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**Report on the assessment of a viable route for the separation of lithium isotopes**

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Authors : Dr. Thomas GIEGERICH (KIT)

TRANSAT - Contract Number: 754586  
TRANSversal Actions for Tritium Project Officer: Angelgiorgio IORIZZO

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### Summary

The objective of this work is to find suitable enrichment processes that fulfil the requirements of lithium enrichment for nuclear fusion and fission economically in the best way. For this purpose, already investigated  ${}^6\text{Li}$  enrichment systems have been listed and discussed.

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### Approval

Date	By
2019-02-21 09:04:41	Dr. Ion CRISTESCU (KIT)
2019-02-27 11:12:11	Mr. Christian GRISOLIA (CEA)

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## Abbreviations

EC DG RTD	European Commission – Directorate General for Research and Technological Development
PQP	Project Quality Plan
DoA	Description of Action
WP	Work package
WPL	Work package leader
GB	Governing Board
PAR	Periodic activity report
PMR	Periodic management report
PR	Periodic report
QA	Quality assurance
PMO	Project Management Office
ECCP	Electronic Collaborative Content Platform
TBM	Test Blanket Module
ITER	International Thermonuclear Experimental Reactor
HCPB	Helium Cooled Pebble Bed
HCLL	Helium Cooled Lithium Lead
DEMO	DEMOstration power plant
PWR	Pressurized water reactor
MSR	Molten salt reactor
ORNL	Oak Ridge National Laboratory
COLEX	Column exchange process
OREX	Organic exchange process
ELEX	Electrochemical exchange process
SSLISC	Solid State Lithium Ion Super Conductor
DC	Direct current
AVLIS	Atomic Vapour Laser Isotope Separation
VDI	German Engineering Society
CHP	Combined Heat and Power
DOE	Department of Energy
TBR	Tritium breeding ratio
WCLL	Water Cooled Lithium Lead
HCCB	Helium Cooled Ceramic Breeder
WCCB	Water Cooled Ceramic Breeder
DCLL	Dual Coolant Lithium Lead concept
SCLL	Self-Cooled Lithium Lead
PP	Port plug
PbLi <sub>eu</sub>	Eutectic lithium lead
HCSB	Helium Cooled Solid Breeder
WCSB	Water Cooled Solid Breeder
DFLL	Dual Functional Lithium Lead
HCML	Helium Cooled Molten Lithium



SCLi	Self-Cooled liquid Lithium
LLCB	Lead Lithium Ceramic Breeder
LL	Lithium Lead
CB	Ceramic Breeder
LIBRETTO	Liquid Breeder Experiment with Tritium Transport Option
TRIEX	TRItium EXtraction
EBBTF	European Breeding Blanket Test Facility
DIADAMO	Facility with gas and PbLi eutectic circuits
PICOLO	Corrosion testing loop
MEKKA	Magnetohydrodynamic Experiments in NaK Karlsruhe
NCCP	Novosibirsk Chemical Concentrates Plant
OSi	Orthosilicates
MTi	Metatitanate
UWTOR-M	Modular stellarator power reactor
PDA	Propylene-di-amine
EDA	Ethylene-di-amine
R&D	Research and Development
DMSO	Dimethyl-sulfoxide
DMC	Dimethyl-cellosolve
THF	Tetrahydrofuran
DMA	N,N'-dimethyl-acetamide
DEF	N,N'-diethylformamide
TFA	Trifluoroacetat
CIEMAT	Spanish research centre for energy, environment and related technologies
HETP	Height equivalent to a theoretical plate
SILEX	Separation of Isotopes by Laser EXcitation
MAGNIS	Magnetically Activated and Guided Isotope Separation
ICR	Ion Cyclotron Resonance
TOF	Time Of Flight
CANDU	CANada Deuterium Uranium reactor
Calutron	California University Cyclotron
SWU	Separative work unit
USEC	United States Enrichment Cooperation
MLIS	Molecular Laser Isotope Separation



## Summary

In future fusion reactors the huge amount of energy that is released by merging the hydrogen nuclei deuterium and tritium will be used to generate electricity. Tritium is a  $\beta$ -radiator and it only exists in nature at negligible amounts. For that reason, it has to be bred inside of so-called breeding blankets of the reactor. The most suitable material for that purpose is the lithium isotope  ${}^6\text{Li}$ . It represents therefore a primary fuel and is consequently crucial for the success of nuclear fusion power generation.

Natural lithium consists to 92.5% of  ${}^7\text{Li}$  and only to 7.5% of  ${}^6\text{Li}$ . This means that the required  ${}^6\text{Li}$  has to be enriched starting with natural lithium. A significant amount of lithium that is enriched in  ${}^6\text{Li}$  will be required in the near future (2025) for the Test Blanket Modules (TBMs) that will be tested in ITER (originally an acronym of International Thermonuclear Experimental Reactor, also Latin for "the way"). ITER is an international project with the objective to prove that it is possible to gain energy by nuclear fusion.

The EU proposes two kind of breeding blanket concepts. One is the HCPB (Helium Cooled Pebble Bed) concept that uses  $\text{Li}_4\text{SiO}_4$  or  $\text{Li}_2\text{TiO}_3$  as ceramic breeding material. For this concept, a  ${}^6\text{Li}$  enrichment level of 40-60% is required. The other concept is the HCLL (Helium Cooled Lithium Lead) concept. The breeding material, which is in this case eutectic  $\text{LiPb}$ , requires a  ${}^6\text{Li}$  enrichment level of more than 90%. An amount of approximately 200 kg 90% enriched lithium will be needed for the EU-TBM. This amount is at the moment hard to afford because of the very high  ${}^6\text{Li}$  price and it's unclear if it will be commercially available. In case the HCLL concept will be chosen for the fusion DEMONstration fusion power plant (DEMO), which should begin to operate in 2035, the huge amount of approx. 60 t of 90% enriched lithium per  $\text{GW}_{\text{el}}$  would be needed.

In nuclear fission  ${}^7\text{Li}$  is required in pressurized water reactors (PWRs). Lithium hydroxide is added to prevent the cooling water of the reactor core from becoming acidic and thus obviate corrosion and possible failures of pipes and other infrastructure. In addition,  ${}^7\text{Li}$  is added to demineralizers, special water purifiers, for filtering out radioactive contaminants from the cooling water. For these purposes lithium-7 needs to be enriched to >99.99%, as lithium-6 would react with nuclear material under release of tritium. Molten salt reactors (MSRs) which are e.g. planed to be built in China require even larger amounts of lithium-7 in a more pure form (99.995% or higher).

The objective of this work is to find suitable enrichment processes that fulfil the requirements of lithium enrichment for nuclear fusion and fission economically in the best way. For this purpose, already investigated  ${}^6\text{Li}$  enrichment systems have been listed and discussed.

In the past  ${}^6\text{Li}$  enrichment occurred primarily for military reasons. USA has been stockpiling lithium-6 for the use of thermonuclear weapons in Oak Ridge National Laboratory (ORNL). Three types of large scale enrichment plants have been established there between 1950 and 1963: the COLEX (column exchange), the OREX (organic exchange), and the ELEX (electrochemical exchange) process. All of these systems made use of the affinity of mercury to  ${}^6\text{Li}$ . The COLEX and OREX systems are chemical extraction systems while the ELEX system separates the isotopes by electrolysis. The COLEX process has been found to be the most effective one. Today no alternative systems have been established for large scale  ${}^6\text{Li}$  enrichment than those used in ORNL.

Nevertheless, many other methods have been found to be applicable. Isotopic selective chemical exchange could be realized for instance by the use of macrocyclic compounds (crown ether or cryptands) that have the ability to complex the lithium ions within their nano cavity. Another possibility of chemical exchange is the use of liquid ammonia which has interesting properties at low temperatures. Several ion exchanger and intercalation systems are also applicable for chemical exchange. Ion exchanger and macrocyclic compounds may also be used as resin material for lithium isotope separation by displacement chromatography. Regarding electrochemical isotope separation, several electrolysis systems beyond the amalgamation have been investigated for  ${}^6\text{Li}$  enrichment. Another electrochemical separation method is electrophoresis with SSLISC (Solid State Lithium Ion Super Conductor) as separation fluid. Electrochemical isotopic exchange may also occur if a DC (direct current) is applied to molten lithium or lithium salt. In this case one speaks of electromigration. Totally different approaches are



methods that use specific laser for isotopic separation. Since isotopes differ not only in their mass but also in their hyper fine electronic structure special laser may excite only one isotope type selectively that could be separated in a next step by a magnetic field.

Up to now, the commercial use of nuclear energy is limited to the use of nuclear fission. Large scale isotopic enrichment of uranium has been established for the civil market since many years. For that reason, the proposed lithium isotope separation systems have been compared to those of the uranium enrichment. It was found that although many lithium separation approaches have been originally developed for uranium enrichment (like for instance the laser based method AVLIS (Atomic Vapour Laser Isotope Separation)), a real comparison is actually quite difficult as the properties of the elements vary widely. The mayor aspect that has to be taken into consideration is that for uranium, a gaseous compound ( $UF_6$ ) exists at room temperature whereas for lithium, no such molecule has been found yet. This leads to the fact that the most frequently used and conventional separation methods for uranium which are gaseous diffusion and gaseous centrifugation are not applicable for lithium enrichment.

For the evaluation of the Li-isotope separation systems an approved systematic method according to a VDI guideline (VDI Guideline 2225-3, Technical-economic examination, German Engineering Society (VDI), 1998) was used. This system offers the opportunity to not only assess the methods according to certain criteria but also to compare and weight the relevance of the criteria themselves. The result of this method was a quality rating for each process related to the estimated respective costs of the process equipment as well as further research and development.

The COLEX process was found to be the most suitable system for nuclear fusion requirements in the near future, especially if reprocessing of burned breeding material is considered. In addition nuclear fission requirements could be fulfilled.



## 1 Introduction

The worldwide economic growth, as well as the technological and industrial enhancements, increases the global energy demand. Today the major part of the world's energy is covered by the use of fossil fuels. The use of fossil fuel has two main disadvantages. Firstly, the resources are limited and secondly their use is associated with greenhouse gas emissions which are held responsible for serious environmental problems like the global warming. Therefore it is essential to replace them with effective and efficient alternatives.

Both nuclear fission and fusion offer a technique of generating electrical energy that is free from greenhouse gas emissions. Nuclear fusion further does not produce long term radioactive waste compared to nuclear fission. Only 100 to 300 years are needed until the produced irradiating material could be recycled [1–3]. Compared to regenerative energies like wind craft or solar energy it has the advantage that its yield is not dependent on environmental conditions like the climate etc. and that a continuous and reliable process can be established.

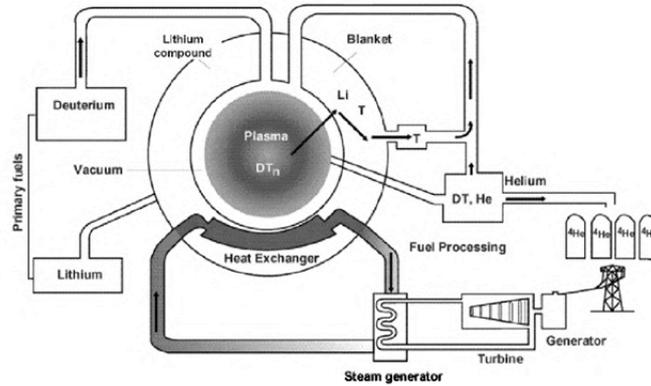
Nuclear fusion is the reaction of two light nuclei forming a heavier one while releasing a large amount of energy per conversion which is caused by the mass difference between the educts and the product. The idea is to use a similar energy source that our sun is using for 4.6 billion years: It burns hydrogen nuclei to helium in its core at 14 million °C and a pressure of  $4 \cdot 10^{11}$  bar. Such a high pressure could not be realized on earth but it is possible to raise the temperature to much higher amounts [1, 3, 4].

The fusion reaction that is considered for the commercial energy generation is the one between the hydrogen isotopes deuterium and tritium (cf. equation (eq.) 1.1). It requires the lowest temperature (approximately 100 million °C) while offering the highest reaction cross section and energy yield among the potential combinations [5–7].



The deuterium reserves seem to be inexhaustible since it makes up about 0.016% of the world's total hydrogen isotope inventory [5]. This means that approximately  $5 \cdot 10^{16}$  kg Deuterium could be found in the oceans [1]. Tritium is a  $\beta$  radiator that has a relatively short half-life of 12.32 years and only exists at negligible amounts in nature. This is why it must be bred artificially by neutronic irradiation of lithium [1, 2, 6]. The lithium resources in the landmass and oceans are estimated to more than  $10^{14}$  kg, which would theoretically be sufficient to breed enough tritium to provide the world's energy demand for more than 30 million years [2]. Therefore the feed material resources for nuclear fusion could be regarded as almost unlimited.

In fusion reactors the gaseous fuel mixture is heated to the already mentioned high temperature of 100 million °C at which it is at the state of plasma. The charged plasma particles (electron and nuclei) are locked in a magnetic cage and form the core of the reactor. Since the neutron that is produced by the fusion reaction (cf. eq. 1.1) is electrically neutral, the magnetic field does not influence it. Thus, it is able to pass the cage and clash onto the inner wall which is covered by the lithium containing tritium breeding blankets. Breeding blankets have basically three functions: The first one is to discharge the kinetic energy of the neutron to a conventional CHP (combined heat and power) generation plant with the help of a cooling agent [cf. Figure 1]. According to the conservation of momentum, approximately 4/5 (ca. 14.08 MeV) of the initial released 17.6 MeV (cf. eq. 1.1) are converted to the kinetic energy of the neutron n. The second function is radiation shielding. [2, 6, 8, 9]



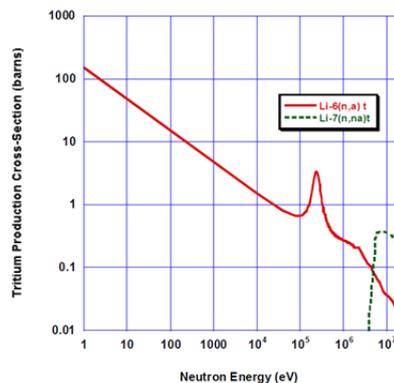
**Figure 1: Schematic drawing of the fusion fuel cycle [6].**

The last function is to breed tritium. Natural lithium consists to 92.5% of  ${}^7\text{Li}$  and to 7.5% of  ${}^6\text{Li}$ . The latter is more of interest for the tritium breeding reaction [2].



The reaction of  ${}^6\text{Li}$  (eq. (1.2)) is exothermic and contributes significantly to the energetic output of the fusion reaction. The energy release of 4.8 MeV per conversion makes 27% of the energy released by the primary fusion reaction (eq. 1.1). The reaction of  ${}^7\text{Li}$  is endothermic and leads to energetic loss.

The cross section of  ${}^6\text{Li}$  especially for thermal neutrons (slow moving neutrons with small kinetic energy) is much higher than for  ${}^7\text{Li}$ . At a neutron velocity of 2'200 m/s which represents a neutron energy of approximately 0.025 eV the tritium producing cross section of  ${}^6\text{Li}$  is ca. 945 barn (1 barn =  $10^{-28}$  cm) while that of  ${}^7\text{Li}$  is negligible [10]. Figure 2 shows that the cross section of  ${}^7\text{Li}$  only surpasses that of  ${}^6\text{Li}$  for neutrons with higher kinetic energies than approximately 5 MeV and yield in only 0.3 barn. Since the neutron increasingly slows down in the blanket it is much more favourable to applicate  ${}^6\text{Li}$  instead of  ${}^7\text{Li}$  [1, 2, 11, 12].



**Figure 2: Tritium production cross section vs. neutron energy (Li-6 and Li-7) [8].**

For this reasons it becomes clear that actually the isotope  ${}^6\text{Li}$  represents the principal fuel beside deuterium and is therefore an absolutely crucial material for successful fusion application. Unfortunately, today  ${}^6\text{Li}$  is very expensive and only commercial available in small amounts (cf. Chapter 3). Since in the near future huge amounts of  ${}^6\text{Li}$  will be needed for the fusion reactors ITER (International Thermonuclear Experimental Reactor or lat. for the way) and DEMO (Demonstration power plant), which should begin to operate in 2025 and 2035 respectively, it is essential to establish an economic large scale enrichment process for the isotope [13, 14].

In nuclear fission, two types of fission reactors require lithium for safe operation: The first one is the pressurized water reactor at which water is pumped under high pressure to the reactor core where



it is heated by the energy released by the fission reaction. The superheated water flows through a steam generator where via a secondary steam system electric energy is produced. For managing the nuclear reaction the core, boron is added to the cooling water and used as neutron absorber. For this reason, lithium hydroxide needs to be used as a pH stabilizer to prevent the water from becoming acidic.  $^7\text{Li}$  is preferred because of its low neutron cross section [15].

The second one is the molten salt reactor (MSR), where lithium fluoride and lithium-beryllium fluorides are used as coolants. These fluoride salts have several advantages: They have very low vapour pressures, good heat transfer properties, low neutron absorption and they are radiation resistant as well as not violently reactive to air or water. The fuel itself is dissolved in the coolant as fuel salt. The fluoride salts of thorium, uranium, and plutonium are all suitable. In short term, batch reprocessing is likely and the fuel life is estimated to be about 4-7 years with high burn-up [16]. The coolant salts of MSRs stay liquid without pressurization from about 500 °C up to 1400 °C. In contrast, a PWR operates at about 315 °C and 150 bar [16]. For both purposes very pure lithium-7 must be used, as otherwise tritium is formed by neutron capture [15, 17].

The only large scale enrichment of  $^6\text{Li}$  in the western world was done between 1950 and 1963 in US at Oak Ridge National Laboratory for the sake of thermonuclear weapons. The most effective process that was used those days was the column exchange process (COLEX) which was basically a counter current extraction of  $^6\text{Li}$  applying a lithium amalgam as extract phase. The DOE (Department of Energy) is reported to have stopped stockpiling  $^6\text{Li}$  since 1963 [15]. In Russia and in China the COLEX process seems still be used today for their military need of  $^6\text{Li}$  [8, 15]. Unfortunately, no further information about the details of these processes was found. The way toxic mercury was treated in Oak Ridge caused serious environmental problems and led to the renunciation of the process in the US. Foreseeing that the application of nuclear fusion for peaceful electricity generation will require  $^6\text{Li}$ , several alternative lithium isotope separation systems have been developed over the last decades.

The scope of this work is to give a survey of the currently available lithium enrichment processes in order to find a suitable method that satisfies the future needs. Therefore, the Li requirements for fusion and fission application are estimated and an overview on the lithium market situation is given. Subsequently the enrichment processes are listed and evaluated. In reference to that it must be mentioned that the given process survey does not claim to be complete. Since today large scale isotope separation methods are used to attain the nuclear fission fuels ( $\text{U}^{235}$  etc.), it is sensible to compare the investigated lithium isotope separation methods to the commonly used processes (cf. Chapter 6).

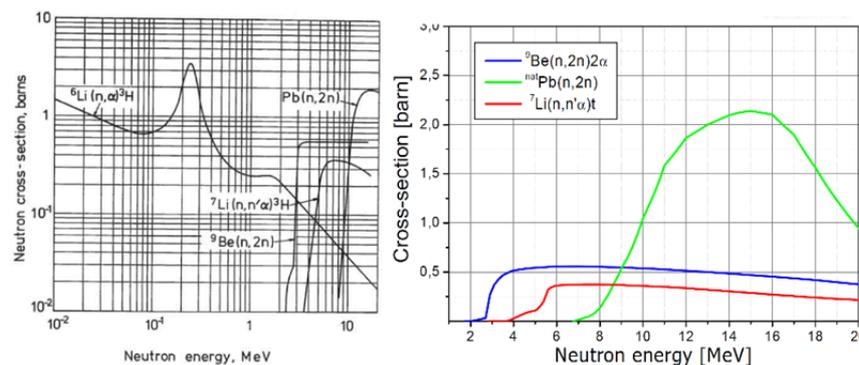
## 2 Lithium requirements

### 2.1 Requirements for fusion application

This chapter refers to the official ITER TBM Programme. However, efforts are underway to align the ITER TBM programme with the European DEMO Blanket programme, and, in this direction, to change the European TBM concepts from HCPB/HCLL to HCPB/WCLL (Water Cooled Lithium Lead). There is even the possibility that the EU TBMs will be reduced to only one of these two options. But the statements given in this chapter for HCLL are expected to do similarly hold for WCLL.

For continuous fusion reactor operation, the amount of tritium bred must at least equalize the amount of tritium burned in the fusion reaction. This would theoretically happen if every fusion neutron would react with one lithium ( ${}^6\text{Li}$ ) nuclei to tritium and if every tritium nuclei would be reprocessed to the fusion core. Unfortunately, in reality this could not be the case. Some neutrons are absorbed by the structural material, some are lost by leakage and since the plasma chamber is not solely covered by blankets a not negligible amount of neutrons is lost by clashing onto the divertor.

Another aspect is the radioactivity of tritium which leads to tritium losses simply by decay into  ${}^3\text{He}$ . Therefore, more tritium must be bred than consumed. The parameter of interest in this case is the tritium breeding ratio (TBR). The TBR defines the ratio of tritium produced in the blanket divided by the tritium consumed in the plasma and by natural decay [2, 4, 6, 8]. To accomplish a TBR higher than one, neutron multipliers are needed. Since the reaction with  ${}^7\text{Li}$  is slightly favourable for the reaction with the initial high energy neutrons (14.6 MeV) while not only producing tritium but also a thermal neutrons, it could also be regarded as multiplier (cf. eq. 1.3). Therefore some advanced breeding concepts employ only liquid lithium. But the even though low cross section of  ${}^7\text{Li}$  and several other reasons (high corrosivity etc.) makes it at the moment favourable to add additional ones (cf. Figure 3) [2, 18]. The most promising neutron multipliers are beryllium and lead.

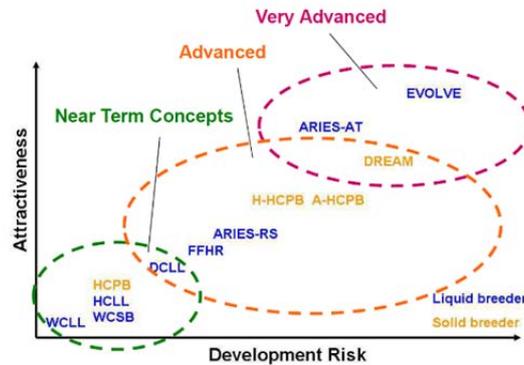


**Figure 3: Cross sections for the reactions [11] on the left, direct comparison of the multiplier cross sections according to reaction on the right [2].**

The resulting two low energy neutrons  $n'$  and  $n''$  in combination with lithium enriched in  ${}^6\text{Li}$  increases the TBR significantly [11].

A variety of breeding blanket concepts has been taken into consideration, ranging from more conservative concepts to higher-risk, higher-payoff concepts for future reactors (cf. Figure 4). Breeding blankets concepts could be generally distinguished according to the aggregate state of the lithium source. Solid breeding blankets will be realized using ceramic lithium containing material in combination with beryllium as multiplier. Since the cross section of Be is not much

larger for high energy neutrons than the one of  ${}^7\text{Li}$  (cf. Figure 3) the required  ${}^6\text{Li}$  enrichment for such solid breeding concepts (e.g. HCPB, HCCB (Helium Cooled Ceramic Breeder), WCCB (Water Cooled Ceramic Breeder)) is comparatively moderate and ranges basically from 30 to 60% [2, 11, 13, 19].



