

Technical Basis for DOE Standard 3013 Equivalency Supporting Reduced Temperature Stabilization of Oxalate-Derived Plutonium Oxide Produced by the HB-Line Facility at Savannah River Site

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June 29, 2012

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EXECUTIVE SUMMARY

The HB-Line (HBL) facility at the Savannah River Site (SRS) is designed to produce high-purity plutonium dioxide (PuO_2) which is suitable for future use in production of Mixed Oxide (MOX) fuel. The MOX Fuel Fabrication Facility (MFFF) requires PuO_2 feed to be packaged per the U.S. Department of Energy (DOE) Standard 3013 (DOE-STD-3013) to comply with the facility's safety basis. The stabilization conditions imposed by DOE-STD-3013 for PuO_2 (i.e., 950 °C for 2 hours) preclude use of the HBL PuO_2 in direct fuel fabrication and reduce the value of the HBL product as MFFF feedstock. Consequently, HBL initiated a technical evaluation to define acceptable operating conditions for production of high-purity PuO_2 that fulfills the DOE-STD-3013 criteria for safe storage. The purpose of this document is to demonstrate that within the defined operating conditions, the HBL process will be equivalent for meeting the requirements of the DOE-STD-3013 stabilization process for plutonium-bearing materials from the DOE complex.

The proposed 3013 equivalency reduces the prescribed stabilization temperature for high-purity PuO_2 from oxalate precipitation processes from 950 °C to 640 °C and places a limit of 60% on the relative humidity (RH) at the lowest material temperature. The equivalency is limited to material produced using the HBL established flow sheet, for example, nitric acid anion exchange and Pu(IV) direct strike oxalate precipitation with stabilization at a minimum temperature of 640 °C for four hours (h). The product purity must meet the MFFF acceptance criteria of 23,600 $\mu\text{g/g}$ Pu (i.e., 2.1 wt %) total impurities and chloride content less than 250 $\mu\text{g/g}$ of Pu. All other stabilization and packaging criteria identified by DOE-STD-3013-2012 or earlier revisions of the standard apply. Based on the evaluation of test data discussed in this document, the expert judgment of the authors supports packaging the HBL product under a 3013 equivalency.

Under the defined process conditions and associated material specifications, the high-purity PuO_2 produced in HBL presents no unique safety concerns for packaging or storage in the 3013 required configuration. The PuO_2 produced using the HBL flow sheet conditions will have a higher specific surface area (SSA) than PuO_2 stabilized at 950 °C and, consequently, under identical conditions will adsorb more water from the atmosphere. The greatest challenge to HBL operators will be controlling moisture content below 0.5 wt %. However, even at the 0.5 wt % moisture limit, the maximum acceptable pressure of a stoichiometric mixture of hydrogen and oxygen in the 3013 container is greater than the maximum possible pressure for the HBL PuO_2 product.

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LIST OF ABBREVIATIONS

$\text{Al}(\text{NO}_3)_3$	aluminum nitrate
BV	bed volume
c	$c=e^{\Delta H/RT}$, where ΔH is the excess heat of adsorption compared to the heat of condensation of the liquid
$^{\circ}\text{C}$	degrees Celsius
CO_3^{2-}	carbonate ion
$\text{C}_2\text{O}_4^{2-}$	oxalate ion
DE	Destructive Examination
DOE	U.S. Department of Energy
F^-	fluoride ion
g	gram
h	hour
HBL	HB-Line
HNO_3	nitric acid
ISSC	Interim Safe Storage Criteria
KF	potassium fluoride
kg	kilogram
L	liter
LANL	Los Alamos National Laboratory
LOI	mass loss on ignition
LTA	Lead Test Assembly
m	meter
M	molar
MFFF	Mixed Oxide Fuel Fabrication Facility
min	minute
MIS	Materials Identification and Surveillance
MOX	Mixed Oxide
NIST	National Institute of Standards and Technology
NO_3^-	nitrate ion
PuO_2	plutonium dioxide
RH	relative humidity
rpm	revolutions per minute
SBL	strongly bound layer
scfm	standard cubic feet per minute

SO ₄ ²⁻	sulfate ion
SRNL	Savannah River National Laboratory
SRS	Savannah River Site
SSA	specific surface area
TGA	thermogravimetric analysis
TGA-MS	thermogravimetric analysis – mass spectrometry
wt %	weight percent

1.0 Introduction

1.1 Purpose

This report documents the technical basis to support a determination that stabilizing high-purity plutonium dioxide (PuO_2) derived from direct strike plutonium(IV) oxalate precipitation at the Savannah River Site (SRS) HB-Line (HBL) facility at no less than 640 °C for a minimum of four hours (h) in an oxidizing atmosphere is equivalent to stabilizing at 950 °C as regards meeting the objectives of stabilization defined for U.S. Department of Energy (DOE) Standard 3013 (DOE-STD-3013) (DOE, 2012) if the material is handled in a way to prevent excessive adsorption of water. Establishing technical equivalency will enable HBL to operate at the lower temperature to produce and package PuO_2 for use by the Mixed Oxide (MOX) Fuel Fabrication Facility (MFFF).

1.2 Background

HBL plans to produce high-purity PuO_2 using conditions appropriate for manufacture of MOX fuel (Christopher, 2011). The HBL mission requires packaging the PuO_2 in 3013 containers for receipt and storage by the MFFF. Reducing the required calcination temperature of the HBL product is of significant benefit to MFFF and is required for MFFF feed stock that is used in direct fabrication of MOX fuel assemblies; however, the 3013 packaging for incoming material is required to meet the MFFF safety basis and support automated handling of the PuO_2 feedstock. Consequently, HBL requested assistance from the Savannah River National Laboratory (SRNL) and Los Alamos National Laboratory (LANL) to develop the technical basis to demonstrate equivalency of lower-temperature stabilization for HBL oxide from oxalate precipitation.

The current HBL facilities were built in the mid-1980s and, along with other DOE-EM missions, have been used for production of Pu-238, Pu-239 and Np-237 oxide products. The process experience associated with these past production campaigns demonstrates the facility's capability to meet rigorous production requirements.

As HBL begins production of PuO_2 under the proposed equivalency, samples of the HBL product will be placed into the MIS Shelf Life Program to evaluate material performance under 3013 storage conditions. The results of the MIS evaluation will support closure of data gaps identified during preparation of this document. Packaging of the HBL PuO_2 in 3013 containers is expected to be deferred for 18 to 48 months as HBL establishes the capability for welding 3013 inner cans.

After production of the HBL product, Interim Safe Storage Criteria (ISSC) will be utilized for packaging and storage of the PuO_2 in the SRS K-Area vault (Hackney, 2011). The analytical requirements and process controls necessary for ISSC are not addressed in this evaluation. However, once the PuO_2 is returned to HBL for 3013 packaging, the moisture limit and other 3013 packaging criteria will be verified to demonstrate conformance with the 3013 Standard. The preliminary design for the HBL inner 3013 can welder includes requirements for a dry nitrogen atmosphere (i.e., <1% O_2 , <5% RH) for packaging.

Prior to packaging PuO_2 produced under this equivalency, an in-depth review of HBL procedures and operational controls will be completed following the detailed "20 Points" process required for shipment of 3013 products to SRS (Gupta et al., 2000). As part of this review, HBL will document the process used for collecting and analyzing moisture samples; controls that are required for deferred packaging; measurement uncertainty associated with furnace temperature, product mass, RH, product purity, etc.

