

PREDICTION OF GAS PRESSURIZATION AND HYDROGEN GENERATION FOR SHIPPING HAZARD ANALYSIS: SIX UNSTABILIZED PLUTONIUM OXIDE SAMPLES

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ABSTRACT

Changes in gas composition and gas pressure for closed systems containing plutonium dioxide and water are studied using a model that incorporates both radiolysis and chemical reactions. The DOE-STD-3013-99 storage standard limits the amount of water to less than 0.5 weight percent. These materials potentially have a wide range of surface areas and the number of equivalent water monolayers for 0.5 weight percent can range from less than one full monolayer to more than twenty. The model is used to investigate the behavior of material stored in storage containers conforming to DOE-STD-3013-99 storage standard. The following theory can be used to compute safety shipping windows for the shipping of radioactive materials that have had a chance to interact with water.

INTRODUCTION

In accordance with non-proliferation concepts, the United States plans to store excess weapons-grade plutonium until an ultimate disposition path can be finalized. Most of this excess plutonium will be stored as stabilized plutonium oxide, since PuO₂ is thought to be thermodynamically stable under storage conditions. Plutonium dioxide is known to absorb small amounts of water, and the radiolysis of water to form hydrogen gas is considered to be the greatest concern for safe long-term storage.

Thermodynamic, chemical, and radiolysis modeling was used to predict gas generation and changes in gas composition within sealed containers containing plutonium bearing materials. The results are used in support of safety analysis for shipping six unstabilized (i.e. uncalcined) samples from Rocky Flats Environmental Technology Sites (RFETS) to the Material Identification and Surveillance (MIS) program at Los Alamos National Lab (LANL). The intent of this work is to establish a time window in which safe shipping can occur. Our calculations show that 5 of the 6 items can be packaged and shipped to Los Alamos National Laboratory inside 200 days or less without exceeding the 5% hydrogen by volume limit as specified in Department of Energy's (DOE) Package Certification Approval Record, Docket No 00-11-9965. Calculations of the gas pressure and changes in gas composition were carried out to one year for each of the six containers. Three containers met the DOE's shipping requirements over the entire year, two containers met these requirements for two hundred days, and one container (ID 39-01483A) met the requirements for only 13 days. Thus five of the six meet DOE'S requirements when shipped with 200 days. If the water in the sixth can (ID 39-01483A) is reduced below 4.3% by weight, the storage container can be shipped, also inside the 200 day window as shown by this model.

Plutonium dioxide absorbs water on its surface. Radiolysis of water to form hydrogen gas is a safety concern for safe storage and transport of plutonium-bearing materials. Hydrogen gas is considered a safety hazard if its concentration in the container exceeds five percent hydrogen by volume, DOE Docket No. 00-11-9965. Unfortunately, water cannot be entirely avoided in a processing environment and these samples contain a range of water inherently.

COMPUTATION

The model we use, which we refer to as Lyman 35, was developed as an Excel spreadsheet. Code available upon request. Assumptions in the model are:

- The chemical composition of PuO₂ is pure. The model hasn't been adapted to calculate the chemical effects of impurities. The volume within the container available for gases is corrected by subtracting the displacement of the impurities. This is a worst-case scenario, because adsorption of water by the impurities will remove water from the close proximity to the plutonium resulting in slower radiolysis.
- The surface of PuO₂ has a top layer of oxygen. This seems to be a valid assumption since uncoordinated saturated atoms of plutonium would be very reactive.
- All of the containers have been sealed and are air-tight. All initial pressures are normalized to 12.9 psi (local pressure at Rocky Flats) and all pressures are given in PSIA.
- Temperature regulation is precise and accurate. Temperature was assumed to be 315 K (107 °F). This temperature was chosen as a worst-case scenario based on the temperature of the savannah river tarmac in the middle of summer and energy released inside the storage container due to radiolysis and the insulation of the storage container.
- The surface area of the oxide is assumed to be 5 m² g⁻¹.⁵
- The water in the first monolayer is assumed to not undergo radiolysis.⁶
- Loss on Ignition (LOI) is assumed to be an accurate analytical method for determining the water content in the sample.

This model assumes that the bulk "impurity" material does not absorb water. If the bulk material absorbs water, then that water will be removed from the majority of the radiolysis field and therefore will undergo radiolysis at a slower rate resulting in a hydrogen pressure smaller than the maximum pressure possible using this model. All of the impurities are being treated as having no interaction with the water; therefore this is a worst case scenario. Since the temperature is unknown, we used a temperature of 315 K (107 °F). At higher temperatures reaction rates increase yielding a shorter time window for safe shipping. The specific surface area (SSA) for these samples has not been measured. Similar materials have been studied and an average SSA of 5 m² g⁻¹ was observed.⁵ We expect the SSA of these materials to be higher because they have not been calcined. As the surface area increases, the final pressure in the storage container at the end of one year will be less, since more water is used in the construction of the first monolayer which is assumed to be nonreactive.⁶ Therefore, we have chosen a SSA of 5 m² g⁻¹ for these calculations.