**Figure 4: Breeding blanket concepts attractiveness vs. development risk [8, 20].**

The major candidates for breeding materials consist of liquid breeders [20]. As liquid breeding materials liquid metals (lithium or eutectic lithium lead) or molten lithium salts ((LiF) n (BeF<sub>2</sub>), (LiF-BeF<sub>2</sub>-NaF)) are considered. In the near term special interest will be paid to the liquid breeding concepts (e.g. HCLL, DCLL (Dual Coolant Lithium Lead), SCLL (Self-Cooled Lithium Lead)), which make use of a homogenous eutectic mixture of liquid lead and lithium (cf. Figure 4). Eutectic lithium lead consists to 15.5% of lithium atoms. These concepts usually require a quite high  ${}^6\text{Li}$  enrichment of more than 90% for a good performance since Pb covers the high neutron energy section quite well (cf. Figure 3) [2, 11, 13, 19, 20].

Within the framework of the ITER Test Blanket Working Group at which 7 members participate (CN, EU, IN, JA, KO, RF, US), several test blanket modules (TBMs) have been proposed to be tested in ITER (cf. Table 1) [21, 22]. For the TBMs program three equatorial ports, particularly port number 2, number 16 and number 18, are designated. Each is connected to one incidental port plug (PP) that is designed to host two irrespective TBMs (cf. Figure 5). Since each PP contains TBMs of two different modules overall six TBMs can be tested simultaneously. In ITER particularly harsh settings with significant neutron wall loads and surface heating of approximately up to 0.78 MW/m<sup>2</sup> and up to 0.5 MW/m<sup>2</sup>, respectively. A complete test system is under development for each of these six concepts with the aim to gain further knowledge for the breeding blanket designs that will be used in DEMO [21, 23].

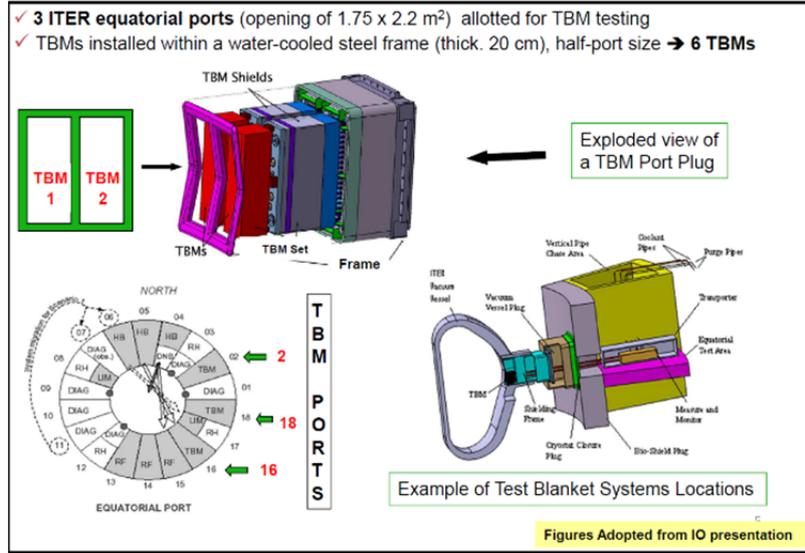


Figure 5: Test blanket systems testing in ITER [22].

In Table 2 the  ${}^6\text{Li}$  mass requirements per half port size TBMs for the different ITER concepts are calculated. The atomic molar masses needed have been extracted from [24] and are summarized in Table 1.

Table 1: Atomic molar mass  $\tilde{M}$  in [kg/kmol]. [25]

$\tilde{M}_{\text{Li-6}}$	$\tilde{M}_{\text{Li-7}}$	$\tilde{M}_{\text{Li,natural}}$	$\tilde{M}_{\text{O,natural}}$	$\tilde{M}_{\text{Si,natural}}$	$\tilde{M}_{\text{Ti,natural}}$	$\tilde{M}_{\text{Pb,natural}}$
6.01512	7.01600	6.941	15.9994	28.0855	47.867	106.421

The calculation occurred as follows:

$$\tilde{M}_{\text{Li,riched}} = \tilde{M}_{\text{Li-6}} \tilde{x}_{\text{Li-6,Li}} + \tilde{M}_{\text{Li-7}} (1 - \tilde{x}_{\text{Li-6,Li}}); \quad (2.3)$$

$$\text{with } [\tilde{x}_{\text{Li-6,Li}}] = \frac{\text{kmol}_{\text{Li-6}}}{\text{kmol}_{\text{Li,riched}}} \quad (2.3.a)$$

$$\tilde{M}_{\text{Breeder}} = \sum_i \tilde{v}_i * \tilde{M}_i \quad (2.4)$$

$$\tilde{M}_{\text{Breeder,Li}_4\text{SiO}_4} = 4 \tilde{M}_{\text{Li,riched}} + \tilde{M}_{\text{Si}} + 4 \tilde{M}_{\text{O}} \quad (2.4.a)$$

$$\tilde{M}_{\text{Breeder,Li}_2\text{TiO}_3} = 2 \tilde{M}_{\text{Li,riched}} + \tilde{M}_{\text{Ti}} + 3 \tilde{M}_{\text{O}} \quad (2.4.b)$$

$$\tilde{M}_{\text{Breeder,LiPb}_{\text{eu}}} = 0.158 \tilde{M}_{\text{Li,riched}} + (1 - 0.158) \tilde{M}_{\text{Pb}} \quad (2.4.c)$$

$$m_{\text{Breeder}} = n_{\text{Breeder}} * \tilde{M}_{\text{Breeder}} \quad (2.5)$$

$$m_{\text{Li,riched}} = n_{\text{Li in Breeder}} * \tilde{M}_{\text{Li,riched}} \quad (2.6)$$

from (2.5.) and (2.6.) follows

$$x_{\text{Li}} = \frac{m_{\text{Li,riched}}}{m_{\text{Breeder}}} = \frac{\tilde{v}_{\text{Li in Breeder}} * \tilde{M}_{\text{Li,riched}}}{\tilde{M}_{\text{Breeder}}} \quad (2.7.)$$

with  $[x_{Li}] = \frac{kg_{Li, enriched}}{kg_{Breeder}}$  and  $\tilde{\nu}_{Li}$  in Breeder is the stoichiometric factor (4, 2, 0.158) for  $Li_4SiO_4$ ,  $Li_2TiO_3$ ,  $LiPb_{eu}$  (eutectic lithium lead) respectively. Therefore:

$$m_{Li, enriched} = m_{Breeder} \cdot x_{Li} \quad (2.8.)$$

With eq (2.8.) follows

$$m_{Li-6} = \tilde{x}_{Li-6, Li} \cdot \tilde{M}_{Li-6} \cdot \frac{m_{Li, enriched}}{\tilde{M}_{Li, enriched}} \quad (2.9.)$$

The mass ratio of the  ${}^6Li$  amount towards the whole breeder mass could be given by

$$x_{Li-6} = \frac{m_{Li-6}}{m_{Breeder}} \quad (2.10.)$$

Conclusively, the  ${}^6Li$  amount needed by each breeder is related to the amount of generated electricity.

**Table 2: Test blanket modules for ITER [26, 27]**

\*The material masses given refer to the material amounts in a half-port size TBM.

TBM-type	Structural material (Name)	Multiplier (Name)	Coolant (Name)	Breeder (Name)	Breeder Mass* (kg)	Li mass* (kg) Calculated	${}^6Li$ enrichment (atomic%)	${}^6Li$ mass* (kg) Calculated	$\frac{x_{Li}}{Breeder\ mass} = \frac{lithium\ mass}{Breeder\ mass}$ (-) Calculated	$\frac{x_{{}^6Li}}{Breeder\ mass} = \frac{lithium-6\ mass}{Breeder\ mass}$ (-)
China HCSB (Helium Cooled Solid Breeder)	Eurofer	Be pebbles	He	$Li_4SiO_4$	51	10.84	80% [56]	8.39	0.2126	0.1646
EU HCSB	Eurofer	Be pebbles	He	$Li_4SiO_4$ or $Li_2TiO_3$	97	21.90 or 11.45	30% for $Li_4SiO_4$ 60% for $Li_2TiO_3$	5.89 or 6.44	0.2258 or 0.1180	0.0607 or 0.0664
Japan HCSB	F82H	Be or $Be_{12}Ti$ pebbles	He	$Li_2TiO_3$ or others	104	-	-(no reference found yet)	-	-	-
Korea HCSB	Eurofer	Be pebbles	He	$Li_4SiO_4$	85.3	19.04	40%	6.92	0.2232	0.0812
RF HCSB (for one submodule)	FS (9CrMoV Nb)	Be (porous blocks)	He	$Li_4SiO_4$	35.5 x2	-	-(no reference found yet)	-	-	-
US HCSB (for 3 unit cells)	F82H or Eurofer	Be pebbles	He	$Li_4SiO_4$ or $Li_2TiO_3$	38.5	-	-(no reference found yet)	-	-	-
Japan WCSB (Water Cooled Solid Breeder)	F82H	Be or $Be_{12}Ti$ pebbles	$H_2O$	$Li_2TiO_3$ or others	91	10.29	90% [54]	9.11	0.1131	0.1001
China DFLL (Dual Functional Lithium Lead)	CLAFM	as the breeder	He	Pb-17Li (also as partial coolant)	2196	23.50	90% [53]	20.80	0.0107	$9.47 \cdot 10^{-3}$
EU HCLL	Eurofer	as the breeder	He	Pb-17Li	2863	30.63	90%	27.12	0.0107	$9.47 \cdot 10^{-3}$
US DCLL	F82H	as the breeder	He	Pb-17Li (also as partial coolant)	1824	19.52	90%	17.28	0.0107	$9.47 \cdot 10^{-3}$
Korea HCML (Helium Cooled Molten)	Eurofer	as the breeder	He	Li	13.9	13.9	90%	12.31	1	0.8853

Lithium)										
RF SCLi (Self-Cooled liquid Lithium)	V-4Cr-4Ti	Be (porous blocks)	-	Li (also as coolant)	11	11	90%	9.74	1	0.8853
Indian LLCB (Lead Lithium Ceramic Breeder) [51]	In-RAFMS [51]	Be-pebbles and as the breeder [51]	He [51]	Pb-17Li (also as coolant) and Li <sub>2</sub> TiO <sub>3</sub> [51]	(no reference found yet)	-	90% for Pb-17Li [53, 54] and 60% for Li <sub>2</sub> TiO <sub>3</sub> [55]	-	0.0107 and 0.1180	-

The European Union has been developing in general two breeding blanket concepts that shall be tested in ITER and afterwards in DEMO. One is the Helium Cooled ceramic Pebble Bed concept (HCPB) which makes use of ternary ceramic pebbles consisting of Li<sub>4</sub>SiO<sub>4</sub> or Li<sub>2</sub>TiO<sub>3</sub> with a lithium-6 enrichment of 30% and 60% respectively as breeding material. The other is the Helium Cooled Lithium Lead (HCLL) concept that uses eutectic lithium lead (LL) with an <sup>6</sup>Li enrichment level of more than 90% as breeding material [21, 26]. It is assumed that a volume of approximately 854 liters of eutectic lithium lead (PbLi<sub>eu</sub>) which consist to 15.8 at% or rather 0.64 w% of lithium will be needed for the EU-HCLL-TBM [13, 19, 28]. The density of eutectic lithium lead is  $\rho_{LL,EU} = \frac{9.4 \cdot 10^3 \text{ kg}}{\text{m}^3}$ .

The lithium lead mass and consequently the lithium mass amount needed per TBM can be calculated to: [13, 19]

$$m_{LL} = V_{LL,EU} \cdot \rho_{LL,EU} = 0.854 \text{ m}^3 \cdot \frac{9.4 \cdot 10^3 \text{ kg}}{\text{m}^3} = 8027.6 \text{ kg} \quad (2.11)$$

With a mass ratio of  $x_{Li,LL_{eu}} = 0.64 \cdot 10^{-2}$ ;  $[x_{Li,LL}] = \frac{\text{Lithium mass (m}_{Li})}{\text{Lithium lead mass (m}_{LL})}$

$$m_{Li, enriched(LL)} = x_{Li,LL_{eu}} \cdot m_{LL} = 0.0064 \cdot 8037 \text{ kg} = 51.38 \text{ kg} \quad (2.12)$$

That means about 51.38 kg lithium per TBM and therefore 154.14 kg for all three TBM ITER phases will be needed (cf. Figure 6). An extra safety margin of 40% is foreseen in case of failures that lead to material loss, but this is not included in the calculations here.

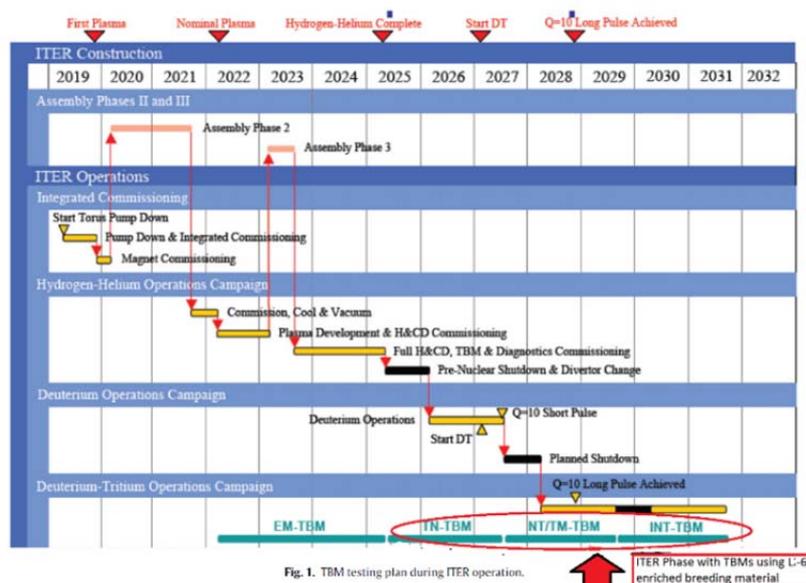


Figure 6: TBM testing plan during ITER operation.



In case of the HCPB concept using  $\text{Li}_4\text{SiO}_4$  as breeding material a total breeder mass for all three test series of 270 kg can be considered (90 kg for each TBM ITER phase). For the mass percentage of 27 w% a total lithium amount of  $m_{\text{Li, enriched(CB)}} = 62.1$  kg can be calculated. Assuming an enrichment of 90% lithium-6 for both cases would lead to a total amount of

$$\begin{aligned} m_{\text{Li, enriched, EU-TBM}} &= m_{\text{Li, enriched(LL)}} + m_{\text{Li, enriched(CB)}} \\ &= 154.14 \text{ kg} + 62.1 \text{ kg} = 216.24 \text{ kg} \end{aligned} \quad (2.13)$$

Since the enrichment of ceramic breeders (CB) is in general smaller than 90% the amount can be approximated to 200 kg of 90%  $^6\text{Li}$  enriched lithium for the European TBM material for ITER. [19] 200 kg of 90% enriched lithium equals a pure  $^6\text{Li}$  amount of

$$m_{\text{pure Li-6}} = m_{\text{Li, enriched, EU-TBM}} \cdot x_{\text{Li-6, Li}} = 200 \text{ kg} \cdot 0.8853 = 177 \text{ kg} \quad (2.14)$$

$$\text{while } x_{\text{Li-6, Li}} = \frac{\tilde{x}_{\text{Li-6, Li}}}{\tilde{x}_{\text{Li-6, Li}} \cdot \left(1 - \frac{\tilde{M}_{\text{Li-7}}}{\tilde{M}_{\text{Li-6}}}\right) + \frac{\tilde{M}_{\text{Li-7}}}{\tilde{M}_{\text{Li-6}}}} = \frac{0.9}{0.9 \cdot \left(1 - \frac{7.01600}{6.01512}\right) + \frac{7.01600}{6.01512}} \cong 0.8853 \quad (2.15)$$

Actually, the amount could be even higher because of the complementary amounts needed for the ongoing experimental programmes: LIBRETTO (Liquid Breeder Experiment with Tritium Transport Option) irradiation, TRIEX (TRitium EXtraction), EBBTF (European Breeding Blanket Test Facility), DIADEMO (facility with gas and PbLi eutectic circuits), PICOLO (corrosion testing loop), MEKKA (Magnetohydrodynamic Experiments in NaK Karlsruhe) and new loops are not considered yet. During the TBM testing a negligible lithium burn up is assumed. This means in reference to lithium enrichment processes that a concept which is suitable for reprocessing of the used breeding material is needed. [13, 19]

For the DEMO Breeding Blankets the needed  $^6\text{Li}$  amounts are even much higher. The volume of 90% enriched liquid lead that is required for DEMO HCLL could be approximated to about 1000  $\text{m}^3$ . This means that the total LL mass could be estimated to:

$$m_{\text{LL, DEMO}} = V_{\text{LL, EU}} \cdot \rho_{\text{LL, EU}} = 1000 \text{ m}^3 \cdot \frac{9.4 \cdot 10^3 \text{ kg}}{\text{m}^3} = 9.4 \cdot 10^6 \text{ kg} = 9400 \text{ t} \quad (2.16)$$

With the mass ratio for eutectic LL ( $x_{\text{Li, LL, eu}} = 0.64 \cdot 10^{-2}$ ) that was already given above, the amount of 90% enriched lithium can be calculated to:

$$m_{\text{Li, enriched(LL)}} = x_{\text{Li, LL, eu}} \cdot m_{\text{LL, DEMO}} = 0.0064 \cdot 9400 \text{ t} = 60.16 \text{ t} \quad (2.17)$$

60 tons of 90%  $^6\text{Li}$  enriched LL only for the EU's HCLL breeder which would mean about 53 tons of pure  $^6\text{Li}$  per DEMO  $\text{GW}_e$  is a quite challenging amount regarding the lithium isotope enrichment process [13]. This consideration lacks the also pretty large amounts needed for the ceramic breeding material of the European DEMO HCPB model as well as further research material. For the DEMO fusion reactor the irradiation aspect becomes much more relevant than for ITER. Impurities, especially in the ceramic breeding materials such as Al, Co and Pt, could easily be activated. Thus a recycling process of the breeding material which is associated with regaining  $^6\text{Li}$  must not only be compatible to unpreventable tritium contaminations but also to further irradiating material [19].



## **2.2 Requirements for fission application**

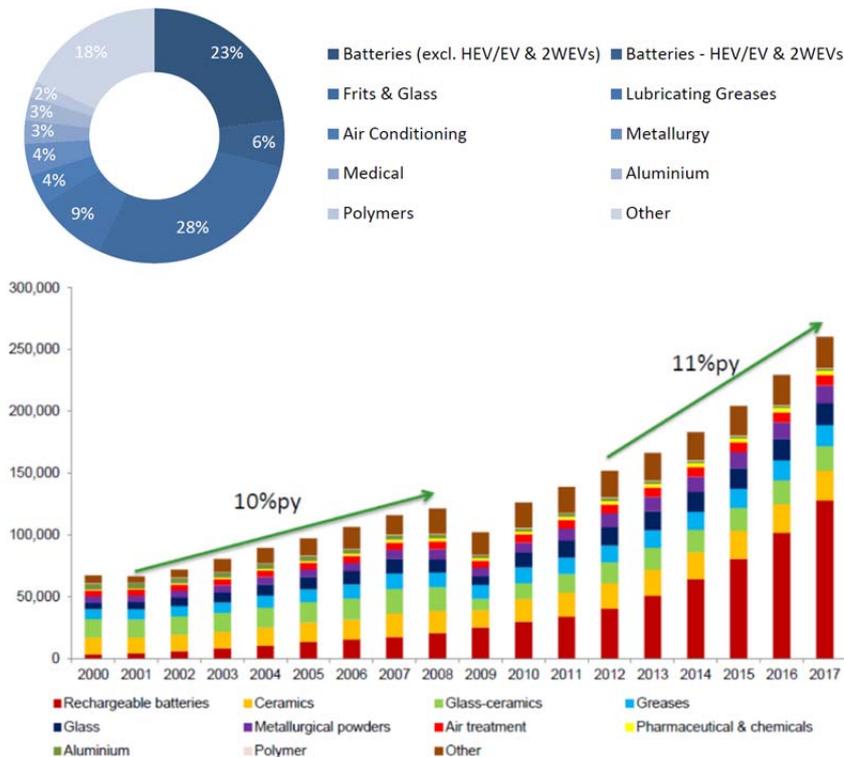
For the operation of two types of nuclear fission reactors  ${}^7\text{Li}$  is required. In pressurized water reactors lithium hydroxide is added to prevent the cooling water from becoming acidic and  ${}^7\text{Li}$  is added to demineralizers for filtering out radioactive contaminants from the cooling water.

The worlds demand for PWRs is about one ton per year. For the 65 pressurized water reactors in the US 300-400 kg of 99.99% enriched lithium-7 are needed each year.

Molten salt reactors which are plant to be built in China e. g. require even larger amounts of lithium-7 in a more pure form (99.995% or higher). Each of these reactors are expected to need thousands of kilograms of lithium-7 to operate [15, 17].

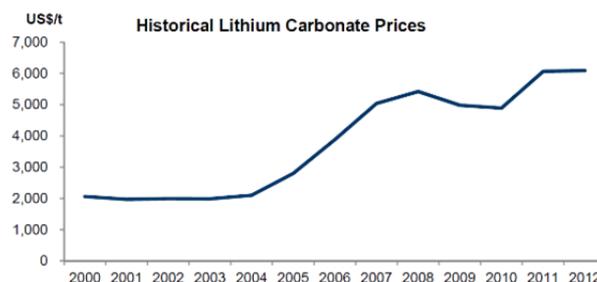
### 3 Lithium market situation

Lithium, the lightest element in the periodic table which is solid at room temperature, exhibits a wide range of economically beneficial properties. It has the highest electrochemical potential of all metals, a very high coefficient of thermal expansion, rather good fluxing and catalytic properties and it acts as a viscosity modifier in glass melts. For these reasons it offers various chemical and technical applications among which the currently fastest growing and the second largest market is that of Li-ion batteries. Figure 7 shows the dues of the most important economical branches as well as the respective world consumption over the last decade [29].



**Figure 7: Lithium applications (2011) and respective world consumption (outlook) by end use (2000-2017) [29].**

The main chemicals lithium is traded with are lithium carbonate, lithium hydroxide, lithium chloride, other lithium halide salts and butyl lithium. Of those lithium carbonate is the most frequently traded one and the lithium market is often represented by the lithium carbonate equivalent. The demand caused by the application of Li-ion batteries increased the lithium (carbonate) price significantly over the last decades (cf. Figure 8).



**Figure 8: Lithium carbonate equivalent price trend (2000-2012) [29].**

Lithium does not occur in nature as a pure element. It is found within mineral deposits or salts. The contained concentration of lithium is generally low and only a limited number of resources from which lithium can be economically extracted exist. The largest part of lithium reserves are found in South America (Bolivia, Chile, Argentina) followed by China, the US and Australia (cf. Figure 9).



**Figure 9: Lithium reserves by country on the left hand, Lithium supply by country (2011) on the right hand side [29].**

The lithium supply by country is mainly consistent with the lithium reserves with the exception of Australia which provides a quite large share of 31% compared to its reserves of 6%.

Regarding nuclear industry, lithium is not only interesting as tritium breeder for nuclear fusion application, but also as buffer needed in pressurized water fission reactors. The lithium application is here dependent on its isotopic composition. As already explained lithium-6 is favourable for the tritium breeding reaction. Enriched lithium-7 is used in the hydroxide form to buffer the cooling water of pressurized water reactors. It prevents the water - which contains other components that are essential to manage the nuclear reaction - from becoming acidic. Since it is most important to suppress tritium breeding in the cooling water, it is required to apply lithium that is highly enriched in lithium-7 [15]. In US, approx. 13% of the whole electricity is produced by pressurized water reactors. Since the US has stopped separating lithium isotopes at industrial scale after dismantling the Oak Ridge enrichment plants (COLEX, ELEX and OREX), it is today dependent on the export of Russia and China. Both still stockpile lithium-6 for military reasons and sell the simultaneously produced lithium-7 on the free market. China as well as Russia applies the COLEX process that was used in Oak Ridge, although it seems that in Russia the electrochemical ELEX process is more frequently used. Russia's Novosibirsk Chemical Concentrates Plant (NCCP) in Siberia is the largest supplier of lithium-7 [17, 30].

