Novel process for the extraction of lithium from β-spodumene by leaching with HF

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ABSTRACT

In this study lithium was extracted from β-spodumene with hydrofluoric acid leaching. The operating parameters studied were: solid–liquid ratio, stirring speed, particle size, temperature, reaction time and HF concentration. Reagents and products were characterized by X-ray diffraction (XRD), X-ray fluorescence (XRF), atomic absorption spectroscopy (AAS), scanning electronic microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS). The lithium extraction efficiency of 90% could be reached with solid–liquid ratio, 1.82% (w/v); temperature, 75 °C; HF concentration, 7% (v/v); stirring speed, 330 rpm and reaction time, 20 min. Al and Si can be precipitated as Na3AlF6 and Na2SiF6 with a recovery of 92%. Lithium carbonate was separated from leach liquor by carbonatation and crystallization during water evaporation, with recovery values of 90%, approximately.

1. Introduction

Lithium is a relatively rare metal, but it 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, which generally is accompanied by quartz, feldspar and mica (Garret, 2004; Habashi, 1980).

Important sources for the obtention of lithium are salt flats and salt lakes. The interest in them has considerably increased in the last two decades. In these sources, lithium is found mainly in a chloride form (Garret, 2004).

In Argentina, main lithium deposits are divided into those from brine deposits and those from spodumene. The salar with the greatest content of lithium is found between Salta and Catamarca provinces. This one is known as "Salar del Hombre Muerto"; it contains a total amount of 800,000 tons of lithium (Garret, 2004). Spodumene main deposits are found in Salta, San Luis and Cordoba provinces. The mineral is associated with quartz, feldspar, plagioclase (oligoclase and albite), muscovite, biotite and sometimes beryl and amblygonite (Galliski, 1994a, 1994b).

Spodumene occurs naturally in α phase, with a monoclinic structure of the pyroxene type. This structure is resistant to the attack of chemical agents, either gaseous or liquid. Spodumene transforms into its β phase through calcination at 1100 °C; this phase is much more reactive and less resistant to ordinary chemical agents. Spodumene has the formula LiAlSi₂O₆, containing up to 8.03% Li₂O (w/w). For this reason it is considered, together with salar brines, one of the best resources for the extraction of lithium (Habashi, 1980).

Lithium is considered a strategic metal, whose use has significantly expanded in the last years. Lithium compounds are used in the preparation of lubricants, in the manufacture of glass and special alloys, and also in the pharmaceutical industry, in the production of drugs used in psychiatry. Lithium and its compounds have recently found use in energy storage devices such as rechargeable lithium-ion batteries (Brandt and Haus, 2010). In this context, it is essential to develop new techniques for the extraction lithium from both minerals and industrial wastes.

The most common industrial processes for the extraction of lithium from spodumene are acid and alkaline digestion, and the ionic exchange method. The products obtained through this methods are lithium carbonate, lithium hydroxide and lithium chloride, respectively. Acid digestion is carried out with concentrated sulphuric acid at temperatures higher than 250 °C, whereas alkaline digestion is carried out with concentrated Ca(OH)₂ at 1040 °C. In the process of ionic exchange, β-spodumene is heated with organic salts of sodium and potassium at temperatures between 825 and 875 °C, depending on the type of salt used (Garret, 2004; Habashi, 1980).

There have been published relevant findings about the dissolution of β-spodumene in an autoclave at temperatures around 250 °C with salts such as CaCO₃, CaSO₄, Na₂CO₃, Na₂SO₄ and NaCl. Others authors suggest processes that combine both pyro and hydrometallurgical routes (Chen et al., 2011; Yan et al., 2012a, 2012b, 2012c). In such processes, β-spodumene is first calcined together with one of the salts mentioned above; then, the mixture obtained is leached with water.

