

Alkaline Process for Extracting Lithium from Spodumene

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ABSTRACT

The growing market demand for lithium is mainly due to its use in the manufacture of batteries for electric or hybrid vehicles and portable equipment (cellphones, tablets, power tools, notebooks, etc.). Currently there is great interest in finding new sources of lithium and technologies for its utilization. Brazil has large lithium pegmatite reserves and spodumene is the most important commercially mined lithium mineral.

There are two main routes to obtain lithium carbonate and lithium hydroxide from mineral concentrates. In the first - the acid process - the mineral concentrate is roasted, sulfated with sulfuric acid and leached with water. Soda ash is added to form lithium carbonate. In the second process - the alkaline one - the mineral concentrate is roasted with lime or limestone, forming a clinker which is leached with water, filtered and crystallized as lithium hydroxide monohydrate. In Brazil, only the acidic process is used, although lithium hydroxide is the product most in demand in the domestic market, used mainly by automotive lubricant manufacturers. Lithium hydroxide is the main product in the alkaline process.

The processing of spodumene concentrate to produce lithium hydroxide via the alkaline process can provide advantages to the production process, especially by replacing expensive chemicals such as sulfuric acid and soda ash with products such as limestone or hydrated lime, which are produced domestically and have more affordable prices.

Thermodynamic modeling using the HSC software 5.1 was conducted to predict different reactions that could occur during roasting of the α -spodumene/CaO system. Lithium extraction from the solid obtained after roasting was also investigated. The results of thermodynamic analysis provided a better understanding of the alkaline process for lithium extraction. The metallurgical tests allowed 84% recovery of the lithium contained in the spodumene concentrate.

INTRODUCTION

At present, lithium carbonate is the compound most commonly used in industry, but lithium hydroxide has been gaining importance in the market. The production of lithium ion batteries grew by 20 % a year between 2000 and 2011, and annual growth of 30 % is forecast until 2020, spurred particularly by the increased production of electric/hybrid vehicles and energy storage systems, as well as expansion of all other applications (Nemaska, 2012).

Lithium hydroxide is the product most in demand to manufacture lithium-iron-phosphate batteries (LFP, or LiFePO_4). These batteries have better power density, longer life cycle and greater safety compared to other types of lithium ion batteries. This is possible because the phosphate used in the cathode consists of nanoparticles (Dinger et al., 2010).

In Brazil, lithium hydroxide is mainly used to manufacture high-performance automotive lubricants (Braga & França, 2011; Saruls, 2018).

The use of alkaline processing to recover the lithium contained in pegmatite minerals, such as spodumene, can have advantages over the acid process currently employed, especially by allowing the replacement of expensive inputs – like sulfuric acid (H_2SO_4) and soda ash (Na_2CO_3) – with limestone (CaCO_3) or hydrated lime [$\text{Ca}(\text{OH})_2$], both of which are widely produced and inexpensive in Brazil. Furthermore, the removal of soda ash from the process of obtaining lithium reduces the probability of contamination of the final product by sodium, since the maximum concentration permitted for the metal in the electrolytes of lithium batteries is 0.0002 % Na.

The objective of this study was to develop a method for direct production of lithium hydroxide starting from a spodumene concentrate with 5.8 % Li_2O content.

METHODOLOGY

Materials and equipment

The lithium extraction tests were conducted in laboratory scale and involved the operations of sampling, homogenization, grinding, roasting in a muffle furnace, followed by aqueous leaching in an agitated reactor to extract the lithium hydroxide formed.

We used a sample of spodumene concentrate with about 5.8 % Li_2O , obtained from ore mined in the region of Araçuaí, Minas Gerais, Brazil. The sample, with particle size distribution below 6 mm, was ground in jaw and roller crushers, and afterwards it was milled in rod and ball mills to obtain a maximum grain size of 100 μm . The spodumene concentrate was divided in a sample splitter, in order to provide samples for mineralogical and chemical characterization and extraction assays. Calcitic limestone and lime were used as sources of calcium.

The evaluation and control of the process were performed by X-ray diffractometry (XRD), gravimetry and flame atomic absorption spectroscopy (FAAS).

Standard roasting and leaching tests

Spodumene is a Li-bearing silicate mineral that is naturally refractory to chemical attack in its α form. Thermal treatment leads to the polymorphic transformation of α -spodumene (monoclinic) into β -spodumene (tetragonal), which is a less dense, more friable and reactive phase. This structural transformation occurs at temperatures between 1,030 and 1,050 °C, enabling ion exchange reactions (Medina et al., 1988; Kotsupalo et al., 2009; Barbosa et al., 2014).

