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Title:

GAS PRESSURIZATION FROM CALCINED PLUTONIUM OXIDES

Author(s):

P. Gary Eller, Richard E. Mason, David R. Horrell,
Steven D. McKee, Nora A. Rink and Craig S. Leasure

University of California
Los Alamos National Laboratory

Submitted to:

Peer Reviewed by:

Materials Identification and Surveillance Working Group
Dr. Ralph H. Condit Lawrence Livermore National Laboratory
Mr. Jeffery B. Schaade Westinghouse Savannah River Company
Dr. Martin G. Seitz Booz-Allen and Hamilton, Inc.
Dr. David C. Moody Los Alamos National Laboratory

ABSTRACT

In this report, studies and observations of gas pressurization from pure and impure plutonium oxides are evaluated within the context of the current (DOE-STD-3013-96) and proposed (DOE-STD-5xxx-99) plutonium stabilization, packaging and storage standards. A conceptual framework for this evaluation is presented. The available information indicates that gas pressures will not exceed the 699 psia design pressure of the welded steel packages if the stabilization and packaging requirements of the standards are followed. Available information shows that the required calcination conditions (950°C for two hours in an oxidizing atmosphere) are sufficiently robust to eliminate all significant sources of pressurization significant with respect to the pressure design criterion, and that actual bounding pressures for such materials are likely to be less than 100 psig.

In sealed packages at anticipated storage temperatures, only moisture readsorbed after calcination is identified as a concern with respect to gas generation. The most problematic materials in this regard appear to be materials with relatively high calcium and / or magnesium content (particularly as chlorides). The requirement of the standards that the moisture content of packaged materials be less than 0.5 wt.%, combined with the effectiveness of hydrogen and oxygen recombination, ensures that pressure from desorption of readsorbed water will not exceed the pressure design criterion. However, appreciable moisture desorption theoretically could lead to early and potentially misleading pressures above the 100 psig indicator threshold of the proposed standard under some circumstances.

A number of peer-reviewed publications, and many unpublished observations from decades of experience, indicate that small amounts of hydrogen, carbon monoxide, and carbon dioxide (but little or no oxygen generation or overall pressurization) can occur in sealed packages of calcined oxides with plutonium content covered by the standards (ranging from impure 30 wt.% plutonium oxide to pure oxide containing 88 wt.% plutonium). Based on the empirical evidence currently available, it appears that the bounding assumption of both standards that water is decomposed entirely to hydrogen gas (and no oxygen) does not occur in practice. Indeed, the preponderance of current evidence suggests that the bounding pressure that actually will be observed may be less than 100 psig due to a number of factors which self-limit gas pressurization.

With the possible exception of moisture desorption under some conceivable circumstances, to date no clearly credible pressure generating mechanism is apparent that would challenge the 699 psig design pressure. However, it is strongly recommended that an effective gas surveillance program be continued well into the storage phase as insurance against surprises from the complex materials being addressed. This surveillance program should be closely integrated between the stabilization / packaging sites, the storage sites, and supporting research and development efforts. Additionally, research should continue to elucidate the nature of the interaction of water with complex oxide materials. Ongoing research should include additional characterization of

impure materials at bounding materials temperatures and evaluation of moisture readsorption between calcination and packaging.

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I. Introduction

A substantial quantity of plutonium-bearing materials which are excess to needs of the United States' defense awaits ultimate disposition. Because disposition may not occur for a considerable length of time, it has been decided to plan for storage of material in a stable form requiring minimal surveillance for a period up to fifty years. Vulnerabilities in the safe storage of plutonium-bearing materials have been documented in recent years in a number of summary reports and reviews. (e.g., see DOE 1994a, 1994b, DNFSB 1994a, Haschke and Martz 1998) Concerns about these vulnerabilities led to issuance of Recommendation 94-1 by the Defense Nuclear Facilities Safety Board (DNFSB 1994b). In response, the U. S. Department of Energy (DOE) issued an implementation plan to resolve the issues raised in the DNFSB recommendation. (DOE 1995) The implementation plan recently has been updated. (DOE 1998)

An existing standard (DOE-STD-3013-1996) which supercedes a prior standard addresses the stabilization, packaging and storage of metals and oxide materials containing at least fifty weight percent (wt.%) plutonium. (DOE 1994c; DOE 1996) A proposed standard (DOE-STD-5xxx-99) would extend the lower concentration of acceptable oxide material to thirty wt.% actinide content and additionally reduce the allowable wattage per package from thirty to nineteen watts. (DOE 1999). A key issue addressed in these standards is elimination of the possibility of sufficient gas generation to compromise the storage container.

The purpose of this report is to evaluate studies and observations related to gas pressurization during long-term storage of pure and impure plutonium oxides, within the context of the current and proposed plutonium stabilization, packaging and storage standards. A conceptual framework for this evaluation is presented. The information surveyed includes scientific journal articles, topical summaries and technical reports published over the past few decades. In addition, a number of recent highly-focused peer-reviewed reports are cited which have resulted from the DNFSB 94-1 Research and Development (R&D) program led by Los Alamos National Laboratory (LANL). The behavior of residues, wastes, unstabilized materials, and other materials outside the scope of the standards are not addressed herein.

A component of the R&D program, the Materials Identification and Surveillance (MIS) project, has characterized thirty three items typical of a substantial portion of the plutonium oxide inventory to be stabilized and packaged at the Rocky Flats Environmental Technology Site (RFETS) and the Hanford Plutonium Finishing Plant (Hanford). A recent MIS report summarizes a large amount of the resulting data (including gas surveillance data). (Mason et al. 1999) The plutonium content in these items ranged from four to eighty six wt.%, compared to the greater than thirty wt.% minimum actinide content acceptable under the proposed standard. The MIS gas surveillance data are interpreted in the present report within the context of the current and proposed standards, together with information from other sources.

II. Conceptual Model for Calcined Impure Plutonium Oxides

Elemental and isotopic characterization has been performed on thirty three RFETS and Hanford oxide items by MIS and the originators of the materials. (Mason et al. 1999) Phase-specific characterization has been conducted by x-ray diffraction on twenty six items. (Mason et al. 1999, Morales and Peterson 1999) In addition, approximately five hundred analyses have been performed recently by scanning electron microscopy / energy dispersive spectroscopy on individual areas of selected as-received and calcined items. (Smith and Neu 1999) Headspace gas pressure and composition data also have been collected for selected items. (Mason et al. 1999)

Based on the data collected to date and the anticipated post-calcination behavior of the dominant impurities known to be present, a conceptual model for impure calcined plutonium oxides has evolved. By its very nature, a conceptual model does not purport to lay to rest all technical aspects of an issue. Instead, a conceptual model provides an intellectual framework for evaluating a broad range of data and for posing relevant hypotheses that can be tested through additional work. The conceptual model is thereby improved as additional data is acquired. Based on information to date, the conceptual model assumes that plutonium in calcined impure oxides exists predominantly as plutonium dioxide, with a minor component of plutonium oxychloride in some cases. Dominant impurity phases are assumed to be of three types: 1) chloride salts of sodium, potassium, calcium, and magnesium, 2) binary and complex oxides involving Fe(III), Cr(III), Ga(III), Ni(II), and Cu(II) with surface water chemical properties similar to those of PuO_2 and 3) alkaline earth oxides (CaO, MgO) with greater affinity for moisture than other oxides. Because effects of impurities are expected to be mass-action driven (e.g., limited by the amount of adsorbed water that can be decomposed or desorbed), trace impurities are assumed to have no significant impact on safe storage. Details of the conceptual model are developed in the remainder of this report.

III. Potential Gas Pressurization Mechanisms

Four types of pressurization mechanisms have been identified for plutonium oxide storage packages prepared according to the standards: thermal heating of the initial gas, helium generation from radioactive decay, gas generation from radiolytic and chemical degradation, and desorption of water adsorbed between calcination and packaging. These mechanisms are evaluated below.

