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SUMMARY OF PLUTONIUM OXIDE AND METAL STORAGE PACKAGE FAILURES

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ABSTRACT

This report compiles available documented information on failures of containers storing plutonium oxide and metal materials within the context of current and newly proposed stabilization, packaging and storage standards. The information was obtained from published DOE-wide plutonium storage safety evaluations, recent workshops, technical reports, scientific journal publications and direct discussion with many subject matter experts. Storage of plutonium-bearing materials has been necessary since the inception of large scale nuclear processing more than five decades ago. However, it is only more recently that significant quantities have been stored outside of nuclear weapons at Department of Energy facilities for extended periods.

This report focuses on the past two decades of plutonium oxide and metal storage, during which package failures were reasonably well documented. However, during this period tens of thousands of containers also have been stored safely despite the lack of uniform packaging protocols. Over time, lessons learned from packaging failures and successes have led to much better understanding of failure modes, improved packaging and surveillance protocols and reduced failure rates.

In this report, two primary failure modes are identified: a) metal oxidation due to non-airtight packages and b) gas pressurization from radiolytic and thermal degradation of inadequately stabilized materials. These failure modes are evaluated in the context of four key aspects of safe storage standards: adequacy of the calcination process, resistance of the container to pressure, container sealing requirements, and container resistance to corrosion and radiation. The evaluation shows that rational explanations exist for all documented failures and that the associated conditions were well outside the envelope defined by both the current and proposed long-term storage standards.

I. INTRODUCTION

Storage of plutonium oxide and metal has been necessary since the inception of large scale nuclear materials processing more than fifty years ago. However, it largely has been within the last twenty to thirty years that significant quantities have been stored outside of nuclear weapons for extended periods at Department of Energy (DOE) facilities. The plutonium environment can be hostile with regard to package integrity. A number of package failures involving plutonium metal, oxide and residues have been well documented in a series of summary reports, reviews and popular articles. (DNFSB 1994a; DOE 1994a,b; Haschke and Martz 1998; Szempruch 1984; Szempruch 1995; Chem. Eng. News 1994; New York Times 1994). Factors that contributed to the failures include container corrosion, gas pressurization, and volume expansion due to metal oxidation. Safety concerns posed by such vulnerabilities led to the issuance in 1994 of Recommendation 94-1 by the Defense Nuclear Facilities Safety Board (DNFSB). (DNFSB 1994b) In response, DOE prepared an implementation plan to address the vulnerabilities. (DOE 1995) The implementation plan recently has been revised. (DOE 1998)

The five major plutonium sites in the DOE complex are Lawrence Livermore National Laboratory (LLNL), Los Alamos National Laboratory (LANL), the Plutonium Finishing Plant (PFP) at Hanford, the Rocky Flats Environmental Technology Site (RFETS), and the Savannah River Site (SRS). While a few significant package failures have occurred at each of these sites, it is equally notable that tens of thousands of packages did not fail, despite the lack of standardized stabilization and packaging protocols. Valuable lessons were learned in assessing the successes as well as the many fewer failures. Primary failure modes were recognized and a relatively small number of dominant package protocols evolved which vastly improved storage of plutonium materials. Improved surveillance procedures also resulted. A notable reduction in failure frequency has resulted complex-wide. Both the current (DOE 1996) and proposed (DOE 1999) plutonium stabilization, packaging and storage standards, and their predecessor (DOE 1994c), use these lessons learned to specify criteria for safe fifty-year storage. The purpose of this report is to consolidate the well-documented failures and to place them in the context of the storage successes and of current and proposed standards.

For the purpose of this report, container failure is defined as compromise of the package's main safety function, specifically containment of radioactive material. Tables 1 and 2 summarize well-documented instances of plutonium storage package failures. In this report we also discuss documented cases of unusual storage occurrences such as bulged or collapsed ("paneled") rim-sealed food-pack cans, where an unusual condition was noted but contamination was not released. Examples of such cases are summarized in Table 3.

In the past, long-term storage of oxide and metal generally was not a concern due to the demand for plutonium. For instances of package failures and unusual occurrences before about 1970, documentation is sketchy at best and very little written record exists. Undocumented failures undoubtedly occurred in this early period but are lost to history. Documentation has improved dramatically since the 1970's and has continued to improve to the present day. In the present study, subject matter experts were surveyed to ensure that significant failure modes were not missed despite the lack of early documentation.

In 1994, DOE adopted DOE-STD-3013-94 as the standard for packaging plutonium metal and oxide materials containing greater than fifty weight percent plutonium. (DOE 1994c) The objective was to avoid container failures during a storage period of fifty years, with minimal surveillance. This standard was revised to DOE-STD-3013-96 in 1996. (DOE 1996) A new standard currently is proposed that, among other changes, lowers the acceptable minimum actinide content from fifty to thirty weight percent and reduces the maximum acceptable wattage per package from thirty to nineteen watts. (DOE 1999) Appendix A of the proposed standard outlines the technical basis for these changes. This report further supports the technical basis of both standards by evaluating documented plutonium storage incidents within the context of requirements of the standards.

Based on the documented information, this report defines two dominant failure modes for plutonium storage package failure:

- Metal oxidation due to non-airtight packages
- Gas pressurization from inadequately stabilized oxides and radiolytic and thermal degradation of organic materials

Four key considerations for safe storage are identified:

- Adequacy of the calcination process
- Container pressure resistance
- Container sealing requirements
- Container corrosion and radiation resistance.

Discussion of the dominant failure modes and safe storage considerations form the focus for the remainder of this report.

II. SOURCES OF INFORMATION

Valuable information for this report was obtained from direct discussions with many active subject matter experts at DOE's five principal plutonium-handling sites. Subject matter experts from other DOE sites, retired personnel, and senior managers from the United Kingdom's Atomic Weapons Establishment (AWE) also were engaged. Some of these subject matter experts are identified at the end of this report. Published information which was surveyed included DOE-wide plutonium storage safety evaluations, technical reports and the peer-reviewed scientific literature. A literature search using technical databases was conducted using the following keywords: plutonium, storage, package, failure, metal, oxide, compounds, and residues. The following databases were searched: INSPEC, Engineering Database, and DOE Energy Science and Technology Database.

