Conversion of Uranium Oxide into Nitrate with Nitrogen Dioxide*

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Abstract
In order to decrease the amount of aqueous liquid waste discharged from nuclear fuel reprocessing, the conversion of uranium dioxide into its nitrate using liquefied nitrogen dioxide was studied. Uranium dioxide powder was immersed in liquefied nitrogen dioxide at 313 K after a pretreatment by the oxidation of the uranium dioxide with nitrogen dioxide and air at 523 K. Seventy-nine % of the uranium dioxide, whose initial feed amount was 0.3 g, was converted into a water soluble compound. Based on an XRD analysis of the compound, uranyl nitrate trihydrate (UO$_2$(NO$_3$)$_3$·3H$_2$O) was confirmed.

Key words: Uranium Oxide, Nitrate, Nitrogen Dioxide, Spent Nuclear Fuel, Reprocessing

1. Introduction

Reprocessing of spent nuclear fuels is one of the key processes in the nuclear fuel cycle. There is an established reprocessing method, called the PUREX process. This method consists of two main steps: 1) the dissolution of uranium and plutonium contained in the fuels using a nitric acid solution, and then 2) extraction of the dissolved actinides with an n-dodecane solution containing tri-n-butylphosphate as the complexing agent. The reprocessing plants employing this method have been in commercial operation around the world, but further development is required to reduce the cost and minimize the waste for the next generation reprocessing.

To decrease the amount of waste discharged from the reprocessing, we propose a reduction of the aqueous solution by replacement of the nitric acid solution with nitrogen dioxide. Nitrogen dioxide is easy to liquefy or gasify by a small change in temperature at atmospheric pressure since its boiling point is 294 K. Liquefied nitrogen dioxide has a higher concentration than its aqueous solution or gaseous state. It is known that liquefied nitrogen dioxide is ionized as follows (1):

\[
2\text{NO}_2 \Leftrightarrow \text{N}_2\text{O}_4 \quad \text{(1)}
\]

\[
\text{N}_2\text{O}_4 \Leftrightarrow \text{NO}^+ + \text{NO}_3^- \quad \text{(2)}
\]

Liquefied nitrogen dioxide might work both as a reactant and reaction medium to convert the actinides into nitrates. Moreover, it could be easily separated from the generated nitrate by increasing the temperature or decreasing the pressure after the conversion. After the separation by depressurization or warming, the nitrogen dioxide can be reused in the conversion process by pressurizing or cooling. If the actinides in the fuels could be converted into nitrates, they can be recovered by crystallization or extraction with supercritical carbon dioxide. Therefore, this will lead to a substantial reduction in the
As a fundamental study, to confirm the possible conversion into nitrates using nitrogen dioxide, we immersed uranium dioxide powder in liquefied nitrogen dioxide in an autoclave at 313 and 353 K, and then its conversion into the nitrate was estimated by the solubility of the product in water. The same conversion procedure was also examined for uranium oxide after the oxidation treatment.

2. Experimental

2.1 Chemicals

Liquefied nitrogen dioxide whose purity was greater than 99.9% was purchased from Sumitomo Seika Chemicals Co., Ltd. The uranium dioxide powder was prepared by grinding pellets of uranium dioxide in a mill (Fritsch, P-7). The grain size of the powder was found to be 5-10 µm by microscopic observation.

2.2 Nitrate Conversion Procedure

Figure 1 shows the experimental apparatus used for the nitration conversion experiment. A 0.30 g sample of uranium dioxide powder was placed in a high pressure vessel of autoclave (TPR-6, Taiatsu Techno Co., Japan) whose volume was 120 cm³.

2.1.1 Nitrate Conversion Procedure with Non-pretreatment of Oxidation

After elevating the autoclave temperature to 313 or 353 K by a heater, a 10 cm³ volume of liquefied nitrogen dioxide at 3.0 MPa was introduced into the autoclave through a syringe pump (260D, Isco, Inc., U.S.A.). The uranium dioxide and nitrogen dioxide was well-mixed by a stirrer for 1 hr.

