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Technical note

Lithium fluoride dissolution in sulfuric acid solution: Optimization and application in the extraction of lithium from fluorinated α-spodumene

Alexander C. Resentera [a,*], Gustavo D. Rosales [a], Marcelo R. Esquivel [b,c], Mario H. Rodriguez [a,*]

[a] Laboratorio de Metalurgia Extractiva y Síntesis de Materiales (MESiMat), Instituto Interdisciplinario de Ciencias Básicas (ICB), UNCUYO-CONICET, Facultad de Ciencias Exactas y Naturales, Universidad Nacional de Cuyo, Padre Contreras 1300, CP 5500 Mendoza, Argentina
[b] Centro Atómico Bariloche (CNEA-CONICET), Av. Bustillo km 9.5, CP 8400 Bariloche, Argentina
[c] Universidad Nacional del Comahue (UNCo), Quintral 1250, CP 8400 Bariloche, Argentina

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ABSTRACT

Fluorination processes have been presented as an alternative to Li extraction and recovery processes from minerals and electronic waste. One of the possible products is LiF, a salt insoluble in water. Depending on market demands, it may be necessary to transform it into another lithium compound for technological applications.

In this work, LiF was synthesized from LiCl and HF and characterized by the XRD and Rietveld method. The dissolution of LiF in sulfuric acid solution was modeled and optimized by Response Surface Methodology (RSM). The operating parameters investigated for leaching LiF were the solid/liquid ratio (A), sulfuric acid concentration (B), and leaching time (C). A mathematical model was obtained using RSM to predict the response at any point in the experimental domain ($R^2 = 0.9970$). Analysis of variance (ANOVA) of the reduced quadratic model indicated that A, B, and AB, A^2, and B^2 interactions were significant. The optimal conditions selected were A = 13.0 LiF g/L, B = 5% *v*/v and C = 15 min to obtain a LiF dissolution of 100 ± 1% in sulfuric acid.

Furthermore, optimal acid leaching conditions were tested on the fluorination products of α-spodumene with NaF. The results indicated that 98 ± 3% of the LiF in the fluorination products dissolves in the acid medium, in agreement with RSM. These results indicate the potential to double the solid/liquid ratio and halve the acid concentration and time to leach lithium from fluorinated α-spodumene, compared to other reported processes.

1. Introduction

Lithium is a critical element for small and large-scale production of energy storage and transportation technologies (Jaskula, 2021; Resentera et al., 2021). This strategic element has an important role in the energy transition toward carbon-free energy sources due to its unique electrochemical characteristics (Graham et al., 2021). Lithium supply security has become a priority for global technology companies (Jaskula, 2021; Resentera et al., 2021). Therefore, research in Li extraction from various sources such as minerals, brines, and residues has been intensified.

In the last decade, different fluorination methods have been presented for the extraction of Li from minerals and electronic waste. Spodumene and lepidolite minerals have been processed by hydrometallurgical methods with HF (Kuang et al., 2012; Rodriguez et al., 2017; Rosales et al., 2013, 2014, 2016, 2017), HF/H_2SO_4 (Guo et al., 2017, 2019a, 2019b, 2021; Kuang et al., 2012), NaF/H_2SO_4 (Rodriguez et al., 2017; Rosales et al., 2022), CaF_2/H_2SO_4 (Catovic, 2017; Rodriguez et al., 2017), and pyrometallurgical methods with NaF by roasting (Resentera et al., 2019; Rosales et al., 2019) with KF (Resentera et al., 2019) or NH_4HF_2 (Resentera et al., 2020, 2021, 2022) followed by acid leaching. Also, spent lithium-ion batteries have been leached with HF (Suarez et al., 2017) and HF/H_2O_2 (Pinna, 2019). All these fluorination processes have shown high extraction efficiency. In many of these processes, the main extraction product generated is solid LiF or a soluble form in an acid medium. Although LiF has wide applications, its low solubility in water (1.34 g/L) makes it difficult to separate it from other insoluble solids produced during roasting (Lide et al., 2016). Furthermore, according to market requirements, it may be necessary to transform LiF into other salts. Therefore, it is of scientific-technological interest to solubilize the LiF formed in fluorination reactions for its separation from other solids or subsequent transformation into other Li salts.

