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**Experimental Studies and Thermodynamic Modeling of Volatilities of
Uranium, Plutonium, and Americium from Their Oxides and from Their
Oxides Interacted with Ash**

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Lawrence
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Abstract

The purpose of this study is to identify the types and amounts of volatile gaseous species of U, Pu, and Am that are produced in the combustion chamber offgases of mixed waste oxidation processors. Primary emphasis is on the Rocky Flats Plant Fluidized Bed Incinerator. Transpiration experiments have been carried out on $\text{U}_3\text{O}_8(\text{s})$, U_3O_8 interacted with various ash materials, $\text{PuO}_2(\text{s})$, PuO_2 interacted with ash materials, and a 3% PuO_2 /0.06% AmO_2 /ash material, all in the presence of steam and oxygen, and at temperatures in the vicinity of 1300 K. $\text{UO}_3(\text{g})$ and $\text{UO}_2(\text{OH})_2(\text{g})$ have been identified as the uranium volatile species and thermodynamic data established for them. Pu and Am are found to have very low volatilities, and carryover of Pu and Am as fine dust particulates is found to dominate over vapor transport. We are able to set upper limits on Pu and Am volatilities. Very little lowering of U volatility is found for U_3O_8 interacted with typical ashes. However, ashes high in Na_2O (6.4 wt%) or in CaO (25 wt%) showed about an order of magnitude reduction in U volatility.

Thermodynamic modeling studies were carried out that show that for aluminosilicate ash materials, it is the presence of group I and group II oxides that reduces the activity of the actinide oxides. K_2O is the most effective followed by Na_2O and CaO for common ash constituents. A more major effect in actinide activity lowering could be achieved by adding excess group I or group II oxides to exceed their interaction with the ash and lead to direct formation of alkali or alkaline earth uranates, plutonates, and americates.

Applying the actinide volatility results found here to the secondary combustor in the Rocky Flats Plant Fluidized Bed Incinerator gives volatilization rates of 1.7×10^{-9} g/y of U, less than 2×10^{-13} g/y of Pu, and less than 2×10^{-17} g/y of Am.

Introduction

This study has been performed primarily for the Rocky Flats Fluidized Bed Incinerator development. Part of the study, i.e., volatility of $^{238}\text{PuO}_2(\text{s})$, was supported by funding from DOE Defense Programs. The objective of this study has been to conduct experiments to identify the types and amounts of volatile gaseous species of U, Pu and Am that are produced in the offgases of mixed waste oxidation processors. The main goal of this phase of the study has been to evaluate the effects of incinerator ash in lowering the volatilities of the actinides. 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.

There is a need for safety reasons to evaluate the emission of U, Pu, and Am in the offgases of thermal oxidation processors for mixed wastes. Prior studies on toxic metals in incinerators show that metals that vaporize in the incinerator preferentially condense onto very fine fly ash particulates or form aerosols that are carried by the offgas [1,2]. These particulates are in a size range ($<0.5\ \mu\text{m}$) that are difficult to remove with air pollution control devices. Complete removal is not possible in flow systems, even with HEPA filters. A knowledge of the volatility levels of U, Pu, and Am produced in the thermal oxidizer offgas is needed for proper process design to limit U, Pu, and Am emissions to acceptable levels.

Workers at EERC have found that the observed amounts of toxic metals volatilized into the offgas for incinerators generally correlate well with the calculated thermodynamic volatilities, provided that the thermodynamic data are available for all of the important volatilizing species, and that the thermodynamics for solid state interactions that limit volatilization are known [1,2]. It is significant that for two apparent contradictions of the thermodynamic predictions, for Cr and As, the correlations came into line after more complete thermodynamic data were made available, which for Cr were data on volatile oxyhydroxide and oxychloride species (provided by Bart Ebbinghaus [3,4]), and for As where data were used to take into account the formation of solid arsenates [1]. Where differences still remain between calculated and observed volatilities, the calculated values are generally somewhat higher than the observed. Thus, the evidence indicates that reaching volatilization equilibrium in the time-temperature regime required for oxidation generally is reasonable. Where equilibrium is not attained, the calculated equilibrium values are conservatively high. Although this discussion is for toxic metals in incineration, we expect it to apply to actinide behavior as well, and to thermal oxidizers in general.

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 passed through the secondary bed. Fly ash produced in the secondary combustor consists of a mixture of a mineral ash 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.

For the operating conditions of the secondary combustor in the Rocky Flats Plant Fluidized Bed Incinerator, we expect the actinide volatility behavior to be as follows. Based on available or predicted thermodynamic data [5-11], 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 $\text{AmO}_2(\text{OH})_2(\text{g})$. $\text{UO}_3(\text{g})$ becomes of importance as a volatile species at temperatures substantially higher than for the Rocky Flats Plant Fluidized Bed Incinerator, i.e., at above $\sim 900^\circ\text{C}$ [12,13]. Similarly, we would expect $\text{PuO}_3(\text{g})$ and $\text{AmO}_3(\text{g})$ to also become of importance above 900°C , although these species have not been identified. If sufficient chlorine is present in the feed to produce HCl concentrations greater than $\sim 0.1\%$ in the gas stream, then the available thermodynamic data [6,14] indicate $\text{UO}_2\text{Cl}_2(\text{g})$ would have a significant volatility under the Fluidized Bed Incinerator conditions. There are no data on Pu and Am oxychloride volatilities, but they would be expected to behave similarly to U. If fluorine were present in the feed, then volatilities of actinide oxyfluorides would also need to be considered. The halogen acid content of the Rocky Flats Fluidized Bed incinerator is expected to be low because of the presence of sodium carbonate in the bed, which acts as a getter for halogen acids and converts them to solid sodium halides. However, the halogen acid removal rate is kinetically controlled, so that a measured verification is needed of the halogen acid level to show that it is sufficiently low to avoid actinide oxyhalide volatilities. The volatilities of the actinides will depend upon their condensed form in the combustor. It is convenient to take the pure oxides $\text{U}_3\text{O}_8(\text{s})$, $\text{PuO}_2(\text{s})$ and $\text{AmO}_2(\text{s})$ as the reference forms. However, interaction of these oxides with incinerator ash, salts, catalyst materials, intentional additives, or any other bed materials can lead to a lowering of the thermodynamic activities of the actinide oxides, and a consequent lowering of their volatilities. The interactions may be to form mixed oxides (e.g., Na_2UO_4), dissolution in a glass, or formation of solid solutions.

In initial work on this project (funded under sub-contract No. 98661GD from EG&G Rocky Flats Plant to LLNL), [7] 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 also carried out a thermodynamic analysis of U and Pu volatilities in the Rockwell International Molten Salt Processor [6], 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 predicted information and the experimental data.

In the first phase of experimental studies on this project [8,10] we used the transpiration method to measure volatilities of Pu and Am from $\text{PuO}_2(\text{s})$ and from $\text{PuO}_2/2\% \text{AmO}_2(\text{s})$ in the presence of steam and oxygen at temperatures of 1230-1430 K. The volatile species were assumed to be $\text{PuO}_2(\text{OH})_2(\text{g})$ and $\text{AmO}_2(\text{OH})_2(\text{g})$ and vapor pressures of $\sim 10^{-10}$ atm and $\sim 10^{-12}$ atm, respectively, were found under measurement conditions. These values are 2-3 orders of magnitude lower than our earlier predictions. Because of the low levels of volatility, we ran into problems of sample contamination from the glovebox environment limiting our accuracy of measurement. PuO_2 dust transport may have also contributed to the observed volatility. The volatility values were therefore observed to be conservatively high. Applying the results to the secondary combustion chamber of the Rocky Flats Plant Fluidized Bed Incinerator and assuming the formation of $\text{PuO}_2(\text{s})$ containing 200 ppm AmO_2 in solid solution gave volatilization rates of 7×10^{-6} g Pu/y and 4×10^{-9} g Am/y.

We have also made transpiration measurements to evaluate the extent of Pu volatilities expected during microwave melting of Pu sludge/glass mixtures for glass encapsulation of Pu sludge wastes in support of the Rocky Flats Plant Microwave Solidification Project [9]. Measurements were made at 2% PuO_2 and 0.03% PuO_2 contents in Pu sludge/glass mixtures and the Pu volatility as $\text{PuO}_2(\text{OH})_2(\text{g})$ was found to be on the order of 10^{-10} to 10^{-11} atm at melt temperatures of 1400 K. Extrapolating the results to the actual expected PuO_2 content of 0.0003%, with an O_2 pressure of 0.2 atm, H_2O pressure of 0.1 atm and a maximum expected melt temperature of 1500 K, gave an estimated $\text{PuO}_2(\text{OH})_2(\text{g})$ pressure of 8×10^{-14} atm. This corresponds to 6 g of Pu volatilized during a 4 h run.

In the current phase of this project, we have carried out both experimental and calculational studies to determine U, Pu, and Am volatilities from incinerator ash in the presence of steam and oxygen. In the experimental studies, the transpiration method is used to measure volatilities of U, Pu, and Am that have been interacted with various ashes. Some volatility measurements are also carried out on volatilities of $\text{U}_3\text{O}_8(\text{s})$ and $\text{PuO}_2(\text{s})$ to better define the volatilities of the reference oxides. Thermodynamic modeling calculations are carried out to obtain a generalized description of ash constituents in lowering of actinide volatilities, and to predict the behavior of additives in lowering of actinide volatilities. Interim results on this phase of the project were reported earlier [8].

Experimental

Transpiration Method:

In the transpiration method, [15] 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,

where $\text{O}_2(\text{g})$ 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, and results in pressure values that are too low. 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 Transpiration Equipment:

Three transpiration units were used: one for the $\text{U}_3\text{O}_8(\text{s})$ experiments, one for the $\text{U}_3\text{O}_8/\text{ash}$ experiments, and one for the $\text{PuO}_2(\text{s})$, PuO_2/ash and $\text{PuO}_2/\text{AmO}_2/\text{ash}$ experiments. The three units were very similar, and are illustrated schematically in Fig. 1. The units for the U experiments were mounted on a bench top, while the unit for the Pu and Pu/Am experiments was set up within an air-flow glovebox. For the U_3O_8 experiments, we used a Marshall tube furnace with Pt/Rh windings rated to 1450°C in air and with a uniform temperature hot zone of ~ 17 cm. An alumina furnace tube, 4.5 cm OD x 60 cm long, was used in the furnace. Stainless steel end caps designed with Viton o-ring seal compression fittings were used to seal off the ends of the furnace tube. An alumina gas inlet tube and an alumina closed-end thermocouple probe tube, each 8 mm OD, were brought in from the upstream side to the hot zone through Viton o-ring sealed fittings. The gas inlet tube extended up to the edge of a 15 cm length of the uniform temperature hot zone, while the thermocouple probe tube extended up to the center of the hot zone. Two alumina discs with appropriate cutouts for the tubes were used to support the tubes at the edge of the hot zone and to contain 6 cm of Kaowool ceramic fiber (composition of 53% SiO_2 and 47% Al_2O_3) insulation to better define the hot zone. A fused silica gas exit tube, 6 mm OD, was placed from the downstream side of a 15 cm length of the hot zone and extended out through a Viton o-ring seal out of the end cap. Alumina discs and Kaowool insulation were located at the hot zone end of the gas exit tube, in similar manner as for the inlet tube side. The gas exit tube served as a collector tube for deposition of volatilized U, and is referred to hereafter as the collector tube. Fused silica boats, 3 cm wide x 6 cm long x 0.85 cm high, were used for most of the $\text{U}_3\text{O}_8(\text{s})$ runs, with Pt boats, 2.5 cm wide x 6 cm long x 1 cm high, for some of the runs. The boats were placed in the center of the hot zone. Hot zone temperatures were measured with a type-S thermocouple located in the probe tube above the center of the boat. The thermocouple was periodically checked against two other type-S thermocouples. No change in readings were found to within ± 2 K. For the $\text{U}_3\text{O}_8/\text{ash}$ experiments, the furnace arrangement was similar to that for the $\text{U}_3\text{O}_8(\text{s})$ experiments, except as follows. The furnace tube was of fused silica, 4.0 cm OD, and end cap seals were made using fused silica to stainless steel ball joints sealed with silicone grease. Both fused silica and Pt boats were again used as above, with the Pt boats being used for $\text{U}_3\text{O}_8/\text{ash}$ samples that were high in CaO or Na_2O contents. Temperature readings were made with a type-S thermocouple in the probe tube above the center of the boat. Periodic comparisons with two other type-S thermocouples showed no change in readings to within ± 2 K. For the $\text{PuO}_2(\text{s})$, PuO_2/ash and $\text{PuO}_2/\text{AmO}_2/\text{ash}$ experiments, we used a Thermcraft Kanthal-heater clamshell furnace rated to 1200°C in air. It provided a uniform-temperature hot zone ~ 7 cm long and an overall heated zone ~ 20 cm long. The furnace tube was of silica glass, 2.6 cm OD x 38.5 cm long with end caps mounted on 35/25 silica glass ball and socket end joints sealed with silicone grease. An 8 mm OD silica glass gas inlet tube was mounted as a sidearm just inside of the end cap seal on the upstream side. A thermocouple probe tube made of 7 mm OD silica glass tubing closed at the end was mounted on the upstream endcap and extended to the center of the hot zone. A silica glass wool insulating plug, 1.5 cm long, was mounted around the tubing up to the beginning of the uniform temperature hot zone. A 9 mm OD x 12 cm long gas outlet and collector tube extended from the downstream side of the uniform temperature hot zone to a 12/30 standard taper joint. The tubing then continued through the end cap.

Figure 1. Schematic of the apparatuses used for the $\text{U}_3\text{Og(s)}$, $\text{U}_3\text{Og/ash}$, $\text{PuO}_2(\text{s})$, PuO_2/ash , and the $\text{PuO}_2/\text{AmO}_2/\text{ash}$ transpiration experiments.

A silica wool insulating plug, 1.5 cm long, was mounted around the inlet end of the collector tube. The standard taper joint was sealed with MoS₂ lubricant, which provided for ease of disassembly when removing the collector tube. Temperatures were measured with type-K thermocouples with inconel sheaths. Fused silica boats, 2.0 cm wide x 4.0 cm long x 0.9 cm high were used for the PuO₂(s), PuO₂/ash, and PuO₂/AmO₂/ash samples. One thermocouple was located on the outside of the furnace tube at its center, and two thermocouples were located in the silica glass thermocouple probe tube just above the sample boat. These various thermocouples were periodically checked and calibrated against two type-S reference thermocouples. The balance of the equipment was identical for the three transpiration units. A water saturator was located upstream of the furnace. The water saturator was made of a 6-mm-thick wall Al vessel with an 800 cm³ capacity and provided with a fritted stainless steel disperser for the carrier gas, which disperser was located 1 cm above the bottom of the vessel. Water level was maintained at 500-600 cm³ during the runs. The vessel was heated with a Glas-col mantle. A desiccant cartridge loaded with Drierite (CaSO₄) was located downstream of the furnace. The cartridge was provided with disconnect fittings to allow weighings to determine water pickup accumulated during a run. Gas lines from the water saturator to the furnace and from the furnace to the Drierite cartridge were of stainless steel. Valves were also of stainless steel with Viton rubber seals. Either Viton o-ring compression fittings, or stainless steel to silica glass ball joints were used to connect with the furnace tubes. Heating tapes were wrapped on the lines from the water saturator to the furnace tube, and from the furnace tube to the Drierite cartridge and maintained at ~150°C during the runs to prevent water condensation. Precision Flow Devices PFD-401 mass flow controllers were used to control O₂ and Ar flow inputs and to monitor the output gas flow. Flow rates were measured in cm³/min at stp. Calibrations for these flow meters were provided by the supplier. The flow meters were intercompared periodically to check for any changes in calibrations. Weighings were carried out on Ohaus GT 2100 electronic balances, with a capacity of 2100 g and an accuracy of ± 0.01 g. Certified weights were used periodically to check the balance calibrations.

Collection Sample Analysis

The uranium deposits on the silica glass collector tubes were dissolved off using 8M HNO₃ to which were added a few drops of concentrated HF. The samples were held in the solvent for twenty four hours to assure complete solution. Repeat solution tests on some samples showed that less than 2 % of the uranium remained in the collector tube. Uranium analyses were carried out by inductively coupled plasma mass spectrometry. This technique is sensitive enough to detect as little as one ng of U, and has an accuracy of ± 5 %.

For the Pu and Pu/Am deposits on silica glass collector tubes, we used warm concentrated HF to leach out the inner surface of the tubes. This was followed by 6N HCl and water rinses. In some of the collector tubes, silica glass wool had been added to aid in the vapor condensation process during the transpiration run. This glass wool was also completely dissolved out. We avoided dissolving material from the outsides of the tubes because of possible pickup of Pu contamination during handling. An aliquot of the solution was dried on a Pt planchet and counted for total alpha dpm using a gas proportional counter with an efficiency of 52 %. For the

$^{239}\text{Pu}/^{241}\text{Am}$ samples, pulse height analysis was performed to separately determine the ^{239}Pu and ^{241}Am alpha activities. Pulse height analysis was also used on the ^{238}Pu samples to evaluate the presence of impurity alpha emitters. Corrections were made for counter background and for isotopic alpha contributions to obtain total Pu and Am.

Starting Materials

$\text{U}_3\text{O}_8(\text{s})$ powder derived from depleted U was obtained from the National Institute of Science and Technology (NIST) as a standard reference material with a stated purity of 99.94%. The material was characterized by X-ray diffraction analysis both before and after use in the transpiration runs. Before use, a mixture of orthorhombic and hexagonal forms of $\text{U}_3\text{O}_8(\text{s})$ were identified with traces of a phase tentatively identified as $\text{UO}_3 \cdot 2\text{H}_2\text{O}(\text{s})$. After use in transpiration runs, the material was identified to be almost pure orthorhombic $\text{U}_3\text{O}_8(\text{s})$ with traces of hexagonal $\text{U}_3\text{O}_8(\text{s})$. $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}(\text{s})$ powder was obtained from J.T. Baker Chemical Co. It had a stated purity of 99.2%. $^{238}\text{PuO}_2(\text{s})$ was obtained as sintered chunks. It was a reactor produced material with an isotopic content of 80.25% ^{238}Pu , 16.60% ^{239}Pu , 2.56% ^{240}Pu , 0.402% ^{241}Pu , and 0.186% ^{242}Pu , all on the basis of metal content. Based on the age of the material, we calculate that 3.3% ^{234}U was also present as a decay product of the ^{238}Pu . $^{239}\text{PuO}_2/2\% ^{241}\text{AmO}_2(\text{s})$ was obtained as a powder. It was a reactor grade material with an isotopic content of 0.056% ^{238}Pu , 80.659% ^{239}Pu , 17.827% ^{240}Pu , 0.989% ^{241}Pu , 0.460% ^{242}Pu , and 2.056% ^{241}Am , all on the basis of metal content. Na_2O powder of 98% purity was obtained from Alpha Inorganics, Inc. NaNO_3 powder of 99.98% purity was obtained from EM Scientific. Na_2CO_3 powder of 99.95% purity and NaCl powder of 100.8% assay (dried basis) were obtained from Mallinckrodt, Inc. Na_2SO_4 powder of 99.8% purity was obtained from J.T. Baker Chemical Co. Oxidation catalyst consisting of 20% $\text{Cr}_2\text{O}_3/80\% \text{Al}_2\text{O}_3$ in the form of porous granules was obtained from Boyce Logsdon at Rocky Flats Plant. Four coal fly ash materials were obtained from NIST as standard reference materials with the designations SRM 1633a, SRM 2689, SRM 2690, and SRM 2691. Compositions provided by NIST for the ashes are listed in Table 1, and the mineralogical assay [16] is given in Table 2.

Preparation and Characterization of Sample Materials

Characterization of the Fly Ash Starting Materials:

We carried out X-ray diffraction analyses of the as-received SRM-ash samples and were able to essentially confirm the mineralogy of the samples as given in Table 2, i.e., the samples are ~70% glass with mullite and quartz generally being the dominant crystalline phases. We then carried out heatings of the ash samples to determine sintering characteristics and to determine phase changes that occur with heat treatment. We needed to determine the maximum temperature conditions under which the samples remain as loose powder to allow equilibration in the transpiration experiments.

Table 1. Composition of NIST standard reference material coal fly ash given in weight percent of constituent oxides.

oxide	SRM 1633a	SRM 2689	SRM 2690	SRM 2691
Na ₂ O	0.23 ± 0.01	0.34 ± 0.04	0.32 ± 0.03	1.47 ± 0.07
K ₂ O	2.26 ± 0.07	2.65 ± 0.04	1.25 ± 0.05	0.41 ± 0.01
MgO	0.75 ± 0.02	1.01 ± 0.08	2.54 ± 0.08	5.17 ± 0.13
CaO	1.55 ± 0.01	3.05 ± 0.08	7.99 ± 0.18	25.82 ± 0.45
SrO	0.10 ± 0.01	0.08	0.24	0.32
BaO	0.17	0.09	0.73	0.74
MnO	0.02 ± 0.01	0.04	0.04	0.03
Al ₂ O ₃	27.02 ± 1.89	24.45 ± 0.40	23.33 ± 0.53	18.54 ± 0.74
Fe ₂ O ₃	13.44 ± 0.14	13.33 ± 0.09	5.10 ± 0.09	6.32 ± 0.04
SiO ₂	48.78 ± 1.71	51.47 ± 0.17	55.30 ± 0.36	36.00 ± 0.26
TiO ₂	1.33	1.25 ± 0.02	0.87 ± 0.02	1.50 ± 0.03
SO ₃	0.45	----	0.37 ± 0.02	2.07 ± 0.12
P ₂ O ₅	----	0.23 ± 0.02	1.19 ± 0.02	1.17 ± 0.05

Table 2. Minerology of NIST coal fly ashes from XRD Data. [16]

compound	SRM 1633a	SRM 2689	SRM 2690	SRM 2691
Ah				1.3
Mu	19.9	9.9	11.2	4.2
Qz	5.7	4.0	11.4	8.4
MI				1.6
C ₃ A				2.8
Mw				5.8
Hm	2.4	3.6		
Sp	6.4	4.9	1.2	1.3
Lm				1.0
Pc				2.4
Gl	65.6	77.6	76.2	71.2

Key:

Ah - Anhydrite (CaSO_4)
Mu - Mullite ($\text{Al}_6\text{Si}_2\text{O}_{13}$)
Qz - Quartz (SiO_2)
MI - Melilite ($(\text{Ca},\text{Na})_2(\text{Mg},\text{Al},\text{Fe})(\text{Si},\text{Al})_2\text{O}_7$)
C₃A - Tricalcium Aluminate ($\text{Ca}_3\text{Al}_2\text{O}_6$)
Mw - Merwinite ($\text{Ca}_3\text{Mg}(\text{SiO}_4)_2$)
Hm - Hematite (Fe_2O_3)
Sp - Ferrite Spinel ($(\text{Mg},\text{Fe})(\text{Fe},\text{Al})_2\text{O}_4$)
Lm - Lime (CaO)
Pc - Periclase (MgO)
Gl - Glass

The four SRM-ash samples were heated to 1000°C in air for 2 hours in Al₂O₃ crucibles. We found the samples remained as a loose powder with very little sintering. This was confirmed by surface area measurements. Surface area determinations showed the ash samples as-received had areas of 0.5-2.0 m²/g, and after the 1000°C heating had areas of 0.2-0.5 m²/g. Only the SRM 2691 was X-rayed after the heating. It showed that the glass content had decreased (partially devitrified), the mullite phase had disappeared, and the major crystalline phases now were 2CaO·Al₂O₃·SiO₂, quartz, and 3CaO·Al₂O₃.

