

Abstract No. duff96

Characterization of Palladium and Ruthenium after Reaction with Tetraphenylborate

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Beamline(s) X23A2

Introduction: Removal of radiocesium by precipitation with dissolved tetraphenylborate (TPB) from High-Level Radioactive Waste (HLW, the waste product associated with the dissolution of spent fuel rods for the recovery of plutonium) is being considered as a waste treatment strategy at the Savannah River Site (SRS). Approximately 130 million L of this waste resides in subsurface tanks awaiting treatment at the SRS. Previous attempts to treat this waste at the SRS with dissolved TPB resulted in the evolution of levels of benzene (a TPB decomposition product), which did not permit the safe operation of the facility at design throughput rates. Although low levels of benzene from the radiolytic and thermal decomposition of TPB were anticipated, the amount of benzene was underestimated. The HLW tanks contain most every element in the periodic chart including catalytic metals such as palladium (Pd) that are capable of decomposing TPB.

Methods and Materials: This abstract describes a second series of X-ray absorption fine structure spectroscopy and chemical analyses to examine the form that Pd and, to a lesser extent, ruthenium (Ru), takes in simulated HLW slurries containing TPB salts. Data collection was conducted at the K absorption edge of Pd and Ru using a Lytle detector.

Results: Based on the analyses and the previous associated studies, we reach the following conclusions. Preliminary studies suggest the formation of nanoclusters of Pd at the onset of catalytic activity occur as a dynamic process with evolution in the cluster speciation over time. Clusters coalesce to larger particles of Pd with time in solutions of TPB and TPB decomposition products. The observations from our EXAFS analyses were corroborated by findings from high-resolution transmission electron microscopic analyses. The clusters are structurally stable after 10 months of air-drying at 25 °C and they do not oxidize over time to Pd(II). Their subsequent reactivity with TPB remains unmeasured at this time. The Ru added as Ru(III), in the 6-month old HLW simulants existed as clusters of Ru(IV) oxide with a structural environment like the tetragonal solid Ru(IV)O₂. Repeated analysis of the previous Ru-XAFS data for the Ru samples indicate Ru in the fresh HLW simulants exists as this oxidized species. The Ru in these tests did not catalyze TPB decomposition and the mechanism by which it was oxidized is not known. WSRC-MS-2001-00723