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Long-term Moisture Adsorption in Packaged Plutonium Oxide

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Contents

1	Introduction	1
2	Methods.....	3
3	Effect of Impurities in stored PuO ₂ on Water Adsorption.....	6
4	Analysis of Water Adsorption by TGA-MS and Mass.....	7
5	Future Directions	12
6	Conclusions	13
7	References	14
8	Acknowledgments	15
9	Acronyms and Abbreviations.....	15

Figures

Figure 1. Splits, masses, containerization, and disposition of samples. “SAVY” refers to the SAVY-4000.	3
Figure 2. Experimental setup for stored PuO ₂ samples analyzed by TGA-MS stored in a 3 quart SAVY-4000.	4
Figure 3. (A) Moisture uptake of PuO ₂ packaged in a SAVY-4000 container measured by TGA-MS over time. Red refers to m/z 17 data and black refers to m/z 18 data. Error bars represent the absolute expanded uncertainty in the measurement. (B) Total increase in mass over time (in wt%) for a 250.034 g PuO ₂ sample. Linear fit equations and R ² values are listed for each data set.	8
Figure 4. Relative humidity and temperature over time where each data point corresponds to a moisture adsorption measurement by (A) TGA-MS or (B) Balance.	9
Figure 5. Relative humidity and temperature vs. the rate of water adsorption in wt%/day for (A and B) TGA-MS and (C) Balance. The wt%/day value was calculated by taking the change in wt% adsorption between two consecutive measurements and dividing by the number of days between the consecutive measurements. This calculated rate of water adsorption was plotted vs. the relative humidity and temperature collected for the second of the consecutive measurements. The 1 st and 2 nd data point for relative humidity and temperature data are excluded TGA-MS measurements (A and B) as these data were not collected when moisture was analyzed by TGA-MS.....	10

Tables

Table 1. samples and their corresponding PuO ₂ mass stored in 20 mL scintillation vials in a 3 quart SAVY-4000 for measurement of water content over time.	4
Table 2. Elements present in a representative sample of the BL by ICP-MS.	6
Table 3. Time to reach specific moisture wt% thresholds and rate of moisture wt% increase over time. These values were calculated from the linear fits found in Figure 3.	8
Table 4. Relative humidity, temperature, and the corresponding wt% moisture measurements by TGA-MS for PuO ₂ stored in a SAVY-4000.	11
Table 5. Relative humidity, temperature, and the corresponding wt% moisture measurements by mass gain as determined with a balance for PuO ₂ stored in a SAVY-4000.....	11

1 Introduction

In 2018, the Department of Energy National Nuclear Security Administration (DOE-NNSA) began implementing dilute and dispose to remove 34 metric tons (MT) of surplus weapons grade plutonium from the US stockpile.¹ Under this plan, surplus plutonium material is converted into plutonium oxide (PuO_2) before being stored in metal containers and sent to the DOE Waste Isolation Pilot Plant (WIPP).¹ The dilute and dispose project was implemented as a more cost-effective method for abiding by the Plutonium Management and Disposition Agreement (PMDA) between the USA and Russia, as compared to producing mixed oxide fuel (MOX). The PMDA was originally signed in 2000 and amended in 2010.² The disassembly of pits and conversion to PuO_2 as part of dilute and dispose is carried out through the Advanced Recovery and Integrated Extraction System (ARIES) developed at Los Alamos National Laboratory (LANL). The dilute portion of dilute and dispose is carried out at Savannah River Site (SRS). With this program in place, it is necessary to ensure the safe, long-term storage of the PuO_2 generated during this process until final disposal at WIPP is accomplished.

In the last 20 years, studies have shown that the steel containers used to house PuO_2 for long-term storage can become corroded over time.³⁻⁵ A variety of factors seem to be at play, but the combination of chloride salts and water in PuO_2 material appears to be particularly detrimental for causing corrosion.³⁻⁷ With this in mind, limits and requirements through DOE-STD-3013-2018 were established to minimize the amount of corrosion occurring in storage containers used for the long-term storage of plutonium materials with the intent of enabling safe, stable storage of the PuO_2 material for 50 years.⁸ A 3013 compliant configuration requires that the nested steel containers are welded shut to ensure that the configuration is leak tight. Limits have also been placed on the allowed water content in the PuO_2 bulk material that must be met prior to storage. Specifically, the Department of Energy requires that the water content of all packaged plutonium materials be no higher than 0.5 wt% (DOE-STD-3013-2018, section 6.1.2.3).^{8,9} As such, this requirement applies to ARIES blend lots (BLs), where a BL is defined as one batch of blended, homogenous plutonium oxide material that has undergone ARIES processing. Additionally, the interface control document between LANL and SRS (the customer for processed PuO_2), requires that the water content in a BL be no higher than 0.1 wt% when packaged in a Dynamic Flow Form (DFF) 3013 container (G-ESR-G-00035).^{10,11}

