ESTIMATION OF THE DEVELOPMENT
POSSIBILITY OF THE ABC/ATW FUEL CYCLE
BASED ON LiF-BeF₂ FUEL SALT

Part II

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1. SOLUBILITY OF FLUORIDS IN FLUORIDE MELTS
— INVESTIGATED AS BASIC SOLVENTS AND FUEL.

Chemical processes occurring in fuel salt in the presence of dissolved fission products compounds are one of the main problems of the fuel composition with the ABC/ATW facility operation as well as they determine physico-chemical properties of the salt components during its reprocessing.

At present there is no any full critical analysis of experimental data on mutual solubility of molten fluorids. Neither is such analysis with reference to fluoride melts used in nuclear power engineering and technology. Special information on this problem can be found in monographs /1-4/ or in the form of journal articles /5-8/.

The major aim of this chapter was generalization of data on solubility and equilibrium states of fission product and actinide fluorides in fluoride salt melts-solvents and fuel composition melts based on LiF-BeF₂ mixture which was proposed as fuel basis for ABC/ATW facility.

1.1. COMPOSITIONS OF FLUORIDE MELT-SOLVENTS

Simultaneous presence of several components in the molten salt can to a certain degree affect their structure and equilibrium properties. One of the possible properties of equilibrium systems is solubility depending on the composition and temperature. For two-component systems, e.g. LiF-BeF₂, its equilibrium property is depicted as a phase diagram (diagram of solubility) (see Fig.1.1).

While using the molten Li and Be fluorides as a liquid fuel for the ABC/ATB facility it is necessary to know the solubility in their molten mixtures of fuel elements (Th, U and Pu) and also of fission products and minor actinides. In spite of the fact that individual fluorides have high melting temperatures, their mixtures in case of a particular components content are characterized by lower melting temperatures. The ranges of such temperatures are indicated on the melting curve-liquidus as its fracture towards low temperatures. To provide a wide working temperature range the greatest interest is laid on equilibrium behaviour of salt mixture components just in these temperature points.
Hypothetic compositions of molten fluoride solvents for fuel corresponding to eutectic compositions pursuant to the differential-thermal analysis data are presented in Tab.1.1 /9-11/.

The phase diagram of LiF-BeF$_2$ mixture has an eutectic point at 350 C and LiF content of 47 mol.%. The composition for the eutectic are presumably characterized by presence of the solid phase of BeF$_2$ from the chemical compound Li$_2$BeF$_4$ and homogenous molten salt according to the differential-thermal analysis. With this fixed composition of the mixture above the eutectic point temperature there will be a homogenous phase of melt.
Hypothetic compositions of molten fluoride solvents.

<table>
<thead>
<tr>
<th>N. n.</th>
<th>Composition of molten fluoride mixture, mol.%</th>
<th>Mixture eutectic point, °C</th>
<th>Investigated temperature range</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>LiF - BeF₂ (47 - 53)</td>
<td>350</td>
<td>500 - 800</td>
</tr>
<tr>
<td>2.</td>
<td>LiF - BeF₂ (66 - 34)</td>
<td>458</td>
<td>500 - 800</td>
</tr>
<tr>
<td>3.</td>
<td>NaF - BeF₂ (56 - 44)</td>
<td>360</td>
<td></td>
</tr>
<tr>
<td>4.</td>
<td>LiF - NaF (60 - 40)</td>
<td>625</td>
<td></td>
</tr>
<tr>
<td>5.</td>
<td>NaF - MgF₂ (77.4-22.6)</td>
<td>824</td>
<td></td>
</tr>
<tr>
<td>6.</td>
<td>LiF - ZrF₄ (50 - 50)</td>
<td>510</td>
<td>600 - 900</td>
</tr>
<tr>
<td>7.</td>
<td>LiF - NaF - ZrF₄ (24 - 41 - 35)</td>
<td>530</td>
<td></td>
</tr>
<tr>
<td>8.</td>
<td>LiF - BeF₂ - ZrF₄ (48 - 50 - 2)</td>
<td>355</td>
<td></td>
</tr>
<tr>
<td>9.</td>
<td>LiF - NaF - KF (46.5 - 42 - 11.5)</td>
<td>492</td>
<td></td>
</tr>
<tr>
<td>10.</td>
<td>LiF - MgF₂ - NaF (47 - 10 - 43)</td>
<td>630</td>
<td></td>
</tr>
<tr>
<td>11.</td>
<td>LiF - MgF₂ - NaF (59 - 29 - 12)</td>
<td>684</td>
<td></td>
</tr>
</tbody>
</table>
For the salt mixture LiF-BeF$_2$ containing 68 mol.% LiF, the melt will have the crystallization temperature 430°C. This example shows that molten fluorides are characterized by high mutual solubility which will have its own minimal melting temperature depending on the mixture composition. In case of the composition 99 mol.% LiF and 1 mol.% BeF$_2$, the melting temperature of salt mixture will be practically equal to the melting temperature of pure LiF.

Similar shape of phase diagrams with the liquidus line fracture in the eutectic composition point is also typical for other double fluoride mixtures given in Tab.1.1. However, the data on phase diagrams of double systems cannot predict which composition will correspond to one or another temperature range, e.g. for the triple system. For instance, the data on double eutectic system LiF-NaF and LiF-ZrF$_4$ cannot precisely predict which melting temperature will be typical for the composition formed by mixing of such systems. Nor can be predicted the melting temperature of a mixture, e.g. LiF-NaF if some amount of zirconium fluoride is added to it.

Prognostication of properties of multicomponent systems containing salts of five or more chemical elements is extremely complicated. Therefore, behaviour of fission product fluorides in molten fuel salt-solvents can be hardly predicted from the phase diagrams of simpler salt mixtures. State of such systems and their composition is likely to be modelled experimentally in an easier manner.

Th-232 (ThF$_4$, 10-12 mol %) is usually used in breeder-reactors for fuel reproduction. Since the ABC/ATW facility is designed to burn actinides, then to provide physico-chemical properties of fuel salt of the required composition the given amount of thorium can be replaced for zirconium fluoride with the optimal composition of fuel salt LiF-BeF$_2$-ZrF$_4$ (65-29-5 mol %) (with about 1 mol % PuF$_3$ added as fuel into the system). Such salt mixture melts at 430°C and is quite satisfactory in terms of its physical properties as a melt-solvent. Fig.1.2 presents a phase diagram of such a system.

While choosing the melt-solvent composition for a fuel component it is required to take into account that use of lithium salts leads to tritium formation. The problem of tritium radiation hazard can be excluded when LiF is replaced by NaF.
Absence of lithium in the fuel salt practically completely excludes tritium formation in the blanket and can provide large radiation "purity" of the ABC/ATW facility. Such replacement changes the thermal-physical properties of composition to a low degree, but increases the melting temperature of salt mixture, and only this phenomenon can complicate further reprocessing of the fuel composition.

Thus, the final choice of the melt-solvent composition of the fuel salt with due account of its operating properties and following reprocessing should be made taking into consideration the tritium "problem".

1.2. ACTINIDE FLUORIDES SOLUBILITY IN MOLTEN MIXTURES ON LiF-BeF₂ BASE

To determine the duration of one operating cycle for the ABC/ATW facility one should know the concentration of fission products in the melt as well as effect of their accumulation on nuclear-physical characteristics of the reactor operation. Probably, during operation of the molten salt reactors (MSR) and ABC/ATW facility with continuous fuel reprocessing there are no problems with separation of fluorides included and formed in the fuel salt when concentrations of fission product fluorides are considerably lower.
than their solubilities. When operating the MSR and ABC/ATW facility without continuous reprocessing there occurs considerable accumulation of fission products in the fuel salt depending on periodicity of its replacement /1/.

The major advantage of MSR is bound up with the relatively high solubility of U and Th compounds in light metal fluorides melts at the melting temperature about 500°C. However, high concentration of U and Th in the salt melt (up to 5-10 mol.%) leads to increase of the melting temperature of salt composition (at the expense of high concentration of heavy elements in the molten salt). Thus, if the melting temperature of LiF-BeF$_2$ eutectics makes up 360°C, 10 mol.% ThF$_4$ added to it increases the melting temperature of the triple system up to 500°C. Therefore for explanation of the crystallization (solubility) curves by the phase diagrams constitutes one of the widely used methods of solubility for interpreting the melts structure.

