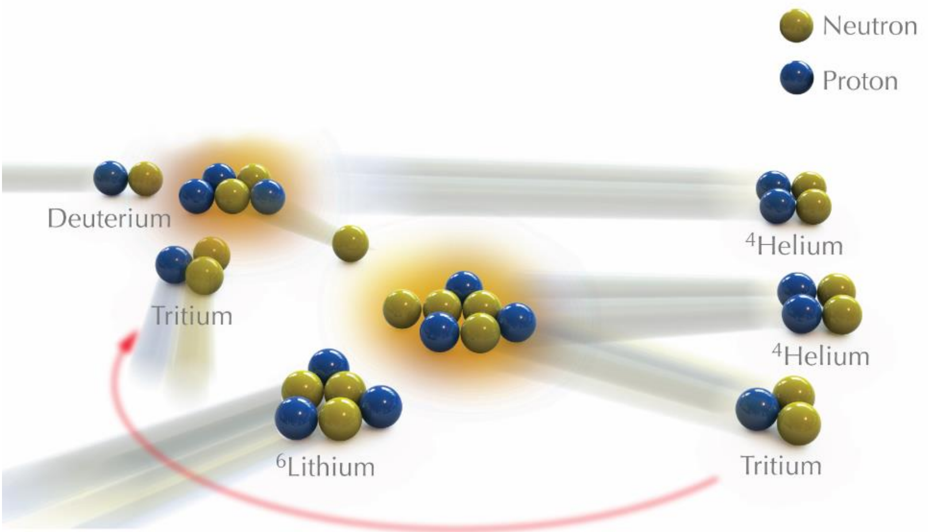
Lithium enrichment issues in the sustainable supply chain of future fusion reactors

Th. Giegerich*, **Chr. Day, R. Knitter, N. Osman**

*** *thomas.giegerich@kit.edu***

INSTITUTE FOR TECHNICAL PHYSICS (ITEP) – VACUUM DEPARTMENT



www.euro-fusion.org

Outline

- Introduction: Lithium enrichment needs
  - …for fusion
  - …for other applications
- Lithium enrichment requirements for tritium breeding
  - …in solid breeders
  - …in liquid breeders
- Lithium-6 market situation
- Available enrichment methods
- Identification of candidate processes for industrial-scale enrichment facilities
- Conclusion and Outlook

Lithium enrichment needs for fusion

- Tritium is not a primary fuel. It has to be bred out of lithium inside the breeding blankets:

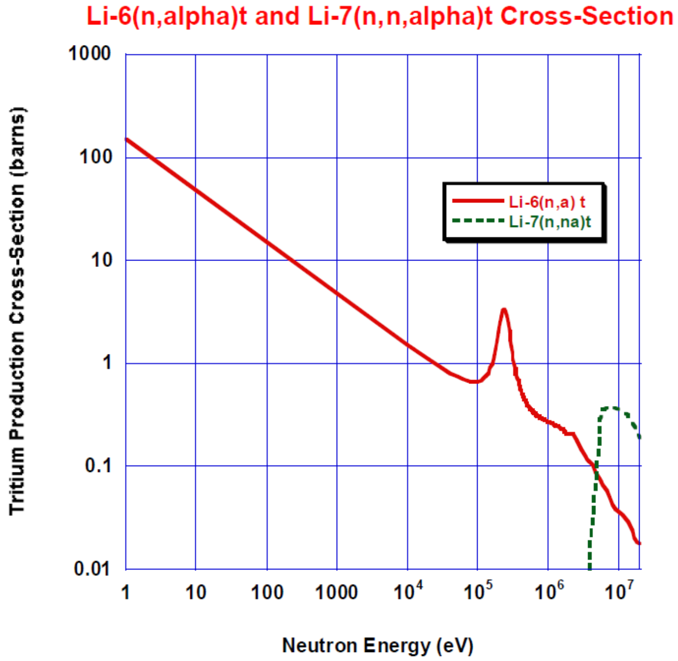
$$^{6}Li + n \rightarrow T + {}^{4}He + 4{,}8\ MeV$$
$$^{7}Li + n \rightarrow T + {}^{4}He + n' - 2{,}466\ MeV$$

- The cross section of the reaction using ^{6}Li is much higher (for thermal neutrons) than the reaction using ^{7}Li

  → It is much more favorable to use ^{6}Li in the blankets than ^{7}Li

- Natural lithium consists to 92.6% of ^{7}Li and to 7.4% of ^{6}Li

  → Enrichment required



Source: W. Biel, Tritium Breeding and blanket technology, Bad Honnef (2014).

