LA-UR-97-3753-Rev. 1

Materials Identification and Surveillance

Evaluation of the Loss-on-Ignition Measurement for Storage of Legacy Plutonium-Bearing Materials

Los Alamos
NATIONAL LABORATORY

*This work was supported by US Department of Energy,
Office of Environmental Management EM-66 Nuclear Materials
Stabilization Office.*

Los Alamos National Laboratory, an affirmative action/equal opportunity employer, is operated by the University of California for the United States Department of Energy under contract W-7405-ENG-36.

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the Regents of the University of California, the United States Government nor any agency thereof, nor any of their employees make any warranty, express or implied, or assume any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product or process disclosed, or represent that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the Regents of the University of California, the United States Government or any agency thereof. Los Alamos National Laboratory strongly supports academic freedom and a researcher's right to publish; as an institution, however, the Laboratory does not endorse the viewpoint of a publication or guarantee its technical correctness.

LA-UR-97-3753 -Rev. 1
Issued: December 1997

Materials Identification and Surveillance

Evaluation of the Loss-on-Ignition Measurement for Storage of Legacy Plutonium-Bearing Materials

Andreas Toupadakis

CONTENTS

FIGURES

TABLES

MATERIALS IDENTIFICATION AND SURVEILLANCE

Evaluation of the Loss-on-Ignition Measurement for Storage of Legacy Plutonium-Bearing Materials

by

Andreas Toupadakis

ABSTRACT

The procedures for the loss-on-ignition analysis followed by Los Alamos National Laboratory, Rocky Flats Environmental Technology Site, Savannah River Site, and Hanford Babcock and Wilcox Site are evaluated and compared. The suitability of LOI analysis in certifying impure plutonium oxide materials for storage is questioned. The processing time required to bring the impure materials into conformance with DOE-STD-3013 varies greatly depending on the identity and concentration of the impurities. The supercritical carbon dioxide fluid extraction method is a promising alternative to LOI analysis for measuring moisture in powders but needs to be demonstrated.

1.0 INTRODUCTION

The need for developing advanced technologies for the stabilization and subsequent long-term storage of legacy plutonium-bearing materials has become apparent. A DOE study identifies the technical issues associated with the storage of plutonium-bearing materials and cites the need to characterize and stabilize materials prior to packaging them in sealed containers.[1]

Potential difficulties associated with plutonium oxide storage arise primarily from a combination of its chemical and physical properties. Oxides with residuals that could over-pressurize the storage container over a 50-year period are not acceptable for storage. Plutonium oxide powder may have a high specific surface area depending on preparation conditions. Such powder could adsorb up to 8% of its weight as moisture.[2] The polar molecules of water are strongly bound to the oxide surface. The storage hazard associated with adsorbed moisture is potential over-pressurization of a sealed oxide container over a prolonged period by the generation of hydrogen gas. Radiolysis of organic materials and chemical reaction of adsorbates hold a potential for generating unacceptably high pressures of non-condensable and reactive gases during storage.

The hazard posed to workers,[3,4] the public, and the environment by possible rupture of an oxide storage vessel is considered to be significant. The time dependence of pressure cannot be predicted because kinetic information for possible pressurization processes is unavailable. As a consequence, the approach that has been adopted is to control the maximum pressure by thermally desorbing reactive species from the oxide and restricting readsorption prior to sealing in the storage vessel.

Impure plutonium oxide must be prepared for long-term storage in accordance with the standard DOE-STD-3013-96,[5] “Criteria for Preparing and Packaging Plutonium Metals and Oxides for Long-Term Storage.” The standard states packaging/storage criteria. Thus, the packaged solids of plutonium oxides shall contain more than 50 mass % plutonium. The quantity of stored plutonium oxide per container should be as close as practical to, but shall not exceed, 5.00 kg (10.97 lb.). Oxides are thermally stabilized by heating in air or an oxidizing atmosphere to 950°C (1742°F) or higher for at least two hours. After calcination, the thermally stabilized oxides shall exhibit less than 0.5 mass % loss on ignition (LOI) and shall retain this characteristic through final packaging. The standard states that the LOI test shall be performed by heating a representative sample of the stabilized oxide in air to 1000°C (1832°F) or higher for at least one hour. The loss-on-ignition test is the standard procedure for confirming the thermal stabilization of plutonium oxide. It is a simple and inexpensive gravimetric method for measuring the mass fraction of volatile residues on the oxide. Unfortunately, in addition to water, the volatile fraction includes other species with significant vapor pressures at 1000°C. Consequently, the method provides a potentially inaccurate measure of the water content of oxide at the time of packaging.

Conditions and essential parameters are adequately defined for preparing, handling, and certifying high-purity PuO_2 prior to storage. A method for effectively removing water and other adsorbates has been verified and the kinetics of water adsorption by fired oxide in air are defined.[6] In contrast, the establishment of procedures for the preparation and handling of impure plutonium dioxide samples is recognized to be a challenge. The difficulties arise from the complex and variable composition of impure oxides. Compositions are often undefined, and the origin of composition changes during the calcination process is uncertain.

In the case of pure plutonium oxide, LOI analysis provides a straightforward way of certifying that little water is present, thus giving confidence for safe storage. In the case of impure plutonium oxide powders, the simultaneous presence of volatile impurities and of impurities that react with oxygen during analysis causes large uncertainty in the validity of the LOI result. A false indication of a small LOI may result from fortuitous equality of mass loss by volatilization and mass gain by oxidation.

2.0 BACKGROUND

In the next four sections the procedures used at different DOE sites for the LOI measurement are presented. Table I summarizes the conditions and materials used at different DOE sites for the LOI measurement.

2.1 Los Alamos LOI Procedure

The detailed step-by-step procedure for performing LOI measurements at Los Alamos is found in the Safe Operating Procedure (SOP) CST15-SOP-600-R00, “Materials Characterization of Radioactive Oxides”. The loss-on-ignition analyses are conducted by CST-15 personnel at TA-55. The technique was qualified prior to use by analyzing a series of plutonium oxide (PuO_2) samples and establishing a statistical base for the technique. The purpose of the study was not to establish an LOI baseline or standard deviation for all oxides analyzed but to qualify the CST-15 procedure.[7]

Table I. Conditions and Materials Used at Different DOE Sites for the LOI Measurement.

Conditions and Materials	Los Alamos National Laboratory	Rocky Flats Environmental Technology Site	Savannah River Technology Center	Babcock & Wilcox Hanford Site
Sample (g)	5-10	< 20	0.99 - 1.01	4-6
Time (h)	2	1	1	2
Temperature (°C)	1000[(a)]	1000	700	1000
Temperature profile	Fig. 1	(b)	(b)	(b)
Calcination crucibles	Fused silica	(b)	Stainless steel	Platinum
LOI crucibles	Platinum or Alumina	Platinum	Porcelain	Platinum
Spoon used	Stainless steel	(b)	Stainless steel	Stainless steel
Preconditioning of furnace	None	(b)	Obtain stable 700°C for 30 min.	None
Preconditioning of crucibles	Ultrasonic cleaning, next heating at 200°C, 1h	(b)	Heating (1h, 700°C) cool in desiccator (1h)	1000°C, 2h

(a) In the past, various temperatures have been used, see LA-12999-MS, Fig. 2.

(b) Information is unavailable.

A summary of the procedure follows: The LOI crucibles used in the LANL procedure are cleaned using an ultrasonic cleaner, and after excess water is wiped off, they are dried in a muffle furnace at 200°C for about 1 h. Crucibles are stored in a desiccator under vacuum prior to use. The powder to be analyzed is introduced to the clean crucibles with lids. Platinum crucibles are used for analysis of samples with plutonium content $\geq$ 80%; otherwise they are made of alumina. Weighed samples (5-10 g) are split and placed in two different crucibles, which are covered and placed in the furnace. The loss-on-ignition run is initiated, and when the heating cycle is completed, the furnace maintains a 200°C waiting period until the samples are removed. Table II and Fig. 1 show a typical temperature profile during the run. The samples are heated isothermally at 1000°C for 2 h. The crucibles are removed from the muffle furnace and placed in a desiccator under argon for 15 min until they cool. The cooled loaded crucibles are weighed again as quickly as possible, and an average weight loss is calculated.

Table II. Typical Temperature Profile During a Los Alamos LOI Analysis.

