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Gas Generation Testing of Neptunium Oxide Generated Using the HB-Line Phase II Flowsheet

by

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**Gas Generation Testing of Neptunium Oxide
Generated Using the HB-Line Phase II Flowsheet**

R. R. Livingston and J. M. Duffey

August 2003

**Westinghouse Savannah River Company
Savannah River Site
Aiken, SC 29808**

Prepared for the U. S. Department of Energy under contract DE-AC09-96SR18500

Gas Generation Testing of Neptunium Oxide

Generated Using the HB-Line Phase II Flowsheet

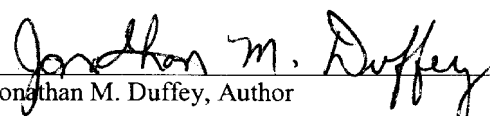
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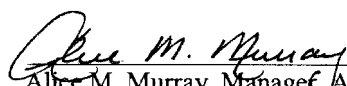
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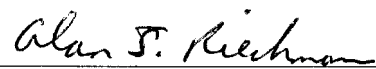
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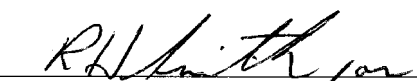
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Gas Generation Testing of Neptunium Oxide

Generated Using the HB-Line Phase II Flowsheet

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Summary

The hydrogen (H_2) gas generation rate for neptunium dioxide (NpO_2) samples produced on a laboratory scale using the HB-Line Phase II flowsheet has been measured following exposure to 75% relative humidity (RH). As expected, the observed H_2 generation rates for these samples increase with increasing moisture content. A maximum H_2 generation rate of 1.8×10^{-6} moles per day per kilogram ($\text{mol} \cdot \text{day}^{-1} \text{ kg}^{-1}$) was observed for NpO_2 samples with approximately one and one-half times ($1\frac{1}{2} \times$) the expected specific surface area (SSA) for the HB-Line Phase II product. The SSA of NpO_2 samples calcined at 650 °C is similar to plutonium dioxide (PuO_2) calcined at 950 °C according to the Department of Energy (DOE) standard for packaging and storage of PuO_2 .¹ This low SSA of the HB-Line Phase II product limits moisture uptake to less than 0.2 weight percent (wt %) even with extended exposure to 75% RH.

Background

Transportation and storage of radioactive materials require extensive understanding of the nuclear material contents to support development of safety analysis reports. One of the key requirements for safe transportation and storage of nuclear materials is demonstrating that the container or transportation package is sufficiently robust to prevent release of the contents under normal and accident conditions. Because radioactive materials are known to generate H_2 gas from radiolysis of water or other hydrogenous materials, the contents of a sealed container must be prepared and packaged in a manner to prevent over pressurization.

The potential for nuclear materials to generate excessive pressure during transportation and storage has long been recognized as a significant safety hazard.^{2,3,4} Recent efforts to control the moisture content of nuclear materials packaged for extended storage are described in the DOE-STD-3013-2000, "Stabilization, Packaging, and Storage of

Plutonium-Bearing Materials,” and the DOE-STD-3028-2000, “Criteria for Packaging and Storing Uranium-233-Bearing Materials.” These standards require the nuclear material to be processed in a manner that precludes over pressurization of the storage container. Measured gas generation rates for oxides tested following stabilization and packaging in the prescribed manner demonstrate the effectiveness of these process conditions.^{5,6}

The DOE-STD-3013-2000 requires that PuO_2 bearing materials be processed at a minimum of 950 °C for two hours. This thermal treatment is designed to remove moisture and reduce the SSA of materials to less than $5 \text{ m}^2 \text{ g}^{-1}$ to limit subsequent adsorption of moisture.⁷ The SSA of an oxide affects the rate and quantity of moisture adsorbed, and SSA is a function of both material origin and calcination temperature.^{8,9,10} Recent efforts by Paffett et al. demonstrate that PuO_2 has similar moisture uptake behavior to that of most other metal oxides.¹¹ NpO_2 is expected to show similar moisture uptake characteristics to PuO_2 , and production controls developed to limit moisture adsorption will benefit from the extensive efforts to characterize moisture uptake by PuO_2 .¹²

Gas generation rates for radiolysis of moisture sorbed on oxide surfaces increase with the moisture content.^{13,14, 15} Gas generation rates of radioactive materials are typically measured by placing a sample in a sealed container and measuring changes in headspace gas composition and pressure with time.^{16,17,18} In many cases, the headspace gas content is known when sealing the container and is typically air, helium or argon depending on the process atmosphere. The headspace gas is then sampled at a later date to determine changes in the gas composition as a function of time. In sealed systems, H_2 and other radiolytic products of water build up to a steady state concentration at which the back reaction of these products to reform water is equal to the rate of their production from water.^{19, 20, 21, 22} Because the net H_2 generation rate decreases as the system approaches steady state, a H_2 generation rate measured at low H_2 pressures may be extrapolated to provide a conservative over-estimate of container H_2 pressure over an extended time frame.

To support the preparation of transportation safety documentation for shipping NpO_2 produced in the HB-Line Phase II facility, about 100 g of NpO_2 were produced in Savannah River Technology Center (SRTC) laboratories for use in gas generation testing.²³ This NpO_2 was produced from the same feed solution source (H-Canyon tank 8.5) to be processed in HB-Line, and the HB-Line flowsheet conditions were maintained as closely as possible given the difference in process scale. The SRTC effort required two anion exchange column runs using a 2¼-inch inner diameter (ID) column containing approximately 1 L of Reillex HPQ resin to concentrate the tank 8.5 solution to approximately 40 g L^{-1} prior to precipitation as neptunium(IV) oxalate, $\text{Np}(\text{C}_2\text{O}_4)_2$. Four separate precipitation batches were produced at 45 to 55 °C by adding oxalic acid to the $\text{Np}(\text{IV})$ anion column product at a controlled rate over 30 to 45 minutes (min). Each batch of $\text{Np}(\text{C}_2\text{O}_4)_2$ was calcined individually and yielded about 22 to 25 g of NpO_2 .

To represent the potential variation in HB-Line furnace operation, two batches of $\text{Np}(\text{C}_2\text{O}_4)_2$ were calcined at 600 °C for two hours and two batches were calcined at 650 °C for 2 hours (h). One of the batches of 600 °C product (600C-2) was not used in gas generation testing due to the inadvertent inclusion of a Teflon coated stir bar in the $\text{Np}(\text{C}_2\text{O}_4)_2$ during calcination.

