LA-UR-18-20970

Title: MIS High-Purity Plutonium Oxide Hydride Product 5501579 (SSR124): Final Report

Author(s):
Veirs, Douglas Kirk
Stroud, Mary Ann
Berg, John M.
Narlesky, Joshua Edward
Worl, Laura Ann
Martinex, Max A.
Carillo, Alex

Intended for: Report

Issued: 2018-02-08

MIS High-Purity Plutonium Oxide Hydride Product 5501579 (SSR124): Final Report

---

Authors:

D. Kirk Veirs
Mary A. Stroud
Max A. Martinez (retired)
Alex Carrillo (retired)
John M. Berg
Joshua E. Narlesky
Laura Worl

MIS High-Purity Plutonium Oxide Hydride Product 5501579 (SSR124): Final Report

Abstract

A high-purity plutonium dioxide material from the Material Identification and Surveillance (MIS) Program inventory has been studied with regard to gas generation and corrosion in a storage environment. Sample 5501579 represents process plutonium oxides from hydride oxide from Rocky Flats that are currently stored in 3013 containers. After calcination to 950°C, the material contained 87.42% plutonium with no major impurities. This study followed over time, the gas pressure of a sample with nominally 0.5 wt% water in a sealed container with an internal volume scaled to 1/500th of the volume of a 3013 container. Gas compositions were measured periodically over a six year period. The maximum observed gas pressure was 124 kPa. The increase over the initial pressure of 70 kPa was primarily due to generation of nitrogen and carbon dioxide gas. Hydrogen and oxygen were minor components of the headspace gas. At the completion of the study, the internal components of the sealed container showed signs of corrosion.

Contents

Figures

Tables

Introduction

The Los Alamos National Laboratory (LANL) Shelf-life Surveillance project was established under the Material Identification and Surveillance (MIS) Program to identify early indications of potential failure mechanisms in 3013 containers.[1] Samples were taken from plutonium processes across the DOE complex. These "representative" materials were sent to LANL to be included in the MIS inventory.[2] The small-scale surveillance project is designed to provide gas generation and corrosion information of the MIS represented materials under worst-case moisture loadings. This information, in combination with material characterization, allows predictions of the behavior of 3013 packaged materials stored at DOE sites. Pressure, gas compositions, and corrosion were monitored in small-scale reactors (SSRs) charged with nominally 10-gram samples of plutonium bearing materials with nominally 0.5 wt% water, the upper limit allowed by the DOE's 3013 Standard.[1]

This report discusses 5501579, a high purity plutonium (Pu) dioxide material from the MIS Program inventory that originated in hydride oxidation in Building 779, Rooms 152A/160A at the Rocky Flats Plant, later known as the Rocky Flats Environment Technology Site (RFETS). The plutonium oxide is representative of hydride oxide from Rocky Flats.[3]

Figure 1. 5501579 upon arrival at LANL.

Material Characterization

The weapons grade plutonium oxide was calcined at 950 °C for 2 hours on July 17, 1997. Several measurements of material characteristics that were obtained on the calcined sample are summarized in Table 1.

Table 1. Material Physical Characteristics

Specific Surface Area (SSA) 5-point (m^2 g^{-1})	0.57 (0.59, 0.55)
Bulk Density (g cm^{-3})	2.7 (2.58, 2.66)
Tap Density (g cm^{-3})	3.8 (3.31 ,4.3)
Pycnometer Density (g cm^{-3})	10.36

Table 2 summarizes the wt% of key elements as well as any impurity present as 0.01 wt% or greater. Oxygen is not measured and it is assumed to make up the difference between the sum of the listed elements plus plutonium and 100%. No measurements of soluble species were conducted for this material. Isotopic Data from calorimetry/gamma isotopics is listed in Table 3.

Table 2. Elemental data. Table 2 lists the major elements with concentrations above 0.01%.

Element	**wt%**
Aluminum	0.018
Calcium	0.004
Carbon	0.012
Chlorine	0.074
Gallium	0.90
Iron	0.069
Magnesium	0.009
Nickel	0.013
Potasium	0.030
Silicon	0.096
Sodium	<0.003
Tantalum	0.024
Uranium	0.3

Table 3. Isotopic data listed as mass fraction (g/g plutonium). Specific power is reported in mW per gram of material, not per gram of plutonium. The isotopics and wattage were measured on 11/25/2003.

Isotope	Mass Fraction (g/gPu)
Pu-238	0.0001862
Pu-239	0.9438426
Pu-240	0.0542669
Pu-241	0.0014543
Pu-242	0.0002500
Am-241	0.0016547

Total Plutonium (calorimetry) (g Pu/g of material)	0.88048
Specific Power (mW/g of material)	2.205

The specific wattage of 5501579 as a function of time from the measurement date is shown in Figure 2.

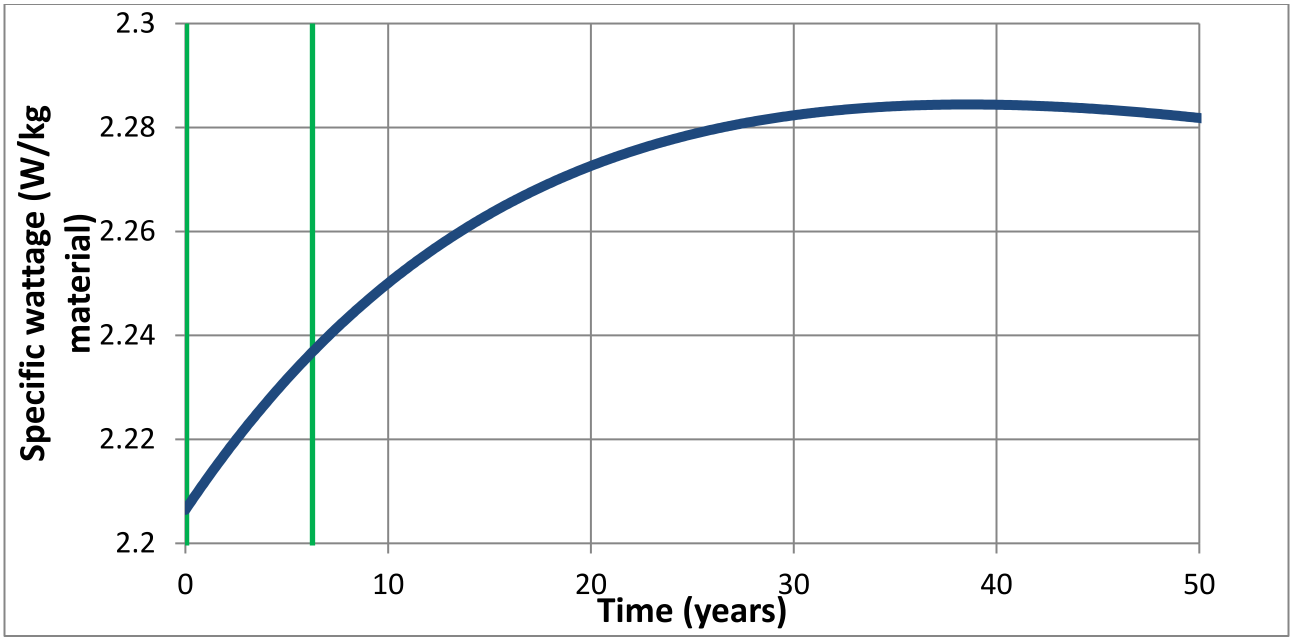


Figure 2. The specific wattage of 5501579 as a function of time from the last measurement date in 2003. The vertical green lines bound the time the sample was in the reactor.

Figure 3 provides information on He evolution as a function of time in 5501579.

