Distribution of ^{59}Fe, ^{60}Co and ^{85}Sr as Low-level Radioactive Wastes Included in Nonflammable Organic Materials in the Decomposition by Supercritical Water with RuO$_2$

T. Yamamura[1], I. Satoh[1], W. Sugiyama[2], M. Takahashi[1],
Y. Shiokawa[1], H. Tomiyasu[3], and T. Ohtsuki[4]

[1] *Institute for Materials Research, Tohoku University, Sendai 980-8577*

[2] *Electric Power Research and Development Center, Chubu Electric Power Co., Inc., Nagoya 459-8522*

[3] *Department of Chemistry and Material Engineering, Faculty of Engineering, Shinshu University, Nagano 380-8553*

[4] *Laboratory for Nuclear Science, Tohoku University, Sendai 982-0826*

We investigated the distribution behavior of iron, cobalt and strontium attached to nonflammable organic materials, in solid, liquid and gas phases during the decomposition of these materials in supercritical water mixed with RuO$_2$. The distributions of these elements were determined by using their radioisotopes as simulated low-level radioactive wastes in order to ease the detection of trace amounts of elements even in solid and gas phases. The obtained results indicate that all of the elements investigated in this study (iron, cobalt, and strontium) can be recovered successfully by this supercritical-water process using RuO$_2$. Consequently, this process is suggested as a predominant candidate for the treatment of nonflammable organic materials in low-level radioactive wastes (LLW).

§1. Introduction

Low-level radioactive wastes (LLW) generated at nuclear power plants can be classified into three categories in Japan: the wastes with (i) very low-level, (ii) relatively low-level and (iii) relatively high-level radioactivity. The conventional method for dealing with these wastes includes compression or incineration before solidification with mortar or concrete, and storing then in 200 L drum containers [1]. Even excluding the above-mentioned category (iii), more than half a million drum containers filled with LLW were being stored at domestic nuclear power plants by the end of FY 2001. One of the reasons why such a huge volume has accumulated is that the main components of the LLW are bulky nonflammable organic materials. No practical method for compressing or decomposing these wastes has been established yet and therefore volume reduction is not achieved satisfactorily.

A method using supercritical water with RuO$_2$ as a catalyst [2] was recently developed for achieving the complete gasification of nonflammable organic compounds, including even such compounds as stable aromatic structures. One of the most important applications of this method would be the decomposition of nonflammable organic materials contaminated with low-level radioactivity, in order to reduce their volume. We have reported on an investigation using this method to decompose nonflammable organic materials used in nuclear power plants [1]. For practical use, what is required is the removal of trace

quantities of radioactive elements attached to these plastics from gas and liquid phases and their concentration in the solid phase.

Radioisotopes contained in the LLW from nuclear power plants can be classified into two types by origin. One type is the radioactivated materials in nuclear power plants, *e.g.* iron-59 and cobalt-60 from the stainless steel (SUS) used as a major construction material, and the other is the fission products of uranium, such as strontium-90, which originate in the nuclear fuel, due to leakage.

In this study, the distribution of the above nuclides into solid, liquid and gas phases were investigated by applying the supercritical-water reaction with RuO_2 for decomposing the nonflammable organic materials. The objective of this study is to elucidate the optimum conditions for the concentration of the radionuclides into the solid phase. In order to detect trace quantities of elements even in the gas and solid samples collected after supercritical-water reaction, radiometric analysis was applied.

§2. Experimental

Laminate sheeting, a popular product used in domestic nuclear power plants, is commercially available from Chiyoda Technol Corp., Japan. Reagents and radioactive reagents were used as purchased. Strontium-85, the tracer of strontium, was prepared by bremsstrahlung irradiation of $SrCO_3$ at the condition of 50 MeV, 100-120 μA, 8 hours with the electron linear accelerator (LINAC) at Laboratory of Nuclear Science, Tohoku University. Radioactive iron and cobalt hydroxides, as simulated radioactive scales of SUS, were prepared as follows already reported [3].

2.1 Supercritical-water reaction conditions

The supercritical batch-wise reactor made of hastelloy C-22 with a nominal inside volume of 10.8 cm^3 was supplied by Taiatsu Techno Corp., Japan. A certain amount of radioactive compound and non-radioactive carrier, 150 mg of laminate sheeting, 30 mg of RuO_2 and 3 mL of water were loaded into the above reactor. By using a temperature controller, the reaction condition of 450ºC-43 MPa was kept for 30 min.

