12/4-4-93 JSD

UCRL-ID-112994

**Measurement of Plutonium and Americium Volatilities
Under Thermal Process Conditions: Final Report**

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April 28, 1993

Lawrence
Livermore
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Laboratory

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Work performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under Contract W-7405-Eng-48.

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Abstract

We have used the transpiration method to measure volatilities of Pu and Am from $\text{PuO}_2(\text{s})$ and $\text{PuO}_2/2\% \text{AmO}_2(\text{s})$ in the presence of steam and oxygen at temperatures of 1230-1430 K. We find the volatile species to be $\text{PuO}_2(\text{OH})_2(\text{g})$ and $\text{AmO}_2(\text{OH})_2(\text{g})$ at vapor pressures on the order of 10^{-10} atm and 10^{-12} atm respectively under measurement conditions. For the Pu volatilization reaction, $\text{PuO}_2(\text{s}) + 1/2 \text{O}_2(\text{g}) + \text{H}_2\text{O}(\text{g}) = \text{PuO}_2(\text{OH})_2(\text{g})$, we obtain a free energy of reaction of $\Delta G^\circ_T = 231.3 - 0.0109 T$ in kJ/mol, and for the Am volatilization reaction, $\text{AmO}_2(\text{s.s. in PuO}_2) + 1/2 \text{O}_2(\text{g}) + \text{H}_2\text{O}(\text{g}) = \text{AmO}_2(\text{OH})_2(\text{g})$, we obtain $\Delta G^\circ_T = 223.9 - 0.0109 T$ in kJ/mol.

We apply these results to the Rocky Flats Plant Fluidized Bed Incinerator to assess the amount of volatile Pu and Am produced in the secondary combustor chamber. Taking operating conditions of 550°C combustor temperature, 40 kmols/h of total gas flow at 1 atm pressure, 0.1 atm $\text{O}_2(\text{g})$, 0.05 atm $\text{H}_2\text{O}(\text{g})$, $\text{PuO}_2(\text{s})$ containing 200 ppm AmO_2 in the bed, and 6000 h of operating time per year, gives volatilization rates of 7×10^{-6} g Pu/y and 4×10^{-9} g Am/y.

Introduction

This study has been performed in support of the Rocky Flats Fluidized Bed Incinerator development. The objective of this study has been to conduct experiments to identify the types and amounts of volatile gaseous species of Pu and Am that are produced in the offgases of mixed waste oxidation processors. The primary emphasis has been on the Rocky Flats Fluidized Bed Incinerator, but the results should be of value as well to other mixed waste oxidation processors.

During operation of a mixed waste incinerator or other mixed waste oxidation processor operating under oxidizing conditions, we expect a limited degree of volatilization of actinides to occur and to be carried off by the combustion gases. The vapor phase actinide species that form under these conditions are expected to condense as aerosol particles associated with ash constituents or as condensates on

fly ash particulate surfaces, and may not be easily removable from the gas stream by filtration or other means. Therefore, it is important to understand the types and amounts of volatile species produced under various operating conditions so as to maintain proper process controls for containment of the actinides.

Based on available or predicted thermodynamic data [1-5], some small amount of volatility is expected for U as $\text{UO}_2(\text{OH})_2(\text{g})$, for Pu as $\text{PuO}_2(\text{OH})_2(\text{g})$, and for Am as $\text{AmO}_2(\text{OH})_2(\text{g})$ for mixed waste incinerators and other mixed waste oxidation processors operating under oxidizing conditions. Thermodynamic data indicate that other possible gaseous actinide species such as oxides, halides, or oxyhalides, are generally much lower in importance than the oxyhydroxides under incinerator operating conditions; unless halogen acids (e.g., HCl or HF) are present at concentrations greater than ~0.1% in the gas stream, in which case actinide oxyhalides may also show significant volatilities. [2] The halogen acid content of the Rocky Flats Fluidized Bed incinerator is predicted to be very low because of the presence of sodium carbonate in the bed, which acts as a getter for the halogen acids and converts them to solid sodium halides.

The Rocky Flats Plant Fluidized Bed Incinerator for mixed wastes containing U, Pu, and Am, uses a primary fluidized bed combustor with a mixed Na_2CO_3 and $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ (oxidation catalyst) bed material operated at 550°C under pyrolysing conditions and a secondary fluidized bed combustor with a $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ bed material operated at 550°C under oxidizing conditions. NaCl and Na_2SO_4 are produced in the primary bed by interactions of acid gases with Na_2CO_3 in the bed. Fly ash produced in the primary combustor is separated out in cyclone separators and the resultant gas stream together with fly ash fines is passed through the secondary bed. Fly ash produced in the secondary combustor consists of mixture of a mineral ash along with $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ catalyst and small amounts of Na_2CO_3 , NaCl and Na_2SO_4 carried through from the primary combustor.

In initial work on this project (funded under sub-contract No. 98661GD from EG&G Rocky Flats Plant to LLNL), [3] thermodynamic modeling was used to estimate the volatilities of U and Pu from both the primary and secondary fluidized bed reaction chambers in the Rocky Flats Plant Fluidized Bed Incinerator. The FACT/EQUILIBRIUM code with its extensive data base was used to carry out these calculations. Additional thermodynamic data on expected $\text{UO}_2(\text{OH})_2(\text{g})$ and $\text{PuO}_2(\text{OH})_2(\text{g})$ vapor species were input into the data base. The data on $\text{PuO}_2(\text{OH})_2(\text{g})$ was estimated using empirical correlations and molecular constant data. Local thermodynamic equilibrium was assumed between the vapor species and the solid materials in the bed. Uranium was found to be present as $\text{Na}_2\text{UO}_4(\text{s})$ and Pu present as $\text{PuO}_2(\text{s})$ in the bed. The volatilization reactions were then given by:

Under the pyrolysis conditions of the primary reaction chamber the volatilities of $\text{UO}_2(\text{OH})_2(\text{g})$ and $\text{PuO}_2(\text{OH})_2(\text{g})$ were found to be quite low ($\sim 10^{-19}$ atm). However, thermodynamic data on other possible volatile U and Pu species that may exist under pyrolysis conditions are limited so that a complete assessment of volatility was not made. Further work would be desirable to check for other possible volatile species. In the secondary chamber, under oxidizing conditions, the dominant vapor species were found to be $\text{UO}_2(\text{OH})_2(\text{g})$ at 1×10^{-13} atm and $\text{PuO}_2(\text{OH})_2(\text{g})$ at 2×10^{-11} atm. The volatility of $\text{UO}_2(\text{OH})_2(\text{g})$ here is substantially lower than if $\text{U}_3\text{O}_8(\text{s})$ had been formed. Thus the formation of the mixed oxide $\text{Na}_2\text{UO}_4(\text{s})$ significantly reduces the $\text{UO}_2(\text{OH})_2(\text{g})$ volatility because of a reduction in uranium oxide activity.

We have also carried out a thermodynamic analysis of U and Pu volatilities in the Rockwell International Molten Salt Processor, [2,6-8] in which we used an independent assessment of the thermodynamic data for $\text{PuO}_2(\text{OH})_2(\text{g})$. The Rockwell International Molten Salt Processor was used to carry out combustion of U- and Pu-containing synthetic laboratory wastes in a molten $\text{Na}_2\text{CO}_3/\text{NaCl}$ bath at ~ 1100 K. We took as the volatilization reactions:

We compared the calculated volatilities of $\text{UO}_2(\text{OH})_2(\text{g})$ and $\text{PuO}_2(\text{OH})_2(\text{g})$ with the amounts of carryover of U and Pu observed in the offgas passages and filters of the Rockwell processor and found agreement to within one to two orders of magnitude. The agreement is as good as can be expected considering the uncertainties in both the calculations and the experimental data.

Applying the two sets of estimated thermodynamic data for volatility of $\text{PuO}_2(\text{OH})_2(\text{g})$ to the secondary chamber of the Rocky Flats Plant Incinerator and assuming Pu to be present as $\text{PuO}_2(\text{s})$ gives volatilities of 2×10^{-11} atm [3] and 7×10^{-13} atm [2] for $\text{PuO}_2(\text{OH})_2(\text{g})$. Thus, the thermodynamic modeling indicates that $\text{PuO}_2(\text{OH})_2(\text{g})$ is an important species, but the predicted volatilities are not very accurate. Experimental measurements would be needed for quantitative data. Also, although $\text{PuO}_2(\text{s})$ is assumed to be present as the combustion product, Pu may interact with the ash formed during combustion or with the fluidized bed materials to form mixed oxides or be incorporated in glass phases. These interactions would lead to a lowering of the $\text{PuO}_2(\text{s})$ activity and a consequent lowering of $\text{PuO}_2(\text{OH})_2(\text{g})$ volatility. The kinetics of the combustion process and its effect on the resultant volatility of $\text{PuO}_2(\text{OH})_2(\text{g})$ also needs to be considered. We expect that both the PuO_2/ash interactions and combustion kinetic effects would lower $\text{PuO}_2(\text{OH})_2(\text{g})$ volatilities as compared to equilibrium volatilization from $\text{PuO}_2(\text{s})$. Our experimental study here of equilibrium volatilities of $\text{PuO}_2(\text{OH})_2(\text{g})$ from $\text{PuO}_2(\text{s})$ should therefore provide us with an upper limit estimate of Pu volatilities in the secondary combustor of the Rocky Flats Plant Incinerator. Similar considerations apply to our study here of $\text{AmO}_2(\text{OH})_2(\text{g})$.

volatilities from a $\text{PuO}_2/2\% \text{ AmO}_2$ solid solution. The effects of actinide/ash interactions on actinide oxyhydroxide volatilities are currently under study in continuing work on this project.

