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BLO-39-11-14-004 (SSR132 and 132A): Final Report

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

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MIS High-Purity Plutonium Oxide Metal Oxidation Product BLO-39-11-14- 004 (SSR132 and 132A): Final Report

Authors:

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

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Abstract

A high-purity, reactor-grade 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. BLO-39-11-14-004 is a high specific power oxide that represents Hanford process plutonium oxides from oxalate process product, oxalate precipitation of impure plutonium and pure mixed uranium/plutonium nitrate solutions, PFP NDA and impure and scrap plutonium oxides 80-85% from PFP and the 300 area. It also represents plutonium oxides from oxalate precipitation at LANL and Savannah River. After calcination to 950 °C, the material contained 80% plutonium and 7% americium 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. A leak occurred in the original reactor (SSR132) which was terminated after 3 years. The sample was reloaded (SSR132A) and an additional set of data was collected. Results from both loadings are discussed. Gas compositions were measured periodically over three (SSR132) and four and a half (SSR132A) year periods. The maximum observed gas pressures were 93 kPa and 94 kPa, respectively. The increase over the initial pressure was primarily due to generation of nitrogen gas. For SSR132, the maximum observed gas pressure for hydrogen was 1.2 kPa and oxygen was 9.3 kPa (includes oxygen from leak). For SSR132A, the maximum observed gas pressure for hydrogen was 5.5 kPa and oxygen was 0.9 kPa. At the completion of the study, the internal components of the sealed container showed limited signs of corrosion.

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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 In this case, however, a 2.5 gram sample was used. The 3013 Standard only allows a total of 19 Watts within a container and the specific power of BLO material, approximately 14 W/kg, results in approximately one-quarter of a normally allowed 5.0 kg loading. The sample used for this study is approximately one-quarter of the normal 10 gram sample.

This report discusses sample BLO-39-11-14-004, a high-purity, reactor-grade plutonium (Pu) dioxide material from the MIS Program inventory that originated in the Hanford continuous oxalate precipitation and calcination process from purified nitrate solution produced in the PFP RMA line. BLO-39-11-14-004 plutonium oxide is representative of oxides generated from the following processes:

- Oxalate Process Product at Hanford
- Oxalate Precipitation of Impure Plutonium Nitrate Solutions at Hanford
- Oxalate precipitation of Pure Mixed Uranium/Plutonium Nitrate Solutions at Hanford
- Oxide from Oxalate Precipitation at Savannah River
- Oxide Precipitation from Nitrate Solutions at LANL³

Figure 1. BLO-39-11-14-004 upon arrival at LANL.

Material Characterization

The reactor-grade plutonium oxide, shown in Figure 1, was calcined at 950 °C for 2 hours on June 19, 1997. Several measurements of material characteristics that were obtained on the calcined sample are summarized in Table 1. The material loaded in the reactor was all calcined to 950 °C. The material was re-calcined to 950 °C in 2017 and the specific surface area (SSA) was measured.

Table 1. Material Physical Characteristics.

Specific Surface Area (SSA) 5-point ($\text{m}^2 \text{g}^{-1}$)	2.4
Bulk Density (g cm^{-3})	2.7
Tap Density (g cm^{-3})	3.4
Pycnometer Density (g cm^{-3})	10.77

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 americium and 100%. No measurements of soluble species were conducted for this material.

Table 2. Elemental weight % of impurities.

Element	wt%
Calcium	0.008
Iron	0.049
Magnesium	0.084
Phosphorus	0.058
Potassium	0.049
Silicon	0.021
Sodium	<0.003
Thorium	0.05

Isotopics and wattage data from calorimetry/gamma isotopics, obtained on the calcined parent material on August 29, 2002, are listed in Table 3.

Table 3. Isotopic data listed as mass fraction (g/g plutonium) obtained from calorimetry/gamma. Specific power is reported in mW per gram of material, not per gram of plutonium.

Isotope	Mass Fraction (g/gPu)	Total Plutonium (g Pu/g of material)	0.80
Pu-238	0.0079654	Total Actinide content (g Pu + Am/g of material)	0.864
Pu-239	0.7709402	Specific Power (mW/g of material)	13.77
Pu-240	0.1954343		
Pu-241	0.02211		
Pu-242	0.0035500		
Am-241	0.0861854		

The specific power of reactor-grade BLO-39-11-14-004 as a function of time from the isotopic measurement date is shown in Figure 2. The high specific power of the material is primarily due to in-growth of Am which reached approximately 7% in the material

Figure 2. The specific power of BLO-39-11-14-004 as a function of time from the isotopic measurement date in August 29, 2002. The vertical green lines bound the time the sample was in SSR132 and vertical purple bound the time for SSR132A.

Figure 3 provides information on He evolution as a function of time in BLO-39-11-14-004.

Figure 3. Rate of He evolved from alpha decay (blue line/left axis) as a function of time and the moles of He per kg material per 0.1 year (red line/right axis). The vertical green lines bound the time the sample was in SSR132 and vertical purple bound the time for SSR132A.

Experimental Procedure

The design of the small-scale reactor (SSR) system has been described previously.⁴ The container's nominally five cm³ 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 body⁵ 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 cm³ was used.⁵ The gas sampling volume located between two sampling valves, 0.05 cm³ (~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. Disassembled 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 material.

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%. For SSR132, 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 small-scale sample. The LOI-200 °C sample was 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 is assumed that the LOI-200 °C material contained additional water as hydroxyls or chemically

adsorbed water which was not removed by heating to 200 °C and was not quantified.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 mass loss water by LOI-200 °C. (No estimate of chemically adsorbed water was included in the sum to 0.5 wt%). For SSR132A, the entire 2.5 g sample was heated for 2 hours at 200 °C to remove adsorbed water. The target amount of water added was 0.5 wt%. In addition, samples from the parents were split and placed in glass vials inside hermetically sealed containers. The water content of both samples were determined by Thermal Gravimetric 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 TGA-MS results were not available at the time of loading.

The procedure to add moisture is described briefly. A 2.5-gram sample of the BLO-39-11-14-004 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 other high-purity oxide samples was measured to and averaged 0.07 wt% per minute.⁷ Therefore 0.05% was assumed to have been lost during the 45 seconds of loading when estimating total moisture content at loading.

The sealed SSR was placed in a heated sample array maintained at 55 °C. Fifty microliter gas samples were extracted through a gas manifold. Fifty microliters corresponds to 0.98% of the free gas volume. The average pressure drop on taking the gas sample was also 0.98%. The gas sample was analyzed using an Agilent 5890 GC (gas chromatograph) calibrated for He, H₂, N₂, O₂, CO₂, CO, CH₄ and N₂O. 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. The relative humidity and temperature in the container were measured using a Vaisala HMT330 sensor and readout after an equilibration time whose length was not measured but thought to be sufficient for 1% accuracy. The material was then removed from the container and the moisture content in the material was determined by performing LOI-200 °C.

