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Superseding
DOE-STD-3013-99
November 1999

DOE STANDARD

STABILIZATION, PACKAGING, AND STORAGE OF PLUTONIUM-BEARING MATERIALS

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

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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 replaces DOE-STD-3013-99, "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 air 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 package surveillance during storage are outlined, and record-keeping requirements are detailed.

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FOREWORD

1. This Department of Energy (DOE) Standard replaces DOE-STD-3013-99, "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.

2. Beneficial comments (recommendations, additions, deletions) and pertinent data that may improve this document should be sent to the Technical Standards Project Office by letter or by using the self-addressed Document Improvement Proposal (DOE F 1300.3) appearing at the end of this document.

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 the following evaluations or determinations should be submitted to the Nuclear Materials Stewardship Project Office (NMSPO), Albuquerque Operations Office:

   - Technical evaluation of an alternate analytical method for stabilization verification;
   - Technical evaluation of a qualified process to reduce testing requirements for stabilized material;
   - 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.

NMSPO will provide a DOE-approved recommendation to the responsible DOE official making the request.

6. Responsibility for management of this Standard has been assigned to the Environmental Management Program, and implementing actions will be taken by NMSPO. Comments and data provided to the Technical Standards Project Office under item 2, above, should also be sent to NMSPO. Questions regarding this Standard should be addressed to NMSPO. Modifications of any kind (Revisions or Change Notices) to this Standard must be submitted to the Office of Environmental Management through NMSPO.

1. Scope

This Standard provides criteria for stabilization of plutonium-bearing materials at DOE facilities to safe and stable forms that can be packaged and placed in 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. 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 WIPP, such as plutonium residues or TRU waste; Irradiated Fuels; sealed sources; 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 product of oxalate precipitation 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. 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 moisture content limitation in this Standard is considered sufficient to avoid significant corrosion.

This Standard addresses the safety envelope of the storage package. 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. However, users of this Standard are advised to consult and assure adherence with other applicable directives while implementing these criteria.

2. Purpose

These criteria provide a basis for assuring that plutonium-bearing materials will be stable forms for safe, long-term storage at DOE facilities in sound Packages 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

10 CFR 830.120, Nuclear Safety Management, Quality Assurance Requirements

49 CFR 178, Specifications for Packagings

ASME Boiler & Pressure Code, Section VIII, July 1, 1998

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

DOE Order 440.1A, Worker Protection Management for DOE Federal and Contractor Employees, March 27, 1998

DOE 5633.3B, Control and Accountability of Nuclear Materials, September 7, 1994

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

DOE-STD-1098-99, Radiological Control, July 1999

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

5. Acronyms and Definitions

5.1 Acronyms

ANSI	American National Standards Institute
ASME	American Society of Mechanical Engineers
CFR	Code of Federal Regulations
DOE	United States Department of Energy
IDC	Item Description Code
LOI	Loss on Ignition
MBA	Material Balance Area
MC&A	Materials Control and Accountability
TID	Tamper Indicating Device
TRU	Transuranic
WIPP	Waste Isolation Pilot Plant

5.2 Definitions

Design Pressure	A characteristic of a sealed container which indicates its ability to withstand internal pressurization. In the language of the 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 package that is available to the fill gas and any gases generated during storage. See Appendix B for further discussion.
Irradiated Fuel	Nuclear material, including Fabricated Fuel, that in its existing form, has been subjected to irradiation in a nuclear reactor or accelerator and that consequently delivers an external radiation dose requiring special containment and handling.
Loss on Ignition	Mass loss measured after a weighed sample is heated in air to a material temperature of 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.
Package	The assembled combination of containers required by this Standard (an inner and an outer), together with the contained plutonium-bearing materials and any additional interior convenience containers into which they have been placed.

Safeguards Termination Limit	The maximum plutonium concentration upon which Materials Control and Accountability and physical protection can be terminated if conditions in DOE Order 5633.3B, Chapter I, Paragraph 1.l are met. If safeguards guidance beyond that contained in the references is applicable to one or more sites, the governing guidance shall be that applicable to the packaging site.
Stabilized Material	Material that will not cause the design basis of the container described in this Standard to be exceeded through pressure generation, corrosion, or excessive stress over a design life of 50 years, and is not reactive in air upon reopening of the container.

6. Stabilization, Packaging and Storage Criteria

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

1. Metal pieces to be packaged shall each weigh at least 50 g. Foils, turnings, and wires shall not be packaged under this Standard.
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.
3. Briquettes made by pressing plutonium turnings shall not be stored under the provisions of this Standard.

6.1.2 Oxides

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.

2. Stabilization Verification: Assurance that materials to be packaged meet Criterion 6.1.2.3 shall be accomplished using one of the following:

    1) Stabilization Testing: Materials that have been stabilized shall have their moisture content measured by using a demonstrated technically appropriate method, such as LOI. Approval for methods other than LOI shall be obtained using the process described in the Foreword, Item 5.

    2) 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, to the satisfaction of an independent review group 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, as described in 6.1.2.2.1, is required only to the extent necessary to show continued process control.

3. Stabilization Acceptance Criterion: The moisture content (weight loss, if using the LOI method) of Oxide to be packaged in any type of sealed container shall be less than 0.5 wt% at the time of packaging.

6.1.3 Engineered Materials

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.

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 meet Criterion 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.

6.2 Containers – the "Packaging"

6.2.1 Container Design Concept

1. The container assembly 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 and an internal pressure indicator. The outer and inner containers shall be sealed by welding. The use of additional sealed or unsealed inner containers, sometimes referred to as material or convenience containers, is optional.
2. Interior containers[*] shall be sized to fit in the next outer container with adequate clearance for welding the next outer container.
3. Both the outer and interior containers shall allow for non-destructive contents verification, inspection, and surveillance (such as by radiography and weighing).
4. The inner container shall allow for a non-destructive indication of a buildup of internal pressure at less than 790 kPa (100 psig)[†].

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

[†] Pressures expressed in kilopascals (kPa) are given in "absolute" terms. The conversion from pounds per square inch (psi) is that 1 psi is equal to approximately 6.9 kPa. Thus, 100 psig (psi gauge), or 115 psia (psi absolute) is equivalent to approximately 790 kPa.

5. The minimum Design Pressure of the outer container shall be 4927 kPa (699 psig).
6. The outer container shall be designed to the requirements outlined in DOE Order 440.1A, Attachment 1, Section 6, and shall be capable of being designated "Safety Class."

6.2.2 Container Construction

1. Both the inner and outer containers shall be fabricated of ductile, corrosion resistant materials, such as 300 series stainless steel or other materials of comparable or better performance (strength, corrosion resistance, etc). Closure welding shall be performed using procedures that minimize sensitization of the stainless steel to stress corrosion cracking. Any additional interior containers shall be made of materials compatible with the inner and outer containers.
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.
3. The loaded and assembled outer container shall fit within a right circular cylinder with the following dimensions:
    1) Inside diameter 126 mm (4.961 in.).
    2) Internal height of 255 mm (10.030 in.).

6.2.3 Container Testing Criteria

1. Design Qualification Testing
    1) The outer container shall remain leak-tight as defined by ANSI N14.5 after a free drop of the Package (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 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 package.
    2) The inner container shall remain leak-tight 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 leak-tight, as defined in ANSI N14.5, after a hydrostatic proof-test to 1.5 times the Design Pressure. The test shall be conducted using containers as specified by 49 CFR 178.601.

2. Testing During Use

   Both the inner and outer containers shall be tested for leak-tightness, as defined in ANSI N14.5, at their time of closure.

6.2.4 Other Criteria

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

6.3.1 Container Fill Gas

1. The atmosphere within any of the containers (including the convenience container, if used) shall not react adversely with the containers or contained materials.
2. The atmospheres within the inner and outer containers shall not preclude leak-testing of the containers.

6.3.2 Mass of Contained Materials

1. The total mass of plutonium and other fissile species within either metal or oxide contents shall not exceed 4.40 kg (9.70 lb.). The total mass of the package contents, whether metal or Oxide, shall not exceed 5.00 kg (11.02 lb.).
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 storage.
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 package shall be at least 0.25 l/kg of Oxide. (For guidance on determination of Free Gas Volume, see Appendix B.)

6.3.3 Packaging Process

1. Obvious, readily-removed tramp materials such as metal fasteners and other debris shall be removed from the material prior to packaging.
2. The Oxide sample taken for stabilization verification shall be representative of the stabilized material placed in the sealed container at the time of packaging. If the material is to be stored for a period of time before packaging, and the provisions of Criterion 6.1.4.1 apply, the sample shall be representative of the material to be placed into a closed container.
3. Contained materials shall not corrode or otherwise adversely affect the structural integrity of the inner or outer container.
4. Only similar materials should be combined in an inner container or convenience container and packaged for storage.