Approach

The approach used here to obtain Pu volatilities is to apply the transpiration technique to experimentally measure Pu volatility from $\text{PuO}_2(\text{s})$ in the presence of $\text{O}_2(\text{g})$ and $\text{H}_2\text{O}(\text{g})$, and similarly, to measure Pu and Am volatilities from a $\text{PuO}_2/2\% \text{ AmO}_2(\text{s})$ mixed oxide in the presence of $\text{O}_2(\text{g})$ and $\text{H}_2\text{O}(\text{g})$. By making measurements on pure $\text{PuO}_2(\text{s})$, we are looking at an upper limit on the volatility, since, as mentioned above, the interactions with ash and the kinetics of vaporization would be expected to lower the volatilities. Use of pure $\text{PuO}_2(\text{s})$ also gives us a well-defined state so that we can obtain thermodynamic data on the volatilized species. In working with Am, we are limited in the amount that we can handle in our glovebox system. We chose the 2% concentration of AmO_2 in PuO_2 to give adequate detectability of volatilized Am. We analyze the results in terms of whether the Am volatility is enhanced or diminished relative to Pu volatility. Measurements are run at temperatures high enough for detectability of volatilized Pu and Am, i.e. temperatures of 900-1200°C. Results are then extrapolated down to 550°C, the operating temperature of the Rocky Flats Plant Incinerator. Measurements are also made at 550°C, to obtain a measured upper limit value for volatility at that temperature.

As a check on the equipment and techniques used to make the transpiration measurements, prior to installing the equipment in the Pu Facility glovebox, we ran some preliminary volatility tests on $\text{WO}_2(\text{OH})_2(\text{g})$ for which the volatility data are well established. [9,10]

Experimental

Transpiration Method:

In the transpiration method, [11] a known amount of carrier gas is slowly passed over a solid or liquid in a furnace chamber, such that any volatile gases produced become entrained in the carrier gas and are swept out of the chamber where the volatilized gas is then condensed and analyzed. The carrier gas may also contain reactive gases that contribute to forming the volatilizing species, such as, for the reaction,

$\text{O}_2(\text{g})$ and $\text{H}_2\text{O}(\text{g})$ are both reactive gases that contribute to production of $\text{PuO}_2(\text{OH})_2(\text{g})$. Variation of flow rate of the carrier gas permits us to establish the conditions under which the carrier gas becomes saturated with the equilibrium vapor pressure of the volatilizing species. At too slow a flow rate, diffusional transport of the volatilized gas out of the furnace chamber results in values apparently higher than the equilibrium vapor pressure. At too high a flow rate the residence time of the carrier gas in the furnace chamber is not long enough for saturation with the equilibrium

vapor pressure to occur. At intermediate flow rates, a "plateau" region is established where the equilibrium vapor pressure persists over a range of flow rates. The vapor pressure of the volatilized gas under equilibrium conditions is determined from the ideal gas law by taking the ratio of moles of volatilized species to total moles of gas passed through the chamber to be proportional to the partial pressure of volatilized species to total pressure of the carrier gas passed. The transpiration method also permits us to obtain information on the formula of the volatilizing species. This is done by varying the partial pressures of the reactive gases and noting the law of mass action effects on the volatilizing species. Thus, for the reaction above, we expect the equilibrium partial pressure of $\text{PuO}_2(\text{OH})_2(\text{g})$ to be proportional to the $1/2$ power of the $\text{O}_2(\text{g})$ pressure and to the first power of the $\text{H}_2\text{O}(\text{g})$ pressure. If the volatilizing species were different than $\text{PuO}_2(\text{OH})_2(\text{g})$, then the power dependence on $\text{O}_2(\text{g})$ and $\text{H}_2\text{O}(\text{g})$ would be accordingly different depending upon the equation stoichiometry.

Description of Apparatus:

The transpiration equipment in use in the Pu Facility is illustrated schematically in Fig. 1. The equipment is located inside of an air-flow glovebox. The furnace is a Kanthal-heater horizontal clamshell furnace rated to 1200°C in air. It provides a uniform-temperature hot zone ~ 7 cm long and an overall heated zone ~ 20 cm long. The furnace tube is of silica glass, 26 mm OD x 385 mm long with 35/25 silica glass ball and socket end joints sealed with silicone grease. The boat used to hold the sample is either of Al_2O_3 or silica glass. Silica glass (or Al_2O_3) wool plugs are used in several locations within the furnace tube: one upstream of the boat to define the hot zone, one just downstream of the boat to provide a dust filter, and either one or two further downstream in the lower temperature zone of the furnace to collect the condensate of the volatilized species. These plugs are surrounded by a Pt wire framework to provide for ease in insertion or removal from the furnace tube, and are sized to fit snugly in the tube. Temperatures are measured with type-K thermocouples with inconel sheaths. One thermocouple is located on the outside of the furnace tube at its center, and either one, two, or three thermocouples are located in a silica glass thermocouple probe tube just above the sample boat. These various thermocouples are periodically checked and calibrated against a type-S reference thermocouple. A water saturator is located upstream of the furnace. The water saturator is made of a 6-mm-thick wall Al vessel with an 800 cm^3 capacity and provided with a fritted stainless steel disperser for the carrier gas, which disperser is located 1 cm above the bottom of the vessel. Water level is maintained at $500\text{--}600\text{ cm}^3$ during the runs. The vessel is heated with a Glas-col mantle. A desiccant cartridge loaded with Drierite (CaSO_4) is located downstream of the furnace. The cartridge is provided with disconnect fittings to allow weighings to determine water pickup. Gas lines from the water saturator to the furnace and from the furnace to the Drierite cartridge are of stainless steel. Valves are also of stainless steel with Viton rubber seals. A stainless steel to silica glass ball joint connection is used to connect with the furnace tube. Heating tapes are wrapped on the lines from the water saturator to the furnace tube, and from the furnace tube to the Drierite cartridge and maintained at $\sim 150^\circ\text{C}$ during the runs to prevent water condensation. Precision Flow Devices PFD-401 mass flow controllers are used to control O_2 and Ar flow inputs and to monitor the output gas. Calibrations for these flow meters are provided by the supplier. The flow meters are intercompared periodically

Fig. 1. Schematic diagram of transpiration equipment.

to check for any changes in calibrations. Weighings are carried out on an Ohaus GT 2100 electronic balance, with a capacity of 2100g and an accuracy of $\pm 0.01\text{g}$. Certified weights are used periodically to calibrate the balance.

Sample Materials:

The sample of $\text{PuO}_2(\text{s})$ used in the runs had been formed from electrorefined plutonium. It was in the form of a very fine powder. Calculation of isotopic Pu and Am contents for April 1, 1992, after correcting for radionuclear changes based on a mass spectrometric analysis of the metal on May 10, 1990 gave an analysis of ^{238}Pu 0.014 %, ^{239}Pu 93.844 %, ^{240}Pu 5.872 %, ^{241}Pu 0.221 %, ^{242}Pu 0.049 %, and ^{241}Am 0.0264 %, all on the basis of metal content. An X-ray diffraction pattern of the PuO_2 starting material taken on a powder camera showed single phase PuO_2 but with broadened lines consistent with a very fine particulate material. An X-ray diffraction pattern taken after the transpiration heatings again showed single phase PuO_2 , but with very sharp spotty lines indicating large crystals. The $\text{PuO}_2/2\% \text{AmO}_2$ sample was a reactor grade material. Using an analysis made on this material on March 5, 1986, and converting for radionuclear changes to June 3, 1992, just prior to the experiments, we obtain ^{238}Pu 0.065 %, ^{239}Pu 80.659 %, ^{240}Pu 17.827 %, ^{241}Pu 0.989 %, ^{242}Pu 0.460 %, and ^{241}Am 2.056 %, all on the basis of metal content. A sample of $^{238}\text{PuO}_2$ reactor grade material was also used for one run. Isotopic analysis on this material was ^{238}Pu 80.33%, ^{239}Pu 16.55%, ^{240}Pu 2.54%, ^{241}Pu 0.398%, and ^{242}Pu 0.183%, all on the basis of metal content. The $\text{WO}_3(\text{s})$ was obtained from Cerac, Inc, as a -325 mesh powder, with a stated purity of 99.9 %. It was yellow green in color as received, but upon heating to 1050°C in $\text{Ar}(\text{g})/\text{H}_2\text{O}(\text{g})$ mixtures for the transpiration runs changed to a dark olive green color. X-ray fluorescence analysis taken after the heatings showed Mo, Zr, and Y to be present as trace impurities. X-ray diffraction patterns taken after the heatings showed the WO_3 to be a mixture of the triclinic [12] and monoclinic [13] forms. The stable form of WO_3 at the temperatures of the transpiration experiments is reported to be a tetragonal structure [14] which is stable only above 720°C . Water used for these experiments had been deionized and then distilled.

