2021 International Nuclear Atlantic Conference – INAC 2021
Virtual meeting, Brazil, November 29 – December 2, 2021

ISBN: 978-65-594-1256-3
9 786559 412563

Fractionation Lithium Isotopes by Inorganic Ion Exchange

João C. Ferreira1, José A. Seneda[1], Vanderlei S. Bergamaschi[1] Maíse P. Gimenez[1] and Oscar V. Bustillos[1]

[1] *jcferrei@ipen.br*
[1] Instituto de Pesquisas Energéticas e Nucleares (IPEN / CNEN - SP)
Av. Professor Lineu Prestes 2242
05508-000 São Paulo, SP

1. Introduction

Lithium has been receiving greater importance in recent years in the electronics and related industries, due to economic and technological interests that lithium can provide to the world. Within this prospect of technological evolution, the Companhia Brasileira de Lítio (CBL) and the Nuclear Energy Research Institute (IPEN/CNEN), which has competence in research and development, signed a partnership, a technique with the purpose of improving the raw material in the purification of compounds from the lithium and in isotopic separation using the ion exchange technique. Natural lithium is composed of two stable isotopes, Li-6 which has an abundance on average of 7.52% and 92.47% of Li-7 which has a Li-6/Li-7 isotope ratio of 0.0813 [1]. In the nuclear industry, Lithium-6 is used as tritium in nuclear reactors and lithium-7 in the form of lithium hydroxide has been used as a moderator to control the pH of the cooling water in the primary circuit of PWR reactors. Due to its chemical properties very similar to the isotopic separation of lithium, it is very complex, and it is necessary to adapt fundamental concepts that make it possible to frequently supply energy to the system [1,2]. As ion exchangers are mass dependent, it associates the difference between the molar fractions of the desired isotope and the other isotope in different parts of the system, which is associated with the speed of movement between the two isotopes and the chemical balance. Two causes are possible, that result in the isotopic phenomenon: the first because the molecules that contain the lighter isotopes have higher speeds and lower bonding energy. The second involves the redistribution of isotopes among several species in a chemical equilibrium process [3,4]. When equilibrium is established, the speed of the direct and inverse reactions are equal and the isotopic abundances in the reactants and products remain constant [4]. To improve the separation efficiency of lithium isotopes, several methods were investigated in the last decades, including amalgam, laser, electro migration, membrane separation, solvent extraction, and ion exchange chromatography. The mercury amalgam method remained superior to others and used in large scale separation of lithium isotopes due to its attractive separation factor (1.054 ± 0.002). However, the use of large volumes of toxic mercury brings serious environmental and biological problems this has awakened interest in extracting solids – liquids for separation of lithium isotopes.

2. Methodology

In this preliminary study, 50 g of dry cationic resin Amberlite 50W-X12 (100-200 mesh) packed in a glass column 120 cm long and 10 mm in diameter was used to evaluate the behavior of ion exchange resins as an exchanger isotopic. An aqueous solution of lithium chloride dissolved in 0.15 M hydrochloric acid with 80% of the methyl alcohol complexing agent was prepared and fed into the column at a temperature of 25 °C, with a flow rate of 0.1 mL min^{-1}. The effluent was collected in 20 mL fractions for isotopic analysis. The analytical techniques of Atomic Absorption and Mass Spectrometry were necessary to monitor the process.
The separation coefficient was calculate using the alpha separation factor (α) relative to the abundance R of the Li-6/Li-7 isotopes in the solution, according to the equation 1.

$$\alpha = R` / R”$$
$$Rn = R_0 .\beta^n \quad (1)$$
$$\beta^n = Rn/ R_0$$
$$\alpha = \beta^2$$
$$R` = x` / 1\text{-}x`$$
$$R” = x” / \ 1\text{-}\ x”$$

Where, x' is the molar fraction of the isotope in the enriched phase and x'' is the molar fraction of the isotope in the depleted phase.

Equation 1 represented by the letter alpha (α) dependent on the abundance R.

The technique used for isotopic determination of Li-6 and Li-7 was inductively coupled plasma mass spectrometry (ICP-MS). This technique is based on the production of a gaseous ion beam on the sample of interest.

3. Results and Discussion

To determine the concentration of Li in the samples, an analytical method was develop by ICP-MS and the analytical curves were constructed from five different concentration points of the lithium standard, as shown in Figure 1. Using the intensity data of each one of the monitored isotopes, the molar ratio of Li-6 and Li-7 was calculated, shown in Table 1.

