ESTIMATED BEHAVIOR OF TITANIUM IN MSBR CHEMICAL PROCESSING SYSTEMS

L. M. Ferris
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Oak Ridge, Tennessee 37830
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L. M. Ferris

ABSTRACT

Available thermodynamic information was used to estimate the behavior of titanium in a fluorination-reductive extraction flowsheet for processing MSBR fuel salt. It was first shown that titanium is likely to be leached from a titanium-modified Hastelloy N containment vessel into a LiF-BeF₂-ThF₄-UF₄ fuel salt at 600°C. The primary reaction would probably be $3\text{UF}_4(\text{d}) + \text{Ti} (\text{Hastelloy}) = \text{TiF}_3(\text{d}) + 3\text{UF}_3(\text{d})$. The estimates showed that, during fluorination, TiF₃ would be oxidized to TiF₄. A large fraction of the TiF₄ would be expected to volatilize during fluorination. Any titanium not volatilized by fluorination would be present in the salt that enters the reductive extraction step. Experimental data confirmed the prediction that titanium would be practically quantitatively extracted from the salt in this step. It was also shown that titanium can be transferred from a bismuth phase to a salt phase by oxidation with gaseous HF, and that HF is not a sufficiently strong oxidant to convert TiF₃ to TiF₄.


1. INTRODUCTION

Hastelloy N (68% Ni--17% Mo--7% Cr--5% Fe) was used for the containment vessel and other metallic components in the Molten-Salt Reactor Experiment (MSRE). However, use of a modified Hastelloy containing up to 2 wt% titanium is being considered for molten-salt breeder reactors (MSBRs) since an alloy of this type is expected to be more resistant to radiation embrittlement than Hastelloy N. In the event that a suitable alloy is developed, it is of interest to know what extent titanium will be leached from the alloy into the molten salt and, if the extent of
leaching is significant, how titanium will behave in an MSBR chemical processing system. The present reference flowsheet\textsuperscript{2,3} for chemically processing an MSBR involves, first, fluorinating the salt to remove uranium as $\text{UF}_6$ and, then, contacting the resultant salt with liquid bismuth containing about 0.002 mole fraction each of lithium and thorium to remove protactinium by reductive extraction. The rare earths remain in the salt during these process steps and are removed in a subsequent metal transfer process. Protactinium and other elements extracted into bismuth will subsequently be transferred to a salt phase by hydro-fluorination of the bismuth in the presence of the salt. The purpose of this report is to estimate the behavior of titanium both in the reactor system and in the various chemical processing steps. The estimates, which were made using the general thermodynamic treatment developed by Baes\textsuperscript{4} could be compared, in some cases, directly with experimental results.

2. THERMODYNAMIC TREATMENT

Baes\textsuperscript{4} has summarized a large amount of equilibrium data involving molten LiF-BeF\textsubscript{2} solutions in terms of standard half-cell potentials ($E^\circ$) referred to the reaction $\text{HF}\,(g) + e^- = F^-(d) + 1/2 \text{H}_2(g)$, for which $E^\circ$ is defined as zero at all temperatures; (g) and (d) denote gaseous and dissolved species, respectively. The standard state for most solutes is the hypothetical unit mole fraction ideal solution in LiF-BeF\textsubscript{2} (66.7-33.3 mole %). The exceptions are LiF, BeF\textsubscript{2}, Be\textsuperscript{2+}, Li\textsuperscript{+}, and F\textsuperscript{-}; the activity of each of these species is defined as unity in the reference salt composition. With LiF-BeF\textsubscript{2} (66.7-33.3 mole %) as the standard state, the activity coefficients for solutes are unity, whereas $\gamma_{\text{LiF}} = 1.5$ and $\gamma_{\text{BeF}_2} = 3$.

The potential for a complete reaction is obtained by algebraically adding the necessary half-cell reaction potentials. For example, at 600°C the equilibrium of pure crystalline chromium metal with U\textsuperscript{4+} dissolved in LiF-BeF\textsubscript{2} (66.7-33.3 mole %) can be expressed as the algebraic sum of the two half-cell reactions:
The standard free energy change for reaction (3) is:

\[ \Delta G^o = -zFE^o = (-2.3RT) \log K \]

in which \( z \) is the number of faradays, \( F \) is the Faraday constant, \( R \) is the gas constant, \( T \) is the absolute temperature, and \( K \) is the equilibrium constant. For our purposes, we will assume that \( E^o \) values (and \( K \)'s derived from them) are the same in LiF-BeF\(_2\)-ThF\(_4\) (72-16-12 mole %), the composition of the MSBR carrier salt, as they are in LiF-BeF\(_2\) (66.7-33.3 mole %). All estimates included in this report were made at 600°C.

