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Actinides/lanthanides separation in molten salt media: application to the liquid fuel reprocessing of molten salt fast reactor (MSFR)

Davide Rodrigues, Sylvie Delpech
CNRS/IN2P3 Univ. Paris Sud, IPN d’Orsay, 15 Rue Georges Clemenceau 91406 Orsay
I. Research framework

2001 - International Forum focused on research and development of nuclear reactor stimulated by the U.S Department of Energy (DOE) [1]

GEN IV Forum established concrete targets for focusing research and development efforts:
- Sustainability (1), safety and reliability (2), economics (3) and proliferation resistance (4)

GIF concept selection:
- Gas-Cooled Fast Reactor (GFR)
- Very-High-Temperature Reactor (VHTR)
- Lead-Cooled Fast Reactor (LFR)
- Sodium-Cooled Fast Reactor (SFR)
- Supercritical-Water Reactor (SCWR)
- Molten Salt Reactor (MSR)

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- **Sustainability (1), safety and reliability (2), economics (3) and proliferation resistance (4)**

GIF concept selection:
- **Molten Salt Reactor (MSR)**

It’s the only one concept to use a liquid fuel, to operate with Th/U fuel cycle and to have an integrated reprocessing

I. Research framework

Molten Salt Reactor (MSR) was first developed by Oak Ridge National Laboratory in the 50’s

- Aircraft Reactor Experiment (ARE) in 1954
- Molten Salt Reactor Experiment (MSRE) from 1965 to 1969
  - Graphite moderator (5 years of lifetime)
  - Thermal Neutron Spectrum
- Molten Salt Breeder Reactor (MSBR)
  - High flow of fuel reprocessing (4000 liters per day)

Inside of MSRE wall protection (8.5MWth)

2. Molten Salt Reactor history

NaF-ZrF$_4$-UF$_4$

LiF-BeF$_2$-ZrF$_4$-UF$_4$  71-16-12-1 mol%

LiF-BeF$_2$-ThF$_4$-UF$_4$  72-16-11-1 mol%

MSRE Reactor (8.5MWth)
3. Molten Salt Fast Reactor concept

Molten Salt Fast Reactor (MSFR) in 2006

- Liquid fuel
- Cycle $^{232}$Th / $^{233}$U:

$$n + ^{232}\text{Th} \rightarrow ^{233}\text{Th} \rightarrow ^{233}\text{Pa} \rightarrow ^{233}\text{U}$$

$t_{1/2}$ Th (233) = 22 Minutes  
$t_{1/2}$ Pa (233) = 27 Days

- Fast spectrum: no graphite moderator
- Operating temperature: 650-750 °C
- Fertile blanket (LiF-ThF$_4$): fissile nuclei production
- Low flow of fuel reprocessing (40 liters per day)

Reprocessing objectives:
- Uranium recovery (used to launch the MSFR)
- Waste management (actinide burner)
- Lanthanides removal which have a low solubility in the liquid fuel and also neutron poison

Reference concept of Forum GEN IV in 2010

LPSC design [2]  
LiF-ThF$_4$-(UF$_4$/UF$_3$)  77-19-4 mol%
I. Research framework

4. Fuel reprocessing

Reaction balance of the reprocessing:

\[ 2 \text{LnF}_3 + 3 \text{H}_2\text{O} \rightarrow \text{Ln}_2\text{O}_3 + 6 \text{HF} \]
II. Reductive extraction


The chemical reaction for the reductive extraction:

\[ MF_z^{(MS)} + z R^{(LM)} \rightarrow z RF^{(MS)} + M^{(LM)} \]

The reducing agent (R) selected, is lithium

The nature of the solvent metal (LM) chosen is bismuth

The particularity of the reprocessing scheme proposed for MSFR treatment is to use the same technique to extract actinides in the first step (2.A) and lanthanides in the second one (2.B)

Actinides extraction must to be selective and with a high efficiency

Lanthanides extraction must to be only with a high efficiency
II. Reductive extraction

2. Analytical description

Extraction efficiency:

\[
\mu(M/Li) = \frac{1}{1 + 10^{\lambda(M/Li)}}
\]

Solvation in the molten salt:

\[
\log \gamma_{M/Li} = \frac{\gamma(MF_2)}{\gamma(LiF)^2}
\]

\[
\lambda(M/Li) = \frac{Z}{m} (E^{\circ}_M - E^{\circ}_Li) - \log \gamma_{M/Li} + \log \frac{\gamma(M)}{\gamma(Li)} + z \log \frac{\chi(LiF)}{\chi(Li)} + \log \frac{n(ML)}{n(MS)}
\]

Database established by extrapolation of literature results [3]

