Materials Identification and Surveillance Project Item Evaluation

Item: Impure Plutonium Oxide (PPSL-365)

Los Alamos
NATIONAL LABORATORY

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by

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ABSTRACT

In this report, we characterize properties relevant to storage of an impure plutonium oxide (82.8 mass % plutonium) in accordance with the Department of Energy (DOE) standard DOE-STD-3013-96. This oxide sample was prepared by direct denitration of plutonium nitrate solution in a vertical calciner operated at 950ºC. This is the fourth impure plutonium oxide sample to be evaluated by this project.

Methods used to characterize the oxide include mass loss-on-calcination (LOC) measurements, mass loss-on-ignition (LOI) measurements, elemental analysis, plutonium and uranium isotopic analysis, particle analyses measurements, x-ray powder diffraction, thermal-desorption mass-spectrometry, and surface-area analyses. Methods used to characterize the container include x-ray radiography and photography.

The LOI value (0.04 mass %) and the specific surface area (0.67 m^2/g) for the powder after stepwise calcination at 600ºC first and next at 950ºC is lower compared to the LOI value (0.06 mass %) and the specific surface area (0.83 m^2/g) for the powder after direct calcination at 950ºC. The calcination effect on the powder appears to be less significant if the powder is calcined in one step directly to 950ºC instead in two steps, first at 600ºC and next at 950ºC.

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 found to be valid for pure PuO_2 in accordance with this standard,[2] questions remain for applying these methods to relatively impure materials. This particular impure plutonium oxide item PPSL-365 has 82.8 mass % plutonium and satisfies the criterion for plutonium content (>50 mass % plutonium). Within the DOE complex there is a large inventory of impure plutonium oxides of varying concentrations of different impurities awaiting stabilization and storage.

The objective of this study is to continue our experimental effort to characterize impure plutonium oxides and to develop preparation methods that convert these materials into forms suitable for storage.

2.0 EXPERIMENTAL METHODS

2.1 Materials

This impure plutonium oxide powder, item PPSL-365 came from a prototype vertical calciner operated at 950^oC at Hanford site. Table I shows the characterization data sent from Hanford site. A description of the Hanford packing configuration follows: The plutonium oxide was placed in a slip-lid steel container and the lid taped closed. This is referred to as the convenience container (CC). The CC is removed from the glovebox in a polyethylene bagout bag then nested and sealed in a crimp-seal food-pack can which is referred to as the inner can. The inner can is the primary contamination barrier. The inner can is then nested and sealed inside a second crimp-seal food-pack can.

2.2 Procedures

To puncture the can the puncture device is epoxied to the top of the can (Fig. 1). The sampling port is mated to the storage can using an O-ring and epoxy seal which allows for a leak-tight connection to the punch assembly and volume-calibrated pressure-vacuum system (PVS). Two type-K thermocouples are also attached to the can. The can, sampling port assembly, and two gas sample vials are connected to the PVS, and the PVS is evacuated and flushed at least three times with high-purity helium gas.

Table I.   Characterization Data Sent from Hanford Site for the Impure Oxide PPSL-365.

Date Processed	1996
Pu (g)	1170
Fissile Material (g)	1098
LOI (wt.%)	0.449
Pu-238 (wt.%)	0.0302
Pu-239 (wt.%)	93.422
Pu-240 (wt.%)	6.0754
Pu-241 (wt.%)	0.4423
Pu-242 (wt.%)	0.0302
Gross Weight (g)	1894.7
Net Weight (g)	1407.2
Calorimetry Date	20 June 1996
Power (watts)	3.1474

After the final flush, the PVS is evacuated to a pressure 5.0×10^{-6} torr and this evacuation is monitored on a residual gas analyzer (RGA). After the helium is pumped off, a rate-of-rise leak test is performed. The leak rate is acceptable if no argon gas is detected after 5 min under static vacuum and the pressure rise in the PVS system does not exceed 5.0 millitorr. All leaks are corrected before proceeding. The gas sample vials are valved out of the system and the PVS is isolated from the vacuum pump. The punch is unlocked and the can lid punctured. The punch is then retracted and locked in its starting (volume calibrated) position. The pressure is allowed to equilibrate between the can and the PVS. The equilibrium pressure and can temperature are recorded. The initial can pressure is calculated based on the expanded equilibrium pressure, the can temperature, and the free volume of the food-pack can. The free volume of the food-pack can is calculated from measurements taken from radiographs of the can. A gas sample is captured in each of the two gas sample vials for future analysis, and the remaining gas in the PVS is analyzed using the RGA. The can puncturing, gas sampling and disassembly process has also been described in summary with photos in a previous report[3].

Next the can is removed from the PVS and opened, and the internal surfaces of the can are visually inspected and photographed. In nested configurations the outer surfaces of the nested can are also photographed. In cases where the nested can is another food-pack can,

Fig. 1. Puncture device being epoxied to the top of the can.

the puncturing process is repeated. The cycle is stopped when the inner can contains the oxide. Next the CC is opened and the temperature of the contents is measured in five places. The plutonium oxide is weighed on a material accountability and safeguards system (MASS) certified balance for accountability purposes. A 30-g sample of the material is then removed from the parent lot. Ten grams are used for thermal desorption mass spectrometry (TDMS), 10 g for long term storage experiments, and 10 grams held as an archive sample. The remainder of the item is sent for calcination and further tests.

The experimental procedures used to measure loss on calcination, loss on ignition (LOI), specific surface area, and particle parameters are described in previous Los Alamos reports.[2,4,5,6]

The sequence of sampling and testing is presented in Figure 2. After samples were taken from the as-received material, (sample S), a portion of the powder was calcined at 600°C to produce sample S′. After samples were taken from the 600°C calcined powder, all of the remaining powder was calcined at 950°C to produce sample S″. Sample S‴ was produced by calcining sample S directly at 950°C without first calcination at 600°C.

Samples S, S′, S″ and S‴ were examined by x-ray powder diffraction. The samples were prepared for x-ray diffraction by light grinding with an aluminum oxide mortar and pestle. A one milligram portion of the sample was then loaded into a 0.2-millimeter quartz capillary. The capillary was cut to the appropriate length, sealed with epoxy, and centered in a Debye-Scherrer camera containing Kodak DEF-392 film. The sample was exposed to nickel-filtered copper radiation for 6.5 hours; the x-ray tube settings were 35 kilovolts and 25 mA.

The same samples were analyzed with a Rheometrics model PL-STA 2000 TGA/DSC which provided thermal gravimetric analysis (TGA) over a given temperature regime. The samples were consistently handled in the following way. Each sample was exposed to air for a maximum of 15 min while that sample was weighed and then loaded into the apparatus. Once the sample was in the apparatus, the sample chamber, whose volume is approximately 15 cm^2, was flushed with high purity nitrogen which passed through Drierite^{TM} canister in series with a Hewlett Packard drying column. The nitrogen gas flow rate was 15 ml/min; the sample chamber was purged for 30 min before the experiment was started. The details of the experiment are as follows. Once the sample chamber was purged, a temperature program was initiated. This program set the temperature to 25°C for a 3-minute isotherm and then ramped the temperature to 950°C at a rate of 10°C /min. During
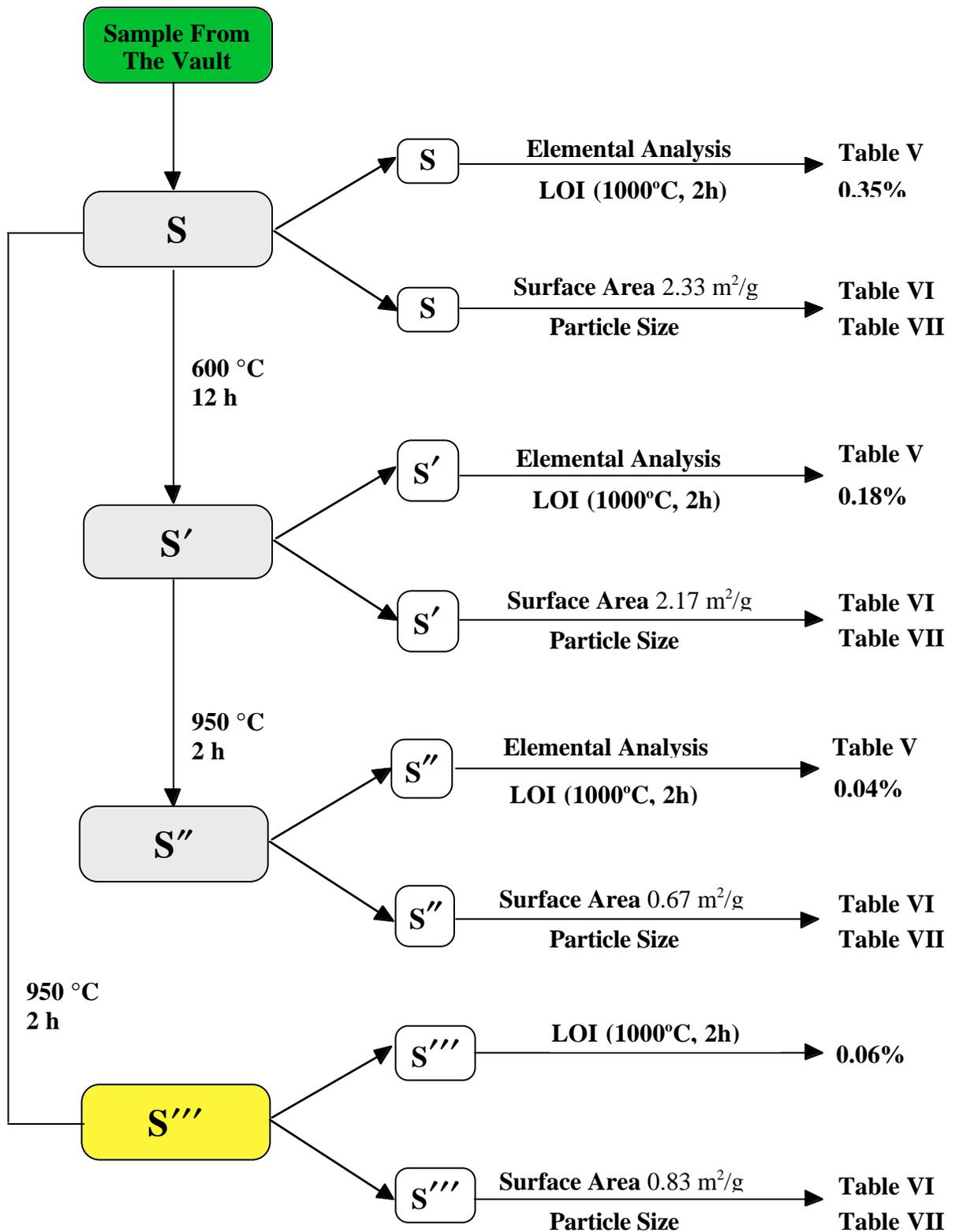
Fig. 2. Characterization of the impure plutonium oxide PPSL-365.

