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GAS GENERATION OVER PLUTONIUM OXIDES IN THE 94-1 SHELF LIFE SURVEILLANCE PROGRAM

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ABSTRACT

The Department of Energy (DOE) is embarking upon a program to store large quantities of plutonium-bearing materials for up to fifty years. The Los Alamos National Laboratory Shelf Life Project was established to bound the behavior of plutonium-bearing material meeting the DOE 3013 Standard. The shelf life study monitors temperature, pressure and gas composition over oxide materials in a limited number of large-scale 3013 inner containers and in many small-scale containers. For the large-scale study, baseline plutonium oxides, oxides exposed to high-humidity atmospheres, and oxides containing chloride salt impurities are planned. The first large-scale container represents a baseline and contains dry plutonium oxide prepared according to the 3013 Standard. This container has been observed for pressure, temperature and gas compositional changes for less than a year. Results indicate that no detectable changes in pressure and gas composition are observed.

INTRODUCTION

The Department of Energy (DOE) standard, DOE-STD-3013-2000,¹ establishes criteria for stabilizing, packaging, and long term safe storage of plutonium bearing materials at DOE facilities. The Standard applies to oxide or metal that contains at least 30 weight percent plutonium plus uranium, where a maximum of 5 kg of material is packaged in a set of two individually sealed containers. The requirements include material stabilization at 950°C, a 0.5 weight percent moisture content or less, and less than nineteen watts of power per sealed container. Although the 3013 package provides for a robust storage system, its long-term safety performance has not been demonstrated. An in-depth understanding of the material's long and short term behavior in sealed containers is being addressed in several ongoing research programs.²⁻⁴

The evolution of hydrogen and other gases from plutonium-bearing residues, inadequately stabilized oxides, and incompatible materials is well known.^{3,5-7} In contrast, documented cases of plutonium storage package failures caused by gas pressurization from reasonably stabilized and packaged oxide materials have not been reported.⁸ Despite these observations, model predictions indicate a pressurization of sealed containers with plutonium oxide due to gas generation mechanisms. Of current concern is the generation of H₂ gas from adsorbed water, the generation of water in the vapor phase at elevated temperatures, and the generation of HCl or Cl₂ gases from the radiolysis of chloride-containing salts, which exist as impurities in the oxides. The combination of chloride bearing gases and condensed water may generate localized corrosion concerns within the 3013 package. Several technical issues remain concerning the kinetics of reactions and compositional effects on gas generation and corrosion over plutonium oxide materials. Ongoing experimental work is planned to address the uncertainty in these issues.^{3,4b}

To ensure failures do not occur while the sealed containers are being maintained, a DOE complex-wide integrated surveillance program is established to define the behavior of these materials. At Los Alamos National Laboratory (LANL), the shelf life project monitors gases over oxide materials in a limited number of large-scale 3013 inner containers and in many small-scale containers with samples taken from site-wide representative materials actually being stored. The small-scale containers allow more sample types and conditions to be studied. This information provides invaluable, defensible results for assuring safe long-term storage of these materials in sealed containers. The engineering design of the LANL surveillance capability and the results for the first large-scale container are discussed.

ENGINEERING DESIGN

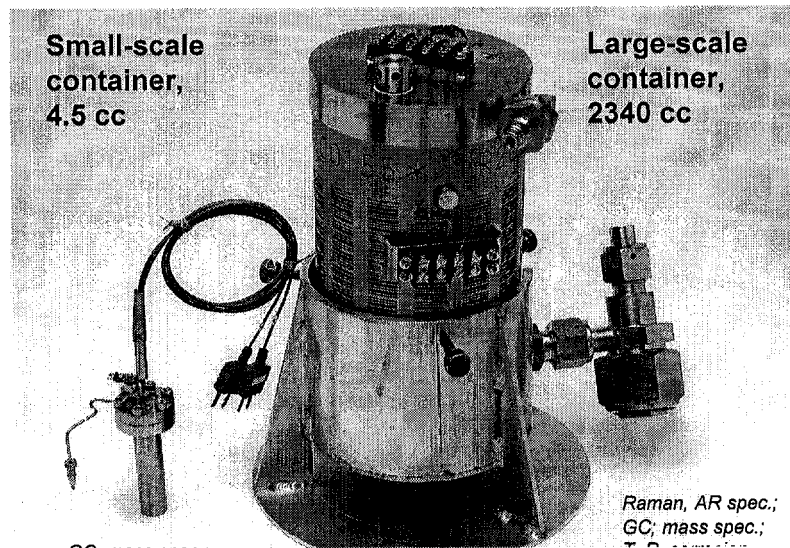
The LANL shelf-life surveillance project has two parallel studies. The small ten gram samples are monitored for relatively short time periods, and a limited number of large samples equivalent in size to the 3013 storage can capacity are monitored for long periods of time. The small samples will allow a database of many material types prepared according to various site-specific packaging methods to be compiled. Large-scale studies will give the behavior of a limited number of samples in the precise geometry and environment in which the material will be stored. Comparison between the two sample types will determine the degree of confidence in small sample experiments and fundamental measurements in predicting the long-term behavior of real materials.

