

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

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February 2013

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Prepared for the U.S. Department of Energy under
contract number DE-AC09-08SR22470.



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Printed in the United States of America

**Prepared for
U.S. Department of Energy**

Keywords: *Oxalate, plutonium
oxide, stabilization, 3013
Standard*

Retention: *Permanent*

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EXECUTIVE SUMMARY

The U.S. Department of Energy (DOE) Standard for Stabilization, Packaging, and Storage of Plutonium-Bearing Materials, DOE-STD-3013, provides requirements for stabilizing oxides containing at least 30 weight percent (wt %) plutonium (Pu) plus uranium by heating in an oxidizing atmosphere to a minimum of 950 °C for at least two hours. In this document, the technical basis for reducing the minimum stabilization temperature to 625 °C for plutonium dioxide (PuO₂) produced in HB-Line at the Savannah River Site (SRS) is provided as an alternative that is technically equivalent in terms of safety.

In alignment with the National Nuclear Security Administration program to disposition 34 metric tons of surplus weapons-grade Pu, the HB-Line facility at SRS will produce high-purity PuO₂ with a targeted stabilization temperature of 650 °C as feed for the Mixed Oxide (MOX) Fuel Fabrication Facility (MFFF). MFFF receipt of PuO₂ feed requires packaging in conformance with DOE-STD-3013 to comply with the facility's safety basis. The HB-Line product will be dissolved in the MFFF for purification by aqueous polishing prior to producing PuO₂ for use in MOX fuel production. The stabilization conditions imposed by DOE-STD-3013 for PuO₂, specifically heating to a minimum of 950 °C for two hours, cannot be met by HB-Line as currently configured. In addition, approximately 250 kilograms of the anticipated 3.7 metric tons of HB-Line product will be used directly in MOX fuel production, which targets calcination at 650 °C based on product specifications. Consequently, HB-Line initiated a technical evaluation to define acceptable operating conditions for stabilization of high-purity PuO₂ that fulfills the 3013 criteria for safe storage. The purpose of this document is to establish the minimum operating conditions for the HB-Line process to produce PuO₂ that meets the material performance requirements of the 3013 stabilization process.

This 3013 equivalency reduces the prescribed minimum stabilization temperature for the HB-Line product from 950 °C for two hours to 625 °C for four hours and requires the product be handled and packaged in a way that precludes formation of a flammable gas mixture within the 3013 container. All other stabilization and packaging criteria identified by DOE-STD-3013 apply. The PuO₂ produced under these conditions will have a higher specific surface area than PuO₂ stabilized at 950 °C and, consequently, will have the capacity to adsorb more water from the atmosphere under identical process conditions. In addition, the product must meet the MFFF acceptance criteria that limit total product impurities (see Appendix, Table A-1 for actual limits).

The PuO₂ produced under the process conditions and material specifications defined in this equivalency presents no unique safety concerns for packaging and storage in the 3013 configuration when handled in a manner that precludes formation of a flammable gas mixture within the 3013 container. However, the details for handling, packaging and associated safety limits that ensure a flammable gas mixture is not generated shall be established and approved as part of the HB-Line "20-Points" documents.

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LIST OF ABBREVIATIONS

AMNMSP	Assistant Manager for Nuclear Materials Stabilization Project
3013	DOE-STD-3013: Stabilization, Packaging, and Storage of Plutonium-Bearing Materials
°C	degrees Celsius
DOE	U.S. Department of Energy
g	gram
kPa	kilopascal
L	liter
LANL	Los Alamos National Laboratory
m	meter
M	molar
MFFF	Mixed Oxide Fuel Fabrication Facility
MIS	Materials Identification and Surveillance
ML	monolayer equivalents
MOX	mixed oxide
Pu	plutonium
PuO ₂	plutonium dioxide
SRNL	Savannah River National Laboratory
SRS	Savannah River Site
TGA	thermogravimetric analysis
TGA-FTIR	thermogravimetric analysis – Fourier transform infrared spectroscopy
TGA-MS	thermogravimetric analysis – mass spectrometry
wt %	weight percent

1.0 Introduction

1.1 Purpose

This report documents the technical basis for determining that stabilizing high-purity PuO₂ derived from oxalate precipitation at the SRS HB-Line facility at a minimum of 625 °C for at least four hours in an oxidizing atmosphere is equivalent to stabilizing at a minimum of 950 °C for at least two hours as regards meeting the objectives of stabilization defined by DOE-STD-3013 (DOE, 2012) if the material is handled in a way to prevent excessive adsorption of water. Establishing technical equivalency will enable HB-Line to stabilize oxalate precipitate at a targeted temperature of 650 °C in order to produce and package PuO₂ for use by the MFFF.

1.2 Background

HB-Line plans to produce high-purity PuO₂ using conditions appropriate for manufacture of MOX fuel (Christopher, 2011) at the MFFF. The MFFF requires incoming material to be packaged in 3013-compliant containers in order to meet the MFFF safety basis and support automated handling of the PuO₂ feedstock. To meet current 3013 Standard requirements, the packaged material must be stabilized at a minimum of 950 °C for at least two hours. The HB-Line process target temperature is 650 °C. Reducing the required stabilization temperature of the HB-Line 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 PuO₂ produced under these conditions will have a higher specific surface area than PuO₂ stabilized at 950 °C, and thus, will have the capacity to adsorb more water from the atmosphere under identical process conditions. Consequently, HB-Line requested assistance from the Savannah River National Laboratory (SRNL) and Los Alamos National Laboratory (LANL) to develop a technical basis to demonstrate 3013 equivalency of lower-temperature stabilization for HB-Line oxide from oxalate precipitation.

The DOE-STD-3013 allows requests for equivalency for certain criteria required by the Standard. Equivalency requests are submitted for approval to the Assistant Manager for Nuclear Materials Stabilization Project (DOE, 2012). Such requests for equivalency may include “determination that a proposed alternative criterion or alternative approach to satisfying one or more criteria is technically equivalent, in terms of safety, to the Standard Criteria.” The DOE has previously approved two submittals (Boak et al., 2002, 2003) for stabilization of chloride-bearing Pu oxides at 750 °C as equivalent following technical evaluation of the proposed alternative stabilization criteria. This request for technical equivalency follows a similar approach to that taken in Boak et al. (2002) to evaluate the effectiveness of the proposed alternative stabilization criteria for meeting the stabilization objectives listed in DOE-STD-3013.

