DOE STANDARD

STABILIZATION, PACKAGING, AND STORAGE OF PLUTONIUM-BEARING MATERIALS

U.S. Department of Energy
Washington, D.C. 20585

AREA PACK

Available on the Department of Energy
Technical Standards Program
Web site at
http://www.hss.energy.gov/NuclearSafety/ns/techstds/

ABSTRACT

This Standard provides guidance for the stabilization, packaging, and safe storage of plutonium-bearing metals and oxides containing at least 30 wt% plutonium plus uranium. It supersedes DOE-STD-3013-2004, "Stabilization, Packaging, and Storage of Plutonium-Bearing Materials," and is approved for use by all DOE organizations and their contractors. Metals are stabilized by removing liquids and corrosion products, and oxides are stabilized by heating in an oxidizing atmosphere at an elevated temperature. Requirements for design, construction, and testing of the storage container are included. Loading limits for the storage container and safety-related requirements for the packaging process are specified. Broad requirements for container surveillance during storage are outlined, and record-keeping requirements are detailed.

INTENTIONALLY BLANK

TABLE OF CONTENTS

TABLE OF CONTENTS (continued)

FOREWORD

1. This Department of Energy (DOE) Standard supersedes DOE-STD-3013-2004, "Stabilization, Packaging, and Storage of Plutonium-Bearing Materials," and is approved for use by all DOE organizations and their contractors. This Standard deals with stabilization, packaging, and storage of plutonium-bearing materials.   Plutonium-bearing materials stabilized and packaged to meet earlier versions of the standard remain DOE-STD-3013 compliant without further evaluation.

2. Responsibility for management of this Standard has been assigned to the Office of Environmental Management (EM), and implementing actions will be taken by Assistant Manager for Nuclear Materials Stabilization Project (AMNMSP), Savannah River Operations Office. Beneficial comments (recommendations, additions, deletions) and pertinent data that may improve this document should be sent to AMNMSP. Questions regarding this Standard should be addressed to AMNMSP. Modifications of any kind (Revisions or Change Notices) to this Standard must be submitted to AMNMSP.

3. DOE technical standards, such as this Standard, do not establish requirements. However, all or part of the provisions in a DOE standard can become requirements under the following circumstances:

   (1) they are explicitly stated to be requirements in a DOE requirements document; or

   (2) the organization makes a commitment to meet the Standard in a contract or in an implementation plan or program plan required by a DOE requirements document.

4. Throughout this Standard, the word "shall" is used to denote actions that must be performed if the objectives of this Standard are to be met. If the provisions of this Standard become requirements through one of the ways discussed above, then the "shall" statements would become requirements.

5. Requests for equivalency for any DOE-STD-3013 criteria or evaluations/determinations listed below shall be submitted in writing to AMNMSP for approval:

- Technical evaluation of an alternate analytical method for stabilization verification;

- Technical evaluation of a qualified process to reduce testing requirements for stabilized material;

- Use of approved evaluations/equivalencies to previous revisions of DOE-STD-3013 for materials yet to be packaged;

- 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; or

- Technical evaluation of a well-defined expansion of scope, under closely controlled conditions.

AMNMSP will provide a DOE-approved recommendation to the responsible DOE official making the request. For copies of approved documents, contact the AMNMSP.

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 contamination because the extent of corrosion is limited by the available moisture, rather than the available chloride. The available moisture limitation in this Standard is considered sufficient to avoid significant corrosion.

This Standard addresses the safety envelope of the storage container. 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

DOE Manual 441.1-1 Nuclear Material Packaging Manual, March 07, 2008

DOE Order 414.1C   Quality Assurance, June 17, 2005

DOE Order 440.1B   Worker Protection Management for DOE Including The National Nuclear Security Administration Federal and Contractor Employees, May 17, 2007

DOE-STD-1098-2008, Radiological Control, October 2008.

ISP 2001   "Establishment of an Integrated Surveillance Program in Support of Stabilization, Packaging, and Long-Term Storage for Plutonium-Bearing Materials," S. M. Sohinki and D. G. Huizenga, July 11, 2001.

LA-14395   LA-14395 "Selection of 3013 Container for Field Surveillance: LA-14310, Revision 1" L. Peppers, E. Kelly, J. McClard, G. Friday, T. Venetz, J. Stakebake (and subsequent revisions of this document)

McCallum 1996   "Additional Attractiveness Level E Criteria for Special Nuclear Material (SNM)", Edward J. McCallum (USDOE/NN51), July 22, 1996

SM 2003   "Approval of Transition of the 94-1 Research and Development Program to the Savannah River Surveillance and Monitoring Program for DOE-STD-3013 Materials", J. H. Roberson, October 23, 2003.

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 835, Occupational Radiation Protection

49 CFR 178, Specifications for Packagings

4.3 Non-Government Documents

ANSI N14.5-97, Standard for Radioactive Materials - Leakage Tests on Packages for Shipment, American National Standards Institute, Inc. (ANSI), New York, NY, 1997

ASME Boiler & Pressure Code, Section VIII, American Society for Mechanical Engineers (ASME), July 1, 1998

5. Acronyms and Definitions

5.1 Acronyms

AMNMSP	Assistant Manager for Nuclear Materials Stabilization Project, 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
LOI	Loss on Ignition
MBA	Material Balance Area
MC&A	Materials Control and Accountability
SARP	Safety Analysis Report for Packaging
TGA	Thermogravimetric Analysis
TRU	Transuranic
WIPP	Waste Isolation Pilot Plant

5.2 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.
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), heat generation rate (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 a time sufficient to meet the Stabilization Criteria in 6.1.2.3, but not less than 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) 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 Acceptance 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 chlorides 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 chlorides 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.

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).

6.2.1.6   The outer container shall be designed to the requirements outlined in DOE Order 440.1B. 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.

---

[*] The term "interior containers" means the inner container and any convenience 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:

1) Inside diameter 127 mm (5.00 in.).

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

6.2.3 Container Testing Criteria

6.2.3.1   Design Qualification Testing

1) 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) 178.603, and shall be conducted using containers as specified by 49 CFR 178.601, loaded with non-radioactive material that simulates the planned loading for the container.

2) 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 178.603, and shall be conducted using containers as specified by 49 CFR 178.601, loaded with non-radioactive material that simulates the planned loading for the container.

3) 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 178.601.

6.2.3.2   Testing During Use
Both the inner and outer containers shall be tested for leaktightness, as defined in

ANSI N14.5, at their time of closure.

6.2.4 Other Criteria

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

6.2.4.2   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. The interior surface shall be similarly contamination-free at least until the inner container is inserted. The removable surface contamination level on the exterior surface of the inner container, at the time of its packaging 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 heat generation rate of the contained materials will not exceed 19 watts at any time during the 50-year storage life.

6.3.2.3   If necessary, the mass of contained materials shall be further limited to ensure that the bounding pressure calculated using the equation derived in Appendix B is less than the outer container Design Pressure. Alternatively, the Free Gas Volume of the 3013 container shall be at least 0.25 l/kg of oxide. (For guidance on determination of Free Gas Volume, see Appendix B.)

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

6.3.2.5   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.

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

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

6.4   Storage - Surveillance of Stored Containers for Safety

An integrated, complex-wide surveillance program has been established and is documented in reference ISP 2001. Additional details of the program are included in reference SM 2003 and of the selection of 3013 containers in reference LA-14395. Sites have the option of participating in the complex-wide program or implementing a site-specific Surveillance Program, approved by the Responsible Authority of the 3013 Standard (Forward, Bullet 5), that meets the minimum requirements defined below.

6.4.1 Surveillance Program

6.4.1.1   Surveillance Programs shall address site-specific operating conditions and quality assurance approaches.

6.4.1.2   The Site Surveillance Program shall specify:

1) A clearly defined approach (which may include statistical measures, anticipated failure rates, consideration of risks inherent in the container contents and other risks, and engineering judgment) by which container selection, frequency, and sample size shall be established, and may be adjusted;

2) The initial surveillance frequency (or time between inspections);

3) The initial size and composition of the sample of containers to be included in the surveillance program; and

4) Provisions for evaluation of any observed off-normal behavior or unanticipated condition.

6.4.1.3   Surveillance prescribed by Surveillance Programs shall include:

1) Initial baseline 3013 Container inspections within 30 days of 3013 Container closure;

2) Initial baseline inspection for pressure indication, required for oxides but not metals, within 30 days of inner container closure.

3) Periodic surveillance throughout the storage period to gather information on container performance and/or the behavior of the container and its contents. The level of scrutiny over time may be adjusted based on observed container behavior.

6.4.1.4   The Site Surveillance Program shall document inspection/surveillance methods and responsibilities.

6.4.1.5   The Site Surveillance Program shall require procedures that:

1) Identify prerequisites for the surveillance (i.e., those actions that must be taken or conditions that must be satisfied before an inspection);

2) Identify acceptance criteria and provide specific instructions for action when any of those criteria are not met; and

3) Establish and maintain a documented surveillance schedule.

6.4.2 Surveillance Parameters

The following parameters shall be included in the non-destructive examination of containers:

1) For oxide bearing material, indication of internal pressure build-up in the inner container.

2) The weight of each container in the surveillance sample.

3) Indications of leakage and/or degradation.

The following parameters shall be included in the destructive examination of containers:

1) Gas composition and pressure.

2) Metallurgical examination of containers for evidence of corrosion.

6.4.3 Evaluation of Surveillance Data

6.4.3.1   Surveillance data from an inspection shall be compared against the baseline measurements to identify any changes to the 3013 container.

6.4.3.2   If at any time an unexpected change in a 3013 container is noted, an evaluation shall be performed and corrective action taken as appropriate. This evaluation shall include, as appropriate, 1) options for opening the 3013 container, 2) consideration for inspecting other similar 3013 containers, based on factors such as contents, origin, and date of closure, and 3) assessment of potential consequences.

6.4.4 Material Surveillance

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

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:

1) Chemical and physical form;

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

3) Quantity (mass) of material contents;

4) 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);

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

6) 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);

7) 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:

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

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

3) 3013 container configuration - quantity and type of containers;

4) Date of packaging for each container;

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

6) Baseline 3013 container gross weight, dimensions, and tare weight;

7) The unique identification number associated with each container; and

8) The manufacturer lot identification number for each container.

9) Baseline inspection for pressure indication (e.g., lid deflection).

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

1) Surveillance results, including analytical data;

2) Records of tests performed;

3) Dates of inspections; and

4) 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.

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.

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 heat generation 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 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.

THE MIS PROGRAM

The Materials Identification and Surveillance (MIS) Program has characterized over 60 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, provided pyrophoric constituents are eliminated and the storage atmosphere is relatively inert. Plutonium oxide with greater than 80-85 wt% plutonium (91-97% PuO_2 and approximately 3-8 wt% impurities) is potentially more complex, but its behavior is reasonably well understood. The oxide materials of greatest concern are those that have more than approximately 8 wt% impurities. Many of these impure oxides contain chloride salt (NaCl, KCl, $CaCl_2$, and $MgCl_2$) impurities. 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.

Fifty years was selected as a reasonable upper limit to the time that material might have to be stored.

Purpose

This Standard supersedes DOE-STD-3013-2004 [USDOE 2004]. 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 have all remained unchanged from DOE-STD-3013-96 [USDOE 1996]):

- Measurement uncertainty must be included for meeting certain criteria which includes stabilization temperature, moisture content, mass of fissionable isotopes, total content mass, heat generation, relative humidity.

- Clarification that TGA, TGA-MS, and TGA-FTIR are preferred moisture measurement techniques and LOI is only approved for > 80 wt% Pu + U.

- Corrosion issues, particularly those involving chlorides, have been addressed and recommendations on container materials and relative humidity controls are provided, specifically, when packaging chloride salts, a maximum relative humidity of 15% is allowed between stabilization and packaging to prevent salt deliquescence.

