REVIEW OF DOE CRITERIA FOR SAFE STORAGE OF PU METALS AND OXIDES

by

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ABSTRACT

A technical review of the DOE criteria for storage of plutonium metals and oxides determined the maximum pressure that could be obtained from 50-year storage of 5.0-kg of PuO₂ powder under the assumed worst-case conditions derived from the DOE standard [1,2]. Those conditions included a final temperature of 400°F and the reaction to yield H₂ gas in accordance with the equation

\[
\text{PuO}_2(c) + x \text{H}_2\text{O} \rightarrow \text{PuO}_2\text{H}_x(c) + x \text{H}_2(g)
\]

where the x moles of sorbed water represents 0.5 wt.% of the PuO₂. The worst-case conditions also included the generation of He gas from the 50-year α-decay of the plutonium, that was considered to be power grade plutonium with the maximum limit of 3% for the short-lived isotope, Pu-238. The free volume for containment of the gases generated in the primary containment vessel, assuming failure of its inner boundary container, was assumed to be 2.5-L value given in the original standard[1].

The worst-case analysis yielded an internal pressure of 426.3 psia, which is marginally lower than the 500-psi qualification pressure specified for the primary containment vessel. One should therefore consider increasing the total free volume of the primary containment vessel or increasing the pressure requirement for the primary containment vessel.

Because PuO₂ particles are small (=100-300 Å average diameter) and highly dispersible and respirable as an aerosol, the containment system must be depressurized before it is opened for sampling or reuse. This paper suggests a cryogenic approach that may be used to depressurize the containment system (cooled to about 15°K) and expand the gas into a 30-fold expansion manifold after 50 years of storage. The approach should prevent contamination of the surrounding area with highly dispersible and respirable PuO₂ aerosol particles.

1. INTRODUCTION

A technical review has been conducted of the U.S. Department of Energy (DOE) criteria [1,2] for long-term (=50 years) storage of 4.4-kg quantities of Pu metal or 5.0-kg quantities of PuO₂. The criteria standard was derived from the analyses and recommendations of an assessment of Pu safety issues at DOE facilities [3]. This paper reviews the criteria standard and includes, where necessary, analysis of the physical significance of certain information contained in the technical assessment document.

The storage containment system given in the standard consists of a boundary container within a primary containment vessel that is qualified for a pressure of 500 psi at 400°F. The standard also includes an option of storing the material in a container within the boundary container. No pressure rating is given for the inner boundary container; so that with its failure, its gaseous content would be released to the primary vessel. Consequently, a design requirement of the primary vessel is that it should accommodate the pressure generated for the worst-case conditions, namely, a free volume at 400°F that contains He gas (from a 50-year direct α-decay of the 238, 239, and 240 isotopes of Pu and from α-decay of Am-241, which is produced from the β-decay of Pu-241) and H₂ gas produced from 100% reaction of PuO₂ powder with water that is physically and chemically sorbed on its surface. The original standard included a provisional requirement of 2.5 L for that free volume. One objective of this paper was to examine the capability of the 2.5-L volume to contain the gas pressure generated by the worst-case conditions. There was no way to verify the attainment of such a free volume because of the limited information available on the dimensions of the boundary container and primary containment vessel.

Because Pu-238 has the shortest half-life of any of the Pu isotopes, its α-decay has the greatest influence on generation of He in stored inventories of PuO₂. Therefore, the worst-case conditions assumed an inventory of power-grade Pu with an upper limit of 3% Pu-238.
Our analysis also examined the practicality of the requirement for opening the containment and reusing the system, in light of the facts that all-welded seals were specified for the boundary vessel and that the particles with sizes characteristic of those for stored PuO₂ [3] could be highly dispersable as respirable Pu aerosols upon opening the pressurized containment vessel.

2. THEORETICAL BACKGROUND

Physical Characteristics of Stored Pu Metals and Oxides

The standard [1] specifies that there shall be no storage of Pu or PuO₂ particles (such as chips or metal turnings) with a surface area greater than 1 cm²/g. It is unrealistic to assume that the friable oxide will not be broken down into smaller particles by the pressures generated by α-decay of the Pu and by its interaction with sorbed water. But, for Pu metal, this appears to be a feasible requirement. Accordingly, a (single) particle diameter d of a sphere, corresponding to its surface-to-mass ratio A/M, is given by

\[
d = 6/\left(19.86(A/M)\right)
\]

where 19.86 is the density of Pu metal in g/cm³ or kg/L. Equation 1 yields an equivalent particle diameter of 0.3 cm or 0.12 in. It is assumed that although the metal may undergo some corrosion, the corrosion is limited because of the formation of a protective oxide film and because the amount of adsorbed water is minimal.