6.4 Storage – Surveillance of Stored Packages for Safety

6.4.1 Surveillance Program

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

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 package contents and other risks, and engineering judgement) by which Package 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 Packages to be surveyed; and
    4) Provisions for evaluation of any observed off-normal behavior or unanticipated condition.
3. Surveillance prescribed by Surveillance Programs shall include:
    1) Initial baseline Package inspections within 30 days of package closure;
    2) Periodic surveillance throughout the storage period to gather information on Package performance and/or the behavior of the container and its contents. The level of scrutiny over time may be adjusted based on observed Package behavior.
4. The Site Surveillance Program shall document safety inspection/surveillance methods and responsibilities.
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 safety surveillance schedule.

6.4.2 Surveillance Parameters

The following parameters shall be included in non-destructive package surveys:

1. Indication of internal pressure build-up in the inner container.
2. The weight of each Package in the surveillance sample.
3. Indications of leakage and/or degradation.

6.4.3 Evaluation of Surveillance Data

1. Surveillance data from an inspection shall be compared against the baseline measurements to identify any changes.
2. If at any time an unexpected change in a Package is noted, an evaluation shall be performed and corrective action taken as appropriate. This evaluation shall include, as appropriate, 1) options for opening the Package, 2) consideration for inspecting other similar Packages, based on factors such as contents, origin, and date of closure, and 3) assessment of potential consequences.

6.5 Documentation

6.5.1 Data Base

An electronic data base shall be maintained as a source of relevant information about stored materials and packages. This data base may consist of several files (which, in themselves, may be data bases), some of which may be classified. For completeness, the data base should be coordinated and generally compatible with the MC&A data base(s).

6.5.2 Data base content elements

1. The data base 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 MBA that generated the material, and IDC), if available;

   6) Specific stabilization conditions to include date, temperature, processing duration and equipment used and atmosphere (and a notation that a qualified process was used, if applicable);
   7) Particle density of the material and method by which determined, or reference to a model that demonstrates such information is not needed to establish a limitation on the mass loading; and
   8) Other information relative to the contents such as expected major impurities with source of impurity data (*e.g.*, process knowledge, destructive analysis, or X-ray fluorescence analysis).

2. The data base shall include, as a minimum, identification of the following package characteristics:
   1) Nominal fill gas composition of each container on sealing (*e.g.*, air, helium, or argon);
   2) Leak test data record for the outer and inner containers in the package;
   3) Package configuration - quantity and type of containers in a package;
   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 Package gross weight, dimensions, and tare weight;
   7) The unique identification number and TID number, if any, associated with each container; and
   8) The manufacturer lot identification number for each container.
3. The data base shall include, as a minimum, the following records from surveillance and inspections:
   1) Surveillance results;
   2) Records of tests performed;
   3) Dates of inspections; and
   4) Names of individuals performing inspections.

4. The data base shall include, as a minimum, specific locations of stored materials in the storage facility.

6.6 Quality Assurance

Quality assurance to meet 10 CFR 830.120 shall be performed in accordance with site Quality Assurance Plans. As a part of site Quality Assurance Plans, the sites are responsible for assuring that oxides being packaged to this Standard are represented by the items accumulated in the Materials Identification and Surveillance Program

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APPENDIX A

Technical Bases for Stabilization, Packaging and Storage of Plutonium-Bearing Materials

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

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

A.1. Scope

This Standard establishes criteria for stabilization, packaging, and safe, long-term storage of plutonium-bearing metal and oxides at DOE facilities. Storage packages 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 pits. The scope of DOE-STD-3013-96 [USDOE 1996] is 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. The scope for this Standard covers essentially all non-fabricated materials of interest to Defense Programs and captures the vast majority of excess materials that will be accepted by the Materials Disposition Program for disposition [USDOE 1998] or conversion to a mixed plutonium-uranium oxide.

Regarding the uranium content, and the implied equivalence of uranium for plutonium, a recent 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 readsorption 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

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Plutonium metal is 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 presents a potentially more complex problem, but its behavior is generally believed to be reasonably well understood. Only about 20% (in terms of the contained plutonium) of the materials destined for disposition are in this category. The oxide materials of greatest concern are those that have more than approximately 3-8 wt% impurities. These impurities generally include appreciable chloride (NaCl, KCl, $CaCl_2$, and $MgCl_2$) content, ranging from less than half of the impurities present to nearly all the impurities. Other common impurities include oxides and other compounds of calcium, magnesium, iron, and nickel. Occasionally, materials containing sulfur and carbon are found. The stabilization process removes about half of the chlorides, converting some to oxides, and, in general, converts the other metal compounds to oxides. Virtually all of the carbon and sulfur are removed.

The vast majority of the plutonium is weapons grade, containing less than approximately 6% ^{240}Pu. However, some materials have significantly higher concentrations of ^{240}Pu and of the higher plutonium isotopes and americium. Also, most of the oxide materials are predominantly plutonium, but some, including the fuels materials, are mostly uranium.

The MIS Program is concluding characterization of approximately 33 items, including 10 that have more than 85 wt% Pu and three that are at or near (two at 30 wt% and one at 31 wt%) the minimum actinide content for this Standard. Several items include significant quantities of uranium, including two in which the uranium content is approximately 80% of the total actinide content. One item contains less than 4 wt% actinides, all plutonium and americium. These 33 items are typical of the materials at RFETS and Hanford that will be stabilized, packaged, and stored, and are intended to represent the bulk of the inventory at those sites. In the future, it is likely that additional items, from RFETS and SRS, will be added. A more complete description of these materials and the characterization results can be found in the report by Mason and others [Mason *et al.* 1999].

storage is underpinned by extensive experience with plutonium-uranium mixed oxide (MOX) fuel in the commercial nuclear power sector.

Acceptability of materials at the Y-12 Plant is determined in accordance with the Y-12 acceptance criteria [USDOE 1997]. In very broad terms, the upper limit for plutonium is set at 5 ppm. This limit has been accepted as the lower limit for plutonium in uranium to be dispositioned by the Materials Disposition Program [USDOE 1998].

The minimum plutonium content for those oxides that have significant quantities of uranium has been set at the safeguards termination limit. This provides a convenient and practical threshold for distinguishing between materials that require continued safeguarding (or, alternatively, further processing to reduce the attractiveness prior to disposition), and those that might be disposable without further processing, regardless of the enrichment level of the contained uranium.

This Standard does not apply to materials destined for WIPP, such as residues and TRU Waste.

"RESIDUES"

The word "residue" does not have a concise, consistent definition from site to site. During the time that weapons were being produced, there were three general categories of plutonium: 1) product metal or oxide or fuels-grade metal and ceramics; 2) residues - materials that were recycled to recover the plutonium; and 3) very lean material designated as waste, which was discarded. The distinction between residues and waste was largely economic. When processing was stopped, some product, residues, and wastes were left in unsatisfactory storage conditions [see *e.g.,* DOE 1994c, DNFSB 1994]. This led to DNFSB Recommendation 94-1 and the DOE 94-1 Implementation Plan (IP), which defined categories for all materials. Categorization was worked out on technical and practical grounds, with oxides and metals >50 wt% Pu comprising one category, and residues and mixed oxides <50 wt% a second. However, the Rocky Flats "Residues EIS" codifies five residue categories, none of which include oxides. Rocky Flats plans to place its oxides in long-term storage, as it is commonly understood that the Fissile Materials Disposition Program will accept all RFETS materials currently categorized as oxides. Thus, at Rocky Flats, and generally throughout the complex, the word residue has come to mean materials to be discarded, not stored long-term.

Most Rocky Flats residues have been declared waste and are destined for appropriate low-level or TRU disposal, although a very small fraction may be processed. Some residues at other sites may also be processed to produce a storable oxide or metal based on practical, programmatic considerations. Since the products of such processing are expected to have impurities and other characteristics similar to the materials already categorized as oxides or metals, they are included in the scope of this Standard.

In summary, oxides are included in the scope of the Standard and residues are not. Broadly speaking, oxides in the EM program are destined for disposition by the Fissile Materials Disposition Program and residues are destined for disposal. Finally, plutonium content is not the distinguishing factor between oxides and residues – the two are separated in the final analysis by programmatic decisions.

The scope of DOE-STD-3013-96 limits the ^{238}Pu content. 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. This makes the percentage limits redundant for purposes of this standard. The limit on ^{233}U concentration has been taken directly from the MD Acceptance Criteria.

Sealed sources and irradiated fuels are excluded from the scope of this Standard, as are unstabilized forms such as solutions.

Even though the DOE Fissile Materials Disposition Program expects to begin processing plutonium-bearing materials for disposition within about 15 years, it is recognized that various factors could potentially delay disposition. Fifty years was selected as a reasonable upper limit to the time that material might have to be stored because of such delays.

A.2. Purpose

This Standard updates DOE-STD-3013-99 [USDOE 1999], which replaced DOE-STD-3013-96 [USDOE 1996]. It changes the allowable contamination on the outer surface of the inner container from that specified in 3013-99. That Standard (3013-99) updated the guidance given in DOE-STD-3013-96 to include a broader concentration and classification range of plutonium-bearing materials. Information developed since issuance of 3013-96 has led to changes implemented in 3013-99 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 (note that the stabilization process, the stability criterion and the container have all remained unchanged from DOE-STD-3013-96):

- Research supporting DOE-STD-3013-96 was performed using pure plutonium dioxide and those results were extrapolated to 50 wt% plutonium content. This Standard includes in its basis considerable research on actual site oxide materials covering the full range of actinide content specified in the scope statement.
- A critical assumption in pressurization analysis for DOE-STD-3013-96 is the reaction with plutonium dioxide that fixes oxygen from adsorbed water and leaves a hydrogen-rich atmosphere. The research supporting this Standard has shown that a second reaction, the recombination of oxygen and hydrogen to form water, is also very effective in removing

oxygen from the package atmosphere. This hereby strengthens the assumption that oxygen will not be present at levels that would cause significant pressurization.