A search of DOE's Occurrence Reporting and Processing System (ORPS) electronic database also was conducted using the keywords plutonium, storage, failure, and vault. The ORPS database search produced no information not acquired through the other means mentioned above.

III. CONTAINER FAILURE MECHANISMS

The information search revealed the documented plutonium storage package failures presented as case studies in Tables 1 and 2. Table 3 lists examples of documented unusual occurrences which did not result in release of contamination from the storage package. Two dominant observed failure modes are discussed in this section, highlighted with a few examples of each failure mode. This survey is restricted to materials categorized as oxides and metal applicable to the long-term storage standards. Failure of packages containing residues, wastes and other materials outside the scope of the standards is not addressed in this report.

1. Metal Oxidation in Non-airtight Packages. The largest number of well-documented package failures involved storage of plutonium metal in containers which were not air-tight (Table 1). In each case, in-leakage of air led to oxidation of the metal to the dioxide, accompanied by a large increase in plutonium material volume which caused mechanical failure of the container. Excellent descriptions of several events of this type are given in Haschke and Martz (1998), Haschke et al. (1998), Dodson (1994) and Stakebake (1995). The roles of moisture, hydriding, nitriding and atmospheric pressure cycling in accelerating oxidation rates are elucidated in these reports.

To illustrate the metal oxidation failure mode, we cite an incident at LLNL which was discussed in detail by Dodson (1994) and summarized as Case SEAL-5 in

Table 1. In this instance, air entered an inner aluminum can through incomplete sealing of the container, followed by conversion of the plutonium metal to oxide and mechanical failure of the container. Failure occurred within three years of packaging. The can was found to be split along its entire length as a result of expansion of the oxidized metal.

2. Gas Pressurization. As indicated in numerous technical reports and publications, failures of packages containing plutonium oxide have occurred because of excessive gas generation. (E.g., see DOE 1994a,b; DNFSB 1994a; Haschke and Martz 1998.) Table 2 shows documented cases of this failure mode. The root cause of this failure mode stems from radiolytic and thermal degradation of inadequately stabilized material.

An illustration of this failure mode is afforded by incidents at PFP (Cases PRESSURE-1 and 2 in Table 2). (Hanford 1975; Szempruch 1984). These incidents involved unstabilized glovebox sweepings packaged in food-pack cans. In both cases gas pressurization and rupture of the containers occurred. In one case the container was ejected from its storage position and gross contamination of the storage vault resulted. The other failure occurred inside a shipping container and resulted in gross contamination of the interior of the shipping container.

An example of failure due to organics degradation is the SRS incident listed as Case PRESSURE-6 in Table 2, reported by Menke and McQuinn. (1981) In this case, an oxide storage package ruptured due to overpressurization, resulting in contamination of a large area of the storage vault. The stored material consisted of glovebox sweepings and reject pressed compacts continuing plutonium dioxide in contact with an aluminum stearate-dodecanol die lubricant. Inspection of similar packages indicated pressurization from buildup of hydrogen and methane due to radiolytic and/or thermal degradation of the organic material.

IV. UNUSUAL STORAGE OCCURRENCES WITHOUT FAILURE

Table 3 tabulates examples of documented cases in which unusual conditions were noted but storage package failures did not occur. Bulging and paneling of food-pack cans dominate this category.

In a 1994 example from SRS (Case PRESSURE-11, Table 3), several food-pack storage cans were observed to be slightly deformed from small internal pressure buildup. (Pierce 1994, Schaade 1994a, Schaade and Walker 1994) The most probable cause of the pressurization was postulated to be a combination of thermal and radiolytic degradation of the PVC bag enclosing the inner container, with a possible small contribution from heating of the can atmosphere. At AWE, pressurization of plutonium oxide containers has only been observed for two containers in recent years, and these were packaged elsewhere under somewhat uncertain conditions and delivered to AWE. (Freestone 1999)

As Table 3 indicates, partial collapse ("paneling") or inward lid deflection of food-pack cans has been observed at PFP and SRS during storage of alpha-phase fuels-grade plutonium metal. An instance at SRS (PANEL-6) apparently involved scrap mixed oxide containing incompletely calcined carbide. (Schaade 1998) Paneling has been observed at AWE only with high-burnup plutonium metal, but not with oxide or weapons-grade metal. (Freestone 1999) A number of reports describe creation of vacuum from reaction of oxygen and nitrogen from air cover gas with plutonium metal. (e.g., see Haschke and Martz 1998, Martz et al. 1994, Stakebake 1992, and references cited therein) None of the paneling cases listed in Table 3 led to release of contamination and no instances are known for weapons-grade metal or metal phases other than alpha. The experience suggests the importance of elevated temperature for the paneling process.

V. DECLINING FAILURE FREQUENCY

For the documented cases presented in Tables 1 and 2, a decline in the frequency of package failures in recent years is evident. Table 3 indicates a greater frequency recently of unusual occurrences without failure, likely a result of more aggressive surveillance and reporting in recent years. The decline in failure rate is attributable to the development and application of improved stabilization and packaging protocols from applying lessons learned from previous packaging failures and successes, in combination with improved surveillance. Forums such as the 1984 DOE training seminar "Prevention of Significant Nuclear Events" have provided a valuable mechanism for information exchange in this regard. (Szempruch 1984)

It is noteworthy that Dodson's 1994 report indicated that only three package failures had been documented or remembered by facility personnel between the start of plutonium operations at LLNL in 1961 and the publication of her report. Only one of these failures was discovered during processing of more than 606 packages containing plutonium during an inventory reduction campaign. No failures have been observed at LLNL since completion of this campaign. Several unusual occurrences without contamination release (e.g., bulging cans containing impure oxides that had not been processed according to the standards) have been reported by LLNL, as indicated in Table 3. (Dodson 1999)

Recently a visual inspection of LANL's entire vault inventory of nearly 8000 plutonium items was conducted. (Boerigter et al. 1997, Fife 1999). This exercise found that 361 containers had some visually observable abnormality. Of these, 82 containers had lost primary containment as indicated by raised lids, corrosion or other factors. None of these primary containment losses led to dispersal of material outside the secondary package. Indeed, during nearly 20 years of operation of the vault at LANL's plutonium facility, no containers of fissile material have failed in an uncontrolled environment. (Boerigter et al. 1997) The most commonly observed cause of primary containment failure was mechanical, for example a bagout bag pushing against a taped slip-lid. A few cases of primary container failure involved corrosive or inadequately dried materials. None of the containers which lost primary containment had been stabilized or packaged in a manner resembling the requirements of the new standard, and all of these cases have rational explanations well outside the envelope defined by the current and proposed standards.