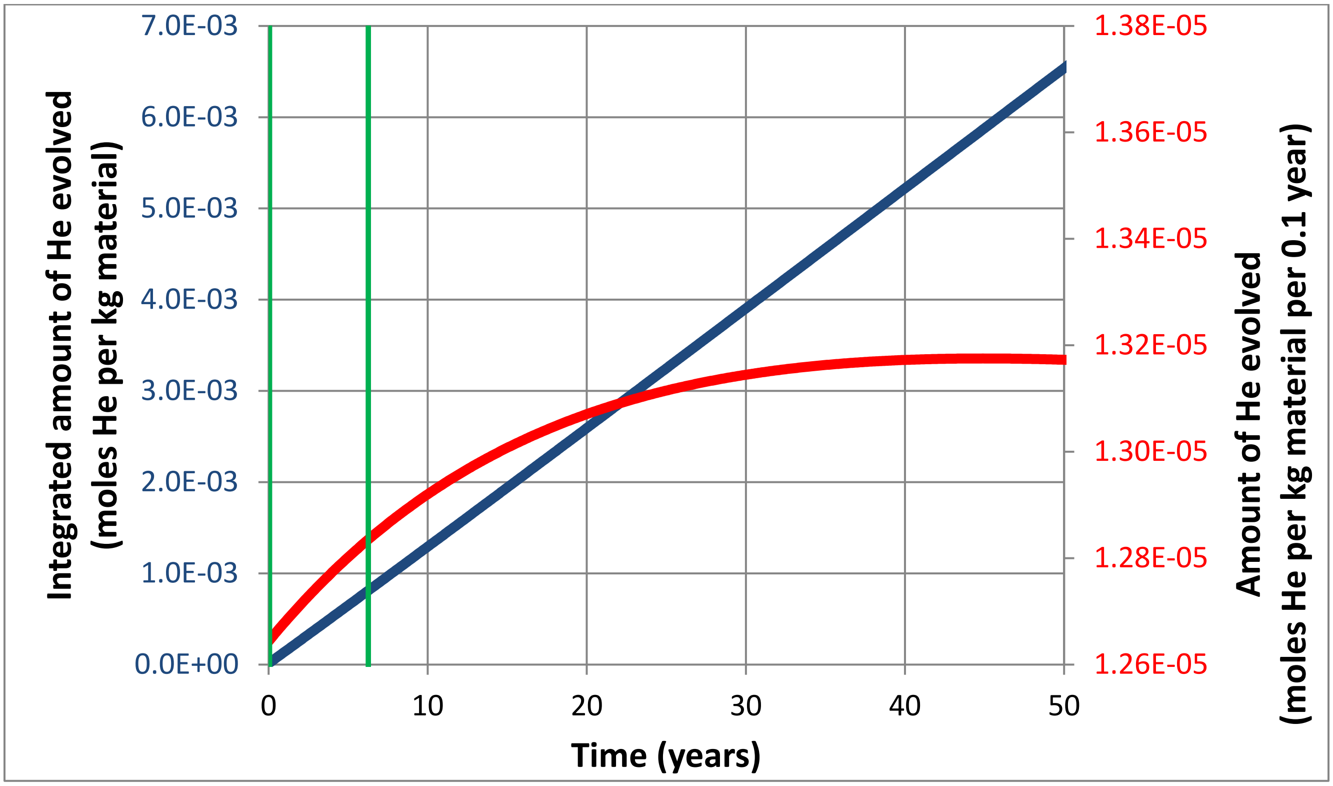


Figure 3. Integrated amount of He evolved from alpha decay from 5501579 as a function of time (blue line and left axis) and the moles of He per kg material per 0.1 year (red line and right axis). The vertical green lines bound the time the sample was in the reactor.

Experimental Procedure

The design of the small-scale reactor (SSR) system has been described previously.[4] The container's nominally five cm^3 internal volume is scaled to ~1/500th of the inner 3013 storage container. The material of construction of the inner small-scale containers is 304L stainless steel. The SSR consists of a container body[5] welded into a Conflat flange and a lid consisting of a Conflat flange with tubing attachments for connections to a pressure transducer and a gas manifold. An inner bucket is used to hold material and is inserted into the container body during the loading activities. The inner bucket allows the fine plutonium oxide powder to be handled with minimal or no spillage. A low-internal-volume pressure transducer and associated low-volume tubing is attached to the lid. Small-scale reactors have interchangeable parts with varying volumes. For this study, a Type H container with a total internal volume of 5.326 cm^3 was used.[5] The gas sampling volume located between two sampling valves, 0.05 cm^3 (~1 % of the SSR volume), allows gas composition to be determined with minimal effect on the internal gas pressure. A disassembled SSR is shown in Figure 4.

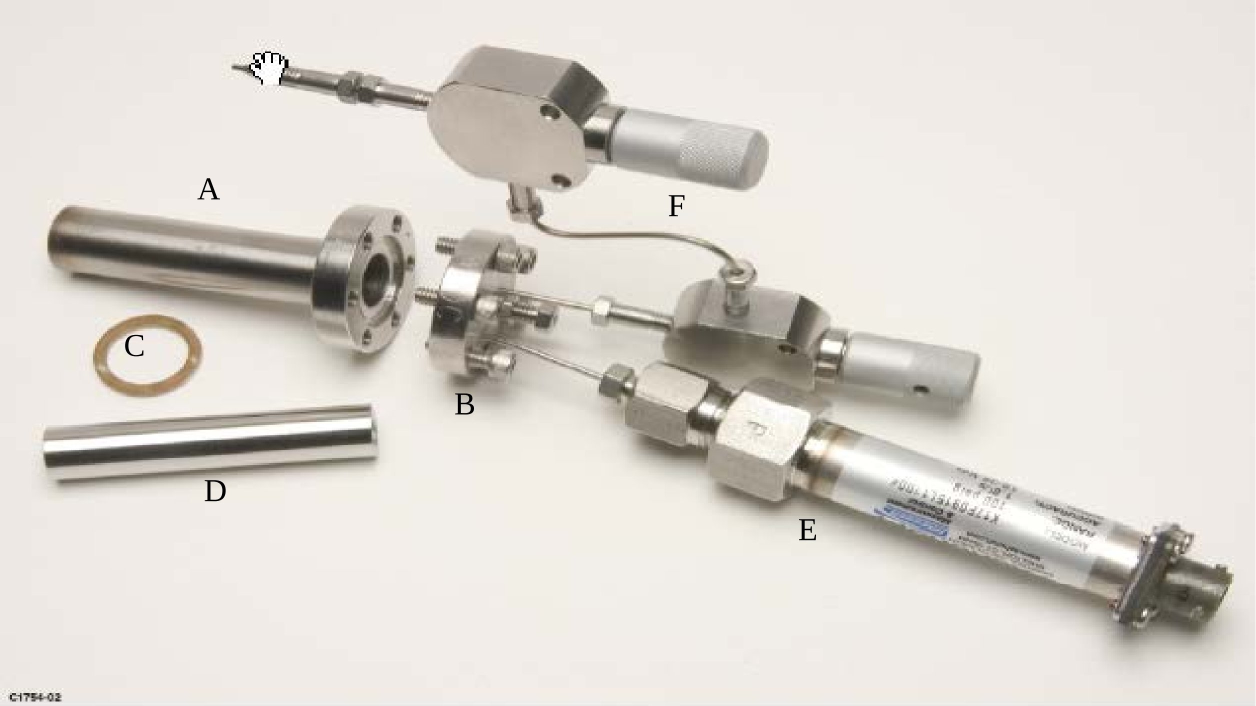


Figure 4. Dissassembled SSR: Conflat container body (A) with conflat flange lid (B), copper gasket (C), inner bucket (D), pressure transducer (E), and a sampling volume between two sampling valves with connection to the gas manifold (F). Inner bucket slides into container body and holds the mateterial.

Gas generation is to be characterized for each MIS represented material at the bounding moisture content of 0.5 wt%. The procedure to achieve 0.5 wt% moisture included (1) estimating the moisture content of the material as it was received for small-scale loading and (2) adding sufficient water to bring the total to 0.5 wt%. The moisture content of the material was estimated by weight loss upon heating to 200 °C (LOI-200 °C) of a one gram sample that was cut from the parent lot at the same time as the 10 g small-scale sample. The LOI-200 °C samples were placed in a glass vial which remained in the glove box line with the small-scale sample until the LOI-200 °C measurement was performed, typically one day or less after the sample split and just prior to SSR loading. LOI-200 °C involved heating nominally one gram of the material for 2 hours at 200 °C, cooling the material for 10 minutes and determining the mass difference of the material before and after heating. The mass loss observed was attributed to adsorbed water. It was assumed that the LOI-200 °C material contained an additional ~1 monolayer equivalent of water, approximately 0.01 wt% for this material, as hydroxyls or chemically adsorbed water which was not removed by heating to 200 °C.[6] The amount of water to be added to achieve 0.5 wt% total moisture was calculated as the difference between 0.5 wt% and the sum of the adsorbed water determined by LOI-200 °C and the chemically adsorbed water assumed to be 0.01 wt%. In addition, a sample from the parent was split and placed in a glass vial inside of a hermetically sealed container. The water content of this sample was determined by Thermal Gravametric Analysis-Mass Spectroscopy (TGA-MS). TGA-MS is inherently more accurate than LOI-200 °C, although there can be errors associated with this method due to handling and excessive times before the sample is run.

The procedure to add moisture is described briefly. A ten-gram sample of the 5501579 material was placed on a balance in a humidified chamber. Weight gain was recorded as a function of time. The sample was then placed into a small-scale reactor. The glove boxes used for loading and surveillance were flushed with He, resulting in a glove box atmosphere of mainly He with a small amount of air. Some moisture loss was expected during transfer from the humidified chamber into the SSR in the very dry glove box atmosphere (relative humidity < 0.1 %). Transfer time from the balance where the final mass measurement is made to when the SSR was sealed was kept to approximately 45 seconds. Weight loss during transfer for high-purity oxides was measured to be 0.07 wt% per minute.[7] This correction was applied to obtain the estimated moisture content.

The sealed SSR was placed in a heated sample array maintained at 55 °C. Fifty microliter gas samples (~1.1 % of the headspace gas per sample) were extracted through a gas mainfold and analyzed using an Agilent 5890 GC (gas chromatograph) calibrated for He, H_2, N_2, O_2, CO_2, CO and N_2O. Water vapor was not measured in these samples. The pressure and array temperature was recorded every fifteen minutes. The pressure data was reduced to weekly average values reported here. Gas composition was sampled at least annually.

At the termination of the experiment, a final GC gas sample was taken, and the SSR was removed from the array and allowed to cool to glove box temperature. The SSR lid was removed and a new lid containing a relative humidity sensor was placed on the container within 20 sec of removal. After allowing 53 minutes for the system to equilibrate, the relative humidity and temperature in the container were measured using a Vaisala HMT330 sensor and readout. The material was then removed from the container and the moisture content in the material was estimated by performing LOI-200 °C.

