RECONSTITUTION OF MSR FUEL BY REDUCING UF₆ GAS TO UF₄ IN A MOLTEN SALT

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RECONSTITUTION OF MSR FUEL BY REDUCING 
$\text{UF}_6$ GAS TO $\text{UF}_4$ IN A MOLTEN SALT 

by 

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RECONSTITUTION OF MSR FUEL BY REDUCING
\[ \text{UF}_6 \text{ GAS TO UF}_4 \text{ IN A MOLTEN SALT} \]

L. E. McNeese
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ABSTRACT

The direct reduction of \( \text{UF}_6 \) to \( \text{UF}_4 \) in a molten salt is proposed as a step in the purification of fuel salt from a molten salt reactor. This step would replace the conventional method of reduction in which \( \text{UF}_6 \) is reduced to \( \text{UF}_4 \) powder in a \( \text{H}_2-\text{F}_2 \) flame. Reduction of the \( \text{UF}_6 \) in a molten salt will result in a shorter and more direct process for fuel salt purification. The reduction is to be effected in two steps which consist of absorption of \( \text{UF}_6 \) into a molten salt containing \( \text{UF}_4 \) and of reduction of the resulting intermediate fluorides to \( \text{UF}_4 \) with hydrogen. Experimental data on the absorption step are presented and information concerning the reduction of intermediate fluorides is considered.

INTRODUCTION

One proposed processing step for Molten Salt Reactor (MSR) fuel is the reduction of purified \( \text{UF}_6 \) to \( \text{UF}_4 \), so that the \( \text{UF}_4 \) can be returned to barren, purified fuel salt.\(^{(1)}\) The usual method for reducing \( \text{UF}_6 \) to \( \text{UF}_4 \) is by use of \( \text{H}_2 \) in a \( \text{H}_2-\text{F}_2 \) flame:

\[ \text{UF}_6 + \text{H}_2 \rightarrow \text{UF}_4 + 2\text{HF}. \]

This reduction is carried out in a tall column where the \( \text{UF}_6 \) and \( \text{H}_2 \) are introduced into a \( \text{H}_2-\text{F}_2 \) flame and dry \( \text{UF}_4 \) powder (finely divided) is collected. It is a routine production operation and there is much available operating information.\(^{(2,3)}\) Such a process would not be desirable for remote operation. It involves a solids handling problem which routinely requires equipment access and process control is sometimes difficult.

It would be desirable to reduce the \( \text{UF}_6 \) to \( \text{UF}_4 \) in a molten salt environment, and thus circumvent the problems of solids handling and fuel make-up. Past experience of other workers has indicated the
feasibility of absorbing $\text{UF}_6$ into molten salt which contains $\text{UF}_4$ and reducing the absorbed $\text{UF}_6$ to $\text{UF}_4$ by sparging with $\text{H}_2$. Kirslis found that corrosion was not severe in absorption of $\text{F}_2$ by molten salt containing $\text{U}$ until the intermediate fluoride of uranium had a fluoride content greater than $\text{UF}_5$. Long found that $\text{H}_2$ would reduce $\text{UF}_4$ to $\text{UF}_3$ in a molten salt and Blood has reduced various metal fluorides in molten salts by use of $\text{H}_2$.

This report presents a proposed continuous processing method for the reduction of $\text{UF}_6$ to $\text{UF}_4$ in a molten salt environment by absorption of $\text{UF}_6$ in the salt and reduction with $\text{H}_2$. The results from a scouting test are analyzed to indicate process feasibility.

**PROPOSED PROCESS AND APPLICATION TO MSR PROCESSING**

The current scheme for processing Molten Salt Reactor (MSR) fuel consists of removal of uranium as $\text{UF}_6$ and volatile fission products (FP) from the salt by fluorination, separation of refractory FP from the salt by distillation, and recombination of the volatilized uranium and purified barren salt for return to the MSR (Fig. 1). During the fluorination step, both uranium and volatile fission products are removed from the salt by the reactions:

$$\text{UF}_4 \text{(in molten salt)} + \text{F}_2 \rightarrow \text{UF}_6,$$

$$\text{FP} \text{(in molten salt)} + \text{F}_2 \rightarrow \text{volatile FP fluorides}.$$  

The $\text{UF}_6$ and volatile FP fluorides will be separated by sorption techniques and the uranium will then be reintroduced as $\text{UF}_4$ to the purified barren salt to form the MSR fuel. Thus, there must be a method for reducing $\text{UF}_6$ to $\text{UF}_4$.