The current HB-Line facilities were built in the mid-1980s, and have been used for production of Pu-238, Pu-239 and Np-237 oxide products along with other DOE Office of Environmental Management missions. The process experience associated with these past production campaigns demonstrates the facility’s capability to meet rigorous production requirements. The glove box atmosphere in HB-Line is filtered ambient air, and up to 70% relative humidity may occur within the processing glove boxes, so one of the challenges is ensuring that the moisture content of the material is properly controlled. To date no material of such high specific surface area has been packaged under the 3013 Standard after exposure to such high relative humidity. However, the Hanford Site was able to package materials containing hygroscopic chloride salts in a humid atmosphere (up to 60% relative humidity) and effectively limit moisture uptake.

High-purity PuO₂ powder with high specific surface area in equilibrium with moist air can generate flammable gas mixtures in a sealed container (Veirs et al., 2012a and Veirs et al., 2012b). Although the 3013 Standard does not specifically address whether flammable gas mixtures are allowed, the safety analysis for transportation of plutonium-bearing oxide contents stabilized to the 3013 Standard relies on the oxygen concentration of the headspace gas remaining below 5% to minimize the impact of postulated transportation accidents. Since the basis for packaging PuO₂ per the 3013 Standard includes an implied

requirement to produce shippable packages, this equivalency specifically prohibits packaging materials that will result in the formation of flammable gas mixtures.

After anion exchange, oxalate precipitation, and calcination, the HB-Line product will be stored at SRS until the capability for welding 3013 inner and outer containers is established. This equivalency defines the requirements for stabilizing HB-Line product during the initial calcination that converts the oxalate to PuO_2 and includes an additional requirement applied at the time of packaging that the material will not generate a flammable gas mixture within the 3013 container. This equivalency does not address the requirements for interim storage between stabilization and packaging. Material can meet the stabilization requirements and still generate a flammable gas mixture as discussed in Section 2.4. The deferred packaging process defined in DOE-STD-3013 section 6.1.4 does not include the requirement that the material will not generate a flammable gas mixture, and therefore, compliance with the 3013 Standard cannot be used to ensure a flammable gas mixture is not generated during interim storage. The K-Area Interim Safe Storage Criteria 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 to ensure a flammable gas mixture is not generated during interim storage are not addressed in this evaluation.

Prior to initiating 3013 packaging under this equivalency, a formal review and approval of the documents identified in Appendix B of the *Savannah River Site Stabilization and Packaging Requirements for Plutonium Bearing Materials for Storage* (Gupta et al., 2000) shall be completed to establish the adequacy of HB-Line procedures and controls to prevent formation of a flammable gas mixture within the 3013 package. The list of 20 documents identified in Appendix B of Gupta et al. (2000) are commonly referred to as “20-Points” documents and the activities associated with development, review, and approval of these documents is called the “20-Points” process. As part of the “20-Points” process, HB-Line will define the process used for collecting and analyzing moisture samples; controls that are required for deferred packaging; and measurement controls associated with furnace temperature, product mass, relative humidity, product purity, etc. The “20-Points” process for material packaged under this equivalency must ensure that procedures are implemented that prevent conditions supporting formation of flammable gas mixtures in the 3013 container or associated Type B shipping containers. The associated “20-Points” documents will be technically reviewed and formally approved by the Assistant Manager for Nuclear Materials Stabilization Project (AMNMSP) at the DOE Savannah River Operations Office. This is the same process and approval authority required for requesting an equivalency under the DOE-STD-3013.

As HB-Line begins production of PuO_2 under this equivalency, samples of representative material will be included in the Materials Identification and Surveillance (MIS) Shelf Life Program to fulfill requirements of the 3013 Standard.

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 Pu oxide;
- 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 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 and formation of flammable gas mixtures 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 3013 Standard specifies that prior to packaging, 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.

Allowing a lower minimum stabilization temperature for high-purity PuO_2 could impact storage because it might be less effective at removing potential gas-producing constituents and will result in material with higher specific surface area. The greater concern here is that material with higher specific surface area will require more care to minimize re-adsorbing gas-producing constituents after stabilization. In particular, the potential to exceed the 0.5 wt % moisture limit will be higher as a result of the lower stabilization temperature, and must be addressed by stabilization verification and subsequent material handling requirements.

The potential for oxygen generation by PuO_2 having a moisture content less than 0.5 wt % must also be addressed in justifying an equivalency, even though this is not an explicit stabilization objective in the 3013 Standard. The 3013 Standard addresses the possibility of oxygen generation only by a limited class of salt-bearing materials, and deems it unlikely. The phenomenon has not been observed for pure oxides stabilized to 950 °C. However, recent studies (Veirs et al., 2012a and Veirs et al., 2012b) show that oxygen generation is more credible for oxide stabilized to lower temperature and subsequently handled in a high relative humidity atmosphere that results in substantial water adsorption. This possibility must be prevented, even though it is not an explicitly stated goal of stabilization in the 3013 Standard, because transportation requirements dictate that a flammable mixture of gases be avoided within the package.

1.4 Problem Definition and Process Description

A process description is provided in the following section to provide an understanding of the overall process and not to specify controls; controls are identified in subsequent sections. The reduced stabilization temperature equivalency will apply only to high-purity PuO_2 containing less than 2.1 wt % total impurities (McAlhany, 2012). The PuO_2 will be produced in the SRS H-Canyon and HB-Line facilities for eventual use as feed into the MFFF process. The chemical impurity limits specified for the oxide product in McAlhany (2012) are listed in the Appendix. The combined H-Canyon/ HB-Line flow sheet (Garrison and Clifton, 2012; Garrison, 2012) is summarized below. The identified flow sheet provides nominal process conditions which may vary during normal facility operations without impacting the conclusion of this evaluation. This flow sheet is similar to the flow sheet that was used by LANL to produce PuO_2 for MOX Lead Test Assemblies 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. Prior to establishing the capability to weld 3013 cans the interim package will consist of a slip lid can that will be bagged and packaged in a secondary filtered can before loading in the 9975.