Time (h)	Temperature (°C)	Time (h)	Temperature (°C)
0	25	10	725
1	200	11	675
2	500	12	600
3	775	13	525
4	1000	14	460
5	1000	15	400
6	1000	16	325
7	925	17	225
8	860	18	200
9	800		

2.2 Rocky Flats LOI Procedure

The procedure for performing LOI measurements at Rocky Flats Environmental Technology Site is found in the document L-4195-A, “Loss on Ignition (LOI) Measurement.” In that document, it is stated that loss-on-ignition (LOI) is a measurement used to determine the amount of volatile material present in plutonium dioxide (PuO_2). The

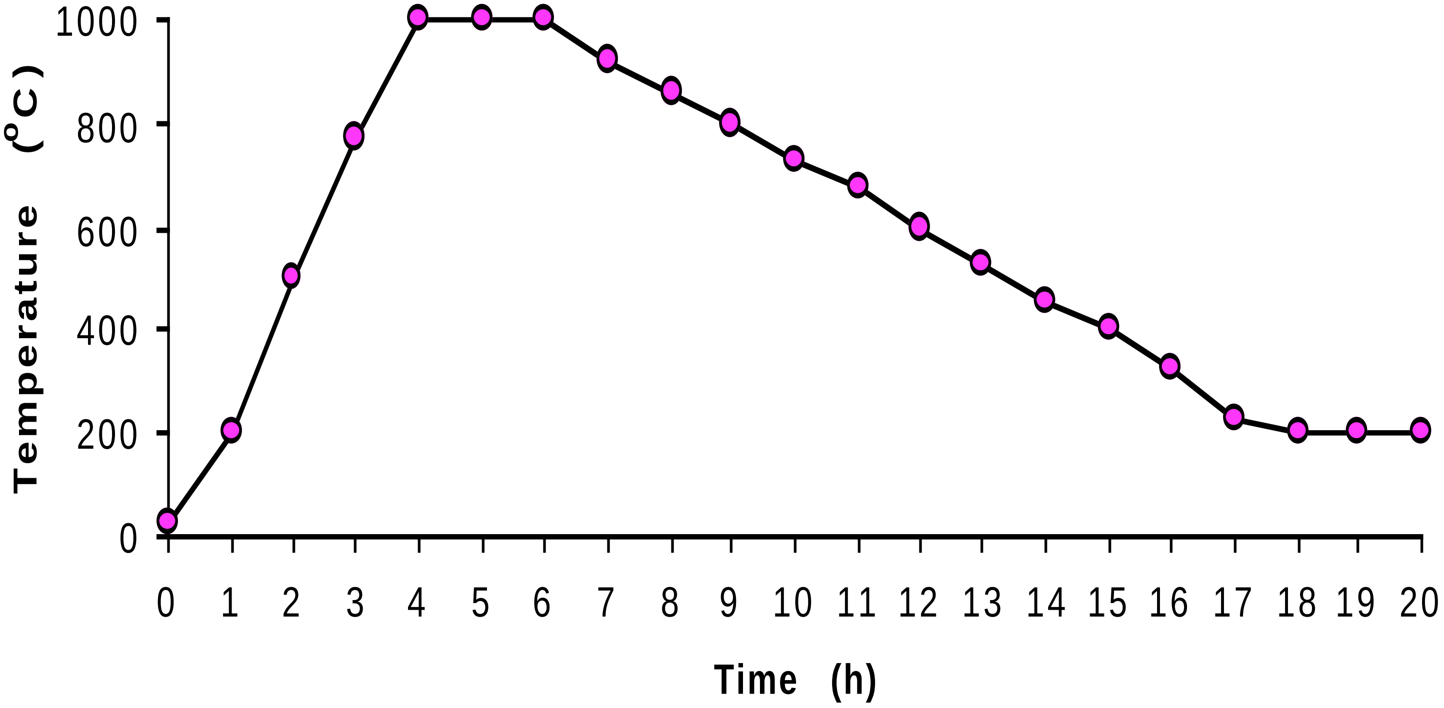

Fig. 1. Typical temperature profile during LOI analysis.

weight loss can come from several sources. The most important are the desorption of water, adsorbed gases, and decomposition of residual peroxide or oxalate intermediates in plutonium oxide processing. The weight loss may also occur from the volatilization of impurities (inorganic salts and oxides), which are reflected in the LOI but would not result in pressurization during storage. In practice it is assumed that the total weight loss is due to adsorbed water. It is not easy to know how much of this total weight loss is due to the volatile impurities other than water.

In summary, the procedure is as follows. A sample of plutonium dioxide not to exceed 20 g is heated isothermally in a platinum crucible at 1000°C for 1 h in a muffle furnace. When the sample cools to 200°C, it is placed in a desiccator and the desiccator is purged with dry argon, helium, or nitrogen gas or evacuated with a small vacuum pump. The samples stay in the desiccator for several hours to ensure that they reach room temperature. Finally, the weight change is determined by taking the difference between the initial weight at room temperature and the final weight at room temperature after the LOI run.

$$LOI \text{ as } \% = [(\text{initial weight} - \text{final weight}) / (\text{initial weight})]100$$

2.3 Savannah River LOI Procedure

The procedure for performing LOI measurements at Savannah River Technology Center is found in the document L3.11-10004, “Weight Loss: Oxide Samples Gravimetric.” In that document, it is stated that the precision of the method is (1) proportional to the magnitude of the weight loss, precision affected by the moisture content of the sample, and (2) a function of the thermal power attributable to specific radioisotopes. In this particular procedure, emphasis is given to the precondition of crucibles and the furnace. However, details of the procedure are not given and the temperature used for the LOI measurement is not mentioned.

Every new crucible used is preconditioned by heating in a muffle furnace at 700°C for 1 h, and cooling in a Desi-Cooler™ for 1 h. It is emphasized that preconditioned crucibles not used within the preceding 24-h period must be refired for 20 min and cooled for 20 min. The balance is calibrated with certified traceable standards before use. The samples are transferred from the sample vial to the porcelain crucible using a stainless steel or ceramic spoon. The crucibles are covered with porcelain covers. The furnace is preheated for 30 min to obtain a stable 700°C temperature.

2.4 Hanford LOI Procedure

The detailed step-by-step procedure for performing LOI measurements at Hanford site is found in the document ZA-510-332 Rev/Mod D-1, "Loss-on-Ignition of Plutonium Bearing Materials." This method was adopted for measuring weight loss of any solid material. Muffle furnace used may be programmed for heating at any temperature up to 1000°C for several hours. A controlled rate of heating allows temperature to increase at a constant rate until desired setting is reached. Timers maintain heat for each desired temperature plateau. In that document, it is stated that this physical test (unlike a chemical analysis) requires only 3 parameters:

- accurate weighing
- sufficiently maintained temperature control
- humidity control

A standard is used mainly to provide a check against improper weighing. Temperature control is dependent on rate of increase and time allowed at each temperature plateau. A glovebox with dry air, having a dew point of less than -23°C (-10°F), or a desiccator is available to cool samples. It is emphasized that balance housing, balance pan, desiccator plate, and sample pans must be clean, and if pan is new, then it must be heated to constant weight at 1000°C prior to use. The pans used are platinum, and the analytical balance is capable of measuring to 0.0001 g. The furnace is muffle type with controller and timers. The desiccator is large enough to hold five sample pans but less than 1.5 liters. The reagents used are plutonium oxide standard (MSDS not available), characterized for weight loss by heating at least four samples, each of 5 g for two hours at 450°C (or at temperature specified on analytical request), and desiccant, indicating, anhydrous calcium sulfate (MSDS 1091). Pans are allowed to cool in desiccator for at least one hour. A standard PuO_2 sample is used mainly to provide a check against weighing errors. The heating cycle consists of three temperatures: 130°C, T°C, and 30°C (T is the temperature specified on analytical request). First temperature is held for 30 min to evaporate any moisture present. After about 30 min, controller programs furnace to an operating temperature which may be 450°C to 1000°C for 2 h. Then the cycle goes to a cooling period, but temperature of furnace may still be read. Heating period is more than enough for quantitative sample weight loss. A complete cycle (30°C $\rightarrow$ 130°C $\rightarrow$ T°C $\rightarrow$ 200°C) takes approximately 5 h at 1000°C.

3.0 IMPACT OF DIFFERENT FACTORS ON LOI

3.1 Impact of the Post-Heating and Cool-Down Procedures

A cursory review of the literature has shown that questions regarding the effect of the post-heating and cool-down procedures on the LOI have not been answered. The impact of the cool-down procedure on LOI has been investigated, though not extensively.[8] A series of LOI runs was conducted in this regard. Each sample was processed for LOI determination according to the LOI procedure. The only deviation from the procedure was in the cool-down phase, specifically when the samples were placed in the desiccator as described in Table III.