- Convenience containers are specifically stated that they shall not be leak tight to assure that gas can get to the inner container pressure indicator.

- Materials of construction are limited to 304L and 316L for the inner and outer containers.

- Surveillance section specifically mentions the Integrated Surveillance Program.

- Clarification that baseline pressure indication is required within 30 days of inner container closure.

Changes in the technical basis section include:

- This Standard includes an understanding of results from the surveillance studies on storage behavior on actual site 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 they could be controlled by the form and quantity of a deliquescent salt and the relative humidity 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, giving products including hydrogen, oxygen, carbon dioxide

and methane. This work has also demonstrated that pressures approaching the design pressure of the container are not observed and are more likely to be less than 100 psia.

Applicability

No further basis provided.

References

No further basis provided.

Acronyms and Definitions

ALARA	As Low As Reasonably Achievable
ARIES	Advanced Recovery and Integrated Extraction System
DDT	Deflagration to Detonation Transition
DE	Destructive examination
IR	Infrared (spectroscopy)
LANL	Los Alamos National Laboratory
LLNL	Lawrence Livermore National Laboratory
LOI	Loss On Ignition
MIS	Materials Identification and Surveillance
MOX	Plutonium-Uranium Mixed Oxide
NDE	Nondestructive examination
QA	Quality Assurance
RFETS	Rocky Flats Environmental Test Site
RH	Relative Humidity
SCC	Stress Corrosion Cracking
SHGR	Specific Heat Generation Rate
SNM	Special Nuclear Material
SRS	Savannah River Site
TGA	Thermogravimetric Analysis

TGA-FTIR   Thermogravimetric Analysis with Fourier Transform Infrared

(spectroscopy)

TGA-MS   Thermogravimetric Analysis with Mass Spectrometer

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.

Stabilized Materials

A.1.1.1 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], Standard 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. 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.1.1.2   Oxides

A.6.1.2.1   The stabilization requirements of this Standard are intended to accomplish the following objectives:

- eliminate reactive materials such as finely divided metal or sub-stoichiometric plutonium oxides;

- eliminate organic materials;

- 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;

- minimize potential for water re-adsorption above the 0.5 wt% threshold; and

- stabilize any other potential gas-producing constituents.

To achieve these objectives, this Standard specifies that oxide material will be placed in a continuously oxidizing atmosphere at a material temperature of at least 950°C for a minimum of two hours. The following discussion outlines the technical basis that ensures that the thermal stabilization requirements of the Standard will accomplish the above objectives.

1) 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, 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 1979, ANS 1980, Katz et al., 1986].

2) 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 6.3.2.4), but the literature indicates that even these will be destroyed by 2hr/950°C thermal stabilization in air.

3) 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.

The water content is distributed as physically adsorbed water on the surfaces of particles, waters of hydration associated with mostly chloride salts, and as dissociated water, i.e. hydroxides, on the surfaces of metal oxides. The mechanisms controlling the loss of each of these types of water is different.

The heat of adsorption of water vapor onto high purity plutonium oxide surfaces is found to be between 44 and 51 kJ mol^{-1} experimentally [Paffett et al., 2003] and 58 kJ mol^{-1} from theoretical calculations [Hay 2006]. The heat of adsorption of water vapor onto UO_2 is 42 kJ mol^{-1} [Paffett et al., 2003]. These are similar to the heat of adsorption of water vapor onto other metal oxide surfaces. Desorption of water from surfaces with this range of heat of adsorption will be complete by 100 to 200 °C. A notably desirable result of 950°C thermal stabilization is that metal impurities are expected to be converted largely or entirely to binary oxides

(e.g., Fe_2O_3, Cr_2O_3, and Ga_2O_3) and complex oxides containing more than one metal cation. While quantitative details will vary with the impurity, the conceptual model for chemisorption and physisorption of moisture on trivalent oxides is expected to be qualitatively similar to moisture interactions with plutonium oxide [Henrich/Cox 1996]. Thus, all physically adsorbed water whether on plutonium oxide, uranium oxide, metal impurities such as Fe_2O_3, Cr_2O_3, Ga_2O_3, etc. or salt surfaces such as NaCl, KCl, etc. will be removed early in the thermal stabilization cycle.

Residual magnesium and calcium chlorides (alkaline earth chlorides), on the other hand, chemically bind substantial amounts of water as stoichiometric hydrates [Smith et al., 1999]. Calcium chloride loses all waters of hydration by 200 °C. [Budovec et al., 1989] Calcium chloride is also hydrolyzed by water vapor above 450 °C releasing HCl vapor. [Lawrence et al., 2000] The thermal behavior of magnesium chloride is more complicated combining loss of water and hydrolysis, which is complete by 500 °C. The hydrolysis of these chlorides, partially or completely, to their respective oxides when heated in the presence of moisture is confirmed by MIS elemental composition and x-ray diffraction results on thermally stabilized impure oxides. [Mason et al., 1999] The calcium and magnesium chloride components are expected to be present as binary or ternary salts ($KMgCl_3$, $KCaCl_3$, $NaKMgCl_6$, and so forth). [Garcia et al., 2007] The behavior of these more complex salts with respect to water loss and hydrolysis is expected to be similar to the pure salts. Thus, all water associated with hydrated chloride salts will be lost by 500 °C.

Plutonium oxide powder forms surface hydroxides upon exposure to air as do many metal oxides. [Farr et al., 2004] [Blesa et al., 1994] Decomposition of the surface hydroxides of plutonium oxide begins at 100 °C and is nearly complete by 590 °C. Iron hydroxides, chromium hydroxide, and nickel hydroxide are reported to have lost all their water in the 200 to 525 °C range. [Galwey 1999] Thus, loss of the hydroxide component of the water associated with plutonium oxide materials is expected to be complete by 650 °C.

Moisture measurements of thermally stabilized material at packaging made during Hanford and Rocky Flats packaging campaigns show that water is nearly all removed by 680 °C (See Figure A-1). The water observed in the measurement is primarily water adsorbed between the end of thermal stabilization and the measurement, the evidence being that most is released far below the thermal stabilization temperature. Rocky Flats TGA-FTIR data were analyzed to determine the amount of water in three nearly equal time segments of the TGA curve. The temperature segments analyzed were ~30 to 365 °C, 365 to 680 °C, and 680 to 1000 °C. The average weight loss during each of these segments was 0.0125wt%, 0.0026wt%, and 0.0013wt% respectively. Measurements on impure

oxides by the MIS project show that residual moisture levels after 950°C thermal stabilization are reliably below the 0.5 wt% criterion, and well below 0.2 wt% in most cases examined to date [Mason et al., 1999].
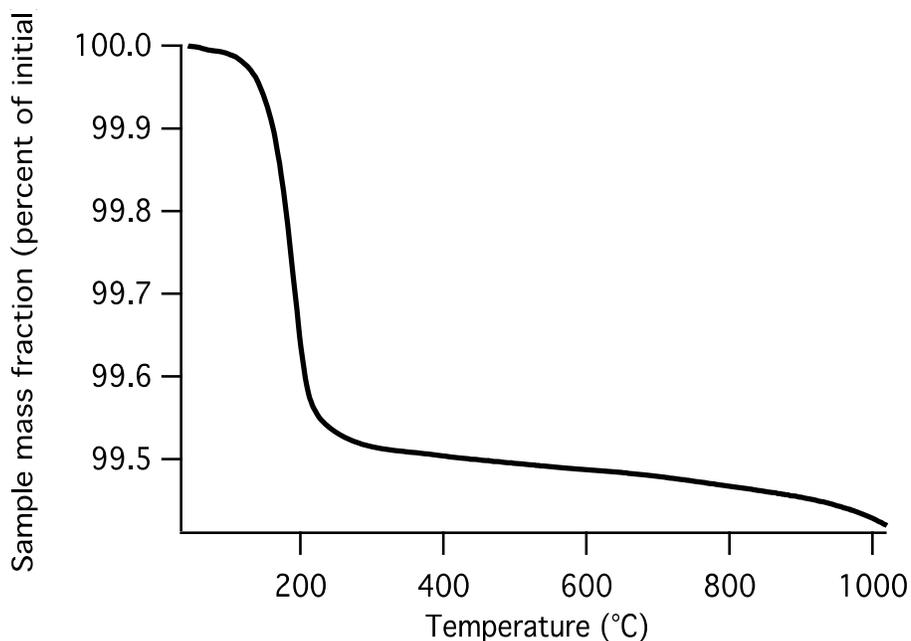

Figure A-1: An example of a TGA mass loss vs. temperature result typical of a sample containing measurable moisture.

Based on process knowledge, MIS measurements of elemental composition and x-ray diffraction patterns, the dominant impurity phases after thermal stabilization are expected to consist of chloride salts of Na, K, Ca, and Mg and binary and compound metal oxides involving Fe(III), Cr(III), Ni(II), Ga(III), Mg(II), etc. [Mason et al., 1999]. MIS elemental analysis on thermally stabilized samples show iron, nickel and chromium as common impurities at levels up to about 5 wt% (iron and nickel) and 1.5 wt% (chromium). The other two most common elemental impurities (other than Na, K, Ca and Mg associated predominantly with chlorides) are gallium (up to about 2.5 wt%) and silicon (up to about 1 wt%). Uranium oxide is expected (and confirmed by MIS x-ray diffraction) to be present predominantly as U_3O_8 after thermal stabilization at 950°C.

4) Minimize potential for water readsorption above the 0.5 wt% threshold.

Water is readsorbed by physically adsorbing to the surfaces, formation of hydrates with principally chloride salts, and 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 pure and impure oxide material surface areas below 5 m^2/gram generally result from thermal stabilization

23

at 950°C for two hours. [Haschke/Ricketts 1995; Haschke/Ricketts 1997; Haschke/Martz 1998; Mason et al., 1999; Manchuron-Mandard/Madic 1996]. A hydroxide layer (equivalent to 0.5 monolayers of water) covered with a monolayer of water on 5 m^2/gram material will result in 0.165wt% adsorbed water (1.5 monolayers of water at 0.22 mg/m^2 for each monolayer). [Haschke/Ricketts 1997] High-purity oxide of less than 5 m^2/gram specific surface area will not re-adsorb sufficient water to exceed the 0.5 wt% limit even when allowed to equilibrate with a controlled atmosphere of about 50% relative humidity. [Haschke/Ricketts 1995]

MIS elemental analysis on materials studied to date shows one of these items has as-received chlorine content above 20 wt%, where the chlorine content after 950°C thermal stabilization was reduced to less than 8 wt%. In general, residual chloride salt is expected (and is observed) to be reduced by thermal stabilization, a factor which will restrict moisture uptake by chlorides before packaging. Sodium and potassium chloride melt below the 950°C thermal stabilization temperature and therefore relatively large particle sizes and low surfaces areas are likely to result for these phases. A literature survey indicates that sodium chloride and potassium chloride will not resorb significant water after thermal stabilization unless the deliquescent relative humidity is exceeded (see Table A-1). [Smith et al., 1999]

Readsorption of water by the alkaline earth chlorides to form hydrated salts occurs at very low water vapor pressure. In addition, small amounts of alkaline earth chlorides when fully hydrated can result in 0.5wt% water, e.g. 0.5wt% of MgCl$_2$ will result in 0.5wt% adsorbed water if the magnesium chloride hexahydrate is formed. The thermodynamics of hydrate formation by MgCl$_2$ is well known.[Pabalan 1987] At room temperature MgCl$_2$ forms the tetrahydrate at less than 1% RH and the hexahydrate by 2% RH. Thermal stabilization substantially reduces the MgCl$_2$ content by hydrolysis forming MgO but does not eliminate MgCl$_2$ entirely. Calcium chloride also readily forms hydrates at low relative humidity. Thermal stabilization of calcium chloride does not typically result in hydrolysis to CaO unless there is water vapor available at high temperatures. [Lawrence et al., 2000]

Thermal stabilization of the alkaline earth chlorides with sodium and potassium chlorides typically result in the formation of more complex salts. [Garcia et al., 2007] However, the behavior of the more complex salts with respect to the formation of the hydrates at low relative humidity is similar to that of the simple alkaline earth chlorides. Because thermal stabilization does not completely convert the alkaline earth chlorides to alkaline earth oxides, control of time and relative humidity between thermal stabilization and packaging is strongly advised when handling plutonium oxides containing magnesium and calcium chloride impurities.

