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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 ($t_{1/2} = 2.1 \times 10^5$ 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 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 $^{93}\text{Nb}(\alpha,2n)^{95\text{m}}\text{Tc}$ 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_2O_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 γ -ray spectra of three phases separated (solid, liquid and gas) and metal pieces. Cesium solution with a tracer of ^{137}Cs was used for a reference of the behavior.

The radioactivity of $^{95\text{m}}\text{Tc}$ 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

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

where D_{phase} designates the distribution ratio, A_{T} and A_{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_2O_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 $\text{Fe}(\text{OH})_3$.

It should be noted that only around 20% of technetium was found in a recovery after SCW-RuO₂ reaction. By measuring γ -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-RuO₂ reaction. On the other hand, fairly amount of technetium was recovered after SCW-H₂O₂ 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 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.

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 H₂O₂ and RuO₂ reactions. 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 treatment.

Reaction	Carrier		$10^2 D_{\text{sol}}^{\ddagger\dagger}$	$10^2 D_{\text{liq}}^{\ddagger\dagger}$	$10^2 D_{\text{gas}}^{\ddagger}$
	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

$^{\ddagger}D_{\text{phase}}$ were determined according to eq. (1).

† Values in parentheses are calculated by $D_{\text{phases}}/(D_{\text{sol}} + D_{\text{liq}} + D_{\text{gas}})$

Table 2. Distribution of Tc and Cs to each site after supercritical water reactions of non-flammable 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
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
SUS304	0	0	0	4.17	1.9	1.95	0	1.2	1.47
Hastelloy	0	0	0	0.63	7.7	0.93	0	3.8	0.62
Inconel	0	0	0	0	1.4	1.38	0	0.9	0.71
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	0	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.