VI. 1. Distribution Behavior of Technetium to Liquid, Solid Phases and onto Metal Surfaces after Supercritical Water Treatment


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Introduction

Above 647 K and 22 MPa, water is a supercritical fluid, which possesses unique solvating and transport properties compared to liquids or gases. Supercritical water (SCW), which shows liquid-like density and gas-like diffusivity, has the ability not only to decompose materials soluble in liquid water but also to promote particular reaction. Gasification of organic materials in the supercritical water using RuO₂ as a catalyst has been developed¹). We applied this gasification method to the decomposition of bulky non-flammable organic materials generated in nuclear power plants, classified as low-level radioactive wastes (LLW)²,³). Radioactive iron, cobalt, cesium, iodine, strontium attached to the organic materials were found to be recovered in the solid phase with or without precipitation reagents and showed no transfer to gas phase.

Appreciable yield of 6.2% in the thermal neutron fission leads to the formation of technetium-99 with long-lived half-life (t₁/₂= 2.1x10⁵ y). The LLW also contains the technetium, which is known to have oxidation states from 0 to VII and shows variety of chemical properties including sublimation of Tc₂O₇ above 584 K⁴). For the decomposition of LLW by the SCW method, the distribution behavior of technetium is to be clarified. In this study, distribution of technetium after supercritical water reaction among solid, liquid and gas phases were determined. The distribution behavior was discussed concerning with differences (i) between SCW reaction with ruthenium oxide (RuO₂) and with hydrogen peroxide (H₂O₂), (ii) with or without its carrier and (iii) between technetium and alkaline metal. Adsorption of technetium on surface of various metal materials, which are
candidates for reactor materials, during the SCW reactions were also discussed.

**Experimental**

Technetium-95m was produced by $^{93}\text{Nb}(\alpha,2n)^{95m}\text{Tc}$ reaction at Cyclotron and Radioisotope Center of Tohoku University and purified by sublimation, followed by dissolution in water to prepare HTcO$_4$. Technetium-99 was used as a carrier. Ruthenium(IV) oxide (purity: >99.9 %) and granular polyethylene (medium density) were purchased from Kishida Chemical Co., Japan and Aldrich Chemical Company, Inc., U.S.A., respectively, and used without further treatment.

A batchwise reactor with 10 mL capacity made of Hastelloy C-22 was used. A small portion of an aqueous solution including about 1 mg of technetium, three pieces of metal plates (SUS304, Hastelloy C-22, Inconel 625, 5x10x1 mm size, polished with #2000), water and either of oxidant (H$_2$O$_2$) or reductant (RuO$_2$ and 150 mg of granular polyethylene) were loaded into the reactor and the supercritical reaction under the condition of "723 K-43 MPa-30 min." was carried out. After cooled off to room temperature, distribution coefficient was determined by measurement of $\gamma$-ray spectra of three phases separated (solid, liquid and gas) and metal pieces. Cesium solution with a tracer of $^{137}\text{Cs}$ was used for a reference of the behavior.

The radioactivity of $^{95m}\text{Tc}$ was determined from the areas of peak at 204.11 keV by using a $\gamma$-ray spectrometer (GEM-28185-P, ORTEC Inc., USA). The distribution of their radioactivity in solid, liquid and gas phases was determined as given by

$$D_{\text{phase}} = \frac{A_{\text{phase}}}{A_T}$$

where $D_{\text{phase}}$ designates the distribution ratio, $A_T$ and $A_{\text{phase}}$ are the radioactivity of initially loaded and the radioactivity of each phase after the supercritical water reaction respectively, and the subscription phase is "sol", "liq" or "gas", referring to the solid phase, the liquid phase and the gas phase, respectively.

**Results and discussion**

*Distribution of technetium with or without carrier and/or precipitating agent*

Amount of technetium found in the solid, liquid and gas phases recovered after supercritical water reaction are indicated with the distribution ratio $D$ in Table 1. Both in H$_2$O$_2$ and RuO$_2$ methods, technetium does not transfer to gas phase in spite of its low
boiling point but limited to solid phase. This distribution of technetium was not affected by addition of its carrier of $^{99}$Tc but shifted to solid phase by addition of Fe(OH)$_3$.

It should be noted that only around 20% of technetium was found in a recovery after SCW-RuO$_2$ reaction. By measuring $\gamma$-rays from inside of the hastelloy reactor, appreciable quantity of technetium was found, in spite of that inside wall were rinsed many times with water after SCW-RuO$_2$ reaction. On the other hand, fairly amount of technetium was recovered after SCW-H$_2$O$_2$ reaction.