<table>
<thead>
<tr>
<th>Element</th>
<th>La</th>
<th>Ce</th>
<th>Nd</th>
<th>Sm</th>
<th>Gd</th>
<th>Tb</th>
<th>Dy</th>
<th>Er</th>
<th>Th</th>
<th>Pa</th>
<th>U</th>
<th>Pu</th>
<th>Am</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a_M)</td>
<td>7.63</td>
<td>7.86</td>
<td>7.87</td>
<td>3.74</td>
<td>8.52</td>
<td>9.62</td>
<td>8.26</td>
<td>9.06</td>
<td>10.74</td>
<td>6.05</td>
<td>9.87</td>
<td>6.82</td>
<td>6.93</td>
</tr>
<tr>
<td>Log (\Gamma_{M/Li}) for (x(LiF) = 77.5) mol %</td>
<td>-0.51</td>
<td>-0.28</td>
<td>-0.27</td>
<td>-1.69</td>
<td>0.38</td>
<td>1.48</td>
<td>0.12</td>
<td>0.92</td>
<td>-0.11</td>
<td>-4.8</td>
<td>1.73</td>
<td>-1.32</td>
<td>-1.21</td>
</tr>
<tr>
<td>Log (\Gamma_{M/Li}) for (x(LiF) = 77.5) mol %</td>
<td>-0.43</td>
<td>-0.20</td>
<td>-0.19</td>
<td>-1.63</td>
<td>0.46</td>
<td>1.57</td>
<td>0.20</td>
<td>1.01</td>
<td>0</td>
<td>-4.69</td>
<td>1.82</td>
<td>-1.24</td>
<td>-1.13</td>
</tr>
<tr>
<td>Log (\gamma(MF_2))</td>
<td>-11.77</td>
<td>-11.03</td>
<td>-10.78</td>
<td>-11.73</td>
<td>-10.06</td>
<td>-9.59</td>
<td>-9.62</td>
<td>-8.73</td>
<td>-7.18</td>
<td>-6.13</td>
<td>-3.93</td>
<td>-8.08</td>
<td>-8.08</td>
</tr>
<tr>
<td>(E^{\circ}_M(V/F_2))</td>
<td>-5.12</td>
<td>-5.08</td>
<td>-5.06</td>
<td>-5.34</td>
<td>-5.11</td>
<td>-5.14</td>
<td>-5.09</td>
<td>-5.09</td>
<td>-4.76</td>
<td>-4.36</td>
<td>-4.54</td>
<td>-4.66</td>
<td>-4.69</td>
</tr>
</tbody>
</table>

Two kinds of parameters:
- Constant (thermodynamical and solvation)
- Adjustable

Adjustable parameters of the process:
- Mole fraction of lithium in bismuth liquid pool
- Volume ratio between metallic phase and salt phase

II. Reductive extraction

3. Extraction efficiency calculations

Influence of the mole fraction of the reducing agent in Bi:

It’s possible to perform the two extraction steps (actinides and lanthanides) by changing the concentration of Li in Bi in the two steps.

For the steps 2.A (actinides extraction):
\[ x(Li)_{Bi} = 0.1 \% \]

For the steps 2.B (lanthanides extraction):
\[ x(Li)_{Bi} = 10 \% \]

Selective and quantitative extraction of actinides (2.A):
\[ x(Li)_{Bi} < 0.001 \]

Quantitative extraction of lanthanides (2.B):
\[ x(Li)_{Bi} > 0.1 \]

Ratio of liquid phases mole number:
\[ \frac{n(MS)}{n(ML)} = 1 \]

MS = LiF-ThF₄ (77.5-22.5 mol%)  
LM = Bi - Li  
T = 873 K  
\[ n(MS)/n(LM) = 1 \]
III. Bi-Li pool production

1. Cyclic voltammetry

Electroactivity domain of the salt with W and Bi working electrode:

Production of the metallic phase Bi-Li in LiF-LiCl

- Electroactivity domain of the salt
- Coulometry
- ICP-AES analysis of the bismuth

Coulometry current set at -0.5 A
Coulometry current set at -0.5 A during 8 hours and 20 minutes:

Theoretical calculations:

\[ Q = n \times z \times F \]
\[ = I \times t \]
\[ Q = 15000 \, C \]

<table>
<thead>
<tr>
<th>Theo. (% mol)</th>
<th>ICP analysis (% mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi</td>
<td>83.1</td>
</tr>
<tr>
<td>Li</td>
<td>16.9</td>
</tr>
</tbody>
</table>

Faraday efficiency
73.6 %

- Electroactivity domain of the salt
- Coulometry
- ICP-AES analysis of the bismuth
### III. Bi-Li pool production