Today commercial available lithium-6 is only sold in small amounts and for very high prices (cf. Figure 10). If you would like to order lithium-6 enriched material, the prices are at pharmaceutical ranges. For example: 1 g of lithium-6 purchased by SIGMA ALDRICH costs 86.50 €, while 100 g of aspirin (acetyl salicylic acid) costs only about 23 € there [31, 32].

**SPEX CertiPrep**  
Inorganic and Organic Certified Reference Materials

Home > Products > Inorganic Standards > Lithium 6 Isotope, 100 ug/mL for ICP-MS, 125 mL

**Product Information**

Part #: ISOT-L16  
Matrix: 2% HNO<sub>3</sub>  
Volume: 125 mL  
Units/Pack: 1  
Storage Condition: Ambient  
Shipping Info: Hazardous  
Method Reference:  
Product Notes:  
SDS

**Lithium 6 Isotope, 100 ug/mL for ICP-MS, 125 mL**

Retail Price: \$ 155.00  
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Claritas PPT Grade Lithium 6 Isotope for ICP-MS, 100 ug/mL (100 PPM), 125 mL, in 2% HNO<sub>3</sub>

Components	Concentration
Lithium 6	100 ug/mL

Related Categories	Alphabetical Listings, I-L, Lithium, Materials Science, Metal and Ceramic Science, More...
InChI Key	WHXSMMKQMYFTQS-BJUDXGMSA-N
isotopic purity	95 atom % <sup>6</sup> Li
form	chunks
mass shift	M-1

### Beschreibung

Packaging	1, 10 g in glass bottle
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SKU-Packungsgröße	Verfügbarkeit	Preis (EUR)	Anzahl
340421-1G	<span style="color: green;">✔</span> Nur noch 4 verfügbar. Mehr ist unterwegs. - ab	86.50	0 <span>★</span> <span>i</span>
340421-10G	<span style="color: green;">✔</span> Der Versand erfolgt am 18.05.18 - ab	432.00	0 <span>★</span> <span>i</span>

**Figure 10: Amounts and prices of lithium-6 offered by common commercial providers; SPEX CertiPrep. on the left hand, SIGMA ALDRICH on the right hand side [32, 33].**

Regarding the European breeding blanket concepts, it is important to consider the production costs of the respective enriched breeding materials meaning the solid  $\text{Li}_4\text{SiO}_4$  or  $\text{Li}_2\text{TiO}_3$ -pebbles as well as the liquid eutectic lithium lead LL. The major part in the total cost of the production of the breeding materials will be represented by the high costs of lithium-6 [13, 19]. In the past the provider of lithium-6 chemicals for enriched orthosilicates (OSi) was the Euriso-top (Saint Aubin, France and Saarbrücken, Germany, resp.), which is a subsidiary of Cambridge Isotope Laboratories (Andover, MA, USA) [19]. It offered 95% enriched lithium-6 metal for 5000 € per 100 g which means a ratio of  $r = \frac{5000 \text{ €}}{95 \text{ g pure Li-6}}$ . In case of ITER OSi-TBM this would mean a price of approximately:

$$r \cdot x_{\text{Li-6,Li}} \cdot m_{\text{Li,enriched(CB,OSi)}} = \frac{5000 \text{ €}}{95 \text{ g pure Li-6}} \cdot 0.3637 \cdot 62.1 \cdot 10^3 \text{ g pure lithium,LL-TBM} \quad (3.1)$$

$$= 1\,188\,724.74 \text{ € for 40\% enriched OSi – TBMs}$$

If the same price and supplier is considered for the production of the  $\text{Li}_2\text{TiO}_3$  (metatitanate, MTi) pebble-TBMs as well as the liquid lithium lead (LL) TBMs the respective prices could be calculated to:

$$r \cdot x_{\text{Li-6,Li}} \cdot m_{\text{Li,enriched(CB,MTi)}} = \frac{5000 \text{ €}}{95 \text{ g pure Li-6}} \cdot 0.5626 \cdot 62.1 \cdot 10^3 \text{ g pure lithium,LL-TBM}$$

$$= 1\,838\,813.68 \text{ € for 60\% enriched MTi – TBMs}$$

$$r \cdot x_{\text{Li-6,Li}} \cdot m_{\text{Li,enriched(LL)}} = \frac{5000 \text{ €}}{95 \text{ g pure Li-6}} \cdot 0.885 \cdot 154.14 \cdot 10^3 \text{ g pure lithium,LL-TBM}$$

$$= 7\,179\,678.95 \text{ € for 90\% enriched OSi – TBMs}$$

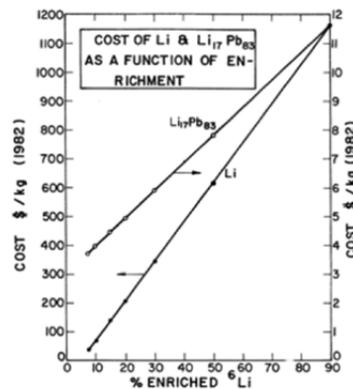
The lithium-6 amount needed for the DEMO LL-breeding blankets would cost under this conditions nearly unaffordable:

$$r \cdot x_{\text{Li-6,Li}} \cdot m_{\text{Li,enriched(LL),DEMO}} = \frac{5000 \text{ €}}{95 \text{ g pure Li-6}} \cdot 53.19 \cdot 10^6 \text{ g pure lithium,LL-DEMO}$$

$$= 279\,947\,368.4 \text{ € for 90\% enriched LL – DEMO blankets}$$

At the moment, it is actually not even possible for the suppliers to offer the amounts needed for ITER (not to mention DEMO...). Therefore, a price estimation based on the current market situation is quite difficult for the large amounts needed. However, the prices for that much more material per order can be usually assumed to be significantly smaller [19].

There were basically two models that tried to predict the lithium price as a function of the  ${}^6\text{Li}$  enrichment level. One model which was developed in 1982 within the framework on the modular stellarator power reactor UWTOR-M shows a linear dependency on the enrichment. This model was developed on the basis of the COLEX enrichment process that will be explained in detail in chapter 4.1.1. Figure 11 shows the price curves based on that model for pure metallic lithium as well as for the eutectic lithium lead breeding material. Since the price for natural lead is higher than for natural lithium the LL-curve begins at a higher price level. But as the price contribution of Pb stays constant and only the smaller amount of lithium in the eutectic alloy rises the price the acclivity of the curve is flatter than that of pure lithium. The intersection point of the price level is suggested to be at an enrichment level of 90% and is assumed to be at the range of 1'150 \$/kg<sub>LL</sub>. Before that point the price level of PbLi-alloy is constantly higher than for pure lithium.



**Figure 11: 1982 UWTOR-M cost estimate based on COLEX enrichment process (by ORNL).**

The other model is the Waganer model. According to that model 90% enriched LiPb would cost 9 \$/kg<sub>LL</sub>. This price per unit was calculated according to the following assumptions:

- The current costs of 99.97% pure Pb with 300 wppm Bi would be  $r_{\text{pb}} = 3 \text{ $/kg}_{\text{Pb}}$ .
- The predicted costs for 90% enriched lithium are about  $r_{\text{Li, enriched}} = 1000 \text{ $/kg}_{\text{Li, enriched}}$ .

The unit price of lithium lead is consequently calculated by summarizing the product of the respective unit ( $r_{\text{Li, enriched}}/r_{\text{Pb}}$ ) cost and mass fraction of the eutectic alloy ( $x_{\text{Pb, LL}}/x_{\text{Li, enriched, LL}}$ ).

$$r_{\text{Pb}}x_{\text{Pb, LL}} + x_{\text{Li, enriched, LL}}r_{\text{Li, enriched}} \quad (3.2)$$

Other variables that influence the material costs according to the Waganer model are:

- The costs of mixing the Pb and Li material to the eutecticum
- The control of Bi impurities that have to be below 50 wppm for irradiation reasons
- The purification system to remove by products

Therefore, it is suggested to consider the additional costs of

- Mixing the alloy
- The online purification system that shall remove Pb byproducts (Bi, Po, Hg radioisotopes) as well as corrosion products (Fe, Ni, Cr radioisotopes)
- The fuel handling and storage which includes the T separation and the replenishment of Li

Currently both estimation models are predicting by far smaller prices for LL as well as for pure lithium than the American and German companies request. The recommended curve shape of the price development over the enrichment level is neither linear as the UWTOP-M model nor convex



(exponential increasing) as the Waganer model but concave as the red curve shown in Figure 12 [34].

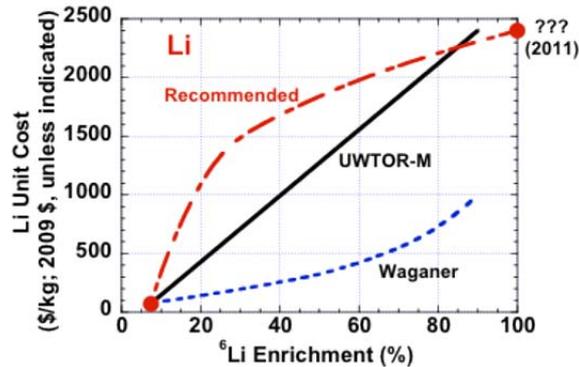


Figure 12: Lithium unit cost trend over the Li-6 enrichment level [34].

It would be therefore favourable to find an enrichment process that offers such a price trend. The way the isotope enrichment process influences the market situation of the appurtenant material can be in case of lithium exemplified by the lithium market development after the establishment of the enrichment plants in Oak Ridge. The overcapacity of lithium produced and stockpiled in Oak Ridge lead to a dramatic decrease of the lithium process costs between the 1940's and the 1960's. The lithium price reached a low of 0.39 \$/kg in 1966 and was less than a third of the original price in 1942 [35]. Assuming that such a scenario would be somehow repeated after establishing the <sup>6</sup>Li-enrichment plants needed for the (peaceful) fusion application, it would strengthen the effect of an economic enrichment process on the <sup>6</sup>Li price by decreasing the price of the raw material.



## 4 Enrichment processes

### 4.1 Chemical exchange systems

According to the second law of thermodynamics the energy required for the separation of isotopes equates at least the energy needed to overcome the entropy of mixing them [35]. In this case, the process is reversible. Unfortunately, a perfect reversible process does not exist in nature. However, it is desirable from an economic point of view to come as close as possible to this point. Chemical equilibrium systems offer the opportunity to that [36]. Chemical equilibrium systems are in general two phase systems that can be classified by their aggregation state. Potential systems are:

- gas / liquid
- gas / solid
- liquid / solid and
- liquid / liquid

It is generally assumed that it would be advantageous if one lithium containing phase would be gaseous (probably because the common ways separating uranium could be used or a simple rectification column could be used for the separation process). But as today lithium compounds that remain gaseous at room temperature are unknown, investigations are limited to liquid-solid and immiscible liquid-liquid systems [10, 36, 37].

The separation occurs due to small differences of chemical properties (solubility) that leads to a slight tendency for lithium-6 to be favoured in one phase and lithium-7 in the other [2, 3]. The extend of the separation effect depends on the fractional differences in isotopic mass  $\Delta m/m$  and the resulting difference in free energy [38].

These differences are accentuated with isotopes of elements of low atomic weight [2]. For small elements like Lithium the molecular vibration frequencies are too high to be fully stimulated at room temperature. Therefore the isotopic differences of the zero-point energies are still perceivable in the free energies. [10, 38]

The magnitude of the single stage isotope separation by two phases at chemical equilibrium is given by the separation factor  $\alpha$ . The separation factor is defined as the quotient of the isotope concentration ratios in the two phases [39].

$$\alpha_7^6 = \frac{([{}^6\text{Li}]/[{}^7\text{Li}])_{\text{phase 1}}}{([{}^6\text{Li}]/[{}^7\text{Li}])_{\text{phase 2}}} \quad (4.1)$$

A value for  $\alpha$  that is larger than 1.03 should be acceptable for chemical lithium-6 enrichment [37]. Since the single stage separation factors for isotopes are very small the desired purity can only be reached by a certain number of equilibrium stages [36].

In the past mainly two liquid phase chemical exchange systems were considered for large scale operation. The required lithium-6 enrichment can be accomplished by running a counter current column in which the solutions passed a cascade of stages [10, 39–41]. If the column contains  $n$  stages and equilibrium is established in each of them the maximum fractionating effect is  $\alpha^n$  [40].

The selection of a suitable liquid/liquid system can be made by the following criteria:

- 1) The isotopes should be evenly distributed between the two immiscible solvents.
- 2) The whole system is out to be chemically stable.
- 3) The isotopic exchange between the two phases should be rapid.
- 4) The solvation environments must be significantly different. It is even preferred that the elements exist in different chemical forms in the two phases.
- 5) The counter current contacting should not be complicated.
- 6) The separation of the two phases and the establishment of a reflux system should be simple and possible on a continuous basis [3, 15, 37].

Unfortunately ordinary aqueous-organic systems show no significant isotope effect ( $\alpha < 1.005$ ) [15]. Lithium compounds are much better soluble in aqueous solvents which leads to the fact that the distribution ratio is greatly in favour of the aqueous phase. Further the state of solvation is almost equal since lithium forms strong solvation shells and carries them along into the organic phase [37, 42].

In the following only suitable processes with significant isotopic selectivity will be discussed.

#### 4.1.1 Lithium-amalgam system

In 1936 Lewis and MacDonald discovered that lithium-6 has a greater affinity for mercury than lithium-7. After producing a lithium amalgam by electrolysis of a lithium carbonate solution using a mercury electrode they separated the isotopes in a large column. In the column, which was filled with an alcoholic lithium chloride (LiCl) solution, they created a counter current flow by creating small droplets (~0.1 mm) of lithium amalgam through a tied silk fabric. This early experiment resulted in a minimum fractionation factor of  $\alpha$  equal to 1.025. In reference to that they determined a difference in electrode potential between the lithium amalgam and the alcoholic solution that was 0.6 mV higher for lithium-7 than for lithium-6.

It is remarkable that the authors were convinced that isotope enrichment will always stay on lab scale and expensive [40] and 14 years later the first and so far known last large scale lithium enrichment plants in the western world were conducted in the Y-12 Plant of Oak Ridge National Laboratory (cf. Figure 13), based on their own idea.

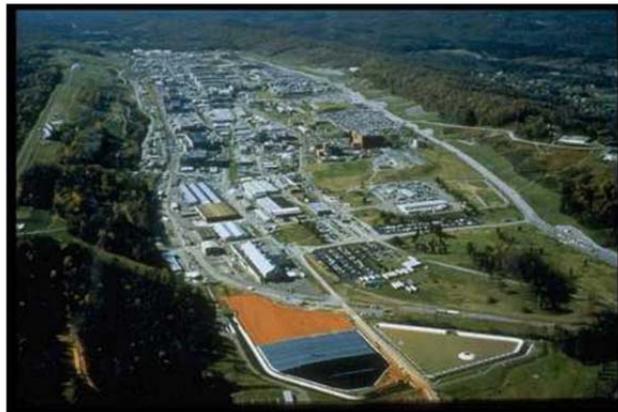


Figure 13: The Y-12 plant at Oak Ridge, Tennessee [41].

The USA have been stockpiling lithium-6 for the use of thermonuclear weapons. Ceramics like lithium-6 deuteride,  ${}^6\text{LiD}$ , was used in the second stage of modern hydrogen bombs. In the primary stage gaseous deuterium and tritium are injected into the fission pit [41] as booster. This way nuclear fission provides the energy and temperature for the nuclear fusion in the first step and the resulting free neutrons react with the  ${}^6\text{LiD}$  in the second step. This boosts the explosion further by 22.4 MeV per converted molecule [10].

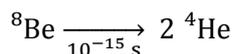


22.4 MeV

Since impurities of lithium-7 would consume neutrons without producing the beneficial tritium by the following equation,



(4.6)



Very pure  ${}^6\text{Li}$  was used for that application [10].

Three kinds of enrichment plants have been running in Oak Ridge National Laboratory between 1950 and 1963 [15, 37, 41]. The first successfully installed pilot plant called ELEX was driven by electrochemical exchange with mercury as cathode. The used process is comparable to the chlorine gas and sodium hydroxide production and is further described in chapter 4.2. The ELEX pilot plant was operating from 1952 till 1958 [41].

The other processes, COLEX (column exchange) and OREX (organic exchange), based on chemical isotopic exchange. Both use lithium amalgam as one phase but differ by the other. The COLEX process uses an aqueous solution of lithium hydroxide (LiOH) as second phase and the OREX an organic solution of lithium chloride in propylene-di-amine (PDA). They were exposed to a sort of inter plant competition to determine which is the more efficient one. The COLEX process won the competition and OREX was dismantled between 1957 and 1959 [41]. Today the COLEX process is still used in Russia and China for military reasons [30]. Two COLEX facilities called Alpha-4 and Alpha-5 were established at the Y-12 plant. The Alpha-4 plant was running from 1955 till 1963 and was placed on standby until the late 1980 when it was finally dismantled. Alpha-5 was operating from 1955 until 1959 and restarted in 1963 for a period of 6 month. It was dismantled between 1965 and 1966. According to the Department of Energy (DOE) the USA has stopped stockpiling lithium-6 isotopes since 1963. [15, 41]



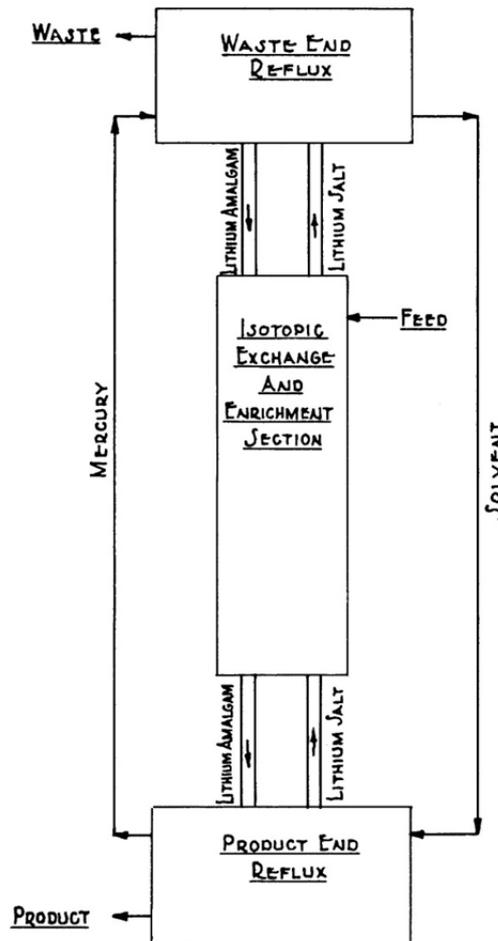
**Figure 14: COLEX facility [41].**



**Figure 15: Lithium hydroxide solution tank [41].**

The major part of investigation on amalgamation systems in the USA was done between the 1940s and the early 1950s [37], since the pressure on national defence was high during the second world war and the directly following arms race with the Soviet Union during the cold war. The focus of that work was to find a suitable system that could be developed into a practical counter current isotope separation plant employing chemical reflux [37, 42]. In Figure 16, a simplified draft of such a process is given. The main facility of the process is the isotopic exchange section that represents the column. Lithium amalgam flows in counter current to a lithium salt solution. The two reflux sections removed the lithium from the phase flowing from the column (enriched in lithium-6) and

insert it into the phase flowing to the column. For continuous operation, several auxiliary processes are needed. The product is enriched in lithium-6 and the waste in lithium-7. [36]



**Figure 16: Simplified block flow diagram of chemical reflux systems for lithium isotope separation [36].**

The separation factor of all so far investigated systems show that  $\alpha$  is a function of temperature.

$$\alpha = \alpha(T)$$

Making use of the fact that  $\alpha$  depends on temperature a dual temperature reflux process which is sketched in Figure 17 can be used. A dual temperature process is most efficient when the possibility of operating an exchange system between two widely separated temperatures is given [36]. The operating ability of the dual temperature reflux system for lithium isotope separation has been confirmed by the Materials Chemistry Division of ORNL. For that purpose, Li-amalgam in contact with LiCl solubilized in either propylene-di-amine (PDA) or ethylene-di-amine (EDA) was used. The PDA system was more advantageous since it shows a wider range of useful temperatures and is stable up to 100 °C. [43] The dual temperature process requires two towers. One must be significantly warmer than the other. The amalgam phase is fed into the cold tower since the equilibrium constant is higher for low temperatures [42, 43]. This tower is called the concentration tower. The other phase, containing the lithium salt, flows in counter current to the feed stream in the hot tower which is called stripping tower. The amalgam feed is first enriched in lithium-6 in the concentration tower. Then in a counter current heat exchanger it is warmed up before entering the stripping tower by the heat of the solution leaving it. In the stripping tower the amalgam is stripped of the enriched lithium-6. Since the separation factor is here smaller the amalgam leaves the stripping tower with a lower concentration in lithium-6 than it entered the

system originally in the feed. The concentrations in lithium-6 between the amalgam leaving the stripping tower and the solution entering the stripping tower are at equilibrium. The solution stream that enters the stripping tower comes from the bottom of the concentration tower where it was just brought into equilibrium with the initial feed. To attain the maximal efficiency it is important to assure equilibrium conditions at the exits of the towers. The highest fraction of the desired  ${}^6\text{Li}$  isotope that could be extracted and concentrated in the product can be estimated as follows:

$$f_{\max} = \frac{\alpha_{\text{concentration column}} - \alpha_{\text{stripping column}}}{\alpha_{\text{concentration column}}} \quad (4.7)$$

This means that the enrichment that could be achieved is accompanied in the region between the two towers and is therefore significantly smaller than the enrichment that could be attained regarding only the cold system [43]. For this reason a dual temperature process needs many more stages than for instance the chemical and electrochemical reflux systems. [36]

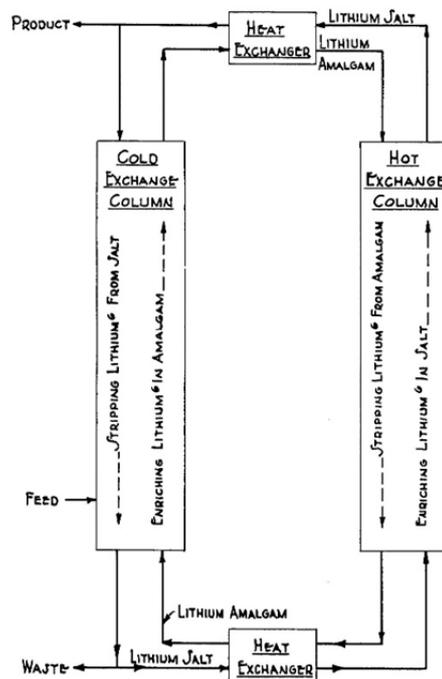


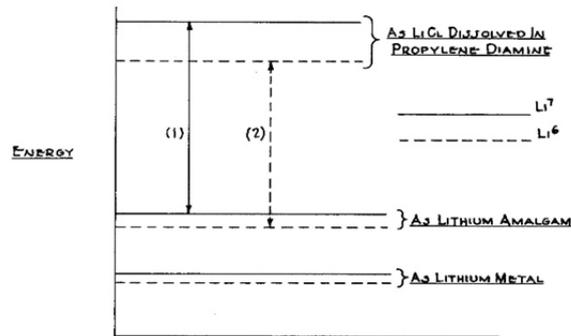
Figure 17: Dual temperature process for lithium isotope separation [36].

Since lithium amalgam is a good reducing agent, the number of salts and solvents that can be used without reacting with it is limited [42]. Reactive solvents such as water or various alcohols decompose lithium amalgam to form lithium hydroxide or lithium alcoholate and hydrogen gas [36]. This way lithium is transferred from the amalgam phase to the aqueous or organic phase and the system becomes unstable. Therefore the use of a reactive solvent is only applicable if the reaction rates of the amalgam decomposition are slow.

