

Divergent Mechanisms of Hydrogen and Oxygen Consumption on Calcined PuO₂: Implications for Long-Term Storage

Will DeBenedetti^{1*}, Joshua Narlesky¹, Laura Worl¹

¹Los Alamos National Laboratory, Los Alamos NM, USA; *wdebenedetti@lanl.gov

The safe and long-term storage of plutonium dioxide requires reliable prediction of headspace gas composition, yet mechanisms governing post-calcination gas consumption remain poorly understood. Radiolytic decomposition of adsorbed water produces both H₂ and O₂ within sealed containers, and the subsequent consumption of these gases by PuO₂ surfaces determines whether conditions evolve toward flammable or pressurized states. Previous work has established that gas generation rates depend on the excess oxygen parameter ($\delta = \text{O/Pu} - 2.0$), specific surface area, local radiation field, and adsorbed water loading, but systematic studies isolating the consumption pathways and their dependence on calcination processing conditions have been lacking.

We present a comprehensive experimental investigation of H₂ and O₂ consumption kinetics across anhydrous PuO₂ samples spanning storage-relevant calcination conditions. The sample matrix includes two source materials (BLO and BLO-C) calcined at 400 °C and 950 °C under both air and argon atmospheres, with specific surface areas ranging from 0.8 to 5.0 m²/g. Small-scale reactors (SSRs) were charged with known quantities of H₂ or O₂ and monitored over periods of months *via* gas chromatography. This geometry delivers ~403× higher radiation dose per gram than full-scale storage containers due to alpha range limitations, enabling accelerated mechanistic studies while maintaining chemical relevance.

Despite occurring on the same PuO₂ surfaces, hydrogen and oxygen consumption proceed through fundamentally different pathways. Hydrogen consumption follows Langmuir chemisorption kinetics characterized by pressure-dependent equilibrium, first-order rate dependence on H₂ partial pressure, and a strong correlation with specific surface area. Calcination temperature is the dominant control parameter: 950 °C processing produces approximately 7× higher adsorption site density than 600 °C, attributed to oxygen vacancy generation and surface defect formation. Reversible surface activation was observed, with a 4× capacity increase upon sequential refilling experiments. No correlation with specific power was detected within constant-power sample sets, establishing that radiolysis *does not drive hydrogen uptake*. The mechanism is best described as $\text{H}_2(\text{g}) + \square_{\text{surface}} \rightleftharpoons \text{H}_2\text{-}\square_{\text{ads}}$, where $\square$ represents oxygen vacancies and coordinatively unsaturated Pu⁴⁺ sites.

Oxygen consumption exhibits markedly different behavior: first-order exponential decay kinetics no meaningful surface area dependence, and dramatic sensitivity to calcination atmosphere. A critical mechanistic reversal was identified in which air calcination enhances O₂ consumption at 400 °C (+11%) while argon calcination dominates at 950 °C (+56%, corresponding to a 3.3× difference in half-life). This crossover is consistent with a dual-mechanism model: at low calcination temperatures, surface the dose to the surface provides reactive oxygen sites that consume headspace O₂ through chemical reduction, while at high temperatures, oxygen vacancy defects created during calcination serve as irreversible sinks for molecular oxygen. Bi-exponential fitting reveals distinct fast and slow site populations, supporting the coexistence of these two pathways.

These mechanistic distinctions carry direct implications for storage optimization. Because H₂ consumption is predictable from surface area while O₂ consumption depends on defect chemistry

imparted by processing history, a single calcination protocol can be identified that simultaneously addresses both gases. Air calcination at 950 °C produces material with low specific surface area (minimizing hydrogen uptake capacity and generation from adsorbed water) while suppressing oxygen vacancy concentration (extending the O₂ half-life to ~349 days versus ~105 days for argon-calcined material). This work provides the mechanistic foundation for optimizing calcination protocols and predicting long-term headspace gas evolution in PuO₂ storage configurations.