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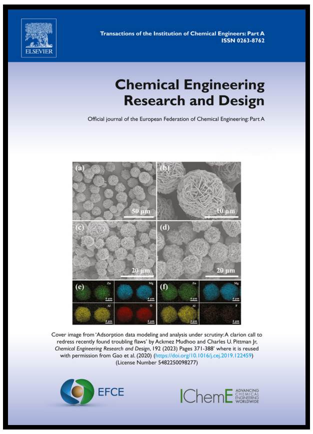

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Acid dissolution of $LiF/(NH_4)_3AlF_6$ mixtures obtained in the fluorination of α-spodumene with NH_4HF_2: modeling and optimization

*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] Servicio de Microscopía Electrónica de Barrido y Difracción de Rayos X - 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.

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

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

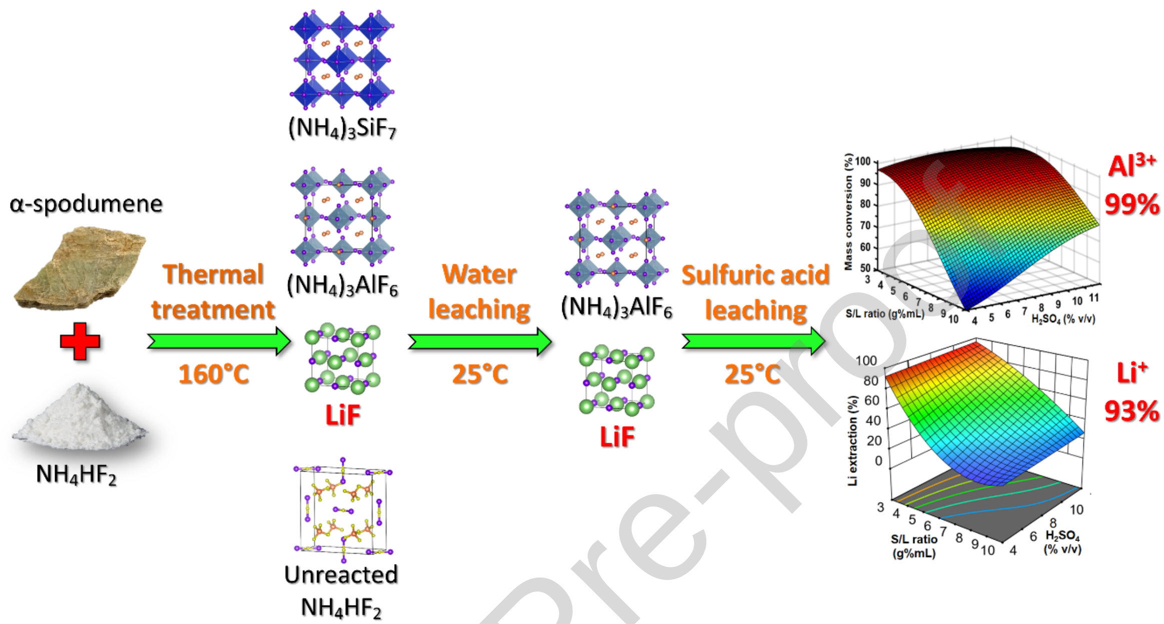
Abstract

Lithium is an essential element in the current energy paradigm shift. Therefore, Li extraction from mineral sources has become a scientific and technological priority. Industrially, the mineral α-spodumene is heated to 1100°C to obtain phase β and then digested with concentrated sulfuric acid at 250°C. As an alternative, the extraction of Li from α-spodumene with molten NH_4HF_2 has been proposed as an efficient alternative method at low temperature (~160°C). However, the LiF obtained requires an acid leaching step to be solubilized and to separate the Li from other products.

This research presents the modeling and optimization of the acid leaching operating parameters of the $LiF/(NH_4)_3AlF_6$ mixture. This mixture was obtained by processing α-spodumene with NH_4HF_2 at low temperatures. The solids were characterized by XRD, SEM/EDS, and the Rietveld method. The leaching operating parameters investigated were solid/liquid ratio, sulfuric acid concentration, and leaching time. $(NH_4)_3AlF_6$ dissolution and Li extraction were analyzed and modeled separately using artificial neural networks and least squares, respectively. The optimization stage of the process leads to $(NH_4)_3AlF_6$ dissolution

of 99% and Li extractions of 93%, working with 6% (v/v) sulfuric acid solution and an S/L ratio of 30 g/L for 24 min.

Graphical abstract



Keywords: Spodumene, Lithium, Ammonium bifluoride, Response surface methodology, Design of experiments, Fluorination

1. Introduction

Energy migration from carbon sources to clean energies and the increasing demand for mobile electronic devices have positioned Li as a critical energy element. This "critical metal" is essential for new technologies manufacture in emerging industries (Pérez et al., 2023; Toro et al., 2022). The Li demand has increased notably due to the market for hybrid and electric cars and large-scale storage systems for public services (Jaskula, 2021, 2020). In particular, global sales of electric vehicles have increased from thousands in 2010 to millions in 2018 (Toro et al., 2022). United States Geological Survey has indicated that the Li supply is one of the main priorities for technology companies (Jaskula, 2021).

Approximately 50% of the world's Li reserves are in the Lithium Triangle, located in brines in Argentina, Chile, and Bolivia (Christmann et al., 2015; González et al., 2020; Karrech et al., 2020). On the other hand, Li minerals (pegmatites) are distributed on all continents (González et al., 2020). Therefore, Li exploitation is critically important due to the unequal global distribution of natural resources. This situation requires efficient processing of all Li sources, i.e., brines (Swain, 2017), salt lakes (USGS, 2014), waste recycling (Pinna, 2019; Pinna et al., 2020), and minerals (Resentera et al., 2019). The predictions of insufficient production of Li compounds have boosted mineral sources on the market. Therefore, it is necessary to develop new extractive methodologies with greater efficiency and lower energy consumption.