1. Thermal Heating. Internal heating of container fill gas from radioactive decay of the plutonium oxide material and the external ambient environment will increase pressure in storage containers. Thermal modeling has been performed on scenarios involving packages containing nineteen watts of oxide, packaged according to the standards and contained in 9975 shipping packages under various conditions. (Hensel 1999a,b) For a bounding shipping scenario with direct solar exposure of the shipping packages, Hensel's reports indicate a maximum oxide material temperature of 275°C could be achieved. In Appendix

A of the proposed standard, an average gas temperature of about 211°C is derived from the average of the maximum oxide material temperature and the maximum container temperature of 147°C for this scenario. (DOE 1999) If one assumes closure of a typical oxide package with an ambient fill gas temperature of 25°C and pressure of about 14 psia and further assumes heating to an average gas temperature of 211°C, the resulting total gas pressure increases to about 23 psia. The pressure increase likely would be realized within a matter of days or weeks under the bounding shipping conditions.

2. Helium from Radioactive Decay. Helium is produced as a direct product of alpha radioactive decay. Appendix B of the proposed standard contains a calculation of the amount of helium produced from 12.4 watts (the approximate wattage of five kilograms of typical pure weapons-grade plutonium oxide) during storage. (DOE 1999) In a typical package configuration with an average gas temperature of 204°C, the theoretical helium pressure was calculated to be about 13 psia after fifty years. In practice, the actual helium gas pressure to be realized will be less than the theoretical value due to trapping of helium in the solid matrices.

3. Radiolytic and Chemical Degradation. Both the current and proposed standards specify calcination at 950°C to minimize or eliminate potential gas-generating constituents such as organics, adsorbed moisture and hydroxides, halides, and oxyanions such as nitrate, sulfate and carbonate. Both standards also specify storage in leak-tested gas-tight steel containers to eliminate the possibility of adsorption of gas-generating constituents during storage. Testing is required by the standards to ensure that moisture readsorption between calcination and storage is limited to less than 0.5 wt.%. The effectiveness of the specified calcination treatment in removing potential gas-generating constituents is discussed below. Figures 1 and 2, discussed later in this report, provide examples of gas surveillance tests from the MIS program. A recent peer-reviewed report summarizing plutonium storage package failures provides an analysis of package failures that supports the adequacy of the standards' calcination conditions to remove gas-generating constituents, since no pressurization failures have been documented for reasonably stabilized and packaged oxide materials. (Eller et al. 1999)

A. Organics. 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. Numerous plutonium storage package failures have been reported that are linked to the presence of organic materials. (e.g., see DOE 1994a, DOE 1994b, DNFSB 1994a, Haschke and Martz 1998, Eller et al. 1999) The technical combustion literature conclusively establishes that plastics less than about one inch in diameter and any other organics likely to accompany unstabilized plutonium materials are completely oxidized in air in less than five minutes at 800°C or above. (ACS 1995, Bockhorn et al. 1996, Panagiotu and Levendis 1996, Wey and Chang 1995, Zevenhoven et al. 1997) It is presumed that larger plastic pieces will be removed after visual examination prior to calcination, but the literature indicates that even these will be effectively destroyed by calcination at

950°C for two hours as prescribed by the standards. The recent MIS data report shows that carbon content was reduced by calcination at 950°C for two hours to 0.24 wt.% or less for thirty three MIS items, even when the as-received carbon content was many tens of wt.%.

B. Halides. The possibility of chlorine gas generation from radiolysis of chloride salt impurities in impure plutonium oxide has been evaluated in a recent peer-reviewed report. (Tandon et al. 1999a) This report concluded that radiolytic effects on chloride constituents are not likely to pose unique and unacceptable safety risks when plutonium materials have been stabilized according to the standards. These conclusions were based on the radiation effects literature, recent technical and summary reports, and direct discussions with numerous subject matter experts with extensive relevant experience in plutonium processing.

The recent MIS data report shows that calcination at 950°C for two hours reduces the chloride content to less than 8 wt.%, even when the initial chloride content was above 20 wt.%. (Mason et al. 1999) The potential for gas generation from chlorides is reduced correspondingly. Significant levels of chlorine or hydrogen chloride have not been observed in the MIS gas surveillance program. Significant corrosion (indicative of chlorine and hydrogen chloride gas evolution) of containers holding plutonium pyrochemical salts has not been reported when highly oxidizing constituents and excess water have been eliminated. (Tandon et al. 1999a)

C. Oxyanions. The technical literature shows that oxalates and nitrates of plutonium are effectively converted to oxides by calcination well below 950°C. (e.g., see Wick 1980 and Waterbury et al. 1961) The literature also indicates that carbonates, nitrates and oxalates with other cations are decomposed effectively at this temperature. As mentioned above, the recent MIS data report shows that carbon content is effectively reduced to nominal levels by the required calcination conditions.

Plutonium sulfate is decomposed effectively by 950°C calcination. (Waterbury et al. 1961) Sulfate is known to be incorporated into plutonium oxide prepared by peroxide precipitation from sulfuric acid solutions. (Leary et al. 1959) The report of Moseley and Wing (1995) shows that 950°C calcination is sufficient to destroy this sulfate constituent. Although sodium sulfate and potassium sulfate are reported to be stable to temperatures well above 950°C, a recent literature review indicates that deleterious amounts of radiolytic gases from residual sulfate is highly improbable. (Weast 1965; Tandon et al. 1999b) The recent MIS data report indicates that calcination reduced residual sulfur content of thirty three MIS items to less than 0.8 wt.% (and usually much less), even when the initial sulfur content was as high as 4.1 wt.%. (Mason et al. 1999)

D. Adsorbed Moisture and Hydroxides. A key element of the technical basis of both the current and proposed standards is that water uptake on calcined plutonium oxide is controlled by the oxide surface area. Published reports indicate that the surface area of plutonium oxide calcined at 950°C is consistently below 5 m^2/g regardless of the oxide origin (e.g., see Haschke and Ricketts 1995, Manchuron-Mandard and Madic 1996). The recent MIS data report indicates this is true not only for the relatively pure oxides but for impure oxides as well. (Mason et al. 1999)

The MIS measurements on pure and impure oxides, and prior work on pure oxides, show that 950°C calcination reduces residual moisture content to under 0.5 wt.%, and typically under 0.2 wt.%. (e.g., see Haschke and Ricketts 1997 and references therein, Mason et al. 1999) Note that in this context, "moisture" refers both to water and related species such as surface-bound hydroxide. These reports indicate that essentially all surface-bound hydroxide is decomposed by 950°C calcination. Many stoichiometric hydroxides also are decomposed below this temperature.

The molar quantity of gas represented by 0.5 wt.% water theoretically could be exceeded if the water is dissociated to significant quantities of both hydrogen and oxygen. However, the available empirical information clearly indicates that substantial pressures of hydrogen and oxygen do not evolve in containers of well-calcined plutonium oxides regardless of purity. Mechanisms that prevent the buildup of substantial pressures of hydrogen and oxygen, or of either alone, under these conditions are discussed in Lloyd et al. (1999) and Section VIII of this report.

Notable scientific reports have been published on pragmatic and fundamental details of water interactions with actinide oxides. (e.g., see Stakebake 1973, Haschke and Ricketts 1997, Ritchie 1981, Baloocha and Hamza 1996, Morales et al. 1999, Manner et al. 1999). While some unresolved scientific issues remain to be clarified, the general outlines of the process are believed to be understood. Figure 3 schematically indicates the behavior of pure water and adsorbed water in a sealed system. Figure 4, taken from Stakebake and Steward (1973), shows the conceptual nature and energetics of moisture adsorption on plutonium dioxide. For a plutonium dioxide surface area of about 5 m^2/gm, 0.1 wt.% moisture content corresponds to approximately two hydration layers. As indicated in Figure 4, the first two layers are reported to be bound with enthalpies of about 20 and 68 kcal/mole. Figure 4 also indicates that additional moisture layers are more weakly bound layers and can be released below 400°C. Similar bonding energetics are expected for the interaction of water with UO_2. Additional aspects of radiolytic and chemical interactions of plutonium oxides with water are discussed later in this report.