Table III. Different Cool-Down Procedures.

Sample	Cool-Down Procedure
A	30 min in desiccator under about 28 L/min argon flow.
B	30 min in desiccator under 24-in. water vacuum.
C	30 min in desiccator under static atmosphere of argon.
D	30 min in glovebox atmosphere.

The cool-down procedures were selected to provide a dramatic difference in technique in an effort to magnify the impact of the cool-down procedure on the LOI. The study indicated that the cool-down procedure does impact the overall LOI. However, this impact is small and does not appear to significantly impact the LOI results. In any case, the obtained results suggested several recommendations.

i. Cooling of the sample under vacuum should probably be avoided because of the large variability associated with this technique.
ii. The cooling of the sample in the glovebox atmosphere should not be used because of the potential susceptibility of the sample to perturbations in the glovebox atmosphere, such as humidity.
iii. The LOI samples should be cooled in a desiccator, using a low flow of argon (about 28 L/min) for 30 min prior to final weight determination.

While deviation in the cool-down procedure, and specifically when the samples were placed in the desiccator, did not show a significant impact on the LOI value for pure PuO_2, deviation in the cool-down rate when the samples are brought from 1000^{o}C to 200^{o}C is expected to show a significant impact on the LOI value for impure oxide samples. Similar significant impact is also expected when the samples are brought from room temperature to 1000^{o}C. Plutonium oxide samples for example containing substantial amounts of volatile impurities such as MoO_3 are expected to give large LOI values. These volatile materials could vaporize at temperatures well below 1000^{o}C, thus the slope of the post-heating and cool-down temperature profile becomes an important determining factor for the LOI value.

3.2 Impact of Calcination and Impurities

As shown by the analytical results for samples E-H in Fig. 2, calcination temperature below 950°C is an important factor in the observed LOI values for this relatively pure dioxide (87.9% Pu). The oxide must be fired at 950°C for about two hours in order to fully remove volatile residues. Results in Fig. 2 also demonstrate that 950°C is necessary for a valid LOI measurement. LOI values are unaltered by heating at higher temperatures, but use of a 1000°C firing temperature is advisable to ensure that all residues are removed.

The effect of calcination temperature on the LOI value of relatively pure dioxide is also apparent in the results of studies by Karraker to determine a satisfactory procedure for calcining Pu(III) oxalate.[9] The starting material in these studies was determined to be $Pu_2(C_2O_4)_3 \cdot 9H_2O$. As shown by the results in Table IV, LOI for the product decreases steadily with increasing calcination temperature. At 750°C, a firing time of three hours is necessary to meet the 0.5% LOI criterion for PuO_2 storage.

The amount of volatile residue measured by LOI analysis of an impure oxide after calcination at 950°C for 2 hours may exceed the 0.5 % criterion. As shown in Fig. 3, calcination of an impure oxide (77.4% Pu, 3.9% Na, 1.2% K, 1.0% C, sample ATL27960)[10] gave an LOI of 0.97%. Figure 4 shows that additional calcination of the impure oxide at 950°C for a total time of ten hours brought the oxide into compliance with the standard. A combined LOI of 3.6% observed during calcination at 950°C (see Fig. 3 and 4) suggests that a longer calcination period may be required for stabilizing impure oxide than for stabilizing pure PuO_2 and that volatilization of non-hydrogenous species is occurring. Investigations are under way to identify volatile products of calcination.

Inconsistent mass-loss behavior is seen in Fig. 5 by comparing mass changes measured during calcination with results obtained by LOI analysis. The oxide mass decreased by 0.6% during the initial two-hour calcination and LOI analysis for the X_2 product showed a loss of 1.3%. However, the mass of the X_2 oxide increased by 1.1% during the subsequent four-hour calcination. LOI analysis of the X_3 product obtained after firing

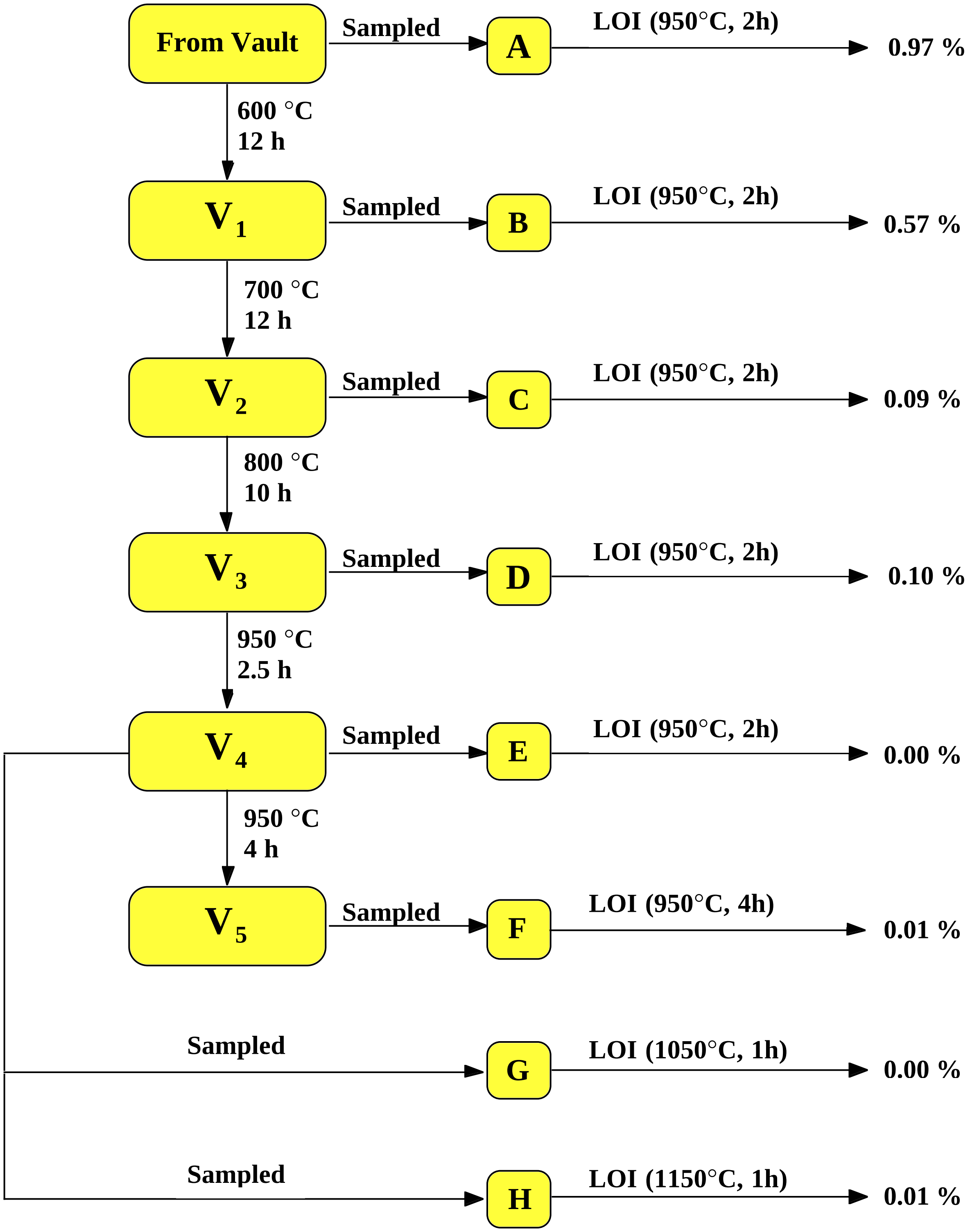

Fig. 2. Characterization of pure plutonium dioxide item MSTPPB1.

Table IV. Impact of Calcination Temperature on the LOI Value for the Pure $Pu_2(C_2O_4)_3 \cdot 9H_2O$ Sample[a].

Calcination Temperature (ºC)	Calcination Time (hr)	Mass Before LOI (g)	Mass After LOI (g)	Mass LOI (%)
600	2	1.871	1.857	0.75
650	2	2.115	2.105	0.52
700	2	2.004	1.994	0.50
750	3	1.980	1.974	0.30
800	2	2.131	2.126	0.23

[a] Error is estimated to be ±0.10%

[b] LOI test (900ºC for 1h).

showed a loss of 1.1%. Though these observations imply that the calcination and LOI processes are different, further analysis of the results also suggests a correlation between mass change and the length of the heating period. Heating for two hours by both methods produced a loss on the order of 1%; calcination for four hours consistently resulted in a mass gain of about 1%.