Transpiration Measurements of $\text{WO}_2(\text{OH})_2(\text{g})$ Volatility:

In order to test out the transpiration apparatus on a cold system prior to installing it in a glovebox in the Pu Facility, we carried out transpiration measurements on $\text{WO}_2(\text{OH})_2(\text{g})$ volatility according to the reaction,

The thermodynamic data for this reaction are well established [9], and accurate transpiration measurement data are also available for this reaction [10] within our temperatures of interest for the Pu and Am volatility studies.

The experimental procedure used was as follows. We loaded a 2.2 g sample of $\text{WO}_3(\text{s})$ into an Al_2O_3 boat, 1.3 cm wide x 7 cm long x 1 cm high, and heated sample and boat in air at 1000°C for 4 hours prior to use in the transpiration experiments. The boat and sample were then weighed and placed in the furnace (see schematic of apparatus, Fig. 1). In one of the runs Al_2O_3 wool plugs were placed in front and behind the boat. In the balance of the runs, plugs were not used. The Drierite cartridge was weighed and placed in the flow system in a valved-off position. The water bath was heated up to constant temperature (e.g., 75°C) and left open to the air through a stainless steel condenser chamber filled full of stainless steel turnings. The furnace was brought up to reaction temperature under Ar flow with the flow rate controlled at the desired flow rate with a flow controller. The Ar exiting the furnace was bypassed around the Drierite cartridge and passed through a flow meter and then exhausted to the air. As the furnace temperature was coming up, the heating tapes were also brought up to temperature. When furnace temperature was reached, the Ar flow was switched to pass through the water bath, with the bath now shut off from the air, and the Ar/ H_2O flow was passed through the furnace, then through the Drierite cartridge and through the exit flow meter and into the air. Upon completion of the run, the Ar flow was diverted to bypass the water bath, the furnace was turned off, and the Ar allowed to flow through the furnace and the Drierite while the furnace cooled. When cool, the boat and sample were removed and weighed to determine sample weight loss, and the Drierite cartridge was weighed to determine the amount of water passed through during the run. The amounts of water found were consistent to within $\pm 10\%$ of the expected values based upon the water bath temperatures and carrier gas flow rates.

The run conditions and results of these transpiration runs are summarized in Table 1. The vapor pressures of $\text{WO}_2(\text{OH})_2(\text{g})$ are calculated on the basis of weight loss of $\text{WO}_3(\text{s})$. These vapor pressures are compared in Table 1 with values obtained from JANAF [9]. Agreement is good at Ar flow rates of 25 or $50 \text{ cm}^3/\text{min}$, but observed vapor pressures are only about half of the literature values at Ar flow rates of $100 \text{ cm}^3/\text{min}$. One run made at $200 \text{ cm}^3/\text{min}$ in a different furnace with a larger diameter furnace tube, showed about two thirds of the literature value, which is consistent considering that there would be a longer residence time for the gas in the hot zone with the larger diameter. The one run made at an Ar flow rate of $50 \text{ cm}^3/\text{min}$ using Al_2O_3 plugs to reduce diffusional losses out of the hot zone showed no difference from a run under similar conditions without plugs, thus indicating no significant diffusional end losses. Carrier gas flow rates used by Glemser and Haeseler [10] in their transpiration studies of $\text{WO}_2(\text{OH})_2$ volatility were $50 \text{ cm}^3/\text{min}$ over the temperature range of 1173-1373 K.

Transpiration Measurements of Pu and Am Oxyhydroxide Volatilities:

The apparatus used for the Pu and Am oxyhydroxide volatilities was the same as that for the $\text{WO}_2(\text{OH})_2(\text{g})$ runs, and experimental procedures were generally the same, except that the volatility determinations were done by collection and analysis of the Pu and Am carryover rather than by weight loss. The availability of analytic support time was limited during the course of this work, so priorities had to be set on the samples that were analyzed, and some runs therefore were not analyzed. Run parameters and

Table 1. Transpiration data on volatility of $\text{WO}_2(\text{OH})_2(\text{g})$ based on the reaction: $\text{WO}_3(\text{s}) + \text{H}_2\text{O}(\text{g}) = \text{WO}_2(\text{OH})_2(\text{g})$.

T, K	time, min	cm ³ /min Ar	g H ₂ O	moles Ar	moles H ₂ O	pH ₂ O, atm	WO ₃ wt. loss, mg	$\frac{p\text{WO}_2(\text{OH})_2 \cdot \text{atm}}{\text{meas.}}$	$\frac{\text{liter}[9]}{\text{liter}[9]}$
1323 ^a	60	200	6.03	0.497	0.335	0.402	141.1	7.3×10^{-4}	11.0×10^{-4}
1319	60	100	2.69	0.248	0.149	0.376	45.4	4.9×10^{-4}	9.8×10^{-4}
1319	60	100	2.91	0.248	0.162	0.395	52.6	5.5×10^{-4}	10.3×10^{-4}
1319	60	50	1.70	0.124	0.094	0.432	47.2	9.3×10^{-4}	11.2×10^{-4}
1317	30	25	0.97	0.093	0.054	0.367	35.4	10.4×10^{-4}	9.3×10^{-4}
1322 ^b	60	50	1.52	0.124	0.084	0.405	40.7	8.4×10^{-4}	10.9×10^{-4}

^a This run was carried out in a separate furnace than used for the work in the Pu Facility. The furnace tube used had an inner diameter of 30 mm compared with 22 mm for the other runs.

^b Al₂O₃ wool plugs were used on either side of the boat in this run.

volatility results for runs with completed analyses are summarized in Tables 2 and 3. A 0.56 g sample of ²³⁹PuO₂ was used in runs 2 to 21, and was contained in an Al₂O₃ combustion boat (from Alfa Products), 2.3 cm wide x 5.8 cm long x 1.3 cm high. A 0.96 g sample of PuO₂/2% AmO₂ was used in runs 23 to 44 and was contained in an Al₂O₃ combustion boat (from Atomergic), 1.7 cm wide x 5.0 cm long x 0.7 cm high.

Water transport that was determined by weight gain of Drierite was consistent with water bath temperatures and carrier gas flow rates for flow rates of 50-100 cm³/min. At the higher gas flow rates of 500-1000 cm³/min, physical carrying of water also occurred from the water bath, and reduced water bath temperatures had to be used to maintain the desired amounts of water vapor flow. In all cases the amount of water picked up by the Drierite was used to determine the amount of water carried.

Temperature profiles were taken of the furnace hot zone, and showed the central uniform temperature hot zone (to within 10°C) was 7 cm long at 1050°C and 5 cm long at 1150°C, with a dropoff of 100 K in 5 cm on each side of the hot zone at each temperature. Because of the shortness of the hot zone and in order to leave room to maintain a dust filter, the center of the boat was displaced 1.3 cm upstream of the center of the hot zone. The purpose of the dust filter was to stop any fine particulates swept by the gas flow while allowing volatilized Pu and Am oxyhydroxides to pass through. Al₂O₃ wool or SiO₂ glass wool located downstream of the dust filter was used to condense out the Pu or Am oxyhydroxides. We expect the volatilities of Pu and Am oxyhydroxides to decrease by about a factor of 5 with a 100 K decrease in temperature, so that a length of 5 cm of wool should condense out about 80% each of the Pu and Am oxyhydroxides. Additional experimental details are given in the Appendix. This includes details on the arrangements of wool filters and collectors used in the various runs, analysis techniques, diagnostics on dust transport and on wall deposits, and sintering effects in the samples.