Lithium enrichment needs for other applications

Applications in fission (^{7}Li)

- For acidity control in water moderated reactors (LiOH)
- Coolant in Gen IV molten salt reactors

→ No generation of tritium desired in these systems

Military applications (^{6}Li)

- ^{6}Li needed to boost nuclear weapons:

$$\begin{array}{l} {}^{6}Li + n \rightarrow {}^{4}He + T + 4{,}8\,MeV \\ D + T \rightarrow {}^{4}He + n + 17{,}6\,MeV \\ \hline \qquad 22{,}4\,MeV \end{array}$$

- ^{7}Li would consume neutrons and weakens this reaction by:

$${}^{7}Li + n \rightarrow {}^{8}Li + \gamma$$

$${}^{8}Li \xrightarrow[0{,}86s]{} {}^{8}Be + e^{-} + \tilde{\nu}_e$$

$${}^{8}Be \xrightarrow[10^{-15}s]{} 2\,{}^{4}He$$

→ Relatively pure ^{6}Li required

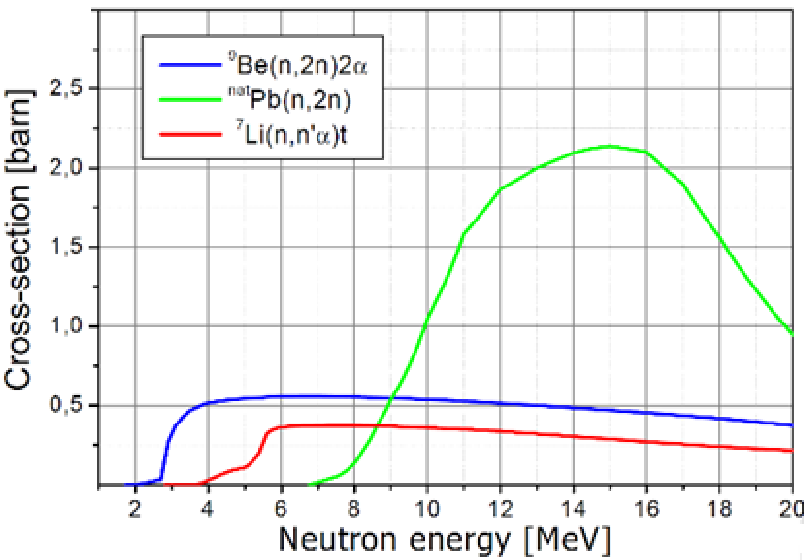
Lithium enrichment requirements for tritium breeding

- In solid breeders, beryllium is used as neutron multiplier
- The cross-section for the formation of thermal neutrons by $^{9}Be(n,2n)2\alpha$ is relatively low and in the same order as the $^{7}Li(n,n')t$ reaction
- A higher ^{7}Li content moderates neutrons and thus allows better breeding

→ Solid breeders typically use lower enriched lithium: ^{6}Li content 30…60%

- In liquid breeders, liquid lead is used as neutron multiplier
- The cross-section for the formation of thermal neutrons is very good
- ^{7}Li is thus not needed for neutron moderation

→ Liquid breeders typically use high enriched lithium: ^{6}Li content ~90%



Source: L.V. Boccaccini, Basic principles of the core design, Karlsruhe, 2015.

- For DEMO the required amount of 90% enriched lithium (per GW_{el}) is about 60 t

Lithium-6 market situation

- In the past in US, three processes have been used in the past for enrichment: COLEX (1955-1963), ELEX (1952-1958) and OREX (1955-1958).
- As far as we know, the ^{6}Li market is supplied up to now by the lithium produced in US by the COLEX process. No industrial-scale facility is existing today that could meet the requirements for fusion power plants.
- Commercial available ^{6}Li today is only sold in small amounts and for very high prices (400€ per 10g).
- To make fusion successful in future, an enrichment plant is needed with a capacity of several tons/day. This would also lead to decreasing prices.
- A number of enrichment methods have been investigated. An assessment is needed to choose a suitable method for future facilities.