The most R&D (Research and Development) among the reactive systems was applied to aqueous lithium hydroxide/lithium amalgam systems which were used to run the COLEX pilot plant [36, 41]. It offers practical advantages for the plant design like for example easy reflux methods [42] which will be discussed later. To eliminate the problem of amalgam decomposition sometimes a holding current was applied to electrolyse the lithium back into the amalgam. This way the concentration of lithium in the amalgam remains constant [42].

Among the stable solvent systems, lithium chloride dissolved in amines and unreactive ethers, propylene-di-amine (1, 2, diamine propane; short: PDA) gained the most attention [36]. It was the system that was used by the OREX pilot plant [41].

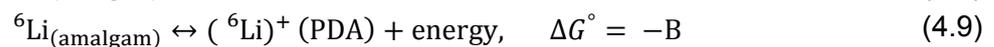
The chemical stability of lithium is higher in the aqueous or organic phase than in the amalgam phase [36]. Since chemical stability is associated with a low free energy (G) level lithium in propylene-di-amine for instance is at a lower free energy level than in the amalgam phase [36] (cf. Figure 18).



**Figure 18: Energy levels of lithium isotopes for different chemical environments [36].**

The fact that lithium-6 is enriched in the amalgam phase means that the loss of free energy by the transition of lithium-7 from the amalgam phase into the organic or aqueous phase is higher. [36]

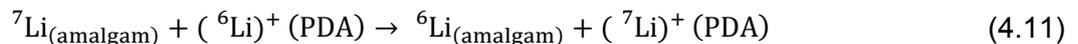
This can be described for example for PDA by the following equations:



and

$$|A| > |B| \quad (4.10)$$

From these equations follows that the difference in free energy between lithium-6 and lithium-7 is negative for the isotopic exchange and this way the whole free energy is lowered [36].



$$\Delta G^\circ = -A + B = -C \quad (4.12)$$

The -C equals approximately -31 cal. at 25 °C [36], that means 129.76 J which is actually quite small.

Due to the definition the separation factor  $\alpha$  and the equilibrium constant are equal. Therefore the dependence of  $\alpha$  on temperature could be given by the van't Hoff equation [36]:

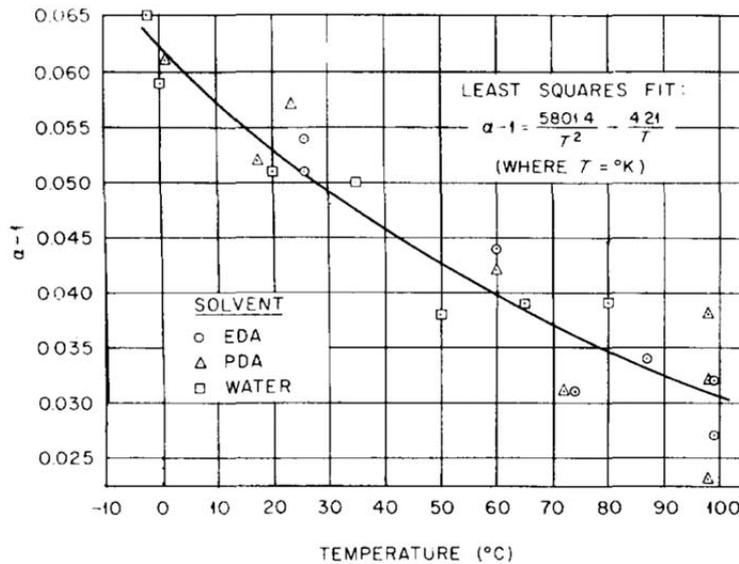
$$\ln(\alpha) = \frac{-\Delta G^\circ}{RT} = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (4.13)$$

Over small changes in temperature the van't Hoff equation can be simplified by binominal approximation [36].

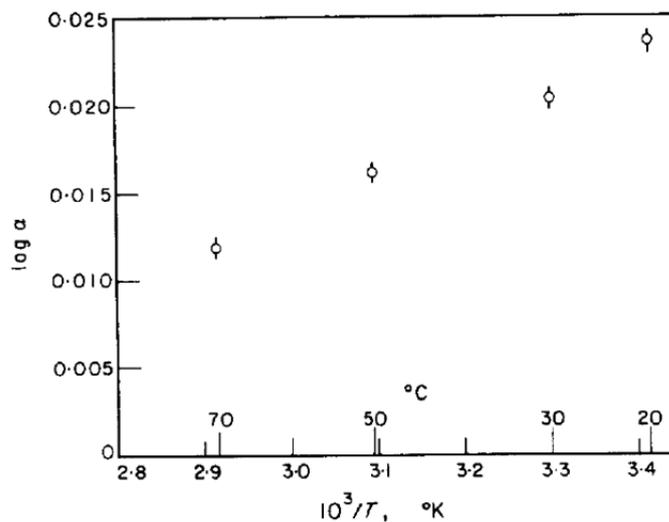
$$\ln(\alpha) \cong \alpha - 1 \quad (4.14)$$

Therefore  $\Delta H$  and  $\Delta S$  are assumed to be independent of temperature. The approximation contains an error of less than 3% for the temperature range in which the separation factors for lithium isotope separation systems were measured. Thus, this assumption is as accurate as the analytical methods for the determination of the isotopic abundance [36].

The compliance with the theory is within the accuracy of data (cf. Figure 19 and Figure 20) [36, 42, 44].



**Figure 19: Separation factor as a function of temperature for the combined Li(amalgam) vs LiOH(aqueous), LiCl(ethylenediamine), LiCl(propylenediamine). [42]**



**Figure 20: The logarithm of the separation factor as a function of  $10^3/T$  (K) for the Li(Hg)Cl(DMSO(dimethyl-sulfoxide)) system; the value at 85 °C was omitted in the calculation of  $(-\Delta H^\circ)$ , it was reported that lithium metal did not react with DMSO up to 80 °C, (2) the irregularity is found at 85 °C. [44]**

A comparison of the experimental plots of Palko, Drury, and Begun [42] and Okuyama, Okada and Saito [44] underlines this assumption. Palko, Begun and Drury plotted their  $\alpha - 1$  values over the temperature while the plot of Okuyama et al. [44] shows the development of the logarithm of  $\alpha$  over the temperature. Although the systems are quite different corresponding the amalgam, in both cases the data show a similar trend over temperature within the same temperature range (~20 °C - 70 °C). The trends are comparable because  $\ln(\alpha)$  and  $\log(\alpha)$  only differ in the constant  $\ln(10)$ .

$$\ln(\alpha) = \log(\alpha) \cdot \ln(10) \quad (4.15)$$

It is noticeable that the separation factor for the aqueous LiOH system is almost similar to the unreactive systems (cf. figure 38) [36], although it needed variable holding currents to maintain the stability. The agreement with the other systems indicates that the rate of electrolysis has probably no effect on the separation factor.

The temperature dependent data for the (LiOH)<sub>aqueous</sub>/Li-amalgam system that was used in the COLEX plant is given in Table 3 [42].

**Table 3: Temperature dependence of the isotopic separation factor for the Li-amalgam vs LiOH(aqueous) system [42].**

Temperature (°C)	Total number of assays	Average mass ratio of <sup>6</sup> Li to <sup>7</sup> Li		Separation factor at 95% C.I.
		Amalgam	Aqueous	
0	16	0.0824	0.0778	1.059 ± 0.014
20	16	0.0817	0.0777	1.051 ± 0.016
35	16	0.0805	0.0766	1.050 ± 0.014
50	16	0.0796	0.0767	1.038 ± 0.007
65	16	0.0799	0.0769	1.039 ± 0.016
80	16	0.0795	0.0765	1.039 ± 0.006
-2	16	0.0817	0.0767	1.065 ± 0.015

The temperature dependent data for the (LiCl)<sub>propylenediamine</sub>/Li-amalgam system that was used in the OREX plant is given in Table 4.

**Table 4: Temperature dependence of the isotopic separation factor for the Li(amalgam) vs LiCl(propylenediamine) system [42].**

Temperature (°C)	Total number of assays	Average mass ratio of <sup>6</sup> Li to <sup>7</sup> Li		Separation factor, $\alpha\left(\frac{\text{amalgam}}{\text{amine}}\right)$ , at 95% C.I.
		Amalgam phase	Amine phase	
1	16	0.0810	0.0763	1.061 ± 0.010
17.5	16	0.0801	0.0762	1.052 ± 0.011
23.5	12	0.0808	0.0764	1.057 ± 0.020
60	12	0.0808	0.0776	1.042 ± 0.014
72	16	0.0811	0.0786	1.031 ± 0.008
98	23	0.0805	0.0787	1.023 ± 0.009
98	16	0.0801	0.0776	1.032 ± 0.009
99	16	0.0817	0.0787	1.038 ± 0.016

Different solvents have varying affinities to lithium ions and different salts dissociate in varying degrees. This affects the separation factor which can for instance be seen in the following data.

**Table 5: Separation factors for lithium salt systems [42].**

TABLE IV. Separation factors for lithium salt systems, Li salt (solvent) vs Li(amalgam).

Organic phase		Temperature (°C)	Total number of assays	Average mass ratio of <sup>6</sup> Li to <sup>7</sup> Li		Separation factor, $\alpha\left(\frac{\text{amalgam}}{\text{amine}}\right)$ , at 95% C.I.
Compound	Solvent <sup>a</sup>			Organic phase	Amalgam phase	
LiCl	THF	1	16	0.0768	0.0804	1.047 ± 0.009
LiCl	THF	27	34	0.0785	0.0812	1.035 ± 0.007
LiCl	THF	57	16	0.0768	0.0797	1.038 ± 0.009
LiCl	IPA	26.5	16	0.0763	0.0805	1.055 ± 0.009
LiCl	DMC	26	16	0.0798	0.0780	1.023 ± 0.013
LiAlH <sub>4</sub>	DMC	~28	16	0.0785	0.0799	1.018 ± 0.014
LiAlH <sub>4</sub>	THF	~28	16	0.0775	0.0803	1.035 ± 0.007

<sup>a</sup>THF = tetrahydrofuran; IPA = isopropyl alcohol; DMC = dimethyl cellosolve.

Three factors limit the selection of organic solvents [36]:

- A limited solubility of lithium salts
- The rapid reactivity of some solvents towards lithium amalgam
- The emulsifying characteristic of some organic solvents towards lithium amalgam.



Of those the emulsification received least attention because probably only a few of them are true emulsions. but form insoluble reaction products that contain physically adsorbed or chemically bonded mercury [36].

Normally ionic salt (NaCl, KCl etc.) solvents need to have large dielectric constants since the dielectric constants are a measure of their ion separating and isolating power. However, in the case of lithium it seems to be the opposite.

Ethylenediamine has a quite low dielectric constant ( $\epsilon_r = 12.9$  at  $25^\circ\text{C}$ ) compared to water ( $\epsilon_r = 81.7$  at  $18^\circ\text{C}$ ) and propylenediamine is expected to have an even lower dielectric constant ( $\epsilon_{r,PDA} \leq \epsilon_{r,EDA}$ ). The solubility of sodiumchloride or potassiumchloride in PDA is a tenth of the solubility in EDA, but the solubility of LiCl is 4 times higher in PDA than in EDA (cf. Table 6) [36].

**Table 6: Dielectric constants and solubility of LiCl, NaCl an KCl in EDA, PDA and water [36].**

Specific Interaction Effects of Selected Solvents I

Solvent	Dielectric Constant	Solubility in moles/liter at $25^\circ\text{C}$		
		LiCl	NaCl	KCl
Ethylenediamine	12.9 ( $25^\circ\text{C}$ ) (17)	0.27 (48)	0.045 (11)	0.0017 (11)
Propylenediamine	12.9	1.0 (47)	0.0048 (60)	0.0001 (43)
Water	81.7 ( $18^\circ\text{C}$ ) (17)	14.0 (56)	5.43 (4)	4.13 (4)

This effect can be explained by the result of the coordination demanded by the lithium ion. The lithium ion has the coordination number 4 which means that 2 EDA or 2 PDA molecules could be tightly bonded. Due to steric effects (additional methyl group) PDA has a better chance to coordinate in the desired way. An even stronger indication to that coordinating effect is given by solvents of cyclic ethers (cf. Figure 21 and Table 7) [36, 42].

Specific Interaction Effects of Selected Solvents II (105)

Solvent	Structure	Solubility of LiCl (moles/liter at $25^\circ\text{C}$ )
Propylene oxide		0.22
Trimethylene oxide		6.0
Tetrahydrofuran		0.78
2-Methyltetrahydrofuran		0.07
Tetrahydropyran		0.08

**Figure 21: Coordinating effect [36].**

Some other systems of lithium compounds have been examined that were found to be stable or at least could be remained stable without much effort.

Palko, Drury, and Begun have been investigating dimethyl-cellosolve (DMC), Tetrahydrofuran (THF) and propylenediamine (PDA) solutions of the lithium adding compounds, benzophenone, benzophenone-anil, and anthracene. The effects of salt and solvent are harder to distinguish in these systems, since a lot of factors must be taken into account. In the solution the lithium compound exists either in the radical form (cf. Figure 22), as a dilithium salt (cf. Figure 23) or as a combination (cf. Figure 24) [42].



Figure 22: The radical form of lithium compound [42].

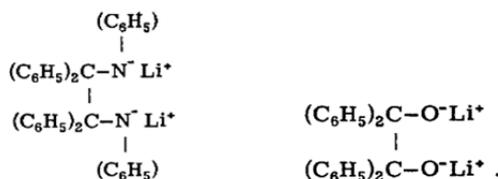


Figure 23: The combination of lithium compound [42].

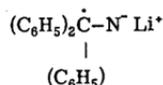


Figure 24: The radical form of lithium compound as combination [42].

The data of these systems is presented in the following table:

**Table 7: Isotopic separation factors for organic-amalgam systems involving lithium addition compounds [42].**

Organic phase		Temperature (°C)	Total number of assays	Mass assay of <sup>6</sup> Li to <sup>7</sup> Li		Separation factor, $\alpha \left( \frac{\text{amalgam}}{\text{amine}} \right)$ , at 95% C. I.
Compound	Solvent <sup>a</sup>			Organic phase	Amalgam phase	
Benzophenone-Li	DMC	27	10	0.0774	0.0818	1.057 ± 0.012
Benzophenone-Li	DMC	26,5	16	0.0769	0.0813	1.056 ± 0.008
Benzophenone-Li	THF	26,5	16	0.0760	0.0794	1.045 ± 0.008
Benzophenone-Li	PDA	26,5	16	0.0760	0.0801	1.055 ± 0.016
Benzophenone anil-Li	DMC	27	10	0.0782	0.0811	1.038 ± 0.011
Benzophenone anil-Li	DMC	26,5	16	0.0771	0.0800	1.037 ± 0.008
Benzophenone anil-Li	THF	26,5	16	0.0762	0.0797	1.046 ± 0.012
Benzophenone anil-Li	PDA	26,5	16	0.0773	0.0809	1.047 ± 0.012
Anthracene-Li	DMC	27	11	0.0764	0.0796	1.042 ± 0.012

<sup>a</sup>DMC = dimethyl cellosolve; THF = tetrahydrofuran; PDA = propylenediamine.

Okuyama et al. measured higher separation factors than at any other so far investigated system by using the dipolar aprotic solvents dimethyl-sulfoxide (DMSO), N,N'-dimethyl-acetamide (DMA) and N,N'-diethylformamide (DEF). [44] The highest  $\alpha$ -value was measured for the Li – amalgam/LiCl<sub>DEF</sub> system. This separation factor is even larger than the theoretical  $\alpha$ -value for the molecular distillation ( $\alpha_{\text{Distillation}} = 1.08$ ).

$$\alpha_{\text{LiCl}_{\text{DEF}}^{\text{Li-amalgam}}}(-15\text{ °C}) = 1.084$$

Among the three solvents used only DMSO is completely stable towards lithium amalgam. DMA and DEF had to be stirred with a glass rod at a velocity of  $200 \frac{\text{rev}}{\text{min}}$  [44]. The advantage of DMA and DEF is that their melting point (m.p.) is lower than for DMSO (cf. Table 8). Therefore the systems can be cooled down to a lower temperature.

**Table 8: Melting points of DMSO, DEF and DMA [44].**

	DMSO	DEF	DMA
m.p.	18.4 °C	-78 °C	-20 °C

Furthermore, the separation factors for DMA and DEF solutions are (in the same temperature range) higher than those for DMSO (cf. Table 9 and Table 10) [44].



**Table 9: Separation factors for DMA and DEF [44].**

Temp. (°C)	Solvents	
	DMA	DEF
-15	1.084 ± 0.004	1.085 ± 0.004
0	1.080 ± 0.003	1.080 ± 0.004
20	1.058 ± 0.004	1.067 ± 0.004
30	1.054 ± 0.002	1.054 ± 0.003
50	1.052 ± 0.003	1.051 ± 0.002
70	1.036 ± 0.004	1.036 ± 0.003
85	1.041 ± 0.003	1.035 ± 0.004

**Table 10: The separation factors for the Li(Hg)-LiCl(DMSO) system [44].**

Temperature (°C)	Total number of assays	Average mass ratio of <sup>6</sup> Li to <sup>7</sup> Li		Separation factor at 95% C.I.
		Amalgam	Aqueous	
0	16	0.0824	0.0778	1.059 ± 0.014
20	16	0.0817	0.0777	1.051 ± 0.016
35	16	0.0805	0.0766	1.050 ± 0.014
50	16	0.0796	0.0767	1.038 ± 0.007
65	16	0.0799	0.0769	1.039 ± 0.016
80	16	0.0795	0.0765	1.039 ± 0.006
-2	16	0.0817	0.0767	1.065 ± 0.015

The effect of the several Li-salts solvated in DMSO on the separation factor was measured and the following trend was obtained:

$$\alpha_{\text{CH}_3\text{COOLi}} \sim \alpha_{\text{LiI}} > \alpha_{\text{LiBr}} > \alpha_{\text{LiCl}} > \alpha_{\text{LiNO}_3}$$

The decreasing order of the halide-salt separation factors (I, Br, Cl) could be explained by the decreasing order of the ion-pair dissociation constant ( $K_{d,\text{LiI}} = 2.0$ ,  $K_{d,\text{LiBr}} = 1.5$ ,  $K_{d,\text{LiCl}} = 0.5$ , at 25 °C). While chloride is a weak electrolyte, iodide is a strong one [44].

The main disadvantage of the systems measured by Okuyama et al. compared to the other systems is the slow rate of isotopic exchange. It took approximately 30 minutes until the equilibria was established [44]. For other systems using Li-amalgam the exchange was so rapid that nearly the only limitation was to bring the two phases in contact [36, 42]. Palko, Begun and Drury estimated half times of less than 2 seconds. [42]

One aspect that contributes to this rapid exchange is the high surface energy of alkali metal amalgams. The application of Gibbs adsorption thermodynamics to the data investigated before 1953 shows surface excess and consequently adsorption of alkali metals at the amalgam surface. Macroscopically, it was obtained that amalgams could be dispersed much better in e.g. PDA than pure mercury. Therefore, it seems to be likely that the amalgam interface has a lower interfacial tension and lowering of interfacial tension by adding an additional compound is the effect of adsorption [36].

The use of mercury has many advantages and disadvantages. The main argument against the use of a high amount of mercury is its toxicity and the environmental pollution that occurred in Oak Ridge.

Between 1950 and 1963 around 11 million kg mercury were used for the <sup>6</sup>Li enrichment in Oak Ridge National Laboratory. Approximately 3% of them were lost to the air, the water, and the soil and rock underneath the facilities [45].



150 tons were released into the Poplar Creek via the East Fork Poplar Creek during the time the plants were operating [46]. The main source was a nitric acid purification system which was used in the COLEX process between 1955 and 1960 [41, 45]. This system drained a diluted neutralized acid waste which contained mercuric nitrate into the East Fork Poplar Creek [41]. Furthermore, the basement sump, which was pumped after 3 sedimentation tanks through a sewer into the East Fork Poplar Creek, was contaminated with mercury from the pills [41]. Today small amounts of mercury still end up in the Creek from diffuse contaminated soil and ground water sources within the Y12 pilot plant [45]. As a result of several waste treatment programmes the mercury concentration in the East Fork Poplar Creek decreased 85% since the 1980's, but the methylmercury concentration in water and fish didn't follow that trend and remained stable [45].

Mercury vapour was released to the air by the buildings ventilation system [16]. Waste gases containing mercury were vented through stack to the environment. Approximately 3600 kg Hg were exhausted through the stacks before scrubbers were installed to prevent that [45]. Additional losses through the air occurred during the mercury recovery process. Site contractors used a furnace in a shed to roast the wastes and sludges for the recovery. In addition, an "open air receiving process" was used to transport the recovered mercury to the COLEX plant [41, 45].

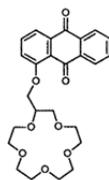
The way toxic mercury was treated during those days shows that the environmental problems are not the result of the system itself, but the result of somehow careless exposure with it.

#### 4.1.2 Cation complexing systems

The environmental problems caused by the use of the toxic mercury and the need for lithium-6 enrichment for nuclear fusion application has led researchers to investigate a number of alternative enrichment methods [47].

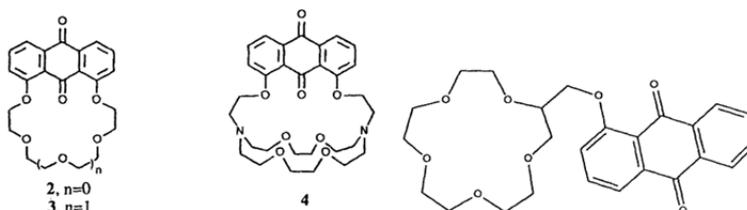
Extraction systems show many advantages for isotope separation at industrial scale, like a high selectivity, high recovery, high capacity, simple equipment and easy automatic control [48]. However, one major problem that made ordinary aqueous organic systems ineffective for the purpose of lithium isotope separation is that lithium salts are much less soluble in organic than in aqueous solvents [26]. Therefore, special attention was paid to the use of cation complexing agents and particularly to cyclic polyethers and cryptands [37, 49]. Cyclic polyethers, especially crown ethers and cryptands, offer the opportunity to solubilize inorganic salts in organic solvents. These mostly at least partially lipophilic agents act like a host for the metallic cation. They complex the metallic ion within their highly selective nano cavities [37, 49]. The cation is bound by the electrostatic interaction between the positive charged metal ion and the partially loaded donor atom, which is usually the electronegative oxygen, in the crown ether or cryptand [37].

With polycyclic ethers, large separation factors can be obtained. Jepson and Cairn discovered the potential use of cycling polyether for the separation of isotopes in 1976 [26]. Their first publication dealt with the separation of calcium isotopes. They were also the first to analyse lithium isotope separation with cation complexing agents (cryptands) in 1979 [8]. The maximal single stage separation factors ( $\alpha = 1.041 \pm 0.006$  and  $\alpha = 1.047 \pm 0.006$ , 25 °C) they achieved were by an aqueous solution of a lithium trifluoroacetate (TFA) and a chloroform solution of lithium [2,2,2] cryptate / lithium [2B,2,2] cryptate respectively [50]. The main disadvantage using [2,2,2] cryptate is that it is quite good soluble in water and therefore not suitable for industrial scale. [2B,2,2] cryptate has a relative slow reaction rate which also limits its application [51]. Nishizawa et al. studied several crown ether systems and observed a quite high value for 12-crown-4 at 0°C ( $\alpha_{\max} = 1.057$ ). The highest so far reported separation values were achieved by using anion radicals of anthraquinone containing crownether macrocycles and macro bicycles [52, 53]. Servando Munzo and Luis Echegoyen measured the reduction potential of the  ${}^6\text{Li}^+$  and  ${}^7\text{Li}^+$  complexes of 9,10-dioxanthracene-1-yloxymethyl-15-crown-5 (short: anthraquinone-15-crown-5 lariat ether, cf. Figure 25). The highest value was achieved ( $12 \pm 3$  mV) for a 2:3 solution of acetonitrile and dichloromethane. This value was calculated to a separation factor of about  $\alpha = 1.6$  [53].