Two samples, SRM 2690 and SRM 2691, were heated to 1075°C in air for 2 hours in Al₂O₃ crucibles. They showed sintering but had not sintered hard, i.e., they could be loosened up with a spatula. The samples were then ground down in a mortar and pestle to pass a 60 mesh screen, and reheated to 1075°C in air for 2 hours. The samples remained as a loose powder. The SRM 2691 material after this treatment was selected as the ash material for preparing PuO₂-loaded ash samples for transpiration tests.

An SRM 2691 sample was heated to 1150°C in air for 2 hours in an Al₂O₃ crucible. The sample had sintered hard. It was ground, passed through a 60 mesh screen and reheated to 1150°C in air for 2 hours. The sample again sintered hard and stuck to the Al₂O₃ crucible used for containment. X-ray analysis after the second heating showed that most of the glass phase, quartz, and minor mineral phases were gone. The major phases present were Ca(Mg,Fe,Al)(Si,Al)₂O₆ and 2CaO·Al₂O₃·SiO₂.

All four ash samples were heated to 1300°C in air for 2 hours in Al₂O₃ crucibles. We found that SRM 2690 and 2691 had melted, and SRM 2689 and 1633a had sintered very hard. SRM 2689 and 1633a were ground to pass 60 mesh and reheated to 1150°C for 2 hours. The samples sintered hard. They were reground to pass 60 mesh and reheated to 1075°C for 2 hours. They now remained as loose powders. The samples were analyzed by X-ray diffraction. The major phases in both samples were glass, mullite, and hematite.

Preparation of Actinide Oxide/Ash Samples:

Two concentrations of uranium oxide in fly ashes, some at 5 wt% UO_{2.67} and some at 0.5 wt% UO_{2.67} were prepared. Some variations in preparative techniques were used for the different samples. The preparations were as follows. An aqueous solution formed from UO₂(NO₃)₂·6H₂O was used to form slurry mixtures with the ashes. An appropriate amount of uranyl nitrate was taken to result in 5 wt% and 0.5 wt% UO_{2.67} in the SRM ashes 1633a, 2689, 2690, and 2691. The slurries were thickened by heating on a hot plate while using a magnetic stirrer, until the stirrer would no longer turn. The slurries were further dried in a vacuum oven at 65°C for 16 hours. The sample with nominally 5 wt% UO_{2.67} in SRM 2690 ash was placed in an Al₂O₃ crucible and slowly heated in air to 1075°C and held there for two hours. It was ground in a B₄C mortar and pestle to pass a 60 mesh screen, and then used for the

transpiration experiments. The remaining dried slurry samples were heated slowly to 450°C in air in Al₂O₃ crucibles, held there for 16 hours (to decompose the uranyl nitrate). Samples of 5 wt% UO_{2.67} in SRM 1633a and 2689 ashes were then heated to 1300°C in air and held there for 4 hours, and the 5 wt% UO_{2.67} in SRM 2691 ash and all of the 0.5 wt% UO_{2.67} samples were heated to 1150°C in air and held there for 4 hours. All of the samples were ground in a B₄C mortar and pestle to pass a 200 mesh screen. The 5 wt% UO_{2.67} in SRM 2691 thus prepared was then used for transpiration experiments. The remaining samples were reheated to 1150°C in air for 4 more hours, then reground to pass a 200 mesh screen. All but the 5%UO_{2.67}/2689 sample were then used in the transpiration experiments. Two other U₃O₈-containing ashes with higher Na₂O contents were prepared. For one sample, 1.172 g of Na₂O was ground fine in an alumina mortar and pestle and blended with the previously prepared and ground samples of 7.868 g of 0.5 wt% UO_{2.67} in SRM 2689 ash and 0.1167 g of 5 wt% UO_{2.67} in SRM 2690 ash. The sample was heat treated at 1050°C for 3 hours under a flow of 10 cm³/min Ar, then ground fine in an alumina mortar and pestle, and used for transpiration experiments. This sample is designated as UO_{2.67}/Ash1. For the other sample, 0.5532 g of NaNO₃ was ground fine in an alumina mortar and pestle and blended with 3.135 g of the previously prepared and ground sample of 0.5 wt% UO_{2.67} in SRM 2689 ash. The sample was heated up slowly to 600°C in a Pt boat under a flow of 25 cm³/min of Ar, held at 600°C for 2 hours, then taken to 1000°C for 3 hours. It was then ground fine in an alumina mortar and pestle and used for transpiration experiments. This sample is designated as UO_{2.67}/Ash2. We prepared PuO₂-loaded ashes as follows. We dissolved ²³⁸PuO₂(s) in concentrated HNO₃ containing a small amount of HF. We formed a slurry of the SRM 2691 ash in the nitric acid solution, using enough ²³⁸PuO₂ content to result in a 3 wt% PuO₂ in ash product. The slurry was slowly dried on a hot plate with stirring. The dry slurry was then transferred to a silica glass boat and placed in the transpiration furnace where it was heated from room temperature to 1050°C over a 2 hour period under a 15 cm³/min flow of O₂, then held at 1050°C for 3 1/2 hours and cooled. The sample was ground in an agate mortar and pestle and then used in the transpiration experiments. We also formed a more dilute PuO₂-loaded SRM 2691 ash by taking 0.10 g of the above 3 wt % PuO₂ ash together with 0.41 g of additional SRM 2691 ash and blended them while grinding in an agate mortar and pestle. The mixture was then heated in a silica glass boat at 1050°C under a 25 cm³/min flow of O₂ for 4 hours, ground in the mortar and pestle again and used in the transpiration experiments. An ash sample was also prepared using ²³⁹PuO₂/2% AmO₂ loading to study Am volatility. 0.05 g of ²³⁹PuO₂/2% AmO₂ was added to 1.60 g of SRM 1633a ash and blended and ground together in an agate mortar and pestle. This was heated in a silica glass boat at 1050°C under 25 cm³/min O₂ flow for 4 hours, then ground in the mortar and pestle and used for the transpiration experiments. For some of the transpiration experiments which were run at 550°C, we also added salts and catalyst to the actinide oxide/ash materials. The salt/catalyst mixture was prepared by blending together 2.596 g Na₂CO₃, 9.048 g NaCl, 1.836 g Na₂SO₄, and 14.528 g of 20 % Cr₂O₃/ 80 % Al₂O₃, where the ingredients had been separately ground in a B₄C mortar and pestle to pass through a 60 mesh screen. Transpiration experiment

samples were then prepared by blending 1/3 by weight of actinide oxide/ash preparations with 2/3 by weight of the salt/catalyst mixture. The various compositions of actinide oxide/ash samples that were used in the transpiration experiments are summarized in Table 3.

Characterization of Uranium Oxide/Ash Samples:

X-ray diffraction analysis of the 5%UO_{2.67}/1633a and 5%UO_{2.67}/2689 samples both showed the presence of mullite (Al₆Si₂O₁₃), hematite (Fe₂O₃), U₄O₉, and glass. No ferrite spinel ((Mg,Fe)(Fe,Al)₂O₄) and little or no quartz (SiO₂) were found in these samples, although present in the original ash samples.

X-ray diffraction analysis of the 5%UO_{2.67}/2690 sample showed the presence of quartz, hematite, anorthite (CaAl₂Si₂O₈), mullite, and glass. In addition, a pattern giving an approximate match for CaU₂O₇ was also present. No ferrite spinel was found in this sample. The presence of hematite and anorthite differs from McCarthy and Thedchanamoorthy's [16] reported results for SRM 2690 ash.

X-ray diffraction analysis of the 5%UO_{2.67}/2691 sample showed the presence of Al-diopside (Ca(Mg,Fe,Al)(Si,Al)₂O₆), melilite (Ca₂(Mg,Al,Fe)(Si,Al)₂O₇), and glass, with the uranium likely present as CaUO₄ or Ca₂U₂O₇. This sample showed the greatest variance in mineralogy from the original fly ash. No anhydrite (CaSO₄), mullite, quartz, tricalcium aluminate (Ca₃Al₂O₆), hematite, ferrite spinel, lime (CaO), or periclase (MgO) were found in this sample. McCarthy and Thedchanamoorthy [16] did not find Al-diopside present in the SRM 2691 ash.

The samples of 0.5%UO_{2.67}/1633a, 0.5%UO_{2.67}/2689, 0.5%UO_{2.67}/2690, and 0.5%UO_{2.67}/2691 were also analyzed by X-ray diffraction. However, no uranium-containing phases were detected. Thus, the uranium was either present as a solid solution in the ashes or the concentration of the uranium containing phases was too low to detect. Otherwise, the mineral contents were essentially the same as the 5wt%UO_{2.67}/ash samples.

Transmission electron microscope analyses were also carried out on the samples 5%UO_{2.67}/1633a, 5%UO_{2.67}/2690, and 5%UO_{2.67}/2691, using a JEM 200CX transmission electron microscope (TEM) with an electron beam size of 75nm. Samples were prepared as follows. The sample of 5%UO_{2.67}/1633a that was used had been densely sintered in a heating in air to 1300°C for 4 hours. The 5%UO_{2.67}/2690 and 5%UO_{2.67}/2691 samples were cold isostatically pressed and then sintered in air at 1150°C for 4 hours. 400 μm slices were cut out of the sintered samples using a diamond wafering saw. 3 mm in diameter discs were cored from the slices, and the discs were ground down to 250 μm thickness by hand with fine SiC lapping film. The centers of the discs were dimpled down on both sides to give a thickness at the center of ~10 μm. The samples were then Ar ion-milled until electron transparent using 5kV accelerating voltage and an 11° angle from the horizontal. A 15 nm layer of carbon was then applied to each surface to minimize charging of the samples under the electron beam. Selected area diffraction, microdiffraction, and

Table 3. Compositions of simulated incinerator ash in weight percent of constituent oxides.

oxide	5%UO _{2.67} / 1633a (wt%)	5%UO _{2.67} / 2690 (wt%)	5%UO _{2.67} / 2691 (wt%)	0.5%UO _{2.67} / 1633a (wt%)	0.5%UO _{2.67} / 2689 (wt%)	0.5%UO _{2.67} / 2690 (wt%)
Na ₂ O	0.23	0.31	1.40	0.24	0.35	0.32
K ₂ O	2.23	1.19	0.39	2.34	2.69	1.25
MgO	0.74	2.43	4.92	0.78	1.03	2.55
CaO	1.53	7.63	24.59	1.60	3.10	8.01
SrO	0.10	0.23	0.30	0.10	0.08	0.24
BaO	0.17	0.70	0.70	0.18	0.09	0.73
MnO	0.02	0.04	0.03	0.02	0.04	0.04
Al ₂ O ₃	26.60	22.28	17.65	27.97	24.82	23.38
Fe ₂ O ₃	13.23	4.87	6.02	13.91	13.53	5.11
SiO ₂	48.03	52.80	34.28	50.50	52.26	55.43
TiO ₂	1.31	0.83	1.43	1.38	1.27	0.87
SO ₃	0.44	0.35	1.97	0.47	—	0.37
P ₂ O ₅	—	1.14	1.11	—	0.23	1.19
U ₃ O ₈	5.38	5.21	5.20	0.520	0.510	0.503
PuO ₂	—	—	—	—	—	—
AmO ₂	—	—	—	—	—	—

oxide	0.5%UO _{2.67} / 2691 (wt%)	0.5%UO _{2.67} / Ash1 (wt%)	0.5%UO _{2.67} / Ash2 (wt%)	3%PuO ₂ / 2691 (wt%)	0.6%PuO ₂ / 2691 (wt%)	3%PuO ₂ / 0.06%AmO ₂ / 1633a (wt%)
Na ₂ O	1.47	13.10	6.37	1.43	1.47	0.24
K ₂ O	0.41	2.33	2.53	0.40	0.41	2.35
MgO	5.17	0.91	0.96	5.04	5.16	0.78
CaO	25.80	2.76	2.91	25.16	25.78	1.61
SrO	0.32	0.07	0.08	0.31	0.32	0.10
BaO	0.74	0.09	0.09	0.72	0.74	0.18
MnO	0.03	0.04	0.04	0.03	0.03	0.02
Al ₂ O ₃	18.53	21.62	23.32	18.06	18.51	28.11
Fe ₂ O ₃	6.32	11.69	12.72	6.16	6.31	13.98
SiO ₂	35.98	45.58	49.10	35.07	35.95	50.74
TiO ₂	1.50	1.10	1.19	1.46	1.50	1.38
SO ₃	2.07	—	—	2.02	2.07	0.47
P ₂ O ₅	1.17	0.22	0.22	1.14	1.17	—
U ₃ O ₈	0.502	0.504	0.479	0.10	0.02	—
PuO ₂	—	—	—	2.9	0.57	3.0
AmO ₂	—	—	—	—	—	0.06

energy dispersive X-ray analysis were used to identify the phases and compositions of the ash constituents.

The 5% $\text{UO}_{2.67}$ /1633a ash was found to be composed of mullite, hematite, crystalline uranium oxide (UO_{2+x} or U_4O_9), and a glassy phase (Al-Si-Ca-O). Uranium was found to be present as small precipitates ranging in size from 7 to 50 nm within the glassy phase. Selected area diffraction of the glass matrix containing the precipitates was consistent with the phases $\text{UO}_{2+x}(\text{s})$ or $\text{U}_4\text{O}_9(\text{s})$. In this ash, the small size of the uranium oxide precipitates indicates to us that the uranium was dissolved in the glass and precipitated out during the cooldown. Because uranium oxide precipitates out of the glass as it cools suggests that the interaction of uranium oxide with this ash is weak.

The 5% $\text{UO}_{2.67}$ /2690 ash was found to be composed of anorthite, quartz, alumina, an iron titanate, and a glassy phase (Al-Si-Ca-O). The uranium was found to be present primarily as precipitates at grain boundaries. Sizes of the precipitates ranged from 10 to 80 nm. Some uranium was also found as precipitates in the interior of the quartz crystals. Sizes of these precipitates ranged from 10 to 200 nm. Microdiffraction of the precipitates in the quartz indicated that the uranium was present either as $\text{UO}_{2+x}(\text{s})$ or as $\text{U}_4\text{O}_9(\text{s})$. No uranium precipitates were found in the glassy phase. However, very little glass was observed in this sample. Some larger dark contrast grains containing uranium were also found. Typically they measured 1 to 2 μm in size. Selected area diffraction of these grains did not match $\text{UO}_{2+x}(\text{s})$, $\text{U}_4\text{O}_9(\text{s})$, or $\text{U}_3\text{O}_8(\text{s})$. Energy dispersive X-ray analysis of the dark contrast grains indicated the presence of uranium, oxygen, and sulfur. Thus, it is possible that the uranium in the dark contrast grains was present as a uranium sulfate. The uranium in this ash seems to be dissolving to a small extent in the quartz and very little if at all in the glass. Therefore, the interaction of uranium with this ash also seems to be weak.

The 5% $\text{UO}_{2.67}$ /2691 ash was found to be composed primarily of crystalline Al-diopside, a calcium uranate (CaUO_4 or $\text{Ca}_2\text{U}_2\text{O}_7$), and a glassy phase (Ca-Si-O). The uranium was located in the calcium uranate and also as small precipitates in the glass. The selected area diffraction data of the uranium in the glass was consistent with the $\text{U}_3\text{O}_8(\text{s})$ structure. In this ash, the uranium seems to be strongly associated with the calcium. Thus, the activity of uranium oxide is expected to be lowest in this ash sample.

Thus, we find that in general the phases found by TEM analysis for the 5% $\text{UO}_{2.67}$ /ash samples are consistent with the X-ray diffraction results. Some uranium oxide seems to dissolve in the glass phase of the ash when it is heated and then precipitates out in the glass as $\text{UO}_{2+x}(\text{s})$, $\text{U}_4\text{O}_9(\text{s})$, or $\text{U}_3\text{O}_8(\text{s})$ upon cooling. The ash with the high calcium content ties up the uranium as a calcium uranate, while free uranium oxides are present in the low CaO ashes.

Analysis of Transpiration Experiment Results

Volatilities of $\text{UO}_3(\text{g})$ and $\text{UO}_2(\text{OH})_2(\text{g})$ from $\text{U}_3\text{O}_8(\text{s})$:

The experimental data on the transpiration runs on $\text{U}_3\text{O}_8(\text{s})$ and $\text{U}_3\text{O}_8/\text{ash}$ are summarized in Tables 4 and 5. The uranium pressure given in Table 5 is calculated from the amount of uranium in the collector tube and represents total uranium species volatilized.

To test for equilibration, a series of runs were carried out on $\text{U}_3\text{O}_8(\text{s})$ volatility at 1373 K with $\text{O}_2(\text{g})$ pressure at 0.4 atm, $\text{H}_2\text{O}(\text{g})$ pressure at 0.6 atm, and with $\text{O}_2(\text{g})$ flow rate varying from 6 to 300 cm^3/min . A plot of total uranium pressure versus log O_2 flow rate (see Fig. 2) shows that a plateau region exists from 10 cm^3/min to about 250 cm^3/min . Flow rates were therefore maintained well within this plateau region to assure equilibration.

We also checked for the effects of water vapor pressure on U species formed in the $\text{U}_3\text{O}_8(\text{s})$ volatility experiments. We know from prior work [12,13] that $\text{UO}_3(\text{g})$ will be present under our experimental conditions, and anticipate the presence of $\text{UO}_2(\text{OH})_2(\text{g})$ as well. We therefore write the following volatility reactions and the associated equilibrium constants.

$$K_4 = p(\text{UO}_3)/a(\text{U}_3\text{O}_8)^{1/3}p(\text{O}_2)^{1/6}.$$

$$K_3 = p(\text{UO}_2(\text{OH})_2)/a(\text{U}_3\text{O}_8)^{1/3}p(\text{O}_2)^{1/6}p(\text{H}_2\text{O}).$$

Taking the activity of $\text{U}_3\text{O}_8(\text{s})$ as unity and rearranging the equilibrium constant expressions, we obtain

$$[p(\text{UO}_3) + p(\text{UO}_2(\text{OH})_2)]/p(\text{O}_2)^{1/2} =$$

$$p(\text{U total})/p(\text{O}_2)^{1/2} = K_4 + K_3p(\text{H}_2\text{O}). \quad (5)$$

This expression indicates that if a significant amount of $\text{UO}_2(\text{OH})_2(\text{g})$ forms in addition to $\text{UO}_3(\text{g})$, we should see a linear increase in the observed total U pressure with increasing water vapor pressure. If significant amounts of U oxyhydroxide species of other stoichiometries form, the power dependence of U volatility on water vapor pressure will differ from unity, according to the formula of the species. Plots of total U pressure versus water vapor pressure are shown at two different temperatures in Figs. 3 and 4. The plots appear linear considering the experimental scatter. The two highest U pressure points in Fig. 4 are particularly uncertain because they were taken at very low flow rates. The solid lines shown are based on the assessed results on $\text{UO}_3(\text{g})$ and $\text{UO}_2(\text{OH})_2(\text{g})$ with proper intercept and slope, which assessed results are

Table 4. Summary of U transpiration experiments on U_3O_8 and U_3O_8 /ash samples.

run #	sample	T_{lum} (K)	O_2 flow (cm ³ /min)	Ar flow (cm ³ /min)	time (min)	T_{bath} (°C)	H ₂ O (grams)
1	5% $UO_{2.67}/2690$	1330	50		240	84.2	6.86
7	$U_3O_8(s)$	1323	50		180	84.6	8.51
8	$U_3O_8(s)$	1323	25		180	84.4	4.07
9	$U_3O_8(s)$	1323	15		180	91.7	4.25
10	$U_3O_8(s)$	1323	25	30.5	180		
11	$U_3O_8(s)$	1323	6		180	97.1	6.21
12	$U_3O_8(s)$	1323	25	30	180		
13	$U_3O_8(s)$	1473		25	180	85.0	4.99
14	$U_3O_8(s)$	1323	25	25	180	86.0	8.88
15	$U_3O_8(s)$	1223	30.5	25	1200		
17	$U_3O_8(s)$	1473	50		120	85.0	6.17
18	$U_3O_8(s)$	1323	9		120	95.0	2.49
19	$U_3O_8(s)$	1323	25	30	180		
20	$U_3O_8(s)$	1373	100		120	84.0	11.71
21	$U_3O_8(s)$	1223	30		1440	79	25.89
22	$U_3O_8(s)$	1373	10		180	85.0	1.39
24	$U_3O_8(s)$	1373	30		180	85.1	(5.38)
25	$U_3O_8(s)$	1373	300		120	85.2	39.76
26	$U_3O_8(s)$	1323	50		180	75.3	4.52
27	$U_3O_8(s)$	1323	50		180	60.1	1.51
31	$U_3O_8(s)$	1573	120		60	85.7	7.95
32	$U_3O_8(s)$	1573	120		60	95.0	32.38
33	$U_3O_8(s)$	1573	50		180	85.0	5.61
34	$U_3O_8(s)$	1573	50		180		
35	5% $UO_{2.67}/2690$	1323	55		360		
36	5% $UO_{2.67}/2690$	1323	25		361	85.0	9.05
37	5% $UO_{2.67}/2691$	1323	55		360		
39	5% $UO_{2.67}/1633a$	1323	55		360		
41	5% $UO_{2.67}/1633a$	1323	55		330		
42	5% $UO_{2.67}/2691$	1323	25		421	95	47.8
43	5% $UO_{2.67}/2691$	1323	25		420	85	11.01
44	5% $UO_{2.67}/2690$	1323	25		360	93.5	31.03
45	1.7% $UO_{2.67}/2690/$ salts/catalyst	827	50		4740	85	243.77
46	$U_3O_8(s)$	1373	50		540		
47	$U_3O_8(s)$	1373	200		120	85.0	26.78
48	1.7% $UO_{2.67}/1633a/$ salts/catalyst	826	50		2915	85	153.71
49	$U_3O_8(s)$	1473	30		240		
50	$U_3O_8(s)$	1273	30		480		
51	5% $UO_{2.67}/2690$	1323	30		390		
52	5% $UO_{2.67}/2690$	1323	30		420	85	10.98
53	5% $UO_{2.67}/2690$	1323	21		420	90	9.02

Table 4. (cont.) Summary of U transpiration experiments on U₃O₈ and U₃O₈/ash samples.