#### 3. Composition salt influence

Different bismuth-lithium pool production in various molten salt:

<table>
<thead>
<tr>
<th>Molten salt</th>
<th>ICP-AES analysis (% mol)</th>
<th>Faraday efficiency (%)</th>
<th>E or I set</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiF-LiCl + ThF$_4$*</td>
<td>Lithium 1.33 / Thorium 0.15</td>
<td>93.5</td>
<td>-1.6 V/Ref.</td>
</tr>
<tr>
<td>LiF-LiCl**</td>
<td>Lithium 12.4 / 9.4 / 8.6</td>
<td>73.6 / 93.8 / 86.4</td>
<td>-0.5 / -0.4 / -0.4 A</td>
</tr>
<tr>
<td>LiF-ThF$_4$</td>
<td>Lithium 0.17 / Thorium 0.04</td>
<td>93.3</td>
<td>-1.2 V/Ref.</td>
</tr>
<tr>
<td>LiCl-KCl</td>
<td>Lithium 17.0 / Potassium 1.8</td>
<td>98.4</td>
<td>-0.4 A</td>
</tr>
<tr>
<td>LiCl-CaCl$_2$</td>
<td>Lithium 1.63 / Calcium 0.55</td>
<td>93.7</td>
<td>-0.5 A</td>
</tr>
<tr>
<td>LiF-CaF$_2$ [6]</td>
<td>Lithium 6.1 / Calcium 5.2</td>
<td>95.0</td>
<td>-0.08 A</td>
</tr>
</tbody>
</table>

Even if the reduction potential of an element occurs at a more cathodic potential compare to lithium reduction on a bismuth liquid electrode, this element will be reduced simultaneously.

The molten salt selected is **LiF-LiCl** for the bismuth pool production.

- Electroactivity domain of the salt
- Coulometry
- ICP-AES analysis of the bismuth

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* 0.060 mol/kg of ThF$_4$
** 3 experiments

V. Reductive extraction experiment

1. Bi-Li / LiF-ThF$_4$ + UF$_4$ + NdF$_3$

Contacting Bi-Li pool with the salt phase LiF-ThF$_4$ at 600°C in two steps:

\[
\log \frac{n(MS)}{n(ML)} = -0.084 \quad \log \chi(Li)_{Bi} = -0.91
\]

Experimental device:
Glassy carbon crucible

4 Li$_{Bi}$ + UF$_4$ → 4 LiF + U$_{Bi}$

Step 1: addition of UF$_4$ to simulate the actinide
Step 2: addition of NdF$_3$ to simulate the lanthanide

3 Li$_{Bi}$ + NdF$_3$ → 3 LiF + Nd$_{Bi}$

Extraction efficiency:

\[\mu (Nd/Li) = 7.5 \%\]
\[\mu (U/Li) = 15.0 \%\]
V. Reductive extraction experiment

2. Bi-Li / LiF-ThF$_4$ + UF$_4$ + NdF$_3$

Contacting Bi-Li pool with the salt phase LiF-ThF$_4$ at 600°C for simulate four stages:

\[ \log \frac{n(\text{MS})}{n(\text{ML})} = 0.696 \quad \log \chi(\text{Li})_{\text{Bi}} = -1.02 \]

4 Li$_{\text{Bi}}$ + UF$_4$ $\rightarrow$ 4 LiF + U$_{\text{Bi}}$

3 Li$_{\text{Bi}}$ + NdF$_3$ $\rightarrow$ 3 LiF + Nd$_{\text{Bi}}$

Increase of extraction efficiency:

\[ \mu_{\text{tot}} (\text{Nd}/\text{Li}) = 18.8 \% \]

\[ \mu_{\text{tot}} (\text{U}/\text{Li}) = 43.7 \% \]
Extraction efficiency of U and Nd with 1 and 4 stages:

\[
\mu(M/Li) = \frac{1}{1 + 10^{\lambda(M/Li)}}
\]

\[
\lambda(M/Li) = \frac{Z}{m} (E^o_{Li} - E^o_M) - \log l_{M/Li} + \log \frac{\gamma(M)}{\gamma(Li)^z} + z\log \frac{x(Li)}{x(Li)} + \log \frac{n(MS)}{n(ML)}
\]

Analytical description

<table>
<thead>
<tr>
<th></th>
<th>U</th>
<th>Nd</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\mu) (%)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 stage (Theo.)*</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>1 stage (Exp.)</td>
<td>15.0</td>
<td>7.5</td>
</tr>
<tr>
<td>Stages number for 95% efficiency (blue number)</td>
<td>19</td>
<td>39</td>
</tr>
<tr>
<td>4 stages (Theo.) (blue number)</td>
<td>47.8</td>
<td>26.8</td>
</tr>
<tr>
<td>4 stages (Exp.)</td>
<td>43.7</td>
<td>18.8</td>
</tr>
</tbody>
</table>