Spodumene is the main industrial mineral resource due to its estimated reserves, distribution, and Li content (8.03% Li_2O theoretical) (Wietelmann and Bauer, 2000). The only industrial process currently used requires the grinding and calcination of the ore at 1100°C to obtain β-spodumene (Peltosaari et al., 2015; Salakjani et al., 2016). Then, a digestion process is carried out with concentrated sulfuric acid at 250°C (Ellestad and Leute, 1950). Soluble Li is separated by various leaching and precipitation processes. The solids generate large amounts of polluting waste without industrial use (Quartarolli et al., 2022). Only 5% of the mineral is used (Rosales et al., 2022). Furthermore, the process requires high energy consumption due to the elevated processing temperatures (Resentera et al., 2021).

Different investigations have been presented to replace the traditional sulfuric acid method. Among them are recent fluorination methods starting from the alpha phase of the mineral, e.g., leaching using HF (Rodriguez et al., 2017) or H_2SO_4/HF mixtures (Guo et al., 2021, 2017) and pyrometallurgical methods with NaF and/or KF (Resentera et al., 2019; Rosales et al., 2023, 2019). However, few of them combine the high profitability and efficiency of the sulfuric acid digestion process. For this reason, they have not been implemented by the industrial sector (Karrech et al., 2020).

Resentera et al. proposed α-spodumene fluorination with molten NH_4HF_2 at low temperatures according to Equation (1) (Resentera et al., 2020, 2019). The operating parameters of the thermal process were optimized by Response Surface Methodology (RSM), obtaining conversions of 96% at 157°C with a molar ratio of 1:17.5 α-spodumene:NH_4HF_2 during 100 min (Resentera et al., 2021). This process considerably reduces the energy requirements of the industrial acid digestion process.

$$\alpha - LiAlSi_2O_6 + 10.5\ NH_4HF_2 \rightarrow LiF + 2\ (NH_4)_3SiF_7 + (NH_4)_3AlF_6 + 1.5\ NH_3 + 6\ H_2O \quad (1)$$

The silicon product and the unreacted fluorinating agent are easily separated by the wet route (high solubility) and purified for industrial use (Resentera et al., 2022). In this way, the mineral is fully used. The mixture of LiF and $(NH_4)_3AlF_6$ remains in the solid due to its low solubility. This process requires solubilizing LiF to transform it into a commercial Li salt. LiF can be solubilized in acid media (Resentera et al., 2023b). However, their leaching conditions have not yet been analyzed when $(NH_4)_3AlF_6$ is in the medium. Reducing costs and maximizing the efficiency of this leaching stage is important to obtain an industrially attractive comprehensive process. Therefore, it is of remarkable scientific-technological interest to model and optimize the dissolution of the LiF/$(NH_4)_3AlF_6$ mixture in an acid medium to separate Al and Li and then obtain other Li salts.

The RSM is an experimental and modeling strategy to find the optimal conditions of a process (Gutiérrez and de la Vara Salazar, 2012). This tool allows the user to fit responses that follow a normal distribution with least squares (LS) or non-linear data for normal distributions using artificial neural networks (ANN) (Giordano et al., 2017; Vera Candioti et al., 2014). Thus, the predictive model obtained explains the importance of each factor and its interactions with the response (Resentera et al., 2021; Teglia et al., 2020). Furthermore, through the multivariate design of experiments (DOE), RSM allows for minimizing the time, effort, and resources compared to the traditional univariate procedure (Goicoechea, 2018).

In this work, the sulfuric acid leaching process of LiF/$(NH_4)_3AlF_6$ products was modeled and optimized using DOE, ANN, and LS. The LiF/$(NH_4)_3AlF_6$ mixture was obtained by processing α-spodumene with NH_4HF_2 at low temperatures. The operating parameters investigated were the solid/liquid ratio, sulfuric acid concentration, and leaching time. A Box-Behnken experimental design was used. $(NH_4)_3AlF_6$ dissolution and Li extraction were analyzed and modeled using ANN and LS, respectively. Finally, the system was optimized using the RSM and experimentally confirmed.

2. Materials and methods

2.1. Equipment

Ore fluorination was carried out in an oven equipped with a temperature controller, gas extraction system, and an aluminum reactor. The leaching tests were carried out in closed PVC reactors in a system with magnetic agitation.

The solid products were characterized by X-ray diffraction (XRD) in a PANalytical Empyrean diffractometer, Cu-Kα operated at 40 kV and 30 mA. Morphological and elemental analyses were performed with an FEI INSPECT s50 scanning electron microscope equipped with an EDAX-Octane Pro energy dispersive X-ray spectrometer. The ore chemical composition was analyzed by X-ray fluorescence (XRF) in a Shimadzu EDX-8000 equipment. Li was determined in a Crudo Camaño Alphanumeric Ionometer flame photometer in the leach liquors. Furthermore, the Al determinations were performed in an AAnalyst 7000 Atomic Absorption Spectrophotometer.