**Figure 25: 9,10-dioxanthracene-1-yloxymethyl-15-crown-5**

Also very large separation factors ( $\alpha = 1.04 - 1.18$ ) for chemical isotope exchange systems were achieved by Zihong Chen and Luis Echegoyen. They used the anthraquinone crown ethers and cryptands presented in Figure 26.



**Figure 26: Reduced anthraquinone crown ether, anthraquinone [2,2] cryptand, 1-hydroxyanthraquinone**

The following aspects could be observed in reference to crown ether complexation [54]:

- Crown ethers usually form the most stable complexes with cations when the cation diameter makes approximately 80% of the cavity diameter.
- Changing an oxygen atom of a crown ether with another donor atom effects the preference of complexing a special kind of cation.
- Harder cations, like alkali and earth alkali metal ions, are better bound by harder donor atoms, like oxygen, than by softer ones and vice versa.
- The basicity of the oxygen atoms in the crown ether ring is an important factor for the stability of the complex that can be influenced by the attached groups.
- Acyclic polyethers which contain one or two carboxyl groups have the convenience that they can complex the cations without their counter ion.

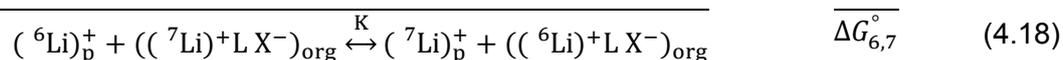
Therefore, the cavity of macrocyclic polyethers can be tuned by [49]:

- Varying the orientation of the donor atom
- Changing the cavity size
- Varying the type of the donor atom (hard or soft donor base)
- Substitution of an electron withdrawing/donating functional group.

The resulting highly specific host/guest interaction between the complexing agent and the cation makes the system applicable for isotope separation [49].

In addition to the characteristics of the complexing agents, a lot of other circumstances could influence the isotopic reaction and must be taken into consideration. Parameters that could be varied by the researcher are for example the solvents the lithium salt or the lithium-complex is dissolved in, the temperature in which the reaction takes place or the counter ion of the lithium salt.

The majority of the so far investigated complexing ligands are more likely to bind lithium-6 within their cavity than lithium-7 which leads to an enrichment of lithium-6 in the organic phase. The isotopic exchange could be simplified to the following equilibrium equations:



Whereas  $X^-$  represents the counter ion of the lithium salt, L stands for the ligand (crown ether, cryptand) and  $((Li)^+L X^-)$  implies the lithium complex. In the organic solvent  $K_6$ ,  $K_7$  and  $K$  represent the equilibrium constants of the respective equation. For the different phases, it was preferred to write the index "p" instead of "aq" since not only water but also other polar solvents, like for instance ethanol or ionic liquids, could be used as initial solvent for the lithium salt. [48, 55]

$\Delta G_6^\circ$  and  $\Delta G_7^\circ$  are both negative ( $\Delta G_6^\circ, \Delta G_7^\circ < 0$ ) because the complexation of lithium ions in general is an exothermic process [49]. Analogue to the amalgam exchange,  $\Delta G_{6,7}^\circ$  can be written as:

$$\Delta G_{6,7}^\circ = |\Delta G_6^\circ| - |\Delta G_7^\circ| \quad (4.19)$$

with 
$$\Delta G_6^\circ = \Delta G_{(({}^6Li)^+L X^-)_{org}} - (\Delta G_{({}^6Li)_p^+} + \Delta G_{X_p^-} + \Delta G_{L_{org}})$$
 (4.20)

and 
$$\Delta G_7^\circ = \Delta G_{(({}^7Li)^+L X^-)_{org}} - (\Delta G_{({}^7Li)_p^+} + \Delta G_{X_p^-} + \Delta G_{L_{org}})$$
 (4.21)

The separation factor can be calculated by the equation:

$$\ln \frac{K_6}{K_7} = \ln K = \ln(\alpha) = \frac{-\Delta G_{6,7}^\circ}{RT} = \frac{-\Delta H_{6,7}^\circ}{RT} + \frac{\Delta S_{6,7}^\circ}{R} \quad (4.22)$$

Since lithium-6 is preferred by the complexing agents,  $\Delta G_{6,7}^\circ$  must be negative. Therefore, an increase in temperature must lead to a decrease in separation factor (cf. Figure 27) [48, 49, 56].

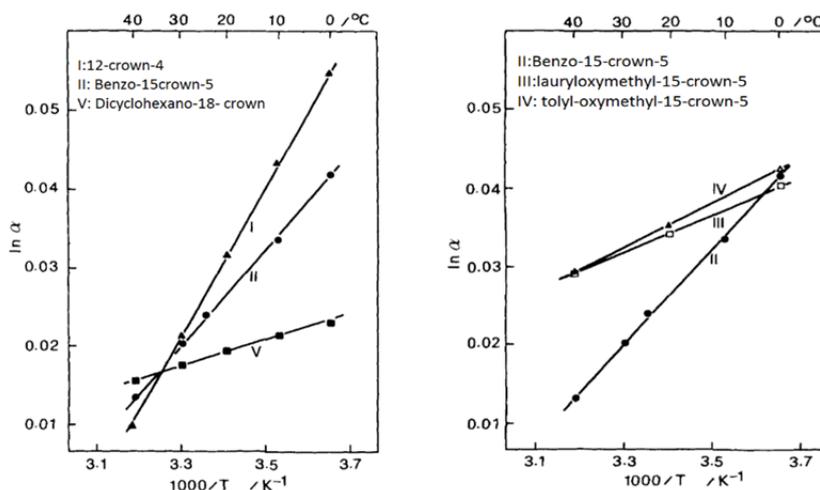


Figure 27: Van't Hoff plots [47].

Figure 27 shows the van't Hoff plots for aqueous LiI equilibrated with the respective crown ether solubilized in chloroform. Among these systems the maximal separation factor could be attained using 12-crown-4 at 0 °C ( $\alpha_{max} = 1.057$ ) [47].

For the cation complexing chemical exchange not only the separation factor but also the distribution factor matters, since it is a measure of the amount of the lithium ions that are complexed by the compound. It may be calculated by the following equation (cf. Figure 28) [51].

$$D = CL^n$$

or

$$\ln D = n \ln L_0 + C'$$

Figure 28: Distribution coefficient [51].

Considerations and calculations for large scale lithium isotope separation have been made for a countercurrent mixer settler cascade system (cf. Figure 30). The focus of that system was on  ${}^7\text{Li}$  enrichment which is needed for pressurized water reactors (PWRs), since it is not sufficiently available within the USA and has to be purchased from China. Nevertheless, the isotope separation simultaneously leads to the enrichment of both isotopes, no matter which out coming flow is regarded as enriched or depleted.

The system chosen for this consideration was an aqueous LiCl solution phase, 15-crown-5-ether as cation complexing compound and chloroform as organic phase. The chosen crown ether represents a compromise between the price and the distribution coefficient of those that were available (cf. Figure 29).

CROWN ETHERS			
PRODUCT	CAS RN	PRICE Information	
		QTY	PRICE
Cyclen	294-90-6	10g	U\$2,100.-
12-Crown-4	294-93-9	1kg	U\$2,100.-
Benzo-18-Crown-6	14098-24-9	50g	U\$1,100.-
Benzo-15-Crown-5	14098-44-3	50g	U\$1,050.-
Benzo-12-Crown-4	14174-08-4	50g	U\$1,100.-
Dibenzo-24-Crown-8	14174-09-5	50g	U\$1,050.-
Dibenzo-18-Crown-6	14187-32-7	1kg	U\$1,300.-
Dicyclohexyl-18-Crown-6	16069-36-6	100g	U\$1,200.-
18-Crown-6	17455-13-9	5kgs	U\$1,400.-
Dibenzo-30-Crown-10	17455-25-3	50g	U\$1,600.-
15-Crown-5	33100-27-5	1kg	U\$1,800.-
1-Aza-18-Crown-6	33941-15-0	25g	U\$1,500.-
Nitrobenzo-18-Crown-6	53408-96-1	50g	U\$1,600.-
Nitrobenzo-15-Crown-5	60835-69-0	50g	U\$1,050.-
1-Aza-15-Crown-5	66943-05-3	25g	U\$1,500.-
Perfluoro-15-Crown-5	97571-68-2	25g	U\$1,800.-

	$D$ at $0^\circ\text{C}$	$\Delta H^\circ$ (kJ/mol)	$\Delta S^\circ$ ( $\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ )
12-Crown-4	$2.0 \times 10^{-5}$	—	—
Benzo-15-crown-5	$7.1 \times 10^{-3}$	-53	-205
Lauryloxymethyl-15-crown-5	$8.1 \times 10^{-3}$	-24	-118
Tolyloxymethyl-15-crown-5	$5.0 \times 10^{-3}$	-26	-129
Dicyclohexano-18-crown-6	$2.8 \times 10^{-2}$	-31	-122

Figure 29: Distribution coefficient of several crown ethers in LiCl water [51], crown ether prices [30].

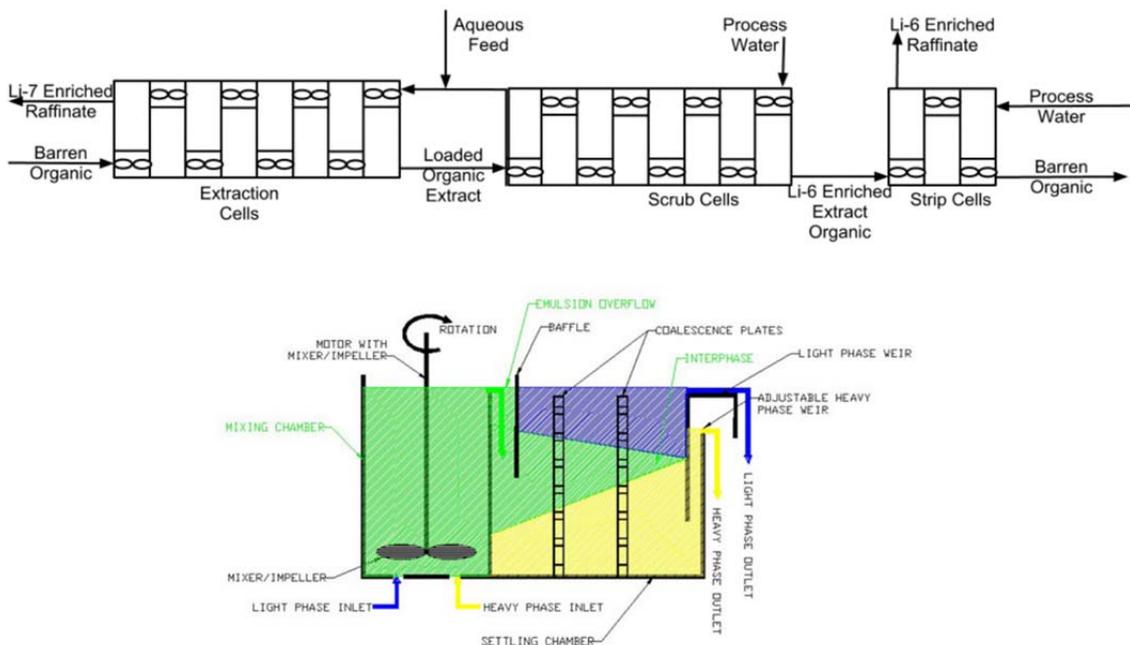
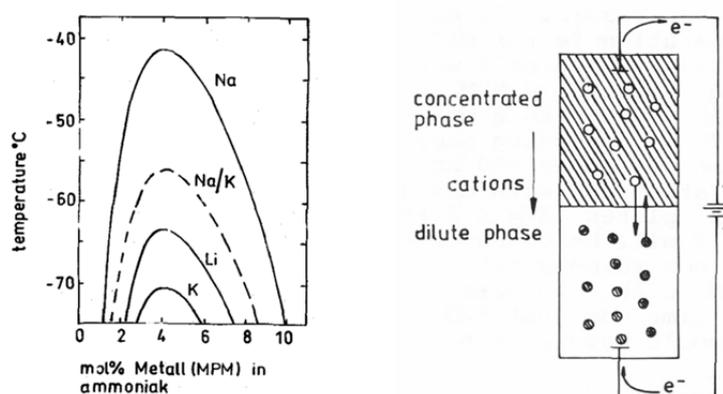


Figure 30: Mixer settler system [30].

#### 4.1.3 Liquid ammonia systems

A solution of alkali metals in liquid ammonia separates into two phases of different densities below a critical temperature of 230 K. The phases vary from each other by their metal concentration. This concentration divergence is dependent on temperature and may vary up to a factor 10. The phenomenon could be used for lithium isotope separation below the critical temperature of (-75 °C)

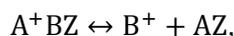
the isotope  ${}^6\text{Li}$  is slightly enriched in the concentration phase. The concentration phase shows more metallic character while the dilute phase could be regarded as electrolyte phase. The single stage separation factor that could be observed for lithium isotopes measured was  $\alpha = 1.01$ . [39] The miscibility gap as well as the critical temperature observed is dependent on the kind of metal solubilized which can be seen in Figure 31 at the left side. For large scale enrichment a counter current column exchange system was proposed. The concentrated “metallic” phase which has a lower density than the diluted electrolyte phase would be consequently separating to the upper region of the column and vice versa. Counter current flow would be established by removing the ammonia at the bottom of the column and adding it to the top of the column (cf. Figure 31). The concentrated phase cannot be diluted and the diluted phase cannot be concentrated due to the miscibility gap. For that reason a concentrated metallic phase would be formed at the bottom of the column and would move up and a dilute electrolytic would be formed at the top of the column and would then descend to the bottom. Unfortunately, this was not shown experimentally for lithium itself, but only for a sodium potassium system instead.



**Figure 31: Miscibility gap for several alkali metals solubilized in liquid ammonia on the left side, counter current column sketch on the right side. [57]**

#### 4.1.4 Chemical exchange with ion exchanger

One of the first attempts to separate lithium isotopes was by chemical exchange with zeolites. If equilibrium is established by shaking a quantity of zeolite with a solution of positive ions for ten to twenty minutes, ion exchange takes place following the equation:



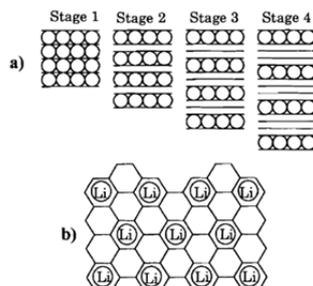
whereby Z stands for the zeolite to which the respective cation is bonded.  $\text{A}^+$  replaces  $\text{B}^+$  up to a specific maximum according to the mass law. The amount of exchange depends on the ratio of the total quantities, but not on the dilution. The separation factor for the lithium isotopes exchange with sodium zeolite was found to be 1.022. The partial separation of lithium isotopes has been conducted using long columns filled with the zeolites. A counter current flow was established with total reflux.

Ammonium peroxodisulfate  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  is a good extractant for lithium ions from  $\text{LiMn}_2\text{O}_4$  extract. It actually extracts  $\text{MnO}_2(\text{Li})$  which preferentially adsorbs  ${}^6\text{Li}^+$ -ions. The isotopic separation factor is  $\alpha = 1.014$  which is pretty high compared to other organic ion exchangers.

Several other ion exchangers with isotopic preference to  ${}^6\text{Li}$  can be found in literature, but to discuss them all would go beyond the scope of this work.

#### 4.1.5 Intercalation systems

Lithium solubilized in 1-methylbutaneoxide is brought into contact with graphite. Through chemical intercalation the lithium is bonded in the layers of the graphite. The phenomenon of sequential formation of these intercalated layers (sheets) is called “staging” (cf. Figure 32) [58].



**Figure 32: Staging. [58]**

The number of the graphene layers between the adjacent intercalate layers is given by the stage index  $n$ . In case of lithium intercalation four different formations can be distinguished.

In Figure 32 b) stage formation one with “in plane” stage Li-graphite intercalation is shown. Lithium-6 always preferred to separate into the graphite phase. The single stage separation factor obtained at room temperature was  $\alpha = 1.023$  (25 °C) [58]. The researchers suggested that if a large isotope effect upon chemical insertion into graphite could be achieved it would be an idea to expose the frequently used lithium ion batteries for enrichment issues. This intercalation system is the technically most interesting one, but there are also other systems that could be found in literature.

## 4.2 Electrochemical separation

### 4.2.1 Electrolysis

Electrolysis using an amalgam cathode has already been applied in the ELEX system for large-scale lithium isotope enrichment at ORNL. A streaming mercury cathode was used flowing countercurrent to an aqueous LiOH solution (cf. Figure 33). Many more stages were required to run the ELEX process compared to the COLEX process. A lithium salt solution is electrolyzed using a mercury cathode in a counter-current flow. The  ${}^6\text{Li}$ -ions are preferentially uptaken by mercury than by  ${}^7\text{Li}$  forming a lithium amalgam. The process is today used by Russia’s Novosibirsk Chemical Concentrates Plant (NCCP) for the production of pure  ${}^7\text{Li}$  for nuclear fission applications. [59]

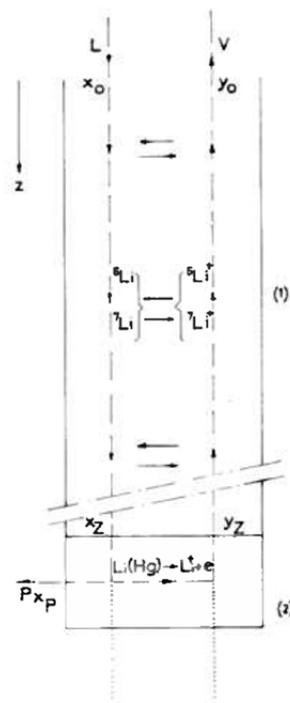


Figure 33: Electrolysis column [59].

Other systems that show lithium isotope effects by electrolysis are for example:

- The electrochemical insertion of lithium isotopes into tin [60]
- The electrochemical insertion of lithium isotopes into zinc [61]
- The electrochemical insertion of lithium isotopes into liquid gallium [62]
- The electrochemical insertion of lithium isotopes into tin IV sulfide
- Lithium isotope effects that are accomplished by electrochemical release from cobalt oxide [63]
- Lithium isotope effects that are accomplished by electrochemical release from manganese oxide [64, 65].

#### 4.2.2 Electromigration

The term electromigration is here basically used as a synonym of the electrolysis of molten lithium or a lithium salt. Since molten lithium is very corrosive molten salts and oxides are preferred. The amounts enriched by electromigration per stage are certainly higher than those by electrolysis and have been examined in dekagram quantities. Principally, the same kind of cathodes that can be used for electrolysis may also be used here (e.g. graphite, zinc, tin etc.) [66–70].

#### 4.2.3 Electrophoresis

Electrophoresis is the motion of disperse solubilized particles (here lithium ions) relative to a separating (viscous) fluid (conductor) that is enforced by a uniform electric field. The isotope separation occurs due to the difference of the velocities of the heavier  $^7\text{Li}$  and the lighter  $^6\text{Li}$  moving through the conducting material.

The “electrophoresis in liquid bath” is considered for large scale separation. It makes use of a so called Li electrolyte-compatible Solid State Lithium Ion Super Conductor (SSLISC) as separating fluid and uses a liquid lithium compound as feed material. Since SSLISC degrades in pure Li, inorganic solid electrolytes (either oxides or non-oxides) are usually selected. The feed chamber is on one side of the membrane and the liquid lithium compound recovery chamber is on the other

side, where Li enriched in  ${}^6\text{Li}$  is stored up. The electrophoresis process for  ${}^7\text{Li}/{}^6\text{Li}$  separation exploits different ionic conductivities in a Li electrolyte-compatible Solid State Lithium Ion Super Conductor (SSLISC) membrane which means that the ions move at different rates and  ${}^6\text{Li}$  is separated and enriched (cf. Figure 34). [65]

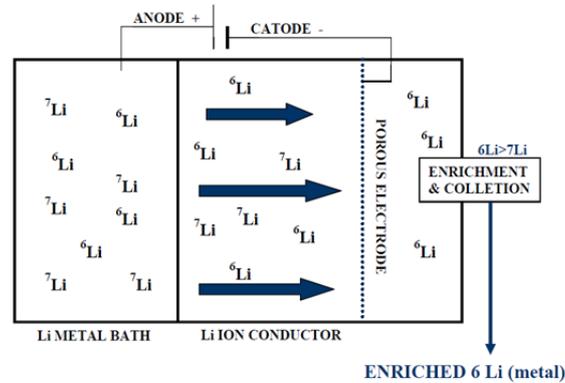


Figure 34: Electrophoresis in liquid bath. [65]

For an electrophoretic cell design the following aspects must be taken into consideration:

- The choice of the suitable electrolyte
- The use of a well-matching SSLISC
- The selection of proper porous electrodes
- The cell housing materials and the cell electric design [71]

A number of possible SSLISCs are given in Table 11.

Table 11: Possible SSLISC materials. [13]

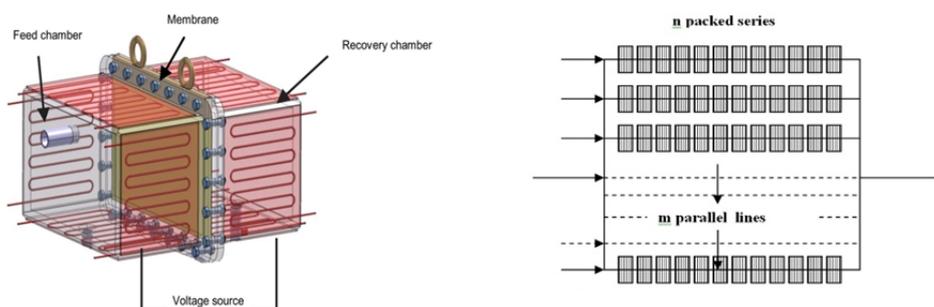
<b>Non-oxide sintered Li single-crystal</b>	$\text{Li}_3\text{N}$
	$\text{LiI}$ (optionally $\text{Al}_2\text{O}_3$ doped)
<b>Amorphous Li compounds</b>	$\text{P2S5-Li2S-LiI}$ ,
<b>Halogenated spinels</b>	$\text{Li}_2\text{MCl}_4$ (M = Mg, Mn, Fe, etc,...)
<b>Li oxides ion conductors</b>	$\text{LiXO}_4\text{-Li}_4\text{YO}_4$ (X = P, As, V, etc.; Y = Si, Ge, Ti, etc.),
	$\text{Li}_{14}\text{Zn}(\text{GeO}_4)_4$ (LISICON),
	$\text{LiTi}_2(\text{PO}_4)_3$
	$\text{LiM}_2(\text{PO}_4)_3$ or NASICON type: $\text{LiM}_2(\text{PO}_4)_4$
	[M: Zr, Ti, Ge, Hf] type,
	$\text{Li}_{1+x}\text{M}_x\text{Ti}_{2-x}(\text{PO}_4)_3$
	[(M = metal element, for M if Al (x =0.3)),
	$\text{Li}_4\text{Ti}_5\text{O}_{12}$ of spinel type,
$\text{La}_x\text{Li}_{0.35}\text{TiO}_3$ , (x = 0.55 or 0.59),.	
	$\text{La}_{0.55}\text{Li}_{0.36}\text{TiO}_3$ ,
<b>alumino-silicates and glasses</b>	$\text{Li}_3\text{BO}_3$ ,
	$\text{Li}_2\text{O-TiO}_2\text{-P}_2\text{O}_5$
	$\text{LiAlSiO}_4$
	$\text{LiAlSi}_2\text{O}_6$ ,
<b>Plumbates</b>	$\text{Li}_4\text{SiO}_4\text{-Li}_2\text{Ti}_3\text{O}_7$
	$\text{Li}_8\text{PbO}_6$ , $\text{Li}_4\text{PbO}_4$
<b>Solid polymeric electrolytes</b>	$\text{PEO-LiClO}_4$ ,
	$\text{PAN-PC-EC-LiClO}_4$

A suitable SSLISC for Li-electrophoretic cell applications should fulfil the following criteria:

- (1) High ionic conductivity of about  $10^{-2}$  S/cm at the operating cell temperature with negligible electronic conductivity over a wide range of Li activity

- (2) Chemical compatibility to the anode and cathode, the electrolyte and cell housing material
- (3) Low hygroscopic characteristics (the presence of water in the material has to be avoided for SSLISC).