The NpO_2 product was analyzed to determine lattice parameters, morphologies, densities, particle sizes, specific surface areas, major impurities and moisture contents.²⁴ The lattice parameters provided by X-ray diffraction analysis indicate the calcination product is NpO_2 , and no major impurities are present. The morphology of the oxide product was determined using a contained scanning electron microscope (CSEM) and appears similar to PuO_2 produced under similar conditions.⁸ X-ray fluorescence measurements using the energy dispersive spectrometry capability of the CSEM indicate no major impurities in the NpO_2 product. Bulk and tap densities were estimated to determine volumes required for shipping the desired mass. Particle size measurements were made to support selection of process equipment. The particle size distribution for the representative HB-Line product is also similar to PuO_2 produced under similar conditions.⁸

The SSA of the NpO_2 produced at 600 °C is $5.4 \text{ m}^2 \text{ g}^{-1}$ and decreases to $3.7 \text{ m}^2 \text{ g}^{-1}$ at 650 °C. As part of this characterization effort, moisture uptake by the various NpO_2 samples was evaluated at 75% RH to represent the upper humidity limit anticipated for production of NpO_2 in HB-Line. The moisture uptake for these samples was difficult to measure with great confidence by either mass change or thermogravimetric analyzer with mass spectrometer detection (TGA-MS) due to the small quantity of moisture adsorbed. Based on TGA-MS results, samples gained less than 0.04 wt % water during exposure to the 75% RH and contained less than 0.15 wt % water following exposure. The NpO_2 calcined at 600 °C has a SSA about 50% greater than NpO_2 calcined at 650 °C and has about 50% more moisture following exposure to 75% RH.

Experimental

Scope

The scope of these experiments includes two sets of tests designed to measure the H_2 generation rate of NpO_2 samples representing HB-Line Phase II product. Each set of tests included four samples of NpO_2 . The test conditions were varied in an attempt to determine the maximum rate of H_2 generation that may be anticipated during transportation of the HB-Line Phase-II product. Each set of tests included two samples calcined at 600 °C and two samples calcined at 650 °C as indicated in Table 1. Both 600 °C samples were taken from a single oxalate precipitation and calcination batch (600-1A & 600-1B), which limits the mass of each sample to approximately 10 g of NpO_2 . The 650 °C NpO_2 samples were from two different oxalate precipitation and calcination batches (650-1 & 650-2) so the sample masses used in these tests were increased to approximately 20 g. Table 1 provides calcination temperature, sample mass, and test conditions used for each sample.

Apparatus

The apparatus used in these experiments is similar to systems used at Los Alamos National Laboratory and Oak Ridge National Laboratory to measure gas generation rates in radioactive materials.^{5,6} Each system has several common components including a stainless steel sample container, pressure transducer, thermocouple, and gas sampling mechanism. The basic function of this apparatus is to contain the sample in a leak-tight environment and monitor pressure and temperature changes during the test period. At the conclusion of each test, the headspace gases are sampled for analysis of gas composition, and the change in gas composition, over the test duration, is used to compute the gas generation rate.

Table 1. Conditions for Tests to Measure H₂ Generation Rate of NpO₂.

Test	Sample Label	Calcination Temperature (°C)	Sample Mass (g)	Exposed to 75% RH (Yes/No)	Fill Gas
1	600C-1A	600	9.845	No	Argon
1	600C-1B	600	9.649	Yes	Argon
1	650C-1	650	20.029	Yes	Argon
1	650C-2	650	19.499	No	Argon
2	600C-1A	600	9.845	Yes	Air
2	600C-1B	600	9.649	Yes	Air
2	650C-1	650	20.029	Yes	Air
2	650C-2	650	19.499	Yes	Air

Sample Containers

The sample containers used in this set of experiments have been upgraded from the container designs used in previous gas generation tests at SRTC. The current design is machined from 304 stainless steel and uses a 2.125-inch Conflat flange closure. This closure allows easier addition and removal of samples than earlier designs. The inside diameter (ID) of this vessel is sized to accept a stainless steel insert. The insert is fabricated with various cavity sizes needed to implement particular test requirements such as minimizing the void volume or selecting a sample fill height. Two different inserts were used in these tests. The smaller cavity is 0.375 inches in diameter and 2.75 inches deep with a volume of approximately 5 cm³, and the larger cavity is 0.530 inches in diameter and 2.75 inches deep with a volume of approximately 10 cm³.

All sample container components were cleaned using a fluorocarbon solvent to remove oil and grease to a level below 50 mg of hydrocarbon per square foot.²⁵ The components were subsequently heated in a vacuum oven at 200 °C to assure that all solvent had been removed from the vessel components.

The vessel lid contains an Omega type J thermocouple (TC) with 0.062-inch diameter 304 stainless steel sheath that is mounted so that the TC junction is centered approximately in the NpO_2 sample. To support gas sampling and analysis, a pair of Valco high-pressure on/off valves is incorporated on the vessel lid and interconnected with a known volume sample loop.^a This pair of sample valves is connected to the vessel lid by a small diameter (0.010-inch ID) tube. This tube is connected to the vessel lid using a Valco fitting with an integral 2 micron sintered metal frit to minimize transfer of the radioactive material during sampling. A second filtered connection is provided to allow connection of a pressure transducer to the vessel lid using a second small diameter tube. All Valco fittings used in these vessels and adjoining connections are 300 series stainless steel. Figure 1 is a photograph of the vessel components.

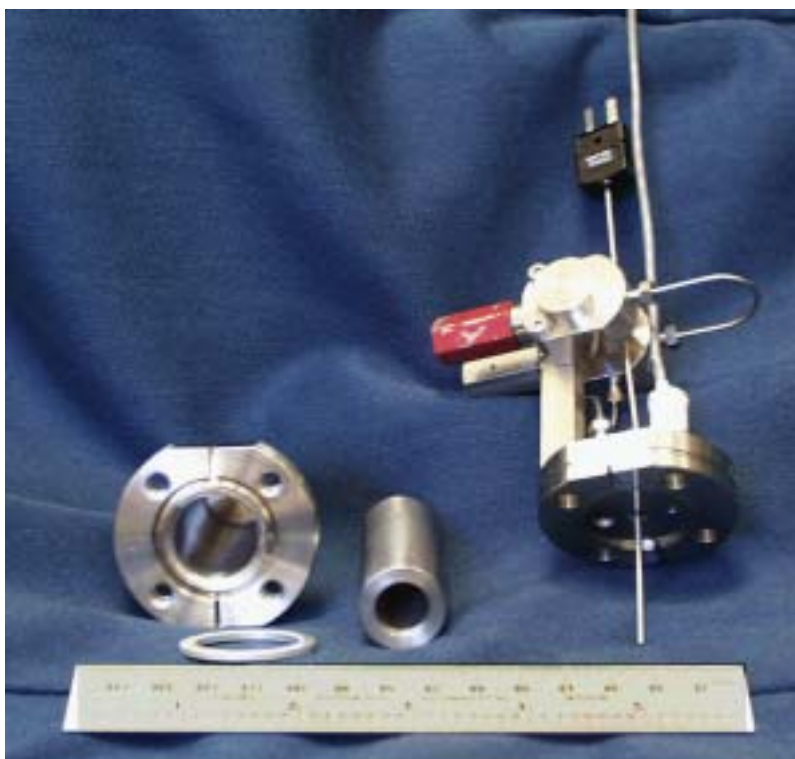


Figure 1. Test vessel components used for NpO_2 gas generation experiments.