The electrochemical behavior of titanium species in molten fluoride salts has been studied voltammetrically by Manning.\(^5\) From this work, Manning\(^5\) estimates the following at 600°C:

\[
\begin{align*}
\text{Ti}^{3+} + \frac{3}{2} \text{Ni}^{2+} &= \text{Ti}^{2+} + \frac{3}{2} \text{Ni}_2^{2+} ; & E^o &= -1.8 \pm 0.1 \text{ V} \\
\text{Ti}^{4+} + \frac{1}{2} \text{Ni}^{2+} &= \text{Ti}^{3+} + \frac{1}{2} \text{Ni}_2^{2+} ; & E^o &= 0.2 \pm 0.05 \text{ V}
\end{align*}
\]

Combining Eq. (5) with

\[
\frac{3}{2} \text{Ni}^{2+} + 3 e^- = \frac{3}{2} \text{Ni}_2^{2+} ; & E^o &= 0.368 \text{ V} \]

yields

\[
\text{Ti}^{3+} + 3 e^- = \text{Ti}^{2+} ; & E^o &= -1.43 \pm 0.1 \text{ V} .
\]
Similarly, from Eqs. (6) and (7) we obtain:

\[ \text{Ti}^{3+} = \text{Ti}^{4+} + e^- \quad ; \quad E^o = -0.568 \pm 0.05 \text{ V} \quad . \quad (9) \]

Use of Eqs. (8) and (9), along with values of \( E^o \) for other appropriate half-cell reactions, allows estimation of the behavior of titanium in a molten-salt reactor system and in the associated chemical processing plant.

3. LEACHING OF TITANIUM FROM TITANIUM-MODIFIED HASTELLOY INTO MSBR FUEL SALT

The question of whether titanium will be leached from a modified Hastelloy into an MSBR fuel salt at a significant rate is a difficult one to answer since the overall rate of leaching would depend both on the rate at which titanium diffuses to the surface of the alloy and on the oxidizing power of the salt. Of the species present in the salt, \( \text{U}^{4+} \) is the most likely oxidant for titanium. The reaction would probably be:

\[ \text{Ti}_{(c)} + 3 \text{U}^{4+} = 3 \text{U}^{3+} + \text{Ti}^{3+} \quad ; \quad E^o = 0.286 \pm 0.1 \text{ V} \quad , \quad (10) \]

for which \( \log K = 4.94 \pm 1.7 \), since the reaction producing \( \text{Ti}^{4+} \), given below, is thermodynamically much less favorable:

\[ \text{Ti}_{(c)} + 4 \text{U}^{4+} = 4 \text{U}^{3+} + \text{Ti}^{4+} \quad ; \quad E^o = -0.282 \pm 0.15 \text{ V} \quad . \quad (11) \]

The value of \( \log K \) for reaction (11) is \(-6.5 \pm 3\). Comparison of the \( E^o \) for reaction (10) with that of reaction (3) confirms earlier predictions\(^6\) that titanium would be much more reactive than chromium to oxidants in the fuel salt. Despite the fact that the thermodynamic driving force for the leaching of titanium from a modified Hastelloy N is much greater than that for the leaching of chromium, it is nearly impossible to estimate the thermodynamic activity of titanium at the surface of the alloy. Not only will the concentration of titanium in the bulk alloy be less than one-third of that of chromium (about 2% vs 7%) but also the diffusion coefficient for titanium in Hastelloy N is about a factor of 10 lower.
than that for chromium. Thus, the titanium activity at the Hastelloy surface at a given time should be considerably lower than the chromium activity. Only direct experimentation can show whether the activity is low enough to offset the large driving force represented by the $E^\circ$ for reaction (10).