[Veirs et al., 2002] Alkaline earth chlorides can also deliquesce which is a more serious condition addressed in Section A.6.1.2.4.

5) 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].

The preceding discussion addresses stabilization issues for plutonium oxide materials that are rooted in safety concerns. An additional issue for these materials, which is based more in operational than safety concerns, is the behavior of salt impurities in plutonium oxides that have resulted from pyrochemical operations. The common impurities NaCl and KCl, which can achieve levels of tens of percent in unstabilized impure oxides being addressed by this Standard, have moderate volatilities above 800°C. The practical impact of moderate volatilities is that materials with these characteristics have difficulty meeting the 0.5 wt% moisture criterion with reasonable thermal stabilization times using mass loss techniques such as LOI and TGA. (Corrosion implications of chlorides during storage are addressed in Section A.6.1.2.4 and A.6.3.2.6 of this Appendix.) A second concern is the maintenance impact of volatilized salts on furnace and off-gas systems. Salt volatilization is much more problematic at 950°C than at 800°C because the vapor pressures of NaCl and KCl are roughly an order of magnitude greater at the higher temperature. This Standard retains the 950°C thermal stabilization criterion of Standard 3013-99 but recommends that operational complications regarding salt evolution be carefully monitored. Section 5 of the Forward, third 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 DOE has approved two submittals as technically equivalent [Boak et al., 2002; Boak et al., 2003]. This process has proved efficient, cost effective, and timely for both Rocky Flats and Richland. The technical equivalency evaluations were based on well-characterized material, with no impurities that could cause pressurization, and subsequently

stabilized materials were tested to the same requirements (moisture content, etc.) previously approved by DOE. The procedure of technical equivalency has allowed the DOE to incorporate new technical basis information into the stabilization process without continuous modification of the Standard. Although not suggested in this Standard, one perceived benefit of thermally stabilizing plutonium oxide is reducing the respirable fraction of the powder [USDOE 1994a]. Haschke and Ricketts reported particle size distributions for plutonium oxide prepared from oxalate precipitation and hydride-catalyzed oxidation of metal after a thermal stabilization cycle that included treatment at 950°C for two hours [Haschke/Ricketts 1995]. The authors' measurements indicated that about 2% of the mass fraction for hydride-derived oxide was below ten microns in size, compared to about 0.05% for oxalate derived oxide, implying that the method of oxide preparation can be a strong determinant of the particle size distribution. This work also indicated that the frequently assumed correlation of specific surface area with particle size is not always valid, due to porosity effects. In other words, the decrease in surface area observed in thermal stabilization is not necessarily accompanied by a decrease in the number of smaller particles. Subsequent work by Machuron-Mandard and Madic [Machuron-Mandard/Madic 1996] examined particle size behavior for oxalate-derived plutonium oxide thermally stabilized at 100°C intervals between 450°C and 1050°C. The studies showed that the number of very small particles increases as the oxide is thermally stabilized at temperatures above 750°C, while the oxides fired at lower temperature are made up of medium size grains. This work thus indicates that for oxalate derived plutonium oxide, the number density of respirable particles may actually increase for thermal stabilization temperatures above 750°C.

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. Thus, verification of adequate stabilization requires only 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 re-adsorbtion 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. This Standard encourages the use of more moisture-specific alternative methods for lower grade materials.

Thermogravimetric analysis (TGA) 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). Use of an inert purge gas mitigates against the potential masking effects of sample oxidation or moisture re-adsorption during cool-down. While it does not directly prevent the mistaking of other volatile components for moisture, experience has shown that the false failure rate is acceptably low for most materials. Where necessary, mass spectrometry or infrared absorption spectroscopy were 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 mass spectroscopy (MS) or infrared (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. However, 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).

After the first 5 years of the Integrated Surveillance Program, 238 nondestructive examinations (NDE) and 43 destructive examinations (DE) had been performed on a total population of approximately 5100 containers. The ages of the containers examined ranged from 3 years to 6 years. All pressures observed have been below 20 psig and gas analyses performed on the DE containers have shown that the gas mixtures are not flammable. In addition, metallurgical examinations of the DE containers have shown only minor corrosion for the chloride salt bearing containers. [JNMM 2010]

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 test 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, 5 kg batches 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 up to 0.5wt% added water were observed 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 given the 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 0.5wt% water, hydrogen gas is generated. [Veirs/Berg 2008] Pyrochemical processing salts can contain an alkaline earth chloride such as $MgCl_2$ or $CaCl_2$ that is not destroyed by thermal stabilization. The alkaline earth chlorides can absorb moisture at low values of relative humidity. The rate of hydrogen generation decreases with time in all cases. The maximum predicted hydrogen partial pressures from the fit are substantially below, falling between 0% and 25% of the hydrogen partial pressures calculated using the aggregate pressure equation [23] in Appendix B. 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 appears 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.

Reproducible tests of one MIS salt-bearing material with 0.5wt% water produced both hydrogen and oxygen in near stoichiometric quantities. [Berg et al., 2007] The gas mixture became flammable within a couple of months. The behavior of the hydrogen and oxygen with time is also unusual in that the partial pressure of both constituents began declining after about one year. These observations suggest both a depletion over time of the source term, water in radiolytically active sites, and a mechanism for subsequent consumption of the hydrogen and oxygen. The data are too sparse to conclusively assign mechanisms. However, it is worth noting that the radiolytic recombination rate of hydrogen and oxygen in the interstitial gas is predicted to be more than sufficient to account for the observed rate of decline in hydrogen and oxygen concentration once the independent generation mechanism slows. [Foy/Joyce 2008] A narrow range of material conditions has been identified for the production of both hydrogen and oxygen. [Berg et al., 2008] In order for oxygen to be generated along with hydrogen the relative concentrations of the alkaline earth chlorides to water must be such that these chloride salts have more than three waters of hydration and the total water content is greater than 0.3wt%. If the alkaline earth chloride content is greater than 1%, then the number of waters of hydration will be less than three when the 0.5wt% water limit is reached and oxygen will not be generated. If the alkaline earth chloride content is low, then the water content must be kept below 0.3wt% 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. Strain measurements on actual 3013 outer containers were slightly less than 2000 μstrain. The authors conclude that "Based on the results of these tests, we 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 containing magnesium and calcium chloride impurities.

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   It is the intent to require control of the relative humidity for materials that are known to contain chloride salts such as from chemical processing, e.g. electrofining or direct oxide reduction, or for materials that have been mixed with, come into contact with, or have been processed in the same equipment as materials known to contain chloride salts. See for instance the criteria used to select containers for field surveillance due to the presence of chloride [Peppers et al., 2009]. It is not the intent to require control of the relative humidity for materials that contain impurity amounts of the element chlorine such as the oxide from direct metal oxidation.

The intent is to avoid packaging any material with liquid present. Chloride salts can form liquids by absorbing water from the atmosphere, a process known as deliquescence. Material with small amounts of deliquesced salts is difficult to detect because the powder still can be a free-flowing powder. The relative humidity at which a particular chloride salt deliquesces is a fundamental chemical property of the salt. The deliquescent relative humidity is independent of other gaseous constituents such as nitrogen, oxygen, or inert gases. The most obvious technical approach to preventing deliquescence of chloride salts is to ensure the relative humidity is below the deliquescent relative humidity of the chloride salts present. When that is not possible, the amount of time that the material is exposed above the deliquescent relative humidity can be limited thereby preventing a liquid from being permanently formed. If the approach is to limit the time, then a technical basis may be developed that justifies the length of time and the relative humidity allowed. Section 5 of the Forward, third 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.

Stress corrosion cracking (SCC) has been identified as being the greatest threat to 3013 container integrity. [Kolman 2001] Room temperature SCC of 304L and 316L stainless steels is reported to occur with the alkaline earth chlorides $MgCl_2$ and $CaCl_2$ commonly present in plutonium processing salts. [Shoji/Ohnaka 1989; Tani et al., 2009] The attack is most aggressive at or slightly above the deliquescent relative humidity of the component salt. The deliquescent relative humidity is the lowest relative humidity at which a solution is formed from the salt and water vapor. The solution formed at the deliquescent relative humidity has the highest chloride concentration possible for the salt. Room temperature SCC of 304L in contact with plutonium oxide with a small amount of $CaCl_2$ and 0.5wt% moisture has been observed in the MIS program. [Zapp/Duffey 2008] The amount of water in these tests is consistent with the formation of deliquesced $CaCl_2$.

The deliquescent relative humidity (RH) of the common plutonium processing salts has been studied in the MIS program. [Veirs et al., 2010] The deliquescent RH for the pure salts is well known. [Greenspan 1977] At room temperature (23 °C), the deliquescent RH for KCl, NaCl, and $MgCl_2$ is 84%, 75%, and 33% respectively. The deliquescent RH 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].

However, in plutonium processing pure salt phases are almost never present. 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 deliquescent RH 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 deliquescent RH 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.

Table A-1. Deliquescent relative humidity of chloride salts used in pyroprocessing across the DOE complex at 25°C (unless otherwise indicated).

Compound	RH(%)	Compound	RH (%)
KCl[a]	84	$MgCl_2 \cdot 6H_2O$ (70°C) [b]	27
NH_4Cl[a]	79	$KCaCl_3$ (70°C) [b]	21
NaCl[a]	75	$CaCl_2 \cdot 4H_2O$[b]	20
$KMgCl_3 \cdot 6H_2O$[b]	57	$CaCl_2 \cdot 2H_2O$ (70°C) [b]	17
$MgCl_2 \cdot 6H_2O$[a]	33	$KCaCl_3$[b]	16
$CaCl_2 \cdot 6H_2O$[a]	29		

a. Lide 2003 page 15-25, Table Constant Humidity Solutions
b. Joyce et al., 2010, Table 1. Data for magnesium chloride also in Garcia et al., 2007.

In order to minimize concerns of SCC, control of exposure above the deliquescent relative humidity is required when handling chloride-containing materials. Oxides suspected to contain chlorides must have the time and relative humidity to which they are exposed after stabilization controlled such that deliquescence does not occur.

A.1.1.3 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.1.1.4 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.

3013 Container

A.1.1.5 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 material container (convenience container) is a container that is used to transfer plutonium-bearing material. A material container is not required in packaging and is not considered an isolation barrier by this Standard. Use of a material container can

reduce the potential for contamination during loading and closure of the inner container, facilitate packaging, and provide an additional material barrier.

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 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 by the mass of oxide specified in Section 6.3.2 under conditions of minimum void volume of 0.25 l/kg, 0.5 wt% moisture, 19 W heat generation, and 211°C (412°F) gas temperature (see Appendix B). 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 Paragraph 6, Pressure Safety Requirements, of Attachment 1 to DOE O 440.1, 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 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, 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. 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.1.1.6 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 failure 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 stress corrosion cracking (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 Report [USDOE 1994a, USDOE 1994c] describes 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 either cleaned or shown to have a de minimis level of organic material.