Since the end result of the $\text{UF}_6$ reduction will be a solution of $\text{UF}_4$ in molten salt rather than $\text{UF}_4$ as a dry powder, it is attractive to carry on the reduction in a molten salt environment and preferably in the purified barren salt. To achieve this requirement, $\text{UF}_6$ can be contacted with a molten fluoride salt containing some uranium as $\text{UF}_4$ where it will be absorbed by reaction with the $\text{UF}_4$ to form an equivalent intermediate fluoride of uranium, such as $\text{UF}_5$, in the salt:
Fig. 1. MSR Fuel Processing with Conventional UF₆ Reduction.
This intermediate fluoride will then be reduced to UF₄ in the salt by means of H₂:

\[ \text{UF}_4(\text{salt}) + \text{UF}_6 \rightarrow \text{UF}_5(\text{salt}) \]

Such a process could be carried out continuously in a column in which the barren salt and UF₆ are introduced at the bottom of the column along with salt containing UF₄ which is recycled from the top of the column (Fig. 2). As the salt and UF₆ progress up the column, the UF₆ will be absorbed in the salt and subsequently reduced to UF₄ as it passes into the H₂ reduction section. The column off-gas will be a mixture of H₂ and HF and a side stream of the overhead molten salt will be ready for return to the nuclear reactor core after filtration since the HF and H₂ sparge usually given make-up salt will have been achieved in the reduction column. When this reduction step is incorporated into the flowsheet, the resulting process is more direct and shorter (Fig. 3).

Initial tests (next sect.) indicate that the absorption step is very rapid, however, it will be desirable to keep the fluoride content of the intermediate fluoride below that equivalent to UF₅ in order to minimize corrosion. The rate of the hydrogen reduction reaction is not known, although the limited data available looks favorable. In studying the reduction of UF₄ to UF₃ in molten salt by H₂ by the reaction:

\[ \text{UF}_4(\text{salt}) + \frac{1}{2}\text{H}_2 \rightarrow \text{UF}_3(\text{salt}) + \text{HF} \]

Long (5) observed that equilibrium was established between a H₂-HF stream and molten salt containing uranium fluorides after the gas bubbles had risen a few inches through the salt. His data also indicate only 1% reduction of UF₄ to UF₃ by a gas stream containing 1% HF in H₂ at a pressure of 1 atm at 600°C.

EXPERIMENTAL EQUIPMENT AND PROCEDURE

The experimental equipment was assembled from existing equipment available as a result of work in support of the Molten Salt Fluoride Volatility Process. Means were provided for contacting UF₄, dissolved in molten salt, with UF₆ in the first step of the reduction process and
Fig. 2. Continuous Reduction of UF₆ by H₂ in a Molten Salt.
Fig. 3. MSR Fuel Processing with Continuous UF₆ Reduction in Molten Salt.
for contacting the resulting uranium fluoride with hydrogen in the second step. Details of the experimental equipment and of the procedure for testing the reduction process are discussed in the following sections.

EQUIPMENT AND MATERIALS

The reduction test was carried out in the vessel shown schematically in Fig. 4. The vessel was constructed from 4-in.-diam Sch 40 nickel pipe and was 26 inches in length. A 3/8-in. nickel inlet line was located in the center of the vessel and terminated 1/4-in. from the bottom of the vessel. A 3/4-in. fitting on the top flange allowed the insertion of a cold, 3/8-in. nickel rod which was used for sampling the salt. The vessel was heated by two nichrome wire resistance furnaces.

A flow diagram for the equipment used in the test is shown in Fig. 5. The equipment included a UF₆ metering system, a hydrogen metering system, means for purging both the UF₆ system and H₂ system with N₂, the reduction vessel, and a NaF trap downstream from the vessel for absorbing UF₆ or HF from the off-gas of the reduction vessel.

The salt charge was prepared by mixing LiF, ZrF₄, and UF₄. The LiF was reagent grade and contained <0.23 wt % impurities (mostly NaF). The zirconium content of the ZrF₄ was found by analysis to be 54.7% which compares favorably with the stoichiometrical value of 54.6%; the uranium content of the UF₄ was found to be 76.9% which also compares favorably with the stoichiometrical value of 75.8%; and the uranium hexafluoride contained less than 200 ppm impurities. Hydrogen that was used contained less than 0.005 vol fraction impurities.