1.3 Purposes of Stabilization

The objectives for stabilization of plutonium-bearing oxides are listed in Appendix A of the DOE-STD-3013 (DOE 2012), Section A.6.1.2.1, p. 20, as follows:

- eliminate reactive materials such as finely divided metal or sub-stoichiometric plutonium oxides;
- eliminate organic materials;
- reduce water content to less than 0.5 wt % and similarly reduce equivalent quantities of species such as hydrates and hydroxides that might produce water;
- minimize potential for water re-adsorption above 0.5 wt % threshold; and
- stabilize any other potential gas-producing constituents.

The first objective is intended to avoid energetic events, for example, when storage containers are opened. The other four objectives are all intended to minimize the potential for pressurization of the container due to chemical, radiolytic, or thermal degradation of impurities, especially water. To achieve these objectives with high confidence for a broad range of materials, the standard specifies that oxide material will be placed in a continuously oxidizing atmosphere at a material temperature of at least 950 °C for a minimum of two hours.

1.4 Problem Definition and Process Description

The reduced stabilization temperature equivalency will be demonstrated for high-purity PuO₂ containing less than 2.1 wt % total impurities (McAlhany, 2012). The PuO₂ will be produced in the SRS H-Canyon and HBL facilities for eventual use as feed into the MFFF process. The chemical impurity limits for the oxide product are listed in Appendix A. The combined H-Canyon/HBL flow sheet, or process (Garrison and Clifton, 2012; Smith, 2012) is summarized below. This flow sheet is similar to the flow sheet used by LANL to produce approximately 330 kg of PuO₂ for MOX Lead Test Assemblies (LTA) during the time frame of 2001 – 2008 (Alwin, 2007; Bluhm, 2005). Figure 1 is a process diagram that shows the basic flow of materials described in the following paragraphs.

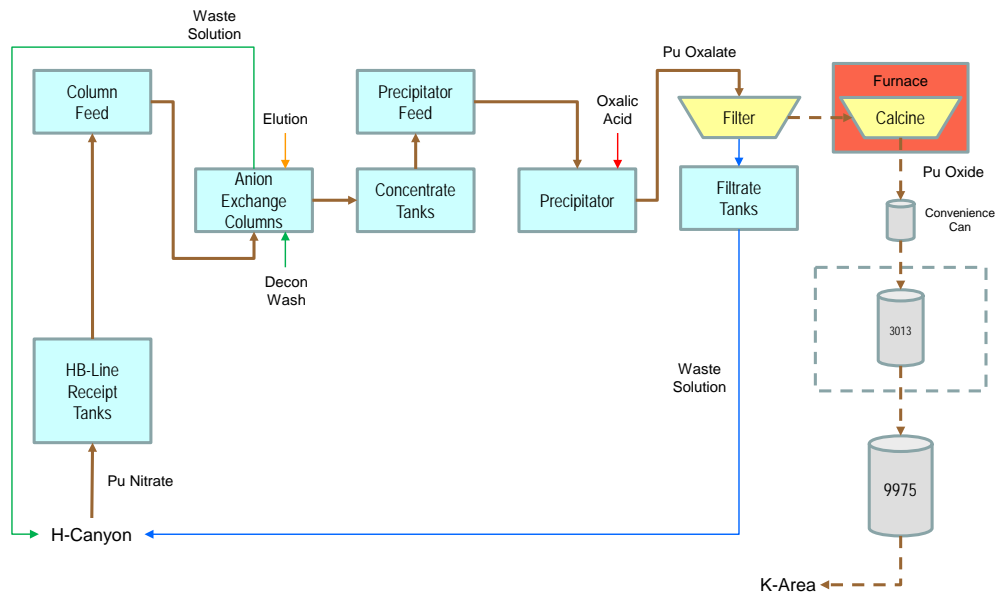


Figure 1. Block diagram of the HBL Phase II process.

1.4.1 Dissolution

H-Canyon will receive Pu metal¹ packaged in dissolvable carbon-steel cans that are sealed to minimize formation of Pu oxide and packaged in nylon bags for contamination control. The Pu metal and associated packaging is dissolved by placing in a boiling solution containing nominally 10 M nitric acid (HNO₃), with about 0.1 M potassium fluoride (KF), for 24–48 hours (h). Gadolinium or boron may be added to the dissolver as a neutron poison (Garrison and Clifton, 2012). After each dissolution cycle, the dissolver solution is expected to contain approximately 1–2 g/L Fe, and other minor impurities. Upon cooling, aluminum nitrate (Al(NO₃)₃) solution will be added to complex fluoride ion (F⁻) prior to transferring solutions to HBL. The Pu concentration in the HBL feed will depend on a number of variables associated with criticality safety controls but is expected to range from 2 to 4 g/L. The impurities associated with H-Canyon dissolution, along with those initially in the Pu metal, are subsequently removed by the HBL anion exchange and precipitation operations.

1.4.2 Anion Exchange

HBL will utilize two anion exchange resin columns in parallel to achieve the desired throughput. None of the column feed or column operation steps are anticipated to introduce additional process impurities. Upon receipt in HBL, the column feed solution will be analyzed to verify HNO₃ concentration prior to loading the anion columns. No valence adjustment step is required based on prior experience for short term storage of low concentration Pu solutions in nitric acid solutions appropriate for anion feed. The columns are conditioned with nominally 8 M HNO₃, loaded with the feed solution from H-Canyon, then washed sufficiently to remove contaminants to meet specifications for the MOX product (Kyser and King, 2012). The Pu feed solutions are passed through a 10- μ m filter (HBL, 2007) prior to loading the anion columns to prevent any solids or other particulate matter from interfering with process operations. Once washed, the column will be eluted with nominally 0.35 M HNO₃. The combined product solution from both columns is expected to contain greater than 40 g/L Pu in low molarity HNO₃ (Smith, 2012; Garrison and Clifton, 2012). Laboratory analysis is used to validate removal of impurities following anion exchange during process start-up and periodically as needed to support the HBL process control strategy.

1.4.3 Precipitation

The anion exchange product solution will be fed to the HBL precipitator, and Pu will be precipitated by the addition of nominally 0.95 M oxalic acid solution (i.e., direct strike precipitation). The precipitator solution temperature will be maintained at approximately 50 \pm 5 °C during precipitation and allowed to digest for 5 min or longer prior to filtration. The total amount of oxalic acid added will be equal to two moles of oxalic acid per mole of Pu plus enough to achieve approximately 0.1 M excess oxalic acid (Smith, 2012).

1.4.4 Filtration

The resulting slurry will be transferred to the HBL filtrate tank with the precipitate collected on a filter boat with a nominally 10- μ m stainless steel screen. During the filtration operation, a wash solution consisting of low molarity HNO₃ and oxalic acid will be utilized to flush the precipitator vessel and wash the plutonium oxalate filtrate to remove additional soluble impurities. When filtration is complete, the filter boat will be lowered and air dried for approximately 60 min by

¹ Although the starting material for the current HBL flow sheet is Pu metal, the arguments for 3013 equivalency would also apply to PuO₂ produced using the same flow sheet but starting with oxide as long as the final product meets the same purity specifications and moisture content at packaging.

pulling air through the filter cake to remove excess moisture prior to calcination (Smith, 2012). Quality of the reagents and process water used for HBL operations are monitored to avoid addition of any undesired contaminants.