In this work, LiF was synthesized from LiCl and HF and characterized

* Corresponding authors.
E-mail addresses: r_alex_07@hotmail.com (A.C. Resentera), mrodriguez@uncu.edu.ar (M.H. Rodriguez).

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Table 1
Experimental design and results for LiF leaching.

Std	Run	Factor A	Factor B	Factor C	Response
		S/L ratio (g/L)	H_2SO_4 (% v/v)	Time (min)	Li extraction (%)
1	14	11.3	3.3	32	98.65
2	4	32.7	3.3	32	56.14
3	3	11.3	8.3	32	98.56
4	17	32.7	8.3	32	79.18
5	1	11.3	3.3	98	99.00
6	9	32.7	3.3	98	57.59
7	8	11.3	8.3	98	98.03
8	2	32.7	8.3	98	82.08
9	12	4.0	5.8	65	99.93
10	15	40.0	5.8	65	60.61
11	7	22.0	1.6	65	53.02
12	6	22.0	10.0	65	96.89
13	10	22.0	5.8	10	93.00
14	13	22.0	5.8	120	91.59
15	16	22.0	5.8	65	93.20
16	5	22.0	5.8	65	92.57
17	11	22.0	5.8	65	93.24

Temperature of 25 °C and stirring speed of 330 rpm.

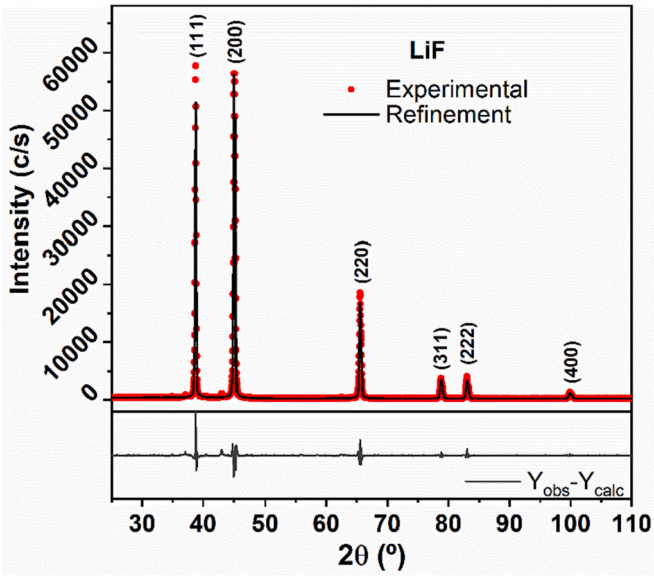

Fig. 1. Diffractogram (red dots) and Rietveld refinement (solid line) of synthesized LiF. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

by the XRD and Rietveld method. The dissolution of LiF in sulfuric acid solution was performed by leaching tests and analyzed and optimized by RSM. From LiCl, LiF was synthesized by a hydrometallurgical route and characterized by XRD and Rietveld method. The operating parameters investigated were leaching time, solid/liquid ratio, and acid concentration. Finally, the optimal conditions were tested on the fluorination products of α-spodumene with NaF to extract lithium in the acid solution.

2. Materials and methods

2.1. Equipment and data analysis

The leaching tests of LiF, synthesized according to the process in Section 2.2, were carried out in a closed 250 mL PVC reactor using a magnetic stirring system. Solid reactants and products were analyzed in a PANalytical Empyrean diffractometer, Cu-Kα operated at 40 kV and 30 mA.

The determination of Li in the liquors and solids (Brumbaugh and Fanus, 1954) was carried out by flame atomic emission spectrometry (FAES) in a Crudo Caamaño, Alphanumeric Ionometer photometer. The chemical composition of the solids was performed on X-ray fluorescence (XRF) in a Shimadzu EDX-8000 (except for Li). Furthermore, the Si and Al determinations of roasting products from α-spodumene were performed in an AAnalyst 7000 Atomic Absorption Spectrophotometer. Sulfates in liquors were determined using the gravimetric Standard Method 4500-SO_4^{2-} C, while the Standard Method 4110 was used for fluorides with a Thermo Scientific Aquion AS-DV USA Ion Chromatograph (Baird et al., 2017).