The data on phase diagrams of the most important fuel and salt compositions are presented in figs.1.3.-1.6. Tab.1.2. gives the compositions of used and proposed fuel compositions for proposed facilities.

In the available literature there are no direct data on studying the solubility of salts UF$_4$, ThF$_4$ in double and triple LiF-BeF$_2$ based mixtures by physico-chemical methods. So it can be assumed that most data on composition and usage of the fuel salts are based on the data on phase diagrams of such systems.

The solubility limit of the salt fuel components in the fluoride mixtures for the preset temperature range can be estimated from the phase diagrams of fluoride mixtures and physico-chemical analysis of plutonium fluorides solubility in the molten salt LiF-BeF$_2$ (66.6-33.4 mol.%), Fig.1.7 /14/.

Proceeding from the obtained data on PuF$_3$ solubility in mixtures LiF-BeF$_2$ (Fig.1.7) and LiF-ThF$_4$ (Fig.1.8.) there has been made an effort to get empiric correlations for calculating the PuF$_3$ solubility in various molten salts at the particular temperature depending on the salt composition.
Fig. 1.3. The system LiF-BeF$_2$-ThF$_4$

Fig. 1.4. The system LiF-BeF$_2$-UF$_4$
Fig. 1.5. The systems NaF-BeF$_2$-ThF$_4$ and NaF-BeF$_2$-UF$_4$

Fig. 1.6. The system LiF-ThF$_4$-UF$_4$. 
Table 1.2

The composition of used and proposed fuel compositions for proposed facilities.

<table>
<thead>
<tr>
<th>Components</th>
<th>APE</th>
<th>MSR-EC</th>
<th>USR</th>
<th>MSGR</th>
<th>DMSR</th>
<th>AMSR</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiF</td>
<td>71</td>
<td>71,6</td>
<td>48</td>
<td>74</td>
<td>64</td>
<td></td>
</tr>
<tr>
<td>BeF₂</td>
<td>27,9</td>
<td>16,0</td>
<td>50</td>
<td>16,5</td>
<td>18</td>
<td></td>
</tr>
<tr>
<td>ThF₄</td>
<td>1,0</td>
<td>12,0</td>
<td></td>
<td>8,25</td>
<td>17,8-</td>
<td></td>
</tr>
<tr>
<td>²³³UF₄</td>
<td>0,1</td>
<td>0,4</td>
<td></td>
<td></td>
<td>0,2-</td>
<td></td>
</tr>
<tr>
<td>ZrF₄</td>
<td>41,2</td>
<td></td>
<td>2</td>
<td></td>
<td>-0,8</td>
<td></td>
</tr>
<tr>
<td>UF₄</td>
<td>5,8</td>
<td></td>
<td></td>
<td>2,2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaF</td>
<td>53,0</td>
<td></td>
<td></td>
<td>0,2</td>
<td></td>
<td></td>
</tr>
</tbody>
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Continuation Table 1.2.

<table>
<thead>
<tr>
<th>Components</th>
<th>MSBR-1</th>
<th>MSBR-2</th>
<th>MOSEL-1</th>
<th>MOSEL-2</th>
<th>MSRE</th>
<th>MSBR</th>
</tr>
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<tbody>
<tr>
<td>LiF</td>
<td>68,75</td>
<td>71,0</td>
<td>71,0</td>
<td>71,0</td>
<td>65,0</td>
<td>71,8</td>
</tr>
<tr>
<td>BeF₂</td>
<td>31,0</td>
<td>20,0</td>
<td>0,0</td>
<td>13,3</td>
<td>29,1</td>
<td>16,0</td>
</tr>
<tr>
<td>ThF₄</td>
<td>0,0</td>
<td>8,75</td>
<td>24,0</td>
<td>13,0</td>
<td>0,9</td>
<td>12,0</td>
</tr>
<tr>
<td>²³³UF₄</td>
<td>0,25</td>
<td>5,0</td>
<td>5,0</td>
<td>2,7</td>
<td>5,0</td>
<td>0,2</td>
</tr>
<tr>
<td>ZrF₄</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>UF₄</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Tab. 1.3. presents the PuF$_3$ solubility in salts at 600 and 700°C calculated by the equation:

$$\log S \text{ (mole \% PuF}_3) = 2.19 - 1.97 \times 10^3/T,$$

(where $S$ is solubility)

and Fig. 1.9 shows the correlation comparison of the calculated and experimentally defined solubility of PuF$_3$. Comparison of solubility for PuF$_3$ in LiF-BeF$_2$-ThF$_4$ (75-5-20 mol.%) with that in LiF-ThF$_4$ (75-25 mol.%) at 600 and 700°C demonstrates that it increases from 2.88 and 3.68 mol.% up to 4.75 and 5.92 mol.%, respectively. In one of the earliest Barton's works /14/ was obtained the less value of PuF$_3$ solubility in the melt LiF-BeF$_2$ which made up 1.33 mol.% (for 28.7 mol.% BeF$_2$) and 0.65 mol.% (for 37.0 mol.% BeF$_2$) at 650°C and depending on the content of beryllium fluoride in the melt.
Table 1.3

Solubility of PuF₃ in LiF-BeF₂-ThF₄ melts as expressed by log solubility

- (mol. %) = A₂ + B₂/T[14]

<table>
<thead>
<tr>
<th>LiF mol.%</th>
<th>BeF₂ mol.%</th>
<th>ThF₄ mol.%</th>
<th>A₂</th>
<th>B₂ *10⁻³</th>
<th>Solubility at 600°C (mol. %)</th>
<th>Solubility at 700°C (mol. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>* 51.7</td>
<td>48.3</td>
<td>0.0</td>
<td>2.77±0.40</td>
<td>2.65±0.34</td>
<td>0.55</td>
<td>1.12</td>
</tr>
<tr>
<td>* 71.3</td>
<td>28.7</td>
<td>0.0</td>
<td>3.24±1.05</td>
<td>2.13±0.92</td>
<td>0.79</td>
<td>1.40</td>
</tr>
<tr>
<td>* 68.1</td>
<td>31.9</td>
<td>0.0</td>
<td>3.39±0.32</td>
<td>3.21±0.27</td>
<td>0.52</td>
<td>1.24</td>
</tr>
<tr>
<td>* 63.0</td>
<td>37.0</td>
<td>0.0</td>
<td>3.14±0.14</td>
<td>3.07±0.13</td>
<td>0.42</td>
<td>0.97</td>
</tr>
<tr>
<td>* 56.3</td>
<td>43.7</td>
<td>0.0</td>
<td>3.00±0.22</td>
<td>2.94±0.19</td>
<td>0.43</td>
<td>0.95</td>
</tr>
<tr>
<td>** 66.6</td>
<td>33.4</td>
<td>0.0</td>
<td>3.22±0.20</td>
<td>3.09±0.17</td>
<td>0.48</td>
<td>1.11</td>
</tr>
<tr>
<td>74.0</td>
<td>22.1</td>
<td>3.9</td>
<td>3.55±0.14</td>
<td>2.97±0.14</td>
<td>1.39</td>
<td>3.11</td>
</tr>
<tr>
<td>76.9</td>
<td>17.1</td>
<td>6.0</td>
<td>3.49±0.23</td>
<td>2.82±0.21</td>
<td>1.81</td>
<td>3.88</td>
</tr>
<tr>
<td>16.7</td>
<td>8.0</td>
<td>3.80±0.05</td>
<td>3.13±0.04</td>
<td>1.64</td>
<td>3.82</td>
<td></td>
</tr>
<tr>
<td>75.3</td>
<td>20.5</td>
<td>11.3</td>
<td>2.98±0.06</td>
<td>2.52±0.06</td>
<td>1.25</td>
<td>2.47</td>
</tr>
<tr>
<td>68.2</td>
<td>16.0</td>
<td>12.0</td>
<td>3.01±0.06</td>
<td>2.41±0.05</td>
<td>1.78</td>
<td>3.42</td>
</tr>
<tr>
<td>*** 72.0</td>
<td>16.2</td>
<td>12.2</td>
<td>2.95±0.07</td>
<td>2.46±0.07</td>
<td>1.36</td>
<td>2.65</td>
</tr>
<tr>
<td>71.5</td>
<td>15.5</td>
<td>13.2</td>
<td>2.62±0.07</td>
<td>2.15±0.06</td>
<td>1.43</td>
<td>2.56</td>
</tr>
<tr>
<td>71.3</td>
<td>14.0</td>
<td>16.0</td>
<td>2.56±0.11</td>
<td>2.06±0.10</td>
<td>1.58</td>
<td>2.76</td>
</tr>
<tr>
<td>70.0</td>
<td>5.0</td>
<td>20.0</td>
<td>2.57±0.14</td>
<td>1.64±0.14</td>
<td>2.88</td>
<td>4.75</td>
</tr>
<tr>
<td>75.0</td>
<td>0.0</td>
<td>20.0</td>
<td>2.62±0.19</td>
<td>1.78±0.19</td>
<td>3.84</td>
<td>6.22</td>
</tr>
<tr>
<td>80.0</td>
<td>0.0</td>
<td>25.0</td>
<td>2.58±0.05</td>
<td>1.76±0.05</td>
<td>3.68</td>
<td>5.92</td>
</tr>
<tr>
<td>75.0</td>
<td>0.0</td>
<td>30.0</td>
<td>2.84±0.07</td>
<td>1.99±0.07</td>
<td>3.60</td>
<td>6.17</td>
</tr>
<tr>
<td>70.0</td>
<td>0.0</td>
<td>35.0</td>
<td>3.01±0.08</td>
<td>2.20±0.08</td>
<td>3.09</td>
<td>5.60</td>
</tr>
<tr>
<td>65.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Calculated from data of C.J.Barton, J.Phy. Cem., 64, 306 (1960)
*** C.E.Bamberger at al, ORNL - 4622, 91 (1971).