Generalizations on water interactions with widely studied metal oxide surfaces typical of impurity phases (e.g., Fe_2O_3 and Cr_2O_3) can be inferred from many past studies. (e.g., see Henrich and Cox 1996, Thiel and Madey 1987) The general nature of the interactions on transition metal oxides are conceptually similar to those with actinide oxides. For example, water reacts with essentially all oxide (and metal) surfaces to produce strongly bound surface adsorbed hydroxyl moieties. These chemisorbed surface species dominate the observed surface chemistry of most (if not all) metal oxides at elevated temperatures. At high temperature, associative recombination of surface hydroxyls occurs to regenerate water vapor (and in many cases, H_2 also). The heat of reaction of the latter process is observed to be material dependent and the oxide surface is regenerated by the water evolution reaction. Water in the second adsorption layer typically desorbs from this hydroxylated surface with an enthalpy value of 15-20 kcal/mole. Subsequent layers of adsorbed water on metal oxide surfaces typically have enthalpies of reaction similar to the that of the vaporization of bulk water, i.e. about 10 kcal/mole.

At elevated temperatures in sealed storage containers, desorbed moisture theoretically could move preferentially from solid phases weakly binding water (e.g., $CaCl_2$) to phases with greater moisture affinity. If desorbed moisture moves to plutonium oxide, the 0.1-0.2 wt.% capacity for strongly-bound moisture normally expected for 950°C calcined oxide could be exceeded, and theoretically the moisture content on the oxide phase could exceed even the equivalent of 0.5 wt.% moisture. This process, if it happens, could affect the radiolytic behavior of the adsorbed water. The ongoing 94-1 R and D program is addressing the possibility of non-uniform water distribution in calcined oxides.

4. Moisture Readsorption, Desorption, and Hydrolysis involving Chloride Salts.

From the preceding discussion, it may be concluded that the calcination requirement of the current and proposed standard is adequate to eliminate all known gas generation mechanisms of significance from plutonium oxides (both pure and impure). Therefore, the issue of gas pressurization sufficient to challenge the 699 psia safety criterion of the standards is reduced to consideration of gases readsorbed from glovebox air in the period between calcination and packaging. Only water should present a significant issue in this regard if, as expected, the period between calcination and packaging is sufficiently small that adsorption of trace atmospheric gases such as CO_2 is inconsequential. In addition, the standards require demonstration that the moisture content of the packaged material is less than 0.5 wt.%. For the maximum material mass of five kilograms allowed by the standards and under anticipated package configurations, the molar quantity represented by this water content will not give rise to pressures exceeding the 699 psia criterion under anticipated conditions. (DOE 1999)

The behavior of common chloride salt impurities in plutonium oxides derived from pyrochemical operations has been considered in the context of the standards. Accordingly, a literature search was conducted on the amount of water retained on NaCl, KCl, $MgCl_2$, and $CaCl_2$ as a function of temperature and relative humidity. (Smith et al. 1999) The available literature, while limited, indicates that heating sodium chloride to about 420°C and potassium chloride to about 300°C removes essentially all adsorbed water. (Smith et al. 1999, Duval 1963) Hydrolysis of these salts to form hydroxides occurs only at higher temperatures and then only to an insignificant extent. (Smith et al. 1999) Kaufman reported that normal mined halide salts have a moisture content ranging from 0 to 0.4 wt.%, depending upon the surface area, and that the deliquescence point of sodium chloride is about 75% relative humidity at room temperature. (Kaufman 1971) It thus is evident that dehydration of sodium chloride will be completed for all practical purposes by 950°C calcination and that moisture readsorption on this phase should not be significant unless exposure to very high glovebox humidities occurs.

While published literature regarding adsorption / desorption of water with potassium chloride is limited, it appears to have lower affinity for moisture than does sodium chloride. (Smith et al. 1999) For example, the deliquescence point of potassium chloride at room temperature is in the range 80-90% relative humidity. (Luna et al. 1998, Tang and Munkelwitz 1994). For an equimolar mixture of sodium and potassium chlorides, Tang and Munkelwitz (1994) reported a deliquescence point of 72% relative humidity.

The high hygroscopicity of calcium and magnesium chloride is well known and both salts will readily deliquesce under common atmospheric conditions. Therefore, particular care must be taken in handling stabilized oxides containing $MgCl_2$ and $CaCl_2$. Both compounds form stoichiometric hydrates which are highly hygroscopic at room temperature yet readily release moisture with modest heating, a property which makes calcium chloride useful as an atmospheric drying agent.

A deliquescence point of 35% relative humidity at room temperature has been reported for calcium chloride. (Tang and Munkelwitz 1994) Calcium chloride hexahydrate is reported to evolve four waters of hydration at 30°C and the remaining two waters at 200°C. (Weast 1965) The analogous hydrate of magnesium chloride has been reported to decompose at 116-118°C, as confirmed by thermogravimetric studies which also indicated complete conversion to magnesium oxide by about 613°C under conditions of the measurement. (Weast 1965, Duval 1963, Duval and Wadier 1960) Assessment of x-ray diffraction and elemental composition data reported by Mason et al. (1999) for plutonium oxides containing appreciable magnesium chloride content shows that appreciable (but not complete) conversion to magnesium oxide occurs as a result of 950°C calcination. (Mason et al. 1999) Calcium oxide could have formed but at levels below the x-ray diffraction detection limit. Beyond these studies, the published technical literature on the rates moisture adsorption / desorption on calcium and magnesium chloride is scant. (Smith et al. 1999)

Relatively large particle sizes for NaCl, KCl, $MgCl_2$ and $CaCl_2$ might be expected because their melting points are well below the 950°C calcination temperature specified by the standards. (As per Weast 1965, the melting points are as follows: 801°C-NaCl, 776°C-KCl, 708°C-$MgCl_2$, 772°C-$CaCl_2$.) However, the particle size behavior in materials containing these chlorides has not yet been addressed definitively. As-received chloride salt content in thirty three MIS items was found to be well under twenty wt.% in all cases except one. (Mason et al. 1999) The MIS data also show that residual chloride salt content was substantially reduced due to distillation of NaCl and KCl during calcination. These factors, occlusion of chlorides by oxide constituents, and coating of $MgCl_2$ by less hygroscopic hydrolytic products will mitigate the moisture affinity of chloride impurities. The finite diffusion times through beds of calcined materials also will retard the rate of readsorption.

Although the 0.5 wt.% moisture criterion ensures that the 699 psia pressure threshold will not be challenged during storage and a number of mitigating factors will be operative, the behavior of readsorbed water on magnesium and calcium chlorides (and to a lesser extent, their oxides) nevertheless is an important consideration for storage. These phases are expected to be the most hygroscopic constituents to be encountered during stabilization and packaging of materials under the standards. They have the additional unfortunate property of readily desorbing water within the range of shipping and storage temperatures being considered. Because dissociation reactions of this type are characteristically very rapid, heating materials containing such constituents could give rise to early and potentially misleading pressure indications. For example, lid deflection at <100 psi from moisture desorption might not necessarily represent an unsafe condition but could be misinterpreted as such if not understood. Ongoing tests in the 94-1 R and D program are evaluating the possibility and extent of such processes.

Figure 3 shows the liquid / vapor curves for pure water (solid curve) and a hypothetical material with adsorbed water (dashed curve) over the temperature range 100-300^{o}C. The horizontal separation of the two curves is determined by the enthalpy of moisture adsorption. The pressure / temperature dependence of an ideal gas also is indicated. Depending upon the amount of water present and the enthalpy of adsorption, it is theoretically possible for appreciable water partial pressures to develop from desorption and even for liquid water to exist in the package at temperatures above 100^{o}C. Although these effects have not actually been reported during storage of pyrochemical salts and a number of mitigating factors work to minimize the possibility (see Section VIII), ongoing experiments are addressing this point. Nevertheless, it is recommended that materials with high calcium and magnesium chloride content be stabilized and packaged with appropriate controls to minimize significant moisture readsorption and the possibility of subsequent desorption.

Unlike sodium and potassium chloride, magnesium and calcium chloride can be converted substantially to their oxides by gas-phase hydrolysis reactions under some circumstances. (e.g., see Coluccia et al. 1987, Duval 1963) X-ray diffraction results summarized in Mason et al. (1999) indicates that this reaction occurs to a detectable extent at least for magnesium chloride as a result of 950^{o}C calcination of some impure plutonium oxides.