Results

Loading

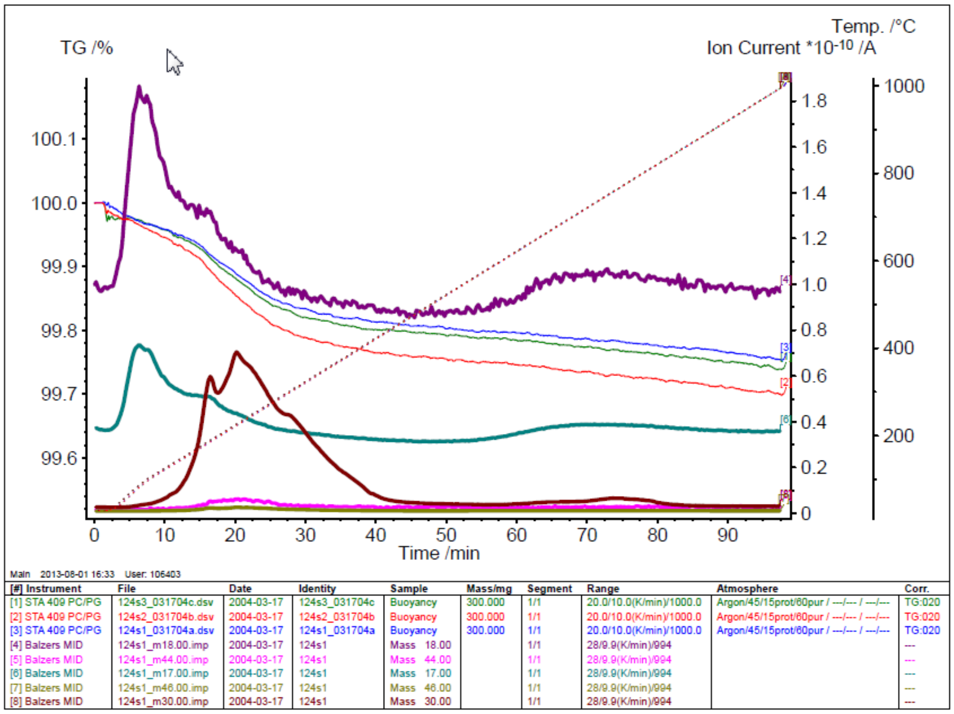
A ten-gram split from the parent was selected for loading into the SSR. The mass of the sample prior to moisture loading, m_{mat}, the volume the material occupies calculated from m_{mat} and the pycnometer density, V_{mat}, and the calculated free gas volume within the SSR, V_{gas}, during the gas generation study are given in Table 4.

Table 4. Mass of sample and results of calculation of free gas volume using approach in *Obtaining G-values and rate constants from MIS data* Appendix A.[5]

Mass of sample m_{mat}	Volume of Material V_{mat}	Volume of SSR V_{SSR}	Free Gas Volume in SSR V_{gas}
10.08 g	0.973 cm^3	5.326 cm^3	4.353 cm^3

TGA-MS Results

TGA-MS data for the sample of the parent material are shown in Figure 5. The sample was large enough to split into three subsamples. TGA traces for all three subsamples and MS traces for channels that were above background for one of the three samples are illustrated. Total moisture content was determined to be 0.090 wt%. The majority of the water was released at low temperature (less than 200 °C) which is reasonably assigned to physically adsorbed (physisorbed) water. A second fraction of water, 0.03 wt%, was released from 500 °C to 950 °C and is interpreted to be chemically adsorbed (chemisorbed) water (hydroxyls). The 0.03 wt% is a low estimate of chemisorbed water since it is expected that additional chemisorbed water was released between 200 °C and 500 °C. Nitrogen oxides are the primary volatiles from 200 °C to 400 °C. During the TGA-MS analysis, 0.13 wt% nitrogen dioxide (~0.013 g in original sample) and 0.004 wt% carbon dioxide (~0.0004 g in original sample) was released. The LOI-200 °C loss of 0.16 wt% overestimates the amount of water for this material, which had been exposed to air for approximately six years prior to the measurement. The presence of surface adsorbed nitrogen and carbon oxide species on aged material limits the accuracy of the LOI-200 °C techniques to estimate water content.



Main 2013-08-01 16:33 User: 106403

[#] Instrument	File	Date	Identity	Sample	Mass/mg	Segment	Range	Atmosphere	Corr.
[1] STA 409 PC/PG	124s3_031704c.dsv	2004-03-17	124s3_031704c	Buoyancy	300.000	1/1	20.0/10.0(K/min)/1000.0	Argon/45/15prot/60pur / ---/--- / ---/---	TG:020
[2] STA 409 PC/PG	124s2_031704b.dsv	2004-03-17	124s2_031704b	Buoyancy	300.000	1/1	20.0/10.0(K/min)/1000.0	Argon/45/15prot/60pur / ---/--- / ---/---	TG:020
[3] STA 409 PC/PG	124s1_031704a.dsv	2004-03-17	124s1_031704a	Buoyancy	300.000	1/1	20.0/10.0(K/min)/1000.0	Argon/45/15prot/60pur / ---/--- / ---/---	TG:020
[4] Balzers MID	124s1_m18.00.imp	2004-03-17	124s1	Mass 18.00		1/1	28/9.9(K/min)/994		---
[5] Balzers MID	124s1_m44.00.imp	2004-03-17	124s1	Mass 44.00		1/1	28/9.9(K/min)/994		---
[6] Balzers MID	124s1_m17.00.imp	2004-03-17	124s1	Mass 17.00		1/1	28/9.9(K/min)/994		---
[7] Balzers MID	124s1_m46.00.imp	2004-03-17	124s1	Mass 46.00		1/1	28/9.9(K/min)/994		---
[8] Balzers MID	124s1_m30.00.imp	2004-03-17	124s1	Mass 30.00		1/1	28/9.9(K/min)/994		---

Figure 5. TGA-MS data for the parent material. Mass 17.00 is H_2O, Mass 30 is NO, and Mass 44 is CO_2. The cracking pattern of NO_2 in the MS instrument results in mass 30 (NO) as the dominant mass fraction for NO_2.

Moisture addition

The measurements and assumptions used to calculate the moisture content at the time of loading are summarized in Table 5. When using LOI moisture measurements, the estimated amount of chemisorbed water is added to the LOI moisture to determine total moisture. Chemically absorbed water may be estimated to be one monolayer (ML) of moisture, 0.01 wt% or when TGA data is available, the TGA data (in this case 0.03 wt% (2.3 ML) may be used to provide a better estimate of chemisorbed water (see Appendix 1). However, the best value for the moisture content at loading, 0.33 wt%, is determined using TGA-MS total moisture data, as given in Table 5 line 12.

Table 5 . Loading moisture data summary.

	Parameter	Value	Units
1	Original Calcination Date	7/17/1997	
2	Loading Date	12/16/2003	
3	Unloading Date	3/2/2010	
4	Initial sample weight (m_{mat})	10.08	g
5	Initial Moisture (Total) by TGA-MS	0.09	wt%
6	Initial Moisture by LOI-200 °C	0.16	wt%
7	Estimated additional (chemisorbed) moisture	0.03 (TGA from 500 °C to 950 °C at loading – 2.3 ML)	wt%
8	Total Moisture added	0.29	wt%
9	Relative Humidity in glove box during loading	0.01/24.8	% / °C
10	Estimated moisture loss during loading	0.05	wt%
11	Estimated Total Moisture in loaded sample (using LOI) = Line 6 + Line7 +Line8 –Line 10	0.43 (33 ML)	wt%
12	Estimated Total Moisture in loaded sample (using TGA-MS) = Line 5 + Line 8 –Line 10	0.33	wt%

The moisture uptake as a function of exposure time to a high humidity atmosphere is plotted in Figure 6. The increase in mass is attributed to water adsorption by the material. Some loss of water occurs between when the material is transferred from the humidified chamber to the balance where the final mass measurement is made. Thus, the total moisture added in Table 5, 0.29 wt%, is slightly less than the mass gain during moisture uptake, 0.31 wt%.

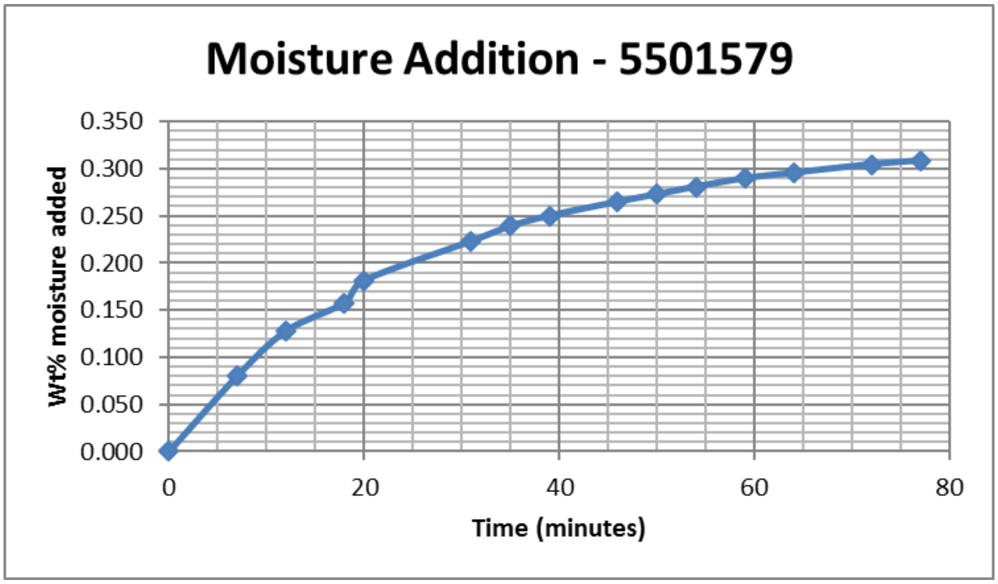


Figure 6. Moisture Addition Curve

Gas Generation

The total pressure in SSR124 as a function of time, as well as the partial pressure of several gasses, is shown in **Error! Reference source not found.**. Detailed information on gas composition and uncertainties is in Attachment 1 and on pressure in Attachment 2.