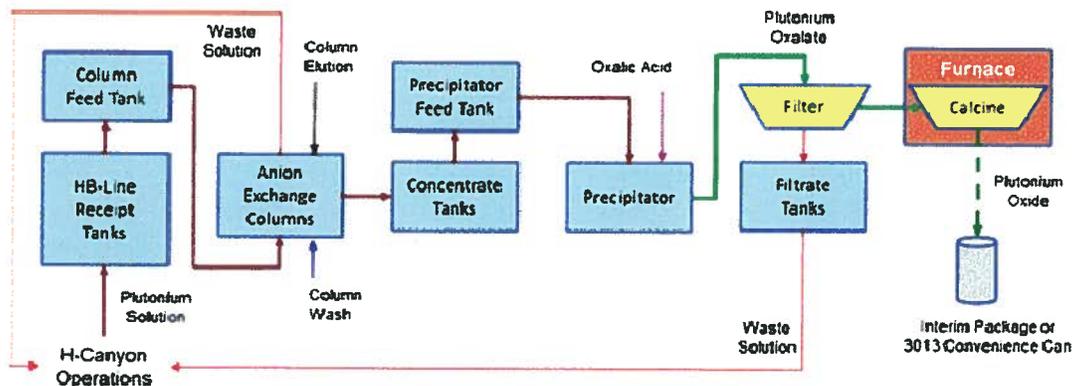


Figure 1. Block diagram of the HB-Line PuO_2 production process.

After establishing 3013 welding capability, HB-Line currently plans to use a stainless steel, crimp sealed Cogema container as the convenience can for DOE-STD-3013 packaging. The Cogema container incorporates features specifically designed for MFFF to accommodate automated processing. Details of the packaging configuration including inner and convenience cans will be documented and submitted for approval per “20-Points” documents, Appendix B, no. 7 (Gupta et al., 2000).

1.4.1 Dissolution

H-Canyon will receive Pu metal packaged in dissolvable carbon-steel cans that are sealed to minimize oxidation of the metal and packaged in nylon bags for contamination control. The quality of the reagents and process water used as part of PuO₂ production are monitored to avoid addition of any undesired contaminants. 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. 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⁻¹ iron, 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 HB-Line. The Pu concentration in the HB-Line feed will depend on a number of variables associated with criticality safety controls but is expected to range from 2 to 4 g L⁻¹. The impurities associated with H-Canyon dissolution, along with those initially in the Pu metal, are subsequently removed by the HB-Line anion exchange and precipitation operations. Although the starting material for the current flow sheet is Pu metal, the arguments for 3013 equivalency apply to PuO₂ produced using the identified flow sheet, as long as the product does not exceed the limits defined for moisture and other impurities.

1.4.2 Anion Exchange

HB-Line 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 HB-Line, the column feed solution will be analyzed to verify nitric acid concentration prior to loading the anion columns. No valence adjustment step is required based on prior experience for short term storage of low concentration (2 to 4 g L⁻¹) Pu in nitric acid solutions. The columns are conditioned with nominally 8 M nitric acid, loaded with the feed solution from H-Canyon, and 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-micron pore size filter (HB-Line, 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 nitric acid. The combined product solution from both columns is expected to contain greater than 40 g L⁻¹ Pu in low molarity nitric acid (Garrison, 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 HB-Line process control strategy.

1.4.3 Precipitation

The anion exchange product solution will be fed to the HB-Line precipitator, and Pu will be precipitated by the addition of nominally 0.95 M oxalic acid solution (direct strike precipitation). The precipitator solution will be maintained at approximately 50 ± 5 °C during precipitation and allowed to digest for five minutes or longer prior to filtration. A total of two moles of oxalic acid will be added per mole of Pu plus enough oxalic acid to achieve approximately 0.1 M excess (Garrison, 2012; Smith, 2012).

1.4.4 Filtration

The resulting slurry will be transferred to the HB-Line filtrate tank and the precipitate collected in a filter boat with a nominally 10-micron pore size stainless steel screen. During the filtration operation, a wash solution consisting of low molarity nitric and oxalic acids will be utilized to flush the precipitator vessel and wash the Pu oxalate filtrate to remove additional soluble impurities. When filtration is complete, the

filter boat will be lowered and air dried for approximately 60 minutes by pulling air through the filter cake to remove excess moisture prior to calcination (Garrison, 2012; Smith, 2012).

1.4.5 Calcination

In HB-Line, the filter boat also serves as the calcination furnace boat. To initiate the calcination step, the filter boat will be raised into the furnace and heated to a minimum bed temperature of 625 °C for at least four hours while pulling air through the filter cake at a minimum of 0.5 standard cubic feet per minute as measured by a downstream rotameter. Figure 2 illustrates the furnace layout and identifies the basic components. The cake temperature probe is located along the centerline of the product bed and will be used to measure a calcination temperature that is anticipated to be near the average cake temperature. The cake temperature probe thermocouple will have been calibrated with traceability to the National Institute of Standards and Technology. The furnace temperature will be controlled to achieve a target product bed temperature of 650 °C; accounting for uncertainty in this temperature, at no location in the product bed will the temperature be less than 625 °C. 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 product will be transferred 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 and prevention of flammable gas formation for the packaged 3013 PuO₂ product.

