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Title: A summary of volatile impurity measurements and gas generation studies on MISSTD-1, a high-purity plutonium oxide produced by low-temperature calcination of plutonium oxalate

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A summary of volatile impurity measurements and gas generation studies on MISSTD-1, a high-purity plutonium oxide produced by low-temperature calcination of plutonium oxalate

Abstract

Plutonium dioxide of high specific surface area was subjected to long-term tests of gas generation in sealed containers. The material preparation and the storage conditions were outside the bounds of acceptable parameters defined by DOE-STD-3013-2012 in that the material was stabilized to a lower temperature than required and had higher moisture content than allowed. The data provide useful information for better defining the bounding conditions for safe storage. Net increases in internal pressure and transient increases in H₂ and O₂ were observed, but were well within the bounds of gas compositions previously shown to not threaten integrity of 3013 containers.[1]

Introduction

The Surveillance and Monitoring Program was instituted by the US Department of Energy Office of Environmental Management to focus on developing the technical basis for safely storing plutonium-bearing materials and validating safe storage. As part of this program, shelf-life studies are conducted at LANL and Savannah River National Laboratory to identify early indications of potential degradation mechanisms, principally internal pressurization and corrosion. These data aid in selection of storage containers to examine in the field and are useful in assessing alternative stabilization and packaging processes for equivalency to the requirements of DOE-STD-3013.[2]

Plutonium oxide in long-term storage has originated from diverse processes and from several facilities, resulting in a wide variety of physical characteristics and chemical impurities. Part of the charge of the shelf-life program is to conduct storage studies on plutonium oxide batches of diverse origins to identify expected and bounding storage behaviors the full range of material being stored under DOE-STD-3013-2012. This report summarizes data collected by the shelf-life program on one such batch of material, designated MISSTD-1. This material differs from most materials included in the shelf-life program in that it was not fully stabilized to the requirements of DOE-STD-3013-2012 and therefore does not directly represent material in storage. However, it has proven useful in studying the effects of high PuO₂ specific surface area on gas generation in storage.

Material Origin and Handling History

MISSTD-1 is the designation of a batch of plutonium oxide created at LANL in 1997 by blending five batches of oxide from low-temperature oxalate calcination. Each of the five batches was produced by aqueous nitrate anion exchange purification, precipitation as plutonium(III) oxalate, and finally a thermal treatment that

combined oxalate destruction and oxide stabilization. The date of original production of those batches ranged from December 1988 to March 1992.

Data sheets and notes on the production of the five batches do not detail the temperature or duration of the thermal treatment. However, conditions can be inferred from the standard operating procedure in place at the time. Based on this procedure, it is likely that the oxalate was air-dried in the filter boat and then calcined in a platinum-lined boat for six hours at 600 °C. The heat-up and cool-down times are not specified in the procedure.

The five batches were removed from the PF-4 vault in March 1997, blended to create MISSTD-1 on 3/27/1997, and sampled for various analyses (discussed below). Then the blend was split into MISSTD-1 and MISSTD-1A.

In April 1997 MISSTD-1, containing the bulk of the blend, was sealed into a welded full-scale test container. The oxide was handled in dry air gloveboxes during the blending, and a helium-atmosphere glovebox for container loading and sealing. It was not heated or otherwise treated to remove adsorbates prior to sealing into the container. The test container was similar to a 3013 with the addition of a sealed bellows in the inner container headspace to be used for radiographic pressure monitoring. It was placed in the PF-4 vault where it resided for most of the subsequent 13 years. It was removed periodically for radiography to measure the bellows length.

MISSTD-1A was stored in an unspecified configuration, probably a taped, slip-lid stainless steel container. Sometime between 1997 and 2005, 30 grams were removed from MISSTD-1A and designated MISSTD-1ASUR for use in small-scale shelf-life tests.