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.1.1.7   Container Testing Criteria

A.6.2.3.1   Design Qualification Testing

1) 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 178.603(a). The target for the drop tests is defined in 49 CFR 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 178.603(e). The simulated contents shall include the mass of any convenience containers. The criterion for passing this test is that it retain its function, (i.e., that it remain leaktight as defined by ANSI N14.5 [ANSI 1997]).

2) The purpose of the 1.3-meter drop test for the inner container is to ensure that a loaded inner container accidentally dropped from the maximum packaging height would not release any material. The simulated contents shall include the mass of any convenience containers.

3) The hydrostatic proof test provides verification that the container will remain leaktight under maximum design conditions, plus a safety margin.

A.6.2.3.2   Testing During Use

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 1997]. 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.

The term "at time of closure" is used for two purposes. First, since a tracer gas (such as helium) is normally used, 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.

A.1.1.8 Other Criteria

A.6.2.4.1 Identification markings are required on all storage containers to facilitate maintenance of an inventory database and management of stored materials.

A.6.2.4.2 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, within the bounds of ALARA principles, but 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, a contamination-free inner 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.

Contents

A.1.1.9 Container Fill Gas

A.6.3.1.1 The stored material condition should not change significantly because of reactions with the container atmosphere. If material stabilization has to be repeated, 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.

A.1.1.10 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 1998] 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. [Clayton 2010] [ANSI/ANS-8.15 1981]

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 wattage (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 Thermal Output and Temperature-Dependent Effects in Plutonium Metal

1) Thermal Output

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 heat generation rate will vary also. The limit is applied to the maximum heat generation rate over the storage period. A discussion of heat generation rates in plutonium is found in Section B.5 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 plutonium metal-stainless steel container interface temperature 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 heat generation rate 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].

Table A-2
Calculated Temperatures (°C) in a 9975 Package

Location	Storage 19 W		Transport 19 W		Storage 30 W
	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.

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 [Beilenberg et al., 2006].

Contributions to the overall thermal conductivity from the container fill gas in pore phase were pressure dependent and the extent of solid to solid particle conduction was determined.   Using the more accurate and experimental determined values for thermal conductivity, the predicted peak centerline oxide temperature were about 50º C lower than those predicted by Hensel for similar

heat loading and the same 3013/9975 configuration, for example 227ºC versus 275ºC for the peak oxide temperature during conditions of transport in a 9975 as shown earlier in Table A-2.

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 heat loads were modeled at 4.7, 10, and 19 watts. A wider range of ambient temperatures were evaluated. Results were generally less than previous thermal models. The study also concluded than 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 - ºC

	Hensel		Bielenberg	Gupta	
Location	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 *	164	211		79	129
Assumed k (watt/m-K)	0.079		0.15	0.45	

*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.

    2) 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, Spearing et al., 1999; Spearing/Veirs 1999; Flanders/Krishnan 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/Veirs 1999; Spearing et al., 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].

3) Metallurgical interactions

Maximum plutonium-container interface temperatures up to approximately 189°C (see 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   The assurance of safe storage embodied in this Standard rests on the premise that the outer storage container is capable of withstanding credible pressure. This is accomplished by ensuring that the design pressure of the container is greater than the theoretical ability of the contained materials to pressurize with time, as determined by the bounding pressure calculation derived in Appendix B. One way to provide this assurance is to provide sufficient free gas volume in the container to accommodate the worst possible gas evolution and expansion. A minimum of 0.25 liters of free volume per kilogram of oxide in the container assures the bounding pressure remains below the design pressure (see Section B.4.2.4 in Appendix B) This was calculated using the design pressure of 4920 kPa (699 psig), a gas temperature of 211°C (412°F), a container heat generation rate of 19 watts, and a moisture content of 0.5 wt%.

A.6.3.2.4   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.6.3.2.5   Because the oxide (including contained impurities) will pick up atmospheric water, it is important that the sample taken for moisture analysis be representative of the material actually packaged into the 3013 container. This can be done, for example, by controlling the glovebox relative humidity and/or packaging within a very few minutes of sampling.

A.6.3.2.6   This Standard prohibits packaging materials that may adversely affect the integrity of the containment system. The primary corrosion mechanisms of interest are pitting and stress corrosion cracking.

General corrosion is not a credible problem 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 addresses radiation induced SCC and hydrogen embrittlement.

These are not anticipated to be issues if, as expected, significant plastic strain is not introduced into the containers and large hydrogen pressures (well above that predicted by the pressure equation) do not develop in the containers. 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.

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

Unlike general corrosion, pitting and stress corrosion cracking (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. 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 two 304L test specimens in contact with PuO_2 powder with 0.90 wt% NaCl, 0.90 wt% KCl, and 0.20 wt% $CaCl_2$ with 0.51 and 0.63 wt% water respectively [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. Nonetheless, a MIS recommended corrosion study is addressing the potential for stress corrosion cracking, and ongoing destructive examination of random and select containers is necessary to provide sufficient long-term assurance of no container failures. [Zapp 2008, SCC Test Plan 2009]

A.6.3.2.7   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.

Storage - Surveillance of Stored Containers for Safety

A Surveillance and Monitoring Plan is necessary to assure that 3013 containers can be safely

stored for up to 50 years. An effective plan should balance the risks (both safety and cost) associated with performing the surveillance examinations against the risks associated with container failures. [ISP 2001]

Where possible, surveillance is to be primarily non-destructive examination to preserve storage container integrity. Limited numbers of containers should be destructively examined to obtain information that cannot be obtained non-destructively. Examples of non-destructive examination methods include the following:

- Radiography to observe physical changes in the stored material (e.g., oxide growth on plutonium metal) and dimensional changes of the inner container from pressure generation, note that surface area on plutonium metal is small thus eliminating the need to radiograph these containers for the purpose of determining dimensional changes of the inner container from pressure generation;

- Weight measurement change, which would indicate a breach in the 3013 container; or

- Additional methods that may become available as technology develops.

Examples of destructive examination include the following:

- Gas composition and pressure

- Metallurgical examination for indications of corrosion.

A.1.1.11 Surveillance Program

A.6.4.1.1   Plans need to be responsive to site policies and practices.

A.6.4.1.2   During the course of packaging and storage of plutonium metal and oxide, there is a very small possibility that some container manufacturing defects may not be detected, that some batches of material may be improperly stabilized or packaged, or that some of the containers may be damaged during handling and storage.   The Quality Assurance (QA) program at the packaging site coupled with the baseline inspections specified in this standard minimizes the likelihood of these problems in storage.   The primary function of the surveillance program is to identify these anticipated low probability errors and flaws in the packaging as well as unanticipated threats to container integrity during storage.

There are two broad classes of "problems" that surveillance is expected to detect. The first class could be called "anomalies" because they are single events that occur more or less randomly in a large population of storage containers. The second class could be called "systemic" because they may affect a significant fraction of the

storage containers, and generally represent an unanticipated condition in those containers. The surveillance program is expected to be able to distinguish between these two classes and to provide information upon which corrective or other action can be based.

The surveillance program should document the surveillance "philosophy" in terms of the characteristics described above. Then, it should apply that philosophy to the specific storage situations that may be encountered. For example, in a facility that relies on 3013 container integrity for public safety (i.e., where the container is designated "safety class") and in which the 3013 containers are easily accessed and inspected, a relatively extensive surveillance inspection would be expected. In a facility that does not rely on 3013 container integrity for public safety, where access to the containers is difficult, and where inspection involves a relatively high personnel radiation dose, the surveillance inspection would be expected to be less extensive than in the previous example.

The surveillance program should identify sources of information/data to be used in establishing inspection frequency, sample size and composition, etc. As information on these containers is accumulated, it should be shared among the sites and included in the information base. It is recommended that samples of materials typical of those being stored be placed in a "shelf-life" program in which the condition of the storage containers can be evaluated over long periods of time to give insight into the behavior of the contained materials and into interactions between the materials and the container; and that this information also be included in the surveillance information base. Finally, it is recommended that the sites storing plutonium metals and oxides and those preparing such materials for storage collaborate to the extent feasible in developing their site programs, so that both consistency in approach and flexibility in storage location can be maintained.

The surveillance program should identify possible courses of action to be taken in the event of an unexpected surveillance finding, and guidance on selecting the appropriate action. This guidance should be directed toward identifying the event as either an anomaly or a systemic issue, and toward establishing a plan for dealing with the matter.

Certain efficiencies may be achieved if the frequency of surveillance is integrated with the physical inventory program as prescribed in DOE M 470.4-6 Change 1.

A.6.4.1.3   Inspections

1) Initial Inspection. Flaws in initial packaging are expected to be detected by inspection of every 3013 Container within 30 days of packaging. Ordinarily, this inspection should be done immediately after packaging, 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.) This initial inspection should provide baseline information on the leak rate of both welded containers (the inner container should be inspected after it is closed and before insertion into the outer container, and the outer container inspected after it is closed), and any other information deemed desirable and attainable through non-destructive examinations such as radiography. This initial inspection may be part of the quality program for verifying 3013 Container integrity.

2) This applied to oxides: Since pressure inside the inner container may change after welding, the baseline non-destructive examination for pressure should be performed as soon as possible after the inner container is welded. This examination may be done either before or after the inner container is welded in the outer container. Allowing up to a maximum 30 day delay accommodates operational considerations.

3) During most or all of the storage period, mechanical failures, if any, are likely to be random or due to an unanticipated failure mechanism. Uniform changes in the storage container population, such as a potential gradual pressure generation in oxide containers, may also occur. Surveillance during this period may include sampling to monitor the behavior of the population. If a "shelf-life" program is established, it may be used to evaluate changes in the contents so that corrective action can be taken in advance of container failure. It should also be used to assess corrosion effects over the long term, particularly stress corrosion cracking in containers containing chlorides.

A.6.4.1.4   Inspection/surveillance methods must be documented to assure consistency. Delineation of responsibilities is needed to assure a consistent management approach and awareness of responsibilities.

A.6.4.1.5   No further basis is provided.

A.1.1.12 Surveillance Parameters

No further basis is provided.

A.1.1.13 Evaluation of Surveillance Data

No further basis is provided.

A.1.1.14 Material Surveillance

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. [Narlesky et al., 2009a] (See MIS Program description A.1 Sidebar and Erickson, 2003) 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.

Documentation

A.1.1.15 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.1.1.16 Database Content Elements

A.6.5.2.1   These parameters allow as complete a characterization 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.

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

A.6.5.2.3   No further basis is provided.

Quality Assurance

No further basis is provided.

INTENTIONALLY BLANK

APPENDIX B. Derivation of Pressure Equation

B.1. Introduction

This appendix provides a derivation of the equation used to bound the internal pressure of storage containers loaded with oxide. It also provides guidance on use of the equation. This equation appears in DOE-STD-3013-96 [USDOE 1996] and is similar to the equation in DOE-STD-3013-94 [USDOE 1994b]. SI units have been used.

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
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}	Pycnometer density of material. Note, 1 g cm^{-3} is equivalent to 1 kg l^{-1}
F_p	---	Packing fraction, ratio of bulk density to pycnometer density.
ρ_{bulk}	g cm^{-3}	Bulk density of material
w_x	---	Mass fraction for component x.
ρ_x	g cm^{-3}	Pycnometer or theoretical 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	number of atoms or mol	Amount of material
N_0	number of atoms or mol	Amount of material at time container is sealed
t	yr	Time since container was sealed
λ	yr^{-1}	Decay constant
$t_{1/2}$	yr	Half-life of a radionuclide
Q	W	Material heat load
E	MeV/event	Decay energy. Note 1 MeV/event = 9.649×10^{10} J mol^{-1}
V_{min}	l	Minimum gas volume required
t_{peak}	yr	Time at which the heat generation rate reaches a maximum

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

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

where P is absolute pressure, V is volume, T is absolute temperature, n is the number of moles of gas, and R is a 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 generated gas of significance anticipated during extended storage is hydrogen from decomposition of adsorbed water. Thus, the combined effect can be expressed as:

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

where P_F, P_{H2}, and P_{He} are the partial pressures of the fill gas, the generated hydrogen, and decay helium, respectively.