Pressure Sensors

The pressure sensors used in the NpO_2 testing are Paroscientific Digiquartz model 6000. These pressure transducers have about 1 cm^3 internal volume and a high accuracy of $\pm 0.01\%$ full scale or approximately ± 0.5 Torr. The model 6000 sensors are temperature compensated over a wide range. Figure 2 shows the calibration verification of the four

^a Real-time sampling and analysis is proposed for future tests so that headspace gas measurements can be made without terminating the test. The gas sample loop provides no real advantage in the current set of experiments; however, the development of this vessel design was completed and components were available for use in these experiments. Volume of the sample loop is selected based on anticipated container pressure and the required volume for analysis by gas chromatograph (GC)

model 6000 sensors performance against a National Institutes of Standards and Technology (NIST) traceable pressure standard.

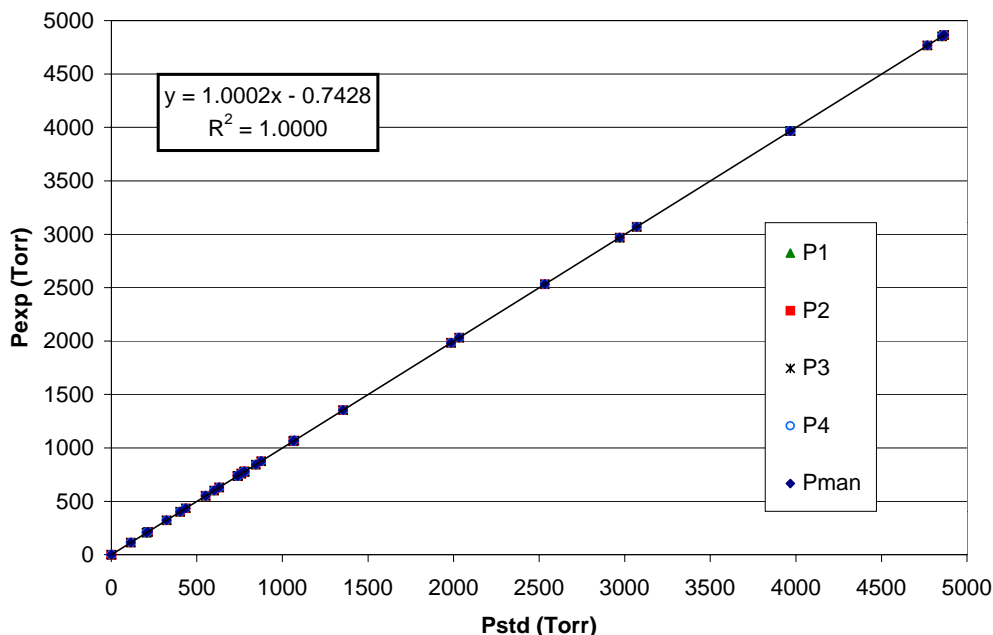


Figure 2. Calibration verification for four Digiquartz pressure sensors.

Helium Leak Testing

Prior to installation in a radioactive containment unit (i.e., glovebox), all components of the gas generation test apparatus were helium leak tested. The vessel bottom and lid were assembled using a silver plated copper gasket identical to the gaskets used when testing nuclear materials. This connection can only be helium leak tested during the initial production of vessels, and then must be maintained by careful handling of the vessel components to prevent damage to the sealing surfaces. All vessels were assembled and leak tested using helium (He) pressure in excess of 100 psig where possible. The design of such vessels incorporating an external pressure transducer required that the connection between the pressure transducer and test vessel be tested using a “hood test” instead of the normal “bell jar test.” The bell jar test is more sensitive to small leaks; however, either test is an excellent measure of leak rate given the low pressures used in NpO_2 gas generation tests.

Helium leak rate measurements demonstrate the apparatus components are properly assembled and have leak rates less than $1 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$. Leak rates for components following installation in the glovebox are done using a “rate of rise” method that requires the container to be evacuated to a low pressure. This method measures the rate of pressure rise in an evacuated system to calculate the leak rate. This type of measurement is less sensitive than a helium leak test and is only for components that are expected to hold gas samples for a short duration.

Sampling Manifold

The outlet on each pair of sample valves is connected to a small manifold to support gas sampling at the end of each test. This small manifold is comprised of Valco fittings and small bore tubing and provides a connection for four sample vessels to the external manifold via a filtered stainless steel line. A diagram of the sampling manifold arrangement is shown in Figure 3. The filters used in the connection to the external manifold are manufactured by Mott Metallurgical from sintered nickel frit. These filters are rated to provide filtration capable of removing 99.99999% of particles down to 0.003 microns at flows up to one standard liter per minute. Two filters are used in this application with one located inside the glovebox to remove most of the particles and a second located outside the glovebox to provide redundant protection.