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Table 2. Summary of conditions of run time and gas flow for $\text{PuO}_2(\text{s})$ and $\text{PuO}_2/2\% \text{AmO}_2(\text{s})$ transpiration runs. Runs #2-21 are for $^{239}\text{PuO}_2(\text{s})$, runs #23-44 are for $^{239}\text{PuO}_2/2\% \text{}^{241}\text{AmO}_2(\text{s})$, and run #73 is for $^{238}\text{PuO}_2$.

run #	time, min	cm ³ /min O ₂	cm ³ /min Ar	g H ₂ O	moles of gas passed			total moles of gas
					O ₂	Ar	H ₂ O	
2	120	500	500	42.31	2.479	2.479	2.349	7.307
4	120	250	250	9.07	1.239	1.239	0.503	2.981
5	60	250	250	4.49	0.620	0.620	0.249	1.489
6	60	250	250	2.01	0.620	0.620	0.112	1.352
8	60	250	250	2.26	0.620	0.620	0.125	1.365
9	120	500		4.48	2.479		0.249	2.728
11	120	500		3.90	2.479		0.217	2.696
19	240	500		8.43	4.957		0.468	5.425
20	120	500		4.05	2.479		0.225	2.704
21	65	500		2.20	1.343		0.122	1.465
23	250	500		8.58	5.164		0.476	5.640
24	125	500		4.20	2.582		0.233	2.815
25	65	500		2.15	1.343		0.119	1.462
28	125	1000			5.164			5.164
32	300	100		18.90	1.239		1.049	2.288
33	180	50		6.10	0.372		0.339	0.711
34	300	50		13.87	0.620		0.770	1.390
36	600	50		33.95	1.239		1.885	3.124
37	600	50		27.84	1.239		1.545	2.784
44	600	50		22.38	1.239		1.242	2.481
73	900	50		30.09	1.859		1.670	3.529

Table 3. Summary of run temperatures, pressures of O₂(g) and H₂O(g), collected amounts of Pu and Am, and derived pressures of PuO₂(OH)₂(g) and AmO₂(OH)₂(g) for PuO₂(s) and PuO₂/2% AmO₂(s) transpiration runs. Runs #2-21 are for ²³⁹PuO₂(s), runs #23-44 are for ²³⁹PuO₂/2% ²⁴¹AmO₂(s) and run #73 is for ²³⁸PuO₂.

run #	T, K	pO ₂ , atm	pH ₂ O, atm	μg Pu	μg Am	pPuO ₂ (OH) ₂ , atm	pAmO ₂ (OH) ₂ , atm
2	1322	0.339	0.321	14.2 ^a	0.0075 ^a		
4	1314	0.416	0.169	0.22		3.09x10 ⁻¹⁰	
5	1413	0.416	0.167	24.9		7.00x10 ⁻⁸	
6	1414	0.459	0.0828	0.975		3.02x10 ⁻⁹	
8	1413	0.454	0.0916	1.3		3.98x10 ⁻⁹	
9	1316	0.909	0.0913	0.26		3.99x10 ⁻¹⁰	
11	811	0.920	0.0804	0.02		3.10x10 ⁻¹¹	
19	1216	0.914	0.0863	0.02		1.54x10 ⁻¹¹	
20	1317	0.917	0.0832	0.04		6.19x10 ⁻¹¹	
21	1415	0.917	0.0828	0.01		2.86x10 ⁻¹¹	
23	1218	0.916	0.0844	0.178	0.016	1.32x10 ⁻¹⁰	1.2x10 ⁻¹¹
24	1331	0.917	0.0828	0.247	0.003	3.67x10 ⁻¹⁰	4.4x10 ⁻¹²
25	1433	0.919	0.0814	0.089	0.003	2.55x10 ⁻¹⁰	8.5x10 ⁻¹²
28	1432	1.000		0.09	0.002	7.29x10 ⁻¹¹	1.6x10 ⁻¹²
32	1434	0.542	0.458	0.037	0.001	6.77x10 ⁻¹¹	1.8x10 ⁻¹²
33	1434	0.523	0.477	0.214	0.004	1.26x10 ⁻⁹	2.3x10 ⁻¹¹
34	1334	0.446	0.554	0.031	0.001	2.44x10 ⁻¹⁰	3.0x10 ⁻¹²
36	1229	0.397	0.603	0.177	<0.001	2.37x10 ⁻¹⁰	<1.3x10 ⁻¹²
37	825	0.445	0.555	0.073	<0.001	1.10x10 ⁻¹⁰	<1.5x10 ⁻¹²
44	1431	0.499	0.501	0.44	0.0088	7.42x10 ⁻¹⁰	1.5x10 ⁻¹¹
73	823	0.527	0.473	0.0032		3.86x10 ⁻¹²	

^aAnalysis of Pu and Am present on dust filter.

Analysis of Results:

We found as these experiments got underway that the Pu volatilities were considerably lower than we had predicted [2,3] (see Fig. 2). This presented us with difficulties in obtaining accurate volatility values. We reject run #5 because of background contamination. In runs #4, 6, and 8, where high gas flow rates and a fine particulate sample were used, some dust transport of PuO₂ may have occurred that contributed to the collected sample. These volatilities may therefore be somewhat high. Extensive sintering had occurred in the source samples used in runs #19, 20, 21, and 32, thus greatly reducing the sample surface area and making it difficult to

obtain equilibration between the carrier gas and the sample. We therefore reject these runs. Runs #25, 33, 34, and 44 also showed evidence for sintering effects and these volatilities appear to be on the low side. Some cross contamination may have also occurred because we reused the same furnace tubes for most of the runs, hence increasing uncertainties in the results. We consider runs #11, 37 and 73 that were run at ~820K to provide only an upper bound to the volatilities, and give a representation of the level of contamination to be expected in handling the collection samples in the glovebox. Considering the various uncertainties in the selected runs, we estimate that the volatility values fall within the range of 1/3 to 3 times the measured values.

We treat the thermodynamics as follows. We take the plutonium volatilization to proceed by the reaction,

The equilibrium constant for this reaction, K_{eq} , is given by,

$$K_{\text{eq}} = [\text{pPuO}_2(\text{OH})_2] / [\text{aPuO}_2][\text{pO}_2]^{1/2}[\text{pH}_2\text{O}], \quad (5)$$

where p indicates partial pressures of the gaseous species in atm and a the activity of the solid phase. Taking the activity of $\text{PuO}_2(\text{s})$ to be unity, and using the partial pressures for $\text{O}_2(\text{g})$, $\text{H}_2\text{O}(\text{g})$, and $\text{PuO}_2(\text{OH})_2(\text{g})$ from Table 3, we obtain K_{eq} values for reaction (2). We make a second-law of thermodynamics plot of $\log K_{\text{eq}}$ versus inverse temperature (see Fig. 2), which should give a linear slope. However, the scatter in the data is too large to obtain a meaningful slope by the second law method. We proceed to analyze the data using the third-law method. The standard free energy change for reaction (2), ΔG°_T , based on the relation $\Delta G^\circ_T = -RT \ln K_{\text{eq}}$, is given in Table 5 for the selected experimental points. The change in free energy function for reaction (2), $(\Delta G^\circ_T - \Delta H^\circ_{298})/T$, is obtained using available free energy function data on $\text{PuO}_2(\text{s})$ from Cordfunke et al.[15], data for $\text{O}_2(\text{g})$ and $\text{H}_2\text{O}(\text{g})$ from JANAF [9], and estimated data for $\text{PuO}_2(\text{OH})_2(\text{g})$ from Krikorian [2]. The estimated free energy function for $\text{PuO}_2(\text{OH})_2(\text{g})$ is given by Krikorian as

$$-(G^\circ_T - H^\circ_{298})/T = S^\circ_{298}[1 + (0.88 + 0.20x + 0.57y)(T - 298.15)(10^{-4})], \quad (6)$$

$$\text{where } S^\circ_{298} = 108.8 + 25.1 \ln(A_M) + 20.9x + 41.8y. \quad (7)$$

Units of $-(G^\circ_T - H^\circ_{298})/T$ are in J/mol-K, x and y are the coefficients for O and OH in the formula $\text{MO}_x(\text{OH})_y$ and A_M is the atomic weight of the central atom M. The $(\Delta G^\circ_T - \Delta H^\circ_{298})/T$ values are given in Table 4 for the experimental points, and are also summarized in Table 5 over a wide temperature range. By appropriately combining

Fig. 2. Plot of $\log K_{eq}$ versus inverse temperature for the reaction $\text{PuO}_2(\text{s}) + 1/2 \text{O}_2(\text{g}) + \text{H}_2\text{O}(\text{g}) = \text{PuO}_2(\text{OH})_2(\text{g})$. Experimental data points are indicated by circles with adjacent run numbers. Darkened circles show data points that are rejected because extensive sintering in the sample prevented equilibration. The experimental curve represents a third-law analysis of the data. An earlier theoretical prediction curve is also given.

the ΔG°_T and $(\Delta G^\circ_T - \Delta H^\circ_{298})/T$ values, we obtain ΔH°_{298} values for each of the data points (see Table 4). The average value of ΔH°_{298} is 232.43 kJ/mol with a standard deviation of ± 15.85 kJ/mol. Using this value of ΔH°_{298} together with the free energy functions in Table 5, we can calculate values for ΔG°_T and $\log K_{eq}$ at various temperatures. These are expressed analytically by the following approximate relationships:

$$\Delta G^\circ_T = 231.3 - 0.0109 T, \text{ kJ/mol}, \quad (8)$$

$$\log K_{eq} = -12,080/T + 0.569, \log \text{ atm}^{-1/2}. \quad (9)$$

The fit of equation (9) to the experimental data is illustrated in Fig. 2.