Results

Loading

A 2.5 gram split from the parent material calcined to 950° C 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. A leak occurred in the original reactor (SSR132) which was terminated after 3 years. The sample was reloaded (SSR132A) and an additional set of data was collected.

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

SSR	Mass of sample m_{mat}	Volume of Material V_{mat}	Volume of SSR V_{SSR}	Free Gas Volume in SSR V_{gas}
132	2.5400 g	0.236 cm ³	5.326 cm ³	5.090 cm ³
132A	2.5061 g	0.233 cm ³	5.326 cm ³	5.093 cm ³

TGA-MS Results

TGA-MS data for the sample from the material used in SSR132 are shown in Figure 5.

Figure 5. TGA-MS data for the parent material loaded into SSR132. Mass 17.00 and 18.00 are H₂O and Mass 44 is CO₂.

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 0.48 wt%. Other than water, carbon dioxide was the primary volatile below 400 °C. During the TGA-MS analysis, 0.02 wt% carbon dioxide (~.0005 g in original sample) was measured. Nitrogen oxides were below quantifiable levels.

A graph of the TGA-MS data for the sample of the parent material in SSR132A is not available. TGA-MS total moisture content was determined to be 0.12 wt%. During the TGA-MS analysis, 0.065 wt% carbon dioxide (~.0016 g in original sample) was measured. Nitrogen oxides were below quantifiable levels.

The presence of surface adsorbed CO₂ on aged material limits the accuracy of the LOI-200 °C techniques to estimate water content. For SSR132, the LOI-200 °C weight loss includes CO₂ loss from this material that had been exposed to air for six to eleven years prior to the measurement.

Moisture addition

The measurements and assumptions used to estimate the true total moisture content at the time of loading are summarized in Table 5. The best estimate for the moisture content at loading is 0.60 wt% for SSR132 and 0.59 wt% for SSR132A, as given in Table 5 line 11, Estimated Total Moisture in loaded sample (using TGA-MS).

Table 5. Moisture data summary at loading.

	Parameter	SSR132	SSR132A	Units
1	Original Calcination Date	6/19/1997	6/19/1997	
2	Loading Date	1/8/2004	6/10/2008	
3	Unloading Date	1/25/2007	1/28/2013	
4	Initial sample weight (m _{mat})	2.540	2.5061	g
5	Initial Moisture (Total) by TGA-MS	0.48	0.12	wt%
6	Initial Moisture (Weakly bound) by LOI-200 °C	0.29	0	wt%
7	Total Moisture added	0.17	0.52	wt%
8	Relative Humidity in glove box during loading	0.1/24.8	0.1/	% / °C
9	Estimated moisture loss during loading	0.05	0.05	wt%
10	Estimated Weakly Bound Moisture in loaded sample (using LOI) = Line 6 +Line7 –Line 9	0.41	0.47	wt%
11	Estimated Total Moisture in loaded sample (using TGA-MS) = Line 5 + Line 7 –Line 9	0.60	0.59	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 during the time when the material is transferred from the humidified chamber to the balance and the final mass measurement is made. The total moisture added to SSR132 in Table 5, 0.17 wt%, is significantly less than the mass gain during moisture uptake, 0.26 wt%, which may be due to a slow transfer.

Figure 6. Moisture Addition Curve.

Gas Generation

The total pressure in SSR132A as a function of time, as well as the partial pressure of several gasses, is shown in Figure 7. Pressures reflect changes in the gasses in the reactor as well the 0.98% pressure drop due to gas sampling. In addition, the vapor pressure of water, estimated to be 4 kPa, is included in the total pressure, i.e. the sum of the partial pressures plotted and 4 kPa for water equals the total pressure. Note that the total pressure increase is less than the partial pressure increases from generated gases mainly due to loss of He partial pressure from sampling. Data for SSR132 was not plotted due to the leak in the reactor. Detailed information on gas composition and uncertainties is in Appendix 1 and on pressure in Appendix 2 and 3.

Figure 7. Total pressure and partial pressure of gases measured using a gas chromatograph as a function of time. He and Total pressure are plotted on the left primary scale.

For SSR132A, the initial pressure of 85 kPa increased over the first three months to 90 kPa, then gradually increased to a maximum pressure of 94 kPa over the next 3.5 years. Hydrogen and oxygen were minor components in the headspace gas. Hydrogen was initially 0 kPa and increased to 5.5 kPa after 100 days then decreased over the next year to a final value of 1-2 kPa. Oxygen began at 0.6 kPa, increased slightly to 0.8 kPa in the first month and decreased to negligible amounts after 3.5 years, remaining low for the rest of the experiment.

The small net increase in total pressure during the experiment was primarily due to the generation of nitrogen and to a lesser extent, hydrogen. Nitrogen slowly increased from 2 to 15 kPa over the first four years of the experiment.

Moisture measurements on unloading

SSR132A was removed from the heated array and placed in a holder to cool. The lid was removed and replaced with a lid modified to hold a RH sensor. The relative humidity and temperature in the container were measured using a Vaisala HMT330 sensor and readout. No details are available for the time taken to complete the measurements. No moisture measurements were obtained for SSR132 at the termination of the experiment. For SSR132A, the weight loss in the material at termination by LOI-200 °C was 0.97 wt%.

The unloading LOI-200 °C (0.97 wt%), was 0.38 wt % greater than the LOI-200 °C (0.59 wt%) at loading. This large increase in the LOI is unexplained and is inconsistent with being moisture because the relative humidity at unloading was low.

The relative humidity in reactor SSR132A at unloading was 15.1%. Given this relative humidity, BET theory predicts approximately 0.7 monolayers (ML) or 0.04 wt% weakly bound water in the reactor (Appendix 4). This corresponds to a reduction of approximately 0.43 wt% or greater than 90% of the weakly bound moisture during the experiment. A similar large reduction in moisture was observed in previous reactors and is probably due, in part, to water condensing in the colder region of the reactor plumbing.⁸

Sample unloading and moisture data are summarized in Table 6.

Table 6. Unloading moisture data summary for SSR132A.

	Parameter	Value	Units
1	Unloading Moisture by LOI-200 °C	0.97	wt%
2	Estimated additional strongly bound moisture of 1.5 ML	0.08	wt%
3	Estimated total moisture at unloading from LOI = Line 1 + Line 2	1.05	wt%
4	Relative Humidity/Temperature in headspace at unloading	15.1/25.9	%/ °C
5	Number of monolayers at unloading RH and temperature using Figure A-1 and $c=7$.	0.7	ML
6	Mass of weakly bound water (RH) using # of MLs in line 5.	0.04	wt%
	Estimated total moisture (RH + 1.5ML strongly bound) at unloading from RH and temperature = line 2 + line 6	0.12	wt%

Corrosion

Images of the inner buckets of SSR132 and SSR132A are shown in Figure 8. No images of the bottom of the bucket were available.

