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ACRONYMS

AMNMS	Assistant Manager for Nuclear Materials Stabilization, Savannah River Operations Office
ANSI	American National Standards Institute
ASME	American Society of Mechanical Engineers
CFR	Code of Federal Regulations
DOE	United States Department of Energy
DSA	Documented Safety Analysis
EM	Office of Environmental Management
IDC	Item Description Code
ISMP	Integrated Surveillance and Monitoring Program
LOI	Loss on Ignition
MBA	Material Balance Area
MC&A	Materials Control and Accountability
MIS-WG	Materials Identification and Surveillance Working Group
SARP	Safety Analysis Report for Packaging
TGA	Thermogravimetric Analysis
TRU	Transuranic
WIPP	Waste Isolation Pilot Plant

1. **SCOPE**

This Standard provides criteria for stabilization of plutonium-bearing materials at DOE facilities to safe and stable forms and packaging for storage with minimal surveillance for up to 50 years. This Standard applies to plutonium-bearing metals and oxides containing at least 30 wt% plutonium plus uranium. For enriched uranium metal, the plutonium content must be sufficiently high that the material is not acceptable at the Oak Ridge Y-12 Plant (Y/LB-15). As a practical limit for oxide materials containing significant quantities of uranium, the plutonium content must be greater than the applicable Safeguards Termination Limit. There is no lower limit for uranium. This Standard does not apply to materials destined for disposal in accordance with waste acceptance criteria for Waste Isolation Pilot Plant (WIPP) or other approved waste disposal sites, such as plutonium residues or transuranic (TRU) waste; Irradiated Fuels; sealed sources; material packaged per DOE M 441.1-1; materials containing greater than 0.5 wt% uranium-233; or plutonium solutions.

A significant portion of the DOE plutonium oxide inventory contains chloride. For example, the oxide material from electrorefining processes can contain percent levels of chloride. The presence of even lower levels of chloride can catalyze stress corrosion cracking in stainless steel, the material specified in this Standard for the containers (Section 6.2.2.1). The Standard does not impose a limit on chloride content because the extent of corrosion is limited by the available moisture, rather than the available chloride. The Standard does require humidity controls to prevent salt deliquescence between thermal stabilization and packaging (Section 6.1.2.4 and Section 6.1.4). The humidity control and the available moisture limitation (Section 6.1.2.3) in this Standard are considered sufficient to avoid significant corrosion.

This Standard addresses the safety envelope of the storage container. The design, construction, and testing criteria (Section 6.2) assure that the outer container will remain a robust barrier during anticipated storage conditions. Low levels of removable contamination (above clean-area limits) are allowed on the exterior of the inner container (Section 6.2.3.2.3) prior to packaging into the outer container. In addition, once the inner is packaged into the outer container, the inner container integrity cannot be assured. This Standard does not address the safety aspects (e.g., contamination inside the outer container, reactivity of metal, internal pressurization, etc.) associated with opening the containers. Storage facility design, safeguards and security interfaces, and transportation requirements are addressed in detail in other DOE directives (e. g., policies and orders) and other agencies' regulations. Such requirements are not repeated in this Standard. Users of this Standard are advised to consult and assure adherence with other applicable directives and implementing documents (for example, Safety Analysis Report for Packaging (SARP) documents, facility-specific Documented Safety Analyses (DSAs), and receiving site acceptance requirements).

2.   PURPOSE

These criteria provide a basis for assuring that plutonium-bearing materials will be stable for safe, long-term storage at DOE facilities requiring minimal surveillance under anticipated handling, shipping, and storage conditions until their final disposition.

3.   APPLICABILITY

All DOE organizations and their contractors may use this Standard.

4.   REFERENCES

4.1.   DOE Documents

AMNMS-15-0014   *Integrated Surveillance and Monitoring Program for Materials Packaged to Meet DOE-STD-3013*, May, 2015.

DOE Manual 441.1-1, Chg 1   *Nuclear Material Packaging Manual*, February 24, 2016.

DOE Order 414.1D, Chg 1   *Quality Assurance*, May 8, 2013.

DOE Order 440.1B, Chg 2   *Worker Protection Management for DOE Including The National Nuclear Security Administration Federal and Contractor Employees*, March 14, 2013

DOE-STD-1098-2008, Chg Notice 1   *Radiological Control*, June 16, 2009.

Y/LB-15, 920/Rev. 1   *Criteria for Acceptance and Technical Assessment for Acceptance of Enriched Uranium at the Y-12 Plant*, March 1997.

4.2.   Other Government Documents

10 CFR Part 835, *Occupational Radiation Protection*

49 CFR Part 178, *Specifications for Packagings*

4.3.   Non-Government Documents

ANSI N14.5-2014, Standard for Radioactive Materials - Leakage Tests on Packages for Shipment, American National Standards Institute, Inc. (ANSI), New York, NY, 2014

ASME Boiler & Pressure Code, Section VIII, American Society for Mechanical Engineers (ASME), 2017

5. DEFINITIONS

3013 Container	The assembled combination of containers required by this Standard.
Design Pressure	A characteristic of a sealed container, which indicates its ability to withstand internal pressurization. In the language of the American Society of Mechanical Engineers (ASME) Boiler and Pressure Vessel Code, it is the "Maximum Allowable Working Pressure."
Fabricated Fuel	Nuclear reactor fuel elements (pins, plates, assemblies, etc.) consisting of plutonium-bearing material completely contained within a cladding (including end fittings), manufactured and maintained with a very high quality and quality assurance.
Free Gas Volume	That portion of the sealed container that is available to the fill gas and any gases generated during storage. See Appendix B for further discussion.
Item Description Code	A site-specific code used to categorize material for Material Control and Accountability (MC&A) purposes that may be indicative of process of origin or chemical impurities.
Irradiated Fuel	Nuclear material, including Fabricated Fuel, that in its existing form, has been subjected to irradiation in a nuclear reactor or accelerator.
Loss on Ignition	For this standard, defined as mass loss measured after a weighed sample is heated in air to 1000 °C for at least one hour, to measure any weight change due to residual volatile species.
Material Temperature	The lowest temperature within a mass of heated material. In other words, all of the material is at or above this temperature.
Oxide	Plutonium oxide with accompanying non-plutonium constituents that have been exposed to oxidizing conditions. Non-plutonium constituents include other actinides, such as uranium and americium, and compounds, such as magnesium oxide and sodium chloride, derived from chemicals used in plutonium or fuel materials processing.

Oxidizing Atmosphere	For this Standard, defined as gaseous atmosphere in which the supplied gas is air or a gas mixture of O_2 and an inert gas such as He, Ar, or N_2, in which the O_2 percentage is equal to or greater than air.
Thermal Power	The rate of heat generated by radioactive decay of the material.
Safeguards Termination Limit	The maximum plutonium concentration upon which Materials Control and Accountability and physical protection can be terminated.
Thermogravimetric Analysis	For this Standard, defined as heating a sample in an inert atmosphere to 1000 °C and measuring weight change during the heating due to residual volatile species.
Thermogravimetric Analysis with Fourier Transform Infrared or Mass Spectrometry	For this Standard, defined as heating a sample in an inert atmosphere to 1000 °C and measuring both the weight change and analyzing the gas generated using either a Fourier Transform Infrared or Mass Spectrometer.

6.   STABILIZATION, PACKAGING, AND STORAGE CRITERIA

When measured values are compared with the following criteria in this Standard, measurement uncertainty must be included to provide confidence that these criteria are met. This applies specifically to material temperature (6.1.2.1), moisture content (6.1.2.3 and 6.1.4), mass of plutonium and other fissionable isotopes (6.3.2.1), total mass of contents (6.3.2.1), total thermal power (6.3.2.2) and relative humidity (6.1.2.4 and 6.1.4).

6.1.   Stabilized Materials

Because of the significant differences in the chemical and physical properties of metals, oxides, and engineered materials (and in their processing methods) criteria are provided for each material category.

6.1.1. Plutonium-Bearing Metals and Alloys

6.1.1.1.   Metal pieces to be packaged shall have a specific surface area less than 1 cm^2/g and in no case shall pieces less than 10 g be packaged. This limit may be implemented by either restricting pieces such that each weighs at least 50 g or by performing calculations for each material type and performing appropriate physical measurements (for example, weight, dimensional measurements, etc.) on each piece. Foils, turnings and wires shall not be packaged under this Standard.

6.1.1.2.   At the time of packaging, metals shall be visually free of non-adherent corrosion products (including oxide), liquids, and organic materials such as plastics and oils.

6.1.1.3.   Briquettes made by pressing plutonium turnings shall not be stored under the provisions of this Standard.

6.1.2. Oxides

6.1.2.1.   Stabilization Conditions: Oxides shall be stabilized by heating the material in an oxidizing atmosphere to a material temperature of at least 950 °C (1742 °F) for at least 2 hours.

6.1.2.2.   (a) Stabilization Verification: Materials that have been stabilized shall have their moisture content measured by using a demonstrated, technically appropriate method. Approved methods are Thermogravimetric Analysis (TGA), TGA with mass spectrometer or infrared spectrometer, Loss on Ignition (LOI) (limited to oxide of 80% or greater plutonium plus uranium), Full-batch LOI, or previously approved alternative measurement techniques per Foreword Item 5.

(b) Process Qualification: Materials that have been stabilized and packaged using a "qualified process" shall be subject to reduced testing requirements. A qualified process is one that has been demonstrated and approved as indicated in the Foreword, Item 5, to consistently produce in a production environment, materials for packaging which meet the requirements of Criterion 6.1.2.3. Once the process has been qualified, material testing is required only to the extent necessary to show continued process control.

6.1.2.3.   Stabilization Verification Criterion: The moisture content of oxide to be packaged in any type of sealed container shall be less than 0.5 wt% at the time of packaging.

6.1.2.4.   Handling after Stabilization: Oxides suspected to contain chloride salts (see A.6.1.2.4) must have the time and relative humidity to which they are exposed after stabilization controlled such that deliquescence does not occur. Specifically, oxides suspected to contain alkaline earth chlorides above trace levels (see A.6.1.2.4) shall not be exposed after stabilization to a relative humidity greater than 15%. This Section also applies to material in Deferred Packaging Section 6.1.4.

6.1.3. Engineered Materials

At the time of packaging, these materials shall be visually free of liquids and organic materials such as plastics and oils.

6.1.3.1.   Unirradiated Fabricated Fuel, consisting of sintered plutonium-uranium oxide pellets clad with zircalloy or stainless steel having adequate quality and surveillance history

to assure its integrity is considered to meet all the requirements of Section 6.1.2 without additional stabilization or testing. Fuel pellets extracted from such fuel are also considered to meet all the requirements of Section 6.1.2 at the time they are declad. Clad metal fuel with a similar assurance of cladding integrity is considered to meet all the requirements of Section 6.1.1.

6.1.3.2. Unclad sintered plutonium-uranium oxide fuel pellets that satisfy Criterion 6.1.2.3 are considered to meet the requirements of Section 6.1.2 without additional stabilization. Sintered plutonium-uranium oxide pellets that cannot meet the requirements of Criterion 6.1.2.3 shall be stabilized according to Criterion 6.1.2.1, and shall be tested and meet Criteria 6.1.2.2 and 6.1.2.3 of this Standard prior to packaging.

6.1.4. Storage after Stabilization – Deferred Packaging

Oxide that has previously been stabilized as specified in Criterion 6.1.2.1, met the testing and stabilization criteria specified in 6.1.2.2 and 6.1.2.3 at the time of stabilization, and was placed in a closed container (such as a convenience can) may be packaged into the inner and outer containers described in this Standard without additional stabilization, provided the container and contents appear unchanged and the moisture content can be shown to be less than 0.5 wt%. The moisture content may be determined, for example, by measurement at the time of packaging into the inner container or by adding any weight gain during the time between stabilization and packaging into the inner container to the moisture content at the time of stabilization. Oxides suspected to contain chloride salts must have the time and relative humidity to which they are exposed after stabilization controlled such that deliquescence does not occur. Specifically, oxides suspected to contain alkaline earth chlorides above trace levels (see A.6.1.2.4) shall not be exposed after stabilization to a relative humidity greater than 15%, same as 6.1.2.4 above.

6.2. 3013 Container

6.2.1. Container Design Concept

6.2.1.1. The container shall consist of a minimum of two individually sealed, nested containers to isolate the stored materials from the environment. The outer container provides the pressure boundary to prevent release of the contents. The inner container provides an additional isolation boundary. It is also an internal pressure indicator for oxides. The outer and inner containers shall be sealed by welding. The use of convenience containers within the inner container is optional when packaging plutonium-bearing metals or alloys and engineered materials, but is required when packaging plutonium-bearing oxides.

6.2.1.2.   Interior containers* shall be sized to fit in the next outer container with adequate clearance for welding the next outer container.

6.2.1.3.   Both the outer and all interior containers shall allow for non-destructive assay of contents by typical MC&A techniques and inspection/surveillance by radiography.

6.2.1.4.   When packaging plutonium bearing oxides, the inner container shall allow for an indication, detectable by non-destructive means, of a buildup of internal pressure of 790 kPa (100 psig) or greater. If a convenience container is used, it shall allow sufficient gas leakage so that this pressure indication is representative of the entire volume of the inner container.

6.2.1.5.   The minimum Design Pressure of the outer container shall be 4920 kPa (699 psig). Appendix B discusses potential pressurization mechanisms and the maximum anticipated pressure.

6.2.1.6.   The outer container shall be designed to the requirements outlined in DOE Order 440.1B, Chg 2, Attachment 1, Section 7, and shall be capable of being designated "Safety Class."

6.2.2. Container Construction

6.2.2.1.   Both the inner and outer containers shall be fabricated of 304L or 316L series stainless steel or equivalent. Closure welding shall be performed using procedures that minimize sensitization of the materials of construction to minimize stress corrosion cracking. Any additional interior containers shall be made of materials compatible with the inner and outer containers.

6.2.2.2.   Neither the outer nor the interior containers* shall include combustible or organic material in their construction. Further, neither elastomeric gaskets nor organic coatings may be applied to any of the containers, including the convenience container.

6.2.2.3.   The loaded and assembled outer container shall fit within a right circular cylinder with the following maximum dimensions:

(a) Inside diameter 127 mm (5.00 in.); and

(b) Internal height of 255 mm (10.04 in.).

6.2.2.4.   Both the inner and outer containers shall have unique permanent identification markings, such as by etching or engraving.

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* The term "interior containers" means the inner container and any convenience containers.

6.2.3. Container Testing Criteria

6.2.3.1. Design Qualification Testing

(a) The outer container shall remain leaktight as defined by American National Standards Institute (ANSI) N14.5 after a free drop of the 3013 container (outer container, inner container, and simulated contents) from a 9-meter (30 ft.) height onto a flat, essentially unyielding, horizontal surface. The drop test shall follow the test procedures specified in applicable portions of 49 Code of Federal Regulations (CFR) Section 178.603, and shall be conducted using containers as specified by 49 CFR Section 178.601, loaded with non-radioactive material that simulates the planned loading for the container.

(b) The inner container shall remain leaktight as defined by ANSI N14.5 after a free drop of the container (including simulated contents) from a 1.3-meter (4 ft.) height onto a flat, essentially unyielding, horizontal surface. The drop test shall follow the test procedures specified in applicable portions of 49 CFR Section 178.603, and shall be conducted using containers as specified by 49 CFR Section 178.601, loaded with non-radioactive material that simulates the planned loading for the container.

(c) The outer container shall remain leaktight, as defined in ANSI N14.5, after a hydrostatic proof-test to 1.5 times the Design Pressure (see 6.2.1.5). The test shall be conducted using containers as specified by 49 CFR Section 178.601.

6.2.3.2. Testing and Inspection Following Container Closure

(a) Both the inner and outer containers shall be tested for leaktightness, as defined in ANSI N14.5, at their time of closure.

(b) Container leak tests shall be performed within 30 days of container closure.

(c) Initial baseline for pressure indication, required for oxides but not metals, shall be performed within 30 days of inner container closure.

(d) The exterior surface of the outer container shall not, at the time of assembly and closure, exceed the removable surface contamination values specified by 10 CFR 835, Appendix D and DOE-STD-1098-2017 at the time of assembly and closure. The interior surface shall be similarly contamination-free at least until the inner container is inserted.

(e) The removable surface contamination level on the exterior surface of the inner container, at the time of its closure into the outer container, shall be as low as reasonably achievable, and shall not exceed 2000 dpm/100 cm^2.

6.3. Contents

6.3.1. Container Fill Gas

6.3.1.1. The atmosphere within any of the containers (including the convenience container, if used) shall not react adversely with the containers or contained materials.

6.3.1.2. The atmospheres within the inner and outer containers shall not preclude leak-testing of the containers.

6.3.2. Contained Materials

6.3.2.1. The total mass of plutonium and other fissionable isotopes within either metal or oxide contents shall not exceed 4.40 kg (9.70 lb.). The total mass of the contents, whether metal or oxide, shall not exceed 5.00 kg (11.02 lb.).

6.3.2.2. If necessary, the mass shall be reduced from that specified in Criterion 6.3.2.1 to ensure that the total thermal power of the contained materials will not exceed 19 watts at any time during the 50-year storage life.

6.3.2.3. Foreign objects shall be removed from the material prior to packaging.

6.3.2.4. The oxide sample taken for stabilization verification shall be representative of the stabilized material to be sealed in the inner container at the time of packaging.

6.3.2.5. Contained materials shall not affect the required performance of the inner or outer container.

6.3.2.6. Only similar materials should be combined in an inner container or convenience container and packaged for storage.

6.3.2.7. Oxide materials packaged to this Standard shall be represented in the Materials Identification and Surveillance Program.

6.4. Storage - Integrated Surveillance and Monitoring Program

Periodic surveillance of 3013 containers is required throughout the storage period to assure continued safe storage of the plutonium-bearing materials. An integrated, complex-wide surveillance and monitoring program (ISMP) has been established and is documented in reference AMNMS-15-0014.

6.4.1. Roles of Materials Identification and Surveillance Working Group (MIS-WG) in the ISMP

The Materials Identification and Surveillance Working Group (MIS-WG) shall direct Shelf-life testing, identify containers for surveillance, define examinations and analyses to be performed, and evaluate the resultant data.

6.4.2. Changes to the ISMP

The MIS-WG may recommend changes to the ISMP as needed. Changes to the ISMP shall be approved by the AMNMS.