For americium volatilization, we express the reaction as

where AmO_2 is present in solid solution in $\text{PuO}_2(\text{s})$. Assuming the AmO_2 to form an ideal solution, we take the activity of AmO_2 to be equal to the mole fraction, or 0.021. The equilibrium constant for reaction (10) is given by

$$K_{eq} = [\text{pAmO}_2(\text{OH})_2] / [\text{aAmO}_2][\text{pO}_2]^{1/2}[\text{pH}_2\text{O}], \quad (11)$$

where $a \text{ AmO}_2$ is taken as 0.021 in our experiments. To calculate K_{eq} values, we review the Am volatility data (see Table 3). Because the Am values are near the limits of detection, we find it convenient to compare the ratios of Pu/Am in the volatilized samples with that in the starting material (see Table 6). The ratio of Pu/Am in the starting material is 47.6. In run #23, the first run made with the $\text{PuO}_2/2\% \text{ AmO}_2$ sample, Am is enriched by about a factor of 4 in the volatilized material with a Pu/Am ratio of 11. In subsequent runs, the Pu/Am ratio in the volatilized material is about equal to or greater than in the starting material. This suggests that the Am volatility may have been high in the initial run but may have been limited by surface depletion of the AmO_2 concentration in subsequent runs. In Table 6, where temperatures for the various runs are shown in addition to the Pu/Am ratios, we see that for the runs made at ~ 1430 K, the Pu/Am ratios for the volatilized material are in the range of 30-54, while at ~ 1330 K, the ratios are ~ 80 , and at 1229 K, the ratio is >177 . This indicates that the replenishment of the AmO_2 concentration at the sample surface is controlled by a diffusional process, with the closest approach to equilibrium in the runs at the highest temperatures, ~ 1430 K, except for the initial run. Recognizing that the $\text{AmO}_2(\text{OH})_2$ volatilities are likely on the low side, we proceed to calculate equilibrium constants for reaction (10). We reject run #32 because of high sintering in the sample. Also, run #28 can not be used because it did not have water vapor present, and runs #36 and 37 showed no detectable Am volatility. K_{eq} values for the remaining runs are summarized in Table 7. We proceed with a third law analysis of the data (Table 7) by taking the $(\Delta G^\circ_T - \Delta H^\circ_{298})/T$ values for the $\text{AmO}_2(\text{OH})_2$ volatilization reaction

Table 4. Summary of thermodynamic data for the reaction $\text{PuO}_2(\text{s}) + 1/2 \text{O}_2(\text{g}) + \text{H}_2\text{O}(\text{g}) = \text{PuO}_2(\text{OH})_2(\text{g})$, based on the experimental results.

run #	T, K	K_{eq} , $\text{atm}^{-1/2}$	ΔG^0_T , kJ/mol	$(\Delta G^0_T - \Delta H^0_{298})/T$, J/mol-K	ΔH^0_{298} , kJ/mol
4	1312	2.84×10^{-9}	214.67	-11.12	229.30
6	1414	5.38×10^{-8}	196.64	-11.86	213.41
8	1413	6.45×10^{-8}	194.51	-11.85	211.26
9	1316	4.58×10^{-9}	210.10	-11.14	224.76
23	1218	1.64×10^{-9}	204.30	-10.77	217.50
24	1331	4.63×10^{-9}	212.37	-11.25	227.34
25	1433	3.27×10^{-9}	232.79	-12.06	250.07
33	1434	3.65×10^{-9}	231.64	-12.07	248.95
34	1334	6.59×10^{-10}	234.30	-11.27	249.33
36	1229	6.24×10^{-10}	216.58	-10.81	229.86
44	1431	2.10×10^{-9}	237.73	-12.04	254.96
					ave. 232.43
					std. dev. ± 15.85

Table 5. Summary of free energy function values for the reaction $\text{PuO}_2(\text{s}) + 1/2 \text{O}_2(\text{g}) + \text{H}_2\text{O}(\text{g}) = \text{PuO}_2(\text{OH})_2(\text{g})$.

T, K	$-(G^0_T - H^0_{298})/T$, J/mol-K				$(\Delta G^0_T - \Delta H^0_{298})/T$, J/mol-K
	$\text{PuO}_2(\text{s})$	$1/2 \text{O}_2(\text{g})$	$\text{H}_2\text{O}(\text{g})$	$\text{PuO}_2(\text{OH})_2(\text{g})$	
700	87.413	106.806	198.465	407.807	-15.123
800	93.946	108.063	201.322	416.801	-13.470
900	100.275	109.276	204.084	425.795	-12.160
1000	106.354	110.438	206.738	434.789	-11.259
1100	112.170	111.546	209.285	443.784	-10.783
1200	117.730	112.604	211.730	452.778	-10.714
1300	123.043	113.614	214.080	461.772	-11.035
1400	128.127	114.579	216.341	470.766	-11.719
1500	132.996	115.501	218.520	479.761	-12.744

Table 6. Pu/Am ratios found in volatilized samples for runs at various temperatures. The Pu/Am ratio in the starting material was 47.6.

Run #	T, K	$\mu\text{g Pu}/\mu\text{g Am}$, in volatilized material
23	1218	11
24	1331	82
25	1433	30
28	1432	45
32	1434	37
33	1434	54
34	1334	81
36	1229	>177
37	825	>73
44	1431	50

(reaction (10)), to be identical to those for $\text{PuO}_2(\text{OH})_2$ volatilization reaction (reaction (2)), as given in Table 5. We obtain an average ΔH°_{298} of 240.5 kJ/mol with a standard deviation of 20.0 kJ/mol for reaction (10). We prefer to give greater weight to run #23, and therefore take ΔH°_{298} to be 225 kJ/mol with an estimated uncertainty of ± 30 kJ/mol. We then obtain the following analytical expressions for ΔG°_T and $\log K_{\text{eq}}$ for reaction (10).

$$\Delta G^\circ_T = 223.9 - 0.0109 T, \text{ kJ/mol}, \quad (12)$$

$$\log K_{\text{eq}} = -11,695/T + 0.571, \log \text{ atm}^{-1/2}. \quad (13)$$

Discussion

The observed volatilities of Pu in these experiments were substantially lower than we had predicted (see Fig. 2). This reduced the accuracy with which we could determine the Pu volatilities. The various problems encountered, i.e., background contamination, carrying of dust (at high flow rates), sintering of the sample, incomplete collection of the volatilized sample on the collection plugs, cross contamination between runs from reuse of the furnace tubes, have all been mentioned. We estimate the accuracy of the measured Pu equilibrium pressures to be within plus a factor of 3 to minus a factor of 1/3 of the selected values. For the measurements on Am volatilities, the same uncertainties apply as for the Pu measurements, plus the uncertainty due to surface depletion. We estimate the accuracy of the measured Am equilibrium pressures to be accurate to within plus a factor of 15 to minus a factor of 1/15 of the selected values.

Table 7. Summary of thermodynamic data for the reaction $\text{AmO}_2(\text{s.s.}, a = 0.021) + 1/2 \text{O}_2(\text{g}) + \text{H}_2\text{O}(\text{g}) = \text{AmO}_2(\text{OH})_2(\text{g})$, based on the experimental results.

run #	T, K	$K_{\text{eq}},$ $\text{atm}^{-1/2}$	$\Delta G^\circ_T,$ kJ/mol	$(\Delta G^\circ_T - \Delta H^\circ_{298})/T,$ kJ/mol-K	$\Delta H^\circ_{298},$ kJ/mol
23	1218	6.9×10^{-9}	190.24	-10.77	203.36
24	1331	2.7×10^{-9}	218.52	-11.25	233.49
25	1433	5.2×10^{-9}	227.27	-12.06	244.55
33	1434	3.2×10^{-9}	233.13	-12.07	250.43
34	1334	3.8×10^{-10}	240.46	-11.27	255.49
44	1431	2.0×10^{-9}	238.43	-12.04	255.66
					ave. 240.5
					std. dev. ± 20.0

The experience gained here is useful in showing how improvements in accuracy of measuring Pu volatilities could be attained in future work. Using $^{238}\text{PuO}_2$ instead of $^{239}\text{PuO}_2$ as the sample material would improve the sensitivity of detection by alpha counting by about a factor of 275 because of the higher specific activity of ^{238}Pu . Temperatures could be held low enough to avoid sintering effects on equilibration, and collection tubes could be used instead of quartz wool to obtain more complete collection of the volatilized samples. This approach was used in one run, run #73, at the end of this study.