Figure 8. Photographs after unloading: a) inner bucket of SSR132 b) inner bucket of SSR132A c) close up of SSR132A section A d) close up of SSR132A section C and e) close up of SSR132A section B.

Limited corrosion was observed in the buckets with no clear distinction between the contact and headspace regions. In image a) corrosion is visible on the cut surface of the inner bucket suggesting that the bucket was exposed to a corrosive environment during or after cutting.

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 and consumed either from radiolysis or from chemical surface reactions.⁵ In order to perform these calculations knowledge of the moisture content of the material during the study and the ionizing radiation 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, BLO-39-11-14-004 was exposed to the glove box environment for six to eleven years after calcination prior to loading. A significant formation of hydroxyls on the oxide surface is expected after this much time. Gases, such as CO_2 or NO_x , would also be adsorbed by the surface and come off of the material slowly over time after moisture is added to the system. The presence of these species may alter the gas generation behavior compared with recently calcined (to 950 °C) plutonium oxide.

H₂ G-value and rate constants

The formation and consumption of H₂ can be represented in a simple scheme as:

where the oxygen in Eq. 1 either enters the gas phase or is consumed by the PuO_2 . Less than 1 kPa of oxygen gas was observed and it was subsequently consumed so both mechanisms occurred. The material present within the sealed container that has the greatest potential to consume H₂ is PuO_2 . The precise nature of the formation and consumption reactions are not known and the product shown in Eq. 2 is for illustration purposes. The important aspect of Eq. 2 is that the H₂ forms a species that does not reform H₂.

The change in H₂ pressure due to the reactions in Eq. 1 and Eq. 2 can be written in differential form as:

$$\frac{dP_{H_2}}{dt} = k_1 A(t) - k_2 P_{H_2} \quad \text{Eq. 3}$$

where P_{H_2} is the partial pressure of hydrogen, $A(t)$ is the active water in the reactor involved in hydrogen generation, expressed in units of pressure using the ideal gas law, t is time in days, and

k_1 and k_2 are the first-order rate constants for the formation and consumption of hydrogen in days⁻¹. The model predicts exponential decay of the active water, $A(t)$, with time as shown in Eq. 4.

$$A_{H_2O}(t) = A_0 e^{-k_1 t} \quad \text{Eq. 4}$$

where A_0 is the amount of active water at $t=0$. Substituting Eq. 4 into Eq. 3 yields equation Eq. 5:

$$\frac{dP_{H_2}}{dt} = k_1 A_0 e^{-k_1 t} - k_2 P_{H_2} \quad \text{Eq. 5}$$

The initial rate of hydrogen generation is calculated by evaluating Eq. 5 at $t = 0$ assuming P_{H_2} is zero at $t=0$. The initial hydrogen generation rate is equal to $k_1 A_0$ (Appendix 6.)

Eq. 5 can be integrated to yield Eq. 6, again assuming P_{H_2} is zero at $t=0$.

$$P_{H_2}(t) = \frac{A_0 k_1}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t}) \quad \text{Eq. 6}$$

The expression for the maximum hydrogen pressure of a system behaving according to Eq. 6 is shown in Eq. 7 where $K = k_2/k_1$.

$$P_{max} = A_0 (K^{K/(1-K)}) \quad \text{Eq. 7}$$

The hydrogen partial pressure versus time observations for SSR132A, fit to Eq. 6, is shown in Figure 9. (Due to the known leak in the system, data from SSR132 was not fit.). The fit to the limited number of data points in Figure 9 is poor suggesting that either the uncertainty in the data is larger than reported in Appendix 1 or that the model is not sufficiently complex. The plateau at long times suggests that a reaction that reforms hydrogen is occurring, resulting in an equilibrium partial pressure of H_2 . Studies of BLO-39-11-14-004 material that may clarify the H_2 behavior with time are being carried out and will be addressed in a later report.

Figure 9. The hydrogen partial pressure and the fit to Equation 6, or first order formation and first order consumption reaction with an r^2 coefficient of 0.85.

The values for the fit parameters yielding the curves in Figure 9 along with the standard error in the parameters are given in Table 7. The function reached a maximum of 4.9 kPa at 116 days. The initial rate of hydrogen generation calculated from these parameters are also reported in Table 7. The fit of the initial points is very good and the estimate of the initial rate, the product of k_1 and A_0 , is minimally affected by the poor fit at long times. However, there is considerably more uncertainty in the individual values of k_1 and A_0 .

Table 7. The fit parameters based on the reaction model, standard errors and initial rate from the hydrogen generation data for SSR132A at 55 °C from Eq 6.

Small-scale Surveillance sample ID	A_0	k_1 (day ⁻¹)	k_2 (day ⁻¹)	Initial Rate (kPa/day) ($k_1 A_0$)
SSR132A	148	0.001099	0.296	0.163
Standard Error	82	0.00034	0.014	

The initial active water from the fit based on the reaction model corresponds to 0.2 wt% or approximately 33% of the initial water loaded on the sample. A plot of $A(t)$, the estimated wt% of water active in hydrogen formation (A) remaining in the system, as a function of time using Eq. 4 is plotted in Figure 10 below.

Figure 10. Graph of the estimated active water, $A(t)$, in SSR132A as a function of time, where A_0 is expressed in terms of wt% of water.

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

Moisture adsorbed on high-purity plutonium dioxide such as BLO-39-11-14-004 is thought to exist as physisorbed (weakly bound) water that behaves according to BET theory⁹ and as chemisorbed (strongly bound) 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 physisorbed and chemisorbed water on the material during the experiment, the SSA, the amount of water in a monolayer, and the RH are needed. RH data was only available at the termination of the experiment.

The difference between the best estimate of the amount of water in SSR132A when the material was loaded (0.015 g from TGA) and unloaded (0.003 g from RH), 0.012 g, is much greater than the amount of water that produced H_2 (0.0002 g) plus the amount of water that would be in the gas phase at unloading (0.00002 g), 0.0002 g. A gradual conversion of physisorbed water to chemisorbed water (hydroxyls) during the experiment would 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, 11}

The additional difference is probably due to water condensing in the colder region of the reactor plumbing.¹¹ During the gas generation study, the condensed moisture in the cold region of the plumbing is located at a sufficient distance from the material that the radiation dose it receives is orders of magnitude smaller than the radiation 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 for $G(H_2)$ in G-value calculations.

Moisture at loading (TGA) overestimates the water receiving radiation dose resulting in gas generation since it includes chemisorbed water and water condensed on the cold region of the reactor. Results based on loading moisture are expected to underestimate the value for $G(H_2)$.