6.4.3. Roles of Packaging and Storage Sites in the ISMP

Sites packaging 3013 containers shall document all baseline data as required by the ISMP. Sites storing 3013 containers shall assure that all baseline and surveillance data are entered into the database (see section 6.5) and shall participate in the activities defined by the ISMP. Additional sites may be added with the approval of the AMNMS.

6.5. Documentation

6.5.1. Database

An electronic database shall be maintained as a source of relevant information about stored materials and 3013 containers. This database may consist of several files (which, in themselves, may be databases), some of which may be classified. For completeness, the database should be coordinated and generally compatible with the Material Control and Accountability (MC&A) database(s).

6.5.2. Database content elements

6.5.2.1. The database shall include, as a minimum, available information on the following material characteristics:

(a) Chemical and physical form;

(b) Best available isotopic distribution including all actinides, and the effective date(s) of analysis;

(c) Quantity (mass) of material contents;

(d) Conditions of material stabilization verification, including test results (if a qualified process has been used for stabilization and packaging, then this entry shall be the mean and standard deviation obtained during qualification testing and results from the three most recent materials measurements for process control);

(e) Source of stored material (e.g., site, facility and Material Balance Area (MBA) that generated the material, and Item Description Code (IDC), if available;

(f) Specific stabilization conditions to include date, temperature, processing duration and equipment used, and oxidizing atmosphere (and a notation that a qualified process was used, if applicable); and

(g) Other information relative to the contents such as expected major impurities with source of impurity data (e.g., process knowledge, destructive examination, prompt gamma analysis, or X-ray fluorescence analysis).

6.5.2.2.   The database shall include, as a minimum, identification of the following 3013 container characteristics:

(a) Nominal fill gas of each container on sealing (e.g., air, helium, or argon);

(b) Leak test data record for the outer and inner containers;

(c) 3013 container configuration - quantity and type of containers;

(d) Date of packaging for each container;

(e) Initial radiation field [gamma and neutron at contact and 300 mm (12 in.)], including how it was measured;

(f) Baseline 3013 container gross weight, dimensions, and tare weight;

(g) The unique identification number associated with each container;

(h) The manufacturer lot identification number for each container;

(i) Baseline inspection for pressure indication (e.g., lid deflection) for oxide containers; and

(j) Contamination measurements of the outer and inner containers.

6.5.2.3.   The database shall include, as a minimum, the following records from surveillance and inspections:

(a) Surveillance results, including analytical data;

(b) Records of tests performed;

(c) Dates of inspections; and

(d) Names of individuals performing inspections.

6.6. Quality Assurance

Activities in accordance with this standard shall be performed in accordance with the DOE-approved site/facility Quality Assurance Program (QAP). The site/facility processes that implement the QAP shall ensure that applicable QA criteria for activities covered by this standard are adequately addressed [DOE Order 414.1D, Chg 1].

APPENDIX A. TECHNICAL BASES FOR STABILIZATION, PACKAGING AND STORAGE OF PLUTONIUM-BEARING MATERIALS

This appendix summarizes the technical bases for the criteria in the body of this Standard. The section numbers in this appendix correspond to the section numbers in the body of the Standard.

The intent of this appendix is to provide the logic underlying the technical bases, to summarize the salient technical points and to provide guidance where applicable. The reader is directed to the primary technical source information for the technical details.

A.1. SCOPE

This Standard establishes criteria for stabilization, packaging, and safe storage of plutonium-bearing metal and oxides at DOE facilities. Storage containers that meet these criteria should maintain their integrity (i.e., should not require repackaging) for a minimum of 50 years.

This Standard applies to plutonium-bearing oxides and metals containing at least 30 wt% plutonium plus uranium. It may be used for metallic weapons components, including those that are classified, but it is not intended for intact weapon components, including pits. The scope of DOE-STD-3013-96 [USDOE 1996] was limited to materials containing at least 50 wt% plutonium. Information developed since the issuance of that standard demonstrates that a broader range of oxide materials, including those with lower plutonium assays, stabilized in accordance with the criteria of this Standard, can be packaged and stored safely. Stabilization data gathered from the Materials Identification and Surveillance (MIS) program and other information sources for oxide materials is considered adequately robust to support selection of 30 wt% plutonium plus uranium as the lower cutoff for this Standard.

Regarding the uranium content, and the implied equivalence of uranium for plutonium, a report [Haschke et al., 1997] assessed the inclusion of mixed plutonium-uranium oxides containing less than 50 wt% plutonium in materials covered by DOE-STD-3013-96. Issues addressed included thermal stabilization, specific surface areas, moisture re-adsorption behavior, loss-on-ignition (LOI) analysis, and criticality safety of the oxide. While some differences in chemical behavior are expected (especially under oxidizing conditions at elevated temperature), the report suggests that "substitution of uranium oxide for plutonium oxide does not detrimentally alter the thermal stabilization behavior or long-term storage behavior of those oxides." The authors specifically concluded that the risk of dispersing plutonium-containing particles should not be altered appreciably in mixed oxides.

Depleted, normal, and enriched uranium have much lower specific activity than plutonium. Therefore, direct radiolytic and thermal reactions in storage containers of high-uranium materials are expected to be strongly diminished or negligible compared to containers containing appreciable plutonium. The suitability of mixed oxides for long-term storage is underpinned by extensive experience with plutonium-uranium mixed oxide (MOX) fuel in the commercial nuclear power sector.

This Standard does not apply to material destined for disposal as TRU Waste.

This Standard does not restrict the isotopic composition of plutonium, but relies instead on the 19-watt thermal power limit to cap the content of short half-life radionuclides. The 19-watt limit restricts the ^{238}Pu content to approximately 33 grams and the ^{241}Am

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THE MIS PROGRAM

The Materials Identification and Surveillance (MIS) Program has characterized an extensive selection of oxide items that are believed to reasonably represent the behavior of the currently identified 3013 oxide material in storage for 50 years. These items are considered part of the MIS inventory. Plutonium metal is not considered in the MIS Program. Metals are generally considered "easy" to store in hermetically sealed containers, provided pyrophoric constituents are minimized and the storage atmosphere is relatively inert. Plutonium oxide is potentially more complex than metal, but its behavior is reasonably well understood with a few exceptions. The oxide materials of greatest concern are those that contain chloride salt impurities (NaCl, KCl, CaCl$_2$, and MgCl$_2$). Other common impurities include oxides and other compounds of calcium, magnesium, iron, and nickel. The stabilization process removes a fraction of the chlorides, volatilizing some and converting some to oxides. In general it also converts the other metal compounds to oxides.

The oxide materials are predominantly plutonium, but some, including the fuels materials, are mostly uranium. Most of the plutonium has a weapons grade isotopic composition, containing approximately 6% ^{240}Pu. However, some materials have significantly higher concentrations of ^{240}Pu, the higher plutonium isotopes, and americium.

The oxides that represent stored 3013 materials are characterized for chemical and physical attributes in the MIS Program. If an item is determined to be unique from characterization data, then the material is examined in storage conditions and placed in instrumented container as part of the shelf-life inventory. The purpose of the shelf-life program is to provide an early warning of storage behavior that could result in container failures in storage facilities. In addition to the materials that are provided by the sites, the MIS Program is including in the shelf-life studies materials that have characteristics that push the limits of the standard to understand the sensitivity of the standard limits to actual phenomena associated with storage container failure.

The performance of materials in storage environments is impacted by moisture content as well as the presence of impurities, their concentration (for some impurities) and their chemical form. Therefore, the most rigorous representation is accomplished by having samples of the major process streams in the MIS inventory. If sites identify process streams that are not yet in the MIS inventory, a sample from that stream may need to be added to the inventory if the behavior of the material could be different from what has already been tested.

content to approximately 165 grams, assuming in each case that no other significant heat generating species are present. Sealed sources and irradiated fuels are excluded from the scope of this Standard, as are unstabilized forms such as solutions.

Fifty years was selected as a reasonable upper limit to the time that material might have to be stored. This is not to imply that the containers may fail after 50 years, but evaluation of surveillance results will be needed to extend the approved life beyond 50 years.

Chloride impurities in oxides are of concern because of the possibility of internal corrosion if significant moisture is also present. The Standard addresses this risk by mandating limits on moisture content and on relative humidity (RH) of the atmosphere in which the material is handled between stabilization and sealing of the inner container. This approach is taken because there are clearer technical bases and technical means for achieving specific moisture limits than there are for setting specific limits on chlorine content. Restricting RH precludes forming significant corrosion sites through formation of liquid droplets inside the container after it is sealed. Restricting the total moisture limits both gas generation and corrosion potential.

A.2. PURPOSE

This Standard supersedes DOE-STD-3013-2012 [USDOE 2012]. Information developed since issuance of that Standard has led to changes that improve the assurance of safety, and/or improve practical aspects of stabilization, packaging and storage without compromising safety. Among those changes are the following in the criteria section (note that the stabilization process, the stability criterion and the container are unchanged from DOE-STD-3013-2012):

- The RH limit after thermal stabilization was clarified to indicate that it applies only when chloride salts may be present in the material.
- Use of convenience containers is required when packaging plutonium-bearing oxides.
- Free Gas Volume limit was deleted based on improved understanding of gas generation, documented in Appendix B.
- All packaging and storage sites are required to participate in the Integrated Surveillance and Monitoring Program (ISMP). The mechanism and approval process for revisions of the ISMP are specified. Criteria for site specific surveillance programs are removed.
- Several criteria are moved to different sections of the Standard for clarification.

Changes in the technical basis section include the following:

- Updated results and implications from the surveillance studies on storage behavior on representative oxide materials covering the full range of actinide

content and bounding moisture conditions specified in the scope statement. These studies and destructive examinations have provided evidence that corrosion events occur within the 3013 container and that they could be controlled by the form and quantity of a deliquescent salt and the RH in the container.

- A critical assumption in earlier versions of the Standard shows a pressurization analysis where the reaction with plutonium dioxide fixes oxygen from adsorbed water and leaves a hydrogen-rich atmosphere. The research supporting this Standard has shown other gas producing reactions can occur. Overall, observed products include hydrogen, oxygen, carbon dioxide, nitrous oxide and methane. This work has also demonstrated that pressures are not observed to approach the design pressure of the container and are more likely to be less than 100 psia.

A.3. APPLICABILITY

No further basis provided.

A.4. REFERENCES

No further basis provided.

A.5. ACRONYMS AND DEFINITIONS

AMNMS	Assistant Manager for Nuclear Materials Stabilization, Savannah River Operations Office
ARIES	Advanced Recovery and Integrated Extraction System
DDT	Deflagration to Detonation Transition
DE	Destructive examination
DOE	U.S. Department of Energy
DRH	Deliquescence relative humidity
IR	Infrared (spectroscopy)
ISMP	Integrated Surveillance and Monitoring Program
LANL	Los Alamos National Laboratory
LLNL	Lawrence Livermore National Laboratory
LOI	Loss on Ignition

MIS	Materials Identification and Surveillance
MIS-WG	Materials Identification and Surveillance Working Group
MOX	Plutonium-Uranium Mixed Oxide
MS	Mass spectrometry
NDE	Nondestructive examination
QA	Quality Assurance
RFETS	Rocky Flats Environmental Technology Site
RH	Relative Humidity
SCC	Stress Corrosion Cracking
SNM	Special Nuclear Material
SRS	Savannah River Site
TGA	Thermogravimetric Analysis
TRU	Transuranic

A.6. STABILIZATION, PACKAGING, AND STORAGE CRITERIA

When measured values are compared with the following criteria in this Standard, measurement uncertainty must be included to provide confidence that these criteria are met. See Standard Section 6.0.

A.6.1. Stabilized Materials

A.6.1.1. Plutonium-Bearing Metals and Alloys

A.6.1.1.1. The ignition temperatures of plutonium metal and alloys are lowered as their specific surface area increases. Limiting the specific surface area of plutonium metal materials therefore reduces the potential for energetic events when such materials are handled, (e.g., when storage containers are opened). Thickness and surface area criteria are specified in the Assessment Report [USDOE 1994a], the Plutonium Handbook [ANS 1980], DOE-STD-3013-96 [USDOE 1996] and other relevant publications [e.g., Haschke/Martz 1998] as a minimum thickness of 1.0 mm (0.04 in.) and a specific surface area less than 1 cm^2/g (71 in^2/lb). However, a limit on

specific surface area is difficult to administer, so one based on weight is used instead. Los Alamos National Laboratory (LANL) evaluated a variety of regular geometric shapes to determine the relationship between limiting specific surface area conditions and piece weight [Haschke et al., 1996]. They determined that pieces approaching the limiting specific surface area generally weighed less than 1 g. Establishing the limit at 50 g provides a margin to account for limited irregularities in shape and other uncertainties. For some materials weighing less than 50 g, oxidation may be an unattractive option. An example would be bonded Pu-Be pieces, which, if oxidized, would create material with very high neutron rates. If pieces less than 50 g are to be packaged, calculations must be performed for each material type and appropriate physical measurements made on each piece to verify compliance with the specific surface area limit. Not allowing pieces less than 10 g to be packaged when using the specific area criteria maintains a factor of 10 margin above the 1 g value discussed above. Foils, turnings, and wires do not conform to the shapes evaluated and can easily have much higher specific surface areas. For this reason, they are excluded from the Standard. Materials rejected under this criterion should be converted to stable oxide powder.

A.6.1.1.2.   Sub-stoichiometric plutonium oxides, formed by partial oxidation of plutonium metal, can be pyrophoric [e.g., see USDOE 1994a, Haschke/Martz 1998]. The pyrophoricity hazard is mitigated by brushing easily removable oxide from plutonium metal prior to packaging the metal. The loose oxides generated by brushing should be stabilized according to this Standard. Oxide removal should not be so aggressive that the adherent oxide layer on the metal surface is removed. This layer is beneficial because it retards further metal oxidation and interdiffusion of metal constituents between the container and stored material [Haschke/Martz 1998, Williamson 1999].

Various reports describe the radiolytic effects of plutonium metal on organic materials such as plastics and oils which lead to corrosion of the plutonium and creation of potentially pyrophoric hydrides [e.g., see USDOE 1994a, Haschke/Martz 1998]. Also, reaction of plutonium metal with water and air can lead to highly reactive hydrides and nitrides under some circumstances [ANS 1980, Haschke/Martz 1998]. Since plutonium metal allowed by this Standard has low specific surface area (see Criterion 6.1.1.1 for details) and is therefore easily examined, visual inspection for free water and organic materials with the unaided eye is sufficient to assure that unsafe quantities of hydrides and nitrides cannot form by this mechanism during storage.

A.6.1.1.3.   Since plutonium turnings pressed into briquettes cannot be examined to determine that they meet the requirements of Criteria 6.1.1.1 and 6.1.1.2, they are not acceptable for storage in 3013 containers. They should be converted to stable oxide powder.

A.6.1.2.   Oxides

A.6.1.2.1.   This Standard requires thermal stabilization of oxide material by heating in an oxidizing atmosphere to at least 950 °C for at least two hours and subsequently verifying that the moisture content is less than 0.5 wt% at packaging. Thermal stabilization to these conditions has been shown to produce oxide that meets several stabilization objectives:

(a) *Reduce the water content to less than 0.5 wt% and similarly reduce equivalent quantities of species such as hydrates and hydroxides that might produce water.*

Water in oxide material can exist as physically adsorbed water on the surfaces of particles, as waters of hydration associated with mostly chloride salts, and as dissociated water, i.e. hydroxides, on the surfaces of metal oxides. The thermal desorption profiles of each of these types of water are different, but all reach completion well below the required 950 °C peak temperature of the stabilization process.

Physically adsorbed water has been shown to desorb from PuO_2 over a temperature range of 100 to 200 °C in a closed system where the vapor remains in contact with the solid [Paffett et al., 2003]. Thermal stabilization operations under this Standard are configured to allow water vapor to escape and so will desorb water from oxide at lower temperatures than a closed system, but the closed system data represents a good bounding case. Thermal stabilization in an oxidizing atmosphere will convert most metal impurities to oxides (e.g., Fe_2O_3, Cr_2O_3, and Ga_2O_3). Adsorption and thermal volatilization of water on these metal oxide particles is expected to be qualitatively similar to moisture interactions with plutonium oxide [Henrich/Cox 1996].

Plutonium oxide powder forms surface hydroxides upon exposure to moisture [Blesa et al., 1994; Farr et al., 2004]. Decomposition of the surface hydroxides of plutonium oxide under vacuum has been seen to begin at 100 °C and to be nearly complete by 590 °C [Farr et al., 2004]. Thermogravimetric data from samples of material heated under ambient pressure show somewhat greater persistence of some hydroxides, with around 0.01-0.02 mass% moisture not desorbed until the 700-950 °C range [Scogin 2016]. These will be removed almost entirely by 950 °C stabilization, and they are far below levels of concern for meeting the moisture content requirement for storage. Many other metal oxides also form surface hydroxides under a wide range of environmental conditions. Iron hydroxides, chromium hydroxide, and nickel hydroxide are reported to decompose and

evolve water in the 200 to 525 °C range [Galwey/Brown 1999].

Residual magnesium chloride and calcium chloride (alkaline earth chlorides) chemically bind substantial amounts of water as hydrates [Smith et al., 1999]. Calcium chloride dehydrates on heating to less than 200 °C [Bukovec et al., 1989]. Magnesium chloride first partially dehydrates and then undergoes hydrolysis to the oxide upon heating to 500 °C. Thus, all water associated with hydrated chloride salts will be lost by 500 °C.

Numerous thermogravimetric moisture measurements have been made on samples from batches of thermally stabilized material during Hanford and Rocky Flats packaging campaigns. These show that water is nearly all removed before the temperature ramp reaches 680 °C [Berg et al., 2010] [Scogin 2016]. Cases where material has failed to meet the moisture content criterion have been attributable to moisture uptake after stabilization rather than to failure of the stabilization to remove adequate moisture.

(b) *Eliminate reactive materials such as finely divided metal or sub-stoichiometric plutonium oxides that are reactive in air.*

The issue addressed by this requirement is avoidance of energetic events, for example, rapid oxidation of small metal pieces by air when storage containers are opened (see Section A.6.1.1 of this Appendix regarding metal reactivity). Other reactive metals or sub-stoichiometric oxides will behave similarly to plutonium metal and will be converted to oxides with thermal stabilization criteria specified in this Standard. The general plutonium technical literature, as well as many decades of operating experience, firmly establishes that sub-stoichiometric plutonium oxide and metal with particle size below the thresholds defined in this Standard (50g as noted in A.6.1.1.1) are completely converted to stable plutonium oxide by thermal stabilization at 950 °C in air for two hours [e.g., ANS 1980; Clark et al., 2008; Cleveland 1979].