Table 1.4

Composition of MSCR salts and the calculated PuF₃ solubility

<table>
<thead>
<tr>
<th>Salt composition mol. %</th>
<th>A(s)</th>
<th>B*10⁻³</th>
<th>Sol. at 500°C mol. %</th>
<th>C* mol. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiF</td>
<td>BeF₂</td>
<td>ThF₄</td>
<td>LiF</td>
<td>BeF₂</td>
</tr>
<tr>
<td>64</td>
<td>32</td>
<td>4</td>
<td>2.09</td>
<td>1.98</td>
</tr>
<tr>
<td>64</td>
<td>30</td>
<td>6</td>
<td>1.97</td>
<td>1.83</td>
</tr>
<tr>
<td>65</td>
<td>27</td>
<td>8</td>
<td>2.19</td>
<td>1.97</td>
</tr>
<tr>
<td>67</td>
<td>23</td>
<td>10</td>
<td>2.56</td>
<td>2.21</td>
</tr>
</tbody>
</table>

* - Calculated data from the data Ref.[14]
For the MSCR reactor, operating with LiF-BeF$_2$-ThF$_3$ molten compositions, the maximum concentration of PuF$_3$ in the salt is 0.2 mol.% (see Tab.1.4). At the same time for criticity of the MSBR reactor it must be dissolved about 0.3 mol.% fissinable materials, e.g. as UF$_4$ (or about 1.0 mol.% PuF$_3$) /2/ (see Tab.1.5).

As follows from the presented data for the MSCR and MSBR reactors the Pu content in the molten salt at 0.5 mol.% is quite achievable. The same concentration of Pu in fuel salt will, probably, be at the ABC/ATW facility (see Fig.1.10).

In order to determine duration of the working cycle for the reactor-converter it is necessary to know some peculiarities of fuel elements behaviour with increase of the fission products concentration. The same question arises when choosing dry methods of reprocessing the MSR fuel.

In ref./1/ it was shown that for the following melts: LiF-BeF$_2$-ThF$_3$-UF$_4$ (72;16;12 and X mol.%, respectively, where X = 0.5-1), increase of the fission products content (CeF$_3$) up to 5 mol.% does not cause yielding of solid phases of uranium and thorium fluorides which provides possibility of the reactor operation without replacing the salt for about 10 years.

<table>
<thead>
<tr>
<th>Salt composition mol. %</th>
<th>A(a)</th>
<th>-B*10$^{-3}$(a)</th>
<th>Sbl at 600$^\circ$ C(b)</th>
<th>C (c) mol. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiF</td>
<td>BeF$_2$</td>
<td>ThF$_3$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>72</td>
<td>20</td>
<td>8</td>
<td>3,23</td>
<td>0,51</td>
</tr>
<tr>
<td>72</td>
<td>18</td>
<td>10</td>
<td>3,13</td>
<td>0,53</td>
</tr>
</tbody>
</table>

**Table 1.5**

Composition of MSBR salts and the calculated PuF$_3$ solubility[14].

For the MSCR reactor, operating with LiF-BeF$_2$-ThF$_4$ molten compositions, the maximum concentration of PuF$_3$ in the salt is 0.2 mol.% (see Tab.1.4). At the same time for criticity of the MSBR reactor it must be dissolved about 0.3 mol.% fissinable materials, e.g. as UF$_4$ (or about 1.0 mol.% PuF$_3$) /2/ (see Tab.1.5).

As follows from the presented data for the MSCR and MSBR reactors the Pu content in the molten salt at 0.5 mol.% is quite achievable. The same concentration of Pu in fuel salt will, probably, be at the ABC/ATW facility (see Fig.1.10).

In order to determine duration of the working cycle for the reactor-converter it is necessary to know some peculiarities of fuel elements behaviour with increase of the fission products concentration. The same question arises when choosing dry methods of reprocessing the MSR fuel.

In ref./1/ it was shown that for the following melts: LiF-BeF$_2$-ThF$_3$-UF$_4$ (72;16;12 and X mol.%, respectively, where X = 0.5-1), increase of the fission products content (CeF$_3$) up to 5 mol.% does not cause yielding of solid phases of uranium and thorium fluorides which provides possibility of the reactor operation without replacing the salt for about 10 years.
However, the papers written by these authors later show that if the composition of fission products gets more intricate and thorium content in the melt is decreased, e.g. the composition LiF-BeF$_2$-ThF$_4$-UF$_4$ (69; 29.5; 1 and 0.5 mol.% respectively) or in the molten salt with the more complex fission products composition, e.g. CeF$_3$-EuF$_3$-ZrF$_4$-LaF$_3$-BaF$_2$-SrF$_2$ (10; 1; 16; 18; 5; 50 mol.%, respectively) indicate that the reactor operation time till replacing the salt mixture will be less. Besides, if addition of up to three mass fractions of the fission products sum into the initial melt did not affect the behaviour of uranium, then increase of FPs up to 5 mass % caused up to 30 % uranium fluoride falling to a solid phase.

Fig.1.11 demonstrates the calculated data on a series of fluorides solubility versus the temperature supposing the formation of ideal solutions (using the Shreder's equation and thermodynamic data /17/). According to these calculations and in sequence of their rising solubility at 550 C fluorides must be placed in the following order ThF$_4$ < LaF$_3$ < UF$_4$ < CeF$_3$ < SmF$_3$ < CeF$_4$ < SrF$_2$. In this case the experimental data /15/ give quite another results. Solubility of uranium and thorium in the LiF-BeF$_2$ melt (70 and 30 %, respectively) is by over one order higher than solubility of rare-earth elements fluorides.
1.3. FISSION PRODUCTS AND OTHER IMPURITIES SOLUBLE IN FUEL SALT.

Operation of the MSR and ABC/ATW facility and reprocessing of their fuel includes as one of the main problems the removal of fission products accumulated in fuel salt as the result of nuclear reactions. Fission products formed can be conventionally divided into four major groups: noble gases, rare-earth elements, "noble" metals and other fission products soluble in fuel salt.

Some fission products produce chemical compounds soluble in the fuel composition. A certain level of such solved impurities must not cause significant change of physico-chemical properties of the fuel mixture.

In the MSBR project there was experimentally studied solubility of Mo, Nd, Sa and La fluorides. It was established that rare-earth elements are accumulated in fuel salt in the form of sufficiently stable fluorides.
In spite of ability of Mo trifluoride for disproportionation, in ref./17/ there was made an effort of experimental determining its solubility in the LiF-BeF₂ melt (67-33 mol %). Under the definite pressure in the system and at temperatures 500-700 °C, MoF₃ did not disproportionate in the melt for several days, though usually transforation of MoF₃ to MoF₆ and metallic Mo took a few hours. Investigations showed that at 700 °C considerable decrease of the MoF₃ concentration in time in the molten salt takes place.

Tab.1.6 /7/ depicts change of MoF₃ solubility in the LiF-BeF₂ melt in the helium atmosphere.