Kumar et al. (2010) reported that the dissolution of aluminum silicates or minerals that contain Al and Si as gangue with HF is

accompanied by the formation of hexafluoroaluminate acid (H_3AlF_6) and hexafluorosilicate acid (H_2SiF_6). The formation of these acids is fundamental to explain the behavior of the system HF–mineral and therefore to achieve precipitation of the dissolved metals. Moreover, these authors propose the addition of Na_2CO_3 in order to increase the pH of the solution, and hence, precipitate the compounds cryolite (Na_3AlF_6) and sodium hexafluorosilicate (Na_2SiF_6). Both compounds are some of the most common alkali-metal fluorides and are widely used in the industry (Jeong and Huh, 2010; Kumar et al., 2006, 2010).

The β-spodumene dissolution with HF can be represented by the following reaction (Rodriguez et al., 2010; Rosales et al., 2013):

$$LiAlSi_2O_{6(s)} + 19HF_{(aq)} \rightarrow LiF_{(aq)} + H_3AlF_{6(aq)} + 2H_2SiF_{6(aq)} + 6H_2O \quad (1)$$
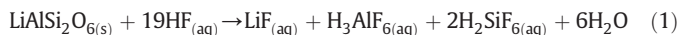
The objective of this study was to establish the optimal operational conditions for a new extraction process of lithium from β-spodumene with HF, in a closed vessel. Furthermore, a novel process for the recovery of Li_2CO_3 from the leach liquors is proposed obtaining Na_2SiF_6 and Na_3AlF_6 as subproducts, both of which having industrial uses.

2. Experimental

2.1. Equipment and materials

The experimental tests were performed in a closed vessel of 500 ml built in PVC and equipped with magnetic stirring and temperature control systems.

The leaching agent was HF (40% w/w), with analytical grade. The reagents used to the recovery essays were NaOH and $CO_{2(g)}$ with analytical and technical grades, respectively.

The mineral used was α-spodumene, extracted from the mine "Las Cuevas", located in the department of San Martín, San Luis, Argentina. The α-phase was calcined at 1100 °C to obtain the β-phase (Habashi, 1980). Characterization of the ore was performed by X-ray fluorescence (XRF) on a Philips PW 1400 equipment and by X-ray diffraction (XRD) in a Rigaku D-Max III C diffractometer, operated at 35 kV and 30 mA. The K_α radiation of Cu and the filter of Ni, $\lambda = 0.15418$ nm were used. Determination of lithium and sodium content in the ore was performed by atomic absorption spectroscopy (AAS) using a Varian SpectrAA 55 spectrometer with a hollow-cathode lamp. Morphological analysis was done by SEM in a microscope LEO 1450 VP which was equipped with an X-ray dispersive spectrometer EDAX, Genesis 2000, used to determine semiquantitative composition of the compounds obtained through of the different process stages by EDS.

The bulk composition of the ore is shown in Table 1, as determined by AAS (Li and Na) and XRF (Si, Al, Fe, Ca, Mg, K and Ti).

The results of the characterization by XRD are shown in Fig. 1.

In Fig. 1(a) XRD patterns show that the sample is mainly composed of α-spodumene (JCPDS 33-786), with the presence of albite (ICDD 96-900-1631) and quartz (JCPDS 33-1161) as gangue. Diffractogram of Fig. 1(b) shows the appearance of β-spodumene (JCPDS 35-797). The α-phase is not detected, indicating that the transformation of α-phase
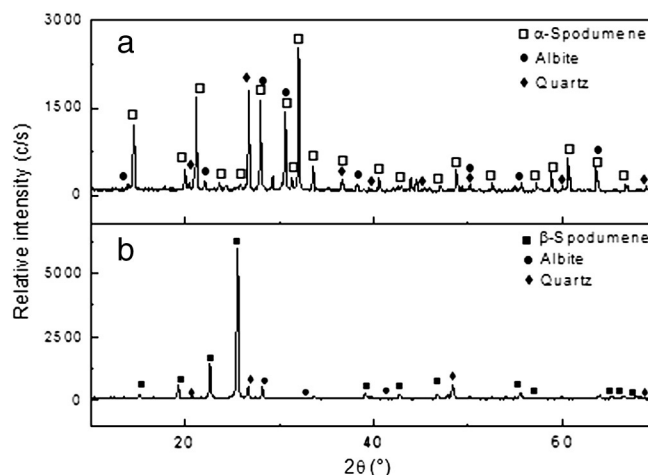
Table 1
The bulk composition of the ore.

