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REVIEW

Lithium Isotope Separation: A Review of Possible Techniques*

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Abstract

Published methods for ^{6}Li–^{7}Li lithium isotope separation have been reviewed. Future demand for ^{6}Li, whose main use will be as a tritium breeder in blankets surrounding the core of DT fusion power reactors, is likely to exceed 5 Mg/a in the next century. The applicability of the various available methods to such a large-scale production rate has been assessed. Research on improving the effectiveness of current lithium isotope separation processes has been carried out worldwide in several major areas during the past decade; these include two-phase chemical exchange systems, ion-exchange resin chromatography, and highly isotope-selective techniques like laser photoactivation and radiofrequency spectroscopy. Chemical exchange systems appear to offer good potential in the near term for ^{6}Li enrichment, but efficient, laser-based methods could probably be developed for large-scale production by early in the next century.

1. INTRODUCTION

There are two naturally occurring isotopes of the element lithium, ^{6}Li at 7.53% and ^{7}Li at 92.47% relative abundance (*1*). Each isotope plays an important role in the nuclear industry. Although natural abundance LiOH is utilized for corrosion control in CANDU pressurized heavy water fission reactors, highly enriched ^{7}Li lithium hydroxide is used for adjustment of coolant pH in pressuried light water reactors (*2*). ^{6}Li, in the form of LiH, is employed as a shield against thermal neutrons (*3*). In the future, lithium compounds containing up to 90% ^{6}Li may be required for the tritium breeder blanket in DT fueled fusion reactors (*4, 5*). The reason

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is that, because of the energy range of the fusion neutrons generated in the blanket material by Reaction (1), ^{6}Li has a much higher neutron capture cross-section for the production of tritium, Reaction (2), than does ^{7}Li, Reaction (3).

$$\begin{aligned} &\mathrm{D} + \mathrm{T} \rightarrow {}^4\mathrm{He} + n && +17.6\ \mathrm{MeV} && (1)\\ &{}^6\mathrm{Li} + n \rightarrow \mathrm{T} + {}^4\mathrm{He} && +4.8\ \mathrm{MeV} && (2)\\ &{}^7\mathrm{Li} + n \rightarrow \mathrm{T} + {}^4\mathrm{He} + n && -2.5\ \mathrm{MeV} && (3) \end{aligned}$$

As of late 1978 no ^{6}Li was being produced in the United States, either in commercial or government plants (*4*). The Colex process (see Section 2.1) facilities at Oak Ridge, Tennessee, were operated between 1955 and 1963 to generate the current US stockpiles of ^{6}Li and ^{7}Li (*4*). However, with the upswing in research in the area of fusion reactor technology there has been renewed interest during the last decade in better processes for ^{6}Li–^{7}Li separation, especially in Japan and the United States.

Although many techniques have been considered over the years for isotope separation in general (*6–8*), not all of them are applicable to the lithium case. In the 1940s and early 1950s most isotope separation work on lithium was done with two-phase equilibrium systems, where the isotopes are distributed between immiscible liquids. A review of data from that period was declassified and published only recently, in 1976 (*9*). After the discovery of new cation complexing agents like crown ethers and cryptands in the 1970s, two-phase liquid systems have come under study again, with encouraging results.

The Japanese in particular have been very active with various types of chromatography for the separation of lithium isotopes. Their publications in this area span at least 15 years (see Section 2.2), with the most recent work covering resin-bound complexing agents. A preliminary design for a 100-kg/a ^{7}Li recovery plant based on ion-exchange resin chromatography has been reported (*10*).

The availability of suitable lasers in the last few years has raised the possibility of their application to ^{6}Li-^{7}Li separation, and both theoretical and experimental results for lithium are now being published (Section 2.3).

All of the above major categories of isotope separation methods are reviewed in detail regarding their applicability to lithium in the following sections of this review. In addition, results for other relevant but less well known methods are summarized in Section 2.4. The potentials of the various methods for large-scale ^{6}Li production are compared in Section 3.

2. A REVIEW OF PUBLISHED METHODS FOR ^{6}Li-^{7}Li SEPARATION

2.1. Two-Liquid-Phase Chemical Exchange Systems

For a lithium compound distributed between two immiscible phases there is a slight tendency for ^{6}Li to be favored in one phase and ^{7}Li in the other, because of small differences in solvation. This is perhaps the most widely studied area for lithium isotope separation. The single stage separation factor, α_7^6, is defined as

$$\alpha_7^6 = \frac{([^6\mathrm{Li}]/[^7\mathrm{Li}])_{\mathrm{phase\ 1}}}{([^6\mathrm{Li}]/[^7\mathrm{Li}])_{\mathrm{phase\ 2}}}$$

Several important criteria must be met before any given two-phase system can provide a useable process with an acceptably large α (>1.03) (*8, 9, 11*). These are:

1. The element should be fairly evenly distributed between the two relatively immiscible solvents
2. The whole system should be chemically stable
3. A rapid exchange of the element should occur between the two phases when they are in contact
4. Preferably, the element should exist in different chemical forms in the two phases; at the least, the solvation environment must be significantly changed from one phase to the other
5. A simple method of countercurrent contacting and separation of the two phases should be possible on a continuous basis

Criterion 4 is critical to the magnitude of α, which is dependent on the extent to which the environment of the element varies between the two phases (*12*). Ideally, a gaseous form of the element is desirable as one phase (*11*), but for lithium no such compounds exist at or near ambient temperature. Second best is a system where the two forms of lithium have different oxidation states; the Colex process, described below, took advantage of this principle. For most cases studied, however, an attempt is made simply to maximize the difference in the types of atoms involved in bonding for the solvation sphere of lithium ions in the two phases. Examples of various systems are given in the following subsections, with a division made between studies done before and after the discovery of cyclic polyether cation complexing agents about 1967.

2.1.1. Reactions Studied before 1967

Chemical exchange methods for lithium isotope separation have been under investigation since the 1930s (*13*). Much experimental work was done in the 1940s in the United States to develop a process for ^{6}Li production, so that tritium could be obtained for thermonuclear weapons research (*4*). In 1976 a report describing much of the earlier work was released (*9*).