However, our understanding of how water content changes over time for stored PuO_2 is limited for PuO_2 that is not packaged in welded, hermetically sealed containers. Recent efforts have been made to transition away from sending ARIES oxide product to SRS in 3013 containers, which are welded shut and known to keep moisture out. Instead, there has been interest in transitioning to SAVY-4000 containers, which are vented. However, SRS still requires that the moisture limits listed in DOE-STD-3013-2018 for plutonium materials be met. Therefore, it is vital that we understand how moisture is adsorbed onto BLs over time when stored in SAVY-4000 containers. Currently, packaging in a SAVY-4000 does not meet the requirements of DOE-STD-3013-2018 both since SAVY-4000 containers are not welded, hermetically sealed containers and since packaging in a SAVY-4000 container is only approved for up to 15 years rather than the 50 years approved for 3013 containers.⁸

Moisture adsorption on PuO_2 materials stored in SAVY-4000 containers is of particular concern for BLs that contain a significant amount of impurities, specifically chlorides. Other impurities that may be of concern include halogens, alkali metals, and alkaline earth metals, which are often hygroscopic. In this study, a highly contaminated BL stored in SAVY-4000 containers was monitored over approximately a year and a half for changes in water content via thermogravimetric analysis mass spectrometry (TGA-MS) and via changes in overall mass as measured by a balance. The results indicated that the rate of water adsorption will result in a water content that no longer meets the limit designated by DOE-STD-3013-2018 and G-ESR-G-00035 in less than 12 years. The remainder of this report will describe the experimental setup, reason for choosing this BL, results, and future experiments that may be useful for expanding our understanding of the rate of water adsorption in PuO_2 materials produced from the ARIES process when those materials are stored or packaged in a SAVY-40000 container.

2 Methods

The design of this set of experiments was originally described in PA-PLAN-01731, *ARIES Test Plan for SAVY-4000 Adsorbed Moisture Quantification*. Two different experiments were conducted, both with the intent of monitoring the rate of water adsorption on PuO_2 material stored in a SAVY-4000 container. All experiments were conducted using material from ARIES BL 97 (OPL0T0097), which consisted of blended, homogenous PuO_2 . A representative sample from BL 97 was analyzed using inductively coupled plasma mass spectrometry (ICP-MS) by the Actinide Analytical Chemistry (C-AAC) group. This was done to determine plutonium and chemical composition of BL 97, and therefore the composition of all samples derived from BL 97. The blend lot was composed from a mixture of pure material and legacy material that was impure. Before any splits, this BL had a net weight of ~ 700 g (Figure 1). Each time a measurement was taken the relative humidity and temperature of the glovebox was recorded.