(c) *Eliminate organic materials.*

The primary issue concerning the presence of organic materials (notably plastics) in stored plutonium oxides is the potential for gas generation (particularly hydrogen) as a result of radiolytic and thermal degradation. The technical literature conclusively establishes that all plastics less than about one inch in diameter and any other organic materials likely to accompany unstabilized plutonium materials are completely oxidized by air in less than five minutes at 800 °C [ACS 1995; Bockhorn et al., 1996; Panagiotou/Levendis 1996; Wey/Chang 1995; Zevenhoven et al., 1997]. It is

presumed that larger pieces will be removed by visual examination prior to thermal stabilization (see Criterion 6.3.2.3), but the literature indicates that even these will be destroyed by 950 °C thermal stabilization in air for two hours.

(d) *Minimize potential for water readsorption above the 0.5 wt% threshold.*

Water can be re-incorporated after stabilization by physically adsorbing to the surfaces, by formation of hydrates of principally chloride salts, and by formation of hydroxides. Reducing the specific surface area limits the amount of water that can be adsorbed onto the surfaces and formation of hydroxides on the surface. MIS measurements on materials stabilized according to this Standard, show that thermal stabilization at 950 °C for two hours generally gives specific surface areas below 5 m^2/gram for both pure and impure oxide material [Haschke/Ricketts 1995; Haschke/Ricketts 1997; Haschke/Martz 1998; Mason et al., 1999; Machuron-Mandard/Madic 1996]. A hydroxide layer (0.5 monolayers) covered with a monolayer of water on 5 m^2/gram material will result in 0.165 wt% adsorbed water (1.5 monolayers). High-purity oxide of less than 5 m^2/gram specific surface area lacks sufficient surface sites to readsorb 0.5 wt% water even with very long exposure to atmospheres with up to 50% RH.

Sodium chloride and potassium chloride will not resorb significant water after thermal stabilization unless subsequently exposed to an atmosphere exceeding their deliquescent relative humidities, which are quite high (see Table A-1). Alkaline earth chloride salts are more problematic because they can form solid hydrates at much lower humidity, as low as 1-2%. Even small amounts of alkaline earth chlorides when fully hydrated can hold sufficient water to exceed the 0.5 wt% limit. For example, conversion of 0.5 wt% of $MgCl_2$ to its hexahydrate would add 0.5 wt% water to a batch of material. Calcium chloride also readily forms hydrates at low RH. Alkaline earth chlorides can deliquesce to form a corrosive aqueous salt solution at low to moderate RH while still meeting the 0.5 wt% total moisture criterion, which is addressed in more detail in Section A.6.1.2.4.

Thermal stabilization reduces the $MgCl_2$ content by hydrolysis to form MgO, and somewhat less effectively converts some calcium chloride to CaO [Lawrence/Bu 2000]. However, the prescribed stabilization conditions do not drive the hydrolysis to completion. Control of time and RH between thermal stabilization and packaging can be used to limit moisture re-incorporation when handling plutonium oxides containing magnesium and calcium chloride impurities [Veirs et al., 2002].

(e) *Stabilize any other potential gas-producing constituents.*

This Standard's thermal stabilization criterion (2 hrs at 950 °C) is intended to ensure that in addition to moisture, all other potential gas-producing impurities in plutonium-bearing oxide materials are eliminated. The technical literature shows that nitrates and sulfates of plutonium are effectively converted to oxides by thermal stabilization at 950 °C [Waterbury et al., 1961]. All other nitrates and carbonates are expected to be decomposed by this procedure. Sulfate is known to be incorporated into plutonium oxide prepared by peroxide precipitation from sulfuric acid solutions [Leary et al., 1959]. The report of Moseley and Wing [Moseley/Wing 1965] shows that 950 °C thermal stabilization is sufficient to destroy this sulfate constituent. Literature searches indicate that deleterious amounts of radiolytic gases from residual sulfate contaminants are unlikely in the long-term storage conditions anticipated for stabilized materials [Tandon et al., 1999 and references therein].

Stabilizing at 950 °C in an oxidizing atmosphere for at least two hours has been shown to reliably meet all of the above stabilization objectives for a broad range of materials. Cases have arisen, however, where those stabilization conditions have been problematic for operational reasons. Item 5 in the Foreword to this Standard outlines a process for evaluating and requesting approval for equivalent alternative approaches to meeting stabilization objectives and criteria. The equivalency determination process has been followed and granted for three specific cases thus far:

- The major salt impurities in plutonium oxides from pyrochemical operations, NaCl and KCl, have moderate volatilities above 800 °C and sublime from the material to a significant degree during 950 °C stabilization. This result is neither necessary to produce a stable storage product, nor is it desirable because the salts deposit elsewhere in the stabilization equipment and cause significant maintenance issues in furnaces and offgas systems. The DOE has approved two submittals, one for the Rocky Flats Environmental Technology Site (RFETS) and one for the Hanford Site, for lower temperature stabilization as technically equivalent for specific chloride-containing materials [Boak et al., 2002; Boak et al., 2003].

- An equivalency employing a lower stabilization temperature for a longer time (four hours) was approved for high-purity PuO_2 produced by a specific process in the HB-Line at the Savannah River Site (SRS). The request was motivated by the determination that 950 °C stabilization of the HB-Line PuO_2 would preclude its use in direct fuel fabrication and reduce its value feedstock for other fuel fabrication processes. Studies showed with high

confidence that the lower stabilization temperature would be sufficient to reduce moisture content to acceptable levels, and that other stabilization objectives would be assured to have been met by a combination of assured product purity and post-stabilization handling and testing requirements [Duffey et al., 2013; Berg et al., 2014a].

- An equivalency allowing a lower stabilization temperature for two hours was approved for high-purity PuO_2 produced from oxidizing specific feed material in the LANL ARIES direct metal oxidation process [Duffey et al., 2013; Berg et al., 2014a]. The motivation for the request was to improve the longevity, reliability and throughput of process equipment. The technical evaluation primarily addressed demonstrating that the stabilization objective of eliminating any reactive finely divided metal would be achieved if oxidation in the first stage of this two-stage process was incomplete.

A.6.1.2.2. The standard accepts two approaches to verification that materials have been adequately stabilized: a) testing essentially every container loading (each container would have a moisture measurement applicable to it, even if the measurement was of a batch sufficient to fill several containers) or b) use of a "qualified process" for stabilization and packaging that would reduce the requirements for materials testing.

(a) Stabilization at 950 °C and appropriate handling prior to packaging ensure that the only significant mechanism for container pressurization is decomposition of readsorbed water into hydrogen gas, and that mechanism cannot produce sufficient gas to exceed the design pressure of the container. Thus, verification of adequate stabilization requires only a moisture measurement to ensure that residual moisture in the packaged material is below the threshold specified in Criterion 6.1.2.3.

This Standard encourages using one or more of the moisture verification methods that have been employed successfully in past stabilization and packaging campaigns. These methods are all based on heating a sample of stabilized material to 1000 °C and measuring the volatilized moisture. The LOI test is accomplished by heating the sample to at least 1000 °C for at least one hour and determining the resulting weight loss after the sample cools. The LOI test is simple, inexpensive and highly practical in a glovebox environment, but it has limitations in cases where mass changes can be caused by processes other than volatilization of hydrogenous material content. The LOI test cannot distinguish moisture from other components that are volatile at temperatures below 1000 °C, so LOI tests on stabilized material containing impurities such as NaCl and KCl will indicate higher moisture content than is actually present. On the other hand, under-

measurement of the moisture content could occur through the masking effect of readsorption of moisture on the sample during the LOI cool-down period prior to the final weight measurement. Mass gain due to air oxidation of minor material phases during LOI would also lead to under-measurement of moisture. Residual sub-stoichiometric oxides that may persist in material from a metal oxidation process are one example. This Standard therefore encourages use of LOI only for high purity plutonium oxide materials that were not prepared by oxidation of metal, and only when the LOI analysis is performed in a dry glovebox [Roberson 2001 and Roberson 2002b]. A variation called Full-batch LOI was used during the packaging campaign at Lawrence Livermore National Lab [Hall 2002]. This Standard encourages the use of more moisture-specific alternative methods for lower grade materials.

Thermogravimetric analysis (TGA) to 1000 °C using an inert carrier gas has been the preferred alternative during packaging campaigns at the Rocky Flats, Hanford and Savannah River DOE Sites. Specific implementations were approved with heating rates restricted to be no greater than 20 °C per minute, and with an inert gas purge of high purity argon (≥99.999%) or helium (≥99.995) [Roberson 2002a,c]. Use of an inert purge gas mitigates against the potential masking effects of sample oxidation or moisture readsorption during cool-down. While it does not directly prevent mistaking other volatile components for moisture, experience has shown that the false failure rate is acceptably low for most materials. Where necessary, mass spectrometry (MS) or infrared absorption spectroscopy (IR) have been used to analyze the evolved gas from the TGA unit to confirm false positives. Heating rate and purge gas specifications were the same as for the TGA implementations. MIS has concluded that TGA coupled with either MS or IR is the preferred method for determining the moisture content of most plutonium bearing materials. Using MS or IR to analyze the off-gas from the TGA has the advantage of quantifying the amount of water that is driven off during the TGA.

Each site has the flexibility to request authorization, with justification, for moisture measurement methods of its selection. Inclusion of other techniques requires independent evaluation and DOE approval consistent with Item 5 of the Foreword.

(b) Qualification of the stabilization and packaging process would permit materials to be stabilized and packaged without the requirement for measuring the moisture content of every batch of material to be packaged [Erickson et al., 2002].

The plan to qualify a process must be developed by the packaging site, consistent with quality assurance requirements and practice at that site. The plan must include the following information:

(1) specific materials to be stabilized and packaged;

(2) process parameters (times, temperatures, glovebox humidity, etc.) that define the process being qualified;

(3) product testing program to demonstrate process stability and product consistency;

(4) post-qualification materials testing needed to verify continued process control;

(5) any changes to storage surveillance requirements needed to assess storage safety; and

(6) actions (such as including the process parameters in the facility Authorization Basis) required to "institutionalize" the qualified process. If the materials to be packaged are to be stored at another site, it is recommended that the storing site be consulted during development of the qualification plan.

Approval of a qualified process will be subject to a technical review of the qualification plan and testing program by an independent technical review team (see Item 5 of the Foreword). The review must include an assessment of the plan and testing results by the storing site, if that site is different than the packaging site.

A.6.1.2.3. The criterion of 0.5 wt% moisture provides a reasonable balance between the difficulty of achieving and measuring lower moisture contents and the cost (of both the container and any ancillary impact on storage facility size) of providing a container that will withstand the pressure theoretically generated by a higher moisture content. The correlation of the weight percent criterion with bounding pressures in storage containers is established in Appendix B (Derivation of Pressure Equation). It should be noted that adherence to this total moisture limit is not sufficient to prevent corrosion in chloride salt bearing containers (see Section A.6.1.2.4).

The 3013 Surveillance Program had performed over 230 nondestructive examinations (NDE) and over 100 destructive examinations (DE) through the end of 2016 on a total population of approximately 5100 containers. The ages of the containers examined range from 3 years to 14 years. All total internal pressures

observed in containers packaged in conformance with the requirements of this Standard have been below 159 kPa (23 psia). One non-conforming package, having a moisture measurement result 25% higher than the acceptance limit, was found to contain just below 301 kPa (44 psia) total pressure. Gas analyses performed on the DE containers have shown that none of the gas mixtures, including that in the non-conforming container, have been flammable.

MIS gas generation studies with represented materials show that actual pressures will be substantially below the bounding pressure. Each 3013 oxide container is represented by one or more Materials Identification and Surveillance (MIS) items that are believed to reasonably predict the behavior of the material in storage for 50 years [Narlesky et al., 2009a]. In small-scale surveillance studies, 10-gram samples are packaged in test containers scaled 1:500 by volume to 3013 inner containers with 0.5 wt% total moisture. Gases that have been observed within these tests containers include hydrogen, helium (from the packaging atmosphere), oxygen, carbon dioxide, nitrogen, carbon monoxide, nitrous oxide, and methane, in order of abundance. A report discussing the carbon dioxide observations proposed that trace carbonates surviving stabilization and CO_2 adsorbed from air exposure after stabilization were two possible source terms, but concluded these observations did not indicate an additional pressurization risk [Berg et al., 2002]. In large-scale surveillance studies, batches of up to 5 kg of material are studied in modified inner 3013 containers. The modifications include pressure and temperature sensors, and the ability to extract gas samples for gas composition determinations. The studies were started in January 2004 and are ongoing. Broad categories of material have been found to exhibit common behaviors.

High-purity oxides with greater than 85% total actinides, less than 200 ppm total chloride and up to 0.5 wt% added water were monitored in both large-scale and small-scale studies. At an initial water surface coverage of one monolayer, water activity was observed to decrease on a time scale of days to weeks and no hydrogen gas was observed. A reasonable hypothesis is that the surface-adsorbed water is slowly consumed by formation of surface hydroxyls. At somewhat higher water surface coverage, hydrogen is observed, but at a small fraction of the maximum possible from total conversion of the initial water content present (approximately 0.1% of the maximum calculated using the aggregate pressure equation [23] in Appendix B). After an initial hydrogen increase in the first month of about 2 kPa, the hydrogen partial pressure is observed to decrease with time. Oxygen is consumed in the presence of water vapor [Veirs 2008]. Carbon dioxide and nitrogen gas generation is observed and attributed to desorption due to competition with water or reaction of surface species with water [Veirs et al., 2008].

In all chloride salt containing materials studied by the MIS program at the bounding condition of 0.5 wt% water, hydrogen gas is generated [Veirs/Berg 2008].

Pyrochemical processing salts can contain alkaline earth chloride salts such as $MgCl_2$ or $CaCl_2$ that are not completely converted to oxide by thermal stabilization. The alkaline earth chlorides can absorb moisture at low values of RH. The rate of hydrogen generation decreases with time in all cases. The maximum predicted hydrogen partial pressures from the fit are substantially below the hydrogen partial pressures calculated using the aggregate pressure equation [25] in Appendix B, falling between 0% and 25% of the calculated pressure. Other gases observed include carbon dioxide, carbon monoxide, and methane, in order of decreasing partial pressure. Carbon dioxide is produced first. As the hydrogen partial pressure increases, carbon monoxide and then methane appear in a ratio of ~20:10:1. If carbon dioxide is not produced, then carbon monoxide and methane do not appear. In a few cases, nitrous oxide is observed at partial pressures of less than 3 kPa.

One MIS representative salt-bearing material reproducibly produced both hydrogen and oxygen in near stoichiometric quantities when loaded with 0.5 wt% water in shelf-life studies [Berg et al., 2007]. The gas mixture became flammable within a couple of months. The hydrogen and oxygen partial pressures both began declining after about one year. The decline is hypothesized as due to hydrogen and oxygen recombination overtaking the rate of hydrogen and oxygen production [Foy/Joyce 2008]. A narrow range of material conditions has been identified for the production of both hydrogen and oxygen [Berg et al., 2008]. Oxygen is only generated along with hydrogen when the concentration ratio of the alkaline earth chlorides to water gives an average of more than three waters of hydration and when the total water content is also greater than 0.3 wt%. If the alkaline earth chloride content is greater than 1 wt%, then the number of waters of hydration will be less than three at the allowed maximum of 0.5 wt% total water content. If the alkaline earth chloride content is low, then the water content must be kept below 0.3 wt% to ensure that oxygen will not be generated along with hydrogen. If hydrogen and oxygen are generated, they can persist as a flammable mixture for long periods of time, e.g. greater than five years.

The 3013 container system is robust and will withstand a deflagration or detonation of hydrogen/oxygen atmospheres at the highest observed hydrogen and oxygen partial pressures. Experimental studies show that a deflagration to detonation transition (DDT) can occur in the confined geometries between the inner and outer containers as well as in the headspace of the inner container and the convenience container. Slightly less than 2000 µstrain was measured during DDT deliberately initiated in testing on actual 3013 outer containers. The authors conclude that "DDT of a stoichiometric hydrogen/oxygen mixture (and mixtures diluted with nitrogen and helium) within the 3013 nested can containment system does not pose a threat to structural integrity of the outer can at initial pressures up to 3.5 bar and temperatures up to 150 °C" [Liang/Shepherd 2007 a, b, c].

Materials with salt impurities containing alkaline earth chlorides are those most likely to reabsorb water after thermal stabilization. When they contain moisture, these materials generate hydrogen and have the potential to also generate oxygen. Because the alkaline earth chlorides can pick up moisture from very low humidity atmospheres, the control of time and atmosphere between thermal stabilization and packaging is strongly advised when handling plutonium oxides suspected to contain more than trace levels of magnesium and calcium chloride impurities (see A.6.1.2.4 for discussion of the term "trace").

Other materials studied in small-scale surveillance include materials from the magnesium hydroxide precipitation process and materials with a high percentage of fluorine. These materials are observed to generate hydrogen but at small partial pressures, nearly an order of magnitude less than chloride salts.

A.6.1.2.4. Stress corrosion cracking (SCC) has been identified as being the greatest threat to 3013 container integrity [Kolman 2001; Lillard et al., 2009a,b]. Room temperature SCC of 304L and 316L stainless steels is reported to occur when in contact with aqueous solutions of the alkaline earth chlorides $MgCl_2$ and $CaCl_2$ commonly present in plutonium processing salts [Shoji/Ohnaka 1989; Tani et al., 2009]. Room temperature SCC of stressed 304L sample coupons in contact with plutonium oxide with a small amount of $CaCl_2$ and 0.5 wt% moisture has been observed in the MIS program [Lillard et al., 2009a; Zapp et al., 2010; Zapp/Duffey 2008]. The moisture content of the material in these tests is consistent with the formation of deliquesced $CaCl_2$.