EXPERIMENTAL PROCEDURE

A salt charge consisting of 5320 g ZrF₄, 863 g LiF, and 61.8 g UF₄ (0.197 gmole UF₄) was placed in the reduction vessel and heated to 600°C. At this temperature the depth of molten salt was 12 inches. The salt mixture had a UF₄ concentration of 1 wt % and a melting point of approximately 510°C. A salt sample (UR-1) was taken by insertion of a cold 3/8-in.-diam nickel rod into the molten salt. A UF₆ flow of 1.5 g/min was then fed through the by-pass around the reduction vessel for 16
Fig. 4. Vessel Used for Reduction of UF₆ to UF₄ in a Molten Salt.
Fig. 5. Flow Diagram for Equipment Used in Reduction of UF₆ to UF₄ in a Molten Salt.
minutes in order to free the system of N₂. The UF₆ flow was then diverted into the dip line of the reduction vessel and was continued for 25 minutes. At this time, the UF₆ flow was stopped and the system was purged with N₂ for 5 minutes after which a salt sample (UR-2) was taken. The quantity of UF₆ fed to the system during this step was 38.2 g (0.108 gmoles). The salt was then purged with H₂ at the rate of 95 st. cm³/min for 25 minutes. A total of 0.107 gmoles H₂ was added during this step. After the system was purged with N₂ for 10 min, a salt sample (UR-3) was taken. The system was then allowed to cool down overnight. The following day the system was heated to 600°C and a salt sample was taken (UR-4). The salt was then sparged with H₂ at a rate of 85 st. cm³/min for 20 min during which a total of 0.076 gmoles H₂ was fed to the system. The system was then purged with N₂ for 10 min and a salt sample (UR-5) was taken. The system was then cooled and the test concluded.

DISCUSSION OF EXPERIMENTAL RESULTS

Two questions related to the experimental work are of primary interest. These are (1) the fraction of UF₆ which was absorbed by the molten salt and (2) the valence of the uranium in the resulting mixture. Also, of interest are the concentration level of trace impurities such as Ni and O₂.

The composition of the various salt samples is given in Table 1. The uranium concentration in the initial salt (UR-1) was found by analysis to be 0.666 wt % which is 11.2% lower than the calculated uranium concentration of 0.75 wt %. The calculated uranium concentration for complete absorption of the UF₆ bubbled through the salt during the 25 min addition period was 1.15 wt %. The average uranium concentration after the UF₆ addition was found by analysis to be 1.07 wt % which is 7% lower than the calculated value. It was concluded that, within the accuracy of the experimental data, complete absorption of the UF₆ had occurred.

It is believed that the addition of UF₆ to a salt containing UF₄ results in the formation of dissolved fluorides of uranium with a valence intermediate between +4 and +6. This behavior is indicated by
Table 1. Composition of Salt Samples Taken During Uranium Reduction Experiment

<table>
<thead>
<tr>
<th>Sample</th>
<th>U wt %</th>
<th>U^{+4} wt %</th>
<th>U^{+6} wt %</th>
<th>Zr wt %</th>
<th>Li wt %</th>
<th>Ni ppm</th>
<th>O_2 ppm</th>
<th>Remarks</th>
</tr>
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<tr>
<td>UR-1</td>
<td>0.666</td>
<td></td>
<td></td>
<td>46.65</td>
<td>3.64</td>
<td>874</td>
<td>4045</td>
<td>Initial salt melt</td>
</tr>
<tr>
<td>UR-2</td>
<td>1.05</td>
<td>.954</td>
<td>&lt; .01</td>
<td></td>
<td></td>
<td>933</td>
<td>4695</td>
<td>After UF_6 addition</td>
</tr>
<tr>
<td>UR-3</td>
<td>1.01</td>
<td>1.074</td>
<td>&lt; .01</td>
<td></td>
<td></td>
<td>1002</td>
<td>4940</td>
<td>After 1st H_2 addition</td>
</tr>
<tr>
<td>UR-4</td>
<td>1.07</td>
<td>0.990</td>
<td>&lt; .01</td>
<td></td>
<td></td>
<td>1007</td>
<td>3050</td>
<td>After cooling overnight and remelting</td>
</tr>
<tr>
<td>UR-5</td>
<td>1.14</td>
<td>0.922</td>
<td>&lt; .01</td>
<td></td>
<td></td>
<td>862</td>
<td>3245</td>
<td>After 2nd H_2 sparge</td>
</tr>
</tbody>
</table>
the fact that quantities of \( \text{F}_2 \) sufficient for the formation of \( \text{UF}_5 \) can be absorbed by molten salt containing \( \text{UF}_4 \) without the evolution of \( \text{UF}_6 \). A similar behavior is also noted in reactions between \( \text{UF}_4 \) and \( \text{UF}_6 \) in the absence of molten salt to yield intermediate fluorides such as \( \text{U}_6\text{F}_{17} \). It is assumed that uranium present in a molten salt as an intermediate fluoride will appear as \( \text{U}^{4+} \) and \( \text{U}^{6+} \) after dissolution in phosphoric acid in preparation for analysis. (7)