2.2. Procedure

2.2.1. Fluorination stage

The α-spodumene used in this work comes from the province of Catamarca, Argentina. Compositional analysis indicates 7.540% Li_2O, 61.228% SiO_2, 26.179% Al_2O_3, 1.652% SO_3, 1.046% Fe_2O_3, and 0.355% others (w/w) (Resentera et al., 2020). In the fluorination step, 70 g of the ore were mixed with NH_4HF_2 (MAG, purity >98%) in a molar ratio of 1:17.5, respectively. The solids were mixed for 15 min in a manual mortar. The sample was then heated to 165°C (2°C/min) and kept isothermal for 120 min (Resentera et al., 2021). After this period, the products were cooled to room temperature and crushed in a mortar for 15 min.

Silicon products and unreacted NH_4HF_2 were separated by wet-route (Resentera et al., 2022). The fluorination products were leached with distilled water for 30 min with a solid/liquid ratio of 126 g/L and magnetic stirring at 300 rpm. The system was filtered, and the solid obtained ($LiF/(NH_4)_3AlF_6$ mixture) was subsequently used for the acid leaching process.

To determine the total amount of Li and Al in the $LiF/(NH_4)_3AlF_6$ mixture (Li_m and Al_m, respectively), 1 g of the sample was leached in 100 mL of 10% (v/v) H_2SO_4 for two hours to ensure complete sample dissolution (Resentera et al., 2021). The Li and Al amounts were analytically determined in the leach liquor.

2.2.2. Acid leaching stage

$LiF/(NH_4)_3AlF_6$ mixtures were leached in sulfuric acid solutions (Alkemit, 98% w/w). The system was studied using a Box-Behnken experimental Design (BBD). The operational parameters investigated were the solid/liquid ratio (30 - 100 g/L), sulfuric acid concentration (4 - 12% v/v), and leaching time (10 - 60 min). Each leaching was carried out in 100 mL of acid solution at room temperature with a stirring speed of 330 rpm. The system was filtered after each experiment. Finally, Al and Li were determined in the leach liquor.

$(NH_4)_3AlF_6$ dissolution and Li extraction were calculated according to Equations (2) and (3), respectively:

$$(NH_4)_3AlF_6\ dissolution\ (\%) = \frac{Al_L}{Al_m} 100\% \tag{2}$$

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

where Li_L and Al_L are the lithium and aluminum amounts in the leach liquor, respectively, and Li_m and Al_m are the total amounts of lithium and aluminum in the $LiF/(NH_4)_3AlF_6$ mixture.

2.3. Data analysis

The phases present in the diffractograms were identified using the ICDD PDF2 database with X'Pert HighScore 2.1.2 software. The mass ratio between the phases of the $LIF/(NH_4)_3AlF_6$ mixture was estimated using the Rietveld method in the FullProf 2017 software.

The BBD results were analyzed by LS in Design-Expert 12 software. Furthermore, non-linear data for normal distributions were analyzed by ANN in SRO_ANN from MatLab. SRO_ANN is a non-parametric tool that uses radial basis functions (RBFs) (Giordano et al., 2017). Finally, the Li extraction conditions were optimized using the desirability function (*D*) with Design-Expert 12.

HSC 6 software was used to perform the thermodynamic calculations and build potential diagrams as a pH function (Eh-pH).

4. Results and discussion

4.1. Obtaining the LiF/$(NH_4)_3AlF_6$ mixture

Figure 1 presents the diffractogram of the fluorination products of α-spodumene with NH_4HF_2. The phases detected are LiF (PDF 01-078-1217), $(NH_4)_3AlF_6$ (PDF 01-076-0117), $(NH_4)_3SiF_7$ (PDF 01-074-0944), and NH_4HF_2 (PDF 01-071-1965). Spodumene is not observed according to the detection limits of the technique. The reaction is properly completed under these conditions according to Equation (1). NH_4HF_2 acts as a powerful fluorinating agent above its melting point (>126°C), completely breaking down the refractory structure of spodumene (Resentera et al., 2023a, 2021). Li extraction of 98 ± 2% from the ore is achieved (Li_m).

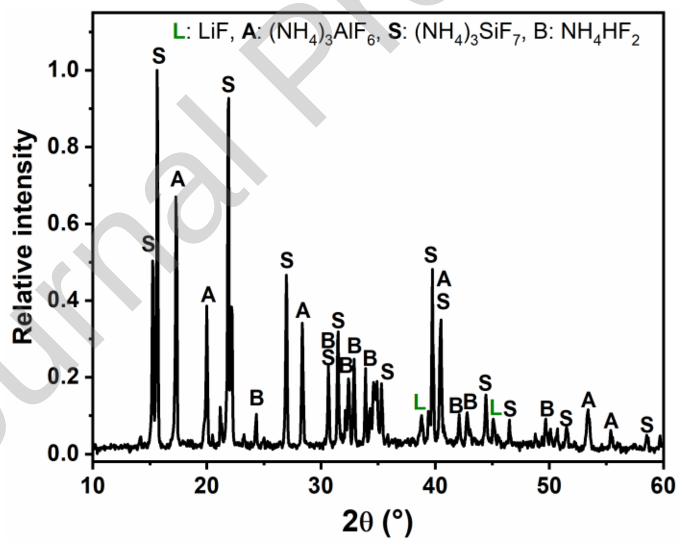


Figure 1. Diffractogram of the fluorination products of α-spodumene with NH_4HF_2.

The fluorination products are washed with distilled water to remove silicon compounds and unreacted fluorinating agent. Figure 2 shows the diffractogram of the solid obtained after washing (solid line) and the fit obtained by the Rietveld method (hollow dots). LiF and $(NH_4)_3AlF_6$ are the main phases detected. The asterisk in Figure 2 indicates a minor impurity that could be identified as $(NH_4)_2SiF_6$, remaining from the wash.