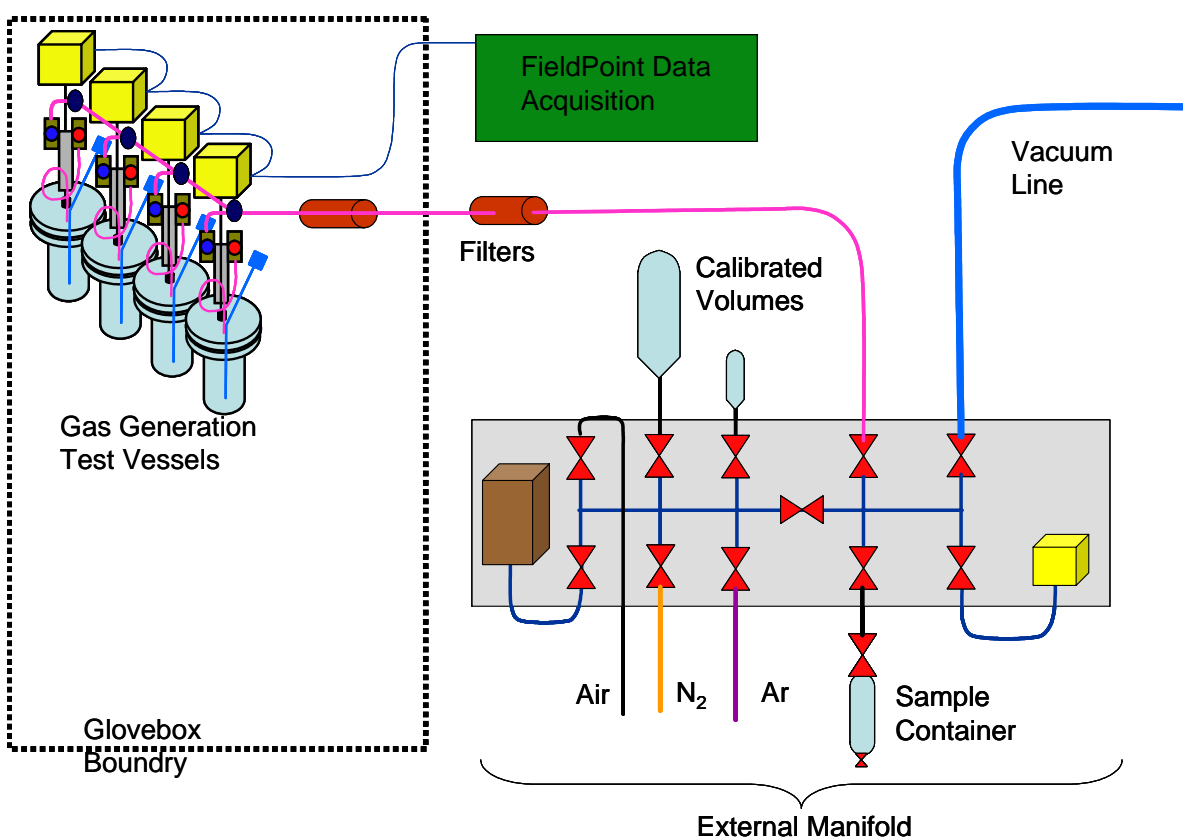


Figure 3. Sample manifold diagram.

The external manifold is connected to a Alcatel Drytel Model 1024 molecular drag pump to provide oil free vacuum down to 1×10^{-6} Torr. The external manifold is used to hook-up small sample containers to collect and transfer a gas samples for analysis by micro-gas chromatograph (micro-GC) for H_2 , oxygen (O_2) and nitrogen (N_2) in the headspace gas collected from test vessels. The external manifold also offers the services required to evacuate and backfill the headspace gases of sample vessels prior to starting a gas generation test. Photos of the various gas generation test components and test equipment are provided in Figures 11 through 17 in Attachment 1.

Data Acquisition

The temperature and pressure sensors installed in each test vessel are connected to a laboratory computer (Dell model Optiplex 260) using National Instruments Field Point modules and RS485 serial communications. The temperature and pressure measurements for each vessel are presented in graphical form and stored in data files using National Instruments LabView software codes developed by SRTC. This code has been validated by inputting known signals and observing recorded results under the various operating modes. Pressure and temperature measurements for manifold pressure and ambient glovebox air temperature are also recorded. The data storage intervals are adjustable but typically set at one data point every 5 to 30 seconds during test set-up and increased to one data point every 300 seconds during extended test periods. The data are stored in a format compatible with Microsoft Excel, which is used for data reduction and subsequent calculations.

Test Protocol

Both sets of gas generation experiments followed a similar protocol that included the following steps:

1. Exposing samples to 75% RH
2. Analyzing samples for moisture
3. Loading test vessels with samples
4. Monitoring pressure and temperature during test
5. Measuring concentration of headspace gases
6. Calculating rates of gas generation

Each step of the test protocol is described individually in the following paragraphs.

Results

Exposing Samples to 75% RH

Details of the moisture uptake efforts are provided in a separate report that describes characterization of the NpO_2 samples.²⁴ Samples were exposed to 75% RH using a saturated NaCl solution based on an ASTM “Standard Practice for Maintaining Constant Relative Humidity by Means of Aqueous Solutions.”²⁶

Test 1

The first set of samples was placed in a small plastic desiccator vessel with the saturated NaCl solution placed in the desiccator below the sample shelf. The NpO_2 samples were contained in small quartz dishes that allowed a thin layer of NpO_2 powder to be exposed to the elevated humidity condition. These samples were allowed to remain in the humid environment for several days with sample weights checked periodically.

In the first set of tests, samples 600C-1B and 650C-1 were exposed to 75% RH and samples 600C-1A and 650C-2 were stored dry in screw-capped glass vials until all four samples were loaded into test vessels.

Test 2

The second set of samples was exposed to 75% RH using a two container apparatus that circulated humidified air from the saturated NaCl solution around the NpO_2 samples. All the samples in this test were exposed to elevated humidity prior to loading in the test vessels. This two container apparatus effectively addressed concerns identified using the single container approach. These concerns included (1) the time required to equilibrate RH in the desiccator following weight measurements, (2) the potential for NaCl solution to contact the sample containers, and (3) the difficulty associated with sealing the small plastic desiccator.

Analyzing Samples for Moisture

About 500 mg of NpO_2 from each sample were analyzed by TGA-MS to evaluate moisture content. Even with the excellent sensitivity offered by TGA-MS, it was difficult to discern differences in the moisture content between samples before and after exposure to elevated humidity conditions.

The analyzed moisture content of these samples did not mirror weight gains observed during storage at 75% RH, and moisture levels determined by MS accounted for only about 30% of the total mass loss observed during TGA operation. The TGA-MS analysis heats a sample to 1000 °C at 20 °C per minute and holds at 1000 °C for one hour. The total weight lost following this protocol is called loss on ignition (LOI).

Although most water appears to desorb from NpO_2 samples at less than about 300 °C, there is some overlap with evolution of other gases (i.e., NO, CO₂, N₂O, NO₂). At this time, good mass balance in TGA-MS operation has yet to be demonstrated. TGA-MS data for test series 1 and 2 are provided in Table 2.

Table 2. TGA-MS Measurement Results for Gas Generation Test Samples.

Test	Sample Label	Exposed to 75% RH (Yes/No)	Total Mass Loss (wt %)	H ₂ O Loss (wt %)	SSA (m ² /g)
1	600C-1A	No	0.304	0.092	5.34
1	600C-1B	Yes	0.290	0.130	5.34
1	650C-1	Yes	0.198	0.091	3.68
1	650C-2	No	0.204	0.077	3.67
2	600C-1A	Yes	0.323	0.130	5.34
2	600C-1B	Yes	0.350	0.140	5.34
2	650C-1	Yes	0.207	0.110	3.68
2	650C-2	Yes	0.213	0.071	3.67

Test 1

The TGA-MS samples were collected during the vessel loading operation following about five days exposure to elevated humidity. Each sample was stored in a small glass vial until analyzed about eight weeks later. Sample analysis was delayed due to the extended installation and set-up time required for TGA-MS in the glovebox containment.