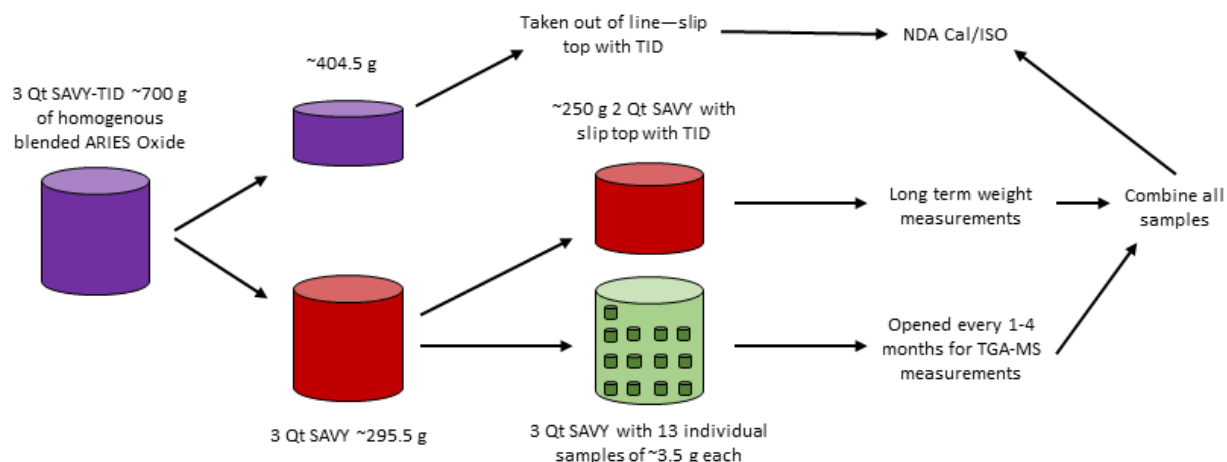


Figure 1. Splits, masses, containerization, and disposition of samples. “SAVY” refers to the SAVY-4000.

Moisture Adsorption Measured by Balance

A 250.0340 g sample of PuO_2 was weighed out using a balance with a range up to 310 g with an uncertainty of 1 mg. This sample was contained in a taped slip top container and placed in a 2 quart SAVY-4000 container. A tamper indicating device (TID) was applied to the SAVY-4000. The performance of the balance used to weigh the SAVY-4000 with the TID was verified prior to each measurement with a 200 g and a 5000 g check weight. Additional mass measurements were collected over 573 days, at intervals of approximately 1-4 months. Relative humidity and temperature measurements were also taken each time the mass was measured. During this time the SAVY-4000 container was staged in a normal air glovebox.

Moisture Adsorption Measured by TGA-MS

A balance with a range up to 310 g and an uncertainty of 1 mg was used to weigh out 13 samples of ~ 3.5 g PuO_2 into 20 mL glass scintillation vials (Figure 2, Table 1). These samples were labeled, then placed into a 3 quart SAVY-4000 container and a TID was applied. A sample

was removed from the SAVY-4000 every one to four months and analyzed for moisture content by TGA-MS over a total of 476 days. Relative humidity and temperature measurements were also taken each time a TGA-MS measurement was done. During this time the SAVY-4000 container was staged in a normal air glovebox. Each time a sample was run on the TGA-MS, the TID on the SAVY-4000 container was broken, a sample was removed, then a new TID was applied.



Figure 2. Experimental setup for stored PuO_2 samples analyzed by TGA-MS stored in a 3 quart SAVY-4000.

Table 1. samples and their corresponding PuO_2 mass stored in 20 mL scintillation vials in a 3 quart SAVY-4000 for measurement of water content over time.

Sample Name	Sample Mass (g)
M1	3.5510
M2	3.4455
M3	3.4305
M4	3.5720
M5	3.5440
M6	3.5385
M7	3.5370
M8	3.4090
M9	3.4180
M10	3.4645
M11	3.5190
M12	3.5480
M13	3.5330

TGA-MS was performed in a normal air glovebox using a Netzsch STA 449 F3 Jupiter coupled to a QMS 403 Aëolos Quadro quadrupole mass spectrometer. All runs were carried out with open-top, 3.4 mL alumina crucibles. Crucibles were cleaned prior to use by heating between 800 and 900 °C overnight in the TGA furnace. Temperature readings measured by the TGA were calibrated at a heating rate of 10 °C/min with National Institute of Standards and Technology (NIST) metal melting point standard reference materials (SRMs), and with high purity metal calibration materials provided by the instrument manufacturer (Netzsch). The MS was calibrated for moisture ($m/z = 17$ and 18) using samples comprised of a combination of gypsum and talc per PMT2-MPR-DOP-015, R12. The NIST SRMs used for weighing samples were calibrated by the LANL Metrology Program and Calibration Laboratory (MPCL). The balance used for measuring samples was verified daily and controlled by the LANMAS measurement control program. Measuring and Test Equipment (M&TE) was utilized for instrument calibration and sample handling.

All TGA-MS measurements were run from 30-1100 °C at a heating rate of 10 °C/min under an argon flow of 50 mL/min. Signals from evolved gases were monitored by the coupled mass spectrometer in the mass-to-charge (m/z) range of 4 to 48. Empty and reference crucibles were first run to determine the TGA baseline on a quarterly basis. Each sample was run once.

3 Effect of Impurities in stored PuO₂ on Water Adsorption

The adsorption of water onto PuO₂ material is of concern for all BLs due to its connection to corrosion. Previous efforts have shown that the presence of impurities tend to exhibit higher water content in BLs. ARIES BLs were analyzed to see if a trend between the concentration of various element ions and water content as measured by TGA-MS existed by looking at previously measured blend lots. In particular, halides, alkali metals, and alkaline earth metals were of concern since salts containing these elements are often hygroscopic.^{12,13} While no clear, linear trend was observed, water content was found to be higher in BLs that contained higher concentration of these hygroscopic impurities.