Moisture at unloading underestimates the water receiving radiation dose resulting in gas generation calculations since it does not include water that reacted during the course of the experiment. Results based on unloading moisture are expected to overestimate the value for $G(H_2)$. Table 8 summarizes estimates of the amount of water on the material at loading and unloading, initial and reacted based on the reaction model, condensed on the piping, in the gas phase, and decomposed to form H_2 expressed as weight percent, moles, grams, and monolayers. The initial active water from the fit to the reaction model may provide the best estimate of the water involved in hydrogen generation for calculating $G(H_2)$.

Table 8. 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 0.0013 g. Calculations use $SSA = 2.4 \text{ m}^2 \text{ g}^{-1}$, $m_{\text{mat}} = 2.51 \text{ g}$ and $V_{\text{gas}} = 5.093 \text{ cm}^3$. The amount of strongly bound chemisorbed water on the material was assumed to be 1.5 monolayers wt% at all times.

Water Source	Amount of Water			
	wt%	g	moles	monolayers
	0.053	0.0013	7.4×10^{-5}	1
In gas at 25.1 °C and 100% RH (3.2 kPa)	0.0045	0.00011	5.9×10^{-6}	0.08 (equivalent)
In gas at 55 °C and 100% RH (15.75 kPa)	0.022	0.00053	2.9×10^{-5}	0.4 (equivalent)
On material at loading: weakly + strongly bound (TGA)	0.59	0.015	8.3×10^{-4}	11.1
Initial active water based on reaction model ($A_0 = 148 \text{ kPa}$)	0.20	0.0049	2.8×10^{-4}	3.8
Reacted to produce H_2 based on reaction model (Figure 10)	0.166	0.0042	2.3×10^{-4}	3.1
Reacted to produce max H_2 in gas at 55 °C (5.5 kPa)	0.0074	0.00018	1.0×10^{-5}	0.14 (equivalent)
In gas at unloading, 25.1 °C and 15.1% RH (0.5 kPa)	0.00069	1.7×10^{-5}	9.6×10^{-7}	0.013 (equivalent)
Presumed condensed on piping and effectively removed from the system = (Loading(TGA) - Unload(RH) - reacted water - strongly bound (1.5ML))	0.31	0.0078	4.3×10^{-4}	5.8

Water Source	Amount of Water			
	wt%	g	moles	monolayers
Presumed condensed on piping and effectively removed from the system = (Loading(TGA)-Unload(RH)-max H2-strongly bound(1.5ML)	0.46	0.012	6.5×10^{-4}	8.8
On material at unloading: weakly bound (LOI)	Results not included: Unexplained LOI result			
On material at unloading: weakly bound (RH)	0.04	0.0009	5×10^{-5}	0.7
On material at unloading: weakly bound (LOI) + strongly (1.5 ML)	Results not included: Unexplained LOI result			
On material at unloading: weakly (RH)+strongly (1.5 ML)	0.12	0.0029	0.00016	2.2

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

A_0 , k_1 , and k_2 are used to calculate $G(H_2)$ and the rate constants for the hydrogen formation and consumption surface reactions using formulas in Appendix 6. Because of the uncertainty in determining the amount of water involved in the hydrogen generation, several values are used for the variable m_{H_2O} . The stopping power ratio for BLO-39-11-14-004 material, $\frac{S_{H_2O}}{S_{mat}}$, is 3.63 (Appendix 5). Results for $G(H_2)$ using the various choices for the amount of water active in producing H_2 using equations from Appendix 6, are reported in Table 9. It is expected that the total water at loading overestimates the amount of water involved in hydrogen generation since it includes strongly bound water (hydroxyls) that is not expected to react as well as water that condensed in the cold part of the piping. Results based on total water at loading bound the lower value for $G(H_2)$.

Table 9. $G(H_2)$ calculated from reaction parameters and estimated moisture content using equation A6-4 in Appendix 6 assuming radiolytic decomposition of water to form H_2 .

<i>Source for the amount of water receiving radiation dose</i>	$G(H_2)$
	molecules $100eV^{-1}$
Total water at loading (TGA)	0.045
Active water based on reaction model (A_0)	0.134
Water reacted to produce max P_{H_2} in gas at 55 °C	3.610
Water on material at unloading: weakly bound (RH)	0.72
Water on material at unloading: weakly bound (RH) + 1.5 ML	0.229

The equations to obtain the rates and rate constants for the surface reactions in Appendix 6 are not dependent on the amount of water and only a single value for each is given in Table 10.

Table 10. Rate constants calculated from the reaction parameters and the estimated moisture content assuming surface catalyzed decomposition of water to form H_2 .

Variable	Eq. in Appendix 6	Value	Units
k_{for}	A6-5	2.12E+12	molecules s^{-1}
k_{con}	A6-6	3.85E+11	molecules s^{-1} kPa^{-1}
R_{for}	A6-8	2.11	nanomoles m^{-2} hr^{-1}
R_{con}	A6-9	0.38	nanomoles m^{-2} hr^{-1}

Figure 11 compares the $G(H_2)$ values determined in this study with those reported previously.¹²

Figure 11. Comparison of calculated $G(H_2)$ plotted against the number of calculated water monolayers determined in this study with those from previous research.

Behavior of CO_2 and NO_2 for SSR132A

While 4×10^{-5} moles of carbon dioxide were detected by TGA-MS on the sample at loading an order of magnitude less CO_2 was observed in the headspace during the experiment. In contrast, no nitrogen oxide was observed in the TGA but 3×10^{-5} moles of N_2 were observed in the gas phase. (The compounds actually bound to the plutonium dioxide surface could have been any of the general forms CO_x and NO_x). Results are summarized in Table 11.

Table 11. 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)
Sample (Loading-TGA-MS)	4×10^{-5}	0	Not measured
Max Detected in Head Space over duration of experiment (GC)	3×10^{-6}	Not measured	3×10^{-5}

Prior to loading the sample in the small-scale reactor, the plutonium dioxide powder was exposed to air for eleven 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 explanation for CO_2 and N_2 observed in the headspace is that the water displaced chemically adsorbed CO_2 and N_2 formed from the NO_x . The CO_2 detected in the headspace during the experiment (Figure 7) was an order of magnitude less than the CO on the surface available. In contrast, significant N_2 was detected which is inconsistent with no NO observed in the TGA-MS and therefore no NO_x on the surface available to form N_2 (Figure 5). The observation of CO_2

and N₂ produced in this high-purity plutonium dioxide materials exposed to air is consistent with other high-purity oxides, however, the magnitude of the partial pressure observed varies with material.^{8,12}

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 He evolution and amount 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 SSR132A is estimated to be 9.8×10^{-6} moles for the 2.5 g sample. This amount of He would result in a gas pressure increase of 5.9 kPa in the 5.1 cm³ 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 5 kPa, which is ~ 0.6 kPa less than the decline expected due to the 8 gas samplings (5.6 kPa). Thus, it appears that 0.6 kPa or 10% of the predicted 5.9 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 BLO-39-11-14-004 was entered into surveillance in June of 2008 and removed from surveillance in January of 2013. The initial amount of water involved in gas generation was estimated to be 0.12 wt% based on the reaction model. The gas generation was dominated by H₂ and N₂. Hydrogen was generated to a maximum partial pressure of 5.5 kPa but declined after reaching this maximum after approximately 105 days. Oxygen was generated to a maximum partial pressure of 0.9 kPa and was then consumed, reaching a final equilibrium partial pressure of approximately 0.1 kPa. Limited corrosion was observed in the reactor buckets with no clear distinction between the contact and headspace regions.