We studied different mass ratios (1:1, 1:2, 1:3, 1:3.5, 1:4 and 1:5) between spodumene and calcitic limestone, both with particle size below 100 μm , to promote the solid-solid reaction in a muffle furnace. The mixtures were placed in alumina crucibles and submitted to thermal treatment at 1,050 °C for 30 minutes.

The calcination-decrepitation-reaction of spodumene with limestone (roasting process) involves three distinct steps: (i) decomposition (calcination) of the limestone at temperatures of 750-800 °C, to form calcium oxide and release carbon dioxide gas; (ii) decrepitation to conversion of α -spodumene (weakly reactive) into β -spodumene (more reactive); and (iii) solid-solid reaction, via contact among β -spodumene and calcium oxide particles, with formation of lithium aluminate and calcium silicate. Steps (ii) and (iii) occur almost simultaneously, at a temperature of 1,050 °C. The resulting clinker, after cooling, was ground in an agate mortar to a particle size smaller than 100 μm (85 % passing) and leached with water at a temperature of 90 °C, at a solid-liquid (S/L) ratio of 10 % p/p. The block diagram in Figure 1 illustrates the tests performed.

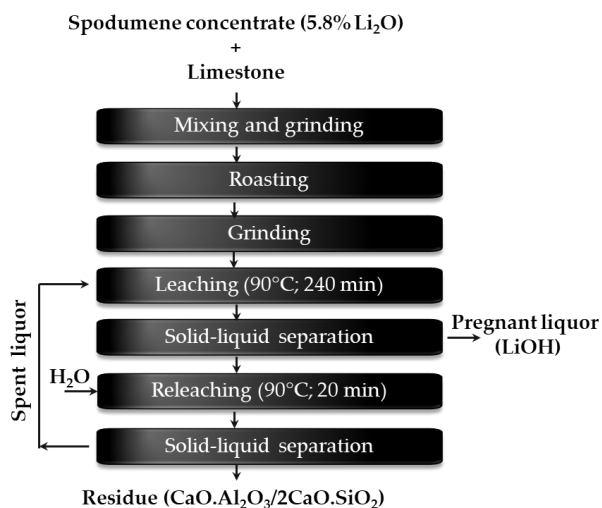
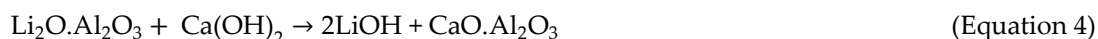


Figure 1 Block diagram of the standard tests

The roasting and leaching test results were evaluated according to the amount of lithium extracted after leaching. The reactions of the process are presented as follow:



Roasting and leaching test with mechanical activation

Mechanical activation modifies particle size and surface area, so it can induce lattice distortion and/or promote phase transformations (Vieceli et al., 2017). As a consequence, it can improve process performance, especially regarding leaching operations. The purpose is to increase the recovery of the target product, mainly in the processing of less common non-ferrous metal ores (Kotsupalo et al., 2010).

We performed complementary extraction tests using mechanical activation, by means of grinding spodumene together with calcium oxide (supplied by Vetec, 95 % purity). The grinding was carried out with a stainless steel rod mill, with capacity of 1 kg of material, for 240 min. After the mechanical activation, the resulting mixture was pressed in an automatic Fluxana press (Vaneox® Technology) with capacity of 40 tons. Briquettes were produced with diameter of 32 mm. The objective of the pressing after grinding was to improve the contact (solid-solid) among the particles of reagents. The briquettes were then treated as shown in Figure 1.

The particle size distribution of the products resulting from the standard and mechanical activation tests was determined by laser diffraction in a Mastersizer 2000, from Malvern Instruments.

RESULTS AND DISCUSSION

Chemical and mineralogical characterization

Table 1 reports the chemical composition of the spodumene concentrate used.

Table 1 Chemical composition (%) of the spodumene concentrate

Li ₂ O	Al ₂ O ₃	SiO ₂	Fe ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O	P ₂ O ₅	Mn ₂ O ₃	LOI
5.80	23.3	56.8	1.07	0.04	0.17	1.40	0.79	0.65	0.14	9.8

LOI - lost on ignition

The results of mineralogical analyses (X-ray diffractometry and stereo microscope analysis), presented in Figure 2 indicated the presence of α -spodumene, the unreactive phase, besides gangue minerals like quartz (Q), feldspars (microcline, Mi and albite, A), muscovite (M) and mica schist, which is the host rock of the pegmatites. The transformation of α -spodumene into β -spodumene is evidenced by the X-ray diffraction patterns (Figure 2), for of the natural and decrepitated samples.