With this in mind, BL 97, which features a variety of impurities including Cl, F, Al, Mg, Ca, Li, Na, and K, was chosen for these experiments. The moisture content of this BL was 0.166 wt% with an absolute error of 0.0014 at the time of initial packaging, which exceeds the 0.1 wt% cutoff for DFF containers. Due to the high concentration of impurities, particularly impurities known to be hygroscopic, this BL represents a worst-case scenario for the presence of impurities, and therefore should provide a worst-case scenario for water adsorption over time. The long-term moisture adsorption experiments described in this document were done on the material with this starting moisture content.

Table 2. Elements present in a representative sample of the BL by ICP-MS.

Elemental Impurity	Concentration (ppm)	% Error
Al	524	10
As	0.753	100
B	25.3	30
Ba	1.55	100
Be	113	10
C	158	10
Ca	7770	10
Cd	0.627	100
Cl	8900	10
Cr	604	10
F	540	10
Fe	1360	10
Ga	3370	10
K	578	10
Li	4.12	100
Mg	7330	10
Na	325	10
Ni	1680	10
Pb	13.2	30
Si	218	10
Total	33515.55	

4 Analysis of Water Adsorption by TGA-MS and Mass

Measurements were taken as described above to investigate the uptake of water in processed PuO₂ BL. TGA-MS measurements looking at m/z of 18 and m/z of 17, corresponding to H₂O and OH respectively, were specifically analyzed to determine the weight percent (wt%) of water in a given sample (Figure 3A). Moisture content was graphed versus time in days to determine how moisture content of a BL may change over time in storage in a SAVY-4000 container. It was found that both ions showed a largely linear trend in the uptake of moisture over time with an R² value of 0.75 and 0.64 for m/z of 18 and m/z of 17 respectively. A linear fit was used to estimate the rate of water adsorption for each data set in terms of wt%/day and wt%/year, which was then used to calculate the time needed for (1) 0.1 wt% uptake, (2) 0.5 wt% uptake, and (3) the time needed for BL 97 to reach 0.5 wt% (Table 3). These values were chosen based on the moisture limits set by the DOE and SRS. Using the m/z 17 data analysis, 0.1 wt% would be gained in 2.295 years and 0.5 wt% would be gained in 11.473 years. Using the m/z 18 data analysis, 0.1 wt% would be gained in 1.860 years and 0.5 wt% would be gained in 9.298 years. Additionally, the time for this BL to reach the 0.5 wt% threshold would be less than 8 years for either mode of analysis. These values correspond to a gain of 0.044 wt% per year and 0.054 wt% per year for m/z 17 and m/z 18 respectively. These data show that under the storage conditions utilized in this experiment, the rate of water uptake will result in a wt% above the limits set by the DOE and SRS in less than 12 years, which is less than the 15-year storage life approved for a SAVY-4000.

Water uptake in this BL was also analyzed by measuring the mass gain over time of a 2 qt SAVY with 250.034 g of material from the BL stored within it (Figure 3B). If it is assumed that all increases in mass can be attributed to water adsorption, then a clear linear trend is observed where the wt% of water increases over time. A linear fit of these data gives a trendline with an R² value of 0.90, a better fit than was achieved by either data set obtained by TGA-MS measurements (Figure 3A). As with the TGA-MS measurements, this linear fit was used to estimate the time needed for (1) 0.1 wt% uptake, (2) 0.5 wt% uptake, and (3) the time needed for BL 97 to reach 0.5 wt% (Table 3). It was found that 0.1 wt% mass would be gained in 1.313 years, that 0.5 wt% mass would be gained in 6.567 years, and that this BL sample would reach the 0.5 wt% threshold in 4.377 years. These values correspond to a gain of 0.076 wt% per year. As such, this experiment suggests a faster rate of water adsorption overall than observed by TGA-MS.