run #	sample	T _{furn} (K)	O ₂ flow (cm ³ /min)	Ar flow (cm ³ /min)	time (min)	T _{bath} (°C)	H ₂ O (grams)
54	5%UO _{2.67} /2690	1323	39		420	75.5	5.13
55	U ₃ O ₈ (s)	1173	25.0		1950	85.3	55.04
56	U ₃ O ₈ (s)	1373	6.0		480	85.0	3.05
58	U ₃ O ₈ (s)	1373	20.0		440	85.0	9.81
59	U ₃ O ₈ (s)	1173	25.0		540		
60	U ₃ O ₈ (s)	1373	50.0		510	85	27.0
61	5%UO _{2.67} /2690	1323	21.0		405	89.5	16.22
63	5%UO _{2.67} /2691	1323	25.0		420	85.5	11.70
64	5%UO _{2.67} /2691	1323	21.0		450	90.0	19.77
65	5%UO _{2.67} /1633a	1323	35.0		1755		
66	5%UO _{2.67} /1633a	1323	25.0		450	85	11.70
67	0.5%UO _{2.67} /1633a	1323	21.0		465	90.5	19.74
68	0.5%UO _{2.67} /1633a	1323	25.0		495	85	12.36
69	0.5%UO _{2.67} /1633a	1323	39.0		450	74	8.32
70	0.5%UO _{2.67} /1633a	1323	50.0		510		
71	0.5%UO _{2.67} /2690	1323	50.0		462		
72	0.5%UO _{2.67} /2690	1323	39.0		435	76	8.96
73	0.5%UO _{2.67} /2690	1323	25.0		475	85.5	13.17
74	0.5%UO _{2.67} /2690	1323	21.0		460	89.7	17.20
75	0.5%UO _{2.67} /Ash1	1323	50.0		1755		
76	U ₃ O ₈ (s)	1273	21.0		440	90.0	17.11
77	0.5%UO _{2.67} /2691	1323	50.0		1695		
78	U ₃ O ₈ (s)	1323	45.0		480	60.0	4.28
79	U ₃ O ₈ (s)	1223	21.0		1890	89.5	68.86
80	0.5%UO _{2.67} /2691	1323	39.0		435	75.5	8.56
83	0.5%UO _{2.67} /2691	1323	21.0		490	91.0	20.49
84	0.5%UO _{2.67} /2691	1323	25.0		440	85	11.11
85	U ₃ O ₈ (s)	1223	35.0		1810	61	13.21
86	U ₃ O ₈ (s)	1223	40.0		1890		
87	0.5%UO _{2.67} /2691	1223	20.0		1890	85	41.53
88	U ₃ O ₈ (s)	1323	18.0		515	94.5	45.86
89	0.5%UO _{2.67} /2691	1223	45.0		1870		
90	U ₃ O ₈ (s)	1323	21.0		475	89.8	18.44
91	U ₃ O ₈ (s)	1223	15.0		1680	94.2	103.51
92	0.5%UO _{2.67} /Ash2	1323	50.0		455		
93	0.5%UO _{2.67} /Ash2	1323	21.0		425	89.7	6.35
94	U ₃ O ₈ (s)	826	20.0		5785	86	132.34
95	0.5%UO _{2.67} /Ash2	1323	25.0		495	85.8	13.06
96	0.5%UO _{2.67} /Ash2	1323	39.0		450	74.5	8.43
97	0.5%UO _{2.67} /Ash2	1223	25.0		1560	86.5	43.76
98	0.5%UO _{2.67} /Ash2	1223	50.0		1500		

Table 5. Summary of U transpiration experiments on U₃O₈ and U₃O₈/ash samples.

run #	moles of gas				p(O ₂) (atm)	p(H ₂ O) (atm)	U (μg)	p(U total) (atm)
	O ₂	H ₂ O	Ar	total				
1	0.495	0.381		0.876	0.565	0.435	5.3	2.54x10 ⁻⁸
7	0.370	0.472		0.843	0.440	0.560	19.3	9.62x10 ⁻⁸
8	0.185	0.226		0.411	0.451	0.549	9.63	9.84x10 ⁻⁸
9	0.111	0.236		0.347	0.320	0.679	9.52	1.15x10 ⁻⁷
10	0.185		0.226	0.411	0.450		7.23	7.38x10 ⁻⁸
11	.0445	0.345		0.389	0.114	0.886	12.4	1.34x10 ⁻⁷
12	0.185		0.222	0.408	0.455		3.03	3.12x10 ⁻⁸
13		0.277	0.185	0.462		0.599	70.4	6.40x10 ⁻⁷
14	0.185	0.493	0.185	0.864	0.215	0.571	13.96	6.79x10 ⁻⁸
15	1.507		1.235	2.742	0.550		1.54	2.36x10 ⁻⁹
17	0.247	0.342		0.590	0.419	0.581	250.9	1.79x10 ⁻⁶
18	.0445	0.138		0.183	0.244	0.756	6.86	1.58x10 ⁻⁷
19	0.185		0.222	0.408	0.455		2.97	3.06x10 ⁻⁸
20	0.494	0.650		1.144	0.432	0.568	72.4	2.66x10 ⁻⁷
21	1.808	1.437		3.245	0.557	0.443	5.9	7.64x10 ⁻⁹
22	.0741	.0880		0.162	0.457	0.543	10.4	2.70x10 ⁻⁷
24	0.222	0.299		0.521	0.427	0.573	29.43	2.37x10 ⁻⁷
25	1.482	2.207		3.689	0.402	0.598	183	2.08x10 ⁻⁷
26	0.370	0.251		0.621	0.596	0.404	9.03	6.10x10 ⁻⁸
27	0.370	.0838		0.454	0.816	0.184	5.2	4.81x10 ⁻⁸
31	0.296	0.441		0.738	0.402	0.598	1980	1.13x10 ⁻⁵
32	0.296	1.797		2.094	0.142	0.858	3150	6.32x10 ⁻⁶
33	0.370	0.311		0.682	0.543	0.457	2080	1.28x10 ⁻⁵
34	0.370			0.370	1.000		2480	2.81x10 ⁻⁵
35	0.370		0.445	0.815	0.454		4.71	2.43x10 ⁻⁸
36	0.372	0.502		0.874	0.425	0.575	15.28	7.34x10 ⁻⁸
37	0.370		0.445	0.815	0.454		0.95	4.90x10 ⁻⁹
39	0.370		0.445	0.815	0.454		3.62	1.87x10 ⁻⁸
41	0.747			0.747	1.000		5.45	3.06x10 ⁻⁸
42	0.433	2.653		3.087	0.140	0.860	14.37	1.96x10 ⁻⁸
43	0.432	0.611		1.044	0.414	0.586	4.18	1.87x10 ⁻⁸
44	0.370	1.722		2.093	0.177	0.823	37.26	7.48x10 ⁻⁸
45	9.757	13.53		23.29	0.419	0.581	0.053	9.56x10 ⁻¹²
46	1.112			1.112	1.000		13.93	5.26x10 ⁻⁸
47	0.988	1.486		2.475	0.399	0.601	162.7	2.76x10 ⁻⁷
48	6.001	8.532		14.53	0.413	0.587	0.207	5.98x10 ⁻¹¹
49	0.296			0.296	1.000		180	2.55x10 ⁻⁶
50	0.593			0.593	1.000		3.02	2.14x10 ⁻⁸
51	0.482			0.482	1.000		3.28	2.86x10 ⁻⁸
52	0.519	0.610		1.128	0.460	0.540	20.85	7.76x10 ⁻⁸
53	0.363	0.501		0.864	0.420	0.580	19.05	9.26x10 ⁻⁸

Table 5. (cont.) Summary of U transpiration experiments on U₃O₈ and U₃O₈/ash samples.

run #	moles of gas				p(O ₂) (atm)	p(H ₂ O) (atm)	U (μg)	p(U total) (atm)
	O ₂	H ₂ O	Ar	total				
54	0.674	0.285		0.959	0.703	0.297	13.6	5.96x10 ⁻⁸
55	2.007	3.055		5.062	0.397	0.603	2.38	1.98x10 ⁻⁹
56	0.119	0.169		0.288	0.412	0.588	30.3	4.42x10 ⁻⁷
58	0.362	0.544		0.907	0.400	0.600	67.4	3.12x10 ⁻⁷
59	0.556			0.556	1.000		1.31	9.90x10 ⁻⁹
60	1.050	1.499		2.549	0.412	0.588	148	2.44x10 ⁻⁷
61	0.350	0.900		1.251	0.280	0.720	21.9	7.36x10 ⁻⁸
63	0.432	0.650		1.082	0.400	0.600	3.13	1.22x10 ⁻⁸
64	0.389	1.097		1.487	0.262	0.738	5.40	1.53x10 ⁻⁸
65	2.529			2.529	1.000		21.1	3.50x10 ⁻⁸
66	0.463	0.650		1.113	0.416	0.584	20.6	7.78x10 ⁻⁸
67	0.402	1.096		1.498	0.268	0.732	20.5	5.75x10 ⁻⁸
68	0.510	0.686		1.196	0.426	0.574	14.20	4.99x10 ⁻⁸
69	0.722	0.462		1.184	0.610	0.390	16.05	5.69x10 ⁻⁸
70	1.050			1.050	1.000		6.08	2.43x10 ⁻⁸
71	0.951			0.951	1.000		5.73	2.53x10 ⁻⁸
72	0.698	0.497		1.196	0.584	0.416	11.93	4.19x10 ⁻⁸
73	0.489	0.731		1.220	0.820	0.180	16.19	5.58x10 ⁻⁸
74	0.398	0.955		1.352	0.294	0.706	20.55	6.38x10 ⁻⁸
75	3.613			3.613	1.000		1.66	1.93x10 ⁻⁹
76	0.380	0.950		1.330	0.286	0.714	5.71	1.80x10 ⁻⁸
77	3.489			3.489	1.000		2.05	2.47x10 ⁻⁹
78	0.889	0.238		1.127	0.789	0.211	9.27	3.46x10 ⁻⁸
79	1.634	3.822		5.456	0.300	0.700	10.57	8.14x10 ⁻⁹
80	0.698	0.475		1.174	0.595	0.405	1.22	4.37x10 ⁻⁹
83	0.424	1.137		1.561	0.271	0.729	1.53	4.12x10 ⁻⁹
84	0.453	0.617		1.070	0.423	0.577	0.94	3.69x10 ⁻⁹
85	2.608	0.733		3.342	0.780	0.220	0.68	8.55x10 ⁻¹⁰
86	3.112			3.112	1.000		0.31	4.18x10 ⁻¹⁰
87	1.556	2.305		3.862	0.403	0.597	0.27	2.94x10 ⁻¹⁰
88	0.382	2.546		2.927	0.130	0.870	39.53	5.67x10 ⁻⁸
89	3.464			3.464	1.000		1.92	2.33x10 ⁻⁹
90	0.411	1.024		1.434	0.286	0.714	23.63	6.92x10 ⁻⁸
91	1.038	5.746		6.783	0.153	0.847	13.78	8.54x10 ⁻⁹
92	0.937			0.937	1.000		0.46	2.06x10 ⁻⁹
93	0.367	0.352		0.720	0.510	0.490	3.68	2.15x10 ⁻⁸
94	4.763	7.346		12.11	0.393	0.607	0.08	2.78x10 ⁻¹¹
95	0.510	0.725		1.234	0.413	0.587	4.12	1.40x10 ⁻⁸
96	0.722	0.468		1.190	0.607	0.393	4.47	1.58x10 ⁻⁸
97	1.606	2.429		4.035	0.398	0.602	2.26	2.35x10 ⁻⁹
98	3.088			3.088	1.000		0.37	5.03x10 ⁻¹⁰

Figure 2. Plot of $\log O_2$ flow rate versus apparent total pressure of uranium where $T = 1373$ K, $p(O_2) = 0.4$ atm, and $p(H_2O) = 0.6$ atm. A plateau region is present from about $10 \text{ cm}^3/\text{min}$ to $250 \text{ cm}^3/\text{min}$.

Figure 3. Plot of $p(\text{U total})/p(\text{O}_2)^{1/6}$ versus $p(\text{H}_2\text{O})$ at 1223 K. The plot increases linearly which indicates that $\text{UO}_2(\text{OH})_2(\text{g})$ gas is formed in the vapor.

Figure 4. Plot of $p(\text{U total})/p(\text{O}_2)^{1/6}$ versus $p(\text{H}_2\text{O})$ at 1323 K. Although there is a lot of scatter in the data, the curve increases linearly with increasing water vapor pressure indicating the presence of $\text{UO}_2(\text{OH})_2(\text{g})$.

given later in this report. The evidence indicates that $\text{UO}_2(\text{OH})_2(\text{g})$ is the other dominant species in addition to $\text{UO}_3(\text{g})$, although minor amounts of other oxyhydroxide species cannot be discounted.

We now derive thermodynamic data for $\text{UO}_3(\text{g})$ and $\text{UO}_2(\text{OH})_2(\text{g})$ from the $\text{U}_3\text{O}_8(\text{s})$ transpiration measurements using the third law method. We take the free energy function for $\text{UO}_3(\text{g})$ from Green [17], see Table 6. The free energy function for $\text{UO}_2(\text{OH})_2(\text{g})$ is calculated using estimated molecular constants. The formulas for the translational, rotational, and vibrational contributions to the free energy function are taken from Lewis, et al. [18]. The formula for the internal rotation contribution to the free energy function is from Ebbinghaus [4]. The electronic contribution to the free energy function is assumed to be negligible. The U-O bond length is estimated as 0.212 nm, and the U-OH bond length as 0.180 nm. The $\text{UO}_2(\text{OH})_2(\text{g})$ molecule is assumed to have a C_{2v} symmetry where the symmetry number of rotation equals two. The vibrational wave numbers are estimated as: 3000, 3000, 776, 765.5, 470, 440, 296, 296, 225, 225, 180, 100, and 100 cm^{-1} . The hydroxide groups are assumed to have a barrier to rotation of 3.1 kJ/mol, a moment of inertia of $1.47 \times 10^{-47}\text{ kgm}^2$, and a symmetry number of rotation equal to one. The free energy function for $\text{UO}_2(\text{OH})_2(\text{g})$ calculated from these molecular constants is given in Table 6. The $\Delta H^\circ_{f,298}$ for $\text{U}_3\text{O}_8(\text{s})$ is from Grenthe et al. [19] and the free energy function is from Glushko et al. [20]. Thermodynamic data for $\text{O}_2(\text{g})$ and $\text{H}_2\text{O}(\text{g})$ are from the JANAF Tables [21].

We first analyze the transpiration data on $\text{UO}_3(\text{g})$ volatility based on reaction (4), using data where only $\text{O}_2(\text{g})$ or $\text{O}_2(\text{g})/\text{Ar}(\text{g})$ mixtures were present. Results are summarized in Table 7, giving a $\Delta H^\circ_{r,298}$ of 403.39 kJ/mol with a standard deviation of ± 12.74 kJ/mol for reaction (4). Ackermann et al. [12] and Dharwadkar et al. [13] have studied this same reaction by the transpiration method, but at higher temperatures. We reanalyze their data by the third law method. The Ackermann et al. data give $\Delta H^\circ_{r,298} = 398.05 \pm 2.23$ kJ/mol and the Dharwadkar et al. data give 396.85 ± 0.75 kJ/mol, where the errors are standard deviations. The agreement is good among the three studies. The $\text{UO}_3(\text{g})$ volatility data is illustrated in Fig. 5 in terms of $\log K_{\text{eq}}$ versus $1/T$. The solid line represents the data derived from the third law treatment of our data, while the dashed line is based upon the combined data of Ackermann et al. and Dharwadkar et al. and is extrapolated down from higher temperatures. We choose to use our data in this study since the measurements were made at lower temperatures. The $\Delta H^\circ_{f,298}$ of $\text{UO}_3(\text{g})$ is calculated to be -788.21 ± 7.0 kJ/mol (see Table 15).

We next analyze the transpiration data on $\text{UO}_2(\text{OH})_2(\text{g})$ volatility based on reaction (3). We obtain values of $\text{UO}_2(\text{OH})_2(\text{g})$ pressures by subtracting out $\text{UO}_3(\text{g})$ pressures (calculated from the selected data) from the total U pressures obtained experimentally (see Table 8). At temperatures above ~ 1400 K, pressures of $\text{UO}_2(\text{OH})_2(\text{g})$ are much lower than $\text{UO}_3(\text{g})$, so that accurate differences cannot be obtained, and so the higher temperature data were not included. Also, because of experimental scatter, runs 27, 78, and 85 gave negative values for $\text{UO}_2(\text{OH})_2(\text{g})$ pressures, and therefore provide no data. Data based on the balance of the points are

Table 6. Free energy functions for $\text{UO}_3(\text{g})$, $\text{PuO}_3(\text{g})$, $\text{AmO}_3(\text{g})$, $\text{UO}_2(\text{OH})_2(\text{g})$, $\text{PuO}_2(\text{OH})_2(\text{g})$, and $\text{AmO}_2(\text{OH})_2(\text{g})$.

$-(G^\circ T - H^\circ_{298})/T, \text{ J/mol-K}$						
T (K)	$\text{UO}_3(\text{g})$	$\text{PuO}_3(\text{g})$	$\text{AmO}_3(\text{g})$	$\text{UO}_2(\text{OH})_2(\text{g})$	$\text{PuO}_2(\text{OH})_2(\text{g})$	$\text{AmO}_2(\text{OH})_2(\text{g})$
800	335.37	353.39	354.36	442.20	460.50	461.46
900	341.00	359.08	360.04	451.82	470.13	471.09
1000	346.60	364.51	365.48	461.00	479.31	480.27
1100	351.88	369.69	370.65	469.74	488.05	489.01
1200	356.93	374.61	375.58	478.06	496.37	497.33
1300	361.76	379.30	380.27	485.99	504.29	505.25
1400	366.37	383.77	384.74	493.54	511.85	512.81
1500	370.78	388.03	389.00	500.75	519.06	520.02
1600	375.01	392.10	393.07	507.65	525.96	526.91

Table 7. Third law treatment for the reaction $1/3 \text{U}_3\text{O}_8(\text{s}) + 1/6 \text{O}_2(\text{g}) = \text{UO}_3(\text{g})$.

run #	T (K)	$\ln K_{\text{eq}}$	$\Delta G^\circ T/T$ (J/mol-K)	$(\Delta G^\circ T - \Delta H^\circ_{298})/T$ (J/mol-K)	ΔH°_{298} (kJ/mol)
10	1323	-16.288	135.43	-165.54	398.24
12	1323	-17.150	142.59	-165.54	407.72
15	1223	-19.765	164.34	-166.86	505.12
19	1323	-17.171	142.77	-165.54	407.96
34	1573	-10.479	87.14	-162.52	392.77
46	1373	-16.760	139.35	-164.91	417.81
49	1473	-12.879	107.08	-163.69	398.90
50	1273	-17.660	146.83	-166.19	398.54
51	1323	-17.370	144.42	-165.54	410.14
59	1173	-18.431	153.24	-167.55	376.35
86	1223	-21.594	179.55	-166.86	<u>423.73</u>
					ave. 403.39 ± 12.74

Figure 5. Plot of $\log K_{eq}$ for the reaction, $1/3 \text{ U}_3\text{O}_8(\text{s}) + 1/6 \text{ O}_2(\text{g}) = \text{UO}_3(\text{g})$, versus $10^4/T$. The solid line is obtained from a 3rd law treatment of our data. The dashed line is obtained from a 3rd law treatment of the combined data of Ackermann, et al. [12] and Dharwadkar, et al. [13].

Table 8. Total pressures of uranium are corrected for $\text{UO}_3(\text{g})$ to give pressures of $\text{UO}_2(\text{OH})_2(\text{g})$.

run #	T (K)	measured $p(\text{U total})$ (atm)	calculated $p(\text{UO}_3)$ (atm)	by difference $p(\text{UO}_2(\text{OH})_2)$ (atm)
7	1323	9.619×10^{-8}	4.861×10^{-8}	4.758×10^{-8}
8	1323	9.839×10^{-8}	4.882×10^{-8}	4.957×10^{-8}
9	1323	1.152×10^{-7}	4.612×10^{-8}	6.908×10^{-8}
11	1323	1.340×10^{-7}	3.884×10^{-8}	9.516×10^{-8}
14	1323	6.792×10^{-8}	4.314×10^{-8}	2.478×10^{-8}
18	1323	1.578×10^{-7}	4.406×10^{-8}	1.137×10^{-7}
20	1373	2.659×10^{-7}	1.845×10^{-7}	8.140×10^{-8}
21	1223	7.638×10^{-9}	2.502×10^{-9}	5.136×10^{-9}
22	1373	2.695×10^{-7}	1.863×10^{-7}	8.320×10^{-8}
24	1373	2.374×10^{-7}	1.842×10^{-7}	5.320×10^{-8}
26	1323	6.105×10^{-8}	5.115×10^{-8}	9.900×10^{-9}
27	1323	4.809×10^{-8}	5.389×10^{-8}	-----
47	1373	2.762×10^{-7}	1.821×10^{-7}	9.410×10^{-8}
55	1173	1.975×10^{-9}	4.328×10^{-10}	1.542×10^{-9}
58	1373	3.123×10^{-7}	1.821×10^{-7}	1.302×10^{-7}
60	1373	2.440×10^{-7}	1.831×10^{-7}	6.090×10^{-8}
76	1273	1.803×10^{-8}	1.069×10^{-8}	7.340×10^{-9}
78	1323	3.456×10^{-8}	5.360×10^{-8}	-----
79	1223	8.138×10^{-9}	2.256×10^{-9}	5.882×10^{-9}
85	1223	8.549×10^{-10}	2.647×10^{-9}	-----
88	1323	5.673×10^{-8}	3.970×10^{-8}	1.667×10^{-8}
90	1323	6.921×10^{-8}	4.526×10^{-8}	2.395×10^{-8}
91	1223	8.535×10^{-9}	2.017×10^{-9}	6.518×10^{-9}

used to obtain values of $\Delta H^\circ_{r,298}$ for reaction (3) (see Table 9). The average value of $\Delta H^\circ_{r,298}$ is found to be 281.82 kJ/mol with a standard deviation of ± 5.93 kJ/mol. This results in a $\Delta H^\circ_{f,298}$ of -1151.61 ± 6.00 kJ/mol for $\text{UO}_2(\text{OH})_2(\text{g})$. Dharwadkar et al. [13] have previously carried out transpiration experiments on $\text{U}_3\text{O}_8(\text{s})$ in the presence of $\text{O}_2(\text{g})$ and $\text{H}_2\text{O}(\text{g})$. They identified the $\text{UO}_2(\text{OH})_2(\text{g})$ species and measured its vapor pressure by subtracting out the $\text{UO}_3(\text{g})$ contribution. We treat their data by the third law method and obtain $\Delta H^\circ_{r,298} = 222.40 \pm 2.73$ kJ/mol for reaction (3), and $\Delta H^\circ_{f,298} = -1211.03 \pm 2.80$ kJ/mol for $\text{UO}_2(\text{OH})_2(\text{g})$. A log K_{eq} versus $1/T$ plot for reaction (3) is presented in Fig. 6, showing our data points along with the third law fit. The Dharwadkar et al. third law results extrapolated down from higher temperatures are shown by a dashed line. Our results differ considerably from those of Dharwadkar et al. We find no clear reasons to account for the discrepancy. We based our results on $\text{UO}_2(\text{OH})_2(\text{g})$ on data obtained at lower temperatures and higher H_2O pressures than Dharwadkar et al., where $\text{UO}_2(\text{OH})_2(\text{g})$ pressures should clearly dominate over $\text{UO}_3(\text{g})$. We believe our results to be correct and use them as our selected values.