**Table 1.6.**

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Reaction Time (hr)</th>
<th>MoF₃ Concentration (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Filtered Sample</td>
</tr>
<tr>
<td>500</td>
<td>2</td>
<td>690</td>
</tr>
<tr>
<td>500-700</td>
<td>2.5</td>
<td>510</td>
</tr>
<tr>
<td>700</td>
<td>3.5</td>
<td>440</td>
</tr>
<tr>
<td>700</td>
<td>7</td>
<td>390</td>
</tr>
<tr>
<td>700*</td>
<td>24</td>
<td>190</td>
</tr>
<tr>
<td>700*</td>
<td>27</td>
<td>&lt;10</td>
</tr>
</tbody>
</table>

* Melt treated with H₂ between 24- and 27-hr samples.

These data confirm that disappearance of MoF₃ from molten salt can be accounted for its disproportionation at 700 °C.

At the same time ref./2/ presents an opinion that noble and semi-noble metals such as Nb, Te, Mo, Rh, Ag, Sb do not produce stable fluorides and are deposited on metallic surfaces of the primary circuit for 2.5 hours.

Study of CeF₃ solubility in the LiF-BeF₂, LiF-BeF₂-ThF₄ melts /13,19/ was carried out with the aim of predicting and comparing the behaviour of PuF₃ with CeF₃ in salt melts (see Fig.1.12). The curve of the obtained results for solubility (mol.%) versus temperature is given in Fig.1.13. Fig.1.14 presents the data on solubility for eight systems LiF-BeF₂-ThF₄ and three binary systems LiF-ThF₄, and Tab.1.7 reflects the generalized results of these and earlier investigations. Fig.1.15 shows the change of CeF₃ solubility in salt mixtures LiF-ThF₄ and LiF-BeF₂ depending on content of thorium and beryllium fluorides at various temperatures, where the CeF₃ solubility values in LiF-ThF₄ according to the phase diagrams data at 800 °C were then extrapolated to the hypothetic solubility value of this salt at 700 and 600 °C.
Fig. 1.12.
Comparison of CeF₃ and PuF₃ solubility in LiF-BeF₂ solvents.

Fig. 1.13.
Solubility of CeF₃ in LiF-BeF₂-ThF₄ (72-16-12 mol. %).

Fig. 1.14. Best-value plots of the solubility of CeF₃ in LiF-ThF₄ and LiF-BeF₂-ThF₄ solvents.

Fig. 1.15. Solubility of CeF₃ in LiF-ThF₄ and LiF-BeF₂ mixtures.
Fig.1.13 demonstrates good coincidence between the results of radiochemical and chemical analyses in these experiments (mixture 1, Tab.1.1). The present results calculated by the least squares method are in Fig.1.13. As mentioned above, these experiments revealed that molar content of ThF₄ and BeF₂ is the decisive factor in binary and quaterary mixtures. The smooth line in Fig.1.16 (where each composition is identified by a number from Tab.1.7) reflects almost linear dependence of CeF₃ solubility \( s = 100[\text{Ce}]/[\text{Ce+Li+Be+Th}] \) to \( u = [\text{Th}]/[\text{Th+Be}] \) according to the equations:

\[
S (600) = 0.50 + 2.60u - 0.40u^2
\]

\[
S (700) = 1.60 + 4.23u - 0.88u^2
\]

\[
S (800) = 3.80 + 5.80u - 0.80u^2
\]

Presentation of the "b" value indicated in Fig.1.16 as an algebraic dependence is caused by existing in the molten mixture LiF-BeF₂-ThF₄ of BeF₂⁻ type complex particles, Th⁴⁺, Ce³⁺ ions and ThF₃⁻ anions as well as presence of "free" LiF in the melt, "b" = 18 mol.%. The values of CeF₃ solubility in the binary mixture LiF-BeF₂ given in Fig.1.17 and enumerated in Tab.1.7 are higher than the same calculated values for LiF-BeF₂ with the higher concentration of BeF₂.

Data on LaF₃ solubility in fluoride melts are extremely small. Thus, according to data of ref./21/ the LaF₃ solubility at 500-600 C is supposed to make up about 1 mol.%. As follows from the calculated solubility increase row of fluorides /15/, solubility in rare-earth elements increases to samarium (0.15; 0.17; 0.5 mol.% for LaF₃; CeF₃ and SmF₃, respectively). This qualitatively coincides with the experimental order of solubility change for rare-earth element (REE) fluorides. However, quantitative calculation gives great values 4.4; 5.0 and 7.9 mol.%, respectively.

Such divergence of calculated and experimental data on REE fluorides and actinides solubility in lithium and beryllium fluoride melts can be accounted for a complex structure of salt melt forming the following molecules:

\[
\text{Li-F} \quad \text{F} \quad \text{Be-F} \quad \text{Li-F}
\]
Table 1.7.
Solubilities and Apparent Heats of Solution of CeF₃ in Mixtures of LiF, BeF₂ and ThF₄

<table>
<thead>
<tr>
<th>Mixture no</th>
<th>Salt composition, mol.%</th>
<th>CeF₃ solubility and std error of fit (95% confidence level), mol.%</th>
<th>Apparent heat of soln and std dev, cal/mol</th>
<th>u = [Th]/[Th+Be]</th>
<th>b=[free LiF], mol.%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>LiF</td>
<td>BeF₂</td>
<td>ThF₄</td>
<td>600°C</td>
<td>800°C</td>
</tr>
<tr>
<td>1</td>
<td>72</td>
<td>16</td>
<td>12</td>
<td>1.62±0.03</td>
<td>(5.28)±0.11</td>
</tr>
<tr>
<td>2</td>
<td>73</td>
<td>0</td>
<td>27</td>
<td>2.65±0.05</td>
<td>8.90±0.18</td>
</tr>
<tr>
<td>3</td>
<td>72.7</td>
<td>4.8</td>
<td>22.5</td>
<td>22.43±0.05</td>
<td>(8.25)±0.17</td>
</tr>
<tr>
<td>4</td>
<td>68</td>
<td>20</td>
<td>12</td>
<td>1.45±0.03</td>
<td>(5.78)±0.12</td>
</tr>
<tr>
<td>5</td>
<td>72.3</td>
<td>11.0</td>
<td>16.7</td>
<td>2.10±0.04</td>
<td>(5.93)±0.12</td>
</tr>
<tr>
<td>6</td>
<td>67.8</td>
<td>25.2</td>
<td>7.0</td>
<td>(1.56)±0.02</td>
<td>(4.92)±0.10</td>
</tr>
<tr>
<td>7</td>
<td>58</td>
<td>30</td>
<td>12</td>
<td>1.13±0.02</td>
<td>4.43±0.10</td>
</tr>
<tr>
<td>8</td>
<td>75</td>
<td>17.9</td>
<td>7.1</td>
<td>(1.52)±0.03</td>
<td>(6.59)±0.13</td>
</tr>
<tr>
<td>9</td>
<td>58.4</td>
<td>20.0</td>
<td>21.6</td>
<td>(1.90)±0.04</td>
<td>6.50±0.14</td>
</tr>
<tr>
<td>10</td>
<td>67</td>
<td>0</td>
<td>33</td>
<td>(2.54)±0.05</td>
<td>7.91±0.17</td>
</tr>
<tr>
<td>11</td>
<td>80</td>
<td>0</td>
<td>20</td>
<td>(3.30)±0.07</td>
<td>(10.07)±0.21</td>
</tr>
<tr>
<td>12</td>
<td>60</td>
<td>0</td>
<td>40</td>
<td>(2.77)±0.06</td>
<td>7.00±0.14</td>
</tr>
<tr>
<td>13</td>
<td>66.7</td>
<td>33.3</td>
<td>0</td>
<td>(0.60)°</td>
<td>(3.7)°</td>
</tr>
<tr>
<td>14</td>
<td>72.7</td>
<td>27.3</td>
<td>0</td>
<td>(0.95)°</td>
<td>(5.7)°</td>
</tr>
</tbody>
</table>

- a Extrapolated from our values to higher temperature
- b Extrapolated from our values to lower temperature
- c Interpolated from literature values and extrapolated to 800°C
- d Negative values of "free" LiF correspond to excess BeF₂ and/or ThF₄ over Li₂BeF₄ and/or Li₂ThF₄, i.e., to acidic compositions in the sense of the Lewis acid-base concept.
- e In this acidic range CeF₃ solubility changes little with composition (see Figure 1 and 5)
Correlation of CeF$_3$ solubility with solvent composition. Smoothlines depict solubility for composition with $b=[\text{LiF}-2\text{BeF}_2-3\text{ThF}_4] \leq 0$ (no "free" LiF). Dotted lines show solubility for $b=18$ (18 mol% "free" LiF).

