Status and Results of Research on PYROSMANI Coordinated Project

Research Institute of Atomic Reactors, Dimitrovgrad
NRC “Kurchatov Institute”, Moscow

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PYROSMANI
PYROchemical processes Study for Minor Actinides recycling in molten salts

Project objective –

to evaluate the feasibility of Minor Actinides recycling by pyro separation in molten salts

To prepare data base concerned the development of pyropartitioning flow sheets, including Chemistry Instrumentation and Monitoring for Molten Salts Streams, for innovative types of fuel in order to improve the sustainability of nuclear power
PYROSMANI
PYROchemical processes Study for Minor Actinides recycling in molten salts

Project duration: 2014 - 2016

Leading institution: JSC “SCC RIAR” (Dimitrovgrad)

Participating institutions: NRC “Kurchatov Institute” (Moscow), IHTE RAS and UFU-UPI (Ekaterinburg)

EU partner: FP7 SACSESS project (DM 2)

CooA between CEA and RIAR signed in March 2014
PYROSMANI: KI activity in 2014

- Measurement of kinematic viscosity and density for molten LiF-AlF₃ and LiF-BeF₂ salt mixtures
- Liquid - liquid extraction of samarium and europium fluorides for LiF-BeF₂ / Bi system
- Salt corrosion and chemistry control
Viscosity and Density

- $\text{85LiF-15 AlF}_3$
- $\text{73LiF-27BeF}_2$
- $(\text{73LiF-27BeF}_2)+\text{1CeF}_3$

Viscosity $10^6$, m$^2$/s

Temperature (C)

Kinematic viscosity $10^6$, m$^2$/s

Temperature (C)

Density (g/cc)

$\beta - \text{NaF}$ (g cm$^{-3}$ K$^{-1}$)

T (K)

$\text{73LiF-27BeF}_2$

$\text{LiF-NaF-BeF}_2$

BeF$_2$ (mol%)
Relative extractabilities of elements are determined by measuring equilibrium distribution coefficients in the two phase system: \( MF_n(melt) + nLi(Bi) \rightleftharpoons M(Bi) + nLiF(melt) \). Distribution coefficient for \( M \) is defined by: \( D = \frac{X_M}{X_{MF_n}} \). Ratio of distribution coefficients (\( \Theta = D_1 / D_2 \)) features the separation of the two components between phases.

\[
\begin{align*}
\text{Lg} D(\text{Nd}) &= 3\text{Lg} D(\text{Li}) + 6.11 \\
\text{Lg} D(\text{La}) &= 3\text{Lg} D(\text{Li}) + 5.91 \\
\end{align*}
\]

73LiF-27BeF₂ at 600°C

LiCl at 650°C
Materials for processing unit

• For areas of processing unit where there is direct contact with the liquid metal (e.g. bismuth) traditional structural materials such as Ni- and Fe- based alloys are not suitable because of (1) increased solubility in the liquid metal or (2) subjecting the mass transfer at exposure system with a temperature gradient.

• Materials showed good compatibility with liquid metals in the limited number of tests include graphite, and refractory metals such as tungsten, rhenium, molybdenum and tantalum. Except tantalum, these materials are difficult to manufacture and compound. All rapidly oxidize in air at temperatures of atmospheric processes and require protection.
There are several methods to manage protective coatings:

- The introduction of non-metallic impurities into the structure of the container materials, including the introduction of liquid metal atoms into the steel (the formation of complex compounds $\text{Me}_x\text{LM}_y\text{O}_z$, where Me-solid metal, LM-liquid metal, O–oxygen and $x, y, z$- stoichiometric ratios)
- Introducing metallic impurities into the structure of container material to form an intermetallic, followed by oxidation and without it
- The precipitation of the compounds formed in the melt and others

$\text{Al}_5\text{FeNi}$ or $\text{Al}_5\text{Fe}_2$. 

*10X15H9C3B1 steel after exposure in Al at 1073 K during 6 hrs*
### Corrosion Systems for studies

<table>
<thead>
<tr>
<th>Solvent</th>
<th>LiF-BeF₂</th>
<th>LiF-AlF₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fuel addition</td>
<td>UF₄, ThF₄</td>
<td></td>
</tr>
<tr>
<td>Liquid metal</td>
<td>Bi-Li</td>
<td>Bi-Mg-Li</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Al-Cu</td>
</tr>
<tr>
<td>Temperature C</td>
<td>650</td>
<td>800</td>
</tr>
<tr>
<td>Exposure time, hrs</td>
<td>100 - 1000</td>
<td></td>
</tr>
<tr>
<td>Container material</td>
<td>Graphite</td>
<td>Mo, W, Ta, Re</td>
</tr>
</tbody>
</table>

### Graph

**E° [U(IV) → U(III)]** = -0.32V
<table>
<thead>
<tr>
<th>[U(IV)]/[U(III)]</th>
<th>HN80MT-VI, enlargement ×160</th>
<th>HN80MTY, enlargement ×160</th>
</tr>
</thead>
<tbody>
<tr>
<td>500 without loading at 735°C</td>
<td>K = 3360 pc×μm/cm; l = 166μm</td>
<td>K = 1660 pc×μm/cm; l = 68μm</td>
</tr>
<tr>
<td>500 25MPa 740°C</td>
<td>K = 8300 pc×μm/cm; l = 180μm</td>
<td>K = 1850 pc×μm/cm; l = 80μm</td>
</tr>
<tr>
<td>100 25MPa 740°C</td>
<td>no</td>
<td>no</td>
</tr>
</tbody>
</table>
Materials for processing unit