The Gibbs free energy changes of the investigated reactions were calculated with the HSC Chemistry 6 (v6.0.0) software. The initial LiF sample was analyzed by Rietveld with FullProf software (June 2019 version). Furthermore, RSM was performed in Design-Expert 12 software.

2.2. Procedure

2.2.1. LiF synthesis

From LiCl, LiF was synthesized according to chemical reaction (1) with HF (Cicarelli, 50% w/w) in stoichiometric quantities. The solution was kept under stirring at 300 rpm for 30 min. The precipitated solid was separated by vacuum filtration, dried in an oven at 80 °C for 12 h, ground in a manual mortar, and characterized.

$$HF_{(l)} + LiCl_{(aq)} \rightarrow LiF_{(s)} + HCl_{(aq)} \quad (\Delta G^0 = -26.69\ kJ) \tag{1}$$

2.2.2. Acid leaching stage

The synthesized LiF was leached using acid solutions prepared with H_2SO_4 Alkemit, 98% w/w. According to the bibliography, the dissolution would occur according to Eq. (2) (Resentera et al., 2021; Rosales et al., 2019). The operating parameters analyzed were leaching time (10–120 min), sulfuric acid concentration (1.6–10% *v*/v), and solid/liquid ratio (4–40 g/L). All leaching experiments were performed at room temperature with a stirring speed of 330 rpm.

$$2LiF_{(s)} + H_2SO_{4\ (l)} \rightarrow 2Li^{+}_{(aq)} + SO^{2-}_{4\ (aq)} + 2HF_{(aq)} \quad (\Delta G^0 = -54.23\ kJ) \tag{2}$$

The Li extraction was quantified from the amount of Li in the leach liquors according to Eq. (3):

$$Li\ extraction\ (\%) = \frac{Li_L}{Li_m} 100\% \tag{3}$$

where Li_L is the amount of lithium in the leach liquor and Li_m is the nominal amount of lithium in the solid.

A rotatable Central Composite Design (CCD) with alpha 1.68179 was

Table 2
Crystallographic data obtained by Rietveld refinement.

Structure (SG[a])	Cell parameters	Ion	Wp[b]	x	y	z	Biso
LiF ($Fm\bar{3}m$)	$a = b = c = 4.02657(2)$ Å	Li^+	4a	0	0	0	1.433(5)
	$\alpha = \beta = \Upsilon = 90°$	F^-	4b	0.5	0.5	0.5	1.098(3)

$\chi^2 = 5.77$, $R_p = 10.9\%$, $R_{wp} = 12.1\%$, $R_{exp} = 5.03\%$, $R_{Bragg} = 0.949$.
[a] SG: Space Group.
[b] Wp: Wyckoff position.

Table 3
ANOVA for reduced quadratic model for Li extraction.

Source	Sum of Squares	df[a]	Mean Square	F-value	*p*-value	
Model	2819.10	5	563.82	605.29	< 0.0001	significant
A - S/L ratio	1989.36	1	1989.36	2135.68	< 0.0001	
B - [H_2SO_4]	307.79	1	307.79	330.43	< 0.0001	
AB	295.24	1	295.24	316.95	< 0.0001	
A^2	289.17	1	289.17	310.44	< 0.0001	
B^2	32.85	1	32.85	35.26	0.0002	
Residual	8.38	9	0.9315			
Lack of Fit	8.11	7	1.16	8.32	0.1115	not significant
Pure Error	0.2784	2	0.1392			
Correlation Total	2827.49	14				
Fit statistics						
	R^2	0.9970		**SD**[b]	0.9651	
	Adjusted R^2	0.9954		**Mean**	88.64	
	Predicted R^2	0.9882		**CV%**[c]	1.09	
	Adequate Precision	69.8494				

Note: Runs 7 and 15 were ignored for this analysis.
[a] **df**: degree free.
[b] **SD**: Standard Deviation.
[c] **CV%**: Coefficient of Variation.

