
Controlling Neptunium and Zirconium in Advanced Extraction Processes

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ABSTRACT:

A number of advanced extraction processes to recover different combinations of actinide elements from used nuclear fuel are under development at various technical readiness levels. Many of these advanced separation processes use tributylphosphate (TBP) as an extractant (e.g. UREX, CoEx, NUEX and CoDCon) or as a phase modifier (e.g. TRUEX and TBP/BTBP-GANEX). Others, for example GANEX-1, are based on solvating extractants (monoamides) that show many similar extraction behaviors to TBP. While these extractants are efficient separating agents for important actinides, a few elements present persistent issues for fuel recycle in these systems. Chief among these are neptunium (Np) and zirconium (Zr). The overall issues with Np and Zr are generally known. Neptunium can easily exist in three different oxidation states and can form cation-cation complexes, both of which affect its partitioning. Zirconium forms soluble and insoluble aggregates that hinder Zr removal and can severely impair extraction performance. However, the fundamental chemical principles that drive these behaviors are not known. The organic phase reduction potentials of Np have never been reported; the composition, nature, and formation energetics of proposed Zr aggregates have never been systematically examined starting with fuel-cycle relevant materials; and how the radiation fields and radiolysis products encountered during fuel recycle drive these specific behaviors of Np and Zr are uncharted.

Recent advances in experimental and theoretical approaches present a critical opportunity to finally understand fundamental molecular-level behaviors of extracted Np and Zr in the presence of radiation fields. Coupling optical and X-ray spectroscopy, small angle scattering, equilibrium thermodynamics, and chemical analysis with the world-class irradiation facilities at INL and recent advances in *biphasic* electrochemistry and computational modeling, we propose to elucidate the specific chemistries underlying the problematic behaviors of Np and Zr in radiation fields. Our objectives are (1) to understand how γ -radiation and radiolysis products in advanced TBP-based separation systems affect the organic phase redox reactions of Np and its chemical speciation in the organic phase, and (2) to understand how Zr aggregates form and coalesce into problematic species in advanced separation systems under irradiation.

These investigations are driven by two hypotheses. First, we hypothesize that the Np oxidation state is influenced by both radiation effects and radiolytic extractant degradation products that stabilize Np(VI) and complicate the recovery of Np. Second, we hypothesize that the formation of organic phase, polynuclear bridged Zr species initiates prior to visible observation of Zr aggregates and impedes Zr recovery by providing the seed for CRUD formation. Understanding the answers to these hypotheses will enable successful execution of advanced separation processes that require rational, finer control of Np and Zr chemistry.