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Comparison of ion exchange methods for lithium-7 isotopic enrichment for application in PWR reactors

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1. Introduction

The Lithium 7 in the chemical form of LiOH monohydrate has a wide temperature range (between 180 to 1340ºC) in which it remains in the liquid state. Due to this property, it is considered an excellent candidate for use as a coolant in PWR (Pressurized Water Reactor) nuclear reactors. Furthermore, it is considered an excellent pH stabilizer to reduce corrosion of reactor primary circuit components.

The isotopes of a chemical element, specifically in the case of lithium, have very similar chemical and physical properties. However, these isotopes behave as completely different substances when used in applications in the nuclear area, mainly in relation to neutron absorption.[1] Consequently, the separation of its isotopes is necessary for this application, but there is a certain complexity in the separation of these isotopes.[2]

In the 1950s, some companies used the Colex method to enrich ^{7}Li, which consists of using mercury amalgam in separation by ion exchange. This method was banned in the USA in 1963 due to the great environmental impact caused by the exposure of mercury as waste, leakage and evaporation in the environment.[2,3] Currently the only sources of enriched ^{7}Li are Russia (80%) and China (20%).[3] Russia obtains ^{7}Li by electrolysis of lithium chloride, which also uses mercury.[3]

The ion exchange technique is a method where the separation of isotopes is carried out by balancing the fractionation of isotopes into two phases, one stationary (ion exchange resin) and the other mobile. There are three main techniques in ion exchange, frontal analysis, elution and displacement. In the frontal analysis, the filler solution itself is used as eluent. In the elution technique, after loading the resin with the problem ion mixture, separation is promoted by the addition of a solution containing ions with less preference than the ions to be separated, but in excess.[4,5]

In the displacement technique, one of the isotopes is adsorbed on the resin forming a band, which moves through the column by interaction with a displacement solution. The adsorption band moves maintaining a constant and distinguishable length of the displacement solution. The isotopes in the band are rearranged in the order of their distribution coefficients. This technique is widely used for isotopes of light elements due to its simplicity and achievement of satisfactory separation factors.[4,5]

In this work, three different procedures were carried out to enrich ^{7}Li by ion exchange using the technique of frontal analysis and displacement chromatography, with the aim of evaluating which technique is most suitable to obtain enrichment of ^{7}Li to 99.95% for application in a PWR reactor.

2. Methodology

To carry out the experiments, glass columns 120 cm long and 13 mm in diameter and acrylic columns 100 cm high and the same diameter were used. The resin used was AG 50w x16 of 200-400 MESH. LiOH and LiCl were used as loading solution. The samples collected from the columns were analyzed in ICP-OES, to determine the concentration, and ICP-MS to determine the isotopic ratio.

The Experiment 1, frontal analysis without saturation, used a feed solution of 400 mL of 0.02 M LiOH in an acidic medium and 30% MeOH, to adsorb on the resin. In three columns (460 mL of resin), this solution was recirculated for 744 cm in length. Then, each column was eluted with an acidic solution with 80% MeOH, and 20 mL samples were collected, which were analyzed in ICP-OES and ICP-MS.
The Experiment 2, frontal analysis with saturation, used the same columns as in Experiment 1, a 0.22 M LiOH solution was percolated in an acidic medium with 30% MeOH until saturation of the 3 columns. Then the separation and enrichment of the isotopes was promoted by circulating 3 L of LiOH solution in an acidic medium with 60%, 70% and 80% MeOH, the columns were eluted individually with 1.0 M HCl with 80% MeOH solution.
The Experiment 3, displacement chromatography, used 4 acrylic columns with resin at a height of 92.5 cm. The 0.15 M LiCl solution was percolated through the first column until saturation, then the band formed was displaced with 0.15 M calcium acetate solution. After 829.5 cm an aliquot was collected and analyzed.