An experimental study conducted several years ago by DeVan and Evans provided evidence that titanium might be leached from Hastelloy N at a higher rate than chromium. In their studies, cast alloys of Ni--17% Mo containing up to 8 wt % of an additive were made into tubing from which thermal convection loops were fabricated. These loops were exposed to NaF-LiF-KF-UF$_4$ (11.2-45.3-41.0-2.5 mole %) for 500 and 1000 hr. The hot-zone temperature of each loop was 815°C, and the cold-zone temperature was 650°C. After each test, the salt was chemically analyzed for the additive. The corrosion susceptibilities (i.e., the amount leached) of the additives increased in the following order: iron < niobium < vanadium < chromium < tungsten < titanium < aluminum. With the exception of tungsten and niobium, the susceptibilities increased in the same order as did the thermodynamic stabilities of the fluoride compounds of the respective elements. It is significant to note that the rate of leaching was much higher during the 500-hr period than during the 1000-hr period. This result suggests that nearly steady-state conditions were established within the first 500 hr.

4. ESTIMATED BEHAVIOR OF TITANIUM DURING FLUORINATION OF MSBR FUEL SALT

In this and the ensuing sections, it will be assumed that titanium is present in measurable concentrations in MSBR fuel salt that enters the chemical processing plant. As noted in Sect. 1, the first chemical processing step is fluorination of the salt to remove uranium as UF$_6$. Fluorination should result in the quantitative oxidation of Ti$^{3+}$ to Ti$^{4+}$:

$$Ti^{3+} + \frac{1}{2} F_2(g) = Ti^{4+} + F^- ; \quad E^\circ = 2.30 \pm 0.1 \text{ V} , \quad (12)$$
for which \( \log K = 13 \pm 1 \). Reaction (12) can also be written as:

\[
\text{TiF}_3(\text{d}) + \frac{1}{2} \text{F}_2(\text{g}) = \text{TiF}_4(\text{d}) \quad (13)
\]

Since the boiling point of TiF\(_4\) is only about 284°C,\(^9\) it is probable that a significant fraction of the titanium would be removed from the salt as TiF\(_4\) during fluorination and would accompany evolved UF\(_6\) to the fuel reconstitution step. An example of the inherent tendency of TiF\(_4\) to volatilize from fluoride melts is provided by the experience of Manning et al.\(^{10}\) They found that, after K\(_2\)TiF\(_6\) was added to molten LiF-NaF-KF or LiF-BeF\(_2\)-ZrF\(_4\) solutions at 550°C, TiF\(_4\) volatilized from the melt and condensed on cooler parts of the system.

5. BEHAVIOR OF TITANIUM IN REDUCTIVE EXTRACTION PROCESSING

Any titanium not removed during fluorination will be present in the salt that enters the reductive extraction step\(^2,3\) for protactinium isolation. In this step, the salt is contacted with a liquid bismuth stream containing about 0.002 mole fraction each of lithium and thorium, protactinium, residual uranium from the fluorination step, zirconium, and some of the noble-metal fission products are transferred to the bismuth phase in this step.

The extraction into liquid bismuth of a solute M\(_n\)\(_F\)_n, present in low concentration in molten LiF-containing salts, can be expressed as the general reaction:

\[
\text{MF}_n(\text{d}) + n \text{Li}(\text{Bi}) = M(\text{Bi}) + n \text{LiF}(\text{d}) \quad , (14)
\]

in which (d) and (Bi) denote the salt and bismuth phases, respectively. This reaction is the sum of the half-reactions

\[
\text{M}^{n+} + n \text{e}^- = M \quad (15)
\]

\[
n \text{Li} = n \text{Li}^+ + n \text{e}^- \quad . (16)
\]
The standard potential for reaction (14), i.e. the algebraic sum of the potentials for reactions (15) and (16), is related to the equilibrium constant as follows:

$$K = \frac{a_M a^n_{LiF}}{a^m_{MF} a^n_{Li}} = e^{(nFE^0/RT)} \quad ,$$

(17)

in which $a$ is activity and the other symbols are as defined previously.

By letting $a = N \gamma$ (where $N$ is mole fraction and $\gamma$ is an activity coefficient) and by defining the distribution coefficient for a given element as $D_M = N_M / N_{MF}$, it was shown by Ferris\textsuperscript{11} that

$$\log K' = \log D_M - n \log D_{Li} = (nFE^0/2.3RT) + n \log \left( \frac{\gamma_{Li}}{\gamma_{LiF}} \right)$$

$$- \log \left( \frac{\gamma_{M}}{\gamma_{LiF}} \right) \quad .$$

(18)

With LiF-BeF\textsubscript{2} (66.7-33.3 mole \%) as the salt phase, Baes\textsuperscript{4} defined $\gamma_{LiF} = 1.5$ and $\gamma_{MF} = 1$. Thus,

$$\log K' = (nFE^0/2.3RT) + n \log \gamma_{Li} - n \log(1.5) - \log \gamma_{M} \quad ;$$