B.2. Derivation

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

Figure B-1. Illustration of the components of free gas volume.
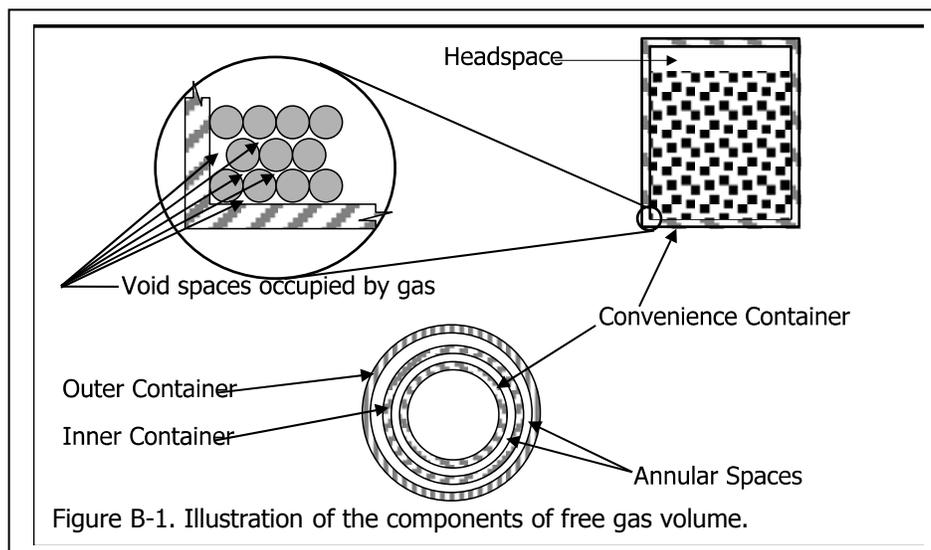
$$V_g = V_c - V_m \qquad\qquad [3]$$

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

B.2.1.1 Containers

Information on the currently used container designs is given in Table B-2. For the RFETS configuration, inner and convenience can volumes were determined from can weights determined by measurements taken during the first 14 destructive examinations at SRS. Volumes for the other configurations were derived from drawings and calculations. The free volume is determined as the interior volume less the material volume of interior containers.

Table B-2. Volumes associated with the container configurations that have been used to date. 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.

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]	0.143±0.001[d] 0.114±0.001[d]	0.143±0.001[d] 0.114±0.001[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±0.001[d]	0.067
Unoccupied volume, V_c	2.168	2.155	2.248	2.168	2.428 2.456	2.384 2.412

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. Calculated from the weight of containers from database at LANL. Uncertainties based on range of weights.

B.2.1.2   Material

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

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

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 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, some alternate methods of estimating the particle density to be used in Equation [4] must be developed.

B.2.1.3   Packing Fraction Method

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, but does not exceed 0.62 [Mason et al., 1999]. Thus, one approach 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). Consequently, 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.

B.2.1.4   Statistical Method

Using the maximum value of the packing fraction can result in a particle density that is too small, especially for materials of low bulk density. For example, Figure B-2 shows the packing fraction as a function of bulk density for the materials in the "shelf life" program. The ratios include material thermally stabilized at 950°C, 800°C, and some that was thermally stabilized

first at 600°C, and then at 950°C. The heavy line that passes through the data points is a statistical regression assuming a linear relationship, and is given by the relationship

$$F_p = 0.2348 + 0.05673 \text{ cm}^3 \text{ g}^{-1} \rho_{bulk} \qquad [5]$$

where F_p is the packing fraction, and ρ_{bulk} is the bulk density. The standard error of an estimate made using this regression is approximately 0.079. A "bounding" estimate can be made by adding twice the error to the estimate, shown in Figure B-2 by the dashed, lighter weight line that is above all the data points. However, using this method to estimate a packing fraction for materials with a bulk density greater than 4.0 results in a packing fraction greater than 0.62. It would not be advisable to use Equation 5 to estimate the density ratio for bulk densities below 2 kg/l, as the equation clearly does not extrapolate correctly to zero bulk density.
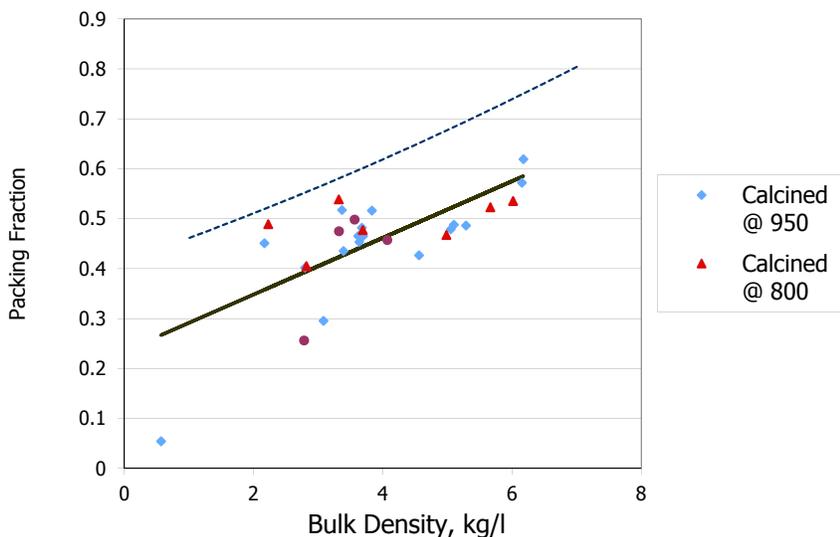

Figure B-2 Statistical model of material density relationship.

B.2.1.5 Material Composition Method

The density of the material can be calculated from knowledge of the material composition and the theoretical density of each constituent. Actinide oxide theoretical 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 density of the material is given by:

$$\rho = \cfrac{1}{\cfrac{w_{PuO_2}}{\rho_{PuO_2}} + \cfrac{w_{U_3O_8}}{\rho_{U_3O8}} + \cfrac{w_{NpO_2}}{\rho_{NpO_2}} + \cfrac{w_{AmO_2}}{\rho_{AmO_2}} + \cfrac{w_{H_2O}}{\rho_{H_2O}} + \cfrac{w_{salt}}{\rho_{salt}}} \qquad [6]$$

where w is the mass fraction of the component and ρ is the 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 pycnometer 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. Reducing the calculated density in Equation [6] by 10% results in a conservative value for the material density for use in Equation [4].
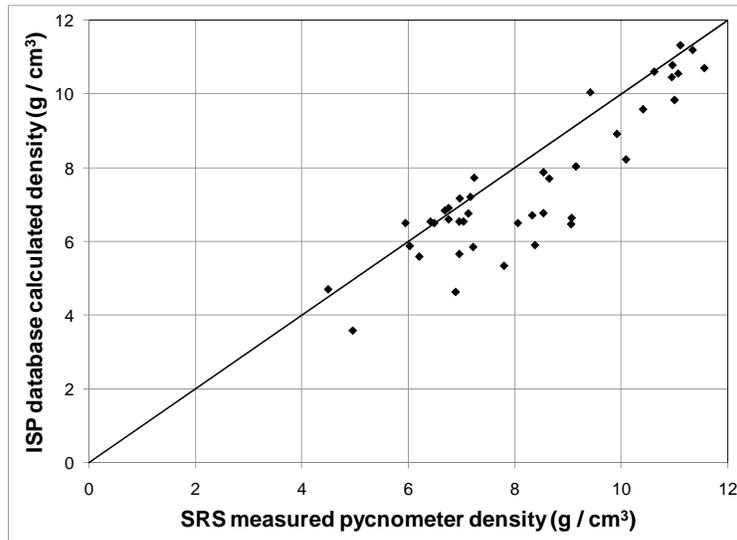

Figure B-3. Comparison of calculated densities to measured pycnometer densities for SRS destructive examination of materials.

Pressure Due to Container Fill Gas

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

$$n_F = P_0 V_g / R T_0 \tag{7}$$

The values of P_0 and T_0 are the pressure and temperature at which the container was loaded and sealed. 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:

$$P_F = n_F R T_1 / V_g = (P_0 V_g / R T_0)(R T_1 / V_g) = P_0(T_1 / T_0) \tag{8}$$

Generated Gases

B.2.1.6 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 conservatively assumes that all the water is decomposed to form hydrogen gas and that the oxygen is consumed by the material. If, in fact, some water is not decomposed, the pressure will be lower.

B.2.1.7 Quantities of Gas 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:

$$n_{H2O} = m w_{H2O}/M_{H2O} \ = \ n_{H2} \tag{9}$$

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

$$P_{H2} = (m w_{H2O}/M_{H2O}) R T_1/V_g \tag{10}$$

which is the middle term of the equation in equation [2].

Decay Helium

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

$$dN/dt = \lambda N \tag{11}$$

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

$$N(t) = N_0 e^{-\lambda t} \tag{12}$$

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

$$n_{He} = \int N(t)dt \ = \ \int \lambda N_0 e^{-\lambda t}dt \ = \ N_0(1 - e^{-\lambda t}) \ \approx \ N_0 \lambda t \tag{13}$$

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,

$$N_0 = wm/M \tag{14}$$

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

$$n_{He}(t) = N_0 \lambda t = (wm/M) \lambda t \tag{15}$$

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

$$P_{He}(t) = n_{He}(t) RT_1/V_g = wm\lambda tRT_1/MV_g \tag{16}$$

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, $\lambda_{239Pu} = 2.87\times10^{-5}$ yr^{-1}, and $M_{239Pu} = 0.239$ kg mol^{-1}. Equation [16] for high-purity oxide with exclusively ^{239}Pu becomes,

$$P_{He}(t) = 1.06\times10^{-4} \text{ mol yr}^{-1} \text{ kg}^{-1} \; mtRT_1/V_g. \tag{17}$$

Equation [17] 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,

$$P_{He}(t) = \sum_i w_i m\lambda_i tRT_1 / M_i V_g = \left(mtRT_1 / V_g\right) \sum_i w_i \lambda_i / M_i \tag{18}$$

In Equation [18], the index i represents all radionuclides that alpha decay. The most important radionuclides to this Standard are given in Table B-5. An alternative formulation of this term is possible that takes advantage of the heat load of the material, which is usually known. The heat generation rate of the contents is given by

$$Q = \sum_i E_i \lambda_i N_i = m \sum_i E_i \lambda_i w_i / M_i \tag{19}$$

where E_i is the radioactive decay energy for radionuclide i and Q is the total heat load 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 [19],

$$Q = Em \sum_i \lambda_i w_i / M_i \tag{20}$$

$$Q/E = m \sum_i \lambda_i w_i / M_i \tag{20a}$$

Substituting the expression for Q/E into equation [18] yields an expression for the pressure due to helium generation from alpha decay as

$$P_{He}(t) = QtRT_1 / EV_g \tag{21}$$

Q can be calculated from the Specific Heat Generation Rate (SHGR) found in Table B-5. Note that 1 MeV/event = 9.649×10^{10} J/mol [Lide 2003]. As can be seen from Equation [21], 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 [21] becomes

$$P_{He} = 6.232 \times 10^{-5} \text{ mol W}^{-1} \text{ yr}^{-1} \; QtRT_1/V_g \qquad [22]$$

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.

Aggregate Equation

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

$$P = P_0(T_1/T_0) + (mw_{H2O}/M_{H2O})RT_1/V_g +$$
$$6.232 \times 10^{-5} \text{ mol W}^{-1} \text{ yr}^{-1} \; QtRT_1/V_g. \qquad [23]$$

B.3. Application of the Pressure Equation

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 [23], 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.