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Appendix 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.

SSR132 (Reactor leaked)

Date	1/8/2004	2/11/2004	2/17/2004	2/18/2004	2/26/2004	2/26/2004	6/9/2004	1/24/2005	8/30/2005	4/19/2006	10/23/2006	1/25/2007
Days	31.0	65.0	71.0	72.0	80.0	80.0	184.0	413.0	631.0	863.0	1050.0	1144.0
CO ₂	0.0	0.6	0.0	0.1	0.0	0.6	1.0	0.4	0.1	0.1	0.0	0.0
N ₂ O	0.0	0.3	0.0	0.0	0.1	0.1	0.3	0.4	0.4	0.3	0.5	0.0
He	77.6	45.2	0.4	0.4	0.5	72.5	73.6	67.5	60.6	57.7	44.3	77.6
H ₂	0.0	0.8	0.0	0.1	0.5	0.3	1.1	0.6	0.4	0.3	0.3	0.0
O ₂	0.1	2.7	1.2	1.3	1.3	2.2	3.4	7.2	8.9	8.2	7.7	0.1
N ₂	0.4	11.3	4.1	4.5	5.3	8.2	8.7	12.6	15.6	16.2	19.3	0.4
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	0.2	0.0	0.0	0.0	0.0	0.3	0.0	0.0	0.0	0.0	0.0
H ₂ O (estimate)	4	4	4	4	4	4	4	4	4	4	4	4
SUM Check	82.10	65.10	9.67	10.30	11.75	87.97	92.49	92.68	90.08	86.88	76.12	82.1

Appendix 1, Gas Generation Partial Pressure Data and Uncertainties in kPa (continued)

Uncertainties

Note: The uncertainties reported here are calculated from the uncertainties associated with the calibration of the GC and the quantification of the peak area of an observed GC peak. Additional uncertainties that are unrelated to the GC and which are variable in time such as minor leaks in the gas manifold are not reported. Thus, the actual uncertainty in the partial pressures of the gases are likely to be somewhat larger than reported.

Date	1/8/2004	2/11/2004	2/17/2004	2/18/2004	2/26/2004	2/26/2004	6/9/2004	1/24/2005	8/30/2005	4/19/2006	10/23/2006	1/25/2007
Days	31.0	65.0	71.0	72.0	80.0	80.0	184.0	413.0	631.0	863.0	1050.0	1144.0
CO ₂	0.00	0.03	0.01	0.02	0.01	0.03	0.04	0.02	0.01	0.01	0.00	0.01
N ₂ O	0.00	0.02	0.00	0.01	0.02	0.02	0.02	0.02	0.02	0.02	0.03	0.02
He	1.60	0.95	0.02	0.02	0.02	1.49	1.52	1.39	1.26	1.20	0.93	1.05
H ₂	0.00	0.02	0.00	0.00	0.02	0.01	0.03	0.02	0.01	0.01	0.01	0.01
O ₂	0.01	0.08	0.06	0.06	0.07	0.07	0.10	0.18	0.22	0.20	0.19	0.15
N ₂	0.02	0.26	0.12	0.12	0.14	0.21	0.21	0.29	0.35	0.36	0.43	0.37
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	0.25	0.00	0.00	0.00	0.00	0.31	0.00	0.01			

Appendix 1, Gas Generation Partial Pressure Data and Uncertainties in kPa (continued)

SSR132A

Date	6/11/2008	6/19/2008	7/8/2008	9/22/2008	12/15/2009	12/2/2010	2/26/2012	1/28/2013
Days	0	8	27	103	552	904	1355	1692
CO ₂	0.0	0.4	1.3	2.2	0.8	0.4	0.0	0.0
N ₂ O	0.0	0.2	0.4	0.4	0.5	0.6	0.0	0.7
He	78.1	73.8	70.8	68.3	68.2	72.7	70.2	72.3
H ₂	0.0	1.0	2.8	5.5	2.1	2.0	1.3	2.0
O ₂	0.7	0.7	0.9	0.9	0.8	0.3	0.0	0.2
N ₂	2.7	2.6	4.1	6.4	11.8	11.2	16.6	13.3
CH ₄	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
CO	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
H ₂ O estimate	4	4	4	4	4	4	4	4
SUM Check	85.6	82.8	84.3	87.8	88.3	91.1	92.1	92.4

Uncertainties

Date	6/11/2008	6/19/2008	7/8/2008	9/22/2008	12/15/2009	12/2/2010	2/26/2012	1/28/2013
Days	0	8	27	103	552	904	1355	1692
CO ₂	0.0	0.0	0.0	0.1	0.0	0.0	0.0	0.0
N ₂ O	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
He	1.6	1.5	1.5	1.4	1.5	1.5	1.5	0.7
H ₂	0.0	0.0	0.1	0.1	0.1	0.0	0.0	0.0
O ₂	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
N ₂	0.1	0.1	0.1	0.1	0.2	0.2	0.2	0.2
CH ₄	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
CO	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