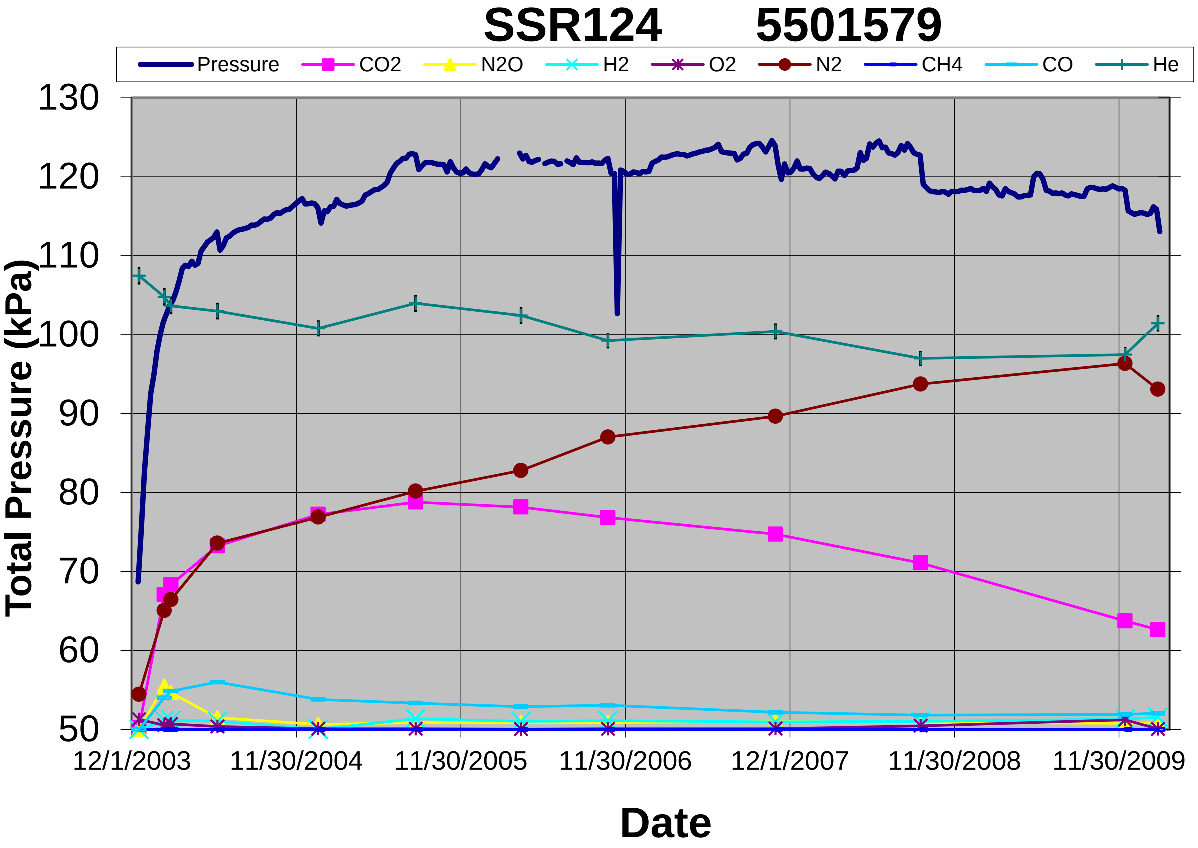


Figure 7 Total pressure and partial pressure of gases measured using a gas chromatograph as a function of time. The error bars are determined from 1 σ uncertainties in the total pressure and 1 σ uncertainties in the GC sensitivities to the various gases which are determined using the calibration of the GC.

The initial pressure of 68 kPa increased to 107 kPa in the first three months and gradually increased to a maximum pressure of 124 kPa over the next 2.5 years. There was a small decrease in the total pressure within the container to 113 kPa over the final 1.5 years. Hydrogen and oxygen were minor components in the headspace gas. Hydrogen was initially not detected and increased to 1.1 kPa within 8 weeks. Hydrogen concentration fluctuatied over the next six years reaching a maximum of 1.6 kPa at the termination of the experiment. Oxygen began at 1.3 kPa and decreased to about 0.5 kPa within eight weeks and then to 0.1 kPa within two years where it remained for approximately 2 years. Over the next sixteen month time range, September 2008 to December 2009, the measured oxygen partial pressure rose to 1.2 kPa before returning to 0.1 kPa for the remainder of the experiment. This observation is assumed to be due to insufficient pump down during sampling.

The net increase in total pressure during the experiment was primarily due to the generation of nitrogen and carbon dioxide both of which increased to approximately 30 kPa over the first 21 months. After 21 months, the amount of nitrogen continued to increase to a maximum value of 46 kPa while the amount of carbon dioxide decreased with time. Similar behavior was observed in the small scale reactor containing TS70701, a high purity oxide from metal oxidation operations.[8] Initially carbon monoxide and nitrous oxide were generated to a maximum pressure of near 6 kPa and then decreased to 1-2 kPa.

Moisture measurements on unloading

The SSR was removed from the heated array and placed in a holder to cool. The lid was removed and within 20 seconds it was replaced with a lid modified to hold a RH sensor. After allowing 53 minutes for the system to equilibrate, the relative humidity and temperature in the container were measured using a Vaisala HMT330 sensor and readout. The moisture content in the material at termination was estimated to be 0.06 wt% by performing LOI-200 °C, which includes the physisorbed water only. To estimate the total moisture at unloading, an additional 0.03 wt% (from TGA at loading) was added to account for chemisorbed water that was not removed by heating to 200 °C. The unloading LOI-200 °C (0.06 wt%) was 0.1 wt % less than the loading LOI-200 °C (0.16 wt%) , but is the same as the wt% water measured in the initial TGA to 500 °C (0.06 wt%). LOI-200 °C also include other gases that desorb at 200 °C (see explanation under TGA-MS Results). Differences in the amount of NOx and CO_2 gases desorbing from the initial and final sample could account for the difference. See section on Behavior of CO_2 and NO_2 for explanation of how much of the initial nitrogen and carbon oxides might still be present at unloading and observable in the LOI-200 °C.

The amount of physisorbed water may also be estimated based on the RH at unloading. (Appendix 2). Given the measured RH of 24.7% at 24.3 °C in the SSR at unloading, BET theory predicts 0.9 to 1.3 (average 1.1) ML or 0.014 wt% physisorbed water was present. Assuming an additional 2.3 ML of moisture is present as chemisorbed water as indicated by TGA moisture from 500 C to 950 C, the RH estimate of the moisture at unloading is 0.04 wt%.

Sample unloading and moisture data are summarized in Table 6.

Table 6. Unloading moisture data summary

	Parameter	Value	Units
1	Unloading Moisture by LOI-200 °C	0.06	wt%
2	Estimated additional (chemisorbed) moisture	0.03 (TGA from 500 °C to 950 °C at loading – 2.3 ML)	wt%
3	Estimated total moisture at unloading from LOI = Line 1 + Line 2	0.09	wt%
4	Relative Humidity/Temperature in headspace at unloading	24.7 / 24.3	%/ °C
5	Number of monolayers at unloading RH and temperature using Figure A-1.	0.9 – 1.3	ML
6	Mass of physisorbed water using average of line 5.	0.014	wt%
	Estimated total moisture at unloading from RH and temperature = line 2 + line 6	0.04	wt%

Corrosion

Images of the inner bucket and copper gasket after unloading are shown in Figure 8. No images of the sides of the inner bucket are available.

Figure 8. Photographs after unloading: a) inner bucket b) bottom of the inner bucket where the staining at the lower right is due to corrosion c) corrosion of the copper gasket.

Corrosion is observed within SSR124 which is unexpected because the material is high-purity plutonium dioxide with only trace amounts of chlorine. Corrosion was observed in the bottom of the inner bucket and on the copper gasket located in the headspace of the reactor. The green coating on the copper gasket is assumed to be a form of copper (II) chloride that is green when hydrated. Corrosion of the copper gasket in the headspace is evidence that gas-phase corrosive species containing chlorine were evolved from the material.

Discussion

A goal of the small-scale surveillance studies is to understand the hydrogen gas generation response of material exposed to moisture over a broad range of materials. Recommendations on the analysis of hydrogen partial pressure curves include calculations to obtain hydrogen G-values and formation and consumption rate constants assuming that the hydrogen gas is formed either from radiolysis or from surface decomposition of water.[5] In order to perform these calculations knowledge of the moisture content of the material during the study and the dose to the moisture is required. We will first discuss the amount of moisture on the material during the study and use the results as input to the $G(H_2)$ and rate constant calculations. We will follow those results with a discussion of the observation of other gases.