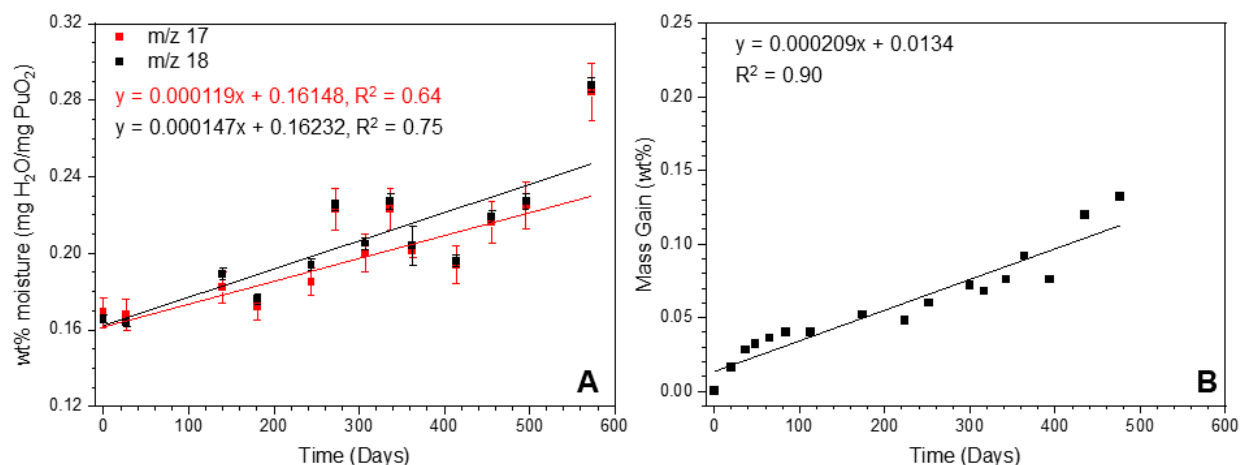


Figure 3. (A) Moisture uptake of PuO₂ packaged in a SAVY-4000 container measured by TGA-MS over time. Red refers to m/z 17 data and black refers to m/z 18 data. Error bars represent the absolute expanded uncertainty in the measurement. (B) Total increase in mass over time (in wt%) for a 250.034 g PuO₂ sample. Linear fit equations and R² values are listed for each data set.

Table 3. Time to reach specific moisture wt% thresholds and rate of moisture wt% increase over time. These values were calculated from the linear fits found in Figure 3.

	TGA-MS		2 QT SAVY Mass Gain
	m/z 17	m/z 18	
Days to 0.5 wt%	2791.062	2264.962	1597.586
years to 0.5 wt%	7.647	6.205	4.377
rate (wt%/year)	0.044	0.054	0.076
years to gain 0.1wt%	2.295	1.860	1.313
years to gain 0.5 wt%	11.473	9.298	6.567

The rate of wt% water increase is higher in the experiments measuring mass increases than in the experiments measuring water content by TGA-MS. This may point to a source of increased mass other than water to which the mass increases should be attributed or that the TGA-MS measurements underrepresent the amount of moisture adsorption. One possibility is that the TGA-MS data shows a rate of increase that is artificially low due to error in the water calibration curve. Alternatively, the 20 mL scintillation vials within the SAVY-4000 container used to store samples measured by TGA-MS may have created a better, though not airtight, seal against airborne moisture as compared to the slip top used to store the sample where moisture adsorption was measured by increases in mass. This could have resulted in an overall decreased water adsorption rate observed in the samples measured by TGA-MS. While some discoloration of the inner plastic of the scintillation vial lids containing samples was observed, no other visible degradation was noted, suggesting that degradation of the seal of the scintillation vials during the course of these experiments was negligible. Another possibility is that the error in either or both sets of measurements have contributed to the difference in calculated adsorption rate. However, all experiments point to an uptake in water adsorption during storage in a SAVY-4000 container, which suggests that PuO₂ BLs may no longer meet the DOE and SRS moisture limits in less than 12 years.