(19)

or, at 600°C,

$$\log K' = n(5.773)E^0 - 0.176n + n \log \gamma_{Li} - \log \gamma_{M} \quad .$$

(20)

In order to calculate $\log K'$ for a given element, we obviously need values of the activity coefficients $\gamma_{Li}$ and $\gamma_{M}$ that are referred to the pure metals as the standard state, in addition to the appropriate $E^0$ values. Values of $E^0$ for a large number of solutes are available from Baes;\textsuperscript{4} those for titanium species were estimated by Manning.\textsuperscript{5} Values of $\gamma_{Li}$ and $\gamma_{M}$ for several solutes were taken from the literature and were summarized by Ferris et al.\textsuperscript{12} These values of $\gamma_{Li}$ and $\gamma_{M}$ are for very dilute solutions of M in liquid bismuth. No information on the activity
coefficient of titanium in liquid bismuth could be found in the literature. Thus we will assume that \( \gamma_{Ti} \) is equal to \( \gamma_{Zr} \). Workers at Brookhaven National Laboratory obtained\(^1\) \( \gamma_{Zr} = 0.012 \) at 700°C. If we assume that the excess chemical potential \( \mu_{Zr} = (2.3RT) \log \gamma_{Zr} \) does not change throughout the temperature range 600-700°C, we can calculate \( \log \gamma_{Zr} = \log \gamma_{Ti} = -2.1 \pm 1 \) at 600°C.

From the above sources, we obtain \( E^\circ = 1.224 \pm 0.1 \) V at 600°C for the reaction

\[
\text{TiF}_3(d) + 3 \text{Li}(c) = 3 \text{LiF}(d) + \text{Ti}(c)
\]

and, using Eq. (20), estimate \( \log K_{Ti}^{3+} = 10.4 \pm 2 \) with LiF-BeF\(_2\) (66.7-33.3 mole \%) as the salt phase. Table 1 compares this value and the values for other selected solutes with values obtained experimentally using LiF-BeF\(_2\)-ThF\(_4\) (72-16-12 mole \%) as the salt phase. The values of \( \log K_{Zr} \) and \( \log K_U \) are those measured earlier by Ferris et al.\(^1\), whereas the value of \( \log K_{Ti} \) was determined in the course of the present work. Note that the values of \( \log K_M \) obtained for LiF-BeF\(_2\)-ThF\(_4\) (72-16-12 mole \%) are somewhat higher than those calculated for LiF-BeF\(_2\) (66.7-33.3 mole \%).

Table 1. Comparison of Values of \( \log K_M \) Calculated for LiF-BeF\(_2\) (66.7-33.3 mole \%) with Those Determined Experimentally at 600°C for LiF-BeF\(_2\)-ThF\(_4\) (72-16-12 mole \%)

<table>
<thead>
<tr>
<th>M</th>
<th>( n )</th>
<th>( \log \gamma_M )</th>
<th>( E^\circ ) (V)</th>
<th>Calculated for LiF-BeF(_2) (66.7-33.3 mole %)</th>
<th>Measured with LiF-BeF(_2)-ThF(_4) (72-16-12 mole %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>1</td>
<td>-4.13</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Zr</td>
<td>4</td>
<td>-2.1</td>
<td>1.226</td>
<td>13.2 \pm 1</td>
<td>14.7 \pm 0.3</td>
</tr>
<tr>
<td>U</td>
<td>3</td>
<td>-3.87</td>
<td>1.143</td>
<td>10.7 \pm 1</td>
<td>11.1 \pm 0.2</td>
</tr>
<tr>
<td>Ti</td>
<td>3</td>
<td>-2.1</td>
<td>1.224</td>
<td>10.4 \pm 2</td>
<td>13.6 \pm 0.4</td>
</tr>
</tbody>
</table>
The experiment to determine the value of log \( K_{Ti}^{'} \) was conducted using the general procedure outlined previously.\(^1\) This experiment was initiated by simultaneously hydrofluorinating, in a molybdenum crucible, LiF-BeF\(_2\)-ThF\(_4\)-CsF (71.7-15.9-12-0.4 mole \%) and bismuth containing dissolved titanium. This treatment resulted not only in the transfer of the titanium to the salt phase but also in the removal of oxide from the system. With the system at 600°C, thorium was added in increments to effect the reductive extraction of titanium from the salt into the bismuth phase. At least 24 hr was allowed for equilibration after each thorium addition before filtered samples of the respective phases were removed for analysis. The salt and metal samples were analyzed for titanium by a colorimetric method; the lithium concentration in the metal phase was determined by flame photometry.

