Efficient extraction of lithium from β-spodumene by direct roasting with NaF and leaching

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ABSTRACT

This research describes the study of a new process for the extraction of Li from β-spodumene by direct roasting with NaF and leaching. Various parameters including roasting temperature, β-spodumene/NaF molar ratio and reaction time were studied. The thermal behavior of the mixture β-spodumene/NaF was studied by simultaneous thermogravimetry and differential thermal analysis. The results indicate that the sample begins to react with NaF at around 540 °C. The optimal conditions for lithium extraction were found to be 600 °C, 1:2 β-spodumene:NaF molar ratio and 60 min of roasting. In these conditions, a lithium extraction degree of 90%, approximately, is reached. The products of the roasting reaction of the mineral with NaF are LiF, nepheline and albite, all identified by XRD. The unreacted NaF can be removed by water washing with minimal lithium loss of 0.36%. Finally, LiF was completely leached with a 10% v/v H_2SO_4 solution, remaining in the solid the compounds albite and nepheline.

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1. Introduction

Lithium is considered a strategic metal with a variety of applications in next generation technologies, such as energy storage, electric mobility and cordless devices. Lithium compounds, however, are also used in a far wider spectrum, e.g. glass, enamel and ceramic industry, lubricating greases, pharmaceutical products or aluminum production (Fröhlich et al., 2017; Martin et al., 2017). In particular, in the last ten years the global lithium industry has experienced a considerable change, doubling its demand (Fröhlich et al., 2017). Lithium is found in many minerals due to its high chemical reactivity. However, there are a few minerals that are useful for the production of lithium compounds. The most important lithium mineral is spodumene (Choubey et al., 2017; Garrett, 2004; Habashi, 1997).

In Argentina, spodumene main deposits occurs in Salta, San Luis and Córdoba provinces. The mineral is associated with quartz, feldspar, albite, muscovite, biotite and sometimes beryl and/or amblygonite (Galliski, 1994). Spodumene is found naturally in its α-phase, with a monoclinic structure of the pyroxene type. This structure is resistant to the attack of chemical agents and may be transformed to its β-phase through calcination at 1050 °C, being this phase much more reactive and less resistant to ordinary chemical agents. The mineral has the formula $LiAlSi_2O_6$, containing up to 8.03% Li_2O (w/w). For this reason, it is considered, together with salar brines, one of the best resources for lithium extraction.

The industrial processes for the extraction of lithium from spodumene are acid and alkaline digestion. In both processes, the ore is calcined at 1050 °C to obtain the β-phase. The products obtained

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through these methods are lithium carbonate and lithium hydroxide, respectively (Choubey et al., 2017; Garrett, 2004; Habashi, 1997).

In recent years, some novel methods have been studied as alternative to industrial processes. In this sense, it was studied the dissolution of β-spodumene with Na_2CO_3 or Na_2SO_4 in an autoclave at temperatures around 250 °C, reaching a lithium extraction of 93% (Chen et al., 2011; Kuang et al., 2018). Other used routes are the pyrometallurgical chlorination of β-spodumene with $Cl_{2(g)}$ or its calcination with $CaCl_{2(s)}$ or a mixture of $NaCl–Na_2CO_3$, at temperatures between 900 and 1100 °C with a mineral conversion degree of 90.2% (Barbosa et al., 2015; dos Santos et al., 2019). There have also been investigated several Li extraction routes using different fluorinating agents. For example, Rosales et al. studied the leaching process of β-spodumene in hydrofluoric acid medium at room temperatures and the recovery of lithium fluoride from lepidolite by leaching with diluted HF at 123 °C (Rosales et al., 2017, 2016; Rosales et al., 2014, 2013). Guo et al. studied the extraction of Li from spodumene and lepidolite by dissolution with a HF/H_2SO_4 mixture reaching high extractions at temperatures close to 125 °C (Guo et al., 2019, 2017). Demyanova et al. investigated the direct fluorination of lepidolite with $F_{2(g)}$ or cold rf-plasma, causing significant changes in the aluminosilicate surface (Demyanova and Tressaud, 2009).

There have been published relevant findings about the extraction of lithium from lepidolite with a combination of both pyro and hydrometallurgical routes. In such processes, lepidolite is firstly calcined together with Na_2SO_4 or K_2SO_4, $FeSO_4$ or FeS at 850 °C. Then, the obtained mixture is leached with water (Hien-Dinh et al., 2015; Kuang et al., 2015; Vieceli et al., 2018; Yan et al., 2012a, b; Yan et al., 2012c).