The pressure of uranium above $\text{U}_3\text{O}_8(\text{s})$ measured at 826 K in run 94, 3×10^{-11} atm, is low, but we believe the amount of U detected is from contamination from handling of the collector tube. Calculation of the uranium pressures under these conditions shows them to be $p(\text{UO}_3) = 8.1 \times 10^{-18}$ atm and $p(\text{UO}_2(\text{OH})_2) = 8.8 \times 10^{-15}$ atm.

The $\Delta H^\circ_{r,298}$ values for reactions (3) and (4) can be combined with the $(\Delta G^\circ_T - \Delta H^\circ_{298})/T$ values given in Table 10. Calculated pressures of $\text{UO}_3(\text{g})$ and $\text{UO}_2(\text{OH})_2(\text{g})$ above $\text{U}_3\text{O}_8(\text{s})$ at 0.1 atm each of $\text{O}_2(\text{g})$ and $\text{H}_2\text{O}(\text{g})$ are shown as a function of temperature in Fig. 7.

Volatilities of $\text{UO}_3(\text{g})$ and $\text{UO}_2(\text{OH})_2(\text{g})$ from $\text{U}_3\text{O}_8/\text{Ash}$:

The experimental data on $\text{U}_3\text{O}_8/\text{ash}$ runs are included in Tables 4 and 5. The measurements were carried out mostly at 1323 K, with a few at 1223 K. The results for the 1323 K runs are illustrated in Figs. 8 and 9 as a plot of $p(\text{U total})/p(\text{O}_2)^{1/6}$ versus $p(\text{H}_2\text{O})$ for the various $\text{U}_3\text{O}_8/\text{ash}$ compositions along with our selected data for the sum of $\text{UO}_3(\text{g})$ plus $\text{UO}_2(\text{OH})_2(\text{g})$ volatilities above $\text{U}_3\text{O}_8(\text{s})$. The volatility data for $\text{U}_3\text{O}_8/1633\text{a}$ ash and $\text{U}_3\text{O}_8/2690$ ash are essentially identical and have been combined in the plots. The lines fitted to the data are assessed values as will be described. The effect of water vapor on total U volatility is apparent in the $\text{U}_3\text{O}_8/\text{ash}$ samples as was the case with $\text{U}_3\text{O}_8(\text{s})$. The extent of U volatility lowering by the 1633a and 2690 ashes is small, while the high Na_2O ash (Ash 1) and the high CaO ash (2691) both show considerable lowering of the volatility.

To analyze the $\text{U}_3\text{O}_8/\text{ash}$ volatility data, it would be desirable to define the chemical form of the uranium. However, the systems are very complex. Our characterization studies indicate that uranium is present both in the glass and in

Table 9. Third law treatment for the reaction $1/3 \text{ U}_3\text{O}_8(\text{s}) + 1/6 \text{ O}_2(\text{g}) + \text{H}_2\text{O}(\text{g}) = \text{UO}_2(\text{OH})_2(\text{g})$.

run #	T (K)	$\ln K_{\text{eq}}$	$\Delta G^\circ_T/T$ (J/mol-K)	$(\Delta G^\circ_T - \Delta H^\circ_{298})/T$ (J/mol-K)	ΔH°_{298} (kJ/mol)
7	1323	-16.145	134.24	-75.91	278.07
8	1323	-16.088	133.77	-75.91	277.45
9	1323	-15.912	132.30	-75.91	275.51
11	1323	-15.685	130.41	-75.91	273.01
14	1323	-16.696	138.81	-75.91	284.13
18	1323	-15.475	128.67	-75.91	270.70
20	1373	-15.619	129.86	-75.61	282.16
21	1223	-18.175	151.12	-76.51	278.44
22	1373	-15.561	129.38	-75.61	281.50
24	1373	-16.051	133.45	-75.61	287.09
26	1323	-17.438	144.99	-75.91	292.30
47	1373	-15.516	129.01	-75.61	280.9
55	1173	-19.631	163.22	-76.82	281.62
58	1373	-15.191	126.31	-75.61	277.28
60	1373	-15.935	132.49	-75.61	285.77
76	1273	-18.184	151.19	-76.21	289.53
79	1223	-18.394	152.94	-76.51	280.66
88	1323	-17.430	144.93	-75.91	292.21
90	1323	-17.002	141.35	-75.91	287.49
91	1223	-18.370	152.74	-76.51	<u>280.42</u>

ave. 281.82 ± 5.93

Figure 6. Plot of $\log K_{eq}$ for the reaction, $1/3 \text{U}_3\text{O}_8(\text{s}) + 1/6 \text{O}_2(\text{g}) + \text{H}_2\text{O}(\text{g}) = \text{UO}_2(\text{OH})_2(\text{g})$, versus $10^4/T$. The solid line is that obtained from a 3rd law treatment of our data. The dashed line is the curve obtained from a 3rd law treatment of the data of Dharwadkar, et al. [13].

Table 10. Free energy functions, $-(\Delta G^\circ T - \Delta H^\circ_{298})/T$, for the reactions:

$-(\Delta G^\circ T - \Delta H^\circ_{298})/T, \text{ J/mol-K}$						
T (K)	eqn (A)	eqn (B)	eqn (C)	eqn (D)	eqn (E)	eqn (F)
800	173.25	78.91	151.44	57.32	152.91	58.79
900	171.66	78.41	149.58	56.64	151.42	58.47
1000	170.10	77.95	147.77	55.93	149.99	58.14
1100	168.60	77.29	146.02	55.19	148.62	57.78
1200	167.18	76.65	144.33	54.44	147.31	57.42
1300	165.84	76.05	142.70	53.69	146.06	57.04
1400	164.58	75.46	141.12	52.93	144.86	56.66
1500	163.37	74.88	139.59	52.16	143.71	56.28
1600	162.21	74.29	138.10	51.40	142.60	55.89

Figure 7. Plot showing $\log p(\text{U})$ for the species $\text{UO}_3(\text{g})$ and $\text{UO}_2(\text{OH})_2(\text{g})$ and maximum $\log p(\text{Pu})$ and $p(\text{Am})$ for $\text{PuO}_3(\text{g})$, $\text{PuO}_2(\text{OH})_2(\text{g})$, $\text{AmO}_3(\text{g})$, and $\text{AmO}_2(\text{OH})_2(\text{g})$ above $\text{U}_3\text{O}_8(\text{s})$, $\text{PuO}_2(\text{s})$, and 1000 ppm AmO_2 solid solution in $\text{PuO}_2(\text{s})$ as a function of temperature where $p(\text{O}_2) = 0.10$ atm and $p(\text{H}_2\text{O}) = 0.10$ atm.

Figure 8. Plot of $p(\text{U total})/p(\text{O}_2)^{1/6}$ versus $p(\text{H}_2\text{O})$ at 1323 K for the 5% $\text{UO}_{2.67}/\text{ash}$ samples. The 5% $\text{UO}_{2.67}/1633\text{a}$ and the 5% $\text{UO}_{2.67}/2690$ data are nearly the same and are shown together. The U volatility above 5% $\text{UO}_{2.67}/2691$ is reduced the most.

Figure 9. Plot of $p(\text{U total})/p(\text{O}_2)^{1/6}$ versus $p(\text{H}_2\text{O})$ at 1323 K for the 0.5% $\text{UO}_{2.67}$ /ash samples. The 0.5% $\text{UO}_{2.67}/1633\text{a}$ and the 0.5% $\text{UO}_{2.67}/2690$ data are nearly the same and are shown together. The U volatility above 0.5% $\text{UO}_{2.67}/2691$ is reduced the most.

crystalline phases, but a complete definitive description is not available, especially at the temperature of the measurements. For convenience in analyzing the data, we use a solution model. We assume that the uranium is dissolved in the host matrix as the oxide U_3O_8 , which for convenience we take as $\text{UO}_{2.67}$. We can then write for the interaction of uranium oxide with ash,

$$\text{UO}_{2.67}(\text{s}) = \text{UO}_{2.67}(\text{sol'n in ash}). \quad (6)$$

The partial molal free energy change for this reaction is given by,

$$\Delta \bar{G}_T = RT \ln a(\text{UO}_{2.67}), \quad (7)$$

which, by assuming the entropy of mixing to be ideal, can be written as

$$\Delta \bar{G}_T = RT \ln \gamma(\text{UO}_{2.67}) + RT \ln x(\text{UO}_{2.67}), \quad (8)$$

where the first term on the right is the partial molal enthalpy of solution and the second term is the partial molal entropy of solution. The partial molal enthalpy of solution is the primary thermodynamic term that describes the uranium volatility reduction in the ash. We expect the partial molal enthalpy of solution to reach a limiting value at low concentrations of $\text{UO}_{2.67}$ (Henry's Law), and to remain nearly constant with temperature.

We therefore analyze the data to obtain values of $RT \ln \gamma(\text{UO}_{2.67})$ for each of the $\text{UO}_{2.67}$ /ash samples. We obtain the γ values from the relation $\gamma = a/x$, i.e., activity coefficient is equal to activity divided by mole fraction. The activities are obtained from the ratio $p(\text{U total})/p^\circ(\text{U total})$, where $p(\text{U total})$ is the measured total U pressure for the U_3O_8 /ash sample and $p^\circ(\text{U total})$ is the calculated sum of the $\text{UO}_3(\text{g})$ and $\text{UO}_2(\text{OH})_2(\text{g})$ pressures above pure $\text{U}_3\text{O}_8(\text{s})$ under the same conditions of temperature and $\text{O}_2(\text{g})$ and $\text{H}_2\text{O}(\text{g})$ pressures. The mole fraction of $\text{UO}_{2.67}$ in each sample is obtained by taking the moles of the ash constituents on the basis of a single metal atom per mole (e.g., $\text{AlO}_{1.5}$, $\text{NaO}_{0.5}$) and taking phosphorous and sulfur to be combined with other metals as phosphate and sulfate. The values of pressures, activities, mole fractions, activity coefficients, and partial enthalpies of solution are summarized for the various runs in Table 11.

We find for the $\text{U}_3\text{O}_8/1633\text{a}$ ash and $\text{U}_3\text{O}_8/2690$ ash samples that there is very little activity lowering for both 5 wt % and 0.5 wt % U_3O_8 contents. The $RT \ln \gamma(\text{UO}_{2.67})$ values are similar for these two ash materials, with a value of about 40 kJ/mol for the 5 wt % U_3O_8 contents and 70 kJ/mol for the 0.5 wt % U_3O_8 contents. Because of the low degree of interaction of U_3O_8 with these ashes, it is not certain that the $RT \ln \gamma(\text{UO}_{2.67})$ values have reached a limiting value at the 0.5 wt % U_3O_8 contents. For the $\text{U}_3\text{O}_8/2691$ ash the activity lowering is substantial, and $RT \ln \gamma(\text{UO}_{2.67})$ goes from 29.89 kJ/mol at 5 wt % U_3O_8 content to 41.30 kJ/mol at 0.5 wt % U_3O_8 contents. The change in $RT \ln \gamma(\text{UO}_{2.67})$ is small, and we have some confidence that the 41.30

Table 11. Calculation of activities, activity coefficients, and enthalpies of solution for U₃O₈/ash samples.

run #	T (K)	p(U total) (atm)	p°(U total) (atm)	a(UO ₂ .67)	x(UO ₂ .67)	γ (UO ₂ .67)	RTln γ (UO ₂ .67) (kJ/mol)
5%UO₂.67/1633a							
39	1323	1.866x10 ⁻⁸	4.889x10 ⁻⁸	0.3817	0.01179	32.37	38.26
41	1323	3.064x10 ⁻⁸	5.575x10 ⁻⁸	0.5496	0.01179	46.62	42.27
65	1323	3.505x10 ⁻⁸	5.575x10 ⁻⁸	0.6287	0.01179	53.32	43.75
66	1323	7.778x10 ⁻⁸	8.300x10 ⁻⁸	0.9371	0.01179	79.48	<u>48.14</u>
							43.11 ± 4.08
0.5%UO₂.67/1633a							
67	1323	5.750x10 ⁻⁸	8.534x10 ⁻⁸	0.6738	0.001095	615.3	70.65
68	1323	4.990x10 ⁻⁸	8.273x10 ⁻⁸	0.6031	0.001095	550.8	69.44
69	1323	5.694x10 ⁻⁸	7.613x10 ⁻⁸	0.7478	0.001095	682.9	71.80
70	1323	2.433x10 ⁻⁸	5.575x10 ⁻⁸	0.4364	0.001095	398.5	<u>65.88</u>
							69.44 ± 2.56
5%UO₂.67/2690							
1	1319	2.542x10 ⁻⁸	9.351x10 ⁻⁸	0.2719	0.01130	24.06	34.88
35	1323	2.428x10 ⁻⁸	4.889x10 ⁻⁸	0.4966	0.01130	43.95	41.62
36	1323	7.345x10 ⁻⁸	8.276x10 ⁻⁸	0.8875	0.01130	78.54	48.01
44	1323	7.480x10 ⁻⁸	8.435x10 ⁻⁸	0.8867	0.01130	78.47	48.00
51	1323	2.861x10 ⁻⁸	5.575x10 ⁻⁸	0.5132	0.01130	45.42	41.98
52	1323	7.763x10 ⁻⁸	8.175x10 ⁻⁸	0.9497	0.01130	84.04	48.75
53	1323	9.265x10 ⁻⁸	8.289x10 ⁻⁸	1.1178	0.01130	98.92	50.55
54	1323	5.957x10 ⁻⁸	7.190x10 ⁻⁸	0.8284	0.01130	73.31	47.25
61	1323	7.357x10 ⁻⁸	8.530x10 ⁻⁸	0.8625	0.01130	76.33	<u>47.69</u>
							44.52 ± 4.88
0.5%UO₂.67/2690							
71	1323	2.531x10 ⁻⁸	5.575x10 ⁻⁸	0.4540	0.001049	432.8	66.78
72	1323	4.192x10 ⁻⁸	7.722x10 ⁻⁸	0.5428	0.001049	517.4	68.75
73	1323	5.576x10 ⁻⁸	6.598x10 ⁻⁸	0.8451	0.001049	805.6	73.62
74	1323	6.384x10 ⁻⁸	8.521x10 ⁻⁸	0.7492	0.001049	714.2	<u>72.29</u>
							70.36 ± 3.15

Table 11. (cont.) Calculation of activities, activity coefficients, and enthalpies of solution for U₃O₈/ash samples.

run #	T (K)	p(U total) (atm)	p°(U total) (atm)	a(UO _{2.67})	x(UO _{2.67})	g(UO _{2.67})	RTlnγ(UO _{2.67}) (kJ/mol)
5%UO_{2.67}/2691							
37	1323	4.896x10 ⁻⁹	4.889x10 ⁻⁸	0.1002	0.01122	8.930	24.09
42	1323	1.956x10 ⁻⁸	8.298x10 ⁻⁸	0.2357	0.01122	21.01	33.50
43	1323	1.874x10 ⁻⁸	8.305x10 ⁻⁸	0.2257	0.01122	20.12	33.02
63	1323	1.216x10 ⁻⁸	8.342x10 ⁻⁸	0.1457	0.01122	12.99	28.21
64	1323	1.526x10 ⁻⁸	8.535x10 ⁻⁸	0.1788	0.01122	15.94	30.46
							29.85 ± 3.86
0.5%UO_{2.67}/2691							
77	1323	2.468x10 ⁻⁹	5.575x10 ⁻⁸	0.04427	0.001042	42.49	41.25
80	1323	4.367x10 ⁻⁹	7.677x10 ⁻⁸	0.05688	0.001042	54.59	44.01
83	1323	4.118x10 ⁻⁹	8.534x10 ⁻⁸	0.04825	0.001042	46.31	42.20
84	1323	3.692x10 ⁻⁹	8.281x10 ⁻⁸	0.04459	0.001042	42.79	41.33
87	1223	2.937x10 ⁻¹⁰	7.058x10 ⁻⁹	0.04162	0.001042	39.94	37.50
89 ^a	1223	2.328x10 ⁻⁹	2.758x10 ⁻⁹	0.8441	0.001042	810.1	68.11 ^a
							41.26 ± 2.38
0.5%UO_{2.67}/Ash1							
75	1323	1.930x10 ⁻⁹	5.575x10 ⁻⁸	0.03462	.0009548	36.26	39.51
0.5%UO_{2.67}/Ash2							
92 ^a	1323	2.063x10 ⁻⁹	5.575x10 ⁻⁸	0.03701	.0009632	38.42	40.14 ^a
93	1323	2.148x10 ⁻⁸	8.006x10 ⁻⁸	0.2682	.0009632	278.4	61.93
95	1323	1.402x10 ⁻⁸	8.309x10 ⁻⁸	0.1688	.0009632	175.2	56.83
96	1323	1.578x10 ⁻⁸	7.627x10 ⁻⁸	0.2068	.0009632	214.7	59.07
97	1223	2.353x10 ⁻⁹	7.083x10 ⁻⁹	0.3322	.0009632	344.9	59.43
98	1223	5.034x10 ⁻¹⁰	2.758x10 ⁻⁹	0.1825	.0009632	189.5	53.34
							58.12 ± 3.23

^aRuns 89 and 92 were not considered when calculating the averages.

kJ/mol is at or close to the level-off value. If we use the $\text{RTln } \gamma(\text{UO}_{2.67})$ value of 41.30 kJ/mol to extrapolate to lower concentrations of U_3O_8 in 2691 ash, we find for example at $x(\text{UO}_{2.67}) = 0.0001$ (0.05 wt % U_3O_8) and 1323 K, that $\gamma(\text{UO}_{2.67}) = 43$, and $a(\text{UO}_{2.67}) = 0.0043$. For U_3O_8 in Ash 1 and Ash 2, runs were only made on 0.5 wt % U_3O_8 content samples. The U_3O_8 activity lowering was substantial in these materials, and the $\text{RTln } \gamma(\text{UO}_{2.67})$ values are probably at or close to the limiting values.

In run 45, we ran a 1.7% $\text{UO}_{2.67}$ /2690 ash/salts/catalyst sample at 827 K and in run 48, we ran a 1.7% $\text{UO}_{2.67}$ /1633a ash/salts/catalyst sample at 826 K, both with 0.4 atm $\text{O}_2(\text{g})$ and 0.6 atm $\text{H}_2\text{O}(\text{g})$ present, and found U pressure values of 1×10^{-11} and 6×10^{-11} atm, respectively. We believe that these values are high and the result of dust transport or contamination during handling of the collector tubes.

Volatilities of $\text{PuO}_3(\text{g})$ and $\text{PuO}_2(\text{OH})_2(\text{g})$ from $\text{PuO}_2(\text{s})$ and from PuO_2/ash :

The experimental data on the transpiration runs on $^{238}\text{PuO}_2(\text{s})$, $^{238}\text{PuO}_2/\text{ash}$ and $^{238}\text{PuO}_2/^{241}\text{AmO}_2/\text{ash}$ are summarized in Tables 12 and 13, and data on $^{239}\text{PuO}_2(\text{s})$ were given in an earlier report [10]. For convenience in illustrating the data, we take the volatilization to occur entirely to $\text{PuO}_3(\text{g})$. The volatilization reaction and the associated equilibrium constant is then:

$$K_9 = p(\text{PuO}_3)/a(\text{PuO}_2)p(\text{O}_2)^{1/2}.$$

We take the $a(\text{PuO}_2)$ for the $\text{PuO}_2(\text{s})$ samples to be unity, and assume that it is also approximately unity for the PuO_2/ash samples. We then plot the data as a $\log p(\text{Pu total})/p(\text{O}_2)^{1/2}$ versus $1/T$ plot (see Fig. 10), which would give a linear curve if the assumptions and data are correct. A similar illustrative plot could have been developed taking the total Pu species to be $\text{PuO}_2(\text{OH})_2(\text{g})$, and the data would show similar effects. The data show considerable problems that need to be discussed.