- Research has shown that oxide materials other than pure plutonium dioxide are unlikely to pass the LOI test even though their moisture content may be acceptably low. Research supporting this Standard has also shown that the stabilization process removes or destroys all materials that pose a threat to the integrity of the container except for readsorbed moisture on the oxide material. This Standard allows moisture-specific measurements to be used as an alternate to the LOI test to verify stability.
- Research and analysis have shown that physical changes that occur in plutonium metal at temperatures that may be achieved within the heat generation limit in this standard during transportation or in storage do not pose a threat to the integrity of the container. The resulting removal of the metal temperature limit allows shipment in conveyances that do not refrigerate their payloads and permits a markedly less expensive design for vault HVAC intake structures.
- The reduction in the wattage limit from 30 w to 19 w reduces anticipated storage temperatures, bringing them more in line with practical storage and experimental experience.
- Corrosion issues, particularly those involving chlorides, have been addressed and recommendations on container materials provided.

A.3. Applicability

No further basis provided.

A.4. References

No further basis provided.

A.5. Acronyms and Definitions

No further basis provided.

A.6. Stabilization, Packaging, and Storage Criteria

A.6.1 Stabilized Materials

A.6.1.1 Plutonium Metals

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 100 mm^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. 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.

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.

3. Since plutonium turnings pressed into briquettes cannot be examined to determine that they meet the requirements of Criteria 6.1.2.1 and 6.1.2.2, they are not acceptable storage package contents. They should be converted to stable oxide powder.

A.6.1.2 Oxides

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 readsorption 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 calcination requirements of the Standard will accomplish the above objectives.

1) Eliminate reactive materials such as finely divided metal or sub-stoichiometric plutonium oxides

   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). 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 are completely converted to stable plutonium oxide by calcination in air at 950°C in air for two hours [*e.g.*, see 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 materials 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 calcination (see Criterion 6.3.3.1), but the literature indicates that even these will be destroyed by 2hr/950°C calcination 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

   A key element of the technical basis for both this Standard and DOE-STD-3013-96 is that water uptake on calcined plutonium oxide is controlled by the oxide surface area. Measurements show that the surface area of pure plutonium oxide calcined at 950°C is consistently below 5 m^2/gram [*e.g.,* see Haschke/ Ricketts 1995 and Manchuron-Mandard/Madic 1996]. MIS measurements show this to be true for impure oxides as well [Mason *et al.* 1999]. MIS measurements on actual site materials to be treated under this Standard and other work show that residual moisture content after calcination at 950°C is well under the 0.5 wt% moisture criterion, and typically well under 0.2 wt%. [*e.g.*, see Haschke/Ricketts 1995 and Mason *et al.* 1999]. Further, the amount of water that can readsorb on plutonium oxide after 950°C calcination, even with exposure to relative humidities up to 50%, also is well below 0.5 wt% [Haschke/Ricketts 1995].

No new physical or chemical processes have been identified which result from lowering the minimum plutonium content from 50 to 30 wt%. Based on process knowledge, well-established thermal properties of likely initial impurity phases, and MIS measurements of elemental composition and x-ray diffraction patterns, the dominant impurity phases after calcination are expected to consist of binary 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 33 calcined site RFETS* and PFP* 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%). 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]. Therefore, moisture affinities and binding energies of oxide impurities are anticipated to be qualitatively similar to those of plutonium oxide.

Uranium oxide is expected (and confirmed by MIS x-ray diffraction) to be present predominantly as U_3O_8 after calcination at 950°C. Like other highly oxidized impurity metal oxides expected after calcination, U_3O_8 represents a large potential sink for any hydrogen gas that might be evolved [e.g., see the free energy/temperature diagram for metal oxide/hydrogen reactions presented as Figure 14-4 in Darker *et al.* 1953].

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* RFETS – Rocky Flats Environmental Technology Site; PFP – Plutonium Finishing Plant, a former plutonium processing facility at Hanford currently being used for storage.

Measurements on impure oxides by the MIS project show that residual moisture levels after 950°C calcination are reliably below the 0.5 wt% criterion, and well below 0.2 wt% in most cases examined to date [Mason *et al.* 1999]. MIS measurements also show that surface areas for these impure oxides are comparable to those of pure oxides after calcination.

MIS elemental analysis on the 33 site materials studied to date shows only one of these items has as-received chloride content above 20 wt%. In all cases, the chloride ion content after 950°C calcination was reduced to less than 8 wt%. In general, residual chloride salt is expected (and is observed) to be strongly reduced by calcination, a factor which will restrict moisture uptake by chlorides before packaging. Sodium and potassium chloride melt below the 950°C calcination temperature and therefore relatively large particle sizes and low surfaces areas are likely to result for these phases. A recent literature survey indicates that these chlorides will not resorb water to an appreciable extent after calcination unless quite high relative humidities are encountered [Smith *et al.* 1999].

Residual magnesium and calcium chlorides, on the other hand, can adsorb and chemically bind as stoichiometric hydrates substantial amounts of water at much lower relative humidities [Smith *et al.* 1999]. However, these chlorides also are known to partially or completely convert to their respective oxides when heated in the presence of moisture, as confirmed by MIS elemental composition and x-ray diffraction results on calcined impure oxides. [Mason *et al.* 1999] Unfortunately, magnesium and calcium chlorides also readily release water with modest heating. At elevated temperature in sealed containers, this moisture potentially could migrate to the plutonium oxide phase and physisorb as weakly bound multiple layers, theoretically exceeding 0.5 wt% equivalent for the oxide phase. This process, if it happens, likely would affect the equilibrium vapor pressure of moisture over plutonium oxide, and possibly affect the radiolytic behavior of the adsorbed water. Therefore, control of time and atmosphere between calcination and packaging is strongly advised when handling plutonium oxides containing magnesium and calcium chloride impurities to avoid the potential for concentrating unacceptable levels of moistures on other phases, and potential initiation of additional gas generation mechanisms. A survey of practical experience in storing pyrochemical salts indicates that with reasonable precautions, moisture readsorption should not pose a major issue [Tandon *et al.* 1999a].

A notably desirable result of 950°C calcination 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. Thermodynamics strongly favors reduction of high valent oxides such as Fe_2O_3 and U_3O_8 by hydrogen, thereby providing a large potential chemical sink for elemental hydrogen generated by chemical or radiolytic means. To illustrate the potential magnitude of this effect, consider that 3 wt% of Fe in a maximum 5 Kg charge or impure oxide corresponds to about 214 grams (about 1.3 moles) of Fe_2O_3. This amount of ferric oxide theoretically is capable of converting about 45 atmospheres (about 660 psi) of hydrogen at 150°C to water in a typical storage package, assuming about one liter of gas void space.

In this Standard, the maximum allowable package heat generation rate (19 watts) is reduced substantially from the 30 watts permitted by DOE-STD-3013-96. As a result, bounding container and material temperatures will be substantially lower. Recent calculations of thermal profiles for one bounding scenario (exposure of a 19 watt 9975 shipping container to diurnal insolation) indicates maximum container and oxide temperatures of 147°C (297°F) and 275°C (527°F) respectively [Hensel 1999a,b] (see Table A-1, Section A.6.3.2.2). From these and related analyses, a solar influence of about 46°C (83°F) on oxide temperature can be deduced. Using a straight line extrapolation from the 30 and 19 watt cases, peak oxide temperatures near 150°C (302°F) and 205°C (401°F) can be estimated for 6 and 12 watt oxide packages, respectively. When the solar factor is subtracted, the resulting temperatures for "normal" storage in 9975 packages (near 105°C at 6 w and 160°C at 12 w) are seen to be within or close to the range experienced during typical vault storage of plutonium oxides. Significantly, the heat generation rates for 5 kg of the 30-50 wt% plutonium materials studied to date in the MIS program are less than 6 watts. All MIS materials studied to date in the 50-80 wt% range have wattage under 12 watts for 5 kg, as should be expected since the wattage of 4.4 kg of typical weapons grade plutonium metal is about 12.5 watts (see Section B.4 in Appendix B).

Therefore, impure materials packaged under this Standard with weapons grade isotopic compositions will never experience the bounding temperatures calculated for the 19-watt solar scenario. The vast preponderance of higher specific wattage material (*e.g.*, fuels or power grade material) to be packaged under this standard is relatively pure "product quality" material at PFP.