It should be noted, however, that the overall recent success in safely storing plutonium in vault environments have involved much lower temperatures than bounding storage scenarios now being considered after packaging according to the standards. (Hensel 1999a,b)

VI. CRITICAL STORAGE STANDARD CONSIDERATIONS

In this section, four key considerations for safe storage of plutonium materials are discussed within the context of the storage standards and the two dominant observed failure modes discussed in Section III. These four considerations are:

- Adequacy of the calcination process
- Container pressure resistance
- Container sealing requirements
- Container corrosion and radiation resistance

1. Adequacy of the Calcination Process. Both the current and proposed standards require calcination at 950^{o}C for two hours to ensure elimination of gas-generating constituents such as organics and nitrates. The moisture content is required to be lower than 0.5 wt.% at the time of packaging. These requirements are intended to eliminate significant gas pressurization. Accordingly, failures and unusual occurrences of this type should be eliminated.

2. Container Pressure Resistance. The plutonium storage container must survive or prevent four types of pressure scenarios:

- Gas vacuum
- Gas pressurization
- Material volume expansion due to metal oxidation
- Metal volume expansion due to phase changes

Tables 1-3 show failures and unusual conditions corresponding to the first three pressure scenarios.

The first pressure scenario (gas vacuum) is addressed in the standards by specification of a storage container with sufficient mechanical strength to withstand total internal vacuum (0 psia).

The second pressure scenario (gas pressurization) is addressed in several ways in the standards. First, a package design working pressure of 699 psia is specified. The burst pressure of the package is nearly two orders of magnitude greater than the burst pressure of food-pack cans commonly used in the past. (Boardman 1997, Fleischman 1993, Coulter 1997) In addition, to minimize the potential for gas generation, the standards require calcination at 950°C to eliminate organic materials, nitrates and other potentially problematic constituents. The standards also require testing to ensure that water content of the packaged materials is below 0.5 wt.%. These criteria were not met for any of the gas pressure-induced failures and unusual occurrences listed in Tables 2 and 3.

A recent peer review report of the AWE interim storage criteria for plutonium-bearing materials contains sections written by representatives from most major DOE plutonium facilities. (Freestone and Shaw 1998) The subreports indicate that, in the experience of the reviewers, no containers of oxide produced and packaged in a well-controlled, reasonably dry atmosphere at a temperature of 400°C or above has exhibited significant container pressurization, even though a loss on ignition value below 0.5 wt. % might not have been attained at this relatively low temperature.

The potential for the third pressurization scenario (oxidation of metal) is minimized by the standards by requiring the use of nested, welded and leak-tested containers to greatly minimize or eliminate the possibility of air in-leakage. The greater mechanical strength of the packages compared to food-pack cans also greatly enhances resistance to failure even if air in-leakage were to occur.

The fourth potential pressurization scenario (metal phase changes) stems from a concern that volume expansions that occur when plutonium metal phase transformations occur near 115^{o}C (alpha/beta) and 185^{o}C (beta/gamma) may exert sufficient mechanical pressure to cause the storage container to fail. Our information survey revealed no documented or anecdotal evidence for this failure mode in containers with far less mechanical strength than those required by the standards. The metal phase change concern has been addressed by worst-case experiments and finite element modeling and is not discussed further in this report. (Spearing et al. 1999; Spearing and Veirs 1999; Flanders and Krishnan 1999)

3. Container Sealing Requirements

As discussed in the preceding section, the standards require that mechanically strong, nested, welded and leak-tested stainless steel containers be used for packaging plutonium metal and oxides for extended storage. This requirement provides high confidence that the containers will be adequately sealed, thereby eliminating the possibility of air in-leakage and the possibility of contamination escaping the container.

4. Container Corrosion and Radiation Resistance

With one possible exception (Case PRESSURE-3, Table 2), none of the oxide and metal storage package failures and unusual occurrences summarized in Tables 1-3 have been caused by corrosion. (Numerous corrosion-related failures of unstabilized residue and waste packages have occurred.) The standards minimize the possibility of corrosion-related failures by allowing only stabilized oxides and metal to be packaged. In addition, the standards specify that corrosive constituents be excluded and that corrosion-resistant container materials (i.e., stainless steel) be used.

The issue of chloride-induced corrosion of storage containers has been addressed by Kolman (1999). Neither the current nor proposed standard specifically excludes chlorides, and both are widely interpreted to permit packaging of chlorides. Kolman's key conclusion is that neither general corrosion nor stress corrosion cracking should pose a threat to the containers under anticipated storage conditions, provided condensed water is avoided. The calcination, moisture and sealing specifications of the standards are intended to avoid any possibility of condensed water in the packages.

Kolman’s report also addresses radiation effects on the stainless steel container. His key conclusion in this regard is that radiation effects are unlikely to be a significant safety issue if good welding practices are followed.

