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Materials Identification and Surveillance

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

Los Alamos
NATIONAL LABORATORY

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CONTENTS

ABSTRACT.....1
1.0 INTRODUCTION 2
2.0 BACKGROUND.....3
2.1 Los Alamos LOI procedure 3
2.2 Rocky Flats LOI procedure 5
2.3 Savannah River LOI procedure.....7
3.0 IMPACT OF DIFFERENT FACTORS ON LOI..... 7
3.1 Impact of post-heating and cool-down procedures.....7
3.2 Impact of calcination - Impact of the Impurities..... 8
3.3 Impact of LOI conditions.....19
4.0 LOI VERSUS CARBON DIOXIDE SUPERCRITICAL FLUID EXTRACTION OF WATER.....20
5.0 CONCLUSIONS 21
ACKNOWLEDGMENTS 22
REFERENCES 23

FIGURES

Fig. 1. Typical temperature profile during LOI analysis..... 6
Fig. 2. Characterization of pure plutonium dioxide item PEOFA..... 9
Fig. 3. Characterization of pure plutonium dioxide item MSTPPB1..... 10
Fig. 4. LOI results of impure plutonium dioxide item ATL27960..... 12
Fig. 5. LOI results after further calcination of impure plutonium dioxide item ATL27960..... 13
Fig. 6. LOI and calcination results after further calcination of impure plutonium dioxide item ATL27960..... 14
Fig. 7. Impact of calcination and LOI conditions on the LOI value for the impure MOX sample PUUOXBC05 and flow diagram for calcination process.....15
Fig. 8. Impact of calcination and LOI conditions on the LOI value for the impure MOX sample PUUOXBC05..... 16
Fig. 9. Impact of calcination temperature on the LOI value for the pure $Pu_2(C_2O_4)_3 \cdot 9H_2O$ sample..... 18

TABLES

Table I. Conditions and Materials Used at Different DOE Sites for the LOI Measurement.....4
Table II. Typical Temperature Profile During LOI Analysis.....5
Table III. Different Cool-Down Procedures..... 8
Table IV. Impact of Calcination Temperature on the LOI Value for the Pure $Pu_2(C_2O_4)_3 \cdot 9H_2O$ Sample.....17
Table V. LOI Results for Pure MOX..... 19

MATERIALS IDENTIFICATION AND SURVEILLANCE

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by

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ABSTRACT

The procedures for the loss-on-ignition analysis followed by Los Alamos National Laboratory, Rocky Flats Environmental Technology Site and Savannah River site are evaluated and compared. Results show that the processing time required to bring the materials into conformance with DOE-STD-3013 vary greatly depending on the identity and concentration of the impurities and suggest that the suitability of LOI analysis in certifying impure plutonium oxide materials for storage is questionable. The supercritical carbon dioxide fluid extraction method as an alternative to LOI analysis for measuring moisture in powders is shown to be promising 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 outer storage container over a 50-year period are not acceptable for storage. Plutonium oxide powder can have a high surface area per unit weight 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 the potential over-pressurization of a sealed oxide container over a prolonged period by the generation of hydrogen gas. Alpha decay of the plutonium, radiolysis, and chemical reaction of the adsorbates hold a potential for producing 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 because a large mass fraction of the material is thought to be in the dispersible size range below 10 μm geometric diameter. 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, whatever that might be, by thermally desorbing reactive species from the oxide and restricting readsorption prior to sealing in the storage vessel.

The preparation of impure plutonium dioxide for long-term storage must meet 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 should contain more than 50 mass % plutonium. The quantity of stored plutonium oxides per container should be as close as practical to, but should not exceed, 5.00 kg (10.97 lb.). The oxides will be thermally stabilized by heating in air or an oxidizing atmosphere to 950°C (1,742°F) or higher for at least two hours. After the calcination treatment, the thermally stabilized oxides will exhibit less than 0.5 mass % loss on ignition (LOI) and will retain this characteristic through final packaging. The

standard states that the LOI test will be based on heating a representative sample of the stabilized oxide in air to 1,000°C (1,832°F) or higher for at least one hour. The loss-on-ignition (LOI) test is the standard procedure for confirming the thermal stabilization of plutonium oxide. It is intended to be a measure of the water content of an 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 apparent difficulties arise from the complex composition of the impure oxide, which many times will be ill-defined, and from the uncertainty as to what this composition changes into during the calcination process.

In the case of pure plutonium oxide samples, the mass LOI criterion provides a straightforward way of making sure that little water is present, thus giving the confidence for storage. In the case of impure plutonium oxide powders, the presence of volatile impurities and also of impurities that could react with oxygen during the LOI test is responsible for obtaining LOI values of uncertain meaning.

2.0 BACKGROUND

In the next three 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 analysis is conducted by CST-15 personnel at TA-55. Before this technique was used it was qualified. A series of plutonium oxide (PuO_2) samples were analyzed for loss on ignition to establish a statistical base for the technique.

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
Sample (g)	5-10	< 20	0.99 - 1.01
Time (h)	2	1	1
Temperature (°C)	1000[a]	1000	700
Temperature profile	Fig. 1	-	-
Calcination crucibles	Fused silica	-	Stainless steel
LOI crucibles	Platinum or Alumina	Platinum	Porcelain
Spoon used	Stainless steel	-	Stainless steel
Preconditioning of furnace	None	-	Obtain stable 700°C for 30 min.
Preconditioning of crucibles	Ultrasonic cleaning next at 200°C, 1h	-	In furnace (1h, 700°C) next in desiccator (1h)

[a]In the past, various temperatures have been used, see LA-12999-MS, Fig. 2 and Fig. 3.

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]

In summary the procedure is as follows: The crucibles used in the procedure are cleaned using ultrasonic cleaner, and after the excess water is wiped off, they are dried in a muffle furnace at 200°C for about 1 h. Until the crucibles are ready to be used they are placed in a desiccator under vacuum. The powder to be analyzed is introduced to the clean crucibles with lids, which are made of platinum in the case of characterizing powder with plutonium content ≥ 80%, otherwise made of alumina. Powder of 5-10 g are placed and weighed in two different crucibles, and the covered crucibles are 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 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 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.