1.4.5 Calcination

In HBL, the filter boat also serves as the calcination furnace boat. To initiate the calcination step, the filter boat is raised into the furnace and heated to a bed temperature of 640 °C or greater for a minimum of 4 h while pulling air through the filter cake at a minimum of 0.5 scfm as measured by a downstream rotameter. Figure 2 illustrates the furnace layout and identifies the basic components. The centerline of the product bed is expected to be the coolest point in the furnace and is used to determine calcination temperature. This thermocouple is calibrated with traceability to the National Institute of Standards and Technology (NIST). The furnace temperature will be controlled to achieve an indicated product bed temperature of nominally 650 °C; however, with associated uncertainty in this temperature reading, the actual product temperature will be no less than 640 °C as proposed for the 3013 equivalency. Following calcination, the oxide product will be cooled to less than 100 °C by pulling glove box air through the furnace shell before lowering the filter boat from the furnace. The process steps followed during product cooling will minimize exposure of the oxide product to the glove box atmosphere and transfer the product to a sealed container as soon as reasonably possible upon cooling to less than 100 °C. This step is noted as an important aspect of moisture control on the 3013 PuO₂ product.

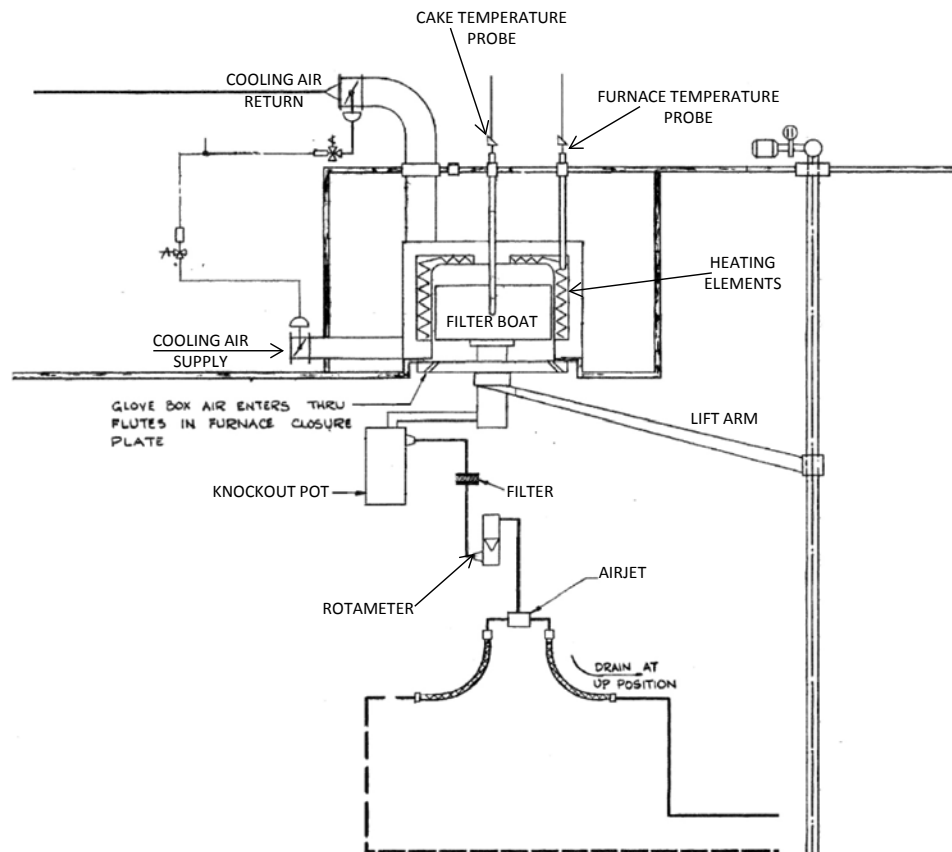


Figure 2. Schematic of the HBL calcination furnace.

Once calcined, the PuO₂ product will be controlled to maintain the RH at the product surface to less than 60% (including measurement uncertainty). The RH is monitored by two independent probes in the processing area; hand-held RH probes may also be used. The RH exposure at the product surface will be determined based on the highest measured RH value and the material temperature. Limiting moisture adsorption is dependent on a combination of multiple process controls beginning with facility HVAC. Additional controls include maintaining product temperature greater than ambient process temperature (e.g., keeping product in the furnace at elevated temperature, transferring product to sealed containers while still warm, evaluating PuO₂ self-heating under various process and package configurations, etc.) and using sealed containers to limit exposure to glove box atmosphere. The benefits of maintaining product temperature above ambient temperature are discussed in Section 2.4.3. If the RH at the product surface is not maintained below 60%, the PuO₂ product will be reconditioned by heating to 640 °C or greater.

1.4.6 Packaging

Each batch of PuO₂ will be transferred after calcination from the filter boat to an interim storage container or product container depending on the batch size. If needed, the interim storage container will be used to combine and store PuO₂ from multiple furnace runs prior to filling the product container or convenience can that is used for storage of PuO₂ prior to packaging in the 3013 inner can. HBL will begin operations using a deferred packaging arrangement that allows the PuO₂ product to be stored in a Type B package² prior to start-up of the 3013 inner canning system. The specific details of this packaging have not been specified at this time; however, the following general principles apply to this and future operations. Moisture controls for the PuO₂ product will be instituted to limit moisture uptake to the greatest extent possible. These controls focus on monitoring glove box RH conditions, minimizing the time product is exposed to the glove box atmosphere, and establishing sampling and moisture analysis methods that provide a reliable yet conservative estimate of product moisture content.

For example, to minimize moisture adsorption during storage in the glove box line, the interim storage container and product containers may be placed into a second container with an elastomeric seal to limit exposure to ambient RH conditions. Once the product container has been filled and is ready for sampling, a core sampling tool will be used to collect a sample for moisture analysis and load into a sample vial with an O-ring seal. The core sample will be pulled from as near as practical to the container wall (i.e., coolest point in the container) and from the full bed depth of oxide in the product can to represent the bulk material. The sample vial will remain sealed until the thermogravimetric analysis (TGA) or TGA-mass spectrometry (TGA-MS) moisture analysis is performed.³ The product container mass will be recorded immediately after sampling to allow tracking of any additional moisture adsorption of the oxide based on container mass. This sample moisture measurement results plus any measured increase in the product container mass will be summed to estimate the total product moisture content. This calculated moisture content along with measurement uncertainty will be considered when comparing to the 3013 standard 0.5 wt % moisture limit.

Details of moisture analysis and deferred packaging will be presented as part of the HBL “20 Points” document used to demonstrate compliance with the 3013 Standard prior to packaging in a

² If the product containers are required to be inerted (e.g., to reduce oxygen content), an “inert” gas such as nitrogen, helium, or argon (rather than, for example, carbon dioxide) will be used to avoid interactions with the product material.

³ Note that TGA/TGA-MS procedures authorized for 3013 moisture analysis (or equivalent) will be used for sample analysis.

3013 compliant configuration and approved by the appropriate technical authority for 3013 operations.