Enrichment methods

- Chemical exchange systems (COLEX, OREX)
- Displacement chromatography
- Ion exchanger methods
- Intercalation methods
- Electrophoreses
- Electrolyses
- Electromigration
- Cation complexing methods
- Liquid ammonia methods
- Electromagnetic separation
- Laser based separation methods
- ...

Chemical exchange systems

- Basic principle: The isotopic mass difference causes a difference in free energy:

$$\Delta G°_{^6Li} \neq \Delta G°_{^7Li} \; and \; \Delta G°_{^6Li} > \Delta G°_{^7Li}$$

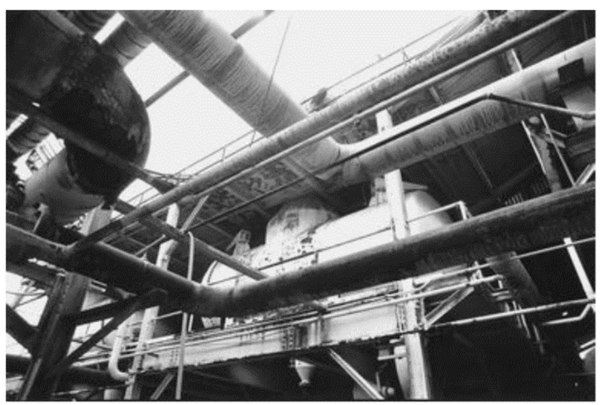
- A single stage separation performance (for a two phase system) at chemical equilibrium is given by the separation factor:

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

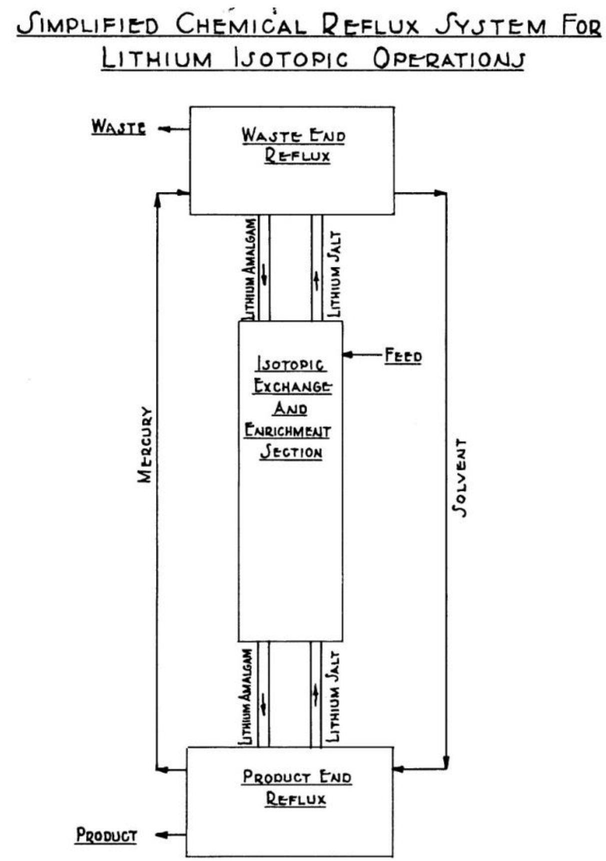
- In general, $\alpha_7^6 > 1.03$ is acceptable for ^6Li enrichment using chemical exchange methods
- If higher enrichment is needed, a cascaded arrangement of separation stages gives an overall separation factor α_{max} for *n* stages of α^n
- In US, the COLEX process was found to be the most efficient one with α_7^6 = 1.057 (at 0°C)

The COLEX process

- The COLEX (column exchange) process was used extensively in the Y12 plant in Oak Ridge, TN, US
- Working principle: Counter-current flow of a LiOH solution (OREX: LiCl in PDA) and lithium amalgam, ^{6}Li accumulates in the amalgam phase
- COLEX was used in the 50s and 60s and caused a strong environmental contamination with mercury (~11‘000 t used, ~330 t lost in waste streams)
- According DOE, the US has stopped stockpiling in 1963



Source: M. Ragheb, Isotopic Separation and Enrichment, Nuclear power engineering course (2015).