We have designed instrumented storage containers that mimic the inner storage can specified in the 3013 standard at both large- and small-scale capacities (2.3 liter and 0.0045 liter, respectively). The containers are designed to maintain the volume to material mass ratio while allowing the gas composition and pressure to be monitored over time. The large-scale cans are instrumented with a Raman fiber-optic probe, a gas chromatography (GC) / mass spectrometer (MS) sampling port, an acoustic resonance chamber, two corrosion monitors, and pressure and temperature sensors. Data collection for the large-scale containers is automated in order to reduce worker exposure. The small-scale containers are designed with a microliter gas-sampling capability (GC and MS) and pressure and temperature sensors. These containers will be stored in a heated array in order to reproduce the increased temperatures arising from radioactive self-heating. Figure 1 shows the large- and small-scale containers.

For the large-scale study, multiple cans containing up to 5 kg of material will be prepared for study. Materials will be sealed in BNFL inner containers that were designed to the DOE 3013 Standard. In order to minimize the effect of invasive gas sampling on the

experiment, an effort is made to limit the gas sampling for gas chromatography / mass spectrometry to 10% of the initial gas loading over the course of the experiment. The majority of the gas compositional data will be obtained through Raman spectroscopy. GC still remains a principal method because of its widespread acceptance as a gas analytical technique and its sensitivity to a wide range of gaseous species. The design limits organic exposure to the oxide by minimizing the organic content of the assembly components. The modified lid is welded to the container inside the glove box after the plutonium oxide has been transferred to the container. The modified lid is designed with a burst disk for pressure release in the event of a highly unlikely scenario of an H₂-O₂ deflagration within the container. A rack system that holds the containers is located in a plutonium glove box. It has a heated gas-manifold to minimize the effect of gas condensation enabling quantitative GC analysis. All data acquisition is controlled remotely so that little or no manipulation in the glove box gloves will be required once the cans are in place.

The containers are monitored for pressure and temperature multiple times an hour, and recorded with data acquisition hardware and software at fifteen minute intervals. In the large-scale containers, gas analysis is done by gas chromatography and Raman spectroscopy. For GC, a gas sample is withdrawn from the container gas decreasing the pressure by 0.04 Torr per gas sample. For the large containers, the primary method of sampling is with Raman spectroscopy with fiber optic coupling, where a sensitivity limit on the order of 0.5 Torr has been demonstrated for most gases.⁹ GC sampling is done periodically to confirm Raman spectroscopy results and offer a quantitative cross-check on the gas constituents for the large containers. It will also be able to detect most monatomic gases (He, Ne, but not Argon) that Raman spectroscopy is unable to detect. GC measurements have been taken for various



calibration mixtures that include gas components that may be observed during the course of the experiments. It is expected that the current configuration allows a gas determination of 1.2 Torr partial pressure in the container.

