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Incineration Method for Plutonium Recovery from Alpha-Contaminated Organic Compounds*

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Incineration of alpha-contaminated organic compounds is the most effective method for plutonium recovery and volume reduction of radioactive wastes. The aim of the work described in this paper was to recover plutonium without production of refractory plutonium oxide and to eliminate the evolution of tar and/or soot during incineration of these organic compounds The proposed method was composed of two stages. The first stage was thermal decomposition of solid or evaporation of liquid organic compounds in a flow of gas containing oxygen in a low ratio at low temperatures. The second stage was complete incineration of thermal decomposition products by catalytic reaction without tar and/or soot. Plutonium could be recovered in the form of oxide in the decomposition or evaporation residues. The experiments were carried out with test samples on an epoxy resin containing plutonium compounds and uncontaminated ion exchange resins.

Experimental and Results

Thermal Decomposition Test for the Epoxy Resin

The weight change and heat evolved during the thermal decomposition of the epoxy resin were measured by a conventional differential thermobalance. About 10 mg of sample were placed in a quartz crucicle and heated up to 800 °C at a rate of 20 °C/min in each run [1]. In order to clarify the effect of oxygen ratios on thermal decomposition of the epoxy resin, experiments were carried out in the flow of the following various kinds of gases: He; 5% O_2–95% Ar mixture; 10% O_2–90% Ar mixture; 20% O_2–80% N_2 mixture; and 100% O_2.

Figure 1 shows the thermogravimetric analyses ot the epoxy resin under different oxygen ratios.