Appendix , Gas Generation: Total Pressure for SSR132

Date	Pressure (kPa)	Date	Pressure (kPa)	Date	Pressure (kPa)	Date	Pressure (kPa)	Date	Pressure (kPa)
12/8/2003		4/12/2004	88.0	8/16/2004	91.4	12/20/2004	92.0	4/25/2005	90.1
12/15/2003		4/19/2004	88.8	8/23/2004	91.6	12/27/2004	92.1	5/2/2005	89.9
12/22/2003		4/26/2004	88.8	8/30/2004	91.7	1/3/2005	92.1	5/9/2005	89.8
12/29/2003		5/3/2004	89.4	9/6/2004	92.0	1/10/2005	91.9	5/16/2005	89.4
1/5/2004		5/10/2004	89.7	9/13/2004	92.3	1/17/2005	91.9	5/23/2005	89.0
1/12/2004	77.5	5/17/2004	90.2	9/20/2004	92.5	1/24/2005	91.9	5/30/2005	88.4
1/19/2004	69.6	5/24/2004	90.6	9/27/2004	92.5	1/31/2005	91.0	6/6/2005	88.1
1/26/2004	66.5	5/31/2004	90.7	10/4/2004	92.4	2/7/2005	91.4	6/13/2005	87.9
2/2/2004	67.0	6/7/2004	90.8	10/11/2004	92.6	2/14/2005	91.6	6/20/2005	87.4
2/9/2004	63.2	6/14/2004	90.1	10/18/2004	92.6	2/21/2005	91.5	6/27/2005	87.6
2/16/2004	0.8	6/21/2004	90.1	10/25/2004	92.6	2/28/2005	91.9	7/4/2005	87.6
2/23/2004	9.5	6/28/2004	90.5	11/1/2004	92.4	3/7/2005	92.1	7/11/2005	87.5
3/1/2004	84.8	7/5/2004	90.7	11/8/2004	92.3	3/14/2005	91.8	7/18/2005	87.6
3/8/2004	85.1	7/12/2004	90.8	11/15/2004	92.3	3/21/2005	91.5	7/25/2005	87.7
3/15/2004	85.8	7/19/2004	90.9	11/22/2004	92.3	3/28/2005	91.3	8/1/2005	88.3
3/22/2004	86.3	7/26/2004	90.8	11/29/2004	92.2	4/4/2005	91.0	8/8/2005	88.5
3/29/2004	86.7	8/2/2004	91.0	12/6/2004	92.2	4/11/2005	90.8	8/15/2005	88.5
4/5/2004	87.1	8/9/2004	91.2	12/13/2004	92.1	4/18/2005	90.5	8/22/2005	88.4

Appendix 2, Gas Generation: Total Pressure for SSR132 (continued)

Date	Pressure (kPa)	Date	Pressure (kPa)	Date	Pressure (kPa)	Date	Pressure (kPa)
8/29/2005	88.6	1/2/2006	84.7	6/19/2006	81.2	10/23/2006	73.1
9/5/2005	87.9	1/9/2006	84.4	6/26/2006	80.7	10/30/2006	73.2
9/12/2005	87.9	1/16/2006	84.2	7/3/2006	80.1	11/6/2006	73.5
9/19/2005	88.0	1/23/2006	84.3	7/10/2006	79.5	11/13/2006	67.0
9/26/2005	88.3	1/30/2006	84.0	7/17/2006		11/20/2006	73.6
10/3/2005	88.2	2/6/2006	83.8	7/24/2006	79.5	11/27/2006	73.8
10/10/2005	88.2	2/13/2006	84.4	7/31/2006	78.3	12/4/2006	73.8
10/17/2005	88.2	2/20/2006	84.6	8/7/2006	77.7	12/11/2006	75.1
10/24/2005	88.2	4/10/2006	85.4	8/14/2006	77.3	12/18/2006	75.3
10/31/2005	87.9	4/17/2006	84.8	8/21/2006	77.0	12/25/2006	75.
11/7/2005	87.9	4/24/2006	84.0	8/28/2006	76.5	1/1/2007	75.5
11/14/2005	88.3	5/1/2006	83.8	9/4/2006	76.1	1/8/2007	75.6
11/21/2005	87.2	5/8/2006	83.4	9/11/2006	75.7	1/15/2007	75.6
11/28/2005	86.8	5/15/2006	83.1	9/18/2006	75.3	1/22/2007	75.
12/5/2005	86.4	5/22/2006	82.8	9/25/2006	74.8		
12/12/2005	86.2	5/29/2006		10/2/2006	74.7		
12/19/2005	84.1	6/5/2006	82.2	10/9/2006	74.3		
12/26/2005	85.3	6/12/2006	81.7	10/16/2006	73.7		

Appendix 3, Gas Generation: Total Pressure for SSR132A

Date	Pressure (kPa)	Date	Pressure (kPa)	Date	Pressure (kPa)	Date	Pressure (kPa)	Date	Pressure (kPa)
6/11/2008	84.68	10/13/2008	89.10	2/23/2009	89.16	6/29/2009	88.53	11/2/2009	90.07
6/16/2008	84.23	10/20/2008	89.24	3/2/2009	89.09	7/6/2009	88.51	11/9/2009	90.36
6/23/2008	83.92	10/27/2008	89.33	3/9/2009	88.99	7/13/2009	88.64	11/16/2009	90.25
6/30/2008	85.41	11/3/2008	89.39	3/16/2009	89.02	7/20/2009	88.67	11/23/2009	90.31
7/7/2008	86.15	11/10/2008	89.21	3/23/2009	89.02	7/27/2009	88.84	11/30/2009	90.25
7/14/2008	86.35	11/17/2008	89.29	3/30/2009	88.95	8/3/2009	88.87	12/7/2009	90.32
7/21/2008	87.37	11/24/2008	89.65	4/6/2009	88.75	8/10/2009	88.84	12/14/2009	90.46
7/28/2008	88.29	12/1/2008	89.52	4/13/2009	88.78	8/17/2009	88.82	12/21/2009	89.79
8/4/2008	88.79	12/8/2008	89.45	4/20/2009	88.71	8/24/2009	88.87	12/28/2009	89.74
8/11/2008	89.36	12/15/2008	89.51	4/27/2009	89.04	8/31/2009	89.02	1/4/2010	89.73
8/18/2008	89.82	12/22/2008	89.54	5/4/2009	89.16	9/7/2009	88.75	1/11/2010	89.97
8/25/2008	90.12	12/29/2008	89.45	5/11/2009	89.22	9/14/2009	88.76	1/18/2010	90.00
9/1/2008	90.29	1/5/2009	89.66	5/18/2009	89.29	9/21/2009	89.84	1/25/2010	89.96
9/8/2008	90.55	1/12/2009	89.55	5/25/2009	90.04	9/28/2009	90.07	2/1/2010	90.17
9/15/2008	90.65	1/19/2009	89.73	6/1/2009	90.35	10/5/2009	90.00	2/8/2010	90.54
9/22/2008	90.70	1/26/2009	89.71	6/8/2009	90.05	10/12/2009	90.03	2/15/2010	90.68
9/29/2008	89.05	2/2/2009	89.66	6/15/2009	89.30	10/19/2009	90.00	2/22/2010	90.41

Appendix 3, Gas Generation: Total Pressure for SSR132A (continued)