Magnesium oxide has been reported to be relatively inert at room temperature to relative humidities less than about 30 %, but to interact rapidly with water at 100% relative humidity. (Smith et al. 1999, Holt et al. 1997) Coluccia et al. (1987) reported that a pellet of magnesium oxide left in contact with water vapor for forty minutes absorbed 2.4 monolayers of water. The rehydration of calcium oxide after calcination at 750-1100^{o}C has been reported. (Machiel-Camacho et al. 1997)

The hygroscopicity of plutonium trichloride, a possible component in some pyrochemical salt mixtures, is well known. (Wick 1980) A weight increase of about 0.5 wt.% was indicated on exposure at 15°C for 2-3 hours to a 74% relative humidity atmosphere. (Rasmussen and Hopkins 1961) At a relative humidity of about 10%, approximately 200 hours of exposure was required to achieve a 0.5 wt.% gain. Plutonium oxychloride has been detected by x-ray diffraction in some MIS impure oxides after calcination, presumably the product of partial hydrolysis of plutonium chlorides. (Morales and Peterson 1999, Mason et al. 1999)

Hydrolysis of chloride salts results in the formation of hydrochloric acid and the respective metal oxide or oxychloride. Consideration of the ionic charge/size ratio and of hydrolysis data in the compendium of Baes and Mesmer (1976) suggests the following tendency to undergo hydrolysis reactions:

$$\mathrm{Pu(IV)\sim Ga(III)\sim Fe(III)>Mg(II)\sim Ni(II)>Pu(III)>Ca(II)}$$

Complete hydrolytic consumption of 0.1 wt.% of moisture in five kilograms of material (equivalent to five grams or 0.28 moles of water) theoretically generates 0.56 moles of hydrogen chloride. Figure 3 illustrates the possible pressure response of this amount of ideal gas. With the assumption of about one liter of gas void space, this amount of hydrogen chloride would generate about 22 atmospheres (about 330 psia) of pressure at 200°C. With partial hydrolytic conversion, therefore, there is potential for forming concentrated hydrochloric acid solutions if liquid water is available. This scenario, if it were to occur, would present a serious concern with respect to stress corrosion cracking of the stainless steel container. However, there is no operational indication that this process actually occurs in sealed containers of plutonium oxide materials. The anticipated very low oxygen gas partial pressures also will tend to mitigate possible stress corrosion cracking. The use of boiling saturated aqueous magnesium chloride in an accelerated ASTM test for stress corrosion cracking of stainless steel implies that hydrolysis of magnesium chloride should not be a significant concern for plutonium storage containers, where conditions should be much less aggressive. (ASTM 1987) Tests currently are being conducted to determine what conditions, if any, would promote undesirable hydrolytic reactions of this type.

IV. Practical Experience with Storage of Calcined Plutonium Oxides

As discussed above, a key concern in storage of plutonium-bearing materials is avoidance of unacceptable gas pressurization. The evolution of appreciable quantities of hydrogen and other gases from plutonium-bearing wastes, residues, inadequately stabilized oxides and incompatible materials is well known. (e.g., see DOE 1994a, DOE 1994b, DNFSB 1994, Haschke and Martz 1998). In contrast, documented cases of plutonium storage package failures caused by gas pressurization from reasonably stabilized and packaged oxide materials have not been reported, as indicated by a recent peer-reviewed assessment of the available information on this topic. (Eller et al. 1999) This review included experience both in the DOE complex and at the United Kingdom’s Atomic Weapons Establishment. (Freestone and Shaw 1998, Freestone 1999). This statement must be tempered with the fact much of the past storage involved food-pack containers, which have exhibited a tendency to be non air-tight, and containers with slip-lids that never were intended to be airtight. Nevertheless, considering the tens of thousands of food-pack cans that have been used to store plutonium oxides of widely varying pedigree calcined under varying conditions in the U.S. and United Kingdom, we judge it to be highly probable that significant gas-generating mechanisms would have been detected during such storage.

V. Gas Pressure Measurements For LANL 3013-94 Type Packages

During a recent processing campaign at LANL, six cans of plutonium oxide were packaged according to the DOE-STD-3013-94 standard. (Mason et al. 1999, Hagan 1996, Hagan and Fry 1999) The material consisted of pure plutonium oxide powder obtained from metal oxidation, with a measured loss of ignition at 1000°C of 0.025 wt.%. Bellows were installed in each can for monitoring pressure changes. To date, the containers have been in vault storage for more than two years. No significant bellows length changes have been observed by radiography for these containers. It is estimated that pressure changes of +/- 1.6 psi can be detected by this method. (Hagan and Fry 1999) Assuming one liter of gas void space at 200°C and five kilograms of material, the molar equivalent of 0.025 wt.% water theoretically could yield a gas pressure of about 39 psia.

In a separate case, a double-welded 3013-type container was loaded with 2.85 kilograms of plutonium oxide containing 85 wt.% plutonium, after storage of the material in a slip-lid container/PVC bag/slip-lid container configuration for about one year in the LANL plutonium facility vault. At the time of packaging in the 3013 container, the measured loss on ignition at 1000°C was 2.1 wt.%, compared to a neutron moderation moisture measurement of about 0.30 wt.% (uncalibrated for matrix effects) and an interstitial gas measurement of 1.1 wt.%. The surface area of the material was 32 m^2/g. Radiographic measurement after about one year showed a shortening of the bellows indicative of a pressure increase of about 8.3 psi during this period. No additional pressurization within the estimated detection limit has been observed after more than one additional year of storage.

In summary, these observations show that relatively pure oxide material with moisture content near or perhaps even somewhat above the 0.5 wt.% moisture does not undergo unacceptable pressurization under vault storage conditions, even after prior storage in slip-lid cans where additional moisture adsorption was possible prior to storage in welded containers. These results are consistent with decades of operational experience in storing oxides under vault conditions.

VI. Headspace Gas Analysis of Aged Hanford Items

Headspace gases of ten sealed containers of plutonium oxide materials recently were characterized, as described in the MIS data report. (Mason et al. 1999) Tables 1 and 2 summarize results from this report. Nine of these items were received from Hanford and had been in vault storage for ten to eighteen years. Five of these items had been received earlier by Hanford from RFETS. One more recently packaged item was chosen from LANL's vault (HRA-905191). A characterization report is available for this item. (Allen et al. 1997) This item originated at Argonne National Laboratory and was repackaged at Hanford prior to shipment to Los Alamos in 1980. The package contained two discrete items of unstabilized material with substantial thorium and organic content. The processing and packaging history of the five ARF samples originating at RFETS unfortunately is not known, although it can be inferred that all except ARF-102-85-114-1 were derived from plutonium pyrochemical processing since they contain appreciable amounts of chloride salts. Sample selection was made by the MIS Working Group, composed of site representatives from the principal DNFSB 94-1 sites at LANL, Hanford, RFETS, the Savannah River Site (SRS), and Lawrence Livermore National Laboratory (LLNL).

The Hanford package configurations consisted of an inner convenience can, at least one inner food-pack can, a bagout can, and at least one outer food-pack can. Each inner and outer can was tested for gas-tightness and total pressures were determined. Mass spectrometry was used to analyze the composition of headspace gases. Of the nine Hanford packages, four of the inner cans and six of the outer cans were determined to be non gas-tight. (Mason et al. 1999) The six gas-tight inner can items are highlighted in Tables 1 and 2, where the inner gas pressures and compositions are presented.