The summary of the parameters refined by the Rietveld method is presented in Table 1. LiF and $(NH_4)_3AlF_6$ crystallize in the cubic system, $Fm\bar{3}m$ and $F\bar{4}3m$, respectively. The phase mass ratio determined by the Rietveld method indicates 12.2(3) and 87.8(1)% for LiF and $(NH_4)_3AlF_6$, respectively. These values are close to the Li_m and Al_m and theoretical values, considering the contents of Li and Al in the ore sample.

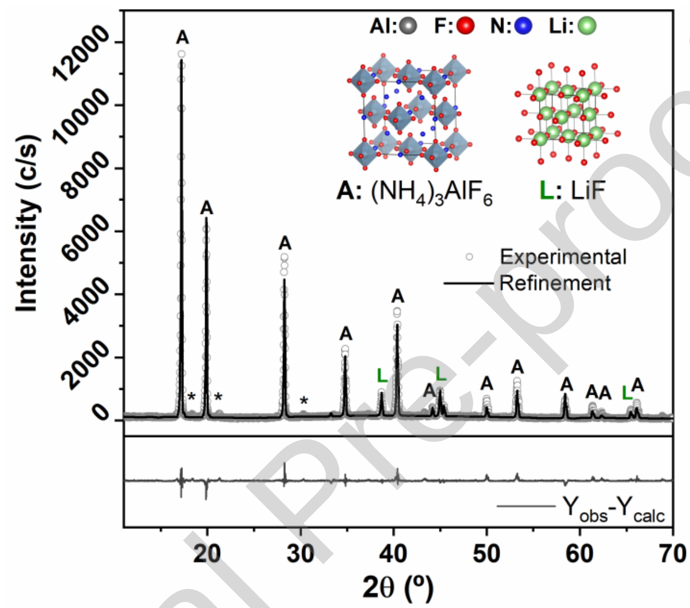


Figure 2. Diffractogram (solid line) and Rietveld refinement (hollow dots) of synthesized LiF/$(NH_4)_3AlF_6$ mixture.

Table 1. Crystallographic data obtained by Rietveld refinement.

Structure (SG[a])	**Cell parameters**	**At.**	**Wp[b]**	**x**	**y**	**z**	**Mass ratio (%)**
$(NH_4)_3AlF_6$ ($F\bar{4}3m$)	$a = b = c =$ 8.93490(4) Å $\alpha = \beta = \gamma = 90°$	N^{3+}	4b	0.5	0.5	0.5	87.8(1)
		N^{3+}	4c	0.25	0.25	0.25	
		N^{3+}	4d	0.75	0.75	0.75	
		Al^{3+}	4a	0	0	0	
		F^-	24f	0	0	0.19471(3)	
LiF ($Fm\bar{3}m$)	$a = b = c =$ 4.02657(2) Å $\alpha = \beta = \gamma = 90°$	Li^+	4a	0	0	0	12.2(3)
		F^-	4b	0.5	0.5	0.5	
χ^2 = 3.21, $(NH_4)_3AlF_6$: R_{Bragg1} = 10.4%, LiF: R_{Bragg2} = 9.92%							

[a]SG: Space Group, [b]Wp: Wyckoff position.

Figure 3 shows a SEM micrograph of the LiF/$(NH_4)_3AlF_6$ mixture. Mainly, the mixture has a poorly developed morphology associated with the growth in a molten medium. The particle in the center of the image displays a different morphology with straight cuts and well-defined edges on a porous surface. This morphology is also associated with crystal development in the cubic crystal system.

Particles with different morphologies also have different compositions. Two linear EDS linescan, L1 and L2, were performed as shown in Figure 3 (b). L1 linescan shows a composition compatible with the LiF compound (Figure 3 (b) top). The Li element is not detectable in this technique. The minimum Al signal in L1 is associated with the volume of the interaction of the electron beam with the particle, which is approximately close to 1 μm^3 at 20 kV (voltage used in the measurement). L2 linescan shows a composition closer to $(NH_4)_3AlF_6$ for N, Al, and F (Figure 3 (b) bottom). The linear scan also shows a low presence of Si in some zones related to an impurity.

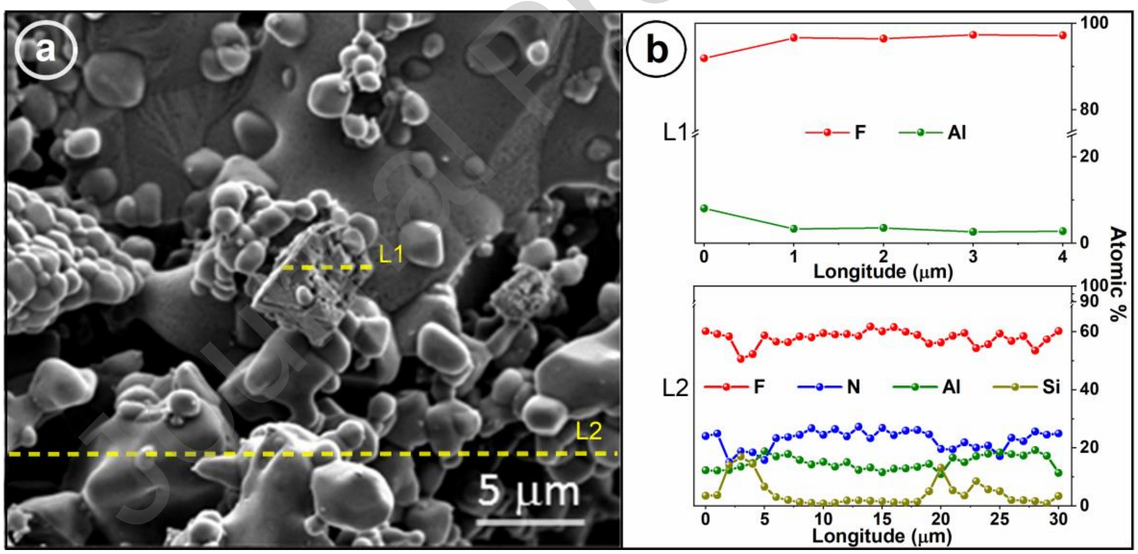


Figure 3. SEM/EDS analysis of the LiF/$(NH_4)_3AlF_6$ mixture. (a) SEM micrograph and (b) EDS linescans L1 and L2. Linescan are shown in (a) in dotted yellow lines.