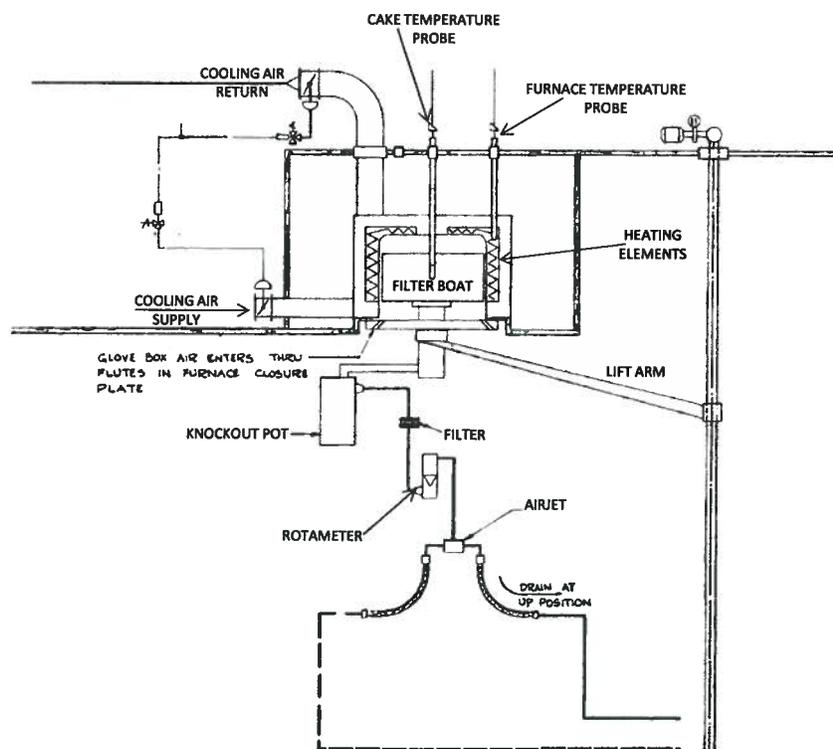


Figure 2. Schematic of the HB-Line calcination furnace.

The relative humidity of the glove box atmosphere will be monitored by two independent probes in the processing area; hand-held relative humidity probes may also be used. The ability to limit moisture adsorption will be dependent on a combination of multiple process controls. Controls may include maintaining the product temperature greater than the ambient glove box 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 the glove box atmosphere. These controls and associated process limits will be defined as part of the “20-Points” process HB-Line will follow to receive DOE approval for packaging under this equivalency. The “20-Points” will address requirements for both deferred packaging of the HB-Line product following interim storage and freshly produced PuO₂ product that is packaged without interim storage.

1.4.6 Packaging

Each batch of PuO₂ will be transferred after calcination from the filter boat to an in process storage container or product container depending on the batch size. If needed, the in process storage container will be used to store and combine 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. HB-Line will begin operations using a deferred packaging arrangement that allows the PuO₂ product to be stored in a Type B package¹ prior to start-up of the 3013 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. Efforts to limit moisture adsorption by the PuO₂ product will be instituted to the greatest extent possible. Verification of limited moisture adsorption is required using established moisture analysis methods that require heating the PuO₂ sample to 1000 °C and measuring the associated mass loss. These methods include mass loss on ignition, thermogravimetric analysis (TGA), thermogravimetric analysis – mass spectrometry (TGA-MS), or thermogravimetric analysis – Fourier transform infrared spectroscopy (TGA-FTIR) (DOE, 2012; Erickson, 2002).

Details associated with qualification of moisture analysis methods for the HB-Line product and establishing requirements for packaging PuO₂ following interim storage (i.e., deferred packaging) will be addressed as part of the “20-Points” process used to demonstrate compliance with the DOE-STD-3013 prior to packaging in a 3013 compliant configuration.

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 storage concerns have been container corrosion and gas generation. In this case, the proposed content will be high-purity PuO₂ with little chlorine (See Table A-1). The maximum content, the standard value that must be met during routine operations, of fluorine plus chlorine is <250 µg g⁻¹ Pu; the maximum exceptional content, the maximum acceptable value as long as the total impurities value is not exceeded, for chlorine is 500 µg g⁻¹ Pu.² The moisture within the package must be less than 0.5 wt %.

General corrosion has been evaluated by the 3013 Standard and is not a credible problem (see section A.6.3.2.6 in DOE, 2012). 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 containing less than 0.5 wt % water by either the SRS destructive examination program or the MIS program (Dunn et al., 2010; Zapp et

¹ If the product containers are required to be inert (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.

² Verification that fluorine plus chlorine levels are <250 µg g⁻¹ Pu will be achieved by measurement of PuO₂ samples.

al., 2010; DOE, 2012). Therefore, this review is primarily focused on the potential for gas generation to impact 3013 container safety.³

Because the material will be stabilized at a minimum of 625 °C rather than at a minimum of 950 °C, the HB-Line product will have a higher specific surface area (Daniel, 2012) and potentially higher carbon content than plutonium-bearing oxide materials represented in the MIS Shelf-Life Program. The higher specific surface area will pose a challenge to limit moisture adsorption. Moisture adsorption must be limited in order to meet the 0.5 wt % moisture limit and also to preclude the eventual formation of a flammable gas mixture within containers of this material while in subsequent storage.

Early small-scale studies had suggested that high surface area PuO₂ produced by calcination of Pu oxalate at temperatures between 600 °C and 700 °C could result in simultaneous generation of H₂ and O₂ if exposed to high relative humidity before storage (Livingston and Duffey, 2001; Duffey and Livingston, 2002). These were short-term tests of a few weeks duration and were not designed to test dependence of gas generation on the relative humidity to which the material had been exposed. These data are discussed in further detail in Veirs et al., 2012a.

The MIS Shelf Life Program conducted longer-term small-scale gas generation tests on two samples of high surface area PuO₂ with a specific surface area of 20–30 m² g⁻¹ produced by oxalate precipitation and calcination to oxide (Berg et al., 2012). The total moisture content in these tests was approximately twice the 0.5 wt % limit for packaging, and while humid atmosphere exposure was used to add known amounts of moisture, no attempt was made to equilibrate the samples at a known relative humidity prior to the tests. Simultaneous generation of H₂ and O₂ was observed in both tests. In the longer duration of the two tests (four years) the gas mixture approached flammable levels and then concentrations decreased.

More recent testing examined the hypothesis that the simultaneous generation of hydrogen and oxygen only occurs if the relative humidity to which the material is exposed exceeds some threshold value, independent of the total moisture content. These tests took samples of PuO₂ from oxalate calcination and exposed them to a known relative humidity for several days, then observed gas generation in sealed containers for several months. The preliminary results suggest that the threshold adsorbed water activity corresponds to an extended exposure at a relative humidity of somewhere between 33% and 72% (Veirs et al., 2012b). Planned studies seek to narrow this range and support HB-Line efforts associated with defining limits that will prevent formation of a flammable atmosphere within the welded 3013 container or associated Type B packaging.