The mechanism of gas formation from water adsorbed on plutonium oxide and impurities is highly relevant to both this Standard and to DOE-STD-3013-96. In both standards, a chemical mechanism described by Stakebake, Haschke *et al.* in several peer-reviewed publications is assumed to define the bounding pressure assumption (hydrogen only, no other gases formed). [Stakebake *et al.* 1993; Haschke/Ricketts 1995; Haschke and Martz 1998] The pertinent chemical reaction is:

$$PuO_2 + x\ H_2O \text{ ------> } PuO_{2+x} + x\ H_2$$

As indicated in this equation, decomposition of adsorbed water occurs by a solid state chemical reaction that generates hydrogen gas and retains oxygen as a superstoichiometric plutonium oxide. The temperature stability field of this oxide is not firmly established, but the compound appears to be stable from room temperature to about 400^{o}C [Morales *et al.* 1999]. A value of x up to about 0.3, corresponding to about 2 wt% moisture in plutonium oxide, appears to be possible in plutonium storage environments [Stakebake *et al*. 1993; Haschke/Ricketts 1995; Haschke and Martz 1998].

Recent work by Morales on the rate of the hydrogen/oxygen reaction in air/hydrogen mixtures over plutonium oxide supports earlier conclusions by Haschke, *et al*. that the surface of plutonium oxide, like many other surfaces, is an effective catalyst for this reaction [Morales 1999; Haschke/Martz 1998]. Accompanying work on hydrogen oxidation in the absence of plutonium oxide shows that stainless steel and other surfaces readily catalyze this reaction at temperatures of interest [Quigley 1998]. A recent literature search also shows conclusively that the H_2/O_2 reaction is readily initiated by alpha and gamma radiation [Lloyd *et al.* 1999 and references contained therein]. Indeed, remarkably high G values (the yield of product for 100KeV of adsorbed radiation energy) for recombination (in excess of 100) have been reported, compared to very much lower G values for liquid or adsorbed water radiolysis (the G value is near one for liquid water radiolysis) [*e.g.*, see Dautzenberg 1989; Dautzenberg 1990; and Kalashnikov, *et al*. 1988]. The cited publications conclusively show that multiple mechanisms exist which should ensure that substantial pressures of hydrogen and oxygen cannot accumulate in plutonium storage environments.

Additional recent data on gas pressurization in plutonium storage environments comes from the MIS program, where headspace gas pressure and composition have been measured for containers from the Plutonium Finishing Plant (PFP) at Hanford [Mason *et al.* 1999]. These containers, which include impure oxides, had been stored for up to 18 years. Common observations for those containers that apparently remained gas-tight are that pressures were found to be near atmospheric, significant hydrogen gas fractions were observed (up to about 50% in one can), oxygen pressures were strongly depressed (or undetectable) and small partial pressures of carbon dioxide and carbon monoxide sometimes were observed.

Similarly, pressures have been monitored over as-received and calcined plutonium-bearing oxides in seven surveillance capsules held at room temperature and monitored for about two years [Mason *et al.* 1999]. These capsules have exhibited little pressure change and, in some cases, an overall pressure drop has been found. As for the PFP samples mentioned above, elevated hydrogen and depressed oxygen partial pressures typically were found.

Additional information comes from practical experience in the United States and United Kingdom weapons complexes over the past five decades. A survey of plutonium storage failures has failed to identify a single instance of gas-induced failure where plutonium oxide materials have been calcined and packaged in a manner similar to that described by this Standard [Eller *et al.* 1999]. It is also notable that no plutonium storage package failures have resulted to date at the United Kingdom's Atomic Weapons Establishment since a good quality-control regime for stabilizing and packaging in food-pack cans was instituted several years ago for interim (10 year) storage [Freestone *et al.* 1998]. The AWE procedure involves calcination at 400°C and an LOI criterion of 2 wt% [Freestone 1998].

A key conclusion from all the work described above is that plutonium container environments have inherent self-limiting mechanisms that prevent accumulation of significant pressures of oxygen and hydrogen over calcined oxides. These mechanisms are very likely to limit buildup of unacceptable pressures of either hydrogen or oxygen alone. Known mechanisms limiting oxygen buildup include recombination with hydrogen and formation of PuO_{2+x} from adsorbed water. Mechanisms that limit hydrogen buildup include recombination with oxygen to produce water and probably reduction of PuO_{2+x} and other high valent materials by hydrogen. It is therefore very likely that the bounding gas assumption made in this Standard (and in DOE-STD-3013-96) is highly conservative.

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

MIS measurements on 33 items from Rocky Flats and Hanford which will be stabilized according to this Standard, show that pure and impure oxide material surface areas below 5 m^2/gram generally result from calcination at 950°C for two hours. [Haschke/Ricketts 1995; Haschke/Ricketts 1997; Haschke/Martz 1998; Mason *et al.* 1999; Manchuron-Mandard/Madic 1996]. This work also shows that post-calcination water readsorption on oxide particles should not pose a practical problem with respect to the 0.5 wt% criterion of this Standard (readsorption onto salt is discussed in the preceding section).

5) Stabilize any other potential gas-producing constituents

This Standard's calcination 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, sulfates and carbonates of plutonium are effectively converted to oxides by calcination 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*. 1957]. The report of Moseley and Wing [Moseley/Wing 1965] shows that 950°C calcination is sufficient to destroy this sulfate constituent. Literature searches indicate that deleterious amounts of radiolytic gases from residual sulfate and chloride contaminants are unlikely in the long-term storage conditions anticipated for stabilized materials [Tandon *et al.* 1999a, Tandon *et al.* 1999b 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% LOI criterion with reasonable calcination times. (Corrosion implications of chlorides during storage are addressed in Section A.6.3 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 calcination criterion of Standard 3013-96 but recommends that operational complications regarding salt evolution be carefully monitored.

Although not suggested in this Standard, one perceived benefit of calcining 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 calcination 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 calcination 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 calcined 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 calcined 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 calcination temperatures above 750°C.

2. The standard accepts two approaches to verification that materials have been adequately stabilized: 1) 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 2) use of a "qualified process" for stabilization and packaging that would reduce the requirements for materials testing.

    1) 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.

       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. The LOI test has great attractiveness for application to stabilized plutonium materials because it is simple, inexpensive and highly practical in a glovebox environment. LOI has the unfortunate characteristic of not directly measuring the parameter of greatest interest – hydrogenous material content. Decades of experience with pure plutonium oxide and recent results in the MIS program with oxides obtained from Hanford and Rocky Flats and tested at LANL indicate that LOI is an adequate test for moisture for fairly pure oxides (plutonium content greater than approximately 80-85 wt%) [Mason *et al.* 1999]. However, the MIS program also shows that lower assay materials of interest to the 94-1 program almost always fail the standard LOI test because of impurities other than water that become volatile at LOI test temperatures. Salt impurities are particularly troublesome in providing false negative indications. This Standard therefore encourages use of LOI for fairly pure plutonium oxide materials and use of moisture-specific alternative methods for lower grade materials.

Because of the shortcomings of the LOI method when applied to impure 94-1 materials, the MIS program has aggressively examined alternative methods for measuring moisture and hydrogenous content. In particular, the following methods have been evaluated carefully.

- Thermal gravimetric analysis/mass spectroscopy
- Supercritical carbon dioxide extraction
- Interstitial gas analysis
- Neutron moderation

A literature review was conducted recently to ensure that promising methods have not been overlooked. [Berg/Eller 1999]

In May 1999 LANL recommended that both neutron moderation and supercritical CO_2 extraction/FTIR methods be deployed [Rubin, *et al.* 1999]. This recommendation was endorsed by a peer review group with representation from SRS, Hanford, RFETS, LLNL, and DOE/HQ. Continued method development was recommended (especially for neutron moderation) to minimize limitations of each technique at their current stage of development. Inclusion of other techniques requires independent evaluation and DOE approval consistent with Item 5 of the Foreword.

2) 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.

   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 appointed by the Albuquerque Operations, Office Nuclear Materials Stewardship Project Office (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.

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) and earlier sections of this Appendix.

A.6.1.3 Engineered Materials

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

A.6.1.4 Storage after Stabilization – Deferred Packaging

The stabilization step, together with verification of stabilization at that time, provides certainty that the material was stable at a point in time. A high degree of confidence that the material is still stable is provided by the observation that the container and material appear unchanged and the moisture content remains acceptably low.

Evidence of change would include, for example, corrosion or substantial pitting of the container, or significant discoloration of the contents. To provide assurance of stability, verification of the moisture content is required, either by measurement, or by some other defensible analysis.

A.6.2 Containers – the "Packaging"

A.6.2.1 Container Design Concept

1. The design goals for the storage package are that it be maintenance free and compatible with existing or planned qualified shipping containers 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 (package) 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.

2. These requirements simply provide functionality in the design.

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.

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) from all known pressurization mechanisms. 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 4927 kPa, or 699 psig).

5. Specifying a minimum design pressure provides compatibility with the safety envelopes for current and planned storage facilities. The specified design pressure of 4927 kPa (699 psig) is sufficient to contain the pressure generated by the mass of oxide specified in Section 6.3.2 under "worst case" conditions of 0.5 wt% moisture, 19 w heat generation, and 211°C (412°F) gas temperature. It thus accommodates bounding storage conditions at most, if not all DOE facilities where plutonium-bearing materials might be stored.