After the reactor was cooled to room temperature, the volume of the gas produced by the supercritical-water reaction was measured using a gas pressure meter and the gas was collected in a 100 mL gas vial; then everything (liquid and solid phases) remaining inside the reactor was recovered and placed in a 10 mL polypropylene test tube. The inner surface of the reactor was rinsed with water three times (total 6 mL) and the washings were collected and added to the contents of the reactor. The supernatant liquid was separated into another polypropylene test tube by centrifuging these contents.

2.2 Determination of distribution factor

The radioactivity of ^{59}Fe, ^{60}Co, and ^{85}Sr were determined from the areas of their peaks at 1099.3, 1173.2, and 514.0 keV, respectively, by using the 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

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

where D_{phase} designates the distribution ratio, A_T and A_{phase} are the total radioactivity of each phase after the supercritical-water reaction and the 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.

§3. Results and discussion

As reported previously [1], the laminate sheeting initially added is completely decomposed without any solid residues by the supercritical-water reaction using RuO_2. Also in this study, only the clear and colorless supernatant solutions and inorganic precipitates are recovered in the all runs. The gases produced during the decomposition of the laminate sheeting may consist of CH_4, CO_2 and H_2, according to our previous study [2]. Experimental conditions, the volume of the gas produced and the distribution in three phases in experiments on ^{59}Fe, ^{60}Co, and ^{85}Sr are summarized in Table 1.

3.1 Distribution of ^{59}Fe and ^{60}Co

There is a tendency for the iron to precipitate almost quantitatively and only a trace amount is transferred to the liquid when a small amount of carrier is added (Table 1). The gas produced during the decomposition of the laminate sheeting contains no activity of ^{59}Fe in any of the runs. This result indicates that both the decomposition of nonflammable plastics and the recovery of iron in the solid phase are successful. In contrast to the results for radioactive iron, about a quarter of ^{60}Co distributes

Table 1. Distribution of Fe, Co, and Sr in three phases after reaction in supercritical-water of nonflammable plastics [3]

Element	Carrier compound	Amount of carrier / mg	Tracer	Activity of tracer added / Bq	Amount of liquid phase / mL	Amount of gas phase / mL[3]	10^2D_{sol}[2]	10^2D_{liq}[2]	10^2D_{gas}[2]
Fe	$Fe(OH)_3$	0.13 [1]	^{59}Fe	3.12×10^5	9	90	97.5±1.5	2.5±0.0	0.0±0.0
		1.3 [1]		0.60×10^5	9	79	99.9±1.6	0.1±0.0	0.0±0.0
		13 [1]		2.94×10^5	9	70	100±1.4	0.0±0.0	0.0±0.0
		130 [1]		3.90×10^5	9	41	100±1.4	0.0±0.0	0.0±0.0
Co	$Co(OH)_3$	2.3 [4]	^{60}Co	8.33×10^4	9	103	75.4±1.0	24.6±0.2	0.0±0.0
		23 [4]		9.02×10^4	9	90	76.7±0.8	23.3±0.2	0.0±0.0
		230 [4]		8.27×10^4	9	27	87.0±0.9	13.0±0.1	0.0±0.0
Sr	$SrCO_3$	trace	^{85}Sr	8.21×10^2	9	65	15.1±0.4	84.9±1.2	0.0±0.0
		5		6.52×10^3	9	60	32.3±0.5	67.7±1.0	0.0±0.0
		50		2.97×10^4	9	44	78.0±0.3	22.0±0.1	0.0±0.0

1) Amount of $Fe(OH)_3$ calculated on the basis of the amount of $Fe(NO_3)_3 \cdot 9H_2O$ used to prepare $Fe(OH)_3$.
2) Value indicates measurement error [8].
3) Value calculated from gas pressure after reaction.
4) Amount of $Co(OH)_3$ calculated on the basis of the amount of $CoCl_2 \cdot 6H_2O$ used to prepare $Co(OH)_3$.