**Distribution of technetium onto metal surfaces**

It is worthwhile to note that technetium shows a large tendency to be adsorbed onto metal surfaces and the adsorbed technetium should be removed by repeating washing by H$_2$O$_2$ method for the next reaction. In order to elucidate the adsorption on metal surfaces, supercritical water reactions were carried out with three types of metal materials (Table 2). Moreover, the results for technetium was compared with those for cesium, which is a member of alkaline metal ion whose character is simple ionic. Technetium was found to adsorbed onto various metal materials. Washing by SCW with H$_2$O$_2$ for 5 times is required to remove the adsorbed technetium from the reactor.

In RuO$_2$ method, technetium may be reduced to colloidal or polymeric TcO$_2$ or TcO(OH)$_2$ which has a great affinity to metal surface$^{5,6}$. The adsorbed TcO$_2$ can be oxidized to TcO$_4^-$ by H$_2$O$_2$ and dissolved in solution. Effect of supercritical water with RuO$_2$ on technetium chemistry requires further investigation.

**Conclusion**

Distribution of technetium after supercritical water reaction was investigated. Technetium does not transfer to gas phase in spite of its low b.p. but distributes to solid phase both in SCW with H$_2$O$_2$ and RuO$_2$ reactions. Furthermore, technetium was found to adsorbed on to various metal materials. Washing by SCW with H$_2$O$_2$ for 5 times is required to remove adsorbed technetium from reactor. The result of adsorption of technetium by SCW with RuO$_2$ and the dissolution by SCW with H$_2$O$_2$ suggested that the reductive atmosphere of SCW with RuO$_2$ may result in the formation of colloidal or polymeric TcO$_2$ or TcO(OH)$_2$ which have a great affinity to metal surface. The supercritical water process can be used for decomposition of non-flammable plastics of LLW with limiting technetium to solid and onto metal surfaces.

**References**

Table 1. Distribution of technetium to three phases after supercritical water treatment.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Carrier</th>
<th>Tc-99 /mg</th>
<th>Fe(OH)₃ /mg</th>
<th>10² D(sol) ‡‡</th>
<th>10² D(liq) ‡‡</th>
<th>10² D(gas) ‡</th>
</tr>
</thead>
<tbody>
<tr>
<td>RuO₂ method</td>
<td>---</td>
<td>---</td>
<td>23.75</td>
<td>0.71 (2.89)</td>
<td>0.00</td>
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<tr>
<td></td>
<td>0.5</td>
<td>---</td>
<td>22.86</td>
<td>0.64 (2.74)</td>
<td>0.00</td>
<td></td>
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<td></td>
<td>0.5</td>
<td>13</td>
<td>17.30</td>
<td>0.12 (0.70)</td>
<td>0.00</td>
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<tr>
<td>H₂O₂ method</td>
<td>---</td>
<td>---</td>
<td>86.54</td>
<td>0.63 (0.72)</td>
<td>0.00</td>
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</tr>
<tr>
<td></td>
<td>0.5</td>
<td>---</td>
<td>41.98</td>
<td>0.90 (2.09)</td>
<td>0.00</td>
<td></td>
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</tbody>
</table>

‡D(phase) were determined according to eq. (1).
†Values in parentheses are calculated by D(phase)/(D(sol) + D(liq) + D(gas))
Table 2. Distribution of Tc and Cs to each site after supercritical water reactions of non-flammable plastics

<table>
<thead>
<tr>
<th>Contents</th>
<th>No reaction ‡</th>
<th>RuO₂ method</th>
<th>H₂O₂ method</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cs-137</td>
<td>Tc-95m</td>
<td>Cs-137</td>
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<tr>
<td>Solid phase</td>
<td>---†</td>
<td>---†</td>
<td>5.8</td>
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<tr>
<td>Liquid phase</td>
<td>83.7</td>
<td>85.5</td>
<td>64.5</td>
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<td>Gas phase</td>
<td>---†</td>
<td>---†</td>
<td>0</td>
</tr>
<tr>
<td>SUS304</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Hastelloy</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Inconel</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1st reaction</td>
<td>3.1</td>
<td>4</td>
<td>6.9</td>
</tr>
<tr>
<td>2nd reaction</td>
<td>1.3</td>
<td>1.6</td>
<td>5.9</td>
</tr>
<tr>
<td>3rd reaction</td>
<td>---</td>
<td>---</td>
<td>2.9</td>
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<tr>
<td>4th reaction</td>
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<td>1.6</td>
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<tr>
<td>5th reaction</td>
<td>---</td>
<td>---</td>
<td>0.8</td>
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<tr>
<td>Total amount recovered</td>
<td>88.1</td>
<td>91.1</td>
<td>88.4</td>
</tr>
</tbody>
</table>

‡Distributions are indicated as percent to the amount initially loaded. †Solutions and specimens were left in the reactor for two hours without supercritical water reaction. ††No solid and gas phases owing to no reaction.