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.

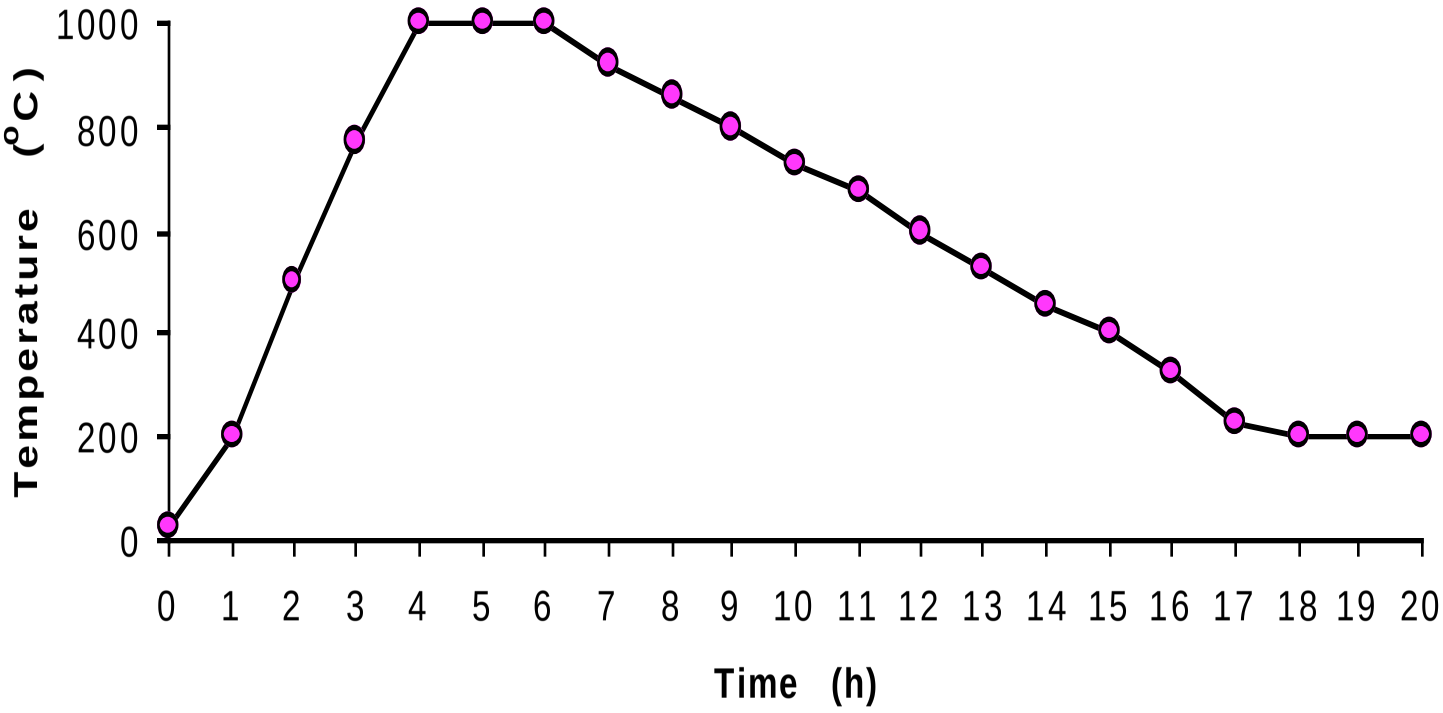

Fig. 1. Typical temperature profile during LOI analysis.

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.

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

2.3 Savannah River Technology Center 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. Before using the balance, it is calibrated with certified traceable standards. 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.

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 exclusively.[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 procedure when the samples are brought from 1000°C to 200°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°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°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 - Impact of the Impurities

The impact of calcination on LOI value as long as the plutonium oxide sample is pure is minimal, see Fig. 2 and 3.

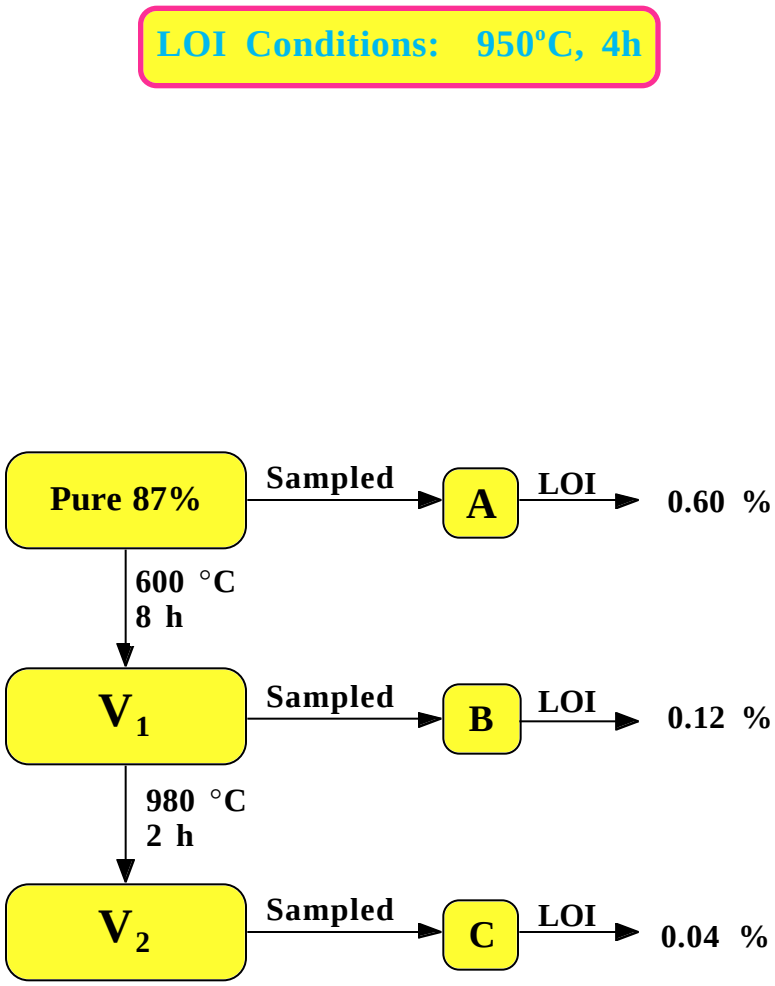

Fig. 2. Characterization of pure plutonium dioxide item PEOFA.