Small-scale shelf-life tests were initiated in 2005 and 2008 using separate 10 gram aliquots from MISSTD-1ASUR. For these tests the material was pretreated in a manner designed to begin the tests with 0.5 wt % moisture on the material. The material was heated to 200 °C for two hours, and then it was exposed to a humid helium atmosphere until it regained 0.5 wt %. Then it was rapidly sealed into the test container. As detailed below in the discussion of TGA-MS data, it later became apparent that 200 °C was not sufficient to desorb most of the moisture from this particular oxide, and the total moisture content in these small-scale tests exceeded 0.5 wt % by a factor of 2 or more.

The small-scale test containers incorporate continuous pressure monitoring and provisions for withdrawing and analyzing gas samples without disturbing the experiment. The 2005 test developed a leak after a few months and was terminated. The 2008 test is ongoing and has produced pressure and gas composition data for almost four years.

Material Characterization Data

Input batches

The Pu content of the five input batches ranged from 87.7 ± 0.2 wt % (4 batches) to 82.2% (1 batch) based on chemical analysis. Carbon at 1.2% was the only significant measured impurity anomaly in the lower-purity batch. The other four batches had carbon at about 500 ppm of the total mass. The lower-purity batch accounted for 29.4% of the mass of the MISSTD-1 blend.

MISSTD-1

Samples were taken from MISSTD-1 on 3/27/1997 (LOI) and 4/2/1997 (SSA, particle size). Mass loss on ignition (LOI) to 1000 °C was measured at 2.13% on 3/31/1997, using a sample split from MISSTD-1 on 3/27/1997, the same day that it was blended from the five input items. Specific surface area was measured three times on 4/3/1997 on a sample collected 4/2/1997, with results of 32 ± 0.8 m²/g, where $\pm$ indicates the total spread of measurements. Trace element analyses were not performed. Plutonium content was assayed at 86.0% and total actinides at 86.0% by calorimetry.

MISSTD-1A

MISSTD-1A was sampled for characterization on 9/14/1999, approximately 2.5 years after it was separated from the parent MISSTD-1. Loss on ignition to 1000 °C was measured on 9/21/1999 and showed 2.35% mass loss. Chemical analysis measured carbon at 2900 ppm (0.29%), which is roughly consistent with what would be expected from the mass-weighted average of the carbon assays on the input items to the blend. No other measured impurities exceeded 200 ppm. An additional sample was taken from MISSTD-1A for surface area and particle size analysis sometime between 2005 and 2011 and analyzed in March 2011. That sample was measured three times for surface area and showed 18.9 ± 0.2 m²/g. An earlier surface area analysis in March 2000 showing 1.4 m²/g is assumed to be erroneous because the instrument was giving problems and was replaced shortly after that measurement.

A sample was split from MISSTD-1ASUR for TGA-MS analysis in 2005 and analyzed in 2007. The sample was stored in a hermetically sealed container for most of the intervening period, but it was unavoidably exposed to ambient air for 10-30 minutes during the transfer into the TGA-MS instrument, so some systematic error in the direction of high moisture content is possible. The data are shown in Figure 1. A total mass loss of 2.9% was observed over the range that volatile species were detected by the mass spectrometer. Calibration of the ion current signals is approximate, but the best estimates are that the total mass loss can be broken down into 1.5% H₂O, 1.0% CO₂, and 0.4% NO_x. The total mass loss exceeds earlier LOI measurements by about 0.6 wt %. This excess could be due to additional moisture uptake during handling of the TGA-MS sample.