1.6 Equivalency of Alternative Processing Pathway

The purpose of stabilization is to ensure the nuclear material can be stored safely for up to 50 years in a specified, sealed, stainless steel container. The basis for determining whether alternative stabilization conditions are equivalent lies in establishing that the new conditions are equally effective in meeting the objectives for stabilization identified in DOE-STD-3013. These objectives are listed in Section 1.3 of this document. Equivalency does not mean that the PuO₂ produced at a calcination temperature of 625 °C will have the same material properties, such as specific surface area, as PuO₂ stabilized at a temperature of 950 °C.

The next section discusses the evidence that high-purity PuO₂ produced in HB-Line and stabilized at no less than 625 °C can be equivalent to material stabilized in compliance with DOE-STD-3013 for each of the stated objectives of stabilization. It is shown that the material must be handled in a way to prevent excessive adsorbed moisture that could occur because of the higher specific surface area. Assurance of adequate stabilization, limited adsorbed moisture, and constraints on material handling to prevent

³ It is critical to the equivalency evaluation that the HB-Line production process and PuO₂ product be isolated from potential chloride contamination associated with future HB-Line activities (e.g., 3013 oxide repackaging).

formation of flammable gas mixtures will be verified by defining appropriate quality assurance and surveillance measures in the “20-Points” documents.

2.0 Discussion of Technical Issues

This section discusses the impacts of the proposed change in stabilization conditions on achieving each of the five objectives for stabilization listed in Section 1.3. Similar to prior 3013 equivalency documents, data gaps and the proposed path forward have been identified, where applicable.

2.1 Elimination of Reactive 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 accidentally breached or when they are intentionally opened in the future. Stabilization is also expected to oxidize substoichiometric Pu oxide to PuO₂. The specific issue is whether stabilization at 625 °C for four hours increases the reactivity or pyrophoricity of the product when compared to stabilization at 950 °C for two hours.

2.1.2 Technical Position

Elimination of pyrophoric materials in the HB-Line product is not a concern because metal cannot credibly survive the aqueous chemical processes leading to Pu oxalate. Substoichiometric oxides are not expected to be a concern for material stabilized in an oxidizing environment at 625 °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.

2.1.3 Discussion of Available Data

Sources of metal in the HB-Line 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 H-Canyon dissolver to HB-Line, 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 625 °C for four hours, they would be too unreactive or too dilute and too highly dispersed within the bulk oxide to be of concern for safe storage.

There is ample evidence in the literature which demonstrates the effectiveness of thermal conversion of both Pu(IV) oxalate 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 an inert atmosphere, although the studies do not focus on trace residual reactant or intermediates. Waterbury et al. (1961) found the oxygen to Pu atom ratios following calcination of Pu(IV) oxalate in air varied from 2.044 at 330 °C to 2.014 after four hours at 1250 °C; thus, substoichiometric oxides are not anticipated in the HB-Line 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 any 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 specific issue is whether stabilization at 625 °C for four hours will result in a product that contains unacceptably high levels of residual organic species.

2.2.2 Technical Position

Published studies indicate that conversion of Pu oxalate to PuO₂ proceeds to completion below 600 °C. Calcination at no less than 625 °C for four hours is expected to destroy oxalate and organics that may credibly be present in the product following oxalate precipitation. This is supported by previous analyses of NpO₂ produced in HB-Line by a similar process which determined the carbon content to be well below 1000 µg g⁻¹ NpO₂ (Duffey, 2008). HB-Line product specifications require the maximum carbon content to be ≤1000 µg g⁻¹ of Pu (≤5000 µg g⁻¹ of Pu for the maximum exceptional limit). The acceptable carbon content must be demonstrated either by carbon measurement for each calcination batch of PuO₂ (Garrison, 2012) or by process qualification with appropriate process controls included in the “20-Points” process.

2.2.3 Discussion of Available Data

The primary source of organic compounds in the HB-Line process is the addition of oxalic acid to precipitate Pu(IV) oxalate. The oxalate ion (C₂O₄²⁻) contains no hydrogen atoms, and therefore, is not a concern for hydrogen gas generation. However, radiolytic or thermolytic decomposition of oxalate species to produce carbon monoxide or carbon dioxide is a plausible source for gas generation (see section 2.5.3 for further discussion). In addition to oxalate, other potential sources of organic material in the HB-Line 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 carbon in NpO₂ produced by HB-Line. They concluded that residues of these materials were not present to any significant degree in the samples of HB-Line NpO₂ product examined, and thermal decomposition of these materials would be observed 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 nitric acid and potassium fluoride solutions such as will be used in this process (Kessinger and Clark, 2004). Organic material remaining in solution after dissolution would be transferred to HB-Line 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. Nylon is a family of thermoplastic polymers, generally referred to as polyamides, consisting of carbon, hydrogen, oxygen, and nitrogen 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 carbon, hydrogen, and fluorine atoms. Boak et al. (2002) report from the literature that decomposition of hydrocarbons and chlorine-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 fluorine-containing organics such as Teflon® begins around 350 °C with no further mass loss obtained above 750 °C.

The DOE-STD-3013 states in section A.6.1.2.1.2 that “all plastics less than about one inch in diameter and any other organic materials likely to accompany unstabilized Pu materials are completely oxidized by air in less than five minutes at 800 °C.” Boak et al. (2003) note in Appendix B that “By the Arrhenius equation, the rate of organic material oxidation at 750 °C would be only about 5% slower than at 800 °C such that ready decomposition of plastics by two hours oxidation at 750 °C would be expected.” Based upon this same argument, the oxidation rate of organic material at 625 °C would be only about 20 percent slower than at 800 °C, so that four hours at 625 °C should be sufficient to completely oxidize any organic material.

Therefore, all three sources of organic material identified above that may conceivably be incorporated in the Pu oxalate precipitate are expected to be decomposed by stabilization to no less than 625 °C in air for

four hours. 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. These data were used to identify intermediate products as well as the temperature at which the conversion to PuO₂ was complete. 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 PuO₂ regardless of whether the initial oxalate compound contained Pu(III) or Pu(IV) and regardless of whether the material was heated in an inert or an oxidizing atmosphere. In these laboratory-scale studies, the conversion to PuO₂ was complete below 400 °C in air and below 600 °C in an inert atmosphere such as argon. 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 carbon as a function of calcination temperature.