The limitation on humidity exposure in this Standard is intended to prevent potential formation of corrosion-enabling droplets of aqueous solution. Some materials may contain hygroscopic chloride salts introduced by chemical processing, e.g. electrorefining or direct oxide reduction, or from mixing with, contacting, or being processed in the same equipment as materials known to contain chloride salts. These salts are susceptible to post-stabilization moisture uptake from the handling atmosphere prior to container closure. They can form liquids by absorbing water from the atmosphere, a process known as deliquescence. The RH at which a particular chloride salt deliquesces is a fundamental chemical property of the salt.

Small amounts of deliquesced salts are difficult to detect in a batch of stabilized material because the powder still can be free-flowing. The most obvious technical approach to preventing deliquescence of chloride salts is to ensure no exposure to RH above their deliquescence relative humidity (DRH). When that is not possible, the amount of time that the material is exposed above the DRH can be limited. If the approach is to limit the time, then a technical basis may be developed that justifies the length of time and the RH allowed. Section 5 of the Foreword, fourth bullet states that "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" may be submitted, technically justified, and approved by the DOE.

The DRH of the common plutonium processing salts has been studied in the MIS program [Veirs et al., 2010]. The DRH for the pure salts is well known [Greenspan 1977]. At 25 °C the DRH levels for KCl, NaCl, and $MgCl_2$ are 84%, 75%, and 33%, respectively. The DRH for these pure materials decreases slightly with increasing temperature. The RH at which calcium chloride forms a liquid is complicated by the various hydrated phases that are stable near room temperature. At 25 °C, calcium chloride can form the hexahydrate, which deliquesces at 29% RH. At 35 °C, calcium chloride tetrahydrate deliquesces at 20% RH before the hexahydrate is formed. At 45 °C to 70 °C, calcium chloride dihydrate deliquesces at 17% RH [Kelly/Wexler 2005].

More complex, ternary salt phases are also expected to be important additional constituents of material from many processes. Identification of the salt phases produced when alkaline earth chlorides are thermally stabilized with NaCl and KCl has been investigated. For magnesium chloride thermally stabilized with an equi-molar mixture of NaCl and KCl, the phase that controls the DRH has been found to be $KMgCl_3$ or carnallite [Garcia et al., 2007]. This salt deliquesces around 57% RH at room temperature. For calcium chloride thermally stabilized with an equi-molar mixture of NaCl and KCl, the phase that controls the DRH has been found to be $KCaCl_3$ or chlorocalcite [Narlesky et al., 2009b]. Chlorocalcite deliquesces at 16% RH at 25 °C and at 21% at 70 °C. The DRH values of known processing salts and a few examples of other salts with low DRH are shown in Table A-1.

Table A-1. Deliquescent RH of chloride salts used in pyroprocessing. DRH values are at 25 °C unless otherwise indicated.

Compound	DRH(%)	Reference
KCl	84	Lide 2003 page 15-25
NH$_4$Cl	79	Lide 2003 page 15-25
NaCl	75	Lide 2003 page 15-25
KMgCl$_3$·6H$_2$O	57	Lide 2003 page 15-25
MgCl$_2$·6H$_2$O	33	Lide 2003 page 15-25
CaCl$_2$·6H$_2$O	29	Lide 2003 page 15-25
MgCl$_2$·6H$_2$O (70 °C)	27	Joyce et al., 2010
KCaCl$_3$ (70 °C)	21	Joyce et al., 2010
CaCl$_2$·4H$_2$O	20	Joyce et al., 2010
CaCl$_2$·2H$_2$O (70 °C)	17	Joyce et al., 2010
KCaCl$_3$	16	Joyce et al., 2010
FeCl$_3$	31	Apelblat/Korin 2002
FeCl$_2$	55-59	McCafferty 1981
LiCl	12	Apelblat/Korin 2002
ZnCl$_2$	10	Shoji/Ohnaka 1989

Limiting exposure during post-stabilization, pre-closure handling to below 15% RH provides a comfortable margin to prevent deliquescence for material suspected to contain alkaline earth chloride salts, which deliquesce at the lowest RH of chlorides that would normally be considered credible. If an unusual chloride impurity is suspected, special evaluation may be needed to establish appropriate handling restrictions.

Materials packaged to this standard frequently do not have quantitative chemical impurity analyses. For this reason, handling of materials should be based on the best available knowledge. If the material originated in a process expected to introduce chloride impurities such as a pyrochemical salt process or a process that uses chloride based chemical processing, this requirement applies. In addition, if prompt gamma analysis indicates the presence of chlorine above background level or if chemical impurity analyses show chlorides are present above trace levels, this requirement applies. For the purpose of this standard, a conservative threshold for trace level is defined as 200 parts per million where the container sets are fabricated from 304 stainless steel or 1000 parts per million if all of the containers in the container set are fabricated from 316 stainless steel. Levels below these thresholds have been shown to be safe for stainless steel equipment in aqueous systems [SSAS, 2001].

A.6.1.3.   Engineered Materials

A.6.1.3.1.   For purposes of this Standard, fabricated fuel made from metals or sintered oxide fuels are considered to be stabilized and contained provided that the cladding has retained its integrity. When there is assurance of cladding integrity, the stabilization requirements of this Standard are deemed to have been satisfied.

A.6.1.3.2.   Sintered oxide fuel pellets qualified for nuclear fuel are quite pure, have controlled stoichiometry, and have been formed at more elevated temperatures than specified in this Standard for stabilization. Consequently, unirradiated pellets need only meet the moisture criterion in Criterion 6.1.2.3 to be considered "stabilized material" and to be eligible for packaging. Pellet materials that do not meet that criterion should be stabilized according to the provisions of Criterion 6.1.2.1 of this Standard.

A.6.1.4.   Storage after Stabilization – Deferred Packaging

The stabilization step, together with verification of stabilization at that time, provides certainty that the material was stable at a point in time. A high degree of confidence that the material is still stable is provided by the observation that the container and material appear unchanged and the moisture content remains acceptably low. Evidence of change would include, for example, corrosion or substantial pitting of the container, or significant discoloration of the contents. To provide assurance of stability, verification of the moisture content is required, either by measurement, or by some other defensible analysis. A deferred packaging which fails to satisfy the Stabilization Acceptance Criterion must be re-stabilized and have its moisture content verified, or it must be treated and verified in an alternative manner approved by AMNMS.

As discussed above in A.6.1.2.4, oxides containing some chloride salts are capable of becoming corrosive after stabilization if they subsequently absorb sufficient moisture from a humid handling or storage atmosphere. Therefore, controls must be put in place to limit such moisture absorption after stabilization.

A.6.2. 3013 Container

A.6.2.1.   Container Design Concept

A.6.2.1.1.   The design goals for the 3013 container are that it be maintenance free and compatible with existing or planned qualified shipping packages without further reprocessing or repackaging.

A sealed container design, rather than a container design with a gas filter, was selected for two reasons: 1) gas filters allow the entry of moist air which could interact with salts and other impurities contained in the stored materials; and 2) if

the container were not always oriented properly, stored powder could plug the filters and later "blow out" causing, at a minimum, a local spread of contamination.

A welded closure is preferred because it is believed to provide the best combination of features such as design qualification test performance, ease of assembly under production conditions in a glove box, container payload capacity, and achievement of a 50-year life.

The convenience container is a container that is used to transfer plutonium-bearing material. A convenience container is not considered an isolation barrier by this Standard. Use of a convenience container is optional when packaging plutonium-bearing metals or alloys, but is required when packaging plutonium-bearing oxides. For oxides, a convenience container reduces the potential for contamination to be transferred to the outer surface of the inner container prior to and during welding, and reduces the risk of weld failure due to oxide incorporation. The convenience container also provides a barrier protecting the inner container from direct contact with potentially corrosive salts during storage.

A.6.2.1.2. These requirements simply provide functionality in the design.

A.6.2.1.3. Storage of plutonium-bearing material must comply with existing material control and accountability (MC&A), safeguards and security, and audit and surveillance directives which rely on nondestructive assays as a technique for validation. The MC&A requirements call for routinely assaying stored materials for process, accountability, and inventory controls. Plutonium packaging and storage should not preclude adherence to these directives.

A.6.2.1.4. Pressure indication, such as a pressure deflectable lid or bellows observable by radiography, will permit early detection of inner container pressurization prior to potential failure. The pressure detection threshold [set at 790 kPa (100 psig) in this Standard] balances the need to minimize "false positives" with the need to eliminate "false negatives." Pressure buildup in the container is expected to yield internal pressures less than 790 kPa (100 psig). Additionally, there are no known mechanisms for pressure buildup in containers holding plutonium metal [Spearing/Crooks 2003]. An internal pressure indication of 790 kPa (100 psig) is therefore adequately indicative of unexpected pressurization, yet far below the design pressure for the outer container (Criterion 6.2.1.5 requires the design pressure to be at least 4920 kPa, or 699 psig).

A.6.2.1.5. Specifying a minimum design pressure provides compatibility with the safety envelopes for current and planned storage facilities. The specified design pressure of 4920 kPa (699 psig) is sufficient to contain the pressure generated under the highly conservative bounding assumptions originally used for the design. It thus

accommodates bounding storage conditions at most, if not all DOE facilities where plutonium-bearing materials might be stored.

A.6.2.1.6.   Section 7, Pressure Safety, of Attachment 1 to DOE O 440.1B, requires that the ASME code or an alternative design code equal or superior to the intent of the ASME code be used for pressure vessels. Since the outer container qualifies as a pressure vessel but cannot be hydrostatically tested when loaded because of its contents, and the final weld is not performed by the manufacturer, it will not be ASME stamped. However, there is precedence in the shipping container qualification process for less than literal adherence to the code. In this Standard, the outer container is designed to ASME requirements and the fabricator manufactures the outer container according to code but does not stamp the outer container as complying with the code. This approach should be used in application of this Standard by designing and manufacturing the outer storage container to ASME specifications (for example, ASME Boiler and Pressure Vessel Code VIII) with exceptions documented to show safety equal to or superior to the intent of the ASME code.

The container may be designated as "Safety Class" in Safety Analysis Reports or other Authorization Basis documents because it provides primary containment.

It should be noted that designation of the outer container as a pressure vessel can arise simply because of the need to contain the internal pressure generated by radioactive decay and by operation at a temperature higher than that at which it was filled and sealed. Beyond that, the outer container's function as the primary containment requires that it be able to contain the pressures that might conceivably be generated by all credible processes.

Finally, it should be noted that the pressure estimates are considered to be highly conservative bounding estimates. Current data indicate that it is unlikely that container pressures will exceed 790 kPa (100 psig) under normal storage conditions during a 50-year storage period [Duffey et al., 2010]. It should also be noted that the container atmosphere may include appreciable percentages of hydrogen in the total gas at the time of opening, and appropriate precautions should be taken.

A.6.2.2.   Container Construction

A.6.2.2.1.   Use of low-carbon stainless steels, such as 304L and 316L, is recommended for the outer and inner container construction, with 316L being preferable to 304L because of its greater corrosion resistance. Both materials are justified on the basis of extensive experience in this and similar types of service. Stainless steels 301, 302, and 303 are not recommended due to their relatively low concentrations of alloying additions. The use of higher alloyed materials is probably beneficial to container

corrosion resistance, but given the less thorough analysis of these alloys in the literature, it may be prudent to avoid their use at this time.

A report on corrosion [Kolman 2001] strongly recommends low carbon grades of stainless steel to avoid sensitization to SCC. The report also notes the importance of welding techniques that will not sensitize the steel to SCC.

A.6.2.2.2. The Assessment Reports [USDOE 1994a, USDOE 1994b] describe radiolytic effects with plastics, hydrogenous compounds, and organic materials during storage of plutonium-bearing materials. Prolonged plutonium storage necessitates exclusion of such materials from sealed containers because radiolysis and thermolysis of organic material can produce combustible and corrosive gases and increase pressure within sealed containers. Radiation and heat also can potentially change the composition of organic materials so that they no longer perform their intended packaging function. Therefore, such materials should not be used in fabricating the inner or outer containers.

Elastomeric seals on food-pack cans have been used for storage of plutonium. Although such containers have been used successfully with little or no significant seal degradation, this Standard conservatively excludes them from use.

Organic materials may not be used as structural components, sealants or coatings of any of the containers. It is understood that organic material may be used as an aid during manufacture. For example, cutting oil is used during the machining of stainless steel containers. After manufacture, the containers should be cleaned to remove such residual oils.

A.6.2.2.3. The 3013 container is sized to fit into existing certified or currently proposed shipping packages. This container design will minimize future handling and avoid unnecessary additional personnel exposure, operational risk, and waste generation.

A.6.2.2.4. Identification markings are required on all storage containers to facilitate maintenance of an inventory database and management of stored materials.

A.6.2.3. Container Testing Criteria

A.6.2.3.1. Design Qualification Testing. These testing criteria are to qualify the design of the containers and not to be applied to loaded containers.

(a) The purpose of the 9-meter drop test of the entire 3013 container is to ensure that a storage container accidentally dropped from the maximum storage height would not release any material. The number of tests, the number of samples per test, and the drop orientation of the samples are specified in 49 CFR Section 178.603(a). The target for the drop tests is

defined in 49 CFR Section 178.603(d). The distance of the drop is measured from the target to the lowest point on the sample container. The drop height specified in the criterion is to be used instead of the heights indicated in 49 CFR Section 178.603(e). The simulated contents shall include the mass of any convenience containers. The criterion for passing this test is that the 3013 container retain its function, (i.e., that it remain leak tight as defined by ANSI N14.5 [ANSI 2014]).

(b) The purpose of the 1.3-meter drop test for the inner container is to ensure that a loaded inner container being handled during packaging operations and not yet sealed in an outer container would not release any material if accidentally dropped from the maximum packaging height. The simulated contents shall include the mass of any convenience containers.

(c) The hydrostatic proof test provides verification that the container will remain leak tight under maximum design conditions, plus a safety margin.

A.6.2.3.2.   Testing and Inspection Following Container Closure

(a) ANSI N14.5, Leakage Tests on Packages for Shipment, specifies that the acceptable maximum leakage rate is 1×10^{-7} std cm^3/sec of dry air at a differential pressure of one atmosphere [ANSI 2014]. Full penetration weld closures provide the highest integrity and longest life seals possible. Welds eliminate gaskets, which may degrade and leak. Mechanical seals using bolts or screwed connections are susceptible to wear, creep relaxation, seizure, or other mechanical failure.

In the context of leak testing, the term "at time of closure" is used for two purposes. First, since the fill gas (such as helium) is normally used as a tracer gas for leak testing, the leak test must be performed soon enough after welding to assure that the gas has not escaped through a possible leak path to the point that the leak test is invalidated. Second, the term is used to clarify that the standard requires an initial leak test, but does not require subsequent leak tests during storage.

(b) Flaws in initial packaging are expected to be detected by inspection, including leak testing, of every 3013 container within 30 days of packaging. Ordinarily, this inspection should be done immediately after closure, but allowing up to a 30-day delay reasonably accommodates operational considerations. (A restriction to less than 30 days may be necessary for leak testing as discussed in Section A.6.2.3.2.a) This initial inspection provides baseline information on the leak rate of both welded containers (the inner container should be inspected after it is closed and before sealing inside the outer

container, and the outer container inspected after it is closed). This initial inspection and test may be part of the quality program for verifying 3013 container integrity.

(c) The requirement for initial pressure indication applies to oxides and not to metals. Stored metals are not considered vulnerable to pressure generation in storage and therefore do not need a baseline indication against which to measure future pressure changes [Spearing/Crooks 2003]. Since pressure inside the inner container may begin to change soon after closure, the baseline non-destructive examination for pressure indication should be performed as soon as possible after the inner container is sealed. This examination may be done either before or after the inner container is welded in the outer container. Allowing up to a maximum 30 days to complete the measurement accommodates operational considerations. The time requirement for initial baseline inspection for pressure indication, within 30 days of inner container closure, is intended to assure that a measurement is made before any significant pressurization has had time to occur between sealing and the measurement. The usual pressure indicator is inner container lid distortion. The initial baseline inspection uses any sufficiently accurate method to measure the lid position at a pressure that is assumed to be equal to that under which the container was sealed. It is important that this be a sufficiently accurate measurement that can be used to compare with a radiographic measurement of the lid position in a future non-destructive surveillance.

(d) The outer container will be placed in and moved through contamination-free areas. It is important that the container not compromise the contamination-free nature of those areas. Furthermore, the outer container, prior to filling or loading, should still be capable of placement in, or transport through, contamination-free areas.

The inner container is the innermost barrier to release of radioactive materials. To ascertain that this barrier has been adequately established, the container is tested to confirm that it is leaktight. Removable contamination should be minimized as much as reasonably achievable, and should not exceed 2000 dpm/100 cm^2, which is the threshold between a "contamination area" and a "high contamination area."

In earlier versions of this Standard, there was a requirement that, at the time of closure of the outer container, the exterior surface of the inner container be contamination-free, as defined in Appendix D to 10 CFR 835. That requirement has now been removed and replaced with the requirement stated above. The reasons for the change are as follows:

- Once the outer container has been sealed, there is no way to determine whether the inner is contaminated or not. On opening the outer, the assumption must be made that the inner is contaminated. Thus, an initially contamination-free inner container provides no benefit after the outer is closed.

- Contamination levels up to 2000 dpm/100 cm^2 do not pose a significant health threat in this application.

- Contamination levels up to 2000 dpm/100 cm^2 do not limit disposal of the outer, which could become contaminated by contacting the inner, as low-level waste.

A.6.3. Contents

A.6.3.1.   Container Fill Gas

A.6.3.1.1.   The stored material condition should not change significantly because of reactions with the container atmosphere. A significant change would be one that increases storage risks from the as-packaged condition. For example, packaging plutonium metal in a container with an air atmosphere can cause a small amount of additional oxidation of the metal, but will not increase the storage risks. If material stabilization has to be repeated to mitigate such risk, there would be additional handling and unnecessary worker radiation exposure.

A.6.3.1.2.   The container atmosphere must not act to mask leak testing and must support leak testing. This requirement can be met by using helium as a major component of the fill gas if helium leak checking is to be used to test the containers.

A.6.3.2.   Contained Materials

A.6.3.2.1.   The mass limit for fissionable materials is based on criticality safety limits for plutonium. The subcritical mass limit given in ANSI/ANS-8.1 for pure ^{239}Pu metal is 5.0 kg [ANSI/ANS-8.1 2014]. The 4.4 kg limit specified corresponds to the limit for some shipping packages and allows a modest additional margin of safety. Note that the mass limit applies to all fissionable species and not just ^{239}Pu. This constraint prevents potential criticality incidents involving stored fissionable materials (i.e., ^{233}U, ^{235}U, ^{237}Np, or higher plutonium isotopes) because the critical masses of fissionable radioisotopes are greater than that of ^{239}Pu [ANSI/ANS-8.15 2014; Clayton 2010].