Component	% w/w
SiO_2	68.3
Al_2O_3	18.6
Fe_2O_3	3.2
CaO	0.52
MgO	0.3
K_2O	0.14
Na_2O	0.8
Li_2O	7.03
TiO_2	0.11
Others	0.1

Fig. 1. Diffractograms of the mineral: (a) α-spodumene; (b) β-spodumene.

to β-phase was completed. Besides, albite and quartz are detected. The quartz content in the sample (b) (8% (w/w)) was determined by XRD, using the standard addition method, diffraction line 26.7° of SiO_2 as standard, (Rosales et al., 2013).

In Figs. 2 and 3 are shown the results of the characterization of the mineral by SEM.

The results of the studies carried out by SEM and EDS on different particles of the sample, with and without thermal treatment, coincided with those obtained by XRD.

The specific surface of the β-spodumene was 1.41 m²/g, determined by BET, by N_2 adsorption at 77 K in a Micromeritics Gemini V.

2.2. Procedures

2.2.1. Leaching assays

For each test, a mass of the ore and a volume of distilled water were placed into the reactor. The mixture was subsequently heated in a water bath, with stirring until the final work temperature was reached. Once the desired temperature was achieved, an appropriate amount of HF was added to the mixture, so as to obtain different acid concentrations. From that moment, the reaction time was calculated. Once the experiment was finished, the solid was filtered, dried at 75 °C, and then weighed.
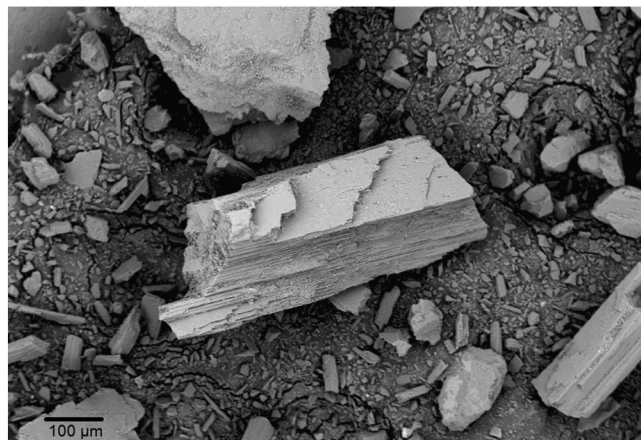

Fig. 2. SEM micrograph of the mineral without thermal treatment (α-spodumene).

Fig. 3. SEM micrograph of the mineral with thermal treatment (β-spodumene).

Fig. 4. Effect of particle size on the lithium extraction efficiency.

Lithium was analyzed by atomic absorption to calculate the extraction percentage in all the experiments by the following equation:

$$\%X = \frac{Li_s}{Li_m}100$$

where: Li_m is the initial amount of Li in the mineral and Li_s is the quantity of Li in the leach liquor.
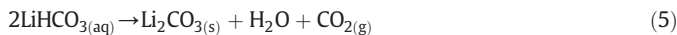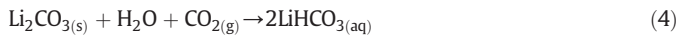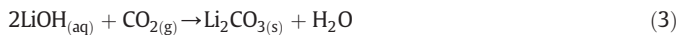
The operational parameters studied were: solid–liquid ratio, stirring speed, particle size, temperature, reaction time and HF concentration.