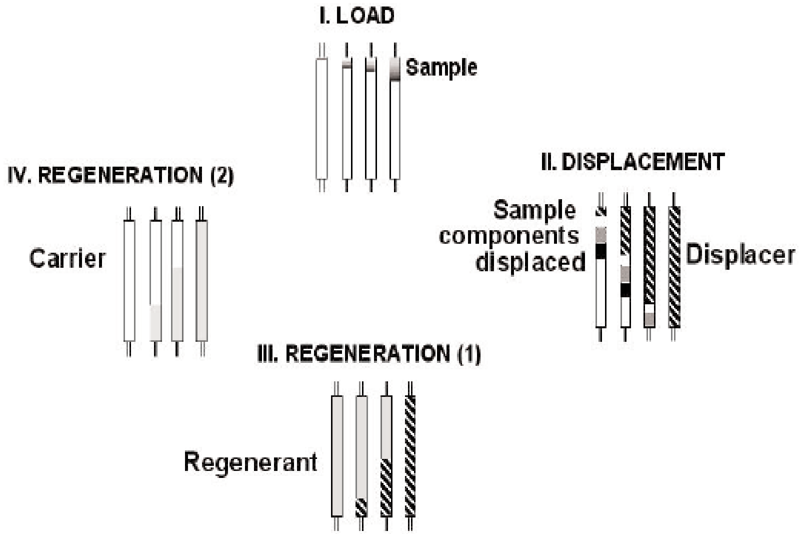


Source: Separation Science and Technology **20** (9-10) 633–651 (1985).

Available enrichment methods

Displacement chromatography

- Batch-process, based on a isotope specific distribution between a mobile phase (lithium solubilized in a liquid) and a stationary phase (e.g. a resin surface)
- Separation facility consists mainly of long columns packed with porous resin material (organic or inorganic)
- Lighter isotopes pass the columns more slowly (better affinity to stationary phase)
- Not very large separation factors per stage achievable
- Upscaling can easily be realized by columns with larger diameters
- A displacer/regenerant is needed
- Industrial scale systems would consist of chromatographic columns arranged in parallel → quasi-continuous operation (successfully demonstrated at lab scale)



Source: Huba Kalász, Journal of Chromatographic Science, Vol. 41, July 2003.

Available enrichment methods (2)

Ion exchanger methods

- Batch-process, based on solid materials (ion exchangers) that replaces ions with equally charged ions in liquids when getting in contact with them
- The exchanger materials usually have a higher affinity to ^{6}Li than to ^{7}Li
- Ion exchanger methods are often used in chromatographic separation systems where they form the resin material,
- Ion exchangers can be organic or inorganic

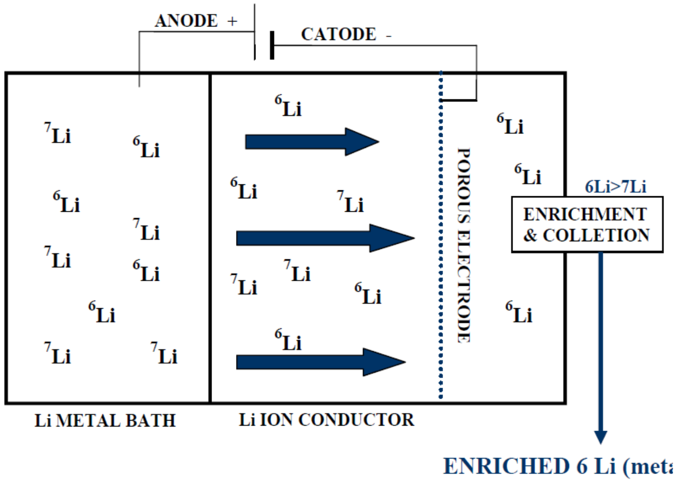
Intercalation methods

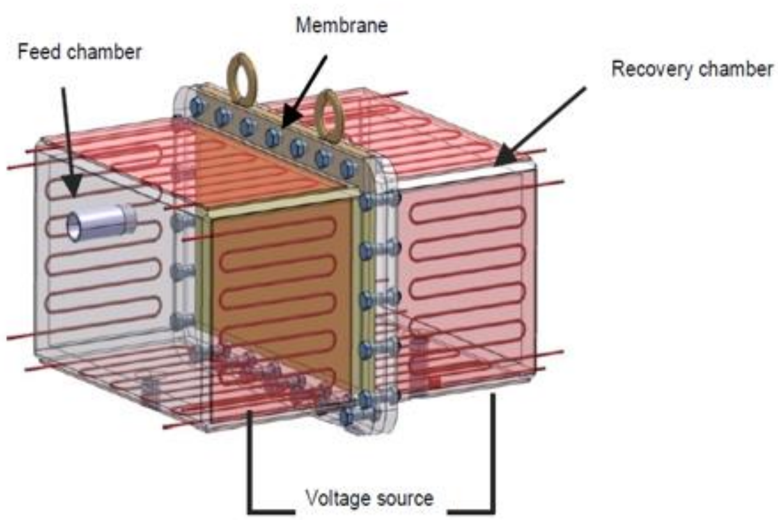
- Reversible insertion of a molecule or ion into a material with layered structures
- Several intercalation materials exist (e.g. graphite) that usually have a greater affinity to insert ^{6}Li than ^{7}Li
- Enrichment takes place in Li ion batteries
- Future perspective: Removal of enriched Li when recycling Li ion batteries?