1.5 Discussion

Prior DOE requests for 3013 equivalency were based on a technical evaluation of feed materials and process conditions (e.g., 750 °C calcination of chloride-bearing oxides) to demonstrate the proposed content would not impact container integrity or storage safety (Boak et al., 2002; Boak et al., 2003). The two processes of concern are corrosion and gas generation. In this case, the proposed content will be high-purity PuO₂ with little chlorine (F plus Cl <250 µg/g Pu).⁴ The RH within the package can be as high as the packaging RH, which may be as high as 70%. General corrosion, which may occur under these conditions, has been evaluated by the 3013 Standard as not a credible problem [A.6.3.2.6]. The small amount of chlorine will be homogeneously distributed throughout the high-purity PuO₂ product by the precipitation and calcination process. In order for the chlorine to cause pitting or stress-corrosion cracking, chloride salts must be present that can deliquesce to form liquids. This has not been observed in sealed containers with high-purity PuO₂ and less than 0.5 wt % water by either the SRS Destructive Examination (DE) program or the MIS program. Therefore, this review is primarily focused on the potential for gas generation to impact 3013 container safety.⁵

Because the material will be stabilized at 640 °C or greater rather than 950 °C, the HBL product is anticipated to have a higher specific surface area (SSA) and potentially higher carbon content than plutonium-bearing oxide materials represented in the MIS Shelf-Life Program. HBL has limited capability to control process glove box RH, and consequently, the higher SSA that results from calcination at lower temperatures poses a challenge to limit moisture re-adsorption.

Limited gas generation data is available for high-purity PuO₂ materials produced by calcination of plutonium oxalate at temperatures between 600 °C and 700 °C and having relatively high SSAs (i.e., between 5 m²/g and 15 m²/g) as expected for the HBL product. Short-term (i.e., 200 h to 400 h duration), small-scale gas generation tests were conducted at the Savannah River Technology Center (now SRNL) with PuO₂ having either weapons grade or fuel grade isotopic mixtures produced by anion exchange purification, precipitation of plutonium(III) oxalate, and calcination in air at 450 °C for 4 h followed by an additional 2 h at 700 °C (Livingston and Duffey, 2001; Duffey and Livingston, 2002). These materials had SSAs of approximately 10 m²/g (Jurgensen et al., 2005). Both weapons grade and fuel grade PuO₂ samples packaged in air with no added moisture (TGA LOI at 950 °C of 1.0 wt % and 0.5 wt %, respectively) consumed O₂ and generated H₂. With approximately 0.3 wt % added water (which was most likely >0.5 wt % total water), the weapons grade samples packaged in air generated H₂ at a much faster rate, but still consumed O₂; and with about 1.0 wt % added water these samples generated both H₂ and O₂. The fuel grade samples with about 0.8 wt % added water generated both H₂ and O₂ when packaged in air, N₂, or Ar. Therefore, while these short-term tests with high-purity PuO₂ having SSA in the range expected for HBL product suggests O₂ is not generated for samples packaged with <0.5 wt % moisture packaged in air, they do not preclude H₂ plus O₂ generation at some longer storage time or when packaged with lower initial O₂ content.

The MIS Shelf Life Program evaluated two samples of a high surface area product identified as MISSTD-1 with a SSA of 20–30 m²/g (Berg et al., 2012). This material was produced by oxalate

⁴ Verification that F plus Cl levels are <250 µg/g Pu will be achieved by measurement of samples of the oxide product.

⁵ It is critical to the equivalency evaluation that the HBL production process and PuO₂ product be isolated from potential chloride contamination associated with future HBL activities (e.g., 3013 oxide repackaging).

precipitation and calcination at 600 °C for 6 h. In the small scale container test, this sample most likely contained 0.7–1.0 wt % moisture and generated a low pressure of H₂ and O₂. The maximum pressure measured in this test was approximately 100 kPa, and the associated gas composition includes about 4 vol % H₂ and 15 vol % O₂. The history of the MISSTD-1 material indicates extended exposure to the glove box atmosphere and is described as “aged” material to indicate this sample was not freshly calcined prior to loading. This same material when loaded into a large scale container did not generate H₂ or O₂; however, a significant quantity of N₂ was produced during this test. Samples analyzed from the large scale test container of MISSTD-1 indicated a moisture content of ~1 wt % and C content also close to 1 wt %. The moisture content, C content, and duration of air exposure for the MISSTD-1 materials were all greater than allowed for HBL product under the proposed 3013 equivalency. However, due to the relatively high SSA of MISSTD-1, coverage of the oxide surface by adsorbed water may have resulted in fewer monolayer equivalents (ML) of adsorbed water than will be possible for the HBL oxide product. The potential for water adsorption by PuO₂ and the implications for gas generation are addressed in section 2.4.

1.6 Equivalency of Alternative Processing Pathway

The basis for determining whether an alternative stabilization is equivalent lies in establishing that it is equally effective in meeting the objectives for stabilization listed in DOE-STD-3013. The final objective of stabilization is to ensure the nuclear material can be stored safely for up to 50 years in a specified, sealed, stainless steel container. For the purpose of this document, equivalency means that the proposed lower temperature stabilization process meets the same objectives as the process requirements set forth in the Standard with the goal of ensuring long-term stability in storage. Equivalency does not mean that the material produced using a calcination temperature of 640 °C has the same material properties, such as SSA, as the material produced at a calcination temperature of 950 °C.

The next section discusses and summarizes the evidence that high-purity PuO₂ produced in HBL and stabilized at 640 °C or greater instead of 950 °C will be equivalent to material stabilized in compliance with DOE-STD-3013 for each of the stated purposes of stabilization. It is shown that the material must be handled in a way to prevent excessive adsorption or readsorption of water that occurs because of the higher SSA. Assurance of adequate stabilization will be verified by defining appropriate quality assurance and surveillance measures including moisture measurement.

2.0 Discussion of Technical Issues

2.1 Elimination of Pyrophoric Materials

2.1.1 Issue Statement

The stabilization process is expected to oxidize any residual metal that may be present in the material so there remains little or no hazard from potential pyrophoric reactions to occur if containers are breached in an accident or when they are opened in the future. Stabilization is also expected to oxidize substoichiometric plutonium oxide to PuO₂. For the HBL oxide product, the question is how stabilization at no less than 640 °C will impact reactivity or pyrophoricity when compared to stabilization at 950 °C.

2.1.2 Technical Position

Elimination of pyrophoric materials in the HBL product will not be a concern because metal cannot credibly survive the aqueous chemical processes leading to plutonium oxalate.

Substoichiometric oxides are not expected to be a concern for material stabilized in an oxidizing environment at 640 °C or greater. Any undissolved metallic fines from the H-Canyon dissolution process are removed by filtration prior to anion exchange, oxidized under the proposed stabilization conditions, or have very limited potential for reaction in air (e.g., platinum, nickel, etc.).

2.1.3 Discussion of Available Data

Sources of metal in the HBL process include Pu metal and the dissolvable carbon-steel cans in which the Pu metal will be repackaged prior to dissolution. The dissolution time and conditions are expected to be sufficient to completely dissolve all metal charged to the dissolver (Pierce, 2011; Rudisill and Pierce, 2012). In the unlikely event that any incompletely dissolved metal particles remain after dissolution and are transferred from the Canyon dissolver to HBL, some of the particles could persist in the process and be collected along with the oxalate precipitate during filtration. However, if any such fine particles were not oxidized by stabilization in air at 640 °C for 4 h, they would be too unreactive or too dilute and too highly dispersed within the bulk oxide to be of concern for safe storage of the PuO₂ product.