The design of a Raman collection chamber is such that gases are detected within an enclosure without sample removal or pre-concentration. The chamber contains an unfiltered, non-imaging fiber-optic probe and a black, colored glass filter tilted to direct reflections away from the probe tip. The fiber-optic probe head consists of a fiber-optic bundle with one center excitation optical fiber and six surrounding collection optical fibers. The container is isolated from the oxide material by a two micron filter.^{4b}

Raman spectra of gas mixtures exhibit distinct scattering peaks characteristic of each gas present in the sample (excluding monatomic gases such as He and Ar). Peak areas are proportional to gas concentration, with the proportionality factor being dependent on the gas and on the instrumentation. In order to compensate for most of the possible variation of the proportionality factors due to changes in instrumentation, peak areas can be compared to an internal standard within the sample being measured. The ratios of the proportionality factor of the gas to be measured and the internal standard can be determined by measuring a known gas mixture. These ratios can then be used to determine unknown gas concentrations of mixtures containing the internal standard at a known concentration

OXIDE MATERIALS

Oxide materials representing inventories destined for long-term storage throughout the DOE complex will be monitored. Thirty-three items from Hanford and Rocky Flats Environmental Technology Site have been evaluated by the LANL 94-1 R&D Program.¹⁰ Residuals from these evaluated items make up the surveillance items to date. In the future, materials may be drawn from the Los Alamos inventory or from other sites to assure that all materials going to storage under the 3013 standard are represented in the LANL Shelf-Life Surveillance Project.

Small-Scale Materials.

The small ten gram samples will allow a database of many material types prepared for storage in various methods.^{4b} For the initial small-scale study, forty-five containers are planned. Forty will contain actual oxide material from the DOE packaging sites, and five will

contain experimental blanks. The five by nine container array is designed so that five independent temperatures can be set for each row of nine small-scale containers.

The samples will be selected to address known existing uncertainties in gas generation and safety considerations associated with specific material types being considered for storage. They will also contain samples of the actual materials going into the large-scale study and offer data validation with ongoing efforts. A percentage of the oxide materials in the small-scale study will be used for data validation of gas generation models in development across the DOE complex. Approximately half of the proposed small-scale samples meet the criteria in the 3013 standard (950°C two hour calcination; greater than 30 weight percent plutonium; less than 19 watts; and less than 0.5 weight percent water). Initial start-up activities during the first six months include both experimental duplicates and blanks. After the initial six months the blanks and duplicates will be phased out and additional oxide samples will be loaded. One blank will reside in the matrix at all times.

Large-Scale Materials.

Ten instrumented inner 3013 containers will be monitored to establish compositional changes in gases over plutonium oxide materials for an extended time. Characterized oxide material, in nine of the containers, will be in varying forms (pure PuO₂, x% H₂O/ PuO₂, PuO₂ with salt, and PuO₂ with other material for example a carbon source). The tenth container will exist as an experimental blank. The material matrix encompasses bounding, safety-driven scenarios for long-term storage.

The oxide materials planned for the large-scale containers will be prepared from calcination following an oxalate precipitation. The typical characteristics of this starting material is 0.5-1.5 weight percent loss on ignition, 20 - 60 m²/gm specific surface area, and 1.8 - 2.0 g/cm³ loose powder density. Several technical issues will be explored through the large-scale experimental array. The first can serves as the baseline and will be pure oxide packaged according to the 3013 Standard. The effect of the specific surface area will be studied in three containers and will determine the effect of free water and gas generation on the oxide surface area. It has been proposed by Veirs¹¹ and others that in the case of high specific surface area, 0.5 weight percent water is bound tightly to the oxide in first few monolayers, thus no water can be found in the vapor phase. On the other hand, a low

specific surface area oxide ($1 \text{ m}^2/\text{g}$) containing 0.5 weight percent contains approximately 20 water monolayers, of which about 18 are loosely bound, generating water in vapor phase. The effect of water on gas generation will be determined by the exposure of the oxides to a humid environment in four comparative containers. A critical corrosion issue within the cans will be addressed with the addition of chloride salts to oxide materials in two containers. The issue of HCl generation, corrosion, and low plutonium content ($<50 \text{ wt.}\%$) will be studied. The generation of hydrogen and CO_2 gases will be explored with the addition of organics and moisture in two different containers. This scenario may result in increased pressures. One can will be heated to a higher temperature to mimic the possible Savannah River Site storage temperature generated inside a sealed can array with added solar heat. The effect of the fill gas will also be studied. If air is the fill gas, the back reaction of generated hydrogen with oxygen from air may actually limit the hydrogen production. And finally one container will be filled with a mixed oxide, which will explore the effect of uranium oxide where U_3O_8 may act as a hydrogen sink and subsequently generate water.