Test 2

The TGA-MS samples were collected from the top of each test vessel insert after about 17-19 days of exposure to 75% RH. Samples were weighed directly into the TGA crucible and analyzed one at a time to limit any errors associated with storing samples. Consequently, samples were analyzed very shortly after being removed from the humid environment. The vessel inserts were returned to the 75% RH environment until day 20 when samples were loaded into test vessels.

Loading Samples

The gas generation test vessels were designed to accept stainless steel inserts to allow for simplified loading and unloading of test materials. The inserts were cleaned as described for other test vessel components. Each vessel was inscribed with a sample designation to prevent misidentification during moisture loading for Test 2. The initial “insert mass” and subsequent changes in the “insert + sample mass” were used to determine the amount of NpO_2 used in given experiment. Two different sized inserts were used based on the available NpO_2 mass. With cavity volumes of 5 and 10 cm^3 , the inserts easily accepted the desired mass of sample given the previously measured bulk density of about 1.9 g cm^{-3} and tap density of 2.5 g cm^{-3} . The actual sample masses for all samples are provided in Table 1.

Test 1

Samples were loaded by pouring the contents of the quartz dish or sample bottle into the stainless steel inserts using a special funnel designed for this purpose. Inserts were filled one at a time to within about 2-5 mm of the insert top and carefully lowered into the test vessel bottom to prevent spilling or contamination of the sample insert. Each vessel top was then installed using a silver-plated copper gasket. Note that vessel top and bottom sections were kept together as mates following the helium leak test performed prior to vessel use for gas generation testing. Once sealed, the test vessel was positioned in a specially designed rack that includes the pressure transducers and small manifold used in gas sampling. Each pressure transducer was connected as a vessel was put into the test rack prior to proceeding to load the next sample. Figure 4 shows a picture of the assembled test apparatus.



Figure 4. Photograph of test vessels loaded with NpO_2 .

Test conditions for the first set of samples required inerting the headspace gas with argon – as proposed for packaging NpO_2 in HB-Line. This gas exchange system hooked to the sample loop outlet and was alternately pressurized with argon to about 4900 Torr and evacuated to about 100 Torr. Pressure transducers and thermocouples were connected to the data acquisition system prior to initiating the inerting protocol. Figure 5 shows the pressure cycles used for inerting all four of the sample vessels in test one. The low pressure used in this effort was limited in an attempt to minimize the moisture removed from these samples during the inerting process. By following this procedure it was estimated that less than 0.01% air would remain in the test vessel. This estimate was based on an assumption that when argon was added to the test vessel, the argon mixed rapidly with the gas content of the test vessel.

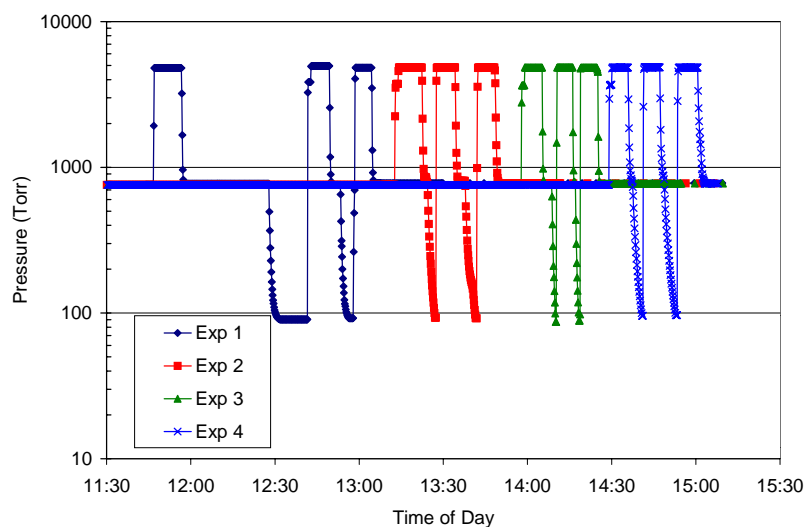


Figure 5. Pressure plot for inerting test vessels.

The volume of each test vessel was calculated during the inerting protocol using pressure and volume calculations at constant temperature. The gas volume in sample lines up to the test vessel were measured by successive expansion of argon gas from small gas cylinders calibrated by the SRTC Standards Laboratory and pressures measured on the external manifold. The volume of each test vessel is provided in Table 3. Error estimates on these volumes suggest an accuracy of $\pm 0.05 \text{ cm}^3$

Table 3. Sample Masses and Test Vessel Volumes.

Test	Sample Label	Sample Mass (g)	Test Vessel Volume (cm^3)
1	600C-1A	9.845	7.27
1	600C-1B	9.649	7.37
1	650C-1	20.029	11.47
1	650C-2	19.499	11.55
2	600C-1A	9.845	7.27
2	600C-1B	9.649	7.37
2	650C-1	20.029	11.47
2	650C-2	19.499	11.55

Following the inerting protocol, the sample vessels were connected to the sample rack gas manifold and data files were initiated to log pressure and temperature for the duration of each experiment.

Test 2

In the second set of tests, samples were exposed to the 75% RH environment in the stainless steel inserts. (Note: In test series 1, the samples were exposed to 75% RH in a small quartz dish.) These samples were weighed then reinstalled into the test vessels as described for test series 1. In this second set of tests, the experiments were conducted in air, so two sets of replicate measurements at elevated moisture content are provided.

Monitoring Pressures and Temperatures during Test

A Paroscientific Digiquartz pressure transducer was used to monitor the pressure changes in each test vessel. The 0.01% accuracy of this sensor provides pressure measurements that are within 0.5 Torr of actual pressure. The Digiquartz sensor electronics have little sensitivity to fluctuations in ambient temperature; however, the pressure in a sealed volume will show significant fluctuations in measured pressure unless corrected for changes in gas temperature.^b The temperature of each test vessel was measured using a type J thermocouples located in the NpO₂ sample. The temperature measurements were used to provide temperature corrected pressure graphs for each sample vessel. Data files are stored on the laboratory computer by the LabView software.

Data presented on the temperature corrected pressure of sample vessels are noisy. The frequent small pressure variations result from inadequately temperature correcting pressure for daily changes in ambient glovebox temperature. However if no attempt was made to correct vessel pressure to a constant temperature, the uncorrected pressure data fluctuate dramatically over the course of an experiment and make visual interpretation of pressure changes nearly impossible. Figure 6 demonstrates the effect of glovebox temperature variation on the measured pressure and the necessity of using temperature corrected pressure data for interpretation of gas generation experiments. Note that when vessel pressure does not correlate with temperature swings in the ambient air temperature, then this behavior is a sure indicator that the vessel is leaking.