A key observation from the data in Table 1 is that pressures in all cans determined to be gas-tight were found to be less than 750 torr. Thus, even after vault storage of highly impure materials with uncertain histories (e.g., HRA-905191, PSU-84-06-05 and ARF-102-85-355; 17, 15 and 45 wt.% plutonium respectively) for up to fourteen years, no significant gas pressurization was observed. It is also noteworthy that moisture content in most cases was relatively low, even in situations where both containers were shown not to be air-tight and the oxide had substantial impurities of magnesium and chloride (e.g., ARF-102-85-295, with chloride content >20 wt.% and magnesium content 6.8 wt.%). (Mason et al. 1999)

Several observations of note can be made from the headspace gas data in Table 2. The first observation is that no significant percentages of any gases were observed other than air components and H_2 (two items, 29 and 48%), NO (one item, 1.8%), CO_2 (up to 14%), and CO (one item, 10%). The CO and NO observations were for BLO-39-11-14, one of the two items in Table 2 with appreciable non-weapons grade plutonium. The other item of this type, PSU-84-06-05, exhibited the highest CO_2 content. Most of the items for which CO and CO_2 were detected also had elevated carbon content, although PSU-84-06 (14% H_2) is a notable exception (as received carbon content was determined to be about 0.04 wt.%).

A second key observation from Table 2 is that only two items generated an appreciable percentage of hydrogen gas. Item HRA-905191 (29% H_2) contained macroscopic quantities of organic material, as noted above. Item ARF-102-85-365 contained detectable carbon (0.4 wt.%), as well as percentage levels of chloride, magnesium, sodium and potassium. The moisture content of this item was found to be 0.51 wt% by interstitial gas analysis and 0.15 wt.% by the supercritical fluid extraction method, compared to a much higher loss on ignition at 1000°C value of 9.32 wt.% presumed to be due to loss of sodium and potassium chloride.

A third key observation from Table 2 is that in the three cases in which oxygen gas was observed, no significant hydrogen gas was detected. Conversely, in the two cases in which hydrogen was measurable, oxygen content was below the detection limit.

A fourth key observation is that in all instances the oxygen concentration was found to be significantly depressed (drastically so in all cases except ARF-102-85-223), even for the containers determinedto be leakers. Depression of oxygen content in the leaking containers indicates that the leaks are small and that oxygen consumption is a dynamic process that exceeds the leak rate.

VII. Headspace Gas Analyses of 10-Gram MIS Surveillance Samples

The recent MIS data report describes gas surveillance of seven gas-tight containers that have held 10-gram samples of MIS plutonium oxides for up to 618 days, as listed in Table 3. (Mason et al. 1999) Total pressures were monitored continuously and headspace gases were analyzed periodically by mass spectrometry. Two examples of gas behavior with time are illustrated in Figures 1 and 2, reproduced from the MIS data report. Substrate selection, fill gas and other experimental protocols for the tests were made by the MIS Working Group. Because of the small size of the samples, the material and gas temperatures were essentially at room temperature.

One set of three ten-gram samples (labeled PPSL-365) was derived from a single as-received Hanford vertical calciner product containing 83 wt.% plutonium and principal impurities of about 5.0 wt.% Mg and 1.6 wt.% Ca. The three samples were sealed with helium fill gas into the surveillance capsules as received, after 600°C calcination, and after 950°C calcination.

A second set of two ten-gram samples (labelled ARF-102-85-295) consisted of RFETS pyrochemical salt material that had been stored at Hanford for more than ten years. Air was used as the fill gas. The as-received item is notable because the material contained only about 30 wt.% Pu and had impurities (wt.%) of Cl (> 20), Mg (6.8), K (5.4), Na (3.7), Fe (2.5), and Ni (2.0). After calcination, the wt.% Pu increased to about 39 wt.% as a result of substantial loss of sodium and potassium chlorides during calcination.

A sixth ten-gram sample (labelled BLO-39-11-12-004) was relatively pure as-received Hanford material containing about 88 wt.% fuels-grade plutonium and appreciable americium. Air was used as a fill gas.

The seventh ten-gram sample (C1407AB) was as-received RFETS oxide containing about 63 wt.% plutonium and 11 wt.% uranium. The principal impurities (wt.%) were Ni (4.3), S (4.1), and Ga (0.8). Nitrogen was used as the fill gas.

Several key conclusions can be derived from the original MIS data report and the data reproduced in Table 3 and Figures 1 and 2. The first conclusion is that significant gas pressurization was not seen for any of the seven samples. A second key conclusion is that ingrowth of only inconsequential quantities (a few micromoles or less, compared to a few millimoles of fill gas) of hydrogen, CO, and CO_2 was observed. A third key conclusion is that substantial depletion of oxygen was observed in all three cases in which the fill gas was air. In the case of the fuels-grade plutonium sample (BLO-39-11-12-004), the oxygen depletion was virtually complete at the first sampling after about 180 days.

The gas surveillance data for the 10-gram tests thus are very consistent with the headspace gas analyses of LANL 3013-94 packages and aged Hanford food-pack containers discussed in Sections V and VI.

VIII. Factors Which Limit Gas Pressurization over Calcined Plutonium Oxides

The conceptual model and empirical information discussed above indicate that water readsorbed after calcination is the only source of gas generation significant with respect to the 699 psia threshold for reasonably calcined and packaged plutonium oxides, even if the oxides are highly impure. The empirical evidence in general shows that gas pressurization from such materials in practice is minimal. This section discusses mechanisms which are known or are likely to be operative to minimize gas generation in sealed containers of calcined plutonium oxide. The discussion is divided into discussions of thermal pressurization and gas generation.

1. Thermal Pressurization. Factors which will minimize pressure increase due to heating of the gas are discussed below.

A. The five kilogram per package maximum material mass specified by the current and proposed standards and simple dilution by impurities will strongly limit wattage per package. For weapons grade oxide, the limits are calculated as <7 watts for 30-50 wt.% Pu material and <11 watts for 50-80 wt.% Pu material. Self-heating will be limited accordingly. Based on Hensel's calculations, bounding oxide material temperatures of about 120°C and 149°C can be inferred for the shipping container/solar scenario discussed earlier for five kilograms of 30 and 50 wt.% weapons grade material. (Hensel 1999a) These temperatures are near or within the range of materials temperatures encountered in decades of storage of calcined plutonium oxides of various purities. Little or none of the higher specific wattage non-weapons grade materials to be stabilized and packaged under this standard consists of impure oxide. (Szempruch 1999)

B. The maximum mass of material per package permitted by the standards is five kilograms. This quantity of many impure plutonium oxide materials physically cannot fit in the storage containers due to their low densities. Wattages and material temperatures will be limited correspondingly.

C. Only a point at the center of the oxide material will be at the bounding material temperature. Material and gas temperatures will grade to the lower temperatures existing at the container wall. For a nineteen watt 9975 shipping scenario that gives a 275°C calculated bounding material temperature, the maximum temperature at the material-container interface was calculated to be 147°C. (Hensel 1999a) In non-shipping 9975 scenarions and during normal vault storage conditions, maximum temperatures will be significantly lower. (Hensel 1999a, Knight and Steinke 1997)

D. The 275°C bounding scenario applies to the shipping scenario, not to anticipated storage scenarios. This scenario may never be experienced in actual practice, and if so, only for a limited time.

2. Gas Generation. Some of the factors which will limit the generation of additional gas are discussed below.

A. As discussed earlier in this report, the only credible source of significant gas generation in calcined oxides appears to be decomposition or desorption of water readsorbed between calcination and packaging.

B. The 0.5 wt.% moisture criterion, anticipated container configuration and temperatures, and expected materials physical properties ensures that even complete decomposition to hydrogen (or equimolar quantity of any other gas) from the maximum allowable five kilogram loading will not exceed the 699 psia pressure threshold.

C. Both standards assume that the dominant decomposition mechanism of adsorbed water is chemical decomposition to form hydrogen and PuO_{2+x} but no molecular oxygen. The empirical evidence indicates that the actual extent of this reaction will be limited, possibly due to reversal of the reaction at modest hydrogen pressures. Tests currently underway at LANL will test this hypothesis.