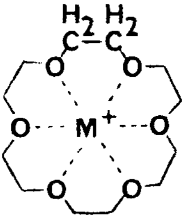
No significant isotope effects ($\alpha > 1.005$) were found for simple aqueous-organic or organic-organic two-phase systems involving distribution of lithium compounds (*9*). Usually the lithium salts were much more soluble in the aqueous phase. However, good results were obtained when one of the phases was a liquid lithium-mercury amalgam. A total of 17 amalgam-aqueous or organic liquid pairs was studied in detail; the effect of solvent and lithium salt on the separation factor α has been tabulated (*9*). For each system ^{6}Li was found to be enriched in the amalgam phase, with α varying between 1.02 and 1.06 at ambient temperature. The system finally chosen for the Colex process was aqueous LiOH contacted with $Li \cdot Hg$ amalgam (*4*). This process was used in the United States between 1955 and 1963 to separate ^{6}Li from ^{7}Li; stockpiles from that period have been available until recently to meet the relatively small demand.

The α for the Colex process ranged between 1.04 at 50°C and 1.06 at 0°C. It is generally believed that any new industrial plants for ^{6}Li enrichment would not be based on the amalgam system, mainly because of the hazards involved in handling huge volumes of toxic mercury (*4*). However, any chemical exchange process replacing the amalgam system will have $\alpha > 1.04$ as a prime target.

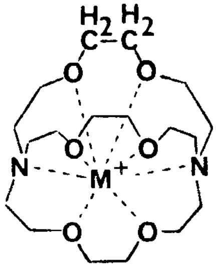
In spite of the health and environmental concerns associated with processes based on mercury, some research is still being done in this area to better define parameters. Japanese scientists have studied $Li \cdot Hg$-organic solvent systems to determine the effects of solvent, anion, salt concentration, and temperature on α (*14*). Impressively large α values were obtained for LiCl in dimethylsulfoxide (1.056 at 20°C), and in diethylformamide or dimethylsulfoxide (1.080 at 0°C, 1.084 at −15°C). The theoretical maximum value of the elementary separation factor for fractionation of lithium isotopes by molecular distillation is $[\text{mass of } ^7\text{Li}/\text{mass of } ^6\text{Li}]^{1/2} = 1.080$ (*14*).

2.1.2. New Cation Complexing Agents Since 1967

A vast literature on complexation of cations by macrocyclic polyethers and their analogues has appeared since Pederson reported the first results in this new field in 1967 (*15*). Many review articles, as well as a comprehensive book (*16*), have been published on the subject. Two representative crown ether and cryptand complexes are shown below, with their common names.



18-crown-6



2,2,2-cryptate

The cation is bound in the ring or inside the three-dimensional molecular cage by electrostatic forces between the positively charged ion and the electronegative oxygen atoms of the host. Significant selectivity can be achieved between cations of different elements in a mixture by optimizing the size of the available cavity for a particular cation, by changing the number of —OCH_2CH_2— groups in the rings. Because many of these compounds are at least partially soluble in organic solvents, or can be made so by attaching organophilic structures to the ring, a new method was found for solubilizing inorganic salts in such solvents. More importantly, when a metal salt is distributed between aqueous solution and an immiscible solvent containing a macrocyclic compound, designated as L below in Eq. (4), the solvation environments of the cation are quite different. This phenomenon was noted by scientists studying metal isotope separation by chemical exchange.

$$ {}^{x}M^{+}_{aq} + {}^{y}ML^{+}_{org} \rightleftarrows {}^{x}ML^{+}_{org} + {}^{y}M^{+}_{aq} \qquad (4) $$

The first reported use of such cyclic polyethers for isotope separation studies involved work by Jepson with calcium salts (*17*). Very recently, Jepson has determined separation factors for lithium isotopes distributed between aqueous solution and chloroform containing a selection of cyclic and polycyclic ethers (*18*). The largest value of α measured at 25°C was 1.036 ± 0.007 for lithium trifluoroacetate and the 2,2,1 cryptand; only the mercury amalgam systems have given higher values (Section 2.1.1).

Two papers have appeared from Chinese scientists studying lithium isotope separation with crown ethers (*19, 20*). Few details are available yet, pending translations, but the effect of many variables on α has been determined.

2.1.3. Other Systems with Some Potential

The desirability of ensuring significantly different lithium ion environments in the two immiscible phases, or if possible an oxidation state change in the element between the phases, was noted in Section 2.1. The following chemical systems offer some potential, although most have not been tested for lithium isotope separation.

Alkali metal/liquid amine mixtures often undergo a phenomenon known as phase separation at low temperature. For example, lithium dissolves in liquid ammonia below −33°C to give a solution of solvated electrons and lithium ions. However, between −63 and −78°C, at 2–8 mol% lithium, a second metallic-liquid phase of lower density exists that is richer in lithium than the solution phase (*21*). Preliminary tests have shown that there is an enrichment of ^{6}Li in the metal-like phase, with an α of 1.01 at −76°C (*21*). Suggestions were made for the general design of a lithium isotope separation process based on this observation, and for an extension of the study to other liquid amines like deuterated ammonia and methylamine (*21*). However, no new published work in this area has been located.

^{7}Li nuclear magnetic resonance spectroscopy has been used to show that the lithium ion in molten salt mixtures of LiCl ($\sim 10^{-2}$ mole fraction) in $AlCl_3$-*n*-butylpyridinium chloride "exists in very different environments on the acidic and the basic sites" (*22*). Acidic sites are present in mixtures containing >0.5 mole fraction $AlCl_3$, and basic sites when the mole fraction of $AlCl_3$ is <0.5. The significant differences in the ^{7}Li line position and shape were ascribed to the formation of two types of mixed chloro complexes with $AlCl_3$ (*22*). The addition of crown ethers to a basic molten salt mixture leads to formation of crown ether complexes of the lithium ion; ligand exchange is fast (*23*). This system may offer advantages for lithium isotope separation if a method of contacting the basic and acidic phases can be developed.