this temperature ramp, the mass of the sample was monitored at a rate of one datum point per second. The experiment concluded when the temperature reached 950 ^{o}C.

Thermal desorption mass spectrometry (TDMS) was performed on the S, S′, S″ and S‴ samples. Ten grams of the plutonium compound are weighed and the mass value recorded. The sample is placed in a tared tantalum cup and the total mass of the tantalum cup and the plutonium compound is measured. The tantalum cup containing the plutonium compound is placed in a stainless steel reactor and the reactor sealed. Contained in the reactor top are 2 type K thermocouples; one which measures the material temperature and the other gas-phase temperature. TDMS experiments are performed under dynamic vacuum. The reactor is attached to the PVS, evacuated and flushed with He gas as described above. After the third flush, the reactor is evacuated to a pressure 1.0×10^{-6} torr followed by a 5-min rate-of-rise leak check. Acceptance criteria are the same as above. The reactor is then opened to the vacuum pump. A 1200 ^{o}C clam-shell furnace is placed around the reactor and the heating cycle started. The heating profile is 6 hours from room temperature to 950 ^{o}C (as measured on the gas-phase thermocouple) followed by a 2-h soak at 950 ^{o}C. A mass spectrum is taken at least every 15 min throughout the test. The scan is normally taken from 1 to 90 amu. The reactor temperature and PVS pressure are recorded on a data acquisition system every 30 s. At the end of the heating profile, the reactor is allowed to cool to room temperature over a 16-h period. The reactor is disassembled and the plutonium oxide weighed. Weight loss during heating is calculated based on the starting and ending compound weights.

3.0 RESULTS AND DISCUSSION

Before the first calcination, 50 g of powder S was set in a glovebox. After 5 days of exposure to the glovebox atmosphere, the weight of powder S increased by 0.006 mass %. After the first calcination at 600 ^{o}C for 12 h, 50 g of powder S′ was set again in the glovebox. After 2 days of exposure to the glovebox atmosphere, the weight of powder S′ increased by 0.022 mass %. And after the second calcination at 950 ^{o}C for 2 h, again 50 g of the powder S″ was set in the glovebox. After 7 days of exposure to the glovebox atmosphere, the weight of powder S″ increased by 0.013 mass %. These results are shown in Table II. It is interesting to notice that all different powders S, S′, and S″ show very similar affinity for water. The values for powder S and S″ in Table II are most likely values for equilibrium loading of water. As we have seen before[3], for the impure plutonium dioxide ATL27960 calcined at 950 ^{o}C for 2 h, one day was enough for equilibrium to be established.

Table II. **Water Uptake Adsorption Measurements for the Impure Oxide PPSL-365**

Time & Amount of Water	Powder S[a]	Powder S′[b]	Powder S″[c]
Time (days)	5	2	7
Mass (g)	0.003	0.011	0.006
Mass (%)	0.006	0.022	0.013

[a]Powder S is the impure oxide from the vault before any calcination.
[b]Powder S′ is obtained after impure oxide S is calcined at 600°C for 12 h.
[c]Powder S″ is obtained after impure oxide S′ is calcined at 950°C for 2 h.

Each time the powder was calcined, the percent mass loss was measured. During the second calcination step the percent mass loss was less than the percent mass loss during the first calcination step. The results are shown below in Table III.

Table III. **Percent Mass Loss During Calcination of Sample PPSL-365**

Sample	Calcination Temperature (°C)	Heating Time (h)	Mass Before Calcination (g)	Mass After Calcination (g)	Mass Loss (%)
S′	600	12	1000	996.4	0.36
S″	950	2	890.2	888.1	0.24

The LOI value (at 1000°C for 2 h) for the 950°C directly at one step calcined powder S‴ is 0.06 mass %. The calcination effect on the LOI value appears to be less if the powder is calcined in one step directly to 950°C instead in two steps (first at 600°C and next at 950°C). The reported Hanford-LOI value is 0.44 mass %. This impure oxide conforms to the DOE-STD-3013-96[1] LOI requirement of <0.5 mass % loss tested at 1000°C for 2 h without any thermal treatment as confirmed by LOI of 0.35% of sample S.

Carbon concentration increased after the 600°C calcining step and subsequently decreased after the 950°C calcining step. Chloride concentration decreased after the 600°C calcining step and remained about the same after the 950°C calcining. Plutonium concentration slightly increased after the 600°C calcining step and remained about the same after the 950°C calcining. Table V shows these results and the elements found.

Table IV.   LOI Analyses Results of the Impure Oxide PPSL-365

LOI Conditions	Powder S[a] LOI (mass %)	Powder S′[b] LOI (mass %)	Powder S″[c] LOI (mass %)
1000^{0}C for 2 h	0.35	0.18	0.04

[a]Powder S is the impure oxide as received from Hanford.
[b]Powder S′ is obtained after impure oxide S is calcined at 600ºC for 12 h.
[c] Powder S″ is obtained after impure oxide S′ is calcined at 950ºC for 2 h.

Table V.   Elemental Analysis of Precalcined Powder S[a] and Calcined Powders S′[b], S″[c] and S‴[d]

Element	Powder S (µg/g)	Powder S′ (µg/g)	Powder S″ (µg/g)	Powder S‴ (µg/g)
Plutonium	828000	834000	835000	835000
Americium-241	1990	not done	not done	not done
Chloride	246	66.17	53	63
Carbon	95	470	15	35
Silver		278		
Aluminum		307		
Arsenic		<5		
Boron		395		
Barium		74		
Beryllium		<2		
Bismuth		46		
Calcium		150		
Cadmium		32		
Cerium		498		
Cobalt		5		
Chromium		958		
Copper		558		
Dysprosium		<1		
Erbium		<1		
Europium		<1		
Iron		8091		
Gallium		7		

Gadolinium	3
Germanium	<17
Hafnium	<1
Holmium	<1
Indium	2
Iridium	<1
Potassium	<610
Lanthanum	5
Lithium	2
Lutetium	<1
Magnesium	683
Manganese	246
Molybdenum	57
Sodium	2517
Niobium	3
Neodymium	4
Nickel	538
Lead	50
Palladium	2
Platinum	<3
Rubidium	<1
Rhenium	<1
Ruthenium	2
Antimony	<2
Selenium	<6
Silicon	<3000
Samarium	<1
Tin	50
Strontium	9
Tantalum	69
Terbium	<1
Tellurium	<3
Thorium	175
Titanium	276
Thallium	<1
Thulium	<1

Vanadium	<141
Tungsten	197
Yttrium	<1
Ytterbium	<1
Zinc	268
Zirconium	28
Caesium	148
Praeseodymium	1
Uranium-238	1996
Uranium-234	39[e]
Uranium-235	492[e]
Neptunium-237	65[e]

[a]Impure oxide before any calcination.
[b]Impure oxide, S, which was calcined at 600℃ for 12 h.
[c]Impure oxide, S′, which was calcined at 950℃ for 2 h.
[d]Impure oxide, S, which was calcined at 950℃ for 2 h.
[e]Semi-quantitative analysis.