2.2.2. Recovery assays

The residual Al and Si in the liquor obtained after the leaching of the mineral were removed as the compounds Na_3AlF_6 and Na_2SiF_6, by using NaOH. The reaction proposed for obtaining a mixture of these compounds is the following (Rosales et al., 2013):

$$5NaOH_{(aq)} + H_3AlF_{6(aq)} + H_2SiF_{6(aq)} \rightarrow Na_3AlF_{6(s)} + Na_2SiF_{6(s)} + 5H_2O \quad (2)$$
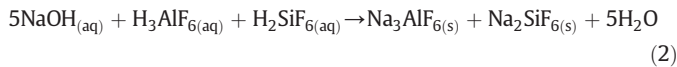
The recovery of Li from the resulting solution after the precipitation of Al and Si can be carried out by any known method. In this case, the carbonation process was used. Lithium was precipitated from alkaline solutions using $CO_{2(g)}$ according to reactions (3), (4) and (5) (Jandová et al., 2010).

$$2LiOH_{(aq)} + CO_{2(g)} \rightarrow Li_2CO_{3(s)} + H_2O \quad (3)$$

$$Li_2CO_{3(s)} + H_2O + CO_{2(g)} \rightarrow 2LiHCO_{3(aq)} \quad (4)$$

$$2LiHCO_{3(aq)} \rightarrow Li_2CO_{3(s)} + H_2O + CO_{2(g)} \quad (5)$$

3. Results and discussion

3.1. Leaching of β-spodumene

3.1.1. Effect of particle size

Fig. 4 shows the effect of particle size on the lithium extraction from the mineral, in range between - 850 and + 45 μm. The remaining variables were kept constant in the following values: temperature, 25 °C; HF concentration, 7% (v/v); solid–liquid ratio, 1.82% (w/v); stirring speed, 330 rpm and reaction time, 35 min.
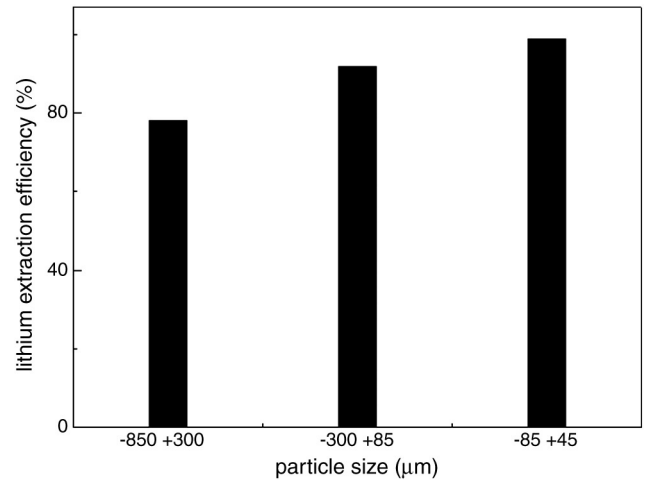
In Fig. 4, it can be observed that an increase in the particle size leads to a marked decrease in lithium extraction efficiency. This can be attributed to an augment in the contact surface between the mineral and the HF when size particle diminishes. For the following assays, a mineral with a particle size between + 45 and - 300 μm was used.

3.1.2. Effect of leaching temperature

In order to investigate the effect of leaching temperature on the lithium extraction, a series of leaching experiments were performed from 10 to 75 °C. Conditions of the leaching process were as follows: solid–liquid ratio, 1.82% (w/v); HF concentration, 7% (v/v); stirring speed, 330 rpm and reaction time, 35 min. The experimental results are shown in Fig. 5.

Fig. 5 illustrates that reaction temperature has an obvious effect on the leaching process. The extraction efficiency increases significantly when the leaching temperature is increased from 10 to 75 °C. The extraction efficiency is 98% when the reaction temperature is 50 °C. However, further increase of the temperature does not result in a clear increase of the extraction efficiency.
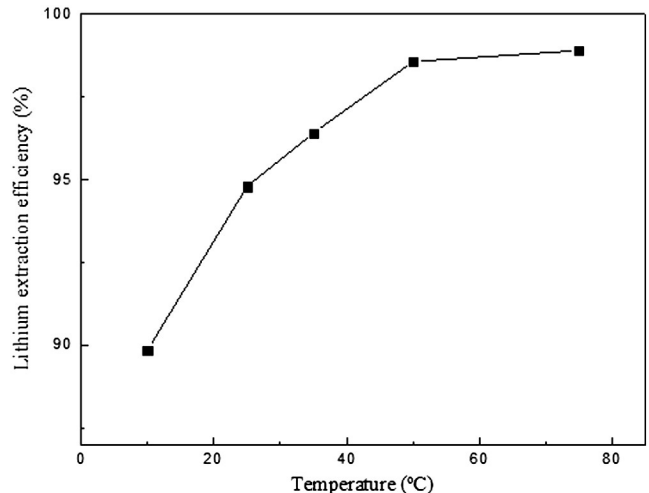

