NENE
International Conference
Nuclear Energy for New Europe

Novel Methods of Isotopic Separation of Lithium 6

Norbert Wegrzynowski
University of Bristol
Wills Physics Laboratory
BS8 1TL, Bristol, United Kingdom
n.wegrzynowski@bristol.ac.uk

Tomas Martin, Thomas Bligh Scott
University of Bristol
Wills Physics Laboratory
BS8 1TL, Bristol, United Kingdom
tomas.martin@bristol.ac.uk, t.b.scott@bristol.ac.uk

ABSTRACT

Nuclear applications often require specific isotopes of an element with the right properties. An example is lithium, which has two isotopes that play a crucial role in the nuclear industry. Lithium-7 is commonly employed as a pH controller in the cooling systems of nuclear reactors, while lithium-6 is vital for tritium production. However, the natural abundance of lithium-6 is only 7.5%, which is insufficient to achieve a high breeding rate of tritium in technically feasible breeder blanket designs. Therefore, increasing the proportion of lithium-6 in any breeder blanket concept presents a significant challenge that needs to be addressed. Prior to the operation of any commercial fusion power plant, it is necessary to establish a facility capable of producing several tons of enriched lithium-6 per year. Currently, no such facility exists. This study explores the different possibility for lithium isotope separation, and assess their viability.

1 INTRODUCTION

Future fusion reactors will most likely operate using a mixture of two hydrogen isotopes: deuterium and tritium. Deuterium occurs naturally, making up around 0.0156% of hydrogen on earth [1], which translates to 1 deuterium atom per 6400 atoms of hydrogen. It is most commonly found in the form of "Heavy water" D_2O, with boiling and freezing points at 3.81°C and 101.42°C as well as a density of 1100 kg/m^3 at 11.23°C. This allows a variety of separation techniques, such as distillation, electrolysis and chemical exchange to be employed in the making of deuterium gas to be used in the reactor. The production of tritium is much more complicated, however.

Tritium is radioactive with a half-life of 12.32 years and thus practically does not occur naturally [1]. Some are generated by cosmic ray resulting in a concentration of 1 per 10^{18} hydrogen atoms. This means that any tritium that will be used in a reactor will have to be made synthetically. Currently, the plan is to utilize lithium-containing "Breeder Blankets" that surround the fusion plasma, generating tritium via splitting of lithium atoms [2]. The key metric used to measure the success of various designs is the tritium breeding ratio (TBR), which is defined as the ratio of tritium production to tritium consumption. A successful design will need to have

a TBR of at least 1. This will allow the fusion reactor to be self-sufficient theoretically but to account for various losses, a TBR of 1.2 is more desirable.

Lithium has two naturally occurring isotopes that can both split to produce tritium, meaning both could potentially be used. The lithium-6 reaction releases energy, as opposed to the lithium-7 reaction that requires energy, as well as having a much larger cross-section at the expected energies. This makes it more desirable and thus breeder blanket design concepts use up to 90% lithium-6. The issue is that the natural abundance of lithium-6 is only around 7.5 at.%. To be able to use lithium-6 at 90% concentration, natural lithium needs to be enriched using some form of isotope separation method. Oak Ridge National Laboratory did operate a lithium-6 enrichment facility employing a column exchange process known as “COLEX” between 1950-1963. However, since decommissioning, the western world does not currently operate any such facilities with most of the worlds demand being met by leftover stockpiles. Some facilities do exist in both Russia and China, employing similar methods to those used in Oak Ridge [3]. Recommissioning old facilities or building new ones based on old technology is not a viable option. The COLEX process requires the use of vast quantities of toxic mercury, thus for environmental reason it cannot be considered moving forward. It can however serve as potentially good starting point for new technologies.

This paper investigates potential isotope separation techniques, with a focus on physical methods. Some attention will be given to techniques on the border between chemical and physical techniques. The following sections are a non-exhaustive summary of available technique, selected to provide a holistic understanding of available methods.