The concentration of \( \text{U}^{6+} \) in the sample after \( \text{UF}_6 \) addition was below the limit of detection of 0.01 wt % and the \( \text{U}^{4+} \) concentration was 0.95 wt %. (Table 1). After the first and second hydrogen sparges, the \( \text{U}^{4+} \) concentration was found to be 1.07 wt % and 0.922 wt %, respectively. Although differences in \( \text{U}^{4+} \) concentration were observed, it is felt that these are within the limits of analytical error and are not meaningful.

Reduction of the \( \text{U}^{6+} \) to \( \text{U}^{4+} \) probably occurred during the addition of \( \text{UF}_6 \) by reaction of the intermediate fluoride with nickel from the vessel wall or with reduced fluorides of nickel, chromium, or iron initially present in the salt. The nickel concentration increased from 874 ppm initially to approximately 1000 ppm during the \( \text{UF}_6 \) addition and the initial hydrogen treatment. This increase in Ni concentration of approximately 130 ppm is sufficient for the reduction of approximately 15% of the \( \text{UF}_6 \) added.

The concentration of oxide in the salt during the test was approximately 4000 ppm.

In the absence of conclusive information on the reduction of uranium fluorides intermediate between \( \text{UF}_4 \) and \( \text{UF}_6 \), reference can be made to data on materials having similar characteristics. The equilibrium between \( \text{UF}_4 \) and \( \text{UF}_3 \) in molten mixtures of LiF and BeF$_2$ has been studied by Long (5) by observing the concentration of HF in \( \text{H}_2 \) in equilibrium with the salt. Equilibrium was observed to have been established during the rise of \( \text{H}_2 \) bubbles through a few inches of molten salt. The data indicated that reduction of \( \text{UF}_4 \) to \( \text{UF}_3 \) could be achieved over a wide range of operating conditions.

The reduction of NiF$_2$, CrF$_2$, FeF$_2$ to the metals by hydrogen is utilized for removal of these contaminants from molten salt. It was also observed that molten salts containing uranium fluoride with a valence \( > 5 \)
are quite corrosive toward nickel metal. Since the reactions:

\[ 2\text{UF}_5 + \text{Ni} \rightarrow 2\text{UF}_4 + \text{NiF}_2 \]
\[ \text{NiF}_2 + \text{H}_2 \rightarrow \text{Ni} + 2\text{HF} \]

are known to occur in molten salts, it is felt that the reaction:

\[ \text{UF}_5 + \frac{1}{2}\text{H}_2 \rightarrow \text{UF}_4 + \text{HF} \]

will also occur.

CONCLUSIONS AND RECOMMENDATIONS

The following conclusions have been made on the basis of the material presented in the preceding sections.

1. Uranium hexafluoride is absorbed rapidly by molten fluoride salt containing approx. 1 wt % UF\(_4\) at 600°C. It is believed that the absorption results in the formation of an intermediate fluoride of uranium.

2. It is likely that reduction of the intermediate fluoride to UF\(_4\) can be accomplished by contact with hydrogen.

3. Incorporation of the proposed reduction step into the flowsheet for MSR processing results in a shorter and more direct process.

It is recommended that experimental work on the reduction of UF\(_6\) to UF\(_4\) in a molten salt environment be continued with emphasis in the following areas:

1. rate of reduction of intermediate uranium fluoride to UF\(_4\) by hydrogen.

2. corrosivity of molten fluoride melts containing intermediate uranium fluorides.

3. adaptation of the reduction process to continuous operation.
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