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Prospects of lithium enrichment on $^7$Li isotope by method of controlled ions electro-migration

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Abstract. This paper deals with a new electro-membrane method of enrichment of $^7$Li isotope. The data are presented on the importance and application fields regarding the use of $^7$Li isotopes. Existing methods and criteria of separation of lithium isotopes are discussed. The principle of new technology, regimes of enrichment experiments, and analysis details of obtained products are briefly described.

I. Introduction
Lithium is a rare element scattered in the Earth's crust; its production, processing and purification are quite costly processes. Li is the lightest metal in nature. Natural lithium consists of two stable isotopes $^6$Li (7.52%) and $^7$Li (92.48%). One of the main sources of primary raw materials is lithium carbonate (Li$_2$CO$_3$). It is known that for industrial production of high purity LiOH·H$_2$O the most preferred method is hydrometallurgical electromembrane technology of conversion of primary lithium carbonate into solution of LiOH with simultaneous removing impurity ions Na$^+$, Ca$^{2+}$, Mg$^{2+}$, Al$^{3+}$ and anions SiO$_3^{2-}$, Cl$^-$ available in original Li$_2$CO$_3$.

In recent years, lithium has been widely used not only in the nuclear industry, but to regulate the water chemical regime, and also in lithium-ion batteries. However, it should be noted that almost all the important application of lithium is associated with isotopes, and a high level of isotopes enrichment is required up to the mono-isotopic purity of one of its stable isotopes.

$^6$Li isotopes are used:
- For production and replenish the fuel tritium 3H in power CTF reactors (controlled thermonuclear fusion).
- In the industrial production of tritium 3H isotope in nuclear reactors. At irradiation of natural mixture of lithium isotopes with neutrons the nucleus of $^6$Li, capturing thermal neutrons, decay into helium and tritium ($^6$Li + n → $^4$He + 3H + 4.78 MeV).

$^7$Li isotopes are used:
- In the development of a wide range of electrical rechargeable batteries, including for portable devices, transportable power sources of electric vehicles and stationary storage of electricity from renewable energy sources to support the utility grid during periods of peak load.
- In nuclear power: the addition of $^7$LiOH·H$_2$O allows to adjust the water-chemical balance of the coolant (pH-factor) in the 1st loop of reactors (boiling and with pressurized water).
Also in water treatment equipment (as part of ion-exchange membranes) of coolant of 1st loop of PW type reactors.

- In medicine: pharmaceuticals on the basis of lithium carbonate (Li₂CO₃) enriched by the \(^7\)Li isotope (rarely by the \(^6\)Li) are used as antidepressants/anxiolytics.

2. Existing technologies of \(^6\)Li and \(^7\)Li isotopes production

For separation of lithium isotopes most often are used the processes of ion exchange, chemical exchange, electrolysis and recently also electro-migration methods by use of ion-exchange membranes [1-3].

As a basis of widespread methods of industrial separation of lithium isotopes is isotope exchange reaction between the solution of lithium compounds and mercury-lithium amalgam. The method is not without a number of drawbacks, the main of which are:

- toxicity and large amounts of mercury, participating in the process
- amalgam trend to decomposition in aqueous solutions
- formation of dangerous mercury-containing waste
- high energy consumption

Therefore the search and development of new, environmentally less hazardous methods of separation of lithium isotopes is of undoubted practical interest.

The main criteria for evaluation of the process prospects of isotope separation are the followings.

Separation factor. Separation (enrichment) factor \(r\) is the ratio of the relative concentration of extracted isotope in the final product (after enrichment) relative to its concentration in the initial (row) mixture of isotopes:

\[
\frac{n'_1}{n'_2} = \frac{n_1}{n_2}
\]

were \(n_1\) and \(n_2\) are concentrations of isotopes with masses \(m_1\) and \(m_2\) before separation, whereas \(n'_1\) and \(n'_2\) are corresponding concentrations after separation.

Productivity - speed of obtaining the desired product.

Safety – level of negative impact on the environment and people health.

Download - original amount of the substance contained in the separation unit.

Startup time is the time from start-up of separation unit until achieving stationary conditions.

Efficiency - efficiency of use of the initial quantity of raw material.

Prime cost - financial costs for producing the mass unit of product.

As already has been noted, now for separation of lithium isotopes the popular is method based on isotope effect which arises during chemical exchange of lithium between lithium amalgam and aqueous solution of lithium compounds.

In this regard it seems interesting is the possibility to enhance the efficiency of isotope exchange [4] with consequent (simultaneous) slowing of reaction of amalgam decomposition which requires its periodic regeneration. This can be realized, for example, by applying electrical potential difference between contacting liquid phases of lithium amalgam and lithium hydroxide circulating countercurrent in conditions of maintaining the high values of ratio between the speed of the interphase chemical exchange of lithium and amalgam decomposition. It should be mentioned that such approach allows to combine the processes of ion and chemical exchange, electrolysis and electro-migration thereby strengthening their joint action.

3. Modification of amalgam method for \(^6\)Li and \(^7\)Li isotope production

3.1. Short description of the process

a) Lithium hydroxide LiOH-H₂O in aqueous solution was preliminarily subjected to a thorough electromembrane cleaning from impurities (Na, Al, Mg, etc.). It is known that lithium ions in solution are characterized by the highest electrode potential, -3.045 V (due to their small size and high degree of hydration). For comparison, the electrode potential of Mg and Na are -2.37 V and -2.71 V,
respectively. This property of lithium ions allows to remove from working compartment of electrodialyzer practically all known impurity cations and anions and to obtain lithium containing solution of very high purity, up to 4-5 (N). Then the purified solution of LiOH-H₂O is sent to the amalgam production unit.

b) In this unit the purified solution of LiOH-H₂O is fed into the working chamber (2) of the electrolytic cell shown in Figure 1. This is a known effective electrolytic method of producing an amalgam [5], which was proposed earlier for extraction of metals from liquid radioactive waste (LRW). The resulting amalgam is sent to the unit for separation of isotopes ⁶Li and ⁷Li.