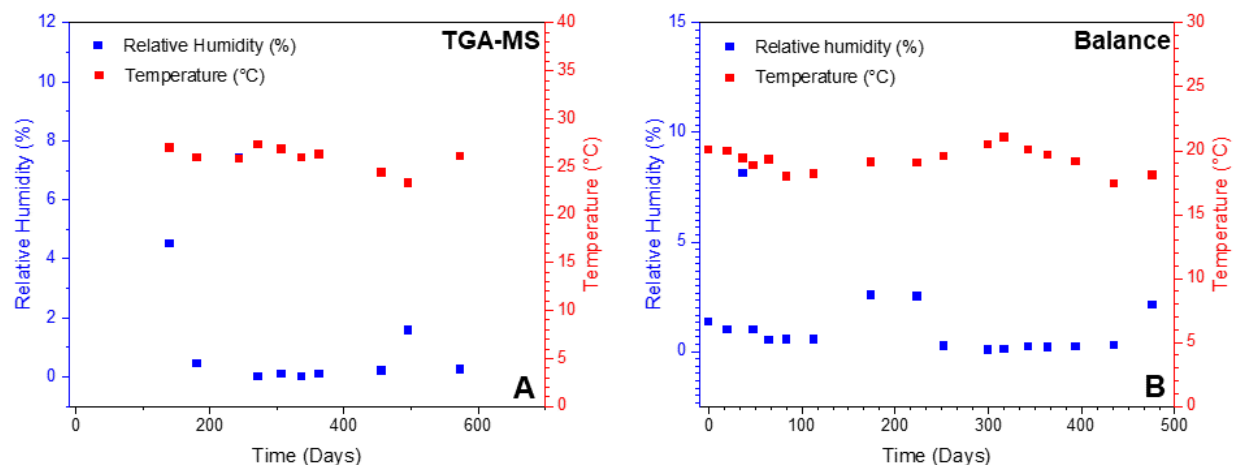


Figure 4. Relative humidity and temperature over time where each data point corresponds to a moisture adsorption measurement by (A) TGA-MS or (B) Balance.

Prior to each TGA-MS and balance measurement, a reading of the relative humidity and temperature were taken (Figure 4 and 5, Table 4 and 5). These data were collected to investigate if temperature or relative humidity affects the rate of water adsorption when stored in a SAVY-4000 container in a temperature and humidity regulated glovebox. The temperature remained relatively constant during all measurements with an average temperature of 25.90 °C in the glovebox used for TGA-MS measurements and an average temperature of 19.25 °C in the glovebox where the 2 QT SAVY-4000 was weighed using a balance. In contrast, the relative humidity jumped up periodically (Figure 4A and 4B). However, there is no clear or consistent correlation observed between these spikes in humidity and the wt% of water in the samples. This lack of correlation between relative humidity or temperature and the rate of water adsorption can be seen even more clearly in Figure 5. Another possible source of variance is the difference in storage methods used for the samples measured by TGA-MS as compared to the samples measured for their increase in mass using a balance.