In this work, we have investigated the effect of the operating parameters on the lithium extraction reaction from β-spodumene by direct roasting with NaF and leaching. In addition, complementary studies were carried out using thermodynamic modeling of the system with HSC software, thermogravimetric and differential thermal analysis and X-ray diffraction with the purpose of finding the pathways through which the reaction occurs. The results of this work could lay the groundwork for the development of a simple and effective way to extract lithium from different mineral resources.

2. Experimental

2.1. Equipment

The roasting tests were performed in a muffle furnace with temperature control system. The samples were held in a platinum crucible in order to correctly perform the mass balance of the process. The temperature was measured with a chromel–alumel thermocouple to within ±5 °C.

The leaching tests were carried out in a closed 500 mL container made of PVC and a control unit equipped with temperature control and magnetic stirring systems.

The determination of the phases present in the solids was performed by X-ray diffraction (XRD) in a Rigaku D-Max III C diffractometer, operated at 35 kV and 30 mA. The Kα radiation of Cu and the filter of Ni, $\lambda = 0.15418$ nm, were used. Morphological analysis was done by scanning electron microscopy (SEM) in a microscope LEO 1450 VP that was equipped with an X-ray dispersive spectrometer EDAX, Genesis 2000, used to determine, by energy dispersive spectrometry (EDS), the semi-quantitative composition of the mineral and final products obtained. The chemical composition of the ore was obtained by absorption spectroscopy (AAS) using a Varian SpectrAA 55 spectrometer with a hollow-cathode lamp, by the method of Brumbaugh and Fanus (Brumbaugh and Fanus, 1954) and X-ray fluorescence (XRF) on a Philips PW 1400 equipment. The thermal behavior of the β-spodumene/NaF mixture was studied by simultaneous thermogravimetry and differential thermal analysis (TG/DTA) using a Shimadzu DTG-60 analyzer.
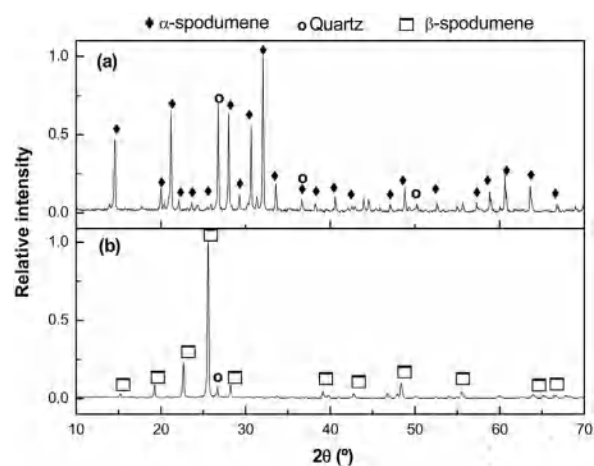
Fig. 1 – Diffractograms of the minerals in its α (a) and β (b) phases.

2.2. Material and methods

The ore sample was extracted from the mine "Las Cuevas", located in the department of San Martín, San Luis, Argentina. The α-spodumene concentrate was calcined from room temperature to 1050 °C in an electric furnace with a heating rate of 10 °C/min during 30 min, in order to transform it into its β-phase, which is more susceptible to the extraction of Li (Habashi, 1997).

The chemical composition of the mineral sample was SiO_2 68.1%, Al_2O_3 18.6%, Li_2O 7.03%, Fe_2O_3 3.1%, Na_2O 1.8% and others 1.37% (Rosales et al., 2016, 2014; Rosales et al., 2013). The average particle size of the sample was 45 μm.

The XRD pattern of the mineral in its α (a) and β (b) phase is shown in Fig. 1.

In Fig. 1(a) XRD patterns show that the sample is mainly composed of α-spodumene (PDF 00-033-0786), with the presence of quartz (PDF 00-033-1161) as gangue. Diffractogram in Fig. 1(b) shows the appearance of β-spodumene (PDF 00-035-0797) after thermal treatment of the ore. The α-phase is not detected, indicating that the transformation of α-phase to β-phase was complete. Besides quartz is also detected.

Fig. 2 shows the results of the SEM characterization of the mineral in its α and β-phases.

