LA-13246-MS

Materials Identification and Surveillance Project Item Evaluation

Items: Impure Plutonium Oxide (ATL27960) and Pure Plutonium Oxide (PEOR3258)

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*Los Alamos National Laboratory is operated by the University of California
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Edited by: Deborah Bacon, Group CIC-1; Margaret Burgess, Group CIC-1
Photocomposition by: Barbara A. Ritchie, Group CIC-1

This work was supported by US Department of Energy, Office of Environmental Management.

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LA-13246-MS

UC-940 and UC-904
Issued: March 1997

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Tom Allen
Quentin Appert
Charles Davis
John Haschke
William Hollis
David Horrell
Aaron Martinez
Richard Mason
Louis Morales
Tom Ricketts
Jim Rubin
Craig Taylor
Andreas Toupadakis

Los Alamos
NATIONAL LABORATORY
Los Alamos, New Mexico 87545

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by
Tom Allen, Quentin Appert, Charles Davis, John Haschke, William Hollis,
David Horrell, Aaron Martinez, Richard Mason, Louis Morales, Tom Ricketts,
Jim Rubin, Craig Taylor, and Andreas Toupadakis

ABSTRACT

In this report, Los Alamos scientists characterize properties relevant to storage of an impure plutonium oxide (74 mass % plutonium) in accordance with the Department of Energy (DOE) standard DOE-STD-3013-96. This oxide is of interest because it is the first impure plutonium oxide sample to be evaluated and it is similar to other materials that must be stored. Methods used to characterize the oxide at certain points during calcination include surface-area analyses, mass loss-on-ignition (LOI) measurements, elemental analysis, moisture-adsorption measurements, and quantitative supercritical-CO_2 extraction of adsorbed water. Significant decreases in the LOI and surface area occurred as the oxide was calcined at progressively increasing temperatures.

Studies indicate that supercritical-CO_2 extraction is an effective method for removing adsorbed water from oxides. We extracted the water from powdered oxides (high-purity ZrO_2, pure PuO_2, and impure plutonium oxide) using CO_2 at 3000 psi pressure and 75°C, and we quantitatively determined it by using gravimetric and dew-point procedures. The effectiveness of the extraction method is demonstrated by good agreement between the amounts of water extracted from pure zirconium and plutonium dioxides and the mass changes obtained from LOI analyses. However, the amount of moisture (0.025 mass %) extracted from the impure plutonium oxide after it had been calcined at 950°C and stored for a period of months is much less than the LOI value (0.97 mass %). These results imply that the impure plutonium oxide is free of adsorbed water after calcination at 950°C, even though the sample does not satisfy the LOI requirement of <0.50 mass % for storage.

1.0 INTRODUCTION

The requirements for extended storage of oxides containing >50 mass % plutonium are described in the Department of Energy (DOE) standard DOE-STD-3013-96.[1] Although procedures are defined for preparing pure PuO_2 in accordance with this standard,[2] similar methods are not established for impure materials. These impure oxides satisfy the DOE criterion for plutonium content, but contain significant concentrations of elements other than plutonium and oxygen and may exhibit markedly different chemical and storage characteristics from those of pure PuO_2. The situation within the DOE complex is further complicated by the need to store diverse, impure, and largely uncharacterized oxides derived from unspecified sources.

The objective of this study is to initiate an experimental effort to characterize impure plutonium oxides and to develop preparative methods that convert these materials into oxide forms suitable for storage. This information will help Los Alamos National Laboratory and other DOE sites establish preparation and handling procedures needed to certify impure plutonium oxides for storage. Also, this information is needed for timely development of implementation plans at storage sites.

Our approach is first to characterize relevant chemical and physical properties of the impure materials before and after calcination and then to examine the suitability of applying calcination procedures for pure PuO_2 to impure plutonium oxides. The need for material characterization was emphasized after the product we obtained by calcining a typical impure plutonium oxide sample at 950°C for 2 h failed to satisfy the 0.5–mass % loss-on-ignition (LOI) requirement of the storage standard. In addition to the surface-area measurements, calcination procedures, adsorption measurements, and LOI techniques used in earlier studies, experimental methods applied in this work include extensive chemical analyses and quantitative extraction of adsorbed water using supercritical CO_2.

Supercritical CO_2 is attractive for use as an extraction solvent because its high diffusivity and low viscosity allow the fluid to penetrate matrices such as loose powders, compact powders, and even fully cemented preforms. Supercritical CO_2 dissolves approximately 0.2 mass % water. Even at this low concentration, an extraction process using a flowing stream of dry supercritical CO_2 is able to quickly dehydrate solid materials and is potentially applicable to inorganic oxides such as PuO_2.

2.0 EXPERIMENTAL METHODS

2.1 Materials

The preparation and characterization of the pure PuO_2 (identification number PEOR3258) by elemental analysis and by surface area measurements (5-point Brunauer-Emmett-Teller [BET] method) have been described previously.[2,3] The plutonium content was reported to be 86.9 mass % by coulometry[3] (the theoretical value for PuO_2 is 88.19 mass % plutonium). The purity of the ZrO_2 is reported to be >99.99%.[4]

The impure plutonium oxide (identification number ATL27960) was produced in the advanced testing line for actinide separation at the Los Alamos Plutonium Facility. The impure oxide (2 077.7 g) was produced by precipitation of plutonium(III) oxalate from a nitrate solution and thermal decomposition of the product at 600°C in air for 4 h in a tube furnace. The sources of the materials used to prepare the nitrate solution are unspecified, and the origin of additional oxide that was apparently combined with the calcined product is unknown. The resulting product was stored for approximately six months prior to being selected for characterization. Uncertainties about the origin and properties of the oxide make it representative of many impure materials that must be prepared for storage.

2.2 Procedures

Our intent was to develop and demonstrate procedures for preparing and handling impure plutonium oxide prior to storage. The experimental procedures used for LOI, supercritical-CO_2 extraction of water from the different oxides, specific-surface-area measurements, calcination, and adsorption have been described previously[2–5] and will not be detailed in this report.