The as-received powder S has a specific surface area of 2.33 m^2/g and the 600℃ calcined powder S′ has a specific surface area of 2.17 m^2/g. The 600℃ first step and 950℃ second step calcined powder S″ has a specific surface area of 0.67 m^2/g. The specific surface area of 600℃ calcined material (sample S′) is slightly smaller than the specific surface area of the as-received material, but the specific surface area of the 600℃ first step and 950℃ second step calcined powder S″, 0.67 m^2/g, is more than three times smaller than the specific surface area of either of the other two specific surface areas. This oxide PPSL-365 shows a similar behavior as the pure plutonium oxide[2] regarding specific surface area change during calcination. The three impure oxides studied so far calcined at 600℃ first step and 950℃ second step very interestingly show almost identical specific surface area values of about 0.7 m^2/g. This value of specific surface area for the impure oxides is about seven times smaller than that for the pure plutonium oxide. This smaller value can be attributed to sintering during the heating process facilitated by the presence of inorganic salts as impurities. The specific surface area for the 950℃ directly at one step calcined powder S‴ is 0.76 m^2/g. Again the calcination effect on the specific surface area as we saw for the LOI value appears to be less if the powder is calcined in one step directly to 950℃ instead in two steps (first at 600℃ and next at 950℃). Table VI shows these results.

Particle analysis results are shown in Table VII.

The tap density and bulk density of the oxide is shown in Table VIII.

Table VI.   Comparison of Specific Surface Area Results with Other Plutonium Oxides (m²/g)

Oxide	As-received	Calcined at 600°C	Calcined at 600 °C & 950°C	Calcined at 950°C
Pure plutonium oxide[a]	11.3	10.2	4.8	–
Impure plutonium oxide[b]	15.6	4.3	0.8	–
Impure plutonium oxide[c]	1.05	1.75	0.78	–
Impure plutonium oxide[d]	2.33	2.17	0.67	0.83

[a]Data for the pure plutonium oxide (PEOR3258) are from Ref. 2.
[b]Data for the impure plutonium oxide (ATL27960) are from Ref. 4.
[c]Data for the impure plutonium oxide (PUUOXBC05) are from Ref. 5.
[d]Data for the impure mixed oxide (PPSL-365) are in this report.

Table VII. Particle Analysis Results of Precalcined Powder S[a] and Calcined Powders S′[b], S″[c] and S‴[d]

Property	Powder S	Powder S′	Powder S″	Powder S‴
Spherical Equivalent Mean (μm)	12.6	16	7.3	18.6
Diameter-by-Volume Mean (μm)	48.05	62.35	33.8	90.15

[a]Impure oxide before any calcination.
[b]Impure oxide, S, which was calcined at 600°C for 12 h.
[c]Impure oxide, S′, which was calcined at 950°C for 2 h.
[d]Impure oxide, S, which was calcined at 950°C for 2 h.

Table VIII. Tap Density and Bulk Density of Precalcined Powder S[a] and Calcined Powders S′[b], S″[c] and S‴[d]

Property	Powder S	Powder S′	Powder S″	Powder S‴
Tap Density (g/cc)	4.76	4.65	4.16	5.12
Bulk Density (g/cc)	4.34	5.26	4.76	4.54

[a]Impure oxide before any calcination.
[b]Impure oxide, S, which was calcined at 600°C for 12 h.
[c]Impure oxide, S′, which was calcined at 950°C for 2 h.
[d]Impure oxide, S, which was calcined at 950°C for 2 h.

The X-ray powder diffraction results for samples S, S′, S″ and S‴ are summarized in Table IX. The "fingerprint" regions for each sample are shown in Fig. 3. These results indicate that the samples are face-centered cubic, space group Fm3m, PuO_2. Table IX contains a listing for each sample of the values for two theta, d, Miller indices, background, peak areas which reflect the intensities of the peaks, and the peak widths. At the end of each listing for a given sample, the table reports the calculated lattice constant for that sample. The lattice constant was calculated by a least squares technique in which the points were weighted by the square root of sine theta. The oxygen-to-plutonium ratio for each sample was calculated from the lattice constant and the data from Gardner et al.[7] The as received material S, was oxygen deficient with a O/Pu ratio of 1.958. Sample S′, fired at 650°C, showed slight oxidation with a O/Pu ratio of 1.977. Samples S″ and S‴ each have an O/Pu ratio of 1.955. These two samples have a O/Pu ratio very close to that for sample S.

The results of the TGA runs are shown in Fig. 4. Samples S, S′, and S″, showed no discernible mass changes with temperature. However, sample S‴ experienced a 1.2 % mass loss which occurred at 150°C and at 550°C. The sample's mass changed from 8.820 mg to 8.71 mg during the course of the experiment with the largest change occurring at 150°C. The 0.11-mg mass loss may be due largely to water loss.

The results of the can puncturing, including the gas composition for the outer and inner can are summarized in Table X. It is known that the outer and inner cans were packaged in air[8]. The outer can gas analysis is generally consistent with air. However, some differences are observed: the CO_2 percentage is a factor of 3 greater then that expected for air, the concentration of H_2 is about 2 orders of magnitude greater than would be expected for normal air, and He is a order of magnitude greater that expected in air. Both the outer and inner cans show elevated concentrations of CO_2, He, and H_2.

Table IX. Summary of the X-ray diffraction results for the PPSL-365 samples.

2-Theta	d(A)	h	k	l	BG	Peak	P%	Area	Area%	FWHM
Sample S										
28.690	3.1090	1	1	1	2746	27625	79.8	10429	61.9	0.340
33.147	2.7004	0	0	2	589	14348	41.5	6646	39.5	0.417
47.559	1.9103	0	2	2	1978	32417	93.7	14887	88.4	0.413
56.437	1.6291	1	1	3	1489	34615	100.0	16838	100.0	0.438
59.143	1.5608	2	2	2	2992	5847	16.9	2107	12.5	0.324
69.470	1.3519	0	0	4	2857	7487	21.6	2232	13.3	0.268
76.837	1.2396	1	3	3	9562	15417	44.5	4931	29.3	0.288
79.139	1.2092	0	2	4	5531	20898	60.4	7779	46.2	0.335
88.473	1.1042	2	2	4	5541	15235	44.0	7911	47.0	0.467
95.450	1.0410	1	1	5	4033	23949	69.2	13629	80.9	0.512
107.378	0.9559	0	4	4	2391	10263	29.6	6609	39.3	0.580
Calculated lattice constant: 5.4117(7)										
Sample S′										
28.770	3.1005	1	1	1	3538	27943	67.3	10682	50.7	0.344
33.288	2.6893	0	0	2	1244	14475	34.8	4775	22.7	0.297
47.656	1.9067	0	2	2	3174	34284	82.5	11947	56.7	0.314
56.524	1.6268	1	1	3	3779	41543	100.0	18590	88.3	0.403
59.229	1.5588	2	2	2	2469	10554	25.4	4137	19.6	0.353
69.602	1.3497	0	0	4	1729	11231	27.0	2950	14.0	0.236
76.906	1.2387	1	3	3	2150	30661	73.8	15028	71.4	0.441
79.252	1.2078	0	2	4	1099	24752	59.6	15695	74.5	0.571
88.599	1.1029	2	2	4	1255	25181	60.6	17222	81.8	0.616
95.560	1.0401	1	1	5	2131	36336	87.5	21061	100.0	0.522
107.452	0.9554	0	4	4	2130	16809	40.5	6624	31.5	0.355
Calculated lattice constant: 5.4043(7)										
Sample S″										
28.668	3.1113	1	1	1	728	33617	67.3	9852	47.0	0.264
33.180	2.6978	0	0	2	410	13204	26.4	4473	21.3	0.305
47.574	1.9098	0	2	2	1745	33045	66.1	10270	49.0	0.280
56.420	1.6295	1	1	3	2726	44556	89.1	14543	69.4	0.294
59.159	1.5604	2	2	2	1458	8835	17.7	3848	18.4	0.392
69.500	1.3514	0	0	4	1851	9412	18.8	2735	13.0	0.262
76.783	1.2403	1	3	3	3334	28974	58.0	11495	54.8	0.357
79.114	1.2095	0	2	4	3986	25300	50.6	8861	42.3	0.315
88.495	1.1039	2	2	4	4251	36545	73.1	13120	62.6	0.323
95.472	1.0408	1	1	5	1864	49981	100.0	20959	100.0	0.377
107.377	0.9559	0	4	4	3770	25025	50.1	8358	39.9	0.301
Calculated lattice constant: 5.4129(7)										

Table IX. Summary of the X-ray diffraction results for the PPSL-365 samples, cont.