The equilibrium constant for the solid state reaction $^7Li(s) + {}^6LiF(s) \rightleftharpoons {}^6Li(s) + {}^7LiF(s)$ has been measured in a vacuum chamber by using electrochemical reversible double cells containing KBF_4 in propylene carbonate (*24*). The equilibrium constant $K = 1.10$ at 23°C was believed to be "the largest lithium isotope effect that has been found experimentally" (exclusive of the later laser system results, Section 2.3). Smaller values of K (1.03–1.05) had been observed earlier by the same authors for comparable LiCl and LiBr systems, so the key is the fluoride ion. Although the cells become chemically unstable after only a few hours, apparently because of solvent decomposition, it may be possible to find a suitable solvent. The author made no reference to applying this exchange equilibrium to separation of lithium isotopes.

Russian scientists recently described metal ion separation/extraction in two-phase systems involving aqueous salt solutions in contact with aqueous polyethylene glycol (PEG) solutions (*25*). A major advantage noted was that the use of "toxic, volatile, combustible, or dangerously explosive" organic solvents could be avoided. The chemically stable liquid PEG, used in the 1500 to 3000 molecular weight range, forms heterogeneous mixtures with water when high salt concentrations (for example, 18 wt% $(NH_4)_2SO_4$) are employed. Such a system may provide sufficiently different solvation states for lithium ions in the two phases to produce a useable separation factor. The addition of a macrocyclic polyether compound could offset the solvation of the cation by water molecules in the PEG-rich phase.

2.2. Displacement Chromatography

2.2.1. Ion-Exchange Resins

Ion-exchange chromatography involves the distribution of selected ions between a moving liquid phase and a stationary phase consisting of ion-exchange resin particles supported in a column. General papers on the theory of isotope separation by chromatography were published in 1958 and 1977 (*26*), but there is a large body of literature data extending back to the 1930s for lithium isotope separation. Strong interest in the application of ion-exchange chromatography to lithium has been shown by Japanese scientists since the late 1960s.

Displacement chromatography was recommended over the more common elution method for isotope production. The latter method provides a greater specific separation, but at the expense of product throughput (*26*). The displacement type of "elution" curve has an almost square shape, with constant element concentration as a function of time. The band soon reaches dynamic equilibrium as the eluant solution is passed through the column, after which the band length remains constant, and self-sharpening phenomena occur at the band boundaries (*27*). The isotope ratio varies within the band, the lighter isotope normally becoming enriched at the rear edge and the heavier isotope at the front edge. The degree of enrichment at each edge increases with the distance traveled through the column by the band, but only until a steady-state condition is reached. Theoretical studies on the application of displacement chromatography to lithium isotope separation appeared in 1969 (*28*), and in 1982 Fujine (*29*) gave a detailed comparison of displacement and standard elution chromatography techniques.

Individual separation factors for ion-exchange (*29*) chromatography are quite small, typically only a few tenths of a percent for lithium (*10, 30*). However, effective separation systems can be designed because columns can be operated very efficiently with a large number of theoretical plates and small HETP (height equivalent to a theoretical plate). Industrial-scale systems would consist of sets of chromatographic columns arranged in series to facilitate moving the adsorption bands continuously over long distances, in order to effect adequate separation of the isotopes (*10*).

Experimental tests have been done with, for example, 22 mm inner diameter and 1 to 2 m long columns packed with H^+-form ion-exchange resin (*30*). The resin was first saturated with a lithium salt, washed to remove the free anion, and then treated with calcium acetate solution as eluant to displace the Li^+ ions. The lithium ion bands were gradually transported through a series of 1 m long columns containing H^+-form resin. In one case, after a displacement of 75 band lengths, the ^7Li concentration at the front boundary was 97.1% and the ^6Li concentration at the rear boundary 14.6%; the initial isotopic composition of the lithium salt was 92.8% ^7Li and 7.2% ^6Li (*30*).

The magnitude of the separation factor has been examined as a function of resin structure, and of cation and anion for the eluant salt solution (*30, 31*). These results have been used by Japanese scientists to test continuous displacement chromatography successfully on a laboratory scale (*10*). They concluded that "the ion exchange method is promising for industrial lithium isotope separation." Construction expenses and the unit cost of separation were estimated for a 100-kg ^7Li/a plant (*10*); details of the calculations have not been translated into English.

The isotope effect that is seen in ion-exchange chromatography is believed to arise from the same basic interaction as for liquid–liquid chemical exchange systems, namely a difference in lithium ion environment in the two phases (*31*). The ions are not as well solvated in the resin phase. Changes in the elution solvent (from water to mixed aqueous–organic) can therefore lead to variation in the α value for $^6Li/^7Li$ on ion-exchange resin columns (*32–34*). In some cases, for example with water–methanol eluant, improvement in α can be achieved relative to the value for water (*34*) because of an enhancement of the difference in Li^+ ion solvation in the liquid and resin phases. Theoretical aspects of isotope effects involving ion-exchange resins in mixed solvents have been considered, and the available experimental data (to 1979) reviewed (*32*). The general conclusion was that mixed-solvent ion-exchange systems would not be suitable for isotope separation on the industrial scale.

Substitution of macroreticular (large pore size) ion-exchange resins for the regular gel types did not change the single-stage isotope separation factor for lithium (*35*). However, the use of such resins did result in higher column efficiency, because faster interphase mass transfer rates for the Li^+ ions lead to a reduction in the HETP (*35*).

The abstract of a very recent Chinese paper refers to the use of high-pressure ion-exchange displacement chromatography for lithium isotope enrichment (*36*), but no details were given.