The average total carbon concentration measured for PuO₂ prepared by SRNL as part of a lab-scale demonstration of the HB-Line flow sheet was $285 \pm 40 \mu\text{g g}^{-1}$ Pu (Crowder and Pierce, 2012), indicating the HB-Line product will meet the $1000 \mu\text{g g}^{-1}$ carbon specification.

2.2.4 Data Gaps

None.

2.3 Reduction of Water Content and Other Water-Producing Species

2.3.1 Issue Statement

To be judged as effective, stabilization must reduce total moisture content of the product to below 0.5 wt %. This objective is intended primarily to mitigate internal pressurization of a container due to radiolysis of moisture. For high-purity PuO₂ from the HB-Line process, the forms of water are weakly bound water and strongly bound water (e.g., surface hydroxides). The specific issue is whether stabilization at 625 °C for four hours will adequately remove both weakly and strongly bound water.

2.3.2 Technical Position

Moisture measurement by an approved method, which includes heating to 1000 °C (DOE, 2012), will verify that less than 0.5 wt % moisture remains in the stabilized HB-Line oxide product. Material failing this criterion will not be packaged without re-stabilization in accordance with the “20-Points” documents. Stabilization at a minimum of 625 °C for at least four hours will drive off virtually all water and hydroxides (Veirs, 2002). It is expected that a small quantity of strongly bound water well below 0.5 wt % will survive stabilization.

2.3.3 Discussion of Available Data

The specific 0.5 wt % moisture limit for the DOE-STD-3013 is based on the limiting case assumption of complete decomposition of all forms of water to hydrogen gas, and the ability of a 3013 container to withstand the resulting internal pressure with an adequate safety margin (DOE, 2012). Previous stabilization and packaging campaigns produced extensive data on the total volatiles after stabilization of PuO₂ to 950 °C using mass loss on ignition or TGA analyses for the purpose of certifying compliance with the 0.5 wt % moisture limit. These measurements assume all weight loss is attributed to water.

However, a smaller set of data is available showing the temperature dependence of the thermal desorption of moisture from plutonium-bearing oxide materials stabilized to 950 °C (i.e., TGA-MS or TGA-FTIR).

Generally the moisture found on these PuO₂ samples is ascribed to the combination of a surface hydroxide layer and one or more monolayers of more weakly bound or physically adsorbed water. These observations indicate that the weakly bound water on the oxide surface will be desorbed using the proposed stabilization process at no less than 625 °C (DOE, 2012; Berg et al., 2012; Veirs et al., 2012a). However, when the oxide is handled in a humid environment, the principal concern for ensuring compliance with the moisture limit is preventing adsorption of water vapor prior to packaging. Because the product oxide from the proposed low temperature stabilization process is expected to have significantly higher specific surface area than oxide stabilized to 950 °C, adsorption has the clear potential to lead to a total moisture content exceeding 0.5 wt %.

Thermal desorption profiles from PuO₂ after stabilization at 650 °C consistently show a small moisture component that is volatilized above the proposed minimum stabilization temperature of 625 °C. For high-purity PuO₂ from oxalate precipitation followed by calcination to 650 °C, the moisture content above 650 °C measured by TGA-MS is significantly less than 0.1 wt %. (Veirs et al., 2012a; Crowder and Pierce, 2012). This is an indication that not all water is removed at 650 °C, but the mass of strongly bound water requiring heating to approximately 1000 °C to remove is small, at less than 0.1 wt %. For high-purity PuO₂ originally calcined at 600 °C, subsequently aged in air during which time the strongly bound layer was fully formed, and then calcined to 650 °C, the water observed by TGA-MS above 650 °C was approximately 0.1 wt % (Veirs et al., 2012a). In both of these cases the specific surface area of the material is greater than 9 m² g⁻¹ which is similar to what is anticipated for the HB-Line product. Based on these observations, the HB-Line product is expected to retain some moisture when calcined at temperatures above 625 °C. It is not expected that after calcination the HB-Line product will contain strongly bound water above 0.1 wt %.

2.3.4 Data Gaps

None.

2.4 Minimization of Potential for Water Adsorption

2.4.1 Issue Statement

The potential for water adsorption after calcination 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. The amount of water adsorbed increases linearly with specific surface area if all other parameters are constant. Thermal stabilization to a 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 HB-Line product, stabilization at 625 °C for at least four hours will result in an increased PuO₂ specific surface area as compared to material calcined to a minimum of 950 °C for at least two hours. In addition, the atmosphere in HB-Line process glove boxes can have high relative humidity (up to 70%) which increases the rate of adsorption and the potential amount of weakly bound water. Together, these conditions significantly increase the potential for exceeding the 0.5 wt % water content criteria and the possibility of generating flammable gas mixtures of H₂ and O₂ are significantly increased. The specific issue is controlling the rate and amount of water adsorption.

2.4.2 Technical Position

The protection from the adsorption of water afforded by low specific surface area (~1 m² g⁻¹) PuO₂ handled in dry glove boxes that is lost under HB-Line processing conditions must be mitigated by institution of rigorous process controls. The required process controls and associated operating limits have not been identified at this time, but these controls must address, at a minimum: (1) how the material will

be kept below 0.5 wt % water before packaging, (2) what measurements can ensure that conditions that result in flammable gas mixtures do not exist, and (3) how the measurements to support these claims are made. These process controls and rework criteria will be addressed by HB-Line as part of the “20-Points” process.

2.4.3 Discussion of Available Data

Water adsorption by high-purity PuO₂ produced from oxalate precipitation is primarily a function of relative humidity, specific surface area, and temperature (Veirs, 2002). The potential for water adsorption is an important consideration for the proposed HB-Line product due to the expected high product specific surface areas (i.e., 5–15 m² g⁻¹) and high relative humidity (i.e., 40–70%) in HB-Line glove boxes. Both the specific surface area and process relative humidity are greater than previously observed during the preparation of PuO₂ for storage in compliance with the 3013 Standard. These conditions increase the potential for the HB-Line product to exceed the 0.5 wt % moisture limit and will increase the potential for hydrogen and oxygen gas generation (Veirs et al., 2012a; Veirs et al., 2012b).