In Fig. 2(a) it is presented the micrograph corresponding to the mineral in its α phase. It can be observed that the particles of the mineral without thermal treatment exhibit an irregular shape and a prismatic structure with a flattened elongated habit, which agrees with the reported in the bibliography (Rosales et al., 2016). From micrographs in Fig. 2(b) and (c), it can be observed that β-spodumene particles have irregular morphologies. This is because when α-spodumene transforms into β-spodumene by the effect of temperature, an augment in the volume of the crystalline structure occurs. The increasing stress due to the volumetric expansion leads to the breakdown of the original particles, obtaining smaller ones with irregular shapes (Salakjani et al., 2016).

β-spodumene was mixed with sodium fluoride of 99% purity (Alkemint) to obtain $β-LiAlSi_2O_6$/NaF mixtures with different molar ratios. Each mixture was dried at 100 °C in a drying oven until reaching constant mass. The mixture was characterized by XRD to be used as a comparison target for the calcination studies.
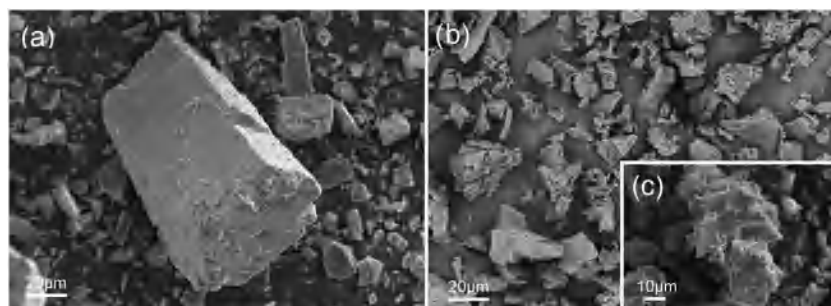
Fig. 2 – SEM micrograph of the mineral in its α (a) and β phase (b and c).

2.3. Procedure

2.3.1. Roasting assays

The sample was mixed with sodium fluoride at different molar ratios of β-spodumene:NaF (1:1 to 1:2.5, respectively). The sample was thoroughly mixed in a mortar for five minutes before being poured into platinum crucibles and then placed into the preheated muffle furnace for roasting. Several durations ranging from 0.5 to 4 h were selected for roasting assays. The temperature study was performed by TG-DTA analysis. A temperature range of 25–900 °C was set for the tests. After roasting, the obtained samples were manually ground in a mortar for five minutes.

2.3.2. Separation assays

The separation of the products from the calcination was carried out in two stages. In *stage* 1, the "calcine" was subjected to washing with distilled water to remove unreacted NaF. Then, in *stage* 2, the "washed-calcine" was leached with a solution of H_2SO_4 to determine the Li extracted in solution, and separate it from the insoluble subproducts.

The experimental conditions set for each stage were the following:

- *Stage* 1: solid/liquid ratio, 194.4 g/L; temperature, 25 °C; stirring speed, 330 rpm and leaching time, 30 min.
- *Stage* 2: solid/liquid ratio, 46.7 g/L; temperature, 25 °C; H_2SO_4 concentration, 10% v/v; stirring speed, 330 rpm and leaching time, 30 min.

The solid/liquid ratio for each stage was calculated taking into account the solubilities of NaF and LiF, 41.3 and LiF 1.34 g/L, respectively (Lide, 2016; Perry et al., 1997; Rankin, 2009).

Li and Na were determined in the liquors by AAS, and solids were dried and characterized by XRD.

The lithium extraction of the β-spodumene/NaF reaction was quantified from the amount of Li in the sulfuric acid "leach liquor" obtained in *stage* 2, by the following equation:

$$X\% = \frac{Li_E}{Li_m} 100\% \tag{1}$$

where:

$X\%$: lithium extracted.

Li_E: amount of lithium in the sulfuric acid leaching, determined by AAS.

Li_m: amount of lithium in the mineral.

To complete the mass balances, Li and Na were measured in the water washing liquor (*stage* 1) to quantify the Li loss and the unreacted NaF in this stage, respectively. Then the

liquor obtained in *stage* 1, was evaporated in a closed vessel to recover the unreacted NaF. The obtained solid was dried, weighed and characterized.

The recovery percentage of unreacted NaF was calculated using the following Eq. (2):

$$X\% = \frac{NaF_{(W)}}{NaF_{(U)}} 100\% \tag{2}$$

where:$X\%$: recovery percentage of unreacted NaF.$NaF_{(W)}$: amount of NaF obtained by precipitation.$NaF_{(U)}$: amount of unreacted NaF dissolved in the washing liquor, obtained by AAS.
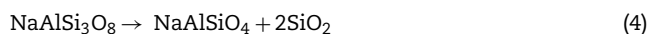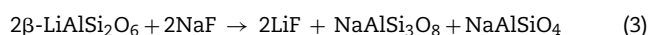
The experimental study of this work was performed by univariate analysis. In order to evaluate the experimental error each test was replicated three times. The average lithium extraction and standard deviation were calculated for each studied parameter.