There is ample literature evidence demonstrating the effectiveness of thermal conversion of both Pu(IV) and Pu(III) oxalate to PuO₂ at lower temperatures than being proposed for this equivalency even in inert atmosphere (Vigier et al., 2007; Myers, 1956). Conversion to PuO₂ is complete by 400 °C in air and by 600 °C in inert atmosphere, although the studies do not focus on trace residual reactant or intermediates. Waterbury et al. (1961) found the O/Pu atom ratios following calcination of Pu(IV) oxalate in air varied from 2.044 at 330 °C to 2.014 after 4 h at 1250 °C; thus, substoichiometric oxides are not anticipated in the HBL product.

2.1.4 Data Gaps

None.

2.2 Elimination of Organic Materials

2.2.1 Issue Statement

The stabilization process has an objective to destroy or drive off organics that may be present in PuO₂ materials to minimize the potential for radiolytic or thermal degradation that may lead to gas generation (particularly hydrogen) during storage. The question is whether stabilization at 640 °C will result in a product that contains unacceptably high levels of residual organic species compared to materials stabilized at 950 °C.

2.2.2 Technical Position

Published studies indicate that conversion of plutonium oxalate to PuO₂ proceeds to completion below 600 °C. Calcination at no less than 640 °C for 4 h is expected to destroy oxalate and any other organics that may credibly be present in the product following oxalate precipitation. This is supported by previous analyses of neptunium dioxide (NpO₂) produced in HBL by a similar process which determined the C content to be well below 1000 µg/g NpO₂ (Duffey, 2008). HBL product specifications require the C content to be ≤1000 µg/g of Pu. Formal requirement that the product specification has been met would assure that the residual carbon content is consistent with essentially complete conversion and not of concern for gas generation in the 3013 container. The acceptable C content must be demonstrated either by C measurement for each batch of PuO₂ or by process qualification.

2.2.3 Discussion of Available Data

The primary source of organic compounds in the HBL process is the addition of oxalic acid to precipitate plutonium(IV) oxalate. Although the oxalate ion ($C_2O_4^{2-}$) contains no H atoms and, therefore, is not a concern for H_2 generation, radiolytic or thermolytic decomposition of $C_2O_4^{2-}$ to produce CO or CO_2 is a plausible source for gas generation. In addition to oxalate, other potential sources of organic material in the HBL product are the nylon bags which contain the dissolvable carbon-steel cans of Pu metal, resin fines that pass through the anion column screen holding the resin in place, and Kynar from the precipitator paddle blades. Residual oxalate, resin, and Kynar were previously investigated by Crowder and Kyser (2009) as potential sources of C in NpO_2 produced by HBL. They concluded that residues of these materials were not present to any significant degree in the samples of HBL NpO_2 product examined, and these materials would have been detectable by TGA-MS analysis of the oxide product if they were present.

The nylon bags used in the dissolution process in H-Canyon have previously been shown to dissolve in HNO_3 -KF solutions such as will be used in this process (Kessinger and Clark, 2004). Organic material remaining in solution after dissolution would be transferred to HBL and either trapped on the resin or washed through the column. If trapped on the resin, some material could be eluted with the Pu product and end up in the oxalate precipitate. It is also conceivable that resin fines from the anion exchange process or Kynar from the precipitator paddle blades could be abraded and be incorporated in the oxalate precipitate.

Nylon is a family of thermoplastic polymers, generally referred to as polyamides, consisting of C, H, O, and N atoms. Reillex™ HPQ is a strong-base macroporous anion exchange resin composed of a copolymer backbone of 1-methyl-4-vinylpyridine and a divinylbenzene mixture (Crooks et al., 2000). Kynar is a thermoplastic fluoropolymer (poly-1,1-difluoroethene) consisting of C, H, and F atoms. Boak et al. (2002) report from the literature that decomposition of hydrocarbons and Cl-containing organics in air is essentially complete by 600 °C, the maximum rate of decomposition of rubbers occurs at less than 470 °C and is complete by 700 °C, and that decomposition of F-containing organics such as Teflon® begins around 350 °C with no further mass loss obtained above 750 °C. Therefore, all three sources of organic material identified above that may conceivably be incorporated in the plutonium oxalate precipitate are expected to be largely or completely decomposed by stabilization to no less than 640 °C in air for 4 h. Furthermore, any significant amount of undecomposed organic material remaining in the stabilized product would result in a failure to meet the product specification for carbon.

Several research groups have studied the thermal decomposition of Pu oxalate under both oxidizing and inert atmospheres. Most researchers followed mass loss as a function of temperature using thermobalances, using that data to identify intermediate products as well as temperature of completion of the conversion to PuO_2 . Some studies have removed material from the thermobalance at intermediate stages of the decomposition to try to identify intermediate products using additional analytical techniques such as X-ray diffraction and infrared or UV-Vis spectroscopy. Early work is summarized in Cleveland (1979). Subsequent studies have added information on the decomposition steps by using techniques such as infrared spectroscopy to identify reaction intermediates (Nissen, 1980; Karelin et al., 1990; Vigier et al., 2007).

There is general agreement that decomposition proceeds to complete conversion to PuO_2 regardless of whether the initial oxalate compound contains Pu(III) or Pu(IV) and regardless of whether the material is heated in an inert or an oxidizing atmosphere. In these laboratory-scale studies, the conversion to PuO_2 is complete below 400 °C in air and below 600 °C in an inert atmosphere such as argon.

2.2.4 Data Gaps

The oxalate decomposition literature regards a reaction as having reached completion when the rate of change is negligible relative to the rate of change early in the process. These studies generally have not focused on quantifying the residual trace C as a function of calcination temperature. It may be necessary to adjust conditions to meet the product C specification of $\leq 1000 \mu\text{g/g Pu}$.

As part of flow sheet evaluation for the proposed HBL process, it is a requirement that the C content of PuO_2 produced according to this flow sheet (Christopher, 2011) is below $1000 \mu\text{g/g Pu}$. Tests currently underway in SRNL to prepare a demonstration batch of PuO_2 per the nominal HBL flow sheet and characterize the product, including measuring total C (Crowder and Duffey, 2011) will help to fill some of the existing data gaps.

2.3 Reduction of Content of Water and Other Water-Producing Species

2.3.1 Issue Statement

To be judged as effective, stabilization must reduce total moisture content to below 0.5 wt %. This objective is intended primarily to mitigate against internal pressurization of a container due to radiolysis of moisture. For HBL oxide, the question is whether stabilization at $640 \text{ }^\circ\text{C}$ will remove water and other water-producing species so the residual water content is $<0.5 \text{ wt } \%$. In general, for oxide materials there is potential for physically adsorbed water, waters associated with hydrated compounds, and the surface hydroxide component of water associated with PuO_2 and other metal oxides. For high-purity PuO_2 from the HBL process, the primary concerns are physically adsorbed water and surface hydroxides.

2.3.2 Technical Position

Moisture measurement by an approved method, which includes heating to $1000 \text{ }^\circ\text{C}$ and measuring the volatilized moisture or the resulting weight loss after the sample cools (DOE, 2012), will verify that less than 0.5 wt % moisture remains in the stabilized HBL oxide product. Any sample failing this criterion will be stabilized again. Stabilization at no less than $640 \text{ }^\circ\text{C}$ for 4 h will drive off virtually all water and hydroxides (Veirs, 2002). It is expected that a small quantity of chemisorbed water (i.e., hydroxyl layer) well below 0.5 wt % will survive stabilization.