PuO₂ produced at LANL for MOX Lead Test Assemblies during the time frame of 2001–2008 using a flow sheet similar to what is planned for HB-Line had measured specific surface areas ranging from 5–15 m² g⁻¹ with an average of 9.8 ± 1.8 m² g⁻¹ ($\pm 1\sigma$) (Alwin, 2007; Bluhm, 2005). A broader survey of the literature on the dependence of specific surface area on calcination temperature (Daniel, 2012) showed that specific surface areas in this range for the HB-Line product would be consistent with that observed in other laboratories. Laboratory-scale PuO₂ samples produced in support of the HB-Line MOX feed mission (Crowder et al., 2012; Crowder and Pierce, 2012; Veirs et al., 2012b) also have specific surface areas 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 1.0–1.5 ML at 30% relative humidity to about 1.7–2 ML at 50% relative humidity and to more than 3 ML at 70% relative humidity (Veirs et al., 2012a). One ML is equal to about 0.22 mg H₂O m⁻² of oxide surface; therefore, PuO₂ with a specific surface area of 10 m² g⁻¹ in equilibrium with a relative humidity of 50% would adsorb an amount of water equal to about 0.44 wt %, and if equilibrated at higher relative humidity would exceed 0.5 wt %. Based upon prior estimates of measurement uncertainty for TGA and TGA-MS, the exposure to moisture must be controlled to demonstrate compliance with the 3013 Standard’s moisture limit.

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

More recent gas generation tests with high-purity PuO₂ show that oxygen is not generated for material equilibrated with $\leq 33\%$ relative humidity, and that sufficient hydrogen and oxygen are generated to produce a flammable atmosphere when the same material is equilibrated with $\geq 72\%$ relative humidity (Veirs et al., 2012b). Results of these studies and planned tests (Berg et al., 2013) will help establish material handling guidelines to ensure the HB-Line product can be packaged in a way that precludes formation of flammable atmospheres. Technical review and evaluation of the proposed conditions will be formally reviewed as part of the “20-Points” process and approved by the AMNMSP at the Savannah River Operations Office.

TGA-MS moisture measurements for PuO₂ produced in SRNL per the nominal HB-Line flow sheet found the moisture content for material with limited exposure (i.e., incidental to handling) to humid air (44 – 60% relative humidity) was about 0.3 wt % and about 0.6 wt % after exposure to humid air for four days

(Crowder and Pierce, 2012). These results highlight the importance of limiting exposure of the HB-Line product to high humidity conditions to meet the 0.5 wt % moisture limit.

High specific surface area material also presents challenges to obtaining accurate moisture measurements. Weakly bound water rapidly adsorbs and desorbs as the relative humidity increases and decreases. For small samples, mass transport limitations on adsorption and desorption rates are much reduced compared to kilogram size batches. Handling small samples in glove boxes where the relative humidity is different (higher or lower) than the atmosphere that the sample is in equilibrium with can result in rapid gain or loss of significant amounts of moisture. For high-purity PuO_2 with $1 \text{ m}^2 \text{ g}^{-1}$ specific surface area, a monolayer of weakly bound water represents about 0.02 wt % moisture which is below the minimum detection limit. Whereas, for high-purity PuO_2 with $15 \text{ m}^2 \text{ g}^{-1}$ specific surface area, a monolayer of weakly bound water represents 15 times more moisture (0.33 wt %) which is close to the maximum amount of water allowed due to analytical uncertainty. In addition, techniques such as TGA-MS use a flowing inert gas with a very low relative humidity ($\ll 1\%$) and have an initial flush to establish instrument stability before water loss measurements begin. High specific surface area material with weakly bound water may lose significant amounts of water in the flowing inert gas during instrument stabilization prior to initiating mass measurements. The potential water loss during this time could result in a non-conservative moisture measurement. This water loss is not an issue for salt-bearing materials because the salts hold water strongly and very little water desorbs. Nor is the water loss a problem for high-purity PuO_2 stabilized to $950 \text{ }^\circ\text{C}$ for two hours because the specific surface area is low and the amount of weakly bound water available for loss is correspondingly low. The HB-Line product (high specific surface area PuO_2 exposed to high relative humidity glove box atmosphere) presents a challenge to moisture measurements. The “20-Points” documents must address conservative moisture measurements with high specific surface area materials and the “20-Points” documents review must determine if procedures are adequate to ensure a conservative moisture measurement.

2.4.4 Data Gaps

The rate of water adsorption of large batches (i.e., 1-3 kilograms per container) of freshly stabilized PuO_2 within HB-Line 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). Material that adsorbs more than 0.5 wt % moisture would still be identified by the pre-packaging moisture measurement process and must be re-stabilized. Avoiding the possibility of O_2 and H_2 co-generation will most likely require handling restrictions to limit moisture uptake. At present, the maximum relative humidity which PuO_2 may safely be equilibrated is poorly defined and should be conservatively assumed to be about 33% (Veirs et al., 2012b) until additional test data are available. The actual process relative humidity limits will be defined by the “20-Points” process and implemented prior to packaging HB-Line product under this equivalency.

2.4.5 Path Forward

Details for handling and packaging must be established and approved as part of the HB-Line “20-Points” documents and must be designed to avoid conditions that could generate a flammable atmosphere. The strategy will probably involve some combination of relative humidity control, restrictions on handling time, keeping the material at an elevated temperature during handling, and/or measuring the equilibrium relative humidity above the material in a sealed container before packaging.

For example, after stabilization the material could be removed from the stabilization furnace while still warm and placed into an in-process storage container having an elastomeric seal to limit exposure to ambient relative humidity. Prior to 3013 packaging, the equilibrium relative humidity within the

convenience container could be measured with a sensor to demonstrate compliance with the threshold value yet to be determined, but presumed to be greater than 33% based on current information.