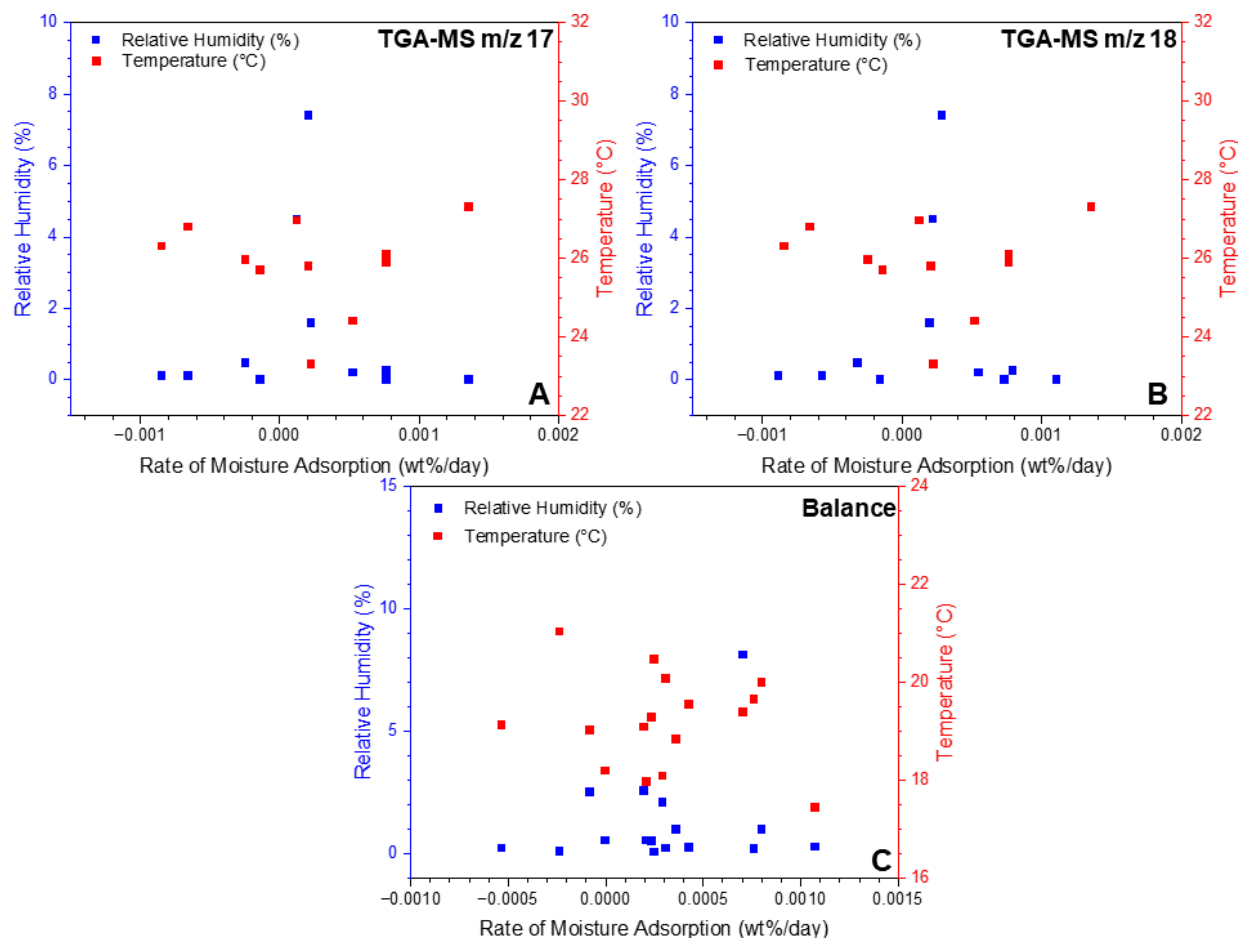


Figure 5. Relative humidity and temperature vs. the rate of water adsorption in wt%/day for (A and B) TGA-MS and (C) Balance. The wt%/day value was calculated by taking the change in wt% adsorption between two consecutive measurements and dividing by the number of days between the consecutive measurements. This calculated rate of water adsorption was plotted vs. the relative humidity and temperature collected for the second of the consecutive measurements. The 1st and 2nd data point for relative humidity and temperature data are excluded TGA-MS measurements (A and B) as these data were not collected when moisture was analyzed by TGA-MS.

While all three methods of analysis suggest a relatively fast rate of water adsorption, there are some important caveats to these experiments that should be kept in mind. First, there are major differences between the experimental setup used here and the storage process used for ARIES BLs. In normal air gloveboxes, the relative humidity and temperature is regulated. The storage areas for the fully packaged ARIES BLs do not regulate temperature or humidity. While these data clearly show that when relative humidity is kept below 15%, in accordance with DOE-STD-3013-2018, and the temperature is kept at approximately room temperature, these factors have no observable impact on the water adsorption rate, this may not be true in conditions where temperature and humidity are not regulated. In fact, studies have shown that high relative humidity can impact the water content in bulk PuO₂ material.^{4,14} As previously discussed, the presence of water, via humidity, in conjunction with chlorides in PuO₂ material plays a role in the corrosion of the stainless steel containers used for packaging PuO₂ material. Second, only one BL was analyzed in this set of experiments. While this BL was carefully chosen to simulate a worst-case scenario, it cannot provide rates of water adsorption that can be universally applied to all stored PuO₂ BLs. Therefore, additional experiments on blend lots with a range of impurities would provide valuable data.

Table 4. Relative humidity, temperature, and the corresponding wt% moisture measurements by TGA-MS for PuO₂ stored in a SAVY-4000.

Days	Relative Humidity (%)	Temperature (°C)	TGA-MS Measured Moisture Content (wt%)	
			m/z 17	m/z 18
0	N/A*	N/A	0.169(8)**	0.166(2)
27	N/A	N/A	0.168(8)	0.164(2)
140	4.50	26.96	0.182(8)	0.189(3)
181	0.46	25.96	0.172(7)	0.176(3)
244	7.40	25.80	0.185(7)	0.194(3)
272	0.00	27.30	0.223(11)	0.225(3)
307	0.10	26.80	0.200(10)	0.205(3)
337	0.00	25.90	0.223(11)	0.227(4)
363	0.10	26.30	0.201(3)	0.204(10)
414	0.00	25.70	0.194(10)	0.196(3)
456	0.20	24.40	0.216(11)	0.219(3)
496	1.58	23.30	0.225(12)	0.227(4)
573	0.25	26.09	0.284(15)	0.288(4)

*N/A = data not recorded

**absolute error in parentheses

Table 5. Relative humidity, temperature, and the corresponding wt% moisture measurements by mass gain as determined with a balance for PuO₂ stored in a SAVY-4000.