2.2.2. Resin-Supported Complexing Agents

The utility of "modern" (post-1967) cation complexing agents like crown ethers and cryptands was referred to in Section 2.1.2. Some of these compounds are available attached to a polymer structure that permits their use as a second phase in an exchange column. The $[2_B,1,1]$ cryptand resin was recently tested in the displacement chromatography mode, starting with the Cs^+-form resin (*37*). A Li^+ adsorption band was formed by adding lithium acetate, and the band was then eluted with sodium acetate solution in methanol. As in ion-exchange chromatography (Section 2.2.1), ^6Li was found to be enriched at the rear boundary and ^7Li at the front boundary of the band (*36*).

A significantly larger single-stage separation factor was measured, 1.014 at 40°C (*37*), compared to ion-exchange chromatography, but the efficiency of the column system tested was no better than for the latter method. It was believed that the cryptand resins could be applicable to industrial lithium isotope separation if the column performance could be improved by decreasing the resin particle size and increasing the resin capacity (*37*).

More encouraging results were reported in 1984 for the $[2_B,2,1]$ cryptand polymer under single-stage contact conditions (*2*). The α found was 1.034 to 1.036 at 40°C and 1.045 to 1.047 at 0°C for LiCl, LiBr and LiI undergoing isotope distribution between methanol solution and the complexing agent. The ^6Li was enriched in the resin-bound complexing agent. Tests with breakthrough chromatography at 30°C lead the author to state that high enrichment of ^6Li should be achievable by using this complexing agent in a chromatographic mode (*2*).

2.2.3. Ion-Exchange Membranes

Results of general electromigration studies are discussed in Section 2.4.3. However, chromatographic electromigration has been examined as a method for lithium isotope separation, with cation-exchange membranes used as the migration media (*38*). A strip of membrane is pulled from the aqueous anode region of the cell through an inert organic liquid phase (CCl_4). The membrane is moved at about 4 cm/h in the direction counter to the cation migration in the membrane, which is the current conductor in the cell. Advantages claimed for the use of an ion-exchange membrane rather than aqueous electrolyte solution for electromigration included negligible remixing of ions by thermal convection and a sharp boundary between the migrating ions (*38*).

^{6}Li is enriched at the front, and ^{7}Li at the rear, of the migrating band. The separation factor S, defined as the ratio of the mobilities of the $^6Li^+$ and $^7Li^+$ ions, was found to be independent of the distance traveled by the band; $S = 1.0037 \pm 0.0004$ (*38*). However, the degree of enrichment does increase with distance traveled, up to a limiting value. For example, in a 3-cm wide band that had been moved 74 cm with the substitution of a calcium salt solution, the ^{6}Li concentration at the front was 13.4%. For a continuous lithium ion supply the ^{6}Li concentration reached 16.8% at the band front after it had migrated 368 cm (*38*). Unfortunately, the degree of enrichment falls rapidly with distance from the band front, and it seems unlikely that such a process could be scaled up to provide the necessary large ^{6}Li production rate.

2.3. Laser Methods

A few papers covering both theoretical and experimental aspects of laser separation of lithium isotopes have appeared in the literature since 1978. These all describe very small scale tests, and no separated isotopic material has been isolated. The main advantage of laser methods is the very high selectivity achievable in a single stage under suitable conditions. However, scale-up from laboratory demonstration to commercial operation is not a simple matter with laser processes.

Mathur et al. were the first to report essentially complete fractionation of ^{6}Li and ^{7}Li by laser, using a thermal energy, molecular lithium beam from an effusion oven and two CW argon ion lasers (*39*). Separation was produced by two-photon, isotope-selective excitation/ionization of Li_2 species to Li_2^+ ions.

Although the Li_2/Li ratio was only ~0.01, Li atoms were not involved in the separation step (*40*). The three product ions $^6Li_2^+$, $^6Li^7Li^+$, and $^7Li_2^+$ were analyzed by mass spectrometry for isotope distribution. Single mode Ar^+ laser operation at 465.8 nm produced ~100% mass 12 species, whereas operation at 476.5 nm could yield either the mass 13 or 14 species with careful adjustment (*40*).

Very recently a comparable theoretical study of isotope separation by means of a molecular lithium beam was reported (*41*). Two different laser wavelengths are employed for the excitation and ionization steps. Essentially 100% separation was predicted for either $^6Li_2$ or $^7Li_2$ from a mixture of the three Li_2 species, and a wide spectrum of wavelengths would be suitable for effective isotope enrichment (*41*). The calculated separation effects were in agreement with the available experimental results, which have been discussed above.

Japanese scientists published some data in 1982 for a two-step photoionization process based on an atomic lithium beam, where a dye laser was used as the exciter at ~670.8 nm and a Nd:YAG laser as the ionizer at ~260.0 nm (*42*). The combined laser beams crossed the collimated atomic Li beam in the ion chamber of a quadrupole mass spectrometer. ^6Li enrichments up to >90% were observed with very low laser power densities in the range 2 to 10 W/cm^2 (*41*). Agreement between experimental and calculated dependence of enrichment on power density was very good.

A Japanese patent was issued in December 1983 to the Japan Atomic Energy Research Institute for a laser-based isotope separation process (*43*). The method involves crossing an atomic beam of lithium with a high intensity laser beam to excite the object isotope selectively, followed by ionization of that isotope and then recovery of the ions using an electric or magnetic field.

2.4. Miscellaneous Methods

2.4.1. Thermal Diffusion

The thermal diffusion technique has been available for the separation of isotopes in gaseous or liquid systems for many decades (*3, 44*). It can be quite effective for separation of elements with atomic weights below about 100 under liquid phase conditions. The method utilizes the tendency of isotopic species to separate along a thermal gradient in a fluid, with the lighter isotope usually migrating to the hotter zone. A pure liquid chemical containing the element is preferred for the working fluid (for example, CS_2 for sulfur, or CH_3Cl for chlorine), which is held in the annulus between two concentric tubes maintained at different temperatures (*45*). However, a salt dissolved in a suitable solvent (for example, $Ca(NO_3)_2$ in water (*46*)) provides an acceptable, if more complicated, system when liquid chemical forms do not exist.

