Identification of Chlorine-Containing Gases Generated by Hydrated PuO_2/Salt Mixtures

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Plutonium is a dynamic, unstable element that presents unique challenges for its safe long-term storage. The Department of Energy (DOE) stores excess plutonium-bearing materials in double nested stainless steel containers. The 3013 Standard (DOE-STD-3013), "Stabilization, Packaging, and Storage of Plutonium-Bearing Materials", defines the stabilization and packaging requirements that assure excess plutonium can be safely stored for 50 years. It requires both stabilization of the plutonium material prior to packaging, to remove volatile components, and a moisture measurement after stabilization to confirm the moisture is less than 0.5 wt%.

Field-destructive examinations of 3013 containers have revealed corrosion in some containers packaged with hydrated PuO_2/salt mixtures. Corrosion was observed in both the contact region, the area where there is contact of the bulk material with the stainless steel, and in the headspace region, the area where there is no contact of the bulk material with the stainless steel. Energy dispersive x-ray (EDX) analyses of corrosion deposits in the headspace showed the presence of chloride (Cl) but no metal cations from hydrated PuO_2/salt mixtures (Na, K, Ca, Mg, or Pu) that would indicate particulate transport of the Cl to that location. This suggests Cl was transported via chlorine-containing gases (i.e., HCl, Cl_2). Chlorine-containing gases with higher redox potentials have been shown to be more corrosive towards stainless steel (i.e., $Cl_2 > HCl$). Therefore, it is important to identify the chlorine-containing gases being generated by the enclosed hydrated PuO_2/salt mixtures to better evaluate the risk of through-wall corrosion in packaged 3013 containers.

Chlorine gas getters were exposed to the headspace gas above recently prepared hydrated PuO_2/salt mixtures and their analyses revealed the successful capture, identification and quantification of HCl and Cl_2 gases. These results suggest the headspace gas above hydrated PuO_2/salt mixtures packaged in 3013 containers contain HCl and Cl_2 gases, and that these gases together with oxygen and moisture cause the corrosion observed when stored containers have been opened and examined. The insights from the present study, in conjunction with future planned studies, are intended to move towards a comprehensive understanding of corrosive gas generation over time for different plutonium-bearing materials. The results will ultimately underpin a science-driven safety basis for effectively monitoring and managing long-term storage of these materials.

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