LARGE SCALE CONTAINER EXPERIMENTAL METHOD

The large-scale container design assembly indicating key components is shown in Figure 2. The lid and base components are cleaned and leak checked prior to placement in the glove box line. The final weld of the lid to the base was completed in the glove box with gas tungsten arc weld. The first oxide container

has nine thermocouples in a linear array across the diameter of the can so that information on PuO_2 thermal conductivity can be obtained.

The plutonium oxide material was prepared for the first large-scale container from an oxalate precipitation followed by calcination at 650°C . Later, the material was screened, blended then calcined at 975°C for four hours and allowed to cool naturally. The measured plutonium content is 87.6% by calorimetry. The impurities in the material are in the parts per million level with the largest impurities being uranium (170 ppm) and nitrate (390 ppm). After calcination, the material specific surface area was $1.07 \text{ m}^2/\text{gm}$, and moisture content was 0.1 weight percent (determined by loss on ignition and supercritical fluid extraction). The specific power of the material was 2.0 watts/kg. After calcination, the material was placed in a convenience can that in turn was placed into a container sealed in air with a Conflat flange for interim storage. This interim storage was done to limit potential moisture uptake on the calcined oxide.

The material was transferred to the first large-scale container after six weeks of interim storage, and the lid was then welded to the bottom of the container in a helium atmosphere. The nuclear material in the container was verified by calorimetry.

The container was prepared for the surveillance rack by a sequence of steps that include leak checking, gas volume determination, and gas exchange with high purity helium. The container was connected to the gas manifold and surveillance rack for monitoring. A final leak check

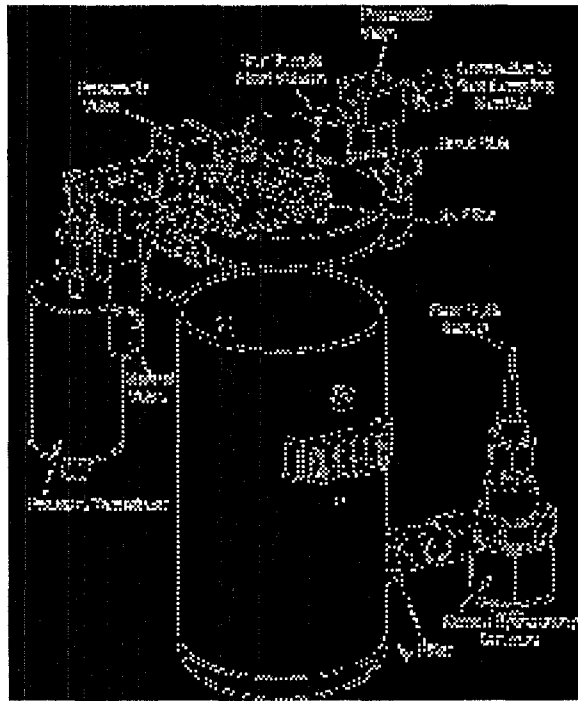


Figure 2. Full-scale can assembly indicating the design major components.

was completed prior to long term surveillance measurements. The container's leak rate was less than 2×10^{-6} atm cm³ per second, which is equivalent to 26 Torr per year. Two blank containers with calibration gas were also prepared for surveillance monitoring.

Gas sampling by Raman, GC and MS was conducted at a specified frequency. Initial sampling was done frequently in the first month. The intrusive gas sampling frequency was reduced after the first two weeks with the container monitored weekly by Raman spectroscopy.

SURVEILLANCE RESULTS

In verification and acceptance testing of the glove box installed equipment, two empty large-scale 3013 containers were installed in the glove box surveillance rack. The containers were filled with calibrated gas mixtures, and the temperature and pressure have been monitored continuously at fifteen minute intervals. The pressure and temperature results for the blank container in position 10 are shown in Figure 3. The pressure readings were corrected for temperature fluctuations by multiplying by the ratio of an average temperature and the temperature of the current reading. The slope indicates a possible leak rate on the order of 0.04 Torr/day. The temperature correction to the pressure does not completely

reflected in the pressure. The slope of the temperature data, if translated to pressure, corresponds to a pressure decrease of 0.06 Torr/day. Thus the data indicate that this container may have no detectable leak at all.