2.5 Stabilization of Other Potential Gas-Producing Constituents

2.5.1 *Issue Statement*

Stabilization must meet the objective of effectively removing other non-moisture, gas-producing constituents such as nitrates (NO_3^-), sulfates (SO_4^{2-}), and carbonates (CO_3^{2-}) in PuO_2 . The specific issue is whether stabilization at no less than 625 °C for four hours is sufficient to eliminate or reduce to acceptable levels these constituents. .

2.5.2 *Technical Position*

With no valence adjustment step in the HB-Line process, there is no credible source of sulfate ions after dissolution (Kyser and King, 2012). Nitrate is plentiful because the process occurs in nitric acid solution, but the bulk of the nitric acid is removed during the anion exchange and oxalate precipitation steps, and residual nitrate species are expected to be decomposed by stabilization at 625 °C or greater for four hours (Boak et al., 2002; Waterbury et al., 1961). Although some residual carbonates could result from incomplete decomposition of oxalate, the relatively small amounts of carbon, as well as nitrogen⁴ and sulfur, allowed by the specification for the HB-Line PuO_2 product ($1000 \mu\text{g g}^{-1}$, $400 \mu\text{g g}^{-1}$, and $250 \mu\text{g g}^{-1}$ 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 carbon dioxide (CO_2) and carbon monoxide (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 carbon dioxide no higher than 5 kilopascals (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 partial pressure of carbon dioxide 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 carbon dioxide 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 carbon dioxide though still far below a level of concern for container pressurization. For example, TS707001 produced a maximum of 30 kPa of carbon dioxide (Duffey et al., 2010). Chemical analysis of the PuO_2 indicated less than 0.01 wt % carbon. The specific surface area of this material was measured at $2.3 \text{ m}^2 \text{ g}^{-1}$, much lower than that of MISSTD-1. Because of the low surface area and a high water loading, water may have effectively displace adsorbed carbon species from the surface resulting in 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.

⁴ H-Area is not required to verify the nitrogen levels (McAlhany, 2012) in the product. MOX Services will confirm the nitrogen limits are met with statistical sampling and analysis prior to dissolving.

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⁻¹ Pu for the HB-Line 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 HB-Line process and associated controls required for supporting the stabilization of PuO₂ at a minimum of 625 °C for at least four hours have been evaluated, and the proposed alternative stabilization criteria determined to be equivalent, in terms of safety, to the DOE-STD-3013 criteria, provided that the product is handled in a way that precludes formation of a flammable gas mixture within the 3013 container. Because the HB-Line product will have a higher specific surface area than PuO₂ stabilized at 950 °C for 2 hours and because the relative humidity in the HB-Line facility may be as high as 70%, the primary concern identified by this report is that the HB-Line product will have a greater tendency to adsorb moisture than PuO₂ stabilized at 950 °C for 2 hours. Furthermore, the specific surface area of the oxide product could fall within a range that would allow multiple monolayers of water to accumulate on the oxide surface without exceeding the 0.5 wt % moisture limit. These multiple layers would be a potential source for generating a flammable mixture of H₂ and O₂ during storage. This evaluation uses available scientific literature for similar materials to support a conservative assessment of product performance. The safety margin associated with this evaluation relies on HB-Line implementing the following controls:

- The Pu oxalate product is stabilized in an oxidizing atmosphere at no less than 625 °C for a minimum of four hours.
- The product does not exceed total product impurities of 23,600 µg g⁻¹ Pu (2.1 wt %). Metallic impurities identified in the Appendix may exceed the defined maximum exceptional limits identified without impacting the proposed equivalency, provided the total impurities remain less than 2.1 wt %. Non-metallic impurities (i.e., B, C, Cl, F, N, P, S, Si) should be constrained to the established maximum exceptional limits provided in the Appendix.
- The HB-Line product shall be packaged in a way that precludes formation of a flammable gas mixture in the 3013 container. These controls shall be documented as part of the “20-Points” process.
- The “20-Points” documents review shall ensure the HB-Line procedures will provide conservative measurements of key parameters including:
 1. moisture content of the product at the time of 3013 packaging is less than 0.5 wt %,
 2. relative humidity or alternate controls identified to preclude formation of a flammable gas mixture in the 3013 container.

The technical team concludes that moisture adsorption by PuO₂ stabilized to a minimum of 625 °C for at least four hours and handled in ambient air with a relative humidity as high as 70% poses the greatest challenge to meeting the DOE-STD-3013 packaging requirements. However, after reviewing the proposed HB-Line flow sheet for high-purity PuO₂ product and available supporting data, the authors concluded that the proposed HB-Line process is capable of producing PuO₂ that poses no safety concern for packaging or storage in the 3013 required configuration, provided the stabilized product is handled consistent with the recommended controls.

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

Table A-1. Chemical Impurity Limits for HB-Line Product

Chemical Component	Maximum Content^a ($\mu\text{g g}^{-1}$ Pu)	Maximum Exceptional Content^b ($\mu\text{g g}^{-1}$ 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 the MFFF safety, process, and product quality.

Distribution:

S. D. Fink, 773-A
T. B. Brown, 773-A
D. R. Click, 773-A
E. N. Hoffman, 999-W
S. L. Marra, 773-A
F. M. Pennebaker, 773-42A
W. R. Wilmarth, 773-A
E. A. Kyser, 773-A
T. S. Rudisill, 773-A
R. A. Pierce, 773-A
M. L. Crowder, 773-A
W. D. King, 773-42A
M. C. Thompson, 773-A
J. M. Duffey, 773-A
D. K. Veirs, LANL
J. M. Berg, LANL
R. R. Livingston, 730-2B
Records Administration (EDWS)

W. E. Harris, 704-2H
J. B. Schaade, 704-2H
S. J. Hensel, 705-K
G. J. Zachman, 225-7H
P.B. Andrews, 704-2H
S.J. Howell, 221-H
K. P. Burrows, 704-2H
K. J. Gallahue, 221-H
J. E. Therrell, 704-2H
J. W. Christopher, 704-2H
S. L. Garrison, 704-2H
W. G. Dyer, 704-2H
M. J. Swain, 703-H
M. J. Lewczyk, 221-H
R. H. Smith, 704-2H
K. D. Scaggs, 704-2H
S. L. Hudlow, 221-H
W. H. Clifton, 704-2H
A. T. Masterson, 704-2H
S. A. Thomas, 703-46A