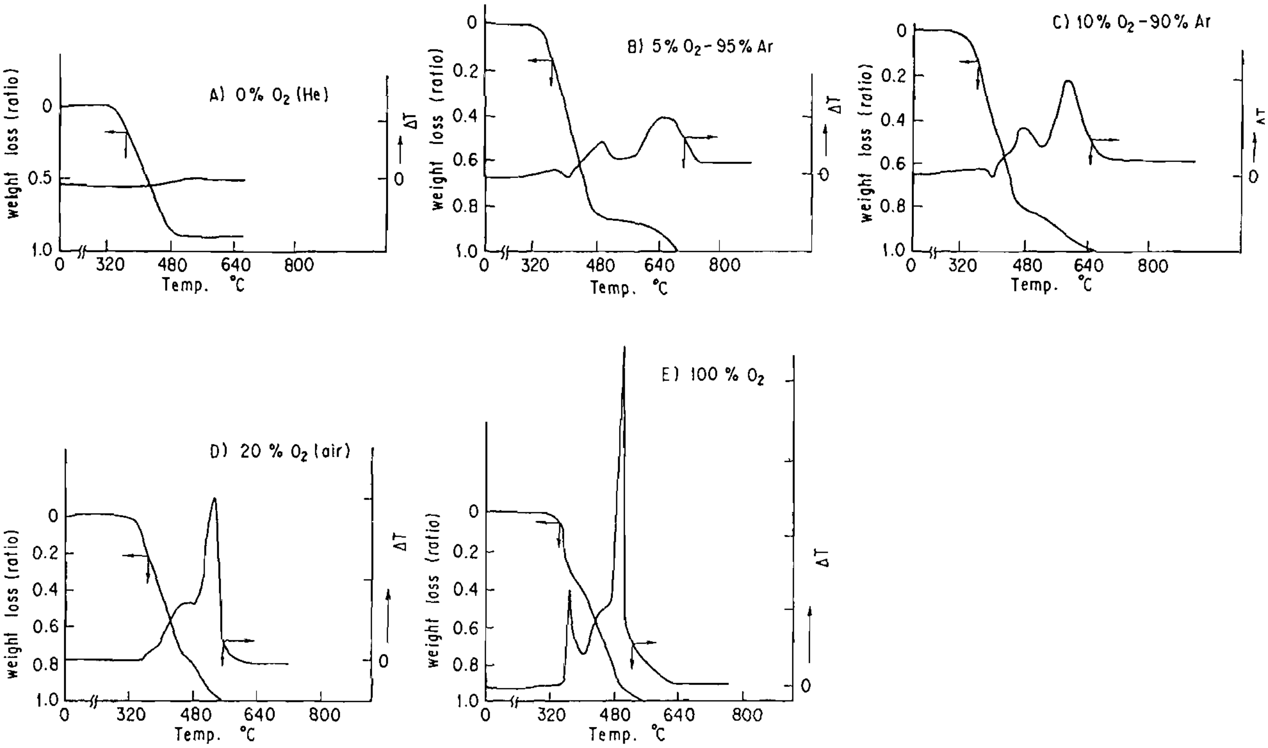

Fig. 1. Differential thermogravimetric curves for the decomposition of epoxy resin.

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The curves A, B, C, D and E in Fig. 1 correspond to He, 5% O_2–95% Ar mixture, 10% O_2–90% Ar mixture, 20% O_2–80% N_2 mixture and 100% O_2, respectively.

He: the weight loss was observed between 340 and 480 °C, but a small amount of carbon remained in the quartz crucible. The DTA curve showed no peaks under inert atmosphere.

5–10% O_2: the weight decrease of the epoxy resin due to the thermal decomposition was considered to proceed in two steps. The first step could be seen in the temperature range of 340 and 480 °C with a large decrease in weight. The second step proceeded from about 480 to 700 °C with a small weight decrease. The peak heights in the DTA curves for the epoxy resin varied with the oxygen ratios. A small endothermic peak which may be caused by the thermal decomposition of the epoxy resin could be seen below 20% O_2.

20–100% O_2: on increasing the oxygen ratio, the second step of the weight decrease of the epoxy resin was shortened. The decomposition products burnt so fast that the sharp increase in temperature might accelerate the decomposition rate and mask the endothermic peaks in the gas atmospheres with higher oxygen ratios.

The thermal decomposition products from the epoxy resin were analysed by mass spectrography at 340 and 550 °C under a vacuum. The species of thermal decomposition products were confirmed to be mixtures of H_2, $C_{1,2}$, CH_4, C_2H_2, N_2 or CO, O_2, CO_2, C_4H_{10}, C_6H_6, etc. There were no differences in the species at the beginning and the end of the decomposition.

If the temperature is raised very high some difficulties may occur; *i.e.*, formation of refractory oxides of plutonium and shortening of the life-time of the furnace, etc. Such problems can be avoided by performing the thermal decomposition reaction with oxygen ratios below 20%.

Figure 2 shows a schematic illustration of the incinerator for the epoxy resin and the oil in the glove box. It was made of a stainless steel tube of 48 mm diameter and *ca.* 1200 mm length. It was separated in two parts: the left side for the thermal decomposition of the epoxy resin or for evaporation of the oil and the right side for complete incineration by the catalytic reaction. Incineration experiments were carried out alternately between the epoxy resin and the oil in the same apparatus.

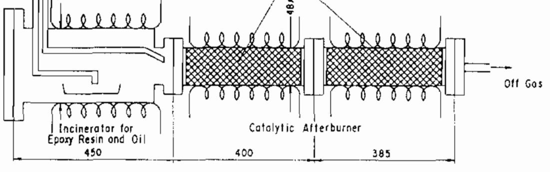

Fig. 2. A schematic illustration of the incinerator for epoxy resin and lubricant oil. Dimensions are in millimeters.

TABLE I. Dissolving Test of Plutonium from Incineration Residues in Nitric Acid[a]

X-ray powder samples of plutonium compounds embedded in epoxy resin (g)	Plutonium and uranium oxides recovered in incineration residues (g)	Residues in conc. HNO_3
7.80	3.12	none detected
6.66	2.19	none detected
5.31	1.53	none detected
7.50	2.15	none detected
6.17	1.52	none detected
5.83	1.44	none detected
8.45	3.03	none detected

[a] The weight difference between columns 1 and 2 in the table corresponds to the weight of epoxy resin.