A recent report on chloride salt radiolytic effects in plutonium storage environments surveys complex-wide experience in storing pyrochemical salts. (Tandon et al. 1999) This survey indicated that significant corrosion problems have not been observed in storage of pyrochemical salts, provided reasonable precautions had been made to avoid excessive moisture. For example, Hanford has stored plutonium-bearing NaCl-KCl salts in food-pack containers for nearly twenty years without observation of significant storage problems (corrosion or otherwise). (Szempruch 1999) These observations are supported by recent observations on pyrochemical salts at RFETS, LANL and AWE. (Stakebake 1998; Boerigter et al. 1997; Freestone 1999) However, it should be noted that much or all of this experience with storage of plutonium/salt mixtures has been at temperatures lower than some anticipated bounding storage conditions for materials packaged according to the standards. (Hensel 1999a,b)

VII. CONCLUSIONS

The evaluation in this report shows that rational explanations exist for all documented cases of failure of storage packages containing plutonium oxide and metal. All documented failures have involved conditions well outside the envelope defined by both the current and proposed standards. Two root causes of documented failures are identified. One cause is volume expansion from oxidation of stored metal in non-airtight packages. The second cause is gas pressurization due to radiolytic and/or thermal decomposition of inadequately stabilized materials. The decrease in failure frequency observed in recent years is attributable to improved packaging and surveillance protocols developed by applying valuable lessons learned from earlier packaging failures and successes. These lessons learned have been applied in both the current and proposed standards.

REFERENCES CITED

Boardman 1997	“Summary Report on the Testing of the PuSPS 3 Can Package”, British Nuclear Fuels, Ltd., Client Report Project Number K0103C/R&P/014/A, February 1997.
Boerigter et al. 1997	“Risk-Based Prioritization for Plutonium Residue Holdings”, S. T. Boerigter, N. S. DeMuth, and G. Tietjen, Los Alamos National Laboratory report LA-UR-97-0426, March 1997.
Bonadie and Szempruch 1999	“Plutonium Inventory Characterization Technical Evaluation Report 3”, E. P. Bonadie and R. W. Szempruch, HNF-SD-CP-TRP-070, Babcock and Wilcox Hanford Co., manuscript in preparation, 1999.
Chem. Eng. News 1994	“Plutonium Storage Containers Aren’t Fail Proof”, Chemistry and Engineering News, June 13, 1994, p. 23.
Condit et al. 1987	“Incident Analysis/Plutonium Burn in Storage Can”, R. H. Condit, D. V. Fix, and H. J. Howe, Lawrence Livermore National Laboratory incident report, January 16, 1987.
Coulter 1997	T. Coulter, “Maximum Allowable Working Pressure for Outer Storage Container V-4003 Based on Burst Tests”, British Nuclear Fuels, Ltd. report Client Report Project K0103/C/R&P/019/B, February 1997.
DNFSB 1994a	“Plutonium Storage Safety at Major Department of Energy Facilities”, Defense Nuclear Facilities Safety Board”, Technical Report DNFSB/TECH-1, April 1994.
DNFSB 1994b	“Defense Nuclear Facilities Safety Board, Recommendation 94-1, “Improved Schedule for Remediation in the Defense Nuclear Facilities Complex”, letter from John T. Conway to Hazel R. O’Leary, Defense Nuclear Facilities Safety Board, May 26, 1994.
Dodson 1994	“Historical Review of Plutonium Storage-Container Failures at Lawrence Livermore National Laboratory”, Karen E. Dodson, UCRL-ID-117333, Lawrence Livermore National Laboratory, May 1994.
Dodson 1999	K. E. Dodson, Lawrence Livermore National Laboratory, personal communication on plutonium materials storage.
DOE 1993	“Potential Worker Contamination from Failed Plutonium Storage Containers”, US DOE Safety Information Safety Letter Issue Number 93-05, U. S. Department of Energy, Washington, D.C., December 1993.

DOE 1994a	“Assessment of Plutonium Storage Safety Issues at Department of Energy Facilities”, DOE/DP-0123T, U. S. Department of Energy, Washington, D. C. , January 1994.
DOE 1994b	“Plutonium Working Group Report on Environmental, Safety and Health Vulnerabilities Associated with the Department’s Plutonium Storage”, U. S. Department of Energy, DOE/EH-0415, November 1994.
DOE 1994c	“Criteria for Preparing and Packaging Plutonium Metal and Oxides for Long-term Storage”, US DOE Standard DOE-STD-3013-94, U. S. Department of Energy, September 1994.
DOE 1995	“Defense Nuclear Facilities Safety Board Recommendation 94-1 Implementation Plan”, U. S. Department of Energy, DOE/EM-0199, 1995.
DOE 1996	Criteria for Preparing and Packaging Plutonium Metal and Oxides for Long-term Storage”, US DOE Standard DOE-STD-3013-96, U. S. Department of Energy, September 1996.
DOE 1998	“Implementation Plan for the Remediation of Nuclear Materials in the Defense Nuclear Facilities Complex (Revision 1)”, U. S. DOE, December 22, 1998.
DOE 1999	“Stabilization and Storage of Plutonium-Containing Materials”, U. S. DOE proposed Standard DOE-STD-5xxx-99 (Draft). U. S. Department of Energy, September 1999.
Fife 1999	K. Fife, Los Alamos National Laboratory, personal communication regarding plutonium materials storage.
Flanders and Krishnan 1999	“Plutonium Alpha-Beta Expansion and BNFL (3013) Inner and Outer Storage Cans Evaluation (U)”, H. E. Flanders, Jr. and R. P. Krishnan, T-CLC-G-00113, Westinghouse Savannah River Company, March 1999.
Fleischman 1993	S. D. Fleischman, “Recommendations for Resolution of Plutonium Storage Issues Outlined in “Master Plan for Evaluation: F-Area Stored Plutonium”, MP-EFB-93-0108”, Savanannah River Site report SRTC-CTS 93-0281.
Freestone and	“Peer Review of AWE’s Proposal for Interim Storage of

Shaw 1998 Plutonium Containing Materials in Rim Sealed Tinplate Containers", V. Freestone and S. J. Shaw, AWE/CMD/T/074/98, United Kingdom Atomic Weapons Establishment, July 1998.

Freestone 1999 V. Freestone, United Kingdom Atomic Weapons Establishment, personal communication regarding plutonium materials storage.

Hanford 1975 "Investigation Report: Contamination Spread, Room 173, 234-5-Z Building, November 9, 1975", ARH-CD-528, Atlantic Richfield Hanford Company, December 20, 1975.

Hanford 1976 " Investigation Report: Leakage of Plutonium Storage Container, Room 2, 2736-Z Building", Atlantic Richfield Hanford Company, 1976.