Data from this experiment are summarized in Table 2, and a plot of log \( D_{Ti} \) vs log \( D_{Li} \) is shown in Fig. 1. The scatter in data points precludes determination of the value of \( n \). However, thermodynamic considerations (Sect. 6) strongly indicate that \( n \) should be 3 (and not 4). The value of log \( K_{Ti}^{'}3^+ \) = 13.6 ± 0.4 is the mean of the values calculated from each data point. This value is somewhat higher than the estimated value (Table 1); however, the agreement is good, considering the uncertainties in the thermodynamic quantities used. Furthermore, the experimentally determined value of log \( K_{Ti}^{'}3^+ \) is consistent with the results of an earlier experiment by Moulton et al., \(^1\) which indicated that log \( K_{Ti}^{'}3^+ \) should be greater than log \( K_{U}^{3+} \). In their experiment, it was found that titanium dissolved in bismuth did not effect detectable reduction of either \( U^{3+} \) or \( Pa^{4+} \) from LiF-BeF\(_2\)-ThF\(_4\) (72-16-12 mole \%) at 600 to 700°C.

During the chemical processing of MSBR fuel salt, it appears certain that titanium, if present in the salt entering the reductive extraction step, will be quantitatively extracted into the bismuth stream along with protactinium and other easily reduced species.

6. ESTIMATED BEHAVIOR OF TITANIUM DURING HYDROFLUORINATION

In the reference MSBR chemical processing method,\(^2\) the bismuth phase from the reductive extraction step used to isolate protactinium would be treated with an HF-H\(_2\) mixture in the presence of a salt phase
Table 2. Distribution Coefficients and Values of $\log K_{Ti^{3+}}$
Obtained at 600°C from Measurements of the Equilibrium
Distribution of Titanium Between Molten LiF-BeF$_2$-ThF$_4$-CsF
(71.7-15.9-12-0.4 mole %) and Liquid Bismuth Solutions

<table>
<thead>
<tr>
<th>Sample</th>
<th>$10^6 N_{Li}$</th>
<th>$10^5 D_{Li}$</th>
<th>D$_{Ti}$</th>
<th>$\log K_{Ti^{3+}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>8.73</td>
<td>1.218</td>
<td>0.038</td>
<td>13.3</td>
</tr>
<tr>
<td>6</td>
<td>16.0</td>
<td>2.226</td>
<td>0.435</td>
<td>13.6</td>
</tr>
<tr>
<td>7</td>
<td>18.7</td>
<td>2.604</td>
<td>0.695</td>
<td>13.6</td>
</tr>
<tr>
<td>8</td>
<td>16.6</td>
<td>2.310</td>
<td>1.06</td>
<td>13.9</td>
</tr>
<tr>
<td>9</td>
<td>27.4</td>
<td>3.822</td>
<td>1.31</td>
<td>13.4</td>
</tr>
<tr>
<td>10</td>
<td>20.8</td>
<td>2.898</td>
<td>1.76</td>
<td>13.8</td>
</tr>
<tr>
<td>11</td>
<td>20.5</td>
<td>2.856</td>
<td>2.33</td>
<td>14.0</td>
</tr>
<tr>
<td>12</td>
<td>33.7</td>
<td>4.704</td>
<td>3.88</td>
<td>13.6</td>
</tr>
<tr>
<td>13</td>
<td>65.0</td>
<td>9.072</td>
<td>5.94</td>
<td>12.9</td>
</tr>
<tr>
<td>14</td>
<td>28.3</td>
<td>3.948</td>
<td>15.7</td>
<td>14.4</td>
</tr>
</tbody>
</table>
Fig. 1. Equilibrium Distribution of Titanium Between Molten LiF-BeF$_2$-ThF$_4$-CsF (71.7-15.9-12-0.4 mole %) and Liquid Bismuth Solutions at 600°C.
to oxidize protactinium and other elements present in order to effect their dissolution in the salt phase. Since titanium could be one of the elements initially present in the bismuth phase, its behavior during hydrofluorination is of interest.