3. Results and discussion

3.1. Thermodynamic analysis of the reaction temperature

The thermodynamic calculations of the amounts of products at equilibrium for the reaction of β-spodumene (β-LiAlSi$_2$O$_6$) with NaF in a molar ratio 1:1, respectively, were performed within the temperature range from 25 to 1000 °C. The equilibrium composition of the Si–Al–Li–O–Na–F system as a function of temperature can be calculated using HSC thermodynamic database software, with the system free energy minimization method (HSC, 2002). The amounts of products at equilibrium as a function of temperature are presented in Fig. 3.

HSC modeling indicates that roasting a β-spodumene/NaF mixture should lead to the formation of NaAlSiO$_4$ (nepheline), NaAlSi$_3$O$_8$ (albite) and LiF (lithium fluoride). The following reactions are predicted to take place during the roasting of the mixture:

$$2\beta\text{-LiAlSi}_2O_6 + 2NaF \rightarrow 2LiF + NaAlSi_3O_8 + NaAlSiO_4 \tag{3}$$

$$NaAlSi_3O_8 \rightarrow NaAlSiO_4 + 2SiO_2 \tag{4}$$

HSC software indicates that LiF is the main lithium compound formed from the reaction of β-spodumene with NaF. Furthermore, the diagram indicates that reaction (3) is favored at room temperature and is slightly reversible at high temperature.
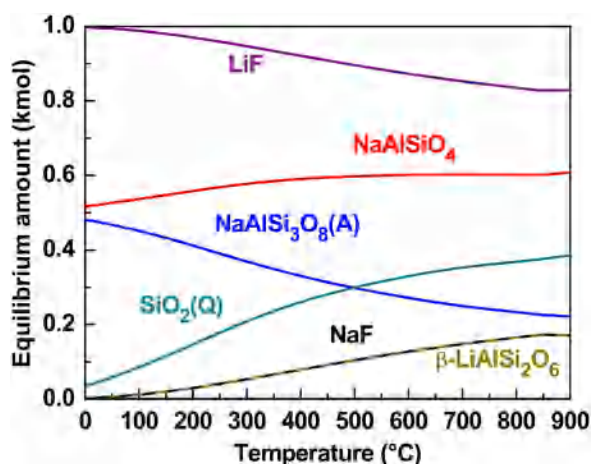
Fig. 3 – HSC modeling of the amounts of products at equilibrium as a function of the temperature for a mixture of β-spodumene and NaF.

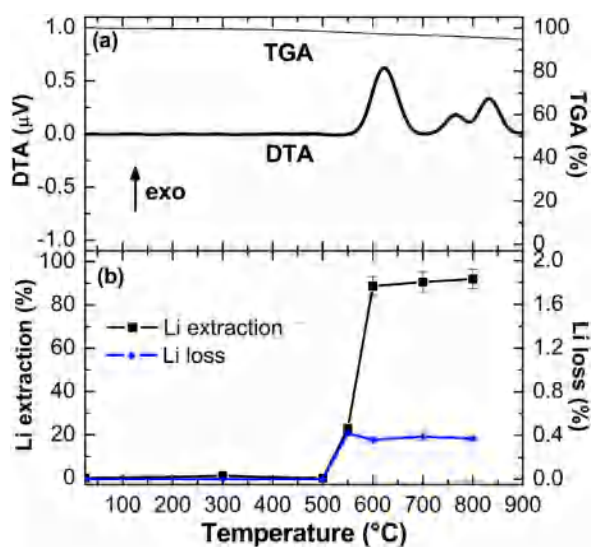
Fig. 4 – (a) TG-DTA curves of the β-spodumene/NaF (1:2) mixture and (b) effect of roasting temperature on lithium extraction.

Fig. 5 – Comparative XRD for mixtures of β-spodumene/NaF (1:2 mol:mol) without roasting (a) and with roasting at 600 (b), 700 (c) and 800 °C (d).

3.2. Roasting assays

3.2.1. Effect of roasting temperature

According to the thermodynamic estimations obtained by HSC software, it can be inferred that the extraction of Li as LiF from the roasting of a β-spodumene:NaF mixture is thermodynamically favored. In order to investigate the effect of roasting temperature, a series of roasting experiments were performed from room temperature to 900 °C in N_2 atmosphere with a heating rate of 5 °C/min using TG-DTA. In addition, lithium extraction was determined for a temperature range of 25–800 °C, under the following experimental conditions: reaction time, 120 min and β-spodumene:NaF molar ratio 1:2, respectively.