^bA test vessel sealed at 760 Torr (atmospheric pressure) and 20°C will increase in pressure by about 2 percent to 772 Torr when heated to 25°C. The gas generation rate for a PuO₂ with similar moisture content as the NpO₂ samples in these tests is about 3.4×10^{-6} mol day⁻¹ kg⁻¹ (see reference 15). Consequently, a 60 day experiment with 10 g of PuO₂ in a 10 cm³ volume at constant temperature of 20°C would produce at most a 3.7 Torr increase in H₂ pressure. This pressure rise is less than the 12 Torr pressure rise expected from a 5°C temperature increase.

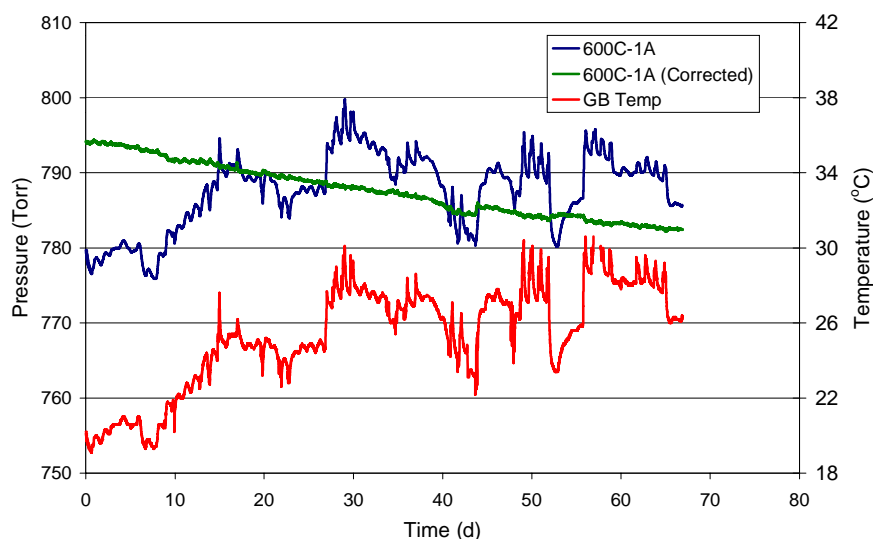


Figure 6. Effect of temperature correction on pressure measurements.

Test 1

Test 1 was run for 67 days. The temperature corrected pressure data for this set of experiments are shown in Figure 7. The samples were started at slightly greater than ambient pressure (about 750 Torr). Container pressures were observed to decrease gradually over the course of the test duration except for sample 650C-1, which had a very slow rise in pressure.

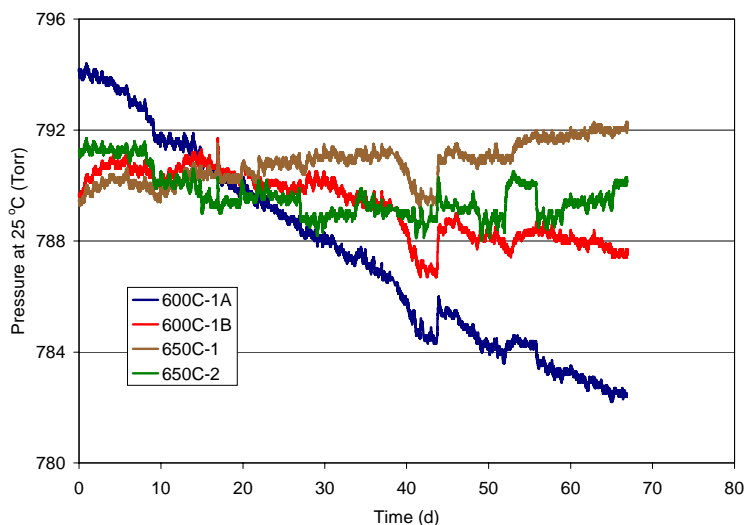


Figure 7. Temperature corrected pressure for test 1. Samples 600C-1B and 650C-1 were exposed to 75% RH and samples 600C-1A and 650C-2 were loaded dry.

Assuming the maximum pressure drop observed in sample 600C-1A was caused by a leak, the leak rate would be about $1 \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$ over the course of this experiment –

about a factor of ten greater than considered reasonable for these containers based on previous helium leak tests. A second potential explanation for the pressure decrease is an ineffective purge of air from the sample vessels.^c Although the argon supply for the inerting procedure is high purity (99.995%), this observation suggests that air was not sufficiently purged from the argon supply lines following installation of a new cylinder.

Test 2

Test two was run for 46 days. The initial headspace gas in this set of experiments is air. The temperature corrected pressure graph for these samples is provided in Figure 8. Samples were started at ambient pressure but at elevated temperature of approximately 30 °C. The initial decrease in pressure associated with the large change in glovebox ambient temperature is not evident in this graph. Over the first four days of this test, the pressures measured for samples 650C-1 and 650C-2 are diverging, which suggests that 650C-1 may not be well sealed. At this point, the ConFlat[®] flanges on all of the sample containers were tightened. The pressure increase observed on day four for each experiment in test series two was caused by decreasing the headspace volume of each vessel when the flange was tightened. The change in behavior for samples 600C-1A and 600C-1B following day four suggests these containers may have also been poorly sealed.

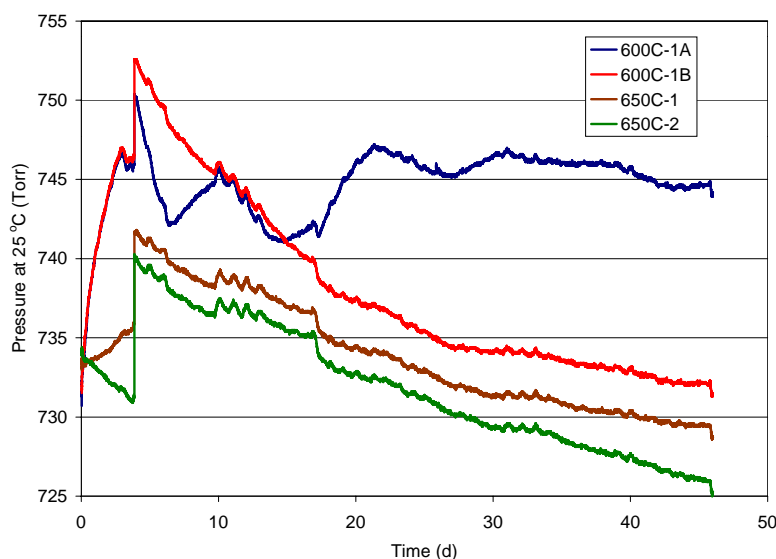


Figure 8. Temperature corrected pressure measurements for test series 2. All samples were exposed to 75% RH prior to loading in test vessels.