D. The G-value of a radiolytic reaction is defined as the number of ions or molecules formed or destroyed per 100eV of adsorbed energy. (Lind 1961) G-values for radiolysis of adsorbed water can be dramatically different than for liquid water. For highly oxidized substrates such as MnO_2 and Cr_2O_3, G-values can be much lower than for liquid water. (e.g., see Lloyd et al. 1999 and references therein) Indeed, because the chemical and physical properties of water in the liquid, gas and adsorbed phases are fundamentally different, secondary radiolysis product ratios will vary substantially. (E.g., see classic radiation chemistry books by Spinks and Wood (1990) and by Draganic and Draganic (1971)). Thus, there is no reason to expect yields of final products from radiolysis of these disparate phases to be the same. An exception is when the number of layers of adsorbed water is sufficiently large that the bulk properties of the outer water layers begin to resemble liquid water. Accordingly, the available empirical evidence shows that little or no molecular oxygen product is observed when the number of adsorbed layers is limited, even when the substrate is not readily oxidizable. A good example has been reported for example for silica, where only hydrogen was observed as a radiolytic gas product. (ORNL 1965)

E. Empirical evidence exists that shows pressures approaching 699 psia of both hydrogen and oxygen, or of either alone, cannot arise in packages of reasonably calcined plutonium oxide, regardless of purity. Indeed, the theoretical, kinetic, thermodynamic and experiential basis appears to be well-grounded that catalytic and/or radiolytic recombination mechanisms will be highly effective in storage containers, thereby essentially excluding the possibility of large pressures of H_2 and O_2 arising. (E.g., see Lloyd et al. 1999 and references therein.)

Chemical catalytic recombination mechanisms have been studied exhaustively for many decades. (Eg., see the classic text on combustion by Lewis and von Elbe 1987 and references therein.) An excellent bibliography of the effect of radiation-induced catalytic activity in many metal oxides has been prepared by Krohn (1963). Recent reports by Morales (1999), Morales et al. (1999), Haschke and Allen (1999) and Haschke et al. (1996) on the rate of the hydrogen/oxygen reaction in systems containing pure and impure plutonium oxides indicate that the surface of plutonium oxide, like many other surfaces, is an effective catalyst for this reaction. (also see Haschke and Martz 1998) Recent work by Quigley (1999) indicates that stainless steel alone readily catalyzes this reaction at temperatures down to at least 200°C. (Quigley 1999) In related work, Beavis (1973) reports that appreciable conversion of hydrogen gas to water occurs on the surface of stainless steel at temperatures as low as 100°C and that the rate increases with temperature.

A recent literature search shows conclusively that the H_2/O_2 recombination reaction is readily promoted by alpha and gamma radiation. (Lloyd et al. 1999 and references contained therein). Indeed, promotion of this reaction by alpha radiation was studied at least as early as 1907. (Ramsay 1907) Lind's classicc 1961 monograph on radiolysis of gases provides an excellent summary of work prior to 1961. Remarkably high G-values for recombination in excess of 100 have been reported under some circumstances, compared to very much lower G-values for liquid, gaseous, or adsorbed water radiolysis (the G-value for formation of hydrogen from liquid water is near one) (e.g., see Dautzenberg 1989, 1990 and Kalashnikov et al. 1988)

F. Molecular desorption of water will be self-limited by the equilibrium nature of the reaction. As discussed above in Section III.4, the 699 psia pressure criterion of the standards cannot be challenged by this reaction. However, pressures exceeding the 100 psig indicator point cannot be excluded categorically when a significant amount of moisture has readsorbed between calcination and packaging. Ongoing tests are determining the significance of water desorption as a function of water content and temperature.

G. Hydrolysis of chloride salts is not expected to be significant during anticipated storage conditions, and therefore should not be a significant source of hydrogen chloride or hydrogen. The extent of hydrolysis in the sealed containers is expected to be limited by the reversibility of the reaction. In contrast, MIS results disccused above indicate tha appreciable hydrolysis is possible in some cases (e.g., $MgCl_2$ and $PuCl_3$) during calcination, where hydrogen chloride product is continuously removed. The lack of observation in practice of any significant container corrosion or hydrogen evolution (from reaction of hydrolytically generated hydrogen chloride with metal containers) strongly indicates that hydrolytic processes are not important under normal storage conditions.

H. The calcination process ensures that impurities such as iron, chromium, gallium, and copper, as well as uranium, will be in highly oxidized states. At least Fe_2O_3 and U_3O_8 are thermodynamically capable of reacting with elemental hydrogen gas. Although the equilibrium reaction rates at normal storage temperatures are likely to be low, the intense radiation environment and elevated temperature of the storage package will accelerate hydrogen reduction. The potential sink provided by such reactions is large. For example, one wt.% of ferric oxide in five kilograms of material at 200°C in a container with one liter of gas void space is theoretically capable of reacting with about 12 atmospheres (180 psi) of hydrogen gas.

I. Chloride ion content has been found to be 8 wt.% or less after calcination for the thirty three MIS items examined to date, which were chosen as typical of most RFETS and Hanford materials to be treated under the standards. Occlusion by other matrix constituents and coating of magnesium chloride by hydrolytic products will occur to some extent. The potential for moisture uptake on chloride impurities and subsequent desorption will be limited accordingly. The finite rate of gas diffusion into macroscopic quantities of the calcined material also will retard moisture readsorption.

J. Sodium and potassium chloride impurities will have limited capacities to readsorb water unless very high relative humidities exist in the glovebox atmosphere.

K. Hygroscopic magnesium and calcium chlorides will be converted partially by hydrolysis to less hygroscopic products during calcination. In MIS items studied thus far, magnesium contents have been less than seven wt.% and calcium content has been less than 9 wt.%. The capacity for moisture adsorption will be correspondingly limited by both hydrolytic reaction and the limited chloride compound content.

L. The surface chemistry, including surface areas and affinity for moisture, after calcination of significant oxide impurities other than magnesium and calcium is expected to be qualitatively similar to that of PuO_2. (E.g., refer to the text on metal oxide surface chemistry by Henrich and Cox 1996.) Based on this information and MIS moisture content data to date on impure plutonium oxides, readsorption of moisture on these calcined oxides is expected to be well under 0.5 wt.% for reasonable glovebox humidities, as it is for PuO_2.

M. Readsorption other than at the surface requires diffusion through the bulk calcined product. For reasonable times between calcination and storage, readsorption will be controlled by the diffusion rates.

N. In both the current and proposed standards, the assumption is made that the bounding pressure will be due to hydrogen only from completion of the following chemical reaction:

$$PuO_2.xH_2O \text{ -------------}\rightarrow PuO_{2+x} + xH_2$$

This reaction has been described in several peer-reviewed scientific journal articles and technical reports. (Stakebake et al. 1993, Haschke and Ricketts 1995, Haschke and Martz 1998, Morales et al. 1999, Haschke and Allen 1999). The temperature stability field of this oxide is not firmly established, but the compound appears to be stable from room temperature to about 400°C. A value of x up to about 0.3, corresponding to about two wt.% moisture, appears to be possible under some conditions. The maximum hydrogen pressures reported to date in these studies is only a few tens of torr, after periods ranging from a few days to about half a year. Using rate constants derived from these low hydrogen pressures and assuming no reversibility of the reaction as hydrogen pressure accumulates, essentially complete moisture decomposition is predicted after tens of years. However, the general lack of observance of significant hydrogen pressures in sealed plutonium packages, including some that have been stored for more than ten years, strongly indicates that the extent of this reaction is limited under storage conditions, possibly due to reversal of the reaction at fairly low hydrogen pressures. Ongoing research is continuing to define the extent and nature of this reaction.

IX. Conclusions

The available information indicates that pressures sufficient to exceed the 699 psia design pressure of the welded steel packages prescribed by the standards are highly unlikely if calcination is performed at 950°C and excessive moisture readsorption is avoided between calcination and packaging. Indeed, the available information discussed in this report indicates that actual maximum pressures under 100 psig are likely under normal storage conditions. The required calcination conditions are sufficient to eliminate all sources of pressurization significant with respect to the pressure design criterion.

The only credible source of significant pressurization for calcined oxide materials is moisture readsorbed between calcination and packaging. The requirement of the standards that the moisture content (or loss on ignition) be shown to be less than 0.5 wt.%, combined with the virtual impossibility that large pressures of hydrogen and oxygen can build up in the package, ensures that pressure from decomposition of readsorbed water likewise will not exceed the pressure design criterion of 699 psi.