Hanford 1979 "Rupture of Plutonium Oxide Storage Container, March 13, 1979", accident investigation report, cover letter by J. J. Fuquay, Battelle-Pacific Northwest Laboratory, June 27, 1979.

Hanford 1980 "Investigation Report of Plutonium Scrap-containing Contamination Incident, Room 230-C, 234-5 Building, October 9, 1980", Rockwell Hanford Operations report RHO-CD-1197.

Hanford 1985 "Event Fact Sheet", August 12, 1985 bulged can observation, SAS-85-002, report dated August 15, 1985.

Hanford 1986 "Event Fact Sheet", March 14, 1986 bulged can observation, SAS-86-001, report dated March 17, 1986.

Hanford 1988 "Event Fact Sheet", August 8, 1988 bulged can observation, 88-324-001, Rev. 1, report dated September 14, 1988.

Haschke et al. 1998 "Oxidation Kinetics of Plutonium in Air: Consequences for Environmental Dispersal", John M. Haschke, Thomas H. Allen and Joseph C. Martz, J. Alloys Comp., 211, 271(1998).

Haschke and Martz 1998 "Plutonium Storage", John M. Haschke and Joseph C. Martz, Chapter in Encyclopedia of Environmental Analysis and Remediation", Robert A. Meyers, Ed., John Wiley and Sons, Inc., 1998.

Hensel 1999a "Thermal Analyses of the 9975 Package with the 3013 Configuration During Normal Conditions of Transport", S. J. Hensel, Westinghouse Savannah River Company report WSRC-TR-98-00420, February 1999.

Hensel 1999b	"Thermal Analyses of the 9975 Package as a Plutonium Storage Container", S. J. Hensel, Westinghouse Savannah River Company report WSRC-TR-98-00203, July 1999.
Kolman 1999	"An Assessment of the Corrosion, Stress Corrosion Cracking, and Embrittlement Susceptibility of 3013 Storage Containers", D. G. Kolman, Los Alamos National Laboratory report LA-UR-98-5762, Revision 1, July 1999.
Martz et al. 1994	"A Mechanism for Plutonium Pyrophoricity", J. C. Martz, J. M. Haschke, and J. L. Stakebake, J. Nucl. Mater., 210, 130 (1994).
Menke and McQuinn 1981	"Investigation of JB-Line Vault Incident", W. A. Menke and R. L. McQuinn, DuPont Savannah River Plant Interoffice Memorandum 221F81-3, Aiken, South Carolina, May 1981.
New York Times 1994	"Stored Plutonium May be a Danger", The New York Times, December 7, 1994, p. A1 and A14.
Pierce 1994	"Pu-oxide Storage Issues - FB-line Can C-39 (U)", R. A. Pierce, WSRC-RP Westinghouse Savannah River Company interoffice memo, August 2, 1994.
Schaade 1994a	"Evaluation of Potential Mechanisms for Can Deformation And Basis for Inspection of FB-Line Can Material in Storage", J. B. Schaade, Westinghouse Savannah River Company Interoffice Memo NMP-EFL-94-0059,, March 15, 1994.
Schaade 1994b	"Results of High Weight Gain SRS Button Repackaging in FB-line Finishing Cabinet", J. B. Schaade, WSRC-RP-94-0757, Westinghouse Savannah River Company internal report, August 3, 1994.
Schaade and Walker 1994	"Inspection of HUA-831 Items in FB-Line Vaults", J. B. Schaade NMP-EFL-94-0057, Westinghouse Savannah River Company interoffice memorandum, March 10, 1994.
Schaade 1995	"Update on Inwardly Deformed Vault Cans", J. B. Schaade, NMS-EFL-95-0104, Westinghouse Savannah River Company memorandum, October 13, 1995.
Schaade 1998	"Repackaging Collapsed Oxide Cans in FB-Line", J. B. Schaade, NMS-ETS-98-0101, Westinghouse Savannah River Site report, December 19, 1998.
Schaade 1999	J. B. Schaade, personal communication regarding 1999 SRS paneled food-pack container, July 1999.

Spearing et al. 1999	"Effect of the Plutonium Alpha-Beta Phase Transition Expansion on Storage Can Integrity", D. Spearing, D. K. Veirs, and F. C. Sprenger, Los Alamos National Laboratory report LA-UR-99-147, 1999
Spearing and Veirs 1999	"Effect of the Plutonium Alpha to Beta Phase Transition", D. Spearing and D. K. Veirs, Los Alamos National Laboratory report LA-UR-99-1363, 1999.
SRS 1979	"Final Report of Special Hazards Investigation No. 338, 200-F Area", Savannah River Site report, 1979.
Stakebake 1992	"Plutonium Pyrophoricity", EG&G Rocky Flats report RFP-4517,, June 2, 1992.
Stakebake 1995	"Failure of Plutonium Storage Containers", J. L. Stakebake, Science Applications International Corporation Technical Report SAIC/OWM-95-001, Golden , Colorado, January 1995.
Stakebake 1998	"Evaluation of Chloride Corrosion of Stainless Steel Cans", J. L. Stakebake, unpublished data from the 1998 Rocky Flats Environmental Technology Site Residue Characterization Program.
Szempruch 1984	"The Effectiveness of Corrective Actions Taken to Preclude Events Involving Tin Cans and Plutonium", R. W. Szempruch, RHO-HS-SA-59 P, May 1984.
Szempruch 1995	"Plutonium Storage Phenomenology", R. W. Szempruch, Westinghouse Hanford Company report WHC-SA-3017-FP, December 1995.
Szempruch 1999	R. Szempruch, B and W Hanford Company, unpublished information.
Tandon et al. 1999	"Information Search on Chloride Salt Radiolytic Effects in Plutonium Storage Environments", L. Tandon, Robert. A. Penneman, and P. Gary Eller, Los Alamos National Laboratory report LA-UR-99-2488, June 1999.
Van Konynen-Burg et al. 1996	"Bulging of Cans Containing Plutonium Residues - Summary Report", R. A. Van Konynenburg, D. H. Wood, R. H. Condit, and S. D. Shikany, Lawrence Livermore National Laboratory UCRL-ID-125115,, March 1996.
Washburn 1983	"Collapsed Plutonium Metal Storage Containers", J. F. Washburn, Rockwell Hanford Operations report SD-RE-TI-106, August 12, 1983.