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 can 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 pressure containment vessel is designed to ASME requirements and the fabricator manufactures the vessel according to code but does not stamp the vessel 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 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, its 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 derived using the pressure equation derived in Appendix B 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.6.2.2 Container Construction

1. Use of low-carbon stainless steels, such as 304 L and 316 L, is recommended with 316 L being preferable to 304 L 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 recent report on corrosion [Kolman 1999] 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. More information from Kolman’s report can be found in Section A.6.3.3.3 of this appendix.

2. The Assessment Report [DOE 1994a, 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.

3. The outer container is sized to fit into existing certified or currently proposed shipping containers (primarily the 9975 and SAFKEG packages). This design will minimize future handling and avoid unnecessary additional personnel exposure, operational risk, and waste generation.

A.6.2.3 Container Testing Criteria

1. Design Qualification Testing

   1) The purpose of the 9-meter drop test of the entire package is to ensure that a storage package 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 criterion for passing the test is that it retain its function, (*i.e.*, that it remain leak tight 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. See A.6.2.3.1 for details of the tests.

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

2. Testing During Use

   ANSI N14.5, Leakage Tests on Packages for Shipment, specifies that the acceptable maximum leak rate is 1 x 10^{-4} std. mm^3/sec (1 x 10^{-7} std. cm^3/sec) of dry air at 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.

A.6.2.4 Other Criteria

1. Identification markings are required on all storage containers to facilitate maintenance of an inventory data base and management of stored materials.
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. Further, the outer container, when open 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 leak-tight. 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.
- Originally (in DOE-STD-3013-94), the packaging concept was that the package would be acceptable for both storage and transportation. It considered the plutonium-bearing materials to be placed into a "boundary container" and that packaged into a "primary containment vessel." The boundary container was required to withstand 150% of the "worst case" internal pressure. The primary containment vessel was expected to pass the same pressure test, all the DOT tests (various drop tests, a crush test, etc.) and to be reusable. The current concept of the 3013 package, which is only for storage, uses the boundary container as the outer and has added a pressure indicating inner container. The outer is not expected to be reused. In short, although the packaging concept has changed dramatically, the criteria regarding removable contamination did not change to reflect the different role that the inner container now fulfills.

In summary, then, allowing a slightly contaminated inner container does not sacrifice any benefits, does not pose any new problems, and does allow correction of an anachronism in the current criteria.

A.6.3 Contained Materials

A.6.3.1 Container Fill Gas

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.
2. The container atmosphere must not act to mask leak testing and must support leak testing.

A.6.3.2 Mass of Contained Materials

1. The mass limit for fissile materials is based on criticality safety limits for plutonium. The fissile mass of an isolated sphere of pure ^{239}Pu that is fully water-reflected and

has a 0.05 margin in k_{eff} is calculated to be 4.53 kg (9.98 lb.). The parameter k_{eff} indicates the criticality status of an assembly of fissile and possibly other materials – a value of 1.0 indicates the critical condition (a self-sustaining reaction) and values less than 1.0 indicate subcriticality, with smaller values signifying greater departures from criticality. A margin of 0.05 (a k_{eff} of 0.95) is commonly used to assure subcriticality. In other words, the smallest amount of plutonium that could go critical is somewhat more than 4.53 kg. 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 fissile species and not just ^{239}Pu. This constraint prevents potential criticality incidents involving stored fissile materials (*i.e.*, ^{233}U, ^{235}U, ^{237}Np, or higher plutonium isotopes) because the critical masses of these fissile radioisotopes are greater than that of ^{239}Pu.

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.

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. The 19-watt-per-package limit ensures that existing transportation containers (primarily the 9975 package at this time) can be used. 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.4 of Appendix B.

The 19-watt limit also caps temperatures that may be reached under normal and off-normal conditions. Calculations performed at the Savannah River Site indicate that the 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

Table A-1

Calculated Temperatures (°C) in a 9975 Package

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

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

results are given in Table A-1. 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 1990]. Note that thermal analyses such as those performed by Hensel should be performed for actual storage configurations to verify the conservatism of the 250°C assumption made for this evaluation.

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 significant 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 recent experiments to address this issue [Flamm 1997; Spearing/Veirs 1999; Spearing *et al.* 1999]. A recent 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 B&PV Code, Section VIII, Division 2 [Flanders/ Krishnan 1999]. Confirmatory tests and analyses at the beta-gamma transition have reinforced the Flanders/Krishnan conclusions [documentation and peer review are underway].

3) Metallurgical interactions

Maximum plutonium-container interface temperatures up to approximately 189°C (see Table A-1) have been postulated for plutonium metal storage containers under bounding conditions. The potential for forming low-melting eutectics has been evaluated recently 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 can 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. 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.

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,

corrosion, *etc.* In the case of pressurization, 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. By using the limiting conditions of a minimum design pressure of 4927 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%, it is straightforward to show that a minimum of 0.25 liters of free volume is required for every kilogram of oxide in the container to keep the bounding pressure below the design pressure (see Section B.3.3.4 in Appendix B).

A.6.3.3 Packaging Process

1. Some oxide packages may contain foreign materials 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.
2. 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 storage container. This can be done, for example, by controlling the glovebox atmosphere and/or packaging within a very few minutes of sampling.
3. This Standard prohibits packaging materials that may corrode the containment system. The primary corrosion mechanisms of interest are general corrosion and stress corrosion cracking. A recent evaluation of both types of corrosion concludes that neither of these mechanisms is likely to be significant under storage environments anticipated by this Standard. [Kolman, 1999]

   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 elemental oxygen present if an air atmosphere was present during packaging is very small, and little or no elemental oxygen is expected to result from catalytic or radiolytic decomposition of water (see Section A.6.1.2 of this appendix). This also makes corrosion pitting highly unlikely.

Unlike general corrosion, stress corrosion cracking (SCC) is not mass limited. While SCC is a definite issue for stainless steel in moist oxidizing environments, Kolman's evaluation concludes that SCC is not a concern if conditions within the storage containers are maintained above the dew point of the contained atmosphere. This conclusion holds even in the presence of chloride salts and temperatures as high as 250°C. The stabilization and packaging criteria of this Standard, the anticipated elevated temperatures during storage, and the affinity of plutonium oxide for water provide confidence that dew points will never be exceeded within the packages. A recent review of experience in storing pyrochemical salts at numerous sites in the DOE complex showed that chloride corrosion has not presented a significant storage problem in the past when liquid water (and other corrosive agents) were avoided, in agreement with the predictions of Kolman [Kolman 1999] regarding storage of materials under this Standard [also see Tandon *et al*. 1999b].

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.

4. To promote material homogeneity for facilitating MC&A measurements and stabilization tests (such as for adsorbed water content), and to preserve characterization information to the greatest extent possible, only similar materials (comparable in form and composition, for example) should be packaged together.

A.6.4 Storage – Surveillance of Stored Packages for Safety

Surveillance is to be primarily non-destructive to preserve storage container integrity. Limited numbers of containers may be destructively examined if the information to be obtained is sufficiently important to warrant the added cost and personnel radiation exposure. Examples of non-destructive testing 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 (pressure change);
- Eddy current or ultrasonic testing of the integrity of the outer container and its welds;
- Weight measurement change, which would indicate a breach in the package; or
- Additional methods which may become available as technology develops.

A.6.4.1 Surveillance Program

1. Plans need to be responsive to site policies and practices.
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 packages may be damaged during handling and storage. The function of the surveillance program is to identify these anticipated low probability errors and flaws in the packaging as well as unanticipated threats to package integrity during storage.

   Essentially all manufactured products exhibit failure rates that graph as a bathtub shaped curve. This type of curve exhibits three distinct phases that occur over the lifetime of the product. There is an early life period, when the failure rate can be relatively high. These failures are generally the result of mistakes made in manufacturing the product that were not detected during production inspections. In the case of storage packages described in this Standard, inadequate stabilization could also contribute to such failures. This is followed by a relatively low failure rate period, which describes most of the life of the product. Then, as the product reaches its end of life, the failure rate again climbs to relatively higher values. The relative magnitude of the three parts of the curve will vary depending on the type of product and manufacturing process. In light of the lack of long-term storage data on these plutonium metal and oxide storage packages, it is reasonable to expect that failures would follow a pattern typified by the bathtub curve. Surveillance Programs should 1) account for the increased failure rate anticipated early in the life of the storage package; 2) recognize the lower inherent "mid-life" failure rate; and 3) monitor for the onset of end of life conditions.

There are at least three possible storage configurations that span the risks associated with plutonium storage. One configuration places the storage package in a vault that relies on the containment function of the storage package to ensure public safety. Another places the storage package in a vault that does not rely on the integrity of the package, and in which the primary risks involve worker safety. A third possible storage configuration places the storage package in some sort of container or over-pack. If the over-pack does not rely on the integrity of the storage package, then the condition of the storage package may not be important to safety, except as it may affect risks associated with opening the over-pack. The surveillance program should take into account the risks associated with storage (*i.e.*, the consequences of failures as well as their probabilities). The program should consider the balance between these risks and surveillance costs, both in terms of economic impact and personnel exposure to radiation or other hazardous environments, in determining the parameters of the surveillance program.