The only results reported to date for lithium involved use of molten

$LiNO_3$ (*47*) and Li_2SO_4 salts (*48*). The ^6Li isotope was concentrated in the hot zone of molten salt held between two horizontal, thermally insulated plates maintained at 268 and 425°C. The average separation factor measured for $LiNO_3$ was 1.0049 ± 0.0002 (*3*). A major practical limitation of the liquid thermal diffusion method is the very small production rate possible, typically a few kg/a (*45*). The problem is that the annulus must be kept very small, usually 0.2 to 0.3 mm, in order to achieve reasonable separation factors. Therefore, this method would not be suitable for production of ^6Li at the 10 to 100 kg/d rate likely needed to supply fuel for a network of fusion reactors in the next century (see Section 3.1).

2.4.2. Radiofrequency Spectroscopy

The separation of ^6Li from ^7Li in a supersonic molecular beam mass spectrometer was recently described (*49*). A supersonic atomic lithium beam seeded with helium is collimated and then directed across an inhomogeneous gradient magnetic field to align the spins of the paramagnetic species. Next the beam traverses a low intensity (~1.5 G) homogeneous magnetic field containing an rf antenna that is selectively tuned to resonance with either the ^6Li (228.528 MHz) or ^7Li (3.191 MHz) species to cause spin flipping of the chosen isotope. Finally, the beam passes through another gradient magnetic field where the spin-reversed species is focused onto the detector. Because the resonance frequencies are isotope-dependent, spatial isotope separation can be obtained.

Under the conditions described, enrichment factors up to 30 were observed (*49*). However, the factor could be increased by using multifrequency rf radiation. The author believed that this single-stage separation process for lithium can be scaled up by employing multiplanar supersonic beams (*49*).

2.4.3. Electromigration

The electrolytic separation coefficient for lithium isotopes in solution was being studied as early as the late 1930s (*50* and references therein). For example, solutions of LiCl in water or in absolute ethanol gave temperature-independent values of 1.055 ± 0.005 for electrolysis of the LiCl at a mercury cathode (*50*). However, the use of molten halides rather than their solutions offers some advantages. The migration velocity of the cations subjected to an electric field gradient is greater, which permits a much higher current, and a tenfold wider range in temperature of operation is available (*51*). As a result, a much larger overall enrichment factor is possible.

Details were published in 1961 for a small-scale process to recover decagram quantities of enriched ^{6}Li by electrolysis of molten LiCl (*51*). The electrolysis cell can be operated in the continuous mode, with a temperature gradient of ~625 to 1375°C. ^{7}LiCl concentrates at the anode, while ^{6}Li metal will accumulate on (and attack) the hollow graphite cathode unless it is quantitatively converted back as it forms to ^{6}LiCl by reaction with Cl_2 gas, which can be recycled from the anode region (*51*). The diaphragm tube diameter chosen depends on the desired enrichment factor, f, and product output. For example, for a yield of several g/d of enriched LiCl ($f = 3$ to 4), a tube diameter of 30 mm was used (*51*).

Similar work has been done at lower temperatures (300 to 500°C) in molten $LiNO_3$, where the electromigration mobilities of ^{6}Li and ^{7}Li have been determined (*52*). The cell contained a platinum anode, and a stainless steel cathode through which a mixture of NO_2 and O_2 was bubbled into the molten salt. Again the ^{7}Li enrichment occurs at the anode and ^{6}Li at the cathode.

The NO_2-plus-O_2 gas feed noted above is not necessary in a molten $LiNO_3$–NH_4NO_3 system (*53*). The ^{6}Li is enriched at the sharp boundary between the $LiNO_3$ band (270°C) and the cooler NH_4NO_3 band (180°C); the latter decomposes and is slowly consumed at the interface to provide reflux for the lithium metal formed by electrolysis at the junction. The author believed the apparatus could be operated for continuous product removal on a laboratory or semi-industrial scale (*53*).

Isotope effects have been measured in the electrolysis of solid Li_2SO_4 maintained below its melting point (*54*). For this salt in the temperature range 575 to 857°C the electrical conductivity and cation self-diffusion coefficient are comparable to those in molten salts, and the cation transport number is unity. The cell consisted of a liquid zinc cathode and a gold anode. The lithium is deposited at the cathode as an alloy with zinc, and is enriched in ^{6}Li, the separation factor being 1.01 (*54*). In the case of solid electrolyte, the salt lattice forms the separation column, which is gradually consumed during the run; for the molten salt, hydrostatic forces in the cell keep the column area filled with electrolyte.

2.4.4. Distillation

Liquid distillation can be an effective method for separating suitable isotopic species (*6, 7*), but no liquid lithium compounds exist at or near ambient temperature. The melting point of lithium metal is relatively low, ~180°C, but most of the thermally stable lithium salts melt above 400°C.

Some tests were done with liquid lithium in the early 1950s, using short-path vacuum distillation columns to produce isotope separation (*55*). Results were obtained for several experimental systems, including six- and eight-stage stainless steel stills. For example, single-stage separation factors of 1.052 to 1.064 were measured for the pot temperature range 535 to 627°C in the six-stage still.

Although the feasibility of molecular distillation for lithium isotope separation has been demonstrated, no indication was given in the 1957 article concerning the relative economics of this approach (*55*).

2.4.5. Fractional Crystallization

Two patents have been issued for isotope-selective, controlled precipitation of lithium salts or complexes from solution (*56*). Few details are provided in the abstracts, but a precipitating agent like ammonium carbonate or phosphate is added to a solution of, for example, lithium aluminum oxalate complex. Multiple fractionation steps were claimed to be possible.

3. PROCESSES SUITABLE FOR LARGE-SCALE ^{6}Li ISOTOPE PRODUCTION

3.1. Projected ^{6}Li Production Requirements

The absolute future demand for ^{6}Li in the tritium breeder blankets of fusion power reactors is difficult to predict. However, a reasonable estimate can be made per reactor, based on the "STARFIRE" report (*57*). The STARFIRE reactor represents the result of the most comprehensive study yet performed (as of 1980) on a commercial fusion reactor concept. The tokamak-style reactor (magnetic confinement) was designed to provide 1200 MW electrical energy (*57*). The production rate of T_2 in the breeder blanket would be approximately 1 kg/d. Since T is formed by the reaction $n + {}^6\text{Li} \rightarrow \text{T} + {}^4\text{He}$, the corresponding consumption of ^{6}Li will be 2 kg/d. Thus, for example, a network of 10 such reactors would "burn up" about 7 Mg of ^{6}Li annually.