This model includes thermodynamics, radiolysis, and chemical reactions listed in Table I. The system is described using the Arrhenius equation, eq. 1. Activation energies, E_a , are listed in Table I. The temperature is T in Kelvins, and the idea gas constant, R , was set to $8.31441 \text{ J K}^{-1} \text{ mol}^{-1}$. Preexponential factors, A , were experimentally determined. The model uses small time steps and a Visual Basic for Applications program to compute a self-consistent field for the coupled reactions listed in Table I. The code was benchmarked against experimental measurements and approximates the experimental work to within +1.5 times of the value measured.⁹

Table I: Radiolysis and Chemical Reactions in Lyman's model 35.

Mechanism	Reaction	A	E_a	N
Radiolysis	$\text{PuO}(\text{OH})_2 \rightarrow \text{PuO}_2 + \frac{1}{2} \text{H}_2(\text{g}) + \frac{1}{2} \text{H}_2\text{O}_2(\text{s})$	$1.56 \cdot 10^{-8}$	0	0
Radiolysis	$\text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{g})$	$2.83 \cdot 10^{-6}$	0	0
Radiolysis	$\text{H}_2\text{O}(\text{s}) \rightarrow \frac{1}{2} \text{H}_2(\text{g}) + \frac{1}{2} \text{H}_2\text{O}_2(\text{s})$	$1.56 \cdot 10^{-8}$	0	0
Radiolysis	$\text{H}_2\text{O}_2(\text{s}) \rightarrow \text{H}_2\text{O}(\text{g}) + \frac{1}{2} \text{O}_2$	$1.4 \cdot 10^{-8}$	0	0
Chemical	$\text{H}_2\text{O}(\text{s}) \rightarrow \text{H}_2\text{O}(\text{g})$	$1.32 \cdot 10^7$	$4.4 \cdot 10^4$	-1
Chemical	$\text{H}_2\text{O}(\text{g}) + \text{S} \rightarrow \text{H}_2\text{O}(\text{s}) \cdot \text{S}$	0.632	0	0
Chemical	$\text{PuO}_2 + \text{H}_2\text{O}(\text{s}) \rightarrow \text{PuO}(\text{OH})_2$	$8.1 \cdot 10^{-4}$	0	0
Chemical	$\text{PuO}(\text{OH})_2 \rightarrow \text{PuO}_2 + \text{H}_2\text{O}(\text{s})$	$5.6 \cdot 10^{-1}$	$1.3 \cdot 10^5$	-1
Chemical	$\text{PuO}(\text{OH})_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{PuO}_2(\text{OH})_2(\text{s})$	$1.4 \cdot 10^{-4}$	$3.9 \cdot 10^4$	0
Chemical	$\text{PuO}_3 + \text{H}_2(\text{g}) \rightarrow \text{PuO}(\text{OH})_2(\text{s})$	$2.7 \cdot 10^{-8}$	0	1
Chemical	$\text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{g})$	$5.9 \cdot 10^{-6}$	0	0
Chemical	$\text{PuO}(\text{OH})_2 + \text{H}_2\text{O}_2(\text{s}) \rightarrow \text{PuO}_2(\text{OH})_2 + \text{H}_2\text{O}(\text{s})$	$1.35 \cdot 10^{-4}$	$3.9 \cdot 10^4$	0

$$K = A \cdot T^N \cdot e^{-E_a/RT} \quad \text{Eq.1}$$

The DOE-STD-3013-99 Standard Appendix B states that the gas volume displaced by plutonium oxide powder can be calculated from the mass and the density of PuO_2 . Experimental data of Veirs et al.⁷ suggests that using the theoretical density of PuO_2 is a reasonable assumption for the PuO_2 in a mixture of plutonium oxide and impurities. For this study, we used the maximum theoretical density of 11.5 g/cm^3 for PuO_2 . M_{PuO_2} is the mass of PuO_2 , ρ is the density of the plutonium dioxide (11.5 g/cm^3), M_B is the mass of the impurities, ρ_B is the density of the impurities, V_t is the volume of the empty storage container, and equation 2 (see below) is used to calculate the volume of the head space for the gas (V_g). The impurities is assumed to be MgO , ρ_B of which is 3.6 g/cm^3 .⁷

$$V_g = V_t - \frac{M_{\text{PuO}_2}(\text{g})}{\rho} - \frac{M_B(\text{g})}{\rho_B} \quad \text{Eq.2}$$

With a large alpha radiolysis field present in the can, an equilibrium is established between water, H₂, and O₂, which favors water formation in general. In order to produce large quantities of H₂, the reaction to form water must be limited by completely consuming the available oxygen. In the model, oxygen is principally consumed in the construction of H₂O₂ which oxidizes the plutonium dioxide to the superoxide. Hydrogen does not build to any appreciable levels until the O₂ is consumed. The 200 day shipping window could be stretched by including more oxygen in the storage container, e.g. filling the container with oxygen instead of air.