* with bibliographic database and extractions condition

\[n_{ext} = n_{init} \times [1 - (1 - \mu(M))^{nbs}]\]

X Determination of activity coefficient of M in the fuel salt

No data in LiF-ThF\textsubscript{4} salt
1. Speciation of thorium

Speciation of thorium by adding lithium fluoride in LiCl-KCl:

- Working electrode (W)
  - $S = 0.50 \text{ cm}^2$
- Scan rate 100 mV/s

Measuring the solvation effect on the equilibrium potential of Th(IV)/Th system

Open circuit potential evolution of a Th working electrode prepared by electrodeposition

The equilibrium potential measured corresponds to the potential of Th(IV)/Th redox system
VI. Activity coefficient of M in the fuel salt: thorium case

2. Mathematical analysis [8]

Simulation of the experimental section:

Nernst relation:

$$\log \alpha_{Th,F} = \frac{nF}{2.3RT} \cdot (E_i - E)$$

Potential for each addition of LiF

Initial potential ($x(LiF) = 0$)

$$\alpha_{Th,F} = 1 + \sum_{i=1}^{i} \beta_i \cdot [F^-]^i_{free}$$

Complexation reaction and equilibrium constant:

$$ThF_4 + iF^- \rightarrow ThF_{(4+i)}^i$$

$$\beta_i = \frac{([ThF_{(4+i)}^i])]}{([ThF_4]) \cdot ([F^-])^i}$$

$$[F^-]_{tot} = [F^-]_{free} + [ThF_4] \cdot \sum_{i=1}^{i} i\beta_i \cdot [F^-]^i_{free}$$

The equilibrium constants $\beta_i$ can be performed by fitting the variation of $(\alpha_{M,F})$ as a function of the total concentration of fluoride ions [7]

The knowledge of $\beta_i$ leads to calculate $(\alpha_{M,F})$ and $[F^-]_{free}$ in fuel salt

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[7] F. Séon, "Réactions d'échange de l'ion oxyde dans l'eutectique LiCl-KCl à 470° C: application à la chloruration sélective d'oxydes métailliques en milieu chlorures fondus", Thèse de doctorat, Université de Pierre et Marie Curie, France (1981)

VI. Coefficient activity of M in the fuel salt

3. Extraction efficiency

The knowledge of βi leads to calculate \((\alpha_{M,F})\) and \([F^-]_{free}\) in fuel salt

Experimental estimation results of activity coefficient \((\gamma(MF_2))\) in fuel salt composition LiF-ThF₄ (77.5-22.5 mol%)

<table>
<thead>
<tr>
<th>M</th>
<th>(\log \Gamma_{M/Li})</th>
<th>(\log \gamma(MF_2)_{MS})</th>
<th>(\mu_{Theo}(M/Li)^*)</th>
<th>(\mu_{Exp}(M/Li))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Th (IV)</td>
<td>-5.03</td>
<td>-5.21</td>
<td>8.5</td>
<td>8.0</td>
</tr>
<tr>
<td>U (IV)</td>
<td>-3.85</td>
<td>-4.03</td>
<td>98.2</td>
<td>15.0</td>
</tr>
<tr>
<td>Nd (III)</td>
<td>-3.50</td>
<td>-3.64</td>
<td>20.5</td>
<td>7.5</td>
</tr>
</tbody>
</table>

\(\*\gamma(\text{LiF})_{MS} = 0.90\)

Theoretical extraction efficiency decrease and closer from experimental efficiency

\[U_{Bi} + 3UF_4 \rightarrow 4UF_3\]
VII. Conclusion and perspectives

Bi-Li pool production:

- Great control of the lithium mole fraction in Bi
- Use of LiF-LiCl necessary to produce pure bismuth-lithium pool

Perspective:

- Stability of the bismuth-lithium pool in LiF-ThF₄ will be studied

Extraction experiments:

- Realization of extraction of U and Nd but also extraction of Th in 1 stage and 4 stages
- Low value of the extraction efficiency

Development of a methodology for activity coefficient calculation:

- Calculation of activity coefficient for Th, U and Nd in the fuel salt

Perspective:

- Calculation of $\gamma_{(LiF)_{MS}}$

The low value requires a lot of stages to attempt a high efficiency:

Reprocessing by reductive extraction?

Another way:

Reprocessing by electrolysis?
Thank you for your attention
Funding and acknowledgement