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Moisture and surface area measurements of plutonium-bearing oxides

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ABSTRACT

To ensure safe storage, plutonium-bearing oxides are stabilized at 950 °C for at least two hours in an oxidizing atmosphere. Stabilization conditions are expected to decompose organic impurities, convert metals to oxides, and result in moisture content below 0.5 wt%. During stabilization, the specific surface area is reduced, which minimizes readsorption of water onto the oxide surface. Plutonium oxides stabilized according to these criteria were sampled and analyzed to determine moisture content and surface area. In addition, samples were leached in water to identify water-soluble chloride impurity content. Results of these analyses for seven samples showed that the stabilization process produced low moisture materials (<0.2 wt%) with low surface area ($\leq$1 m^2/g). For relatively pure materials, the amount of water per unit surface area corresponded to 1.7–3.4 molecular layers of water. For materials with chloride content >360 ppm, the calculated amount of water per unit surface area increased with chloride content, indicating hydration of hygroscopic salts present in the impure PuO_2-containing materials. The low moisture, low surface area materials in this study did not generate detectable hydrogen during storage of four or more years.

1. Introduction

In the past two decades, significant quantities of plutonium (Pu) have been stabilized as the dioxide for storage at Department of Energy facilities. Prior to long-term storage in sealed containers, research [1,2] was performed to determine the stabilization conditions necessary to ensure safe storage. Generally, plutonium-bearing materials were heated in air at 950 °C for at least two hours, resulting in moisture content below 0.5 wt% [3]. (Some salt-bearing species, including Sample 6 in this study, were stabilized at 750 °C.) The low moisture level minimizes concerns about corrosion of storage vessels by halide-containing materials, and also reduces the potential for radiolytic hydrogen generation and subsequent pressurization of sealed vessels. Stored plutonium-bearing oxides have a wide range of plutonium contents and contain various impurities, including uranium oxides and chloride salts. Some chloride (Cl^-) phases, such as $MgCl_2$, are known to be quite hygroscopic. Past investigation has shown that the specific surface area of pure and impure Pu-bearing oxides is reduced as the calcination temperature is increased [4,5]. Calcination at 950 °C effectively reduces the specific surface area (SSA), which limits the amount of moisture that is re-adsorbed by the surface. Because of the expected low surface area and low moisture of these materials, this study did not investigate the presence of PuO_{2+x}, which has been reported in high surface area plutonium oxides in the presence of water [6]. The results presented demonstrate the effectiveness of the plutonium stabilization process through the characterization of materials that have been stored in sealed containers for more than four years, after being packaged at the Department of Energy's Rocky Flats site.

2. Experimental

Sealed containers of plutonium-bearing oxide were opened and sampled immediately. These samples were analyzed by Thermogravimetric Analysis-Mass Spectroscopy (TGA-MS) using a Netzsch STA 409 Luxx model TGA connected to a Pfeiffer ThermoStar MS. The permanent gases pass from the TGA portion of the instrument through a heated transfer tube maintained at $\geq$150 °C to the MS. During analyses, samples were heated from ambient to 1000 °C (at 15 °C/min) under a flowing argon gas stream which was analyzed by the MS. Gypsum standards were used to develop an MS moisture calibration curve, as described elsewhere [7,8]. Additional samples from the same parent container were analyzed for surface area with a Micromeritics Gemini 2360 analyzer using the Brunauer–Emmett–Teller (BET) method with nitrogen adsorbate. All analyses were performed in duplicate unless otherwise indicated. Soluble chloride salt content was determined by leaching 0.5-g samples in water at 90 °C for one hour. After cooling, aliquots were analyzed to determine selected anions (by ion chromatography) and selected cations (by inductively coupled plasma-emission spectroscopy). In addition to the oxide sample characterization, gas samples from the headspace of the cans (collected during storage vessel opening) were analyzed by gas chromatography.

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Table 1
Characterization data for plutonium-bearing oxide samples.

#	% Pu	% U	Soluble Cl^- μg/g	SSA m^2/g	TGA mass loss wt%	MS moisture wt%	Water/surface area mg H_2O/m^2	Molecular layers 0.21 mg ea
1	87.5	–	BDL	0.47	0.03	0.04	0.63	3.0
2	85.0	1.32	BDL	0.82	0.03	0.05	0.37	1.7
3	86.5	–	120	0.94	0.04	0.05	0.42	2.0
4	85.8	–	320	0.99	0.07	0.10	0.71	3.4
5	84.1	0.22	360	0.58	0.16	0.05	0.86	4.1
6	67.9	–	110,000	0.58	0.44	0.14	2.4	11[b]
7	51.4	–	170,000	0.58	4.1	0.19[a]	3.3	16[b]

BDL = Below Detection Limit.

[a] Value based on single value of MS replicate. Initial analysis had an MS error.

[b] Values provided for comparison, since moisture tends to hydrate Cl^- salts, not form additional layers.

