

PURIFICATION OF LITHIUM CARBONATE BY ION-EXCHANGE PROCESSES FOR APPLICATION IN NUCLEAR REACTORS

Mariana N. Andrade¹, Glaucia A. C. Oliveira¹, Débora A. Pirani¹, João F. Coutinho¹, Vanderlei S. Bergamaschi¹, Jose A. Seneda¹ and José O. V. Bustillos¹.

¹ Instituto de Pesquisas Energéticas e Nucleares (IPEN / CNEN - SP)
Av. Professor Lineu Prestes 2242
05508-000 São Paulo, SP
mariana.no vaisandrade@gmail.com

ABSTRACT

Lithium Compounds have applications in strategic areas for intern consumption of a country as well as international commerce. In nuclear industry, the lithium is used for the cooling of PWR reactors as a pH stabilizer. Based on this assumption, the generation of knowledge to master the processing cycle of these compounds is essential. The high degree of purity of lithium compounds is determinant to have success in these applications. Lithium hydroxide LiOH and lithium carbonate Li₂CO₃ are the main forms in which lithium is used industrially. To improve the quality of the starting product, purifying process were used until obtaining an adequate purity level of raw material (> 99%). The present work aims to make feasible a purification of Li₂CO₃ through ion-exchange chromatography from a 98.5% purity compound. The impurities present in higher content are sodium and calcium. To separate these two elements from lithium or at least to lower their concentrations, a column with cationic resin was used to fix lithium. The determination of lithium, sodium and calcium contents in the solutions was performed by inductively coupled plasma optical emission spectrometry, ICP-OES. The experiments performed to evaluate the best lithium purification condition were based on the variation of the main operational parameters: pH, flow and elution solution. The results indicate increased purity from the application of ion exchange operations obtaining a suitable condition for nuclear uses.

1. INTRODUCTION

Lithium is an alkali metal, the smallest and lightest atom between all the metals of the periodic table, under normal conditions of temperature and pressure. The name lithium comes from the Greek *lithos*, which means rock. It is the 25th most abundant element in the earth's crust (20 ppm) but is very dispersed. It was discovered in Sweden in 1817 by Johan August Arfwedson, a chemist, while examining the petalite mineral which discovery was made by a Brazilian, José Bonifácio de Andrada e Silva.

The obtainment of lithium compounds, specifically lithium carbonate, Li₂CO₃, is the result of extraction processes from several minerals. Its most abundant minerals are the lepidolite, K(Li, Al)₃(Si, Al)₄O₁₀(F, OH)₂, and spodumene, LiAl(SiO₃)₂, from which lithium is most frequently obtained and it's the main source of lithium in Brazil, Australia and Canada.

The increasing technological importance of lithium has highlighted the concern with world reserves and the obtaining of the element. Products with a purity of about 85% in Li₂CO₃ are used for applications in synthetic enamels, adhesives, greases and lubricants. However, for uses in nuclear industry, it's necessary a high level of purity, > 99%.

The lithium-7 isotope can be used as a coolant in high temperature reactors due to its low vapor pressure, good thermohydraulic properties and demonstrated compatibility at high temperatures. A nuclear reactor coolant circulates through the reactor core to absorb the heat it generates. The heat is withdrawn from the reactor and is then used to generate steam.

Despite all technological and economic potential, Brazil currently produces only technical-grade lithium compounds, in other words, lithium chemicals (lithium carbonate and lithium hydroxide) with a purity of less than 99%. The present work aims to develop a process for the purification of lithium carbonate via ion exchange.

Ionic exchange is a high efficiency technique that separates the ions through ion exchange chromatography. In ion exchange chromatography, the anions in the sample are charged through an ion exchange resin (stationary phase). Ion exchange resins are polystyrene spheres that have been treated to attach ion exchange sites on the surface of their granules. Depending on the type of resin, they may be of the acid type (cationic resins) which retain most of the cations by replacing these by H^+ or the base type (anionic resins) which retain most of the anions by replacing these by OH^- .

Since in aqueous solution, the lithium will be in the form of Li^+ , cationic resins are frequently used. Several are the cationic resins and the experimental conditions that can be used to obtain such purification. The purity level achieved by this operation varies according to the experimental conditions of this ion exchange operation, the purity of the starting compound, and the impurities present.

The major impurities that may be present and which make it difficult to obtain high purity values in lithium compounds are sodium, calcium and other alkali metals and alkaline earth metals, since all these and even the lithium present very similar chemical characteristics thus making difficult the fractionation between these elements of the two groups.

2. MATERIALS AND METHODS

In the purification of lithium carbonate, the materials, reagents, equipment and methods listed below were used.