The results are shown in Fig. 4(a) and (b), respectively.

In Fig. 4(a), one exothermic peak at about 620 °C is observed in the DTA curve. This peak starts at 540 °C and would be associated to the ionic exchange reaction of the mineral with NaF, as proposed in Eq. (3) and the enthalpy of the reaction was $\Delta H° = −13.186$ kcal/mol (HSC, 2002).

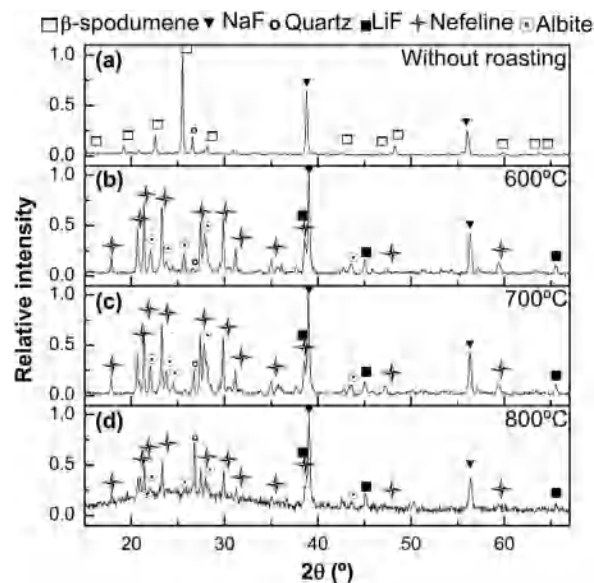Two exothermic peaks are observed at about 770 and 830 °C, respectively, which match with the melting point of LiF in the liquidus curve for the system LiF–NaF (Holm et al., 1965).

Fig. 4(b) indicates that, working at temperatures below 500 °C, no extractions of Li are obtained (black line). This was in accordance with the results presented in the DTA curve (Fig. 4(a)). Then, it is observed that the reaction temperature strongly affects the extraction of Li from β-spodumene, obtaining the highest extraction values at 600 °C (88.2%). Statistical analysis of the results indicates that there is an average standard deviation of 1.21%. The blue line indicates the loss of lithium in the *stage* 1, with an average lithium loss of 0.4%.

In Fig. 5 it is presented a comparative analysis of the XRD of mixtures of β-spodumene/NaF (1:2 mol:mol) without roasting and with roasting at 600, 700 and 800 °C during 120 min.

In Fig. 5(a) the diffraction lines corresponding to unreacted β-spodumene (PDF 00-035-0797), NaF (PDF 01-073-1922) and quartz (PDF 01-078-2315) are observed. In the mixtures roasted at 600, 700 and 800 °C (Fig. 5(b)–(d), respectively) the total disappearance of the β-spodumene phase and the formation of LiF (PDF 01-078-1217), $NaAlSi_3O_8$ (PDF 01-076-1819) and $NaAlSiO_4$ (PDF 01-079-0994) can be observed. These data confirm that the mechanism proposed for the system through thermodynamic study (Eqs. (3) and (4)) is the most likely.

3.2.2. Effect of β-spodumene:NaF molar ratio

Fig. 6 presents the HSC modeling of the amounts of products at equilibrium as a function of NaF amount at 600 °C. It can be seen that the best extraction value of Li is achieved with 2 kmol of NaF for 1 kmol of β-spodumene. These values indicate that the roasting reaction does not follow a 1:1 (β-spodumene:NaF) stoichiometric ratio.

Based on these results, the experiments were conducted in the following conditions: β-spodumene:NaF molar ratio, between 1:1 and 1:2.5; temperature 600 °C and roasting time 120 min. The obtained results are illustrated in Fig. 7.