The observed time dependence of mass change is consistent with occurrence of two competing reactions occurring at different rates. A possible set of mass change-time curves that account for the observed results is presented in Fig. 6. One curve is characterized by a steady mass gain and the other by a rapid and finite mass loss. As defined by the difference in the two curves, the net mass-change curve in Fig. 6 accounts for the observed values of -1% and 1% at heating times of 2 and 4 h, respectively.

The hypothetical curves in Fig. 6 are consistent with plausible chemical reactions of impurities in the ATL27960 oxide. Stable ternary oxides reported for the Na-Pu-O system include Na_6PuO_6, Na_4PuO_5, and Na_3PuO_4, which are prepared by high temperature reaction of PuO_2 with stoichiometric amounts of Na_2O or Na_2CO_3 (thermally decomposed to $Na_2O + CO_2$) in the presence of oxygen.[11] Plutonium is present in these compounds as Pu(V) or Pu(VI). Idealized reactions for formation of Pu(VI) compounds from sodium oxide, plutonium dioxide and oxygen at 400-500°C are given by Equations 1 and 2:

$$3\ Na_2O + PuO_2 + 1/2\ O_2 \rightarrow Na_6PuO_6. \qquad (1)$$

$$2\ Na_6PuO_6 + PuO_2 + 1/2\ O_2 \rightarrow 3\ Na_4PuO_5. \qquad (2)$$

LOI Conditions: 950°C, 4h

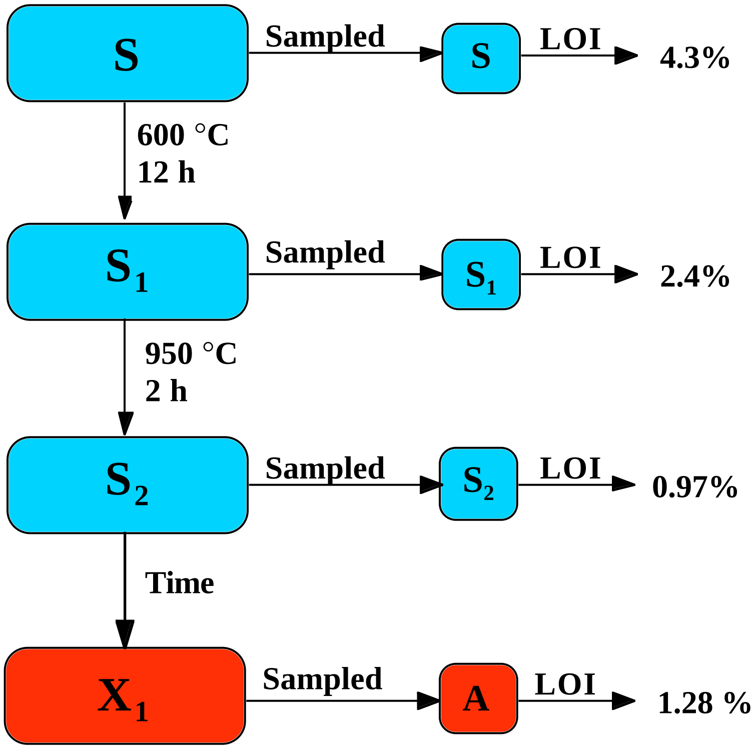

Fig. 3. LOI results of impure plutonium dioxide item ATL27960.

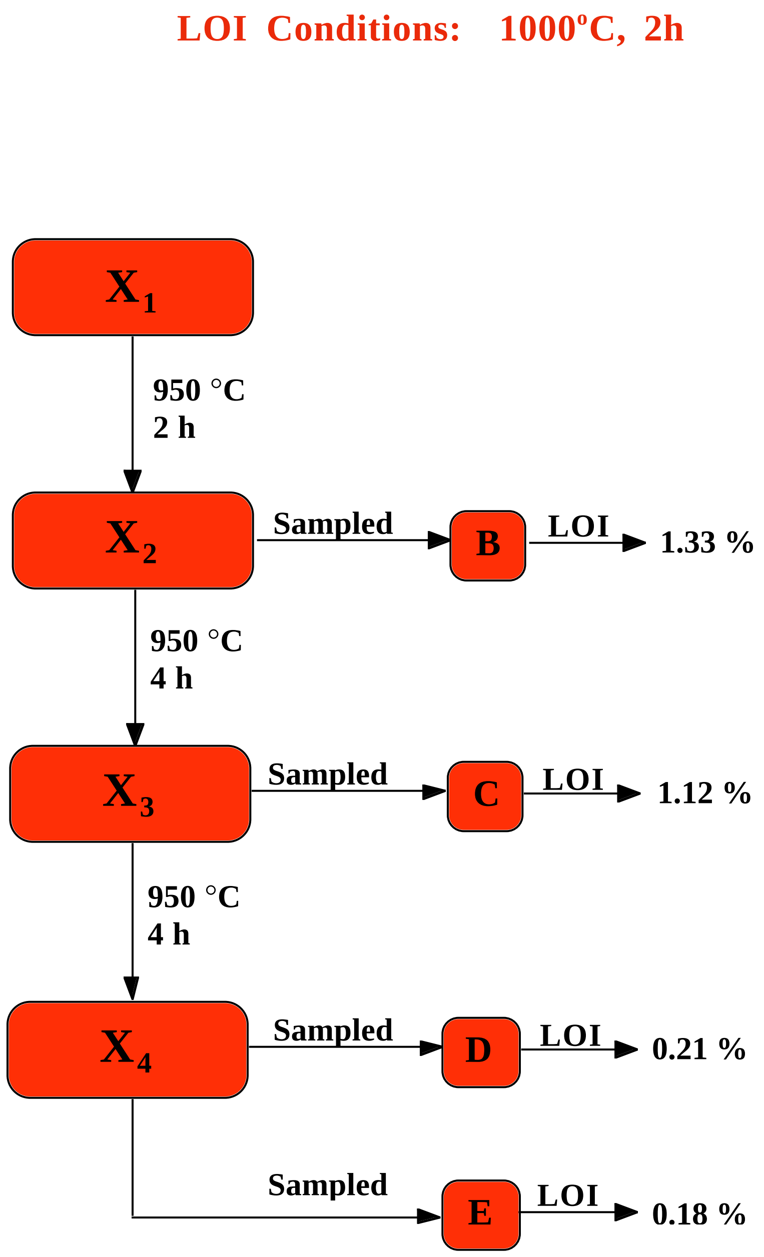

Fig. 4. LOI results after further calcination of impure plutonium dioxide item ATL27960.