If the above rate seems high, even larger values were predicted by Rhinehammer and Wittenberg for tritium requirements to the year 2020 (*4*). The estimate for 11,500-MW(e) fusion reactor capacity in the year 2020 ranged from 46 to 276 Mg ^{6}Li annual consumption. However, statements made then are still very relevant now, although the date is no longer realistic: "The blanket-breeder concept finally selected will strongly affect the cumulative quantities of lithium required. Quantities of needed lithium must still be considered speculative until data are accumulated from operation of the first experimental power reactor in 1986–88 and subsequent demonstration reactors" (*4*). Similarly the extent of ^{6}Li enrichment for the lithium to be used in the blanket will depend on the design(s) chosen. But one point is quite clear: if fusion reactors become a reality, the process(es) chosen for ^{6}Li separation must be capable of supplying a ^{6}Li market that will be at least 5 Mg/a by early in the next century.

3.2. Processes Suitable For Scale-Up

With annual demands for ^{6}Li probably exceeding 5 Mg early in the next century (Section 3.1), small-scale processes limited by technology will not be able to play a significant role, regardless of how large a separation factor they have. For example, thermal diffusion is known to be suitable only for providing enriched isotopes at a rate of a few kg/a (*45, 50*) (Section 2.4.1). Electromigration in molten salts was considered to be practical only for laboratory or semi-industrial scale (*53*). Electromagnetic mass separators (*7*) (calutrons, not discussed before) are appropriate only for small-scale separations, not high volume production (*58*).

Methods that must have a gas-phase stream at some point in the separation process, such as those involving lasers (Section 2.3) and radiofrequency spectroscopy (Section 2.4.2), would seem, at first glance, to be unable to meet such a large production rate. However, the AVLIS (atomic vapor laser isotope separation) process currently being developed at least in the United States (*59*) and France (*60*) for ^{235}U enrichment has a projected total mass throughout of 10^7 kg/a (10^4 Mg/a) for a full-scale plant (*61*). This laser process is claimed to provide a significant reduction in cost for uranium isotope separation compared with current gaseous diffusion and gas centrifuge technologies (*59, 60*). Thus it would appear that laser and rf spectroscopy may ultimately be capable of the large-scale production rates envisaged for ^{6}Li. Laser isotope separation may someday be practical, but that time will be at least 10 years in the future (*58*).

The question of cost for lithium isotope separation by lasers is a different matter. Guidelines for comparing possible laser-based processes against efficient "standard chemical processes utilizing temperature and pressure control of reactions" have recently been reviewed by Davis and Rockower (*61*). For a decision on selecting a laser-based approach over a conventional two-phase chemical contacting process, questions of capital and operating costs, and market value and volume of the product, must be assessed. High value, high volume products (a relatively rare situation) can favor selection of the laser approach (*61*). Economic value must be assigned to ^{6}Li before a choice could be made between chemical exchange and laser photochemistry.

French scientists have also been working on a chemical exchange process, known as Chemex (*60*), for ^{235}U enrichment. No detailed cost comparison between the AVLIS and Chemex methods has been found, but the laser approach may ultimately provide a cheaper product (*60*). The modular Chemex system should be more cost effective than current centrifuge and diffusion plants. Several advantages and disadvantages for both the Chemex and AVLIS processes have been noted (*60*).

4. CONCLUSIONS

The chemical exchange (Section 2.1) and displacement chromatography (Section 2.2) routes are the most likely candidates to be used to produce the necessary quantities of ^{6}Li, at least early in the age of fusion power. Research is continuing actively in both areas, as scientists search for ways to improve the separation factors. The present author believes that there is more scope in the near term for new discoveries in the field of chemical exchange for ^{6}Li–^{7}Li separation.

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REFERENCES

1. E. Michiels and P. De Bièvre, "Absolute Isotopic Composition and the Atomic Weight of a Natural Sample of Lithium," *Int. J. Mass Spectrom. Ion Phys.*, *49*, 265 (1983).

2. K. Nishizawa, H. Watanabe, S. Ishino, and M. Shinagawa, "Lithium Isotope Separation by Cryptand (2_B,2,1) Polymer," *J. Nucl. Sci. Technol.*, *21*, 133 (1984).

