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

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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:
  \[ ^{6}\text{Li} + n \rightarrow T + ^{4}\text{He} + 4.8\text{ MeV} \]
  \[ ^{7}\text{Li} + n \rightarrow T + ^{4}\text{He} + n' - 2.466\text{ MeV} \]

- The cross section of the reaction using \(^{6}\text{Li}\) is much higher (for thermal neutrons) than the reaction using \(^{7}\text{Li}\)
  → It is much more favorable to use \(^{6}\text{Li}\) in the blankets than \(^{7}\text{Li}\)

- Natural lithium consists to 92.6% of \(^{7}\text{Li}\) and to 7.4% of \(^{6}\text{Li}\)
  → 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:
  \[
  \begin{align*}
  ^6\text{Li} + n &\rightarrow ^4\text{He} + T + 4.8 \text{ MeV} \\
  D + T &\rightarrow ^4\text{He} + n + 17.6 \text{ MeV} \\
  &\rightarrow 22.4 \text{ MeV}
  \end{align*}
  \]
- \(^7\)Li would consume neutrons and weakens this reaction by:
  \[
  ^7\text{Li} + n \rightarrow ^8\text{Li} + \gamma
  \]
  \[
  ^8\text{Li} \xrightarrow[0.86\text{s}]{0.86}\ ^8\text{Be} + e^- + \bar{\nu}_e
  \]
  \[
  ^8\text{Be} \xrightarrow[10^{-15}\text{s}]{10^{-15}} 2\ ^4\text{He}
  \]
→ 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 $^9\text{Be}(n,2n)2\alpha$ is relatively low and in the same order as the $^7\text{Li}(n,n')t$ reaction.
- A higher $^7\text{Li}$ content moderates neutrons and thus allows better breeding.
  → Solid breeders typically use lower enriched lithium: $^6\text{Li}$ 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.
- $^7\text{Li}$ is thus not needed for neutron moderation.
  → Liquid breeders typically use high enriched lithium: $^6\text{Li}$ content ~90%.

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

Source: L.V. Boccaccini, Basic principles of the core design, Karlsruhe, 2015.
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 $^6\text{Li}$ 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 $^6\text{Li}$ 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
- ...

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

\[ \Delta G^{\circ}_{\text{Li}^6} \neq \Delta G^{\circ}_{\text{Li}^7} \text{ and } \Delta G^{\circ}_{\text{Li}^6} > \Delta G^{\circ}_{\text{Li}^7} \]

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

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

In general, \( \alpha^6 > 1.03 \) is acceptable for \( ^6\text{Li} \) enrichment using chemical exchange methods.

If higher enrichment is needed, a cascaded arrangement of separation stages gives an overall separation factor \( \alpha_{\text{max}} \) for \( n \) stages of \( \alpha^n \).

In US, the COLEX process was found to be the most efficient one with \( \alpha^6 = 1.057 \) (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 ($\sim 11'000$ t used, $\sim 330$ t lost in waste streams)

- According DOE, the US has stopped stockpiling in 1963
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)

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)

Electrophoresis

- 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 $^7\text{Li}$ and the lighter $^6\text{Li}$ 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

Available enrichment methods (4)

**Electrolysis**
- A lithium salt solution is electrolyzed using a mercury cathode in a counter-current flow
- $^6\text{Li}$ 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 $^7\text{Li}$ 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
- $^6\text{Li}$ 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 $^6\text{Li}$ ion is preferably bounded within the nanocavity of the complexing agent
- High single stage separation factors achievable

Liquid ammonia methods
- Below 230 K, a lithium - liquid ammonia solution forms two phases with different densities and a large difference in metal ion concentration
- $^6\text{Li}$ 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)

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

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.

<table>
<thead>
<tr>
<th>Weighting</th>
<th>Lithium amalgam chemical exchange</th>
<th>Liquid ammonia chemical exchange</th>
<th>Cation Complexing chemical exchange</th>
<th>Ion exchanger (organic)</th>
<th>Ion exchanger (inorganic)</th>
<th>Intercalation systems</th>
<th>Electrolysis (mercury cathode)</th>
<th>Electrolysis (other cathode)</th>
<th>Electrophoresis</th>
<th>Electromigration</th>
<th>Separation by laser methods</th>
</tr>
</thead>
<tbody>
<tr>
<td>( p )</td>
<td>( p \times q )</td>
<td>( p \times q )</td>
<td>( p \times q )</td>
<td>( p \times q )</td>
<td>( p \times q )</td>
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<td>( p \times q )</td>
<td>( p \times q )</td>
<td>( p \times q )</td>
<td>( p \times q )</td>
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<tr>
<td>Good scalability of the process</td>
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<td>4</td>
<td>20</td>
<td>4</td>
<td>20</td>
<td>1</td>
<td>5</td>
<td>4</td>
<td>20</td>
<td>4</td>
<td>20</td>
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<tr>
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<td>4</td>
<td>8</td>
<td>4</td>
<td>8</td>
<td>2</td>
<td>4</td>
<td>8</td>
<td>4</td>
<td>8</td>
<td>3</td>
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<tr>
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<td>4</td>
<td>48</td>
<td>14</td>
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<td>0</td>
<td>0</td>
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<tr>
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<td>3</td>
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<tr>
<td>No use of toxic operation fluids</td>
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<td>2</td>
<td>1</td>
<td>3</td>
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<td>2</td>
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<tr>
<td>Well proven process</td>
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<td>4</td>
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<td>0</td>
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<td>2</td>
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<tr>
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<td>30</td>
<td>3</td>
<td>30</td>
<td>2</td>
<td>20</td>
<td>2</td>
<td>20</td>
<td>2</td>
<td>20</td>
</tr>
</tbody>
</table>

**Sum:**

|                       | 56 | 197 | 139 | 103 | 86 | 113 | 112 | 164 | 109 | 010 | 86 | 172 | 124 | 119 | 120 |

**Quality rating** \( W \):

|                        | 87,9 | 62,1 | 46,0 | 38,4 | 50,4 | 50,0 | 73,2 | 48,7 | 45,1 | 38,4 | 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.

Preliminary results:

![Graph showing quality rating vs. costs for process equipment and R&D (in % compared with the most expensive case).]
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 ($^6\text{Li}$ vs. $^7\text{Li}$)
- 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 $^6\text{Li}$ 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 $^6\text{Li}$:
  - 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.