In brief, LOI data were obtained as follows. Weighed samples of pure PuO_2 and impure plutonium oxide were calcined in platinum crucibles. All samples were heated in the LOI furnace at the same time. We ramped the temperature to 950°C over a period of several hours, held the samples at 950°C for 2 h, and cooled them to 200°C in 3 h. The samples were held at 200°C, transferred from the furnace to a desiccator for cooling to room temperature, and weighed. We determined the LOI values for ZrO_2 by measuring the mass loss that occurred during heating at 140°C for 16 h.

Using standards of pure ZrO_2 and PuO_2, we investigated the use of the supercritical-CO_2 extraction method for determining the amount of water adsorbed on oxide.[4] The quantitative results were evaluated by comparing them with LOI data. Real-time extraction experiments were conducted by flowing supercritical CO_2 (3000 psig, 75°C) over a weighed oxide sample and measuring the dew point of the solvent after expansion to a measured pressure of about 12 psia. We determined the integral quantity of extracted water by summing the amounts derived from moisture analyses of sequential gas aliquots of the total solvent flow. After periods of 1.3–2.4 h, water content of the aliquots became negligible and extraction was discontinued. We employed similar procedures for extraction measurements on impure plutonium oxide. The flow chart (Fig. 1) shows the step-by-step experimental procedures we followed for characterizing the impure plutonium oxide.

2.3 Characterization of the Impure Plutonium Oxide

The sample of impure plutonium oxide from the vault, identification number ATL27960, was introduced into the glovebox. The powder was a dull yellowish-green, and conglomerates were evident. We processed the powder in three phases.

Phase I. We sieved the “as-received” plutonium oxide powder through a 20-mesh (850 μm) sieve and rod-milled the oxide particles >850 μm to meet size requirements. The oxide was combined, resieved, and blended for homogeneity. We took samples of this material, which is designated “S” (see Fig. 1), for measurements of LOI, surface area, plutonium content, isotopes, metallic impurities, and carbon impurity.

Phase II. We calcined the plutonium oxide powder S at 600°C for 12 h and allowed it to cool. After calcination, the material (now denoted S′) was light gray. With minimal exposure to the glovebox atmosphere, we took samples for LOI and surface-area measurements and for adsorption experiments.

Phase III. We then calcined the plutonium oxide powder S′ at 950°C for 2 h. The color after calcination was dark gray-black, and the oxide in contact with the bottom of the fused silica boat was fused to the container. The fused layer was approximately 1/32-in. thick and was difficult to remove. The top layer of the oxide had formed a crust, but it was easily broken up when sieved through a 20-mesh sieve. Once the material (now denoted S″) had cooled, we took samples for LOI and surface-area measurements, adsorption experiments, elemental analyses, and supercritical-CO_2 extraction experiments.

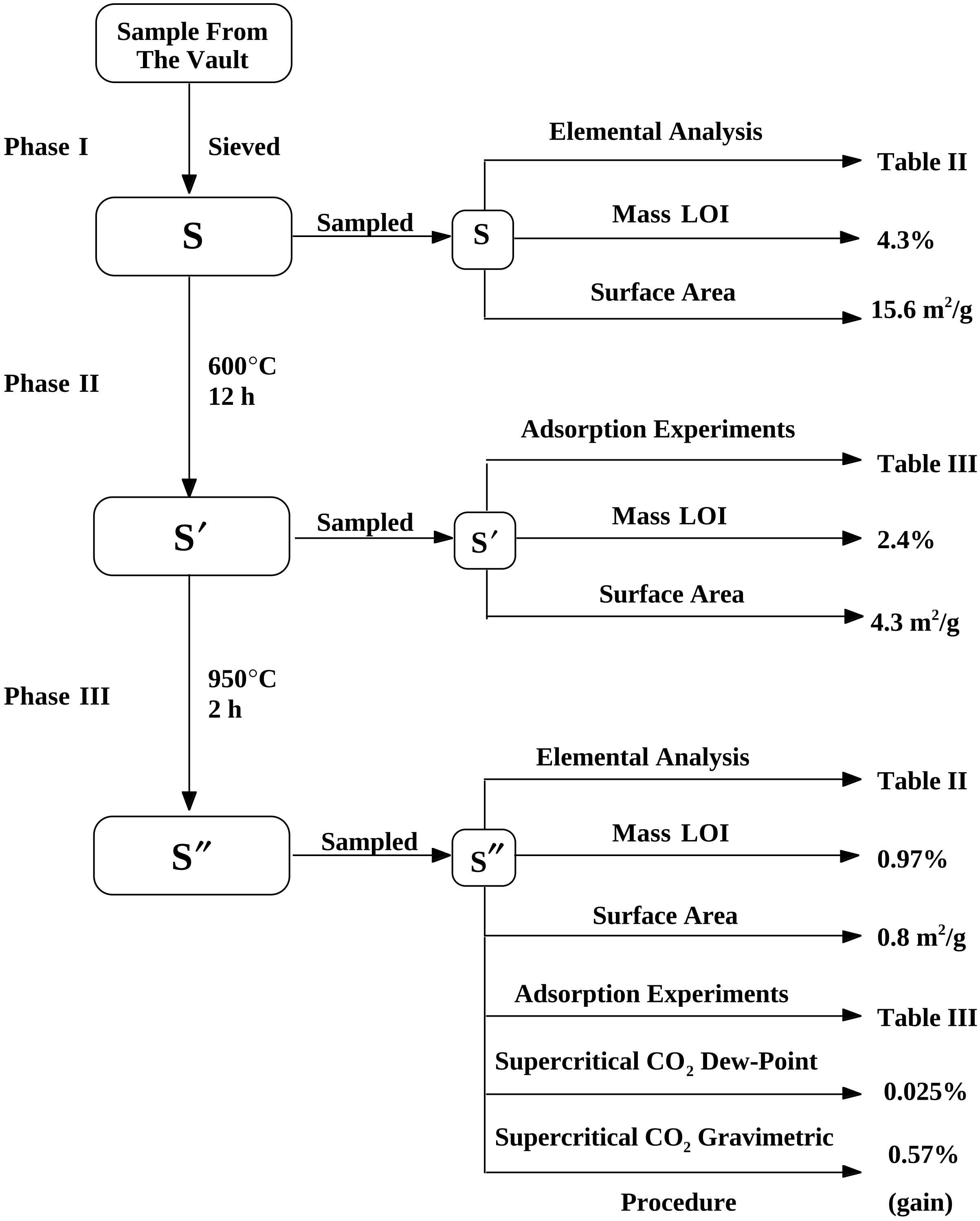

Fig. 1. **Characterization of the impure plutonium oxide, identification number ATL27960.**