Example Calculations

B.3.1.1 Example Pressure Calculation for Weapons Grade Oxide

Assume that a RFETS container will be loaded with 5.0 kg of weapons grade oxide that has a pycnometer density of 10 kg/l (and is therefore assumed to be fairly pure) and a moisture content of 0.5 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 heat generation rate is 2.8 W/kg times 4.4 kg of Pu, or 12.4 W. The evaluation temperature is 204.4 + 273 or 477.4 K, and the loading temperature is 30 + 273 or 303 K. The values of the parameters used in the pressure equation are summarized in Table B-3.

Table B-3
Values of Parameters used to Calculate Pressure

Symbol	Quantity	Value	Symbol	Quantity	Value
P	Container pressure	kPa	V_g	Gas volume of container	1.690 l
P_0	Fill gas pressure at filling	101 kPa	m	Mass of material	5.0 kg
T_1	Evaluation temperature	477.4 K	ρ	Density of material	10 kg/l
T_0	Fill gas temperature at filling	303 K	Q	Container energy generation	12.4 W
w_{H2O}	Water mass fraction	0.005	t	Storage time	50 yr

The gas volume is determined by subtracting the material volume (mass of 5.0 kg divided by density of 10 kg/l to yield 0.5 l) from the 2.190 l free volume of the RFETS container system.

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

$P = 101$ kPa *(477.4 K/ 303 K) +

(5 kg * 0.005/.018 kg/mol) *8.3145 kPa l mol^{-1} K^{-1} *477.4 K / 1.690 l +

6.232x10^{-5} mol W^{-1} yr^{-1} * 12.4 W * 50 yr *8.3145 kPa l mol^{-1} K^{-1} *477.4 K / 1.690 l

  =160 kPa + 3260 kPa + 91 kPa

  = 3510 kPa

This calculation is comparable to calculations prescribed in DOE-STD-3013-04 and yields comparable results. For "pure oxide" a pressure of approximately 3510 kPa (~500 psia) is bounding.

B.3.1.2 Example with Unknown Density, 19 W Heat Load

Assume that a RFETS container will be filled with 5 kg of material with an unknown density. The other parameters given above remain unchanged except for the heat generation rate, which is now assumed to be 19 W. Since the density is unknown but the bulk material fills the

convenience container, we use the packing fraction method to determine the density as 5.0 kg/(1.856 l x 0.62) or 4.345kg/l. Using that density, we calculate the free gas volume as 2.190 – 5/4.345, or 1.039 l.

P = 160 kPa + (5 kg * 0.005/.018 kg/mol)* 8.3145 kPa l mol^{-1} K^{-1} * 477.4 K / 1.039 l +

6.232x10^{-5} mol W^{-1} yr^{-1} *19 W * 50 yr * 8.3145 kPa l mol^{-1} K^{-1} * 477.4 K /1.039 l

= 160 kPa + 5300 kPa + 226 kPa

= 5690 kPa

In this example, the pressure is higher than the design pressure, and in order to meet the design pressure of 4920 kPa, it would be necessary to reduce the loading by about 14% to remain within the standard criterion or limit the free void volume as discussed under section B.3.2.4.

B.3.1.3   General Behavior of Pressure Equation – Example of Statistical Method

The material density model that was developed in B.2.1.4 can now be used to estimate the bounding internal pressure as a function of bulk density. The parameters are as before, except that the bulk density is allowed to vary over a significant range, and the particle density is estimated by using the equation

$$F_p = 0.3928 + 0.05673 \text{ cm}^3 \text{ g}^{-1} \rho_{bulk}$$

This is the regression equation developed in B.2.1.4 (Equation [5]) plus twice the error.

For this example, it is assumed that only weapons grade material will be considered. The SHGR is 2.81 w/kg Pu, or about 12.5 W for 5 kg of plutonium oxide. To be conservative, a value of 15 W will be used for the heat generation rate. The calculations by Hensel (Table A-2) indicate that a linear approximation of 6°C per watt of heat generation can be used to estimate temperatures for different heat generation rates. This would yield a temperature of 187°C for a 15-W package subjected to solar radiation.

The bounding pressure estimate for these conditions is shown in Figure B-4. The behavior shown is characteristic of the relationship between pressure and density. Starting from the right side of Figure B-4 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 4760 kPa (690 psia or 675 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-4. Bounding pressure as a function of bulk density for the statistical model in B.3.2.3
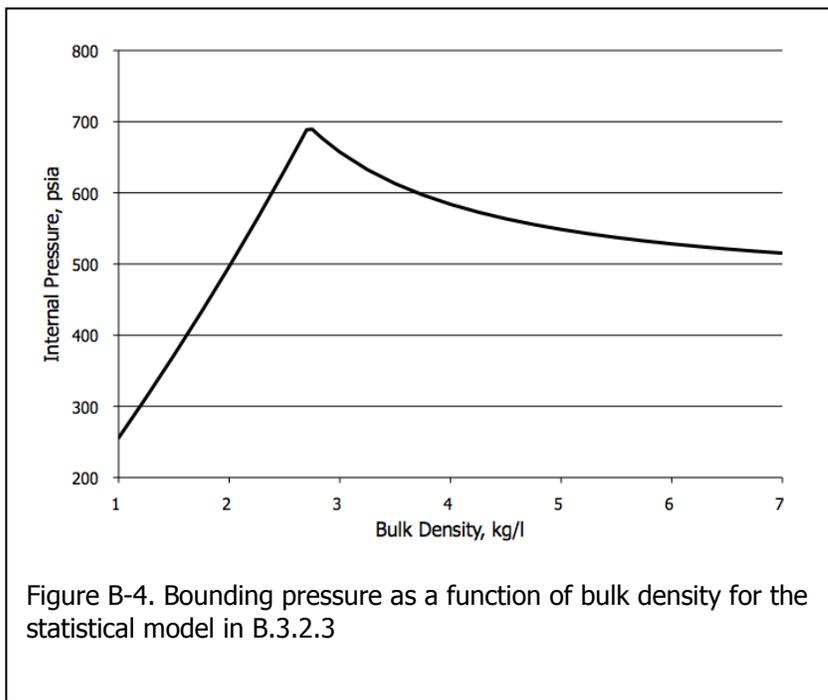
B.3.1.4   Minimum Required Free Gas Volume per Kilogram

Assume now that we wish to find the minimum required free gas volume of a container with a heat generation rate of Q and a moisture content of 0.5 wt%. The other parameters are as assumed before, except that an evaluation temperature of 211°C will be used, representing a configuration in which the 3013 container is in a 9975 transportation package in the sun. The resulting pressure is required to be 4920 kPa.

$$4920 \text{ kPa} = 161 \text{ kPa} + (m * 0.005/0.018 \text{ kg/mol})*8.3145 \text{ kPa l mol}^{-1} \text{ K}^{-1} *484 \text{ K} / V_{min}+$$

$$6.232 \times 10^{-5} \text{ mol W}^{-1} \text{ yr}^{-1} * Q *50 \text{ yr} *8.3145 \text{ kPa l mol}^{-1} \text{ K}^{-1} *484 \text{ K} / V_{min}$$

After rearranging, the equation becomes

$$4920 \text{ kPa} = 161 \text{ kPa} + 1118 \text{ kPa l kg}^{-1}*m/V_{min} + 12.54 \text{ kPa l W}^{-1} Q/V_{min}$$

$$V_{min} = 0.2348 * m \text{ l kg}^{-1} + 0.002628 \ Q \text{ l W}^{-1}.$$

With the worst case heat load of 19 W, the expression for V_{min} can be solved

$$V_{min}/m = 0.234 \, l + 0.050/m \, l,$$

where V_{min}/m is the minimum volume per kg. The minimum specific volume is 0.285 l/kg at 1 kg and decreases to 0.245 l/kg as the mass increases to 5 kg, Table B-4. The pycnometer density of material resulting in 0.285 l/kg at 1 kg loading is 0.52 g cm^{-3}, which is unrealistically low. The lowest material pycnometer density measured by SRS during destructive examination is greater than 4 g/cm^3. For minimum volumes of greater than 0.25 l/kg, the material pycnometer density is always less than 4 g/cm^3. Therefore, a value of V_{min}/m of 0.25 l/kg is conservative and is used in the Standard.

Table B-4. The minimum volume per kg of material, material volume, and density that results in the design pressure when loaded with 0.5wt% water in the RFETS container configuration.

m (kg)	V_{min}/m (l/kg)	V_m (l)	ρ (g/cm^3)
1	.285	1.905	0.52
2	.260	1.670	1.20
3	.252	1.434	2.09
4	.248	1.198	3.30
5	.245	0.965	5.15

B.4. Plutonium Radioactive Decay and Heat Generation

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 heat generation rate as a function of time for a variety of isotopic mixes. This material is not intended to replace methods of determining heat generation rates that the sites may decide to use in conjunction with this Standard.

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 heat generation 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-5 contains pertinent data for these isotopes, and for some uranium isotopes of interest.

Table B-5
Decay Energy for Relevant Nuclides

Radio-nuclide	Half-life [a], yr	Decay constant [b], yr^{-1}	Decay Energy[c], Mev/event	SHGR[d], Watts/kg
^{233}U	1.59E+05	4.35E-06	4.909	0.281
^{235}U	7.04E+08	9.85E-10	4.679	6.00E-05
^{238}U	4.47E+09	1.55E-10	4.269	8.51E-06
^{238}Pu	87.7	7.90E-03	5.593	568
^{239}Pu	24110	2.87E-05	5.244	1.93
^{240}Pu	6564	1.06E-04	5.256	7.07
^{241}Pu	14.35	4.83E-02	0.0208	12.8
^{242}Pu	3.73E+05	1.86E-06	4.984	0.112
^{241}Am	432	1.60E-03	5.638	115

a. Half-life data from Audi et al., 2003.
b. Decay constant calculated using $\lambda = \ln(2)/t_{1/2.}$
c. Decay energy calculated from isotopic masses in Audi et al., 2003, see http://nucleardata.nuclear.lu.se/database/masses/.
d. SHGR is calculated from the decay energy, the decay constant, and the atomic weight.