- In the short term, from an engineering point of view the use of graphite block pyrochemical processing will require the least amount of research.
- Also, the use of graphite as the main structural material block pyrochemical reprocessing require the development of a class of compounds of special graphite - graphite and graphite - metal.
- Results for material compatibility and flowsheet development unit reprocessing received soon will determine the degree of follow-up for each of these materials.
PYROSMANI: RIAR activity in 2014

- PrF$_3$ and AmF$_n$ solubility measurements in Li, Na, K/F eutectics by three different methods:
  - Isothermic saturation
  - Reflectance spectroscopy
  - Electrochemical method of limiting deposition current
The method of isothermal saturation

1– cell, 2-pellet’s supply tube
3 - crucible made of Nickel
4,8,11,12 - Thermocouples
5,10 - Argon supply; 6 – Furnac
Reflectance spectroscopy

beam inlet - 1, collimator - 2, mirror - 3, divider (splitter) - 4, molten salt - 5, window - 6, collimator - 7, channel optical fiber - 8, shutter - 9, reference - 10, catcher - 11, water-cooled case - 12, heater - 13, container - 14, mirror - 15, Pt-Rh
Electrochemical methods

2 – carbon auxiliary electrode;  
3 – Mo working electrode;  
5 – Pt quazi reference electrode;  
6 – thermocouple;  
14 – glass graphite crucible;  
15 – melt

Cyclic voltammograms

LiF-NaF-KF+PrF₃

Pulse-differential voltammetry

Normal-differential voltammetry

LiF-NaF-KF+AmF₃ at 873 K
## Individual Solubility in FLiNaK Eutectics

### PrF<sub>3</sub>, mol. %

<table>
<thead>
<tr>
<th>Temperature, K</th>
<th>Isothermal saturation</th>
<th>Electrochemical methods</th>
<th>Reflectance spectroscopy</th>
</tr>
</thead>
<tbody>
<tr>
<td>773</td>
<td>(8,87)</td>
<td>10,1±1,0</td>
<td>13,3±1,3</td>
</tr>
<tr>
<td>823</td>
<td>(13,35)</td>
<td>13,7±1,0</td>
<td>17,7±1,7</td>
</tr>
<tr>
<td>873</td>
<td>19,0±1,1</td>
<td>18,9±1,0</td>
<td>22,2±2,2</td>
</tr>
<tr>
<td>923</td>
<td>26,6±1,4</td>
<td>(34,2)</td>
<td>(26,7)</td>
</tr>
<tr>
<td>973</td>
<td>36,2±1,8</td>
<td>(40,8)</td>
<td>(31,2)</td>
</tr>
<tr>
<td>1023</td>
<td>45,3±2,3</td>
<td>(48,3)</td>
<td>(35,6)</td>
</tr>
</tbody>
</table>

Equation: \( \log S = 3,8731 - 2261,2/T \)

### AmF<sub>3</sub>, mol. %

<table>
<thead>
<tr>
<th>Temperature, K</th>
<th>Isothermal saturation</th>
<th>Electrochemical methods</th>
<th>Reflectance spectroscopy</th>
</tr>
</thead>
<tbody>
<tr>
<td>773</td>
<td>(12,5)</td>
<td>(8,3)</td>
<td>12,9±1,1</td>
</tr>
<tr>
<td>823</td>
<td>18,0±1,8</td>
<td>12,8±1,0</td>
<td>17,9±1,8</td>
</tr>
<tr>
<td>873</td>
<td>31,7±3,1</td>
<td>18,8±1,0</td>
<td>22,9±2,3</td>
</tr>
<tr>
<td>923</td>
<td>34,0±3,4</td>
<td>(26,6)</td>
<td>(27,9)</td>
</tr>
<tr>
<td>973</td>
<td>43,4±4,3</td>
<td>(36,3)</td>
<td>(33,0)</td>
</tr>
<tr>
<td>1023</td>
<td>(55,5)</td>
<td>(48,0)</td>
<td>(38,0)</td>
</tr>
</tbody>
</table>

Equation: \( \log S = 3,75 - 2051,6/T \)

In brackets are the data obtained as a result of their calculation and the approximation by the equations.
PrF$_3$ Solubility in FLiNaK Eutectics

![Graph showing solubility vs. temperature](image-url)
AmF$_3$ Solubility in FLiNaK Eutectics
Individual Solubility in FLiNaK Eutectics

Isothermal saturation

Solubility, mol.

Temperature, K

UF4
ThF4
PuF3
NdF3
PrF3
CeF3
AmF3

RIAR Radiochemical Division
Solubility and Viscosity in FLiNaK Eutectics

Isothermal saturation

<table>
<thead>
<tr>
<th>T, °C</th>
<th>Individual Solubility, mol.%</th>
<th>Joint Solubility, mol. %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PuF₃</td>
<td>UF₄</td>
</tr>
<tr>
<td>550</td>
<td>6.1±0.6</td>
<td>15.3±0.8</td>
</tr>
<tr>
<td>600</td>
<td>11.1±1.1</td>
<td>24.6±1.2</td>
</tr>
<tr>
<td>650</td>
<td>21.3±2.1</td>
<td>34.8±1.7</td>
</tr>
<tr>
<td>700</td>
<td>32.8±3.3</td>
<td>44.7±2.2</td>
</tr>
<tr>
<td>750</td>
<td>21.0±1.1</td>
<td>19.0±1.0</td>
</tr>
<tr>
<td>800</td>
<td>22.5±1.2</td>
<td>20.0±1.1</td>
</tr>
</tbody>
</table>
Key Papers’ 2014-2015


- **Zagnit’ko A and Ignat’ev V (2015)** The equilibrium distribution of samarium and europium between the molten fluoride salts and liquid bismuth, *Russian Journal of Physical Chemistry*, to be published