We did not study the water-adsorption behavior of the impure plutonium oxide type S, but we did study the water-adsorption behavior as a function of time for each calcined sample (S′ and S″) in two different configurations. For one configuration we used a 50-ml beaker, and for the other we used a watch glass with a diameter of approximately 3.5-in. The time dependence of adsorption was determined by measuring the mass change of the oxide sample with an analytical balance. We placed an accurately weighed sample of calcined oxide in one of the two identified configurations, and determined the mass at time intervals of between 15 min and 1 h, depending on the observed adsorption behavior. We monitored the relative humidity in the glovebox during the time we conducted these experiments. The highest moisture level in the glovebox during exposure to its atmosphere was 0.5% relative humidity. The moisture level remained constant during the exposure.

In the case of S′, the sample in beaker #1 weighed 26 g, the sample in beaker #2 weighed 27 g, and the sample on the watch glass weighed 22.6 g. We monitored these weights for approximately 50 h. The results are presented as a graphic representation of adsorption measurements as a function of time in Fig. 2. In the case of S″, the sample in beaker #1 weighed 30 g, the sample in beaker #2 weighed 19 g, and the sample on the watch glass weighed 31 g. These weights were monitored for approximately 25 h. The results are presented as a graphic representation of adsorption measurements as a function of time in Fig. 3.

3.0 RESULTS AND DISCUSSION

It has been established that adsorbed water on pure ZrO_2 and pure PuO_2 can be efficiently removed and measured by supercritical-CO_2 extraction. Results from the supercritical-CO_2 extraction are in excellent agreement with results from LOI analysis of the pure PuO_2.[4] After testing the ability of supercritical CO_2 to extract adsorbed water from these metal oxide surfaces, the method was applied to the impure plutonium oxide. A short discussion is presented of data on the characterization of the pure oxides ZrO_2 and PuO_2 before the new results are presented on the characterization of the impure oxide and compared with the results obtained previously.[4] The mass-loss results for ZrO_2, pure PuO_2, and impure plutonium oxide S″ are summarized in Table I.

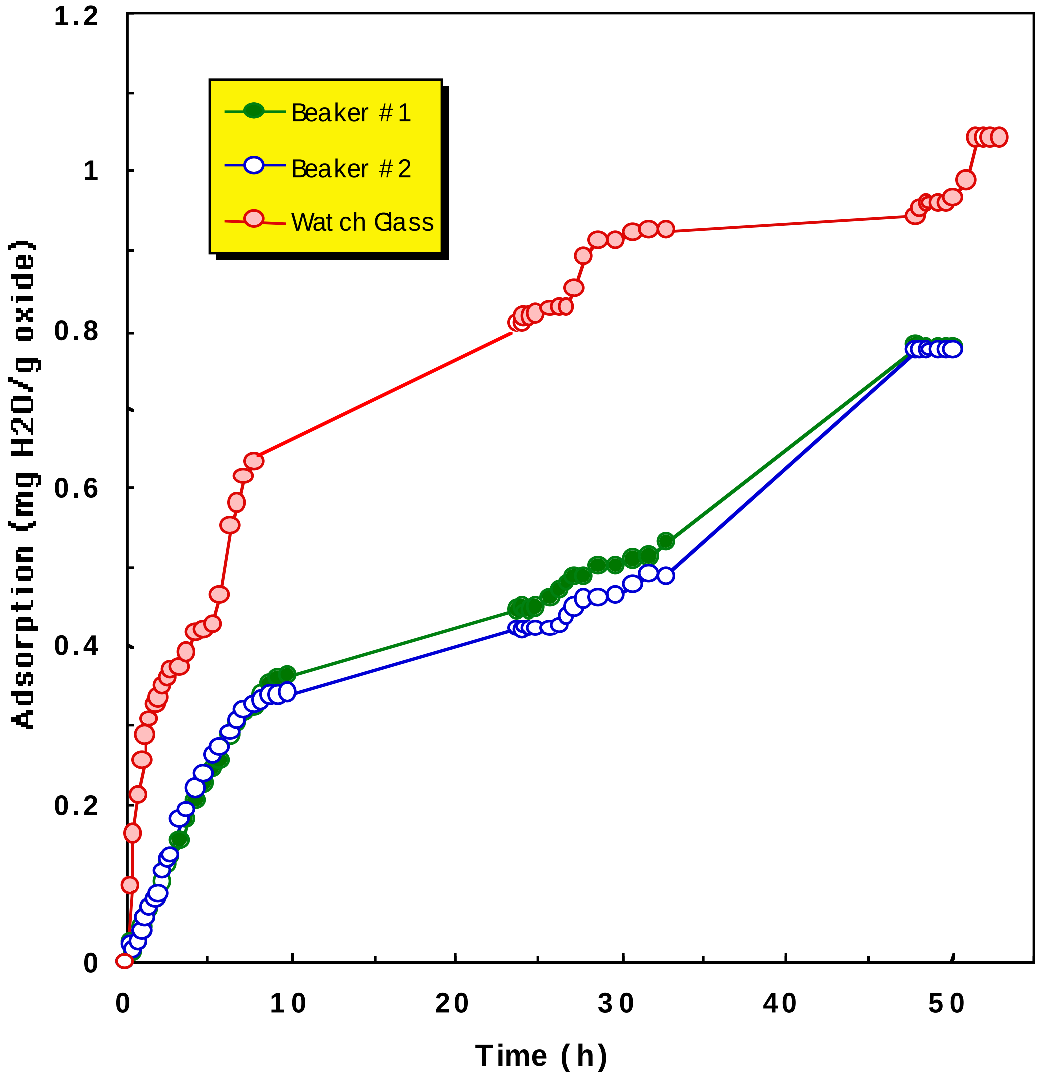

Fig. 2. Adsorption measurements over time of impure plutonium oxide S′.