Table B-6 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-6
Isotopic Mix and Heat Generation Rates in Various Grades of Plutonium

Nuclide	Pure ^{239}Pu	Weapon Grade	Fuel Grade	Power Grade	Hanford 4-7%	Hanford 10-13%	Hanford 16-19%
^{238}Pu		0.05%	0.1%	1.0%	0.01%	0.09%	0.24%
^{239}Pu	100.0%	93.50%	86.1%	63.0%	93.77%	86.94%	80.66%
^{240}Pu		6.00%	12.0%	22.0%	6.00%	11.81%	16.98%
^{241}Pu		0.40%	1.6%	12.0%	0.20%	1.00%	1.44%
^{242}Pu		0.05%	0.2%	3.0%	0.03%	0.17%	0.69%
^{241}Am					0.14%	0.86%	2.80%
Initial SHGR, W/kg	1.93	2.53	3.15	8.95	2.46	4.02	7.20
Maximum SHGR, W/kg	1.93	2.81	4.48	18.5	2.61	4.72	7.92

Figure B-5 shows how the heat generation rate changes with time for each of the materials
given in Table B-5, except for the power grade material. A chart showing the heat generation in that is given in Figure B-6, where it can be compared with the other two grades of plutonium. Several characteristics are immediately evident: 1) the maximum is very flat and broad; 2) the variation between initial and maximum SHGR 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 SHGR is only about 15% greater than the initial SHGR. Figure B-6 provides an extreme example of the increase in SHGR 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

Figure B-5. Heat Generation rates in various grades of plutonium as a function of time. The legend refers to the isotopic mix in Table B-6.
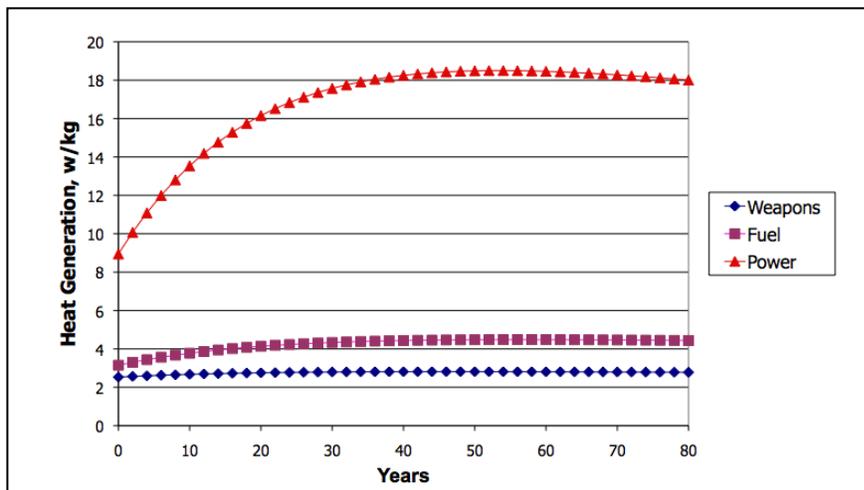
Figure B-6. Heat generation rate as a function of time for three grades of plutonium

material, after 20 years of storage and the consequent decay of the ^{241}Pu into ^{241}Am, the subsequent increase in heat generation rate is only about 15%.

As a rule of thumb, the peak heat generation rate 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 heat generation rate 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 heat generation rate. 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:

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

Where t_{peak} is the time until the peak heat generation rate

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.

APPENDIX C, References

Reference	Citation
ACS 1995	"Fire and Polymers II, Material and Tests for Hazard Prevention," G. L. Nelson, Editor, American Chemical Society, 1995
ANS 1979	*The Chemistry of Plutonium*, J. M. Cleveland, American Nuclear Society, La Grange Park, Ill., 1979
ANS 1980	*Plutonium Handbook,* O. J. Wick, ed., Volumes I and II, The American Nuclear Society, La Grange Park, Ill., 1980
ANSI 1997	"American National Standard for Radioactive Materials – Leakage Tests on Packages for Shipment," American National Standards Institute, New York, 1997, ANSI N14.5-97
ANSI/ANS-8.1 1998	American National Standard for Nuclear Criticality Safety in Operations with Fissionable Materials Outside Reactors, ANSI/ANS-8.1-1998, American Nuclear Society, LaGrange Park, IL, 1998.
ANSI/ANS-8.15 1981	American National Standard for Nuclear Criticality Control of Special Actinide Elements, ANSI/ANS-8.15-1981, American Nuclear Society, LaGrange Park, IL, 1981.
Arnold 2008	"Volume determination for RFETS, SRS and Hanford 3013 convenience cans", Arnold, M., U-CLC-K-00007, Savannah River Site, Aiken, SC, January, 2008.
Audi et al., 2003	"The NUBASE evaluation of nuclear and decay properties", G. Audi, O. Bersillon, J. Blachot, and A.H. Wapstra, Nuclear Physics A, 2003, vol. 729, page 3-128.
Berg et al., 2002	"Gas Generation over Plutonium Oxides in the 94-1 Shelf Life Surveillance Program," LA-UR-02-0583 (2002) John M. Berg, David Harradine, Dallas D. Hill, James T. McFarlan, Dennis D.Padilla, F. Coyne, Prenger, D. Kirk Veirs, Laura A. Worl, 2002
Berg et al., 2007	"Predicting the future gas composition of MIS material 011589A", J.M. Berg, A. Carrillo, M.A. Martinez, D.K. Veirs, L.A. Worl, D.M. Harradine, and R.E. McInroy, LA-UR-07-7870; Los Alamos National Laboratory: Los Alamos, NM 87545, 2007.
Berg et al., 2008	"The effect of moisture content on oxygen generation for 011589A substitute materials", J.M. Berg, E. Garcia, G. Long, M.A. Martinez, J.E. Narlesky, D.K. Veirs, C. Williams, and L.A. Worl, L. A., LA-UR-08-2546 Los Alamos National Laboratory: Los Alamos, NM, 2008.

Reference	Citation
Bielenberg et al., 2006	"The effects of pressure on thermal transport properties in plutonium oxide powder", International Journal of Heat and Mass Transfer, Volume 49, Issues 17-18, August 2006, Pages 3229-3239
Blesa et al., 1994	"Chemical Dissolution of Metal Oxides Chapter 9.1 Hydration and Hydroxylation" M.A. Blesa, P.J. Morando, and A.E. Regazzoni, CRC Press, Boca Raton, 1994.
Boak et al., 2002	"Technical Basis for Equivalency to DOE Standard 3013 Requirements of Lower-Temperature Stabilization for Electrorefining-Derived Plutonium Oxides, Revision 1", Boak, P.G. Eller, R.M. Erickson, A. Murray, G.D. Roberson, LA-UR-02-6054, 2002
Boak et al., 2003	"Recommendations on Stabilization of Plutonium Material Shipped to Hanford from Rocky Flats," Boak, E. A. Conrad, C. H. Delegard, A. M. Murray, G. D. Roberson. T. J. Venetz, LA-14070 (October 2003)
Bockhorn et al., 1996	"Investigation of the Kinetics of Thermal Degradation of Commodity Plastics", H. Bockhorn, A. Hornung, U. Hornung, S. Teepe, and J. Weichmann, Combust. Sci. and Tech., 1996, Vol. 116-117, pp. 129-151
Bukovec et al., 1989	"TG and DSC investigation of $CaCl_2 \cdot 6H_2O$, a phase change material for energy storage", N. Bukovec, P. Bukovec, and V. Arbanas, Thermochimica Acta 148 (1989) 281-288.
Clayton 2010	"Anomalies of Nuclear Criticality" E. D. Clayton, PNNL-19176, 2010
Erickson et al., 2002	"Technical Basis for Process Qualification of Stabilization of Plutonium-Bearing Oxide Materials," R. M. Erickson, P. G. Eller, R. E. Mason, LA-UR-01-6288, June 2002
Erickson 2003	"Representation of Items Packaged to DOE-STD-3013-2000, Randall M. Erickson, LA-14016-MS, February 2003
Farr et al., 2007	"Surface chemistry of Pu oxides", J.D. Farr, R.K. Schulze, and M.P. Neu, J. Nuclear Materials 328 (2004) 124-136.
Flamm 1997	"The Effect of Thermal Cycling on the Integrity of Long Term Storage Cans Containing Alpha Plutonium," B. F. Flamm, LA-UR-97-439, 1997
Flanders/Krishnan 1999	"Plutonium Alpha-Beta & BNFL (3013) Inner and Outer Storage Cans Evaluation (U)", H. E. Flanders and R. P. Krishnan, T-CLC-G-00113, Savannah River Site, 1999
Foy/Joyce 2008	"Gas-phase Radiolysis in Plutonium Dioxide Powder", B.R. Foy, and S.A. Joyce, LA-UR-08-2627; Los Alamos National Laboratory: 2008.

Reference	Citation
Friday et al., 2008	"A method for estimating gas pressure in 3013 containers using an ISP database query", G. P. Friday, L.G. Peppers, and D.K. Veirs, WSRC-STI-2008-00214; Savannah River National Laboratory: Aiken, SC, July 2008, 2008.
Galwey/Brown 1999	"Thermal Decomposition of Ionic Solids Chapter 8 Thermal Dehydration of Hydroxides", A.K. Galwey and M.E. Brown, Elsevier Science B.V.; Amsterdam, 1999.
Garcia et al., 2007	"Deliquescent behavior of $KMgCl_3$, K_2MgCl_4, $K_3NaMgCl_6$, and electrorefining salts", E. Garcia, O.W. Gillespie, S.A. Joyce, D.K. Veirs, and L.A. Worl, LA-UR-07-4356 (2007).
Greenspan 1977	"Humidity Fixed Points of Binary Saturated Aqueous Solutions", L. Greenspan, Journal of Research of the National Bureau of Standards - A. Physics and Chemistry 1977, 81A, (1), 89-96.
Gupta 2007	Thermal Model for the 3013 Containers in KAMS, M- CLC-K-00720, Savannah River National Laboratory, 10/15/2007
Hackney 2007a	"Volume determination for Rocky Flats Environmental Site (RFETS) 3013 containers", Hackney, E.R., U-CLC-K-00006, Savannah River Site, Aiken, SC, November, 2007.
Hackney 2007b	"Volume determination for SRS and Hanford 3013 inner containers", Hackney, E.R., U-CLC-K-00006, Savannah River Site, Aiken, SC, November, 2007.
Haschke/Martz 1998	"Plutonium Storage", J. M. Haschke and J. C. Martz, pp. 3740-3755 in *Encyclopedia of Environmental Analysis and Remediation*, Robert A. Meyers, Ed., John Wiley and Sons, Inc., 1998{111l, 112}
Haschke et al., 1996	"Nuclear Materials Stabilization and Packaging Quarterly Status Report, January 1 – March 31, 1996", J. M. Haschke, D. R. Horrell. C. W. Hoth, K. W. Fife, J. B. Nielsen, S. W. Pierce, T. E. Ricketts, N. A. Rink, M. A. Robinson, LA-13162-SR, Los Alamos National Laboratory, Los Alamos, New Mexico, August 1996
Haschke et al., 1997	"White Paper on Possible Inclusion of Mixed Plutonium-Uranium Oxides in DOE-STD-3013-99," LA-13236-MS, November 1997
Haschke/Ricketts 1995	"Plutonium Dioxide Storage: Conditions for Preparation and Handling", J. M. Haschke and T. E. Ricketts, LA-12999-MS, Los Alamos National Laboratory, Los Alamos, New Mexico, August 1995
Haschke/Ricketts 1997	"Adsorption of Water on Plutonium Dioxide," J. M. Haschke and T. E. Ricketts, J. Alloys and Compounds **252** (1997) 148-156

Reference	Citation
Hay 2006	"Theoretical Studies of Hydrogen and Water Adsorption on Actinide Oxide Surfaces," Materials Research Society Symposium Proceedings Vol 893. Actinide 2005- Basic Science, Applications and Technology. pg 363.
Hecker/Stevens 1999	"Preliminary Review of the Experiment on 'Effect of the Plutonium $\alpha - \beta$ Phase Transition Expansion on Storage Can Integrity,'" S. Hecker and M. Stevens, LA-UR-99-399, January 1999
Henrich/Cox 1996	"The Surface Science of Metal Oxides", V. E. Henrich and P. A. Cox, Cambridge University Press, 1996
Hensel 1998a	"Thermal Analysis of the 9975 Package with the 3013 Configuration as a Plutonium Storage Container," S. J. Hensel, WSRC-TR-98-00203
Hensel 1998b	"Thermal Analysis of the 9975 Package with the 3013 Configuration During Normal Conditions of Transport," S. J. Hensel, WSRC-TR-98-00420
ISP 2001	"Establishment of an Integrated Surveillance Program in Support of Stabilization, Packaging, and Long-Term Storage for Plutonium-Bearing Materials," S. M. Sohinki and D. G. Huizenga, July 11, 2001.
JNMM 2010	*Journal of Nuclear Material Management* Articles in the Winter and Spring Issues, 2010
Joyce et al., 2010	"Salt phases in calcined materials and their hydration properties" Joyce, S. A., J. E. Narlesky, D. K. Veirs, E. Garcia, O.W. Gillispie, J.M. Jackson, B. Scott, and L. A. Worl.. *Journal of Nuclear Material Management* 37, pg. 70, 2010.
Katz et al., 1986	"The Chemistry of the Actinide Elements. Volume 1. Chapter 7: Plutonium", J. J. Katz, G. T. Seaborg, and L. R. Morss, Eds., Chapman and Hall, London/New York, 1986.
Kelly/Wexler 2005	"Thermodynamics of carbonates and hydrates related to heterogeneous reactions involving mineral aerosol", J.T. Kelly and A.S. Wexler, Journal of Geophysical Research 2005, 110, (D11) and references cited.
Kolman 2001	"A Review of the Potential Environmentally Assisted Failure Mechanisms of Austenitic Stainless Steel Storage Containers Housing Stabilized Radioactive Compounds", D.G. Kolman, *Corrosion Science*, Vol. 43, No. 1, pp. 99 - 125 (2001)
Kolman et al., 2004	"The Microstructural, Mechanical, and Fracture Properties of Austenitic Stainless Steel Alloyed with Gallium", D.G. Kolman, J.F Bingert and R.D. Field, *Metallurgical and Materials Transactions A*, Vol. 35A, No. 11, pp. 3445 - 3454 (2004)