Fig. 7 illustrates that the increase in the amount of NaF has a marked effect on the roasting process, which fits well with the results obtained from HSC software. The best extraction value (90%) was obtained for β-spodumene:NaF molar ratios
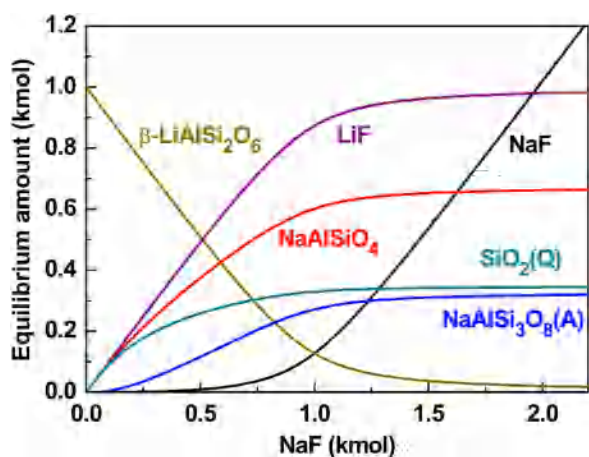
Fig. 6 – HSC modeling of the amounts of products at equilibrium as a function of NaF amount at 600 °C for a mixture β-spodumene and NaF.
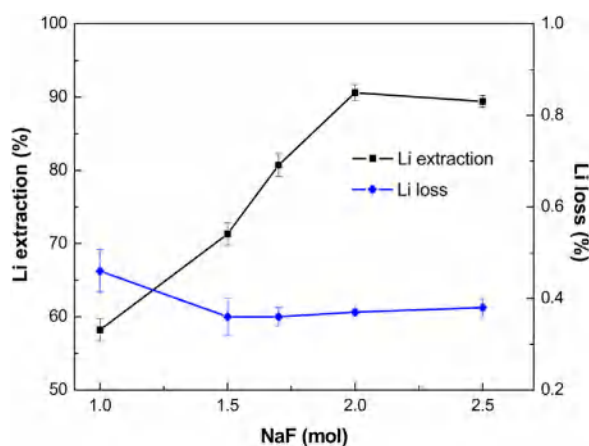

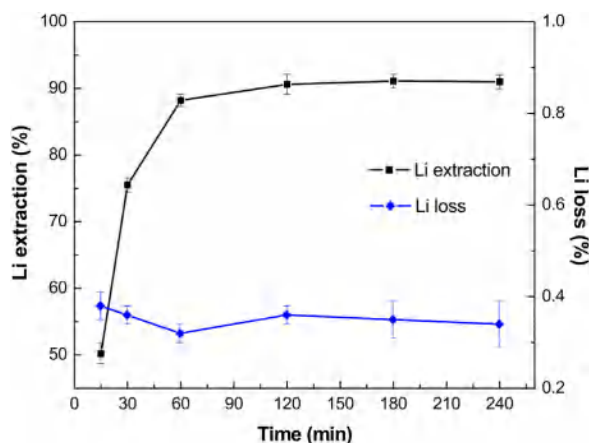**Fig. 7 – Effect of β-spodumene:NaF molar ratio on lithium extraction.**

Fig. 8 – Effect of reaction time on lithium extraction.

of 1:2 and 1:2.5. Statistical analysis of the results indicates that there is an average standard deviation of 1.29%. The average lithium loss was around of 0.35%.

3.2.3. Effect of roasting time

To study the effect of reaction time on lithium extraction of β-spodumene, the experiments were performed at 600 °C of temperature and 1:2 β-spodumene:NaF molar ratio, respectively.
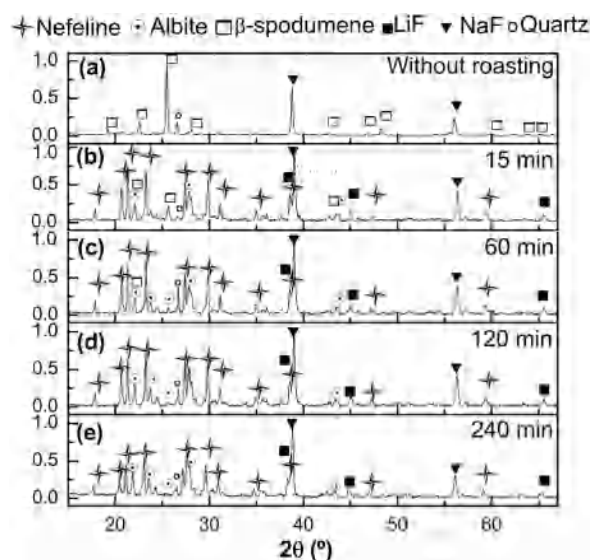

Fig. 9 – Diffractograms of the samples without roasting (a) and roasted at 15 (b), 60 (c), 120 (d) and 240 min (e).