Table 2. Distribution of Co and Sr in three phases when 200 mg of non-radioactive iron hydroxide[1] was added for coprecipitation [3]

Element	Carrier compound	Amount of carrier / mg	Tracer	Activity of tracer added / Bq	Amount of liquid phase / mL	Amount of gas phase / mL[3]	$10^2 D_{sol}$[2]	$10^2 D_{liq}$[2]	$10^2 D_{gas}$[2]
Co	CoCl$_2$·6H$_2$O	not added	^{60}Co	2.19×10^5	9	27	98.5±0.9	1.5±0.0	0.0±0.0
		5		2.18×10^5	9	27	99.4±1.0	0.6±0.0	0.0±0.0
Sr	SrCO$_3$	0.5	^{85}Sr	2.66×10^3	9	20	7.3±0.1	92.7±1.0	0.0±0.0
	SrCO$_3$	5		4.55×10^4	9	21	91.7±0.3	8.3±0.10	0.0±0.0
	Sr(NO$_3$)$_2$	5		5.82×10^3	9	16	97.2±0.6	2.8±0.1	0.0±0.0

1) 200 mg of Fe(OH)$_3$ calculated on the basis of the 500 mg of FeCl$_3$·6H$_2$O used to prepare Fe(OH)$_3$.

2) Error indicates measurement error [8].

3) Value calculated from gas pressure after reaction.

to the liquid phase. In order to shift the distribution to the solid phase, 200 mg of non-radioactive iron hydroxide was added to the reactor and the supercritical-water reaction was examined (Table 2). Cobalt is quantitatively transferred to the solid phase, as seen only in the case of iron (Table 1). This dramatic improvement could be explained by the coprecipitation of the cobalt with the iron. The gas produced during the decomposition of laminate sheeting contains no activity of ^{60}Co in any run.

3.2 Distribution of ^{85}Sr

Table 1 indicates that ^{85}Sr mainly stays in the liquid phase, and only a small amount is transferred to the solid phase, even when SrCO$_3$ carrier is added. The gas produced during the reaction contained no ^{85}Sr in any run. To recover radioactive strontium as a solid, two additional examinations were performed: (1) adding the non-radioactive iron hydroxide to the reactor before the reaction and (2) adding a precipitation reagent to liquid obtained after the reaction. In the case of examination (1), 200 mg of the non-radioactive Fe(OH)$_3$ was added to the reactor before the reaction (Table 2), and the strontium quantitatively transferred to the solid phase as seen only in the case of iron (Table 1). This dramatic improvement in the recovery of strontium in the solid phase could be explained by the coprecipitation of the strontium with the iron. In the case of examination (2), Na$_2$CO$_3$ or NaHCO$_3$ aqueous solution was added to radioactive Sr(NO$_3$)$_2$ aqueous solution as follows: A certain amount of non-radioactive Sr(NO$_3$)$_2$ as the carrier and ^{85}SrCO$_3$ dissolved in a 1 M HNO$_3$ aqueous solution, which is the simulated solution obtained after the supercritical-water reaction, was mixed into 3 mL of water in a polypropylene test tube. By adding 1 mL of 0.4 M Na$_2$CO$_3$ or NaHCO$_3$ aqueous solution to the above-mentioned solution, a white suspension was obtained in all runs. After centrifuging, the supernatant liquid phase was transferred to another polypropylene test tube with a polyethylene dropper. The determined distribution of ^{85}Sr in this examination (Table 3) indicates that Na$_2$CO$_3$ and NaHCO$_3$ are excellent precipitate reagents for strontium. Thus, strontium dissolved in the liquid obtained after the supercritical-water reaction could be precipitated with Na$_2$CO$_3$ and NaHCO$_3$ aqueous solution.

Table 3. Distribution of Sr in solid and liquid phases after adding precipitation reagent to simulated solution obtained after reaction by supercritical-water mixed with RuO_2 [3]

Element	Precipitate reagent	Carrier compound	Amount of carrier / mg	Tracer	Activity of tracer added / Bq	$10^2 D_{sol}$[1]	$10^2 D_{liq}$[1]
Sr	Na_2CO_3 [2]	$Sr(NO_3)_2$	0.5	^{85}Sr	$5.03×10^3$	99.1±0.7	0.9±0.0
	Na_2CO_3 [2]		5		$5.13×10^3$	99.2±0.7	0.8±0.0
	$NaHCO_3$ [2]		0.5		$4.87×10^3$	99.1±0.7	0.9±0.0
	$NaHCO_3$ [2]		5		$4.81×10^3$	99.1±0.5	0.9±0.0

1) Error indicates measurement error [8].
2) Adding 1 mL of Na_2CO_3 or $NaHCO_3$ aqueous solution.