Available enrichment methods (3)

<u>Electrophoresis</u>

- Motion of lithium ions relative to a viscose separating fluid (conductor) driven by a uniform electric field
- Isotope separation occurs due to the different travel velocities of the heavier ^{7}Li and the lighter ^{6}Li through the conducting fluid
- *Electrophoresis in liquid bath* could be used for large scale separation: it applies the so-called Li electrolyte-compatible Solid State Lithium Ion Super Conductor (SSLISC) as separating fluid and uses liquid metallic lithium as feed material





Source: A.I. Barrado et al., FED 86 (2011) 2662–2665.

Available enrichment methods (4)

Electrolysis

- A lithium salt solution is electrolyzed using a mercury cathode in a counter-current flow
- ^{6}Li ions are preferentially uptaken by mercury forming a lithium amalgam
- A large scale enrichment facility has been tested in Oak Ridge National Laboratory (ELEX process)
- Process is today used in Russia's Novosibirsk Chemical Concentration Plant (NCCP) for the production of pure ^{7}Li for nuclear fission applications
- Other cathodes are also possible (e.g. Zinc-, Graphite-, Tin-, Manganese cathodes)

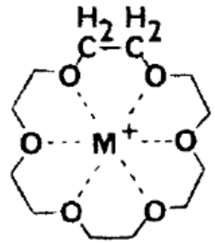
Electromigration

- A DC current is applied between a cathode and a liquid lithium (molten lithium or molten lithium salt) anode
- ^{6}Li usually accumulates on the hollow cathode (e.g. graphite- or stainless steel)

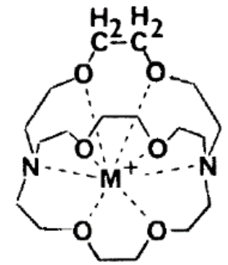
Available enrichment methods (5)

Cation complexing methods

- Basically lithium salts solubilized in organic solvents (crown ether or cryptands)
- Complexation due to interaction between the positive charged ion and the dipolar bounded donor atoms (in general oxygen)
- The ^{6}Li ion is preferably bounded within the nanocavity of the complexing agent
- High single stage separation factors achievable



18-crown-6



2,2,2-cryptate

source: Separation Science and Technology **20** (9-10) 633–651 (1985).

Liquid ammonia methods

- Below 230 K, a lithium - liquid ammonia solution forms two phases with different densities and a large difference in metal ion concertation
- ^{6}Li is slightly enriched in the concentrated phase
- Only relatively low enrichment factors achievable
- Counter-current processing for technical-scale facilities is suggested but not experimentally investigated yet

Available enrichment methods (6)

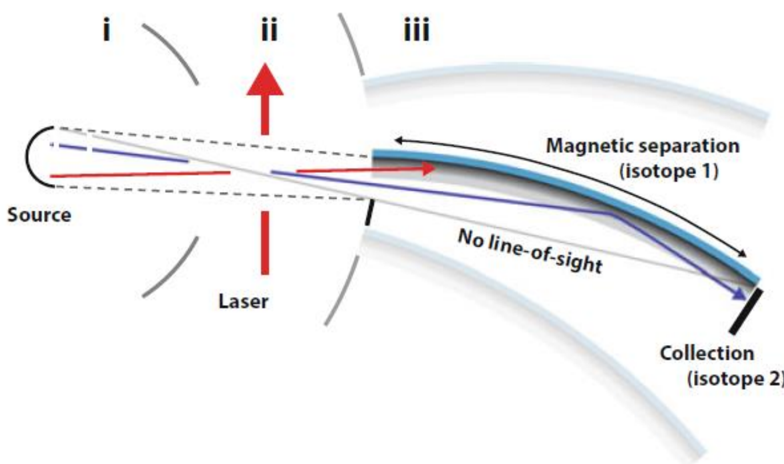
Karlsruhe Institute of Technology

Electromagnetic separation

- Evaporation of the lithium metal feed (vaporization of elemental material in a source for producing an atomic flux)
- Electric or magnetic activation
- Magnetic separation by using a planar magnetic field gradient for filtering the atoms