2 TWO PHASE CHEMICAL EXCHANGE SYSTEMS

Compounds are often soluble in various phases, with some of them being immiscible. These compounds will usually be made of elements with multiple stable isotopes, which can have different affinities to a particular phase resulting in small differences in solvation. If this is the case, then when two immiscible phases containing the compound are mixed an isotope effect will be present. This will result in the enrichment of each isotope in their preferred phase. The level of enrichment can be quantified using the single stage separation factor α shown in equation 1. It is defined as the ratio between concentration of each isotope in each phase.

$$\alpha_b^a = \frac{\left([^a\mathrm{X}]/[^b\mathrm{X}]\right)_{\text{phase 1}}}{\left([^a\mathrm{X}]/[^b\mathrm{X}]\right)_{\text{phase 2}}} \tag{1}$$

Here the α between isotopes a and b of element X in phase 1 and phase 2 is shown. $[^a\mathrm{X}]$ denotes the concentration of the a isotope of element X. For a chemical exchange isotope separation processes to be successful it needs to meet the following requirements [4, 5]:

1. Large separation factor. This is especially important as $[\alpha - 1]$ is usually already close to zero. Thus, this is usually the limiting factor of the success of any method.

2. Fast isotope exchange. The diffusion of isotopes between phases need to be high so that the equilibrium can be setup quickly. The shorter this takes the shorter the phases to be in contact with each other, allowing quicker through put and smaller devices.

3. Possibility of a repeating cascade of separation stages that maximize separation. The phases used have to allow for quick reflux. The desired isotopes have to be easily removed to allow for this as well the separation of the two phases from each other. This means the solubility of the phases in each other has to be near zero, meaning they are immiscible. This pairs with the following point.

4. Total reflux of enriched product and phases. The target isotope not only has to be removed quickly but completely. Any leftover product will reduce the amount of enrichment possible, reducing α. In addition to this, no chemical reaction should take place, as this will reduce the total amount of phase for the isotopes to dissolve in.

These requirements are usually best met with system where one phase is a gas and the other a liquid. This however may not be possible at near room temperatures as no gaseous, stable, lithium containing compounds have been found. Thus, most researched has focussed on immiscible liquid-liquid systems [6], with the only method successfully employed at a large scale being COLEX.

2.1 Mercury systems

The COLEX process is the most well known mercury involving process taking advantage of the fact that lithium-6 has a greater affinity for mercury than lithium-7. This affect arises due to the slight differences in size and therefore different charge and spin distributions. This results in small difference in electronegativity between the isotopes where lithium-7 has a slightly higher value than lithum-6. The process involves mixing of a liquid metal alloy of lithium and mercury, known as lithium amalgam, with an aqueous lithium hydroxide solution. Due to the greater affinity of lithium-6 for the mercury, it diffuses out of the aqueous solution into the amalgam. Simultaneously the lithium-7 diffuses in the opposite direction. These two phases can then be separated, and the lithium extracted creating an enriched lithium-6 product from the amalgam and an enriched lithium-7 tail in the form of lithium hydroxide from the aqueous phase. This process can be repeated to achieve a batch cascade system. This is done by redissolving the lithium-6 product from the first stage into fresh phases and repeating the mixing and separation process. An equilibrium will once again be setup, creating a more enriched lithium-6 product alongside a depleted tail. This depleted tail from the second stage can be reused in the first stage to increase efficiency.

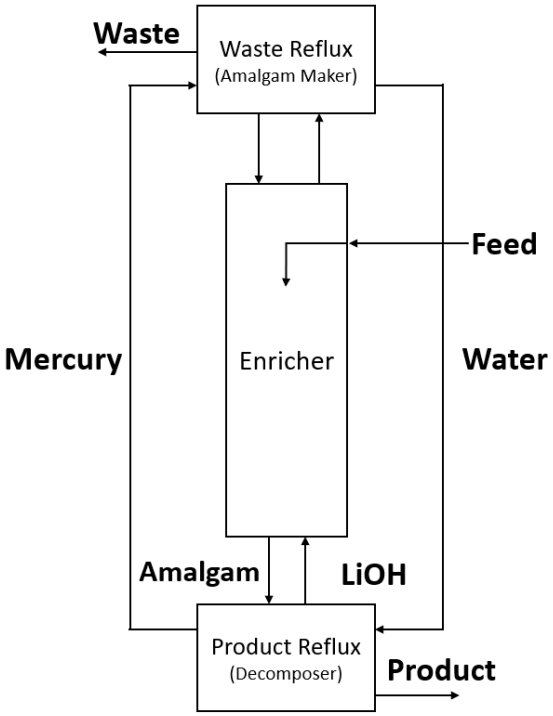

Figure 1: A simple schematic showing the column exchange process. This could easily be adapted to use with any liquid-liquid two phase chemical exchange system

The COLEX method conducted at Oak Ridge, was a constant flow-through process utilizing counter-flow columns that greatly increase throughput at the cost of a larger facility. A schematic of such a system is shown in figure 1. Lithium amalgam enters through the top and sinks to the bottom of the column contacting with the aqueous lithium hydroxide. The requirements described in section 2 determine the dimensions of this column. A slower exchange results in longer columns allowing more time for the exchange to take place. The “waste” and “product” are refluxed before being used as the feed for the stages before and after.