4.2. Modeling and optimization of sulfuric acid leaching

The operating parameters of the LiF/$(NH_4)_3AlF_6$ mixture leaching with sulfuric acid are investigated from a BBD. Table 2 presents the design matrix used for the analysis and the experimental results obtained.

Table 2. BBD matrix and its experimental responses obtained.

Std. order	Run	Factor A	Factor B	Factor C	Response 1	Response 2
		S/L ratio (g/L)	H_2SO_4 (% v/v)	Time (min)	$(NH_4)_3AlF_6$ dissolution (%)	Li extraction (%)
1	11	30	4	35	96.6	92
2	10	100	4	35	51.3	25
3	3	30	12	35	97.6	96
4	7	100	12	35	97.1	30
5	2	30	8	10	98	96
6	13	100	8	10	93.8	17
7	15	30	8	60	99.5	92
8	1	100	8	60	89.6	25
9	6	65	4	10	94.1	27
10	9	65	12	10	97.2	63
11	4	65	4	60	99.6	32
12	12	65	12	60	96.9	77
13	14	65	8	35	97.7	50
14	5	65	8	35	98.1	42
15	8	65	8	35	98.3	40

$(NH_4)_3AlF_6$ dissolution data are nonlinear for normal distributions (Figure S1, Supplementary Material), so they are analyzed by ANN. The generated model has an architecture of three input neurons, ten hidden neurons, and one output neuron. Data training results indicated a good fit, where R^2 = 0.998, SD = 0.669, CV% = 0.714, pure error = 0.306, and a significant lack of fit (p = 0.185). Figure 4 presents the three-dimensional model obtained by ANN. Figure 4 shows the three-dimensional model graph that highlights the influence of the S/L ratio and sulfuric acid concentration (a), the S/L ratio and time (b), and time and sulfuric acid concentration (c).

According to Figure 4, the ANN model indicates that the main effects affecting $(NH_4)_3AlF_6$ dissolution are the S/L ratio and the acid concentration. The dissolution model clearly shows that acid concentration has a positive effect, S/L ratio has a negative effect, and time has little influence.

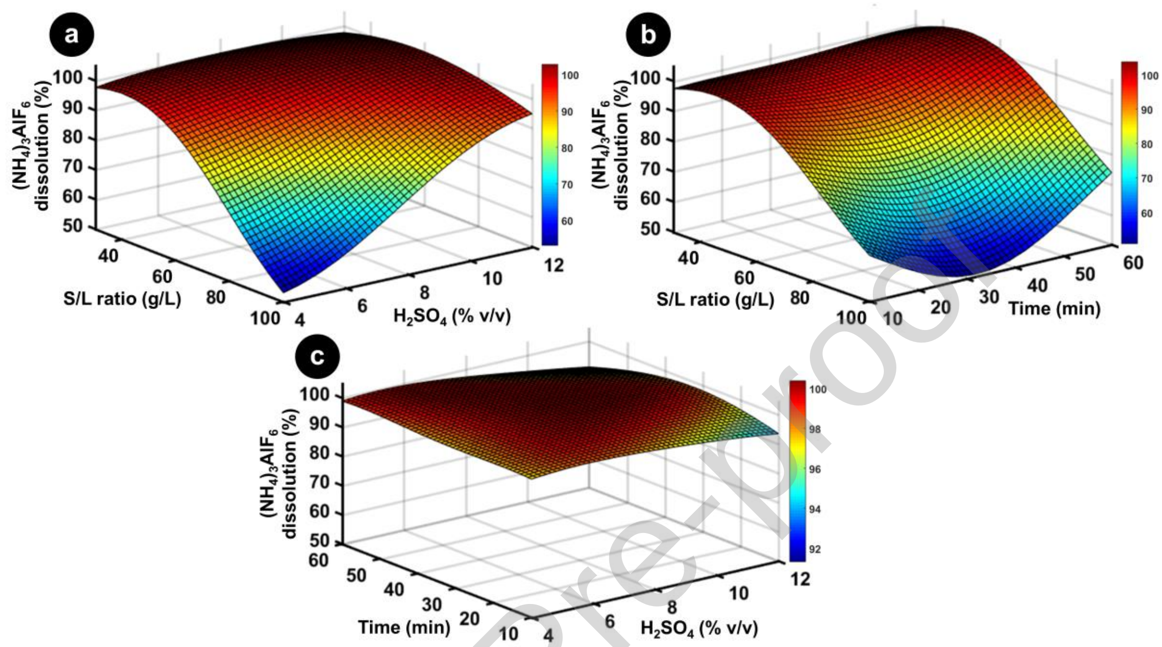


Figure 4. Modeling of $(NH_4)_3AlF_6$ dissolution by ANN.

The Li extraction is analyzed by LS to obtain a predictive mathematical model of the system (linear for normal distributions). Table 3 summarizes the results obtained by ANOVA for Li extraction.