Unlike plutonium-bearing materials currently stored in 3013 containers throughout the DOE complex, 5501579 was exposed to the glove box environment for nearly six years after calcination prior to loading. A significant formation of hydroxyls on the oxide surface is expected after this much time. Gases, such as NOx and CO_2, would also be adsorbed to the surface as indicated in the TGA-MS, Figure 5. The presence of these species may alter the gas generation behavior compared with recently calcined plutonium oxide.

Estimation of the amount of moisture on the material during the gas generation study

Moisture adsorbed on high-purity plutonium dioxide such as 5501579 is thought to exist as physisorbed water that behaves according to BET theory[9] and as chemisorbed water with very low chemical activity (very low water vapor pressure). The latter water can be described as surface hydroxyls and is removed from the plutonium dioxide surface only at high temperatures. In order to use BET theory to estimate the amount of water on the material during the experiment, the SSA, the amount of water in a monolayer, and the RH are needed.

The difference between the best estimate of the amount of water in the reactor when the material was loaded (0.033 g from TGA) and unloaded (0.004 g from RH), 0.029 g, is much greater than the amount of water that produced H_2 (0.00005g) plus the amount of water that would be in the gas phase at unloading (0.00002), 0.00007 g. A gradual conversion of physisorbed water to chemisorbed water (hydroxyls) during the experiment would also contribute to lower measured moisture content at the termination of the experiment than at the beginning because more water would be inaccessible to the LOI-200 °C measurement. The conversion of weakly-bound water to strongly-bound water over time is expected to be less than 1.0 monolayers of water, which corresponds to approximately 0.001 g for this sample, much less than the difference between the moisture at loading and unloading.[10, 8]

The additional difference is probably due to water condensing in the colder region of the reactor plumbing.[8] During the gas generation study, the moisture in the cold region is located at a sufficient distance from the material that the dose it receives is orders of magnitude smaller than the dose the water associated with the material receives. This water is NOT expected to contribute to gas generation and would result in a low value in G-value calculations. Moisture at unloading should provide the better value for gas generation calculations. Table 7 summarizes the amount of water on the material, in the gas phase, and decomposed to form H_2 expressed as weight percent, moles, grams, and monolayers.

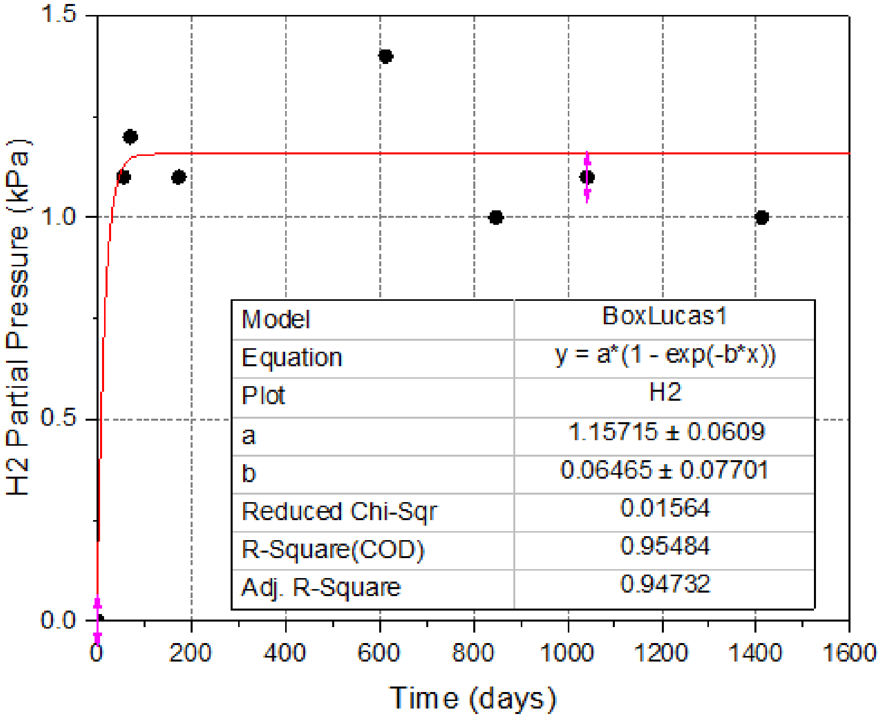
Table 7. The amount of water adsorbed on the material, in the gas phase, and decomposed to form H_2 expressed as moles, grams, and monolayers. The mass of water in a monolayer is 0.00126 g. Calculations use SSA = 0.57 $m^2\ g^{-1}$, m_{mat} = 10.08 g and V_{gas} = 4.353 cm^3. The amount of chemisorbed water on the material was assumed to be 0.03 wt% at all times.

Condition	**Amount of Water**			
	wt%	g	moles	monolayers
	0.013	0.0013	7x10^{-5}	1
In gas at 25 ^{0}C and 100% RH (3.170 kPa)		9.1x10^{-5}	5.1x10^{-6}	0.072 (equivalent)
In gas at 55 ^{0}C and 100% RH (15.752 kPa)		4.5x10^{-4}	2.5x10^{-5}	0.36 (equivalent)
In gas at unloading, 24 ^{0}C and 25% RH (0.746 kPa)		2.1 x10^{-5}	1.2x10^{-6}	0.017 (equivalent)
Reacted to produce max H_2 in gas at 55 ^{0}C, (1.6 kPa)	4.6 x10^{-4}	4.6x10^{-5}	2.6x10^{-6}	0.036 (equivalent)
On material at loading: physi+chemisorbed (TGA)	0.33	0.033	1.8x10^{-3}	26
Presumed condensed on piping 25 ^{0}C and effectively removed from the system	0.29	0.029	1.6x10^{-3}	23
On material at unloading: physisorbed (LOI)	0.06	0.006	3.4x10^{-5}	4.8
On material at unloading: physisorbed (RH)	0.014	0.0014	2.5 X10^{-6}	1.1
On material at unloading: physi (LOI)+chemisorbed (2.3 ML)	0.09	0.009	5.0 X10^{-4}	7.1
On material at unloading: physi (RH)+chemisorbed (2.3 ML)	0.04	0.004	2x10^{-4}	3.2

(Note: Additional moisture could have been consumed in formation of the corrosion products such as iron hydroxide)

The H_2 G-value and rate constants

It is recommended that *G(H_2)* and rate constants be calcuated for materials where H_2 is observed. The mathematical formalism is given in *Obtaining G-values and rate constants from MIS data*.[5] First, the hydrogen partial pressure versus time observations are fit to a single exponential function. The initial H_2 generation rate is determined from the first eight measurements of hydrogen partial pressure (excluding the zero value) taken over the first 1041 days of the experiment. The results are given in Table 8.



Model	BoxLucas1
Equation	y = a*(1 - exp(-b*x))
Plot	H2
a	1.15715 ± 0.0609
b	0.06465 ± 0.07701
Reduced Chi-Sqr	0.01564
R-Square(COD)	0.95484
Adj. R-Square	0.94732

Figure 9. The hydrogen partial pressure and the fit to Equation 1, or zeroth order formation and first order consumption reaction.

The H_2 partial pressure increased by 1.1 kPa the first 56 days, indicating a lower limit for the initial production rate of 0.02 kPa/day or 1.9 X 10^{16} molecules/day. The hydrogen gas generation rate was determined by fitting the hydrogen partial pressure data to Equation 1 which expresses H_2 pressure as a function of time,

$$\boldsymbol{p = a(1 - e^{-bt})} \qquad \textbf{Equation 1}$$

where *a* has units of kPa and *b* has units of day^{-1}. Detailed information on the derivation of the equation and interpretation of the fit parameters may be found elsewhere.[5]

The values for the fit parameters yielding the curves in Figure 9 are given in Table 8. We will use these values to calculate *G(H_2)* and the rate of the hydrogen consumption reactions.

Table 8. The fit parameters and standard errors from the hydrogen generation data

Small-scale Surveillance sample identification	$a = k_1/k_2 = P_{max}$ (kPa)	$b = k_2$ (day^{-1})
SSR124	1.16	0.065

The fitting constants are used to calculate *G(H2)* and reaction rate constants. The variable m_{H2O} is taken from the total water mass at loading (which is not representative of the water physically present on the material during the experiment), the mass of water associated with the H_2 gas pressure, the mass associated with the physisorbed water at unloading (from RH and for comparison from LOI), and the mass associated with both the chemisorbed and physisorbed water at unloading. The stopping power ratio is 3.69.

Table 9. *G(H2)* and rate constants calculated from the reaction parameters and the estimated moisture content using Equations from Reference 6.