In the earlier work with $^{239}\text{PuO}_2(\text{s})$ [10], because of the low levels of Pu volatilized we found that the results were complicated by problems of: PuO_2 dust transport, collection of the volatilized samples on quartz wool plugs, cross-contamination of collection samples between runs, and background contamination from the glovebox environment during sample handling. We also believed that sintering of the samples may have reduced the approach to equilibrium. In retrospect, after seeing the current results with $^{238}\text{PuO}_2(\text{s})$, sintering was not the main contributor to the problem, but rather dust transport and sample contamination. We believe that in runs 4, 6, 8 and 9 (see Fig. 10), dust transport was very pronounced because of the

Table 12. Summary of Pu transpiration experiments on PuO₂, PuO₂/ash, and PuO₂/AmO₂/ash samples.

run #	sample	T _{furn} (K)	O ₂ flow (cm ³ /min)	Ar flow (cm ³ /min)	time (min)	T _{bath} (°C)	H ₂ O (grams)
46	3% ²³⁸ PuO ₂ /2691	1228	50.0		600	81.0	21.07
47	3% ²³⁸ PuO ₂ /2691	1330	50.0		600	81.0	22.10
52	3% ²³⁸ PuO ₂ /2691	1330	50.0		600	92.8	67.61
53	3% ²³⁸ PuO ₂ /2691	1279	50.0		870	92.9	93.14
54	3% ²³⁸ PuO ₂ /2691	1355	50.0		600	95.4	110.36
55	1.1% ²³⁸ PuO ₂ /2691/ salts/catalyst	829	50.0		1110	85.6	51.29
63	0.6% ²³⁸ PuO ₂ /2691	1228	50.0		630	85.8	34.45
64	0.6% ²³⁸ PuO ₂ /2691	1280	50.0		600	85.8	34.61
65	0.6% ²³⁸ PuO ₂ /2691	1330	50.0		600	85.9	32.95
66	0.6% ²³⁸ PuO ₂ /2691	1179	50.0		600	85.8	32.21
67	0.6% ²³⁸ PuO ₂ /2691	1381	50.0		540	82.9	20.77
69	3% ²³⁹ PuO ₂ / 0.06% ²⁴¹ AmO ₂ /1633a	1228	50.0		600	82.7	22.81
70	3% ²³⁹ PuO ₂ / 0.06% ²⁴¹ AmO ₂ /1633a	1178	50.0		600	82.7	22.07
71	3% ²³⁹ PuO ₂ / 0.06% ²⁴¹ AmO ₂ /1633a	1279	50.0		600	82.6	22.77
72	3% ²³⁹ PuO ₂ / 0.06% ²⁴¹ AmO ₂ /1633a	1329	50.0		600	82.7	23.23
73	²³⁸ PuO ₂	824	50.0		900	82.6	30.09
74	²³⁸ PuO ₂	1076	50.0		1030	82.7	37.30
75	²³⁸ PuO ₂	1177	50.0		600	82.8	23.42
76	²³⁸ PuO ₂	1277	50.0		540	82.7	21.14
77	²³⁸ PuO ₂	1327	50.0		600	82.7	25.32
78	²³⁸ PuO ₂	1325	50.0		600		
79	²³⁸ PuO ₂	1327	25.0	24.9	840		
80	²³⁸ PuO ₂	1326	12.5	37.5	1050		
81	²³⁸ PuO ₂	824	50.0		900	85.3	31.26
82	²³⁸ PuO ₂	1076	50.0		1010	82.7	39.24
83	²³⁸ PuO ₂	1176	50.0		600	82.7	24.02
84	²³⁸ PuO ₂	1277	50.0		590	82.7	25.92
85	²³⁸ PuO ₂	1326	50.0		480	82.7	20.44
86	²³⁸ PuO ₂	1326	50.0		600		
87	²³⁸ PuO ₂	1326	25.0	24.9	890		
88	²³⁸ PuO ₂	1325	12.5	37.5	860		
89	²³⁸ PuO ₂	824	50.0		600	82.7	23.18
90	²³⁸ PuO ₂	1176	50.0		480	82.7	20.17

Table 13. Summary of Pu transpiration experiments on PuO₂, PuO₂/ash, and PuO₂/AmO₂/ash samples.

run #	moles of gas				p(O ₂) (atm)	p(H ₂ O) (atm)	Pu (ng)	p(Pu total) (atm)
	O ₂	H ₂ O	Ar	total				
46	1.239	1.170		2.409	0.515	0.485	0.0900	1.57x10 ⁻¹³
47	1.239	1.227		2.466	0.503	0.497	4.84	8.24x10 ⁻¹²
52	1.239	3.753		4.992	0.248	0.752	3.75	3.16x10 ⁻¹²
53	1.797	5.170		6.967	0.258	0.742	1.20	7.23x10 ⁻¹³
54	1.239	6.126		7.365	0.168	0.832	39.75	2.27x10 ⁻¹¹
55	2.293	2.847		5.140	0.446	0.554	0.256	2.10x10 ⁻¹³
63	1.301	1.912		3.214	0.405	0.595	0.0765	1.00x10 ⁻¹³
64	1.239	1.921		3.160	0.392	0.608	0.238	3.16x10 ⁻¹³
65	1.239	1.829		3.068	0.404	0.596	1.148	1.57x10 ⁻¹²
66	1.239	1.788		3.027	0.409	0.591	2.23	3.09x10 ⁻¹²
67	1.115	1.153		2.268	0.492	0.508	3.65	6.76x10 ⁻¹²
69	1.239	1.266		2.505	0.495	0.505	<.0034	<5.7x10 ⁻¹⁵
				(2.6 pg Am, p(Am total) = 4.31x10 ⁻¹⁵)				
70	1.239	1.225		2.464	0.503	0.497	2.20	3.74x10 ⁻¹²
				(64 pg Am, p(Am total) = 1.08x10 ⁻¹³)				
71	1.239	1.264		2.503	0.495	0.505	7.59	1.27x10 ⁻¹¹
				(176 pg Am, p(Am total) = 2.92x10 ⁻¹³)				
72	1.239	1.290		2.529	0.490	0.510	0.31	5.13x10 ⁻¹³
				(8.4 pg Am, p(Am total) = 1.38x10 ⁻¹⁴)				
73	1.859	1.670		3.529	0.527	0.473	4.05	4.82x10 ⁻¹²
74	2.128	2.071		4.199	0.507	0.493	0.0076	7.65x10 ⁻¹⁵
75	1.239	1.300		2.539	0.488	0.512	0.163	2.69x10 ⁻¹³
76	1.115	1.173		2.288	0.487	0.513	0.0082	1.50x10 ⁻¹⁴
77	1.239	1.406		2.645	0.469	0.531	0.0348	5.52x10 ⁻¹⁴
78	1.239			1.239	1.000		0.0313	1.06x10 ⁻¹³
79	0.868		0.864	1.732	0.501		0.0006	1.52x10 ⁻¹⁵
80	0.542		1.627	2.169	0.250		0.0035	6.83x10 ⁻¹⁵
81	1.859	1.735		3.594	0.517	0.483	0.0895	1.05x10 ⁻¹³
82	2.086	2.178		4.264	0.489	0.511	0.0076	7.49x10 ⁻¹⁵
83	1.239	1.333		2.572	0.482	0.518	1.92	3.14x10 ⁻¹²
84	1.219	1.439		2.658	0.459	0.541	0.0003	4.90x10 ⁻¹⁶
85	0.991	1.135		2.126	0.466	0.534	0.0159	3.14x10 ⁻¹⁴
86	1.239			1.239	1.000		0.0022	7.42x10 ⁻¹⁵
87	0.919		0.916	1.835	0.501		0.0007	1.65x10 ⁻¹⁵
88	0.444		1.332	1.776	0.250		0.173	4.08x10 ⁻¹³
89	1.239	1.287		2.526	0.491	0.509	<.0006	<9x10 ⁻¹⁶
90	0.991	1.120		2.111	0.470	0.530	0.0004	8.11x10 ⁻¹⁶

Figure 10. Plot of $\log p(\text{Pu total})/p(\text{O}_2)^{1/2}$ versus $10^4/T$ for $\text{PuO}_2(\text{s})$ and PuO_2/ash runs.

very fine $^{239}\text{PuO}_2(\text{s})$ material used, and the high gas flow rates. In runs 19, 20, and 21, the material showed considerable sintering, and in spite of high gas flow rates ($500 \text{ cm}^3/\text{min}$) and without the use of a dust filter, the apparent volatility was down to that observed for the 550°C run (run 11). Using a new sample material, $^{239}\text{PuO}_2/2\% ^{241}\text{AmO}_2$, higher volatilities were observed when the sample was ground in a mortar and pestle prior to the runs (see runs 33, 36, and 44 in Fig. 10), then if a sample was reheated after a previous high temperature run (runs 23, 24, 25, 28, 32, 34, and 37). We can conclude for these previous measurements, that because of problems of dust transport and sample contamination, the total Pu volatility lies below $3 \times 10^{-11} \text{ atm}$ at $0.1 \text{ atm H}_2\text{O}$ pressure, 0.9 atm O_2 pressure and 1415 K (see run 29 in ref. [10]).

We discuss next the $^{238}\text{PuO}_2(\text{s})$ experiments, even though these followed the PuO_2/ash experiments. We made a number of experimental improvements to avoid or reduce the problems encountered in the earlier work [10]. ^{238}Pu was used for greater sensitivity of detection. Temperatures were kept below 1330 K to avoid extensive sintering. A collection tube was used instead of quartz wool for sample collection. Quartz wool was placed inside of the collection tube to facilitate condensation in runs 73-77, but not in the balance of the runs. No difference in results was noted. Solvent was added to only the inside of the collection tubes to leach out the Pu deposit for analysis, thus avoiding any contamination picked up on the outside of the tubes. The $^{238}\text{PuO}_2$ sample was ground in a mortar and pestle before the first run, but no further grinding was used on succeeding runs. Using alpha counting for ^{238}Pu analysis, we found that the Pu volatilities were somewhat higher than for the $3\%^{238}\text{PuO}_2/2691$ ash samples. However, a check on alpha peaks using pulse height analysis showed that the alpha counts came primarily from a 4.75 MeV peak corresponding to either ^{234}U , ^{237}Np or ^{233}U . A thin film sample was prepared by hot filament evaporation onto a planchet and analyzed by pulse height analysis for fine structure and showed that the 4.75 MeV peak was essentially all ^{234}U . These pulse height analysis results on the $^{238}\text{PuO}_2(\text{s})$ runs contrasted to the earlier $3\%^{238}\text{PuO}_2/2691$ ash runs where we had found nearly all of the alpha counts to originate from ^{238}Pu . We proceeded to reanalyze all of the ^{238}Pu runs (including the ash runs) by pulse height analysis to obtain both ^{238}Pu and ^{234}U values. The ^{238}Pu values were corrected to total Pu based on the isotopic mix, and results are given in Table 13. The amounts of ^{234}U found are given in Table 14.

Analyzing the results of the $^{238}\text{PuO}_2(\text{s})$ runs, we find a high Pu volatility value for run 73 at 824 K , where the sample had been ground prior to the heating. We attribute this to PuO_2 dust transport. In runs 81 and 89, also at 824 K , we find successively lower values for Pu volatility, indicating successively lower values of dust transport. The Pu volatility results for runs 81 ($p(\text{Pu total}) = 1.05 \times 10^{-13} \text{ atm}$) and 89 ($p(\text{Pu total}) = <9 \times 10^{-16} \text{ atm}$) fairly well bracket the observed volatilities at the higher temperatures. This indicates that even the higher temperature volatilities result from dust transport. There is one particularly spurious point for run 83 at 1176 , that gives a high volatility value, but is not born out by data at higher temperatures. At the highest

Table 14. Summary of ^{234}U volatility data from transpiration experiments on $^{238}\text{PuO}_2$ and $^{238}\text{PuO}_2$ /ash samples. Calculated values of ^{234}U pressures are shown for comparison based on the assumption that 3.3% $^{234}\text{UO}_{2.67}$ is in ideal solution in $^{238}\text{PuO}_2$.

run #	T (K)	gas (mol)	p(O_2) (atm)	p(H_2O) (atm)	^{234}U (μg)	measured p(U tot) (atm)	calculated p(U tot) (atm)
3% $^{238}\text{PuO}_2$/2691:							
46	1228	2.409	0.515	0.485	0.036	6.39×10^{-11}	2.42×10^{-10}
47	1330	2.466	0.503	0.497	0.56	9.70×10^{-10}	3.14×10^{-9}
52	1330	4.992	0.248	0.752	1.1	9.42×10^{-10}	3.31×10^{-9}
53	1279	6.967	0.258	0.742	6.8	4.17×10^{-9}	9.91×10^{-10}
54	1355	7.365	0.168	0.832	2.2	1.28×10^{-9}	5.77×10^{-9}
1.1% $^{238}\text{PuO}_2$/2691/salts/catalyst:							
55	829	5.140	0.446	0.554	n.d.		
0.6% $^{238}\text{PuO}_2$/2691:							
63	1228	3.214	0.405	0.595	0.02	2.66×10^{-11}	2.64×10^{-10}
64	1280	3.160	0.392	0.608	0.13	1.76×10^{-10}	9.74×10^{-10}
65	1330	3.068	0.404	0.596	0.25	3.48×10^{-10}	3.25×10^{-9}
66	1179	3.027	0.409	0.591	n.d.		7.41×10^{-11}
67	1381	2.268	0.492	0.508	0.36	6.78×10^{-10}	1.05×10^{-8}
$^{238}\text{PuO}_2$:							
73	824	3.529	0.527	0.473	n.d.		
74	1076	4.199	0.507	0.493	n.d.		3.71×10^{-12}
75	1177	2.539	0.488	0.512	0.045	7.57×10^{-11}	6.50×10^{-11}
76	1277	2.288	0.487	0.513	3.2	5.98×10^{-9}	8.59×10^{-10}
77	1327	2.645	0.469	0.531	1.5	2.42×10^{-9}	2.96×10^{-9}
78	1325	1.239	1.000		6.0	2.07×10^{-8}	1.94×10^{-9}
79	1327	1.732	0.501		9.0	2.22×10^{-8}	1.83×10^{-9}
80	1326	2.169	0.250		12.3	2.42×10^{-8}	1.59×10^{-9}
81	824	3.594	0.517	0.483	n.d.		
82	1076	4.264	0.489	0.511	n.d.		3.81×10^{-12}
83	1176	2.572	0.482	0.518	0.087	1.45×10^{-10}	6.37×10^{-11}
84	1277	2.658	0.459	0.541	1.6	2.57×10^{-9}	8.74×10^{-10}
85	1326	2.126	0.466	0.534	8.0	1.61×10^{-8}	2.91×10^{-9}
86	1326	1.239	1.000		1.8	6.21×10^{-9}	2.00×10^{-9}
87	1326	1.835	0.501		5.4	1.26×10^{-8}	1.78×10^{-9}
88	1325	1.776	0.250		4.6	1.11×10^{-8}	1.54×10^{-9}
89	824	2.526	0.491	0.509	n.d.		
90	1176	2.111	0.470	0.530	0.45	9.11×10^{-10}	6.45×10^{-11}

temperature, 1326 K, we found the Pu volatility values to be in the range of 2×10^{-15} to 4×10^{-13} atm, with no obvious dependence on $\text{H}_2\text{O}(\text{g})$ or $\text{O}_2(\text{g})$ pressures. We are unable to make a positive identification of the amounts of $\text{PuO}_3(\text{g})$ and $\text{PuO}_2(\text{OH})_2(\text{g})$ under these very low volatility conditions because of the dust problem, but we can set maxima of 1×10^{-13} atm each for $\text{PuO}_3(\text{g})$ and $\text{PuO}_2(\text{OH})_2(\text{g})$ at pressures of 0.5 atm each of $\text{H}_2\text{O}(\text{g})$ and $\text{O}_2(\text{g})$ and 1326 K.

We need to evaluate the presence of ^{234}U in the collected samples from the $^{238}\text{PuO}_2$ runs for any additional information it may yield. In the runs at temperatures of 824-1076, little or no ^{234}U was found in the collected samples (see Table 14), indicating little or no change from the original $^{238}\text{PuO}_2$ sample material, and hence indicating dust transport. At higher temperatures, increasing amounts of ^{234}U are found with increasing temperature, indicating U volatility accompanying dust transport. We can do a rough check on the U volatility. Values are obtained for $p(\text{U tot})$ based on the measured ^{234}U amounts (see Table 14). We can also calculate U volatilities based on taking $\text{UO}_{2.67}$ being present as an ideal solution in PuO_2 with an activity of 0.033 corresponding to the ^{234}U content. Using the thermodynamic data generated for $\text{UO}_3(\text{g})$ and $\text{UO}_2(\text{OH})_2(\text{g})$ in this report, we calculate the $p(\text{U tot})$ values shown in Table 14. We find a rough agreement between the measured and calculated, with the measured values generally higher than the calculated values.

Pu volatility results for the PuO_2/ash samples are also illustrated in Fig. 10. The same improved techniques were applied in the PuO_2/ash experiments as described above for the $^{238}\text{PuO}_2$ experiments, except silica glass wool was used in all of the collection tubes, and samples were all ground in a mortar and pestle prior to each heating. The grinding was done to provide a large sample area to assure equilibration. Examination of the data shows Pu volatility values that exceed those over pure $^{238}\text{PuO}_2(\text{s})$. This is not reasonable. Pu volatilities would be reduced if PuO_2 interacted with the ash to give a lowered activity. Here again we must attribute the observed volatilities as resulting from dust transport. Run 73 for $^{238}\text{PuO}_2(\text{s})$ and run 55 for the 1.1% $^{238}\text{PuO}_2/2691/\text{salts}/\text{catalyst}$ mixture that had both been ground were run at ~825 K give Pu volatility values that should be indicative of dust transport. These values do roughly bracket the observed higher temperature volatilities of the PuO_2/ash samples. Interestingly, the higher temperature data do show a trend of Pu volatility with temperature for the $^{238}\text{PuO}_2/\text{ash}$ samples. However, the trend also follows the sequence of the heatings, the runs were made starting with lower temperatures and going to higher temperatures. The increased grinding with subsequent runs could have increased the amount of dust transport. The amounts of volatilized ^{234}U in the $^{238}\text{PuO}_2/\text{ash}$ runs were about an order of magnitude lower than with the $^{238}\text{PuO}_2(\text{s})$ runs (see Table 14), thus indicating an interaction of the U with the ash as was found in our $\text{U}_3\text{O}_8/2691$ ash experiments. The Pu volatility data for the 3% $^{239}\text{PuO}_2/0.06\%^{241}\text{AmO}_2/1633\text{a}$ runs are also consistent with dust transport. From these data on Pu volatilities from PuO_2/ash , it is not possible to obtain any information on PuO_2 activity lowering from ash interactions.

From the maximum values set above for $p(\text{PuO}_3)$ and $p(\text{PuO}_2(\text{OH})_2)$ from $\text{PuO}_2(\text{s})$ at 1326 K with 0.5 atm each of $\text{H}_2\text{O}(\text{g})$ and $\text{O}_2(\text{g})$, we can set up thermodynamic data to extend these maximum pressure values to other temperatures. The two volatility reactions are given by equation (9) above and

$$K_{10} = p(\text{PuO}_2(\text{OH})_2)/a(\text{PuO}_2)p(\text{O}_2)^{1/2}p(\text{H}_2\text{O}).$$

Taking the activity of $\text{PuO}_2(\text{s})$ as 1, we calculate $K_9 = 1.414 \times 10^{-13} \text{ atm}^{1/2}$ and $\Delta G^\circ_{r,1326} = 326.19 \text{ kJ/mol}$. Similarly for reaction (10), we calculate $K_{10} = 2.828 \times 10^{-13} \text{ atm}^{-1/2}$ and $\Delta G^\circ_{r,1326} = 318.55 \text{ kJ/mol}$. Free energy functions for $\text{PuO}_3(\text{g})$ and $\text{PuO}_2(\text{OH})_2(\text{g})$ are obtained by the molecular constant method. We use the same molecular constants as for $\text{UO}_3(\text{g})$ and $\text{UO}_2(\text{OH})_2(\text{g})$ except for taking the mass of Pu as 239, and using ground state multiplicities of 9 for both $\text{PuO}_3(\text{g})$ and $\text{PuO}_2(\text{OH})_2(\text{g})$ resulting from the two unpaired f electrons. These free energy function values are summarized in Table 6. Thermodynamic data for $\text{PuO}_2(\text{s})$ are taken from Cordfunke et al. [22] and for $\text{O}_2(\text{g})$ and H_2O from JANAF [21]. From these data we obtain $-(\Delta G^\circ_{1326} - \Delta H^\circ_{298})/T = 142.29 \text{ J/mol-K}$ for reaction (9) and 53.49 J/mol-K for reaction (10). Combining with the $\Delta G^\circ_{r,1326}$ values above, we obtain $\Delta H^\circ_{r,298} = 514.86 \text{ kJ/mol}$ for reaction (9) and $\Delta H^\circ_{r,298} = 389.48 \text{ kJ/mol}$ for reaction (10). From the $\Delta H^\circ_f,298$ values for $\text{PuO}_2(\text{s})$ given by Cordfunke, et al. [22] and for $\text{H}_2\text{O}(\text{g})$ given in the JANAF tables [21], the minimum $\Delta H^\circ_f,298$ values for $\text{PuO}_3(\text{g})$ and $\text{PuO}_2(\text{OH})_2(\text{g})$ are calculated to be -540.94 kJ/mol and -908.15 kJ/mol , respectively.

The $\Delta H^\circ_{r,298}$ values for reactions (9) and (10) can now be combined with the appropriate free energy functions to calculate maximum $\text{PuO}_3(\text{g})$ and $\text{PuO}_2(\text{OH})_2(\text{g})$ pressures at various temperatures. $-(\Delta G^\circ_T - \Delta H^\circ_{298})/T$ values as a function of temperature are summarized in Table 10 for reactions (9) and (10). Calculated maximum values of $\text{PuO}_3(\text{g})$ and $\text{PuO}_2(\text{OH})_2(\text{g})$ pressures above $\text{PuO}_2(\text{s})$ at 0.1 atm each of $\text{O}_2(\text{g})$ and $\text{H}_2\text{O}(\text{g})$ pressure are shown as a function of temperature in Fig. 7.

Volatilities of $\text{AmO}_3(\text{g})$ and $\text{AmO}_2(\text{OH})_2(\text{g})$ from $\text{PuO}_2/\text{AmO}_2/\text{ash}$:

In analyzing the Am volatility data from $\text{PuO}_2/\text{AmO}_2/\text{ash}$ (see Tables 12 and 13), we find that we have the same dust transport problem because the $3\%^{239}\text{PuO}_2/0.06\%^{241}\text{AmO}_2/1633\text{a}$ material used is the same as used for Pu volatility tests. In run 72 at 1329 K (the highest temperature run), the Am pressure was found to be $1.38 \times 10^{-14} \text{ atm}$. The ratio of Am/Pu in the collected sample for this run is 0.027 compared with 0.021 in the original material, which indicates a 29% enrichment in Am which could be attributed to volatilization. Taking 29% of $1.38 \times 10^{-14} \text{ atm}$ value as the volatilized portion, gives $4.0 \times 10^{-15} \text{ atm}$ for the total Am pressure. As a rough check on this, if we assume that $\text{AmO}_3(\text{g})$ and $\text{AmO}_2(\text{OH})_2(\text{g})$ volatilities above

AmO₂(s) are the same as PuO₃(g) and PuO₂(OH)₂(g) volatilities above PuO₂(s), and that AmO₂(s) forms an ideal solution in the PuO₂(s) without interacting with the ash. Using the maximum values of 1×10^{-13} atm each of PuO₃(g) and PuO₂(OH)₂(g) at 1326 K gives for 0.021 mole fraction AmO₂, $2 \times 10^{-13} \times 0.021 = 4.2 \times 10^{-15}$ atm as a maximum for the total pressure of Am species. The volatilities seem to be in agreement although uncertainties are very high.

For purposes of a best estimate for calculating maximum Am volatilities, we will take maximum AmO₃(g) and AmO₂(OH)₂(g) volatilities above AmO₂(s) to be the same as that of maximum PuO₃(g) and PuO₂(OH)₂(g) volatilities above PuO₂(s). AmO₂(s) will be assumed to form an ideal solution in PuO₂(s) so that the Am volatilities will be reduced in proportion to the AmO₂(s) content in PuO₂(s). The volatility reactions and equilibrium constant expressions are:

$$K_{11} = p(\text{AmO}_3)/a(\text{AmO}_2)p(\text{O}_2)^{1/2},$$

$$K_{12} = p(\text{AmO}_2(\text{OH})_2)/a(\text{AmO}_2)p(\text{O}_2)^{1/2}p(\text{H}_2\text{O}).$$

Taking the activity of AmO₂(s.s.) as 1, we calculate $K_{11} = 1.414 \times 10^{-13} \text{ atm}^{1/2}$ and $\Delta G^\circ_{r,1326} = 326.19 \text{ kJ/mol}$. Similarly for reaction (12), we calculate $K_{12} = 2.828 \times 10^{-13} \text{ atm}^{-1/2}$ and $\Delta G^\circ_{r,1326} = 318.55 \text{ kJ/mol}$. Free energy functions for AmO₃(g) and AmO₂(OH)₂(g) are obtained by the molecular constant method. We use the same molecular constants as for UO₃(g) and UO₂(OH)₂(g) except for taking the mass of Am as 241, and using ground state multiplicities of 11 for both AmO₃(g) and AmO₂(OH)₂(g). These free energy function values are summarized in Table 6. Thermodynamic data for AmO₂(s) are taken from Cordfunke et al. [22] and for O₂(g) and H₂O from JANAF [21]. From these data we obtain $-(\Delta G^\circ_{1326} - \Delta H^\circ_{298})/T = 145.75 \text{ J/mol-K}$ for reaction (11) and 56.94 J/mol-K for reaction (12). Combining with the $\Delta G^\circ_{r,1326}$ values above, we obtain $\Delta H^\circ_{r,298} = 519.45 \text{ kJ/mol}$ for reaction (11) and $\Delta H^\circ_{r,298} = 394.05 \text{ kJ/mol}$ for reaction (12). From the $\Delta H^\circ_{f,298}$ values for AmO₂(s) given by Cordfunke, et al. [22] and for H₂O(g) given in the JANAF tables [21], the minimum $\Delta H^\circ_{f,298}$ values for AmO₃(g) and AmO₂(OH)₂(g) are calculated to be -412.75 kJ/mol and -779.98 kJ/mol , respectively. These minimum $\Delta H^\circ_{f,298}$ values are given in Table 15 along with the minimum $\Delta H^\circ_{f,298}$ values for PuO₃(g) and PuO₂(OH)₂(g) and the $\Delta H^\circ_{f,298}$ values for UO₃(g) and UO₂(OH)₂(g).