The surface areas of PuO₂ powders are many orders of magnitude larger than the surface areas of Pu. The technical reference document [3] gives surface areas in the range of 17-50 m²/g, with corresponding adsorbed water values of 28-82 mg per g of PuO₂, and states that =1/3 of the adsorbed water is chemisorbed. Because of the large surface areas, 17-50 m²/g, and probably because of the partial dipolar nature of its Pu-O bonds, PuO₂ can bind monolayers of other partially dipolar molecules, such as water, to those surfaces. A conceivable picture for water adsorption is that the negatively polarized oxygen atoms in water molecules bind to positively polarized Pu surface atoms to form a chemisorbed (monomolecular) layer. Physically sorbed water layers, perhaps two or three, then could be formed by weaker H-O dipole interaction binding between successive layers of water.

The oxide particles are not necessarily spherical and presumably each of the surface areas in the technical reference document [3] refer to a particle-size distribution. But neither this information nor the experimental basis for the quoted surface areas was given in the technical reference document. Therefore, assuming a characteristic particle size for PuO₂ surface areas, and assuming the given relationship of particle diameter to surface area (Eq. 1) but with a theoretical density of 11.45 g/cm³ for PuO₂, the particle diameters that corresponds to 17 and 50 m²/g surface areas are 308 and 105 Å, respectively.

The particles with a 308-Å diameter (154-Å radius) have a volume of 1.53 x 10⁻¹⁷ cm³ and a mass of 1.75 x 10⁻¹⁶ g and, at a water adsorption value of 28 mg/g of oxide, the amount of sorbed water per particle is 4.9 x 10⁻¹⁸ cm³. The outer radius of the sorbed water layer may then be determined from the relationship

\[
r = \left[(3/4\pi) \times (1.53 \times 10^{-17} + 4.9 \times 10^{-18})\right]^{1/3} \times 10^8 \text{ Å},
\]

which gives an outer radius of 169 Å or a water-surface layer thickness of 15.0 Å.

Similarly, for the 105-Å particles the surface layer thickness is estimated to be 13.2 Å. Therefore, because the technical reference document states that 1/3 of the water is chemisorbed, the thickness of the chemisorbed layer is =4.5-5 Å, or approximately the same thickness as a monomolecular layer. That amount of chemisorbed water corresponds to the 0.5% loss-on-ignition (LOI) requirement of the standard [1,2].

Chemical Considerations for Stored Pu Metals and Oxides

If PuO₂ is exposed to H₂, it can be reduced to such material particulates as Pu₂O₃, Pu, or PuH₂. The PuH₂, in turn, can be oxidized by moisture to regenerate H₂. Under certain conditions, the PuO₂ can be oxidized to yield PuO₂₃ by the reaction
Initially [1], it was assumed that for stored oxide powders of Pu, the primary source of pressure from moisture in the system was 100% radiolysis of the water sorbed by the oxide to yield \( \text{H}_2 \) and \( \text{O}_2 \). The more recent standard [2] assumes that a more plausible, but less conservative, basis for generation of \( \text{H}_2 \) in stored \( \text{PuO}_2 \) powders is the reaction of the oxide with its adsorbed water in accordance with the reaction

\[
\text{PuO}_2(c) + x \text{H}_2\text{O(adsorbed)} \rightarrow \text{PuO}_2(x)(c) + x \text{H}_2
\]  

Approximately 2/3 of the sorbed water, i.e., the amount that is physically sorbed, is lost at the temperatures below 1000°C; and most of the remainder, the chemisorbed water, is lost at ≈1000°C. High temperatures are used to thermally stabilize the powder, i.e., to oxidize all of the lower valent impurities to \( \text{PuO}_2 \), and drive off most of the sorbed moisture so the loss on ignition (LOI) would be no greater than 0.5 wt.% for a time period specified by the certification procedures. Therefore, the worst-case calculation assumes that all of the water remaining in the stored oxide, which corresponds to an LOI of 0.5%, reacts with the \( \text{PuO}_2 \) to yield \( \text{H}_2 \), mole for mole, in accordance with Eq. 4. The compaction of the oxide powders in pellet form has been considered, but this does not eliminate the problem because the pellets are friable and will break up under relatively low pressures.