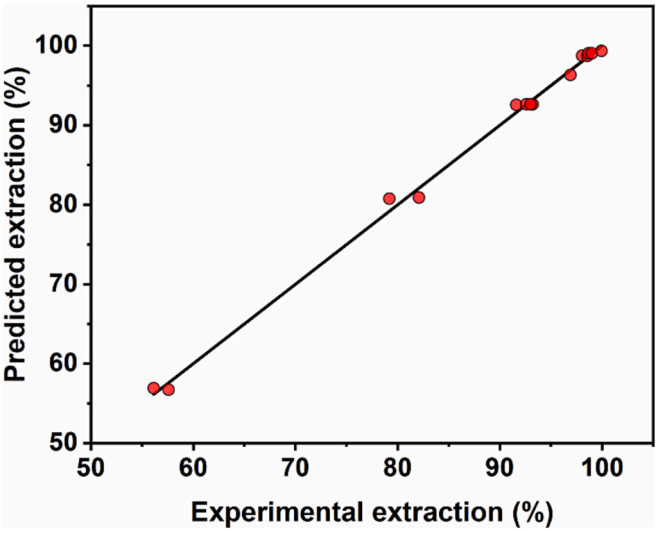

Fig. 2. Comparison of the actual and predicted values of the RSM model for the LiF dissolution.

used to obtain a predictive mathematical model that describes the process, revealing the correlation between the factors and the response. The CCD consisted of 17 experiments with three central point replicates (Table 1). The experimental data were fitted with a second-order or higher polynomial function to build a mathematical model according to the following regression model:

$$y = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \beta_{ii} X_i^2 + \sum_{1 \le i \le j}^{k} \beta_{ij} X_i X_j + \varepsilon \quad (4)$$

where y is the response, β_0 is the general average effect, β_i represents the effect of the factors (variables) X_i and, β_{ij} is the effect of the interaction between the factors X_i and X_j, β_{ii} which correspond to the quadratic terms. The term ε is a random error component and represents other sources of variability not taken into account in the model. Analysis of variance (ANOVA) test was used to analyze the importance of the model and the factors (Vera Candioti et al., 2014).

2.2.3. Verification stage in LiF/mineral system of fluorinated α-spodumene

According to the previous studies, LiF, $NaAlSiO_4$ (Nefeline), and $NaAlSi_3O_8$ (Albite) are the products of the extraction process of Li from

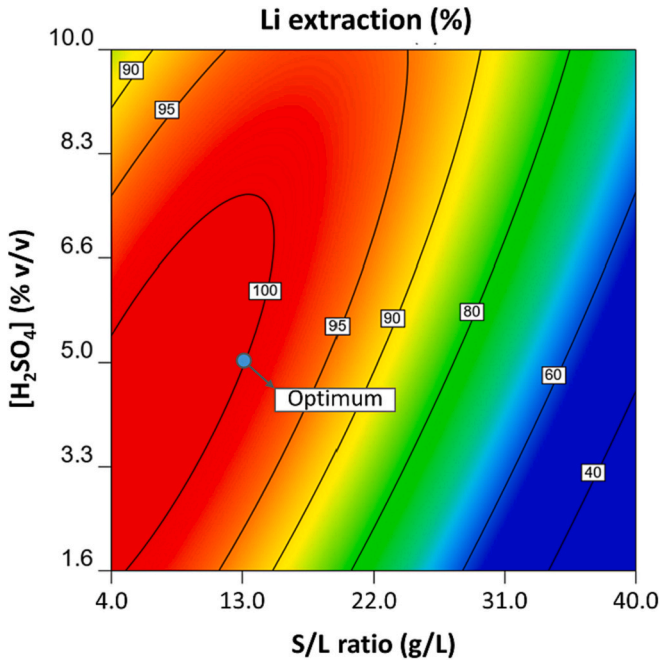

Fig. 3. Contour plot of the reduced quadratic model for the dissolution of LiF in sulfuric acid.

α-spodumene with NaF, Eq. (5) (Resentera et al., 2019; Rosales et al., 2019).

$$LiAlSi_2O_6 + NaF \rightarrow LiF + 0.5NaAlSiO_4 + 0.5NaAlSi_3O_8 \ (\Delta G^0 = -5.89\ kJ) \quad (5)$$

In the verification stage, 5 g of α-spodumene was mixed with 2.35 g NaF (Alkemint, 99% *w*/w) in a manual mortar for 5 min. The mineral contains 7.54% w/w Li_2O; a complete characterization is presented in (Resentera et al., 2020, 2021). The mixture was placed in a muffle furnace and heated at 750 °C for two hours, as specified in previous studies (Resentera et al., 2019). The calcine was washed in 100 mL of distilled water to remove unreacted NaF. Finally, the solid products were leached under the optimal conditions determined in Section 2.2.2. The Li extraction in the liquor was determined according to Eq. (3).