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MATERIALS IDENTIFICATION AND SURVEILLANCE WORKING GROUP

For several years, Los Alamos National Laboratory has led the DNFSB Research and Development project funded by DOE to resolve technical issues in implementing the national DNFSB 94-1 program. A crucial element of this program is the Materials Identification and Surveillance (MIS) project, in which representative materials from the principal DNFSB 94-1 sites are subjected to detailed characterization. The MIS effort is intended to detect unanticipated conditions that might arise during stabilizing, packaging and storing plutonium materials at the respective sites.

An essential element in focusing the MIS effort and interpreting the resulting information is an active working group comprised of senior subject matter experts with significant management and technical responsibilities at the respective 94-1 sites. Weekly teleconferences, quarterly multi-day workshops, frequent technical data and report reviews, and other frequent information exchanges form the core of this effort. The membership of the MIS Working Group as of June 1999 is as follows:

Hanford Plutonium Finishing Plant	Richard W. Szempruch
Lawrence Livermore National Laboratory	Karen E. Dodson
Los Alamos National Laboratory	Richard E. Mason Nora A. Rink
Rocky Flats Environmental Technology Site	Jerry L. Stakebake Stephen C. Wing
Savannah River Site	James W. McClard

SUBJECT MATTER EXPERTS DISCUSSIONS

Discussions on plutonium storage container failures were held with many subject matter experts other than the MIS Working Group and reviewers of this document. A few of these individuals are listed below. Information was specifically solicited on documented plutonium storage package failure events. Information was collected over the past year in a variety of meetings around the United States during the development of the proposed standard and in numerous individual conversations.

Los Alamos National Laboratory:
- Keith D. Fife
- Larry R. Avens
- Stephen D. McKee
- David R. Horrell

Hanford Plutonium Finishing Plant
- Theodore Venetz

Savannah River Site
- Jeffrey. B. Schaade

TABLE 1. FAILURES FROM METAL OXIDATION OR CORROSION

Case Number (Reference)	Year/Facility	Case Details	Cause of Failure	Failure Avoided by Standards?
SEAL-1 (Szempruch 1984)	1969 Hanford	A fuels-grade plutonium metal button weighing 2 Kg oxidized and ruptured food-pack can after 13 months in storage due to radial growth of oxide. Vault was grossly contaminated. Personnel contaminated upon entering the vault	Leak in the sealed can. Air inleakage oxidized metal and resultant radial pressure caused container failure.	Yes. Container sealing requirements (leak tested welded closure) and redundant barriers prevent air entry.
SEAL-2 (Szempruch 1984)	1970 Hanford	A fuels-grade plutonium metal ingot weighing 2.2 Kg oxidized and ruptured food pack can after about two years in storage vault. Can configuration was sealed can-plastic bag-taped slip lid can. Oxide that formed packed space in can. Radial growth caused failure of can sidewall. Vault was grossly contaminated. Personnel contaminated and internal deposition received upon entry into vault.	Leak in the sealed can. Air inleakage oxidized metal and resultant radial pressure caused container failure.	Yes. Container sealing requirements (leak tested welded closure) and redundant barriers prevent air entry.
SEAL-3 (Szempruch 1984)	1972 Hanford	Plutonium metal oxidized and food-pack can split open in glovebox. Powder accumulation outside can. Contamination confined to glovebox.	Leak in the sealed can. Air inleakage oxidized metal and resultant radial pressure caused container failure.	Yes. Container sealing requirements (leak tested welded closure) and redundant barriers prevent air entry.
SEAL-4 (Stakebake 1995)	1982 Rocky Flats	Two out 27 3-kg alpha plutonium cylinders breached their containers. Packaging was in aluminum cans with steel crimp sealed lid and stainless steel overpack. The overpack closure was a close tolerance fit lid sealed with silicone polymer sealant. These assemblies were submerged in water in experiments. The handling area was contaminated. Upon opening one of the ruptured containers for inspection in a air glovebox, the plutonium and corrosion products spontaneously ignited and the metal burned completely.	Leak in the sealed can. Air inleakage oxidized metal and resultant radial pressure caused container failure.	Yes. Container sealing requirements (leak tested welded closure) and redundant barriers prevent air entry.

SEAL-5 (Dodson 1994; Condit et al. 1987)	1992 Livermore	A seamless aluminum can with screw type lid was filled with 1108 g of Pu metal in 1989. This can was bagged out of the glovebox and placed in a one-gal can for storage. After 32 months, the package was retrieved for processing and the contents of the gallon can transferred into a glovebox. Upon removal of the plastic bags, the aluminum can as found to have split lengthwise due to oxidation of the metal. Approximately 622 g of metal had oxidized.	Leak in the sealed can. Air inleakage oxidized metal and resultant radial pressure caused container failure.	Yes. Container sealing requirements (leak tested welded closure) and redundant barriers prevent air entry.
SEAL-6 (Stakebake 1995)	1992 AWE	A Pu metal button packaged in 1985 inside a screw-top aluminum can as bagged from a glovebox and placed in a metal food pack can with crimp sealed lid. By 1990, the Pu had gained only 3 g of oxygen and by 1992, the plutonium was totally oxidized. The increase in volume of the oxide exerted a radial pressure that destroyed the aluminum can and ultimately caused the food pack cans to rupture, contaminating the storage bin.	Leak in the sealed can. Air inleakage oxidized metal and resultant radial pressure caused container failure.	Yes. Container sealing requirements (leak tested welded closure) and redundant barriers prevent air entry.
SEAL-7 (DOE 1993)	1993 Los Alamos	In 1979, 2.5 kg of cast Pu metal was enclosed in 2-in.-diam vessel made of steel tubing with welded end caps. The cylinder was bagged out of the glovebox and stored in an 8-in.-diam by 15-in.-tall steel can with taped slip-lid closure and stored in a vault. Upon movement of the item to a processing area 14 y later, the handler's protective clothing and a transfer cart became contaminated. The inner welded steel vessel had one end torn away. Evidence was not seen of plutonium metal; only yellow-green oxide powder was observed. Hydride-catalyzed Pu corrosion suspected. Faulty weld on stainless steel container caused leak in the sealed can.	Faulty weld on stainless steel container caused leak in the sealed can. Air inleakage oxidized metal, and resultant radial pressure caused container failure.	Yes. Container sealing requirements (leak tested welded closure) and redundant barriers prevent air entry.
SEAL-8 (Stakebake 1995)	1993 Los Alamos	In 1984, 5 Kg of plutonium metal was removed from a glovebox in a plastic bag and placed in a second plastic bag inside a lead-lined can with a	Comingling of incompatible materials (plastic and plutonium metal) led to formation of pyrophoric	Yes. The standards prohibit the presence of plastic materials in the storage package.