The container filled with plutonium oxide was initially evacuated and filled with 1000 Torr helium to verify a leak free container. During the container evacuation, the centerline temperature increased to over 100°C, which is attributed to a very low thermal conductivity of the plutonium oxide powder. At 1000 Torr of He, the centerline temperature was 47 °C. The container pressure was later reduced to 610 Torr helium. A 2.5°C increase in the container centerline temperature was observed with the pressure modification. The temperature profiles are shown in Figure 4. The graph includes the temperature distribution initially and when the container came to equilibrium with 1000 Torr then with 610 Torr of helium. The graph also includes two curves calculated using the thermal conductivity of helium at two different pressures. The agreement between observed and calculated at equilibrium is quite good. The variation of temperature observed when the pressure is lowered from 1000 to 610 Torr may be attributed to a change in the thermal conductivity of the powder due to repositioning of the particles within the powder, or a pressure dependence of the

thermal conductivity of the gas. This is under current investigation.

Pressure measurements have been recorded on the first container for over eight months and currently indicate no pressure changes due to gas compositional changes. Current pressure readings are just under 610 Torr.

Gas sampling was done during the evacuation and leak check phase, which included times when the oxide was above 100°C. The initial gas samples indicated that CO₂ was present. After the container was stabilized on the rack in a 1000 Torr and 610 Torr helium atmosphere, subsequent gas analysis indicated no CO₂ was present in the gas phase. The source of the carbon is not known, but it could be impurity carbon in the oxide powder or carbon in the stainless steel of the container. We speculate that CO₂ was probably produced during the first few weeks when the oxide was exposed to air within the sealed interim storage container and that CO₂ sorbs on the surface of the oxide with some heat of

adsorption. This sorbed CO₂ and will have an equilibrium partial pressure that increases with increasing surface temperature.

Currently, at the stabilized temperatures, no detectable gases are observed with Raman and GC measurements. Currently, over twenty Raman and eight GC measurements have been conducted on the container filled with plutonium oxide. All ongoing measurements indicate that no polyatomic gases are being generated in the first oxide container.

From the specific surface area, and the amount of material and moisture in the material, the available free water can be estimated.¹⁰ Using this approach, it is estimated that there are approximately four molecular water layers available on the surface of the oxide. The water layers under these conditions must be unreactive to hydrolysis because no hydrogen formation is observed at this point. The CO₂ or carbonate sorbed on the oxide surface may influence the observed chemistry.