Fig. 1.17. Correlation of apparent heat of solution with solvent composition.
These molecules can be considered as complex ions \( \text{Li}_2\text{F}^+ \) and \( \text{BeF}_3^- \). There are no reasons to deny their existence in molten salts, as their formation is accompanied by considerable power excess (as to calorimetry data).

Under more severe account of other impurities effect, the physico-chemical properties of the molten salt it should be noted that in industry-produced salts there is already a certain fraction of "adverse" compounds (Ni, Fe, Cr, Si, Al, Mn chlorides and sulphates) with the total content no more than \( 10^{-2} \) %.

When monitoring the content of impurities in salt melts used for heat transfer study it was established for the melt \( 67.5\text{LiF}-20\text{BeF}_2-12\text{ThF}_4-0.5\text{UF}_4 \) that their mass content makes up:

- Fe - \( 78\times10^{-4} \)%; Ni - \( 20\times10^{-4} \% \); Cr - \( 25\times10^{-4} \% \); and in the melt \( 72\text{LiF}-16\text{BeF}_2-12\text{ThF}_4-0.3\text{UF}_4 \):
- Fe - \( 45\times10^{-4} \)%; Ni - \( 70\times10^{-4} \% \); Cr - \( 85\times10^{-4} \% \).

Another source of impurities intake to the fuel salt is structural materials corrosion. However, pursuant to current estimations the corrosion products concentration in the salt does not exceed \( 0.02 \) %, and these products do not practically affect the fuel salt chemically.

Therefore, on the basis of the available information one can expect that the ultimate permissible concentration of fission products remaining in the fuel salt is limited by their solubility which is about \( 5 \) % at \( 700 \) °C /2/. Depending on the energy release level and total volume of fuel in the ABC/ATW facility this concentration can be achieved in 10-12 or 30 years.

At the same time on the basis of the available laboratory and reactor investigations at present one can anticipate that the fission products concentration only at the 1-2 % level does not influence significantly the physico-chemical properties of Li, Be, Th and U fluoride melts /1/. As to higher concentrations of rare-earth metal fluorides, this issue requires additional investigations, in our opinion.
2. PROVISIONAL DESCRIPTION OF TECHNOLOGICAL COMPLEX FOR FISSION PRODUCTS AND ACTINIDES REMOVAL FROM IRRADIATED FUEL SALT OF THE ABC/ATW FACILITY

Previously were proposed several possible variants of arranging the molten salt processing of the ABC facility /1/. Since at present the salt composition and main characteristics of the ABC/ATW facility are determined /2/, it is expedient to decide on one of the variants with the aim of fission products and actinides removal out of the salt fuel.

This chapter is devoted to description of processes proposed for the chemical-technological complex of the ABC/ATW facility and their physico-chemical peculiarities. Partially the data presented in the section are proposals developed on the basis of RIAR technological experience.

2.1. GENERAL APPROACHES TO FUEL PROCESSING

The following parameters should be emphasized from the main parameters of the ABC facility which are essential for considering and estimating the variants of arranging its fuel cycle /2/: fuel composition - LiF (65%) - BeF₂ (29%) - ZrF₄ (5%), Pu content - less than 1 mol.% (about 0.34 % after 10 years, about 0.46 % after 20 years) fuel amount - mass = 22000 kg
volume = 9.7 m³
Pu inventory for 10-year lifetime - 250 kg
inventory of other actinides for 10 years - 100 kg.

The most acceptable from the authors' viewpoint will be a variant based on three operations of melt processing, two of which must be conducted during the continuous operation of the ABC facility:

1. Inert gas processing of the molten salt fuel for removal of gaseous fission products and fission products generating volatile fluorides and aerosols;

2. "Fuel - active metal" interaction for removal of "noble" and "semi-noble" fission products which can form deposits on metallic parts of fuel circuit.

Such a partial processing will provide the facility operation provided there is gradual accumulation in the REE fuel and Cs, Sr, Rb, I, Br.
(3) Chemical reprocessing of salt with aim of removal of actinides and remaining fission products, the fluorides of which are not removed during partial fuel processing, will be performed at a separate facility after the project-determined fission products accumulation.

Let us consider each of these operations in particular.

2.2. GAS PROCESSING OF MOLTEN SALT

Molten fuel prior to or after the heat exchanger passes through the device in which it mixes with the inert gas. In this case dissolved radioactive gases and, partially, fission products volatile fluorides are transformed into the milled gas bubbles via the "gas-salt" interface surface.

The solubility constant Kr and Xe in the LiF-BeF₂ melt is less than \( 10^{-8} \text{ mol/(cm}^3\text{*atm)} \) /1/, so inert gases are transformed into the gaseous phase practically completely.

Besides, as MSRE experience showed, some other fission products are also captured. (see Tab.3.11 /1/).

Within the frames of the MSBR project developed was an optimal system for gaseous fission products removal that is presented in Fig.2.1. The fuel salt flux passes the by-pass circuit in which there is a bubbler 1 saturating the salt with gas bubbles. At the same time He is also supplied to fuel pump 2. Gaseous phase is separated from salt in gas separator 3. Such a device developed earlier /3/ is given in Fig.2.2. The carrier-gas containing Xe, Kr and aerosols with fission products is fed to settling tank 4 followed by delay for short-lived isotopes decay. Through filter 5 the gas goes to delay line 6 with activated carbon as a sorbent (for 47 hours). Then the main part of the flow returns to bubbler 1, and some part - for deep purification from T, Xe, Kr.

This system in full scope can be recommended for realization in the ABC project. However, some important engineering problems must be solved:
- cooling system of the settling tank;
- replacement system of sorbent and filters;
- system tightness.

Argon could be used instead of helium in developing the gas removal system. Argon has less penetrating power which will allow its more technological use without leakages and losses. Technological properties of argon as a carrier-gas are not worse that those of helium. Besides, the technology of argon use as protective gas is quite well developed in sodium coolant fast reactors /4/, and some technical methods can be used in the ABC/ATW project.
Fig. 2.1. Flow sheet of the gases purification and removal system in the MSBR reactor
1. bubbler; 2. fuel pump; 3. separator; 4. settling tank; 5. purification from aerosols; 6. delay line (47 hours); 7. membrane system; 8. delay line (90 hours); 9. purification; 10. filter; 11. storage tank.

Fig. 2.2. Bubble separator design for gas system technology facility. [3]
2.3. SYSTEM OF "NOBLE" AND "SEMI-NOBLE" FISSION PRODUCTS REMOVAL

The second operation of fuel processing in the continuous operating mode of the ABC facility must be its contact with active metal. Its purpose is noble fission products removal from the molten salt. As shown in the report /1/, it is necessary for removal of impurities which can interact with structural materials of fuel circuit and blanket circuit or can increase corrosion, or form uncontrolled deposits on metallic and graphite surfaces inside the blanket and in the heat exchanger.

Since salt fuel contains zirconium fluoride, it is reasonable to let salt contact the metallic zirconium. In this event there will occur the reactions of fission products fluorides - zirconium exchange. All fission products - metals whose fluorides are less resistant than zirconium fluoride for the given system - will belong to this fission products group (noble and semi-noble).

Reactions that will occur during these operations are as follows (calculation of free energy for 650 C as to Tab.3.2, report /1/ and /5/):

\[
3 \text{Zr} + 4 \text{MoF}_3 = 3 \text{ZrF}_4 + 4 \text{Mo} \quad (\Delta G = -1814 \text{ kJ})
\]

\[
5 \text{Zr} + 4 \text{RuF}_5 = 5 \text{ZrF}_4 + 4 \text{Ru} \quad (\Delta G = -5244 \text{ kJ})
\]

\[
\text{Zr} + 4 \text{AgF} = \text{ZrF}_4 + 4 \text{Ag} \quad (\Delta G = -1114 \text{ kJ})
\]

\[
\text{Zr} + 2 \text{TeF}_2 = \text{ZrF}_4 + 2 \text{Te} \quad (\Delta G = -877 \text{ kJ})
\]

Impurities of structural materials will react in the same way:

\[
\text{Zr} + 2 \text{FeF}_2 = \text{ZrF}_4 + 2 \text{Fe} \quad (\Delta G = -532 \text{ kJ})
\]

\[
\text{Zr} + 2 \text{CrF}_2 = \text{ZrF}_4 + 2 \text{Cr} \quad (\Delta G = -380 \text{ kJ}).
\]

This operation will allow timely removal of many fission products (As, Se, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Cd, Te, Zn, Ga, Ge, In, Sn, Sb) and corrosion products (Ni, Fe, Cr and other elements if they are used, e.g. Ti, V, W, etc.) from fuel salt. Data on fluorides stability in LiF-BeF₂ fuel are published not for all fission products, however, general trends of fluorides stability (see Section 3.1 and
Tabs. 3.1, 3.2, 3.4, 3.5, report /1/ state that only REE, actinides, alkali and alkali-earth elements as well as iodine and bromine will stay in the melt.