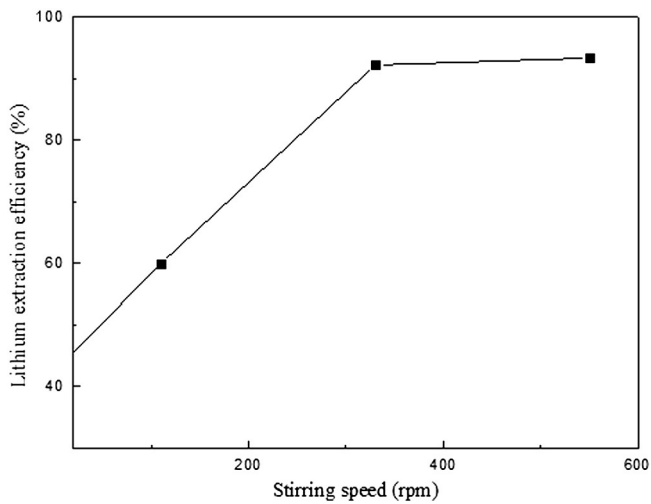Fig. 5. Effect of leaching temperature on the lithium extraction efficiency.

Fig. 6. Effect of stirring speed on the lithium extraction efficiency.

Fig. 8. Effect of reaction time on the lithium extraction efficiency.

3.1.3. Effect of stirring speed

To study the effect of stirring speed on the lithium extraction efficiency, experiments were performed on conditions of solid–liquid ratio, 1.82% (*w/v*); reaction time, 35 min; HF concentration, 7% (*v/v*) and temperature, 25 °C. The experimental results are shown in Fig. 6. It illustrates that stirring speed has an obvious effect on the leaching process.

When the stirring speed is over 330 rpm, the lithium extraction efficiency will remain constant. This fact indicates that once this stirring speed is reached, the thickness of the film surrounding the solid is minimal, and hence it does not affect HF transference rate from the solution to the particles surface. Then 330 rpm is considered as the optimum stirring speed.

3.1.4. Effect of solid–liquid ratio

Solid–liquid ratio effect on lithium extraction efficiency was investigated from 0.9 to 7.2% (*w/v*). The leaching conditions were as follows: reaction time, 35 min; temperature, 25 °C; HF concentration, 7% (*v/v*) and stirring speed, 330 rpm. The results are plotted in Fig. 7, which shows that the solid–liquid ratio has a slight effect on the extraction efficiency. When the solid–liquid ratio is over 1.82% (*w/v*), the lithium extraction efficiency will remain constant. A solid–liquid ratio of 1.82% (*w/v*) is considered to be optimal for both the economic and efficient reasons.
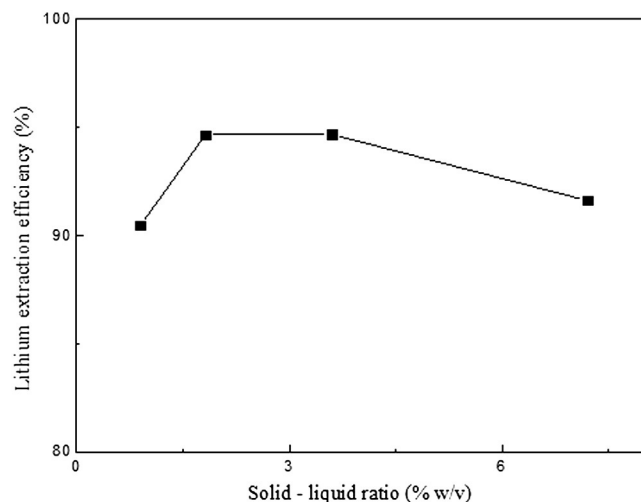
3.1.5. Effect of reaction time

To study the effect of reaction time on the lithium extraction, experiments were conducted on conditions of the solid–liquid ratio, 1.82% (*w/v*); HF concentration, 7% (*v/v*); temperature, 25 °C and stirring speed 330 rpm. The results are plotted in Fig. 8, which shows that leaching time has a remarkable effect on lithium extraction. As time increases from 5 to 20 min, lithium extraction efficiency raises from 61 to 95%. As reaction time increases to 35 min, the extraction efficiency remains almost constant.