Because of the low accuracy of measurement of Pu volatilities, we were not able to establish the formula of the volatilizing species through tests based on the variation of O_2 and H_2O pressures. We have assumed $\text{PuO}_2(\text{OH})_2(\text{g})$ to be the predominant volatilizing species based on estimated bond energy and entropy considerations of possible species, as discussed in ref. [2]. But, considering that the $\text{PuO}_2(\text{OH})_2(\text{g})$ volatility is lower than we had predicted, the next most likely species to consider that might make contributions to the volatility are $\text{PuO}_3(\text{g})$ and $\text{PuO}_2\text{OH}(\text{g})$. For example, in the analogous case for U, $\text{UO}_3(\text{g})$ is known to make a significant contribution to the volatility in addition to $\text{UO}_2(\text{OH})_2(\text{g})$ at temperatures in the vicinity of 1400 K [16], and in the analogous case for Cr, volatilities of $\text{CrO}_3(\text{g})$ and $\text{CrO}_2\text{OH}(\text{g})$ are each an order of magnitude below that for $\text{CrO}_2(\text{OH})_2(\text{g})$ [17]. We find, however, that even if $\text{PuO}_3(\text{g})$ or $\text{PuO}_2\text{OH}(\text{g})$ are important at the temperature range of our measurements, ~ 1400 K, the dropoff in volatilities of $\text{PuO}_3(\text{g})$ and $\text{PuO}_2\text{OH}(\text{g})$ with decreasing temperature would be much more rapid than for $\text{PuO}_2(\text{OH})_2(\text{g})$, so that $\text{PuO}_3(\text{g})$ and $\text{PuO}_2\text{OH}(\text{g})$

become unimportant at 823 K under the conditions of the Rocky Flats Plant incinerator. For example, let us assume that all of the experimentally observed Pu volatility is due to $\text{PuO}_3(\text{g})$ according to the reaction,

From the experimental data, we calculate appropriate values of K_{eq} and ΔG°_T . We use the same free energy function for $\text{PuO}_3(\text{g})$ as for $\text{UO}_3(\text{g})$ [15], and free energy functions for $\text{PuO}_2(\text{s})$ from ref. [15] and for $\text{O}_2(\text{g})$ from ref. [9], to obtain $(\Delta G^\circ_T - \Delta H^\circ_{298})/T$ values that range from -146.63 J/mol-K at 800 K to -136.99 J/mol-K at 1500 K. An average value of ΔH°_{298} based on the experimental data is then calculated to be 423.7 kJ/mol with a standard deviation of 18.5 kJ/mol. This leads to the expression

$$\Delta G^\circ_T = 406.0 - 0.125 T, \text{ kJ/mol}, \quad (15)$$

for reaction (14). We then use this expression to calculate that in the presence of 0.1 atm $\text{O}_2(\text{g})$, the assumed volatility of $\text{PuO}_3(\text{g})$ would drop from 7.6×10^{-10} atm at 1400 K to 1.8×10^{-20} atm at 823 K. Thus we see that even if $\text{PuO}_3(\text{g})$ makes a significant contribution to the Pu volatility at ~1400 K, it drops to a negligible level relative to $\text{PuO}_2(\text{OH})_2(\text{g})$ at 823 K. We can similarly show that $\text{PuO}_2\text{OH}(\text{g})$ drops off to a negligible level at 823 K. We conclude that although it has not been experimentally established that $\text{PuO}_2(\text{OH})_2(\text{g})$ is the species responsible for the volatilities observed in our experiments, other possible contributing species become of negligible importance under the Rocky Flats Plant incinerator conditions. Therefore, assuming all of the experimental volatility to result from $\text{PuO}_2(\text{OH})_2(\text{g})$ gives us a conservatively high value for Pu volatility under the Rocky Flats Plant incinerator conditions. We can make similar arguments to show that $\text{AmO}_2(\text{OH})_2(\text{g})$ is the dominant species under Rocky Flats Plant incinerator conditions.

We now proceed to calculate the Pu and Am volatilities produced in the secondary fluidized bed combustor of the Rocky Flats Plant incinerator. We take as operating conditions for the bed [18,19], a temperature of 823 K, 40 kmols/h of total gas flow at a pressure of 1 atm, 0.1 atm O_2 , and 0.05 atm H_2O . We assume that Pu and Am are present in the bed in the form of $\text{PuO}_2(\text{s})$ containing 200 ppm of AmO_2 in solid solution. (Note, however, that if insufficient Pu and Am are present in the waste to form a $\text{PuO}_2(\text{s})$ phase with dissolved $\text{AmO}_2(\text{s})$, then the volatilities of Pu and Am will be lower than calculated here.) We take 6000 hours of operating time per year. From equations (5) and (9), we obtain a $\text{PuO}_2(\text{OH})_2(\text{g})$ pressure of 1.2×10^{-16} atm; and from equations (11) and (13), and using an activity of 2×10^{-4} for AmO_2 , we obtain an $\text{AmO}_2(\text{OH})_2(\text{g})$ pressure of 7.3×10^{-20} atm. Taking the ratio of partial pressure of $\text{PuO}_2(\text{OH})_2$ to total gas pressure to be equal to the mole fraction of $\text{PuO}_2(\text{OH})_2$ in the gas, and multiplying this mole fraction by the molar flow rate of gas, we obtain a $\text{PuO}_2(\text{OH})_2(\text{g})$ transport rate of 4.9×10^{-12} moles Pu/h, or 1.2×10^{-9} g Pu/h. At 6000 h of operation per year, this amounts to 7.1×10^{-6} g Pu/y. Similarly, for $\text{AmO}_2(\text{OH})_2(\text{g})$,

we obtain a transport rate of 7.0×10^{-13} g Am/h or 4.2×10^{-9} g Am/y. We need to assess the uncertainties in these values. For $\text{PuO}_2(\text{OH})_2(\text{g})$, a factor of 3 uncertainty on the high side results from the errors in the measured vapor pressures, and we add an additional factor of 5 uncertainty on the high side because of the error introduced from the estimated free energy function for $\text{PuO}_2(\text{OH})_2(\text{g})$. This gives a total estimated error of a factor of 15 on the high side. For $\text{AmO}_2(\text{OH})_2(\text{g})$, the uncertainty is a factor of 15 on the high side from the measured vapor pressure and a factor of 5 on the high side from the estimated free energy function for a total estimated error of a factor of 75 on the high side. Taking the high side error estimates, the Pu transport rate becomes 1.8×10^{-8} g Pu/h or 1.1×10^{-4} g Pu/y, and the Am transport rate becomes 5.2×10^{-11} g Am/h or 3.1×10^{-7} g Am/y.

The thermodynamic data generated here on $\text{PuO}_2(\text{OH})_2(\text{g})$ and $\text{AmO}_2(\text{OH})_2(\text{g})$ can be applied to other mixed waste incinerators as well, to obtain equilibrium amounts of $\text{PuO}_2(\text{OH})_2(\text{g})$ and $\text{AmO}_2(\text{OH})_2(\text{g})$. In doing so, we need to recognize that these volatilities may be reduced because of interactions of $\text{PuO}_2/\text{AmO}_2$ with incinerator ash thus lowering the $\text{PuO}_2/\text{AmO}_2$ activities. Also, if a high halogen content is produced in the combustion gases, gaseous oxyhalides of Pu and Am may add to the overall Pu and Am volatilities. For purposes of illustration, we take the incinerator operating conditions as 1 atm total pressure with 0.1 atm $\text{O}_2(\text{g})$ and 0.1 atm $\text{H}_2\text{O}(\text{g})$, and a gas flow rate of 40 kmols/h. Incinerator temperatures are taken over the range of 550 C to 1500 C. Operational time is taken as 6000 h/y. PuO_2 containing 200 ppm AmO_2 in solid solution is assumed to be present in sufficient quantity to maintain the solid $\text{PuO}_2/\text{AmO}_2$ phase in the ash. Results are given in Table 8. We see that the volatilities of Pu and Am are strongly dependent upon temperature, as for example, an incinerator that operates at 1000°C, shows a 10^5 increase in Pu and Am volatilities as compared with an incinerator that operates at 550°C.

Summary and Conclusions

We find by transpiration experiments that Pu and Am show very low but measurable volatilities at 1230-1430 K from interactions of $\text{O}_2(\text{g})$ and $\text{H}_2\text{O}(\text{g})$ with $\text{PuO}_2(\text{s})$ and $\text{PuO}_2/2\% \text{AmO}_2(\text{s})$. The volatile species are taken to be dominantly $\text{PuO}_2(\text{OH})_2(\text{g})$ and $\text{AmO}_2(\text{OH})_2(\text{g})$ with vapor pressures of $\sim 10^{-10}$ atm $\text{PuO}_2(\text{OH})_2(\text{g})$ and $\sim 10^{-12}$ atm $\text{AmO}_2(\text{OH})_2(\text{g})$ under the measurement conditions. We estimate the accuracy to be within plus a factor of three to minus a factor of 1/3 in the $\text{PuO}_2(\text{OH})_2(\text{g})$ pressure measurements and within plus a factor of 15 to minus a factor of 1/15 in the $\text{AmO}_2(\text{OH})_2(\text{g})$ pressure measurements. Using thermodynamic relations to extend the data to the conditions of the secondary combustion chamber of the Rocky Flats Plant Fluidized Bed Incinerator, we obtain volatilization rates of 7×10^{-6} g Pu/y and 4×10^{-9} g Am/y.

