

Behavior of Technetium in Supercritical Water: Distribution to Liquid, Solid Phases and onto Metal Surfaces

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The distributions of technetium among solid, liquid and gas phases in supercritical water reactions were investigated for the decomposition process of nonflammable plastic materials contaminated with technetium. In addition to supercritical water (SCW) methods with or without H₂O₂ which have been investigated extensively for decomposition method for the plastics, SCW with RuO₂, developed by us, characteristic of reductive reaction was investigated for technetium distributions. The distributions of technetium were determined by using ^{95m}Tc tracer with or without its carrier ⁹⁹Tc. The gases produced during the decomposition of the organic material contain no radioactivity under all conditions in this study. Also, technetium shows a tendency to transfer to solid phase but not to liquid phase in SCW with RuO₂. These results indicate that this process is suggested as a predominant candidate for the treatment of nonflammable organic materials in low-level radioactive wastes (LLW).

1. 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 dissolve materials soluble in liquid water but also to promote particular reaction. Using the supercritical water, gasification of organic materials using RuO₂ as a catalyst has been developed.¹ 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 ($t_{1/2} = 2.1 \times 10^5$ 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 K.⁴ 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. In addition, adsorption of technetium on surface of various metal materials, which are candidates for reactor materials, during the SCW reactions were discussed.

2. Experimental

Technetium-95m was produced by ⁹³Nb(α, n)^{95m}Tc reaction at Cyclotron and Radioisotope Center of Tohoku University and purified by sublimation, followed by dissolution in water to prepare HTcO₄. NH₄⁹⁹TcO₄, possessed by Faculty of Science, Tohoku University, 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 C22, Inconel 625, 5 × 10 × 1 mm size, polished with #2000), water and either of oxidant (H₂O₂) or reductant (RuO₂ 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 γ -ray spectra of three phases separated (solid, liquid and gas) and metal pieces. Cesium solution with a tracer of ¹³⁷Cs was used for a reference of the behavior.

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

$$D_{\text{phase}} = \frac{A_{\text{phase}}}{A_T}, \quad (1)$$

where D_{phase} designates the distribution ratio, A_T and A_{phase} are radioactivity of sample before the supercritical-water reaction and radioactivity of each phase respectively, and the subscription phase is "sol", "liq" or "gas", referring to the solid phase, the liquid phase and the gas phase, respectively. The radioac-

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tivity of each radioisotope in a sample was extrapolated to the time point at which the radioactivity, loaded into the supercritical-water reactor, was measured before the supercritical-water reaction. The typical time periods required for the γ -ray measurements were 30 minutes for the solid phase, 3 hours for the liquid phase and 48 hours for the gas phase.

3. Results and Discussion

3.1. Preliminary experiment. In a preliminary experiment for examining reaction of technetium with supercritical water, only around 10% of technetium was found in a recovery (liquid phase and solid phase) when SCW-RuO₂ reaction including technetium was performed (Figure 1, 1st reaction). Technetium was not detected in recovered gas phase at all. By measuring γ -rays from inside of the hastelloy reactor, appreciable quantity of technetium was found in the reactor, in spite that inside walls were rinsed many times with water after SCW-RuO₂ reaction. In order to remove adsorbed technetium, SCW-H₂O₂ reaction without technetium was examined and more than 80% of technetium to loaded quantity was recovered (Figure 1, 2nd reaction). According to these results, SCW-H₂O₂ reaction effectively removes technetium adsorbed inside the hastelloy reactor, whereas SCW-RuO₂ reaction has not show such ability. Actually, SCW-RuO₂ reaction was examined again in 3rd reaction, but only less than 1% of technetium was recovered, which is in clear contrast to further SCW-H₂O₂ reaction done in 4–7 reactions which remove technetium significantly. Since in the 5th reaction by SCW-H₂O₂ yield only less than 2% of technetium, we decided that 5 times of SCW-H₂O₂ reaction should be done for finishing a supercritical water experiment with technetium.