2.3.3 Discussion of Available Data

The specific 0.5 wt % limit is based on the limiting case assumption of complete conversion of the hydrogen content of water to H_2 gas, and the ability of a 3013 container to withstand the resulting internal pressure with an adequate safety margin (DOE, 2012). Achievement of this objective is the primary purpose of the 3013 requirements of thermally stabilizing to $950 \text{ }^\circ\text{C}$ for two hours followed by analysis of the residual moisture. Previous stabilization and packaging campaigns produced extensive data on the total volatiles after stabilization of PuO_2 to $950 \text{ }^\circ\text{C}$, all of which was assumed to be moisture for the purposes of certifying compliance with the 0.5 wt % moisture limit. A much smaller set of data is available showing the temperature dependence of the thermal desorption of moisture from oxide stabilized to $950 \text{ }^\circ\text{C}$. Generally the moisture found on the material is ascribed to a combination of a surface hydroxide layer and one or more monolayers of more loosely bound adsorbed water molecules. There is strong evidence that the loosely-bound monolayers of H_2O on the oxide surface will be desorbed using the proposed stabilization process at $640 \text{ }^\circ\text{C}$ or greater (DOE, 2012; Berg et al., 2012; Veirs et al., 2012). The principal concern for this form of moisture would be prevention of adsorption or re-adsorption between stabilization and packaging. Because the product oxide from the proposed low

temperature stabilization process is expected to have significantly higher SSA than oxide stabilized to 950 °C, adsorption or re-adsorption has the clear potential to lead to a total moisture content exceeding 0.5 wt %.

Thermal desorption profiles from PuO₂ after stabilization at 950 °C also consistently show a small moisture component that is volatilized above the proposed stabilization temperature of 640 °C or greater. The data suggest, but do not prove, that this component may form over weeks to months from H₂O already on the material in other forms or from H₂O vapor available in the storage atmosphere (Veirs et al., 2012). It is possible that material with a higher specific surface area would have significantly greater capacity for moisture that would not be removed under the proposed stabilization conditions. In that case, the result would be high rates of failure to meet the 0.5 wt % moisture criterion, which would be identified by the required moisture measurements prior to packaging.

2.3.4 Data Gaps

Existing data show that some moisture incorporated into batches of pure PuO₂ is not thermally volatilized at the proposed stabilization temperature (Berg et al., 2012; Veirs et al., 2012). No test data has been identified that quantifies the capacity for such moisture in the case of higher surface area PuO₂. If the ultimate capacity for such tightly-bound moisture is high enough to result in potential failure to meet the 0.5 wt % criterion, information on kinetics of its formation would be important in avoiding high failure rates. The data gaps indicate unknown risk of failure to meet the 0.5 wt %, a risk that could not be mitigated by restrictions on post-stabilization handling of the oxide. Moisture measurements and moisture uptake studies planned for PuO₂ that will be produced in SRNL per the nominal HBL flow sheet (Crowder and Duffey, 2011) are expected to fill some of the data gaps. However, non-compliant material would still be identified by the pre-packaging moisture measurement process.

2.4 Minimization of Potential for Adsorption or Readsorption of Water

2.4.1 Issue Statement

The potential for water adsorption depends on the availability of water, usually as water vapor in the post-stabilization handling atmosphere, and on the affinity of the material for moisture, whether through surface adsorption or chemical incorporation. Thermal stabilization to higher temperature than strictly required for oxalate decomposition serves to reduce the material surface area, thereby reducing the potential of the stabilized material to adsorb water upon cooling. For the HBL product, the question is whether stabilization at 640 °C for 4 h will be sufficient to reduce the oxide SSA and decrease potential for water adsorption so the product can be maintained at <0.5 wt % water if allowed to equilibrate with the handling atmosphere, or whether measures will be necessary to prevent the equilibrium condition from being achieved.

2.4.2 Technical Position

Moisture measurement will verify that less than 0.5 wt % moisture remains in the stabilized HBL oxide product immediately after stabilization and at the time of packaging. Any sample failing this criterion will be stabilized again. Process controls (which may include additional moisture measurements) and an integrated surveillance program will confirm the moisture content remains below 0.5 wt % including measurement uncertainty for packaged materials. This approach does not require specific limits on handling time and handling conditions except as necessary to assure that the measured moisture on the sample remains representative or bounding of the moisture on the parent batch at the time of packaging. However, due to the increased potential for hydrogen plus oxygen generation for high-purity oxide exposed to high RH, the RH at the stabilized oxide

surface (i.e., lowest material temperature) should be limited to 60% (Veirs et al., 2012). Furthermore, it is necessary to minimize exposure of the batch to a humid atmosphere, as the SSAs will be large enough that the material will fail the 0.5 wt % moisture criterion if equilibrated with such an atmosphere.

2.4.3 Discussion of Available Data

Water adsorption by high-purity PuO₂ produced from oxalate precipitation is primarily a function of RH, SSA, and temperature (Veirs, 2002). The potential for water adsorption is an important consideration for the proposed HBL product due to the expected high product SSAs (i.e., 5–15 m²/g) and high processing RH (i.e., 40–70%) in HBL. These conditions increase the potential for the HBL product to exceed the 0.5 wt % moisture limit and will increase the potential for H₂ and O₂ gas generation (Veirs et al., 2012).

PuO₂ produced at LANL for MOX LTA during the time frame of 2001–2008 using a flow sheet similar to what is planned for HBL had measured SSAs ranging from 5–15 m²/g with an average ($\pm 1\sigma$) of 9.8 ± 1.8 m²/g (Alwin, 2007; Bluhm, 2005). A broader survey of the literature on the dependence of SSA on calcination temperature (Daniel, 2012) shows that SSAs in this range for HBL product would be consistent with that observed in other laboratories. Laboratory-scale PuO₂ samples produced in support of the HBL MOX feed mission (Crowder and Duffey, 2011; Crowder et al., 2012) also have SSAs in this range.

Based on Brunauer-Emmett-Teller (BET) adsorption isotherm theory as well as experimental observations of water adsorption on PuO₂ (Haschke and Ricketts, 1997), the number of monolayer equivalents (ML) of water adsorbed by PuO₂ at equilibrium increases from about 1.5 ML at 30% RH to about 2 ML at 50% RH and to more than 3 ML at 70% RH (Veirs et al., 2012). One ML is equal to about 0.22 mg H₂O/m² of oxide surface; therefore, PuO₂ with a SSA of 10 m²/g in equilibrium with a RH of 50% would adsorb an amount of water equal to about 0.44 wt %, and if equilibrated at higher RH would exceed 0.5 wt %.

Based on a review of the available data for O₂ generation by high-purity PuO₂, Veirs et al. (2012) also conclude that a minimum of 2 ML of adsorbed water is required for production of H₂ and O₂. Furthermore, under HBL processing conditions it is possible to produce PuO₂ that will adsorb 2 ML of water with <0.5 wt % total water content.