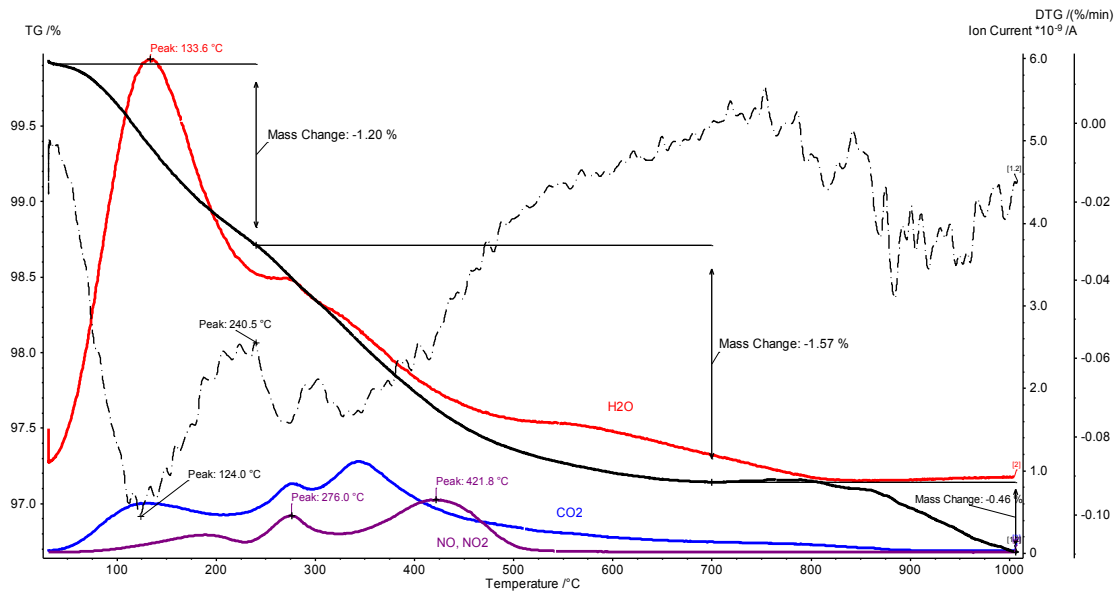


Figure 1: TGA-MS data on sample of MISSTD-1A material prior to start of small-scale test loading. In addition to the fractional mass change with temperature (left axis), the graph also shows the time derivative of the mass change, and mass spectrometer ion currents for the parent ions of H₂O, CO₂ and NO released into the gas phase.

Gas generation results

MISSTD-1 Full-scale Test

The results of the radiographic measurements of the pressure-indicating bellows in the full-scale test are shown in Figure 2.

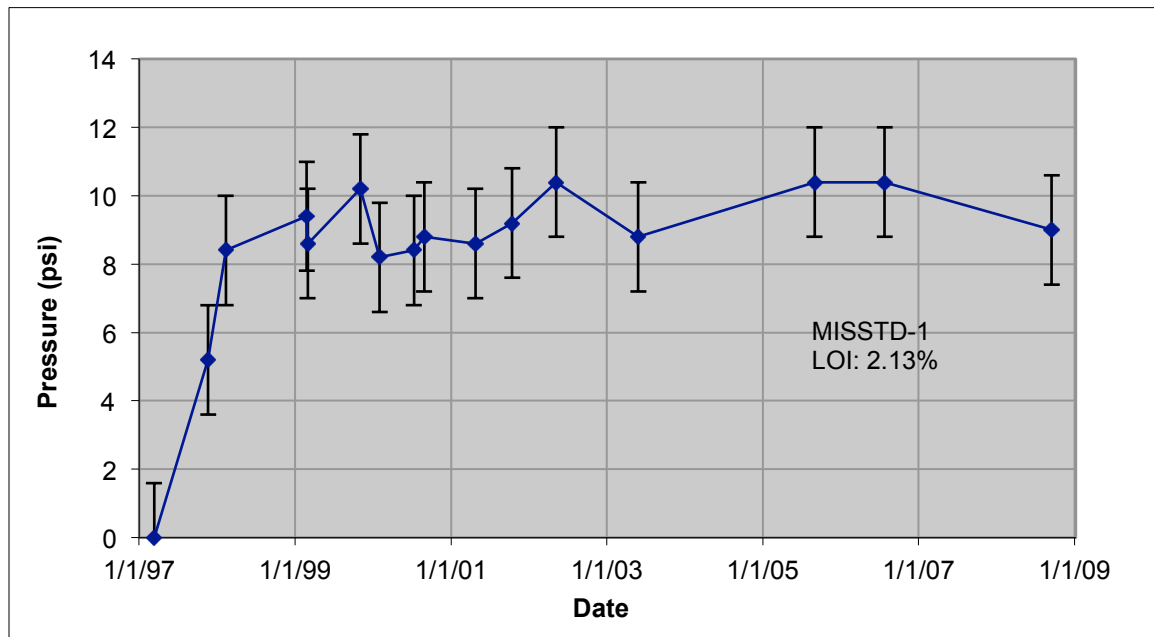


Figure 2: Internal pressure change from the initial value at closure (internal psig) of container with MISSTD-1 as determined from radiographic measurement of internal sealed bellows.