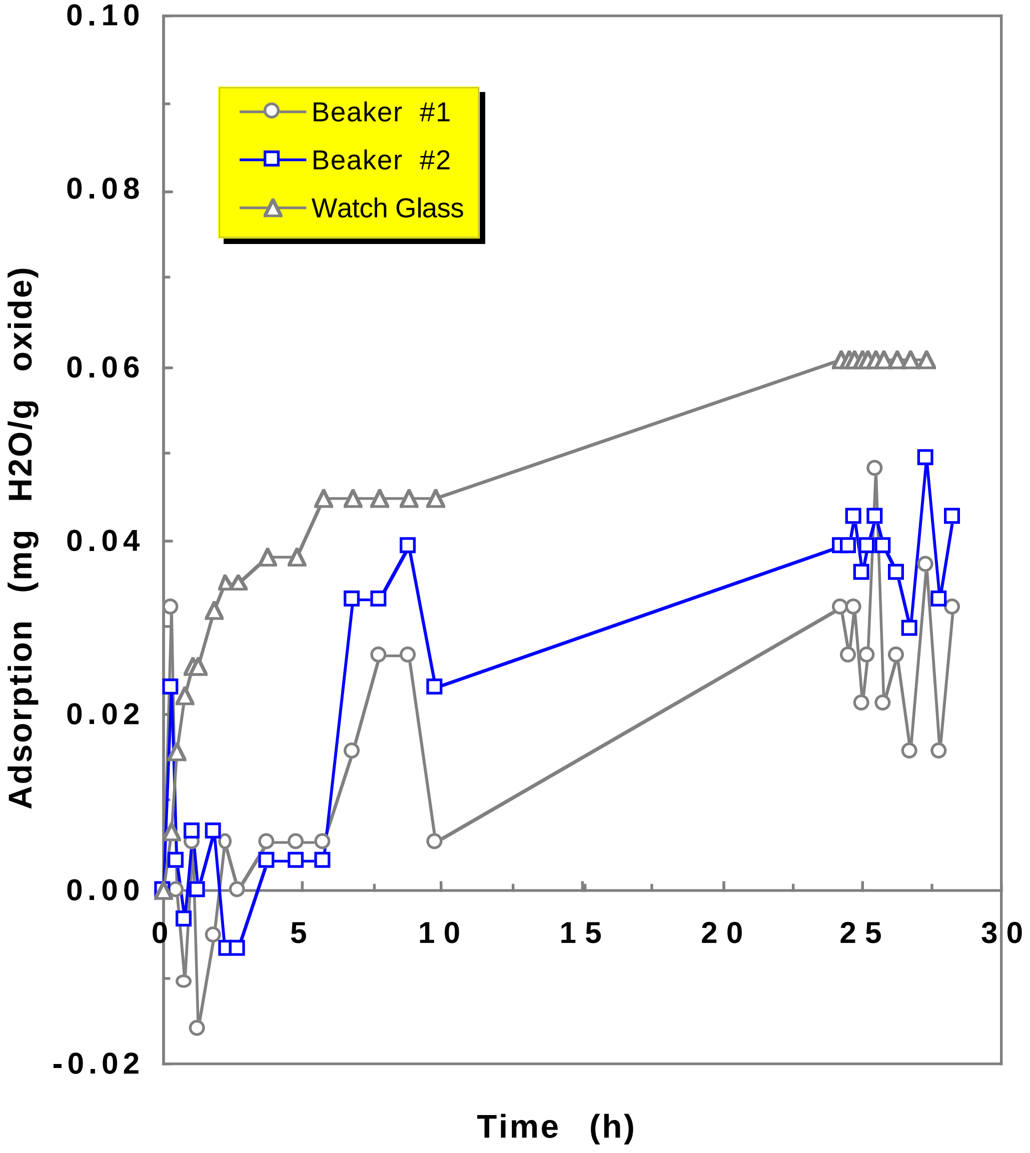

Fig. 3. Adsorption measurements over time of impure plutonium oxide S″.

3.1 Characterization of the Pure ZrO_2 Standard

A. Mass Loss after Thermal Treatment. Three ZrO_2 samples were heated in a furnace at 140°C for 16 h, and the average mass loss was 0.0948%.

B. Calculated Mass Loss after Supercritical-CO_2 Extraction. The mass loss determined from the real-time dew-point measurements was 0.0950%.

C. Gravimetric Mass Loss after Supercritical-CO_2 Extraction. The total gravimetric mass loss (0.0978%) is the sum of the mass loss (0.0414%) of the adsorbed water removed by supercritical–CO_2 extraction and the mass loss (0.0564%) of the adsorbed CO_2 removed in a second step by thermal treatment (CO_2 correction).

Comparing A and B, there is excellent agreement between the mass loss produced by thermal treatment and the calculated mass loss produced by supercritical-CO_2 extraction (0.0948% vs 0.0950%). Comparing C with A or B, again an excellent agreement exists, but only after a CO_2 correction was made. The observed additional mass loss (0.0564%) is attributed to removal of CO_2 adsorbed during supercritical-CO_2 extraction of water, but this explanation has not been verified. The above data are summarized in Table I.

Table I. Results of Supercritical-CO_2 Extraction and LOI Analyses of Oxides[a]

Oxide	Mass of Oxide[b] (g)	Extracted Water[c] (mass %)	LOI (mass %)	Change in Oxide Mass[d] (mass %)
ZrO_2	13.643	0.0950	0.0948	0.0414 (loss)
PuO_2	7.6987	0.017	0.01595[e]	0.056 (loss)
PuO_2	7.1315	0.014	0.02430[e]	0.011 (loss)
PuO_2[f]	8.2460	0.025	0.97	0.57 (gain)

[a] Data from Ref. 4.
[b] Mass of oxide for the supercritical-CO_2 experiments.
[c] Calculated mass loss after supercritical-CO_2 extraction.
[d] Gravimetric mass change after supercritical-CO_2 extraction, before any CO_2 corrections were made.
[e] Approximately a 5-g sample for each aliquot.
[f] Impure plutonium oxide S″; see Fig. 1.