2-Theta	d(A)	h	k	l	BG	Peak	P%	Area	Area%	FWHM
Sample S‴										
28.607	3.1179	1	1	1	2000	37896	50.8	12392	67.1	0.294
33.088	2.7051	0	0	2	8745	10496	14.1	2763	15.0	0.237
47.514	1.9121	0	2	2	5352	42464	57.0	13832	74.9	0.293
56.362	1.6310	1	1	3	2591	74555	100.0	18467	100.0	0.223
59.120	1.5614	2	2	2	858	15901	21.3	4579	24.8	0.259
69.505	1.3513	0	0	4	2146	16719	26.4	4423	23.1	0.238
76.779	1.2404	1	3	3	6795	35029	47.0	13031	70.6	0.335
79.114	1.2095	0	2	4	7814	32480	43.6	9602	52.0	0.266
88.400	1.1049	2	2	4	5478	46806	62.8	17811	96.4	0.342
95.338	1.0419	1	1	5	1808	53349	71.6	16609	89.9	0.280
107.151	0.9573	0	4	4	1335	22883	30.7	6923	37.5	0.272
Calculated lattice constant: 5.4128(6)										

The inside surfaces of the outer can were non-remarkable, that is, they were consistent with normal food-pack cans. Some minor surface blemishes were noted; however, it is known that the cans are imperfect when placed in service, and there was no evidence that these blemishes were the result of mechanical or chemical degradation. The outer surface of the inner can was similarly non-remarkable.

The gas analysis results for the inner can show a marked shift with respect to room air. There are substantial increases in N_2 and CO_2 concentrations, and a substantial decrease in O_2 concentration. He and H_2 concentrations are also greater than would be expected for normal air. These results suggest that both chemical and radiological reactions have occurred during the storage period. The H_2 is probably due, in part, to minor radiolytic and thermal decomposition of the polyethylene bagout bag. It must be noted that there was no PuO_2 on the polyethylene bag, which suggests a small gamma or neutron flux through the CC walls. The increase in N_2 percentage is consistent with the consumption of O_2 and the production of CO_2. The calculated can pressure is also consistent with a net loss of O_2. The increased concentration of CO_2 does not account for all of the oxygen consumed. Work[9] shows that O_2 can react with PuO_2 in the presence of water to form a superstoichiometric plutonium dioxide (PuO_{2+x}) and H_2.
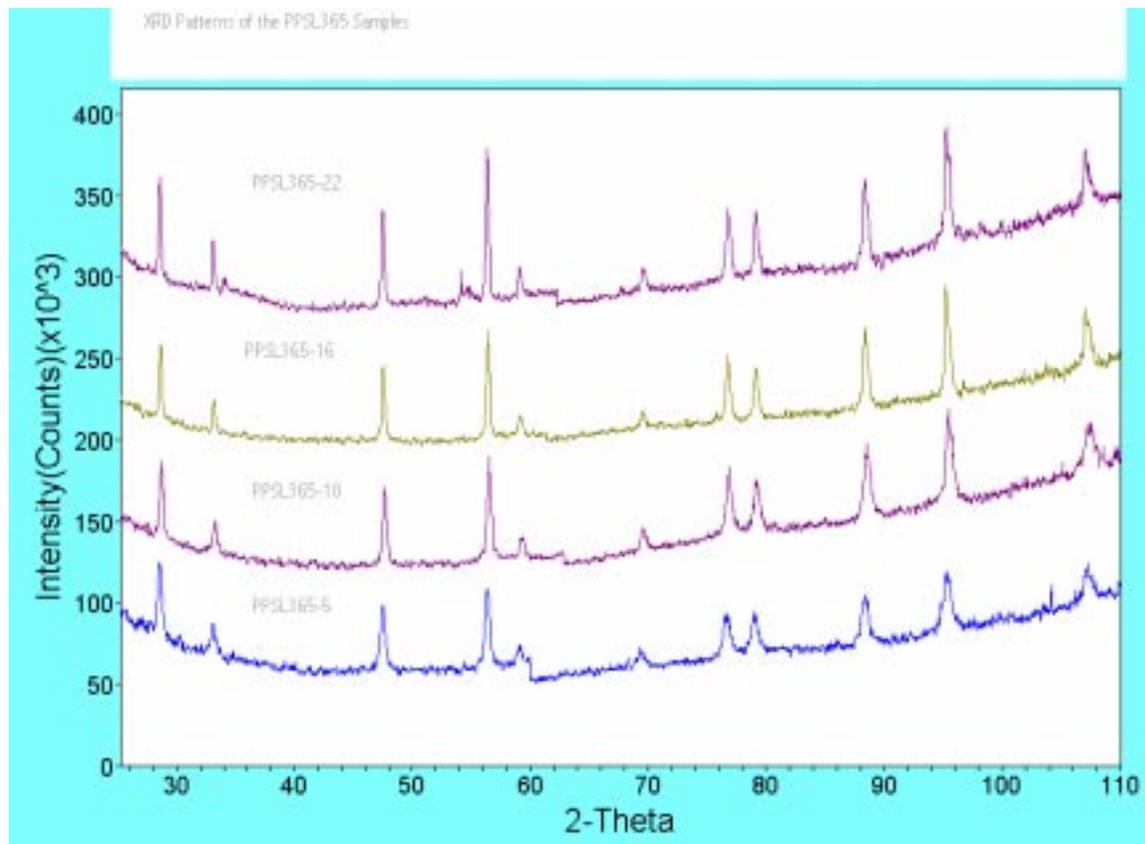
Fig. 3. X-ray diffraction results for the PPSL-365 samples
(S_5 is S, S_{10} is S′, S_{16} is S″, and S_{22} is S‴).
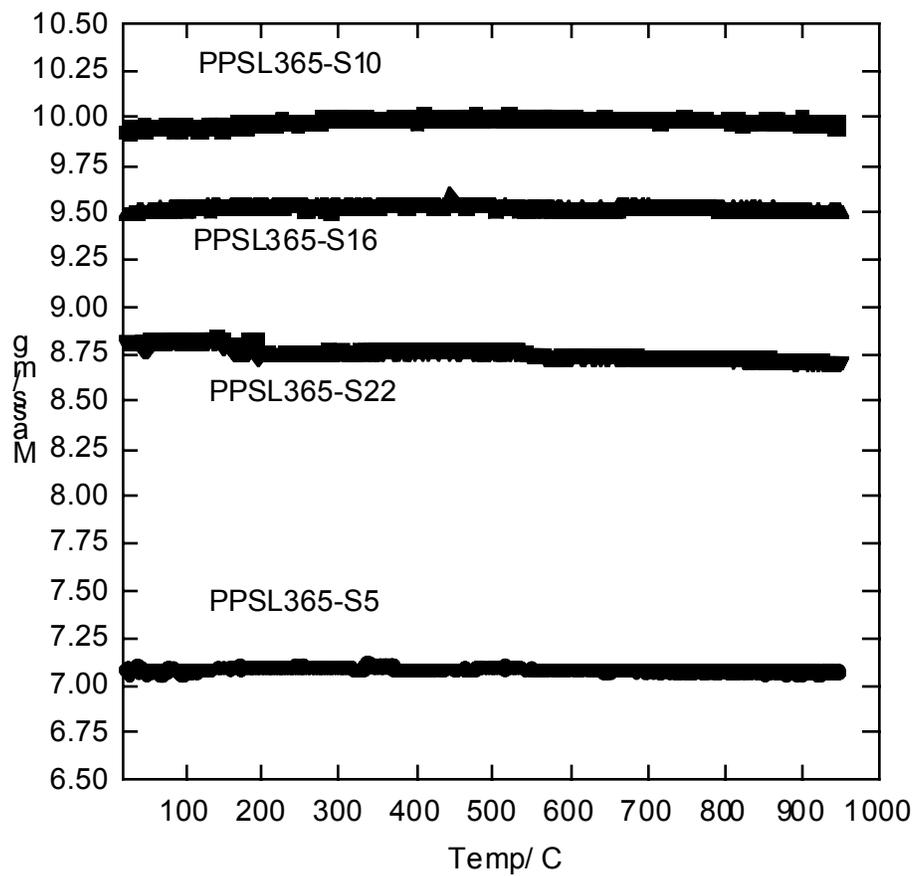
Fig. 4. Thermal gravimetric analysis results for the PPSL-365 samples
(S$_5$ is S, S$_{10}$ is S′, S$_{16}$ is S″, and S$_{22}$ is S‴).

Table X.   Can Puncturing Results and the Gas Composition for the Outer and Inner Can.

Property	Outer Can	Inner Can	Air
Age	one year	one year	
Temperature (^{o}C)	25.9	33.1	
Equilibrium Pressure (Torr)	440.9	443.8	
Calculated Pressure (Torr)	636.9	585.6	
Can Seal	No Leak	No Leak	
Gas Species (mole %)			
N_2	79.2	91.03	78.08
O_2	19.3	4.86	20.94
Ar	0.86	0.86	0.934
CO_2	0.098	2.91	0.0314
He	0.0039	0.33	5.24×10^{-5}
H_2	0.0045	0.13	5.0×10^{-5}
H_2O	0.059	0.051	
CH_4		0.10	

The H_2 then reacts with atmospheric O_2 to form additional H_2O on the PuO_2 surface followed by the formation of more PuO_{2+x}. The cycle continues until all of the O_2 in the can is consumed.