2.1. Materials

- Glass column, 20 cm x 2 cm;
- 15 and 50 mL centrifuge tubes in polypropylene, with lid;
- 50 mL glass beaker;
- Long stem glass funnel of approximately 50 mL capacity;
- Filter paper, slow filtering, Whatman;
- 100 ml glass Erlenmeyer.

2.2. Reagents

- Hydrochloric acid, HCl, 37%, Merck Millipore;
- Nitric acid, HNO_3 , 65%, Merck Millipore;
- Methanol, MeOH, Merck Millipore;

- Lithium carbonate, Li_2CO_3 , 98.5% purity, CBL;
- Strong acid cationic resin AG 50W-X (H), Bio-Rad Labs. INC.

2.3. Equipment

- Optical Emission Spectrometry with Argon Plasma Source, ICP-OES, Spectro Flame M120, Modula, Spectro Analytical Instruments;
- Peristaltic metering pump, Milan Equipamentos Científicos LTDA;
- pHmeter , Model 420A, Orion Analyser;
- Magnetic stirrer, Quimis;
- Heating plate, Eletolab.

2.4. Methods

Initially, for the ion exchange procedure, the column was coupled to a peristaltic metering pump and packed with the resin conditioned with a solution of HNO_3 and MeOH. A lithium solution was prepared from the lithium carbonate powder (load solution) and added to the column.

Centrifuge tubes were used to collect the aliquots during the ion exchange experiments. The aliquots with MeOH were first filtered (slow filtration) and brought to the heating plate at 80 ° C to evaporate the MeOH. Then they were again filtered to ensure a clear aliquot to the initial volume in order to not damage the analytical equipment.

For the determination of lithium, sodium and calcium in the aliquots, analyzes were performed by Optical Emission Spectrometry with Argon Plasma Source, ICP-OES, and from this it was possible to verify the data and compare what method would apply to the purification of Li_2CO_3 .

3. RESULTS AND DISCUSSION

Countless experiments were performed in order to obtain the purification of Li_2CO_3 and in each of them, the parameters used were modified in amount of resin, pH in which it was conditioned, MeOH concentration, HNO_3 concentration, flow time and solution concentration of Li_2CO_3 .

Since the starting compound (Li_2CO_3) had 98.5% in Li purity, the result shown below is most significant obtaining a higher than 99% purity. The purification observed in the form of the chromatographic resolution of the peaks of the main cations present was obtained in more than one working condition.

The result of the ion exchange was the resolution of the cations peaks, where Li is the first cation to be eluted, followed by Na and Ca. Thus, the fractions containing these cations can be collected individually which means obtaining a fraction containing lithium where the concentrations of sodium and calcium are extremely low.

Figures 1 and 2 show the graphs where the separated Li, Na and Ca peaks are observed during the run of this operation.