With allowance for the fact that plutonium is in a three-valent state in the ABC facility fuel, the following reaction should not seem dangerous:

\[ 4 \text{PuF}_4 + Zr = 4 \text{PuF}_3 + ZrF_4, \]

since such interaction will stabilize the oxidation-reduction potential of molten salt. Metallic plutonium will not deposit in this system:

\[ 4 \text{PuF}_3 + 3 Zr = 4 \text{Pu} + 3 ZrF_4 \quad (\Delta G = +128 \text{ kJ}). \]

This operation can be performed by several technical methods:

(A) Interaction of fuel with Zr chip (or other milled form) in a special by-pass. The scheme of such a device is depicted in Fig. 2.3. The device should have special inner additional appliances or filters for trapping the metallic fission products suspensions. The fission products precipitation device should be detachable and it should include the "cold trap" principle as it was developed in the fast reactors technology when purifying the coolant-sodium from oxides and fission products /4/. Solid particles that might be present in fuel will be trapped.

(B) Passing of fuel through the device with zirconium plates, like one illustrated in Fig. 2.4. The whole device should be periodically replaced in this case.

The speed of accumulation and sliming of these devices is to be defined experimentally. It is advantageous that the reaction zone be subject to additional heating for decomposition of instable fluorides.

This method can be realized only in the case if in metallic structures of fuel flow there will be no electrochemical couples that can enhance the fuel circuit corrosion. To provide protection against this effect one may isolate zirconium metallic parts or chip from contact with the circuit metal (pipelines) via special ceramic inserts.
Fig. 2.3. Device for removal of noble fission products with Zr chip

1. Zr chip  
2. Insulating layer  
3. Area of suspensions precipitation

Fig. 2.4. Device for removal of noble fission products with Zr-plates

1. Zirconium plates  
2. Insulators
It is important to note that during the facility operation period this method can be described as automatic replacement of burnt-up plutonium or actinides for zirconium. Tab. 2.1. presents estimations on fission products and zirconium accumulation in fuel salt. Additional supply of Zr into fuel salt for 10-year lifetime will not exceed 0.4 mass.% which will change its composition just a little.

Both operations (removal of gases and "noble" fission products) are simple in their technical exercise which permits creations of the compact and productive equipment for their realization. On the whole, fuel processing described in 2.2 and 2.3 will allow its freeing from subsequent fission product groups:

- Noble gases - Kr, Xe (and tritium, in partial);
- Noble and semi-noble metals - Se, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Cd, In, Sn, Sb, Te (and Zn, Ga, Ge, As);
- Corrosion products - Ni, Fe, Cr.

If this scheme is realized, there is no sense to speak of the degree of fuel purification from the enumerated impurity groups, for the residual element content in the melt will be a factor determining purification efficiency. The speed of removing these impurities will depend on the speed of fuel passing through processing devices and will not exceed a few minutes.
Table 2.1
Calculation of FP accumulation at complete fuming out of 250 kg of Pu and 100 kg minor actinides on data of [11].

<table>
<thead>
<tr>
<th>Fission products</th>
<th>Total content in fuel, kg</th>
<th>FP content in fuel, mas.%</th>
<th>Amount of Zr supplied into fuel during exchange, kg</th>
<th>Amount of Zr supplied into fuel during exchange, mas.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kr</td>
<td>3.8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Xe</td>
<td>41.0</td>
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</tr>
<tr>
<td>Br</td>
<td>0.36</td>
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<tr>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rb</td>
<td>3.4</td>
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<td></td>
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<tr>
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<td>37.8</td>
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<td></td>
</tr>
<tr>
<td>Sr</td>
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</tr>
<tr>
<td>Ba</td>
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<td>~0.09</td>
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</tr>
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<td></td>
<td></td>
</tr>
<tr>
<td>Sm</td>
<td>0.7</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Eu</td>
<td>0.4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dy</td>
<td>0.93</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zr</td>
<td>(40.3)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nb</td>
<td>41.6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mo</td>
<td>42.6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ru</td>
<td>42.6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rh</td>
<td>10.4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pd</td>
<td>28.3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag</td>
<td>11.6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tc</td>
<td>96.3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cd</td>
<td>1.6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>In</td>
<td>1.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sn</td>
<td>0.7</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sb</td>
<td>3.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Se</td>
<td>1.8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Te</td>
<td>7.8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K</td>
<td></td>
<td></td>
<td>92.3 kg</td>
<td>(0.41 mas.%)</td>
</tr>
</tbody>
</table>
2.4. FULL CHEMICAL REPROCESSING OF FUEL SALT

Full chemical (pyroelectrochemical) reprocessing of fuel salt must be conducted at the special facility portion by portion. Such a facility can be placed separately from the ABC facility and can receive fuel salt both as liquid and solid form.

Fuel salt will contain actinides (Np, Pu, Am, Cm) and those fission products which do not react zirconium (i.e. rare-earth, alkali-earth and alkali metals as well as halogens).

The aim of reprocessing should be maximal release of fission products to wastes with minimal actinides removal. The reprocessing strategy depends on stability of the enumerated fission products fluorides. According to the literature data (section 3.1 of the report /1/) the row of stress for the system is like this:

\[
\text{Zr - Np - Pu - Am,Cm - REE - Sr,Ba - (Be) - Cs,Rb,Li}
\]

This sequence must be taken into account in developing the reprocessing operations.

2.4.1. ZIRCONIUM REMOVAL.

Since the melt comprises a large amount of zirconium fluoride (~5 mol %), zirconium will be the first to participate in electrochemical and exchange reactions (see sections 3.1.4 and 3.2.1, report /1/). That is why before the operation of actinides and fission products separation it is required to remove zirconium from fuel salt.

Two methods are possible:
- exchange on liquid melt containing lithium, e.g. Bi-Li;
- electrolysis of melt with zirconium release either to a solid cathode product or to liquid-metallic alloy.

The first method based on the reaction:

\[
\text{ZrF}_4 + 4 \text{Li(Bi)} = 4 \text{LiF} + \text{Zr(Bi)}
\]
is not acceptable, as it requires large amount of metallic lithium with isotope $^7\text{Li}$ enrichment.

The second method can be realized using the known electrolyzer types for fluoride salts. Reactions proceeding on electrodes:

on a cathode:

$$ \text{Zr}^{4+} + 4 e^- \rightleftharpoons \text{Zr} \text{ (or alloy in Bi)}, $$

on an anode:

$$ 2 \text{F}^- - e^- \rightleftharpoons \text{F}_2. $$

In this event there must be released fluorine on the anode (which is unlikely) and it can be used at other stages of reprocessing, or using special graphite anodes there can be produced fluoro-carbons that are less corrosive:

$$ n \text{F}^- + m \text{C (anode)} - n e_- \rightleftharpoons \text{C}_m\text{F}_n. $$

Electrolysis should be conducted prior to release of the Zr bulk, but provided the capture of actinides by the cathode deposit or alloy must be excluded.

For getting solid zirconium there will be formed the dendrite cathode zirconium that will capture the salt. Though the difference in potentials of Zr and Pu deposition might be evaluated as 0.5-0.6 B (due to Tab.3.5, report /1/), this salt will comprise Pu and should provide for the operation of captured salts removal from the cathode deposit, which can be made by vacuum processing in the inert atmosphere. This will cause extratechnological problems.

The most convenient variant is one using the bismuth cathode. Judging from the evaluations of conditional alloy potentials (see Appendix), the difference in standard potentials on liquid bismuth Zr and Pu deposition is about 0.4 B (at 650 C), thus, conduct of electrolysis at least up to their content equalization in fuel salt is expedient. Pu content in the cathode alloy Bi-Zr will be on the traces level.