This process can account for the additional O_2 reacted in excess of that used to produce CO_2. No analytical measurements were performed to verify the stoichiometry of this oxide.

The PuO_2 temperatures are shown in Table XI and are measured at four positions clockwise and in the center of the material. The thermocouple is inserted to about 50% of the total PuO_2 depth.

The inside surfaces of the inner can were in good condition. There was no visual indication of corrosion of the food-pack can or on any visible surface of the convenience container that could be directly traced to the storage conditions. Small blemishes were observed on the food-pack can; however, the cans may have been put in service in a blemished condition. The outer surface of the CC was covered with lead tape to reduce the radiation flux.

Table XI.   PuO$_2$ Temperatures.

Position (clockwise)	Temperature (ºC)
12 o'clock	39.7
3 o'clock	44.7
6 o'clock	50.0
9 o'clock	43.9
Center	49.2

The polyethylene bagout bag was abraded by the lead tape, which in turn caused minor discoloration of the bag. However, the polyethylene bag and the plastic tape used to seal the CC were still pliable, and there was no visible heat or radiation damage. The oxide in the container was green, and the particle size was varied. The particle distribution was not measured.

In mass spectroscopy, the gas molecules that comprise the analyte are ionized. The ions are then accelerated across a potential difference, through a mass filter, to a detector. The mass filter separates the ions so that only a specific ion reaches the detector. The results are generally displayed as a table or graph showing the ratio of ion mass to charge in contrast to the ion current (in amperes). The ion current is directly proportional to the amount of that ion present in the analyte. The quantitative analysis of mass spectra requires that each mass peak be identified as a parent or daughter peak of the neutral precursor in the analyte. After each peak is identified, it is normalized to nitrogen, based on the ionization cross section for that compound. The quantity of that molecule is directly related to the total normalized ion current for that molecule. The quantity of a specific molecule in a given analyte is calculated using the sample pressure, molecule ion current, and the total ion current for the analyte. In the data from this test it was not possible to identify all of the peaks and, therefore, the quantitative results described above are not presented. The ratio of the ion current of a specific peak over the total ion current is presented in the tables below and represents approximately a ±10% error in the amount of a given molecule when compared with real quantitative results. The numbers in the following tables show the quantity of each species as ratios expressed as %. The TDMS results for samples S, S′, S″ and S‴ are summarized as follows.

Sample S

TDMS is performed under dynamic vacuum. One of the limitations to this method is that it does not reproduce the exact processing conditions used for thermal stabilization. Compounds that are observed in vacuum may be oxidized at similar temperatures in air. Therefore, an attempt was made to perform the as-received TDMS in a partial pressure of O_2 equivalent to that at Los Alamos atmospheric pressure (588 torr). Gas samples were taken at the sampling port and analyzed. Then, the O_2 pressure was adjusted for the gas removed and the reactor temperature so that a constant O_2 activity was maintained above the oxide. It was expected that the off-gas from the oxide would diffuse from the reactor to the sampling port. This did not occur, and it was not possible to measure the changes in the reactor gas mixture at the sampling port. In addition, the gas samples were compromised by an air leak in one of the sampling valves. Therefore, the gas analysis data from this run are unusable. The calculated loss-on-ignition (LOI) is 0.623% which does not meet the 3013 storage requirement.

Sample S′

The bulk PuO_2 was calcined at 600ºC for 12 hr in air. A 10-gram aliquot of this oxide was used for TDMS analysis. This TDMS was performed explicitly as described in the experimental section of this report. The mass spectrum results are shown in Table XII and the pressure-temperature data in Fig. 5. Regions P1 through P4 on the pressure curve are anomalies in the pressure transducer and not pressure perturbations caused by off-gassing from the oxide. This is confirmed because concurrent and independent pressure measurements made on the RGA do not show similar pressure changes. Also, this is true for Fig. 6 and Fig. 7.

Analysis of the mass spectrum results show that H_2O and CO_2 are the major gas constituents throughout the run. Also, small amounts of H_2, C_2H_2, and CH_4 are observed which suggest the decomposition of hydrocarbons. A 28 peak (N_2 and CO) is also seen throughout the run. This mass analyzer is limited to one amu resolution, therefore, it is not possible to distinguish between N_2 and CO using only the 28 peak. However, by comparing the peak intensities of the daughter peaks from N_2, CO, and contributing components (such as CO_2), an estimate can be made on the gross distribution of CO and N_2. There is a mixture of N_2 and CO at temperatures below 740ºC, and above 780ºC, N_2 is the only contributor to the amu 28 peak. Helium is evolved early in the process then goes

Table XII.   Results of the TDMS Gas Analysis for Sample S′.

TEMP	H_2O	CO_2	28 (N_2,CO)	O_2	H_2	He	CH_4
32.8	0	31.6	0	0	0	0	0
35.8	0	0	29.36	0	41.29	0	0
87.4	0	91.88	3.6	0	0	0.69	3.14
120.1	0	95.82	0	0	0	0.3	3.79
163.5	10.55	84.41	0.55	0	0.54	0.48	3.29
206.1	69.27	26.47	0.51	0	1.16	0.09	0.85
241.6	72.97	22.45	0.43	0	1.53	0.09	0.96
286.7	70.22	22.71	0.61	0	2.51	0.09	2.24
333.2	63.6	27.22	0.64	0	2.77	0	4.26
374.3	57.49	21.1	3.13	0	2.57	0	6.1
401.6	58.97	28.76	1.1	0	2.21	0	7.13
445.4	55.02	30.2	1.67	0.03	2.94	0	8.27
486.1	52.62	30.53	3.51	0	2.68	0	8.79
532.8	50.25	32.82	3.39	0.03	2.66	0	9.14
561.4	51.77	33.18	2.59	0	2.38	0	8.66
607.6	55.76	33.3	1.56	0	2.12	0	4.78
650.6	63.29	28.26	2.04	0	2.22	0.1	1.78
740.5	72.44	20.35	2.2	0	2.67	0.21	0.52
738.3	72.76	18.91	2.97	0.03	3.07	0.3	0.31
781.7	71.69	17.18	4.74	0	4.08	0.29	0.19
825.4	68.86	15.43	8.71	0.04	4.82	0.31	0.13
838.9	66.68	13.58	12.34	0	5.5	0.13	0.09
842.7	63.8	13.75	14.38	0	5.47	0	0.24
844.5	60.57	12.47	17.81	0	6.32	0.24	0.12
844.7	56.51	14.64	18.93	0	7.04	0.26	0.11
845.3	54.87	12.74	23.76	0	7.2	0	0.12
846.2	53.82	12.83	25.17	0	6.26	0	0.15
849.2	49.72	13.52	28.63	0	5.48	0	0.15

Table XII.   Results of the TDMS Gas Analysis for Sample S′, cont.

Temp	C_2H_2	27,30	31	40	42	45	50	78
32.8	0	0	0	0	0	0	0	0
35.8	0	0	0	0	0	0	0	0
87.4	0	0	0	0	0	0	0	0
120.1	0	0	0	0	0	0	0	0
163.5	0	0	0	0	0	0	0	0
206.1	0	0	0	0	0	0	0	0
241.6	0	0.03	0	0	0	0	0	0
286.7	0.03	0.03	0	0	0.03	0	0	0
333.2	0.03	0.06	0	0	0.03	0	0	0
374.3	0.06	0.12	0	0.03	0.03	6.97	0	0
401.6	0.09	0.15	0	0.03	0.03	0	0.03	0
445.4	0.09	0.18	0.05	0.03	0.03	0	0.06	0
486.1	0.09	0.12	0.05	0.03	0	0	0	0.12
532.8	0.14	0	0.05	0	0	0	0	0.03
561.4	0.1	0	0	0	0	0	0	0
607.6	0.05	0	0	0	0	1	0	0
650.6	0	0	0	0	0	0.78	0	0
740.5	0	0	0	0	0	0	0	0
738.3	0	0	0	0	0	0	0	0
781.7	0	0	0	0	0	0	0	0
825.4	0	0	0	0	0	0	0	0
838.9	0	0	0	0	0	0	0	0
842.7	0	0	0	0	0	0.82	0	0
844.5	0	0	0	0	0	0.86	0	0
844.7	0	0	0	0	0	0.94	0	0
845.3	0	0	0	0	0	0	0	0
846.2	0	0	0	0	0	0	0	0
849.2	0	0	0	0	0	1	0	0