Days	Relative Humidity (%)	Temperature (°C)	2 QT SAVY mass gain (g)	2 QT SAVY mass gain (mg)	2 QT SAVY mass gain (wt%)
0	1.35	20.07	0.00	0	0.00
20	1.00	19.99	0.04	40	0.02
37	8.12	19.39	0.07	70	0.03
48	1.00	18.83	0.08	80	0.03
65	0.52	19.28	0.09	90	0.04
84	0.56	17.97	0.10	100	0.04
113	0.56	18.19	0.10	100	0.04
174	2.58	19.09	0.13	130	0.05
224	2.52	19.03	0.12	120	0.05
252	0.25	19.55	0.15	150	0.06
300	0.08	20.46	0.18	180	0.07
317	0.11	21.03	0.17	170	0.07
343	0.23	20.07	0.19	190	0.08
364	0.20	19.65	0.23	230	0.09
394	0.24	19.12	0.19	190	0.08
435	0.29	17.44	0.30	300	0.12
476	2.11	18.09	0.33	330	0.13

5 Future Directions

While important insight can be gained from this set of experiments, there are a variety of experiments that would add to our understanding of water adsorption for PuO₂ material stored in SAVY-4000 containers. Some possible future experiments and the insights that could be gained from them are outlined below.

1. It would be valuable to see how the rate of wt% water changes for BLs with different impurities as analyzed by ICP-MS. Repeating the experiments described in this technical report using 5-10 BLs with varying concentrations of impurities and from a variety of sources would allow us to compare the rate of water adsorption. Additionally, it would allow for error to be more accurately calculated given that most statistical analysis methods require at least 3 data points to be meaningful. These proposed experiments would also demonstrate whether the presence of impurities after processing changes the rate of water adsorption.
2. After processing a largely pure BL as determined by ICP-MS, it would be valuable to make 3-5 samples with impurities of interest doped in at a certain weight percent (i.e. 0%, 1%, 5% and 10%) and perform the experiments previously described in this report. Possible compounds of interest to include are compounds containing halogens, alkali metals, or alkaline earth metals. This would reveal if the rate of moisture adsorption changes should specific compounds/salts be present in higher concentration after processing.
3. It would be valuable to repeat the same experiment while storing the samples somewhere outside of a normal air glovebox, such as the vault or a safe. This would mimic actual storage conditions used for BLs, and thus allow us to determine if storing samples in a normal air glovebox provides data that can be extrapolated to actual storage conditions. This experiment would require that a temperature and humidity measurement in the storage location be collected regularly, such as every workday or once a week.
4. Last, it would be interesting to run these experiments over multiple years. This would provide insight into whether water adsorption continues to be linear after the first year or two. It is possible that after a certain amount of time, an equilibrium moisture concentration would be reached, causing the rate of water adsorption to decrease or level out.

6 Conclusions

The long-term moisture adsorption experiments described in this report suggest that water adsorption in PuO_2 material stored in a SAVY-4000 container may occur faster than initially predicted, which is of concern due to the known impact of water on the stable storage of PuO_2 . It is therefore imperative that we gain a more holistic understanding of long-term water adsorption in stored PuO_2 , then use that knowledge to develop better packaging and storage techniques.

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9 Acronyms and Abbreviations

Acronym	Definition
AMPP	Actinide Material Processing and Power
ARIES	Advanced Recovery and Integrated Extraction System
BL	Blend lot
BLs	Blend lots
C-AAC	Chemistry Division Actinide Analytical Chemistry
DFF	Dynamic flow form
DOE	Department of Energy
ICP-MS	Inductively coupled plasma mass spectrometry
LANL	Los Alamos National Laboratory
MOX	Mixed oxide fuel
MT	Metric ton
MPCL	Metrology Program and Calibration Laboratory
M&TE	Measuring and Test Equipment
NIST	National Institute of Standards and Technology
NNSA	National Nuclear Security Administration
PMDA	Plutonium Management & Disposition Agreement
SRM	Standard Reference Materials
SRS	Savannah River Site
TID	Tamper indicating device
TGA-MS	Thermogravimetric analysis mass spectrometry
WIPP	Waste Isolation Piolet Plant
wt%	Weight percent