Plutonium base metals do not exhibit large surface areas or polar binding sites for sorption of water and organic matter; and the generation of \( \text{H}_2 \) from corrosion of the metal would be orders of magnitude lower than that generated from the surface reaction between \( \text{PuO}_2 \) and its sorbed water. Furthermore, the \( \text{He} \) generated by radioactive decay of the Pu is trapped in the interstices of the metal, whereas \( \text{He} \) generated by decay of \( \text{PuO}_2 \) powder would be completely released. Therefore, the worst-case analysis was based on \( \text{PuO}_2 \) powder, which would generate much greater pressure than the metal.

**Gases Available under Worst-Case Conditions with PuO₂**

1. **Gases from the Reaction of Sorbed Water with PuO₂**

   Assuming for an LOI of 0.5%, 0.5% water is retained in the \( \text{PuO}_2 \) and that it is available to release \( \text{H}_2 \) from the reaction

   \[
   \text{PuO}_2(c) + x \text{H}_2\text{O(adsorbed)} \rightarrow \text{PuO}_2(x)(c) + x \text{H}_2
   \]  

   under the worst-case conditions, then the \( \text{H}_2 \) that is available to 5.0 kg of oxide in this scenario is given by

   \[
   n(\text{H}_2) = 0.005 \times 5000/18.016 = 1.388 \text{ moles}
   \]  

2. **He Gas Available from 50-y α-Decay of Pu Isotopes**

   The technical reference document [3] states that the amount of \( \text{He} \) that is available from the decay of Pu is 1.055 \( \times 10^4 \) moles/(kg-PuO₂)/y. Assuming a molecular weight of 239 for Pu, this is 1.196 \( \times 10^4 \) moles/(kg of Pu)/y. With a Pu-239 half-life of 2.41 \( \times 10^4 \) y, or a decay constant \( \lambda \) of 2.876 \( \times 10^{-5} \) y⁻¹, the moles of \( \text{He} \), \( n(\text{He}) \), calculated from the relation

   \[
   n(\text{He}) = \frac{1}{0.239} [1 - \exp(-\lambda t)] = \frac{\lambda}{0.239} = 1.203 \times 10^4 \text{ moles/(kg of Pu)/y}
   \]  

agrees quite well with the value given in Ref. 3. However, this value does not account for \( \text{He} \) generated from the \( \alpha \)-decay of Pu isotopes other than Pu-239. For example, the 87.7-\( y \) decay of Pu-238, even at contents of a few percent, contributes significantly to the \( \text{He} \) inventory.

Furthermore, Pu-241 decays according to the following equation:

\[
\text{Pu-241} \rightarrow \beta + \text{Am-241} \rightarrow \alpha + \text{Np-237} \rightarrow \alpha + \text{Pa-233}
\]
The half-lives for the decay of Pu-241, Am-241, and Np-237 are 14.4, 432.7, and 2.14 x 10^6 years, respectively. So, neglecting the He produced from the decay of Np-237, it can be shown that the moles of He produced from this decay scheme over 50 years is given by

\[ n(\text{He}) = (4.4/MW)f_{241}(1 - \frac{\lambda_{241}}{\lambda_{241} + \lambda_{241}})\left[1 - \exp\left(-50\lambda_{241}\right) - \exp\left(-50\lambda_{241}\right)/\Delta\right] \]  

(9)

where MW is the molecular weight of a particular grade of Pu in kg, determined from its isotopic composition; \( f_{241} \) is the mole-fraction of Pu-241; \( \lambda_{241} \) and \( \lambda_{241} \) are the decay constants for Pu-241 and Am-241, respectively; and \( \Delta = (\lambda_{241} - \lambda_{241}) \).

With this parent-daughter decay scheme, 50-year \( \alpha \)-decays were calculated for 5.0 kg of PuO2 (4.4 kg of Pu) at the isotopic compositions of weapons, fuel and power grade Pu given previously [1]. The half-lives used for Pu-238, Pu-239, and Pu-240 were 87.7, 2.42 x 10^4, and 6.56 x 10^3 years, respectively, and each isotopic decay constant was 0.69315/tlm In addition, a separate calculation was performed for power-grade Pu, with a Pu-240 content of 20% and an increase in Pu-238 content to 3%. The following table gives the moles of He and H2 determined for each of the above cases.

<table>
<thead>
<tr>
<th>Grade of Plutonium</th>
<th>Moles of He</th>
<th>Moles of H2</th>
<th>Total He + H2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weapons</td>
<td>3.78 x 10^{-2}</td>
<td>1.388</td>
<td>1.426</td>
</tr>
<tr>
<td>Fuel</td>
<td>5.59 x 10^{-4}</td>
<td>1.388</td>
<td>1.389</td>
</tr>
<tr>
<td>Power</td>
<td>0.2167</td>
<td>1.388</td>
<td>1.605</td>
</tr>
<tr>
<td>Power at 3% Pu-238</td>
<td>0.3601</td>
<td>1.388</td>
<td>1.748</td>
</tr>
</tbody>
</table>

The number of H2 + He gas moles available under the worst-case conditions is thus 1.748 moles.