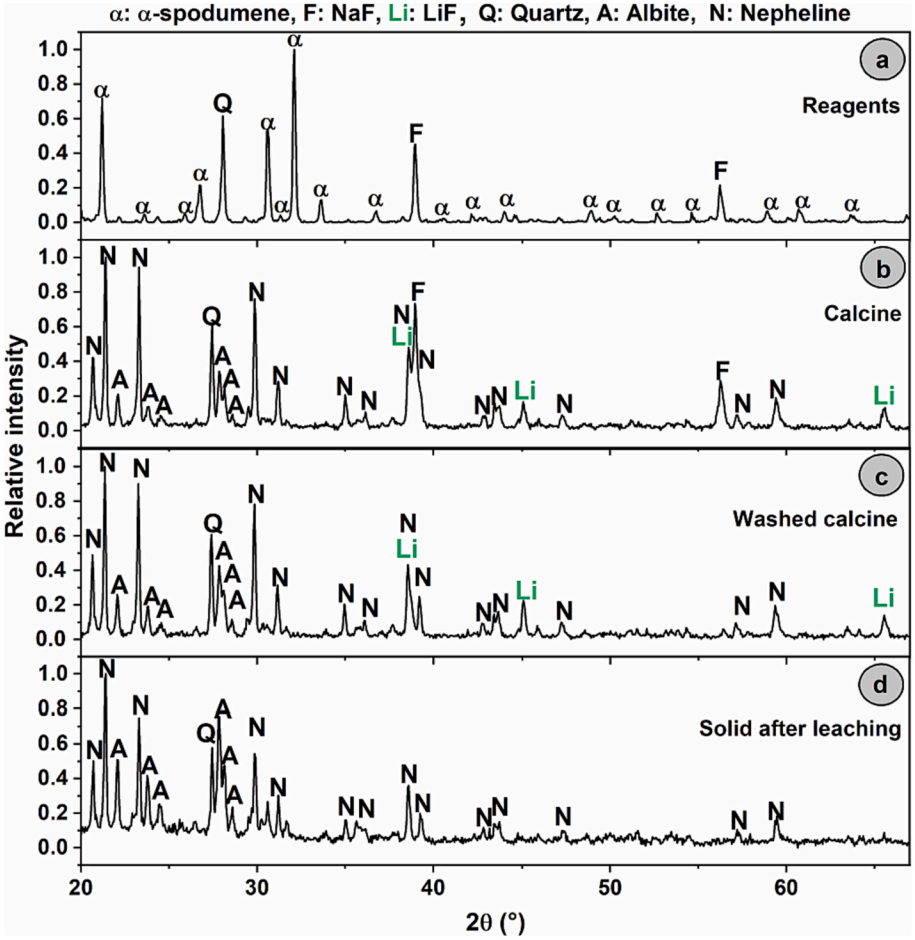

Fig. 4. Comparative XRD (a) mixture of reagents α-spodumene/NaF, (b) fluorination products after calcination with NaF, (c) washed calcine, and (d) solid after acid leaching at optimal conditions (leaching time 15 min, S/L ratio 13.0 LiF g/L, and H_2SO_4 5% *v*/v).

Table 4
Mass balance of the process stages.

Stage	Cumulative mass loss (%)		Mass (g)	
	Experimental	Theoretical	Before	After
Calcination	0.05 ± 0.02	0	7.355 ± 0.002	7.353 ± 0.002
Water leaching	18.3 ± 0.3	18.5	5.248 ± 0.002	4.29 ± 0.01
Acid leaching	30.8 ± 0.1	27.2	4.003 ± 0.006	3.39 ± 0.08

3. Results and discussion

3.1. Characterization of the synthesized LiF

Fig. 1 shows the synthesized LiF diffractogram (continuous line) and the fit obtained by the Rietveld method (red dots). The summary of the refined parameters is presented in Table 2. The diffraction pattern is identified as LiF (PDF 01–078-1217), which crystallizes in the cubic system according to the space group $Fm\bar{3}m$. The basic structure consists of a face-centered cubic (FCC) unit cell with all occupied octahedral holes, coordinate six for all atoms, and Li—F bond lengths of 2.01328(2) Å.