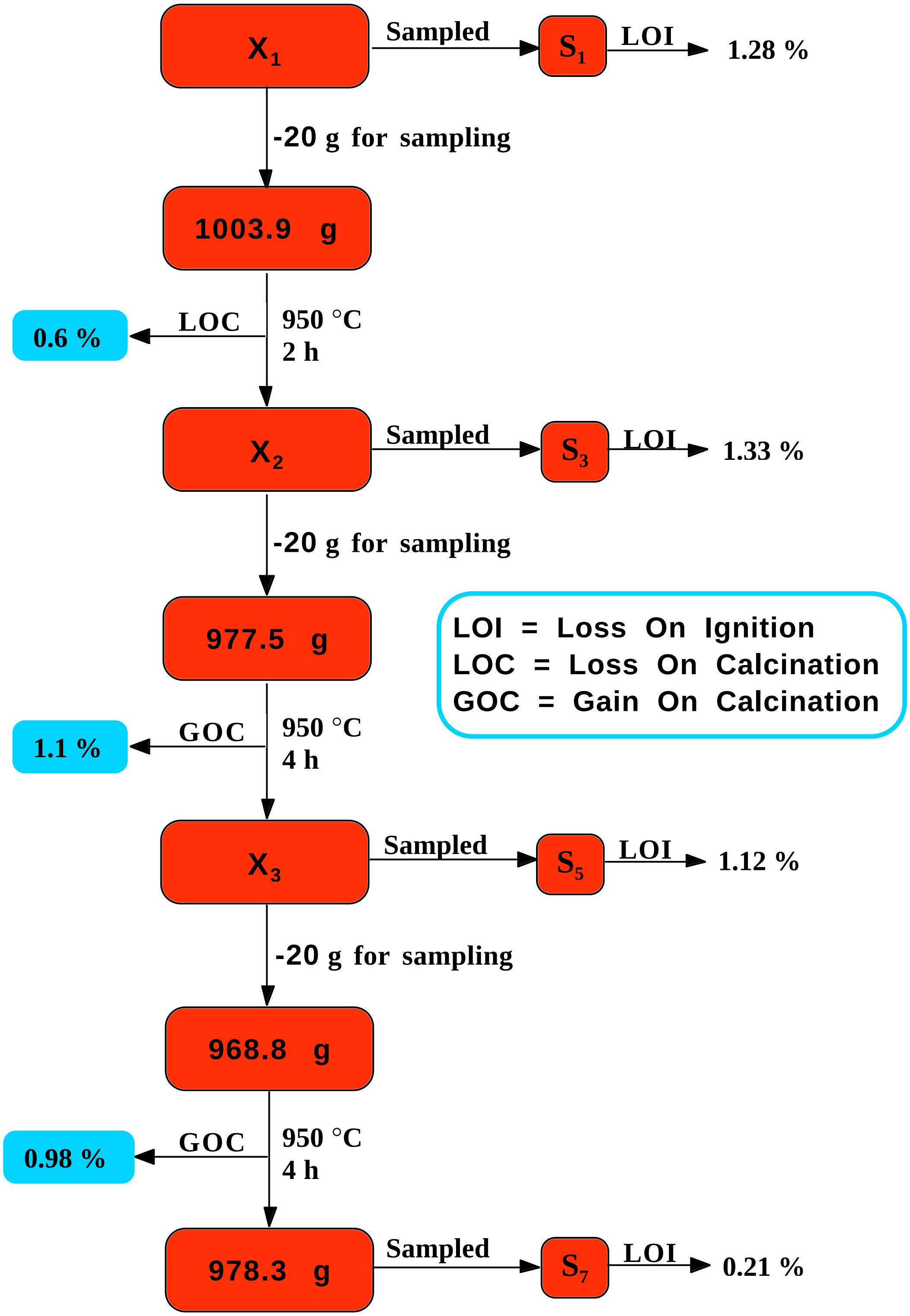

Fig. 5. LOI and calcination results after further calcination of impure plutonium dioxide item ATL27960.

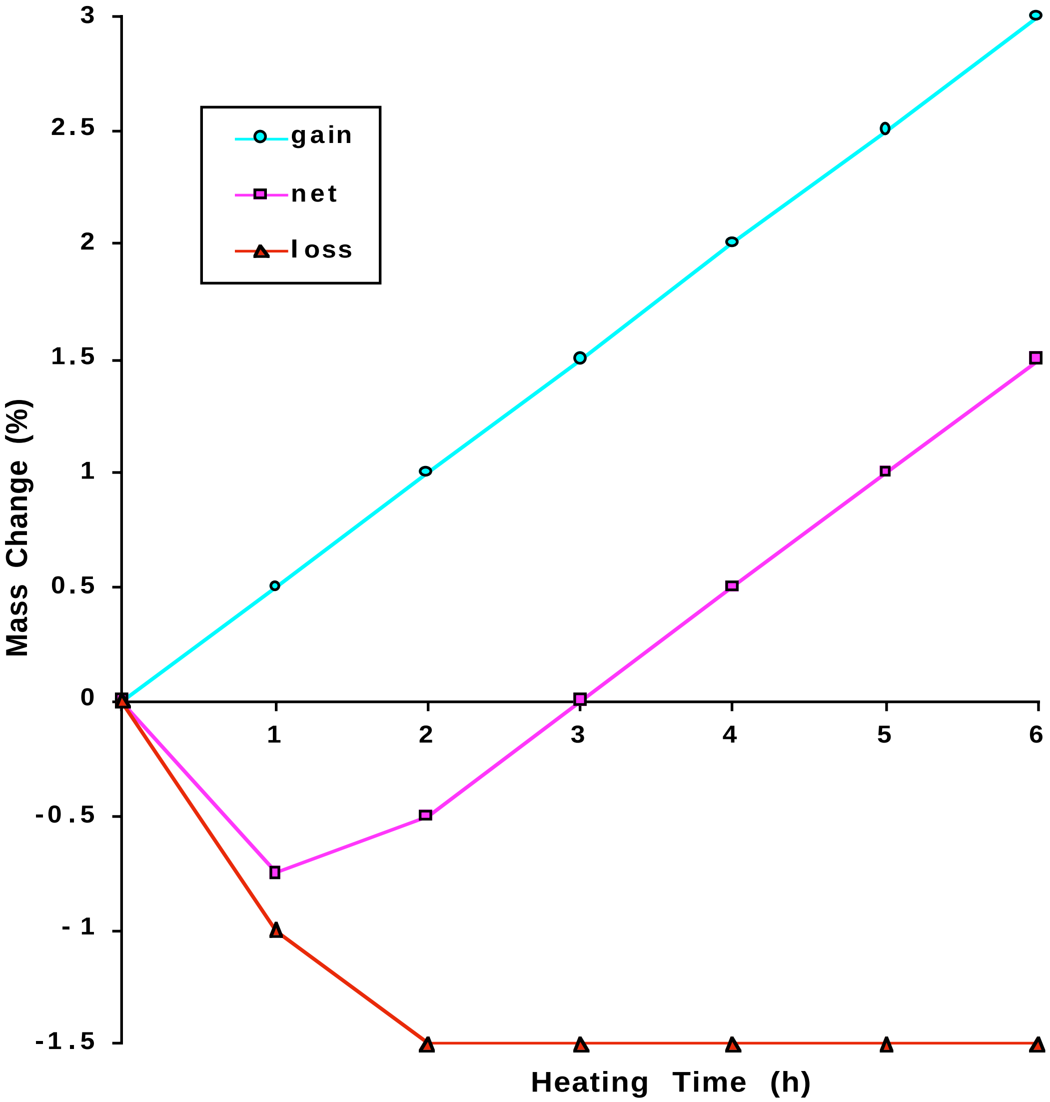

Fig. 6. Hypothetical curves of mass change as a function of time.

Studies of the Na-U-O system, show that additional compounds (Na_2UO_4 and $Na_2U_2O_7$) of U(VI) exist.[12-14] Reactions describing the formation of the corresponding compounds of Pu follow:

$$Na_4PuO_5 + PuO_2 + 1/2\ O_2 \rightarrow 2\ Na_2PuO_4. \qquad (3)$$

$$2\ Na_2PuO_4 + 2\ PuO_2 + O_2 \rightarrow 2\ Na_2Pu_2O_7. \qquad (4)$$

The net reaction defined by Equations 1-4 is given by Equation 5:

$$2\ Na_2O + 4\ PuO_2 + 2\ O_2 \rightarrow 2\ Na_2Pu_2O_7. \qquad (5)$$

At the 0.5:1 molar ratio of Na to Pu in ATL27960, 50% transformation of available plutonium to $Na_2Pu_2O_7$ is possible with a total mass increase of about 3%.

Ternary oxides of Pu(VI) are unstable relative to compounds of Pu(V) at temperatures encountered during calcination or LOI analysis.[11] Formation of Na_3PuO_4, the stable phase above 900°C, is described by Equation 6:

$$3\ Na_2O + 2\ PuO_2 + 1/2\ O_2 \rightarrow 2\ Na_3PuO_4. \qquad (6)$$

As indicated by the example in Equation 7, Pu(VI) oxides are expected to form as calcination products cool in air:

$$4\ Na_3PuO_4 + 1/2\ O_2 \rightarrow 3\ Na_4PuO_5 + PuO_2 \qquad (7)$$

Equations 1-7 suggest a possible mechanism for mass change-time curves like those in Fig. 6. A progressive mass increase accompanies the reaction of Na_2O with PuO_2 and O_2 to form the ternary oxide of Pu(V) according to Equation 6. Though the oxides of Pu(VI) are unstable in air at 950-1000°C, they form as calcined material cools to room temperature in air. Heating of calcined oxide during LOI analysis produces a rapid initial loss due to decomposition of high-composition oxide. Over a two-hour period, this loss is large compared to the mass gain associated with ternary oxide formation and a net mass loss is observed. If the material is heated for hours, net mass increase results because the process dominated by the continuous mass gain accompanying ternary oxide formation.