3.2 Characterization of the Pure PuO_2 Standard

A. Mass Loss after Thermal Treatment. A 10-g sample, split into two 5-g aliquots, was measured for mass LOI. We heated the samples in air at 950°C for 9 h, and the average mass loss was 0.0201%. The individual weight losses of the two aliquots were 0.01595% and 0.02430%.

B. Calculated Mass Loss after Supercritical-CO_2 Extraction. The average mass loss that we determined from the real-time, dew-point measurements for two pure PuO_2 samples was 0.0155%. The mass losses of the two aliquots were 0.017% and 0.014%.

C. Gravimetric Mass Loss after Supercritical-CO_2 Extraction. We weighed the pure PuO_2 samples before and after extraction to determine the mass loss due to extraction. The average mass loss was 0.033%. The individual mass losses of the two aliquots were 0.056% and 0.011%.

Comparing A and B, we see excellent agreement between the mass loss produced by thermal treatment and the calculated mass loss from supercritical-CO_2 extraction (0.0201% compared with 0.0155%). However, it is apparent that the mass losses of the individual aliquots were more consistent in the latter case than they were in the former. In C we have interpreted the large difference between the mass-loss values of the individual aliquots as resulting from vibrations that interfered with the microbalance readings made in the glovebox. Whatever might be the cause, it is clear that results based on gravimetric measurements (A and C methods) are less consistent than results based on nongravimetric measurements (B method). Comparing C with A or B, however, we note that although the individual values of gravimetric mass loss in C are not very consistent, the average value is reasonably consistent with both the mass loss on thermal treatment and the calculated mass loss (0.033% vs 0.020% or 0.015%) after supercritical-CO_2 extraction.

It must be noted that the mass-loss values reported in case C are not corrected for the adsorption of CO_2. If a similar loading of CO_2 was present on PuO_2 as on ZrO_2 (0.0564%), then the values in case C would deviate from the values of either A or B (0.089% vs 0.020% or 0.015%). Studies of CO_2 adsorption on pure PuO_2 should be done before we can compare mass-loss values in C with values in A or B. Nevertheless, these adsorption studies are not a high priority because the most important and reliable water analyses come from the supercritical-CO_2-extraction dew-point measurements.

3.3 Characterization of the Impure Plutonium Oxide

Sample S. The surface area of S was 15.6 m^2/g. The results from the elemental analysis of this sample are presented in Table II; as indicated, chemical analysis by coulometry shows a plutonium content of about 74 mass %.

A. Mass Loss after Thermal Treatment. The mass LOI was 4.3%.

B. Calculated Mass Loss after Supercritical-CO_2 Extraction. No extraction was done.

C. Gravimetric Mass Loss after Supercritical-CO_2 Extraction. No extraction was done.

This impure plutonium oxide sample was originally prepared by firing oxalate at 600°C for 4 h, and then stored for about six months in the vault. Before we performed an LOI analysis on it, we homogenized the sample. The mass LOI value of 4.3% is high, and it is not possible to say how much of this 4.3% mass loss is due to hydrogenous compounds, primarily water, and how much loss is due to volatilization of nonhydrogenous compounds, primarily inorganic salts. Elemental analysis (see Table II) shows that the predominant metallic impurities are sodium and potassium and, to a lesser extent, calcium, aluminum, iron, magnesium, chromium, nickel, lead, and americium. The carbon concentration was 2 mass %.

Sample S′. The surface area of S′ was 4.3 m^2/g. The maximum water adsorption for the impure plutonium oxide (in the watch-glass configuration) calcined at 600°C for 12 h is 1.04 mg H_2O per gram plutonium oxide over approximately 50 h. The results of the adsorption experiments are shown in Fig. 2.

A. Mass Loss after Thermal Treatment. The mass LOI was 2.4%.

B. Calculated Mass Loss after Supercritical-CO_2 Extraction. No extraction was done.

C. Gravimetric Mass Loss after Supercritical-CO_2 Extraction. No extraction was done.

Table II. Elemental Analysis of Precalcined Powder S[a] and Calcined Powder S″[b]

Element	Powder S (μg/g)	Powder S″ (μg/g)	Concentration Change (μg/g)
Pu	740 600	774 300	+ 33 700
Ag	<1	<1	-
Al	960	1020	+ 60
Am	335	350	+ 15
B	10	13	+ 3
Be	<2	<2	-
Bi	<4	<4	-
Ca	1000	1030	+ 30
Cd	<0.5	<0.5	-
C	20 000	10 000	- 10 000
Cr	610	820	+ 210
Fe	840	800	- 40
K	14 000	12 000	- 2000
Mg	620	470	- 150
Mn	11	13	+ 2
Mo	80	130	+ 50
Na	44 000	39 000	- 5000
Ni	520	620	+ 100
Pb	390	210	- 180
Si	65	440	+ 375
Sn	<0.3	<0.3	-
Ta	<0.1	<0.1	-
Th	<0.2	<0.2	-
W	<0.3	<0.3	-

[a] Impure oxide from the vault before any calcination.

[b] Impure oxide (S) that was calcined in two steps, first at 600°C for 12 h and next at 950°C for 2 h.

The smaller mass LOI of 2.4% for sample S′ compared with 4.3% for sample S is not a surprise because S′ is simply S after calcination at 600°C for 12 h. But again, the fraction of the change that is due to water or any other hydrogenous compounds is unknown. The surface area for sample S′ (4.3 m^2/g) was much smaller than that for sample S (15.6 m^2/g). We attribute this substantial decrease to sintering during calcination.