The pressure measurements show a pressure increase of 60 kPa (9 psi) over the first year, and no changes within the uncertainty of the measurement for the subsequent 10 years.

The gas inside the container was sampled in 2010 just prior to opening it for destructive examination. The gas analysis results are shown in Table 1. The dominant net change in the gas over the 13 years of storage was a net increase of 77 kPa in N₂ gas, which was consistent with the net pressure increase over the test. No H₂ or O₂ was observed above the detection limit. Carbon dioxide was only a trace constituent in the gas phase.

Immediately after opening the container the relative humidity inside was measured and found to be less than 1%. Then a sample of the oxide was collected and stored in a sealed sample vial until it could be analyzed by TGA-MS. The results are shown in Figure 3. A total mass loss of 2.28% was observed between ambient temperature and 1000 °C, which is consistent with the LOI measurement on a sample of material taken before the test began. The mass spectrometer data indicate that CO₂ and H₂O were the major volatiles, producing m/e=44 and m/e=18 ion currents, respectively, of roughly equal intensity and over nearly coincident broad temperature ranges. Smaller amounts of nitrogen oxides were also volatilized as evidenced by the m/e=30 trace. Comparison of the m/e=18 integrated area against that from calibration samples yields an estimated moisture content of 1.1 wt %. An alternative analysis of these data involving deconvolution of the mass loss rate into components that correlate with the mass spectrometer traces suggests 1.5 wt % CO₂ and a smaller amount of H₂O, estimated at 0.6 wt %. The broad conclusion with regard to storage is that despite exceeding the 3013 Standard requirement for H₂O in the sample and despite the relatively high total carbon and adsorbed CO₂, there was no detectable net generation of H₂ or O₂, and the CO₂ was very low.

Table 1: Gas composition over MISSTD-1 after 13 years in 3013-scale container

	Fraction	Pressure (kPa)
CO ₂	0.01%	0.02
N ₂ O	0.58%	0.91
He	49.91%	78.15
H ₂	0.01%	0.02
O ₂	0.01%	0.02
N ₂	49.48%	77.49
CH ₄	0.00%	0.00%
CO	0.00%	0.00%