5501579				
Variable	m_{H2O}	Equation in Ref 6	Value	Units
$G(H_2)$ from water at loading (physisorbed+chemisorbed)	0.033 g	6	.05	molecules $100eV^{-1}$
$G(H_2)$ from H_2 max pressure	N/A	8	50.0	molecules $100eV^{-1}$
$G(H_2)$ from LOI at unloading (physisorbed)	0.006g	6	0.3	molecules $100eV^{-1}$
$G(H_2)$ from RH at unloading (physisorbed)	0.0014 g	6	1.2	molecules $100eV^{-1}$
$G(H_2)$ from water at unloading (physisorbed (LOI) +chemisorbed)	0.009g	6	0.18	molecules $100eV^{-1}$
$G(H_2)$ from water at unloading (physisorbed (RH) +chemisorbed),	0.004 g	6	0.4	molecules $100eV^{-1}$
k_1	--	10	8.4E+11	molecules s^{-1}
k_2	--	10	7.2E+11	molecules s^{-1} kPa^{-1}
R_{for}	--	12	0.87	nanomoles m^{-2} hr^{-1}
R_{con}	--	13	0.75	nanomoles m^{-2} hr^{-1} kPa^{-1}

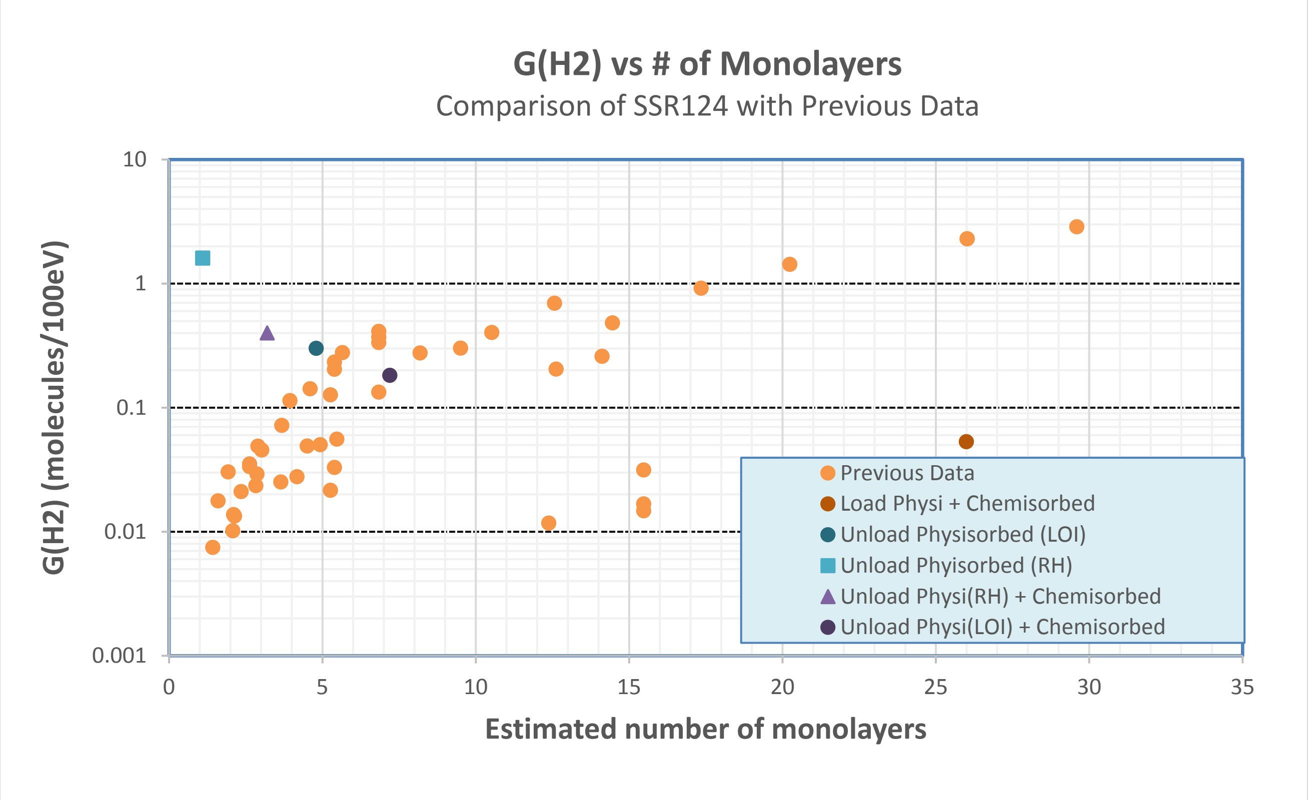


Figure 10. Comparison of calculated G(H2) plotted against the number of calculated water monolayers determined in this study with those from previous research.

Behavior of CO_2 and NO_2

The carbon dioxide and nitrogen dioxide detected by TGA-MS on the 10 g sample at loading are a possible source for the CO_2 and N_2 observed in the gas phase. (The compounds actually bound to plutonium dioxide surface could have been any of the general forms COx and NOx). The number of moles of nitrogen gas and carbon dioxide present in the head space at the termination of the experiment were calculated using the ideal gas law, n = PV/RT, where V = 4.353 cm^3, T = 328 K, and P = partial pressure of the gas (P_{CO2}=13 kPa at termination and 29 kPa at maximum and P_{N2} = 43 kPa at termination and 46 kPa at the maximum). Results are summarized in Table 10.

Table 10. Amount of nitrogen species detected on the surface prior to loading compared to the amount detected in the gas phase.

	CO_2 (moles)	**NO_2 (moles)**	**N_2 (moles)**	**N (moles)**
Sample (Loading-TGA-MS)	9×10^{-64}	2.8×10^{-4}	Not measured	2.8×10^{-4}
Head Space (Termination-GC)	2.0×10^{-5}	Not measured	6.9×10^{-5}	1.4×10^{-4}
Max Detected in Head Space over duration of experiment (GC)	4.6×10^{-5}	Not measured	7.4×10^{-5}	1.5×10^{-4}

Approximately 5 times as much carbon dioxide was released than was detected by TGA-MS, and approximately 50% of the nitrogen in the NOx gases detected by TGA-MS was released from the surface as N_2 by the termination of the experiment. Prior to loading the sample in the small-scale reactor, the plutonium dioxide powder was exposed to air for six years (nitrogen and oxygen with small amounts of water and carbon dioxide). The sample was placed in a helium atmosphere within the small-scale reactor with a large partial pressure of water. A possible explantion for the increase in CO_2 is that the water displaced chemically adsorbed CO_2 from the surface sites. The excess CO_2 over the TGA-MS measurement is not explained. The production of N_2 from the NOx species adsorbed on the surface suggests that the reaction to form NOx from radiolysis of air is reversible in the alpha radiation environment on the surface.

Behavior of He

The alpha decay of the Pu and Am creates He, which may escape the oxide into the gas phase. The amount of He created depends upon the mass of the material and the rate of decay of the various isotopes. The rate of decay can be illustrated graphically as the specific wattage calculated from the reported isotopics, Figure 2. Results were calculated using the last reported isotopics measurements taken on December 3, 1997 that are reported in Table 3. The integrated and differential amount of He evolved as a function of time are shown in Figure 3.

The amount of He created due to alpha decay over the time the material was in the SSR is estimated to be 8×10^{-6} moles for the 10 g sample. This amount of He would result in a gas pressure increase of 5.1 kPa in the 4.353 ml of gas volume and gas temperature of 328 K, if all the He was released into the gas phase. Instead, the He pressure declined by approximately 6 kPa, which is 2.1 kPa less than the expected 8.1 kPa decline due to the 12 gas samplings. Thus, it appears that 2.1kPa or ~40% of the predicted 5.1 kPa of generated He was released into the gas phase. This analysis does not account for any leaks in the system or the large uncertainties associated with the He gas measurements.

Conclusions

The MIS item 5501579 was entered into surveillance in December of 2003 and removed from surveillance in March of 2010. The amount of water on the material during the gas generation study was estimated to be 0.02 wt%. The gas generation was dominated by N_2 and CO_2. Hydrogen was generated to a maximum partial pressure of 1.6 kPa with an estimated equilibrium value of approximately 1.2 kPa. The oxygen that was initially present (1.3 kPa) was mainly consumed and a partial pressure of approximately 0.1 kPa seemed to be the final equilibrium value. Corrosion was observed in the headspace that appears to be due to a corrosive chlorine containing gas. Corrosion was also observed in the material phase.

Acknowledgements

Funding for this work was provided to the MIS Program by the Assistant Manager for Nuclear Materials Stabilization, Savannah River Operations Office, Department of Energy’s Office of Environmental Management.