Reference	Citation
Kolman/Chavarria 2004	"The Liquid Metal Embrittlement of 316L SS by Ga", D.G. Kolman and R. Chavarria, *Corrosion*, Vol. 60, No. 3, pp. 254 - 261 (2004)."
Lawrence/Bu 2000	"The reactions between Ca-based solids and gases representative of those found in fluidized-bed incinerator", A.D. Lawrence and J. Bu, Chem. Eng. Sci. 55 (2000) 6129-6137.
Leary et al., 1959	"Plutonium Peroxide Precipitation," J. A. Leary, A. N. Morgan, & W. J. Maraman, Industrial & Engineering Chemistry, <u>51</u> (1959) 27
Liang/Shepherd 2007a	"Explosion Testing of Nested Can Containment System Part I: Planar Gap", Z. Liang, and J.E. Shepherd, FM2007.001; California Institute of Technology: 2007.
Liang/Shepherd 2007b	"Explosion Testing of Nested Can Containment System Part II: Thick Walled Tube", Z. Liang, and J.E. Shepherd, FM2007.001; California Institute of Technology: 2007.
Liang/Shepherd 2007c	"Explosion Testing of Nested Can Containment System Part III: 3013 Outer Can", Z. Liang, and J.E. Shepherd, FM2007.001; California Institute of Technology: 2007.
Lillard et al., 2009	"Test Plan for Determining the Susceptibility of 3013 Containers to Stress Corrosion Cracking" R.S. Lillard, D.K.Veirs, J.M.Berg, L.A.Worl, J.M. Duffey, K.A. Dunn, R.R. Livingston, P.E.Zapp, J.W. McClard, LA-UR-09-02953, 2009.
Lide 2003	Lide, D.R., ed. 2003. *CRC Handbook of Chemistry and Physics*. 84th ed: CRC Press
Louthan 1998	"Storage Criteria and plutonium Metal Interactions with Container Materials," Savannah River Technology center Inter-office Memorandum, M. R. Louthan, Jr., SRT-MTS-98-2020, 1998
Machuron-Mandard/ Madic 1996	"Plutonium Dioxide Particle Properties as a Function of Calcination Temperature," X. Machuron-Mandard and C. Madic, J. Alloys and Compounds 235 (1996) 216-224
Mason et al., 1999	Materials Identification and Surveillance: June 1999 Characterization Status Report", LA-UR-99-3053, R. Mason, T. Allen, L. Morales, N. Rink, R. Hagan, D. Fry, L. Foster, E. Wilson, C. Martinez, M. Valdez, F. Hampel, and O. Peterson.{111a,e}
Moseley/Wing 1965	"Properties of Plutonium Dioxide," J. D. Moseley & R. O. Wing, RFP-503, August 1965
Narlesky et al., 2009a	"Complex-Wide Representation of Material Packaged in 3013 Containers", J.E. Narlesky, L.G. Peppers, and G.P. Friday, LA-UR-09-14396; Los Alamos National Laboratory: Los Alamos, NM, 2009.

Reference	Citation
Narlesky et al., 2009b	"Establishing Deliquescence Relative Humidity for Packaged Materials Part II: Understanding the Salts", J.E. Narlesky, J.M. Berg, E. Garcia, S.A. Joyce, T. Ruf, B. Scott, D.K. Veirs, and L.A. Worl, LA-UR-09-01498, Los Alamos National Laboratory: Los Alamos, NM, 2009.
Pabalan/Pitzer 1987	"Thermodynamics of concentrated electrolyte mixtures and the prediction of mineral solubilities to high temperatures for mixtures in the system Na-K-Mg-Cl-SO$_4$-OH-H$_2$O", R.T. Pabalan and K.S. Pitzer, Geochimica et Cosmochimica Acta 1987, 51, 2429-2443.
Paffett et al., 2003	"A critical examination of the thermodynamics of water adsorption on actinide oxide surfaces", M.T. Paffett, D. Kelly, S.A. Joyce, J. Morris, and K. Veirs, J. of Nuclear Materials 322 (2003) 45-46.
Panagiotou/Levendis 1996	"Observations on the Combustion of Pulverized PVC and Poly(ethylene)," T. Panagiotou and Y. A. Levendis, Combust. Sci. and Tech. 112 (1996) 117-140
Peppers et al., 2009	"Selection of 3013 Container for Field Surveillance: LA-14310, Revision 1" L. Peppers, E. Kelly, J. McClard, G. Friday, T. Venetz, J. Stakebake, LA-14395, 2009
Pruvost/Paxton	"Nuclear Criticality Safety Guide", N. L. Pruvost and H. C. Paxton, LA-12808, September, 1996
Shoji/Ohnaka 1989	"Effects of relative humidity and kinds of chlorides on atmospheric stress corrosion cracking of stainless steels at room temperature", S. Shoji, and N.Ohnaka, Boshoku Gijutsu 1989, 38, (2), 92-97.
Smith et al., 1999	"Hydration of Plutonium Oxide and Process Salts, NaCl, KCl, CaCl$_2$, MgCl$_2$; Effect of Calcination on Residual Water and Rehydration", D. M. Smith, M. P. Neu, E. Garcia, and L. A. Morales, LA-UR-99-261, February 1999
Spearing et al., 1999	"Effect of the Plutonium $\alpha - \beta$ Phase Transition Expansion on Storage Can Integrity", D. Spearing, D. K. Veirs, and F. C. Prenger, LA-UR-99-147, January 1999
Spearing/Veirs 1999	"Effect of the Plutonium Alpha-Beta Phase Transition Expansion on Storage Can Integrity: Experimental Results", D. Spearing and D. K. Veirs, Los Alamos National Laboratory, LA-UR-99-1363, 1999
Spearing et al., 2001	"Effect of the expansion associated with the plutonium α-β-γ phase transitions on storage can integrity," Dane R. Spearing, D. Kirk Veirs, F. Coyne Prenger, Journal of Nuclear Materials 299 pp. 111-123 (2001)
Spearing/Crooks 2003	"Gas Generation Mechanisms in Pu Metal Bearing DOE-3013 Containers," Dane R. Spearing and William J. Crooks III, LA-UR-03-1214, Rev. 2, April 21, 2003

Reference	Citation
Tandon et al., 1999	"Information Search on Chloride Salt Radiolytic Effects in Plutonium Storage Environments," L. Tandon, R. A. Penneman & P. G. Eller, LA-UR-99-2488, June 1999
Tani et al., 2009	"Initiation and Propagation of Stress Corrosion Cracking of Stainless Steel Canister for Concrete Cask Storage of Spent Nuclear Fuel", J.-I. Tani, M. Mayuzumi, and N. Hara, Corrosion 2009, 65, (3), 187 - 194.
USDOE 1994a	"Assessment of Plutonium Storage Safety Issues at Department of Energy Facilities," U. S. Department of Energy, DOE/DP-0123T, 1994
USDOE 1994b	"Criteria for Safe Storage of Plutonium Metals and Oxides", US DOE Standard DOE-STD-3013-94, U. S. Department of Energy, Washington, D. C., December 1994
USDOE 1994c	"Plutonium Working Group Report on Environmental, Safety and Health Vulnerabilities Associated with the Department's Plutonium Storage", U. S. Department of Energy, DOE/EH-0415, 1994
USDOE 1996	"Criteria for Preparing and Packaging Plutonium Metals and Oxides for Long-Term Storage", US DOE Standard DOE-STD-3013-96, United States Department of Energy, Washington, D. C., September 1996
USDOE 2004	"Stabilization, Packaging and Storage of Plutonium-Bearing Materials", US DOE Standard DOE-STD-3013-2004, United States Department of Energy, Washington, D. C., September 2004
USDOE 2006	"Nuclear Material Control and Accountability", US DOE Manual, DOE M 470.4-6 Chg 1, United States Department of Energy, Washington, D. C., August 2006
Veirs et al., 2002	"Technical Basis for Packaging Glovebox Moisture Content", D.K. Veirs, R. Mason, R. Erickson, LA-UR-02-560; Los Alamos National Laboratory: Los Alamos, NM, 2002.
Veirs 2008	"Gas generation from pure plutonium oxide: implications to Pu-238 drums", D. K Veirs LA-UR-08-1488; Los Alamos National Laboratory: Los Alamos, NM, 2008.
Veirs et al., 2008	"Alpha radiolysis in plutonium-bearing materials: Long-term studies of gas generation" D.K. Veirs, L.A. Worl, M.A. Martinez, D.M. Harradine, R.E. McInroy, LA-UR-08-0804; Los Alamos National Laboratory: Los Alamos, NM, 2008.
Veirs/Berg 2008	"Maximum hydrogen pressure predicted in MIS salt-bearing materials", D.K. Veirs, and J.M. Berg, LA-UR-08-06289; Los Alamos National Laboratory: Los Alamos, NM, 2008.

Reference	Citation
Veirs et al., 2010	"Relative humidity and the susceptibility of austenitic stainless steel to stress corrosion cracking in an impure plutonium oxide environment". Veirs, D. K., L. A. Worl, J. M. Berg, P. E. Zapp, J. M. Duffey, P. S. Lam, and K.A. Dunn. *Journal of Nuclear Material Management* 37 2010.
Waterbury et al., 1961	"Thermogravimetric Behavior of Plutonium Metal, Nitrate, Sulfate, and Oxalate," G. R. Waterbury, R. M. Douglass, and C. F. Metz, Analytical Chem., <u>33</u> (1961) 1018.
Wey/Chang 1995	"Kinetic Study of Polymer Incineration," M. Y. Wey and C. L. Chang, Polymer Degradation and Stability, <u>48</u> (1995) 25
Williamson 1999	"Plutonium Storage: Phase Equilibria Issues", M. A. Williamson, LA-UR-99-136, January 1999
Zapp/Duffey 2008	"Status report for SRNL 3013 corrosion tests", P.E. Zapp, J.M. Duffey, WSRC-STI-2008-00046; Savannah River National Laboratory: Aiken, SC, August 2008, 2008.
Zevenhoven et al., 1997	"Combustion and Gasification Properties of Plastics Particle", R. Zevenhoven, M. Karlsson, M. Hupa and M. Frankenhaeuser, Journal of the Air and Waste Management Association, <u>47</u> (1997) 861

CONCLUDING MATERIAL

Review Activity: **Preparing Activity:**

<u>Programs</u>   <u>Field Offices</u>   Savannah River Operations/AMNMSP

DP   AL

EH   ID   **Project Number:**

EM   RF   PACK-0017

MD   RL

                    SR

<u>National Laboratories</u>

    LLNL

    LANL