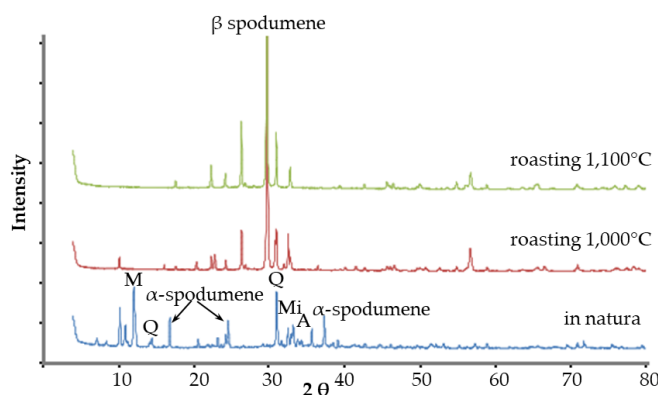


Figure 2 X-ray diffraction patterns of the natural and decrepitated spodumene

Note the appearance starting at 1,000 °C of peaks referring to β -spodumene, which is chemically reactive, with higher crystallinity degree at 1,100 °C, for a calcination time of 30 minutes. The calcined samples did not present peaks referring to α -spodumene, evidencing the efficiency of the decrepitation. Although Garrett (2004) indicated that this phase transformation occurs near 1,040 °C, it is possible to observe that the peaks referring to the calcined sample at 1,000 °C are similar to those of the calcined sample at 1,100 °C.

Thermodynamic study

We performed a thermodynamic study of the α -spodumene/CaO using the HSC Chemistry 5.11 software. This part of the work is very important, because it allows determining the viability of the reaction for the proposed system.

The effect of temperature on the reaction to extract lithium is presented in Figure 3 indicating that the reaction is thermodynamically favorable, throughout the proposed temperature range (25-1,000 °C), for a mineral:CaO molar ratio of 1:2. According the model of the HSC software, the reaction products are calcium silicate (Ca_2SiO_4) and lithium aluminate (LiAlO_2). Based on these results, we propose the following roasting reaction:

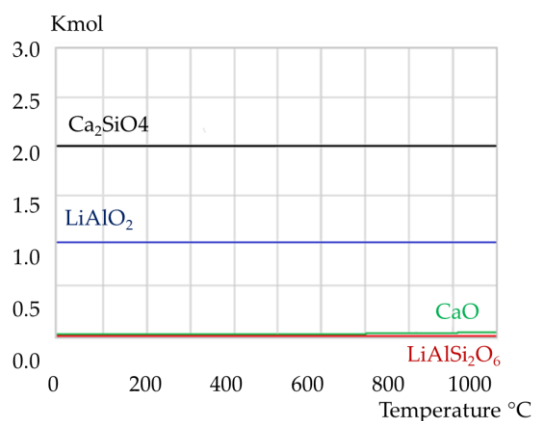
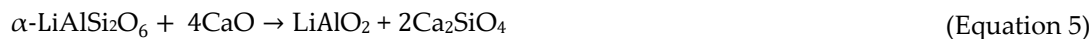


Figure 3 HSC model for the α -spodumene ($\text{LiAlSi}_2\text{O}_6$): CaO mixture

Standard roasting and leaching test

Figure 4A shows the lithium extraction percentages for reactions with different spodumene:limestone mass ratios and different leaching times (30 and 240 min), for a fixed roasting time of 30 min. It can be noted that at the 1:1 and 1:2 ratios, there was basically no ion exchange reaction, evidenced by the low lithium extraction, with values of 2 and 13 %, respectively. For the mass ratio of 1:3, the extraction was slightly better, reaching levels in the range of 30 %, but still considered low. The most promising results were obtained at the highest ratio (1:5), with lithium extraction of 64 % after leaching for 4 hours.

Figure 4B depicts the lithium extraction values at different spodumene:limestone ratios and different extraction times (30 and 240 min), for a fixed reaction time of 120 min. It can be noted that the lithium extraction efficiency was low compared to the extractions performed with reaction time of 30 min (Figure 4A), probably due to the sintering or vitrification of the resulting product during the roasting, hampering the extraction of the lithium contained in the clinker.