References

1. U. S. Department of Energy, Stabilization, Packaging, and Storage of Plutonium-Bearing Materials. U.S. Department of Energy: Washingon, D.C., 2012.
2. Narlesky, J. E.; Peppers, L. G.; Friday, G. P. *Complex-Wide Representation of Material Packaged in 3013 Containers*; LA-UR-14396; Los Alamos National Laboratory: Los Alamos, NM, 2009.
3. Narlesky, J. E. P., Peppers, L. G.; Friday, G. P. *Complex-Wide Representation of Material Packaged in 3013 Containers*; LA-UR-14396; Los Alamos National Laboratory: Los Alamos, NM, 2009.
4. Veirs, D. K.; Worl, L. A.; Harradine, D. M.; Martinez, M. A.; Lillard, S.; Schwartz, D. S.; Puglisi, C. V.; Padilla, D. D.; Carrillo, A.; McInroy, R. E.; Montoya, A. R. *Gas generation and corrosion in salt-containing impure plutonium oxide materials: Initial results for ARF-102-85-223*; LA-UR-04-1788; Los Alamos National Laboratory: Los Alamos, NM, 2004.
5. Veirs, D. K.; Berg, J. M.; Stroud, M. A. *Obtaining G-values and rate constants from MIS data*; LA-UR-17-23787; Los Alamos National Laboratory: Los Alamos, NM, 2017.
6. Veirs, D. K.; Berg, J. M.; Crowder, M. L. *The effect of plutonium dioxide water surface coverage on the generation of hydrogen and oxygen*; LA-UR-12-22377; Los Alamos National Laboratory: Los Alamos, NM, 2012.
7. Worl, L., Berg, John, Bielinberg, Patricia, Carrillo, Alex, Martinez, Max, Montoya, Adam, Veirs, Kirk, Puglisi, Charles, Rademacher, Dave, Schwartz, Dan, Harradine, David, McInroy, Rhonda, Hill, Dallas, Prenger, Coyne, Steward, Jim *Shelf Life Surveillance for PuO2 Bearing Materials FY04 Second Quarterly Report*; Los Alamos National Laboratory: 2004.
8. Veirs, D. K. S., Stroud, M. A.; Martinez, M. ; Carrillo, A.; Berg, J.; Narlesky, J.; Worl, L. *MIS High-Purity Plutonium Oxide Metal Oxidation Product TS707001 (SSR123): Final Report*; LA-UR-17-27172; Los Alamos National Laboratory: Los Alamos, NM, 2017.
9. Brunauer, S.; Emmett, P. H.; Teller, E., Adsorption of Gases in Multimolecular Layers. *Journal of the American Chemical Society* 1938**,** *60*.
10. Veirs, D. K.; Berg, J. M.; Hill, D. D.; Harradine, D. M.; Narlesky, J. E.; Romero, E. L.; Trujillo, L.; Wilson, K. V. *Water radiolysis on plutonium dioxide: Initial results identifying a threshold relative humidity for oxygen gas generation*; LA-UR-12-26423; Los Alamos National Laboratory: Los Alamos, NM, 2012.
11. Haschke, J. M.; Ricketts, T. E., Adsorption of water on plutonium dioxide. *Journal of Alloys and Compounds* 1997**,** *252*, 148-156.

Attachment 1: Gas Generation Partial Pressure Data and Uncertainties in kPa

Note: Total pressure values used to determine partial pressures were reduced by 4kPa to correct for the estimated partial pressure of water vapor. Partial pressures were corrected for variation in the sensitivity of the GC with time. The average manifold background pressure was subtracted from the partial pressures.

Date	12/17/2003	2/11/2004	2/26/2004	6/8/2004	1/18/2005	8/22/2005	4/13/2006	10/23/2006	10/30/2007	9/16/2008	12/14/2009	2/25/2010
Days	0.0	56.0	71.0	174.0	398.0	614.0	848.0	1041.0	1413.0	1735.0	2189.0	2262.0
CO_2	0.2	17.1	18.3	23.2	27.2	28.8	28.2	26.8	24.7	21.1	13.7	12.6
N_2O	0.0	5.5	4.6	1.5	0.6	0.9	0.9	0.9	1.0	0.9	0.8	0.8
He	57.5	54.8	53.6	53.0	50.8	54.0	52.4	49.2	50.4	47.0	47.5	51.4
H_2	0.0	1.1	1.2	1.1	0.0	1.4	1.0	1.1	1.0	1.0	1.3	1.6
O_2	1.3	0.5	0.7	0.4	0.1	0.1	0.0	0.1	0.1	0.5	1.2	0.1
N_2	4.4	15.1	16.4	23.6	26.9	30.2	32.8	37.0	39.7	43.7	46.3	43.1
CH_4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
CO	0.0	4.0	4.9	6.0	3.8	3.3	2.9	3.1	2.2	1.8	1.9	2.1

Uncertainties

Date	12/17/2003	2/11/2004	2/26/2004	6/8/2004	1/18/2005	8/22/2005	4/13/2006	10/23/2006	10/30/2007	9/16/2008	12/14/2009	2/25/2010
CO_2	0.02	0.37	0.40	0.49	0.57	0.61	0.59	0.56	0.53	0.46	0.31	0.29
N_2O	0.00	0.14	0.12	0.05	0.03	0.04	0.04	0.03	0.04	0.04	0.04	0.04
He	1.13	1.09	1.07	1.06	1.02	1.08	1.05	0.99	1.01	0.94	0.95	1.03
H_2	0.00	0.03	0.03	0.02	0.00	0.03	0.02	0.02	0.02	0.02	0.03	0.04
O_2	0.04	0.03	0.03	0.02	0.01	0.01	0.01	0.01	0.01	0.03	0.05	0.01
N_2	0.11	0.32	0.35	0.49	0.56	0.63	0.68	0.76	0.81	0.89	0.94	0.87
CH_4	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CO	0.00	0.11	0.12	0.15	0.10	0.10	0.08	0.08	0.07	0.07	0.07	0.07

Attachment 2: Gas Generation: Total Pressure (p. 1 of 3)

Date	Pressure (kPa)	Date	Pressure (kPa)	Date	Pressure (kPa)	Date	Pressure (kPa)	Date	Pressure (kPa)
12/8/2003		4/12/2004	109.3	8/16/2004	113.6	12/20/2004	116.6	4/25/2005	116.9
12/15/2003	68.7	4/19/2004	108.8	8/23/2004	113.9	12/27/2004	116.6	5/2/2005	117.7
12/22/2003	75.1	4/26/2004	109.0	8/30/2004	113.9	1/3/2005	116.7	5/9/2005	117.8
12/29/2003	82.6	5/3/2004	110.6	9/6/2004	114.0	1/10/2005	116.6	5/16/2005	118.1
1/5/2004	87.7	5/10/2004	111.2	9/13/2004	114.3	1/17/2005	116.1	5/23/2005	118.3
1/12/2004	92.6	5/17/2004	111.7	9/20/2004	114.6	1/24/2005	114.1	5/30/2005	118.4
1/19/2004	94.8	5/24/2004	112.0	9/27/2004	114.6	1/31/2005	115.7	6/6/2005	118.6
1/26/2004	97.9	5/31/2004	112.3	10/4/2004	114.8	2/7/2005	115.6	6/13/2005	118.9019
2/2/2004	100.0	6/7/2004	113.0	10/11/2004	115.2	2/14/2005	116.2	6/20/2005	119.3217
2/9/2004	101.6	6/14/2004	110.7	10/18/2004	115.4	2/21/2005	116.2	6/27/2005	120.4637
2/16/2004	102.6	6/21/2004	111.3	10/25/2004	115.4	2/28/2005	117.1	7/4/2005	121.1122
2/23/2004	103.7	6/28/2004	112.2	11/1/2004	115.6	3/7/2005	116.6	7/11/2005	121.6931
3/1/2004	104.4	7/5/2004	112.5	11/8/2004	115.8	3/14/2005	116.4	7/18/2005	121.9621
3/8/2004	105.4	7/12/2004	112.8	11/15/2004	115.9	3/21/2005	116.3	7/25/2005	122.3351
3/15/2004	106.8	7/19/2004	113.1	11/22/2004	116.3	3/28/2005	116.4	8/1/2005	122.3461
3/22/2004	108.4	7/26/2004	113.3	11/29/2004	116.6	4/4/2005	116.4	8/8/2005	122.8559
3/29/2004	108.8	8/2/2004	113.4	12/6/2004	117.0	4/11/2005	116.5	8/15/2005	122.9361
4/5/2004	108.6	8/9/2004	113.5	12/13/2004	117.2	4/18/2005	116.7	8/22/2005	122.7808

Attachment 2: Gas Generation: Total Pressure (p. 2 of 3)

Date	Pressure (kPa)	Date	Pressure (kPa)	Date	Pressure (kPa)	Date	Pressure (kPa)	Date	Pressure (kPa)
8/29/2005	120.9158	1/2/2006	120.29	5/8/2006	121.85	9/11/2006	121.78	1/15/2007	120.5992
9/5/2005	121.3737	1/9/2006	120.37	5/15/2006	122.07	9/18/2006	121.87	1/22/2007	120.6569
9/12/2005	121.7501	1/16/2006	120.89	5/22/2006	122.19	9/25/2006	121.70	1/29/2007	121.7176
9/19/2005	121.7943	1/23/2006	121.63	5/29/2006		10/2/2006	121.74	2/5/2007	121.945
9/26/2005	121.8015	1/30/2006	121.32	6/5/2006	121.66	10/9/2006	121.66	2/12/2007	122.1275
10/3/2005	121.671	2/6/2006	121.14	6/12/2006	121.85	10/16/2006	122.11	2/19/2007	122.4901
10/10/2005	121.5722	2/13/2006	121.70	6/19/2006	121.98	10/23/2006	122.33	2/26/2007	122.4647
10/17/2005	121.58	2/20/2006	122.26	6/26/2006	121.93	10/30/2006	120.4164	3/5/2007	122.5224
10/24/2005	121.52	2/27/2006		7/3/2006	121.58	11/6/2006	120.4135	3/12/2007	122.7152
10/31/2005	120.61	3/6/2006		7/10/2006	121.64	11/13/2006	102.652	3/19/2007	122.8145
11/7/2005	121.91	3/13/2006		7/17/2006		11/20/2006	120.8563	3/26/2007	122.9311
11/14/2005	121.10	3/20/2006		7/24/2006	121.99	11/27/2006	120.694	4/2/2007	122.8018
11/21/2005	120.60	3/27/2006		7/31/2006	121.80	12/4/2006	120.2702	4/9/2007	122.8335
11/28/2005	120.44	4/3/2006		8/7/2006	121.54	12/11/2006	120.3227	4/16/2007	122.6245
12/5/2005	120.48	4/10/2006	122.99	8/14/2006	122.40	12/18/2006	120.5987	4/23/2007	122.7567
12/12/2005	120.99	4/17/2006	122.24	8/21/2006	121.79	12/25/2006	120.5369	4/30/2007	122.8857
12/19/2005	120.49	4/24/2006	122.68	8/28/2006	121.81	1/1/2007	120.3555	5/7/2007	122.9902
12/26/2005	120.32	5/1/2006	121.90	9/4/2006	121.77	1/8/2007	120.6645	5/14/2007	123.1327