The impurities most likely to readsorb moisture from the glovebox atmosphere are chlorides of magnesium and calcium. Desorption of water from these compounds at elevated temperatures theoretically could lead to misleading pressure indications and even to liquid moisture under some theoretical conditions. The presence of liquid water would raise the possibility of stress corrosion cracking and consequent reduction of pressure resistance of the package. Simple good operating practices should be effective in limiting readsorption between calcination and packaging and reducing the possibility of this occurrence to negligible levels. Such practices include controlling glovebox humidity and exposure time and covering the material in the period between calcination and packaging. Packaging while the material is still warm would be beneficial as well.

While no credible and significant gas generation mechanisms are apparent, with the possible exception of those due to moisture readsorption between calcination and packaging, it is strongly recommended that an effective surveillance program be established and be continued well into the storage phase to provide insurance against surprises from the complex materials being stored. This surveillance program should be closely integrated between the stabilization/packaging sites, the storage sites, and supporting research and development efforts. The latter specifically should include additional characterization of impure materials at bounding materials temperatures and evaluation of moisture readsorption between calcination and packaging.

Table 1. Gas Pressure Data for One LANL and Nine Hanford As-received MIS Items Stored in Food-pack Containers. Can leak-tightness, pressure and item descriptions for one Los Alamos and nine Hanford cans of plutonium oxide. Data in this table are from Tables 2, 3, 5 and 11 of Mason et al. 1999. Items for which the innermost can was gas-tight are highlighted. Moisture content was measured by the supercritical carbon dioxide extraction method.

Item	As Recd. Wt.% H2O	Wt.% Pu	Description	Age (yrs)	Leaking Inner Lid?	Leaking Outer Lid?	Inner Can Pressure (torr)	Nominal Site Pressure (torr)
HRA-905191	Not measured	17	Unstabilized LANL vault item containing thorium and organics. Origin unknown.	Unknown	N/A	No	563	Unknown
PPSL 365	0.01	83	Hanford vertical Calciner product	1	No	No	586	742
ARF-102-85-295	0.04	28	RFETS item stored at Hanford	12	Yes	Yes	707	742
BLO-39-11-14-004	0.58	86	Fuel-grade Pu oxide with Am	18	Yes	Yes	620	742
PBO-4709-012-023	0.04	87	Reactor-grade Pu Oxide	10	Yes	Yes	603	742
PSU-84-06-05	0.13	15	Mixed oxide with 63% U and fuel-grade Pu	13	No	No	593	742
ARF-102-85-365	0.15	59	RFETS item stored at Hanford	13	No	Yes	668	620

ARF-102-85-114-1	0.00	86	RFETS item stored at Hanford	13	No	Yes	576	620
ARF-102-85-223	0.14	64	RFETS item stored at Hanford	13	Yes	No	592	620
ARF-102-85-355	0.22	45	RFETS item stored at Hanford	14	No	Yes	525	742

Table 2. Headspace Gas Analyses for One LANL and Nine HanfordAs-received MIS Items Stored in Food-pack Containers. Data are from Tables 3 and 4 of Mason et al., 1999. Percentages of total gas are listed. Estimated errors in compositions are roughly +/- 10%. Highlighted rows are for items determined to have non-leaking inner containers. Gas compositions are for the innermost containers of the packages.

Item	Total Press-ure (torr)	N_2	O_2	Ar	CO_2	H_2O	H_2	He	CO	CH_4	SO_2	NO	HCl
Air	-	78.1	20.9	0.93	0.07	-	-	-	-	-	-	-	-
HRA-905191	563	49.6	-	0.4	10.0	-	28.9	-	-	-	-	-	-
PPSL 365	586	91.3	4.9	0.9	2.9	0.1	0.1	0.3	-	0.1	-	-	-
ARF-102-85-295	707	97.6	-	0.7	1.0	-	-	0.6	-	-	-	-	-
BLO-39-11-14-004	620	77.4	2.2	0.8	5.4	-	-	0.1	9.9	-	-	1.8	-
PBO-4709-012-023	603	97.8	0.7	0.9	0.1	0.1	-	0.2	-	-	-	0.1	-

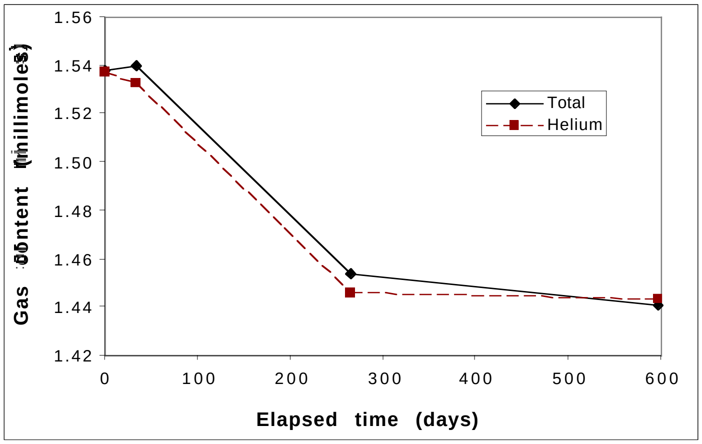
PSU-84-06-05	593	81.5	0.1	0.7	14.5	-	0.3	0.3	-	-	-	-	-
ARF-102-85-365	668	47.3	-	0.7	-	0.2	47.5	4.2	-	-	-	-	-
ARF-102-85-114-1	576	97.4	-	0.9	0.4	-	-	1.0	-	-	-	0.2	-
ARF-102-85-223	592	86.9	12.1	0.7	-	-	0.1	-	-	-	-	0.1	-
ARF-102-85-355	525	93.6	-	0.9	3.9	-	0.9	0.4	-	0.2	-	-	-

Table 3. Gas Data for 10-gram MIS Surveillance Samples. Data are from Table 15 and Figures 2-16 of Mason et al. 1999.

Item	Processing Status	Starting Pressure (torr)	Current Pressure (torr)	Fill Gas	Elapsed Time (days)	Comments
PPSL-365-ARLT	As Recd.	760	757	He	596	Traces N_2, CO_2 observed
PPSL-365-600LT	600°C Calcination	614	425*	He	618	Trace N_2 observed
PPSL-365-900LT	950°C Calcination	578	572	He	578	Trace N_2, H_2 observed
ARF-102-85-295-ARLT	As Recd.	593	555	Air	564	Trace CO_2 observed
ARF-102-85-295-900LT	950°C Calcination	539	440	Air	243	Trace CO_2 observed
BLO-39-11-12-004-ARLT	As recd.	612	251*	Air	530	Strong O_2 depletion and trace He, H_2, CO_2 observed
C1407AB-ARLT	As recd.	551	537	N_2	41	Little or no trace gas observed

* Possible gas loss during sampling.

Figure 1. Gas Pressure Changes for 10-gram MIS Surveillance Sample of as-received Hanford Item PPSL-365. Data are from Figures 2 and 3 of Mason et al. 1999.