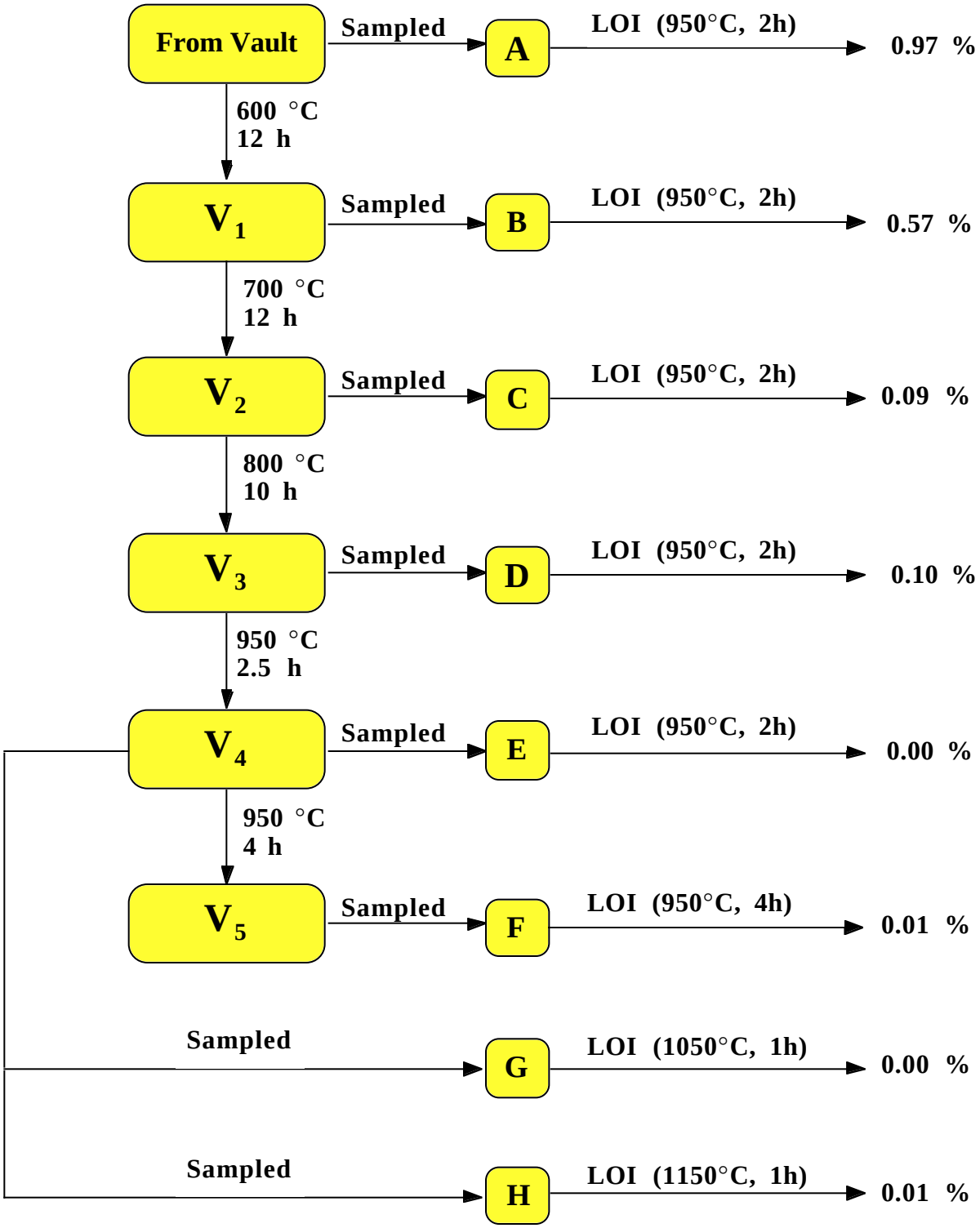

Fig. 3. Characterization of pure plutonium dioxide item MSTPPB1.

However, if the oxide contains volatile impurities, then the impact of calcination on the LOI is proportional to the concentration of the volatile impurities, see Figs. 4-6.

The weight loss measured by loss on ignition (LOI) for the impure PuO_2 sample ATL27960 was 0.97 mass %, which exceeds the specified maximum of 0.5 mass % set forth in DOE-STD-3013, see Fig. 4.[9] Additional calcination verified that a constant mass could be reached. Thus, revisiting the impure plutonium oxide ATL27960, it was found that longer calcination period brought the sample in compliance with the standard. These results are shown in Fig. 5. The large weight loss, 0.97 mass %, measured by LOI and the longer calcination period necessary for LOI stabilization indicates that volatilization of inorganic, nonhydrogenous material is taking place during calcination. This assumption is under verification and studies are under way to identify volatile species removed during calcination. It should be noted that for impure sample ATL27960, during the last stages of thermal treatment using longer calcination times (4 h) a substantial mass gain instead of mass loss was observed (Fig.6). This sample did not contain uranium that could be oxidized and thus explain the observed mass gain, and the calcination boats did not show any observable surface change, even though no analysis was performed on the material to see if any silicon was diffused into the sample. Thus this weight gain cannot be explained at this point.

Another example for studying the impact of calcination on the LOI value is the impure MOX sample PUUOXBC05. In contrast to the previous impure plutonium dioxide sample ATL27960, this impure oxide contains uranium. This oxide met the LOI criterion without the need to use long calcination periods, and during calcination a mass loss was observed. The item did not gain weight, even though uranium was present, see Figs. 7 and 8.