3.1.6. Effect of HF concentration

In order to investigate the effect of HF concentration on the lithium extraction, a series of leaching experiments were performed from 5 to 30% (*v/v*). Conditions of the leaching process were as follows: solid–liquid ratio, 1.82% (*w/v*); stirring speed, 330 rpm; temperature, 75 °C and reaction time, 35 min. The results are plotted in Fig. 9.

In Fig. 9, when working with the two lowest values of HF concentration, a slight increase in the extraction of Li can be observed. Then, when the HF concentration increases it can be seen a decrease in the extraction efficiency.

This can be explained considering that, for values above those stoichiometrically required for reaction (1), complete dissolution of β-spodumene is achieved and albite present in the sample begins to be dissolved, reaction (6). This leads to the formation of cryolithionite

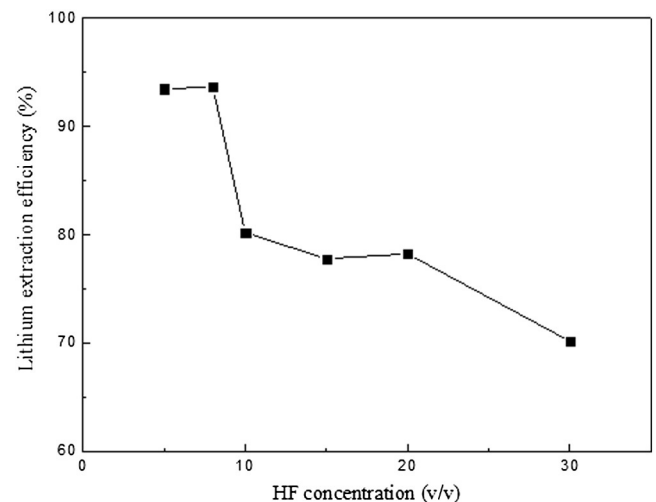**Fig. 7.** Effect of the solid–liquid ratio on the lithium extraction efficiency.

Fig. 9. Effect of HF concentration on the lithium extraction efficiency.
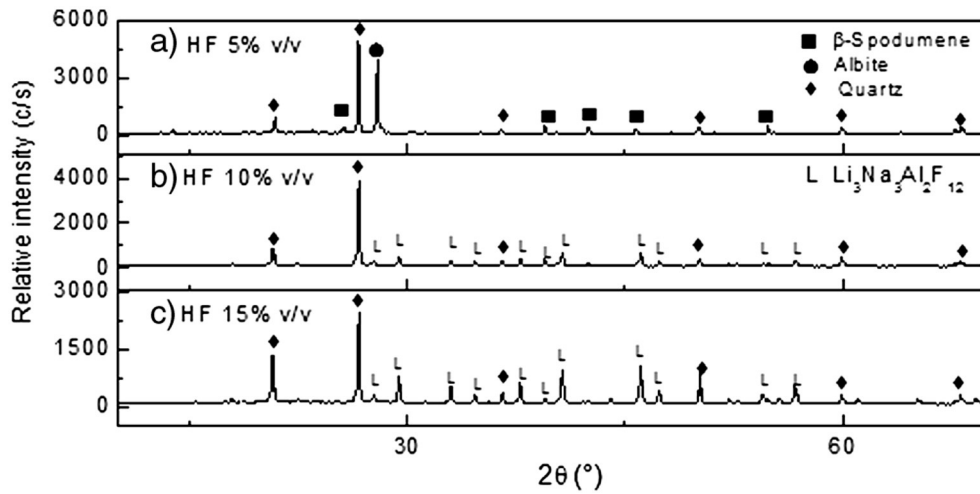
Fig. 10. Diffractograms of the leaching waste obtained with different concentrations of HF: (a) 5% (*v/v*), (b) 10% (*v/v*) and (c) 15% (*v/v*).