Sample S″. We found the surface area of S″ to be 0.8 m^2/g. The maximum water adsorption for the impure plutonium oxide (in the watch-glass configuration) calcined at 950°C for 2 h is 0.06 mg H_2O per gram plutonium oxide over approximately 25 h. The results from the elemental analysis of this sample are presented in Table II, and the results from the adsorption experiments can be seen in Fig. 3.

A. Mass Loss after Thermal Treatment. The mass LOI was 0.97%.

B. Calculated Mass Loss after Supercritical-CO_2 Extraction. The mass loss determined from the real-time, dew-point measurements was only 0.025%.

C. Gravimetric Mass Loss after Supercritical-CO_2 Extraction. We found the gravimetric mass change after supercritical-CO_2 extraction to be a mass *gain* of 0.57% instead of a mass loss.

The even smaller mass LOI for sample S″, 0.97% compared with 2.4 % for sample S′, is again not surprising because we obtained S″ by calcining S′ at 950°C for 2 h. Further conglomeration is consistent with the additional calcination and with a reduced surface area (0.8 m^2/g compared with 4.3 m^2/g). This decrease in surface area is supported by adsorption experiments that show a significant difference in the readsorption of water on the oxide S′ (0.9 mg H_2O per gram S′) and the oxide S″ (0.06 mg H_2O per gram S″). See Fig. 4 for the 25-h period. Because the moisture level in the glovebox remained constant during the exposure, the origin of step-like features in the adsorption curves (Figs. 2–4) is not known at this time. Table III shows a comparison of adsorption results for pure and impure plutonium oxide at room temperature.

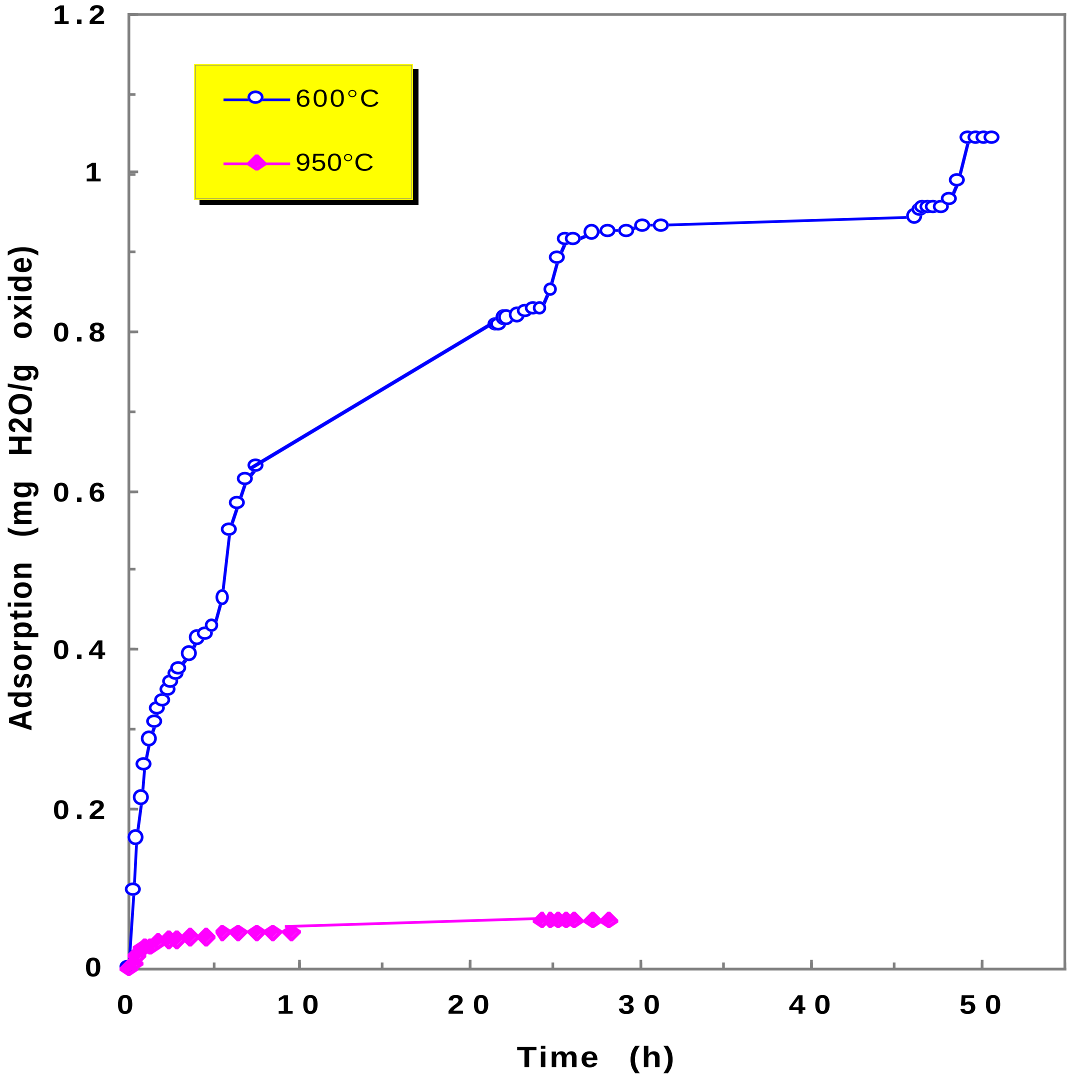

Fig. 4. Adsorption measurements over time of impure plutonium oxide on a watch glass.

Table III. Comparison of Adsorption Results for Pure[a] and Impure Plutonium Oxide at Room Temperature

Oxide	Calcination Temperature (°C)	Specific Surface Area of Oxide (m^2/g)	Initial Adsorption Rate of Water (mg/m^2h)	Equilibrium Concentration of Water (mg/m^2)
Pure	700	8.1	0.27[b]	0.17[b]
Pure	950	4.8	0.37[b]	0.16[b]
Impure	600	4.3	0.06[c]	0.24[c,d]
Impure	950	0.8	0.03[c]	0.09[c]

[a] Data for pure oxide are from Ref. 2.
[b] Relative humidity of 1%.
[c] Relative humidity 0.5%; watch glass configuration.
[d] It is not certain if equilibrium has been reached; see Fig. 4.