The effect on the LOI value of the calcination temperature during preparation of pure plutonium dioxide is apparent. D. G. Karraker from Savannah River Technology Center performed studies to determine a satisfactory procedure for calcination of Pu(III) oxalate. He found that three hours at 750°C and above was necessary to pass the loss-on-ignition requirement of less than 0.5 wt. % for PuO_2 storage.[10] During these studies, the starting material's composition was calculated to be $Pu_2(C_2O_4)_3 \cdot 9H_2O$. In Table IV and Fig. 9, it is seen that the LOI value decreases as the calcination temperature increases. In this case the volatile components are only water and carbon oxides.

D. G. Karraker has also performed scoping studies to determine a satisfactory procedure for calcination of a pure MOX sample (35 wt. % PuO_2 and 65 wt. % UO_2) in order to meet the LOI criterion.[11] The outcome of these studies was that the LOI measurement can not be trusted as a method for ensuring safe storage of MOX materials.

LOI Conditions: 950°C, 4h

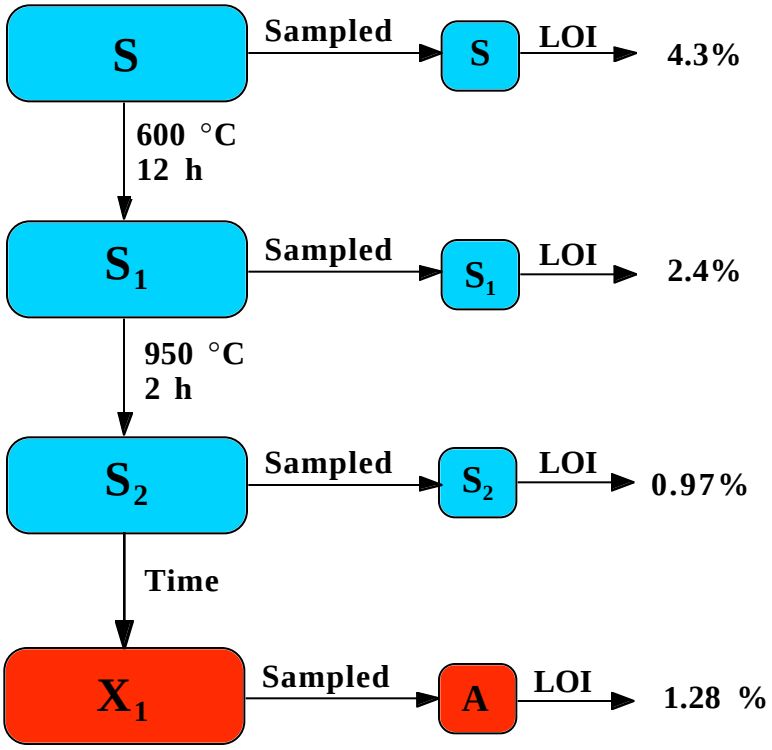

Fig. 4. LOI results of impure plutonium dioxide item ATL27960.

LOI Conditions: 1000°C, 2h

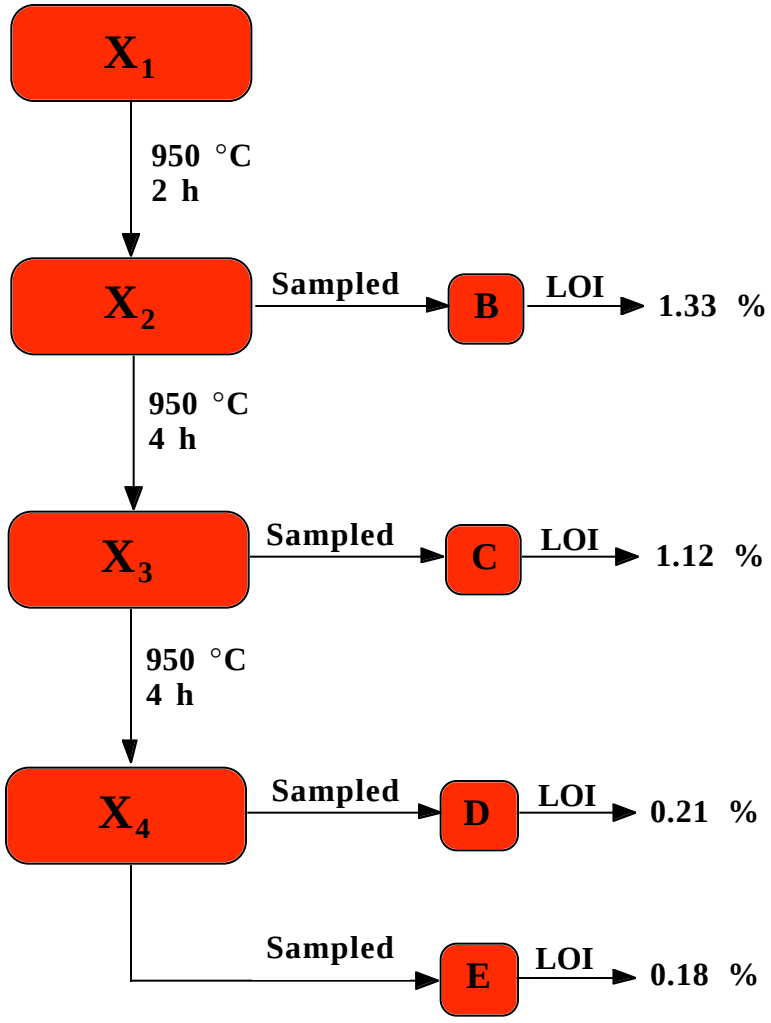

Fig. 5. LOI results after further calcination of impure plutonium dioxide item ATL27960.