In terms of plutonium mass, 5.00 kg (11.02 lb.) of plutonium oxide is equivalent to 4.40 kg (9.70 lb.) of plutonium metal. The oxide weight limit refers to the total mass of the plutonium-bearing materials present, not just to the plutonium oxide content.

This constraint provides additional assurance of subcriticality by making the conservative assumption that all the contents are pure plutonium dioxide. Mass limits may be further limited by facility-specific considerations including administrative criticality, radiation, and thermal power (heat output) constraints. Note that the mass limit does not imply subcriticality of arrays and the normal, more facility-specific analyses are required to demonstrate criticality safety in storage and transportation.

For consistency, and through a similar reasoning process, the total mass of metal, including alloying additions and other non-fissile species, is also limited to 5.0 kg (11.02 lb.).

Finally, keeping the mass of the contents at or below 5.0 kg (11.02 lb.) ensures that the safety envelope established through the container certification (drop testing) program is maintained.

A.6.3.2.2.   Total Thermal Power and Temperature-Dependent Effects in Plutonium Metal

(a) Total Thermal Power

The thermal output is limited to assure compliance with limits at existing and planned storage facilities as well as for possible future shipment off-site. Because the mix of plutonium isotopes (and americium) will vary during storage, the thermal power will vary also. The limit is applied to the maximum thermal power over the storage period. A discussion of thermal power in plutonium is found in Section B.4 of Appendix B.

The 19-watt limit also caps temperatures that may be reached under normal and off-normal conditions. Calculations performed at the Savannah River Site indicate that the temperature of the interface between the plutonium metal and the stainless steel container will not exceed approximately 189 °C (372 °F) even when the container is placed in a 9975 transportation package, exposed to diurnal solar heating and an ambient temperature of 37.8 °C (100 °F), provided the thermal power of the contents does not exceed 19 watts [Hensel 1998b]. These calculations have also shown that the centerline temperature of the plutonium metal will not exceed approximately 202 °C (397 °F) under the same conditions. These and other results are given in Table A-2. In evaluating temperature dependent phenomena in plutonium metal, it was conservatively assumed that the plutonium and the plutonium-steel interface were at 250 °C (482 °F), thereby providing considerable margin to the calculated maximums [Williamson 1999].

A detailed model to more accurately predict thermal conductivity (k) in high-purity plutonium oxide was developed in 2006 by using experimental data

taken in support of MIS large scale shelf life studies [Bielenberg et al., 2006]. Contributions to the overall thermal conductivity from the container fill gas in the pore phase were pressure dependent and the extent of solid to solid particle conduction was determined. Using the more accurate and experimentally determined values for thermal conductivity, the predicted peak centerline oxide temperatures were about 50 °C lower than those predicted by Hensel for similar thermal power and the same 3013/9975 configuration, for example 227 °C versus 275 °C for the peak oxide temperature during conditions of transport in a 9975 as shown earlier in Table A-2.

Table A-2. Calculated temperatures (°C) in a 9975 package

	Storage 19 W		Transport 19 W		Storage 30 W
Location	Oxide	Metal	Oxide	Metal	Oxide
Top	93.9	77.8	142	126	120.6
Bottom	91.7	86.7	140	134	117.2
Side	98.9	85.6	147	133	128.3
Pu/Can		148.9		189	
Pu Peak	229.4	165	275	202	331.7
Average Gas	164		211		230

From Hensel 1998a, 1998b. Average gas temperature estimated as midway between Pu Peak and Side temperatures. Calculations assumed a 37.8 °C ambient temperature and temperatures under "Transport" are peak temperatures when exposed to diurnal solar radiation. "Top," "Bottom" and "Side" refer to locations on the outer container, and "Side" is at the middle height of the contents.

Additional thermal modeling of the 3013/9975 storage configuration was performed in 2007 for Rocky Flats and Hanford storage configurations [Gupta 2007]. Fill gas was assumed to be 75% He and 25% air by volume. Various oxide densities and resultant fill height and thermal power were modeled at 4.7, 10, and 19 watts. A wider range of ambient temperatures was evaluated. Results were generally less than previous thermal models. The study also concluded that uncertainty in thermal conductivity of the powder had only a very small effect on the average gas temperatures in the containers.

Comparative results from all three models are presented in Table A-3.

Table A-3. Comparative models for oxide at 19 watts calculated temperatures (°C)

Location	Hensel[a]		Bielenberg[b]	Gupta[c]	
	Storage in 9975	Transport in 9975	Transport in 9975	Storage in bare 3013	Storage in 9975
Ambient T	37.8	37.8	37.8	33.1	33.1
Top	93.9	142		53	110
Bottom	91.7	140		73	114
Side	98.9	147	147	69	121
Peak Oxide (centerline)	229.4	275	227	110	160
Average Gas[d]	164	211		79	129
Assumed k (watt/m-K)	0.079		0.15	0.45	

    a. Hensel 1998a, Hensel 1998b
    b. Bielenberg et al., 2006
    c. Gupta 2007
    d. Average gas temperature estimated as midway between Pu Peak and Side temperatures.

Potential metal storage issues related to metal temperature include 1) volume changes associated with plutonium metal phase transitions and 2) metallurgical interactions between plutonium metal and the container walls. These two issues are discussed below.

    (b) Plutonium metal phase changes

        The alpha to beta phase transition of plutonium metal, which occurs near 119 °C, is accompanied by a 10% volume increase [ANS 1980; Flanders/Krishnan 1999; Spearing et al., 1999; Spearing/Veirs 1999;]. This volume change typically is not fully recovered when the metal is returned to the alpha phase by cooling below the transition temperature. Concern that cycling of alpha plutonium metal through the alpha-beta phase transition could cause enough radial growth in the contained metal to damage or breach the container led to experiments to address this issue [Flamm 1997; Spearing et al., 1999; Spearing/Veirs 1999]. A peer review of these experiments concluded that "the only potential failure mode that we could anticipate is one of fatigue resulting from repeated cycles" [Hecker/Stevens 1999]. Experimentally, it is observed that plutonium volume expansion occurs anisotropically in a cylinder with more expansion in the axial direction than in the radial direction. Also, the fraction of expansion occurring in the axial direction increases as the strength of the can increases. The peer review

concluded that cycling through the beta-gamma transition alone near 185 °C would be less demanding on the container than the alpha-beta transition cycling because 1) the volume change is significantly less for this transition and 2) the strength of stainless steel decreases more slowly with temperature than the strength of plutonium. Finite element analysis using the alpha-beta transition experiment data evaluated the fatigue loading on the storage containers and showed that the storage containers meet the requirements of the ASME Boiler and Pressure Vessel Code, Section VIII, Division 2 [Flanders/Krishnan 1999]. Confirmatory tests and analyses at the beta-gamma transition have reinforced the Flanders/Krishnan conclusions [Spearing et al., 2001].

(c) Metallurgical interactions

Maximum plutonium-container interface temperatures up to approximately 189 °C (see "Pu/Can" row in Table A-2) have been postulated for plutonium metal storage containers under bounding conditions. The potential for forming low-melting eutectics has been evaluated based on the available phase diagram data, diffusion data, and effect of surface oxides [Williamson 1999]. This study concluded that the storage of Pu metal and Pu-Ga alloys in stainless steel containers will not lead to the formation of liquids, or result in direct release of plutonium by means of diffusion mechanisms, as a result of storage at temperatures up to 250 °C. The lowest melting liquid system identified in this study (about 400 °C) results from the addition of small amounts of Ga (~1 wt%) to a two-phase Pu-Pu_6Fe mixture. The margin of about 150 °C between the melt temperature and the conservatively assumed metal storage temperature of 250 °C is judged to be adequately safe.

However, while directly applicable data are limited, this study could not categorically exclude the possibility of reduction of inner storage container mechanical strength due to Fe diffusion into Pu. If a 250 °C theoretical storage condition extended for a long time period (10 years or more) and the plutonium metal intimately contacts the container, the wall thickness of the container could be reduced. However, these analyses were very conservative in not taking credit for protective oxide films and the small surface area of metal-metal contact that will occur in practice. In addition, problems of this type have not been observed in numerous applications involving direct plutonium-stainless steel interactions, including stainless steel clad nuclear fuels [Louthan 1998]. Failure of inner welded cans by this mechanism therefore appears to be highly unlikely.

A.6.3.2.3.   Some oxide to be packaged may include foreign objects such as metal items and processing debris. These materials should be removed from the oxide prior to

packaging. Items may be removed manually or by screening the powder, and can be removed either before or after stabilization.

A.6.3.2.4.   Because the oxide (including contained impurities) can absorb water from the handling atmosphere, care must be exercised to ensure that the sample taken for moisture analysis be representative, at the time of its analysis, of the material actually packaged into the 3013 container. This can be done, for example, by controlling the glovebox RH and/or packaging within a very few minutes of sampling.

A.6.3.2.5.   This Standard prohibits packaging materials that may adversely affect the integrity of the containment system. The primary corrosion mechanisms of interest are pitting and SCC.

General corrosion is not a credible failure mechanism because the quantity of oxidizer (oxygen or water) available to react with the thick-walled containers is too limited to be significant. The initial amount of gas phase oxygen present if an air atmosphere was present during packaging plus the maximum oxygen that could be produced from catalytic or radiolytic decomposition of water would not be sufficient for general corrosion to affect the 3013 container integrity [Kolman 2001].

Kolman's paper also discusses a number of other potential container failure mechanisms. Hydrogen embrittlement is not anticipated to be an issue if, as expected, large hydrogen pressures (well above that predicted by the pressure equation) do not develop in the containers. Ionizing radiation at the anticipated flux levels is not expected to alter container material properties enough to increase the susceptibility to corrosion. Preliminary accelerated corrosion susceptibility tests of stainless steel weld specimens support this conclusion. Kolman's paper states that it is critical that welding practices do not result in sensitization of the stainless steel container. To avoid sensitization, the use of low carbon grades of stainless steel is strongly recommended, as is the use of weld filler material. Moreover, the use of stress-relieved container materials is strongly recommended [Kolman 2001].

Likewise, it is concluded that gallium embrittlement is unlikely to be a significant issue [Kolman et al., 2004; Kolman/Chavarria, 2004].

Unlike general corrosion, pitting and SCC are not mass limited. While SCC is a definite issue for stainless steel in the presence of deliquesced chloride salts, SCC is not a concern if water activities (relative humidities) within the storage containers are too low for an aqueous liquid phase to form and persist. The stabilization and packaging criteria of this version of the Standard provides confidence that aqueous phases will not be formed within containers packaged. Salt-bearing materials packaged under atmospheric conditions of greater than 16% RH, as allowed in

earlier versions of this standard, have the potential for localized liquids from deliquesced salts.

Stress Corrosion Cracking (SSC) has been observed at room temperature in shelf-life studies in which 304L test specimens were placed contact with PuO_2 powder with 0.9 wt% NaCl, 0.9 wt% KCl, 0.3 wt% $CaCl_2$ and 0.5 wt% water, respectively [Mickalonis/Duffey 2012; Zapp/Duffey 2008;]. The consensus opinion of MIS and corrosion experts is that the multiple, nested, robust design of the 3013 container system will prevent failure during storage, even if the unlikely conditions (salt composition, water content, internal humidity) are found to occur [Roberson 2008; Worl et al., 2008]. Nonetheless, an MIS-recommended corrosion study is addressing the potential for SCC, and ongoing destructive examination of random and select containers is necessary to provide sufficient long-term assurance of no container failures [Berg et al., 2014b; Zapp/Duffey 2008].

A.6.3.2.6. To promote material homogeneity for facilitating MC&A measurements and to preserve characterization information to the greatest extent possible, only similar materials (comparable in form and composition, for example) should be packaged together.

A.6.3.2.7. The performance of materials in storage environments is impacted by the presence of impurities, their concentration (for some impurities) and their chemical form. Therefore, the most rigorous representation is accomplished by having samples of the major process streams in the MIS inventory [AMNMS 2015; Narlesky et al., 2009a] (see MIS Program description A.1 Sidebar). If sites identify process streams that are not yet in the MIS inventory, a sample from that stream may need to be added to the inventory if the behavior of the material could be different from what has already been tested. Prediction of material storage behavior over time is dependent on extensive observations conducted on representative materials within the MIS program. Therefore, it is crucial that materials packaged to this Standard be represented in the MIS Program.

A.6.4. Storage - Integrated Surveillance and Monitoring Program

Surveillance and monitoring of 3013 containers is necessary to assure that the containers can be safely stored for up to 50 years. An effective surveillance program balances the risks (both safety and cost) associated with performing the surveillance examinations against the risks associated with container failures. A DOE complex-wide integrated surveillance program was initiated in 2001 [ISP 2001]. The current program is documented in AMNMS-15-0014. The program uses a combination of (1) Field Surveillance, which non-destructively or destructively examines containers randomly selected from the storage inventory plus containers selected by the MIS Working Group (MIS-WG) based on its engineering judgment, and (2) Shelf-life testing where

representative and other materials are tested in an accelerated manner to evaluate potential degradation mechanisms. Packaging of plutonium-bearing materials into 3013 containers began in 2001, Shelf-life testing began in 2001, and Field Surveillance began in 2005.

A.6.4.1.   Roles of Materials Identification and Surveillance Working Group (MIS-WG) in the ISMP

The MIS-WG is a DOE multi-site technical working group that provides the oversight and expertise needed to direct Shelf-life testing and Field Surveillance and evaluate the results from the surveillance program. The MIS-WG includes representatives from the plutonium storage sites and most of the plutonium packaging sites.

A.6.4.2.   MIS-WG May Recommend Changes to the ISMP

Based on the results from the surveillance program, the MIS-WG may decide that modifications to the program are needed. Any changes to the program must be approved by the AMNMS.

A.6.4.3.   Roles of Packaging and Storage Sites in the ISMP

A significant amount of information has been gathered from surveillance of the 3013 container storage inventory. Packaging sites have included Rocky Flats Environmental Technology Site, Hanford, Lawrence Livermore National Laboratory, Los Alamos National Laboratory, and Savannah River Site. Current storage sites for 3013 containers are the Savannah River Site and Los Alamos National Laboratory. Sites storing 3013 containers shall participate in the activities defined by the ISMP. Additional sites may be added with the approval of the AMNMS. If packaging and/or storage begins at other sites, information on the materials must be provided to the AMNMS for approval of inclusion in the ISMP. If sites temporarily store or stage material for a different site, the programmatic owner of the material may be designated to be responsible for some or all of the activities defined by the ISMP.

A.6.5. Documentation

A.6.5.1.   Database

An electronic database is specified because a manual database would be overly cumbersome. The architecture is not specified here to allow maximum flexibility to interface with existing databases and files. Some data will be classified, partly because Category I quantities of Special Nuclear Material (SNM) will be stored in the storage facility.

A.6.5.2.   Database Content Elements

A.6.5.2.1.   The material characteristics parameters in the database should provide as complete a description of the contents as is possible without undertaking additional characterization. The intent is to capture all available relevant information, and not to require additional characterization beyond that which is already available.

Packaging sites are required to report verification analytical moisture results using one of the methods specified in 6.1.2.2. However, some of those techniques are known to have high biases as measures of moisture content. For example, when using TGA to 1000 °C, the total observed mass loss is reported as moisture even though that mass loss often includes significant other volatile components including alkali chloride salts. More accurate assessment of moisture content can sometimes be obtained by further analysis of the verification data to correct for known bias, for example by excluding mass losses at high temperature where chloride salts become volatile in the TGA, or by analyzing moisture-specific data on volatiles such as that collected in TGA-MS or TGA-FTIR techniques.

Such data and assessments are included in the database as well, when available, as they may be useful for interpreting surveillance observations and predicting storage behavior. For example, the analysis of storage gas generation in Appendix B makes use of what has been judged to be the most accurate of the available analyses for packaging moisture for each container. These are currently reported as "best moisture" values for each container in the database, and are generally less conservative than the stabilization verification values.

A.6.5.2.2.   Container data can meet a number of needs. For example, if a 3013 container exhibits unexpected behavior, these data can help identify other, similar containers that may require inspection. These data also allow disposition processing to be optimized.

The results of the baseline inspection for pressure indication at the time of container closure are included in the database so that there is a basis for comparison to detect pressurization at the time of later surveillance inspections.

A.6.5.2.3 No further basis is provided.

A.6.6. Quality Assurance

No further basis is provided.

APPENDIX B.   DERIVATION AND GUIDANCE ON USE OF THE PRESSURE EQUATION

B.1.   INTRODUCTION

This appendix provides a derivation of the equation used to calculate the maximum expected internal pressure of storage containers loaded with plutonium oxide under normal operations. It also provides guidance on use of the equation. The pressure equation in this version of the 3013 Standard contains the same three terms as previous versions of the 3013 Standard, but modifies the two terms relating to (1) the generation of hydrogen gas and (2) the helium produced by alpha decay. The modifications are multipliers for each term that decreases the amount of hydrogen and helium entering the gas phase. The multiplier for hydrogen is derived from observations of the amount of hydrogen gas formed by the decomposition of water in 3013 containers as measured when they undergo destructive evaluation. The DE data is complimented by hydrogen gas observations in shelf-life studies, which are described in Section A.6.1.2.3. The multiplier for helium released into the gas phase comes from the literature. The values of the multipliers are derived from empirical observations. SI units have been used.

This Standard addresses conditions during normal operations. The gas behavior within the container during abnormal events is not evaluated. In particular, the temperature of the material during a facility fire can far exceed temperatures during normal operations. The water that has not formed hydrogen gas may still be present and can contribute to pressurization under high-temperature conditions in a manner not captured by the pressure equation. The helium will diffuse more rapidly at higher temperatures and enter the gas phase at higher rates. Evaluations of the gas pressure within 3013 containers during off-normal conditions with high temperatures should consider using a value of 1 for the hydrogen and helium multipliers.