Attachment 2: Gas Generation: Total Pressure (p. 3 of 3)

Date	Pressure (kPa)	Date	Pressure (kPa)	Date	Pressure (kPa)	Date	Pressure (kPa)	Date	Pressure (kPa)
5/21/2007	123.2095	9/24/2007	124.23	1/28/2008	119.9542	6/2/2008	123.7457	10/13/2008	118.1209
5/28/2007	123.3504	10/1/2007	123.74	2/4/2008	119.7576	6/9/2008	124.2463	10/20/2008	118.0705
6/4/2007	123.3821	10/8/2007	123.13	2/11/2008	120.1205	6/16/2008	124.5308	10/27/2008	117.9924
6/11/2007	123.5316	10/15/2007	123.83	2/18/2008	120.5855	6/23/2008	123.658	11/3/2008	118.1342
6/18/2007	123.7263	10/22/2007	124.57	2/25/2008	120.4201	6/30/2008	123.7535	11/10/2008	118.0405
6/25/2007	124.1027	10/29/2007	123.92	3/3/2008	120.0953	7/7/2008	123.0198	11/17/2008	117.7597
7/2/2007	123.1834	11/5/2007	121.37	3/10/2008	119.7151	7/14/2008	122.9211	11/24/2008	118.1556
7/9/2007	123.068	11/12/2007	119.65	3/17/2008	120.6999	7/21/2008	122.7347	12/1/2008	118.1107
7/16/2007	123.013	11/19/2007	121.62	3/24/2008	120.6784	7/28/2008	123.0773	12/8/2008	118.113
7/23/2007	122.9842	11/26/2007	120.4752	3/31/2008	120.1644	8/4/2008	123.9388	12/15/2008	118.2969
7/30/2007	122.9588	12/3/2007	120.5852	4/7/2008	120.7164	8/11/2008	123.3524	12/22/2008	118.2833
8/6/2007	122.13	12/10/2007	121.1156	4/14/2008	120.7935	8/18/2008	124.2117	12/29/2008	118.3584
8/13/2007	122.36	12/17/2007	122.0086	4/21/2008	120.8238	8/25/2008	123.7074	1/5/2009	118.5163
8/20/2007	122.87	12/24/2007	120.9944	4/28/2008	121.0966	9/1/2008	123.0219	1/12/2009	118.27
8/27/2007	122.93	12/31/2007	120.9744	5/5/2008	123.0615	9/8/2008	122.8264	1/19/2009	118.25
9/3/2007	123.74	1/7/2008	121.0844	5/12/2008	122.0692	9/15/2008	122.7396	1/26/2009	118.27
9/10/2007	124.07	1/14/2008	121.0541	5/19/2008	122.3432	9/22/2008	119.0273	2/2/2009	118.51
9/17/2007	124.19	1/21/2008	120.3898	5/26/2008	124.1581	9/29/2008	118.6114	2/9/2009	118.13

Attachment 2: Gas Generation: Total Pressure (p. 3 of 3)

Date	Pressure (kPa)	Date	Pressure (kPa)	Date	Pressure (kPa)	Date	Pressure (kPa)	Date	Pressure (kPa)
2/23/2009	118.71	6/29/2009	118.18	11/2/2009	118.42				
3/2/2009	118.37	7/6/2009	117.89	11/9/2009	118.63				
3/9/2009	117.68	7/13/2009	117.94	11/16/2009	118.83				
3/16/2009	117.56	7/20/2009	117.85	11/23/2009	118.65				
3/23/2009	118.49	7/27/2009	117.95	11/30/2009	118.45				
3/30/2009	118.13	8/3/2009	117.68	12/7/2009	118.50				
4/6/2009	117.96	8/10/2009	117.57	12/14/2009	118.30				
4/13/2009	117.82	8/17/2009	117.84	12/21/2009	115.68				
4/20/2009	117.44	8/24/2009	117.73	12/28/2009	115.43				
4/27/2009	117.43	8/31/2009	117.62	1/4/2010	115.24				
5/4/2009	117.60	9/7/2009	117.51	1/11/2010	115.35				
5/11/2009	117.64	9/14/2009	117.53	1/18/2010	115.46				
5/18/2009	117.70	9/21/2009	118.48	1/25/2010	115.37				
5/25/2009	119.97	9/28/2009	118.65	2/1/2010	115.21				
6/1/2009	120.45	10/5/2009	118.62	2/8/2010	115.35				
6/8/2009	120.36	10/12/2009	118.48						
6/15/2009	119.63	10/19/2009	118.39						
6/22/2009	118.26	10/26/2009	118.45						

Appendix 1: Estimating the monolayer coverage

Surface Area: The number of monolayers of moisture on the sample surface may be calculated if the mass of moisture or water, the mass of the sample, and the SSA of the sample are known. One approach is to determine the weight percentage for one monolayer of water. The number of monolayers of water can be calculated by dividing the total weight percentage of water (mass of water/mass of the sample) by the weight percentage of one monolayer of water.[11] The weight percentage of one monolayer of water is the product of the weight of water in a monolayer of 1 m^2 and the SSA:

$$\text{wt\% of 1 ML} = 0.00022\ \text{g m}^{-2}\text{ML}^{-1} \text{ x SSA m}^{2}\ \text{g}^{-1} \text{ x } 100 \text{ wt\%}$$

$$= 0.022 \text{ wt\% ML}^{-1} \text{x SSA.} \qquad \text{Equation A1-1}$$

For the material 5501579 with a SSA of 0.57 m^2 g^{-1}, the weight percentage of one monolayer of water is 0.01254 wt% ML^{-1}.

Dividing the weight percentage of water by the weight percentage of water in one monolayer yields the number of monolayers of water. Applying this to the measured weight percentage of water upon loading and unloading results in:

Loading Condition: 0.33 wt% / 0.01254 wt% ML^{-1} = 26 ML

Unloading Condition: 0.04 wt% / 0.01254 wt% ML^{-1} = 3.2 ML

BET Theory: The number of monolayers can also be estimated based upon the relative humidity in the container using Brunauer-Emmett-Teller (BET) theory.[9] BET theory is the standard model for quantifying the equilibria between multiple physically adsorbed layers on a surface and the adsorbing species in the gas above the surface. The specific relationship between the RH above a surface and the number of monolyers of weakly bound water on the surface predicted by BET theory is illustruated in Fig. A-1.

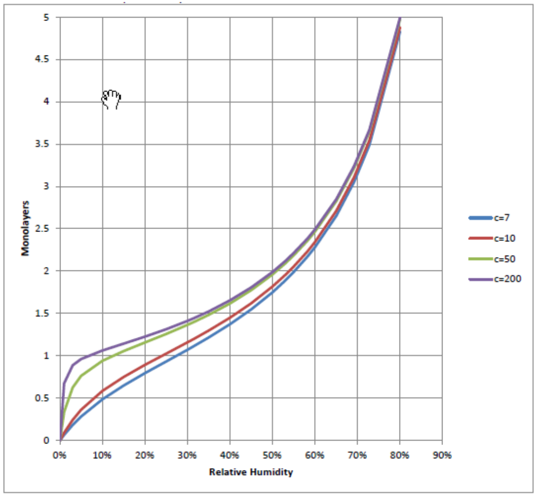


Figure A-1. Adsorption Isotherm Calculated from BET Theory.

Appendix 2: Stopping power ratio

The ratio of the stopping power due to the water and the stopping power due to the material is calculated using the approach in Appendix B of Reference 6. Elements with greater than 0.3 wt% were included.

Element or Compound	Integrated Stopping Power from 0 to 5.2 MeV (mg^{-1} cm^{-2})	Elemental Mass Fraction	Elemental Stopping Power (mg^{-1} cm^{-2})
H2O(g)	7.946	0.0000	0
H2O (l)	7.708	0.0067	0.05164
F	6.645	0.0000	0
O	5.901	0.0000	0
Na	5.304	0.0000	0
C	5.190	0.0000	0
S	5.117	0.0000	0
Mg	5.100	0.0000	0
Si	4.852	0.0000	0
Al	4.702	0.0000	0
K	4.652	0.0000	0
Cl	4.575	0.0000	0
Ca	4.461	0.0000	0
Cr	3.688	0.0000	0
Fe	3.504	0.0000	0
Ni	3.184	0.0000	0
Cu	2.871	0.0000	0
Zn	2.860	0.0000	0
Ga	2.786	0.0090	0.02507
UO2	2.081	0.0034	0.00707
PuO2	2.081	0.99	2.0552
		Smat	2.087
		Swat	7.708
		S	3.693