Table 15. Enthalpies of formation for $\text{UO}_3(\text{g})$, $\text{PuO}_3(\text{g})$, $\text{AmO}_3(\text{g})$, $\text{UO}_2(\text{OH})_2(\text{g})$, $\text{PuO}_2(\text{OH})_2(\text{g})$, and $\text{AmO}_2(\text{OH})_2(\text{g})$.

species	$\Delta H^\circ_{\text{f},298}$ (kJ/mol)
$\text{UO}_3(\text{g})$	-788.21 ± 7.0
$\text{PuO}_3(\text{g})$	-540.94^*
$\text{AmO}_3(\text{g})$	-412.75^*
$\text{UO}_2(\text{OH})_2(\text{g})$	-1151.61 ± 7.5
$\text{PuO}_2(\text{OH})_2(\text{g})$	-908.15^*
$\text{AmO}_2(\text{OH})_2(\text{g})$	-779.88^*

*Minimum values

The $\Delta H^\circ_{r,298}$ values for reactions (11) and (12) can now be combined with the appropriate free energy functions to calculate maximum $\text{AmO}_3(\text{g})$ and $\text{AmO}_2(\text{OH})_2(\text{g})$ pressures at various temperatures. $-(\Delta G^\circ_T - \Delta H^\circ_{298})/T$ values as a function of temperature are summarized in Table 10 for reactions (11) and (12). Calculated maximum values of $\text{AmO}_3(\text{g})$ and $\text{AmO}_2(\text{OH})_2(\text{g})$ pressures above a 1000 ppm AmO_2 solid solution in $\text{PuO}_2(\text{s})$ at 0.1 atm each of $\text{O}_2(\text{g})$ and $\text{H}_2\text{O}(\text{g})$ pressure are shown as a function of temperature in Fig. 7.

Thermochemical Modeling Study of Interactions of Uranium, Plutonium, and Americium Oxides with Incinerator Ash and Its Constituents

Interactions of Actinides with Oxides:

We have observed that additions of Na_2O and CaO to ash will lower uranium volatility. The decrease in volatility is a result of the interactions of the uranium oxides with the alkali, group I, and alkaline earth, group II, oxide constituents in the ash. The other primary constituents of the ash, SiO_2 , Al_2O_3 , and Fe_2O_3 , seem to interact weakly or not at all with the uranium oxides. No data are available that would suggest how Pu and Am oxides would interact with ash materials. However, there are some data which indicate how U oxides would interact with ash materials.

The known phase equilibria for the systems $\text{SiO}_2\text{-UO}_2$ [23], $\text{UO}_2\text{-Al}_2\text{O}_3$ [24], and $\text{UO}_2\text{-Fe}_3\text{O}_4$ [25] show that no intermediate phases are formed and that little or no solid solubility is observed. Thus, U in the form of $\text{UO}_2(\text{s})$ would not be expected to react with the primary ash constituents. However, U in incinerator environments would normally be expected to oxidize to $\text{U}_3\text{O}_8(\text{s})$ which seems to behave differently than $\text{UO}_2(\text{s})$. Schreiber [26] has shown that the +5 and +6 oxidation states of U are more soluble than the +4 in aluminosilicate melts. Thus, the interaction of $\text{U}_3\text{O}_8(\text{s})$ with aluminosilicates is greater than the interaction of $\text{UO}_2(\text{s})$. Schreiber [26] has found that glasses of the compositions 55.7 wt% SiO_2 , 17 wt% Al_2O_3 , 16.4 wt% CaO , 7.4 wt% MgO , and 3.5 wt% Na_2O and 61.4 wt% SiO_2 , 17.6 wt% Al_2O_3 , 9.5 wt% CaO , 4.5 wt% MgO , and 7.1 wt% Na_2O will dissolve up to 15 wt% U_3O_8 at 1250°C under oxidizing conditions, but under reducing conditions the same glasses can dissolve only 4 to 5 wt% UO_2 . In addition, Schreiber's results indicate that greater U_3O_8 solubility is observed in glasses which contain Na_2O . Under oxidizing conditions an aluminosilicate of the composition 51.6 wt% SiO_2 , 2.3 wt% Al_2O_3 , 19.2 wt% MgO , 26.9 wt% CaO can dissolve only about 8.5 wt% U_3O_8 at 1500°C, which is considerably less than Schreiber's other aluminosilicate melts which had 15 wt% U_3O_8 solubility at 1250°C. The greater the U_3O_8 solubility, the stronger the interaction of uranium with the glass. Hence, the addition of Na_2O seems to increase the strength of the interaction of uranium with the glass which is consistent with what we have observed in our volatility measurements. Schreiber's results [26] also show that for an aluminosilicate melt at 1500°C about 30% of the U is in the +6 state, about 65% is in the +5 state, and about 5% is in the +4 state. Thus, the overall oxidation state of U in the glass is +5.25 which is nearly the same as the oxidation state of +5.33 in $\text{U}_3\text{O}_8(\text{s})$. This is also consistent with the uranium in ash volatility data herein. The

plots in Figs. 8 and 9 seem to show that the volatility of U in ash has the same $O_2(g)$ and $H_2O(g)$ pressure dependence as $U_3O_8(s)$. Thus, the oxidation state of U in the ashes is about the same as U in $U_3O_8(s)$.

The ashes we used in the actinide volatility experiments also contained some TiO_2 , but the amounts were too small to ascertain if larger amounts would help tie up the actinides and, consequently, lower the actinide volatility. Some data exists which suggests that additions of TiO_2 may be helpful. Vance, et al. [27] have shown that uranium containing glasses of the composition 6.6 mol% Na_2O , 5.1 mol% Al_2O_3 , 16.5 mol% CaO , 14.8 mol% TiO_2 , and 57.0 mol% SiO_2 with 0.1 to 2.0 mol% U substituted for Ca will tie up the U in the phase $CaUTi_2O_{7+y}$. Abrajano, et al. [28] found that a U-Ti-O phase formed in a glass of the composition 45.8 wt% SiO_2 , 13.2 wt% Fe_2O_3 , 10.8 wt% B_2O_3 , 9.6 wt% Na_2O , 5.4 wt% Al_2O_3 , 4.1 wt% Li_2O , 4.1 wt% MnO_2 , 1.5 wt% NiO , 1.4 wt% MgO , 1.0 wt% CaO , 1.0 wt% U_3O_8 , 0.7 wt% TiO_2 , and other trace elements totaling 1.0 wt%. Also, various titanates such as used in the SYNROC waste form process are known to incorporate actinides into their structures [29]. Perovskite, $CaTiO_3$, is known to incorporate +3 actinides and zirconolite, $CaZrTi_2O_7$, is known to incorporate +4 actinides. The resulting mixed oxides are known to have very low leachability which suggests that the actinides are held tightly in these materials. However, it is known that uranium oxide in the form of $UO_2(s)$ will not react with $TiO_2(s)$ [30] which indicates a very weak interaction between the two oxides. Similarly, the interaction of $U_3O_8(s)$ with $TiO_2(s)$ is expected to be weak unless group I or II oxides are also present.

Since the group I and II oxides seem to be the only oxides which by themselves interact strongly with the actinide oxides, we have applied thermochemical modeling only to these oxides. In order to calculate stabilities of these mixed oxides and activities of actinide oxides in these mixed oxides, the formation enthalpies, $\Delta H^\circ_{f,298}$, the entropies, S°_{298} , and heat capacities, C_p , are needed. However, limited thermodynamic data are available for mixed actinide oxides, especially the Pu and Am mixed oxides. Therefore, thermodynamic estimates primarily for the $\Delta H^\circ_{f,298}$ values are needed where data are lacking. In this study, existing thermodynamic correlations have been revised in an effort to better estimate $\Delta H^\circ_{f,298}$ values of mixed actinide oxides for which data are lacking. Using estimated $\Delta H^\circ_{f,298}$ values, which agree well with experimental values in most cases, the stability and activity of the actinide oxides in various mixed oxide equilibria are then calculated. The relative effectiveness of the group I and II oxides as additives are then generalized.

Formation Energy of Mixed Oxides - Correlations:

The actinide oxides react with many of the group I and II oxides to form stable mixed oxides. Much of the available data on reactions of this type are summarized by Morss [31]. U, Pu, and Am are expected to oxidize to U_3O_8 , PuO_2 , and AmO_2 in incinerator environments. Respectively, the oxidation states of U, Pu, and Am are +5.33, +4, and +4. In general, the oxidation state of the actinides in the oxide will differ from that in the mixed oxides. For example, Morss [31] has shown that each of these

actinides tend to form mixed oxides in the +6 and +5 state, although, Pu and Am are also known to form mixed oxides in the +4 state. The discussion herein is limited to the +6 actinides in mixed actinide oxides since more experimental data are available on these types of mixed oxides. In addition, incinerator environments are typically oxidizing enough such that +6 actinide mixed oxides are expected to be important.

Tardy and Garrels [32-34] have shown that the Gibbs formation energy from the constituent oxides is proportional to the difference in a parameter which they identify as ΔO^{2-}_M . Thus, for a reaction of the type

the free energy of formation from the constituent oxides is given by

$$\Delta G^\circ_{r,298} = K[\Delta O^{2-}_A - \Delta O^{2-}_B]. \quad (20)$$

The ΔO^{2-}_M parameter is defined as

$$\Delta O^{2-}_M = 1/z [\Delta G^\circ_{f,298}(MO_z(s)) - \Delta G^\circ_{f,298}(M^{2z+}(aq))], \quad (21)$$

where $\Delta G^\circ_{f,298}(MO_z(s))$ is the Gibbs formation energy of the constituent oxide and $\Delta G^\circ_{f,298}(M^{2z+}(aq))$ is the Gibbs formation energy of the aqueous metallic ion. Initially we used Tardy and Garrels' method to estimate Gibbs formation energies of mixed oxides [8]. This correlation was adequate to make rough estimates of the formation energies of the mixed oxides, but a correlation which better fit the experimental data was desired.

Morss and Mensi [35] show that the formation enthalpies of ABO_3 perovskites from the constituent oxides correlate well with the Goldschmidt tolerance factor [36]. Thus, for a reaction of the type

the $\Delta H^\circ_{r,298}$ values fit the equation

$$\Delta H^\circ_{r,298} = K (r_{AO})/[2^{1/2}r_{BO}] + C, \quad (23)$$

where r_{AO} and r_{BO} are the nearest neighbor bond distances in the constituent oxides. Goudiakas, et al. [37] have used this correlation with good success to include additional thermodynamic data on ABO_3 perovskites.

Although the two correlations appear quite different, they are actually quite similar. For Tardy and Garrels' method the free energy of formation is used and for Morss and Mensi's method the enthalpy of formation is used. For reactions from the oxides to form mixed oxides as in eqns (19) and (22), the change in entropy and the change in heat capacity are expected to be small. Thus, to a good approximation

$$\Delta G^{\circ}_{r,T} = \Delta H^{\circ}_{r,T}. \quad (24)$$

In other words, $\Delta H^{\circ}_{r,298}$ and $\Delta G^{\circ}_{r,298}$ are interchangeable in eqns (20) and (23).

Fuger [38] has shown that

$$\Delta H^{\circ}_{f,298}(\text{MO}_z(\text{s})) - \Delta H^{\circ}_{f,298}(\text{MO}^{2z+}(\text{aq})) = C_M/r_{\text{MO}} + C. \quad (25)$$

This correlation is valuable for estimating the $\Delta H^{\circ}_{f,298}$ values for oxides when the $\Delta H^{\circ}_{f,298}$ values for the aqueous ions are known. If the $\Delta H^{\circ}_{f,298}$ terms in eqn (25) are replaced with $\Delta G^{\circ}_{f,298}$ terms, then eqn (25) can be substituted into eqns (20) and (21) to yield

$$\Delta H^{\circ}_{r,298} = C_A/r_{\text{AO}} + C_B/r_{\text{BO}} + C. \quad (26)$$

This correlation is similar to that given by Morss and Mensi [35] in the respect that the $\Delta H^{\circ}_{r,298}$ values are proportional to $1/r_{\text{BO}}$.

For eqn (19) the $\Delta H^{\circ}_{r,298}$ value is also given by

$$\Delta H^{\circ}_{r,298} = a\Delta U_{\text{LE}}(\text{AO}_x) + b\Delta U_{\text{LE}}(\text{BO}_y) - \Delta U_{\text{LE}}(\text{A}_a\text{B}_b\text{O}_{ax+by}), \quad (27)$$

where ΔU_{LE} is the lattice energy of the constituent oxide or mixed oxide. For ionic compounds, the lattice energy represents a reaction of the type

and is given by the Born lattice energy equation

$$\Delta U_{\text{LE}}(\text{MO}_z) = A (1 - 1/n_{\text{MO}})/r_{\text{MO}}. \quad (29)$$

Since oxides are partly ionic in character, it might be expected that the $\Delta H^{\circ}_{r,298}$ values could be fitted to a relationship of the form

$$\Delta H^{\circ}_{r,298} = C_A(1 - 1/n_{\text{AO}})/r_{\text{AO}} + C_B(1 - 1/n_{\text{BO}})/r_{\text{BO}} + C, \quad (30)$$

where n_{AO} and n_{BO} are the Born repulsion terms which appear in the Born lattice energy equation r_{AO} and r_{BO} are the nearest neighbor bond distances in the mixed oxide. Eqn (30) and eqn (26) differ only by the Born repulsion terms.

Upon fitting data on a number of mixed oxide systems using eqns (20), (23), (26), and (30), we found that eqn (30) most accurately fits the experimental data. We therefore select the form of eqn (30) for calculating $\Delta H^{\circ}_{r,298}$ values for group I and II mixed oxides with the +6 actinides.

In addition to relating formation energies to the nearest neighbor bond distances in the constituent oxides, a relationship which relates mixed oxides of different stoichiometries is needed. Many binary oxide systems form several mixed oxides. In the SrO-UO₃ system, for example, at least 5 different mixed oxides are known, Sr₃UO₆, Sr₂UO₅, SrUO₄, Sr₂U₃O₁₁, and SrU₄O₁₃ [40]. Tardy [34] has proposed a method to relate the Gibbs formation energies of mixed oxides of different stoichiometry. For reactions of the type in eqn (19), Tardy proposes that the Gibbs free energies of formation for different stoichiometries are related by

$$\Delta G^{\circ}_{f,298} = K [axby/(ax + by)]. \quad (31)$$

In the denominator, Tardy uses the total number of oxygen atoms in the mixed oxide per formula unit. In order for the relationship to be independent of the way the formula is written, the total number of atoms, which includes the metal atoms, in the mixed oxide formula unit should be used in the denominator. Making this adjustment and using the relationship in eqn (24) we obtain

$$\Delta H^{\circ}_{f,298} = K [axby/[a(1 + x) + b(1 + y)]]. \quad (32)$$

The complete expression for calculating $\Delta H^{\circ}_{f,298}$ = values as based on eqns (30) and (32) is given later in this report.

Formation Enthalpies for NpO₃(s), PuO₃(s), and AmO₃(s):

In order to calculate $\Delta H^{\circ}_{f,298}$ values for the Pu and Am mixed oxides in the +6 valence state, estimates of the $\Delta H^{\circ}_{f,298}$ values for PuO₃(s) and AmO₃(s) are needed. The $\Delta H^{\circ}_{f,298}$ value for NpO₃(s) is also calculated so that available formation data for +6 Np mixed oxides can be included in the mixed oxide formation energy correlation.

Using a modified form of Fuger's correlation [38],

$$\Delta H^{\circ}_{f,298}(\text{MO}_3(\text{s})) - \Delta H^{\circ}_{f,298}(\text{MO}_2^{2+}(\text{aq})) = \frac{A[(1 - 1/n_{\text{MO}})/r_{\text{MO}}] + C, \quad (33)$$

the $\Delta H^{\circ}_{f,298}$ values for NpO₃(s), PuO₃(s) and AmO₃(s) can be estimated. Taking the $\Delta H^{\circ}_{f,298}(\text{MO}_2^{2+}(\text{aq}))$ for WO₂²⁺(aq) and MoO₂²⁺(aq) from Dellien, et al. [41], the $\Delta H^{\circ}_{f,298}(\text{MO}_2^{2+}(\text{aq}))$ for UO₂²⁺(aq) and the $\Delta H^{\circ}_{f,298}(\text{MO}_3(\text{s}))$ value for UO₃(s) from Grenthe, et al. [40], the $\Delta H^{\circ}_{f,298}(\text{MO}_3(\text{s}))$ values for MoO₃(s) and WO₃(s) from the JANAF tables [21], and the r_{MO} and n_{MO} values given in Table 16 gives $A = -1040.86$ nm-kJ/mol and $C = 4613.27$ kJ/mol for eqn (33). Using the $\Delta H^{\circ}_{f,298}(\text{MO}_2^{2+}(\text{aq}))$ values for NpO₂²⁺(aq), PuO₂²⁺(aq), and AmO₂²⁺(aq) from Fuger [38], the $\Delta H^{\circ}_{f,298}(\text{MO}_3(\text{s}))$ values for NpO₃(s), PuO₃(s), and AmO₃(s) are calculated to be -1052.8 kJ/mol, -995.4 kJ/mol, and -809.5 kJ/mol, respectively.

Table 16. Nearest neighbor bond distances, r_{MO} , for coordination number of 6, the Born repulsion term, n_{MO} , and the factor s_{MO} used in eqns (20) and (22).

$$s_{MO} = (1 - 1/n_{MO})/r_{MO}$$

oxide	r_{MO} (nm)	n_{MO}	s_{MO} (nm ⁻¹)
+1:			
Li ₂ O	0.20003	4.75	3.9468
Na ₂ O	0.24023	7	3.5680
K ₂ O	0.27868	8	3.1398
Rb ₂ O	0.29180	8.75	3.0353
Cs ₂ O	0.29155	9.5	3.0689
+2:			
BeO	0.18609	4.75	4.2424
MgO	0.21060	7	4.0700
CaO	0.24054	8	3.6376
SrO	0.25795	8.75	3.4337
BaO	0.27610	9.5	3.2406
+6:			
AmO ₃	0.21024	10	4.2808
PuO ₃	0.21098	10	4.2658
NpO ₃	0.21189	10	4.2475
UO ₃	0.21251	10	4.2351
WO ₃	0.19207	9.5	4.6584
MoO ₃	0.18969	8.75	4.6693
CrO ₃	0.16587	8	5.2752

Additionally, the $\Delta H^\circ_{f,298}$ values for $\text{NpO}_3(\text{s})$ and $\text{PuO}_3(\text{s})$ can be estimated by assuming that

$$\begin{aligned} \Delta H^\circ_{f,298}(\text{MO}_3) - \Delta H^\circ_{f,298}(\text{UO}_3) = \\ \Delta H^\circ_{f,298}(\text{aAO}_x \cdot \text{MO}_3) - \Delta H^\circ_{f,298}(\text{aAO}_x \cdot \text{UO}_3). \end{aligned} \quad (34)$$

Morss, et al. [39] used this relationship to estimate $\Delta H^\circ_{f,298} = -1076 \pm 6$ kJ/mol for $\text{NpO}_3(\text{s})$. The difference in formation energy of a number of +6 mixed actinide oxides are given in Table 17. The average difference between +6 Np mixed oxides and +6 U mixed oxides is 139.6 ± 10.5 kJ/mol and the average difference between +6 Pu mixed oxides and +6 U mixed oxides is 228.9 ± 14.6 kJ/mol. From these differences and from the $\Delta H^\circ_{f,298}$ value for $\text{UO}_3(\text{s})$ from Grenthe, et al. [40], the $\Delta H^\circ_{f,298}$ values for $\text{NpO}_3(\text{s})$ and $\text{PuO}_3(\text{s})$ are calculated to be -1084.2 ± 10.5 kJ/mol and -994.8 ± 14.6 kJ/mol, respectively.

For $\text{NpO}_3(\text{s})$ we take the average of the two estimated values while weighting the second value twice to give a $\Delta H^\circ_{f,298}$ value of -1073.7 ± 22 kJ/mol. For $\text{PuO}_3(\text{s})$ we average the two estimated values to give a $\Delta H^\circ_{f,298}$ value of -995.1 ± 11 kJ/mol. For $\text{AmO}_3(\text{s})$ we have only one estimate, -809.5 ± 25 kJ/mol. These formation enthalpies are given in Table 18 along with $\Delta H^\circ_{f,298}$ values for other relevant oxides [22,40,43,44].

Calculated Formation Enthalpies for Mixed Actinide Oxides:

For a reaction of the type

where A is a group I or group II metal and B is a + 6 cation, the enthalpies of reaction are best fit by an equation which combines the forms given in eqns (30) and (32) to yield

$$\Delta H^\circ_{r,298} = D_{ab}[C_A^s \text{AO} + C_B^s \text{BO} + C_{ab}], \quad (36)$$

where

$$s_{\text{MO}} = (1 - 1/n_{\text{MO}})/r_{\text{MO}}, \quad (37)$$

$$D_{ab} = axby/[a(1 + x) + b(1 + y)], \quad (38)$$

and

$$C_{ab} = A[ax/(ax + by)] + B[by/(ax + by)]. \quad (39)$$

Table 17. Enthalpies of formation of + 6 neptunium and plutonium mixed oxides minus enthalpies of formation of +6 uranium mixed oxides.

compound	M = Np $\Delta H^\circ_{\text{f},298}$ (kJ/mol)	M = Pu $\Delta H^\circ_{\text{f},298}$ (kJ/mol)
$\text{UO}_3 \cdot \text{H}_2\text{O}(\text{s})$	154.4	
$\text{UO}_3(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}(\text{s})$	159.0	
$\text{Cs}_2\text{UO}_4\text{Cl}_2(\text{s})$	148.1	
$\text{Ba}_2\text{MgUO}_6(\text{s})$	149.0	250.6
$\text{Ba}_2\text{CaUO}_6(\text{s})$	136.4	228.0
$\text{Ba}_2\text{SrUO}_6(\text{s})$	134.7	233.5
$\text{Sr}_3\text{UO}_6(\text{s})$	136.4	219.7
$\text{Ba}_3\text{UO}_6(\text{s})$	124.7	213.0
$\text{Li}_2\text{UO}_4(\text{s})$	133.9	
$\text{Na}_2\text{UO}_4(\text{s})$	137.2	
$\text{K}_2\text{UO}_4(\text{s})$	126.8	
$\text{Cs}_2\text{UO}_4(\text{s})$	132.2	
$\text{Na}_4\text{UO}_5(\text{s})$	141.8	
Ave.	139.6 ± 10.5	228.9 ± 14.6

Data on uranium compounds are from ref. [25].