Table B-1. Symbols and units

Symbol	Units	Description
P	kPa	Absolute Pressure
P_0	kPa	Initial pressure at time container is sealed
V	L	Volume in liters
n	mol	Amount of material in moles
R	kPa L K^{-1} mol^{-1}	Universal gas constant, 8.3145 kPa L K^{-1} mol^{-1}
T	K	Average gas temperature
P_F	kPa	Partial pressure of the fill gas
P_{H2}	kPa	Partial pressure of the generated hydrogen gases
P_{He}	kPa	Partial pressure of the helium produced by alpha decay
V_c	L	Unoccupied volume of the outer container
V_g	L	Volume of the outer container occupied by gas

Symbol	Units	Description
V_m	L	Volume of the contained material
V_{oc}	L	Interior volume of the outer container
V_i	L	Volume of the material of the inner container
V_{cc}	L	Volume of the material of the convenience container
m	kg	Mass of material
ρ	g cm^{-3}	Particle density of material. Note, 1 g cm^{-3} is equivalent to 1 kg L^{-1}
ρ_{bulk}	g cm^{-3}	Bulk density of material
w_x	---	Mass fraction for component x.
ρ_x	g cm^{-3}	Crystal density of material component x
n_x	mol	Amount of gas or material component x
T_0	K	Initial average temperature of the gas within the container at the time the container is sealed
T_1	K	Average temperature of the gas within the container at the time the container is evaluated
M_x	kg mol^{-1}	Atomic or molecular weight of gas or material component x
N	mol	Amount of material
N_0	mol	Amount of material at time zero
t	yr	Time since container was sealed
λ	yr^{-1}	Decay constant
$t_{1/2}$	yr	Half-life of a radionuclide
Q	W	Total material thermal power
q	W kg^{-1}	Specific thermal power of material
E	MeV/event	Decay energy. Note 1 MeV/event = 9.649x10^{10} J mol^{-1}
t_{peak}	yr	Time at which the material thermal power reaches a maximum
η_{H2}	---	Fraction of water that decomposes to from hydrogen gas
η_{He}	---	Fraction of helium from alpha decay that enters the gas phase

It is assumed that the ideal gas law applies to the conditions and gases important to the calculations. According to that law

$$PV = nRT \qquad\qquad [1]$$

where P is absolute pressure, V is volume, T is absolute temperature, n is the number of moles of gas, and R is the gas constant with units consistent with those chosen for P, V, and T.

For ideal gases, the pressure of a mixture of gases can be determined as the sum of the partial pressures of the individual gases. There are three gas sources that require consideration in a plutonium storage container: 1) the container fill gas, 2) any gases evolved during storage in the sealed container through radiolysis, chemical reactions, or desorption, and 3) helium produced by alpha decay of the contained radioactive species. The only evolved gas of significance anticipated during extended storage is hydrogen from decomposition of adsorbed water. Thus, the combined effect can be expressed as:

$$P = P_F + \eta_{H2}P_{H2} + \eta_{He}P_{He} \qquad [2]$$

where P_F, P_{H2}, and P_{He} are the maximum possible partial pressures of the fill gas, the generated hydrogen, and decay helium, respectively and η_{H2} and η_{He} are empirical values less than one that reduce the hydrogen and helium pressure from their theoretical maximum values.

B.2. DERIVATION

B.2.1. Geometry Consideration

The outer container is the credited pressure vessel. The following discussion conservatively assumes the inner container is breached and all gas spaces within the outer container are at the same pressure. If the inner container remains intact, the pressure on the outer container will be less than calculated here.

The volume occupied by the gas at the evaluation temperature, V_g, will be called the "free gas volume" of the container. This volume can be calculated as the unoccupied volume of the outer container (V_c) i.e., interior volume of the outer container (V_{oc}) less the volume occupied by the materials comprising internal containers (V_i and V_{cc}), less the volume occupied by the contained material (V_m). These volumes, which are illustrated in Figure B-1, can be represented as

$$V_g = V_c - V_m \qquad [3] \text{ and}$$

$$V_c = V_{oc} - V_i - V_{cc} \qquad [3a]$$

B.2.1.1.   Containers

Information on the currently used container designs is given in Table B-2. The inner and convenience can volumes were determined from dimensions on technical drawings

and/or can weights when available. In Table B-2, all volumes are in liters. The outer container unoccupied volumes are obtained using the minimum outer container volumes and the maximum inner and convenience container material volumes.
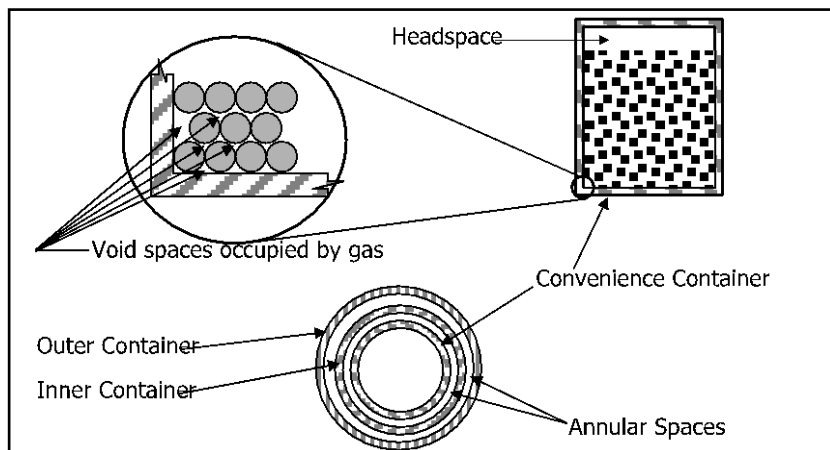

Figure B-1. Illustration of the components of free gas volume.

Table B-2. Volumes associated with the container configurations that have been used to date. All volumes are in liters.

Component	RFETS	Hanford	SRS	LLNL	LANL	ARIES
Outer Container Interior Volume, V_{oc}	2.608±0.012[a]	2.608±0.012[a]	2.608±0.012[a]	2.608±0.012[a]	2.608±0.012[a]	2.608±0.012[a]
Inner Container Material Volume, v_i	0.143±0.045[a]	0.216±0.015[b]	0.216±0.015[b]	0.143±0.045[a]	0.110±0.031[d]	0.110±0.031[d]
Convenience Container Material Volume, v_{cc}	0.218±0.022[c]	0.191±0.019[c]	0.106±0.011[c]	0.218±0.022[c]	0.022±0.002[d]	0.067±0.007[d]
Minimum Unoccupied Volume, V_c [e]	2.168	2.155	2.248	2.168	2.432	2.382

a. Volumes calculated from dimensions on technical drawings. Uncertainties based on specified tolerances [Hackney 2007a].
b. Volumes calculated from dimensions on technical drawings. Uncertainties based on specified tolerances [Hackney 2007b].
c. Volumes calculated from dimensions on technical drawings and verified using container weight. Uncertainties based on specified tolerances [Arnold 2008].
d. Volumes calculated using the equations in [Hackney 2012], with input value ranges adjusted to match the dimensional tolerances in the referenced drawings.
e. Minimum unoccupied volume is calculated from the nominal container volume values above minus the sum of their uncertainties.

B.2.2. Material

A straightforward method to determine the volume occupied by the contained material is the mass of material divided by the material density:

$$V_m = m/\rho \qquad\qquad [4]$$

The difficulty with this approach is that the density is most likely unknown. To facilitate discussion, definitions of different types of density are provided:

- Bulk density: This is the mass of material divided by the volume that it occupies. In the case of a powder, it is assumed to be the density achieved after the powder has been poured into the container.
- Crystal density: This is the theoretical density of a crystal of the material in question.
- Particle density: For purposes of this discussion, the particle density is the average density of the individual particles of powder. This will be greater than the bulk density because the interstitial gas spaces are not included in the volume. It will be less than the crystal density because the particles will have some porosity that cannot be accessed by the gas. A gas pycnometer measures the average particle density.

The correct density to use in Equation [4] is the particle density. However, it is extremely unlikely that the particle density of material will be known. Accordingly, a method of estimating the particle density to be used in Equation [4] is described below.

B.2.2.1.   The Material Composition Method for Determining Particle Density

This method can be used when the mass fractions of the actinides, water, and impurities are known. Knowledge of these quantities is required for a package to be compliant with the Standard. The density of the material can be estimated from knowledge of the material composition and the crystal density of each constituent. Actinide oxide crystal densities are well known. The remaining impurities of either salts or oxides will have a range of densities that are estimated using a single value of 2.5 g cm^{-3}. The overall particle density of the material is given by:

$$\rho = \cfrac{1}{\dfrac{w_{PuO_2}}{\rho_{PuO_2}} + \dfrac{w_{U_3O_8}}{\rho_{U_3O8}} + \dfrac{w_{NpO_2}}{\rho_{NpO_2}} + \dfrac{w_{AmO_2}}{\rho_{AmO_2}} + \dfrac{w_{H_2O}}{\rho_{H_2O}} + \dfrac{w_{salt}}{\rho_{salt}}} \qquad [5]$$

where w is the mass fraction of the component and ρ is the crystal density of that fraction. [Friday et al., 2008]. The material composition method is used by the ISP database. The calculated density is compared to material particle densities measured

at SRS as part of the destructive examination program in Figure B-3. A conservative calculated density with respect to determining the material volume would be less than the measured density, i.e. lying below the line in Figure B-3. As seen in the plot, most values are below the line. There are a number of reasons that calculated densities may be below the measured densities, the primary one being that many of the metal oxides have densities greater than 2.5 g cm^{-3}. However, some of the values in the plot are slightly above the line. This could be due to occluded voids in the particles or uncertainties associated with the actinide measurements. Reducing the calculated density in Equation [6] by 10% results in a conservative value for the particle density for use in Equation [4].
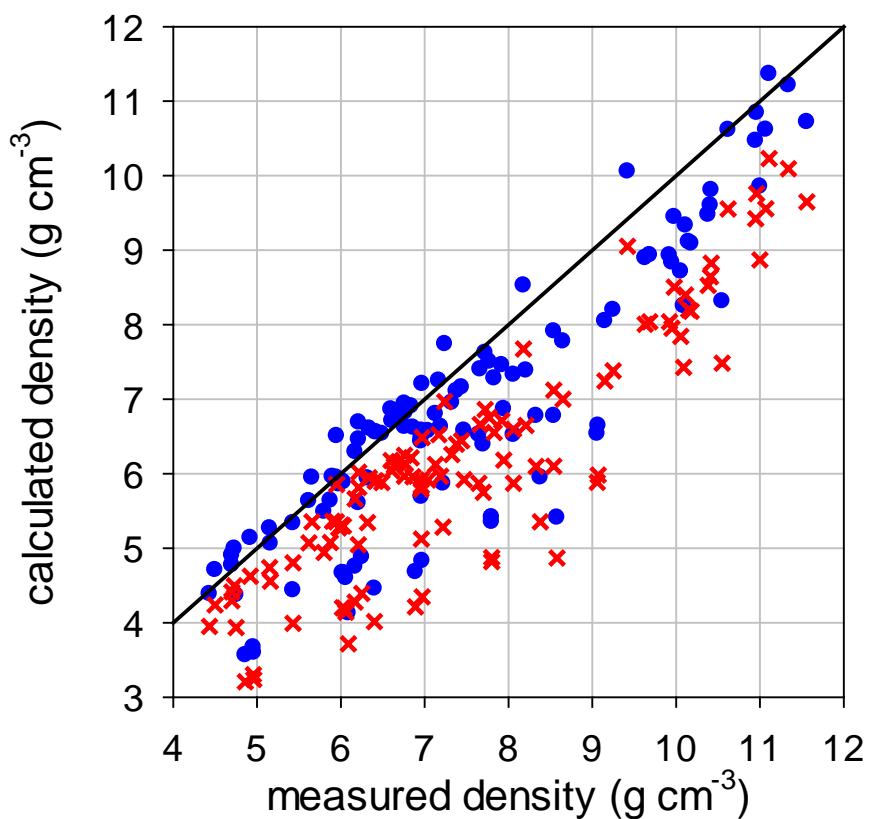

Figure B-2. Comparison of calculated densities to measured particle densities for SRS destructive examination of materials. The blue dots are the calculated densities using Equation 6. The red x's are 90% of the calculated densities.

B.2.2.2.   The Material Packing Fraction

The packing fraction is especially useful for bounding calculations where both the bulk density and the particle density are needed. Any powder poured into a container has a bulk density less than the particle density for the material. Measurements of particle density by gas pycnometer and comparison with bulk density have shown that the packing fraction, which is the ratio of bulk density to particle density, varies over a fairly wide range. A maximum value of the packing fraction will ensure a minimum particle density for any given bulk density, and therefore a minimum free gas volume and maximum pressure. Measurements of the packing fraction for MIS represented material and from 3013 containers show that it does not exceed 0.62 [Mason et al., 1999][. Figure B-4 shows the packing fraction as a function of bulk density for materials from 3013 containers and MIS represented materials. One approach to estimating the material volume of an unknown particle density would be to determine the bulk density and divide by 0.62, realizing that the true particle density can be no less than this value (a higher density value would result in a smaller volume occupied by the particles and, hence, a lower theoretical gas pressure).For instance, if 3.6 kg of oxide filled a 1.8 liter convenience container, the bulk density would be 2.0 kg/L and the estimated particle density would be 2.0 kg/L / 0.62, or 3.226 kg/L, giving a material volume of 1.116 liters.
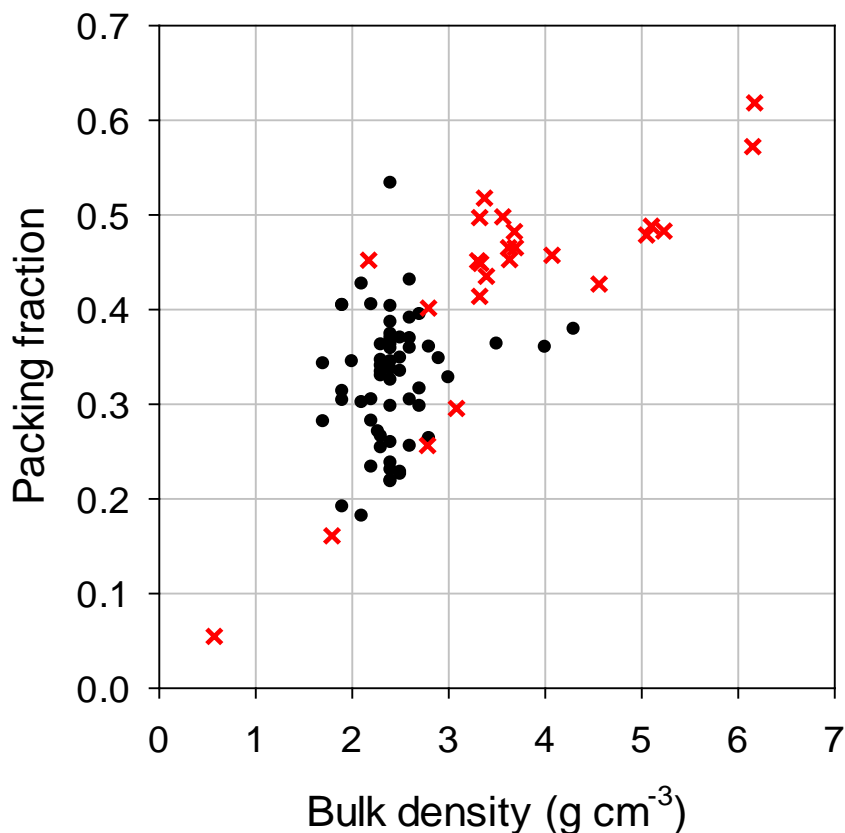
Figure B-3. The packing fraction of MIS represented material (red x's) and material from 3013 containers that have undergone destructive evaluation through 2010 (black circles).

B.2.3. Defining the pressure terms

B.2.3.1.   Pressure Due to Container Fill Gas

The amount of fill gas, n_F, at the time a container is sealed is given by:

$$n_F = P_0 V_g / R T_0 \qquad [6]$$

The values of P_0 and T_0 are the pressure and temperature at which the container was loaded and sealed. It is conservative to assume that the amount of fill gas does not change during storage, therefore at any time in the future when the temperature is given by T_1, the pressure due to the container fill gas is given by:

$$P_F = n_F R T_1 / V_g = (P_0 V_g / R T_0)(R T_1 / V_g) = P_0 (T_1 / T_0) \qquad [7]$$

B.2.3.2.   Gases of Concern

The only generated gas of significance during extended storage is hydrogen from decomposition of adsorbed water. Maximum credible hydrogen pressures are expected to be maintained well within the storage container pressure design basis. The technical basis for these expectations is provided in Section A.6.1.2 of Appendix A of this Standard. The derivation assumes that all the water is decomposed to form hydrogen gas and that the oxygen is consumed by the material. This assumption has always been considered to be conservative. For instance, an unexpected pressure has always been defined as 100 psig or greater in Section A.6.2.1.4 in previous issues of the 3013 Standard. Measurements that challenge this assumption were not available when the Standard was originally written. Measurements are now available from both destructive evaluation of 3013 containers and shelf-life studies [Veirs et al 2017]. In order to account for these observations, an empirical factor, η_{H2} referred to as the H_2 fraction, is introduced to reduce the calculated hydrogen pressure.

B.2.3.2.1.   Quantities of Hydrogen Produced

Starting with m kg of material with a moisture content of w_{H2O} (mass fraction by weight; note that the mass fraction is equivalent to the per cent by weight divided by 100%), the amount of water is given by the following equation and converted to moles of hydrogen:

$$n_{H2O} = m w_{H2O} / M_{H2O} = n_{H2} \qquad [8]$$

where M_{H2O} is the molecular mass of water, 0.018015 kg mol^{-1}. The amount of hydrogen, which is equal to the amount of water, results in a pressure rise

$$P_{H2} = (m w_{H2O} / M_{H2O}) R T_1 / V_g \qquad [9]$$

which is the maximum value for the middle term of the equation in equation [2] when η_{H2} is taken to be 1.

