*. https://chemaust.raci.org.au/article/march-2016/lithium-production.html
Seetharaman, S., A. McLean, R. I. L. Guthrie, and S. Sridhar. 2014. *Treatise on process metallurgy*, Vol. 3. Oxford: Elsevier.
SGS. 2013. T3 1001 hard rock lithium processing.
SME. 2019. *SME mineral processing & extractive metallurgy handbook*. Englewood, Colorado: Society for Mining, Metallurgy & Exploration.
Talens Peiró, L., G. Villalba, and R. Ayres. 2013. Lithium: sources, production, uses, and recovery outlook. *JOM* 65 (8):986–96.
Terence, B. 2020. www.thebalance.com/lithium-production-2340123#citation-1.
Umar, A. 2020. Are mining companies jumping the gun on lithium? *Mining Technology*. https://mining-technology.com/features/are-mining-companies-jumping-the-gun-on-lithium/
Xing, P., C. Y. Wang, L. Zeng, B. Ma, L. Wang, Y. Chen, and C. Yang. 2019. Lithium extraction and hydroxysodalite zeolite synthesis by hydrothermal conversion of α-spodumene. *ACS Sustainable Chemistry & Engineering* 7 (10):9498–9505.
Zhao, C., Y. Zhang, H. Cao, X. Zheng, T. Van Gerven, Y. Hu, and Z. Sun. 2019. Lithium carbonate recovery from lithium-containing solution by ultrasound assisted precipitation. *Ultrasonics Sonochemistry* 52:484–92.