Table 8. Illustration of the dependence of $\text{PuO}_2(\text{OH})_2(\text{g})$ and $\text{AmO}_2(\text{OH})_2(\text{g})$ volatilization on incineration temperature in mixed waste incinerators. Pu and Am are assumed to be present as $\text{PuO}_2(\text{s})$ with 200ppm AmO_2 in solid solution. Incinerator operating conditions are taken as 1 atm total pressure with 0.1 atm $\text{O}_2(\text{g})$ and 0.1 atm $\text{H}_2\text{O}(\text{g})$, and a gas flow rate of 40 kmols/h. Operational time is taken as 6000 h/y.

t , °C	$p\text{PuO}_2(\text{OH})_2$, atm	$p\text{AmO}_2(\text{OH})_2$, atm	g Pu/y	g Am/y
550	2.5×10^{-16}	1.5×10^{-19}	1.4×10^{-5}	8.4×10^{-9}
600	1.7×10^{-15}	9.5×10^{-19}	9.8×10^{-5}	5.5×10^{-8}
700	4.5×10^{-14}	2.3×10^{-17}	2.6×10^{-3}	1.3×10^{-6}
800	6.5×10^{-13}	3.0×10^{-16}	3.7×10^{-2}	1.7×10^{-5}
900	5.9×10^{-12}	2.5×10^{-15}	3.4×10^{-1}	1.5×10^{-4}
1000	3.8×10^{-11}	1.5×10^{-14}	2.2	8.9×10^{-4}
1100	1.9×10^{-10}	7.2×10^{-14}	11.0	4.1×10^{-3}
1200	7.4×10^{-10}	2.7×10^{-13}	42.0	1.6×10^{-2}

Appendix

Additional Experimental Details:

The arrangements of the wool filters and collectors for the various runs were as follows: In runs #1 to 3, a 1.5 cm long Al_2O_3 wool plug was placed just upstream of the boat, a 1.5 cm long Al_2O_3 wool plug (the dust filter) was placed immediately downstream of the boat, another 1.5 cm long Al_2O_3 wool plug followed that, and then a 5 cm long Al_2O_3 wool plug. Run #1 was an initial heating of the $^{239}\text{PuO}_2$ sample in an Ar/O_2 gas flow (without H_2O) to 1325 K for 2 hours. In runs #2 and 3, the $^{239}\text{PuO}_2$ was exposed to $\text{Ar}/\text{O}_2/\text{H}_2\text{O}$ mixtures at 1322 K for 2 hours. The Al_2O_3 plugs downstream of the boat were submitted for Pu analyses for these three runs. However, we were unable to dissolve off the Pu from the Al_2O_3 wool, using hot HNO_3/HF , or several other acids or acid mixtures that were tried. The dust filter plug on run #2 showed a high alpha count, sufficient for analysis by gamma counting. It was therefore analyzed by gamma counting and showed a Pu content of 14.2 micrograms and an Am content of 0.0075 micrograms (see Table 3). This value is useful for setting an upper bound to the amount of PuO_2 dust carryover to be expected for the very fine particulate PuO_2 sample used here. Activities on the Al_2O_3 plugs downstream were much lower indicating that the filter had effectively filtered out most of the PuO_2 dust, or had reacted with the $\text{PuO}_2(\text{OH})_2(\text{g})$ to form a solid compound of

Pu. The amount of Am present in the deposit is enriched by a factor of 2 relative to Pu as compared with the starting sample, thus suggesting that $\text{AmO}_2(\text{OH})_2(\text{g})$ has a proportionately higher volatility than $\text{PuO}_2(\text{OH})_2(\text{g})$, and that a portion of the activity on the dust filter originated from reactive condensation of the gaseous Pu and Am oxyhydroxides. No further analyses were attempted on runs #1 to 3.

Because of the problems of using Al_2O_3 wool plugs for dust filters and collectors, we switched to silica glass wool dust filters and collectors in all subsequent runs except for runs #44 and 73, in which we used silica glass collection tubes. The following wool plug arrangements were used for the remaining runs. For runs #4 to 11, we used a 1.5 cm long Al_2O_3 wool plug upstream of the boat, a 1.5 cm long SiO_2 glass wool dust filter immediately downstream of the boat followed by a 0.5 cm gap and then a 5 cm long SiO_2 glass wool collector plug. For runs #19 to 21, we used a 1.5 cm long SiO_2 glass wool plug upstream of the boat, and two 5 cm long SiO_2 glass wool collector plugs placed immediately downstream of the boat. No dust filter was used in these runs. In runs #23 to 37, we used a 1.5 cm long SiO_2 glass wool plug upstream of the boat, a 1.5 cm long SiO_2 glass wool dust filter immediately downstream of the boat followed by a 0.5 cm gap and then two 5 cm long SiO_2 glass wool collector plugs. In runs #44 and 73, we again used a 1.5 cm long SiO_2 glass wool plug upstream of the boat, a 1.5 cm long SiO_2 glass wool dust filter immediately downstream of the boat followed by a 0.5 cm gap, and then a 1.5 cm dia x 12 cm long SiO_2 glass collector tube joined on the downstream side with a 12/30 standard taper joint to a tube exiting the furnace. A SiO_2 glass wool plug was wrapped around the sampling tube near the entrance end to provide a diffusion barrier inside the furnace tube, and SiO_2 glass wool was loosely placed inside the sampling tube to provide additional surface area for condensation.

Cotton swabs were also used for diagnostic tests on a number of the runs to test for residual Pu or Am deposits on the furnace tube walls in the region of the silica glass wool collectors and further downstream. These cotton swab tests are described further down in this report.

We found that the Pu and Am could be dissolved from both the silica glass wool and from the cotton swabs by digesting in an acid mixture containing 8M HNO_3 , 0.1M HF , and 0.1M H_2SO_4 . After digestion, each solution from the PuO_2 tests was filtered, and an aliquot evaporated to dryness on a 2.5 cm dia planchet. In samples from the $\text{PuO}_2/2\% \text{AmO}_2$ tests, each filtered solution was passed through an ion exchange column to separate Pu and Am into fractions prior to evaporation on a planchet. Gross alpha activity on the planchets was measured using a dual chamber Ortec alpha spectrometer system composed of models 778, 6719 and 576 counter, timer, and chamber components. The system was standardized for Pu and Am determinations with standard solutions of Pu of appropriate isotopic composition and a standard ^{241}Am solution. The concentrations of Pu and Am were calculated taking into account the measured alpha counts, the volumes of the digested solutions and of the aliquots evaporated on the planchets, the specific activity of the Pu isotopic mix or separated ^{241}Am fraction, and the counting system efficiency. For the silica glass collection tubes, which also contained some silica glass wool packing inside the tubes, we used

a mixture of concentrated HCl and HF for the dissolution. This dissolved the Pu and Am and also dissolved the silica glass wool and etched the surface of the silica tube. The dissolved silica was removed as $\text{SiF}_4(\text{g})$ by heating with excess HF, then aliquot portions were taken of the solution, taken to dryness on planchets and counted for alpha activity using pulse height analysis to determine both Pu and Am. On two of the $^{239}\text{PuO}_2$ runs (runs #6 and #8), we carried out analyses on the collector plugs by gamma counting, and then analyzed them by the chemical dissolution and alpha counting method. For run #6, we obtained 1.1 μg Pu by gamma counting and 0.85 μg Pu by alpha counting, and for run #8, we obtained 1.2 μg Pu by gamma counting and 1.4 μg Pu by alpha counting. The agreement appears to be within about 20% by the two methods. We have used the average of the two types of analytic results for runs #6 and 8 in Table 3.

Beginning with run #6, diagnostic surveys were carried out using surface alpha counting of silica glass plugs and cotton swabs to evaluate PuO_2 dust transport, condensate on the furnace tube walls, and background contamination problems from the glovebox system. Surface measurements were made with a self-contained alpha survey count-rate-meter, LLNL model LEA75-1854. With this instrument, 0.1 μg of Pu (93.8% ^{239}Pu), dried from solution onto a planchet, measured 9,000-10,000 counts per min at approximately 2 cm. We had found a spuriously high level of Pu deposit on the silica glass wool plug in run #5 (see Table 3), that even exceeded the amount of Pu found on the dust filter of run #2 (see Table 3). We believe that the high level of Pu occurred from pickup of background Pu during handling of the collector plug in the glovebox. After run #6, to check the background Pu level inside the glovebox, we took paper swipe samples on the gloves, glovebox floor and walls, and apparatus surfaces and found alpha activity ranging from 4000-50,000 counts/min. This can be compared with 30,000 counts/min of alpha found on the surface of the collector plug from run #5. Before proceeding further, we wiped down all of the glovebox interior surfaces and the exposed equipment surfaces with lab wipes (paper towelettes) dampened with "Swish" (aqueous detergent cleaner). Then, to further minimize the pickup of background Pu contamination, we used the following procedures for handling of collector plugs and diagnostic swabs. The silica glass wool plugs were brought into the glovebox in a sealed plastic bag. The bag was opened and the plug inserted into the furnace tube using the bag as a holder to make the insertion. A metal rod with a disk on the end was cleaned with "Swish" on a lab wipe, and used to push the plug into position. After the run, a wire with a hook on the end was wiped off with "Swish" on a lab wipe, and used to pull the plug out of the furnace tube and drop it into a clean screwcap plastic container. After removal of the collector plug, a long-handled cotton swab with a plastic handle was removed from a sealed plastic bag, wet with water and used to wipe down the inside walls of the furnace tube on the downstream side up to just short of the dust filter. The cotton swab was then snipped away from the handle and dropped into a clean screwcap plastic container. A second cotton swab was used to dry off and further wipe the same region of furnace walls, and was similarly

transferred to a separate screwcap plastic container. The collector plugs and swabs were transferred to a hood, removed from the containers and counted with the alpha survey meter that had been checked against the 0.1 μg ^{239}Pu reference.