Table 3. ANOVA for reduced cubic model for Li extraction.

ANOVA						
Source	**Sum of Squares**	**df**[a]	**Mean Square**	**F-value**	***p*-value**	
Model	11914.17	5	2382.83	70.21	< 0.0001	significant
A - S/L ratio	9730.13	1	9730.13	286.72	< 0.0001	significant
B - H_2SO_4	1640.25	1	1640.25	48.33	< 0.0001	significant
AB	0.2500	1	0.2500	0.0074	0.9335	not significant
A^2	523.30	1	523.30	15.42	0.0035	significant
A^2B	648.00	1	648.00	19.09	0.0018	significant
Residual	305.43	9	33.94			
Lack of Fit	249.43	7	35.63	1.27	0.5078	not significant
Pure Error	56.00	2	28.00			
Correlation Total	12219.60	14				

FIT STATISTICS			
R^2	0.9750	**SD**[b]	5.83
Adjusted R^2	0.9611	**Mean**	53.60
Predicted R^2	0.9237	**CV%**[c]	10.87

Adequate Precision	20.1527

[a]**df**: degree free. [b]**SD**: Standard Deviation. [c]**CV%**: Coefficient of Variation.

The reduced cubic model is significant according to the F value of 70.21. Statistical fit reveals a value of R^2 0.9750. The predicted R^2 and the adjusted R^2 are in good agreement, i.e., the difference is less than 0.2. Terms A, B, A^2, A^2B are significant from the model (*p*-values <0.05). The term AB (*p*-value = 0.9335) is included to maintain a model hierarchy since A^2B is significant. Furthermore, the non-significant lack of fit and Adequate Precision show that the model can be used to navigate the design space. Equation (4) presents the mathematical representation of the model with real variables that describes the extraction of Li:

$$Li\ extraction\ (\%) = 237.47886 - 6.08754\,A - 10.57398\,B + 0.479337\,AB + 0.039052\,A^2 - 0.003673\,A^2B \quad (4)$$

where A and B are the S/L ratio (g/L) and the sulfuric acid concentration (% v/v), respectively. The equation predicts the response over the entire design space (in the original units of each factor). Figure 5 shows the three-dimensional model graph that highlights the influence of the S/L ratio and sulfuric acid concentration (a) and the S/L ratio and time (b).

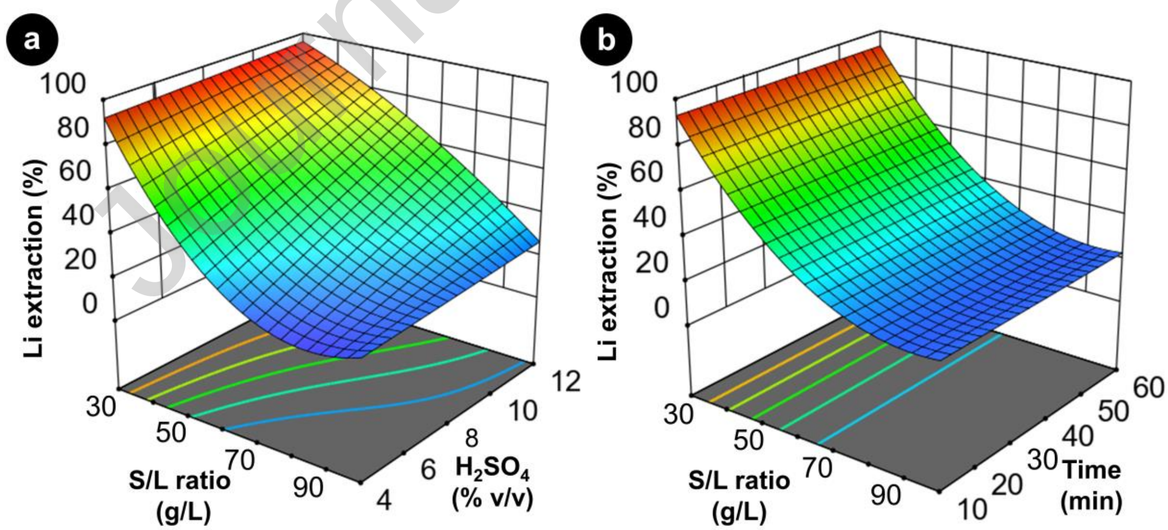


Figure 5. Modeling of Li extraction by LS.

Figure 5 (a) shows that Li extraction improves with increasing acid concentration and decreasing S/L ratio. Similar to what was observed for $(NH_4)_3AlF_6$ dissolution. Furthermore, the interaction between both parameters is revealed in the apparent convexity of the surface. As the acid concentration increases, there is greater availability of the leaching agent to react and form products (Pinna et al., 2017). In turn, by decreasing the S/L ratio, the solution is less saturated, favoring contact with the solid and mass transport. Furthermore, Figure 5 (b) shows that time has a non-significant influence on the system. The lack of residence time would allow the use of continuous process systems.

For both responses, factors A and B are of significant importance. However, the surfaces of the $(NH_4)_3AlF_6$ dissolution model show concave trends (Figures 4 (a) and (b)), unlike the Li extraction model (Figures 5 (a) and (b)). This reveals that $(NH_4)_3AlF_6$ is more soluble than LiF in an acid medium. I.e., $(NH_4)_3AlF_6$ dissolves completely with a lower S/L ratio and acid concentration than LiF. Also, as $(NH_4)_3AlF_6$ dissolves, less acid would be available to dissolve LiF.