The results are plotted in Fig. 8, which shows that roasting time has a remarkable effect on lithium extraction. As time increases from 15 to 60 min, lithium extraction efficiency raises from 52 to 88% and as reaction time increases up to 240 min, it remains almost constant. Statistical analysis of the results indicates that there is an average standard deviation of 1.17%. The average lithium loss was 0.38%.

Fig. 9 shows XRD patterns of the samples without roasting and calcined at 600 °C at different reaction times (between 15 and 240 min).

In Fig. 9(b) for 15 min of roasting, a pronounced decrease in the relative intensities of β-spodumene can be seen; and the formation of LiF, nepheline and albite. After 60 min, Fig. 9(c), β-spodumene phase almost totally disappears. By increasing the reaction time (Fig. 9(d) and (e), respectively), the diffraction lines of LiF, nepheline and albite become sharper, which would indicate that their crystallinity increases. These results coincide with the extraction experiments presented in Fig. 8.

### 3.2.4. Characterization SEM-EDS of the product of calcination

Fig. 10 shows the micrographs of the particles that comprise the reacted sample at 600 °C and 240 min. In Table 1 the chemical composition of the particles marked in Fig. 10(b) is presented.

In Fig. 10, the presence of two types of particles, well differentiated by their morphology, can be observed (particles "L" and "A"). The β-spodumene particles morphology observed in Fig. 2(b and c) does not coincide with the morphologies of the particles analyzed in Fig. 10. The chemical composition obtained for the particles "L" (Fig. 10(b) and Table 1) indicates that this particle is mainly composed by fluorine. However, since Li cannot be detected by EPMA analysis, these particles must correspond to the LiF compound, observed in the diffractograms of the sample calcined at 600 °C and later confirmed by AAS. The presence of low amounts of Na could be attributed to part of NaF remaining unreacted, or to the fact that the equipment detected the Na of particles "A".

The chemical composition for the particle "A" is in good agreement with albite and nepheline theoretical compositions (Table 1).

Table 1 – Chemical compositions of the marked particles in the micrograph (Fig. 10(b)), in atomic %.

Element	Chemical composition							
	Theoretical		Measure (EDS)					
	Albite	Nepheline	L1	L2	L3	A1	A2	A3
O	48	45	–	–	–	45.01	46.05	28.93
Si	32	20	–	–	–	32.6	34.23	38.95
Al	11	19	–	–	–	12.82	5.3	15.01
Na	9	16	8	5	–	4.8	8.86	11.87
F	–	–	92	95	100	3.07	5.56	3.18
Fe	–	–	–	–	–	1.63	–	2.06
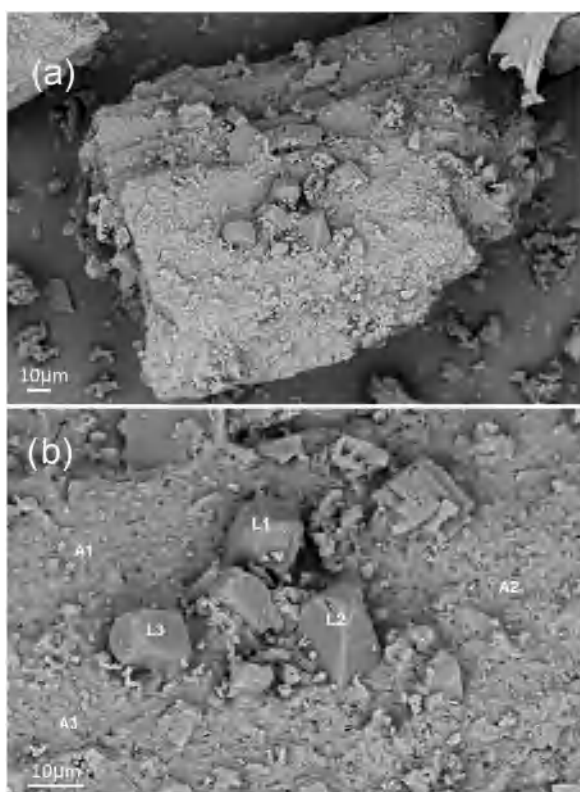
**Fig. 10 – SEM micrograph of the calcine obtained (a) 1000×
and (b) 2500×.**

The presence of the LiF crystals in the surface of the albite
and nepheline structures would indicate that the reaction of
the mineral and NaF occurs from the interaction surface by an
ionic exchange between the Li of the spodumene and the Na of
the NaF. This behavior usually occurs in solid/solid reactions.