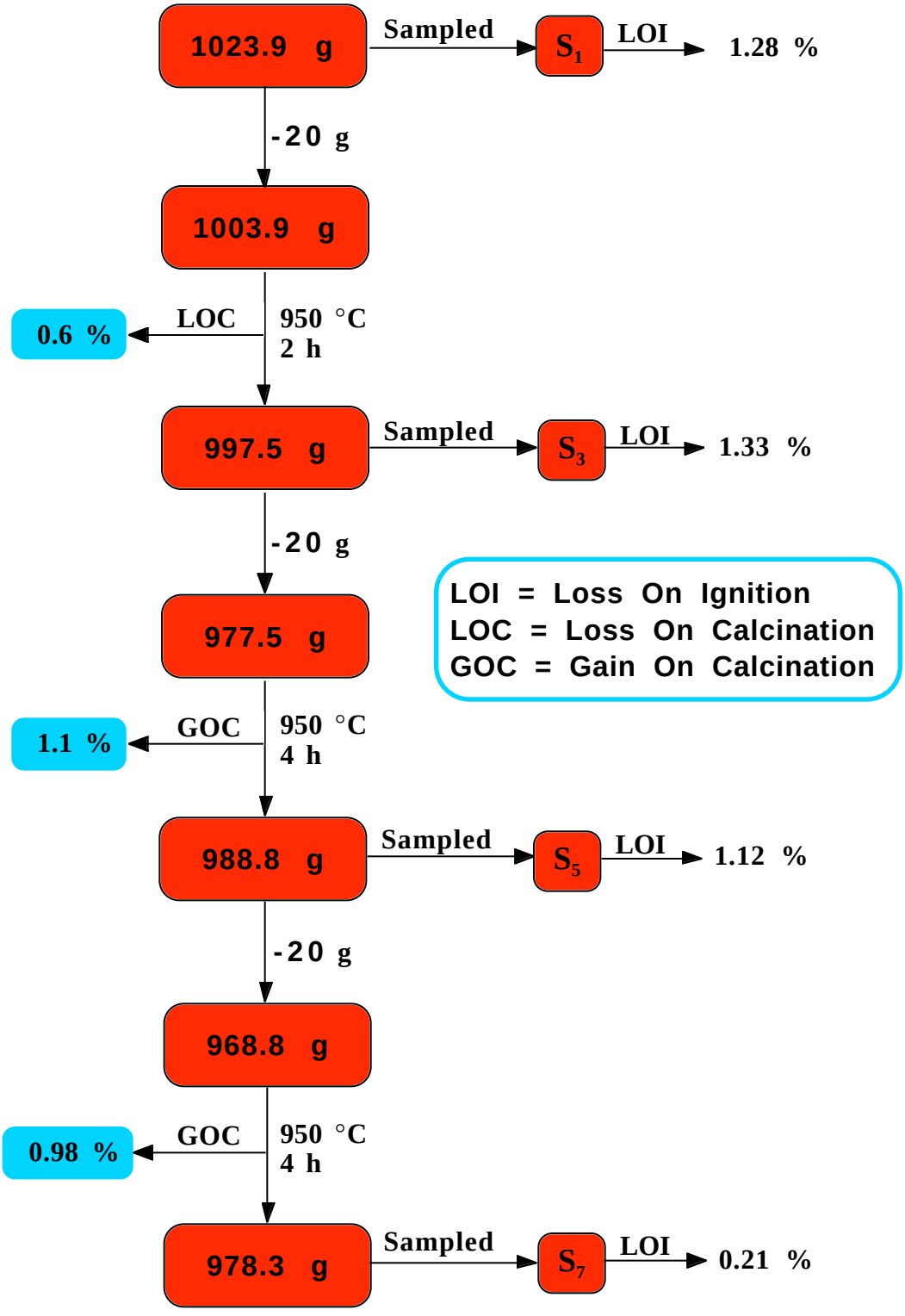

Fig. 6. LOI and calcination results after further calcination of impure plutonium dioxide item ATL27960.