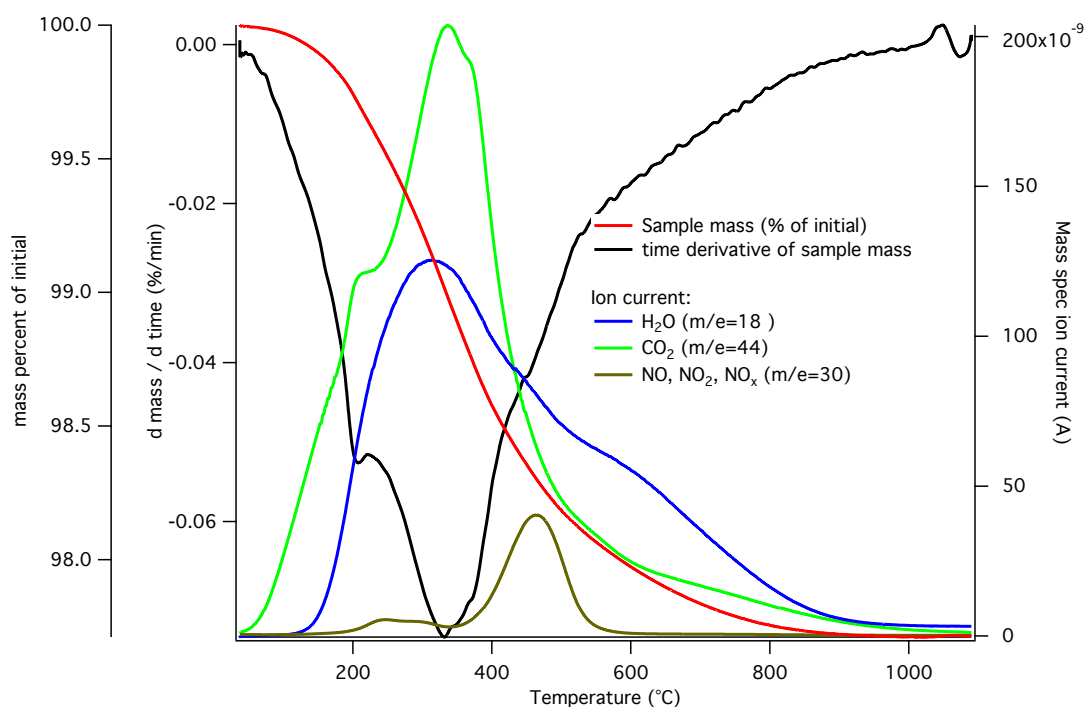


Figure 3: Thermogravimetric analysis with mass spectrometer signals for H₂O, CO₂ and nitrogen oxides obtained from a sample of MISSTD-1 after removal from full-scale test container. The red and black traces are the mass loss and the derivative of the mass loss with respect to temperature.

MISSTD-1A Small-scale Tests

Material from the 1997 blend batch was also included in two small-scale shelf-life tests, one initiated in August 2005, and one in June 2008. In both cases 10 grams of the material was placed into a shallow round crucible of approximately 5 cm diameter and heated to 200 °C for two hours, and upon cooling it was weighed and found to have lost approximately 0.5% of its initial mass. It was then exposed to water vapor within the enclosure of an analytical balance until it increased 0.5% in mass. Bed depth during this exposure was no more than a few millimeters. The process of 200 °C drying followed by exposure to water vapor was performed three times on the same material as it became necessary to re-initialize the gas generation experiment to correct experimental problems. Each time the sample gained 0.5% mass in approximately 15 minutes. The mass gain data during exposure for the third of the three exposures to water vapor are shown in Figure 4. The peak mass gain rate was 3.0% per hour, and the average was 2% per hour. The relative humidity was measured by a probe inside the enclosure and is only approximate because the system did not reach a steady state during the 15 minute exposure. The rate of mass gain was not noticeably faster above 10% RH than it was at 5% RH.

