Lithium extraction from α-spodumene by low-temperature fluorination with NH_4HF_2

A. Resentera[1], G. Rosales[1], M. Esquivel[2,3], and M. Rodriguez[1]

[1]Laboratorio de Metalurgia Extractiva y Síntesis de Materiales (MESiMat), ICB-UNCUYO-CONICET, FCEN, Universidad Nacional de Cuyo, Padre Contreras 1300, CP 5500, Mendoza, Argentina.

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

[3]UNCo-Bariloche, Quintral 1250, CP 8400, Bariloche, Argentina.

Currently, lithium is considered a "critical energy element" worldwide, mainly due to its applications in energy storage technologies. [1] The "security of lithium supply" is a top priority for technology companies due to the continued increase in the consumption of mobile electronic devices, the demand for hybrid and electric vehicles, and the policies of adoption of energy storage systems in different countries of the world. [1] Furthermore, according to the growing world demand for lithium, world production is expected to be insufficient in the coming years. This situation has competitively positioned lithium mineral sources in the market. [1]

α-spodumene (4-8.03% Li_2O) is the main mineral considered for the extraction of Li. The only industrial Li extraction process is digestion with concentrated sulfuric acid. [2] The mineral is calcined at 1100°C to generate a phase change (β-spodumene) and digested with concentrated H_2SO_4 at 250°C. The main disadvantages of the process include the high consumption of energy required and that only 5% of the mineral is used, generating environmental liabilities. [1]

This work describes a novel method for Li extraction from α-spodumene by thermal treatment with NH_4HF_2 at low-temperature. The thermal analysis of the reactive mixture is carried out by thermogravimetry and differential thermal analysis (TG-DTA). The operational parameters of the thermal treatment (temperature, α-spodumene/NH_4HF_2 molar ratio, and reaction time) are analyzed and modeled using artificial neural networks (ANN) to maximize Li extraction. [1,2]

The α-spodumene (7.54% Li_2O), from the province of Catamarca Argentine, was mixed with NH_4HF_2 (commercial grade, ≥98%) in different molar ratios (1:10.5 to 1:21, respectively). The samples were thermal-treated in an oven equipped with a gas recovery system at 2°C/min between 100 and 170°C for reaction times of 60 to 120 min. The solids obtained were leached first with water, to eliminate the unreacted NH_4HF_2 and the ammonium fluorosilicates generated, and secondly with 100 mL of H_2SO_4 at 10% v/v (Alkemit) to dissolve the extracted Li. The solids were dried and characterized by XRD, and Li was determined in the liquors by flame photometry.

Figure 1 shows the results of the TG-DTA analysis. The curves indicate six apparent endothermic stages with associated mass losses during the process. The first event (124°C) agrees with the NH_4HF_2 fusion. The second peak appears at 145°C as a shoulder and is associated with the reaction between α-spodumene and NH_4HF_2 (reaction (1)). [1] The third peak (152°C) is mainly due to the maximum decomposition of NH_4HF_2. The events observed at 158, 212, and 227°C correspond to the decomposition of the products of Si and Al, obtained in reaction (1). The mineral fluorination and the NH_4HF_2 decomposition occur simultaneously in a limited range of temperatures, between 100 and 170°C, approximately. [1]

$$\alpha - LiAlSi_2O_6 + 10,5\ NH_4HF_2 \rightarrow LiF + 2\ (NH_4)_3SiF_6 \cdot F + (NH_4)_3AlF_6 + 1.5\ NH_{3(g)} + 6\ H_2O \quad (1)$$

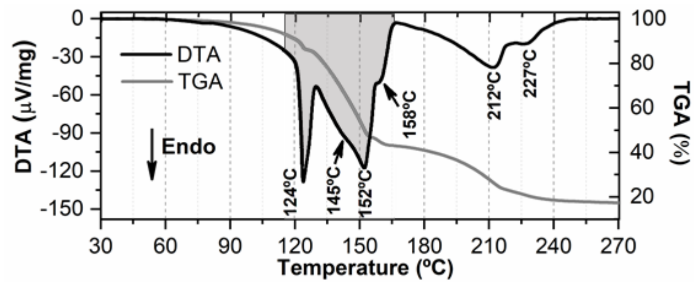

Figure 1. TG-DTA analysis of the α-spodumene/NH_4HF_2 mixture at 2°C/min.

Figure 2 presents the results of the Li extraction analyzed ANN. The data training results shows a good fit, with values of R^2 = 0.99801, SD = 1.4701 and CV% = 1.9747.
According to the model, the temperature has the greatest influence on Li extraction because it controls the rate of fluorination reaction and NH_4HF_2 decomposition. The amount of NH_4HF_2 and time also have a positive influence on the process. These allow to improve the diffusion of the liquid NH_4HF_2 through the mineral structure, increase the contact surface and the interaction time.

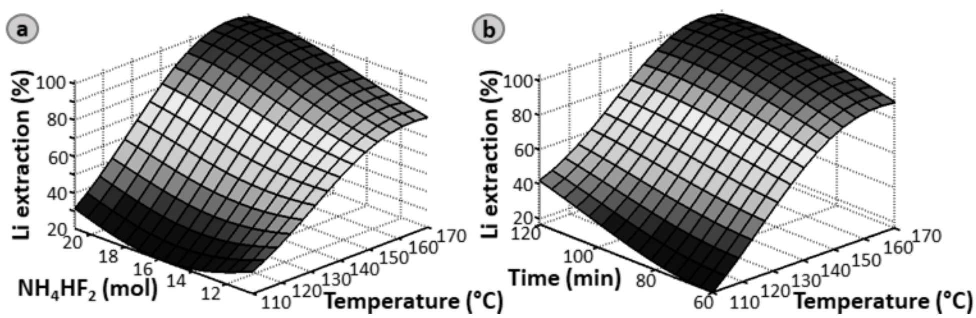

Figure 2. Modeling of Li extraction by ANN. (a) Influence of the NH_4HF_2 amount and temperature and (b) effect of time and temperature.

Li extraction values of 99% are obtained with a molar ratio of α-spodumene:NH_4HF_2 of 1:17.5 at 155°C for 120 min. Also, the water leach liquor can be evaporated to obtain $(NH_4)_3SiF_6 \cdot F$ as by-product. These can be used directly in the synthesis of mesoporous zeolites or amorphous silica.

Keywords: Lithium, Spodumene, Ammonium bifluoride, Artificial neural networks

References:
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