Results of the diagnostic surveys are summarized in Table A-1. Run #6A was a test for PuO_2 dust transport. With the upstream wool plug, PuO_2 and boat, and dust filter in place, two clean silica glass wool plugs each 2 cm long were inserted downstream of the dust filter, and Ar was run through the furnace tube at 500 cm^3/min for 1 hour. After the run, we found 250 counts/min alpha activity on a dry swab sample taken of the furnace tube wall downstream of the plugs. We found 6000 counts/min alpha activity on the first collector plug (nearest the boat) and only 500 counts/min on the second plug. A dry swab taken of the furnace tube wall downstream of the dust filter after removal of the plugs showed 2000 counts/min alpha. These results may be indicative of some dust pickup by the first plug, or the plug may have picked up some contamination from the furnace tube walls from prior runs. There was no evidence that any dust had gotten past the plugs, or it would have been picked up by the first swab. Run #10 was another test for PuO_2 dust transport. A new clean tube, a clean dust filter, and clean collection plug were used for the test, with the PuO_2 sample and boat and the upstream filter in place. The tube had a constriction between the dust filter and the collector plug that narrowed the passage to 1 cm in diameter, which arrangement channels the flow and the dust particles through the center of the dust filter, thus minimizing any leakage between the dust filter and the wall. The run was made at 823 K for 2 hours under 500 cm^3/min flow of O_2 , but without H_2O present. No volatility of Pu is expected without H_2O . From 200-500 counts/min of alpha activity were found for the collector plug and for the wet and dry swabs. We surmise that this is the level of Pu activity to expect because of background contamination from the glovebox environment during handling of the collector plugs and swabs. Because of the low level of activity, we conclude that PuO_2 dust transport did not occur. Run #13 was made to test for variation of Pu condensate with distance in the collector plugs. Eight plugs each 1.3 cm long, were placed next to each other, and a run was made at 1430 K for 1 hour with 500 cm^3/min O_2 flow and 0.078 atm of H_2O present. Alpha counts were found to all be low and randomly distributed at 100-200 counts/min, so that a distribution of Pu condensate could not be distinguished. This run was also indicative of no PuO_2 dust transport. In runs #19, 20, and 21, dust filters were not used. There was no evidence for dust transport in these runs, nor any evidence for volatility above the background level of up to about 500 counts/min of alpha associated with handling of the samples in the glovebox. We believe the low levels of dust transport and volatility observed here are a result of the high degree of sintering that has occurred in the PuO_2 sample (see more discussion later). In run #23, in which we made the first run with the $\text{PuO}_2/2\%$ AmO_2 sample, with run conditions of 1218 K for 250 min with 500 cm^3/min O_2 flow and 0.084 atm H_2O , we carried out chemical analyses for Pu and Am on the separate collector plugs and swabs and obtained: collector plug #1, 0.044 μg Pu and 0.003 μg Am; collector plug #2, 0.008 μg Pu and 0.004 μg Am; wet swab, 0.062 μg Pu and 0.004 μg Am; and dry swab, 0.064 μg Pu and 0.004 μg Am. It is apparent that a significant fraction of the Pu and Am condensate was picked up by the swabs. On subsequent runs therefore we combined

Table A-1. Summary of alpha activity surveys of dust filters, collector plugs, and wet and dry swabs used to wipe off the inner walls of the furnace tubes. The alpha activity is measured with an alpha survey meter at ~2 cm from the surface of the sample.

run #	furnace tube ^a	alpha activity, counts per min				
		dust filter	collector plug # 1	collector plug # 2	wet swab	dry swab
4	B					
5	B	30,000				
6	B		4000		2000	2000
6A ^b	B		6000	500		2000
8	B		8000		800	1000
9	B		4000		600	
10 ^c	D		300		500	200
11	D	10,000	1000		3000	2000
13 ^d	D		100-200 ^d		400	300
19 ^e	D		100	200	300	300
20 ^e	D		400	100	300	1000
21 ^e	D		200	200	400	500
23	D		2000	1000	1000	4000
24	D		2000	600	600	400
25	D		6000	400	300	500
28	D		1000	2000	300	
32	E		4000	2000	400	2000
33	E	60,000	2000	500	1000	400
34	E		2000	400	2000	10,000
35 ^f	E		4000	4000	400	300
36	E		500	5000	600	3000
37	1	30,000	1000	2000	200	300
44	8		2000 ^g			
73	15					

^aFurnace tubes D and E had a constriction in the tube between the dust filter and the first collector plug, narrowing the passage to 1 cm in diameter. Furnace tubes B, 1, and 8 were smooth bore. New tubes were used for runs 4, 10, 37, 44, and 73.

^bThis was a run made to check for dust transport. With the front plug, PuO₂ sample and boat, and dust filter in place, two clean silica glass wool plugs each 2 cm long were placed in the tube past the dust filter and Ar was run through at 500 cm³ for 1 hour with the furnace cold.

^cThis was a run made to check for dust transport. It was run at 823 K for 2 hours under 500 cm³/min flow of O₂.

^dThis run was made to check for variation of Pu condensate with distance along the length of the collector plug. Eight plugs, each 1.3 cm long, were placed next to each other, and a run was made at 1430 K for 1 hour with 500 cm³/min O₂ flow and 0.078 atm H₂O present. Surface alpha counts on the plugs were all found to be low at 100-200 counts/min.

^eDust filters were not used in these runs.

^fThis was a run without furnace operation in which the clean collector plugs were inserted into position and then removed and checked for alpha counts.

^gCounts are for plug supporting inlet to the sampling tube.

the two collector plugs and two swabs in one batch for analysis, except for run #28, where we only used the two collector plugs, and for runs #44 and 73, where we used silica glass collector tubes. In run #34, which was made at 1334 K for 5 hours with 50 cm³/min O₂ flow and 0.458 atm H₂O, we found a fairly high activity of 10,000 counts/min alpha on the dry swab. To test the effect of transfer of any residual deposit to the next run, we carried out a dry run (run #35) in which clean collector plugs were inserted into position and then removed without operating the furnace. This was followed by a wet and dry swab. The collector plugs showed fairly high activity at 4000 counts/min of alpha each, while the counts on the swabs had dropped to background. This indicates that the collector plugs (which fit snugly in the furnace tube) were effective in removing the residual Pu and Am from the previous run off the walls. We expect that some transfer of Pu and Am condensate occurred in all the runs where we reused the tubes.

We noted the effect of sample sintering resulting in low volatility in runs #19, 20, and 21. Prior to run #19, the PuO₂ sample had accumulated run times of 17 hours at 1330 K plus 5 1/2 hours at 1430 K. The presence of water vapor probably accelerated the sintering. Visual observation showed the sample to have the appearance of grains of sand. X-ray diffraction showed a spotty pattern indicating large crystals. The low surface area from the sintering would make it more difficult to attain equilibrium, especially at the high gas flow rates used in these runs. The amounts of Pu analyzed in the collection plugs for these three runs are very low and subject to background contamination during handling, so that the actual volatilized amounts are even less than shown. In the runs on the PuO₂/2% AmO₂ samples, we followed the effects of sintering on equilibration more carefully. After an initial heat treatment of the sample at 1330 K for 4 hours, we made run #23 at 1218 K and run #24 at 1331 K and obtained the expected Pu volatilities for these runs (see Fig. 2 where log K_{eq} for the volatilization reaction is shown as a function of 1/T). In run #25 made at 1433 K for 65 min, we found an apparent drop off in Pu volatility, although probably within experimental error. This would suggest sintering was becoming important at 1433 K. By run #32, the PuO₂/2% AmO₂ sample had accumulated run times of 6 hours at 1330 K plus 11 hours at 1430 K. Run #32 was made at 1434 K for 6 hours with an O₂ flow rate of 100 cm³/min, which was a much lower flow rate than in previous runs. The volatility obtained for Pu was found to be considerably reduced in run #32, which we attribute to sintering. The lower flow rate of gas used should have improved the approach to equilibrium because of the longer residence time of the gas, but the lowered surface area of the sample from sintering apparently was a more significant factor. For run #33, we ground up the PuO₂/2% AmO₂ sample in a mortar and pestle, and carried out the run at 1434 K for 3 hours with an O₂ flow rate of 50 cm³/min. The volatility of Pu was considerably increased in this run but still appeared somewhat low (see Fig. 2). Some sintering may still have occurred since the sample was at 1434 K for 3 hours. The sample was rerun (run #34), without grinding, at 1334 K for 6 hours with an O₂ flow rate of 50 cm³/min, and showed a lowered Pu volatility similar to run #33. Apparently no further sintering occurred at this lower temperature. The sample was reground and run again in run #36 at 1229 K for 10 hours under 50 cm³/min O₂ flow. The Pu volatility was found to be up to the expected level (see Fig. 2). Again no significant sintering seems to occur at this low temperature. The sample was then

used without grinding for the low temperature run, run #37, at 825 K. It was next used for run #44 at 1431 K for 10 hours with 50 cm³/min O₂ flow. The sample was first ground prior to the run. The run was made for 7 hours and stopped. The sample was ground again, and the run continued for an additional 3 hours. The Pu volatility was found to be somewhat below the expected curve as was the case with runs #25, 33, and 34, suggesting again sintering effects at 1430 K.

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