Because there is a possibility that HBL product may produce H₂ and O₂, determination of the maximum attainable pressure is required to demonstrate packaging integrity. Veirs et al. (2012) conclude that the maximum pressure that could be generated in a 3013 container by 5000 g of high-purity PuO₂ with SSA in the range expected for HBL product equilibrated with 60% RH and containing <0.5 wt % water is 277 kPa (Table 1). This calculated pressure assumes (1) that both a strongly bound layer (SBL) of chemisorbed water equivalent to 0.5 ML and up to two ML of molecular (physisorbed) water are not available to generate pressure by radiolysis, and (2) all of the water beyond these first 2.5 ML is completely converted to a stoichiometric mixture of H₂ and O₂ gas. Figure 3 illustrates the sensitivity of the maximum calculated pressure to changes in equilibrium RH (i.e., the pressure increases about 60 kPa for every 1% RH increase) for 5000 g of the same high-purity material using the same conditions evaluated in Table 1. The conditions selected for calculating the pressure data presented in Table 1, are considered most representative of the HBL product (Veirs et al., 2012). The expression for c as used in the construction of Table 1 and Figure 3 is $c = e^{\Delta H/RT}$, where ΔH is the excess heat of adsorption compared to the heat of condensation of the liquid.

Table 1. Calculated maximum pressures in kPa as a function of the mass of oxide and the RH the material experiences using $T = 35\text{ }^{\circ}\text{C}$, $c = 7$, and $\text{SBL} = 0.5$.

Mass (g)	70%	65%	60%	55%	50%
5000	876	579	277	0	0
4500	770	509	243	0	0
4000	669	442	211	0	0
3500	572	378	181	0	0
3000	480	317	152	0	0
2500	391	258	124	0	0
2000	306	202	97	0	0
1500	225	149	71	0	0
1000	147	97	46	0	0

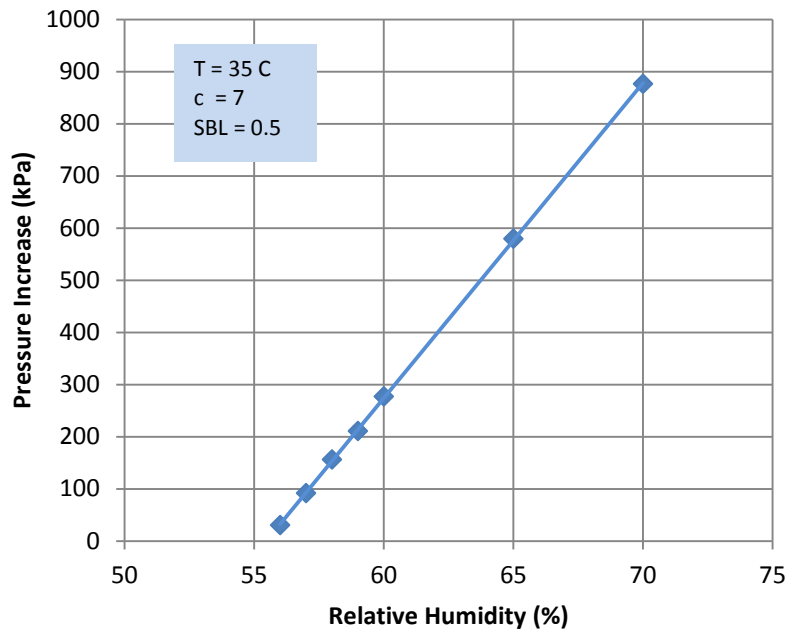


Figure 3. Calculated maximum pressure as a function of equilibrium RH for 5000 g of PuO₂.

Rawls et al. (2010) carried out a series of tests to determine the threshold for deflagration-to-detonation transition (DDT), structural loading, and structural response of the 3013 container in the event of an accidental explosion of evolved gas within the storage container (Liang and Shepherd, 2007a-c). They concluded that DDT of a stoichiometric mixture of H₂ and O₂, as well as mixtures diluted with nitrogen and helium, within the 3013 container at initial pressures up to 3.5 bar (350 kPa) does not threaten the structural integrity of the outer container. Furthermore, Rawls (2012) evaluated the possibility of an HBL 3013 container explosion with an initial pressure of 380 kPa (i.e., approximately 100 kPa nitrogen and approximately 280 kPa stoichiometric hydrogen-oxygen) and concluded there is sufficient structural capacity in the 3013 container to prevent failure. Therefore, generation of both H₂ and O₂ by HBL product exposed to

≤60% RH and containing up to 0.5 wt % water is not expected to exceed the conditions evaluated by Rawls (2012) and will not pose a threat to the structural integrity of the 3013 container.

2.4.4 Data Gaps

The rate of water adsorption of large batches (i.e., 1-3 kg per container) of freshly stabilized oxide within HBL is not known. The rate is likely conservatively bounded by laboratory small-scale studies, since deeper oxide beds will provide more resistance to water diffusion and mass transfer than the shallow samples used in laboratory testing. Nevertheless, laboratory sample equilibration times are relatively low (i.e., minutes to hours) and would lead to the expectation that the surface would be fully equilibrated by adsorbing moisture prior to packaging (Berg et al., 2012; Haschke and Ricketts, 1997). In any case, non-compliant material would still be identified by the pre-packaging moisture measurement process.

2.5 Stabilization of Potential Gas-Producing Constituents

2.5.1 Issue Statement

Stabilization must meet the objective of effectively removing other non-moisture, gas-producing impurities such as nitrates (NO_3^-), sulfates (SO_4^{2-}), and carbonates (CO_3^{2-}) in PuO_2 . The question is whether stabilization at 640 °C for 4 h will be sufficient to eliminate or reduce to acceptable levels such impurities in the HBL product.

2.5.2 Technical Position

With no valence adjustment step in the HBL process, there is no credible source of SO_4^{2-} after dissolution (Kyser and King, 2012). Nitrate is plentiful because the process occurs in HNO_3 solution, but the bulk of the HNO_3 is removed during the anion exchange and oxalate precipitation steps, and residual NO_3^- is expected to be decomposed by stabilization at 640 °C or greater for 4 h (Boak et al., 2002; Waterbury et al., 1961). Although some residual CO_3^{2-} could result from incomplete decomposition of oxalate, the relatively small amounts of C, as well as N^6 and S, allowed per specification in the HBL PuO_2 product (1000 µg/g, 400 µg/g, and 250 µg/g of Pu, respectively) do not pose a significant gas generation concern. Significantly higher levels of each impurity have been present in material stored for five to ten years in 3013 containers (Kessinger et al., 2010), and in material subjected to shelf-life tests for up to ten years (Berg et al., 2012), and in no case have they led to levels of gas generation that are of concern for over-pressurizing a 3013 container (Almond et al., 2010).

2.5.3 Discussion of Available Data

Both shelf-life studies and destructive examinations of production containers have shown that some thermally stabilized impure oxides can release minor quantities of CO_2 and CO into the container headspace during storage (Duffey et al. 2010; Almond et al., 2010). The quantities are far below levels of concern for pressurization. Destructive evaluations of containers with up to 1.4 wt % total carbon have shown partial pressures of CO_2 no higher than 5 kPa after more than five years of storage.