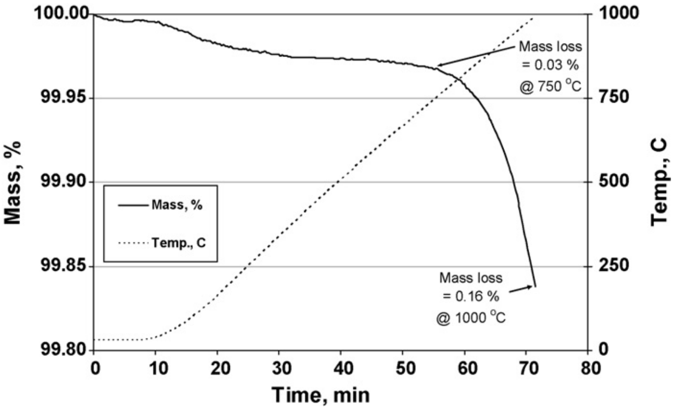

Fig. 1. Thermogravimetric analysis of chloride-bearing sample #5.

3. Results

Typical TGA and combined TGA-MS curves are shown in Figs. 1 and 2, which have the same temperature versus time profile. Detailed analytical results are shown in Table 1 with samples listed in order of increasing Cl^- content. Note that pure Pu oxide has an assay of 88.2% Pu for common isotopic mixtures. Uncertainties in the values reported in Table 1 are ±5% for TGA mass loss, ±10% for soluble Cl^- and SSA, and an estimated ±30% for MS moisture content. Table 1 also contains the number of molecular layers of water present on each material, based on the value of 0.21 mg/m^2, an average estimate for the molecular coverage on plutonium dioxide [1]. Results for water-soluble cation contents are shown in Table 2. Finally, analysis of the gas inside the sealed Pu storage vessels did not detect appreciable hydrogen for the seven samples in this study [9].

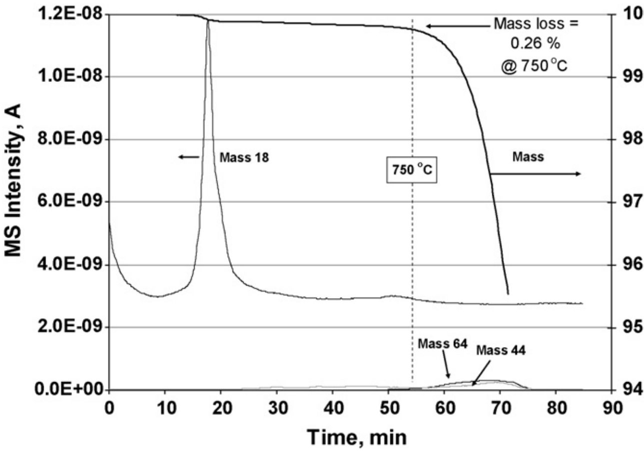

Fig. 2. TGA-MS of sample #7 containing 17 wt% chloride.

Table 2
Water-soluble cation contents.

#	Ca (μg/g)	K (μg/g)	Mg (μg/g)	Na μg/g
6	30	61,000	5,200	37,000
7	430	76,000	7,200	47,000

4. Discussion

As shown in Table 1, the four samples with the highest purity exhibited a total mass loss of 0.03–0.07 wt%. During development of the moisture calibration curve, the linear relation between MS peak area for Mass 18 versus mass of moisture was assigned an intercept of (0, 0). Using a zero intercept gave the reported MS results a small positive bias for low moisture materials; however, TGA and MS moisture results agree within the uncertainties of the measurement methods.

For the relatively pure Samples 1–4, the amount of water per unit surface area corresponded to 1.7–3.4 molecular layers of water. Pure materials have been shown to contain nominally two molecular layers of moisture [1].

For Samples 5–7, the chloride contributes significantly to the total mass loss, especially above 750 °C, the temperature at which chlorides salts begin to volatilize. For all samples, the majority of moisture release, which occurred by the time the sample reached 400 °C, is generally ascribed to physisorbed moisture. For Samples 1–3 and 5–7, moisture release from 750 to 1000 °C was ≤0.015 wt%. However, Sample 4, which had the highest surface area of the samples tested and contained modest Cl^-, showed moisture release of 0.03 wt% between 750 and 1000 °C, an indication of some strongly chemisorbed moisture.

Generally, the surface areas for these samples were quite low, ranging from 0.47 to 0.99 m^2/g. Reduced surface area tends to minimize rehydration of the oxide. Thus, the materials in this study compare favorably with the thirteen samples reported by Leasure et al. [4] that had been calcined at 950 °C and had surface areas ranging from 0.20 to 3.16 m^2/g with a median value of 1.21 m^2/g. Similarly, Machuron-Mandard and Madic [5] calcined PuO_2 at 750, 850, and 950 °C and found specific surface areas of 2.0, 2.6, and 2.1 m^2/g, respectively. For samples in this study containing chloride salts, particularly Sample 6 stabilized at 750 °C, the low specific surface areas may be due in part to the presence of the salt.

The absence of hydrogen in the headspace above the plutonium-bearing materials in this study indicates minimal generation of hydrogen by either radiolysis of water or by chemical reaction of water and PuO_2. It is unlikely that H_2 was generated and later consumed. Thus, the low moisture, low surface area materials in this study were stable during storage in terms of hydrogen generation.

5. Conclusions

Seven samples which represent a portion of the types of plutonium-bearing oxides stabilized for long-term storage were tested. Characterization of these samples provides an initial indication that the stabilization process effectively produces materials with low surface area, $\leq 1\,m^2/g$, and moisture content <0.2 wt% for the materials in this study. The relatively pure samples tested in this study contained 2–3 molecular layers of water, which is consistent with earlier studies on pure Pu oxides. Materials containing appreciable chloride exhibited increased mass loss when heated to 1000 °C, and these samples exhibited increased water content.

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