		taped lid seal. Radiolysis of the plastic produced hydrogen, which reacted with the plutonium to form plutonium hydride and/or nitride. The container was opened inside a hood in 1993. Disruption of the brittle plastic caused a massive breach and spontaneous ignition occurred. Both the operator and hood were contaminated.	hydride. Inappropriate containment and handling led to release of the plutonium material.	

TABLE 2. FAILURES FROM GAS PRESSURIZATION

Case Number (Reference)	Year/Facility	Case Details	Cause of Failure	Failure Avoided by Standards?
PRESSURE-1 (Hanford 1975)	1975 Hanford	Can of less than 300 g of plutonium glovebox sweepings ruptured and ejected from storage position in vault. Container was a food-pack can sealed and placed in storage about four days before the event took place. Scrap powder from oxalate precipitation process oxide production line was involved. Some powder from the precipitator/calciner glovebox, reported to be dry and free-flowing, was sealed out and stored without thermal stabilization. Visible oxide contamination of storage vault floor resulted.	Gas generation from unstabilized oxide constituents. Material spilled from oxalate precipitation process glovebox was added to can without calcination.	Yes. The 500-500°C calcination temperature of the subject process produced tons of well-behaved PuO_2 that had measured LOI of <0.5%. The 950°C of the standards far exceeds the demonstrated temperature for this type of material.
PRESSURE-2 (Szempruch 1984)	1984 Hanford	Very similar to case PRESSURE-1, involivng food-pack can of plutonium glovebox sweepings. In this instance, the can was being stored in a shipping container that was closed but not bolted closed for shipment as only temporary storage was intended. The shipping container was so badly contaminated that it had to be discarded.	Gas generation from unstabilized oxide constituents. Material spilled from oxalate precipitation process glovebox was added to can without calcination.	Yes. The 500-500°C calcination temperature of the subject process produced tons of well-behaved PuO_2 that had measured LOI of <0.5%. Thermal stabilization at 500-600°C was used routinely at Hanford during the mid-1980’s . Over a thousand containers of product with LOI (done at 450°C) in the range 0.2-1.0% range resulted. These items have not presented pressurization problems in the 15 years of subsequent storage. The 950°C of the standards far exceeds the demonstrated temperature for this type of material.
PRESSURE-3 (Szempruch 1984)	1976 Hanford	Can of plutonium scrap discovered slightly bulged and leaking an oily appearing substance on storage vault. Slight contamination of storage rack resulted.	Packaging of unstabilized material led to gas generation and corrosion of container. The tin-plated steel containers were designed to hold dry, stabilized materials.	Yes. The 950°C of the standard is adequate to remove gas-generating constituents. Also, corrosive materials are prohibited by the standards.

PRESSURE-4 (Hanford 1979)	1979 Hanford	A storage container containing high decay heat plutonium oxide ruptured, releasing a plutonium oxide aerosol. The room, equipment, and three workers were contaminated. The can had been sealed and removed from the glovebox on the previous day and was in a shipping container for about 12 h just prior to the rupture. The material contained lumps up to 0.5-in. suspected of not being fully heated to the 450 C calciner temperature. The lumps may have been avoided during sampling, making the sample taken not representative. Analysis was specific for water and would not have indicated potential for nitrate decomposition.	Gas generation from insufficient conversion of nitrate to oxide, promoted by self-heating of the high-heat material.	Yes. The 950°C calcination temperature is sufficient to decompose all nitrate constituents.
PRESSURE-5 (Hanford 1980)	1980 Hanford	Enriched uranium/plutonium scrap oxycarbide material was contained in a 1-pound, slip-lid can and enclosed in two layers of plastic. The material spontaneously ignited, causing the container to breach during handling outside of a glovebox. This occurred immediately as the item was taken from the glovebox after being packaged. The room and two operators directly involved with the repackaging operations were contaminated. The material identified was an oxycarbide that had been stored for about 15 years in a brass vial thought to contain kerosene. The event took place within a hour of opening the brass vial. Spontaneously ignited and pressurized can. Gross contamination of room and personnel resulted.	Gas pressurization from inadequately stabilized material, plus formation of pyrophoric products. Interaction with residual hydrocarbons was suspected.	Yes. The 950°C calcination temperature is sufficient to completely convert oxycarbides to stable oxide products.
PRESSURE-6 (Menke and	1980 Savannah River Site	An oxide storage package ruptured due to overpressurization, resulting in contamination of	Radiolytic and/or thermal degradation of organic material present in the	Yes. The 950°C calcination temperature is sufficient to

McQuinn 1981)		a large area of the storage vault. The stored material consisted of glovebox sweepings and reject pressed compacts containing plutonium oxide in contact with an aluminum stearate-dodecanol die lubricant. Inspection of similar packages indicated pressurization from build-up of hydrogen and methane due to radiolytic and/or thermal degradation of the organic material.	plutonium oxide resulted in pressurization and rupture of the storage can.	eliminate organic constituents and produce stable oxides.
PRESSURE-7 (SRS 1979)	1979 Savannah River Site	During removal of cans from a welded stainless steel capsule shipped in an FL-10-1 shipping container, pressure and contamination were released into and out of a plastic containment hut. Pressurization of the capsule occurred during post loading leak testing of the shipping container with helium. Porosity in the capsule closure weld allowed injection of helium into capsule. The capsule end broke away from the body during opening with a pipe cutter. Release of helium pressure from welded capsule during opening of capsule released plutonium oxide into the room and contaminated personnel.	Inadequate leak testing procedures and weld quality.	Yes. Helium leak testing of both inner and outer containers at time of packaging provides assurance that helium cannot leak into container in subsequent testing. Quality assurance requirements on welds should prevent inadequate weld quality.