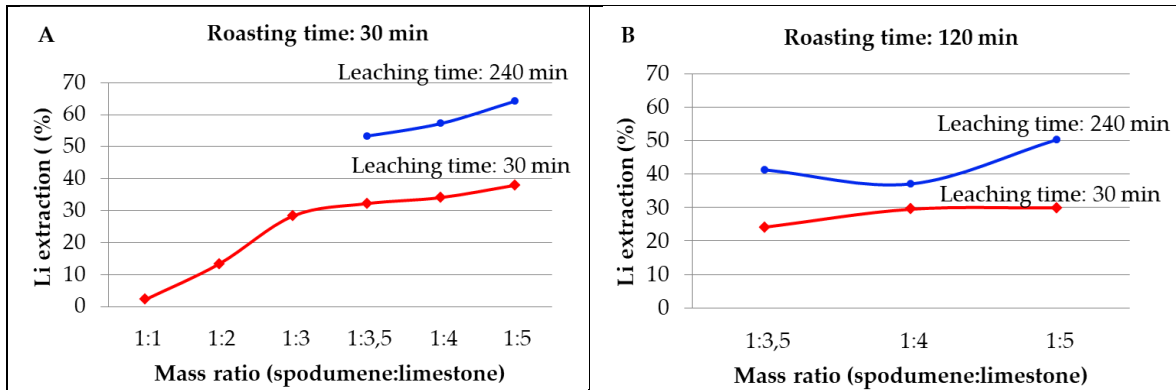


Figure 4 Extraction of lithium at different spodumene:limestone mass ratios and roasting (30, 120 min)

The low extraction of lithium from the mixtures prepared at the 1:1 and 1:2 (spodumene:limestone) ratios can be explained by a stoichiometric imbalance, i.e., the lack of CaO for the final reaction step, which occurs during the leaching process, necessary to transform lithium aluminate into lithium hydroxide and calcium aluminate, as described in Equation 4.

Roasting and leaching test with mechanical activation

Figure 6 shows the particle size distribution and specific surface area (S) of the mixtures used in the standard and mechanical activation tests. There was an increase of 46 % in the specific surface area of the mixture produced (spodumene and lime) in the test with mechanical activation in relation to the mixture of the standard test, corroborated by a reduction of the average particle diameter (d_{50}), caused by the insertion of the grinding step.

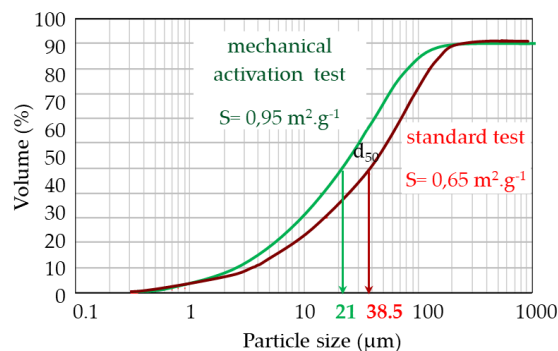


Figure 6 Particle size and specific surface area of the mixture used in the standard tests and those with mechanical activation

The lithium extraction obtained in the test with mechanical activation, spodumene:lime mass ratio of 1:2 and other conditions according to the standard test (roasting = 30 min; leaching = 240 min) was 84 %. This increase of extraction in relation to the standard test corroborates the results reported by Kotsupalo et al. (2010), who observed that mechanical activation of α -spodumene in planetary mills altered the structure of the mineral and caused cleavage of the Li-O and Al-O bonds, favoring its extraction.

CONCLUSION

The results of the standard roasting and leaching tests of spodumene with limestone (Figure 4) indicated that the best spodumene:limestone mass ratio is 1:5, which enabled lithium recovery of around 64 %. These tests were conducted using a discontinuous and static muffle furnace.

The use of lime instead of limestone substantially reduced the mineral:reagent ratio (1:5 \rightarrow 1:2), allowing working with larger mineral quantities, meaning increased productive scale.

The prolonged exposure of the mixture to heat during the roasting process can lead to the formation of a sintered product, from which it is hard to extract lithium.

The mechanical activation of the α -spodumene/lime mixture and its subsequent briquetting enhanced the solid-solid contact and the overall recovery of lithium to a level near 84 %.

The cost of production (OPEX) by the alkaline process is around 20 % higher than the acid one. In the other hand, capital (CAPEX) and environmental costs must be considered in the acid process, due to emission of sulfur gases and, in the case of Brazil, the dependence of imports of soda ash and sulfur, inputs not produced domestically.

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