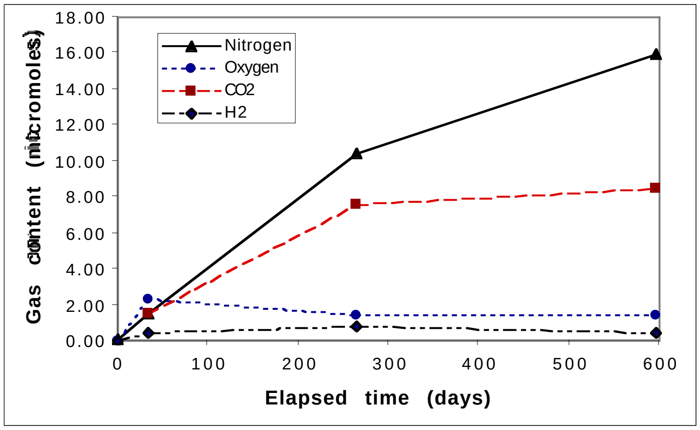
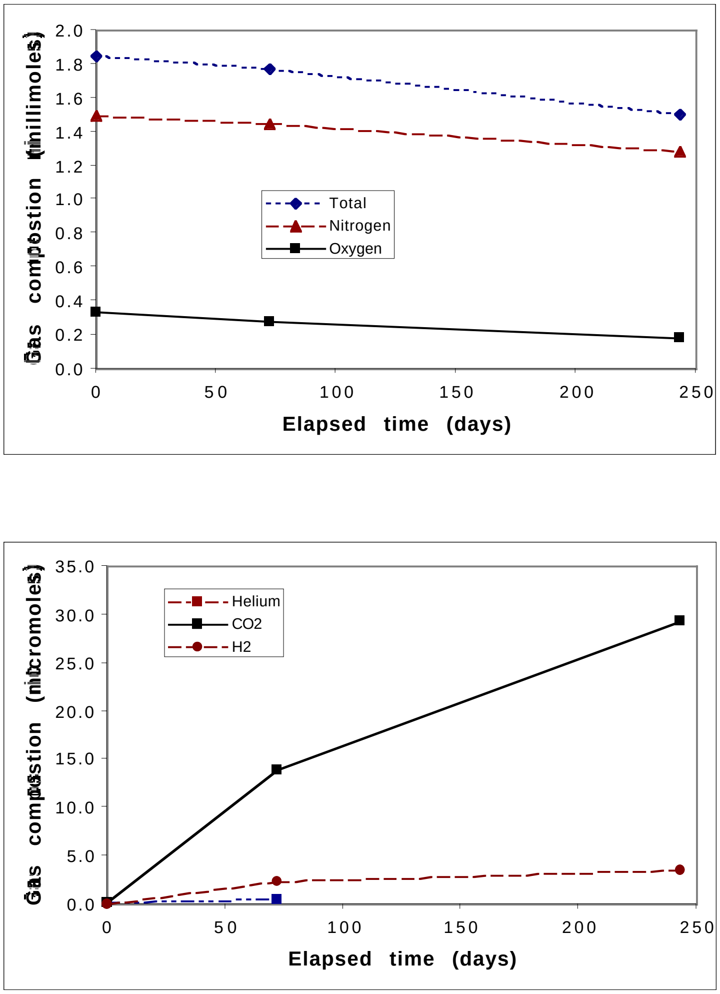


Figure 2. Gas Pressure Changes for 10-gram MIS Surveillance Sample of 950ºC-calcined Hanford Item ARF-102-85-295. Data are from Figures 11 and 12 of Mason et al. 1999.



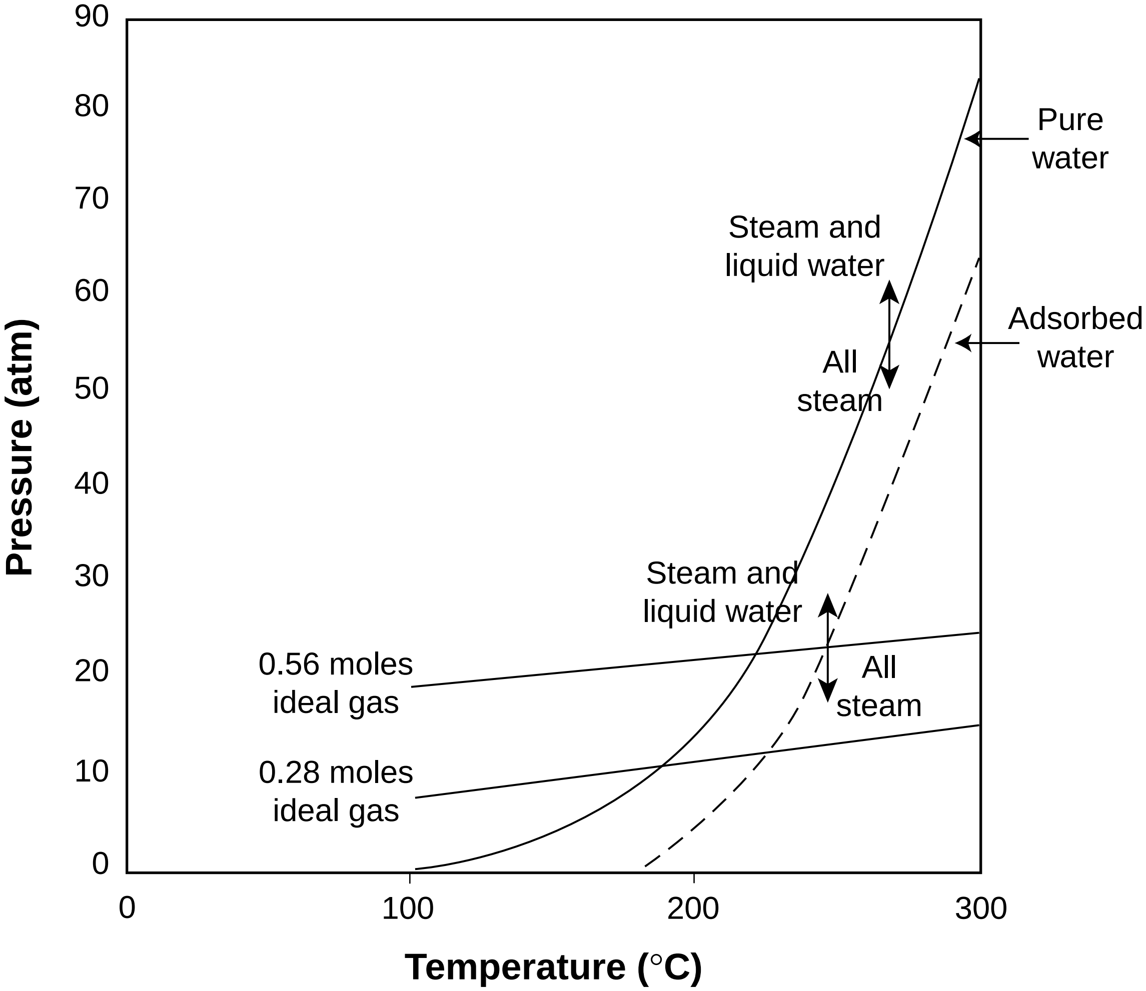
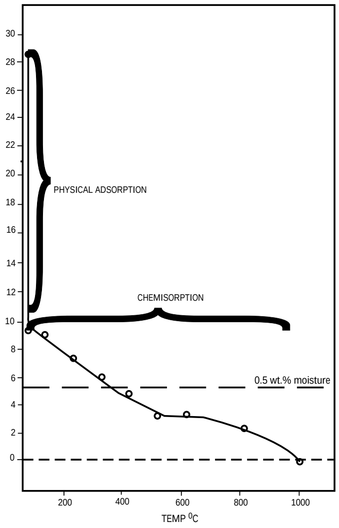
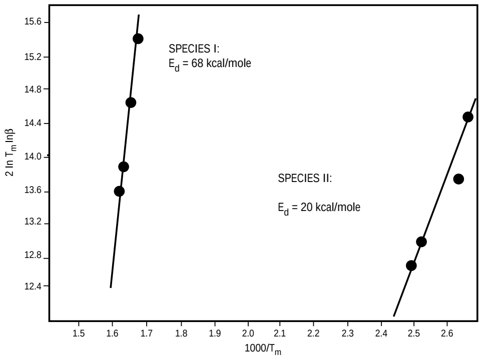


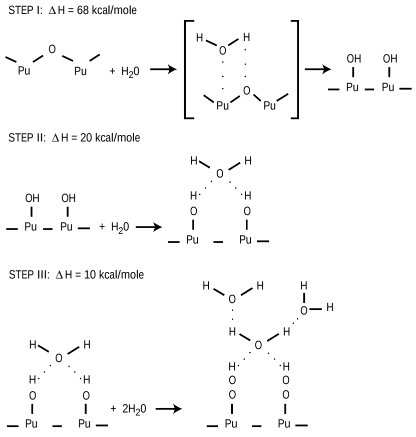
Figure 3. Behavior of water in sealed systems. 0.1 wt.% moisture in 5 Kg material is equivalent to 0.28 moles. The temperature shift between the pure water and adsorbed water curves represents the enthalpy of adsorption.



Gravimetric desorption of water from plutonium dioxide.



Activation energies for the desorption of chemisorbed water from plutonium dioxide.



Adsorption of water on plutonium dioxide.

Figure 4. Interaction of water with plutonium dioxide.
Figures are from Stakebake and Steward, 1973.

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