3.3. Separation assays

3.3.1. Recovery of unreacted NaF
Due to the difference in solubility and the effect of the com-
mon ion between LiF and NaF in water (1.34 and 41.3 g/L at
25 °C, respectively), it is possible to recover the remaining NaF
from the products of the reaction of β-spodumene with NaF,
by washing with water, without significant losses of Li (Lide,
2016; Perry et al., 1997; Rankin, 2009).

The theoretical calculation of the LiF solution, using the
LiF Kps values (1.84×10^{-3}) and the estimated unreacted NaF
concentration, indicated losses of less than 0.36% of Li, which
coincides with the results presented in Figs. 4(b), 7 and 8.

The washing assays indicated that $98.0 \pm 0.3\%$ of the unre-
acted NaF is dissolved with a negligible Li loss, 0.37% in average
(Figs. 4(b), 7 and 8).
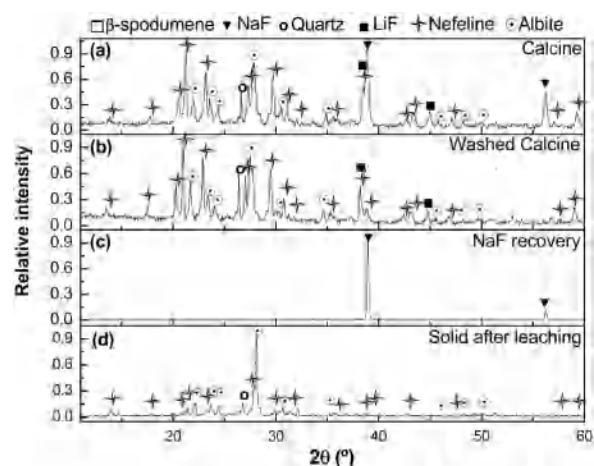
**Fig. 11 – Comparative XRD (a) calcine obtained in optimal
conditions, (b) washed-calcine, (c) NaF recovery and (d)
solid after leaching.**

The obtained water washing liquor was evaporated to
dryness, and then weighed and characterized. The obtained
results indicated a $96 \pm 2\%$ recovery of the unreacted NaF.

Fig. 11 shows the diffractograms of: (a), the solid
obtained after calcination at 600 °C during 60 min with a β-
spodumene:NaF molar ratio of 1:2 (optimal conditions); (b), the
solid obtained after the water washing of the calcine; (c), the
unreacted NaF obtained after the evaporation of the washing
liquor and (d), the solid obtained after leaching with H_2SO_4.

Fig. 11(a) and (b) show that there are no significant changes
in the diffraction lines of the LiF, $NaAlSi_3O_8$ and $NaAlSiO_4$
phases, while those corresponding to NaF disappear com-
pletely. This indicates that all the NaF was dissolved under
these conditions. Fig. 11(c) shows the diffractogram of the solid
obtained by drying the washing liquor, where only the diffrac-
tion pattern corresponding to NaF (01-073-1922) is observed
with no other crystalline impurities. Finally, in Fig. 11(d) the
characteristic diffraction lines of $NaAlSi_3O_8$, $NaAlSiO_4$ and
$SiO_2(Q)$ are observed, while the diffraction lines of LiF are not
observed, indicating that the complete dissolution of this com-
pound was achieved.

4. Conclusions

The thermodynamic analysis shows that the roasting reac-
tion of β-spodumene with NaF should lead to the formation of
$NaAlSiO_4$ (nepheline), $NaAlSi_3O_8$ (albite) and LiF (lithium flu-
oride). The DTA analysis indicates that the reaction between
β-spodumene and NaF, begins at 540 °C, with an enthalpy reac-
tion of $\Delta H° = -13.186$ kcal/mol (HSC).

Experimental results indicate that Li extraction is favored with increasing roasting temperature, β-spodumene:NaF molar ratio and reaction time. The characterization of the reaction products shows that LiF, nepheline and albite were produced. The optimal conditions for the roasting process are 600 °C, 1:2 β-spodumene:NaF molar ratio and 60 min.

LiF could be completely leached with a 10% v/v H_2SO_4 solution, remaining in the solid the compounds albite and nepheline. In these conditions, a lithium extraction degree of 90%, approximately, is reached. In addition, the unreacted NaF can be removed by water washing without considerable lithium loss (0.36%).

Therefore, this process could be used as an alternative way for the extraction of lithium from the mineral spodumene, obtaining as valuable subproducts the compounds albite and nepheline. Furthermore, given that the first stage of the proposed process is the calcination of β-spodumene with NaF, this could be done continuously during cooling of the ore after it being transformed from α-phase to β-phase in the acid industrial process.

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