away and returns at 600ºC. A very small amount of NO (amu 30) is observed between 445ºC and 530ºC. The 41 and 45 peaks are attributed to C, N, and H containing compounds based on searches of the NIST mass spectral database[10]. The remaining peaks 40, 42, 50, and 78 are assigned to unspecified hydrocarbons again based on searches of NIST mass spectral database. The calculated LOI is 0.280%, and meets the 3013 storage requirement.
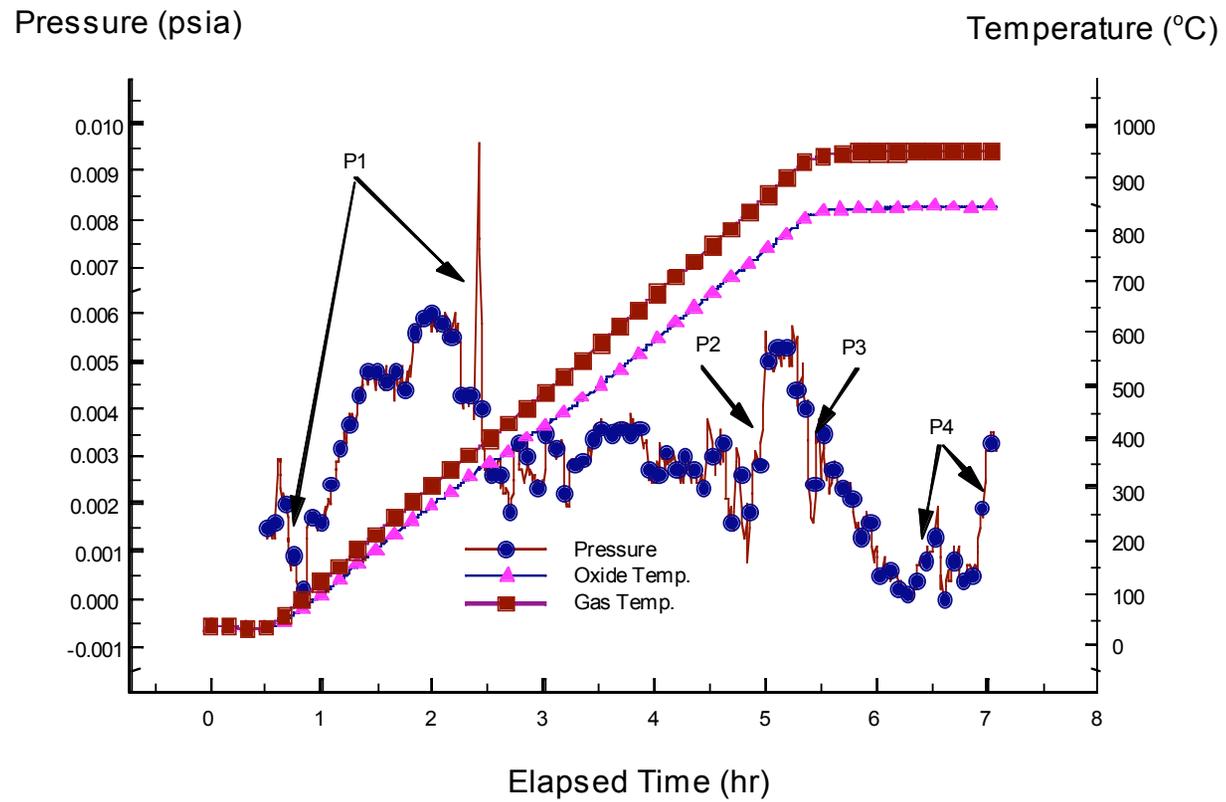
Fig. 5. TDMS pressure-temperature data for sample S′.
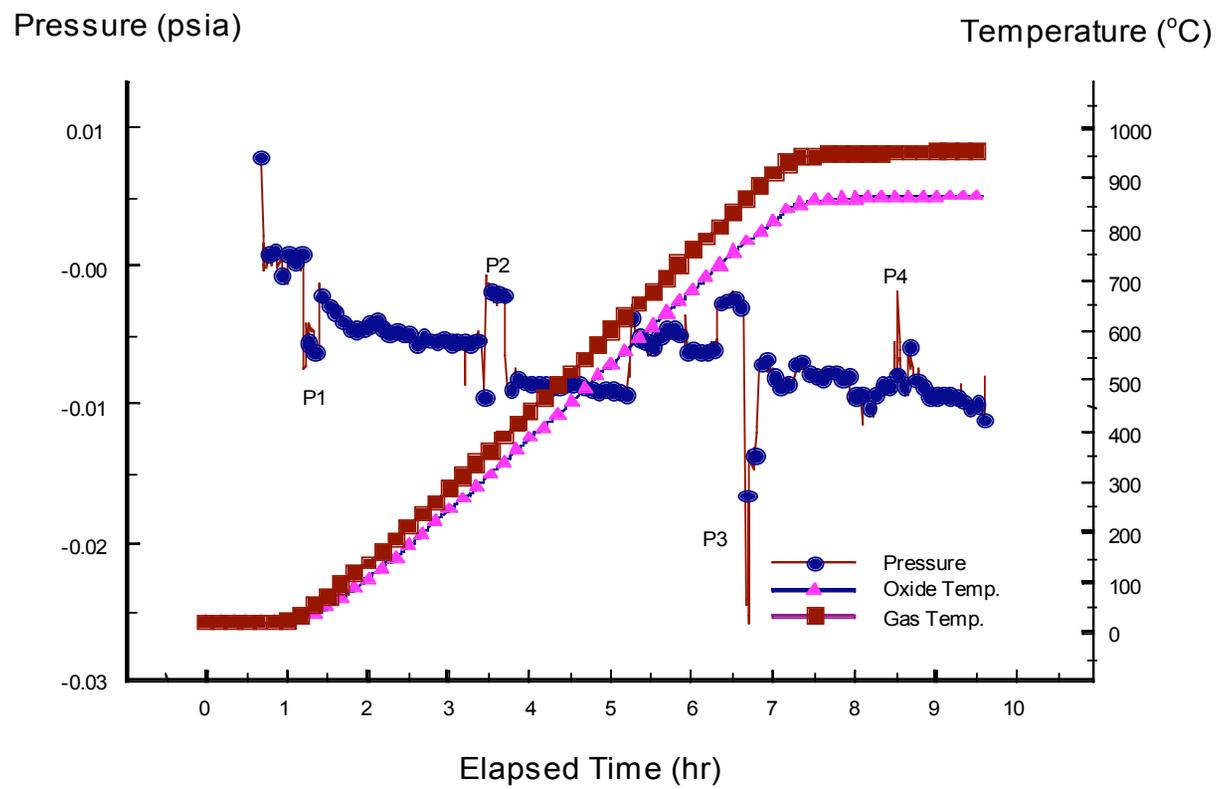
Fig. 6. TDMS pressure-temperature data for sample S″.
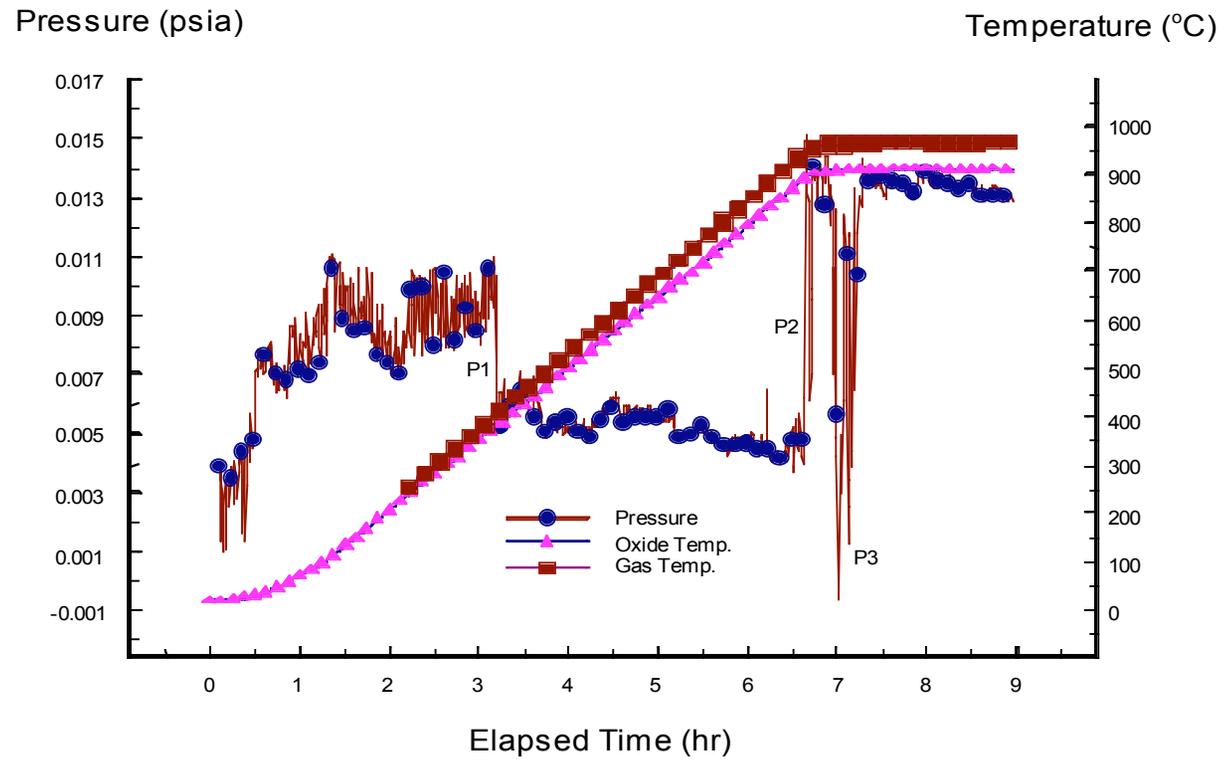
Fig. 7. TDMS pressure-temperature data for sample S‴.