4.3. Optimization

The optimization stage is important to maximize the dissolution of the compound and minimize operating costs. The desirability function allows us to quantify optimization conditions to find the best compromise results for both response and operating parameters (Resentera et al., 2021).

At this stage, only the Li extraction model is optimized. The experimental ranges studied were used as optimization limits. The details of the criteria followed for the Li extraction optimization are presented in Table 4.

Table 4. Optimization criteria for Desirability function.

Parameter	Goal	Lower limit	Upper limit	Lower weight	Upper weight	Importance
A - S/L ratio	Maximize	30	100	0.25	1	3
B - H_2SO_4	Minimize	4	12	1	1.5	3
C - Time	In range	10	60	1	1	3
Li extraction	Maximize	90	100	1	1	3

A maximum global desirability value of 0.339 is obtained. The optimal conditions suggested are an S/L ratio of 30 g/L, a sulfuric acid concentration of 6% (v/v), and a time of 24 min. Figure 6 shows the results obtained in the optimization stage. The Li extraction model predicts an extraction value of 93 ± 5% (95% confidence interval). This prediction allows obtaining high extractions of Li, considerably reducing the amount of sulfuric acid and the leaching time (Resentera et al., 2021). The optimal conditions suggested were confirmed experimentally in triplicate, obtaining values of 92 ± 4%. Furthermore, under these conditions, $(NH_4)_3AlF_6$ dissolution of 99.3 ± 0.6% were obtained in agreement with the ANN model.

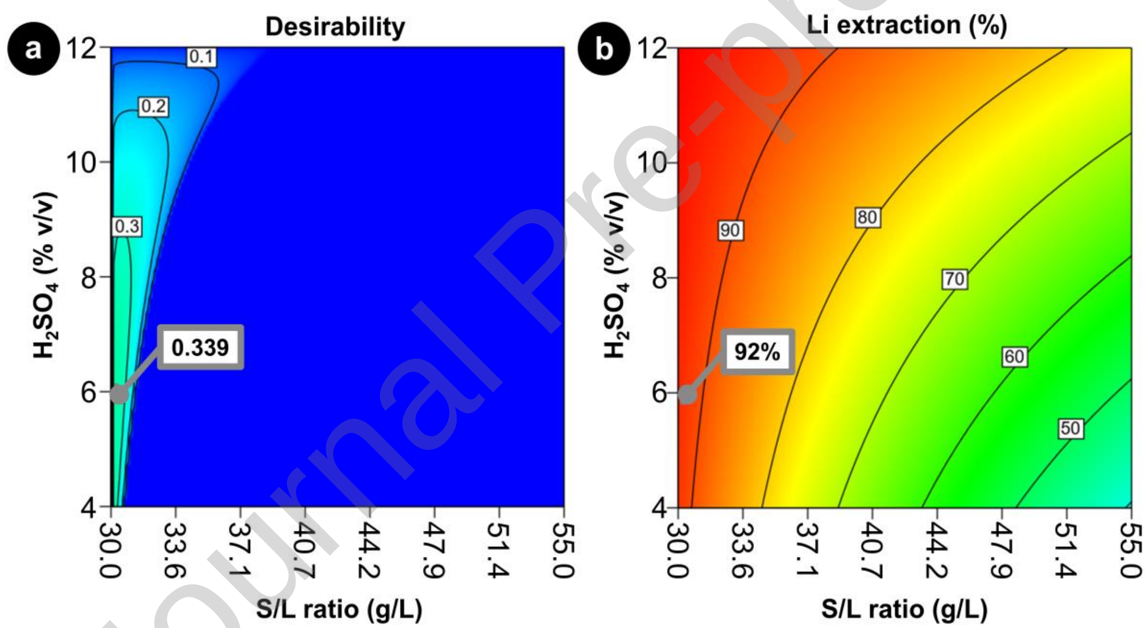


Figure 6. Process optimization results.

4.4. Proposition of dissolution reactions

An Eh-pH diagram was constructed to propose the possible dissolution reactions for LiF and $(NH_4)_3AlF_6$. The Eh-pH diagram for the Li-Al-F-S-N-H_2O system can be seen in Figure 7. It should be noted that there are no thermodynamic data for solid $(NH_4)_3AlF_6$. The dissolution of the species occurs at pH<7. The increase in pH leads to the precipitation of LiF. All the acid concentrations used in the BBD led to pH 1. The proposed dissolution reactions are presented in equations (5) and (6), according to the stable species observed at pH 1.

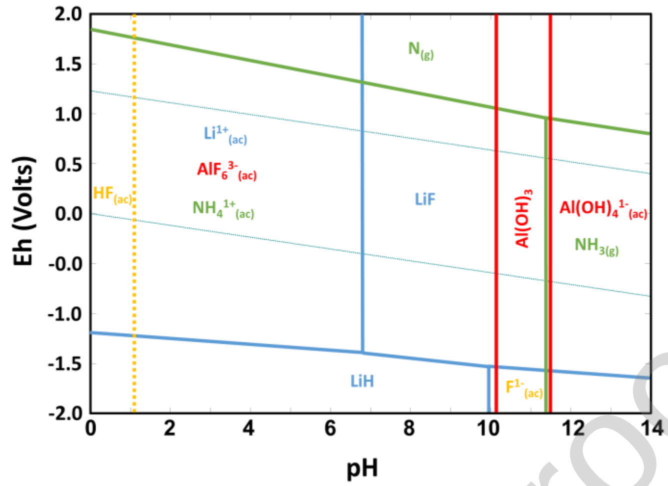


Figure 7. composite Eh-pH diagram for the Li-Al-F-S-N-H_2O system.