TABLE 3. EXAMPLES OF UNUSUAL OCCURRENCES WITHOUT FAILURE

Case Number (Reference)	Year/Facility	Case Details	Cause of Failure	Failure Avoided by Standards?
PANEL-1 (Szempruch 1984)	1975 Hanford	Several cans received in a single shipment of fuels-grade plutonium metal were found to be punctured, paneled, charred, or deformed inward. One such deformed can contained about 350 grams of corrosion product. Contamination was observed on inside of several shipping containers.	High decay heat caused abnormally high temperatures in shipping container causing discoloration of cans. The high temperature also enhanced reaction of plutonium with air in the cans, causing paneling. Similar later occurrences indicated formation of plutonium nitride at similar temperatures.	Yes. Containers will be strong enough to withstand total vacuum.
PANEL-2 (Washburn 1983)	1983 Hanford	Two cans containing fuels grade metal buttons were found to be paneled. Decay heat of each button was about 10 W. The buttons had been in storage in food pack cans for 4 and 14 years at the time of the discovery. No contamination was released. Washburn 1983 also mentions two previous similar occurrences. One was Case PANEL-1 and the other was a single Hanford can found collapsed in 1981.	Partial vacuum from metal reaction with air sufficient to panel straight-walled food-pack can.	Yes. Containers will be strong enough to withstand total vacuum.
PANEL-3 (Dodson 1994)	1986 Livermore	Approximately 186 g of Pu scrap metal was bagged out of a glovebox in a pint can, placed in a gallon can and stored in a vault. After 15 months in storage, the gallon can was found to have collapsed under vacuum.	Partial vacuum from metal reaction with air was sufficient to panel can.	Yes. Containers will be strong enough to withstand total vacuum.
PANEL-4 (Schaade 1995)	1995 Savannah River Site	Two vault stored items containing fuels-grade plutonium metal exhibited inward can wall deformation on the outer cans. No contamination was released.	Partial vacuum from metal reaction with air was sufficient to panel can.	Yes. Containers will be strong enough to withstand total vacuum.
PANEL-5 (Bonadie and Szempruch 1999)	1998 Hanford	One of the buttons discussed in Case PANEL-1 spontaneously ignited when opened in an air glovebox in 1975. Oxidation was assumed to be complete when burning ceased. The resultant	Partial vacuum from metal reaction with air was sufficient to panel food-pack can.	Yes. Containers will be strong enough to withstand total vacuum. The 950°C calcination temperature will be

		oxide was placed in two cans and placed in storage. Thirteen years later, the outer can of one of the items was found to be paneled.		sufficient to convert all metal fines to stable oxide.
PANEL-6 (Schaade 1999)	1998 Savannah River Site	A can of scrap mixed oxide derived from Pu/U carbide from FFTF fabrication program was discovered paneled. The container had been stored for about 15 years and paneling had not been observed during previous routine surveillance. The material apparently contained residual Pu/U carbide.	Partial vacuum from carbide reaction with air was sufficient to panel food-pack cans.	Yes. Containers will be strong enough to withstand total vacuum. The 950°C calcination temperature will be sufficient to convert all carbide to stable oxide.
PANEL-7 (Bonadie and Szempruch 1999)	1996 Hanford	Six paneled inner cans were observed in a population of 52 metal items examined by radiography. The cans contained metal ingots each with approximately 12 W decay heat. No rupture of containers was observed. No contamination was detected during handling to obtain radiographs.	Partial vacuum from metal reaction with air was sufficient to panel food-pack can.	Yes. Containers will be strong enough to withstand total vacuum.
PANEL-8 (Schaade 1998)	1998 Savannah River Site	A food-pack container of oxide from LLNL was discovered to be paneled.	The material was not fully oxidized and contained small metal particles. Partial vacuum from metal reaction with air was sufficient to panel food-pack can.	Yes. The 950°C calcination temperature will be sufficient to convert all metal particles to stable oxide. Also, containers will be strong enough to withstand total vacuum.
SEAL-9 (Schaade 1994b)	1993 Savannah River Site	A can containing a Pu metal button was observed to steadily gain weight over a period of 4 years since original packaging. When opened, the inner can was found to have a defective seal. The oxide formed in the inner can filled the can but did not mechanically rupture the can. No contamination was released from the container.	Defective seal allowed entry of air into inner can with subsequent oxidation of metal.	Yes. Container sealing requirements (leak tested welded closure) and redundant barriers to prevent air entry.
PRESSURE-8 (Van Konynen-burg et al 1996)	1994 Livermore	During routine surveillance, two sealed packages, each consisting of concentric double food-pack cans containing calcined plutonium mixed oxide residues, were discovered to have bulging lids.	Gas generation from inadequately stabilized materials.	Yes. The 950°C of the standard is adequate to remove gas-generating constituents.
PRESSURE-9 (Hanford 1985)	1985 Hanford	A container of uncalcined mixed oxide gel sphere material was observed to be bulged.	Gas pressurization from inadequately stabilized materials.	Yes. The 950°C of the standards is adequate to remove gas-generating constituents.

PRESSURE-10 (Hanford 1988)	1986 Hanford	A bulged can was observed. The nature of the contained material was not included in the event fact sheet.	Gas pressurization from inadequately stabilized materials.	Yes. The 950°C of the standards is adequate to remove gas-generating constituents.
PRESSURE-11 (Pierce 1994, Schaade 1994a, Schaade and Walker 1994)	1994 Savannah River Site	Several food-pack containers were observed to be slightly deformed, indicative of an internal pressure of about 10psig.	Most probably caused by a combination of thermal and radiolytic degradation of the PVC bag enclosing the inner container, with a possible small contribution from heating of the can atmosphere.	Yes. The standard does not allow organics in the storage package. Also, containers will be strong enough to withstand total vacuum.