Sample S″

After calcination at 600ºC, the bulk oxide was again calcined at 950ºC for 2 hr.   A 10-g sample of this oxide was used for TDMS analysis. The mass spectrum results are shown in Table XIII, and the pressure-temperature data in Fig. 6.

Pressure measurements show that the total amount of volatile component from the oxide is very small. The pressure drops continually throughout the run. H_2O and CO_2 are major components of the vapor fraction which is consistent with the TDMS results from the 600ºC calcination. The same analysis of the 28 peak was performed on these data and the results show that above 500ºC CO is evolved and at temperatures below, a mixture of CO and N_2 are evolved. Small amounts of CH_4 are produced throughout the run. C_2H_2 is seen between 250 and 775ºC. When compared with the results from the TDMS for the oxide calcined at 600ºC, although much smaller quantities, a larger fraction of it belongs to C-N-H compounds (amu 41 and 45) and unidentified hydrocarbons (amu 27, 40, 42, 50, 54, 55, 56, 57, 77, and 78). It is noteworthy that no He was detected. The calculated LOI is 0.130% which meets the 3013 storage requirement.

Sample S‴

Because of processing limitations in the calcination furnace, all of the PPSL-365 batch could not be processed simultaneously. Therefore, we held a quantity of the original batch to be calcined one time only, to 950ºC. TDMS was run on a 10-g aliquot of this material. The mass spectrum results are shown in Table XIV, and the pressure-temperature data in Fig. 7.

Comparison of the gas analysis results from the material calcined at 600ºC and 950ºC (950-1) Table XIII and the material calcined only at 950ºC (950-2) Table XIV show that they are quite similar. Differences are found at amu's 4, 41, and 57. amu 4 is helium gas, amu 41 is assigned, at this point, to carbon-hydrogen-nitrogen compounds, and amu 57 suggest hydrocarbons. The difference in He can be attributed to the time held at elevated temperatures with 950-1 losing most of its He while 950-2 retains some. At this time there is no explanation for the differences observed in amu 41 or 57. The calculated LOI is 0.286% which meets the 3013 storage requirement.

Table XIII. Results of the TDMS Gas Analysis for Sample S″.

Temp.	H_2O	CO_2	2 8 (N₂, CO)	O_2	H_2	He	CH_4
21.7	0	0	23.63	33.54	42.83	0	0
24.4	0	0	0	0	0	0	0
37	49.17	12	15.07	1.85	15.87	0	0
57.4	4.58	65.2	4.93	0	0	0	0
84	14.38	65.87	0.85	0	0	0	2.05
111.1	55.19	36.81	0.61	0.2	0	0	0
150.2	72.7	19.86	0.91	0	0	0	0.36
184.3	75.73	19.14	1.25	0	1.14	0	0.23
234	64.86	23.13	1.95	0	2.73	0	0.59
257.2	55.47	32.24	3.58	0	3.17	0	1.23
297	40.35	42.15	6.03	0	3.27	0	2.45
325	32.17	48.28	7.54	0.12	2.52	0	3.36
362.9	28.75	50.57	7.71	0	3.8	0	3.75
396.2	27.9	47.96	8.26	0	5.81	0	3.29
431.9	25.05	45.74	14.51	0	7.76	0	2.88
468.3	21.47	42.11	20.49	0	6.96	0	2.3
507.7	24.87	32.92	28.44	0	8.02	0	2.2
543.9	22.28	33.37	33.27	0	6.04	0	2.15
576	18.71	32.9	37.68	0	6.1	0	1.92
614	17.44	33.96	39.21	0	5.37	0	1.71
653.9	19.73	34.27	36.78	0	5.31	0	1.67
691	22.83	39.69	27.27	0	4.73	0	1.68
726.7	26.09	45.02	20.89	0	4.89	0	1.95
762.9	27.28	46.01	16.87	0	4.18	0	1.86
802	33.16	47.12	13.84	0	3.43	0	1.49
838.4	32.56	47.25	11.78	0.11	3.71	0	1.56
851.9	33.89	48.13	9.76	0.12	3.59	0	1.56
858.3	37.51	44.54	9.2	0.13	3.65	0	1.65
860.2	40.32	41.29	10.49	0.14	5.13	0	1.3
863	42.56	41.22	8.7	0.16	4.9	0	1.41
861.5	42.63	39.09	10.11	0	5.67	0	1.15
862.9	44.39	38.16	9.69	0	5.47	0	1.01
862.6	42.69	37.51	8.89	0.18	4.7	0	0.87
865.5	44.39	38.16	9.69	0	5.47	0	1.01
866.8	44.07	34.33	10.22	0	5.19	0	0.98
867.4	44.64	32.2	10.85	0.19	5.81	0	0.94

Table XIII. Results of the TDMS Gas Analysis for Sample S″, cont.

Temp.	26 (C$_2$H$_2$)	27	30 (NO)	31	40	41	42	45	54	56
21.7										
24.4	0	0	0	0	0	0	0	0	0	0
37	0	0	0	0	0	0	0	0	0	0
57.4	0	0	0	0	0	0	0	0	0	0
84	0	0	7.05	0	0	0	0	8.71	0	0
111.1	0	0	6.3	0	0	0	0	9.4	0	0
150.2	0	0	3.26	0.34	0	0	0	0	0	0
184.3	0	0	1.37	0.21	0	0	0	2.84	0	0
234	0	0	0	0	0.11	0.34	0.23	0	0	0
257.2	0	0.13	0	0	0.38	0.9	0.38	3.1	0	0
297	0.14	0.14	0	0	0.42	1.12	0.84	0	0	0
325	0.24	0.24	0	0	0.61	1.69	1.21	0	0	0
362.9	0.21	0.42	0	0	0.73	1.67	0.94	0	0.1	0.1
396.2	0.29	0.38	0	0	0.48	1.14	0.76	0	0.1	0
431.9	0.18	0.36	0	0	0.36	0.64	0.45	3.08	0	0.09
468.3	0.27	0.55	0	0	0.27	0.45	0.45	0	0	0.09
507.7	0.27	0.62	0	0	0.27	0.44	0.53	2.18	0	0.09
543.9	0.24	0.6	0.21	0	0.24	0.36	0.36	0	0	0
576	0.25	0.5	0.21	0	0.25	0.25	0.25	0	0	0
614	0.22	0.33	0	0	0	0.11	0.11	1.05	0	0
653.9	0.19	0.28	0	0	0	0.19	0	0	0	0
691	0.19	0.38	0	0	0	0.19	0.1	0.95	0	0
726.7	0.18	0.28	0	0	0	0.09	0.09	2.21	0	0
762.9	0.1	0.1	0	0	0	0.1	0.1	0	0	0
802	0.09	0.19	0	0	0	0.09	0	2.84	0	0
838.4	0	0.1	0	0	0	0.1	0.1	0	0	0
851.9	0	0.11	0	0	0	0.11	0	2.46	0	0
858.3	0	0.12	0	0	0	0.11	0	1.93	0	0
860.2	0	0.12	0	0	0	0	0	2.34	0	0
863	0	0.12	0	0	0	0	0	0	0	0
861.5	0	0.14	0	0	0	0	0	0	0	0
862.9	0	0	0	0	0	0.15	0	0	0	0
862.6	0	0	0	0	0	0	0	0	0	0
865.5	0	0	0	0	0	0.16	0	4.26	0	0
866.8	0	0	0	0	0	0	0	0	0	0
867.4	0	0	0	0	0	0	0	4.28	0	0
	0	0	0	0	0	0.18	0	4.58	0	0

Table XIV. Results of the TDMS Gas Analysis for Sample S′′′.