Finally, 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 packages. The second class could be called "systemic" because they affect a significant fraction of the storage packages, and generally represent an unanticipated condition in those packages. 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 package integrity for public safety (*i.e.*, where the container is designated safety class") and in which the packages are easily accessed and inspected, a relatively extensive surveillance inspection would be expected. In a facility that does not rely on package integrity for public safety, where access to the packages 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 packages 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 packages 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 a 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 5633.3B.

3. Inspections

   1) Initial Inspection. Flaws in initial packaging are expected to be detected by inspection of every package within 30 days of packaging. Ordinarily, this inspection would be done immediately after packaging, but 30 days delay reasonably accommodates operational considerations. 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),

verification of contents through NDA measurements, and any other information deemed desirable and attainable through non-destructive measurements such as radiography. This initial inspection may be part of the quality program for verifying package integrity.

2) Early failures are caused by mistakes, missteps, or other problems in the manufacturing, stabilizing or packaging processes that result in flawed or defective packages that are not detected during the initial inspection. To detect these types of failures, the initial program plan should consider alternatives such as: 1) provisions to inspect each package at least once during the first few years of storage; 2) an inspection of each package as it is put into storage; 3) inspection of all "high risk" packages identified based on their material contents, whether the container was among the first manufactured, whether it was non-conforming and accepted "as-is", *etc*. and inspection of only a pre-determined sample of other packages; and 4) inspections appropriate to the "random failure" approach, but with a higher frequency or larger sample size.

   During most or all of the storage period, mechanical failures, if any, are likely to be random. Uniform changes in the storage package 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 package failure. It should also be used to assess corrosion effects over the long term, particularly stress corrosion cracking in containers containing chlorides. The program plan should include provisions to assess the failure rate and to detect any changes that might signal an end to the "early failure" period, or the onset of an "end of life" period.

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.

5. No further basis is provided

A.6.4.2 Surveillance Parameters

The parameters specified by the criterion are the measurable indicators identified in Sections 6.2 and 6.3, above. These parameters provide an indication of material stability and package integrity.

A.6.4.3 Evaluation of Surveillance Data

These evaluations confirm the safety of the package.

A.6.5 Documentation

A.6.5.1 Data Base

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

A.6.5.2 Data Base Content Elements

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.
2. Package data can meet a number of needs. For example, if a package exhibits unexpected behavior, these data can help identify other, similar packages that may require inspection. These data also allow disposition processing to be optimized
3. No further basis is provided.
4. No further basis is provided.

A.6.6 Quality Assurance

This is a natural extension of the responsibilities the sites already have to assign materials to “oxide” and “residue” categories and to select items for the MIS Program.

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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 packages 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]. For simplicity in comparing the equation derived here with that used in the 3013 Standard, SI units have not been used. Instead, pressures are given in psi.

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. If a gas is at some standard condition, described by P_0, V_0, and T_0, then the quantity nR can be evaluated as

$$n\,R = P_0V_0/T_0. \qquad [2]$$

And the pressure under different conditions can be determined by

$$P_1 = nRT_1/V_1 = P_0(V_0/V_1)(T_1/T_0). \qquad [3]$$

In the above equation, T_1 is the temperature at which P_1 is to be evaluated. V_1 is the volume occupied by the gas at the evaluation temperature.

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. Thus, the combined effect can be expressed as:

$$P = P_F + P_G + P_{He} \qquad [4]$$

where P_F, P_G, and P_{He} are the partial pressures of the fill gas, the evolved gases and decay helium, respectively.

B.2. Derivation

B.2.1 Geometry Consideration

The volume occupied by the gas at the evaluation temperature, V_1, will be called the "free gas volume" of the package. This volume can be calculated as the unoccupied volume (V_c) of the outer can (*i.e.*, interior volume of the outer can less the volume occupied by the materials comprising internal containers), less the volume occupied by the contained material. These volumes, which are illustrated in Figure B-1, can be represented as

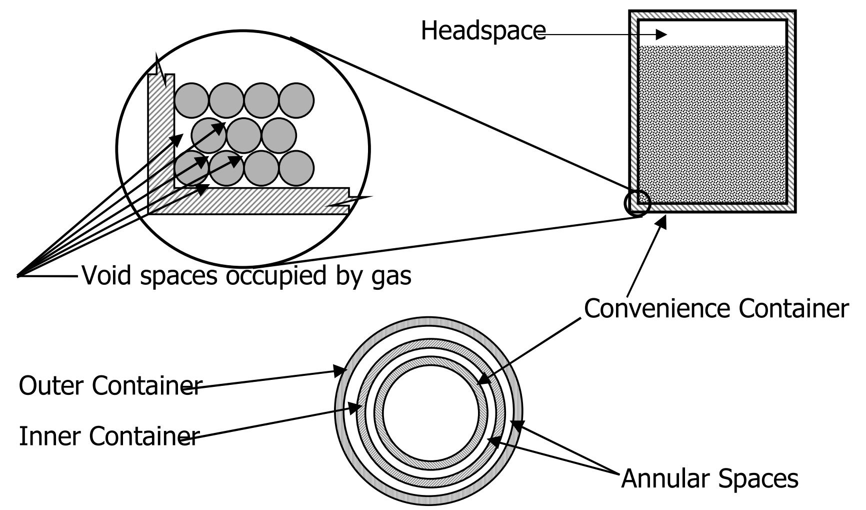

Figure B-1. Illustration of the components of free gas volume.

$$V_1 = V_c - V_m \quad [5]$$

and $$V_c = V_o - v_i - v_{cc} \quad [5a]$$

where V_o is the interior volume of the outer container,

v_i is the volume of the material of the inner container,

v_{cc} is the volume of the materials making up the convenience container, and

V_m is the volume of the contained material.

B.2.2 Container Fill Gas

The appropriate equation for pressure as a function of temperature is simply the gas law:

$$P_F = P_0(V_0/V_1)(T_1/T_0). \quad [6]$$

Since the initial volume and the final volume are the same, this reduces to

$$P_F = P_0(T_1/T_0). \qquad [7]$$

The values of P_0 and T_0 are the pressure and temperature at which the container was loaded and sealed. This is the first term of the equation given in DOE-STD-3013-96.

B.2.3 Evolved Gases

B.2.3.1 Gases of Concern

The only evolved gas of significance anticipated 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. If, in fact, some water is not decomposed, but is desorbed, the results are the same.

B.2.3.2 Quantities of Gas Produced

Starting with m kg of oxide with a moisture content of L (in percent by weight), there will be 10mL/18 moles of water in the container. Since one mole of water can theoretically produce one mole of hydrogen gas, hydrogen production, G, in moles, is assumed to be given by:

$$G = 10mL/18 \qquad [10]$$

B.2.3.3 Calculation of Gas Pressure

Since a mole of gas has a volume of 22.4 l at STP (14.7 psia and 273°K), a generated quantity of gas would occupy a volume (in liters) given by

$$V = 22.4\ G. \qquad [11]$$

In using the ideal gas law, this volume could be considered the initial volume so that the pressure attributable to this gas would be

$$P_G = (14.7)(22.4\ G)(T_1/273)/V_1 = 1.206\ GT_1/V_1. \qquad [12]$$

$$P_G = 0.67mLT_1/V_1 \qquad [13]$$

which is the middle term of the equation in DOE-STD-3013-96, if the free gas volume, V_1, is defined as

$$V_1 = (V_c - m/\rho)$$

where ρ is the density of the oxide.

B.2.4 Decay Helium

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

$$h = \lambda N \qquad [14]$$

where λ is the decay constant and N is the number of atoms of the decaying material. As a function of time, N is given by

$$N = N_0 e^{-\lambda t}. \qquad [15]$$

The total amount of helium generated, H, over a period of time τ is therefore

$$H = \int h\, dt = \int \lambda N_0 e^{-\lambda t}\, dt = N_0(1 - e^{-\lambda\tau}). \qquad [16]$$

For values of $\lambda\tau$ which are small, the term in parentheses can be replaced by its linear approximation, $\lambda\tau$. This approximation is conservative because $\lambda\tau \geq 1 - e^{-\lambda\tau}$. Also, since the units of H are the same as the units of N_0, it is possible to consider both as moles, rather than as atoms, and the volume of helium thus produced (in liters at STP) is

$$H = 22.4(1000\ m/271)\lambda\tau \qquad [17]$$

where m is the oxide mass in kg, and 271 is the molecular weight of PuO_2.

The pressure due to this volume of helium is

$$P_{He} = (14.7)[22.4(1000\ m/271)\lambda\tau](T_1/273)/V_1$$

$$P_{He} = 4.4507 m\lambda\tau T_1/V_1. \qquad [18]$$

If it is assumed that the radioactive species is ^{239}Pu with a half-life of 24,110 years, then Equation [18] becomes

$$P_{He} = 1.28\text{x}10^{-4}\ m\ \tau T_1/V_1. \qquad [19]$$

Equation [19] is the same as the third term of the equation in DOE-STD-3013-96.