Though the proposed reactions described by Equations 1-7 cannot be verified, that type of complex chemical process must occur to cause the erratic behavior observed for the impure oxide during calcination and LOI analysis. As shown in Fig. 4, the LOI requirement is ultimately satisfied after extended firing, but confidence is diminished because the acceptable result may result from fortuitous interaction of competing processes.

Another opportunity for studying the impact of calcination on the LOI value is provided by the impure MOX ($U_yPu_{1-y}O_{2+x}$) sample PUUOXBC05.[15] In contrast to the impure oxide ATL27960, this material contained uranium (17.8% U, 43.8% Pu, 8.1% O at the

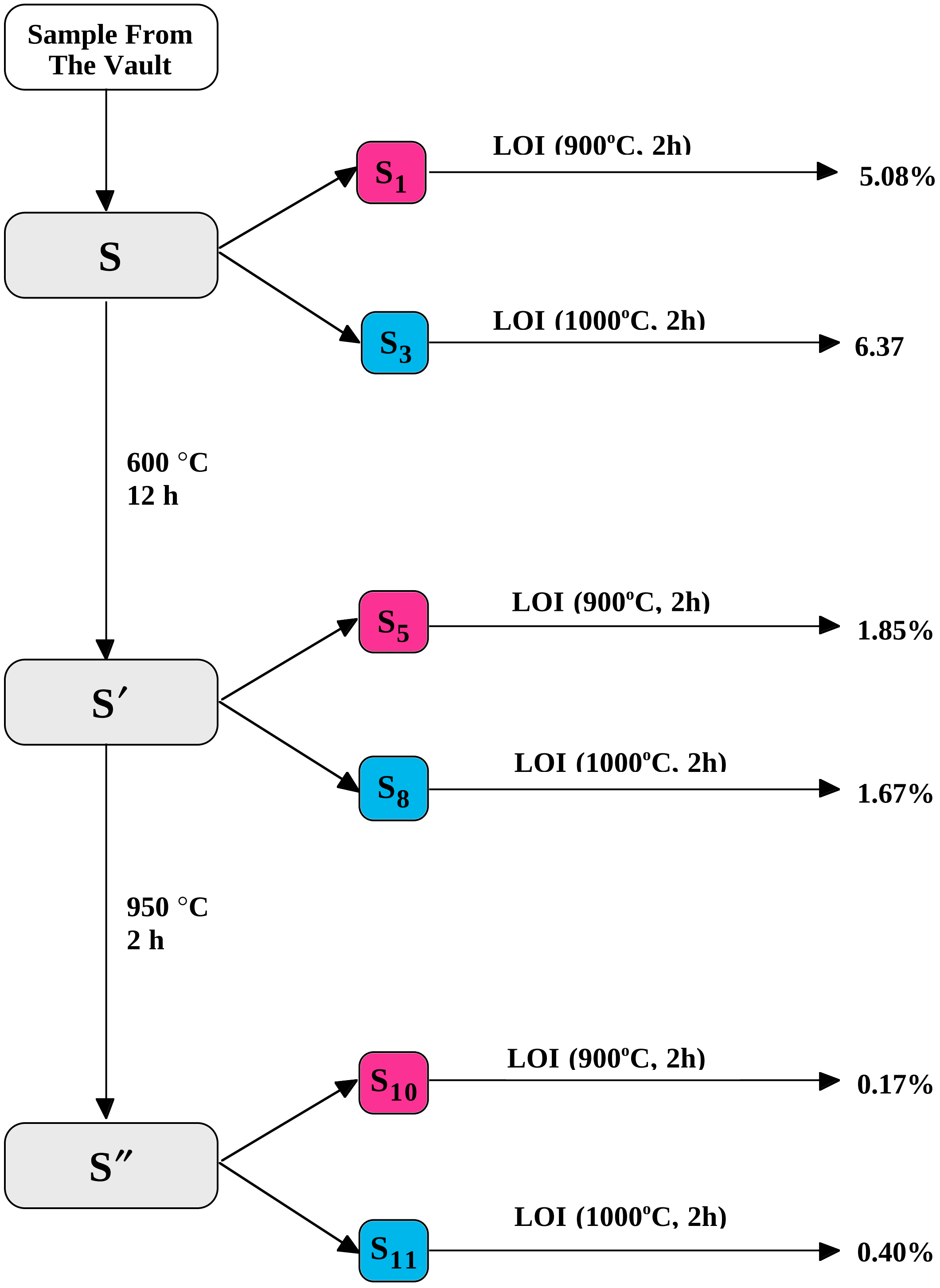

Fig. 7. Impact of calcination and LOI conditions on the LOI value for the impure MOX sample PUUOXBC05 and flow diagram for calcination process.

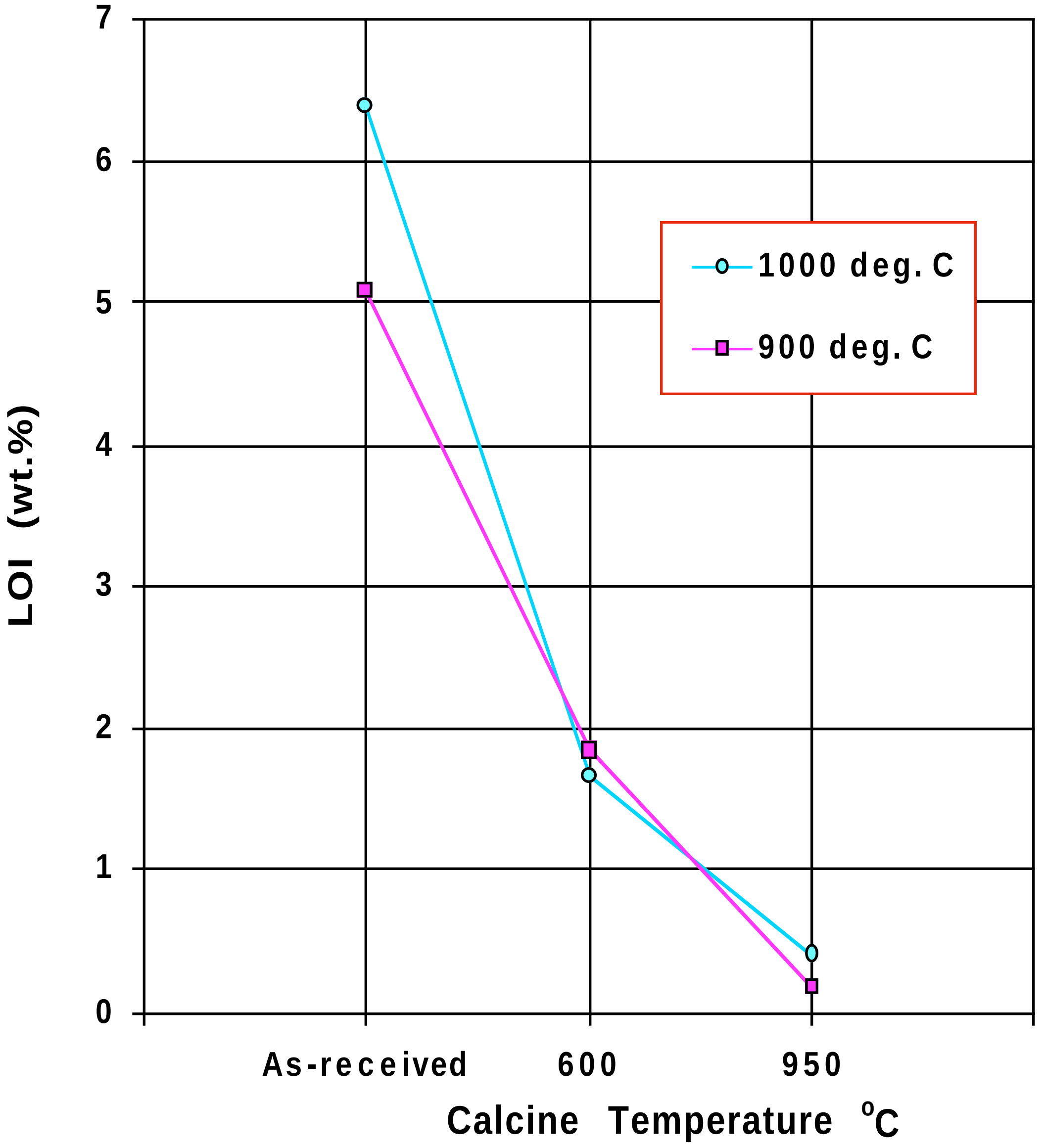

Fig. 8. Impact of calcination temperature and LOI temperature on the LOI value for the impure MOX sample PUUOXBC05.