B.2.3.2.2.   The Hydrogen Fraction

The maximum hydrogen pressure generated by plutonium-bearing materials within sealed containers is difficult to measure because of the long times required to reach the maximum pressure and the need to continuously measure the gas composition and pressure. The MIS shelf-life studies has conducted these difficult measurements on a number of represented materials [Bailey et al., 2000; Berg et al., 2007; Duffey et al., 2010; Veirs 2005; Veirs et al., 2004; Veirs/Berg 2008; Worl et al., 2000]. The results of these measurements for shelf-life studies in small-scale reactors have indicated that the maximum hydrogen pressure is at most one-quarter that predicted by Equation [10]. Relative radiation dose to the gas-phase is smaller in small-scale

reactors than in 3013 containers, resulting in potentially higher hydrogen pressures in small-scale reactors than would be expected in 3013 containers if gas-phase reactions consume hydrogen [Foy/Joyce 2008]. Surveillances of containers by destructive examination after many years of storage have also measured hydrogen pressures that are much less than predicted by Equation [9]. In order to quantify the ratio of the actual amount of hydrogen generated to the maximum expected from Equation [9], the H_2 fraction term is defined as

$$\eta_{H2} = n_{H2,obs} / n_{H2O} \tag{10}$$

where $n_{H2,obs}$ is the number of moles of hydrogen observed in the gas phase and n_{H2O} is the number of moles of water in the container. A plot of the measured hydrogen fraction versus the wt% of moisture for the 3013 DE containers is given in Figure B-4 [Veirs et al 2017].
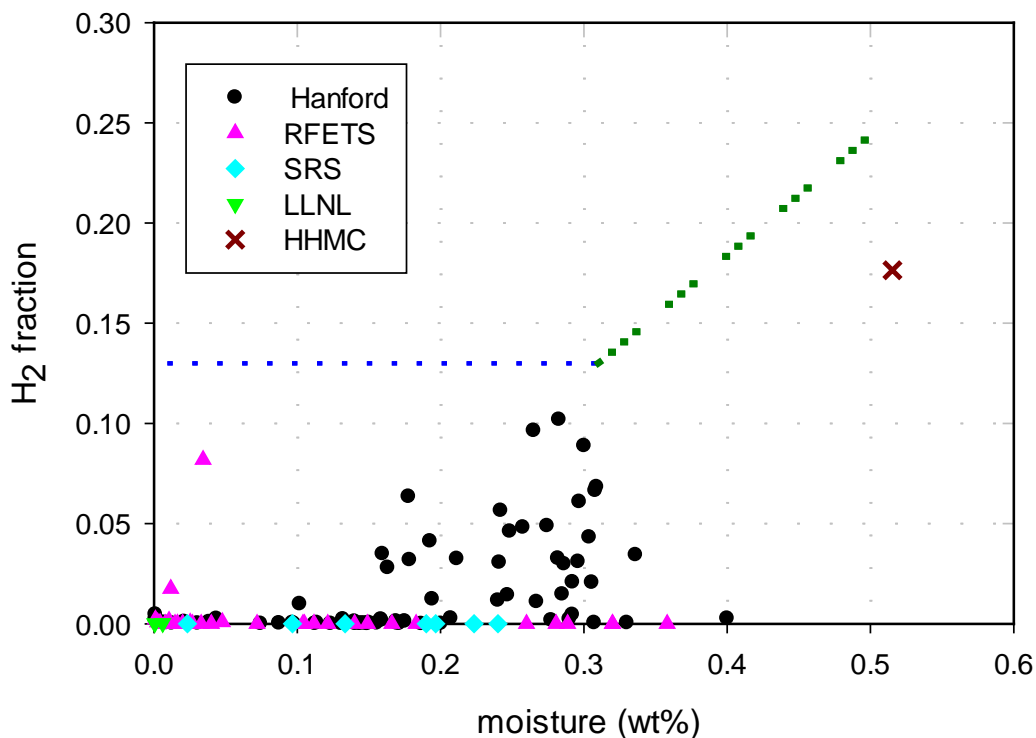
Figure B-4. Plotted are the calculated H_2 fractions observed during DE of compliant 3013 containers for the four packaging sites and for the non-compliant Hanford High Moisture Container (HHMC). The blue dashed line is the H_2 fraction bounding value from statistical analysis of the DE data excluding the HHMC. The green dash-dot line is an empirical boundary that ties the H_2 fraction statistical value of 0.13 to the bounding value for the entire DE population of 0.25.

The blue dashed and the green dash-dot lines bound the DE observations in Figure B-4. These lines are derived entirely from the DE observations of 3013 containers, although the observations from shelf-life studies are consistent with these lines even though the shelf-life SSR studies have a lower radiation dose-rate to the headspace gas that should result in higher H_2 concentrations and H_2 fractions. The value of the H_2 fraction as a function of moisture wt% given by these lines can be used to reduce P_{H2} calculated using Equation [9] to predict a maximum hydrogen pressure that is more consistent with the observations of hydrogen in sealed containers. Parameters describing these lines are given in Table B-3, and their derivation is detailed in Veirs et al 2017.

Table B-3. The bounding values of the H_2 fraction for use in the pressure equation that results in the lines in Figure B-4.

Moisture (wt%)	H_2 fraction
0 to 0.31	0.13
0.31 to 0.5	0.600 (1/wt%) x wt% - 0.056

The expected maximum hydrogen pressure is given is given by Equation [11]

$$\eta_{H2} P_{H2} = \eta_{H2} (mw_{H2O}/M_{H2O}) RT_1/V_g \qquad [11]$$

where η_{H2} is calculated from the relation given in Table B-3. Equation [11] is the middle term in Equation [2].

B.2.3.2.3. Decay Helium

For a radioactive species, the decay rate (and, hence, the helium generation rate for alpha decay) is

$$dN/dt = \lambda N \qquad\qquad [12]$$

where λ is the decay constant and N is the amount of the decaying material [note: the decay constant is related to the half-life by $\lambda = \ln(2)/t_{1/2}$]. As a function of time, N is given by

$$N(t) = N_0 e^{-\lambda t} \qquad\qquad [13]$$

For alpha decay, each atom or mole of atoms that decays results in an atom or mole of helium produced. The total amount of helium generated, n_{He}, over a period of time, t, is therefore

$$n_{He} = N_0 - N(t) = N_0(1 - e^{-\lambda t}) \approx N_0 \lambda t \qquad\qquad [14]$$

For values of λt, which are small, the term in parentheses can be replaced by its linear approximation, λt. This approximation is conservative because $\lambda t \geq 1 - e^{-\lambda t}$. The amount of a radionuclide is calculated from the mass fraction, the total mass, and the atomic mass at the time the container is sealed,

$$N_0 = wm/M \tag{15}$$

The amount of helium generated from the decay of this radionuclide can be calculated for any time t,

$$n_{He}(t) = N_0 \lambda t = (wm/M)\,\lambda t \tag{16}$$

The pressure resulting from the helium generated by the decay of this radionuclide at time t is,

$$P_{He}(t) = n_{He}(t)RT_1/V_g = wm\lambda t RT_1/MV_g \tag{17}$$

For high-purity oxide consisting of a single isotope of plutonium, ^{239}Pu, the mass fraction, decay constant, and atomic mass are w_{239Pu} = 0.239 kg mol^{-1}/0.271 kg mol^{-1} = 0.8819, λ_{239Pu} = 2.87x10^{-5} yr^{-1}, and M_{239Pu} = 0.239 kg mol^{-1}. Equation [16] for high-purity oxide with exclusively ^{239}Pu becomes,

$$P_{He}(t) = 1.06\text{x}10^{-4} \text{ mol yr}^{-1} \text{ kg}^{-1} \, mtRT_1/V_g. \tag{18}$$

Equation [18] is the same as the third term of equation [2]. In order to account for the generation of helium from all isotopes present one must sum over all radionuclides that alpha decay,

$$P_{He}(t) = \sum_i w_i m \lambda_i t RT_1 / M_i V_g = \left(mtRT_1/V_g\right)\sum_i w_i \lambda_i / M_i \tag{19}$$

In Equation [19], the index i represents all radionuclides that alpha decay. The most important radionuclides to this Standard are given in Table B-9. An alternative formulation of this term is possible that takes advantage of the thermal power of the material, which is usually known. The thermal power of the contents is given by

$$Q = \sum_i E_i \lambda_i N_i = m \sum_i E_i \lambda_i w_i / M_i \tag{20}$$

where E_i is the radioactive decay energy for radionuclide i and Q is the total thermal power of the material. For simplicity, consider that all alpha decay energies are similar with a value near 5 MeV per event. Using a single value for the decay energy simplifies Equation [20],

$$Q = Em\sum_{i} \lambda_i w_i / M_i \qquad\qquad [21]$$

$$Q / E = m\sum_{i} \lambda_i w_i / M \qquad\qquad [21a]$$

Substituting the expression for Q/E into equation [19] yields an expression for the pressure due to helium generation from alpha decay as

$$P_{He}(t) = QtRT_1 / EV_g \qquad\qquad [22]$$

Q can be calculated from the specific thermal power (q) for individual isotopes found in Table B-9. Note that 1 MeV/event = 9.649×10^{10} J/mol [Lide 2003]. As can be seen from Equation [22], the conservative evaluation is achieved by using a relatively low value for E. A reasonable selection is the value for [239]Pu. When that value is used, Equation [22] becomes

$$P_{He} = 6.232 \times 10^{-5} \text{ mol W}^{-1} \text{ yr}^{-1} QtRT_1/V_g \qquad\qquad [23]$$

Note also that the contribution from decay of uranium isotopes is negligible, with the possible exception of [233]U. As an extreme case, consider an oxide material with a composition of approximately 88 wt% [235]U, 0.1 wt% [239]Pu, and 0.5 wt% [233]U. In such a material, the contribution from [235]U would be only about 3% of the Pu contribution, and that from [233]U, although comparable to that from Pu, would still represent an insignificant source of pressurization.

B.2.3.2.4. The Helium Fraction

Similar to the case for hydrogen, not all of the helium gas predicted by Equation [23] is seen in the gas-phase. In the case of helium, the alpha particles overwhelmingly end their trajectory in the material phase after being emitted. A portion of these eventually diffuse to the surface and enter the gas phase as helium, but the rest remains trapped in the solid. The fraction released into the gas-phase is defined as η_{He} for use here. Equation [23] conservatively assumes all of the alpha decay results in gas-phase helium, i.e. η_{He} is one.

Also similar to hydrogen, it is difficult and expensive to conduct studies over many years in sealed containers in order to quantify η_{He} and no studies for this purpose are available. However, observations of helium in sealed $^{238}PuO_2$ fuel containers has been used to determine the helium fraction [Mulford 2014].

Measurements of the helium pressure within 21 sealed containers of $^{238}PuO_2$ was analyzed and the observations expressed as the ratio of the pressure observed to

the pressure calculated from alpha decay which is equivalent to η_{He} as used here.[4] The age of the containers ranged from 23 to 34 years and the temperature during that time was assumed to be 350 ⁰C. The temperature is higher than expected for 3013 containers during storage so the value for η_{He} observed under these conditions should be larger than the value under 3013 storage conditions if diffusion is the dominant mechanism that releases helium from the material into the gas phase. The average value for the ratio of the helium pressures was 0.26 and the largest observation was 0.37. Adding measurement uncertainty results in a bounding value slightly less than 0.5.

The recommended value for η_{He} is 0.5. The expected helium pressure is given is given by Equation [24]

$$\eta_{He}\, P_{He} = \eta_{He}\ 6.232\text{x}10^{-5}\ \text{mol W}^{-1}\ \text{yr}^{-1}\ QtRT_1/V_g \qquad [24]$$

where η_{He} is 0.5. Equation 24 is the last term in Equation [2].

B.2.3.3.   Aggregate Equation

Summing the three partial pressures using Equation 2 and the terms given above yields the aggregate equation for the total pressure:

$$P = P_0(T_1/T_0) + \eta_{H2}\ (mw_{H2O}/M_{H2O})\,RT_1/V_g + \eta_{He}\ 6.232\text{x}10^{-5}\ \text{mol W}^{-1}\ \text{yr}^{-1}\ QtRT_1/V_g.$$
$$[25]$$

B.3.   APPLICATION OF THE PRESSURE EQUATION

B.3.1. Estimated Temperatures

The average gas temperature is impractical to measure and it is necessary to calculate it. In this appendix, we are only interested in providing guidelines for use of Equation [25], and so will use "worst case" temperatures that might be encountered. Calculations at the Savannah River Site by Hensel for a configuration in which a storage container generating 19 W is placed in a 9975 transportation package indicate an average gas temperature of approximately 164 °C for normal storage conditions in an ambient temperature of 37.8 °C (100 °F) (see Table A-2). These calculations also indicate an average gas temperature of approximately 211 °C for transportation conditions (exposure to solar heating). These temperatures are probably bounding and may be used when other information is not available. Each storage facility should evaluate average gas temperatures under the conditions anticipated at that facility, such as loss of cooling events, to determine appropriate evaluation conditions.

B.3.2. Example Calculations

B.3.2.1. Example Material Composition Density Calculation

Consider a material that contains plutonium, uranium, neptunium, and americium oxides, with the maximum wt% of water, and impurities, with mass fractions as given in Table B-4.

Table B-4. Values of parameters used to calculate particle density

Symbol	Quantity	Value	Symbol	Quantity	Value
w_{PuO_2}	PuO_2 mass fraction	0.64	ρ_{PuO_2}	Crystal density of PuO_2	11.5 g cm^{-3}
$w_{U_3O_8}$	U_3O_8 mass fraction	0.05	$\rho_{U_3O_8}$	Crystal density of U_3O_8	8.38 g cm^{-3}
w_{NpO_2}	NpO_2 mass fraction	0.00	ρ_{NpO_2}	Crystal density of NpO_2	11.1 g cm^{-3}
w_{AmO_2}	AmO_2 mass fraction	0.005	ρ_{AmO_2}	Crystal density of AmO_2	11.7 g cm^{-3}
w_{H_2O}	Water mass fraction	0.005	ρ_{H_2O}	Density of liquid water	1.00 g cm^{-3}
w_{salt}	Salt[a] mass fraction	0.30	ρ_{salt}	Density of salt[a]	2.50 g cm^{-3}

[a] because much of the impurities are salts, the subscript "salt" is used for all non-actinide impurity material

The densities for the materials specified in Equation 5 are given by [Friday et al., 2008] and listed in Table B-4. The particle density of the composite material is

$$\rho = \cfrac{1}{\cfrac{0.64}{11.5 \text{ kg L}^{-1}} + \cfrac{0.05}{8.38 \text{ kg L}^{-1}} + \cfrac{0.00}{11.1 \text{ kg L}^{-1}} + \cfrac{0.005}{11.7 \text{ kg L}^{-1}} + \cfrac{0.005}{1.00 \text{ kg L}^{-1}} + \cfrac{0.30}{2.50 \text{ kg L}^{-1}}}$$

[26]

$$= 5.35 \text{ kg L}^{-1}.$$

[26A]

B.3.2.2. Example Pressure Calculation for a Typical Loading of a Container

Assume that a RFETS container will be loaded with 2.4 kg of a stabilized material with the composition used in B.3.2.1 and with a moisture content of 0.31 wt%. The container was loaded at 86 °F (30 °C), and could encounter conditions in the storage vault in which the gas temperature might reach 400 °F (204.4 °C). The thermal power is calculated from the actinide composition given in Table B-4 and the specific thermal power (q) given in Table B-9 assuming the Pu isotopics of weapons grade material. The thermal power of the material is 1.93 W/kg times 2.4 kg of material, or 4.68 W. The evaluation temperature is 204.4 + 273 or 477.4 K, and the loading temperature is 30 + 273 or 303 K. The pressure in the container is to be evaluated

after a storage time of 50 years. The values of the parameters used in the pressure equation are summarized in Table B-5.

Table B-5. Values of parameters used to calculate pressure of a typical loading

Symbol	Quantity	Value	Symbol	Quantity	Value
P	Container pressure	kPa	Vg		
P_0	Fill gas pressure at filling	101 kPa	m	Mass of material	2.4 kg
T_1	Evaluation temperature	477.4 K	ρ	Density of material	5.35 kg/L
T_0	Fill gas temperature at filling	303 K	Q	Container thermal power	4.63 W
W_{H2O}	Water mass fraction	0.0031	t	Storage time	50 yr
V_c	Unoccupied volume of RFETS container	2.168 L	η_{H2}	H_2 fraction for 0.31 wt% water = 0.60x0.31 – 0.056	0.130

The gas volume is determined by subtracting the material volume from the 2.168 L free volume of the RFETS container system:

$$V_m = \frac{m}{\rho} = \frac{2.4\ kg}{5.35\ kg\ L^{-1}} = 0.449\ L \tag{27}$$

$$V_g = V_c - V_m = 2.168\ L - 0.50\ L = 1.719\ L \tag{28}$$

Substituting the parameters into Equation 24 yields:

$P\ =\ $ 101 kPa *(477.4 K/ 303 K) +
0.130 2.45 kg * 0.0031/.018 kg/mol) *8.3145 kPa L mol^{-1} K^{-1} *477.4 K / 1.719 L +

0.5 6.232x10^{-5} mol W^{-1} yr^{-1} *4.68 W * 50 yr *8.3145 kPa L mol^{-1} K^{-1} *477.4 K / 1.719 L

$$\tag{29}$$

$$=159\ kPa + 124\ kPa + 17\ kPa \tag{29A}$$

$$=\ 300\ kPa \tag{29B}$$

This calculation yields substantially less pressure than prescribed in previous versions of DOE-STD-3013. For this material the pressure is 300 kPa (43.5 psia or 28.8 psig).

B.3.2.3.   Example with Unknown Density, 19 W Thermal Power

Assume that a RFETS container will be filled with 5 kg of material with an unknown particle density. The other parameters given in Table B-6.