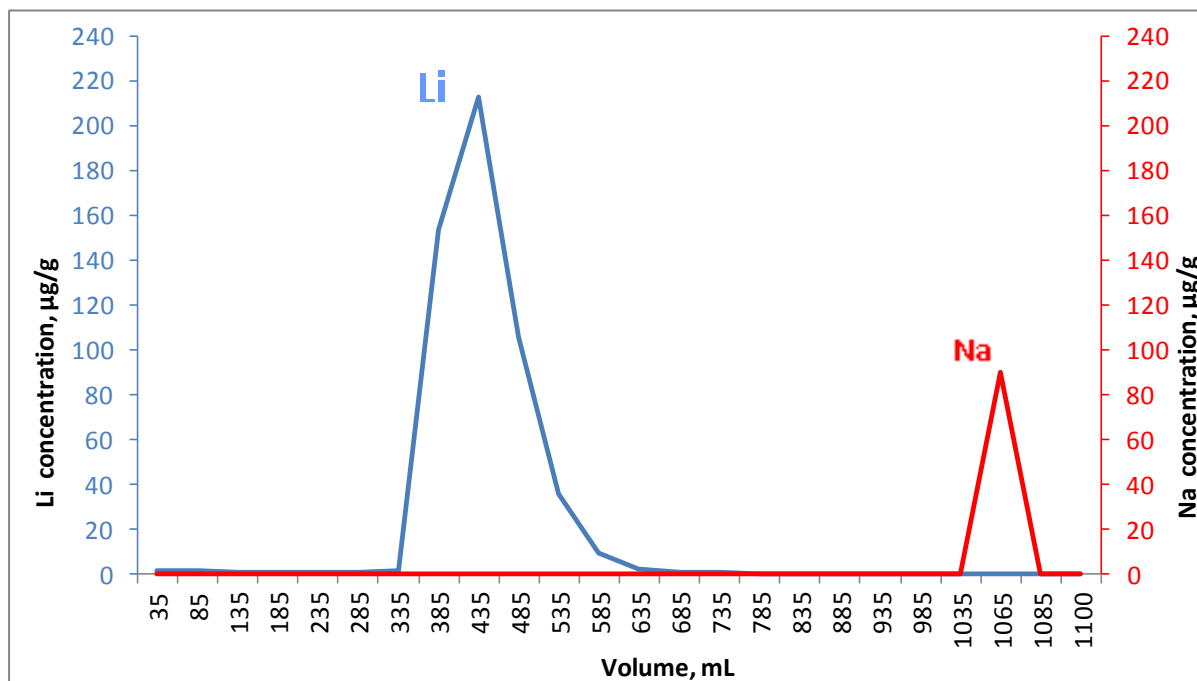


Figure 1: Chromatographic profiles of the Li and Na cations in the experiment.

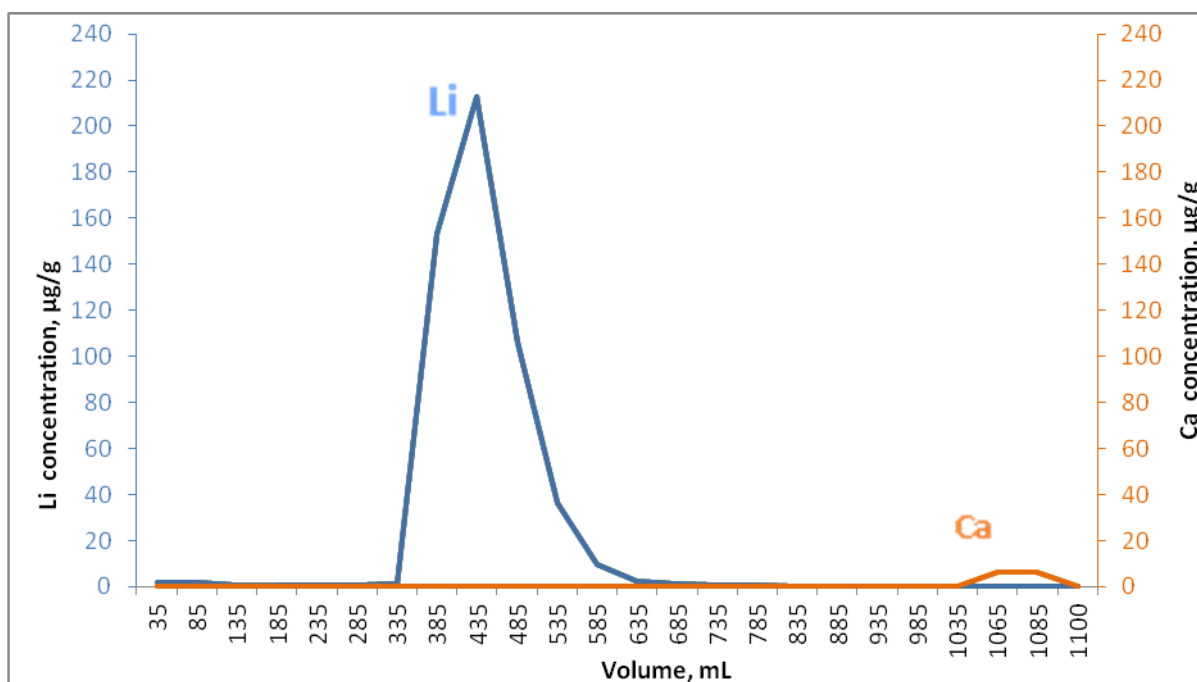


Figure 2: Chromatographic profiles of the Li and Ca cations in the experiment

From the analysis and evaluation of the results and experimental conditions, it is considered that the resolution/separation of the peaks of these cations is positive, and three are the parameters of greatest influence: 1) flow during the cation elution step (in mL min⁻¹); 2) the nature of the eluent composition (MeOH, HNO₃ and H₂O) and the respective concentrations; 3) the amount of resin/cation amount ratio.

4. CONCLUSIONS

Although lithium and sodium exhibit similar behavior when in aqueous solution, a satisfactory separation was obtained through the ion exchange. A great advantage of this process is that it dispenses with the use of large amounts of water. Even though still on bench scale, the whole cycle of this process can be easily reproduced for higher scales as a pilot assembly or even on an industrial scale. The reagents used are easy to acquire in the national market and do not require the need for special equipment or the elaborate experience of the possible operators.

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