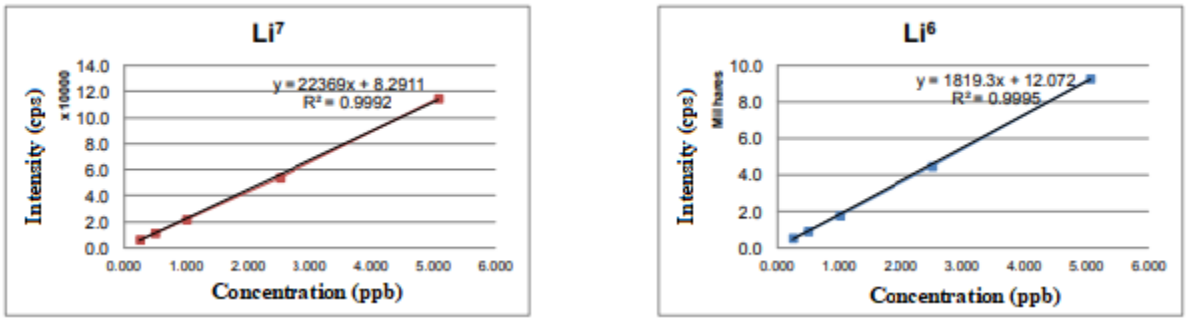

Figure 1: Analytical Curves of Li-6 and Li-7

Table 1: Results of Li-6 and Li-7 molar ratio by ICP – MS

Sample Description	% Li^6 (mass)	% Li^7 (mass)	Molar ratio Li^6/Li^7
Initial Solution	6.52	93.48	0.0813
Fraction 1	7.47	92.58	0.0940
Fraction 2	7.39	92.61	0.0930
Fraction 3	7.33	92.66	0.0927
Fraction 4	7.38	92.62	0.0929
Fraction 5	7.30	92.70	0.0925

In the present work, the value of the isotopic coefficient was determined by calculating the average of the molar ratios of the 5 sequential fractions, obtaining a value of 0.09302. The Molar Ratio depleted charge solution was keep with the initial ratio of 0.0813, used in the calculation of the separation factor.
The molar ratio, in the initial solution and the average, was used to calculate the upper separation factor (β = 1.0144) according to equation 1. This B factor was used to calculate the isotopic separation factor (α = 1.029), close to the literature reference for this resin 50 W– X12. In general, the isotope separation coefficients depend on the concentration of isotopes in both the solution and resin phases, for this reason, the use of a resin with a high degree of crossover is necessary to continue this study.

4. Conclusions

It was observed that the specifications of the resin that the experiment had selectivity conditions which enable to carry out the isotopic separation of lithium by the ion exchange method. The separation coefficient obtained was 1.029, which values for the 50W-X12 resin are in the range of 1.006 to 1.026, thus showing the effectiveness of the process. This study is in line with the lithium project developed by IPEN/CNEN-SP and CBL to seek sustainable isotopic separation alternatives. Resins with higher % DVB rate, complexing resins, adsorbent associated with solvent extraction technique, macrocyclic with low hydration coefficient and others are studied, obtaining a selectivity condition close to 1.054 produced by the Amalgam Hg-Li method.

Acknowledgements

The authors would like to thank the “Companhia Brasileira de Lítio” - CBL and IPEN for all the support in this research.

References

[1] MACEDO, S. H. G, F. Separação Isotópica de Litio:Estudos preliminares. Dissertação de Mestrado, Universidade Federal, Rio de Janeiro, 1998.
[2] NOMURA, Y.B. M., FUJII, Y. Chromatographic Separation of Lithium Isotopes with Silica Based Monobenzo-15-crown-5 Resin, Journal of Nuclear Science and Technology, 39:3, 279-281 (2002).
[3] NISHIZAWA., K., WATANABE, H., ISHINO, S., SHINAGAWA, M. Lithium Isotope Separation by Cryptand (2B, 2, 1) Polymer, Journal of Nuclear Science and Technology, 21:2, 133-138 (1984).
[4] FERREIRA, A.I.A.J.V. Espectrometria de massa de razões isótopicas. Faculdade de Ciências. Tese de doutorado, Universidade de Lisboa, 2008.