Throughout the operation of the Oak Ridge plant, over 11000 tons of mercury were used with about 330 tons of that lost in waste streams via evaporation or spills [7]. The mercury would be received in open air with flasks being poured into pipes leading to the plant. Mercury vapour was exhausted from the plant into the environment using the building’s ventilation system. This is obviously an environmental disaster [8, 9] and any future lithium isotope separation method will either have to greatly increase the care taken when operating or omit the use mercury all together.

Investigations have been conducted into the effectiveness of using various solvents and lithium salts [10]. Organic solvents like dimethylformamide, tetrahydrofuran, n-propylamine, dimethyl sulfoxide, however there was very little difference in separation factor between using these and water. Similarly, the use of various lithium salts did not seem to pose a large benefit. The maority of halide salts were tested as well as nitrates and ethanoate. Within these small differences, LiCl or LiOH dissolved in water seemed to be the best performing, with separation factors of approximately 1.05. This combined with the abundance of these salts and solvents made it an obvious choice for COLEX.

2.2 Alternate Two-Phase Systems

Not only can the salts and solvents be varied to optimize for the best separation factor, but the secondary phase can also be varied. Most research has been centred around using organic macrocyclic compounds known as crown ethers which were found to have specific selectivity to certain metal ions in back as the 1960s [11]. Research in to these compounds continued throughout the 1980s [12, 13] up until present day [14, 15, 16]. All have shown promising results with separation factors in the region of 1.02-1.04 reaching a maximum of 1.044 ± 0.003 [12]. Chemical equilibrium was reached in around 5 seconds, and with such high separation factors both the first and second requirement from section 2 are met. Benzo-15-crown-5 was selected, as it is highly soluble in organic solvents that would be immiscible with water, satisfying requirement number 3. The lithium was extracted from the organic phase by scrubbing using water, allowing the lithium ions to react with it and be washed away. This simplicity satisfies the last requirement.

A variation of the lithium amalgam method included the addition of electrolysis. Instead of the lithium being present in both phases, which were then contacted and allowed to establish an exchange equilibrium, the lithium is only present in the aqueous phase and is electrochemically inserted into the mercury, acting as the cathode, forming lithium amalgam. This method has shown slight improvements over the purely contacting method [10] with separation factors reaching 1.056 [17]. In a similar case to macrocyclic compounds in the contacting method, mercury does not need to be used as the cathode in the electrolysis. Materials such as graphite, gallium, tin, zinc and nickel have been used with over separation factors of 1.025, 1.031, 1.015, 1.023 and 1.031 respectively [6]. Inspiration could potentially be taken from this and use one of the secondary phases tested like liquid gallium in a purely two-phase exchange system.

3 LASER ISOTOPE SEPARATION

Properties of isotopes can often be very similar with only small differences being present. Most isotope separation techniques rely on the differences in masses of the isotopes and the resulting changes in behaviour of the atoms be it chemical or physical. Laser isotope separation is based on the differences in atomic structure. Lithium 6 has a nuclear spin of $I = 1$ whereas lithium 7 has nuclear spin of $I = 3/2$ leading to very slight differences in the location of the $2p$ excited state electron levels. The two levels of interest are the $^2P_{1/2}$ and $^2P_{3/2}$. The maximum possible difference in energy is between the ^{6}Li$^2P_{1/2}$ and ^{7}Li$^2P_{3/2}$ corresponding to a difference in wavelength of exciting light of only 0.0315nm. This is depicted in figure 2 by the green arrow. From this diagram its also visible that the difference between ^{6}Li$^2P_{3/2}$ and ^{7}Li$^2P_{1/2}$ is smaller still, only around 0.0158nm.