3. REVIEW OF BASIC CRITERIA FOR THE STANDARD

Estimate of Vessel Pressure for Worst-Case Conditions

As stated previously, taking into consideration failure of the boundary container, the free volume of gases in the primary container plus the available volume within the interstices of powdered oxides, is assumed to be 2.5 L. The assessment below evaluates the capability of that volume to contain the pressure generated under the estimated worst-case conditions. For that assessment, assume that the boundary container and primary vessel were initially loaded to a pressure of 1 atm at an initial temperature, \( T_0 \), of 298°K. Then, the pressure, \( P \), calculated from the highest possible noncondensable gas inventory after 50-year storage at the maximum reference temperature, \( T \), of 477.6°K (400°F) would be

\[ P = P_0\left(\frac{T}{T_0}\right) + \left[n(\text{He}) + n(\text{H}_2)\right](RT/V) = (1 \times 477.6/298 + 1.748 \times 0.08205 \times 477.7/2.5) \times 14.7 \text{ psia} \]  

(10)

or 426.3 psia. This is a very conservative upper pressure limit that the total 2.5-L free volume of the system could attain during a 50-year storage period.

Even at the given 100°C steady-state temperature [1], the boundary container would rupture to give a primary-vessel pressure, \( P \), of

\[ P = 426.3 \times 373.2/477.6 \text{ psia}, \]  

(11)

or 333.1 psia.

Opening the Containment System for Sampling and Re-use

A potential problem could occur when the containment system is opened for gas sampling and/or reuse to meet the requirements specified in the original standard [1] because fine particulate oxide could be spread as an aerosol into the surrounding area.
This potential problem can be prevented by the following approach. Chill the primary vessel cryogenically to ≈15°K, bleed its 2.5-L free volume into a 75-L manifold at a nominal room temperature of 298°K, and then allow the primary vessel to warm back up to approximately nominal room temperature.

The total gas inventory \( n_p \) in the 2.5-L free volume of the primary vessel with the failed boundary container would be

\[
n_p = \left(\frac{426.3}{14.7} \times 2.5\right) / (0.08205 \times 477.6) = 1.850 \text{ moles}
\]  

(12)

and its pressure, \( P_p \), at 15°K would be

\[
P_p = 426.3 \times \frac{15}{477.6} = 13.39 \text{ psia}
\]

(13)

This is less than the 1 atm pressure of the 75-L collection manifold, which would have a gas inventory, \( n_m \), given by

\[
n_m = \frac{75}{(0.08205 \times 298)} = 3.067 \text{ moles}
\]

(14)

With the whole system, i.e., primary vessel plus manifold, at 298°K after expansion of the primary-vessel gases into the expansion manifold, the system pressure, \( P_s \), would be

\[
P_s = \left(\frac{1.85 + 3.067 \times 0.08205 \times 298 \times 14.7}{77.5}\right) = 22.8 \text{ psia},
\]

(15)

i.e., 8.1 psig, which could be handled with an all-glass manifold.

4. CONCLUSIONS

The pressure calculated for the specified worst-case conditions in the DOE criteria [1] was 426.3 psia at 400°F. The estimate assumed complete release and 100% reduction of the water sorbed by 5.0 kg of PuO₂ powder, i.e., water sorbed to 0.5% of the PuO₂ mass, to yield \( \text{H}_2 \); \( \text{He} \) from the 50-year \( \alpha \)-decay of the Pu at the assumed isotopic content for power-grade Pu, but with Pu-238 added to the 3% limit specified in Ref. [1]; and a 400°F temperature of the 2.5-L free volume for the contained gases. The calculated 426.3 psi pressure for the worst case is only marginally lower than the 500 psi qualification pressure for the primary containment vessel at 400°F. Thus, the required free volume of the containment system and/or the pressure requirement for the primary containment vessel should be increased.

The standard [1] appears to contain two conflicting requirements, namely, that the boundary container and primary containment vessel contain all-welded seals and that there be provisions for opening the containment and reusing the system. The standard requires that the containment system be designed as both a storage and shipping package and that the containment system be opened for sampling of the contained gases and then resealed prior to shipment. To prevent the spread of fine oxide particles upon opening the containment system, we suggest a cryogenic approach that can be used to depressurize the system (cooled to ≈15°K) and allowing it to expand into a 30-fold expansion manifold after 50 years of operation.