3. G. Vasaru, *Separation of Isotopes by Thermal Diffusion*, Report ERDA-tr-32, Translation of Romanian Report, 1972. Technical Information Center, U.S. Energy Research and Development Administration, 1975.
4. T. B. Rhinehammer and L. J. Wittenberg, *An Evaluation of Fuel Resources and Requirements for the Magnetic Fusion Energy Program*, Mound Facility Report MLM-2419, Monsanto Research Corp., Miamisburg, Ohio, 1978.
5. D. P. Jackson et al., *Fusion Breeder Blanket Study. Part I*, CFFTP Report #F84033, *AECL-8631, Atomic Energy of Canada, Chalk River, Ontario, 1984.*
6. J. Kistemaker, J. Bigeleisen, and A. O. C. Nier (eds.), *Proceedings of the* (first) *International Symposium on Isotope Separation*, Interscience, New York, 1958.
7. H. London (ed.), *Separation of Isotopes*, Newnes, London, 1961.
8. J. Bigeleisen, "Gilbert N. Lewis and the Beginnings of Isotope Chemistry," *J. Chem. Educ.*, *61*, 108 (1984).
9. A. A. Palko, J. S. Drury, and G. M. Begun, "Lithium Isotope Separation Factors of Some Two-Phase Equilibrium Systems," *J. Chem. Phys.*, *64*, 1828 (1976).
10. S. Fujine, K. Saito, Y. Naruse, K. Shiba, M. Kosuge, T. Itoi, and T. Kitsukawa, *The Outline of the Processes for Lithium Isotope Separation by Ion Exchange Method*, Japan Atomic Energy Research Institute, Tokai Research Establishment, Report no. JAERI-M-9735 (body of report in Japanese).
11. N. M. Zhavoronkov, D. A. Knyazev, A. A. Ivlev, and G. D. Klinskii, "Principles of the Selection of Chemical Systems for the Separation of Isotopes," *Russ. J. Phys. Chem.* (*Engl. Transl.*), *52*, 513 (1978); "Thermodynamic Classification of Chemical Isotope Exchange Reactions," *Ibid.*, *51*, 1 (1977).
12. R. H. Betts and J. Bron, "A Discussion of Partial Isotope Separation by Means of Solvent Extraction," *Sep. Sci.*, *12*, 635 (1977).
13. T. I. Taylor and H. C. Urey, "On the Electrolytic and Chemical Exchange Methods for the Separation of Lithium Isotopes," *J. Chem. Phys.*, *5*, 597 (1937).
14. K. Okuyama, I. Okada, and N. Saito, "The Isotope Effects in the Isotope Exchange Equilibria of Lithium in the Amalgam-Solution System," *J. Inorg. Nucl. Chem.*, *35*, 2883 (1973).
15. C. J. Pederson, "Cyclic Polyethers and Their Complexes with Metal Salts," *J. Am. Chem. Soc.*, *89*, 7017 (1967).
16. G. A. Melson (ed.), *Coordination Chemistry of Macrocyclic Compounds*, Plenum, New York, 1979.
17. B. E. Jepson and R. DeWitt, "Separation of Calcium Isotopes with Macrocyclic Polyether Complexes," *J. Inorg. Nucl. Chem.*, *38*, 1175 (1976).
18. B. E. Jepson, *Equilibrium Separation Factors for Lithium Isotopes in Chemical Exchange with Macrocyclic Compounds*, Preprint of Paper in Draft, August 1984.
19. S. Fang, K. Zhi, L. Fu, Z. Yao, Z. Gao, and F. Zhang, "Use of Crown Ether C401 for Lithium Isotope Separation," *Chem. Abstr.*, *99*, 147994e (1983).
20. H. Sheng, S. Li, Y. Chen, P. Jin, and Q. Cai, "Effect of Anions on the Extractive Separation of Lithium Isotopes by the Crown Ether B15C5," *Ibid.*, *101*, 62198h (1984).
21. U. Schindewolf, "Solvated Electrons—Starting Point for New Technologies," *Nachr. Chem. Tech. Lab.*, *28*, 580 (1983) (in German).
22. F. Taulelle and A. I. Popov, "Nuclear Magnetic Resonance Study of Aluminum Chloride-*n*-Butylpyridinium Chloride Melts," *Polyhedron*, *2*, 889 (1983).
23. R. R. Rhinebarger, J. W. Rovang, and A. I. Popov, "Multinuclear Magnetic Resonance Studies of Macrocyclic Complexation in Room-Temperature Molten Salts," *Inorg. Chem.*, *23*, 2557 (1984).
24. J. C. Hall, L. F. Sylvester, G. Singh, and P. A. Rock, "Thermodynamics of Lithium

Isotope Exchange Reactions. IV. Exchange between Isotopic Metals and Solid Fluorides," *J. Chem. Phys.*, *59*, 6358 (1973).

25. T. I. Zvarova, V. M. Shkinev, B. Ya. Spivakov, and Yu. A. Zolotov, "Liquid Extraction in Aqueous Salt Solution–Aqueous Polyethylene Glycol Solution Systems," *Proc. Acad. Sci. USSR, Chem.*, *273*, 347 (1983) (English Translation).
26. E. Glückauf, "Theory of Chromatography. Part II. Enrichment of Isotopes by Chromatography," *Trans. Faraday Soc.*, *54*, 1203 (1958); H. Kakihana, T. Oi, and T. Nomura, "Theory of Chromatographic Separation of Isotopes," *J. Nucl. Sci. Technol.*, *14*, 572 (1977).
27. Z. Hagiwara and Y. Takakura, "Enrichment of ^{6}Li and ^{7}Li by Ion Exchange Column," *J. Nucl. Sci. Technol.*, *6*, 326 (1969).
28. Z. Hagiwara, "Theoretical Treatment of Ion-Exchange Systems Used for Lithium Isotope Separation," *Ibid.*, *6*, 508 (1969).
29. S. Fujine, "Theoretical Study of Lithium Isotope Separation by Displacement Chromatography," *Sep. Sci. Technol.*, *17*, 1049 (1982).
30. Z. Hagiwara and Y. Takakura, "Enrichment of ^{6}Li by Ion Exchange," *J. Nucl. Sci. Technol.*, *6*, 153 (1969); "Separation Factor of Lithium Isotopes in Ion Exchange Chromatography," *Ibid.*, *6*, 279 (1969).
31. D. A. Lee and G. M. Begun, "The Enrichment of Lithium Isotopes by Ion Exchange Chromatography. I. The Influence of the Degree of Crosslinking on the Separation Factor," *J. Am. Chem. Soc.*, *81*, 2332 (1959); D. A. Lee, "II. The Influence of Temperature on the Separation Factor," *J. Phys. Chem.*, *64*, 187 (1960); "III. The Influence of the Nature of the Solution Phase on the Separation Factor," *J. Am. Chem. Soc.*, *83*, 1801 (1961).
32. A. R. Gupta, "Isotope Effects in Ion-Exchange Equilibria in Aqueous and Mixed Solvent Systems," *Sep. Sci. Technol.*, *14*, 843 (1979).
33. H. Kakikana, T. Nomura, and Y. Mori, "The Separation Factor of Lithium Isotopes with Ion Exchangers," *J. Inorg. Nucl. Chem.*, *24*, 1145 (1962).
34. D. Nandan and A. R. Gupta, "Lithium Isotope Effects in Ion-Exchange Equilibriums in Mixed Solvents," *Indian J. Chem.*, *16A*, 256 (1978).
35. S. Fujine, K. Saito, and K. Shiba, "The Effects of Temperature and the Use of Macroreticular Resins in Lithium Isotope Separation by Displacement Chromatography," *Sep. Sci. Technol.*, *18*, 15 (1983).
36. D. Ling, Z. Zheng, T. Yue, H. Xu, K. Yang, and Y. Wang, "Enrichment of Lithium Isotopes by High-Pressure Ion-Exchange Displacement Chromatography. (III). Semicontinuous Operation," *Chem. Abstr.*, *100*, 181843d (1984).
37. S. Fujine, K. Saito, and K. Shiba, "Lithium Isotope Separation by Displacement Chromatography Using Cryptand Resin," *J. Nucl. Sci. Technol.*, *20*, 439 (1983).
38. Y. Fujii, H. Kakikana, M. Okamoto, T. Oi, and Y. Sakuma, "Separation of Isotopes of Lithium and Uranium by Electromigration Using Cation-Exchange Membranes," *Isotopenpraxis*, *15*, 203 (1979).
39. B. P. Mathur, E. W. Rothe, G. P. Peck, and A. J. Lightman, "Two-Photon Ionization of Li_2: Isotopic Separation and Determination of IP(Li_2) and D(Li_2^+)," *Chem. Phys. Lett.*, *56*, 336 (1978).
40. B. P. Mathur, E. W. Rothe, and G. P. Peck, "Isotope Fractionation in Two-Step Photoionization of Li_2," *Ibid.*, *53*, 74 (1978).
41. P. Cremaschi, "A Theoretical Study of the Isotope Separation of Li_2 Using Different Laser Wavelengths for the Excitation and Ionization Processes," *Ibid.*, *106*, 286 (1984).
42. T. Arisawa, Y. Maruyama, Y. Suzuki, and K. Shiba, "Lithium Isotope Separation by Laser," *Appl. Phys. B*, *28*, 73 (1982).