Table 5
Elemental mass balance in the process stages.

Material	Mass (g)	Volume (L)	Chemical analysis						
			Unit	Li	Al	Si	Na	F	S
α-spodumene	5.004	–	% w/w	3.518[a]	13.859	28.573	–	–	0.661
NaF	2.351	–	% w/w	–	–	–	54.761	45.201	–
Calcine	7.355	–	% w/w	2.407[a]	9.368	19.375	17.525	14.448	0.450
Wash liquor	–	0.07	g/L	3×10^{-4}	–	–	10.170	8.388	–
H_2SO_4 (5% v/v)	–	0.05	g/L	–	–	–	–	–	29.28
Leach liquor	–	0.05	g/L	3.450	0.711	1.475	0.173	9.502	29.16
Leach residue	5.085	–	% w/w	0.069[a]	12.655	26.247	10.553	–	–
Total mass input of elements			g	0.177	0.689	1.430	1.287	1.063	1.497
Total mass output of elements			g	0.176	0.679	1.409	1.257	1.062	1.46

[a] Li measured by Brumbaugh and Fanus method (Brumbaugh and Fanus, 1954).

3.2. Modeling and optimization

The CCD results were analyzed using RSM to obtain a predictive model. Thus, the relationship between the operating parameters and the response is modeled mathematically. Table 3 summarizes the results obtained after the least squares analysis.

According to the ANOVA analysis, the p-value of the reduced quadratic model <0.0001 implies that it is significant ($p < 0.05$). Also, the factors A, B, AB, A^2, and B^2 are significant terms of the model. The statistical results show a good fit. The Predicted R^2 of 0.9882 is in reasonable agreement with the Adjusted R^2 of 0.9954 (the difference is <0.2).

On the other hand, the lack of fit is not significant about the pure error, implying that the model fits adequately. Furthermore, Adequate Precision indicates an adequate signal. This model can be used to navigate the design space. Eq. (6) presents the mathematical representation of the model with real variables that affect the Li extraction:

$$Li\ extraction\ (\%) = 99.18765 - 0.208725\,A + 1.47522\,B + 0.227138\,AB - 0.056995A^2 - 0.353926B^2 \quad (6)$$

where A and B are S/L ratio (LiF g/L) and sulfuric acid concentration (% *v*/v), respectively. This equation allows predictions about the response within the experimental space. Fig. 2 presents a comparative plot between the experimental values and those predicted by the model. The points are distributed almost in a straight line with a high determination indicating that the reduced quadratic model fits adequately.

Fig. 3 shows the contour plot of the model. This plot highlights the effect of operating parameters on extraction efficiency. The model indicates that dissolution increases with increasing acid concentration and decreasing S/L ratio. Furthermore, interaction is observed between both parameters, as indicated by Eq. (6). The positive effect of increased acid concentration is typically associated with the greater availability of the leaching agent to react with the solid and form the products (Pinna et al., 2017), according to Eq. (2). On the other hand, by decreasing the S/L ratio, the solution is less saturated, favoring contact between the leaching solution and LiF and mass transport. As can be seen in Table 3, time is not a significant parameter in dissolution. This could be because the synthesized LiF is pure and finely ground. In LiF/mineral type systems, times of 30 to 120 min could be required since LiF is sintered with other roasting products (Resentera et al., 2019; Rosales et al., 2019).

Finally, according to the response surface, the optimum point is selected at an acid concentration of 5% (*v*/v), S/L ratio of 13.0 g/L, and leaching time of 15 min to obtain 100 ± 1% of Li extraction. Optimum conditions tested experimentally by triplicate resulted in Li extractions of 99.7 ± 0.2%, confirming the predicted results.