Finally, from the information given in the technical assessment document for the standard [3], it was estimated that the characteristic PuO₂ particle size is in the range of 100-300 Å, with an adsorbed surface layer thickness in the range of 13.2-15 Å before thermal stabilization to reduce the amount of adsorbed material. Therefore, we question the advisability of long-range storage of such highly dispersible oxides. Other options should be explored, such as conversion to the base metal or incorporating the PuO₂ into borosilicate glass.

NOMENCLATURE

A/M Surface-to-mass ratio of stored Pu metal or PuO₂ powder, in units of \( \text{cm}^2/\text{g} \) or \( \text{m}^2/\text{g} \), respectively

\( \alpha \)-decay Decay of Pu-238, Pu-239, Pu-242, Am-241 and Np-241 in Pu with emission of \( \alpha \) particles
Decay of Pu-241 in Pu to emit $\beta, \gamma$ radiation in the decay scheme:

$$Pu-241 \rightarrow \beta + Am-241 \rightarrow \alpha + Np-237 \rightarrow \alpha + Pa-233$$

**Chemisorption**
Sorption of moisture and other volatile materials with strong dipolar bonding between unlike molecules at a boundary layer surface, i.e., between the surface molecule and the sorbed molecule.

**d**
Characteristic diameter of a Pu oxide particle of radius $r$, both expressed in Å.

**DOE**
The U.S. Department of Energy.

**$f_i$**
Mole fraction of Pu isotope $i$ for a particular Pu metal or oxide inventory.

**LOI**
Loss-on-ignition, or the mass loss measured when a representative thermally stabilized Pu-bearing oxide is heated to confirm the elimination of residual moisture and other volatile materials from the thermally stabilized material.

**$\lambda_i$**
Decay constant of a given Pu or Pu daughter isotope in $y^{-1}$, where

$$\lambda_i = 0.69315/t_{1/2}$$

**MW**
Molecular weight of a particular grade of Pu in g or kg.

**$n(He)$**
Number of gram-moles of He generated by a particular Pu metal or oxide inventory through $\alpha$-decay over a particular time interval.

**$n(H_2)$**
Number of moles of $H_2$ generated during 50-y storage of 50.0 kg of PuO$_2$.

**$n_m$**
Number of moles of gas in a 75-L expansion manifold, initially at 1 atm pressure and 298°K, for capture of high-pressure gases from the primary vessel.

**$n_p$**
Number of moles of gas in the free volume of the primary vessel that contains the breached container after 50 year storage of 50.0 kg of PuO$_2$.

**P**
Pressure of the breached boundary container and primary vessel at 477.6°K, under the worst-case conditions after 50-year storage of 50.0 kg of PuO$_2$.

**Physical sorption**
Sorption with rather weak dipolar bonding of like molecules at a surface, such as bonding of water layers (past the surface boundary layer) to a PuO$_2$ particle.

**$P_0$**
Original pressure of the as-sealed boundary container and primary vessel, taken as 1 atm pressure, at 298°K.

**$P_p$**
Pressure of the breached boundary container and primary vessel cooled from 477.6 to 15°K after 50 year storage of 50.0 kg of PuO$_2$.

**$P_s$**
Pressure of the combined system (boundary container, primary vessel and expansion manifold), at 298°K after expansion of the high-pressure primary-vessel gases into the expansion manifold.

**R**
Ideal-gas constant, in units of L atm mol$^{-1}$ deg$^{-1}$.

**Sorption**
General term for surface adsorption of a particular substance to a surface; could be either chemisorption or physical sorption.

**Storage**
Method of safely maintaining items in a retrievable form (for use or disposition) under conditions calculated for 50-year storage of 50.0 kg of PuO$_2$. 
\( t_{1/2} \quad \text{Half-life of a particular isotope in years} \)

\( T_a \quad \text{Initial temperature of the as-sealed boundary container and primary vessel, taken as 298^\circ K} \)

\( T \quad \text{Final temperature of the plenum of a primary vessel with 50.0 kg of PuO}_2 \text{ stored for 50 years, taken as 477.6^\circ K} \)

Thermal stabilization \( \quad \text{A process that exposes Pu-bearing material in air to an elevated temperature for the time required to convert reactive constituents to oxides and to remove adsorbed moisture and other volatile species} \)

\( V \quad \text{Combined free volume of a breached boundary container and primary vessel, including the interstitial volume within 50.0 kg of stored PuO}_2 \)

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