Only the highest conductivities are used for large-scale  ${}^6\text{Li}$ -enrichment. Among the available material lithium oxides SSLISC show the highest chemical stability with liquid electrolytes (except liquid lithium) and they also have the highest conductivities. The most advantageous are  $\text{Li}_{1+x}\text{T}_{2-x}\text{O}_4$  of spinel type,  $\text{Li}_2\text{Ti}_3\text{O}_7$  of ramsdellite type,  $\text{La}_{0.55}\text{Li}_{0.35}\text{TiO}_3$  of perovskite type and plumbates with the highest number of exchangeable Li atoms in their lattices [13]. A prototype of an electrophoretic cell was designed and a layout of  $n$  series in  $m$  packed lines was proposed by CIEMAT ('Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas', Spanish research centre for energy, environment and related technologies) (cf. Figure 35).



**Figure 35: Electrophoretic cell prototype on the right side and a plant lay-out based on electrophoresis on the left side. [13]**

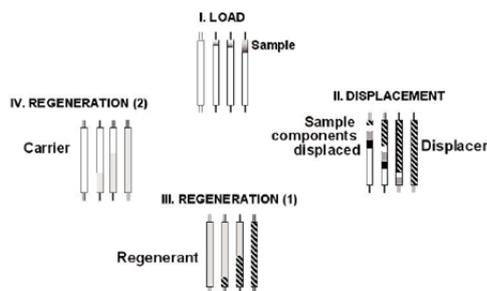
### 4.3 Displacement chromatography

The chromatographic separation of lithium isotopes is generally based on a chemical interaction between the lithium solubilized in the liquid mobile phase and the lithium adsorbed at the resin surface [72]. The exchange resin particles are packed in a column, while the mobile phase flows through that column. The ions are distributed between the resin and the liquid phase. The distribution is based on the slightly higher affinity of the solid resin phase towards the desired lithium-6 isotope. [37, 73, 74]

Displacement chromatography was preferred over the usually used elution chromatography, since it provides a greater throughput [37]. The main difference between the two methods is that the elution type employs only one or several similar solutions (eluent) and that the separation occurs due to an increasing distance between the phases that should be separated. The displacement chromatography employs three basically different mobile phases and the separation occurs within a band of constant length. The phases needed for displacement chromatography are:

1. The carrier
2. The displacer
3. The regenerant.

The carrier is used to relieve the loading process. It must be able to solute the sample components especially those that have to be separated (in our case the lithium ions). The carrier is also used to retard the samples flow through the column (cf. Figure 36). The next step is the displacement of the sample by the displacer. During that step the isotope exchange takes place. The displacer is strongly bound to the resin and pushes the sample components through the column. Finally, the column is emptied by the regenerant, which removes the displacer from the resin. The process is sketched in Figure 36. [75]



**Figure 36: Displacement chromatography scheme. [76]**

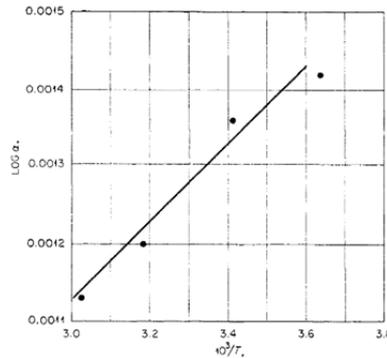
The elution curve shows an almost constant concentration as a function of time and has therefore nearly square shape [37]. The band reaches dynamic equilibrium when the band length remains constant and “self-sharpening” phenomena can be obtained at its boundaries. The lighter isotope lithium-6 is usually enriched at the rear edge and the heavier isotope (lithium-7) at the front edge because the resin phase has a higher affinity to bind  ${}^6\text{Li}$  and therefore retards the flow of it. The enrichment of the respective isotopes at each edge increases with the distance [37]. The isotopic equilibrium between the resin and the mobile phase can be described by the following equation:



The index solid represents the ion exchange resin phase and the index liquid represents the mobile phase [77]. In early attempts to separate lithium isotopes by chromatography the enrichment of lithium-6 was very small [78]. Therefore, the Li adsorption band had to be carried over a long distance to achieve the desired enrichment. Nevertheless, the process remained interesting for scientists since it was believed that it could easily be scaled up with a larger diameter of the column [77]. Columns could be carried out efficiently with a large number of theoretical plates and small HETP (height equivalent to a theoretical plate). For industrial scale systems, a set of chromatographic columns would be arranged in series through which the adsorption bands would have to cover a long distance. Fujine et al. successfully tested continuous displacement chromatography on laboratory scale [37, 79]. Based on these results the construction and unit costs were estimated for a 100 kg  ${}^6\text{Li}$  per year plant [37].

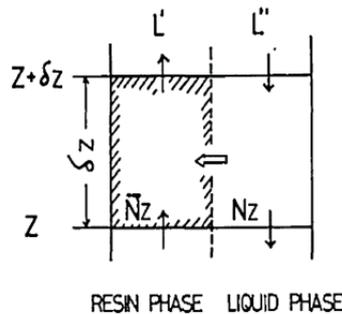
For a successful separation of lithium isotopes by chromatography, it is decisive that the chromatographic boundaries between the two isotopic species are as sharp as possible [6]. Since in displacement chromatography the separated bands do not move away from each other, the efficiency of the separation depends on the width of the separation zone. Therefore, the consideration of several aspects like temperature, grain size, flow rate, diffusion constants in both phases and the concentration of the eluent are of essential importance [78].

Due to the thermodynamic consideration of chemical isotope separation, which is already shown in chapter 4.1.1 and 4.1.2, the equilibrium constant and therefore the separation factor decreases with increasing temperature. One major concern within displacement chromatography is the diffusion term. A reduction of temperature would not only increase the separation factor, but also decrease the diffusion coefficient in the resin  $D_r$  and in the eluent phase  $D_s$ . Therefore, a reduction of temperature is very advantageous for the chromatographic separation [78]. The van't Hoff plot for the chromatographic separation factor values measured by Lee and Begun is given in Figure 37.



**Figure 37: Resin(sulfonated polystyrene-divinylbenzene Dowex X-16 ground to 200-400 mesh) vs. eluent (LiCl dissolved in HCL solution). [80]**

In displacement chromatography the adsorption band is considered as a square cascade or a distillation column that operates in total reflux. The height equivalent to a theoretical plate (HETP) is defined as the height of a section of the resin bed from which the two streams leaving in the opposite directions are in equilibrium (cf. Figure 38).



**Figure 38: Infinitesimal mass transfer unit (band) profiles at steady state. The HETP is the fraction of the length of the band to the theoretical stage number [81].**

Since a former equation which was deduced by Glueckauf et al. did not agree well with the experimental results, an equation to estimate HETP at steady state in the bands was derived for chromatographic lithium isotope separation by Fujine et al. [78, 82].

$$HETP = \left( \frac{C_0}{q_0 + \varepsilon C_0} \right) \frac{0.071 r_0^2}{\bar{D}} \bar{u} + \left( \frac{q_0}{q_0 + \varepsilon C_0} \right) \frac{0.133 r_0^2 \bar{u}}{\bar{D}(1 + 70 r_0 \bar{u})} + \frac{\varepsilon E}{\bar{u}} \quad (4.24)$$

While

- $C_0$  is the initial concentration of the eluent
- $q_0$  is the ion exchange capacity
- $\varepsilon$  is the porosity
- $\bar{D}$  is the self distribution coefficient
- $r_0$  is the particle radius
- $\bar{u}$  is the superficial velocity
- $E$  is the effective diffusivity.

The influence of physiochemical properties on HETP are considered in this equation. The first term on the right-hand side is contributed by the slow diffusion in particles, the second term considers the slow diffusion in the boundary layer of the liquid, and the third accounts for the liquid mixing [82].

The term for diffusion in particles is approximately 10 times higher than the term for diffusion in the boundary layer and is therefore the main resistance regarding isotope separation by chromatography. The diffusion terms increase proportional to the superficial velocity and the liquid mixing term decreases proportional to its inversion. The molecular diffusion term is also small compared to the liquid mixing term and could therefore be eliminated in most cases. The equation was found to agree well with the experimental data [82].

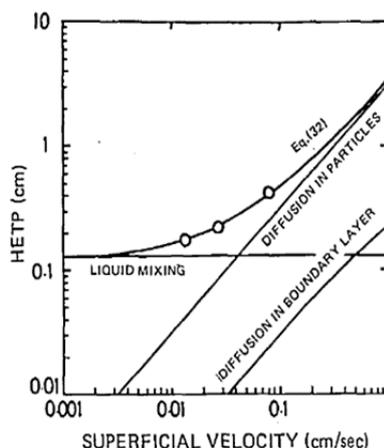


Figure 39: Influence of superficial velocity on HETP. [81]

Studies have been made to find a suitable resin material that is able to rise the small separation factor. Especially resin material containing cation complexing compounds showed promising results. The resin materials with the lowest enrichment factors are the ordinary organic resin materials used like for instance the Dowex 50W-X(12-16) resin material. This tendency may be seen comparing the resin materials in Table 12.

Table 12: Ion exchangers. [13]

Literature data for lithium-isotope fractionation during uptake into macrocyclic compounds and inorganic exchangers such as clay minerals.

Study	Exchanger	Eluant/solution phase	$\alpha_{\text{solid-solution}}$	Isotope in solid phase	T (°C)
<i>Macrocyclic compounds</i>					
Ban et al. (2002)	Monobenzo-15-crown-5	0.55 M LiCl in methanol, 12 M HCl	0.9873	<sup>6</sup> Li	35
Kim (2002)	Cyclic N <sub>3</sub> O <sub>3</sub> trimerrifield peptide resin (18C6)	4 M NH <sub>4</sub> Cl	1.028	<sup>7</sup> Li	20
Kim et al. (1991)	Monobenzo-15-crown-5	5% H <sub>2</sub> O in acetonitrile	0.947	<sup>6</sup> Li	23
Kim et al. (1995)	Dibenzo pyridino diamide azacrown (DBPDA)	Acetonitrile	0.966	<sup>6</sup> Li	20
Kim et al. (1997)	Cyclic triazetetramerrifield resin	1 M NH <sub>4</sub> Cl	0.932	<sup>6</sup> Li	20
Kim et al. (1998)	Azacrown tetramerrifield peptide resin	0.5 M NH <sub>4</sub> Cl	1.00127	<sup>7</sup> Li	25
Kim et al. (1998)	NTOE	0.01 M HCl	1.0242	<sup>7</sup> Li	25
Kim et al. (1999)	N <sub>4</sub> O <sub>2</sub> azacrown	0.01 M NH <sub>4</sub> Cl	1.038	Unclear	20
Kim et al. (2000)	Amino benzo-15-crown-5	1 M NH <sub>4</sub> Cl	1.026	<sup>7</sup> Li	20
Nishizawa and Watanabe (1986)	Cryptand (2B,2,1)		0.959	<sup>6</sup> Li	Room temp.
Nishizawa et al. (1984)	Benzo-15-crown-5		0.965–0.998	<sup>6</sup> Li	Room temp.
Nishizawa et al. (1984)	Cryptand (2B,2,1)	Methanol solution of LiX	0.953–0.965	<sup>6</sup> Li	
Nishizawa et al. (1988)	Benzo-15-crown-5		0.960–1.000	<sup>6</sup> Li	20
Ooi et al. (1999)	Ti-phosphate exchanger	0.05 M (NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub>	0.993	<sup>6</sup> Li	20
Otake et al. (2006)	Phenol type benzo-15-crown-5	Methanol-HCl mix	0.967	<sup>6</sup> Li	35
Kim et al. (2003)	Aminobenzo-18-crown-6	2 M NH <sub>4</sub> Cl	1.0095	<sup>7</sup> Li	20
Oi et al. (1991)	Cation exchange resin		1.00089–1.00171	<sup>7</sup> Li	
<i>Inorganic materials</i>					
Pistiner and Henderson (2003)	Gibbsite		0.985	<sup>6</sup> Li	
Zhang (1998)	Kaolinite and vermiculite		0.972–0.979	<sup>6</sup> Li	25
Vigier (2008)	Smectite		0.984	<sup>6</sup> Li	3
Wimpenny (2010)	Fe-oxyhydroxides		0.98	<sup>6</sup> Li	
Chan and Hein (2007)	Fe-Mn crusts		0.978–0.999	<sup>6</sup> Li	
Taylor and Urey (1938)	Zeolite		0.978	<sup>6</sup> Li	

#### 4.4 Laser methods

The method is generally based on the selective excitation of the desired isotope and its subsequent separation from the feed stream. Two large laser based enrichment facilities have been planned by General Electric for Wilmington, North Carolina. One of these facilities is called SILEX (Separation of Isotopes by Laser EXcitation) another is a commercially ready Hitachi laser plant [30]. Both should primarily enrich uranium isotopes (cf. chapter 6). Another process that has also been considered for uranium enrichment is the AVLIS (Atomic Vapour Laser Isotope Separation). With the AVLIS process the isotopic mixture is firstly vaporized by an electronic beam. Afterwards the desired isotope is selectively ionized by a laser with a suitable wavelength (usually a dye laser). Then the ionized isotope is separated by an electric field (e.g. attraction by negatively charged plates) [83–86]. In Figure 40 there is an illustration of such an installation.

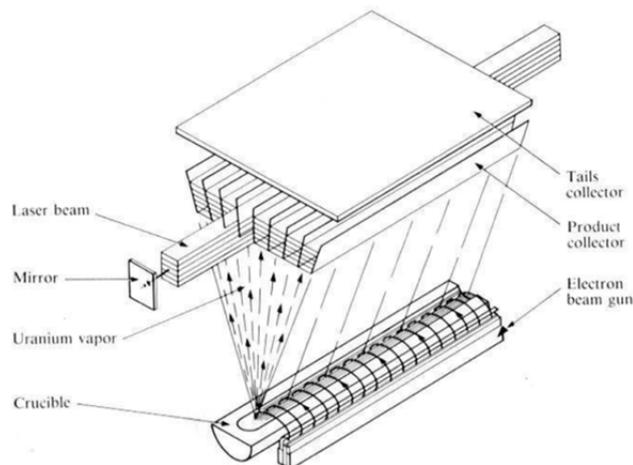


Figure 40: AVLIS. [41]

Another possibility to separate the ionized isotopes is the MAGNIS (Magnetically Activated and Guided Isotope Separation) system. The isotopes here are also vaporized, but are not ionized by the laser beam, but optically pumped according to Figure 41 [87, 88].

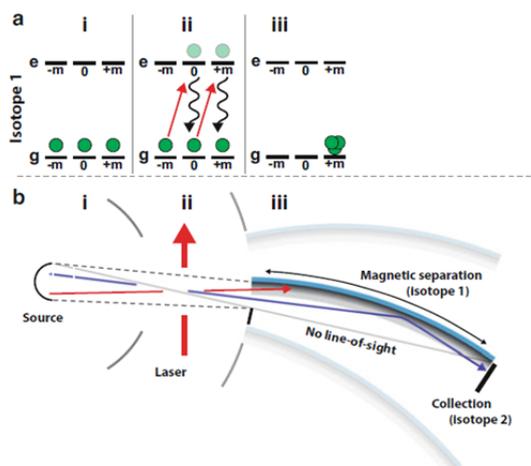


Figure 41: MAGNIS. [87]

This way they are magnetically activated and may be separated by the subsequent magnetic field according to the charge to mass ratio. The optical pumping is what distinguishes this method to ordinary plasma ICR (Ion Cyclotron Resonance) methods, which is basically a mass spectrometer process where the isotopes are heated to plasma and then separated in a magnetic field. Another pathway is the two step laser photoionization, which uses two dye lasers at once to excite and ionize the vaporized feed. Since here both isotopes are ionized, they are separated subsequently

by a TOF (Time Of Flight) spectrometer. The set up may be seen in Figure 42. Since the isotopic electronic structure of isotopes differs only in its hyperfine structure, the selective excitation laser beams require a very narrow linewidth [86, 89–92].

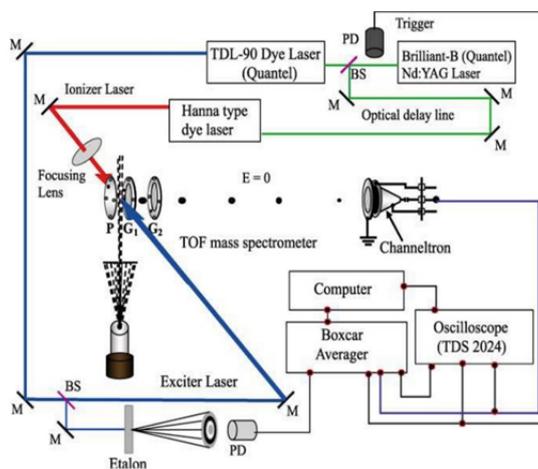


Figure 42: The two step laser photoionization. [92]



## 5 Technical and economical evaluation of the processes

Many methods have been investigated for the purpose of isotope separation (cf. Chapter 4). Each of those has its own advantages and disadvantages. Even among one method class there are large differences between the proposed systems. Not every effective separation method fulfils the requirements of nuclear fusion. Out of those difficulties a certain systematic method according to a VDI guideline (VDI Guideline 2225-3, Technical-economic examination, German Engineering Society (VDI), 1998) was used for the evaluation process.

### 5.1 Overview of the identification process

The identification process basically follows four steps:

- 1) Definition of assessment criteria
- 2) Pairwise comparison
- 3) Calculation of the quality rating
- 4) Technical-economic examination.

These approaches are commonly used in product development and have also been used last year to develop the new reference architecture of the EU DEMO fuel cycle. It offers the opportunity to find out which of the available methods will meet the fusion requirements the best way in order to avoid expensive development efforts with unknown results.

The identification process starts with the definition of the assessment criteria. This is a very important step, since reliable results can only be achieved, if all relevant requirements are considered. The next step is a pairwise comparison of the different requirements the lithium enrichment process should accomplish. The pairwise comparison approach is a method to obtain a ranking in an arbitrary list of different requirements. The main advantage of this procedure is that it is easier to compare two aspects with each other than giving a full list a certain order. The pairwise comparison approach determines the relevance of each requirement [32]. These values are needed in the following step for the calculation of the quality rating. The quality rating expresses in a quantitative way (values between 0 and 100%) how good an enrichment method meets the requirements of the pairwise comparison. The values approached by the quality rating are for the last step plotted against the estimated cost (comprising R&D and the equipment needed to realize the respective process) relative to the most expensive solution.

### 5.2 Definition of assessment criteria

A summary of the requirements used for the pairwise comparison approach is given in Table 13.

**Table 13: Requirements used for pairwise comparison.**

Requirements used for the pairwise comparison approach
Good scalability of the process
Low complexity of the process
Usability for reprocessing of the blanket material
No production of toxic waste
No use of toxic operation fluids
Well proven process
Good energy efficiency of the process
Low facility investments



Due to the large amounts of  ${}^6\text{Li}$  isotope that will be needed in the near future within the nuclear fusion program (cf. Chapter 2), it is important that the process chosen for its enrichment is well scalable. Otherwise it would be almost impossible to fulfil that need.

Complexity is almost always related to a lot of engineering problems and difficulties. Therefore, it is desirable that the complexity of the process is as low as possible for an industrial application. As already mentioned in chapter 2, a significant amount of  ${}^6\text{Li}$  breeding material will not react during the lifetime of the breeding blanket. Thus, the process should also be applicable for reprocessing. Since it is not avoidable that this material is associated with tritium and other activated nuclei, it must be assured that the enrichment system is usable under these circumstances. The tritium contamination may also lead to the production of toxic or irradiating waste, dependent on the enrichment system and its associated materials. It is crucial to avoid that as much as possible, since an increasing amount of irradiating toxic material would not only lead to the logistic problems of their treatment and storage, but would also increase the running costs significantly and damage the image of nuclear fusion as alternative energy source due to environmental issues accompanied.

The major concern that is associated with the use of toxic operation fluids is that it could be released to the environment and destroys the nature or influence the ecosystem in a harmful way. An appropriate engineering and the establishment of a closed fluid cycle could prevent that. Another aspect that should be taken into consideration is the little time left until the first enriched material breeding blankets shall be tested in ITER (cf. Chapter 2). For that reason the process chosen should be well proven so that it does not need much time and effort to establish it. Since the isotope should be used for the generation of electric energy, it is not reasonable that its enrichment method consumes a lot of it. Further, a high energy demand produces running costs which influences the isotope price negatively. As illustrated in Chapter 3 the actual price of the desired isotope is much too high. To set up an economic process that offers the opportunity to produce the isotope to a cheaper price, it is important to consider the facility investments needed. These should be of course as low as possible.

### **5.3 Pairwise comparison**

The pairwise comparison is done according to the following scheme: If one category is more important than the other, a 2 is given; if it is less important, a 0 is given; if both categories are of the same importance, a 1 is given. The results are given in Table 14.



**Table 14: Pairwise comparison results for <sup>6</sup>Li enrichment process requirements.**

	Good scalability of the process	Low complexity of the process	Usability for reprocessing	No production of toxic waste	No use of toxic operation fluids	Well proven process	Good energy efficiency of the process	Low facility investments	SUM	ORDER
Good scalability of the process	1	0	1	2	1	0	0	0	5	5
Low complexity of the process	1	1	0	0	1	0	0	0	2	7
Usability for reprocessing	2	2	1	2	2	1	2	2	12	1
No production of toxic waste	1	2	1	1	2	2	1	0	9	4
No use of toxic operation fluids	0	2	0	0	0	0	0	0	2	7
Well proven process	1	1	0	0	2	1	0	1	5	5
Good energy efficiency of the process	2	2	1	1	2	2	1	1	11	2
Low facility investments	2	2	0	2	2	1	1	1	10	3

The order of importance for each criterion, determined by this method, is shown in the very right column. The quantitative weighting, required for the following calculation of the quality ranking, is given in the neighbouring column (SUM value). For filling the matrix diagram, it is sufficient to fill only the numbers on the right side of the diagonal line (indicated in black). Therefore, the question has to be answered if the horizontal aspect is more, less or equally important than the vertical aspect. The numbers in grey are resulting and can be calculated by two minus the value reflected on the diagonal line.

#### 5.4 Calculation of a quality rating

The quality rating is conducted in such a way that it is checked to what extent an enrichment method or rather an enrichment method class meets the categories already used for pairwise comparison. For this purpose, the resulting weighting value g (SUM value) for each category is taken and multiplied with a rating number p according to the German guideline for this approach. The value of the rating number has to be chosen from p = 0 (dissatisfying), 1 (inadequate), 2 (sufficient), 3 (good) or 4 (very good, ideal). Finally, the quality rating W is given in a relative way, related to the maximum number of points that is 4 (best rating) x 56 (sum of all weighting values) = 224, and expressed as a number in per cent. The results are shown in Table 15.