Date	Pressure (kPa)	Date	Pressure (kPa)	Date	Pressure (kPa)	Date	Pressure (kPa)	Date	Pressure (kPa)
3/8/2010	90.55	7/12/2010	91.39	11/15/2010	92.62	3/21/2011	92.34	7/25/2011	85.84
3/15/2010	90.72	7/19/2010	91.21	11/22/2010	92.80	3/28/2011	92.47	8/1/2011	93.00
3/22/2010	90.73	7/26/2010	91.12	11/29/2010	92.74	4/4/2011	92.27	8/8/2011	93.03
3/29/2010	90.83	8/2/2010	91.07	12/6/2010	91.60	4/11/2011	92.25	8/15/2011	92.95
4/5/2010	90.64	8/9/2010	90.93	12/13/2010	91.75	4/18/2011	92.27	8/22/2011	92.84
4/12/2010	90.71	8/16/2010	91.03	12/20/2010	91.61	4/25/2011	92.31	8/29/2011	92.85
4/19/2010	90.69	8/23/2010	91.18	12/27/2010	91.73	5/2/2011	92.47	9/5/2011	93.06
4/26/2010	90.69	8/30/2010	91.13	1/3/2011	91.43	5/9/2011	92.49	9/12/2011	93.03
5/3/2010	90.71	9/6/2010	91.46	1/10/2011	91.59	5/16/2011	92.43	9/19/2011	93.38
5/10/2010	91.03	9/13/2010	91.19	1/17/2011	91.60	5/23/2011	92.32	9/26/2011	93.56
5/17/2010	90.98	9/20/2010	91.73	1/24/2011	91.67	5/30/2011	92.21	10/3/2011	93.52
5/24/2010	91.10	9/27/2010	92.77	1/31/2011	91.70	6/6/2011	92.21	10/10/2011	93.56
5/31/2010	91.19	10/4/2010	91.46	2/7/2011	91.66	6/13/2011	92.53	10/17/2011	93.79
6/7/2010	91.24	10/11/2010	90.86	2/14/2011	91.84	6/20/2011	92.40	10/24/2011	93.46
6/14/2010	91.46	10/18/2010	90.76	2/21/2011	91.98	6/27/2011	92.60	10/31/2011	93.41
6/21/2010	91.46	10/25/2010	91.40	2/28/2011	91.98	7/4/2011	92.71	11/7/2011	93.43
6/28/2010	91.52	11/1/2010	92.53	3/7/2011	92.15	7/11/2011	92.92	11/14/2011	93.45

Appendix 3, Gas Generation: Total Pressure for SSR132A (continued)

Date	Pressure (kPa)	Date	Pressure (kPa)	Date	Pressure (kPa)	Date	Pressure (kPa)
11/28/2011	93.13	4/2/2012	92.53	8/6/2012	93.40	12/10/2012	92.87
12/5/2011	93.29	4/9/2012	92.58	8/13/2012	93.42	12/17/2012	92.56
12/12/2011	93.36	4/16/2012	92.68	8/20/2012	93.33	12/24/2012	92.88
12/19/2011	93.24	4/23/2012	92.77	8/27/2012	93.27	12/31/2012	93.06
12/26/2011	93.31	4/30/2012	92.35	9/3/2012	93.23	1/7/2013	93.01
1/2/2012	92.87	5/7/2012	92.60	9/10/2012	93.58	1/14/2013	92.96
1/9/2012	93.31	5/14/2012	93.55	9/17/2012	93.45	1/21/2013	93.00
1/16/2012	93.49	5/21/2012	93.76	9/24/2012	93.40	1/28/2013	93.35
1/23/2012	94.15	5/28/2012	93.77	10/1/2012	93.48		
1/30/2012	93.94	6/4/2012	93.71	10/8/2012	93.30		
2/6/2012	93.65	6/11/2012	94.07	10/15/2012	93.37		
2/13/2012	93.61	6/18/2012	93.84	10/22/2012	93.44		
2/20/2012	93.68	6/25/2012	93.76	10/29/2012	93.49		
2/27/2012	92.62	7/2/2012	93.68	11/5/2012	93.38		
3/5/2012	92.65	7/9/2012	93.50	11/12/2012	93.27		
3/12/2012	92.80	7/16/2012	93.55	11/19/2012	93.23		
3/19/2012	92.70	7/23/2012	93.36	11/26/2012	93.32		

Appendix 4, Estimating the monolayer coverage

Surface Area: The number of monolayers of moisture on the sample surface may be calculated if the mass of moisture/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.¹³ The weight percentage of one monolayer of water is the product of the weight of water in a monolayer of 1 m² and the SSA:

$$\begin{aligned}\text{wt\% of 1 ML} &= 0.00022 \text{ g m}^{-2}\text{ML}^{-1} \times \text{SSA m}^2 \text{ g}^{-1} \times 100 \text{ wt\%} \\ &= 0.022 \text{ wt\% ML}^{-1} \times \text{SSA.}\end{aligned}\quad \text{Equation A1-1}$$

For the material BLO-39-11-14-004, with a SSA of 2.4 m² g⁻¹, the weight percentage of one monolayer of water is 0.053 wt%.

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:

	Total Moisture Loading (TGA)	
	SSR 132	SSR132A
Wt% Moisture	0.60	0.59
ML	11.3	11.1

Appendix 4, Estimating the monolayer coverage (continued)

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 monolayers of weakly bound water on the surface predicted by BET theory is illustrated in Fig. A-1. We will use $c=7$ for high-purity plutonium dioxide because it is within the range observed.¹⁴

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

Appendix 5, 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 ($\text{mg}^{-1} \text{cm}^{-2}$)	Elemental Mass Fraction	Elemental Stopping Power ($\text{mg}^{-1} \text{cm}^{-2}$)
H ₂ O(g)	7.946	0.0000	0
H ₂ O (l)	7.708	0.0067	0.05164
F	6.645	0.0000	0
O	5.901	0.0084	0.049521
Na	5.304	0.0000	0
C	5.190	0.0021	0.0109
S	5.117	0.0000	0
Mg	5.100	0.0006	0.003264
Si	4.852	0.0000	0
Al	4.702	0.0000	0
K	4.652	0.0003	0.001442
Cl	4.575	0.0010	0.004575
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	0.0000	0
(Pu+U+Am)O ₂	2.081	.988	2.055050
		S _{mat}	2.124755
		S _{wat}	7.708
		S	3.63

Appendix 6, Obtaining G-values and rate constants

As discussed in the H₂ G-value and rate constants section, a double exponential growth function fits the time dependence of the partial pressure curve for hydrogen in many of the MIS studies. The double exponential has three fitting parameters, A₀, the initial active water, k₁ the hydrogen formation rate constant and k₂, the hydrogen consumption rate constant. These fitting parameters can be used along with information of material properties and container geometry to calculate the initial rate, the hydrogen G-value, and empirical rate constants. This appendix documents the methodology for obtaining this information.