The continuing erratic behavior of 600C-1A has not been explained. Pressure measurements during sampling indicate that there was not a problem with the Digiquartz

^c In testing and storage of PuO₂ in air, the O₂ content of the headspace is frequently depleted and pressures are observed to drop. The fate of O₂ removed in this manner is explained as chemical reaction to oxidize PuO₂ to PuO_{2+x}. Similarly, the radiolysis of moist air will also result in a reduced O₂ content for a storage container.²⁷

transducer. During sampling it was noted that the sample valves on this vessel were not closed as tightly as the other containers, so additional follow-up efforts to evaluate of this potential source of error are warranted. To offset the potential for H_2 to leak from these containers during the first four days of testing, the gas generation rates were calculated based on the experiment duration of 42 days, instead of the total 46 days.

Measuring Concentration of Headspace Gases

Headspace gas samples were collected in the same manner from each set of tests. Four small gas sample containers were designed for these samples with a volume of approximately 12 cm^3 . Each container included a large metal bellows valve with face seal connections (Swagelok SS-4BG-V51) on one end and a Valco miniature high pressure on/off valve on the other end. A picture of this sample container is shown in Figure 9. The large valve was used to connect to the external manifold and the small valve was used to connect to the micro-GC for sample analysis. The sample containers were leak tested prior to use by the rate of rise methodology and indicated no pressure increase over about 16 hours. This equates to a leak rate of $\leq 1 \times 10^{-7}\text{ cm}^3\text{ s}^{-1}$.



Figure 9. Gas sample container for headspace sample analysis.

Prior to collecting a gas sample, the gas sample container was connected to the external manifold. The gas sample container and all tubing between the gas sample container and inner sample loop valve were evacuated to about 3×10^{-5} Torr (pressure reading at the vacuum pump). The manifold valve to the vacuum pump valve was closed, and a minimum volume path established between the test vessel and the gas sample container. This volume included a Digiquartz sensor installed on the external manifold. At this point, the inner sample loop valve was opened and headspace gas from the test vessel expanded into the evacuated sample line and gas sample container. Once pressures between the external manifold and test vessel equilibrated, the valves were closed and the gas sample container was disconnected. This process was repeated for each experiment. The gas pressure in the gas sample container available for micro-GC analysis was about 120 to 170 Torr depending on the initial test vessel headspace volume and pressure. Figure 10 shows the pressure measurements recorded while sampling.

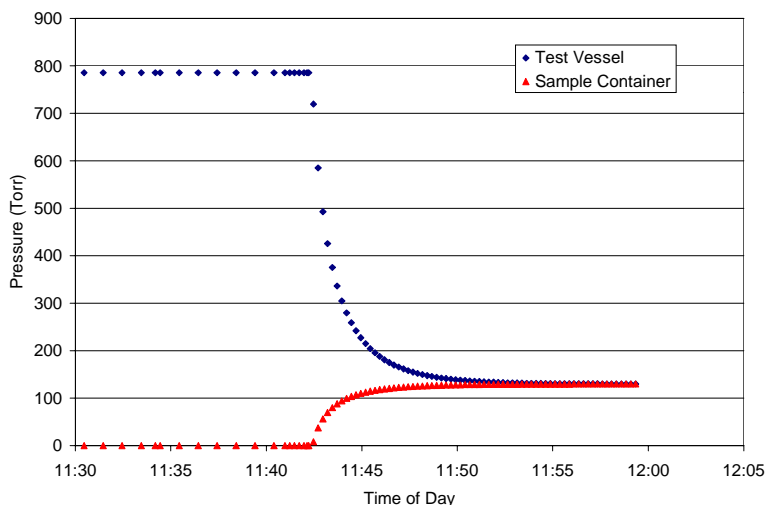


Figure 10. Pressure measurements during gas sampling of test vessels.

The micro-GC results for tests 1 and 2 are provided in Table 4. The micro-GC provides an accurate measurement of H_2 , O_2 , and N_2 concentrations of gas samples even at low pressures and concentrations of H_2 gas.²⁷ The ratio of $N_2:O_2$ for air is 3.7 and an increase in this ratio indicates oxygen depletion.

Table 4. Gas Content of Headspace Gas Determined by Micro-GC Analysis.

Test	Sample Label	$H_2\%$	$O_2\%$	$N_2\%$	$N_2:O_2$
1	600C-1A	0.08	3.11	16.18	5.20
1	600C-1B	0.14	0.69	5.65	8.19
1	650C-1	0.07	0.11	0.42	3.82
1	650C-2	0.02	0.04	0.20	5.00
2	600C-1A	0.07	17.04	74.20	4.35
2	600C-1B	0.24	16.38	78.81	4.81
2	650C-1	0.25	18.52	77.48	4.18
2	650C-2	0.23	16.75	75.98	4.54

The presence of N_2 and O_2 in the first test series indicates that the inerting protocol was not effective in removing air from the samples and observed pressure drops in these four experiments were a result of oxygen consumption. This consumption of oxygen should be expected base on radiolysis of moist air.²⁸

Calculating Rates of Gas Generation

Hydrogen gas generation rates were calculated from the experimental data as follows:

$$rate = \frac{n_{H_2}}{t \cdot m}$$

where:

$rate$ = moles of hydrogen generated per day per kilogram of NpO_2

n_{H_2} = moles of hydrogen produced,

t = test duration in seconds,

m = mass of NpO_2 in kilograms,

The number of moles of hydrogen produced (n_{H_2}) was calculated as follows:

$$n_{H_2} = \frac{c_{H_2} \cdot p \cdot V}{R \cdot T}$$

where:

c_{H_2} = volume fraction of hydrogen in container at end of test,

p = final container pressure in atmospheres,

V = container volume in liters,

R = the ideal gas constant, 0.08206 L·atm/mol·K,

T = absolute temperature in Kelvins (K).

The calculated gas generation rates are provided in Table 5 along with mass, pressure, volume and. Duration for each experiment.

Table 5. H_2 Gas Generation Rates for NpO_2 Tests.

Test	Sample ID	Sample Mass (g) ^d	Pressure (atm) ^e	Volume (L)	Duration (days)	Rate (mol day ⁻¹ kg ⁻¹)
1	600C-1A	9.8446	1.030	0.00727	66.90	0.36 x 10 ⁻⁶
1	600C-1B	9.6488	1.036	0.00737	66.90	0.67 x 10 ⁻⁶
1	650C-1	20.0288	1.042	0.01147	66.90	0.24 x 10 ⁻⁶
1	650C-2	19.4998	1.040	0.01155	66.90	0.08 x 10 ⁻⁶
2	600C-1A	9.3538	.980	0.00722	41.93	0.57 x 10 ⁻⁶
2	600C-1B	9.1397	.964	0.00733	41.93	1.81 x 10 ⁻⁶
2	650C-1	19.3138	.964	0.01140	41.93	1.33 x 10 ⁻⁶
2	650C-2	18.9956	.955	0.01151	41.93	1.30 x 10 ⁻⁶

^d A dry sample mass is calculated by subtracting the loss on ignition result from the measured sample mass.