Later the obtained product (Bi-Zr alloy) can be used as the Zr source to prepare salt for reirradiation after fission products removal.

The scheme of an electrolyzer for conducting this operation is presented in Fig.2.5.
2.4.2. ACTINIDES REMOVAL FROM FUEL SALT.

The following operation should be performed with the produced molten salt, the composition of which can be defined as:

\[
\text{LiF-BeF}_2-\text{PuF}_3(<1 \text{ mol\%}) - \text{ZrF}_4(<0.5 \text{ mol\%}) - \text{MAF}_3-\text{FPF}_n(<1 \text{ mol\%}).
\]

While its processing all actinides must be removed in order to have the maximal possible amount of fission products at the next stage and to dissolve actinides from the produced alloy to the purified salt afterwards.

Actinides removal can be performed by two methods:
- electrolysis into liquid-metallic cathode;
- exchange interaction with alloy, e.g. Bi-Li.

Principal thermodynamic foundations of these methods are close, and like in the case of the bismuth cathode use and in the case of Bi-Li this process can be calculated. The separation degree for the alloy and electrochemical process is defined practically by the same thermodynamical parameters /1/, so it is sufficient to estimate by the exchange reaction:

\[
\text{PuF}_3 + 3 \text{Li(Bi)} = \text{Pu(Bi)} + 3 \text{LiF}
\]

Calculation and substantiation of the Pu separation factors and of some REE are given in Appendix. Tab.2.2 presents their estimated values in the system "LiF-BeF$_2$-ThF$_4$ melt and Bi-Li alloy", as it is only for this system there are data on Pu behaviour. Properties of this fuel mixture slightly differ from the assumed fuel LiF-BeF$_2$-ZrF$_4$, therefore, analogous indices on actinides and REE separation can be expected.

Nevertheless, data on the separation factors do not reveal the process as it is, since they determine the system equilibrium state. For the precise description use should be made of a definition "purification factor" /6/ which is related to the separation factor in the following way:
where \( C \) - initial content, \( C' \) - final content.

It is clear from this expression that for 90% \( \text{Pu} \) extraction from salt, the purification factor will be by one order less than the separation factor. To make 99.9% \( \text{Pu} \) extraction its value will be 1000 times less.

Thus, in order to extract \( \text{Pu} \) (or neptunium) completely from the salt it is necessary to capture REE into the alloy partially.

Estimations of the purification factors of \( \text{Pu} \) from REE are shown in Tab.2.3.

Operation of actinides extraction from fuel salt can be performed in electrolyzers depicted in Fig.2.5 and 2.6.

### Table 2.2

<table>
<thead>
<tr>
<th>( M^{n+} )</th>
<th>( \text{Zr}^{4+} )</th>
<th>( \text{Np}^{3+} )</th>
<th>( \text{Pu}^{3+} )</th>
<th>( \text{La}^{3+} )</th>
<th>( \text{Pr}^{3+} )</th>
<th>( \text{Eu}^{2+} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \log \frac{D_M}{D_U} )</td>
<td>14,7</td>
<td>10,5</td>
<td>10</td>
<td>6,5</td>
<td>5,6</td>
<td>3,7</td>
</tr>
<tr>
<td>( K_{\text{separ}}(\text{Pu}) )</td>
<td>5*10^4</td>
<td>3,2</td>
<td>1</td>
<td>3,2*10^{-4}</td>
<td>4*10^{-5}</td>
<td>5*10^{-7}</td>
</tr>
<tr>
<td>( \log \ K_{\text{separ}} )</td>
<td>0,5</td>
<td>-3,5</td>
<td>-4,4</td>
<td>-4,4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \log \ K_{\text{equil}} )</td>
<td>28,8</td>
<td>-22,6</td>
<td>-22,6</td>
<td>-22,6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \Delta E^{**, V} )</td>
<td>-0,44</td>
<td>-0,03</td>
<td>0</td>
<td>+0,21</td>
<td>0,27</td>
<td>0,69</td>
</tr>
<tr>
<td>( (E^{<strong>}_{\text{Pu}} - E^{</strong>}_M) )</td>
<td>-0,44</td>
<td>-0,03</td>
<td>0</td>
<td>+0,21</td>
<td>0,27</td>
<td>0,69</td>
</tr>
</tbody>
</table>
Fig. 2.5. Electrolyzer for Zr and actinides extraction
1. mixer  
2. Bi alloy removal  
3. vessel  
4. anode assembly  
5. anode of graphite material  
6. tube for salt transfer  
7. heater

Table 2.3
Purification factor of Pu from REE versus the degree of Pu removal from salt

<table>
<thead>
<tr>
<th>Degree of Pu removal from salt</th>
<th>La (K_{separ} = 3.2\times10^{-4})</th>
<th>Pu (K_{separ} = 4\times10^{-3})</th>
<th>Eu (K_{separ} = 5\times10^{-4})</th>
</tr>
</thead>
<tbody>
<tr>
<td>at 90 %</td>
<td>3.2\times10^{-3}</td>
<td>4\times10^{-4}</td>
<td>5\times10^{-6}</td>
</tr>
<tr>
<td>at 99 %</td>
<td>3.2\times10^{-2}</td>
<td>4\times10^{-3}</td>
<td>5\times10^{-5}</td>
</tr>
<tr>
<td>at 99.9 %</td>
<td>0.32</td>
<td>0.04</td>
<td>0.005</td>
</tr>
</tbody>
</table>
Fig. 2.6. Bipolar electrolyzer for fuel salt reprocessing

1. furnace
2. anode assembly
3. electrolyzer vessel
4. salt melt
5. liquid Bi alloy
6. mixer
7. non-conductive barrier
8. cathode assembly
2.4.3. SALT PURIFICATION FROM REE

Salt with removed actinides should be transferred to another apparatus that is designed for salt purification from the remaining REE and, probably, alkaline-earth metals.

This procedure can be based on two methods:

(A) Deposition of REE oxides with an inert oxide matrix:

\[ 2 \text{EuF}_3 + 3 \text{CaO} = \text{Eu}_2\text{O}_3 + 3 \text{CaF}_2 \quad (K = 10^{11}) \]

\[ 2 \text{LaF}_3 + 3 \text{CaO} = \text{La}_2\text{O}_3 + 3 \text{CaF}_2 \quad (K = 10^{11}) \]

\[ 2 \text{CeF}_3 + 3 \text{CaO} + 0.5 \text{O}_2 = 2\text{CeO}_2 + 3 \text{CaF}_2 \quad (K = 10^{29}) \]

In this connection it is required to choose some reagents for precipitation, as such fission products as Sr and Ba are likely to be deposited.

After precipitation of fission products oxides it is necessary to separate solid particles from the melt, and electrochemical processing of the melt to remove the oxygen-containing impurities.

(B) Exchange interaction with the lithium-containing alloy up to full REE removal:

\[ \text{LnF}_3 + 3 \text{Li}(\text{Bi}) = 3 \text{LiF} + \text{Ln}(\text{Bi}) \]

The procedure is analogous to the operation of actinides removal from fuel salt and its foundations are described in section 3.2, report /1/. Electrochemical REE extraction into the melt is possible, the known electrolyzer types being used.

As the result of this operation the salt will be practically wholly purified from REE and, partially, from Sr and Ba. For high-temperature processes the salt can be purified by a factor of 100-1000 /8/.

2.4.4. REDUCTION OF FUEL SALT COMPOSITION

After purification the salt can be sent to the electrolyzer once again where actinides were removed.

There should be conducted an electrochemical operation of the anode actinides introduction to fuel salt:
reaction on the anode: \( \text{Pu(Bi)} - 3e^- = \text{Pu}^{3+} \)

Operations of actinides removal from one salt portion and their anode dissolution in another portion of the purified salt can be joined when using a bipolar electrolyzer that is schematically depicted in Fig.2.6. Such layout will allow optimal arrangement of the flow sheet if fuel salt is re-used.

2.5. FUEL SALTS REPROCESSING WASTES

The described technological methods will result in formation of the following waste types:

(A) Off-gas system wastes;

The treatment methods were developed previously /7/. (The authors did not study this problem in detail)

(B) Trapping system wastes of noble and "semi-noble" metals:

Waste can include replaceable devices with zirconium parts (Fig.2.3 and 2.4). They can be processed with extracting the noble metals /9/ and other valuable fission products or sent for disposal after removal of the fuel salt residues.