**Table 15: Quality rating calculation results for lithium enrichment process classes.**

	Weighting	Lithium amalgam chemical exchange		Liquid ammonia chemical exchange		Cation complexing chemical exchange		Ion exchanger (organic)		Ion exchanger (inorganic)		Intercalation systems		Electrolysis (mercury cathode)		Electrolysis (other cathodes)		Electromigration		Electrophoresis	
		p	p x g	p	p x g	p	p x g	p	p x g	p	p x g	p	p x g	p	p x g	p	p x g	p	p x g	p	p x g
Good scalability of the process	5	4	20	4	20	4	20	4	20	4	20	1	5	4	20	4	20	4	20	4	20
Low complexity of the process	2	4	8	4	8	4	8	4	8	4	8	2	4	4	8	4	8	3	6	2	4
Usability for reprocessing	12	4	48	4	48	0	0	0	0	0	0	4	48	4	48	3	36	2	24	3	36
No production of toxic waste	9	4	36	4	36	0	0	0	0	3	27	3	27	4	36	2	18	1	9	1	9
No use of toxic operation fluids	2	1	2	0	0	1	2	0	0	0	0	1	2	1	2	1	2	1	2	1	2
Well proven process	5	4	20	0	0	2	10	1	5	1	5	1	5	4	20	1	5	4	20	1	5
Good energy efficiency of the process	11	3	33	2	22	3	33	3	33	3	33	1	11	0	0	0	0	0	0	0	0
Low facility investments	10	3	30	3	30	3	30	2	20	2	20	1	10	3	30	2	20	2	20	1	10
<b>Sum:</b>	<b>56</b>	<b>197</b>	<b>164</b>	<b>103</b>	<b>86</b>	<b>113</b>	<b>112</b>	<b>164</b>	<b>109</b>	<b>101</b>	<b>86</b>										
<b>Quality rating W:</b>		<b>87.9</b>	<b>73.2</b>	<b>46.0</b>	<b>38.4</b>	<b>50.4</b>	<b>50.0</b>	<b>73.2</b>	<b>48.7</b>	<b>45.1</b>	<b>38.4</b>										

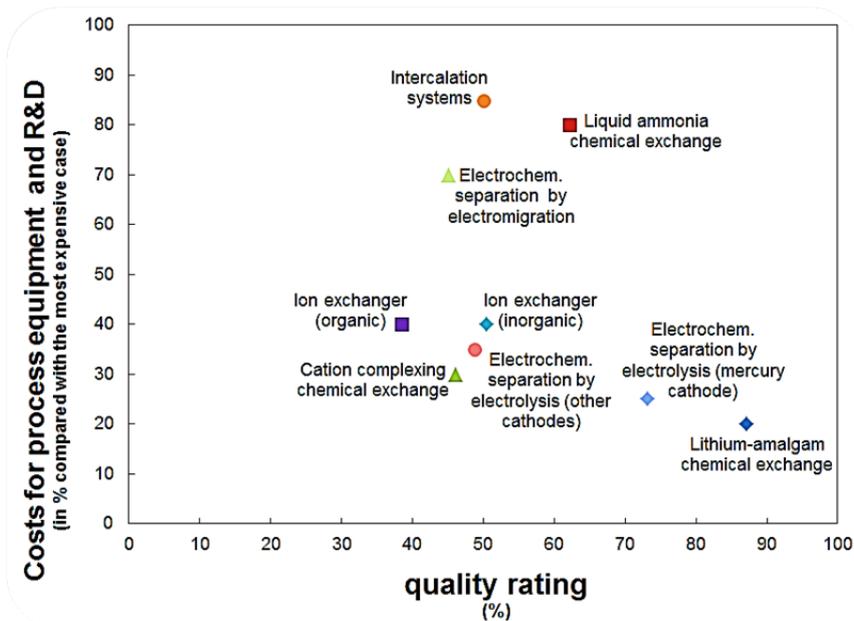


Continuation Table 15.

	Weighting		Displacement chromatography (inorganic resin)		Displacement chromatography (organic resin)		Separation by laser methods	
	p	p x g	p	p x g	p	p x g	p	p x g
	Good scalability of the process	5	3 15	3	15	3	15	1
Low complexity of the process	2	4 8	4	8	4	8	1	2
Usability for reprocessing	12	3 36	3	36	0	0	4	48
No production of toxic waste	9	3 27	3	27	1	9	4	36
No use of toxic operation fluids	2	1 2	1	2	4	8	4	8
Well proven process	5	2 10	2	10	2	10	2	10
Good energy efficiency of the process	11	4 44	4	44	4	44	1	11
Low facility investments	10	3 30	3	30	3	30	0	0
<b>Sum:</b>	<b>56</b>	<b>172</b>	<b>172</b>	<b>124</b>	<b>124</b>	<b>120</b>	<b>120</b>	<b>120</b>
<b>Quality rating W:</b>		<b>76.8</b>	<b>55.4</b>	<b>55.4</b>	<b>53.6</b>	<b>53.6</b>	<b>53.6</b>	<b>53.6</b>

### 5.5 Technical-economic examination

For the technical and economical examination the values obtained by the quality rating are deallocated to a percentage assessment of the cost that would be caused by the research and development and by the process equipment required to establish the particular method. For the purpose of an appropriate comparison between the methods the system that is estimated to cause the highest costs, which is in case of Li-enrichment the laser method, is set to 100%. The best result of the technical and economical evaluation is the system that is found in the rear right edge as close to the quality rating axis (x-axis) as possible. It was found that the 'classical' COLEX process has the highest quality value at a low development effort. Generally the mercury based methods show the highest quality values since they are on the one hand well established and on the other hand applicable for reprocessing.



**Figure 43: Technical and economical evaluation.**

The COLEX process has the advantage that it is a well proven process for large scale lithium isotope separation. Therefore, the effort that has to be invested in research and development is relatively low which leads to the fact that it may be established more quickly than the other not that well experienced systems. As chemical extraction system it is easily scalable by the number of equilibrium stages. It is also a pretty simple and robust process which basically only needs an extraction column, a waste and product end reflux system and pumps that convey the operation fluids. Due to the setup of the process, it could be regarded as relatively energy efficient, since basically only the pumps and the reflux systems require a perceptible amount of electrical energy. Therefore, the fraction of the produced electricity that will be consumed by a future fusion power plant would be relatively low. It may be assumed that such a simple process only requires relatively low facility investments which will probably contribute significantly to lower the price of  $^6\text{Li}$ .

Another major aspect that distinguishes the COLEX process from most of the other chemical exchange systems is that it is usable for the recycling of the tritiated burned breeding material. Mercury does not interact with hydrogen and particularly not with the tritium impurities which are in case of reprocessing almost unavoidable. Therefore, no toxic waste will be produced that has to be stored elsewhere and does not only produce additional costs, but also represents a threat for nature and environment. The main disadvantage of the COLEX process is the use of toxic mercury as operation fluid. This is soberly considered more a problem of the negative reputation caused by the former experience in Oak Ridge than a serious threat. Engineers working in the nuclear energy section are approved to handle much more critical materials than mercury which is still used today in many products (like e.g. dental amalgam which is used for tooth fillings) and industrial applications (like for instance the chlorine caustic soda production). Almost all the environmental problems that occurred in Oak Ridge could be avoided by a proper engineering and design.

Chemical exchange systems in general are well scalable, thus also the liquid ammonia system. However, due to its small separation factor many more stages than for the COLEX system would be required. The separation system itself could be regarded as even simpler than the COLEX system, since only two components must be taken into consideration. Reprocessing would also be possible, since tritium probably does not destroy the ammonia molecule nor produce any waste. Nevertheless, isotopic exchange between the hydrogen atoms of the ammonia molecule and the tritium contaminations presumably lead to the formation of tritiated ammonia which therefore represents a toxic (and radioactive!) operation fluid. The main disadvantages of that process are that it is not well proven and that it is more energy consuming compared to the other chemical exchange systems (since the ammonia must be cooled down to quite low temperatures of less than 230 K).

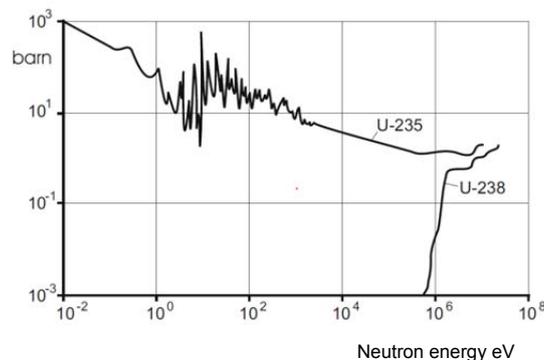


The main difficulty with the cation complexing systems is that they are absolutely not usable for reprocessing. Isotopic exchange between the hydrogen atoms of the organic system and tritium may change the highly specific build molecules and probably makes them ineffective and even toxic. This way, a lot of hazardous irradiating waste would be produced. Since the prices for the complexing compounds are quite high (cf. Chapter 4.1.2.), this would cause a great loss. Similar problems must be generally considered for all organic compounds. This is why for the evaluation of the chemical exchange with ion exchanger as well as for the displacement chromatography the involved compounds have been separated into the categories organic or inorganic. Obviously, the ion exchange systems that work with inorganic ion exchangers as well as the chromatography that uses inorganic resin material therefore have a better quality ranking than the others. However, it should be mentioned that this discrimination is only valid for inorganic ion exchanger that do not include hydrogen atoms in their molecule.

Regarding the electrochemical separation systems, the main disadvantage is that they require an appreciable amount of electrical energy which cannot be counterbalanced by their separation performance.

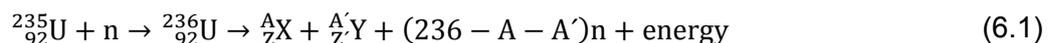
## 6 Comparison with enrichment processes in fission

The commercial use of nuclear energy is up to now limited to the use of nuclear fission. Contrary to nuclear fusion the energy in nuclear fission is not released by melting two (light) nuclei but by splitting a heavy one. Nuclei that might be used for nuclear fission could be distinguished into fissile nuclei (e.g.  $^{233}\text{U}$ ,  $^{235}\text{U}$ ,  $^{237}\text{Np}$ ,  $^{239}\text{Pu}$  and  $^{241}\text{Pu}$ ) and fissionable nuclei (e.g.  $^{232}\text{U}$ ,  $^{234}\text{U}$ ,  $^{238}\text{U}$  and  $^{232}\text{Th}$ ). Fissionable nuclei need neutrons of significant kinetic energy to overcome the fission barrier equally to  $^7\text{Li}$ . For fissile nuclei thermal neutrons are sufficient to induce the fission reaction same as for  $^6\text{Li}$  [41]. The only fissile nuclei that could be found in nature in significant amounts is the  $^{235}\text{U}$ . Natural uranium consists to 99.3% of  $^{238}\text{U}$  and only to 0.7% of  $^{235}\text{U}$ . Therefore, the natural isotopic composition of uranium could be regarded as much less favourable than that of lithium (92.4%  $^7\text{Li}$  and 7.6%  $^6\text{Li}$ ). Also the relative mass difference between the lithium isotopes is much higher than that between the uranium isotopes. The reason why  $^{235}\text{U}$  is preferred to  $^{238}\text{U}$  for nuclear fission is comparable to that why  $^6\text{Li}$  is preferred to  $^7\text{Li}$ . The neutronic cross section of  $^{235}\text{U}$ , especially for thermal neutrons, is higher than that of  $^{238}\text{U}$  (cf. Figure 44).



**Figure 44: Neutronic cross section for fission of  $^{235}\text{U}$  and  $^{238}\text{U}$ . [93]**

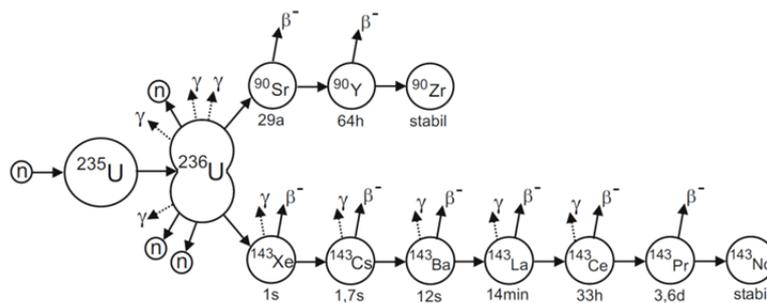
The energy released by the neutron capture of  $^{235}\text{U}$  (about 7 MeV) excites the nucleus that much that it is splitted. The fission process of  $^{235}\text{U}$  can be symbolized by the following equation [93]:



The energy released can be approximated to about 200 MeV per fission reaction. This value is at the first glance much higher than the 17.6 MeV of nuclear fusion. But related to the fuel mass the value for nuclear fusion is more than a hundred times higher than that of nuclear fission. Nevertheless, this is a huge amount of energy which can be seen by comparing the values to those of conventional fossil fuels (cf. Table 16) [94]. X and Y represent fractions of the former nuclei and n the free neutrons released by the fission process. The capital A stands for the atomic mass and Z represents the number of protons in the nuclei. X and Y are in general different which means that their numbers of protons vary. It is also quite unusual that both have the same atomic mass. Both store a higher binding energy per nucleon than the original  $^{235}\text{U}$  and both are radioactive. They irradiate further in a specific decay chain like for instance the one shown in Figure 45.

**Table 16: Comparison of chemical and nuclear reactions. [94]**

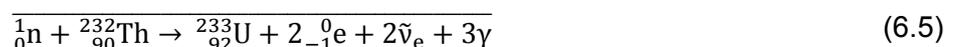
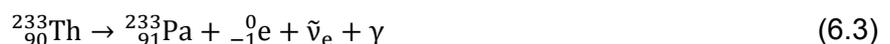
	Chemical reaction	Nuclear fission	Nuclear fusion
Reaction example	$C + O_2 \rightarrow CO_2$	$^1_0n + ^{235}_{92}U \rightarrow ^{144}_{92}Ba + ^{89}_{36}Kr + 3^1_0n$	$^2_1D + ^3_1T \rightarrow ^4_2He + ^1_0n$
Fuel	coal, oil and air	enriched uranium	deuterium and tritium
Typical temperature (K)	1 000	1 000	100 000 000
Released energy per kg fuel ( $\frac{MJ}{kg}$ )	33	$2.1 \cdot 10^6$	$3.4 \cdot 10^8$



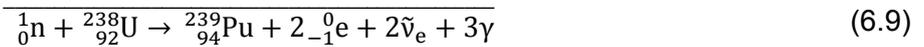
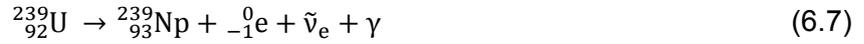
**Figure 45: Possible decay chain of uranium-235 fission products. [93]**

The fission reaction itself produces about 2-3 high energetic neutrons of approximately 2 MeV. To maintain a continuous chain reaction in which the produced neutrons per fission initiate a successive reaction, it is necessary to moderate the neutrons to thermal velocities. Moderators could be either conventional (light) water (H<sub>2</sub>O), heavy water (D<sub>2</sub>O) or graphite. All have the characteristic to scatter the fast neutrons. This way the neutrons lose kinetic energy and become slower. If light water is used - as for about 90% of the existing commercial nuclear reactors - fission neutrons may be absorbed by hydrogen nuclei to form D<sub>2</sub>O out of H<sub>2</sub>O. Since this way neutrons are lost, the uranium applied has to be enriched in <sup>235</sup>U. Heavy water reactors (like for instance the CANDU (CANada Deuterium Uranium) reactor) and reactors working with graphite as moderator do not need any uranium enrichment, since they do not absorb neutrons. Not all neutrons lead to further fission reactions. Some are lost by leakage, some are absorbed by the structural material and some are used to “breed” further nuclei. For that purpose there are principally two mechanisms that possibly occur [93]:

The first one is a reaction between <sup>232</sup>Th traces in the breeding material and thermal neutrons. This reaction produces fissile <sup>233</sup>U by the following way:



The second and most frequent one makes use of neutrons that still have a moderately high velocity and breeds fissile  $^{239}\text{Pu}$  out of  $^{238}\text{U}$  in the following way:



As fissile material is bred by this reactions the fission material for peaceful electricity generation only needs a relative moderate isotopic enrichment of about 3%  $^{235}\text{U}$  compared to lithium which has to be at least enriched to 30% for ceramic breeders (cf. Chapter 2). The effect of such small enrichment amounts can be illustrated by the following deliberations:

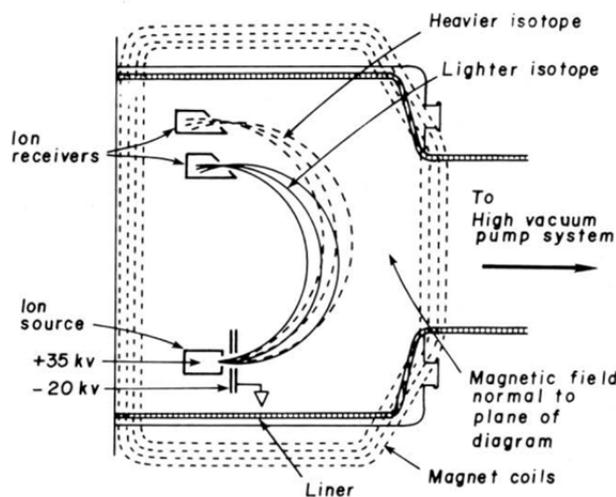
If  $\sigma_a$  represents the cross section for the absorption of a neutron and  $\sigma_f$  represents the cross-section for the fission initiation the probability that a moderated thermal neutron leads to nuclear fission ( $w_f$ ) could be calculated by:

**Table 17: Neutronic fission and absorption cross-sections. [93]**

	$\sigma_{f,^{235}\text{U}}$	$\sigma_{a,^{235}\text{U}}$	$\sigma_{f,^{238}\text{U}}$	$\sigma_{a,^{238}\text{U}}$
barn	583	78.5	0	2.74

For natural uranium (0.7%  $^{235}\text{U}$ , 99.3%  $^{238}\text{U}$ ) the probability is therefore 55%. For enriched uranium (3%  $^{235}\text{U}$ , 97%  $^{238}\text{U}$ ) this value increases up to 78%.

Historically, uranium enrichment was first realized at large scale by the “Calutrons” (California University Cyclotron). This method invented by Ernest Lawrence in 1930 can be used for the separation of all isotopes. It is based on the separation of the by electrons ionized isotopes according to their charge to mass ratio. Figure 46 shows the principle of a Calutron. [38]



**Figure 46: Principal of a Calutron. [38]**

The feed material is first vaporized by a heated source. A fraction of particles in this vapour is then ionized by an arc discharge. After that, the ions are accelerated into a large surrounding chamber

by an appreciable potential difference of about 40 keV. The resulting speed  $v$  for an ion of mass  $m$  is as a result of equilibrium of the force of initial and the Lorentz force, given by

$$v = \sqrt{\left(\frac{2eV}{m}\right)} \quad (6.10)$$

while  $e$  represents the charge and  $m$  the mass of the isotope. The static magnetic field  $B$  which deflects the ions into circular trajectories is generated by large current carrying coils which surround the chamber. Due to the Lorentz forces the radius  $r$  for the respective isotope may be given by the following equation:

$$r = \frac{1}{B} \cdot \left(\frac{2eV}{m}\right) \quad (6.11)$$

From this equation it is obvious that the heavier isotope is distracted on a circuit with a larger radius. Within the World War II Manhattan District Project these machines were used to separate  $^{235}\text{U}$  in kilogram quantities. The principle of that process is essentially that of a largescale mass spectrometer. It was used after the end of the World War II to separate many other kinds of isotopes [38, 41, 95]. Principally, Calutrons would be also applicable for lithium enrichment, but since they require a huge amount of electricity, they are economically not feasible for that purpose [41].

Another enrichment plant that was used simultaneously to the Calutrons and, in fact, that was pre-enriching the uranium before it was separated by the Calutrons was the S-50 thermal diffusion plant in the ORNL (cf. Figure 47).

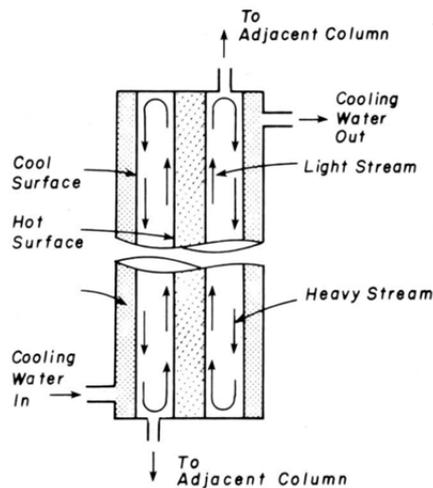


**Figure 47: S-50 Thermal diffusion plant at Oak Ridge, Tennessee. [41]**

Thermal diffusion relies on the kinetic gas theory which predicts that atoms or molecules of different atomic weights differ in their diffusion rates. Gaseous mixtures that are subjected to a temperature gradient show also a concentration gradient according to the temperature difference. This means for isotopic separation that there is a tendency for one kind of isotope to concentrate in the cold region and the other type in the hot region [41].

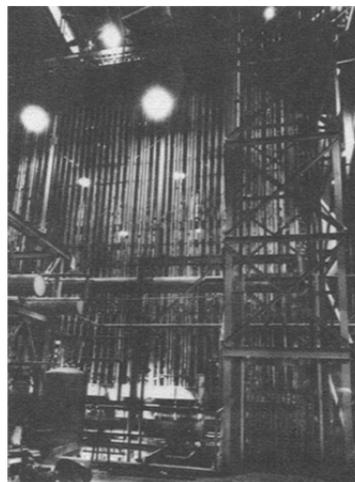
H. Clausius and G. Dickel invented the thermal diffusion column in 1938. A long vertical cylinder confines the gaseous fluid between a hot inner wall and a cool outer wall. Due to thermal convection a counter current flow is created in which the outside cold gas sinks to the bottom of the column and the hot gas at the inner side rises to the top of the column. Applied to uranium this means that the gaseous compound  $\text{UF}_6$  is circulating in the annual region between the two pipes in vertical direction. A higher concentration of the lighter isotopes ( $^{235}\text{U}$ ,  $^{234}\text{U}$ ) may be found near the hot surface than near the cold surface. Isotopic exchange occurs between the rising and the

descending current comparable to that in the counter current extraction column like COLEX (cf. Figure 48).



**Figure 48: Thermal diffusion column. [38]**

Since at different levels along the column length the horizontal slices of the column act as unit separation stages, the counter current vertical flows multiply the small isotopic concentration difference (less than 1%) between the walls. This way, a single column contains a large number of separating stages. A system of two 1.5 m long tubes with an outer diameter of 0.03 m and a size of gap between the tubes of 2 mm would produce a 40% difference in concentration of the rare isotope between the column ends. To produce 1 g of 90% enriched uranium per day one needs an installation of 1000 of such columns (cf. Figure 49).



**Figure 49: Liquid thermal diffusion rack. [41]**

A light water fission reactor that produces 1.2 GW electrical energy requires about 100 t of low enriched (< 4-5%  $^{235}\text{U}$ ) uranium dioxide [93]. These amounts are comparable to those of lithium needed for the DEMO reactor. Obviously, the amounts of enriched material that may be produced by these early methods are not satisfying. Especially gaseous diffusion would require much more effort for lithium than for uranium, since no lithium compound that is gaseous at room temperature has yet been found. This is generally the problem comparing the enrichment methods used for the uranium separation to those of the lithium separation. The most frequently used uranium separation methods that are used today are gaseous diffusion and gaseous centrifugation. Both require gaseous components of the respective isotopes as can be seen in the following.

Most of the  $^{235}\text{U}$  that was produced during the Second World War was separated by gaseous diffusion. It represents the first commercial separation method and today still 40% of the worlds enriched uranium is separated by this process [41]. The first nation that has used gaseous diffusion for uranium enrichment was the USA (also within the Manhattan Project), followed by Russia, the UK, France, China and Argentina. Gaseous diffusion today is only used to produce significant amounts of enriched uranium in the USA and in France.