Temp	H_2O	CO_2	28 (N_2, CO)	O_2	H_2	He	CH_4
134.4	82.12	12.08	0.78	0.14	0.93	0	0
100.1	70.29	23.22	1.07	0.17	1.64	0.48	0.41
223.7	70.13	19.38	2.91	0.1	2.15	0.29	0.39
255.1	63.23	23.55	4.12	0.18	2.34	0	0.58
31.7	54.69	5.86	10	1.47	12.58	9.73	0
278.3	49.06	35.85	5.43	0.2	3.61	0	1.35
68.6	45.4	34.45	4.43	0.67	4.13	1.92	2.9
921.3	41	37.19	15.58	0.18	3.82	0	1.19
22.9	40.96	3.18	7.99	2.98	10.96	29.69	0
909.6	40.38	42.82	9.3	0.24	3.24	0	1.58
911.6	39.92	42.18	11.66	0.26	3.68	0	1.26
912	38.76	38.72	12.43	0.27	4.25	0	1.36
314.1	38.39	43.36	6.44	0.09	3.7	0.27	1.76
911.1	38.02	38.96	15.46	0.3	5.05	0	1.26
874.4	37.77	43.43	0	0.22	3.8	0.33	1.55
843.4	37.69	45.48	19.47	0.12	4.05	0	1.5
911.9	37.17	38.39	17.17	0.15	4.57	0	1.31
911.3	36.66	38	18.19	0.32	4.28	0	1.32
901.1	35.86	44.47	10.09	0.2	2.84	0.3	1.54
805.5	34.41	44.76	10.58	0.12	4.35	0.35	1.69
757.5	33.29	43.65	14.07	0.26	5.85	0	2.09
358.2	32.83	46.09	8.08	0.17	4.2	0	2.07
721.6	30.93	38.39	20.14	0.13	6.06	0.4	1.8
695.9	28.37	35.74	23.48	0.14	6.94	0.43	1.9
498.5	25.83	28.47	29.64	0.11	9.58	0	1.77
540.6	25.34	27.56	31.52	0.27	9.88	0	1.86
406.1	23.02	42	10.93	0.07	7.39	0	1.87
643.1	22.2	34.35	31.64	0.12	6.93	0	1.95
608	20.05	32.78	36.55	0.12	7.26	0	1.94
586.7	20.02	31.85	36.77	0.13	7.79	0	1.93
425.5	19.94	40.13	12.41	0.07	9.05	0	2.02
454.9	19.37	37.06	14.18	0.07	8.67	0	1.94

Table XIV. Results of the TDMS Gas Analysis for Sample S‴ cont.

Temp	26	27	30	31	40	41	42	45
134.4	0	0	0.65	0	0	0	0	1.2
100.1	0	0	1.15	0	0	0	0	0
223.7	0	0	0	0	0.34	0.42	0.34	1.62
255.1	0.09	0	0	0	0.27	0.72	0.51	2.5
31.7	0	0	0	0	0	0	0	0
278.3	0.09	0	0	0	0.45	1.18	0.72	0
68.6	0	0	2.31	0	0	0	0	1.59
921.3	0	0	0	0	0	0	0	0
22.9	0	0	0	0	0	0	0	0
909.6	0	0	0	0	0	0	0	1.7
911.6	0	0	0	0	0	0	0	0
912	0	0	0	0	0	0	0	3.42
314.1	0.16	0	0	0	0	0	0.93	2.9
911.1	0	0	0	0	0	0	0	0
874.4	0	0	0	0	0	0	0	1.52
843.4	0	0	0	0	0	0	0	1.55
911.9	0	0	0	0	0	0	0	0
911.3	0	0	0	0	0	0	0	0
901.1	0	0	0	0	0	0	0	3.54
805.5	0	0	0	0	0	0	0	2.76
757.5	0	0	0	0	0	0	0	0
358.2	0.31	0	0	0	0	0	1.12	3.01
721.6	0.12	0	0	0	0	0	0	1.33
695.9	0.24	0	0	0	0	0	0	2.05
498.5	0.21	0.66	0	0	0	1.11	0.42	0
540.6	0.24	0.41	0.13	0	0.24	0.12	0.15	0.79
406.1	0.26	0	0	0	0	4.68	1.99	2.6
643.1	0.11	0.14	0	0	0	0.12	0	1.81
608	0.1	0.24	0	0	0	0	0	0
586.7	0.11	0.26	0	0	0	0.2	0	0
425.5	0.45	0	0.21	0	0	5.97	2.65	0
454.9	0.44	0	0.33	0	0	6.22	3.21	0
	26	27	30	31	40	41	42	45

Table XIV. Results of the TDMS Gas Analysis for Sample S‴, cont.

Temp	50	54		55	56	57	64	77	78
134.4	0			0	0	0	0	0	0
100.1	0			0	0	0	0	0	0
223.7	0			0	0	0	0	0	0
255.1	0			0	0	0	0	0	0
31.7	0			0	0	0	0	0	0
278.3	0			0.09	0.09	0	0	0	0
68.6	0			0	0	0	0	0	0
921.3	0			0	0	0	0	0	0
22.9	0			0	0	0	0	0	0
909.6	0			0	0	0	0	0	0
911.6	0			0	0	0	0.12	0	0
912	0			0	0	0	0	0	0
314.1	0			0.08	0.08	0	0	0	0
911.1	0			0	0	0	0	0	0
874.4	0			0	0	0	0	0	0
843.4	0			0	0	0	0	0	0
911.9	0			0	0	0	0	0	0
911.3	0			0	0	0	0	0	0
901.1	0			0	0	0	0.09	0	0
805.5	0			0	0	0	0	0	0
757.5	0			0	0	0	0	0	0
358.2	0			0.16	0.23	0	0	0	0
721.6	0			0	0	0	0	0	0
695.9	0			0	0	0	0	0	0
498.5	0.1	0		0.1	0.21	0.1	0	0.1	0.31
540.6	0	0		0	0	0	0	0	0.24
406.1	0.13	0	7	0.33	0.86	0.66	0	0.07	0.26
643.1	0			0	0	0	0	0	0
608	0			0	0	0	0	0	0
586.7	0			0	0	0	0	0	0
425.5	0.19	0	6	0.38	1.27	0.89	0	0.06	0.32
454.9	0.19	0.1	2	0.5	1.37	0.93	0	0.06	0.31

LOI calculations show that volatile adsorbates are being removed as a function of calcination. This is consistent with both RGA and pressure data. TDMS for the 600ºC calcination shows a pressure peak at temperatures between 200ºC and 300ºC. RGA data show that the largest components are H_2O, CO_2, CH_4, and H_2. The same temperature region for the 950-1 calcination shows no pressure peak. There is substantially less total gas and the species distribution is somewhat different. Water and CO_2 make up the largest fractions, CH_4 is present, followed by N_2 and amu 41. The same region for the 950-2 calcination shows a small pressure peak. The gas fractions are quite similar to 950-1 with larger quantities. The definitive assignment of the smaller peaks in the mass spectra is very difficult because there is insufficient gas quantity to determine the difference between parent and daughter peaks. Searches of the NIST database indicate that most of compounds associated with peaks 41 and 45 contain C, H, and N and with peaks 40, 42, 43, 50, 51,52, 54, 54, 64, 77, and 78 contain C and H. They account for a very small amount of the total and their significance, if any, can not be determined at this time; however, it is unlikely that they will have a deleterious effect during storage.

Gas analysis of the outer food-pack can atmosphere shows that some changes may be occurring; however, the results are within experimental error for air. Gas analysis of the inner food-pack can shows that a chemical reaction has occurred. O_2 was consumed by two pathways, the formation of CO_2, and the formation of PuO_{2+x}. The He comes from the alpha decay of plutonium (PuO_2), and H_2 is released in the formation of PuO_{2+x}, with the possibility of some contribution from radiolytic and thermal decomposition of the polyethylene bag. There was no obvious degradation of the storage containers that could be directly related to the chemical or mechanical storage environment. Neither the outer nor inner cans were leaking.

These results show that for this impure oxide LOI was met even for sample S before any calcination. After calcination at 600ºC and 950ºC, the 3013 LOI criterion was also met. Mass spectral results show that water and carbon dioxide are major contributors throughout the temperature range of all runs.

Minor gas species change with respect to processing temperatures. The minor mass spectral peaks are difficult to definitively assign; however, they appear to fall into two major categories; C-H-N and C-H compounds. These compounds are not expected to play any role during storage life times.

The isotopic distribution of plutonium was also measured for the as-received powder S and the results are shown in Table XV.

Table XV.   Isotopic Distribution of Plutonium for the "As-received" Powder S.

Isotope	Mass %
Pu-238	0.0301
Pu-239	92.9943
Pu-240	6.5125
Pu-241	0.4339
Pu-242	0.0292
Total	100

4.0 CONCLUSIONS

- The precalcined S, and the calcined S′ and S″ powders show very similar affinity for water.

- During the first calcination step, the percent mass loss was more than the percent mass loss during the second calcination step.

- The calcination effect on the LOI value appears to be less if the powder is calcined in one step directly to 950°C instead in two steps (first at 600°C and next at 950°C).

- The calcination effect on the specific surface area also appears to be less significant if the powder is calcined in one step directly to 950°C instead in two steps (first at 600°C and next at 950°C).

- The three impure oxides studied so far calcined at 600°C, first step, and 950°C, second step, very interestingly show almost identical specific surface area values of about 0.7 m^2/g. This value of specific surface area for the impure oxides is about seven times smaller than that for the pure plutonium oxide. This smaller value can be attributed to sintering during the heating process facilitated by the presence of inorganic salts as impurities.

- Both the outer and inner cans show elevated concentrations of CO_2, He, and H_2.

- The gas in the inner can had reacted with the powder to give a decreased oxygen content, increased hydrogen content, and increased CO_2 content.

- Mass spectral results show that water and carbon dioxide are major contributors throughout the temperature range of all thermal desorption runs. Minor gas species change with respect to processing temperatures.

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