2.2.2 Nitrate Conversion Procedure with Pretreatment of Oxidation

The uranium dioxide powder was first oxidized by air and a small amount of nitrogen dioxide. It is known that the air oxidation of uranium dioxide does not proceed beyond U₃O₈. However, uranium tetraoxide is known to be formed from uranium dioxide in a 1% nitrogen dioxide-air mixture at 523 K. In this study, the uranium dioxide was oxidized in the autoclave containing air and nitrogen dioxide, whose volume was 0.5 cm³ at
3 MPa, by heating at 523 K prior to the conversion procedure mentioned above.

2.3 Analyses

The product was obtained from the autoclave after cooling and purging with argon gas, then subjected to a solubility test in water and XRD (Mini Flex, Rigaku, Japan) analyses. The solubility test was carried out as follows: the product was dissolved to a certain amount of pure water, and uranium concentration in the water was measured by ICP-AES (ICPS-7000, Shimazu, Japan). The conversion was defined as follows:

\[
\text{(Conversion, \%) = \frac{\text{Amount of uranium dissolved in water, g}}{\text{Initial amount of uranium, g}}} \times 100
\]

(3)

3. Results and Discussion

3.1 Nitrate Conversion with No Pretreatment by Oxidation

Both uranium products obtained from the uranium dioxide powders in contact with nitrogen dioxide at 313 and 353 K were a dark brown-black color. There seemed to be no change in the color of the uranium compound before and after the immersion in nitrogen dioxide; i.e., it was considered that there was no chemical change. Table 1 shows the conversion into the nitrate estimated by the solubility test in water. Although no significant change in color was observed in the product, approximately 30% of the uranium was dissolved in water. This might be reasonable if the nitrogen dioxide remained with the uranium oxide powder, and formed nitric acid in the water during the solubility test. Based on these results, the conversion of uranium dioxide into its nitrate seemed to be difficult by only the immersion in nitrogen dioxide. The uranium in uranyle nitrate is hexavalent, but that in uranium dioxide is tetravalent. The oxidation treatment might be effective for the conversion of uranium dioxide using nitrogen dioxide.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>(\text{UO}_2, \text{ g})</th>
<th>(\text{NO}_2, \text{ cm}^3)</th>
<th>Temp., K</th>
<th>Conversion, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.3</td>
<td>20</td>
<td>313</td>
<td>31</td>
</tr>
<tr>
<td>2</td>
<td>0.3</td>
<td>20</td>
<td>353</td>
<td>34</td>
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</table>

3.2 Nitrate Conversion by Oxidation Pretreatment

By immersion in nitrogen dioxide at 313 K, 79% of the uranium dioxide converted into the water soluble compound (Run 3). The color of uranium compound changed from dark brown-black to yellow-brown. The XRD analysis was conducted using the sample obtained from Run 3 at 0.5 and 1.5 hr after recovery from the autoclave. The results are shown in Fig. 2. In the XRD pattern of the product just recovered from the reactor, there were many peaks. They were different from those of the reactant, uranium dioxide (c), and the oxidized one, uranium tetraoxide (d). By comparing these patterns at 0.5 and 1.5 hr ((a) and (b)), it was found that some of the peaks, which were indicated by arrows, disappeared, while others became sharper with time. For some of the latter ones, it was confirmed that they were the peaks of uranyl nitrate trihydrate (\(\text{UO}_2(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}\)) based on the PDF data (e). It was found that uranium dioxide was converted into its nitrate by immersion in liquefied nitrogen dioxide combined with the oxidation pretreatment.
4. Conclusion

By combining the oxidation pretreatment by heating uranium dioxide with nitrogen dioxide and air at 523 K, 79 % of the uranium dioxide was converted into a water soluble compound after immersion in liquefied nitrogen dioxide at 313 K. Based on the XRD analysis, the peaks of uranyl nitrate trihydrate \((\text{UO}_2\text{(NO}_3\text{)}_2\cdot3\text{H}_2\text{O})\) were detected in the product. It was found that the conversion of uranium dioxide into the nitrate using nitrogen dioxide combining with the oxidation treatment was possible.

References