($Li_3Na_3Al_2F_{12}$) according to the following reactions (Rosales et al., 2013):

$$NaAlSi_3O_{8(s)} + 25HF_{(aq)} \rightarrow NaF_{(aq)} + H_3AlF_{6(aq)} + 3H_2SiF_{6(aq)} + 8H_2O \tag{6}$$

$$3Li^+_{(aq)} + 2H_3AlF_{6(aq)} + 3Na^+_{(aq)} \rightarrow Li_3Na_3Al_2F_{12(s)} + 6H^+_{(aq)} \tag{7}$$
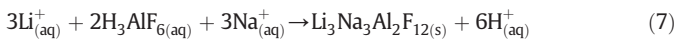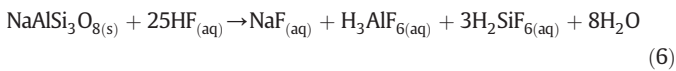
Fig. 10 shows the diffractograms of the leaching residues at 75 °C and a reaction time of 35 min, with different concentrations of HF.

It can be inferred from Fig. 10 that the increase of HF concentration favors the dissolution of the β-spodumene and enhances the intensity of the peaks corresponding to the $Li_3Na_3Al_2F_{12}$ structure (Fig. 10(b) and (c)). The formation of $Li_3Na_3Al_2F_{12}$ according to reactions (1), (6) and (7) is due to the opening of the ore with the consequent release of Li^+, Na^+ and Al^{+3} ions from spodumene ($LiAlSi_2O_6$) and albite ($NaAlSi_3O_8$), initially present in the sample. These metal ions, then, react with fluoride ions of the leaching agent to form $Li_3Na_3Al_2F_{12}$. At HF concentrations below the stoichiometric value for reaction (1) the formation of the compound $Li_3Na_3Al_2F_{12}$ is not observed because the dissolution of albite does not occur (Fig. 10(a)) (Rosales et al., 2013).

The results indicate that the extraction efficiency of Li decreases with the augment of HF concentration because this augment favors the formation of $Li_3Na_3Al_2F_{12}$.

3.2. Recovery of Li, Al and Si

3.2.1. Recovery of residual Al and Si

The result of XRD characterization of the solids precipitated is shown in Fig. 11.

In Fig. 11 the appearance of diffraction lines that correspond to the structure of Na_2SiF_6 (ICDD 96-901-1051) and Na_3AlF_6 (ICDD 01-082-0227) can be observed, which agrees with the proposed reaction (2).

To determine the recovery values of Na_3AlF_6 and Na_2SiF_6, different tests were carried out, by adding different amounts of NaOH to the leach liquor, in a range above and below the stoichiometric values, necessary for the occurrence of the reaction (2). The maximum value

Table 2
Purity of the compounds Na_3AlF_6 and Na_2SiF_6.

Purity of Na_3AlF_6 (%)	Components of the sample					
	Na	Al	Si	F	O	Others
93%	37.3	19.6	–	36.1	5.4	1.6
Purity of Na_2SiF_6 (%)	Components of the sample					
	Na	Al	Si	F	O	Others
98.2%	36.2	–	24.2	37.8	–	1.8

