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Gas Generation by Pure and Impure Plutonium Oxide Materials in Sealed Containers

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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. For oxide material a maximum of 5 kg of material is packaged in a nested set of two individually welded containers and the requirements include material stabilization at 950°C, 0.5 weight percent moisture content or less, and less than nineteen watts of power per sealed container. The welded containers ensure that any gas generated due to radiolysis will be retained within the container. Although the 3013 package provides for a robust storage system, its long-term safety performance has not been demonstrated.

To ensure failures do not occur while the sealed containers are being stored for up to 50 years, a DOE complex-wide integrated surveillance program has been established to measure the gas generation rates 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 charged with 5 kg of material and in many small-scale containers with 10 gram 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. Initial results on gas generation are presented.

Results

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, two corrosion monitors, and pressure and temperature sensors. The primary method of sampling is with Raman spectroscopy, as each GC sample perturbs the system by reducing the overall gas pressure by 4 Torr. Raman sensitivity is on the order of 0.5 Torr for most gases. GC sampling is done periodically to confirm Raman spectroscopy results with a sensitivity of 1.2 Torr. Pressure and temperature are recorded every fifteen minutes. 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. Initial small-scale gas compositions were obtained with MS.

The first large-scale container was filled with 5 kg of plutonium oxide material prepared from an oxalate precipitation followed by calcination at 650^{0}C. The material was then screened, blended, calcined at 975^{0}C for four hours, and allowed to cool naturally. The measured plutonium content is 87.6% by calorimetry. The major impurities were uranium (170 ppm) and nitrate (390 ppm). After calcination, the material specific surface area was 1.07 m^2/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 fourteen months of observations of the first large-scale container there has been no increase in pressure and no hydrogen or any other impurity gas generated.

The characteristics of the oxide material that has been sealed in the small-scale surveillance containers and the results of the final gas analysis are documented in the shelf-life project's year-end report.[2] The experimental observations conveniently fall into two basic categories. For materials packaged with He as fill gas, in which an air leak can be definitively ruled out, there is no generation of impurity gases. For materials packaged in air as fill-gas, typically there is oxygen depletion and the generation of carbon dioxide and nitrogen oxide (N_2O). These results are independent of the amount of impurities in the plutonium oxide materials as long as the water content is less than 0.5wt%. The time evolution of the gases observed in the headspace of a small-scale container with a calcined plutonium oxide material containing 20% chlorine with 6.8% magnesium, 5.4% potassium, 3.7% sodium, 2% nickel, and 2.5% iron is shown in Figures 1.

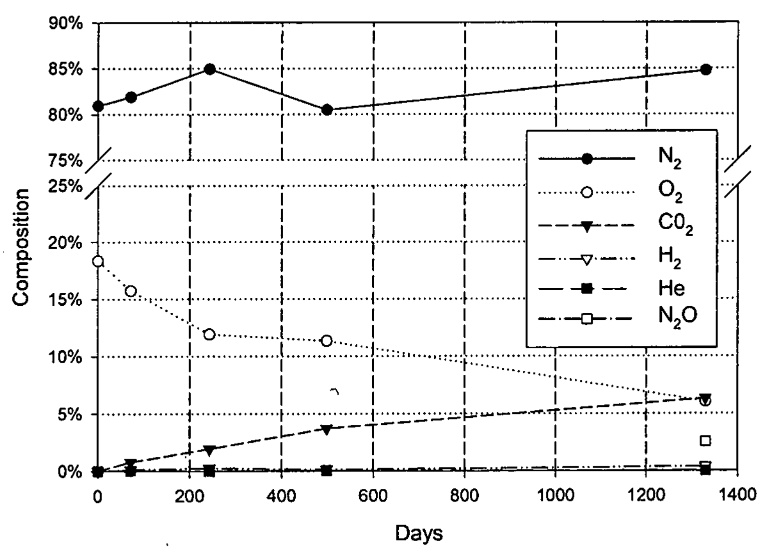

Figure 1. Gas composition over time for ARF-102-85-295 packaged after calcination at 900°C.

Discussion

A shelf life surveillance study has been developed for understanding gas generation concerns in sealed containers of plutonium oxide for long-term storage. Observations on a large-scale container representing a baseline that contains dry plutonium oxide prepared according to the 3013 Storage Standard shows no detectable changes in pressure and gas composition. Under the conditions of this container, no hydrogen has been detected.

For more complex material such as plutonium oxide mixed with chloride salts and packaged in air, the results shows depletion of oxygen and generation of carbon dioxide and nitrogen oxide.

These results show there is no generation of significant quantities of undesirable gases such as hydrogen in containers with pure or impure plutonium oxide materials studied to date and prepared according to DOE's 3013 Standard for stabilization and packaging. Future work using representative materials from DOE's sites will provide critical information to DOE and the sites to assure that properly stabilized materials in approved containers are safe in long-term storage.

Acknowledgement

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References

1. "Stabilization, Packaging, and Storage of Plutonium-Bearing Materials," DOE-STD-3013-2000, U. S. Department of Energy, Washington, DC.

2. Worl, L.A.; Berg, J.M.; English, D.; McFarlan, J.T.; Padilla, D.D.; Veirs, K.; Harradine, D.; McInroy, R.; Hill, D.D.; Prenger, F.C.; Morris, J.S., "MIS Small and Large Scale Sample Surveillance 2002 Year End Status Report", LA-UR-02-7356, Los Alamos National Laboratory Report.