43. Japan Atomic Energy Research Institute, "Isotope Separation Method," Japanese Patent 58,219,925 (December 21, 1983), *Chem. Abstr.*, *100*, 217679w (1984).

44. W. M. Rutherford, "Separation of Isotopes in the Thermal Diffusion Column," *Sep. Purif. Methods*, *4*, 305 (1975).

45. W. M. Rutherford, "Separation of the Stable Isotopes of Chlorine, Sulfur, and Calcium," in *Stable Isotopes*, Elsevier, Amsterdam, 1982.

46. W. M. Rutherford and K. W. Laughlin, "Separation of Calcium Isotopes by Liquid Phase Thermal Diffusion," *Science*, *211*, 1054 (1981).

47. S. Gustafsson and A. Lunden, "Thermal Diffusion of Lithium Isotopes in Pure Molten Lithium Nitrate," *Z. Naturforsch.*, *17a*, 550 (1962) (in German).

48. K. Lindqvist and A. Lunden, "Thermal Diffusion of Lithium Isotopes in Solid Lithium Sulfate," *Ibid.*, *16a*, 626 (1961).

49. A. Amirav and U. Even, "Lithium and Potassium Isotope Separation Using Radiofrequency Spectroscopy," *Chem. Phys. Lett.*, *86*, 331 (1982).

50. H. L. Johnston and C. A. Hutchison, "Efficiency of the Electrolytic Separation of Lithium Isotopes," *J. Chem. Phys.*, *8*, 869 (1940).

51. M. M. Benarie, "Enrichment of the ^{6}Li-Isotope in Dekagram Quantities by Electromigration in Molten Lithium Chloride," *J. Inorg. Nucl. Chem.*, *18*, 32 (1961).

52. A. Lunden and A. Ekhed, "The Temperature Dependence of the Isotope Effect for Electromigration of Lithium Ions in Molten Lithium Nitrate," *Z. Naturforsch.*, *24a*, 892 (1969).

53. I. Okada and N. Saito, "Enrichment of Li-6 by Countercurrent Electromigration with Molten $LiNO_3$-NH_4NO_3 System," *J. Nucl. Sci. Technol.*, *11*, 314 (1974).

54. A. Lunden, "Isotope Effects in Solid Li_2SO_4 at 600–790°C," *J. Chem. Phys.*, *60*, 259 (1963).

55. D. B. Trauger, J. J. Keyes Jr., G. A. Kuipers, and D. M. Lang, "Some Experiments on the Separation of Lithium Isotopes by Molecular Distillation," in *Proceedings of the* (first) *International Symposium on Isotope Separation* (J. Kistemaker, J. Bigeleisen, and A. O. C. Nier, eds.), Interscience, New York, 1958.

56. K. Peters, "Process for the Separation of Lithium Isotopes," British Patent 866,720 (April 1961), *Nucl. Sci. Abstr.*, *15*, 17223 (1961). "Separation of Lithium Isotopes," Austrian Patent 204,052 (June 1959), *Chem. Abstr.*, *53*, 14769c (1959).

57. Argonne National Laboratory, *STARFIRE—A Commerical Tokamak Fusion Power Plant Study*, Report ANL/FPP-80-1, 1980.

58. W. R. Wilkes, W. M. Rutherford, B. E. Jepson, and E. D. Michaels, "Developments in Thermal Diffusion and Chemical Exchange Isotope Separation," in *Synthesis and Applications of Isotopically Labeled Compounds*, (W. P. Duncan and A. B. Susan, eds.), Elsevier, New York, 1983.

59. *Atomic Vapor Laser Isotope Separation*, Report 1-587-055/16, U.S. Government Printing Office, 1982.

60. "France is Gearing Up for Laser Enrichment," News Story in *Nucleonics Week*, p. 10 (June 7, 1984).

61. J. I. Davis and E. B. Rockower, "Lasers in Materials Processing," *IEEE J. Quantum Electron.*, *QE-18*, 233 (1982).

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