Shelf-life studies of gas generation at LANL have included several tests on material (MISSTD-1) from a parent lot of pure oxide that was prepared by calcining Pu(III) oxalate at 600 °C for six hours (Berg et al., 2012). Total carbon content of the parent was measured as 0.29 wt %. The

⁶ H-Area is not required to verify the nitrogen levels in the product. MOX Services will confirm the nitrogen limits are met with statistical sampling and analysis prior to dissolving.

partial pressure of CO₂ in 1:500 scale containers with 10 grams of material heated to 55 °C had risen to 1.1 kPa three months after the start of the test and was at the same value one year later. A kilogram-scale test on the same material showed only 0.02 kPa CO₂ when the headspace gas was sampled after approximately 10 years.

Other LANL shelf-life experiments on pure oxides calcined to 950 °C observed somewhat higher levels of CO₂, though still far below a level of concern for container pressurization. For example, TS707001 produced a maximum of 30 kPa of CO₂ (Duffey et al., 2010). Chemical analysis indicated less than 0.01 wt % carbon. The SSA of this material was measured at 2.3 m²/g, much lower than that of MISSTD-1. Because of the low surface area and high water loading, H₂O may effectively displace adsorbed carbon species from the surface and lead to a higher proportion in the gas phase. But even in these cases, volatile carbon-containing species are far below pressures that would raise concerns about container integrity.

In summary, all container surveillance and shelf-life studies indicate that carbon-containing species (CO₂, CO, etc.) are not significant contributors to headspace pressure even after years of storage. The carbon content of some of the materials in these studies has significantly exceeded the allowed level of 1000 µg/g Pu for the HBL product. Where carbon is present, operating experience indicates that it remains almost entirely in non-volatile forms.

2.5.4 Data Gaps

None.

3.0 Conclusions and Recommendations

The HBL process and associated controls required for supporting the stabilization of PuO₂ at no less than 640 °C for 4 h have been evaluated and determined to generate a product equivalent, relative to meeting the DOE-STD-3013 criteria, to plutonium-bearing oxides currently packaged under the 3013 standard. The primary limitation identified by this report is the high-purity oxide produced in HBL will have a greater tendency to adsorb moisture than PuO₂ stabilized at 950 °C. By maintaining the RH at the product surface to 60% or less (including measurement uncertainty) and total moisture content to less than 0.5 wt % (including measurement uncertainty), the composition and pressure of gas generated by this product is bounded by the maximum acceptable pressure of a stoichiometric mixture of hydrogen and oxygen in the 3013 container (Rawls, 2012). This assessment is based on evaluation of available scientific literature for similar materials to define a conservative estimate of product performance. The margin associated with this evaluation relies on HBL implementing the following controls:

- Plutonium(IV) oxalate product is stabilized in an oxidizing atmosphere at no less than 640 °C for a total of 4 h or longer.
- The total product impurities shall be less than 23,600 µg/g Pu (2.1 wt %). Chloride plus fluoride content is limited to 250 µg/g Pu and carbon content is limited to 5000 µg/g Pu. Variation in metallic impurities identified by MFFF limits are not a direct concern for this evaluation.
- RH at the product surface, taking into account any difference between ambient temperature and product temperature, needs to remain below 60% RH.
- Moisture samples will be collected near the container wall and represent the full volume of the product can. Any increase in mass by the product following sampling shall be conservatively addressed as part of the moisture analysis.
- Moisture analysis will use TGA or TGA-MS methods approved by the 3013 Standard and assure samples are heated to 1000 °C as part of the analysis. Total moisture content

shall be less than 0.5 wt % including analytical uncertainty.⁷ Representative samples of the HBL product will be placed in the MIS program to validate material performance at the 0.5 wt % moisture limit with samples representing both the high and low SSA values that are expected by the HBL process.

- Product wattage is limited only by restrictions on content imposed by the 3013 Standard “to ensure the heat generation rate of the contained materials will not exceed 19 watts at any time during the 50-year storage life” (DOE, 2012).

After reviewing the proposed HBL flow sheet for producing high-purity PuO₂ for feed to the MFFF and available supporting data, the authors conclude that the proposed HBL process conditions are capable of producing PuO₂ that poses no safety concern for packaging or storage in the 3013 required configuration, provided the stabilized product is handled in a way to minimize adsorption of water. The technical team also concludes that moisture adsorption by PuO₂ stabilized to at least 640 °C for 4 h and handled in ambient air with a RH as high as 70% poses the greatest challenge to meeting the DOE-STD-3013 packaging requirements. As the RH increases above 60%, the equilibrium moisture content increases to levels that increase the risk of exceeding the 0.5 wt % moisture content limit in a practical handling time.

The anticipated gas generation pressures and compositions for this product packaged with less than 0.5 wt % moisture will be within the limits of observations for materials previously evaluated by the MIS Shelf Life program. In all cases, the acceptable pressure of a mixture of hydrogen and oxygen in the 3013 container (Rawls, 2012) is greater than the maximum pressure calculated for the proposed HBL product. Incorporation of samples of actual HBL product into the MIS Shelf Life Program will ultimately validate the anticipated gas generation behavior of these materials.

⁷ Previously, DOE sites have imposed measurement limits of 0.4 wt % mass loss for TGA and 0.32 wt % moisture by TGA-MS to ensure compliance with the 0.5 wt % moisture limit (see, e.g., McNew, 2003).

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Appendix A. Chemical Impurity Limits for HB-Line Feed to MFFF

Table A-1. Chemical Impurity Limits for HB-Line Feed to MFFF

Chemical Component	Maximum Content^a ($\mu\text{g/g Pu}$)	Maximum Exceptional Content^b ($\mu\text{g/g Pu}$)
Ag (silver)	250	10,000
Al (aluminum)	500	10,000
B (boron)	100	1000
Be (beryllium)	100	2000
Bi (bismuth)	100	1000
C (carbon)	1000	5000
Ca (calcium)	500	10,000
Cd (cadmium)	10	1000
Cl (chlorine)	(+F <250)	500
Co (cobalt)	100	10,000
Cr (chromium)	1000	1500
Cu (copper)	100	500
Dy (dysprosium)	1	1000
Eu (europium)	1	1000
F (fluorine)	(+Cl <250)	350
Fe (iron)	2000	3000
Ga (gallium)	12,000	12,500
Gd (gadolinium)	3	250
In (indium)	20	1000
K (potassium)	300	10,000
Li (lithium)	400	10,000
Mg (magnesium)	500	10,000
Mn (manganese)	100	1000
Mo (molybdenum)	100	1000
N (nitrogen) ^c	400	400
Na (sodium)	1000	10,000
Nb (niobium)	100	3500
Ni (nickel)	5000	12,000
P (phosphorus)	200	1000
Pb (lead)	200	1000
S (sulfur)	250	1000
Si (silicon)	200	200
Sm (samarium)	2	1000
Sn (tin)	100	2500
Ta (tantalum)	200	500
Ti (titanium)	100	2500
Th (thorium)	100	100
V (vanadium)	300	2500
W (tungsten)	200	2500
Zn (zinc)	150	1000
Zr (zirconium)	50	1000
Total Impurities^d	23,600	

^a “Maximum content” is the standard value that the feedstock shall meet during routine operations.

^b “Maximum exceptional content” is the maximum value for which the feed is acceptable as long as the total impurities value is not exceeded.

^c H-Area is not required to verify the nitrogen levels in the product. MOX Services will confirm the nitrogen limits are met with statistical sampling and analysis prior to dissolving.

^d Impurities that are not listed are assumed present at levels that do not affect MFFF safety, process, and product quality.

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