(C) Zr (alloy) extraction wastes:

If Zr extraction is carried out on a liquid cathode (e.g., Bi), either its direct disposal or anode Zr extraction to the salt melt is possible for re-use.

In the second case the remaining alloy will comprise impurities of some fission products. It can be purified for multiple use.

(D) REE removal wastes out of salt:

In case of oxide fission products precipitation these wastes will be as an oxide powder that can be directly applied for vitrification of high-level wastes after separation from salt.

In case of using a liquid-metallic electrode one can perform an operation of fission products concentrating with multiple application of the alloy.

(E) Wastes after actinides release to fuel salt (alloy):
This waste type will constitute an alloy containing fission products impurities in small quantities and will be used multiply. On completion of reprocessing it can be regenerated for re-use of the metal-alloyformer.

(F) Wastes of the fuel reprocessing facility equipment:
At present no estimation can be made, as structural materials for chemical processes conduct are not determined.

(G) Anode gases of electrochemical processes:
A simple compact system of gas purification should be developed, since this wastes type can contain corrosion-active fluorine.

Wastes of metallic alloy (e.g., based on Bi) for positions (C) and (E) can be reprocessed in electrolyzers with the similar design as those in Fig.2.5 and 2.6.

Complete estimations of waste flows can be made when concrete processes are chosen. However, proceeding from operating experience with salt melts during oxide fuel reprocessing /10/, one can expect that yield of solid high-active wastes (excluding the equipment) will exceed several percent of the reprocessed salt volume.

2.6. GENERAL SCHEME OF SALTS REPROCESSING

Due to all the above procedures, fuel salt will be freed from fission products and impurities. Table 2.4 shows the methods and periods of fission products removal from fuel salt.

The scheme of fuel treatment is given in Fig.2.7. It can be stated on the whole that the purification factor of Pu from REE will make up several tens (20-50), and the purification factor of salt from impurities - 100 to 500. The degree of Am and Cm separation from REE can not be determined precisely due to the available data, but 2-5 fold purification is quite possible. This value can be increased while replacing Bi by the alloyformer with the greatest selectivity of Am and Cm separation from REE.

The degree of actinides purification from fission products is defined by a few factors, namely, by mass relation in fuel salt, the permissible level of actinides content in wastes and by the separation methods. New experimental data for correct estimation of these indices must be obtained.
The described scheme after the salt reprocessing 2 or 3 times during the ABC/ATW facility operation will allow retain other long-lived isotopes subject to transmutation in fuel salt: Cs, Sr, I. Still, technetium will be removed in fuel purification from noble and "semi-noble" fission products, since its fluorides are unstable.

---

**Fig. 2.7.** The scheme of fuel cycle of ABC/ATW complex.

1. Heatexchanger  
2. Assembly of gas removal  
3. Assembly of deposition of noble Fd  
4. Plant of fuel reprocessing  
5. First apparatus (the electrolyser)  
6. Second apparatus
### Table 2.4.

**Methods and period of FPs and impurities removal from fuel salt**

<table>
<thead>
<tr>
<th>Group</th>
<th>Components</th>
<th>Period of removal</th>
<th>Operation of removal</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Inert gases</strong></td>
<td>Kr, Xe</td>
<td>0.5-1 min</td>
<td>Removal into gaseous phase by inert carrier-gas</td>
</tr>
<tr>
<td><strong>Noble and seminoble metals</strong></td>
<td>Se, Nb, Mo, Tc, Ru,</td>
<td>several min</td>
<td>Precipitation on surface of metallic Zr from fuel flow in a special device</td>
</tr>
<tr>
<td></td>
<td>Rh, Pd, Ag, Cd, In,</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sn, Sb, Te</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Corrosion products</strong></td>
<td>Ni, Fe, Cr</td>
<td>several min</td>
<td>Precipitation on surface of metallic Zr from fuel flow in a special device</td>
</tr>
<tr>
<td><strong>Actinides</strong></td>
<td>Pu, Np, Am, Cm</td>
<td>10 years (20 years)</td>
<td>Removal to liquid metals during reprocessing</td>
</tr>
<tr>
<td><strong>Halogens</strong></td>
<td>Br, I</td>
<td>10 years (20 years)</td>
<td>Removal in anode salt processing during fuel reprocessing</td>
</tr>
<tr>
<td><strong>Rare-earth elements</strong></td>
<td>Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb</td>
<td>10 years (20 years)</td>
<td>Precipitation as oxides or alloy during full fuel reprocessing</td>
</tr>
<tr>
<td><strong>Alkaline-earth elements</strong></td>
<td>Sr, Ba</td>
<td>10 years (20 years)</td>
<td>Precipitation as oxides or alloy during full fuel reprocessing</td>
</tr>
<tr>
<td><strong>Alkaline metals</strong></td>
<td>Rb, Cs</td>
<td>20 years</td>
<td>While full removal of salt for disposal</td>
</tr>
<tr>
<td><strong>Salt components</strong></td>
<td>Li, Be, Zr</td>
<td>20 years</td>
<td>While full removal of salt for disposal</td>
</tr>
</tbody>
</table>
CONCLUSION

The present report is the continuation of the report /1/ and is devoted to detailed interpretation of two problems:

- solubility of actinides and fission products in liquid-salt fuel;
- description of proposals on the reprocessing facility structure in the ABC/ATW complex and on the fuel reprocessing methods.

It was demonstrated that solubility of actinide fluorides can be sufficient to maintain serviceability of the salt molten fuel.

Reprocessing of fuel salt can be made by various modifications of the well-known methods. Nevertheless, previous papers were devoted to somewhat other systems with liquid-salt fuel, and their adaptation to the ABC/ATW complex problems should be carried out after a series of investigations, the basic trends of which are suggested in chapter 5, report /1/. 
LITERATURE FOR CHAPTER 1.


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7. Хомяков В.И., Шишков Ю.Д., Галкин Н.П. Использование фторидных расплавов для извлечения некоторых продуктов деления и америция из смесей различных фторидов, имитирующих по составу остатки от фторирования топлива реактора на быстрых нейтронах.- Радиохимия, 1977, t.19, N4, c.549-554.


16. Изучение координационных свойств актинидных и осколочных элементов и их поведение при фазообразовании в галийных расплавах: Отчет.Кн.1./Радиевый институт АН СССР; Руководитель работы В.Р. Клокман - 1-11-01-01-091(3208) - Ленинград, 1975-61с.


**LITERATURE FOR CHAPTER 2.**


2. Report LANL on ABC/ATW Project on JASON Committee (Jan.1994)


6. В.А.Лебедев. Избирательность жидкокометаллических электродов в расплавленных галогенидах. Челябинск; Металлургия. 1993 г.


APPENDIX

Method for alloy conditional standart potentials estimation from data on equilibrium distribution of elements

Conditional Standart potential of alloy for pair Me /Me (Me):

\[ E_{\text{standart potential for Me /Me Me}} = E_{\text{standart potential}} + \frac{RT}{nF} \ln \frac{f(1)}{1} - \frac{RT}{Y(1) nF} \ln Y(1) \]

where \( E \) - standart potential for Me /Me,

\[ E_{\text{standart potential for Me /Me Me}} = E_{\text{standart potential}} + \frac{RT}{nF} \ln f_{\text{Me ions in molten salt}} - \frac{RT}{Y(1) nF} \ln Y_{\text{Me atoms in molten alloy with Me}} \]

Utilization of alloy conditional standart potentials makes easier thermodynamics calculations. For calculation of separation factor of Me and Me on alloy with Me:

\[ K = \frac{c_{\text{Me}} x_{\text{1}}}{c_{\text{Me}} x_{\text{2}}} \]

\[ \ln K = \frac{nF(n-m)FE + mFE}{nFe} - \frac{nF}{2} \]

If \( n=m \), separation factor does not depend from alloy potential (E):

\[ \ln K = \frac{RT}{2} \]

Equilibrium constant for exchange reaction:

\[ n^+ \text{Me (Me)} + m^+ \text{Me} = m^+ \text{Me (Me)} + n^+ \text{Me} \]

can be described from reagents contents:
It is also depended from alloy conditional standart potentials:

\[
\ln K = \frac{-n^m F}{RT} (E_2 - E_1)
\]

These equations was used for calculations of differences of alloy conditional standart potentials of elements on Bi alloys (tabl. 2.2).