Laser based separation methods

- Makes use of the differences in the hyperfine electronic levels between the isotopes
- Selective ionization of ^{6}Li by irradiation with the suitable wavelength (usually using dye laser)
- Magnetic separation



Source: T.R. Mazur, Magnetically Activated and Guided Isotope Separation, 1st ed., Springer International Publishing, Cham, 2016.

Assessment of enrichment methods

- An assessment is needed
  - to find out which of the available methods will meet the fusion requirements
  - to avoid expensive development efforts with unknown results
- Therefore, a multi-stage approach has been done (*see next slides*):
  - **Definition of assessment criteria**
  - **Pairwise comparison**
  - **Calculation of the quality rating**
  - **Technical-economic examination** → Results
- 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
- Detailed description of the process: *VDI Guideline 2225-3, Technical-economic examination, German Engineering Society (VDI), 1998*

Definition of assessment criteria

For the assessment, the following criteria shall be used:

- **Good scalability** of the process (weighting from pairwise comparison: 5)

A production rate of ~ton/day must be easily achievable

- **Low complexity** of the process (weighting: 2)

Simple and robust processes are desirable for industrial facilities

- **Use for reprocessing** of the blanket material (weighting: 12)

Material from activated/tritiated blankets must be reprocessed

- **No production of toxic waste** (weighting: 9)

No toxic or radioactive residuals of the process must be produced (→ waste problem)

- **No use of toxic operating fluids** (weighting: 2)

If possible, toxic operating fluids should be avoided

- **Well proven** process (weighting: 5)

Avoid expensive development efforts with unknown results

- **Good energy efficiency** of the process (weighting: 1)

To be economically attractive, the enrichment process must not consume a large fraction of the electricity produced by the fusion power plant

- **Low facility investment** (weighting: 10)

Required to keep costs for electricity in fusion low

Calculation of a quality rating

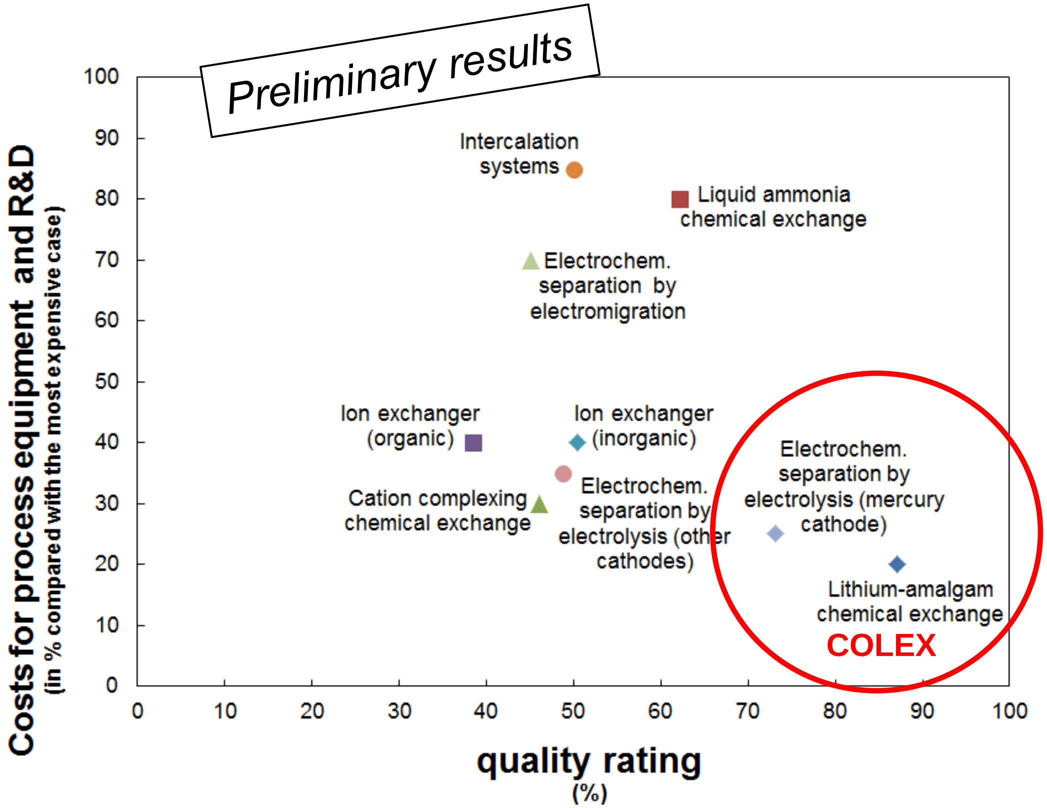
- The quality rating expresses (in %) how good a method (shown in the columns) meets the different criteria (shown in the rows)
- Values (p) between 0 and 4 express how good the method meets the criterion