3.3 Precipitation mechanism in the case of Fe and Co

Under the conditions with small amounts (0.13 and 1.3 mg) of the non-radioactive iron hydroxide as the carrier, iron is not recovered in the solid completely and still remains in the liquid (Table 1). One possible explanation of these results is that the iron(III) could be simultaneously reduced to iron(II) during the reductive decomposition of the nonflammable organic materials. To obtain information on the oxidation state of the dissolved iron under these conditions, 2,2′-bipyridyl, a colorimetry reagent for Fe^{2+}, were added to the liquid obtained after the supercritical-water reaction with 0.13 and 1.3 mg of the non-radioactive iron hydroxide. The liquid turned pink and the absorption spectrum in the visible region showed an absorption band at 520 nm, which is attributed to Fe^{2+} [4]. In the case of cobalt, the color of the liquid obtained after reaction was initially pale pink and changed to golden yellow when 2,2′-bipyridyl was added. Also non-radioactive condition, we prepared a cobalt(II) aqueous solution using $CoCl_2 \cdot 6H_2O$. The color of this solution was initially pale pink and changed to golden yellow when 2,2′-bipyridyl was added. These results indicated the production of Fe^{2+} in the liquid by the reactions with 0.13 and 1.3 mg of the non-radioactive iron hydroxide and also Co^{2+} in the liquid by supercritical-water reaction. These results show that iron(II) and cobalt(II) generated in the liquid after reaction. Iron and cobalt added into the reactor before the reaction was $Fe(OH)_3$ and $Co(OH)_3$, respectively. Therefore, iron(III) and cobalt(III) were respectively reduced to iron(II) and cobalt(II), and this means that a reductive mechanism is operating in the reaction using supercritical water mixed with RuO_2. It is worthwhile to note that the reduction of Co(III) to Co(II) requires very reductive conditions, as indicated by the standard electrode potential of -1.92 V vs. SHE [5] in comparison with that of Fe(III) to Fe(II), which is -0.771 V vs. SHE [5]. Once the divalent metal ion is formed, the cobalt(II) ion should have greater solubility than the iron(II) ion on the basis of the solubility product K_{sp} obtained at the ambient temperature for $Fe(OH)_2$ and $Co(OH)_2$ $8 × 10^{-16}$ [6] and $1.6 × 10^{-15}$ [7], respectively.

Furthermore, all of the solids obtained after the supercritical-water reaction of iron showed ferromagnetism when checked with a magnet. Thus, a non-radioactive sample was prepared by the procedure wherein 200 mg of non-radioactive $Fe(OH)_3$, 30 mg of RuO_2, 150 mg of laminate sheeting and

3 mL of water reacted under standard conditions. The X-ray powder diffraction (XRD) was performed at RINT 2000 (Rigaku Corp., Japan) using $CuK_{\alpha 1}$. The XRD pattern of the obtained solid agreed very well with Fe_3O_4. Since the corresponding radioactive cobalt samples also exhibited ferromagnetic behavior, the non-radioactive sample was prepared by the same way of iron samples. the XRD pattern of the obtained solid agreed well with CoO. A detailed analysis of the solid obtained after the reaction using supercritical water mixed with RuO_2 is now underway.

With reference to the gasification mechanism proposed in ref. [2] for the decomposition of nonflammable organics using supercritical water with RuO_2 catalyst, the atmosphere of the supercritical-water reaction is suggested to be reductive. The above analysis of the solid phase obtained in the reaction also supports this reductive mechanism, where a portion of iron(III) and all of cobalt(III) are reduced to iron(II) and cobalt(II), respectively.

§4. Summary

The present investigation indicates that during the decomposition of laminate sheeting, the produced gas contains no radioactivity in any run. The distribution of Fe, Co, and Sr was determined by radiometric analysis after laminate sheeting was decomposed using supercritical water mixed with RuO_2. Iron, cobalt and strontium were recovered as solids after the present supercritical-water reaction by the addition of an excessive quantity of iron hydroxide before the reaction. In the case of strontium, almost all radioactivities were found in the liquid phase. However, by adding precipitate reagents to the liquid phase obtained in the reaction, strontium can be recovered in the solid phase. This method should be a very effective way to decompose the nonflammable organic materials of LLW generated by nuclear power plants.

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