Plutonium Recovery from the Epoxy Resin Containing Plutonium

About 10 pieces (each 18 mm length, 20 mm width and 1.5 mm thickness) of X-ray powder samples of uranium–plutonium mixed carbides embedded in the epoxy resin were charged in the boat as shown in Fig. 2. The samples were heated at 500 °C in a stream of air for 2 h. Decomposition products of the epoxy resin were contacted with copper oxide at about 500 °C; tar and/or soot were not observed in the off gas. Mixtures of uranium and plutonium oxides could be recovered from the ash of the epoxy resin.

Oxides obtained from incineration residues could be completely dissolved in nitric acid containing a small amount of hydrofluoric acid, as reported in Table I. This fact suggests the successful separation of the heavy metal oxides from the epoxy resin.

Thermal Decomposition Test of the Ion Exchange Resin

The weight change during the thermal decomposition of the ion exchange resins was measured by a thermobalance. About 30 mg of sample were placed in a quartz crucible and heated up to 600 °C at a rate of 30 °/min in each run. The experiments were carried out in a flow of the following various kinds of gases: 0% O_2–100% N_2; 10% O_2–90% Ar mixture; 20% O_2–80% N_2 mixture; and 30% O_2–70% Ar mixture. The curves A and B in Fig. 3 correspond to

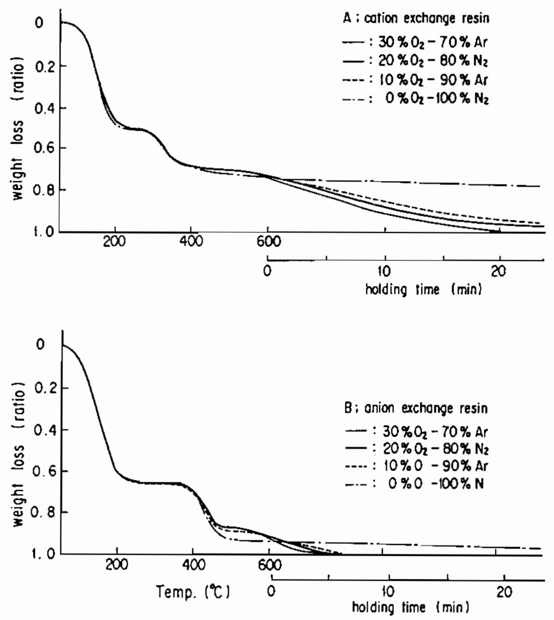

Fig. 3. Thermogravimetric curves for the decomposition of ion exchange resins.

cation (Diaion SKN-1) and anion exchange resin (Diaion SAN-1) in the oxygen ratios of 0% O_2–100% N_2, 10% O_2–90% Ar mixture, 20% O_2–80% N_2 mixture and 30% O_2–70% Ar mixture, respectively.

Decrease of the resins could be observed in three steps: the first step was the evaporation of water at about 100 °C; the second was the decomposition of functional groups, namely sulfonic acid for cation and trimethyl ammonium for anion exchange resin at 300 and 400 °C, respectively; and the final step was the thermal decomposition of resin base polymer above 500 °C. Matsuda *et al.* reported that the sulfur in the cation exchange resin made the resin base polymer thermally stable [2]. As shown in Fig. 3, the cation exchange resin was somewhat more stable than that of the anion exchange resin. Sulfur may have stabilized the resin base polymer in this case.

The effects of oxygen ratios on the thermal decomposition rate were not observed significantly below 500 °C, but the decrease in the resin base was accelerated by high oxygen ratios at *ca.* 600 °C. In the inert atmosphere, the resin base polymer was not perfectly decomposed and formed carbon in the crucible.