Data on neptunium and plutonium compounds are from ref. [32,33,41].

Table 18. Standard enthalpies of formation of relevant oxides.

oxide	$\Delta H^\circ_{f,298}$ (kJ/mol)
UO ₂ (s)	-1085.0 ± 1.0 ^a
UO _{2.6667} (s)	-1191.6 ± 0.8 ^a
UO ₃ (s)	-1223.8 ± 1.2 ^a
NpO ₂ (s)	-1074.0 ± 2.5 ^b
NpO ₃ (s)	-1073.7 ± 22 ^b
PuO ₂ (s)	-1056.2 ± 0.7 ^b
PuO ₃ (s)	-995.1 ± 11 ^c
AmO ₂ (s)	-932.2 ± 2.7 ^b
AmO ₃ (s)	-809.5 ± 25 ^c
Li ₂ O(s)	-597.9 ± 0.3 ^d
Na ₂ O(s)	-417.1 ± 4.2 ^d
K ₂ O(s)	-362.3 ± 2.5 ^d
Rb ₂ O(s)	-338.9 ± 13.3 ^d
Cs ₂ O(s)	-346.0 ± 0.8 ^d
MgO(s)	-601.2 ± 0.6 ^e
CaO(s)	-635.1 ± 0.9 ^e
SrO(s)	-592.0 ± 3.3 ^e
BaO(s)	-548.1 ± 2.1 ^e

a from ref [25]

b from ref [11]

c estimated in text

d from ref [30]

e from ref [31]

r_{MO} is calculated from the tables given by Ziötkowski [42] assuming a coordination number equal to 6. n_{MO} is the repulsion term in the Born lattice energy equation. D_{ab} is a normalization factor which relates the enthalpies of formation of mixed oxides of different stoichiometries. Although C_{ab} was given as the constant C in eqn (30), we find that a better fit of the data is obtained if it is allowed to vary linearly with the oxide constituent compositions as shown in eqn (39).

Using data from a number of sources [22,40,41,45-51], the enthalpies of formation from the constituent oxides of the mixed oxides with +1 and +6 cations are fit to the equation

$$\Delta H^{\circ}_{r,298} = D_{ab}[575.010s_{AO} - 203.639s_{BO} + C_{ab}], \text{ kJ/mol}, \quad (40)$$

where

$$C_{ab} = -2115.803[ax/(ax + by)] - 1639.523[by/(ax + by)]. \quad (41)$$

From available data in the literature [40,41,52,53], the enthalpies of formation from constituent oxides of the mixed oxides with +2 and +6 cations are fit to the equation

$$\Delta H^{\circ}_{r,298} = D_{ab}[464.439s_{AO} - 160.940s_{BO} + C_{ab}], \text{ kJ/mol}, \quad (42)$$

where

$$C_{ab} = -1029.067[ax/(ax + by)] - 1348.827[by/(ax + by)]. \quad (43)$$

Comparisons between the experimental and calculated formation energies using eqns (40) and (41) are given in Table 19 for mixed oxides with +1 and +6 cations and using eqns (42) and (43) are given in Table 20 for mixed oxides with +2 and +6 cations. The values of r_{MO} and n_{MO} used are given in Table 16.

Using eqns (40) to (43) and then using the $\Delta H^{\circ}_{f,298}$ values for the constituent oxides given in Table 18, the $\Delta H^{\circ}_{f,298}$ values for a number of mixed actinide oxides are calculated and given in Tables 21 and 22.

Activities of Actinide Oxides in Mixed Oxides:

We now proceed to calculate the activities of actinide oxides for group I with +6 actinide mixed oxides and group II with +6 actinide mixed oxides. Results are given for a temperature of 1300K (see Tables 24 and 25). Computational details follow.

In order to evaluate the effectiveness of additives, the activities of the U, Pu, and Am oxides are calculated as a function of group I or II oxide content. For consistency and comparison purposes, we calculate the activities of the oxides per mole of actinide metal constituent. Thus, $U_3O_8(s)$ is treated as $UO_{2.67}(s)$. Using the data given in Tables 18, 21, and 22 and also by knowing the free energy of reaction as a function of temperature for each of the reactions

Table 19. Comparison of experimental enthalpies of formation of mixed oxides with +1 and +6 cations from the constituent oxides versus calculated enthalpies of formation using eqns (40) and (41) in the text.

compound	D _{ab}	experimental $\Delta H^\circ_{f,298}$ (kJ/mol)	calculated $\Delta H^\circ_{f,298}$ (kJ/mol)
Li ₂ NpO ₄	3/7	-153.7	-151.9
Na ₂ NpO ₄	3/7	-270.5	-245.2
K ₂ NpO ₄	3/7	-346.0	-350.6
Cs ₂ NpO ₄	3/7	-366.9	-368.2
Na ₄ NpO ₅	6/10	-405.0	-386.2
Na ₂ Np ₂ O ₇	6/11	-323.9	-284.1
K ₂ Np ₂ O ₇	6/11	-417.7	-418.4
Rb ₂ Np ₂ O ₇	6/11	-422.6	-451.0
Li ₂ UO ₄	3/7	-146.5	-150.6
Na ₂ UO ₄	3/7	-256.8	-243.9
K ₂ UO ₄	3/7	-334.6	-349.4
Rb ₂ UO ₄	3/7	-360.0	-375.3
Cs ₂ UO ₄	3/7	-358.2	-366.9
Li ₄ UO ₅	6/10	-219.8	-254.0
Na ₄ UO ₅	6/10	-398.5	-384.5
Li ₂ U ₂ O ₇	6/11	-168.1	-164.0
Na ₂ U ₂ O ₇	6/11	-339.1	-282.8
K ₂ U ₂ O ₇	6/11	-440.6	-417.1
Rb ₂ U ₂ O ₇	6/11	-445.5	-449.8
Cs ₂ U ₂ O ₇	6/11	-426.4	-439.3
Li ₂ U ₃ O ₁₀	9/15	-168.1	-168.2
Na ₆ U ₇ O ₂₄	63/37	-1533.0	-868.2
Li ₂ WO ₄	3/7	-162.5	-187.4
Na ₂ WO ₄	3/7	-286.4	-281.2
K ₂ WO ₄	3/7	-375.9	-386.6
Na ₂ W ₂ O ₇	6/11	-297.9	-329.7
Li ₂ MoO ₄	3/7	-176.1	-188.7
Na ₂ MoO ₄	3/7	-307.4	-282.0
K ₂ MoO ₄	3/7	-389.6	-387.4

Table 19. (cont'd) Comparison of experimental enthalpies of formation of mixed oxides with +1 and +6 cations from the constituent oxides versus calculated enthalpies of formation using eqns (40) and (41) in the text.

compound	D _{ab}	experimental $\Delta H^\circ_{f,298}$ (kJ/mol)	calculated $\Delta H^\circ_{f,298}$ (kJ/mol)
Rb ₂ MoO ₄	3/7	-402.3	-413.4
Cs ₂ MoO ₄	3/7	-423.0	-405.0
Na ₂ Mo ₂ O ₇	6/11	-337.8	-333.0
Cs ₂ Mo ₂ O ₇	6/11	-466.5	-487.4
Li ₂ CrO ₄	3/7	-206.3	-241.4
Na ₂ CrO ₄	3/7	-335.6	-334.7
K ₂ CrO ₄	3/7	-451.4	-440.2
Rb ₂ CrO ₄	3/7	-482.3	-466.1
Cs ₂ CrO ₄	3/7	-494.5	-457.7
Na ₂ Cr ₂ O ₇	6/11	-385.8	-398.3
K ₂ Cr ₂ O ₇	6/11	-522.6	-532.6
Rb ₂ Cr ₂ O ₇	6/11	-540.6	-565.3
Cs ₂ Cr ₂ O ₇	6/11	-566.1	-554.8

Table 20. Comparison of experimental enthalpies of formation of mixed oxides with +2 and +6 cations from the constituent oxides versus calculated enthalpies of formation using eqns (42) and (43) in the text.

compound	D _{ab}	experimental $\Delta H^\circ_{f,298}$ (kJ/mol)	calculated $\Delta H^\circ_{f,298}$ (kJ/mol)
Sr ₃ PuO ₆	9/10	-274.0	-252.7
Ba ₃ PuO ₆	9/10	-357.0	-333.5
Sr ₃ NpO ₆	9/10	-278.1	-250.2
Ba ₃ NpO ₆	9/10	-366.0	-330.5
BeUO ₄	3/6	>0.0	10.0
MgUO ₄	3/6	-31.9	-30.1
CaUO ₄	3/6	-143.6	-130.5
SrUO ₄	3/6	-175.5	-177.8
BaUO ₄	3/6	-222.1	-223.8
Sr ₂ UO ₅	6/8	-231.1	-231.0
Ca ₃ UO ₆	9/10	-176.9	-163.2
Sr ₃ UO ₆	9/10	-268.6	-248.1
Ba ₃ UO ₆	9/10	-342.8	-328.9
BaU ₂ O ₇	6/10	-241.7	-287.9
Sr ₂ U ₃ O ₁₁	18/16	-390.8	-424.7
SrU ₄ O ₁₃	12/18	-434.5	-274.1
BeWO ₄	3/6	-61.1	-24.3
MgWO ₄	3/6	-73.0	-64.0
CaWO ₄	3/6	-163.2	-164.4
SrWO ₄	3/6	-208.8	-212.1
BaWO ₄	3/6	-312.1	-256.9
Sr ₂ WO ₅	6/8	-276.1	-282.0
Ca ₃ WO ₆	9/10	-182.9	-224.3
Sr ₃ WO ₆	9/10	-309.2	-309.6
BeMoO ₄	3/6	-26.3	-25.1
MgMoO ₄	3/6	-54.2	-64.9
CaMoO ₄	3/6	-166.0	-165.3
SrMoO ₄	3/6	-208.4	-213.0
BaMoO ₄	3/6	-253.7	-257.7
MgCrO ₄	3/6	-152.3	-113.8
CaCrO ₄	3/6	-170.5	-214.2
SrCrO ₄	3/6	-249.4	-261.5
BaCrO ₄	3/6	-307.3	-306.3

Table 21. Calculated enthalpies of formation from the elements for various mixed actinide oxides with +1 and +6 cations using eqns (40) and (41) in the text.

	M = U $\Delta H^\circ_{f,298}$ (kJ/mol)	M = Pu $\Delta H^\circ_{f,298}$ (kJ/mol)	M = Am $\Delta H^\circ_{f,298}$ (kJ/mol)
$\text{Li}_2\text{M}_2\text{O}_7(\text{s})$	-3209.4	-2755.4	-2385.9
$\text{Li}_2\text{MO}_4(\text{s})$	-1972.4	-1728.4	-1562.1
$\text{Li}_4\text{MO}_5(\text{s})$	-2673.4	-2448.5	-2264.7
$\text{Li}_6\text{MO}_6(\text{s})$	-3343.3	-3119.0	-2935.5
$\text{Na}_2\text{M}_2\text{O}_7(\text{s})$	-3147.4	-2693.5	-2323.9
$\text{Na}_2\text{MO}_4(\text{s})$	-1884.9	-1658.9	-1474.6
$\text{Na}_4\text{MO}_5(\text{s})$	-2442.5	-2217.6	-2033.8
$\text{Na}_6\text{MO}_6(\text{s})$	-2951.7	-2727.4	-2543.9
$\text{K}_2\text{M}_2\text{O}_7(\text{s})$	-3226.9	-2773.0	-2403.4
$\text{K}_2\text{MO}_4(\text{s})$	-1935.6	-1709.6	-1525.3
$\text{K}_4\text{MO}_5(\text{s})$	-2480.6	-2255.7	-2071.9
$\text{K}_6\text{MO}_6(\text{s})$	-2957.8	-2733.4	-2549.9
$\text{Rb}_2\text{M}_2\text{O}_7(\text{s})$	-3236.3	-2782.3	-2412.8
$\text{Rb}_2\text{MO}_4(\text{s})$	-1938.0	-1712.0	-1527.7
$\text{Rb}_4\text{MO}_5(\text{s})$	-2469.9	-2244.9	-2061.2
$\text{Rb}_6\text{MO}_6(\text{s})$	-2929.2	-2704.8	-2521.3
$\text{Cs}_2\text{M}_2\text{O}_7(\text{s})$	-3232.9	-2778.9	-2409.4
$\text{Cs}_2\text{MO}_4(\text{s})$	-1936.8	-1710.8	-1526.5
$\text{Cs}_4\text{MO}_5(\text{s})$	-2472.5	-2247.5	-2063.8
$\text{Cs}_6\text{MO}_6(\text{s})$	-2937.1	-2712.7	-2529.3

Table 22. Calculated enthalpies of formation from the elements for various mixed actinide oxides with +2 and +6 cations using eqns (42) and (43) in the text.

	M = U $\Delta H^\circ_{f,298}$ (kJ/mol)	M = Pu $\Delta H^\circ_{f,298}$ (kJ/mol)	M = Am $\Delta H^\circ_{f,298}$ (kJ/mol)
MgM ₂ O ₇ (s)	-3105.5	-2651.1	-2281.3
MgMO ₄ (s)	-1855.1	-1628.9	-1444.5
Mg ₂ MO ₅ (s)	-2435.4	-2210.4	-2026.6
Mg ₃ MO ₆ (s)	-3009.7	-2785.4	-2602.0
CaM ₂ O ₇ (s)	-3259.9	-2805.4	-2315.2
CaMO ₄ (s)	-1989.4	-1763.2	-1578.8
Ca ₂ MO ₅ (s)	-2653.8	-2428.8	-2245.0
Ca ₃ MO ₆ (s)	-3292.1	-3067.8	-2884.4
SrM ₂ O ₇ (s)	-3273.6	-2819.2	-2449.4
SrMO ₄ (s)	-1993.7	-1767.4	-1583.0
Sr ₂ MO ₅ (s)	-2638.6	-2413.6	-2229.9
Sr ₃ MO ₆ (s)	-3248.0	-3023.8	-2840.3
BaM ₂ O ₇ (s)	-3283.5	-2829.1	-2459.3
BaMO ₄ (s)	-1994.6	-1763.4	-1584.0
Ba ₂ MO ₅ (s)	-2618.1	-2393.1	-2209.3
Ba ₃ MO ₆ (s)	-3197.0	-2972.8	-2789.4

and

the activities of $\text{UO}_{2.67}(\text{s})$, $\text{PuO}_2(\text{s})$, and $\text{AmO}_2(\text{s})$ as a function of temperature can be calculated. The free energy functions for $\text{U}_3\text{O}_8(\text{s})$, $\text{UO}_3(\text{s})$, $\text{PuO}_2(\text{s})$, $\text{AmO}_2(\text{s})$, and $\text{O}_2(\text{g})$ are taken from Cordfunke, et al. [22]. The free energy functions for $\text{PuO}_3(\text{s})$ and $\text{AmO}_3(\text{s})$ are assumed to be the same as the free energy function for $\text{UO}_3(\text{s})$. The calculated free energy changes for eqns (44) to (46) as a function of temperature are given in Table 23.

Many of the compounds listed in Tables 21 and 22 are unstable. The stability of mixed oxides in each binary system can be ascertained from the Gibbs formation energy of each mixed oxide. In the Na_2O - PuO_2 system, for example, the free energy of the reactions

at 1300 K are calculated to be 33.6 kJ/mol, -86.8 kJ/mol, -228.4 kJ/mol, and -321.1 kJ/mol, respectively. Since the $\Delta G^\circ_{f,1300}$ value for eqn (47) is positive, $\text{Na}_2\text{Pu}_2\text{O}_7(\text{s})$ is unstable. If the common tangent rule is applied, then $\text{Na}_2\text{PuO}_4(\text{s})$ is also predicted to be unstable. In other words, the estimated thermodynamics predict that $\text{Na}_2\text{PuO}_4(\text{s})$ will dissociate to $\text{Na}_4\text{PuO}_5(\text{s})$ and $\text{PuO}_2(\text{s})$. Mixed oxides that are not expected to form at 1300 K are designated as unstable in Tables 24 and 25.

As an example of how the activity of the actinides can be calculated consider the equilibria between $\text{Li}_2\text{UO}_4(\text{s})$ and $\text{Li}_4\text{UO}_5(\text{s})$.

If the free energy of reaction is known, then the equilibrium constant can be calculated by

$$\Delta G^\circ_{f,T} = -RT \ln K_{\text{eq}}, \quad (52)$$

Table 23. Free energy of reaction of actinide oxides to form trioxide as a function of temperature.

	$\frac{1}{3} \text{U}_3\text{O}_8(\text{s}) \frac{1}{6} \text{O}_2(\text{g}) = \text{UO}_3(\text{s})$ (A) $\text{PuO}_2(\text{s}) + \frac{1}{2} \text{O}_2(\text{g}) = \text{Pu}_2\text{O}_3(\text{s})$ (B) $\text{AmO}_2(\text{s}) + \frac{1}{2} \text{O}_2(\text{g}) = \text{AmO}_3(\text{s})$ (C)		
T (K)	eqn (A) $\Delta G^\circ_{r,T}$ (kJ/mol)	eqn (B) $\Delta G^\circ_{r,T}$ (kJ/mol)	eqn (C) $\Delta G^\circ_{r,T}$ (kJ/mol)
600	-12.35	104.95	166.67
700	-8.77	112.53	174.03
800	-5.10	120.21	181.41
900	-1.38	128.00	188.81
1000	2.73	135.87	196.22
1100	6.22	143.82	203.62
1200	10.08	151.84	211.02
1300	13.98	159.92	218.41
1400	17.89	168.06	225.77
1500	21.83	176.25	233.11
1600	25.78	184.48	240.42

Table 24. Activities of actinide oxides are given at 1300 K with $p(\text{O}_2) = 0.10$ atm for two phase regions for alkali-actinide mixed oxides. The two phase region consists of the designated phase and the one next lower in actinide content. Unstable phases are indicated.

	M = U a($\text{UO}_{2.67}$)	M = Pu a(PuO_2)	M = Am a(AmO_2)
$\text{Li}_2\text{M}_2\text{O}_7(\text{s})$	unstable	unstable	unstable
$\text{Li}_2\text{MO}_4(\text{s})$	6.54×10^{-2}	unstable	unstable
$\text{Li}_4\text{MO}_5(\text{s})$	2.07×10^{-4}	unstable	unstable
$\text{Li}_6\text{MO}_6(\text{s})$	4.34×10^{-13}	4.55×10^{-7}	8.39×10^{-5}
$\text{Na}_2\text{M}_2\text{O}_7(\text{s})$	1.49×10^{-1}	unstable	unstable
$\text{Na}_2\text{MO}_4(\text{s})$	3.71×10^{-4}	unstable	unstable
$\text{Na}_4\text{MO}_5(\text{s})$	4.79×10^{-8}	5.93×10^{-2}	unstable
$\text{Na}_6\text{MO}_6(\text{s})$	3.79×10^{-19}	3.97×10^{-13}	7.33×10^{-11}
$\text{K}_2\text{M}_2\text{O}_7(\text{s})$	1.04×10^{-2}	unstable	unstable
$\text{K}_2\text{MO}_4(\text{s})$	1.06×10^{-6}	unstable	unstable
$\text{K}_4\text{MO}_5(\text{s})$	3.78×10^{-12}	4.60×10^{-6}	9.22×10^{-4}
$\text{K}_6\text{MO}_6(\text{s})$	5.35×10^{-26}	5.66×10^{-20}	1.04×10^{-17}
$\text{Rb}_2\text{M}_2\text{O}_7(\text{s})$	5.43×10^{-3}	unstable	unstable
$\text{Rb}_2\text{MO}_4(\text{s})$	2.53×10^{-7}	3.41×10^{-1}	unstable
$\text{Rb}_4\text{MO}_5(\text{s})$	3.71×10^{-13}	4.64×10^{-7}	9.04×10^{-5}
$\text{Rb}_6\text{MO}_6(\text{s})$	1.14×10^{-27}	1.20×10^{-21}	2.22×10^{-19}
$\text{Cs}_2\text{M}_2\text{O}_7(\text{s})$	6.66×10^{-3}	unstable	unstable
$\text{Cs}_2\text{MO}_4(\text{s})$	4.02×10^{-7}	5.41×10^{-1}	unstable
$\text{Cs}_4\text{MO}_5(\text{s})$	7.78×10^{-13}	9.72×10^{-7}	1.93×10^{-4}
$\text{Cs}_6\text{MO}_6(\text{s})$	3.94×10^{-27}	4.16×10^{-21}	7.61×10^{-19}

Table 25. Activities of actinide oxides are given at 1300 K with $p(\text{O}_2) = 0.10$ atm for two phase regions for alkaline earth-actinide mixed oxides. The two phase region consists of the designated phase and the one next lower in actinide content. Unstable phases are indicated.

	M = U $a(\text{UO}_{2.67})$	M = Pu $a(\text{PuO}_2)$	M = Am $a(\text{AmO}_2)$
MgM ₂ O ₇ (s)	4.56×10^{-1}	unstable	unstable
MgMO ₄ (s)	3.33×10^{-1}	unstable	unstable
Mg ₂ MO ₅ (s)	unstable	unstable	unstable
Mg ₃ MO ₆ (s)	unstable	unstable	unstable
CaM ₂ O ₇ (s)	7.11×10^{-2}	unstable	unstable
CaMO ₄ (s)	4.59×10^{-4}	unstable	unstable
Ca ₂ MO ₅ (s)	3.67×10^{-6}	unstable	unstable
Ca ₃ MO ₆ (s)	1.51×10^{-6}	unstable	unstable
SrM ₂ O ₇ (s)	2.98×10^{-2}	unstable	unstable
SrMO ₄ (s)	5.08×10^{-5}	unstable	unstable
Sr ₂ MO ₅ (s)	7.13×10^{-8}	9.25×10^{-2}	unstable
Sr ₃ MO ₆ (s)	5.70×10^{-10}	5.92×10^{-4}	1.09×10^{-1}
BaM ₂ O ₇ (s)	1.30×10^{-2}	unstable	unstable
BaMO ₄ (s)	6.45×10^{-6}	unstable	unstable
Ba ₂ MO ₅ (s)	1.68×10^{-9}	2.18×10^{-3}	4.45×10^{-1}
Ba ₃ MO ₆ (s)	3.26×10^{-13}	3.39×10^{-7}	6.18×10^{-5}

where

$$K_{eq} = a(\text{UO}_{2.67})p(\text{O}_2)^{1/6}. \quad (53)$$

For the reaction

the $\Delta H^\circ_{f,298}$ value can be calculated from the data in Tables 18 and 21. Since the change in heat capacity and entropy are expected to be small for this reaction, the assumption in eqn (24) can be used. Therefore, the $\Delta G^\circ_{r,T}$ value for eqn (54) at every temperature is roughly equivalent to the $\Delta H^\circ_{f,298}$ value. If eqn (44) is subtracted from eqn (54), then eqn (51) is obtained. Using the data in Tables 18, 21, and 23, the $\Delta G^\circ_{f,1300}$ for eqn (51) is then calculated to be 33.6 kJ/mol and K_{eq} is calculated to be 4.46×10^{-2} . Assuming $p(\text{O}_2) = 0.10$ atm and a temperature of 1300 K, the activity of $\text{UO}_{2.67}(\text{s})$ is calculated from eqn (53) to be 6.54×10^{-2} . Using the same procedure, the activities for a number of other two phase mixed oxide equilibria are given in Tables 24 and 25.