3. Results and Discussion

Isotopic analysis was performed by Inductively Coupled Plasma – Mass Spectrometry ICP-MS ELAN DRC II – Perkinelmer. As a reference solution, the certified lithium carbonate isotope standard (International Atomic Energy Agency – IAEA) was used with a natural ratio of 0.08215 (^{6}Li 7.591% and ^{7}Li 92.409%). The ICP-MS analysis method was set to a concentration of 50 µg L^{-1}. The collected samples were analyzed in relation to the concentration in the ICP-OES and then analyzed in relation to the isotopic ratio. Table 1 shows the method parameters on ICP-MS.

TABLE 1. ICP-MS Method Parameters

Nebulizer Gas Flow	1.1 L min^{-1}
Radio Frequency	600 W
Gas flow rate	1.2 L min^{-1}
Peak Hoping mode	-
Dwell time	80 ^{6}Li 480 ^{7}Li
Sweeps per reading	50

The ^{7}Li enrichment result is presented in the abundance format of this isotope, as shown in Figure 1 below.

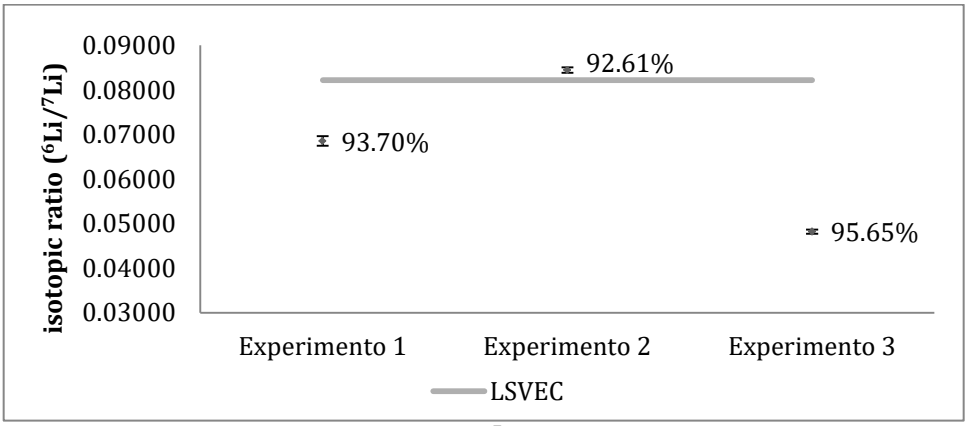

Figure 1. Abundance of ^{7}Li in each experiment.

The distance traveled by Li ions in experiment 1 was 744 cm and in experiment 3 it was 829.5 cm, in other words, experiment 3 was 11% longer than the experiment 1. However, the enrichment obtained in experiment 3 was 2.5 times greater than that obtained in experiment 1.

4. Conclusions

The ^{7}Li enrichment experiment did not reach the desired 99.95%, however preliminary results indicate that the ion exchange procedure using the displacement chromatography technique is more appropriate in relation to the frontal analysis technique to obtain the separation and enrichment of this isotope.

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References

[1] BAN, Y.; NOMURA, M.; FUJII, Y. 2022. Chromatographic Separation of Lithium Isotopes with Silica Based Monobenzo-15-crown-5 Resin. Journal of Nuclear Science and Technology, v. 39, nº 3, p. 279–281

[2] XIAO, J.; JIA, Y.; SHI, C.; WANG, X.; YAO, Y.; JING, Y. 2016. Liquid-liquid extraction separation of lithium isotopes by using room-temperature ionic liquids-chloroform mixed solvente system contained benzo-15-crown-5. Journal of Molecular Liquids, v. 223, 1032-1038.

[3] WNA – World Nuclear Association. "Lithium". Acessado em 30/07/2023. Disponível em [https://world-nuclear.org/information-library/current-and-future-generation/lithium.aspx]

[4] DING, X. & LIU, X. 2012. Nitrogen isotope separation by ion exchange chromatography. Em: Ion Exchange Technologies. Londres: Intechopen Limited, pp. 343 - 366.

[5] ABRÃO, A., 1972. Operações de troca iônica. 2014 ed. São Paulo: s.n.