3.2. Distribution of technetium with or without carrier

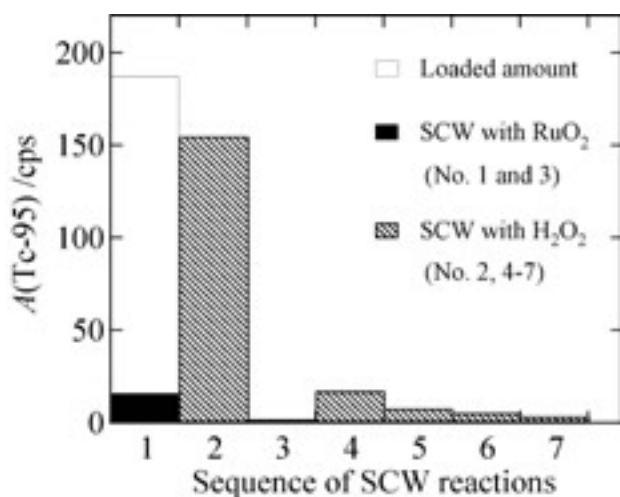


Figure 1. Activity of Tc-95 loaded and found in recovered samples obtained by supercritical water with RuO₂ and polypropylene (No. 1 and 3) or with H₂O₂ (No. 2 and 4-7).

and/or precipitating agent. Amount of technetium found in the solid, liquid and gas phases recovered after supercritical water reaction (i.e. not including the recovery of washings by SCW with H₂O₂ reaction to remove adsorbed technetium inside of the reactor) are indicated in ratio *D* in Table 1. Both in H₂O₂ and RuO₂ 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 ⁹⁹Tc but shifted to solid phase by addition of Fe(OH)₃. Summarizing the results, technetium can be recovered in solid phase without transfer to gas phase.

3.3. 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 H₂O₂ 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 H₂O₂ for 5 times is required to remove the adsorbed technetium from the reactor.

In RuO₂ method technetium may be reduced to colloidal or polymeric TcO₂ or TcO(OH)₂ which has a great affinity to metal surface.^{5,6} The adsorbed TcO₂ can be oxidized to TcO₄⁻ by H₂O₂ and dissolved in solution. Effect of supercritical water with RuO₂ on technetium chemistry requires further investigation.

4. 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 in SCW and SCW with RuO₂. Furthermore, technetium was found to adsorbed on to various metal materials. Washing by SCW with H₂O₂ for 5 times is required to remove adsorbed technetium from reactor. The result of adsorption of technetium by SCW with RuO₂ and the dissolution by SCW with H₂O₂ suggested that the reductive atmosphere of SCW with RuO₂ may result in the formation of colloidal or polymeric TcO₂ 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.

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TABLE 1: Distribution of Technetium to Three Phases After Supercritical-Water Reactions

Reaction	Carrier		10 ² <i>D</i> _{sol} ^{‡†}	10 ² <i>D</i> _{liq} ^{‡†}	10 ² <i>D</i> _{gas} [‡]
	Tc-99 /mg	Fe(OH) ₃ /mg			
RuO ₂ method	---	---	23.75 (97.11)	0.71 (2.89)	0.00
	0.5	---	22.86 (97.26)	0.64 (2.74)	0.00
	0.5	13	17.30 (99.30)	0.12 (0.70)	0.00
H ₂ O ₂ method	---	---	86.54 (99.28)	0.63 (0.72)	0.00
	0.5	---	41.98 (97.91)	0.90 (2.09)	0.00

[‡]Values of *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 Nonflammable Plastics[¶]

Contents		No reaction [‡]		RuO ₂ method			H ₂ O ₂ method			
		Cs-137	Tc-95m	Cs-137	Cs-137 + CsNO ₃	Tc-95m	Tc-95m + Tc-99	Cs-137	Tc-95m	Tc-95m + Tc-99
Phases recovered after reaction	Solid phase	---	---	5.8	15.63	33.9	65.75	1.9	17.8	16.75
	Liquid phase	83.7	85.5	64.5	80.29	0.5	0.76	80.2	1.5	23.62
	Gas phase	---	---	0	0	0	0	0	0	0
Metal specimens	SUS304	0	0	0		1.9	1.95	0	1.2	1.47
	Hastelloy	0	0	0		7.7	0.93	0	3.8	0.62
	Inconel	0	0	0		1.4	1.38	0	0.9	0.71
Washings with SCW-H ₂ O ₂ reaction	1st reaction	3.1	4	6.9	4.17	22.6	24.12	12.1	51.8	28.55
	2nd reaction	1.3	1.6	5.9	0.63	4.8	1.79	2.4	3.8	5.58
	3rd reaction	---	---	2.9	0.17	2.3	0.52	1.1	1.7	1.11
	4th reaction	---	---	1.6	0.12	3.8	0.41	1.3	1.3	0.26
	5th reaction	---	---	0.8		1.4	0.38	0.5	0.8	0.51
Total amount recovered		88.1	91.1	88.4	101.01	80.3	97.99	99.5	84.6	79.18

[¶]Distributions are indicated as percentile 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.

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