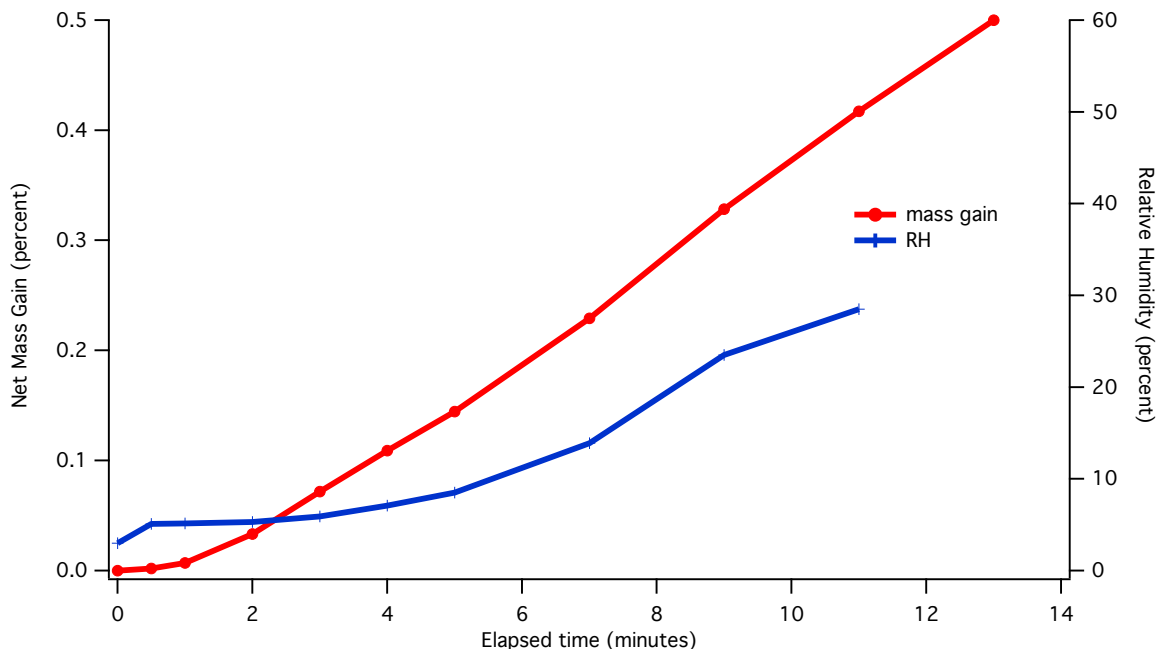


Figure 4: Mass gain as a fraction of initial mass for a 10 gram sample of MISSTD-1A during exposure to humidified helium prior to loading in a sealed test vessel for a small-scale gas generation test. The relative humidity measured by a probe suspended near the sample is also plotted. Prior to this exposure to water vapor, the sample was partially dried by heating to 200 °C for two hours.

After adsorption of water vapor, the material was quickly transferred to a test vessel of 1:500 of 3013 scale and sealed. The vessel was placed in a heated well in a test array and kept at 55 °C for the duration of the test. Pressure was monitored continuously, and gas samples were periodically withdrawn for analysis by gas chromatography.

The 2005 test showed a pressure rise of 10 kPa over the first two months. Gas samples showed ingrowth of O₂, N₂ and H₂. Decreasing total pressure and He partial pressure were taken as indications of a leaking vessel after the first two months and the test was eventually terminated. The data are useful for qualitative confirmation of the observations from the second test.

Data from the second test, initiated in 2008, are shown in Figure 5. Again the most significant change in overall pressure occurred in the first two to three months of the test. The gas chromatography data show that the pressure change correlated with a relatively rapid initial ingrowth of O₂, and somewhat lesser amounts of N₂ and H₂. As the test has progressed for more than three additional years, the O₂ and H₂ partial pressures have slowly decreased from their peak values, with O₂ currently at 20% of its peak and H₂ at 45% of its peak. The partial pressure of N₂ has continued to increase, though at a slower rate than in the initial two months. If these trends continue, the gas inside this test vessel may eventually resemble what was observed after 13 years in the full-scale test: the initial He charge, accompanied by a nearly equal amount of N₂ and only trace amounts of other gases including CO₂.