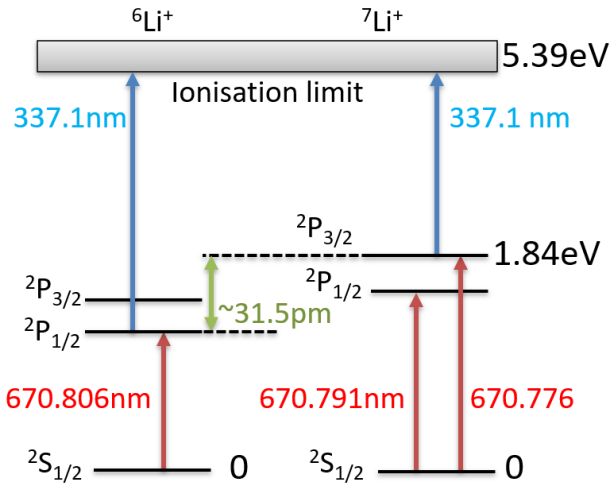

Figure 2: Diagram depicting the hyperfine structure of the electron energy levels

The differences are so small in fact that they are smaller than the isotopic shift, or the full shift in spectral line due change from one isotope to another. This forces the use of very narrow linewidth lasers capable of resolving the differences in fine structure levels. The slight differences in energy levels can be used to selectively excite and then ionize the lithium atoms. In this way only one type of isotope will be ionized. The desired isotope can then be separated out using electric fields leaving behind the other isotope that remained neutral. Due to the selective nature of the technique the single stage enrichment of these methods is very high. The concept has been demonstrated as far back as 1977 [18]. Research has continued with various studies demonstrating this effect [19, 20] and showing increases in the concentration of lithium 6 from natural abundance to between 47%-90% [21, 22, 23]. The majority of these utilized a two-step process, first exciting the isotope to the intermediate $^2P_{1/2}$, then ionizing with a laser from that level. Separation of isotopes was usually done with the use of a mass spectrometer

4 ADAPTING METHODS FROM LARGER INDUSTRIES

Another major industry that requires extensive isotope enrichment is the cousin to fusion, fission. The nuclear fission industry requires vast quantities of uranium with a content of the isotope uranium 235 at a level between 3-5%. This is reached through enrichment from the natural abundance of around 0.7% . Many techniques have been researched of the years, but a few have stood out as best performing. Gas-centrifugation has been a particularly successful method. The basic principle behind the functioning of a gas centrifuge is utilizing the different

amounts of centripetal force felt by the two isotopes due to their mass. This difference in forces creates a net flux of isotopes allowing for separation to occur. This affect can be amplified by using a counter-current gas centrifuge, shown in figure 3. In this setup the initial separation gradient is set up thanks to the rotation, this is amplified by the flow of the fluid inside the centrifuge. The flow at the center and outside edge of the centrifuge pushes the isotope in opposite direction creating an additional separation gradient in the vertical direction. Taking inspiration from this, could it be possible to repurpose the uranium enrichment technology for lithium?