The initial water-adsorption rate for the impure plutonium oxide at 0.5% relative humidity (0.03 mg/m^2h) is about 12 times lower than the initial water-adsorption rate of the pure PuO_2 at 1% relative humidity (0.37 mg/m^2h), after calcination at 950°C.[2] The difference in initial adsorption rate cannot be explained by the small difference in relative humidity (0.5% in contrast to 1%). Evaluation of the initial water-adsorption rate for pure PuO_2 at 10% relative humidity (0.39 mg/m^2h) shows that a 10-fold increase in relative humidity does not alter the initial adsorption rate.[6] Thus, the 12-fold decrease in initial adsorption rate in the case of the impure plutonium oxide appears to be due to the presence of the impurities.

Although the rate of adsorption by the impure plutonium oxide is slow compared with that of pure PuO_2, the equilibrium concentrations of water adsorbed by the impure oxide (0.09 mg/m^2) and pure PuO_2 (0.16 mg/m^2) after calcination at 950°C are in good agreement at room temperature and similar relative humidity. The slightly higher value of 0.16 mg/m^2 in contrast to 0.09 mg/m^2 is understandable because of higher relative humidity (1% in contrast to 0.5%). These results suggest that the affinity of impure plutonium oxide for water is similar to that of pure PuO_2.

The results of supercritical-CO_2-extraction experiments on the impure plutonium oxide are summarized in Table I. Results of dew-point measurements show that the amount of water removed (0.025%) is comparable with the amounts of water removed from ZrO_2 and pure PuO_2. This value also agrees with the equilibrium adsorption results in Table III: for a surface area of 0.8 m^2 per gram of impure plutonium oxide, 0.025% of extracted water corresponds to 0.31 mg H_2O per square meter on the impure oxide prior to extraction. The slightly higher surface concentration of water on the S″sample used for extraction is consistent with exposure to atmospheres having greater than 0.5% relative humidity during shipping and handling. The agreement also supports the conclusion that supercritical-CO_2 extraction is an effective method for removing adsorbed water from inorganic oxides.

It was a surprise to find out that the gravimetric measurements after supercritical-CO_2 extraction of S″ show a mass gain (0.57%) instead of a mass loss. Supercritical-CO_2 extraction removes water and probably some other impurities such as organics. Because we observed a mass gain instead of a mass loss and because it appears that ZrO_2 may absorb CO_2, we assume that CO_2 is being adsorbed on the surface of the impure plutonium oxide. To verify this hypothesis, CO_2 adsorption-desorption studies should be carried out on pure and impure PuO_2.

The mass gain observed after extraction may also be attributed to the partial conversion of oxides to carbonates. This possibility should be verified by desorption studies on oxides after extraction. The reported[4] formation of uranium carbonate salts using a slurry of UO_3 in the presence of CO_2 at 100°C and 250–800 psia does resemble the temperature conditions of extraction (75°C). However, the pressure conditions of the supercritical-CO_2-extraction method (3000 psig) are much different. Most importantly, using an aqueous slurry of UO_3 in the presence of CO_2 means that the carbonate ions are already formed and are ready to react. On the other hand, during the supercritical-CO_2 extraction, the oxide is at almost anhydrous conditions.

3.4 Discussion on the Results of Elemental Analysis

The origin of the difference between the mass LOI of 0.97% and the water loss of 0.025% during supercritical-CO_2 extraction is important because DOE-STD-3013-96 for long-term storage of plutonium oxide states that "…thermally stabilized oxides shall exhibit less than 0.5 mass percent loss-on-ignition (LOI)."[1] For the time being, an incomplete, but nevertheless helpful, explanation for this observed difference is given by comparing the results from the elemental analyses of samples S and S″ (see Table II). It is interesting to note that the largest decrease observed is for carbon, which is probably removed from the sample as CO_2 during calcination. The presence of carbon is consistent with the history of the sample, which in large part came from the decomposition of Pu^{3+} oxalate that precipitated from a nitrate solution. Incomplete removal of oxalate residues during the calcination process (at 600°C for 4 h) could result in the relatively high carbon concentration (2 mass %) of sample S. The large mass loss of 0.97% during the LOI test of sample S″ could be explained by oxidation of 1-mass-% residual carbon from sample S″

during the LOI test. After carbon, the next largest change comes from sodium. The sodium loss may result from its volatilization in some chemical form, but the results are far from conclusive.

The results in Table II and in Ref. 4 do not agree. The results in Ref. 4 were obtained by using the direct-current arc spectrographic technique and were later determined to be questionable because of the high salt (sodium and potassium) content. The sample was rerun by inductively coupled plasma-mass spectrometry and inductively coupled plasma-atomic emission spectrometry, the appropriate techniques for this type of material. The results in Table II are the accepted values.

Lead shows almost the same mass-percent decrease as carbon (46 mass % decrease for lead in contrast to 50 mass % decrease for carbon). The significance of the lead mass loss cannot be ignored for future impure oxide samples with high levels of lead. We speculate that the small, but noticeable, increase in silicon content comes from a reaction between the oxide and the silica vessel during calcination. The analytical results suggest that nonmetallic elements, in addition to carbon, are lost during calcination and emphasize the need for qualitative and quantitative analysis of off-gases produced during calcination of impure plutonium oxide.

3.5 Possible High-Temperature Chemistry and Suggested Techniques for Characterization of the High-Temperature Chemistry

We cannot ignore the chemical reactions that can possibly take place between the different species present in an impure plutonium oxide. During calcination, new compounds and phases may form, and their behavior could affect the result of the LOI test. In a possibly similar scenario, PuO_2 and MgO mixtures appear to form a simple binary eutectic system. More interesting, during the melting stage both PuO_2 and MgO lose oxygen.[7] Oxygen from superstoichiometric plutonium oxide, PuO_{2+x}, may also contribute to mass loss seen at high temperatures. In addition, we must consider the loss of oxygen from metal oxides and from decomposition of residual oxalate, hydroxide, superoxide, and nitrate anions.

