Gas Generation in Pu-O-H System -ABSTRACT

The behavior of plutonium (Pu) oxides in the presence of water/moisture in a confined environment and the associated issues of hydrogen and oxygen generation due to radiolysis have important implications for the storage and transportation of plutonium-bearing materials. According to the U.S. Department of Energy (DOE) Standard for Stabilization, Packaging, and Storage of Plutonium-bearing Materials, DOE-STD-3013-2004, there are inherent self-limiting mechanisms that prevent accumulation of significant pressures of oxygen and hydrogen over calcined oxides limiting oxygen buildup, including recombination with hydrogen and formation of $PuO_{2+x}$ from adsorbed water. Formation and stability of $PuO_{2+x}$ as a sink for oxygen is the key in preventing Pu-bearing materials stored in cans from reaching the flammability range.
This paper will review results of recent studies of gas generation in the Pu-O-H system, including determination of release rate via engineering measurement and modeling using multiple chemical reaction rate theories. The paper will also discuss recent scientific advances in the investigations of the Pu-O-H system using state-of-the-art ab initio electronic structure calculations, as well as advanced synchrotron techniques to determine the valence structure of the various Pu-containing phases. Of particular interest is the possibility of entropy-induced transition of intermediate phases on the long-term stability of $PuO_{2+x}$. Investigation of this possibility is suggested experimentally by using pressure transducers and oxygen sensors, and theoretically by ab initio electronic structure calculations.
Implications of gas generation in Pu-O-H system on the storage and transportation of Pu-bearing materials will be discussed, along with the consequences of breaching the flammability limits. Based on synthesis of these recent developments, a framework is suggested for the next stage of development of science-based, engineering-tested guidelines for the storage and transportation of Pu-bearing materials.