Gaseous uranium hexafluoride flows from a high pressure chamber to a low pressure chamber through a barrier with very fine holes. Since the driving force which is the pressure difference is the same for both isotopes, their kinetic energy must be the same either [41].

$$\frac{1}{2} m_{^{238}\text{UF}_6} v_{^{238}\text{UF}_6}^2 = \frac{1}{2} m_{^{235}\text{UF}_6} v_{^{235}\text{UF}_6}^2 \quad (6.12)$$

Therefore, the lighter  $^{235}\text{UF}_6$  has a higher velocity than the heavier  $^{238}\text{UF}_6$ . This way the gas that passes the barrier (the permeate) is slightly enriched in  $^{235}\text{UF}_6$ . The rest of the gas, which has not passed the barrier, will be consequently impoverished (cf. Figure 50).

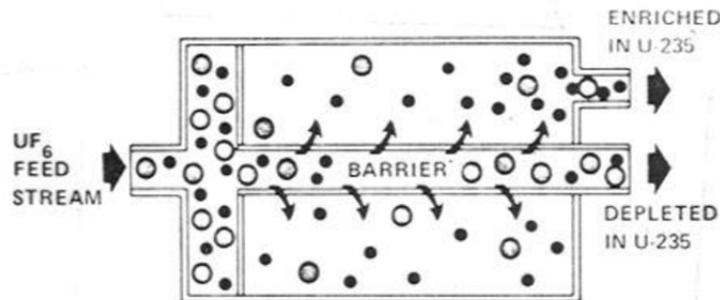


Figure 50: Gaseous diffusion cell [41].

Out of eq. (6.12) it becomes obvious that the ratio of the respective isotopic velocities is equal to the square root of the inverse mass ratio [41]:

$$\frac{v_{^{235}\text{UF}_6}}{v_{^{238}\text{UF}_6}} = \sqrt{\frac{m_{^{238}\text{UF}_6}}{m_{^{235}\text{UF}_6}}} \quad (6.13)$$

while  $v$  stands for the respective velocity and  $m$  for the respective molecular mass. Here it must be mentioned that the fluoride atom only exists in one isotopic form ( $^{19}\text{F}$ ) which means that it does not contribute to the mass difference of the molecules. The resulting ideal separation factor  $\alpha$  for a mixture of the two components equals the ratio of the velocities, since the diffusion rate is directly proportional to it.

$$\alpha = \sqrt{\frac{m_{^{238}\text{UF}_6}}{m_{^{235}\text{UF}_6}}} = \sqrt{\frac{352}{349}} = 1.00429 \quad (6.14)$$

Here it becomes obvious that this method would probably be more effective for lithium, since as already mentioned the relative mass difference of the lithium isotopes is higher than that of the uranium isotopes. The low separation factor indicates that a lot of enriching stages in a counter current cascade are required to achieve a perceptible enrichment degree (cf. Figure 51).

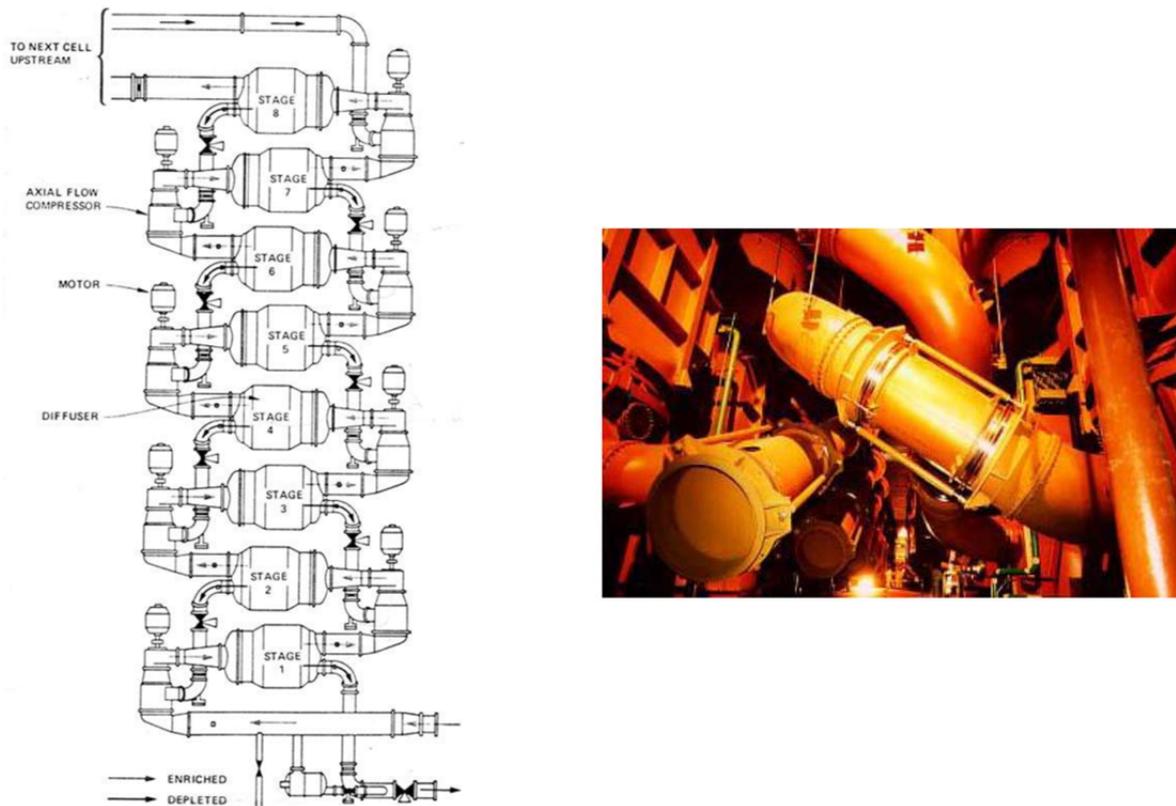


Figure 51: Gaseous diffusion cascade. [41]

Before the permeate of the previous stage enters the next one it must be recompressed. The power needed for the compressor between each stage accounts significantly to the high electrical energy requirement of such enrichment plants. Approximately 70 percent of the running costs are those that have to be spend on electricity.

To separate the feed of natural uranium up to an enrichment level of 3%  $^{235}\text{U}$  an “ideal cascade” of varying size would require 1272 stages. To achieve an enrichment level of 90% which is a level that is probably only needed for the production of nuclear weapons, one would require 3919 stages [95]. The capacity of a separation facility is usually given by the separative work unit (SWU) which is a measure of the quantity of separation achieved in dependence on the separation performance [93]. It can be calculated by the following equation:

$$SWU = P \cdot V(\tilde{x}_p) + W \cdot V(\tilde{x}_w) - F \cdot V(\tilde{x}_f) \quad (6.15)$$

and

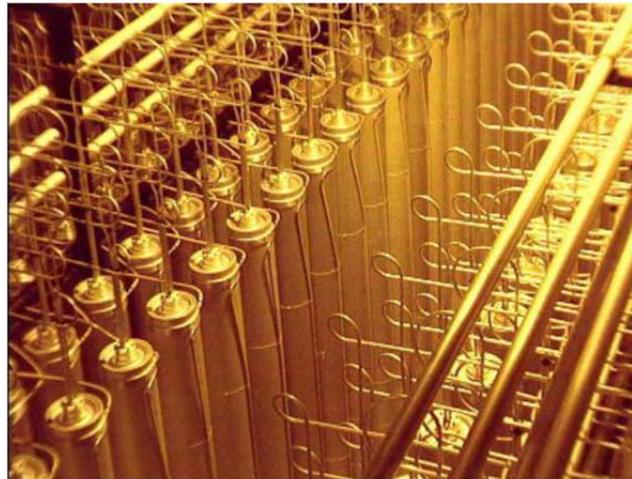
$$V(\tilde{x}_i) = (2\tilde{x}_i - 1) \cdot \ln\left(\frac{\tilde{x}_i}{1 - \tilde{x}_i}\right); \text{ and } i = P, W, F \quad (6.16)$$

with  $\tilde{x}_i$  representing the molar fraction of the desired isotope ( $^{235}\text{U}$ ) in the respective material. The P stands for the product amount, W for waste amount and the F for feed amount. The indexes P, W, F refer to the respective molar fraction. The unit of the SWU is usually kg [93].

In the USA the large USEC (United States Enrichment Cooperation) plant which was originally developed for the nuclear weapon production produces about 8 million kg SWU per year. A more modern gaseous diffusion plant in France (Tricastin) produces 10.8 million kg SWU per year. A typical 1 GW fission reactor requires about 1-1.2 million kg SWU. The gaseous diffusion plants are however at the end of their design life and will be probably soon replaced by gaseous

centrifugation plants since they are much more energetic efficient. Gaseous diffusion plants require about 900 MJ per SWU and gaseous centrifugation plants only about 180 MJ per SWU [41, 95].

Today gaseous centrifugation is the most recommended uranium enrichment method. Gas centrifugation was also among the methods considered by the Manhattan Project, but it was gaseous diffusion that was preferred. The Soviet Union on the contrary chose this method concurrently to gaseous diffusion with the help of its war prisoner the German Gernot Zippe. Industrial capacity of gas centrifugation plants was reached by Russia, Germany, China, UK, USA, Japan, Pakistan, Brazil and Iran [95]. The four Russian plants, which are placed in Seversk, Zelenogorsk, Angarsk and Novouralsk, produce 40% of the world's capacity. Enrichment plants at commercial level are also employed in the EU by a British, German and Dutch company called Urenco which runs enrichment plants in all three member countries (cf. Figure 52) [41, 95].



**Figure 52: Centrifuge banks at the European Urenco plant [41].**

The technology is based on the principle that due to the centrifugal forces the heavier molecule  $^{238}\text{UF}_6$  flows to the walls while the lighter molecule  $^{235}\text{UF}_6$  remains more in the middle of the centrifuge. The operation occurs as follows: The gas is fed into a series of tubes. The tubes are 1-2 m long and have a diameter of 0.15-0.20 m. Each tube contains a rotor which rotates very rapidly with about 50000-70000 rpm. The heavier  $^{238}\text{UF}_6$  concentrates at the outer edge and the lighter  $^{235}\text{UF}_6$  in the centre. The application of a temperature gradient, heating the lower part of the centrifuge's rotor and keeping the upper part cool, leads to move of the lighter molecule towards the upper part due to thermal convection similar to the thermal diffusion method. Such a centrifuge using a temperature gradient is called "Zippe" centrifuge (cf. Figure 53) [19, 95]. As usual the enriched gas makes the feed gas for the next stage while the depleted gas flows back to the previous stage.

A radial separation factor is the result of the difference between the relative partial pressures at the wall and the cylinder axis. It highly differs with the rotation speed of the cylinder. A cylinder that rotates with a peripheral velocity of 300 m/s e. g. shows a pressure ratio of 550:1, while a cylinder that rotates with a peripheral velocity of 500 m/s shows the huge ratio of  $3.9 \cdot 10^7:1$  [41]. The maximum separation factor may be calculated by the ratio of the enrichment factor  $\alpha$  between the feed stream and the product stream and the depletion factor  $\beta$  between the feed stream and the depleted waste stream.

$$r_{\max} = \frac{\alpha}{\beta} = e^{\frac{1}{2} \Delta m v^2 \frac{1}{RT} \sqrt{2} \frac{l}{d}} \quad (6.17)$$

where  $\Delta m$  represents the mass difference between the isotopes,  $R$  is the universal gas constant,  $T$  stands for the absolute temperature,  $l$  is the rotor length,  $d$  is the diameter of the rotor, and  $v$  is the peripheral velocity. For a peripheral speed of 300 m/s the radial separation factor for the uranium isotopes at 27 °C would be about 1.055, which is much higher compared to the separation factor for gaseous diffusion (1.004). Therefore, an enrichment of 4-5% needs about 1000 stages with gaseous diffusion, but only ten stages in a centrifugation cascade. Regarding eq. (6.17), it becomes significant that this kind of enrichment method would not be as effective for lithium isotope separation as for uranium isotope separation, because the separation factor value is raised by the absolute mass difference and not by the relative one, which is about 3 u between the uranium isotopes and only 1 u between the lithium isotopes.

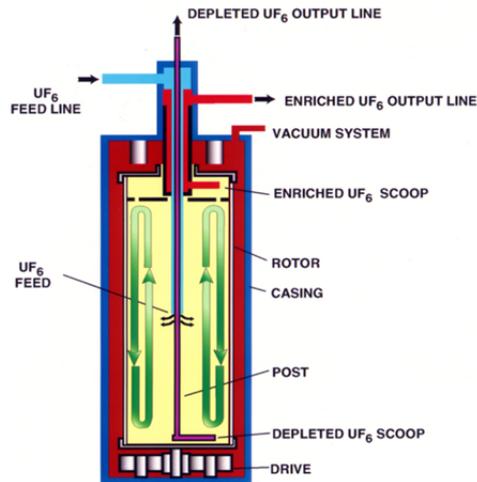


Figure 53: Gas centrifuge. [95]

The laser based methods considered for lithium isotopes have originally been developed for uranium isotope separation. Beyond laboratory scale there are basically three methods that have been developed: [95]

- AVLIS (Atomic Vapour Laser Isotope Separation)
- MLIS (Molecular Laser Isotope Separation) and
- SILEX (Separation of Isotopes by Laser EXcitation).

Of those only the AVLIS system may be applied at industrial scale. The AVLIS method uses molten uranium which is firstly vaporized by an electronic beam, secondly selectively ionized by a laser that emits a wavelength of 50273 angstrom and thirdly separated by an electric field. The main disadvantage of this method is that molten uranium is used instead of  $UF_6$ .

The excitation mechanism of the MLIS and the SILEX system is equal. The  $^{235}UF_6$  is firstly selectively excited by an infrared laser. Afterwards it is dissociated to solid  $^{235}UF_5$  by an ultraviolet laser. This way one gains the enriched precipitate. The main difference between the MLIS and the SILEX process is that the SILEX process utilizes a carrier gas [41, 95]. Some attempts such as the separation of lithium and uranium isotopes with chromatography, electromigration, using a cation exchange membrane [96] have been made, but did not seem to be of relevance for large technical separation plants.

Conclusively, it can be said that the properties and therefore the enrichment processes of uranium and lithium isotopes are quite different.

## 7 Conclusions

Lithium isotope enrichment is crucial for the success of the nuclear fusion energy since  ${}^6\text{Li}$  represents a primary fuel. The EU requires an amount of approximately 200 kg 90% enriched lithium for the ITER TBM testing. The estimations for the DEMO reactor predict a much higher quantity of more than 60 t of 90% enriched lithium per  $\text{GW}_{\text{el}}$ . The lowest price for  ${}^6\text{Li}$  that has been found up to now is that of Eurisotop, who offer 95% enriched lithium-6 metal for 5000 € per 100 g. In spite of the high prices, the lithium for the ITER TBM could still be paid for, but it is unclear whether sufficient Li-6 will be available. In addition, DEMO at the latest requires an enrichment system and the development process until then is expected to be long. Thus, work should start now to ensure lithium availability.

In addition, for nuclear fission reactors like PWRs and MSRs one to thousands of tons of highly enriched (>99.99%)  ${}^7\text{Li}$  are required.

Many lithium enrichment systems have been found in literature. The most important ones are listed in Table 18:

**Table 18: List of the most important enrichment systems.**

Enrichment system	Description
Chemical exchange with lithium amalgam	<ul style="list-style-type: none"> <li>Mercury has a higher affinity to <math>{}^6\text{Li}</math> than to <math>{}^7\text{Li}</math></li> <li>Counter current extraction system with enrichment in the amalgam phase</li> <li>Approved large scale enrichment method that has been militarily used to produce thermonuclear weapons</li> <li>The column exchange (COLEX) system (Li-amalgam vs. LiOH-aqueous solution) has been chosen as the most efficient one by ORNL</li> <li>The COLEX process is today still applied by Russia and China for military reasons</li> <li>The investigated enrichment factor for the COLEX system yields in <math>\alpha(0\text{ }^\circ\text{C}) = 1.059</math></li> </ul>
Chemical exchange with liquid ammonia	<ul style="list-style-type: none"> <li>Below 200 K, a lithium - liquid ammonia solution forms two phases with different densities and a large difference in metal ion concentration</li> <li><math>{}^6\text{Li}</math> is slightly enriched in the concentrated phase</li> <li>Only relatively low enrichment factors achievable</li> <li>Counter-current processing for technical-scale facilities is suggested, but particularly for lithium not experimentally investigated yet</li> </ul>
Cation complexing based chemical exchange	<ul style="list-style-type: none"> <li>Macrocyclic compounds (basically crown ether and cryptands)</li> <li>Offer the opportunity to solubilize inorganic Lithium salts in organic solvents</li> <li>Establishment of ordinary immiscible aqueous/organic equilibrium systems</li> <li>Highly selective host guest chemistry: <ul style="list-style-type: none"> <li>The Li-6 ion is preferably bounded within the nano cavity of the complexing agent</li> <li>The complexation occurs due to interaction between the positive charged ion and the dipolar bounded donor atoms (in general oxygen)</li> </ul> </li> </ul>



	<ul style="list-style-type: none"> <li>• The single stage separation factors are comparable or even larger than those of the amalgamation processes (for 12-crown-4 at 0 °C (<math>\alpha_{\max} = 1.057</math>) which is almost the same as for the COLEX system)</li> <li>• Considerations and calculations for large scale lithium isotope separation have been made for a counter current mixer settler cascade system</li> <li>• The focus of that system has been on <math>^7\text{Li}</math> enrichment which is needed for PWRs, since it is not sufficiently available within the USA and has to be purchased from China</li> <li>• The system chosen for this considerations was an aqueous LiCl solution phase, the cation complexing compound 15-crown-5-ether and chloroform as organic phase</li> </ul>
Chemical exchange using ion exchanger	<ul style="list-style-type: none"> <li>• Batch-process, based on solid materials (ion exchangers) that replace ions with equally charged ions in liquids when getting in contact with them</li> <li>• The exchanger materials usually have a higher affinity to <math>^6\text{Li}</math> than to <math>^7\text{Li}</math></li> <li>• Ion exchanger methods are often used in chromatographic separation systems where they form the resin material</li> <li>• Ion exchangers can be of organic or inorganic nature</li> <li>• Systems have been up to now only investigated at lab scale</li> </ul>
Intercalation methods	<ul style="list-style-type: none"> <li>• Reversible (or partially reversible) insertion of a molecule or ion into a material with layered structures</li> <li>• For lithium isotope separation, several intercalation materials (e.g. graphite) exist that usually have a greater affinity to insert <math>^6\text{Li}</math> than <math>^7\text{Li}</math> → enrichment takes place in Li ion batteries</li> <li>• E.g. intercalation into graphite (<math>\alpha_{\max} \sim 1.023</math>)</li> <li>• A future perspective could be the removal of enriched <math>^6\text{Li}</math> when recycling Li ion batteries</li> </ul>
Electrochemical separation by electrolysis	<ul style="list-style-type: none"> <li>• A lithium salt solution is electrolyzed using a mercury cathode in a counter-current flow</li> <li>• <math>^6\text{Li}</math> ions are preferentially uptaken by mercury than <math>^7\text{Li}</math> forming a lithium amalgam</li> <li>• A large scale enrichment facility has been tested in Oak Ridge National Laboratory (ELEX process)</li> <li>• Process is today used by used in Russia's Novosibirsk Chemical Concentrates Plant (NCCP) for the production of pure <math>^7\text{Li}</math> for nuclear fission applications</li> <li>• Other cathodes are also possible (e.g. zinc, graphite, tin, manganese cathodes)</li> </ul>
Electrophoresis	<ul style="list-style-type: none"> <li>• Motion of disperse solubilized particles (here lithium ions) relative to a separating (viscose) fluid (conductor) that is enforced by a uniform electric field</li> <li>• The isotope separation occurs due to the different velocities the heavier <math>^7\text{Li}</math> and the lighter <math>^6\text{Li}</math> moving through the conducting material</li> <li>• "Electrophoresis in liquid bath" is considered for large scale separation, it makes use of so called Li electrolyte-compatible Solid State Lithium Ion Super Conductor (SSLISC) as separating fluid and uses liquid metallic lithium as feed material</li> </ul>



	<ul style="list-style-type: none"> <li>An electrophoretic cell prototype was designed and a plant layout of n parallel series in m packed lines was proposed by CIEMAT</li> </ul>
Displacement chromatography	<ul style="list-style-type: none"> <li>Batch-process, based on an isotope specific distribution between a mobile phase (lithium solubilized in a liquid) and a stationary phase (resin surface)</li> <li>Separation facility consists mainly of long columns packed with porous resin material (organic or inorganic)</li> <li>Band length remains constant (reaches dynamic equilibrium) after the eluent solution passed the whole column</li> <li>Isotope separation within the bands by “self-sharpening”: → Lighter isotope enriches at the rear edge (<math>{}^6\text{Li}</math> has generally a better affinity to the stationary phase), the heavier isotope at the front edge</li> <li>The single stage separation factors for the so far investigated chromatography systems do not reach those of the amalgamation processes</li> </ul>
Laser methods	<ul style="list-style-type: none"> <li>Makes use of the differences in the hyperfine electronic levels between the isotopes</li> <li>AVLIS (Atomic Vapour Laser Isotope Separation) <ul style="list-style-type: none"> <li>Selective ionization of <math>{}^6\text{Li}</math> by irradiation with the suitable wavelength (usually using dye laser)</li> <li>Separation by an electric field</li> </ul> </li> <li>General Electric has planned two laser facilities for Wilmington, North Carolina (for uranium enrichment): <ul style="list-style-type: none"> <li>a demonstrative isotopic laser facility called SILEX (Separation of Isotopes by Laser EXcitation)</li> <li>a commercially ready Hitachi laser facility</li> </ul> </li> <li>MAGNIS (Magnetically Activated and Guided Isotope Separation) <ul style="list-style-type: none"> <li>Selective optical pumping of the desired isotope and atoms → magnetic activation</li> <li>Separation of the activated isotope in a magnetic field</li> </ul> </li> </ul>

It was tried to compare these enrichment methods with the enrichment methods in fission (enrichment of uranium), but a serious comparison between the uranium enrichment methods and the lithium enrichment methods was actually quite difficult. The properties of the elements vary widely. Not only the atomic weight and the relative mass difference between the uranium and lithium isotopes are quite different, but also the natural abundance (92.4% of  ${}^7\text{Li}$ /7.6% of  ${}^6\text{Li}$  vs 99.3% of  ${}^{238}\text{U}$ /0.7% of  ${}^{235}\text{U}$ ). But the mayor aspect regarding the difference in enrichment probability is that for uranium a gaseous compound ( $\text{UF}_6$ ) exists at room temperature and for lithium not. Therefore, the most frequently used and conventional separation methods for uranium which are gaseous diffusion and gaseous centrifugation are not applicable for lithium enrichment.

For lithium isotope separation the COLEX process was found to be the most convenient one for the requirements of nuclear fusion and fission technology. The mayor advantages of COLEX over the other processes are that it is on the one hand suitable for reprocessing and on the other hand already approved in large scale lithium isotope separation. Therefore, it may be established faster than the others without much time and cost intensive research and development. This is important because the time frame to ITER and DEMO is quite short.

Furthermore, the facility investments and the running costs can be regarded as relatively low, since the facility setup is quite simple and the one-time investment in the quite large amounts of mercury



needed is due to the establishment of a recovery circle not accounting on the long run. However, since the application of mercury might harm the reputation of nuclear fusion technology, it might make sense to find a compromise or to establish an alternative on the long run. A compromise could be for instance to use the COLEX process primarily for the reprocessing of the breeding material and to run simultaneously a facility using cation complexing compounds, since the separation performance of these systems is at least comparable to the COLEX system and as quite simple extraction system the establishment would not make much effort. Further research and development in that direction is already advanced.

On the long run it might be a good idea to invest in the development of extraction systems using inorganic ion exchanger with good separation performances which are suitable for reprocessing.

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