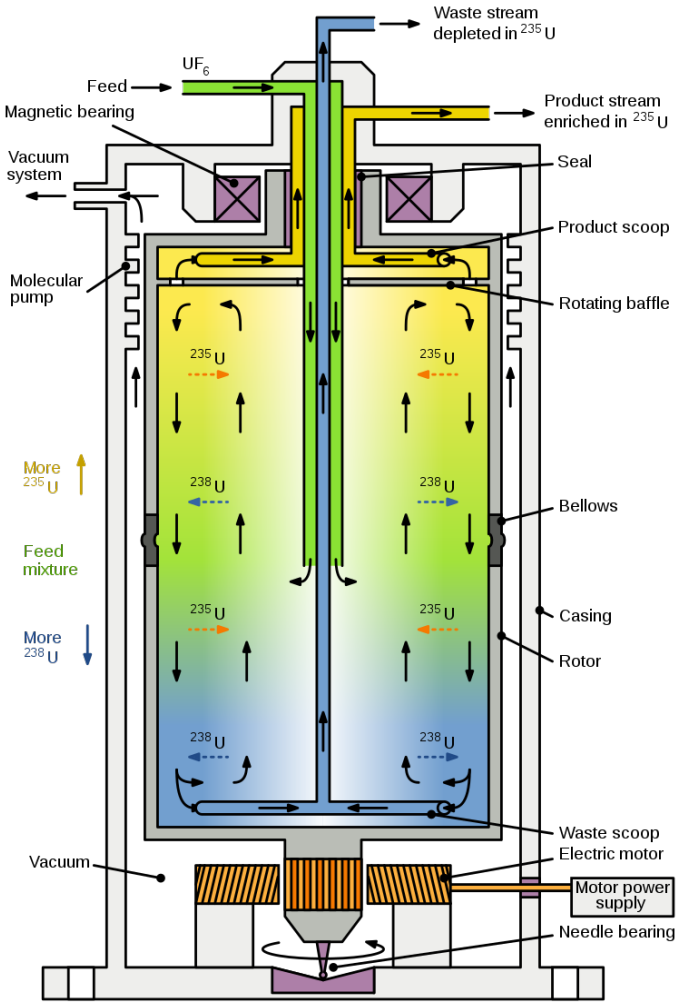

Figure 3: Diagram depicting the simplified inner workings of a modern counter-current gas centrifuge. Credit to [24]

No stable lithium containing compounds have been found that are gaseous at room temperature. However, raising the temperature to just around $150°$C could provide to potential compounds, namely n-hexyl-lithium and phenyl-lithium with boiling points around $69°$C and $140°$C respectively. These compounds are commonly used in chemistry as chemical reagents used in many applications. It may be possible to use these compounds in current gas centrifuge.

Alternatively, a recent study that centrifugation of salt solutions could be an effective method of isotope separation [25]. Very large separation factors of around 1.05 have been found for lithium. The study also investigated centrifugation for calcium, molybdenum and oxygen. They simply dissolved lithium containing salts like LiCL in water and centrifuged at high speeds for up to a period of 72 hours. Tests were conducted with range of concentration from 0.1M to 5M as well various lithium salts including: LiCl, Li_2SO_4, LiBr, LiI, Li_2MoO_4,

LiOH, $Li_2C_2O_4$, $LiNO_3$. Various non-aqueous solvents were also tested including: propylene carbonate, dimethyl sulfoxide, triethyl phosphate, but the selectivity was low and did not accede 1.0054. The most promising result for lithium came from centrifugation of approximately 5ml of 1M aqueous solution of LiCl for a period of 72 hours. This could potentially be easily reproduced.

5 CONCLUSION

Many methods not mentioned in this paper have shown promising results, however, out the techniques selected in this paper, two are of particular interest. Firstly, two-phase exchange systems involving liquid gallium. It feels like a natural alternative to mercury and could prove to be interesting, warranting some attention. Secondly, inspiration should also be taken from larger more established isotope separation industries like those used for uranium. What form that should take is up for debate but some form of counter-current flow centrifugation could be a good final goal considering its effectiveness in the uranium enrichment sector.

ACKNOWLEDGMENTS

The organizer gratefully acknowledges the work done by all Organizing Committees of the International Conferences Nuclear Energy in New Europe who prepared the first and the improved versions of the template.

REFERENCES

[1] A. Keçebaş and M. Kayfeci, “Chapter 1 - hydrogen properties,” in *Solar Hydrogen Production* (F. Calise, M. D. D’Accadia, M. Santarelli, A. Lanzini, and D. Ferrero, eds.), pp. 3–29, Academic Press, 2019.

[2] Y. Wu and S. Şahin, “3.13 fusion energy production,” in *Comprehensive Energy Systems* (I. Dincer, ed.), pp. 538–589, Oxford: Elsevier, 2018.

[3] T. Ault, K. Brozek, L. Fan, M. Folsom, J. Kim, and J. Zeismer, “Lithium isotope enrichment: feasible domestic enrichment alternatives,” *University of California: Berkeley, CA, USA*, pp. 3–4, 2012.

[4] T. Ishida and Y. Ono, “Early history of chemical exchange isotope enrichment and lessons we learn,” *Journal of nuclear science and technology*, vol. 43, no. 4, pp. 391–399, 2006.

[5] E. A. Symons, “Lithium isotope separation: a review of possible techniques,” *Separation Science and Technology*, vol. 20, no. 9-10, pp. 633–651, 1985.

[6] A. Murali, Z. Zhang, M. L. Free, and P. K. Sarswat, “A comprehensive review of selected major categories of lithium isotope separation techniques,” *physica status solidi (a)*, vol. 218, no. 19, p. 2100340, 2021.

[7] M. Ragheb, “Chapter 10 isotopic separation and enrichment,” 2021.

[8] H. King, M. Sollenberger, D. Sparkman, R. Reynolds, and G. Wayland, “Surveillance and maintenance report on decontamination and decommissioning and remedial action activities at the oak ridge y-12 plant, oak ridge, tennessee. fiscal year 1996,” tech. rep., Oak Ridge Y-12 Plant, 1996.