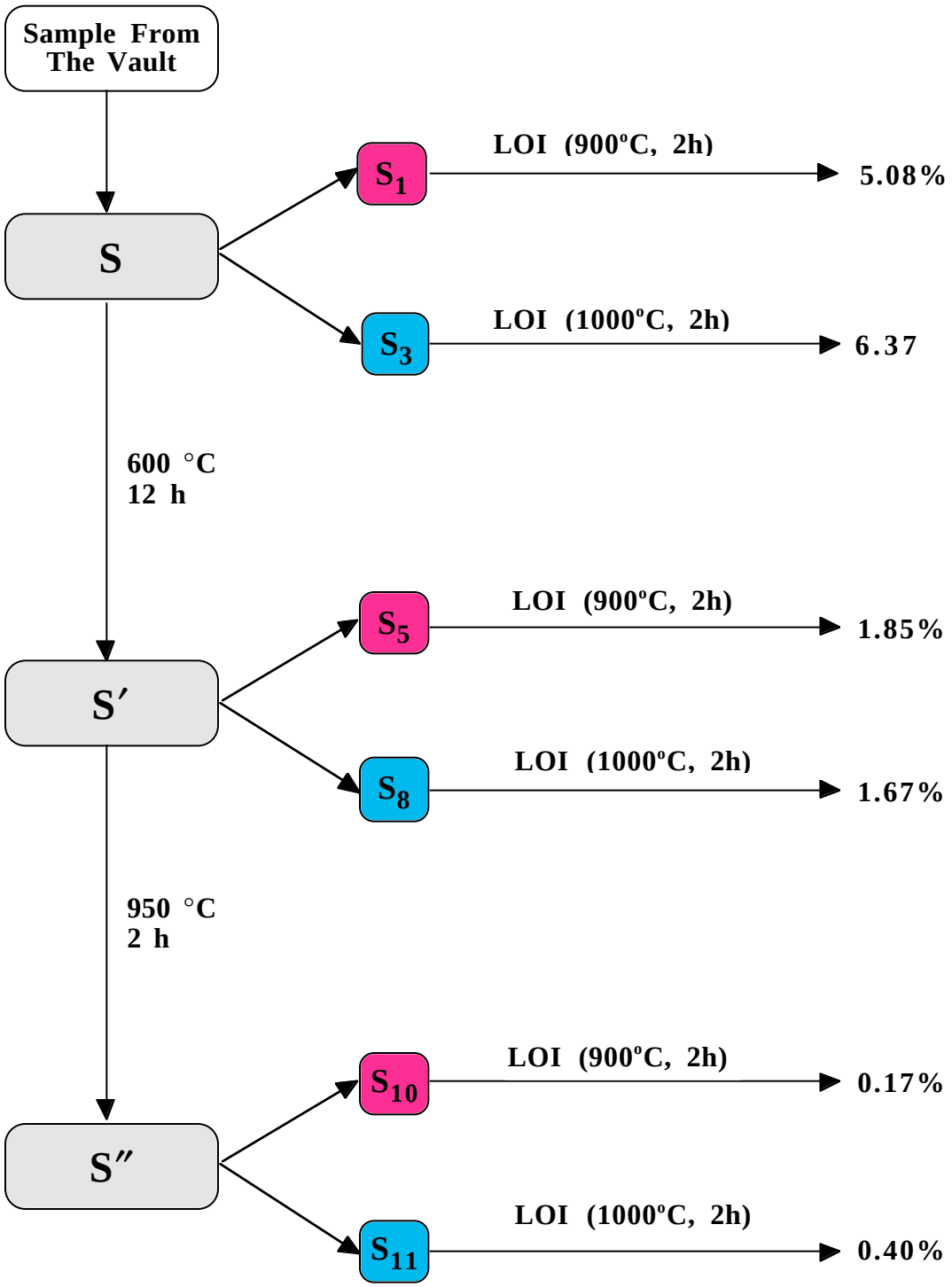

Fig. 7. Impact of calcination and LOI conditions on the LOI value for the impure MOX sample PUUOXBC05 and flow diagram for calcination process.

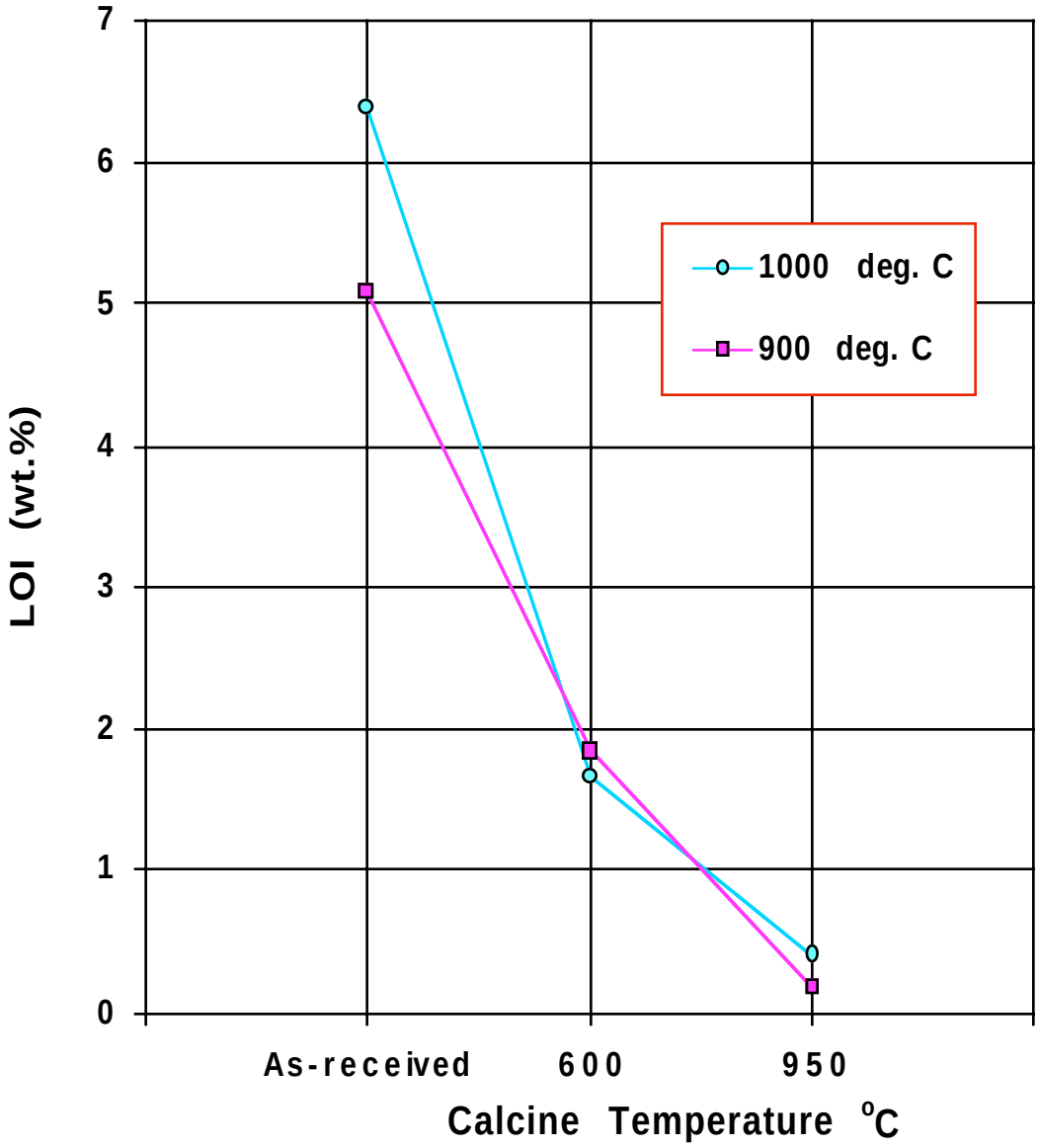

Fig. 8. Impact of calcination and LOI conditions on the LOI value for the impure MOX sample PUUOXBC05.

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 (°C)	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 (900°C for 1h).