$$2LiF_{(s)} + H_2SO_{4\,(aq)} \rightarrow 2Li^{+}_{(aq)} + SO^{2-}_{4\,(aq)} + 2HF_{(aq)} \quad (5)$$

$$2(NH_4)_3AlF_{6\,(s)} + 3H_2SO_{4\,(aq)} \rightarrow 6NH^{+}_{4\,(aq)} + 3SO^{2-}_{4\,(aq)} + 2AlF^{3-}_{6\,(aq)} + 6H^{+}_{(aq)} \quad (6)$$

5. Conclusions

This work presents the modeling and optimization of the acid leaching operating parameters of the LiF/$(NH_4)_3AlF_6$ mixture. LiF and $(NH_4)_3AlF_6$ were obtained from α-spodumene processing with NH_4HF_2 at low temperatures. The mixture was characterized by XRD, SEM/EDS, and the Rietveld method. DOE and RSM were used to investigate the leaching operating parameters: solid/liquid ratio (A), sulfuric acid concentration (B), and leaching time (C). Two responses were modeled, Li extraction by LS and $(NH_4)_3AlF_6$ dissolution by ANN. Models indicate that $(NH_4)_3AlF_6$ dissolves more easily than LiF. A and B were the parameters that most influenced the responses. The optimization stage of the process shows Li extractions of 93% and $(NH_4)_3AlF_6$ dissolution of 99%, working with 6% (v/v) sulfuric acid solution and an S/L ratio of 30 g/mL for 24 min.

Finally, Figure 8 shows a complete scheme of the Li extraction process from α-spodumene with ammonium bifluoride. This scheme incorporates the optimization of thermal treatment operating parameters with that of LiF/$(NH_4)_3AlF_6$ mixture acid leaching. In this way, the entire process minimized operating costs and maximized the extraction of valuable metals from the mineral.

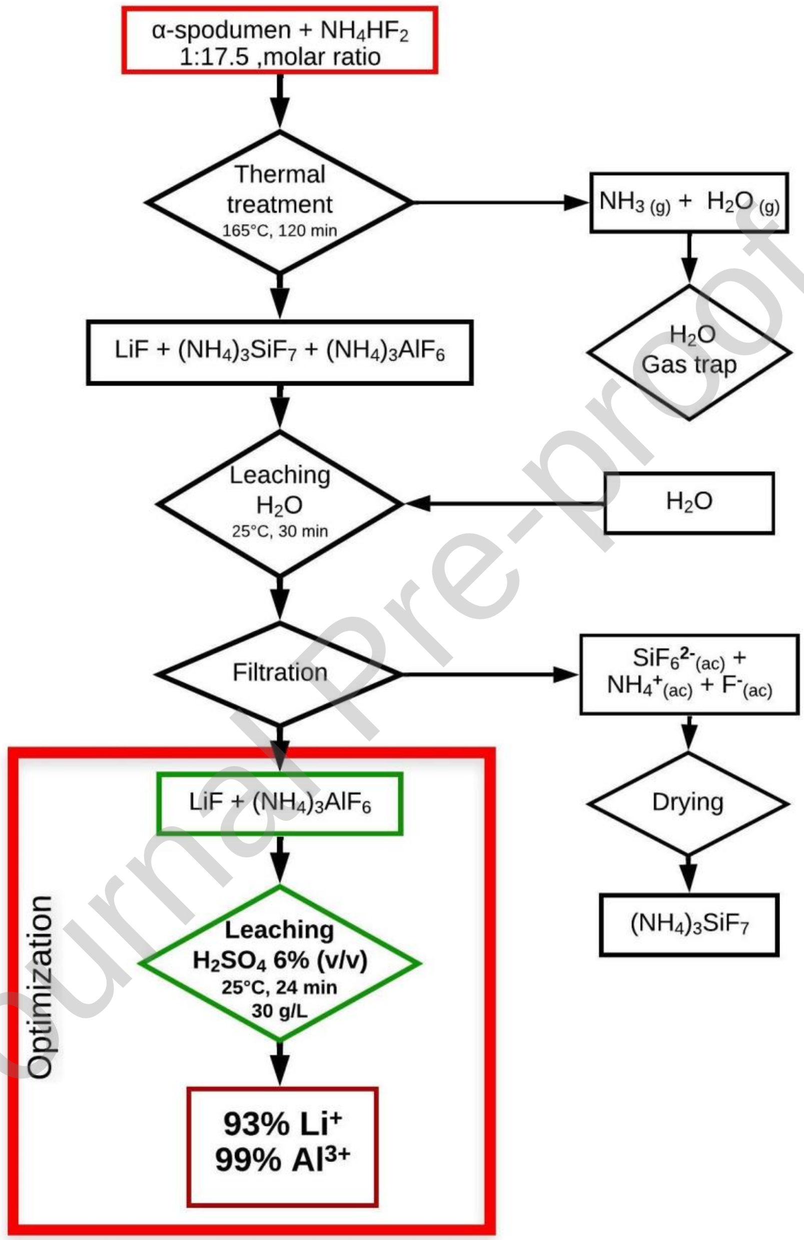


Figure 8. Scheme of the Li extraction process from α-spodumene with ammonium bifluoride.

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Declaration of interests

☒ 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.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Highlights

- The LiF/$(NH_4)_3AlF_6$ mixture is obtained by processing spodumene with NH_4HF_2.
- The LiF/$(NH_4)_3AlF_6$ dissolution is analyzed in an acid medium.
- Predictive models for LiF dissolution and total mass conversion are presented.
- Leaching time, S/L ratio, and acid concentration are analyzed.
- The optimal conditions tested led to Li extractions of 93%.