3.3. Optimum leaching test in LiF/mineral system of fluorinated α-spodumene

The products LiF, albite, and nepheline were obtained by thermal fluorination of spodumene with NaF, as shown in Eq. (5). In previous studies, the three products were subjected to leaching with acid to obtain up to an experimental Li extraction of 91% after 30 min at an S/L ratio of 6.6 LiF g/L and 10% v/v H_2SO_4 (Resentera et al., 2019; Rosales et al., 2019). Since albite and nepheline are not significantly affected by H_2SO_4, this system offers a practical example for testing the dissolution of LiF produced, Eq. (5), during acid treatment according to Eq. (2).

The model obtained in Section 3.2 adequately predicts the results presented by Rosales et al., 2019, i.e., a value of 90 ± 3% Li extraction (see Fig. 3). Furthermore, the optimal conditions selected in Section 3.2 were tested in this work to halve the amount of acid and double the S/L ratio used in the system (acid concentration of 5% *v*/v, S/L ratio of 13.0 g/L, and leaching time of 15 min). Fig. 4 (a) shows the diffraction patterns of the α-spodumene (PDF 01–075-1091) and NaF (PDF 01–073-1922) reagents. Fig. 4 (b) shows the diffractogram of the fluorination products after calcination with NaF: LiF (PDF 01–078-1217), nepheline (PDF 01–079-0993), albite (PDF 01–071-1150), and unreacted NaF in agreement with the literature and Eq. (5) (Resentera et al., 2019; Rosales et al., 2019). The absence of unreacted α-spodumene in Fig. 4 (b) within the detection limits of the technique suggests a complete reaction. Fig. 4 (c) shows the XRD pattern of the washed calcine, with no evidence of unreacted NaF as it dissolved completely during washing. However, the other products remained in the washed calcine due to their low solubility in water.

Once the unreacted NaF was removed by washing, the solid was leached following the optimum conditions described in Section 3.2: leaching time 15 min, S/L ratio 13.0 LiF g/L (contained in the washing calcine), and H_2SO_4 5% v/v. The Li extractions of 98 ± 3% obtained in these tests are in good agreement with the prediction of the model Fig. (3). Fig. 4 (d) presents nepheline and albite as final products in the leach residue after acid dissolution of LiF according to Eq. (2).

Table 4 presents the mass balance of the Li extraction process from α-spodumene. Theoretical calculations consider Eq. (5) in the calcination stage, the removal of unreacted NaF (concerning the Li amount in the α-spodumene) in the water leaching (washing) of calcine, and only the dissolution of LiF in the acid leaching leaving behind quartz, albite and nepheline.

In the calcination stage, no significant mass loss was observed from the total mass of 7.355 g of α-spodumene and NaF (Table 4), in agreement with that reported in the bibliography (Resentera et al., 2019; Rosales et al., 2019). In the water leaching stage, the experimental mass loss of 18.3 g which is only slightly lower than the theoretical value of 18.5 (Table 4).

Table 5 shows the elemental mass balance and confirms that the washing of the calcine dissolved 98% of the unreacted NaF along with 0.05% of the LiF due to their solubilities and common ion effect (see input and output in columns for Na and Li). In the mass balance for the acid leaching stage in Table 4, the experimental value of 30.8 g is higher than the theoretical value of 27.2 g. According to Table 5, nearly all LiF and NaF are removed from the solid phase during acid leaching. Furthermore, ~6% of albite and nepheline are dissolved by the HF formed in situ due to the reaction between LiF and unreacted NaF in the acid medium, see Supplementary material, according to Table 5 and the literature (Guo et al., 2017; Rosales et al., 2013).

4. Conclusions

In this research, LiF was synthesized and characterized by XRD and Rietveld. Dissolution of synthesized lithium fluoride was optimized in sulfuric acid solution. A mathematical model was obtained using RSM to predict the response at any point in the experimental domain (R^2 = 0.9970). The operating parameters investigated were LiF leaching time, S/L ratio, and sulfuric acid concentration. Leaching time 15 min, S/L ratio 13.0 LiF g/L, and H_2SO_4 5% *v*/v were selected as the optimal combination to obtain 100 ± 1% Li extraction.