Calculation of G(H₂)

G(H₂) can be calculated by equating the initial rate of hydrogen generation to the product of the rate of dose to the water and G(H₂),

$$\frac{dn_{H_2}}{dt} = \dot{D}_{H_2O} G(H_2)$$

Equation A6-1

where N_{H2} is the number of molecules of hydrogen and $\dot{D}_{H_2O}$ is the rate of adsorbed dose to the water with units eV s⁻¹. The initial rate is given by the differential

$$\frac{dP_{H_2}}{dt} = k_1 A_0 e^{-k_1 t} - k_2 P_{H_2}$$

evaluated at time zero in units of molecules per second rather than kPa per day, given P_{H2} is zero at t = 0.

$$\begin{aligned} \left. \frac{dP}{dt} \right|_{t=0} &= k_1 A_0 e^{-k_1 t} \Big|_{t=0} = k_1 A_0 \\ \frac{dn_{H_2}}{dt} &= \frac{dP}{dt} \frac{V_g N_A}{R T} = k_1 A_0 \frac{V_g N_A}{R T} \frac{\text{day}}{86400 \text{ s}} \\ k_1 A_0 \frac{V_g N_A}{R T} \frac{\text{day}}{86400 \text{ s}} &= \dot{D}_{H_2O} G(H_2) \end{aligned}$$

Equation A6-2

In Equation A6-2, V_g is the gas volume within the reactor, N_A is Avogadro's number, R is the universal gas constant, T is the temperature in the gas phase during the time the data was collected. The method for calculating V_g within an SSR is shown in the Loading section. The dose rate to the water is given by

Appendix 6, Obtaining G-values and rate constants (continued)

$$\dot{D}_{H_2O} = P_{mat} \frac{6.2418 \times 10^{18} \text{ eV}}{\text{s W}} m_{mat} f_{H_2O} \frac{S_{H_2O}}{S_{mat}}$$

$$f_{H_2O} = \frac{m_{H_2O}}{m_{mat}}$$

$$\dot{D}_{H_2O} = P_{mat} \frac{6.2418 \times 10^{18} \text{ eV}}{\text{s W}} m_{H_2O} \frac{S_{H_2O}}{S_{mat}}$$

Equation A6-3

where P_{mat} is the specific power of the material in W g^{-1} , m_{mat} is the mass of the material, f_{H_2O} is the fraction of water, and the ratio S_{H_2O}/S_{mat} is the ratio of the stopping power of alpha particles in water to the stopping power in the material. An approach for calculating S_{H_2O}/S_{mat} is given in Appendix B. For high-purity plutonium dioxide with adsorbed water and no impurities the ratio S_{H_2O}/S_{mat} for 5.2 MeV α -particles is ~ 3.70 . Combining Equation A6-2 and Equation A6-3 yields a general expression for $G(H_2)$ using the fitting parameters k_1 and A_0 , and the material properties,

$$G(H_2) = k_1 A_0 \frac{V_g N_A}{R T} \frac{\text{day}}{86400 \text{ s}} \frac{1}{P_{mat} \frac{6.2418 \times 10^{18} \text{ eV/100}}{\text{s W}} m_{H_2O} \frac{S_{H_2O}}{S_{mat}}} \frac{1}{\frac{S_{H_2O}}{S_{mat}}}$$

Equation A6-4

Conversion of rate constants

The surface formation rate constant, k_{for} , is determined from the initial rate and can be expressed in terms of molecules of hydrogen produced per second using Eq. A6-5.

$$k_{for} = k_1 A_0 \frac{V_g N_A}{R T} \frac{\text{day}}{86400 \text{ s}}$$

Equation A6-5

The consumption rate constant, k_2 , expressed in units of days^{-1} , can be expressed in terms of molecules of hydrogen consumed per second per kPa of hydrogen using Eq. A6-6.

$$k_{con} = k_2 \frac{V_g N_A}{R T} \frac{\text{day}}{86400 \text{ s}}$$

Equation A6-6

Appendix 6, Obtaining G-values and rate constants (continued)

Calculation of rate constants for surface catalyzed decomposition of water to form H₂

The surface catalyzed decomposition of water to form H₂ has been proposed by Haschke and co-workers.¹⁵ The reaction is described by,

Equation A6-7

The reaction “contributes to H₂ pressurization of sealed storage containers until the equilibrium pressure of Equation A6-7 is reached.”^{15a} The amount of solid plutonium dioxide and water is large compared to the amount of H₂ and higher oxide produced. The initial reaction rate will be essentially constant throughout the reaction. The H₂ consumption reaction, in this case a true back reaction, is first order in H₂ partial pressure and in the amount of the higher oxide. The rate was found to be independent of adsorbed water over a wide range of adsorbed water. The observed initial rate of formation is divided by the total surface area of the material to obtain values that can be compared to Haschke’s reaction rates,

$$R_{\text{for}} = A_0 k_1 \frac{\text{day}}{24 \text{ hr}} \frac{V_g}{R T} \frac{1}{SSA m_{\text{mat}}}$$

Equation A6-8,

where *SSA* is the specific surface area of the material and *m_{mat}* is the mass of the plutonium dioxide. This formation rate, *R_{for}*, is expressed in units of moles m⁻² hr⁻¹ kPa⁻¹ of active water. The rate of the surface catalyzed consumption reaction is given by

$$R_{\text{con}} = k_2 \frac{\text{day}}{24 \text{ hr}} \frac{V_g}{R T} \frac{1}{SSA m_{\text{mat}}}$$

Equation A6-9.

Appendix 7, Symbols and Conversion Factors

Symbols

Symbol	Units	Description
A	kPa	Active water or the water involved in hydrogen generation
A_0	kPa	Initial active water (fitting parameter based on the reaction model)
k_1	day ⁻¹	Rate constant for the formation of hydrogen from water (fitting parameter based on the reaction model)
k_2	day ⁻¹	Rate constant for the consumption of hydrogen (fitting parameter based on the reaction model)
$\dot{D}_x$	eV s ⁻¹ or J s ⁻¹ or W	Rate of adsorbed dose to x
$G(x)$	molecules 100 eV ⁻¹	Number of molecules of x produced per 100 eV of adsorbed dose
f_x	---	Fraction of material x in the total material
m_x	g	Mass of x
N_x	molecules	Number of molecules of substance x
N_A	molecules mol ⁻¹	Avogadro's number
p_x	kPa	Partial pressure of x
P_x	W g ⁻¹ or eV s ⁻¹ g ⁻¹	Specific power of x
S_x	m	Stopping power of x to alpha radiation
SSA	m ² g ⁻¹	Specific Surface Area of the material
t	s or day or yr	Time
T	K	Temperature
V_g	cm ³	Volume that the gas occupies

Appendix 7, Symbols and Conversion Factors (continued)

Unit conversions

1 W	$6.2418 \times 10^{18} \text{ eV s}^{-1}$
1 day	86400 s
1 day	24 hr
N_A	$6.0221367 \times 10^{23} \text{ molecules mol}^{-1}$
R	$8.314510 \text{ J mol}^{-1} \text{ K}^{-1}$ $8.314510 \text{ kPa L mol}^{-1} \text{ K}^{-1}$ $8314.510 \text{ kPa cm}^3 \text{ mol}^{-1} \text{ K}^{-1}$