^e Pressure measurements are corrected to 25°C or 298K

The H₂ generation rates have an estimated error of $\pm 5\%$ relative standard deviation with the greatest uncertainty contributed by the uncertainty in the hydrogen concentration.

Discussion

The empirical measurement of H₂ generation rates for a nuclear material is not a simple task, as indicated by the foregoing description of SRTC efforts. These tests required the laboratory scale production of NpO₂ to represent the HB-Line Phase II product and extensive characterization of the NpO₂ to support interpretation of the gas generation test results. The test variables used in these experiments included calcination temperature, elevated humidity, and fill gas. Each of these variables has a noticeable impact on the H₂ generation rate measured for NpO₂. The primary reason these variables impact gas generation rates is their effect on moisture adsorption by the NpO₂ samples.

Calcination Temperature

Calcination temperature and material origin are the key parameters that control the SSA of an actinide oxide. The NpO₂ that was generated for these gas generation experiments used the HB-Line Phase II flowsheet started with the same process stream to be used in HB-Line Phase-II (i.e. Tank 8.5 solution). The NpO₂ samples included materials calcined at the anticipated process temperature of 650 °C and also at 600 °C. Samples calcined at 600 °C have higher SSA than samples calcined at 650 °C, so these samples should bound moisture uptake in the HB-Line process.

The SSA achieved following calcination at 600°C or 650°C is sufficiently small to prevent adsorption of more than about 0.2 wt % moisture at the maximum anticipated RH expected in HB-Line under normal operating conditions. The nominal HB-Line product calcined at 650 °C has a SSA in the same range as PuO₂ materials described in the DOE-STD-3013-2000 that have been calcined at 950 °C for 2 hours. Reducing the calcination temperature to 600 °C resulted in a 50% increase in SSA and subsequent increase in moisture adsorbed following exposure to 75% RH.

Elevated Humidity

The moisture uptake methodology used in these experiments exposed open containers of NpO₂ to 75% RH for five days, or longer. The samples of dry NpO₂ sealed following calcination in SRTC were shown to increase in moisture content by up to 0.2wt % when exposed to 75% RH. In HB-Line the containers of NpO₂ will be much larger (e.g., about 5 kg) and will be sealed until inerting and packaging in the shipping container. These factors should limit the amount of moisture adsorbed on actual HB-Line products and these products are likely to have moisture content similar to the levels associated with NpO₂ tested “as calcined” (i.e. samples 600C-1A and 650C-2 in test 1).

Based on experience with PuO₂, the potential for moisture adsorption dramatically increases at RH greater than 80% as described by Paffett et al. This type of rapid moisture adsorption above 80% RH has been observed by Icenhour at ORNL on a sample

of NpO_2 calcined at 650 °C. In Icenhour's test, when the sample was exposed to 97% RH, a rapid increase in sample weight was recorded and the calculated moisture content reached about 0.9 wt % after several days exposure. The moisture on this sample rapidly returned to about 0.1 wt % when removed from the elevated humidity conditions.²⁹

Fill Gas

The process used to inert the test samples with argon appears to have removed a significant fraction of the adsorbed moisture and significantly reduced the H_2 generation rates by about 3 to 5X. The inerting effort produced a greater change in the low SSA products (i.e., 5X) than the high SSA product (i.e., $2\frac{1}{2}\text{X}$). These changes in rate are consistent with moisture being more easily removed from NpO_2 calcined at 650 °C.

Moisture Content of NpO_2 Samples

The moisture measurements provided by TGA-MS in general tend to support prediction of relative changes in H_2 generation rates. However the very small differences in moisture content between samples maintained "as calcined" with minimal exposure to humid conditions and samples exposed to 75% RH for an extended duration limits the value of this tool for process control. The currently proposed LOI test is of questionable value because it cannot distinguish between weight loss due to moisture and other impurities. A large fraction of the observed weight loss (50-70%) for the HB-Line Phase II NpO_2 product is from other impurities.

Conclusions

The H_2 gas generation rate for NpO_2 samples produced on a laboratory scale using the HB-Line Phase II flowsheet has been measured both dry and following exposure to 75% RH. A maximum H_2 generation rate of $1.8 \times 10^{-6} \text{ mol} \cdot \text{day}^{-1} \cdot \text{kg}^{-1}$ was observed for NpO_2 samples with approximately $1\frac{1}{2}$ times the expected SSA for HB-Line Phase II product.

The nominal HB-Line flowsheet includes calcination at 650 °C, inerting the packaging prior to shipping, and limiting moisture exposure of the NpO_2 product by storing in sealed containers. The NpO_2 sample tested under these conditions (650C-2, Test 1) generated H_2 at a rate equal to about 5% of the maximum observed rate. The HB-Line Phase II product should produce H_2 at a similar rate if the desired process conditions are achieved and the inerted storage container remains sealed to minimize exposure to the glovebox atmosphere.

Based on the limited value of LOI for the NpO_2 product, alternate process controls, such as calcination temperature and relative humidity, are needed to assure the SSA and moisture uptake of the HB-Line product are within the range described by these experiments. The moisture content of the Phase II process cabinets needs to be maintained at less than 75% RH when producing or handling the NpO_2 product in open containers. Lower humidity conditions will decrease the moisture adsorbed by NpO_2 and

improve gas generation behavior of the packaged product. The calcination of $\text{Np}(\text{C}_2\text{O}_4)_2$ should be at 650 °C for at least 2 hours to achieve the lower SSA described in this report. Consideration should be given to measuring the actual SSA of the HB-Line process during the initial process runs to validate controls on furnace operation are sufficient. By implementing process controls on RH and calcination temperature, the HB-Line Phase II NpO_2 product should eliminate the need for routine moisture measurements to apply the test results provided in this document

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Attachment 1 Photographs of Test Equipment



Figure 11. Exposure of NpO₂ to 75% RH prior to test 1.



Figure 12. Equipment used in loading test vessel inserts.



Figure 13. Test vessel bottom loaded with NpO_2 .



Figure 14. Installing test vessel top for NpO_2 gas generation test.



Figure 15. Test apparatus for NpO₂ gas generation experiments.



Figure 16. Photograph of external manifold and laboratory computer.



Figure 17. Alcatel Drytel Model 1025 vacuum pump installed in radioactive containment.