A fluidized bed was used for the incineration of the ion exchange resin. The incinerator consisted of nine parts: two screw feeders; an air compressor; a preheater; 90 mm diameter, 1250 mm high stainless incinerator chamber; one cyclone as a fly ash separator; a sintered metal filter; a catalytic afterburner; and an off-gas scrubber.

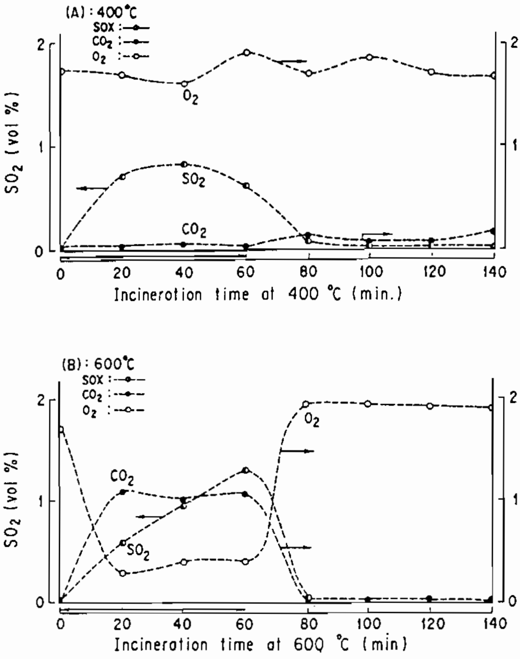

Fig. 4. Composition of off gases during thermal decomposition of cation ion exchange resin without $Ca(OH)_2$ at 400 °C (A) and 600 °C (B).

Both the ion exchange resin and calcium hydroxide as SO_2 fixer could be fed by the screw feeder. The temperature could be measured at various points of the incinerator, the pipe line and the catalytic afterburner.

The analyses of the thermal decomposition products and the evolved gas were performed on line: O_2, CO_2, CO, SO_2 and CH_4.

Figure 4 shows the analyses of off gases from the fluidized bed incinerator. The curves A and B in Fig. 4 correspond to cation exchange resin at 400 and 600 °C, respectively. The resin was fed at 4.76 g/min for 1 h in each run without calcium hydroxide. At 400 °C, the O_2 and CO_2 contents did not change throughout the experiment; the incineration of resin did not occur at this temperature. SO_2 could be observed after the decomposition of the functional group of the resin. At 500 and 600 °C, O_2 was decreased and on the contrary CO_2 was increased by the incineration of the resin; SO_2 could also be observed.

A mixture of cation and anion exchange resin (ratio 1:2) was fed at 4.76 g/min with a small excess over the stoichiometric amount of calcium hydroxide for fixing SO_2. In this case, SO_2 was fixed with calcium hydroxide to form calcium sulfate. The resin did not remain in the fluidized bed incinerator [3, 4].

Conclusions

Plutonium recovered from low temperature incineration residues was easily dissolved in nitric acid. Generally, plutonium-contaminated organic compounds were decompsoed below 600 °C and decomposition products could be perfectly incinerated using a catalyst. Therefore, the incineration method combined with thermal decomposition and catalytic reaction is suitable for plutonium recovery.

References

1 T. Yahata, J. Abe, M. Kato and M. Kurihara, *J. Nucl. Sci. Technol.*, *22*(8), 669 (1985).
2 M. Matsuda, K. Funabashi, T. Nishi and H. Yusa, *Nucl. Technol.*, *75*, (Nov.) (1986).
3 M. Valkiainen and M. Nykyri, *Nucl. Technol.*, *58*, (Aug.) (1982).
4 L. J. Meile, F. G. Meyer, A. J. Johnson and D. L. Ziegler, 'Rocky Flats Plant Fluidized-bed Incinerator', *Rocky Flats Plant, RFP-3249*, March, 1982.