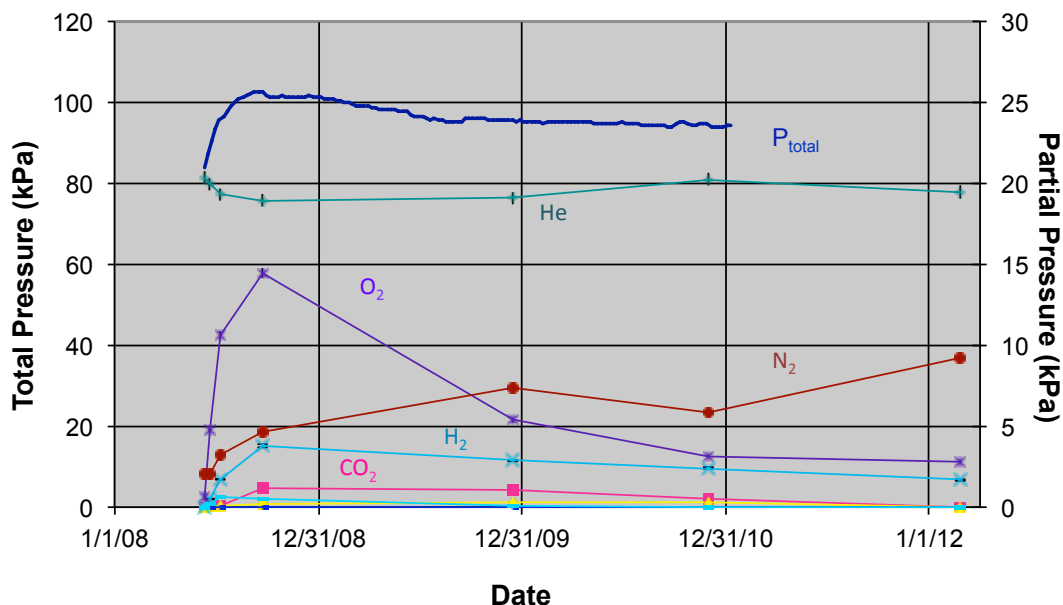


Figure 5: Pressure and gas composition inside the small-scale test container loaded in 2008.

Summary and relevance

Adsorbed species

The measured moisture in the sample collected after termination of the full-scale test and in the sample collected prior to the small-scale test suggests that both had surface H_2O coverages exceeding 1.5 monolayer equivalents and as high as 3 monolayer equivalents if one assumes a specific surface area of $20 \text{ m}^2/\text{g}$ of PuO_2 and a monolayer mass of $0.22 \text{ mg}/\text{m}^2$.

In addition to H_2O , the TGA-MS data from both the full-scale and small-scale samples clearly show the presence of oxides of both carbon and nitrogen, observed in the gas phase as CO_2 and NO . The TGA-MS was not calibrated for quantification of these gases, but the mass changes coincident with their MS detection suggest desorbed masses similar to that of H_2O , on the order of 1 wt % total.

The TGA-MS data indicate that the chemical forms of the adsorbates differed between the full-scale and small-scale samples. The sample prior to the small-scale test showed relatively more H_2O desorbed at low temperature, perhaps indicating recent adsorption from exposure to ambient atmosphere during handling, and overall a greater amount of H_2O relative to CO_2 and NO_x . The sample collected after the full-scale test, in contrast, showed a relatively larger amount of CO_2 and more tightly bound forms of all of the adsorbates, particularly H_2O .

Gas generation

The small-scale tests using MISSTD-1 material show that while it is possible to generate both H₂ and O₂ when oxide with high surface area is allowed to substantially exceed 0.5 wt % moisture, the combination of H₂ and O₂ only approached flammable levels for a period of a few months during the first year, and never approached a level of concern for affecting container integrity. Furthermore, the H₂ and O₂ are not persistent in the container. They have been declining back towards zero in the ensuing 3.5 years. The other persistent long-term trend has been a slow increase in the N₂ partial pressure. The levels and rates of increase of N₂ are not of concern for storage.

In the full-scale test a net ingrowth of N₂ was the only significant change from the initial He gas charge. The data do not rule out the possibility that the full-scale test experienced an initial transient ingrowth of O₂ and H₂, which then disappeared over the subsequent 12 years as in the small-scale test. These results support the expectation that oxide of high surface area with 0.5 wt % moisture will not produce either excessive pressures or persistent reactive gases in the long term.

Neither the full-scale nor the small-scale test showed significant CO₂ or other carbon species in the gas phase, despite the presence of 0.3 wt % carbon in the solid phase and the TGA-MS evidence of thermal desorption/decomposition of 1% or more of the material mass as CO₂. These results suggest that a low-temperature stabilization process for oxalate need not be accompanied by an additional requirement for post-stabilization carbon analysis specifically to preclude CO₂ pressurization. The appearance of nitrogen in the gas phase may be due to slow reduction of nitrate or other NO_x species that were incorporated into the MISSTD-1 material during the several years between its last calcination and the initiation of the tests. Nitrogen levels observed are far below what could be deemed a pressurization concern. Furthermore, preventing long-term air exposure between stabilization and packaging should limit the formation of precursor species forming on the oxide surface, and result in lower N₂ levels.

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