This conclusion has been outlined by John Haschke et al. in a paper titled "White Paper on Possible Inclusion of Mixed Plutonium-Uranium Oxides in DOE-STD-3013-94."[12] The net weight gain of 0.68%, see Table V, shown by the as-received MOX sample during the LOI test was interpreted as a result of the larger weight gain due to the partial conversion of UO_2 to U_3O_8 compared to the smaller weight loss due to elimination of water and carbon dioxide. The constant mass observed during LOI analysis of the calcined mixed oxide MOX was interpreted as a result from a serendipitous equality of mass loss and mass gain. X-ray diffraction analysis results showed that the single-phase as-received mixed oxide was partially converted to U_3O_8 during the calcination step at 750°C. Similar X-ray analysis of the product after LOI analysis of the calcined MOX showed that the relative intensities of reflections for U_3O_8 had increased. This result suggests that additional U_3O_8 formed during the LOI test at 900°C.

In contrast, for pure samples of PuO_2, as was pointed out in the beginning of this section, it has been found that the DOE-STD-3013 of 0.5 mass % LOI requirement for storage is met without the use of long calcination periods (Figs. 2 and 3).[13] Longer calcination periods did not alter the LOI value (Fig.3). Additional studies are needed to evaluate the use of longer calcination periods for meeting the DOE-STD-3013 of 0.5 mass % LOI requirement for storage of impure plutonium oxides.

The fused-silica boats used for calcination in Los Alamos were chosen because of their availability and low cost. It is important to notice that kilogram quantities of high-purity (>88 mass % Pu) oxides were obtained from sources that might be encountered during typical repackaging operations.[6] No interactions between pure plutonium oxide and the

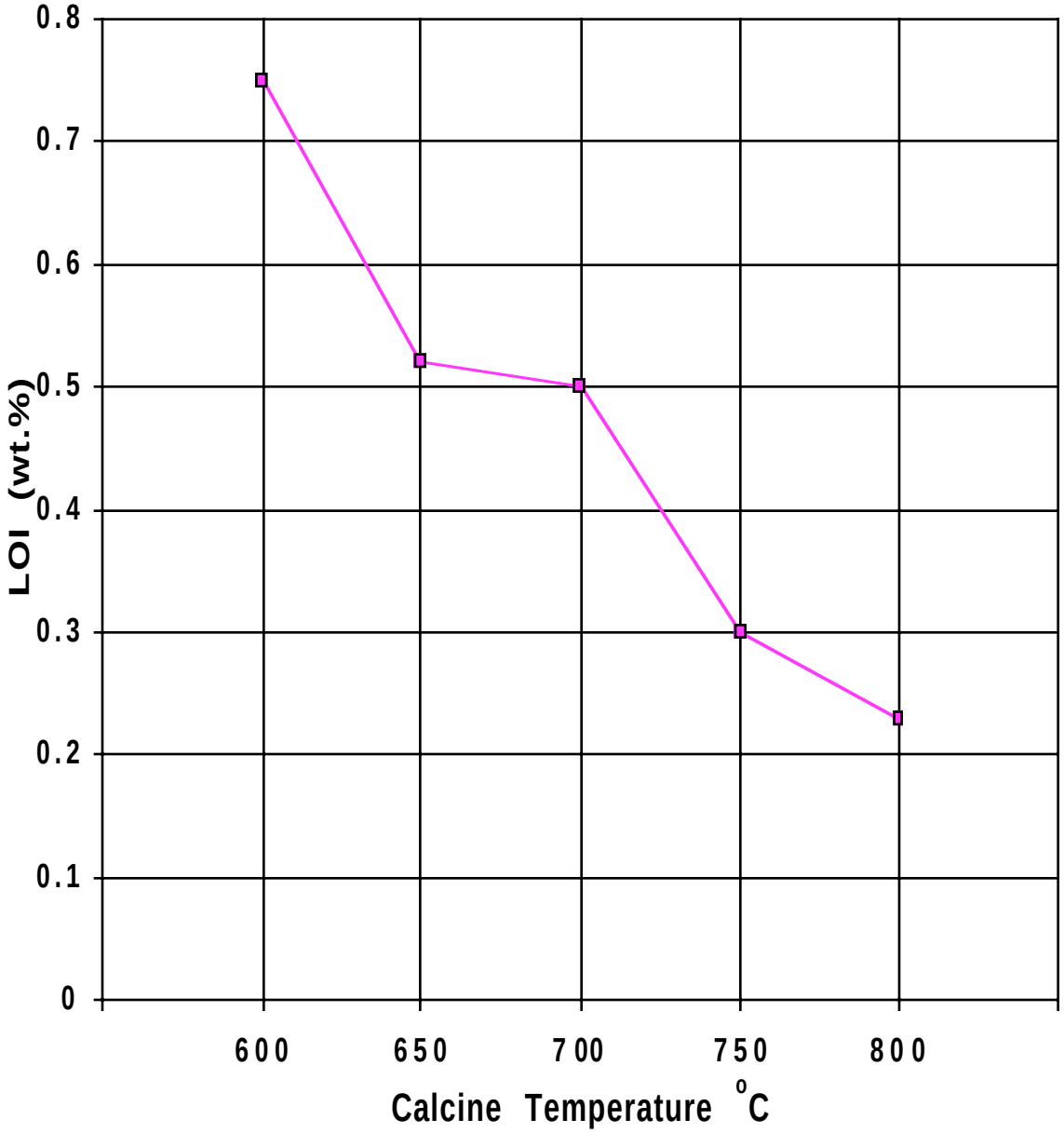

Fig. 9. Impact of calcination temperature on the LOI value for the pure $Pu_2(C_2O_4)_3 \cdot 9H_2O$ sample.

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 (750°C for 3h); LOI test (900°C for 1h).

surface of the boats were observed. In contrast, in the case of impure plutonium oxide samples containing metals such as sodium and potassium, the oxide in contact with the bottom of the fused silica boat was fused to the container.[9] Nevertheless such behavior does not affect the storability of the materials.