![Figure 1. Electrolytic method for obtaining amalgam. 1 – electrolytic cell, 2 – solution of LiOH, 3 – residue, 4 – anode, 5 – cathode, 6 – diaphragm, 7 – mercury, 8 – amalgam.](image1)

c) Experiments were conducted in the separation unit [6] shown in the Figure 2 which presents an electrolytic cell with the following operating parameters: I = 150mA, U = 10 V, S = 100cm², V_mercury = 50cm³, V_solution = 300 cm³ and lithium content of 15g. Lithium containing solution is pumped in a closed loop.

Under the influence of an applied electric voltage between electrodes, cations of ⁷Li and ⁶Li isotopes migrate in solution with different speeds.

The spatial separation of isotopes in the cell volume occurs as follows. More movable and light ⁶Li⁺ ions will migrate faster through the membranes and bind to mercury amalgam, while the main part of ⁷Li⁺ ions is “lagging behind”. Some part of cations of isotope ⁷Li⁺ having time to migrate through the membrane are raised on the upper surface of the mercury cathode under the influence of the eddy currents generated on the side surface of the mercury amalgam.

![Figure 2. Scheme of electrolytic cell for separation of lithium isotopes. 1 – mercury, 2 – LiOH solution, 3 – dielectric, 4 – cation-exchange membrane.](image2)
Thus in this case the enrichment on lithium isotopes is controlled (simultaneously and interconnected) by three different factors: electro-migration through an ion exchange membrane (the probability of passing $^{6}\text{Li}$ isotopes) is high; the binding of isotopes in amalgam (the probability of binding $^{6}\text{Li}$ isotopes in mercury cathode) is high; and finally, Eddy currents - the $^{7}\text{Li}$ isotopes most likely are extracted from the side surface of mercury cathode on its upper surface.

We think that $^{6}\text{Li}$ isotopes are enriched in the bulk of mercury cathode, while $^{7}\text{Li}$ ions accumulated on the top surface of the mercury cathode and in the working chamber.

After three-hour operation, samples were taken from the anode (working) compartment, from the solution over the mercury cathode and from the solution after amalgam decomposition.

3.2. Method of measurement of $^{7}\text{Li}/^{6}\text{Li}$ ratio

Analyze to determine the isotope ratio were conducted by the mass spectrometer ICP-MS ELAN 9000, which gives a good opportunity to identify rare and trace elements and isotopes in a wide range with accuracy up to ng/l.

In experiments the standard solutions of $^{6}\text{Li}$, $^{7}\text{Li}$ (Perkin Elmer) were used.

As matrix solution the bidistilled 2% nitric acid in deionized water purified in apparatus Easypure II (18.2 MOm·cm) was used. For plasma formation and spraying the argon of 99.998% purity was used. Samples were injected into the system by a peristaltic pump in a cross-flow nebulizer, wherein their conversion in aerosol was occurred. Parameters of the analysis are shown in Table 1.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Discharge power</td>
<td>1400 W</td>
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<tr>
<td>Consumption of plasma generating gas</td>
<td>15 l/min</td>
</tr>
<tr>
<td>Consumption of atomizing gas</td>
<td>0.86 l/min</td>
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<tr>
<td>Scan mode</td>
<td>Peaks determination</td>
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<tr>
<td>Replicates (number of parallel measurements)</td>
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<tr>
<td>Integration time</td>
<td>5000 microsecond</td>
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<tr>
<td>Solution feed rate</td>
<td>1.3-1.4 ml/min</td>
</tr>
<tr>
<td>Input cones</td>
<td>Nickel</td>
</tr>
</tbody>
</table>

Analyses were carried out as follows: blank – standard – sample respectively. To reduce the “memory” effect the capillaries were washed with a 3% nitric acid during about 5-7 minutes. Results of $^{7}\text{Li} / ^{6}\text{Li}$ ratio were compared with the ratios in standard solutions and initial solution of lithium hydroxide respectively.

3.3. Preliminary results

$^{7}\text{Li}$ isotope separation coefficient $r$ measured according to procedure described above is equal to 1.178, confirming the prospects of this method of enrichment of lithium isotopes.

Experiments simulating the cascading process (when solution enriched by $7\text{Li}$ in first cell was used as an initial for second cell) have shown that values of separation coefficient can be kept on the level achieved in the first cascade.

Estimation of scalability made on the basis of performed experiments show that this method is able to provide the production of isotope $^{7}\text{Li}$ enriched up to 99.95% or higher in a continuous mode.

4. Conclusions

Thus, the proposed electromembrane method of isotopes separation is characterized as following:

- it is a modified version of the amalgam method of lithium isotope enrichment with a broad new opportunities for controlling the parameters;
• it allows to expect the obtaining of enriched lithium isotopes or mono-isotopic compounds in solution (hydroxides);
• it is characterized by high efficiency and profitability due to low power consumption for isotope separation;
• it has the prospect of scaling up to production on industrial scale;
• it is environmentally more attractive, more technological than existing methods for the separation of isotopes of lithium.

References