Table B-6. Values of parameters used to calculate pressure for material with unknown density

Symbol	Quantity	Value	Symbol	Quantity	Value
P	Container pressure	kPa	V_c	Unoccupied volume of RFETS container	2.168 L
P_0	Fill gas pressure at filling	101 kPa	m	Mass of material	5.0 kg
T_1	Evaluation temperature	477.4 K	Q	Container thermal power	19 W
T_0	Fill gas temperature at filling	303 K	t	Storage time	50 yr
W_{H2O}	Water mass fraction	0.005	η_{H2}	H$_2$ fraction for 0.5 wt% water = 0.60x0.5 – 0.056	0.244

Since the density is unknown but the bulk material fills the convenience container, we can use the volume of the convenience container, which for RFETS is 1.856 L to determine the bulk density and the packing fraction to determine a minimum particle density:

$$\rho_{\text{bulk}} = \frac{5 \text{ kg}}{1.856 \text{ L}} = 2.694 \text{ kg L}^{-1} \qquad [30]$$

$$\rho = \frac{\rho_{\text{bulk}}}{0.62} = 4.345 \text{ kg L}^{-1} \qquad [31]$$

Using that density, we calculate the material volume and the free gas volume:

$$V_m = \frac{m}{\rho} = \frac{5 \text{ kg}}{4.345 \text{ kg L}^{-1}} = 1.151 \text{ L} \qquad [32]$$

$$V_g = V_c - V_m = 2.168 \text{ L} - 1.151 \text{ L} = 1.017 \text{ L} \qquad [33]$$

The pressure terms are now:

P = 159 kPa + 0.244 (5 kg * 0.005/.018 kg/mol)* 8.3145 kPa l mol^{-1} K^{-1} * 477.4 K / 1.017 L +

0.5 6.232x10^{-5} mol W^{-1} yr^{-1} *19 W * 50 yr * 8.3145 kPa L mol^{-1} K^{-1} *477.4 K /1.017 L

[34]

$$= 159 \text{ kPa} + 1323 \text{ kPa} + 116 \text{ kPa} \qquad [34a]$$

$$= 1597 \text{ kPa} \qquad [34b]$$

In this example, the maximum amount of material, maximum moisture content, and the maximum thermal power are used resulting in a maximum value for the pressure. The free gas volume is independent of the amount of material as long as the limiting value for the packing fraction of 0.62 holds. In order to obtain a material with a smaller value for the particle density, the amount of material must be less. This results in the same free gas volume but less water due to the smaller mass of material. The result would be a smaller pressure. Thus, the pressure calculated in this example is the highest expected pressure. The pressure of 1597 kPa (231 psia) is ~32% of the design pressure of 4920 kPa. There is no need to limit material density as was required by previous DOE-STD-3013 versions.

B.3.2.4. General Behavior of Pressure Equation – Effect of changing bulk density

The effect of changing the bulk density is examined using the bounding parameters specified in B.3.2.3. The maximum packing fraction can be used to estimate the internal pressure as a function of bulk density. The bulk density is allowed to vary over a significant range, and the particle density is estimated by using the equation

$$\rho = \frac{\rho_{\text{bulk}}}{0.62} \qquad [35]$$

For this example, it is assumed that only weapons grade material will be considered. The specific thermal power for weapons grade plutonium dioxide is 2.23 W/kg oxide, or about 11.2 W for 5 kg of plutonium oxide. To be conservative, a value of 19 W will be used for the thermal power. The calculations by Hensel (Table A-2) indicate that a linear approximation of 6 °C per watt of thermal power can be used to estimate average gas temperatures for different material thermal powers. This would yield an average gas temperature of 211 °C for a 19 W package subjected to solar radiation.

The bounding pressure estimate for these conditions is shown in Figure B-5. The behavior shown is characteristic of the relationship between pressure and density. Starting from the right side of Figure B-5 and moving to the left, as the density decreases, the free gas volume decreases, and the bounding pressure increases. However, this behavior continues only until the innermost container (convenience container) is full. After that, as the density is further reduced, the mass of material is reduced, the amount of moisture is correspondingly reduced and the pressure decreases. The maximum pressure occurs at the bulk density at which the convenience can is just full. In this case, the maximum bounding pressure is 1597 kPa (231 psia or 216 psig). Note that this particular model demonstrates compliance with Criterion 6.3.2.3 for all material densities and would eliminate the need to measure density or determine free gas volume. The development and use of such a model will be governed by the Quality Assurance program applicable to the packaging site (and acceptable to the storing site) in terms of regression coefficients and confidence levels.
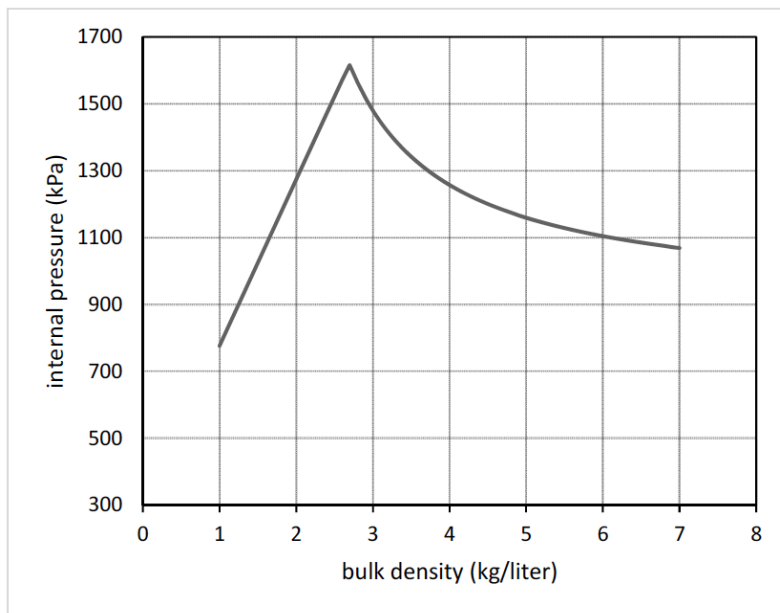
Figure B-5. Bounding pressure as a function of bulk density for the statistical model in B.3.2.3.

B.3.2.5.   General Behavior of Pressure Equation – Effect of moisture

Using the bounding starting conditions given in Section B.3.2.3, the moisture content is varied. The value for η_{H2} decreases as the moisture wt% decreases. The result is that the pressure falls more rapidly than the amount of moisture. For instance, a reduction of the amount of moisture of 40% from 0.5 wt% to 0.3 wt% results in a pressure drop of approximately 56% from 1597 kPa to 697 kPa. The temperature is 477.4 K, volume is 1.017 liter, thermal power is 19 watts, η_{He} is 0.5, the initial pressure is 101 kPa, and the amount of material is 5 kg at a density of 4.345 kg/L. The results are given in Table B-7

Table B-7. The effect of moisture content on the maximum pressure.

Moisture (wt%)	η_{H2}	P_f (kPa)	$\eta_{H2}P_{H2}$ (kPa)	$\eta_{He}P_{He}$ (kPa)	P (kPa)	P (psia)
0.5	0.244	159	1323	116	1597	232
0.4	0.184	159	798	116	1072	156
0.3	0.13	159	423	116	697	101
0.2	0.13	159	282	116	556	81
0.1	0.13	159	141	116	415	60

B.3.2.6.   General Behavior of Pressure Equation – Effect of material mass

Using the bounding starting conditions given in Section B.3.2.3, the material mass is varied. The material mass affects the temperature, the free gas volume and the amount of water. For this example, the moisture is 0.5 wt% and η_{H2} is 0.244, the material density is 4.345 kg/L, the specific thermal power is 3.8 W/kg, η_{He} is 0.5 and the temperature is reduced by 6 degree / watt. The results are given in Table B-8.

Table B-8. The effect of material mass on the maximum pressure.

Material mass (kg)	Thermal Power (W)	T (K)	V (liter)	P_f (kPa)	$\eta_{H2}P_{H2}$ (kPa)	$\eta_{He}P_{He}$ (kPa)	P (kPa)	P (psia)
5	19	477.4	1.017	159	1322	116	1597	232
4	15.2	454.6	1.247	152	821	72	1045	152
3	11.4	431.8	1.478	144	494	43	681	99
2	7.6	409	1.708	136	270	24	430	62
1	3.8	386.2	1.938	129	112	10	251	36

B.4.   PLUTONIUM RADIOACTIVE DECAY AND THERMAL POWER

This portion of Appendix B is intended to provide basic information about the various radionuclides of interest to the Standard, and to illustrate the behavior of the specific thermal power as a function of time for a variety of isotopic mixes. This material is not intended to replace methods of determining the thermal power that the sites may decide to use in conjunction with this Standard.

B.4.1. Expected Isotopic Compositions

Plutonium is produced in a nuclear reactor, and the vast majority of plutonium in the Complex was produced either in Hanford production reactors or Savannah River

production reactors. It is produced by irradiating uranium, and in these production reactors the uranium has a low enrichment and is in a metallic form often referred to as a "target." The ^{238}U accepts a neutron and is converted to ^{239}Pu after beta decay through neptunium. The ^{239}Pu thus produced is exposed to the neutron flux as the target remains in the reactor. Most, but not all neutron absorptions in ^{239}Pu cause fission, but some produce ^{240}Pu. That isotope will accept a neutron to produce ^{241}Pu, which, in turn, will accept another to produce ^{242}Pu, provided the ^{241}Pu does not fission. In addition, through a similar chain of neutron absorptions, ^{235}U in the target will be converted through ^{236}U and ^{237}Np to produce ^{238}Pu. Consequently, plutonium can be expected to have isotopes from 238 to 242 in noticeable quantities. The exact mix of isotopes will depend on the irradiation time and the target and reactor characteristics, with longer irradiation times producing more of the higher isotopes, higher target enrichment producing more ^{238}Pu, and reactor characteristics having effects that are less easily described. Note that ^{238}Pu and ^{241}Pu both require three neutron absorptions, and, as a consequence, their concentrations as a function of time will behave in a similar fashion.

Once the target is discharged from the reactor, production of these isotopes stops, and any further changes are the result of radioactive decay. With the exception of ^{241}Pu, all the plutonium isotopes decay by alpha decay. For the time spans of interest here, their progeny are not important in terms of thermal power or helium production with the exception, again, of ^{241}Pu. That isotope decays fairly rapidly by beta decay into ^{241}Am, which then decays somewhat more slowly by alpha decay. Table B-9 contains pertinent data for these isotopes, and for some uranium isotopes of interest.

Table B-10 provides expected isotopic compositions for a variety of circumstances. The three columns with various "grades" of plutonium refer to material that has been recently discharged from a reactor and reprocessed (recovering the plutonium from the uranium target is called "reprocessing"). In each case, the americium content is zero because any that was formed during irradiation or any cooling period prior to reprocessing, has been removed during reprocessing. The last three columns, pertaining to Hanford materials, are for plutonium that has been "aged" for 10-30 years, and has experienced a significant buildup of americium, and decay of ^{238}Pu and ^{241}Pu. The percentage ranges refer to the ^{240}Pu content of the material. Note that the first two categories of Hanford plutonium are similar to the Weapon Grade and Fuel Grade categories in terms of the ^{240}Pu content. The similarity is more apparent if the americium content is added to that of the ^{241}Pu, which, for these decay times, provides a reasonable estimate of the original ^{241}Pu content.

Table B-9. Decay energy for relevant nuclides

Radio-nuclide	Half-life[a], (yr)	Decay constant[b] (yr^{-1})	Decay Energy[a] (MeV/event)	Specific Thermal Power[c] (W/kg)
^{233}U	1.592E+05	4.35E-06	4.909	0.281
^{235}U	7.04E+08	9.85E-10	4.689	6.01E-05
^{238}U	4.468E+09	1.55E-10	4.269	8.51E-06
^{238}Pu	87.7	7.90E-03	5.593	568
^{239}Pu	2.411E+04	2.88E-05	5.244	1.93
^{240}Pu	6564	1.06E-04	5.256	7.07
^{241}Pu	14.35	4.83E-02	0.0054	3.31
^{242}Pu	3.75E+05	1.85E-06	4.986	0.116
^{241}Am	432.2	1.60E-03	5.638	115

a. Half-life data and decay energy taken from ICRP 2008.
b. Decay constant calculated using $\lambda = \ln(2)/t_{1/2}$.
c. Specific thermal power (q) is calculated from the decay energy, the decay constant, and the atomic weight, Eq. 20.

Table B-10. Isotopic mix and specific thermal power for various grades of plutonium oxide

Nuclide	Pure ^{239}Pu	Weapons Grade	Fuel Grade	Power Grade	Hanford 4-7%	Hanford 10-13%	Hanford 16-19%
^{238}Pu		0.05%	0.1%	0.99%	0.01%	0.09%	0.24%
^{239}Pu	100.0%	93.50%	86.1%	62.38%	93.77%	86.94%	80.66%
^{240}Pu		6.00%	12.0%	21.78%	6.00%	11.81%	16.98%
^{241}Pu		0.40%	1.6%	11.88%	0.20%	1.00%	1.44%
^{242}Pu		0.05%	0.2%	2.97%	0.03%	0.17%	0.69%
^{241}Am					0.14%	0.86%	2.80%
Initial q, W/kg oxide	1.70	2.23	2.76	7.73	2.17	3.57	6.52
Maximum q, W/kg oxide	1.70	2.48	3.96	16.2	2.31	4.20	7.18

The two plots in Figure B-6 show how the specific thermal power changes with time for each of the seven oxides given in Table B-10. Several characteristics are immediately evident: 1) the maximum is very flat and broad; 2) the variation between initial and maximum specific thermal power is a function of the initial ^{241}Pu content (and the ^{238}Pu content, although that is not as obvious); and 3) for the Hanford material, the maximum
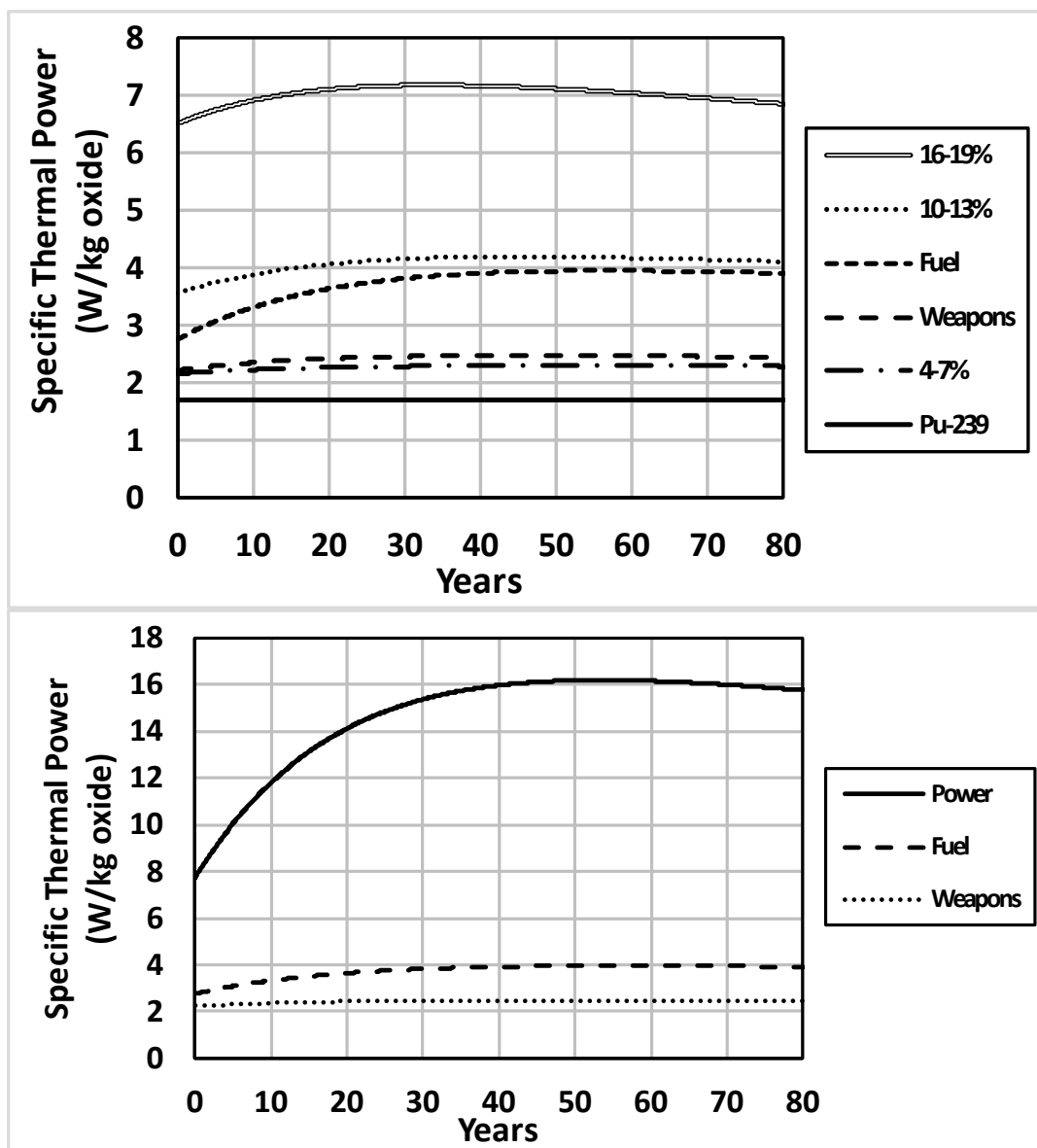
**Figure B-6. Specific thermal power as a function of time
for several grades of plutonium oxide.**

specific thermal power is only about 15% greater than the initial specific thermal power. The Power Grade material in Figure B-6 provides an extreme example of the increase in specific thermal power with time. This is due to the considerable buildup of ^{241}Pu, representing a source of ^{241}Am and hence a future heat generation capability.

Fortunately, the Power Grade curve is not characteristic of any significant quantity of plutonium to be packaged under this Standard. However, even for this material, after 20 years of storage and the consequent decay of the ^{241}Pu into ^{241}Am, the subsequent increase in thermal power is only about 15%.

As a rule of thumb, the peak specific thermal power occurs about 40-60 years after discharge from the reactor. Thus, after 20 years of storage, the peak is still some 20-40 years in the future. A reasonable approach to determining the peak thermal power is to treat the ^{241}Pu as though it was ^{241}Am. An alternative approach is to attempt to estimate the timing of the peak and then use the radioactive decay equations to determine the isotopic composition and the thermal power. Because the peak is so flat, a very accurate estimate of its time of occurrence is not necessary. To estimate the timing of the peak the following equation can be used:

$$t_{peak} = -20.78 \ln(0.0312 + 0.0302\, w_{51}/\,w_{41} + 0.5716\, w_{48}/\,w_{41})\ \text{yr} \qquad [36]$$

Where t_{peak} is the time until the peak thermal power

w_{41} is the mass fraction of ^{241}Pu

w_{48} is the mass fraction of ^{238}Pu, and

w_{51} is the mass fraction of ^{241}Am.

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APPENDIX D.   CONCLUDING MATERIAL

Review Activity: **Preparing Activity:**

Programs   Field Offices   Savannah River Operations/AMNMS

NA   AL

AU   ID   **Project Number:**

EM   RL   PACK-xxxx

MD   SR

National Laboratories

LLNL

LANL