An alternative formulation of this term is possible. The heat generation rate of the contents is given by

$$Q = E\lambda N = E\lambda N_0 e^{-\lambda t} \qquad [20]$$

where E is the energy emitted/generated during radioactive decay. For simplicity, consider only the initial heat generation. Then solve for N_0, substitute the result into the equation for helium produced, and use the linear approximation for the exponential, yielding

$$H = Q_0\tau/E. \qquad [21]$$

Using this relationship, the pressure equation becomes

$$P_{He} = 14.7x22.4(Q_0\tau/E)(T_1/273)/V_1$$

$$P_{He} = 1.2061(Q_0\tau/E)T_1/V_1 \qquad [22]$$

Note that for Q_0 in watts and τ in years, the quantity E must be in watt-years/mole. Table B-5 (found in Section B.4.1) provides decay energies for radionuclides of interest in both Mev and watt-yr/mole. As can be seen from the values in that table, Equation [22] produces pressures that are relatively insensitive to the radioactive species chosen because the value of E is relatively constant over the species considered. The conservative evaluation is achieved by using a relatively low value for E. A reasonable selection is the value for ^{239}Pu. When that is used, Equation [22] becomes

$$P_{He} = 7.517x10^{-5}\ Q_0\tau T_1/V_1 \qquad [23]$$

Note that Q_0 is the Specific Heat Generation Rate (SHGR) (from the last column of Table B-5) times the mass of plutonium in the container. If the value in Table B-5 for ^{239}Pu (1.93 w/kg) is used, and a conversion to use kg of oxide (instead of kg of plutonium) is also made to give the relationship $Q_0 = 1.7$ m, the resulting equation is the same as the one above based on mass (Equation [19]):

$$P_{He} = 7.517x10^{-5}\ (1.7\ m)\tau T_1/V_1$$

$$= 1.28x10^{-4}\ m\tau T_1/V_1 \qquad [19a]$$

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

B.2.5 Aggregate Equation

Summing the three partial pressures:

$$P = P_F + P_G + P_{He}. \qquad [24]$$

Using the terms given above:

$$P = P_0(T_1/T_0) + 0.67\ mLT_1/V_1 + 7.517\text{x}10^{-5}\ Q_0\tau T_1/V_1 \qquad [25]$$

where the symbols have the meanings indicated in Table B-1.

Table B-1

Meaning of Symbols in the Pressure Equation (Eq. 25)

Symbol	Quantity	Units	Symbol	Quantity	Units
P	Container Pressure	psia	V_1	Free Gas Volume	liters
P_0	Fill Gas Pressure at Filling	psia	m	Mass of Oxide	kg
T_1	Evaluation Temperature	K	τ	Storage Time	years
T_0	Fill Gas Temperature at Filling	K	Q_0	Container Heat Generation Rate	watts
			L	Moisture content	wt%

B.3. Application of the Equation

B.3.1 Example Calculation of Free Volume using the "BNFL" Containers

Information on the "BNFL" container design is given in Table B-2. Can weights and volumes in that table were determined by J. Stakebake [Stakebake 1997]. Volumes were derived from BNFL drawings and calculations. The interior volume of the inner container does not take into account the curvature of the can bottom. The free volume is determined as the interior volume less the material volume of interior containers. The free volumes shown for the inner and outer containers were agreed upon by SRS and RFETS contractor personnel and used by BNFL for design at the direction of DOE.

Table B-2

Container Volumes

Component	Interior Volume in liters	Mass in grams	Material Volume in liters	Free Volume in liters
Convenience Can	1.839	1580	v_{cc} = 0.198	V_c = 1.839
Inner Can	2.266	1600	v_i = 0.200	2.068
Outer Can	V_o = 2.602	4026		2.204

B.3.2 Determining the Free Gas Volume

B.3.2.1 Density Method

A straightforward method to determine the free gas volume of the container is to first estimate the volume occupied by the contained material as the mass of material divided by the material density:

$$V_m = m/\rho, \qquad [26]$$

The free gas volume is then obtained by subtracting the volume defined in Equation [26] from the container unoccupied volume given in Equation [5a]. 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 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 (see Figure B.1) 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. The particle density can be measured with a gas pycnometer.

The correct density to use in Equation [26] is the particle density. However, it is extremely unlikely that the particle density of material in every container will be measured. Accordingly, some alternate methods of estimating the density to be used in the equation must be developed.

B.3.2.2 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 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 l convenience container, the bulk density would be 2.0 kg/l and the estimated particle density would be 2.0/0.62, or 3.226 kg/l, giving a material volume of 1.116 l.

B.3.2.3 Statistical Method

The packing fraction approach is generally useful only when the bulk density is known. The bulk density is easily determined if the container is full, but a partially full container makes the situation more complicated because of lack of knowledge about the volume of material. In principle, a series of density measurements could be made to develop a statistical model of the powder, and from that the appropriate density could be determined. For example, Figure B-2 shows the ratio of bulk density to pycnometer density as a function of bulk density for the materials in the "shelf life" program. The ratios

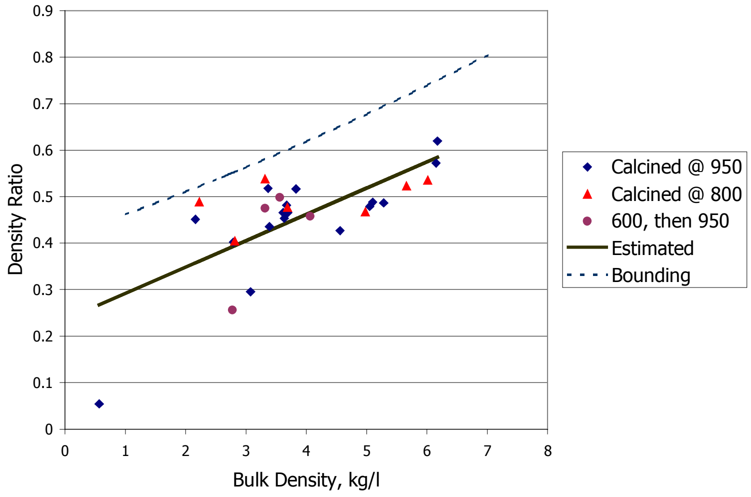

Figure B-2. Statistical model of material density relationship include material calcined at 950°C, 800°C, and some that was calcined first at 600°C, and then at 950°C. The heavy line that passes through the data points is a statistical regression, and is given by the relationship

$$F_p = 0.2348 + 0.05673\,\rho_{bulk} \qquad [27]$$

Where F_p is the density ratio, 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. That is shown in Figure B-2 by the dashed, lighter weight line that is above all the data points.

B.3.3 Estimated Temperatures

The final parameter required for use of Equation [25] is the gas temperature. As it is impractical to measure this quantity, 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 package 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-1). These calculations also indicate an average gas temperature of approximately 211°C for transportation conditions (exposure to solar heating). These temperatures are probably bounding and may be used when other information is not available. Each storage facility should evaluate average gas temperatures under the conditions anticipated at that facility, such as loss of cooling events, to determine appropriate evaluation conditions.

B.3.4 Example Calculations

B.3.4.1 Example Pressure Calculation for Weapons Grade Oxide

Assume that a BNFL container will be loaded with 5.0 kg of weapons grade oxide that has a density of 10 kg/l (and is therefore assumed to be fairly pure) and a moisture content of 0.5 wt%. The package 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	psia	V_1	Gas Volume of Container*	1.704 l
P_0	Fill Gas Pressure at Filling	14.7 psia	m	Mass of Oxide	5.0 kg
T_1	Evaluation Temperature	477.4 K	ρ	Density of Oxide	10 kg/l
T_0	Fill Gas Temperature at Filling	303 K	Q_0	Container Energy Generation	12.4 w
L	Water Content	0.5 wt%	τ	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 2.204 l free volume of the BNFL container system.

$$P = P_0(T_1/T_0).+ 0.67\ mLT_1/V_1 + 7.517\text{x}10^{-5}\ Q_0\tau T_1/V_1$$

$$= 14.7*(477.4/303) + 0.67*5*0.5*477.4/1.704 +$$

$$+ 7.517\text{x}10^{-5}*\ 12.4\ *50*477.4/1.704$$

$$= 23.2 + 452.5 + 13.1$$

$$= 489 \text{ psia}$$

This calculation is comparable to calculations prescribed in DOE-STD-3013-96 and yields comparable results. For “pure oxide” a pressure of approximately 500 psia is bounding.

B.3.4.2 Example with Unknown Density, 19 w Heat Load

Assume that a BNFL 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/1.839 l/0.62 or 4.385kg/l. Using that density, we calculate the free gas volume as 2.204 – 5/4.385, or 1.064 l. Not too surprisingly, this is also equal to 38% of the convenience container volume plus the two annular spaces in the container system (1.839 x 0.38 + 0.229 + 0.136 = 1.064 l)

$$P = 23.2 + 0.67*5*0.5*477.4/1.064 + 7.517\text{x}10^{-5}*19*50*477.4/1.064$$

$$= 23.2 + 751.7 + 30.1$$

$$=805 \text{ psia}$$

In this example, if the design pressure were 699 psig (714 psia), it would be necessary to reduce the loading by about 7% to remain within the standard criterion. In other words, a mass loading of 4.70 kg would increase free volume to 1.132 l and would reduce the last two terms to 663.9 and 26.5, for a total of 713.6, just under the 714 psia limit.