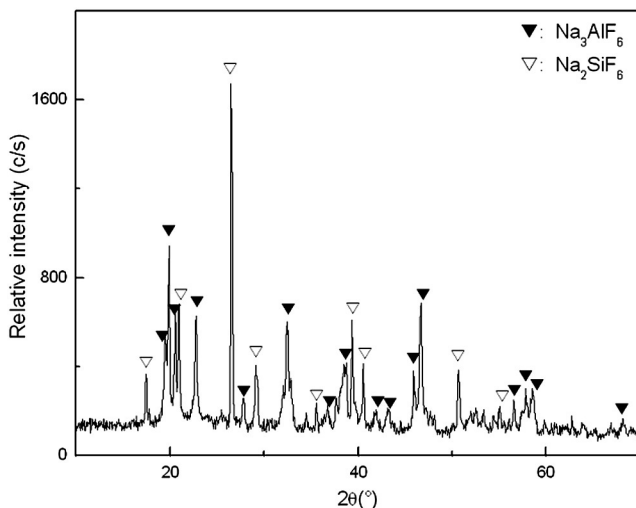**Fig. 11.** Diffractogram of the solids precipitated by the addition of NaOH.
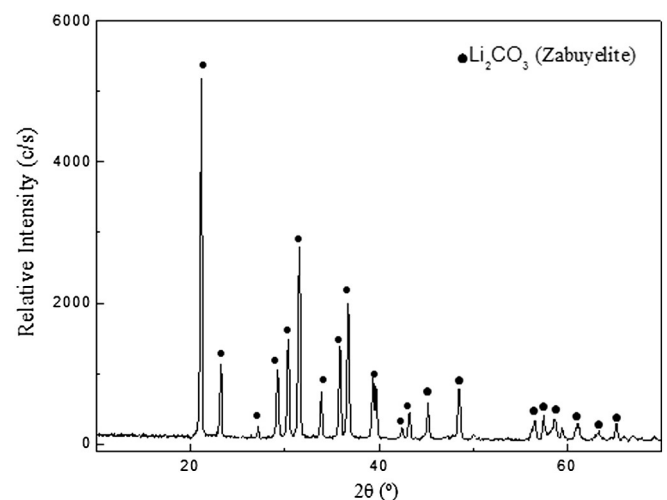
Fig. 12. XRD patterns of the obtained Li_2CO_3.

Table 3
Purity of Li_2CO_3.

Purity of Li_2CO_3 (%)	Content of major impurities				
	Na	K	Ca	Mg	Others
98.3	0.09	0.03	0.04	0.005	1.53

of recovery achieved was 92%, with an amount of NaOH of 8 g. This amount of NaOH corresponds to the stoichiometric value calculated from the reaction (2).

Na_2SiF_6 and Na_3AlF_6 can be separated by an adjustment in pH when NaOH is added, according to the reported by Kumar et al. (2010).

The resulting compounds Na_3AlF_6 and Na_2SiF_6 were analyzed by microanalysis EDS and XRF to determine the purity of the precipitate.

Table 2 shows the purity of the compounds Na_3AlF_6 and Na_2SiF_6.

3.2.2. Recovery of Li as Li_2CO_3

The liquor obtained after the recovery of Al and Si were evaporated until the concentration of Li was 20 g/L (An et al., 2012). After this, the pH of the solution was adjusted between 13 and 14, adding NaOH. Then, $CO_{2(g)}$ was dissolved into the solution until pH lowered down to 6.5. Finally, the solution was heated at 95 °C for 20 min, leading to the precipitation giving place the precipitation of Li as Li_2CO_3 (Jandová et al., 2010).

Fig. 12 shows the diffractogram of the Li_2CO_3 obtained.

Fig. 12 shows that the compound Li_2CO_3 was obtained without other phases as impurities.

Gravimetric analysis showed that the recovery of Li as Li_2CO_3 was close to 90%.

The resulting lithium carbonate was analyzed by AAS to determine the purity of the precipitate.

The concentration of major impurities in the lithium carbonate is shown in Table 3.

4. Conclusions

In summary, a process including the leaching with HF was employed to extract lithium from β-spodumene. The experimental results indicate that the optimal conditions to achieve a lithium extraction higher than 90% were: solid–liquid ratio, 1.82% (w/v); temperature, 75 °C; HF concentration, 7% (v/v); stirring speed, 330 rpm and reaction time 10 min. The compounds Na_3AlF_6 and Na_2SiF_6 can be obtained as subproducts of the process with a recovery percentage of 92%. The dissolved lithium can be separated by precipitating it as Li_2CO_3, with recovery values of 90%, approximately.

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