$(U,Pu)O_2$ composition, and 7.7% impurities). The LOI criterion was met without the need for a long calcination period. As seen in Fig. 7 and 8, erratic mass changes were not observed during firing. Formation of a higher stoichiometry oxide is anticipated because U(V) and U(VI) are stable oxidation states of uranium in air. As determined by X-ray diffraction measurements, contraction of the mixed-oxide lattice during firing indicates that a substantial fraction of the uranium was oxidized to U(V) with an accompanying mass increase of 0.7%. Though compliant with the storage standard, the LOI result is clouded by uncertainty.

Karraker has also performed scoping studies to define a satisfactory calcination procedure for MOX. The test material was a pure mixed oxide (65% UO_2 and 35% PuO_2).[16] LOI analysis showed a zero mass loss after firing and suggested that the method was suitable for MOX stabilization. A different conclusion was reached by Haschke et al. in a reevaluation of the MOX study by Karraker.[17] As indicated in Table V, LOI analysis of the as-received MOX showed a mass gain of 0.68%. X-Ray diffraction data showed that the single-phase, as-received oxide was partially converted to U_3O_8 during calcination at 750°C and the observation of a positive LOI was attributed to partial oxidation of the sample during analysis. X-Ray analysis of the product after LOI analysis showed an increase in the relative intensities of the U_3O_8 reflections, an indication that additional oxidation of the sample had occurred during analysis. This observation suggest that the zero LOI value observed after calcination may have resulted from the fortuitous equality of mass-loss and mass-gain processes.

In contrast to results of LOI studies on pure PuO_2, LOI results for impure oxides are unpredictable and uncertain. In one case (Fig. 5), the LOI requirement was met only after extended calcination. In other instances (Fig. 7 and Table V), the 0.5% requirement was satisfied after one or two calcination steps. In all cases, uncertainties exist regarding the validity of the LOI results. Major difficulties with LOI analysis are the inability to determine if the observed LOI is the net result of competing processes involving mass loss and mass gain and to determine if hydrogen-containing species are volatilized during the mass-loss process. Additional studies are needed to establish the suitability of the LOI method for certifying the compliance of impure oxides with DOE-STD-3013.

An additional impact of impurities is seen in their alteration of materials compatibility. The fused-silica calcination boats used at Los Alamos were chosen because of their availability and low cost. Although no interaction is evident between SiO_2 and pure PuO_2, reaction is observed between the boats and impure oxides containing Na and K impurities. After calcination, the impure oxide in contact with the boat adhered to the surface and spectroscopic analysis of the product showed increase levels of Si.[10] This behavior is attributed to the well-known reaction of Na_2O with SiO_2 to form soda glass, a material with a noticeably lower softening point (1000-1100°C) than that (1400-1500°C) of silica. However, such behavior does not alter the storability of the material.

Table V. LOI Results for Pure MOX[a,b].

Sample	Mass Before LOI (g)	Mass After LOI (g)	Mass Change (g)	Mass LOI (%)
MOX before calcination	1.172	1.180	+ 0.008	+ 0.68
MOX after calcination	1.468	1.468	0	0

[a] This sample analyzed 35 wt. % PuO_2 by alpha count/PHA; 65 wt. % UO_2 by difference.
[b] Calcination (750ºC for 3h); LOI test (900ºC for 1h).

3.3 Impact of LOI Conditions

Conditions of the LOI analysis are important determinants of the LOI values measured for impure oxides. Evaluation of recent data for calcination and LOI analysis suggests that modification of procedures may be required and that increased consistency in their execution is needed. Incorporation of changes to the DOE standard might be necessary in order to adequately define conditions for certifying impure plutonium oxides for long-term storage. This is demonstrated by considering two scenarios for LOI analysis of the same impure oxide containing a sizable fraction of material that is volatile at 700-1000°C. During the first analysis, a sample of calcined oxide is fired at 1000°C for one hour. During the second LOI analysis, an identical sample is fired at 1100°C for two hours. Both procedures are consistent with the DOE standard which states that “the LOI test shall be based on heating of a representative sample of the stabilized oxide in air to 1000°C or higher for at least one hour.” Based on results of the study on impure oxide ATL27960, the first sample might be expected to pass the LOI test, whereas the second might be expected to fail. An example relevant to this discussion is provided by observations for PUUOXBC05 showing that a 100°C increase in the LOI temperature (900 to 1000°C) during a two-hour firing increased the LOI of S″ (Fig. 7) from 0.17 to 0.40 mass %.

The temperature profile of calcination is an important concern. It is not only within the horizontal part of the temperature profile that the experimentalist will have to be consistent. Consistency will have to be observed in both non-horizontal regions of the temperature profile, i.e. at the positive and negative slope region. The critical temperature increment will be approximately between 700°C and 1000°C. Impure oxides with high concentrations of inorganic volatile impurities in this temperature region will exhibit large weight loss if a temperature profile with a small slope is followed. In conclusion, it should not be a surprise to see such samples not pass the LOI test if the temperature profile is such that the temperature change from about 700°C to 1000°C to 700°C takes place at a longer time than usual.

Calcination procedures must also be consistent. Oxides with high concentrations of volatile materials will most likely pass the LOI test if they are calcined for a long time at a high temperature. Oxides treated for short times at low temperatures are less likely qualify for long-term storage.

Essential elements of calcination and LOI procedures are the definition and maintenance of conditions necessary to stabilize and analyze the material. Attainment of stabilization rests on experimental development and verification of quality-assured procedures. Unfortunately, stabilization is sensitive to the nature of the impurity and a single procedure is most likely not applicable to all impure oxides. Adequate R&D must be devoted to development of each procedure. In part, these difficulties stem from a fundamental weakness of the LOI method: volatile species are not identified and the observed mass loss is assumed to result solely from desorption of water. However, the strength of this assumption is its provision of a highly conservative basis for safe extended storage of plutonium oxides. Expansion of the DOE standard to include other certification methods is necessary.

4.0 Other Methods

4.1 Thermal Desorption Mass Spectrometry

Thermal desorption mass spectrometry (TDMS) is a definitive method for identifying non-condensable species produced by thermal decomposition of solid materials in vacuum. During a TDMS measurement, a sample is placed in the reaction vessel of a sealed vacuum system connected to a mass spectrometer. A selected mass range is periodically swept to analyze gaseous products formed as the reactor is heated. Though the volatile species formed during TDMS analysis differ from those produced during calcination of a material in air, the evolution of hydrogen and hydrogen-containing species is detected and the relative amounts of all volatile impurities are determined as a function of temperature. Condensable products, which deposit in cooler regions of the reactor, may be sampled and analyzed by other methods.

The value of TDMS is demonstrated by results obtained for the impure MOX sample (PUUOXBC05).[15] Water was the primary gaseous product formed as the oxide was heated to 950°C over an eight-hour period. The largest amount of water was evolved between 175 and 340°C; its relative abundance was approximately 150 times that of other gaseous products. A minimum in the gas evolution rate between 350 and 450°C was followed by a second release that continued at a constant rate up 950°C. The major products were water and carbon dioxide, which appeared in a 1:1 ratio at a five-fold to ten-fold greater rate than other species (carbon monoxide, methane, ethane oxygen , hydrogen).

In addition to use in identifying the thermal decomposition products of impure oxides, the TDMS method holds potential for complementing the LOI results. Identification of the volatile species formed during TDMS analysis of impure oxide after calcination would help in determining if hydrogen-containing residues remained. If properly used, these data could assist in certifying the adequacy of calcination procedures for impure oxides.

4.2 Supercritical Carbon Dioxide Extraction

Supercritical fluid extraction (SFE) of water from inorganic solids with CO_2 is a potential alternative method for removing and quantifying the water content of impure oxides. Carbon dioxide is abundant, inexpensive and environmentally compatible. Water extracted from solid materials by an SFE stream is quantitatively determined by measuring the humidity of the expanded CO_2.

Results obtained by using CO_2 extraction to determine the amount of water adsorbed on pure ZrO_2 and PuO_2 standards are compared with LOI data.[10,18] The results are in good agreement. However, a similar comparative study with the impure oxide ATL27960 shows that the amount of water removed by SFE (0.025%) is much less than the LOI (0.97%), suggesting that calcination is effective in removing water from impure oxides or that the extraction method is ineffective or residual carbon with other impurities were eliminated during the LOI measurement. If CO_2 extraction is a quantitative method for determining the water content of solids, it would be valuable in certifying calcination processes for various types of impure oxides.