B.3.4.3 General Behavior of Pressure Equation – Example of Statistical Method

The material density model that was developed in B.3.2.3 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

$$F_p = 0.3928 + 0.05673\ \rho_{bulk}$$

This is the regression equation developed in B.3.4.3 (Equation [27]) 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-1) 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-3. The behavior shown is characteristic of the relationship between pressure and density. As the density decreases, the free gas volume decreases, and the bounding pressure increases. However, this behavior continues only until the innermost container (convenience can) is full. After that, as the density is further reduced, the mass of material is reduced, the amount of moisture

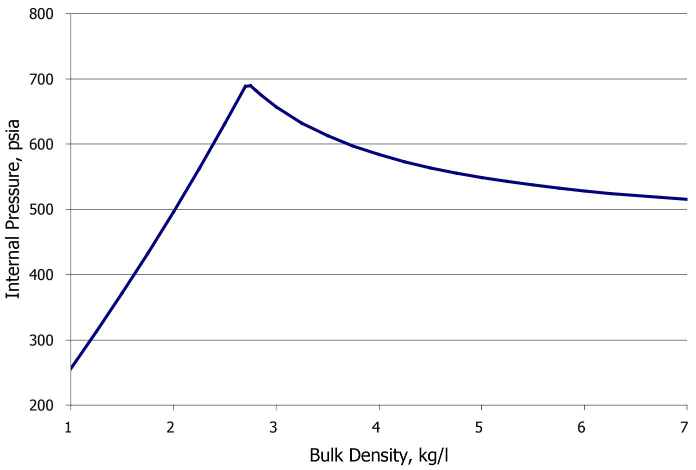

Figure B-3. Bounding pressure as a function of bulk density for the statistical model in B.3.2.3

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 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.

B.3.4.4 Minimum Required Free Gas Volume per Kilogram

Assume now that we wish to find the minimum required free gas volume of a container holding 1 kg of material that has a heat generation rate of H_S w 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 storage package is in a 9975 transportation package in the sun. The resulting pressure is required to be 714 psia (699 psig).

$$714 = 23.2 + 0.67*1*0.5*484/V_{min} + 7.517x10^{-5}* H_S *50*484/V_{min}$$

After rearranging, the equation becomes

$$V_{min} (714-23.2) =.67*1*0.5*484+ 7.517x10^{-5}* H_S *50*484$$

$$V_1 = 0.2348 + 0.00263H_S \text{ l.}$$

Based on the previous example, the worst case is when the maximum loading just fills the innermost container. For that case, H_S will be 19/5, or 3.8 w/kg oxide, and V_{min} will be 0.246 l per kilogram of material, or 1.230 l for the 5 kg loading. Table B-4 provides results for other heat generation rates. In each case, the limiting combination of heat generation and mass loading are used to determine the total free gas volume required. For the BNFL container system, a free gas volume of 0.996 l corresponds to a density ratio of 0.656, which is larger than density ratios observed in the shelf life items. That, in turn, implies that such a value is conservative. For simplicity, a value of 0.25 is used in the Standard.

Table B-4

Minimum Free Gas Volumes

SHGR w/kg	Loading kg	V_{min} l/kg	FGV* l
4.3	5	0.246	1.230
5.4	4	0.249	0.996
7.2	3	0.254	0.762
10.8	2	0.263	0.526
21.5	1	0.291	0.291

* FGV is the minimum container free gas volume for the mass loading indicated

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.

B.4.1 Expected Isotopic Compositions

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

Once the target is discharged from the reactor, production of these isotopes stops, and any further changes are the result of radioactive decay. With the exception of ^{241}Pu, all the plutonium isotopes decay by alpha decay. For the time spans of interest here, their progeny are not important in terms of 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, Yr.**	**Decay Energy, Mev/event**	**Decay Energy, Watt-yr/mole**	**SHGR, Watts/kg**
^{233}U	160,000	4.909	15,021	0.581
^{235}U	7.1×10^8	4.681	14,333	0.00006
^{238}U	4.5×10^9	4.195	12,836	0.000008
^{238}Pu	87.84	5.593	17,113	567
^{239}Pu	24,110	5.244	16,046	1.93
^{240}Pu	6,537	5.255	16,079	7.10
^{241}Pu	14.4	0.0205	62.7	12.52
^{242}Pu	376,000	4.983	15,246	0.116
^{241}Am	432.2	5.637	17,248	114.8

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-4 shows how the heat generation rate changes with time for each of the materials given in Table B-6, except for the power grade material. A chart showing the heat generation in that is given in Figure B-5, 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-5 provides an extreme example of the increase in SHGR with time. This is due to the considerable buildup of 241Pu, representing a source of 241Am and hence a future heat generation capability. Fortunately, the "power grade" curve is not

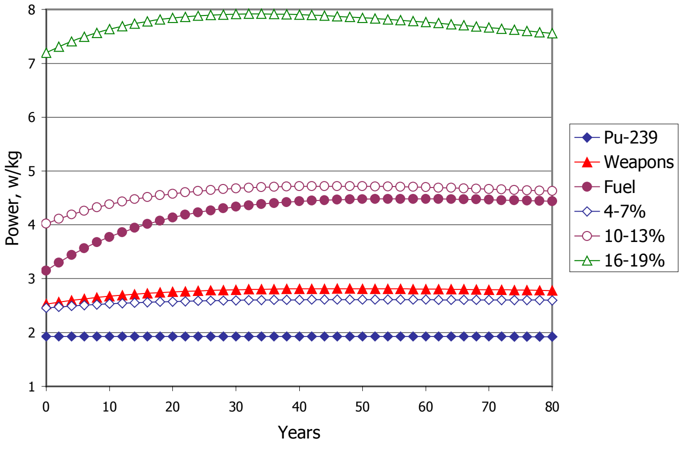

Figure B-4. Heat Generation rates in various grades of plutonium as a function of time.

characteristic of any significant quantity of plutonium to be packaged under this Standard. However, even for this material, after 20 years of storage and the consequent decay of the ^{241}Pu into ^{241}Am, the subsequent increase in heat generation rate is only about 15%.

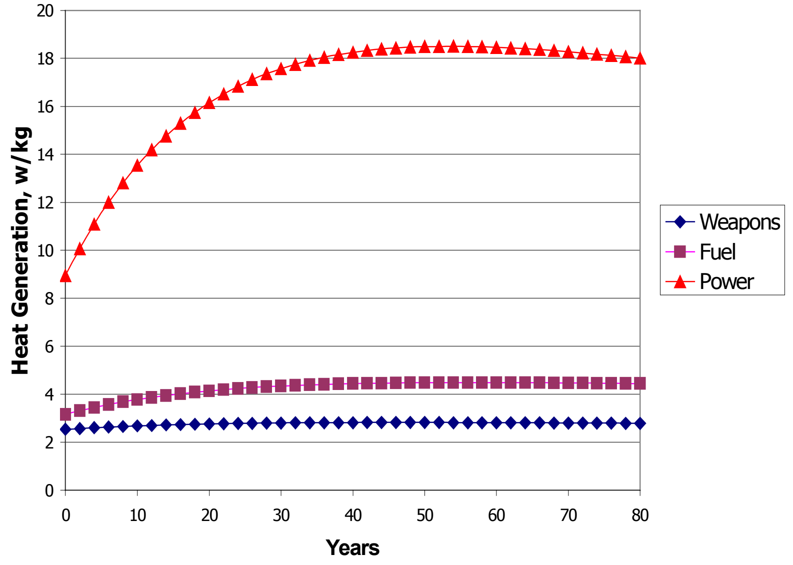

Figure B-5. Heat generation rate as a function of time for three grades of plutonium

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:

$t_{peak} = -20.78 \ln(0.0312 + 0.0302\ f^{51}/f^{41} + 0.5716\ f^{48}/f^{41})$

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

f^{41} is the concentration of ^{241}Pu (wt% or mass fraction)

f^{48} is the concentration of ^{238}Pu (wt% or mass fraction)

f^{51} is the concentration of ^{241}Am (wt% or mass fraction)

APPENDIX C

References

References are dominated by three types of information:

a) Operational experience in the United States and United Kingdom over the past five decades, involving tens of thousands of plutonium storage containers

b) Published technical literature

c) New reports and unpublished information from the Materials Identification and Surveillance (MIS) project of the DNFSB 94-1 Research and Development program led by Los Alamos National Laboratory

All recent LANL and SRS reports referenced in this Standard have been peer reviewed and are openly available.

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CONCLUDING MATERIAL

Review Activity:

Programs

DP
EH
EM
MD

Field Offices

AL
ID
RF
RL
SR

National Laboratories

LLNL
LANL

Preparing Activity:

AL/NMSPO

Project Number:

PACK-0014