The model obtained was successfully tested on a LiF/mineral system of the fluorinated α-spodumene, such as those obtained in different Li extraction processes. The optimum point was tested for the dissolution of the LiF obtained as a fluorination product of α-spodumene with NaF. The results indicated that 98 ± 5% of the LiF in the fluorinated system was dissolved in acid as $Li^+_{(aq)}$, in agreement with RSM. In this way, Li is efficiently separated reducing high water and acid consumption in the conventional process.

CRediT authorship contribution statement

Alexander C. Resentera: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Writing – original draft, Writing – review & editing. **Gustavo D. Rosales:** Methodology, Visualization, Validation, Investigation, Writing – review & editing. **Marcelo R.**

Esquivel: Visualization, Investigation, Resources, Writing – review & editing, Supervision, Project administration, Funding acquisition. **Mario H. Rodriguez:** Methodology, Visualization, Resources, Writing – review & editing, Supervision, Project administration, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.hydromet.2023.106027.

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SUPPLEMENTARY MATERIAL

Lithium fluoride dissolution in sulfuric acid solution: Optimization and application in the extraction of lithium from minerals

Alexander C. Resentera [a,*], *Gustavo D. Rosales* [a], *Marcelo R. Esquivel* [b,c], *Mario H. Rodriguez* [a,**]

[a] Laboratorio de Metalurgia Extractiva y Síntesis de Materiales (MESiMat), Instituto Interdisciplinario de Ciencias Básicas (ICB), UNCUYO-CONICET, Facultad de Ciencias Exactas y Naturales, Universidad Nacional de Cuyo, Padre Contreras 1300, CP 5500, Mendoza, Argentina.

[b] Centro Atómico Bariloche (CNEA-CONICET), Av. Bustillo km 9.5, C.P.8400, Bariloche, Argentina.

[c] Universidad Nacional del Comahue (UNCo), Quintral 1250, CP 8400, Bariloche, Argentina.

[*] r_alex_07@hotmail.com (Alexander C. Resentera)

[**] mrodriguez@uncu.edu.ar (Mario H. Rodriguez)

A. XRD characterization of LiF low dissolution assays

In order to show that other solid species are not formed during the leaching, Figure S1 presents an XRD of the solid obtained after the Std 11 experiment (Li extraction 53.02%).

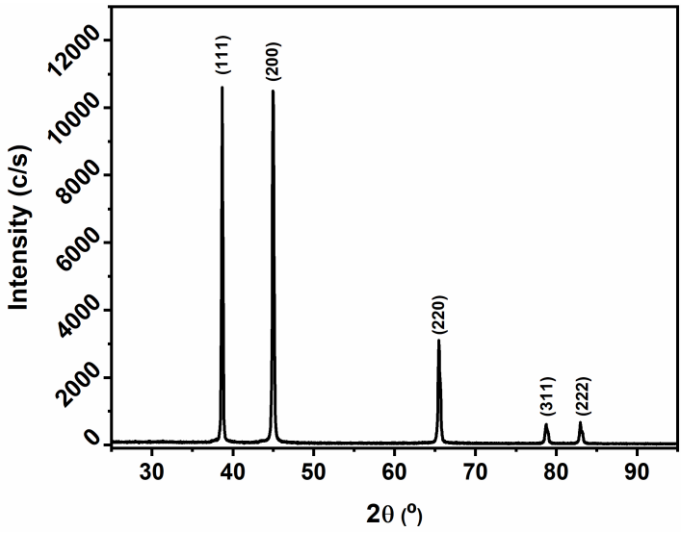

Figure S1. XRD of the solid obtained after experiment std 11.

The result shows that the only solid species is undissolved LiF. Also, the decrease in intensity shows the effect of sample dissolution with respect to Figure 1.

B. Albite/Nepheline dissolution calculations in acid medium

According to Table 5, 0.475 g of HF are generated by dissolution of LiF and unreacted NaF in an acid medium. This amount of HF dissolves 0.253 g of albite and nepheline generated according to reaction (S1), i.e., approximately 6%. These results are in good agreement with the amount of Al and Si observed in Table 5 (Leach liquor).

$$NaAlSiO_{4(s)} + NaAlSi_3O_{8(s)} + 38HF_{(aq)} \rightarrow 2NaF_{(aq)} + 2H_3AlF_{6(aq)} + 4H_2SiF_{6(aq)} + 12H_2O \text{ (S1)}$$