	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)		Electrophoresis		Electromigration	
		p	p x g	p	p x g	p	p x g	P	p x g	p	p	p x g	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	15	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	0	3	8	4	8	4	8	2	4	4	8	4	88	3	6	2	4
Usability for reprocessing	**12**	4	48	4	14	0	0	0	0	0	0	4	48	4	36	3	36	2	24	3	36
No production of toxic waste	**9**	4	36	1	30	0	0	0	0	3	27	3	27	4	18	2	18	1	9	1	9
No use of toxic operation fluids	**2**	1	2	1	3	1	2	0	0	0	0	1	2	1	2	1	2	1	2	1	2
Well proven process	**5**	4	20	0	1	2	10	1	5	1	5	1	5	4	5	1	5	4	20	1	5
Good energy efficiency of the process	**11**	3	33	2	0	3	33	3	33	3	33	1	11	0	0	0	0	0	0	0	0
Low facility investments	**10**	3	30	3	15	3	30	2	20	2	20	1	10	3	20	2	20	2	20	1	10
Sum:	**56**	**197**		**139**		**103**		**86**		**113**		**112**		**164**		**109,0**		**101**		**86**	
Quality rating W:		**87,9**		**62,1**		**46,0**		**38,4**		**50,4**		**50,0**		**73,2**		**48,7**		**45,1**		**38,4**	

	Displacement Chromatography (inorganic resin)		Displacement Chromatography (organic resin)		Electromagnetic separation		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	3	15	3	15	1	5	1	5
Low complexity of the process	4	8	4	8	1	2	1	2
Usability for reprocessing	3	36	0	0	4	48	4	48
No production of toxic waste	3	27	1	9	4	36	4	36
No use of toxic operation fluids	1	2	4	8	4	8	4	8
Well proven process	2	10	2	10	4	20	2	10
Good energy efficiency of the process	4	44	4	44	0	0	1	11
Low facility investments	3	30	3	30	0	0	0	0
Sum:	**172**		**124**		**119**		**120**	
Quality rating W:	**76,8**		**55,4**		**53,1**		**53,6**	

Results of the assessment

- In a technical-economic examination, it was found that the 'classical' COLEX process has the highest quality value at a low development effort
- In general, mercury based methods (chemical exchange, electrolysis) show highest quality values
- Other methods have been tested in lab-scale or even technical scale but never reached high values
- Major reasons:
  - Bad scalability and/or high complexity
  - Use for reprocessing of the (tritiated) waste from the blankets is not possible



Results of the assessment (2)

- During the assessment, interesting synergies between fusion and fission have been found
  - In view of the enrichment methods (e.g. R&D done for laser based methods)
  - In view of isotope purity requirements (^{6}Li vs. ^{7}Li)
- It is planned to have a closer look on this topic in future to evaluate the results in view of different requirements for fusion and fission
- A proposal for such a project is currently underway on EU level

Conclusion and Outlook

- Lithium has to be enriched in ^{6}Li from 7.4% towards 30…90% for tritium breeding applications in fusion
- Unavailability of Li enrichment facilities that could meet DEMO requirements is a threat to the success of fusion
- Enrichment methods used in the past (cold war) relied on mercury based methods (chemical exchange, electrolysis)
- In future it is proposed to follow two development paths in order to reduce unavailability risks of ^{6}Li:
  - Develop Hg based methods further (proven technique, reliable and simple but needs improvement in view of environmental aspects)
  - Spend additional R&D efforts to investigate alternative methods