Studies to investigate the capabilities of CO_2 extraction for removing bulk water from oxides, hydroxides, and crystalline hydrates have been initiated.[19] SFE removes H_2O from $Ca(OH)_2$ and produces $CaCO_3$. Results for crystalline hydrates show that some materials can be fully dehydrated, while others are only partially dehydrated, and still others are unaffected. For example, studies with $CaSO_4{\cdot}2H_2O$ show that waters of crystallization are not extracted by SFE; only adsorbed water is removed. Similar extraction experiments with $MgSO_4{\cdot}7H_2O$ show that five waters of crystallization are removed.

The effectiveness of CO_2 extraction as a general quantitative method for dehydration from solids seems doubtful. Extraction of water from alkali and alkaline earth hydroxides is energetically favorable because stable carbonates form during the process. Water molecules of crystallization are extracted only if they are rather weakly bound; i.e., are thermally removed below 150°C. The free energy of solution of H_2O in supercritical CO_2 is apparently insufficient to remove strongly bound waters of crystallization. Thermodynamic data for $Pu(OH)_4$ and PuO_2 show that the tetrahydroxide is unstable ($\Delta G° = -10$ kcal/mol) relative to the dioxide and water at room temperature[20] and SFE may prove effective. This uncertainty can be eliminated by experiments in which $Pu(OH)_4$ is extracted after precipitation from aqueous solution and vacuum drying at room temperature. Effectiveness of the extraction could be determined by LOI, TGA (thermogravimetric analysis) and TDMS analyses of the solid product.

5.0 Conclusions

The primary objective of this report is to compare the LOI procedures used at different DOE sites and identify factors that may alter the results. The inadequacies of LOI as a method of certifying impure oxides for storage have also been addressed and status of possible alternative methods has been reviewed. A summary of conclusions follows:

- Different DOE sites emphasize different parts of the LOI procedure in an effort to improve precision. For example, precision is directly affected by the amount of oxide used in analysis.
- Different DOE sites use different temperatures, times, and thermal profiles for LOI analysis.
- Different DOE sites use different crucible materials for LOI analysis. Different materials are sometimes used at the same site.
- Rigorous consistency during calcination and LOI analysis is essential in order to develop a reliable technical basis for decisions about storage of impure oxides.

- Reactions involving sodium oxide, potassium oxide, uranium oxide and other impurities may result in unpredictable mass changes during calcination and LOI analysis.
- The suitability of LOI analysis in certification of impure oxides for storage is doubtful. Results are misleading and additional work is needed to determine the contribution of hydrogenous materials to the analytical result.
- Thermal decomposition mass spectrometry is effective in identifying volatile hydrogen-containing species formed at different temperatures during calcination and LOI analysis.
- The suitability of supercritical CO_2 extraction as a method for removal and quantitative determination of water in pure hydrated oxides of plutonium has not been demonstrated.
- Supercritical extraction does not remove water from common crystalline hydrates, and therefore, the method does not appear suitable for analysis of impure oxides in which such materials are known to be present.
- The problem of certifying impure oxides for storage after calcination is unresolved. Two approaches for addressing the problem follow: (1) Development of a hydrogen-specific analytical method for certifying impure oxides. Neutron absorption spectroscopy is a promising option. (2) Certification of calcination procedures for classes of impure oxides by demonstrating that representative calcination products are free of hydrogen. Thermal decomposition mass spectrometry is a promising option.

ACKNOWLEDGMENTS

The author thanks Mr. Charles Davis for the LOI measurements, and Mr. Jeremy Trujillo and Mr. Quentin Appert for the calcination studies on revisiting sample ATL27960. He also thanks Mr. Thomas E. Ricketts for providing the LOI results on the pure plutonium dioxide item MSTPPB1.

REFERENCES

1. "Assessment of Plutonium Storage Safety Issues at Department of Energy Facilities", U.S. DOE Report DOE/DP-O123T, U.S. Department of Energy, Washington, DC, January 1994.
2. J. L. Stakebake and M. R. Dringman, "Desorption from Plutonium Dioxide", U. S. DOE Report RFP-1248, The Dow Chemical Company, Golden, CO, November 1968.
3. "Potential Worker Contamination from Failed Plutonium Storage Containers" in *Safety Information Letter*, Issue Number: 93-05, US Department of Energy, Washington, DC, December 1993.
4. "Plutonium Storage Containers Aren't Fail-Proof", *Chem. Eng. News*, June 13 (1994), 23.
5. "Criteria for Preparing and Packaging Plutonium Metals and Oxides for Long-Term Storage," Department of Energy document DOE-STD-3013-96 (September 1996).
6. J. M. Haschke and T. E. Ricketts "Plutonium Dioxide Storage: Conditions for Preparation and Handling", Los Alamos National Laboratory Report LA-12999-MS, Los Alamos National Laboratory, Los Alamos, NM, (August 1995).
7. Quarterly Status Report, April 1- June 30, 1995. LA-UR-95-2646. The Nuclear Materials Packaging and Repackaging Project and The Vault Work-Off Project.
8. LA-UR-96-372. Quarterly Status Report, October 1-December 31, 1995. Nuclear Material Stabilization and Packaging, (February 1996).
9. D. G. Karraker, "Plutonium Dioxide Calcination Scoping Studies," Savannah River Technology Center Letter SRT-CTS-95-0011, Westinghouse Savannah River Company, Aiken, SC, (January 1995.).
10. 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, "Materials Identification and Surveillance Project Item Evaluation: Impure Plutonium Oxide ATL27960 and Pure Plutonium Oxide PEOR3258," Los Alamos National Laboratory report LA-13246-MS (March 1997). http://lib-www.lanl.gov/la-pubs/00326225.pdf
11. C. Keller, L. Koch, and K. Walter, J. Inorg. Nucl. Chem., 27 (1965) 1205.
12. W. Ruedorff and H. Leutner, Z. Anorg. Allgem. Chem., 292, (1957) 193.
13. L. M. Kovba, E. A. Ippolitova, Yu. P. Simanov, Vikt. A. Spitsyn, Doklady Akad. Nauk. S.S.S.R. 120 (1958) 1042.

14. K. M. Efremova, E. A. Ippolitova, Yu. P. Simanov, Vikt. A. Spitsyn, Doklady Akad. Nauk. S.S.S.R. 124 (1959) 1057.
15. Tom Allen, Quentin Appert, Charles Davis, John Haschke, William Hollis, David Horrell, Aaron Martinez, Richard Mason, Louis Morales, Jim Rubin, Craig Taylor, John Telford, Andreas Toupadakis, Jeremy Trujillo, "Materials Identification and Surveillance Project Item Evaluation: Impure Mixture of Plutonium Oxide and Uranium Oxide (PUUOXBCO5)," Los Alamos National Laboratory report LA-13295-MS (June 1997). http://lib-www/la-pubs/00326289.pdf
16. D. G. Karraker, "Plant PuO_2 and Mixed UO_2-PuO_2 Calcination Studies," Savannah River Technology Center Letter SRTC-CTS-95-0037, Westinghouse Savannah River Company, Aiken, SC, (February 1995).
17. J. M. Haschke, T. Venetz, R. Szempruch and J. W. McClard "White Paper on Possible Inclusion of Mixed Plutonium-Uranium Oxides in DOE-STD-3013-94," Los Alamos National Laboratory Report LA-13236-MS, Los Alamos National Laboratory, Los Alamos, NM. (Draft).
18. J. B. Rubin, W. K. Hollis, A. M. Martinez, and C. M. V. Taylor, "Supercritical Carbon Dioxide Extraction of Water from Pure and Impure PuO_2 Oxides," Los Alamos National Laboratory report LA-UR-96-3692 (November 1996).
19. J. B. Rubin, W. K. Hollis, K. V. Wilson, L. A. Morales, A. M. Martinez, and C. M. V. Taylor, "Extraction of Water from Oxides and Hydrates Using Supercritical-Fluid Carbon Dioxide" Los Alamos National Laboratory report LA-UR-97-2082 (June 1997).
20. L. R. Morss, "Thermodynamic Properties," in The Chemistry of the Actinide Elements, J. J. Katz, G. T. Seabog, and L. R. Morss, eds., Chap. 17, Chapman and Hall, New York, 1986.

Los Alamos
NATIONAL LABORATORY
Los Alamos, New Mexico 87545