3.3 Impact of the LOI conditions

LOI conditions appear to be important for determining the LOI value for impure oxides. Taking into account the new data obtained from the thermal treatment of impure oxides, it is clear that some practices and more caution for consistency will have to be observed while the preparation of the impure oxides is taking place, and also, during the LOI test. Moreover, some additions might need to be incorporated into the DOE standard in order to cover more precisely the conditions for the correct certification of impure plutonium oxides for long-term storage. This becomes clear if one considers the following two different scenarios taking place in determining the LOI value for the same impure oxide sample, which happens to have a considerable amount of volatile materials at between 700°C and 1100°C. During the first LOI test, the impure oxide is fired in air at 1,000°C for one hour. During the second LOI test, the impure oxide is fired in air at 1,100°C for two hours. Both times, the experimentalist has followed the DOE standard which states that "the LOI test shall be based on heating a representative sample of the stabilized oxide in air to 1,000°C or higher for at least one hour." Results from the study of the impure oxide ATL27960 point out clearly that it should not be a surprise if the first sample passes the LOI test but the second does not. Ironically, both samples come from the same oxide. A good example in regard to the above discussion is the impure mixed oxide

(PUUOXBCO5). We see that for a 100°C increase (i.e., 1000°C for 2 h instead of 900°C for 2 h) an LOI of 0.40 mass % was found instead of 0.17 mass % for the calcined sample S″ (Fig. 7).[14]

However, 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. Last, the thermal treatment of the sample before the LOI test will have to be consistent. Samples with high concentrations of volatile inorganic materials treated for longer times at higher temperatures will most likely pass the LOI test, while samples treated for shorter times and lower temperatures might not qualify for long-term storage. Rigorous consistency will aid in making decisions for storage involving impure oxides.

4.0 LOI VERSUS CARBON DIOXIDE SUPERCRITICAL FLUID EXTRACTION OF WATER

Supercritical CO_2 has become a popular solvent because it is abundant, relatively inexpensive, and environmentally benign. The use of the CO_2 extraction method for determining the amount of water adsorbed on oxide was investigated using standards of pure ZrO_2 and PuO_2. Quantitative results were evaluated by comparison with LOI data.[9,15] 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 indicated that the supercritical-CO_2-extraction method could be suitable for quantitative determination of adsorbed water on plutonium oxide. Consequently similar studies were done using impure plutonium dioxide samples. The weight loss measured by loss on ignition (LOI) for the impure PuO_2 sample (ATL27960) was 0.97 mass %, which exceeds the specified maximum of 0.5 mass % set forth in DOE-STD-3013. As it was mentioned before, additional calcination verified that a constant mass was reached, thus meeting the < 0.5 mass % LOI requirement for storage. However, for the same impure PuO_2 sample ATL27960 the weight loss measured by supercritical CO_2 real-time extraction was

0.025 mass %, which is well within the specifications. The amount of water (0.025 mass %) removed from the impure plutonium oxide by CO_2 SFE after calcination and equilibration with air was in good agreement with the equilibrium concentration measured during adsorption tests but did not account for the LOI value of 0.97 mass %. The 0.97 mass % LOI of the calcined impure oxide could be explained if residual carbon or other impurities were eliminated during the LOI measurement.

Thermal desorption mass spectrometry (TDMS) studies were initiated to identify volatile species removed during calcination, and the first results of these TDMS studies on a MOX sample have been published.[9] In these initial studies only non-condensable species were analyzed. There were also solids which were condensed in the cooler parts of the experimental device which are being analyzed. It is very interesting to notice that chemisorbed water is the primary gaseous product observed during calcination of the oxide and appears throughout the TDMS process. The largest quantity of water is seen between 175°C and 340°C. The CO_2 that evolves during thermal desorption at low temperatures should be due to the desorption of adsorbed CO_2. The CO_2 that evolves during thermal desorption at high temperatures suggests the decomposition of carbonates that formed during storage. Water and carbon dioxide were the major gases formed between 450 and 950°C. Besides water and carbon dioxide there were other species identified such as CO, ethane, methane, oxygen and hydrogen. Even though the water which is seen throughout the process has not been quantified it is important to know if it can be removed by the CO_2 SFE method. In this regard, in addition to the oxides, additional studies have been performed in Los Alamos by the CO_2 SFE group on several hydroxide and crystalline hydrates in order to evaluate the efficacy of the method in removing water of constitution and water of crystallization, respectively. Initial results showed that there is not a clear cut answer. Thus some hydrates were fully dehydrated, while others were only partially dehydrated, and still others were not affected at all.[16]

Clearly, additional studies to fully determine the capabilities of the CO_2 SFE method are necessary and are in place. The supercritical extraction apparatus has been upgraded to allow for quantitative, simultaneous, real-time analysis of water and hydrocarbons.

5.0 CONCLUSIONS

The intention of this document was to bring together the different LOI procedures used throughout the DOE complex, compare them, and point out the different factors which affect the LOI value. Some interesting points have become noticeable by reviewing the LOI measurement as practiced within the DOE complex:

- Sites are emphasizing different phases of the procedure in regard to precision for the LOI measurement.
- Sites are using differing amounts of plutonium dioxide sample. This affects the precision.
- Sites are using differing (temperature, time) LOI conditions, and in general, differing LOI temperature profile.
- Sites are using crucibles for the LOI measurement that are not always made of the same material. Sometimes this is observed even within the same DOE site.
- The suitability of LOI analysis in certifying impure plutonium oxides for storage is fallacious, and additional work is needed. This additional work should focus on determining of how much of the weight loss on ignition is due to hydrogenous materials.
- Only by being rigorously consistent during calcination and LOI measurement will it be perhaps possible to make decisions with confidence for storage involving impure oxides.
- Initial results indicate that supercritical fluid extraction is an effective analytical method for the determination of water content in inorganic matrices, but the method needs to be further developed in order to include hydrogenous organic substances and relatively strong-bonded water such as hydration water or fixed water (OH groups).
- Supercritical fluid extraction could be used as a supplementary method to LOI method.

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