From the previous discussion on the elemental analysis data, it appears that for sample S″, the difference between the mass LOI value (0.97%) and the supercritical-CO_2-extraction dew-point value (0.025%) is most likely due to the volatilization of inorganic, nonhydrogenous material. We will verify this assumption in the near future. Some techniques that could help us understand the chemistry that is involved at these high temperatures are x-ray diffraction for identifying crystallographic structures and calculating the arrangement of the surface atoms, auger electron spectroscopy for finding the elemental composition of the surface, secondary ion-mass spectroscopy for determining the composition of the surface and the adsorbate, x-ray fluorescence spectroscopy for elemental analysis, and computer simulations for thermochemical modeling of the high-temperature processes. After we have developed and evaluated the above conceptual and empirical models for characterizing impure plutonium oxide sample ATL27960, we will use the applicable techniques to characterize impure plutonium oxides from other sources. We expect that the behavior of these impure plutonium oxides will depend on the types and concentrations of impurities.

3.6 Future Considerations

Taking into account the new data we obtained from the thermal treatment of the impure plutonium oxide, it is clear that improved procedures and practices will be necessary both during the preparation of impure plutonium oxides and during LOI analysis. Moreover, modifications of DOE-STD-3013-96[1] may be necessary in order to cover conditions for certification of impure plutonium oxides for long-term storage.

The LOI values we presented for impure plutonium oxide are large. Each value is based on the mass change that occurred during a single heating at 950°C for 2 h. Additional calcination could verify that a constant mass has been reached. This verification is accomplished by measuring weight changes that occur when the LOI sample is heated (1) for additional time at 950°C and (2) at higher temperatures (such as 1000, 1050, and 1100°C) for 2-h periods. The <0.5–mass % LOI specified in DOE-STD-3013-96[1] might be satisfied if we extend the calcination time at 950°C or increase the calcination temperature. However, higher temperatures or longer times could cause sintering of the material as we observed it during this work. If sintering would occur and to what extent it would occur, would depend on the kind and concentration of the impurities present. Sintering could negatively impact the processing of the material. Results of LOI tests will provide essential information.

Preliminary results indicate that supercritical-CO_2 extraction and dew-point analysis provide a method for quantitative determination of water adsorbed on plutonium oxide. However, we must resolve some important issues. It seems certain that we can remove physisorbed molecular water by this extraction method, but in this study we have not addressed extracting chemisorbed water (that is, OH groups) or water of hydration using supercritical CO_2. Tests with nonnuclear materials, such as $Fe(OH)_3$, $Ca(OH)_2$, and $CuSO_4 \cdot 5H_2O$, would provide a range of thermodynamic stability for bound H_2O and would help us to assess the suitability of supercritical-CO_2 extraction for removing tenaciously held water. In addition, the discrepancies arising from apparent retention of CO_2 or formation of carbonates during extraction must be resolved before we can apply the method confidently.

Only by being rigorously consistent will it be possible to make decisions for storage involving impure oxides. Impurities already present introduce many new parameters into our equation that make it important not to ignore the above-mentioned suggestions.

4.0 CONCLUSIONS

We have established the conditions for preparing and handling pure PuO_2 for long-term storage,[2] and we have initiated studies to define the conditions for preparing and handling impure plutonium oxide for long-term storage. We have also begun investigations to see if these impure materials are storable after firing them at 950°C or higher for at least 2 h, even though they do not pass the LOI test. The following conclusions were reached in the course of this study:

- An LOI value of 4.3 mass % was determined for the “as-received” impure plutonium oxide (74.06 mass % plutonium) characterized in this study.
- The DOE requirement of <0.5-mass % LOI for storage is not satisfied after a single calcination at 600°C for 12 h and then a calcination at 950°C for 2 h; the measured LOI of the calcined oxide is 0.97%.
- Additional calcination could verify that a constant mass has been reached.
- The specific surface area of the calcined impure plutonium oxide (0.8 m^2/g) is lower than values observed for calcined pure PuO_2.
- The initial rate at which the calcined impure plutonium oxide adsorbs moisture is more than 10 times slower than that for calcined pure PuO_2.
- The equilibrium concentration of water adsorbed by the impure plutonium oxide after calcination (0.09 mg/m^2) equals that for pure PuO_2 and suggests that the materials have similar affinities for water.
- Good agreement observed between the amounts of water removed from ZrO_2 and PuO_2 standards by supercritical-CO_2 extraction and by LOI analysis indicates that the supercritical-CO_2-extraction method is suitable for quantitative determination of adsorbed water on plutonium oxide, but uncertainty exists about retention of CO_2 by the oxides.

- The amount of water (0.025 mass %) removed from the impure plutonium oxide after calcination and equilibration with air is in good agreement with the equilibrium concentration measured during adsorption tests but does not account for the LOI value of 0.97 mass %.
- The source of the large LOI observed for the "as-received" impure plutonium oxide (4.3 mass %) is not revealed by comparing results of metallic-element and carbon analyses of the initial and calcined material.
- The 0.97–mass % LOI of the calcined impure oxide is explained if 1-mass-% residual carbon is eliminated during the LOI measurement.
- The concentrations of sodium and potassium are high (4.4 mass % and 1.4 mass %, respectively) in the "as-received" impure plutonium oxide and are not significantly altered (3.9 mass % sodium and 1.2 mass % potassium) by calcination.
- Because of its uncertain origin and complex properties, the impure plutonium oxide investigated in this study is considered representative of (but not identical to) impure materials that must be stored at several sites in the DOE complex.

Additional studies are needed to identify volatile species removed during calcination, to evaluate the use of a longer calcination period for meeting the <0.5–mass % LOI requirement for storage, to define the chemical properties of the impure plutonium oxide, to fully determine the capabilities of supercritical-CO_2 extraction, and to characterize other impure plutonium oxides.

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Los Alamos
NATIONAL LABORATORY

Los Alamos, New Mexico 87545