RESULTS AND DISCUSSION

Container ID 39-01356A contains 61 g (16.156 Ci) Pu, 115 g of bulk material, at 4.3 weight percent water by loss on ignition. The pressure inside the container at 365 days is predicted to be 16 psia. Gas phase hydrogen is predicted to reach 5 percent by volume at 206 days, see Table II.

Container ID 39-01356B contains 58 g (15.397 Ci) Pu, 111 g of bulk material, at 4.3 weight percent water by loss on ignition. The pressure inside the container at 365 days is predicted to be 16 psia. Gas phase hydrogen is predicted to reach 5 percent by volume at 218 days, see Table II.

Container ID 39-01483A contains 61 g (16.074 Ci) Pu, 269 g of bulk material, and 23.3 weight percent water by loss on ignition. The pressure inside the container at 365 days is predicted to be 62 psia. Gas phase hydrogen is predicted to reach 5 percent by volume inside 13 days. If the container was treated to reduce the water content below 4.3 weight percent water, the material and storage container would be shippable inside the 200 day window.

Container ID 07242326A contains 69 g (17.588 Ci) Pu, 429 g of bulk material, at 0.33 weight percent water by loss on ignition. The pressure inside the container at 365 days is predicted to be 14 psia. Gas phase hydrogen remains below 5 percent by volume for the entire year, see Table II.

Container ID 101707001A contains 61 g (14.957 Ci) Pu, 295 g of bulk material, at 0.58 weight percent water by loss on ignition. The pressure inside the container at 365 days is predicted to be 14 psia. Gas phase hydrogen remains below 5 percent by volume for the entire year, see Table II.

Container ID 07242243A contains 57 g (14.297 Ci) Pu, 218 g of bulk material, no water was found by loss on ignition. The pressure inside the container at 365 days is predicted to be 13 psi. One would expect that with no water, no pressure could be generated. The reason why this can be pressurized to 13 psia is that $1 \cdot 10^{-8}$ g of water was added to the simulation to avoid division by zero errors. Gas phase hydrogen remains below 5 percent by volume for the entire year, see Table II.

Table II: Pressure and H₂ generation in the six containers.

ID (Headspace filled with Air)	Max Pressure (psia)	H ₂ generated (moles)	Time required for the headspace to reach 5% H ₂ (days)
39-01356A	12 at 206 days 16 at one year	$1.8 \cdot 10^{-3}$ at 206 days $1.3 \cdot 10^{-2}$ at one year	206
39-01356B	12 at 218 days 16 at one year	$1.8 \cdot 10^{-3}$ at 218 days $1.2 \cdot 10^{-2}$ at one year	218
39-01483A	14 at 13 days 62 at one year	$2.1 \cdot 10^{-3}$ at 13 days 0.14 at one year	13
07242326A	14	$7.0 \cdot 10^{-3}$	Over one year
101707001A	14	$6.4 \cdot 10^{-3}$	Over one year
07242243A	13	$7.7 \cdot 10^{-3}$	Over one year

CONCLUSION

The calculations were performed in order to elucidate allowable times for shipping without exceeding packing requirements. We predict that 5 of the 6 items can be packaged and shipped to Los Alamos National Lab in 200 days or less without exceeding the 5% hydrogen by volume limit. If the water in the sixth can (ID 39-01483A) is reduced below 4.3% by weight, the storage container can be shipped, also inside the 200 day window.

As expected, at one year the can with the most water had the highest pressure (61 psia) and highest hydrogen content (0.14 moles) and exceeds the shipping requirements at 13 days. The final pressures in Table II, can be lowered and the time for the gas phase composition of the sample to reach five percent hydrogen by volume increased by removing the water and to a lesser extent to use a gas mixture with more oxygen, because oxygen is a sink for the hydrogen ($\text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{g})$). The storage container can not start to pressurize until all the oxygen has been depleted, therefore, the window can be extended by sealing the can with an oxygen environment instead of an air environment.

Our calculations show that 5 of the 6 items can be packaged and shipped to Los Alamos National Laboratory inside 200 days or less without exceeding the 5% hydrogen by volume limit as specified in Department of Energy's (DOE) Package Certification Approval Record, Docket No 00-11-9965. If the water in the sixth can (ID 39-01483A) is reduced below 4.3% by weight as measured by loss on ignition, then the item can be shipped, also inside the 200 day window.

Due to the requirements to ship material around the complex (i.e. Savannah river and WIPP) windows of opportunity have to be calculated. This system can be extended easy into other chemical, thermodynamic, and radiolysis reactions that could be present in other systems by adding the activation energy and the preexponential factor in the table of Arrhenius equations.

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