[9] D. O. T. UUU, “Y-12 plant decontamination and decommissioning technology logic diagram for building 9201-4,” 1994.

[10] A. A. Palko, J. S. Drury, and G. M. Begun, “Lithium isotope separation factors of some two-phase equilibrium systems,” *The Journal of Chemical Physics*, vol. 64, pp. 1828–1837, Feb. 1976.

[11] C. J. Pedersen, “Cyclic polyethers and their complexes with metal salts,” *Journal of the American Chemical Society*, vol. 89, no. 26, pp. 7017–7036, 1967.

[12] K. Nishizawa, S.-i. Ishino, H. Watanabe, and M. Shinagawa, “Lithium isotope separation by liquid-liquid extraction using benzo-15-crown-5,” *Journal of nuclear science and technology*, vol. 21, no. 9, pp. 694–701, 1984.

[13] N. Kazushige, I. Shin-ichi, W. Hisashi, and S. Mutsuaki, “Lithium isotope separation by liquid-liquid extraction using benzo-15-crown-5.,” *Journal of Nuclear Science and Technology*, vol. 21, no. 9, pp. 694–701, 1984.

[14] Q. Zhang, Y. Jia, J. Sun, P. Zhang, C. Huang, M. Wang, Z. Xue, C. Wang, F. Shao, F. Tong, Y. Xiao, and Y. Jing, “Lithium isotope separation effect of n-phenylaza-15-crown-5,” *Journal of Molecular Liquids*, vol. 330, p. 115467, May 2021.

[15] J. Xiao, Y. Jia, C. Shi, X. Wang, S. Wang, Y. Yao, and Y. Jing, “Lithium isotopes separation by using benzo-15-crown-5 in eco-friendly extraction system,” *Journal of Molecular Liquids*, vol. 241, pp. 946–951, Sept. 2017.

[16] M. Davoudi and M. H. Mallah, “Enrichment of 6li using dispersive liquid–liquid microextraction as a highly efficient technique,” *Annals of Nuclear Energy*, vol. 62, pp. 499–503, Dec. 2013.

[17] M. FUJIE, Y. FUJII, M. NOMURA, and M. OKAMOTO, “Isotope effects in electrolytic formation of lithium amalgam,” *Journal of Nuclear Science and Technology*, vol. 23, pp. 330–337, Apr. 1986.

[18] M. Shimazu, Y. Takubo, and Y. Maeda, “Selective two-step photoionization of lithium atoms,” *Japanese Journal of Applied Physics*, vol. 16, no. 7, p. 1275, 1977.

[19] N. Karlov, B. Krynetskii, V. Mishin, and A. Prokhorov, “Laser isotope separation of rare earth elements,” *Applied Optics*, vol. 17, no. 6, pp. 856–862, 1978.

[20] I. E. Olivares, A. E. Duarte, E. A. Saravia, and F. J. Duarte, “Lithium isotope separation with tunable diode lasers,” *Applied optics*, vol. 41, no. 15, pp. 2973–2977, 2002.

[21] T. Arisawa, Y. Maruyama, Y. Suzuki, and K. Shiba, “Lithium isotope separation by laser,” *Applied Physics B*, vol. 28, pp. 73–76, 1982.

[22] M. Saleem, S. Hussain, M. Rafiq, and M. A. Baig, “Laser isotope separation of lithium by two-step photoionization,” *Journal of Applied Physics*, vol. 100, Sept. 2006.

[23] V. Saini, S. Talwar, V. Subrahmanyam, and S. Dixit, “Laser assisted isotope separation of lithium by two-step photoionization using time of flight mass-spectrometer,” *Optics & Laser Technology*, vol. 111, pp. 754–761, Apr. 2019.

[24] Inductiveload, “Countercurrent gas centrifuge,” 2023. Available online: `https://en.wikipedia.org/wiki/Gas_centrifuge#/media/File:Countercurrent_Gas_Centrifuge.svg` (Accessed on 30/08/2023).

[25] J. F. Wild, H. Chen, K. Liang, J. Liu, S. E. Cox, A. N. Halliday, and Y. Yang, “Liquid solution centrifugation for safe, scalable, and efficient isotope separation,” *arXiv preprint arXiv:2303.14168*, 2023.