The reaction of primary interest is:

\[3 \text{HF}(g) + \text{Ti}(c) = \frac{3}{2} \text{H}_2(g) + \text{TiF}_3(d)\quad ; \quad E^\circ = 1.43 \pm 0.1 \text{ V}, \quad (22)\]

for which \(\log K = 25 \pm 2\) at 600°C. Despite the fact that the activity coefficient for titanium in liquid bismuth is of the order of \(10^{-2}\), thermodynamic considerations led us to expect titanium to be easily hydrofluorinated from a bismuth phase into a molten fluoride salt phase. This expectation was confirmed (at least under one set of conditions) in the initial phase of the experiment described in Sect. 5. In this experiment, bismuth and LiF-BeF₂-ThF₄-CsF (71.7-15.9-12-0.4 mole %), contained in a molybdenum crucible, were simultaneously hydrofluorinated at 600°C to remove oxides from the system. After sparging with purified argon, sufficient titanium metal was added to give a titanium concentration of 2500 wt ppm in the bismuth phase. Analysis of a sample of this phase confirmed that all the titanium was dissolved in the bismuth. The two-phase system was then sparged at 600°C for about 20 hr with HF-H₂ (50-50 mole %). Analyses of the respective phases showed that all of the titanium had been transferred to the salt phase during the hydrofluorination period.

Gaseous HF does not appear to be a sufficiently strong oxidant to convert Ti³⁺ to Ti⁴⁺; consequently, hydrofluorination of a bismuth-salt system should leave the titanium in the salt as TiF₃. This conclusion is based on the following estimate at 600°C:

\[\text{Ti}^{3+} + \text{HF}(g) = \frac{1}{2} \text{H}_2(g) + \text{Ti}^{4+} + \text{F}^-\quad ; \quad E^\circ = -0.59 \pm 0.05 \text{ V}, \quad (23)\]

for which \(\log K = -3.3 \pm 0.3\). Since the activity coefficients for the solutes are defined as unity, the expression for the equilibrium constant for reaction (23) will give:
Expressing the partial pressures in atmospheres, we find that, even with nearly pure HF as the gas phase, the equilibrium concentration of Ti\(^{4+}\) is extremely low as compared with the Ti\(^{3+}\) concentration:

\[
\left(\frac{N_{\text{Ti}^{4+}}}{N_{\text{Ti}^{3+}}}\right) = K\left(\frac{p_{\text{HF}}}{p_{H_2}}\right)^{\frac{1}{2}}.
\]  

(24)

<table>
<thead>
<tr>
<th>(p_{\text{HF}}/p_{H_2})</th>
<th>(N_{\text{Ti}^{4+}}/N_{\text{Ti}^{3+}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0004</td>
</tr>
<tr>
<td>10</td>
<td>0.002</td>
</tr>
<tr>
<td>100</td>
<td>0.005</td>
</tr>
</tbody>
</table>

7. BEHAVIOR OF TITANIUM IN OXIDE PRECIPITATION PROCESSES

Oxide precipitation is being studied as an alternative to fluorination--reductive extraction for isolating protactinium and subsequently removing uranium from MSBR fuel salt.\(^{16}\) Protactinium would be precipitated as \(\text{Pa}_2\text{O}_5\);\(^{17,18}\) consequently, the salt would have to be treated with an oxidant such as HF to convert \(\text{Pa}^{4+}\) to \(\text{Pa}^{5+}\) prior to the precipitation step. As shown in Sect. 6, HF is not a sufficiently strong oxidant to convert \(\text{Ti}^{3+}\) to \(\text{Ti}^{4+}\). No information could be found in the literature on the behavior of \(\text{Ti}^{3+}\) in molten fluoride salts containing dissolved oxide. Experimental work would be required to determine this behavior.

Some information on the apparent solubility of \(\text{TiO}_2\) in fluoride melts is available. Mailen\(^{19}\) had indications that \(\text{TiO}_2\) was less soluble than \(\text{UO}_2\) in LiF-BeF\(_2\)-ThF\(_4\) (72-16-12 mole %) at 600°C. Similarly, Bamberger and Baez\(^{20}\) equilibrated \(\text{TiO}_2\) with LiF-BeF\(_2\)-ThF\(_4\) (72-16-12 mole %) at 600°C. The equilibrium titanium concentration in the salt was about 40 wt ppm, which is lower than the solubility of \(\text{UO}_2\) in this salt.

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