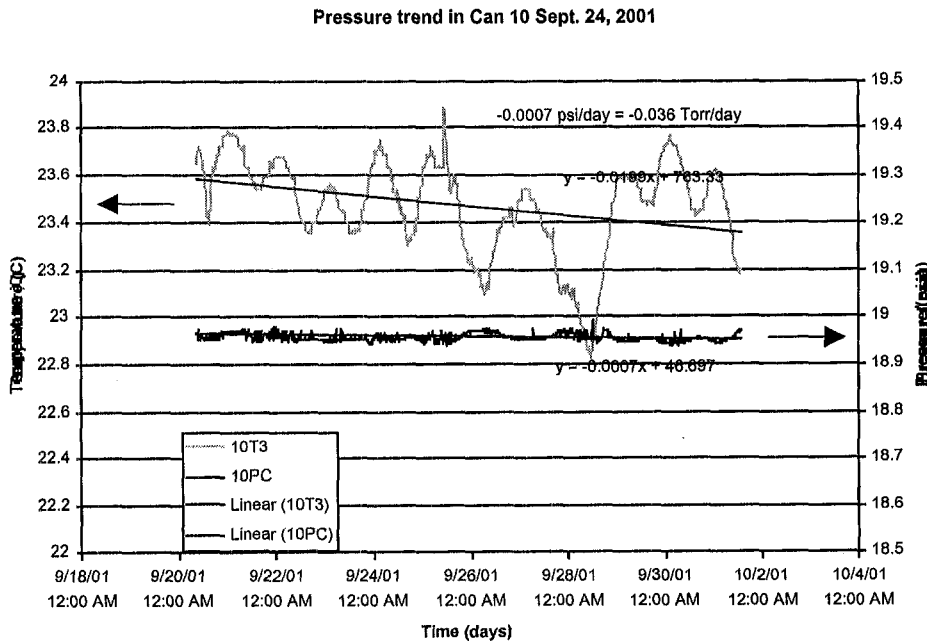


Figure 3. Temperature and pressure data for the calibration container in position 10 on the surveillance rack. In order to have reliable leak-checking data, the cans must be filled with an overpressure of over 1000 Torr of helium and monitored for a week.

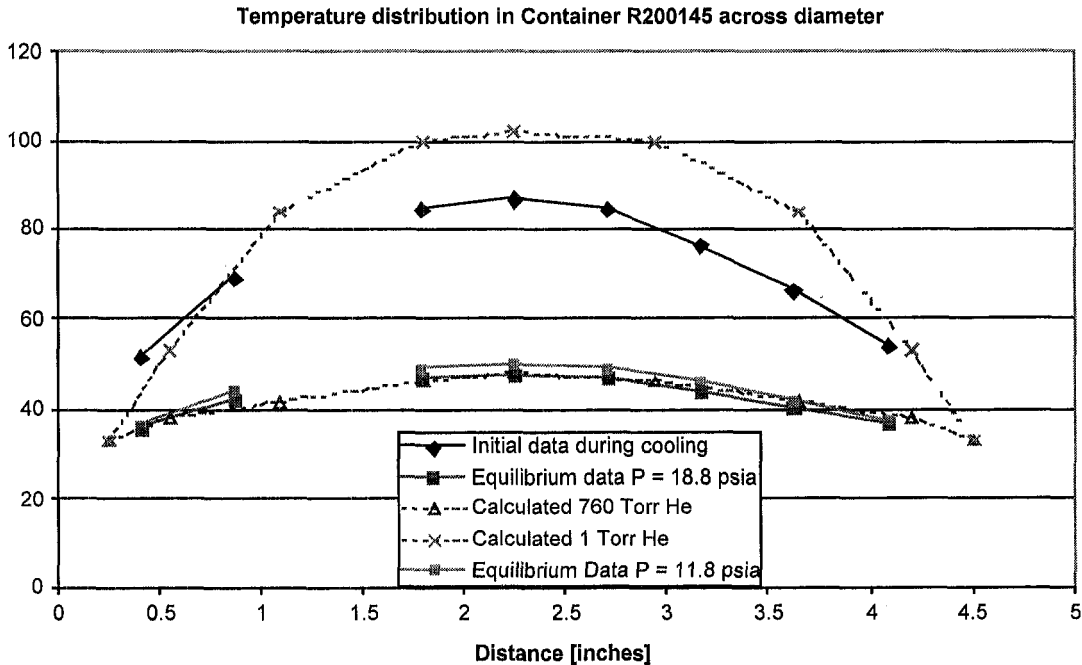


Figure 4. Temperature distribution across diameter of first oxide container.

CONCLUSIONS

A shelf life surveillance study is being developed for understanding gas generation concerns in sealed containers of plutonium oxide.

The first large-scale container represents a baseline and contains dry plutonium oxide prepared according to the 3013 Storage Standard. This container has been sealed in a helium environment with 5 kg of plutonium oxide. Initial activities during the container evacuation and leak check indicated the presence of CO_2 at temperatures greater than 100°C .

The first large-scale container has been observed for pressure, temperature and gas compositional changes for less than a year. Results indicate that no detectable changes in pressure and gas composition have been observed at equilibrium temperatures less than 50°C . Under the conditions of the first container, no hydrogen has been detected.

In summary, the results of the work performed here will provide critical information to DOE and the sites to assure that representative stabilized materials in approved containers are safe in long-term storage. We will provide guidance on what may or may not cause a

container to pressurize, understand the changes in gas composition over time, and study the effect of corrosive gas generation in the cans. This information from this project will also be important to the formation of a site wide surveillance program for the extensive amount of material packaged according to the DOE Standard.

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