The activities calculated in Tables 24 and 25 are all based on the calculated enthalpies of formation given in Tables 21 and 22. The activities calculated using enthalpy of formation data in the literature for mixed oxides where available seem to agree well with the activities calculated using the estimated $\Delta H^\circ_{f,298}$ values given in Tables 21 and 22. For example, Grenthe, et al. [40] give $\Delta H^\circ_{f,298}$ values of -1989.6 ± 2.8 kJ/mol, -2635.6 ± 3.4 kJ/mol, and -3263.4 ± 3.0 kJ/mol for $\text{SrUO}_4(\text{s})$, $\text{Sr}_2\text{UO}_5(\text{s})$, and $\text{Sr}_3\text{UO}_6(\text{s})$, respectively. Using these values and the data in Table 23, the activity of $\text{UO}_{2.67}(\text{s})$ at 1300 K in each of the two phase equilibria SrUO_4 - Sr_2UO_5 , Sr_2UO_5 - Sr_3UO_6 , and Sr_3UO_6 - SrO is calculated to be 8.22×10^{-5} , 2.83×10^{-6} , and 1.37×10^{-10} , respectively. This agrees roughly with the $\text{UO}_{2.67}(\text{s})$ activities of 5.08×10^{-5} , 7.13×10^{-8} , and 5.70×10^{-10} given in Table 25.

Keller, et al. [54] have studied the stability of actinide mixed oxides which contain Li_2O and Na_2O . In general, their results on the stability of the mixed oxides agree with Table 24. Their results show that in the U_3O_8 - Na_2O system, the phases $\text{Na}_2\text{U}_2\text{O}_7(\text{s})$, $\text{Na}_2\text{UO}_4(\text{s})$, $\text{Na}_4\text{UO}_5(\text{s})$, $\text{Na}_6\text{UO}_6(\text{s})$ all form and in the U_3O_8 - Li_2O system, the phases $\text{Li}_2\text{U}_2\text{O}_7(\text{s})$, $\text{Li}_2\text{UO}_4(\text{s})$, $\text{Li}_4\text{UO}_5(\text{s})$, and $\text{Li}_6\text{UO}_6(\text{s})$ all form. In the PuO_2 - Na_2O system, only the phases $\text{Na}_4\text{PuO}_5(\text{s})$ and $\text{Na}_6\text{PuO}_6(\text{s})$ form and in the PuO_2 - Li_2O system, only the phases $\text{Li}_4\text{PuO}_5(\text{s})$ and $\text{Li}_6\text{PuO}_6(\text{s})$ form. In the AmO_2 - Na_2O system, only the phases $\text{Na}_4\text{AmO}_5(\text{s})$ and $\text{Na}_6\text{AmO}_6(\text{s})$ form and in the AmO_2 - Li_2O system only the phases $\text{Na}_4\text{AmO}_5(\text{s})$ and $\text{Na}_6\text{AmO}_6(\text{s})$ form. Although $\text{Na}_4\text{PuO}_5(\text{s})$, $\text{Li}_4\text{PuO}_5(\text{s})$, $\text{Na}_4\text{AmO}_5(\text{s})$, and $\text{Li}_4\text{AmO}_5(\text{s})$ are not listed as stable phases at 1300 K in Table 24, the data in Tables 18, 21, and 23 indicate that they are

stable at lower temperatures. Thus, the stabilities of mixed oxides in the Pu and Am mixed oxides systems calculated from the data herein are consistent with the observations of Keller, et al.

Because the free energy changes in Table 23 increase with temperature, the stability of the +6 mixed actinide oxides are calculated to decrease with temperature. This suggests that at lower temperatures the activities of $\text{UO}_{2.67}(\text{s})$, $\text{PuO}_2(\text{s})$, and $\text{AmO}_2(\text{s})$ in the two phase regions of the mixed oxides are lower. The free energy changes in Table 23 indicate that the drop in actinide oxide activity at lower temperatures will be largest for the Am mixed oxides and smallest for the U mixed oxides. This implies that mixed actinide oxides, primarily Pu and Am mixed oxides, with smaller fractions of the group I and II oxides will decompose to higher compositions of group I or II oxide plus free actinide oxide with temperature. This is similar to some observations by Keller, et al. [54]. At about 573 K, they observed that $\text{Na}_4\text{AmO}_5(\text{s})$ will decompose to $\text{Na}_6\text{AmO}_6(\text{s})$ plus $\text{AmO}_2(\text{s})$. In contrast, however, they observe a reverse trend at higher temperatures. For example, Keller et al. find that at 923 K, $\text{Na}_6\text{NpO}_6(\text{s})$ will decompose to $\text{Na}_4\text{NpO}_5(\text{s})$. Then at 1073 K, $\text{Na}_4\text{NpO}_5(\text{s})$ will decompose to $\text{Na}_2\text{NpO}_4(\text{s})$, and then at 1273 K, $\text{Na}_2\text{NpO}_4(\text{s})$ will decompose to $\text{NpO}_2(\text{s})$. In addition, Keller, et al. [54,55] find that +5 Np, Pu, and Am in mixed oxides are stabilized at higher temperatures. Thus, +5 and maybe +4 oxidation states of Pu and Am are probably important in mixed oxides under some incinerator environments.

Application and Discussion

General Treatment of Actinides Interacted with Ash:

This discussion will be concerned primarily with the $\text{U}_3\text{O}_8(\text{s})$ interactions with ash since definitive experimental results were not obtained on $\text{PuO}_2(\text{s})$ and $\text{AmO}_2(\text{s})$ interactions with ash.

The U_3O_8 /ash volatility data can be generalized as a function of temperature by using the partial enthalpy of solution values for $\text{UO}_{2.67}$ in ash, as given by $\text{RTln } \gamma(\text{UO}_{2.67})$. The activity of $\text{UO}_{2.67}(\text{s})$ is given by the relationship

$$\text{RTln } a(\text{UO}_{2.67}) = \text{RTln } x(\text{UO}_{2.67}) + \text{RTln } \gamma(\text{UO}_{2.67}), \quad (55)$$

where $x(\text{UO}_{2.67})$ is the mole fraction of $\text{UO}_{2.67}$ in the ash. The mole fractions are calculated based on oxide formulas which are normalized to one metal atom.

The U volatilities as a function of temperature for the 0.5 wt % U_3O_8 in the various ashes (except for Ash 1) are calculated using activities for $\text{UO}_{2.67}$ based on the $\text{RTln } \gamma(\text{UO}_{2.67})$ values. For these calculations, $\text{U}_3\text{O}_8(\text{s})$ is designated as $\text{UO}_{2.67}(\text{s})$, and the pressures of $\text{O}_2(\text{g})$ and $\text{H}_2\text{O}(\text{g})$ are each assumed to be 0.10 atm. The volatility reactions and the associated equilibrium constants are:

$$K_{57} = p(\text{UO}_3)/a(\text{UO}_{2.67})p(\text{O}_2)^{1/6}.$$

$$K_{58} = p(\text{UO}_2(\text{OH})_2)/a(\text{UO}_{2.67})p(\text{O}_2)^{1/6}p(\text{H}_2\text{O}).$$

The selected thermodynamic data for $\text{UO}_3(\text{g})$ and $\text{UO}_2(\text{OH})_2(\text{g})$ are used to carry out these calculations. The volatilities above $\text{U}_3\text{O}_8(\text{s})$ are carried out as well. These results are presented in Fig. 11 as a plot of $\log p(\text{U total})$ versus temperature. These calculations indicate that the activity lowering of U_3O_8 is more effective at higher temperatures. For 0.5% $\text{UO}_{2.67}/1633\text{a}$ and 0.5% $\text{UO}_{2.67}/2690$ ashes, the data indicate that the uranium volatility below 1250 K is the same as that above $\text{U}_3\text{O}_8(\text{s})$, and similarly for 0.5% $\text{UO}_{2.67}/\text{Ash 2}$, the volatility becomes the same as for $\text{U}_3\text{O}_8(\text{s})$ below 1000 K. The 0.5% $\text{UO}_{2.67}/2691$ ash is the most effective at activity lowering with a factor of 50 decrease at 1600 K dropping to a factor of 3 at 850 K.

Also shown in Fig. 11 are the calculated U pressures above the two phase mixtures $\text{CaU}_2\text{O}_7\text{-CaUO}_4$ and $\text{CaUO}_4\text{-Ca}_2\text{UO}_5$. The pressures of $\text{O}_2(\text{g})$ and $\text{H}_2\text{O}(\text{g})$ are each assumed to be 0.10 atm. These calculations were carried out using the data in Tables 18, 22, and 23. For the $\text{CaU}_2\text{O}_7\text{-CaUO}_4$ equilibria the U activity lowering is given by following reaction and its associated equilibrium constant.

$$K_{59} = a(\text{UO}_{2.67})p(\text{O}_2)^{1/6}.$$

The free energy change is given by the sum of free energy changes for the reactions

The free energy change for eqn (60) is given in Table 23, and the free energy change for eqn (61) is equal to the $\Delta H^\circ_{r,298}$ value given in Tables 18 and 22. The activity of $\text{UO}_{2.67}$ can then be calculated as a function of temperature. By combining eqn (60) with eqn (61) the U volatility above the two phase mixture of $\text{CaU}_2\text{O}_7\text{-CaUO}_4$ is calculated. In a similar manner, the U activity lowering for the two phase mixture of $\text{CaUO}_4\text{-Ca}_2\text{UO}_5$ is given by the following reaction and its associated equilibrium constants.

$$K_{62} = a(\text{UO}_{2.67})p(\text{O}_2)^{1/6}.$$

Figure 11. Plot of $\log p(\text{U total})$ versus T above $\text{U}_3\text{O}_8(\text{s})$, $\text{U}_3\text{O}_8/\text{ash}$, and CaO-UO_3 mixed oxides where $p(\text{O}_2) = 0.1 \text{ atm}$, $p(\text{H}_2\text{O}) = 0.1 \text{ atm}$.

The free energy for this reaction is obtained by combining the free energy of eqn (60) obtained from Table 23 and the free energy of the reaction

obtained from the $\Delta H^\circ_{f,298}$ values in Tables 18 and 22. As shown in Fig. 11, the $\text{UO}_{2.67}(\text{s})$ activity lowering is calculated to be greater at lower temperatures for two phase regions of the mixed oxides.

For the U_3O_8 /ash interactions, the activity lowering is calculated to be greater at higher temperatures and smaller at lower temperatures. Our treatment of the data assumes that the U_3O_8 dissolves homogeneously throughout the ash sample. A large fraction of the ash is glass, and if the actinide oxide dissolves in the glass as some of our TEM work on the U_3O_8 /ash samples shows, then this assumption is reasonable. However, the TEM work on the U_3O_8 /ash experiments also shows that the U may be associated with other crystalline phases in the ash. If the actinide oxide is associated with minor phases in the ash, then the entropy of solution will be less positive than if it dissolves homogeneously through out the sample. The net result will be an increase of the extrapolated activity at higher temperatures and a decrease at lower temperatures. In other words, the calculated actinide volatility extrapolated to lower temperatures using our treatment of the data will be greater than the real volatility.

General Effectiveness of Additives:

From the data in Tables 24 and 25, it is clear that the group I oxides interact stronger with the actinides than the group II actinides. It is also clear that the group I and II oxides interact stronger with $\text{UO}_{2.67}$ than with PuO_2 and stronger with PuO_2 than with AmO_2 . In addition, the interactions of the actinide oxides with the group I and II oxides increase going down a row in the periodic table. For example, the interaction of K_2O with the actinide oxides is stronger than the interaction of Na_2O . These conclusions seem to be consistent to what we have observed experimentally. The interaction of Na_2O with $\text{UO}_{2.67}(\text{s})$ in the ash is stronger than the interaction of CaO with $\text{UO}_{2.67}(\text{s})$. This is demonstrated by the $\text{UO}_{2.67}(\text{s})$ activities at 1323 K of 1.89×10^{-1} in 0.5% $\text{UO}_{2.67}$ /Ash1 which has 6.4% Na_2O and of 6.28×10^{-1} in 0.5% $\text{UO}_{2.67}$ /2690 which has 8.0% CaO .

Although we know that additives of group I and II oxides will lower the activities of the actinide oxides, very little can be said quantitatively about the amount of volatility reduction that will occur when large amounts of ash are present. For binary oxide systems with a group I or group II oxide and an actinide oxide, the stability can be predicted and activities for two phase equilibria can be calculated. However, incinerator ash will contain large amounts of SiO_2 and Al_2O_3 . In some cases, other oxides like TiO_2 and Fe_2O_3 may also be present in substantial amounts. Each of these oxides also reacts strongly with group I and II oxides. Thus, small additions of group I or II oxides to an incinerator ash may interact with the other oxide constituents thus lowering group I and II oxide activities and reducing the reactivity with the actinide oxides. Hence, this interaction depends on the relative stability of the group I and II oxides with silica and alumina versus their reaction with the actinide oxides.

Therefore, large amounts of additive may be required before actinide volatility reduction occurs. In order to better understand actinide volatility from incinerator ashes, a better understanding of the types of phases which form and their thermodynamics is needed. This modeling study suggests that K_2O may be a better additive than Na_2O . Hence, some volatility experiments to determine the effectiveness of K_2O would be valuable.

The discussion of mixed actinide oxides species herein is limited to actinides in the +6 valence state. U, Pu, and Am are all known to form +5 mixed oxides and Pu and Am are known to form +4 mixed oxides [31]. Estimates for thermodynamics of formation of these mixed oxides could also be made using the correlation technique used herein for the +6 actinide mixed oxides. For Pu and Am, the +4 and +5 mixed oxides are expected to be important in incinerator environments when smaller amounts of group I or II oxides are present or at higher temperatures such as was observed by Keller, et al. [54,55]. When larger amounts of the group I or II oxide are present or at lower temperatures, the +6 mixed actinide oxides are expected to be more important.

Application to the Rocky Flats Plant Incinerator:

Initial work on this project predicted that $Na_2CO_3(s)$ present in the bed material in the Rocky Flats Plant Incinerator would react with $U_3O_8(s)$ to form $Na_2UO_4(s)$ [7]. $PuO_2(s)$ was not expected to react with $Na_2CO_3(s)$ to form any mixed oxides. Although experimental data are available on the formation energies of many of the mixed oxides in the $Na_2O-U_3O_8$ system, no experimental data are available on formation energies of mixed oxides in the Na_2O-PuO_2 and the Na_2O-AmO_2 systems. At 800 K, the data in Tables 18, 21, and 23 predict that in the Na_2O-PuO_2 system, $Na_4PuO_5(s)$ and $Na_6PuO_6(s)$ are stable phases, and in the Na_2O-AmO_2 systems, $Na_4AmO_5(s)$ and $Na_6AmO_6(s)$ are stable phases. From the free energy of the reaction

at 800 K taken from data in the JANAF tables [21] and assuming $p(CO_2) = 0.10$ atm, the activity of $Na_2O(s)$ is calculated to be 5.52×10^{-13} . Using the data in Tables 18, 21, and 23, the activity of $Na_2O(s)$ in the equilibria $Na_6PuO_6-Na_4PuO_5$ and in the equilibria $Na_4PuO_5-PuO_2$ is calculated to be 8.86×10^{-7} and 1.77×10^{-8} , respectively. Likewise, the activity of $Na_2O(s)$ in the equilibria $Na_6AmO_6-Na_4AmO_5$ and in the equilibria $Na_4AmO_5-AmO_2$ is calculated to be 8.47×10^{-7} and 1.54×10^{-7} , respectively. Since the activity of $Na_2O(s)$ is lower in $Na_2CO_3(s)$, neither $PuO_2(s)$ nor $AmO_2(s)$ would react with $Na_2CO_3(s)$ to form a mixed oxide in the Rocky Flats Plant Fluidized Bed Incinerator.

In the Rocky Flats application, we expect that little or no lowering of Pu and Am volatility will occur due to interaction with the ash except perhaps when large amounts of CaO, Na_2O , or K_2O are present. Although U may react with ashes to lower its

volatility the strongest interaction is expected to be with the Na_2CO_3 bed material in the primary combustor to form $\text{Na}_2\text{UO}_4(\text{s})$. Taking the reactions

and

as the volatilization reactions in the secondary combustion chamber of the Rocky Flats Plant Incinerator, we calculate the volatilities of U, Pu, and Am. The vapor pressures of the actinide trioxides are insignificant at 823 K relative to the vapor pressure of the oxyhydroxides and are therefore not considered. Only maximum values can be given for the $\text{PuO}_2(\text{OH})_2(\text{g})$ and $\text{AmO}_2(\text{OH})_2(\text{g})$ volatilities. The $\Delta H^\circ_{\text{f},298}$ values for $\text{UO}_2(\text{OH})_2(\text{g})$, $\text{PuO}_2(\text{OH})_2(\text{g})$, and $\text{AmO}_2(\text{OH})_2(\text{g})$ are given in Table 15. The $-(\Delta G^\circ - \Delta H^\circ_{298})/T$ values for reactions (2) and (67) are taken from Table 10 and the free energy functions for $\text{UO}_2(\text{OH})_2(\text{g})$ are given in Table 6. The free energy functions and $\Delta H^\circ_{\text{f},298}$ values for $\text{H}_2\text{O}(\text{g})$, $\text{O}_2(\text{g})$, and $\text{Na}_2\text{CO}_3(\text{s})$ are taken from the JANAF tables [21], and the free energy function and $\Delta H^\circ_{\text{f},298}$ value for $\text{Na}_2\text{UO}_4(\text{s})$ are taken from Grenthe, et al. [19]. Assuming $T = 823 \text{ K}$, $p(\text{O}_2) = 0.10 \text{ atm}$, and $p(\text{H}_2\text{O}) = 0.05 \text{ atm}$, and $p(\text{CO}_2) = 0.10 \text{ atm}$, pure $\text{Na}_2\text{UO}_4(\text{s})$ and $\text{PuO}_2(\text{s})$ with AmO_2 at 200 ppm in the PuO_2 in the combustion chamber, the pressure of U vapor species is calculated to be $3.00 \times 10^{-20} \text{ atm}$, and the pressures of Pu and Am are calculated to be less than $2.90 \times 10^{-24} \text{ atm}$ and $3.53 \times 10^{-28} \text{ atm}$, respectively. Assuming an offgas flow rate of 40 kmol/h and a total operational time of 6000 h/y, the volatilization rate from the combustion chamber for U is $1.7 \times 10^{-9} \text{ g/y}$, and for Pu and Am is less than $1.7 \times 10^{-13} \text{ g/y}$ and $2.0 \times 10^{-17} \text{ g/y}$, respectively.

Application to Incinerators in General:

For application to incinerators in general, we assume that $\text{U}_3\text{O}_8(\text{s})$ and $\text{PuO}_2(\text{s})$ are the source materials for the volatilized U and Pu. AmO_2 is taken to be at 1000 ppm AmO_2 in PuO_2 . The pressures of $\text{O}_2(\text{g})$ and $\text{H}_2\text{O}(\text{g})$ are both assumed to be 0.1 atm, the offgas flow rate is assumed to be 40 kmol/h, and the operational time is assumed to be 6000 h/y. From these conditions, the maximum amount of U, Pu, and Am volatilized in the incinerator combustion chamber per year is calculated as a function of temperature (See Fig. 12). The $\text{HCl}(\text{g})$ and $\text{HF}(\text{g})$ concentrations in the offgas are assumed to be negligible, and hence, actinide volatilities arising from the formation of actinide oxychlorides and oxyfluorides are not considered in Fig. 12. At low operating temperatures, i.e. 800 K, the volatilization rates of U, Pu, and Am are calculated to be $2.1 \times 10^{-5} \text{ g/y}$, $6.6 \times 10^{-14} \text{ g/y}$, and $4.0 \times 10^{-17} \text{ g/y}$, respectively. At moderate operating temperatures, i.e. 1200 K, the volatilization rates are calculated to be $7.9 \times 10^{-1} \text{ g/y}$, $3.8 \times 10^{-5} \text{ g/y}$, and $3.5 \times 10^{-8} \text{ g/y}$, respectively. At high operating temperatures, i.e. 1600 K, the volatilization rates are calculated to be $8.0 \times 10^5 \text{ g/y}$, 4.8

Figure 12. Plot of $\log gU/y$, $\log gPu/y$, and $\log gAm/y$ versus T above $U_3O_8(s)$, $PuO_2(s)$, and 1000 ppm AmO_2 solid solution in $PuO_2(s)$ where $p(O_2) = 0.1$ atm, $p(H_2O) = 0.1$ atm, offgas flow rate is 40 kmol/h, and operation time is 6000 h/y.

g/y, and 5.9×10^{-3} g/y, respectively. The volatilization rates for the Pu and Am are upper limit values. Roughly the actinide volatility is a factor of 10^8 greater at 1200 K than at 800 K and a factor of 10^{12} greater at 1600 K than at 800 K.

Summary and Conclusions

Transpiration experiments have been applied to determine the volatility of U from $\text{U}_3\text{O}_8(\text{s})$ in the presence of steam and oxygen at 1173-1573 K. The volatile species have been identified as $\text{UO}_3(\text{g})$ and $\text{UO}_2(\text{OH})_2(\text{g})$, and thermodynamic data have been developed for these species. Transpiration experiments have also been carried out at 1223-1323K on U_3O_8 interacted with several flash materials to evaluate U volatility lowering because of U_3O_8 activity lowering. Very little lowering of U volatility is found with typical flashes. However, ashes with high Na_2O (6.4 wt%) contents or with high CaO (25 wt%) contents both showed U volatility lowerings by about a factor of ten. Transpiration experiments were also carried out at 1228-1381 K to determine Pu volatilities from $\text{PuO}_2(\text{s})$ and PuO_2 interacted with flyash, and to determine Am volatilities from a 3% $^{239}\text{PuO}_2$ /0.06% AmO_2 /ash material. These experiments showed the volatilities of Pu and Am to be extremely low, with the Pu and Am carried over in the experiments to be dominated by dust transport. The results allow us to set upper limits on the volatilities of $\text{PuO}_3(\text{g})$, $\text{PuO}_2(\text{OH})_2(\text{g})$, $\text{AmO}_3(\text{g})$, and $\text{AmO}_2(\text{OH})_2(\text{g})$.

Thermodynamic modeling studies were carried out that show that for aluminosilicate ash materials it is the presence of group I and group II oxides that enhances activity lowering of the actinide oxides. K_2O is the most effective followed by Na_2O and CaO for common ash constituents. To obtain more major effects in actinide activity lowering, excess amounts of group I or II oxides would need to be added to exceed their interaction with ash and lead to direct formation of alkali or alkaline earth uranates, plutonates, and americates.

Applying the actinide volatility results found here to the secondary combustor in the Rocky Flats Plant Fluidized Bed Incinerator, we find volatilization rates of 1.7×10^{-9} g/y of U, less than 2×10^{-13} g/y of Pu, and less than 2×10^{-17} g/y of Am.

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