Speciation and Behavior of Neptunium and Zirconium in Advanced Separation Process

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ABSTRACT:

Tributyl phosphate (TBP) is the technologically most important extractant for nuclear fuel reprocessing. TBP selectively removes tetra- and hexavalent actinides from solutions of used fuel dissolved in nitric acid (3-4M). Trivalent (Am and Cm), pentavalent (Np) actinides, and most fission products remain in the aqueous raffinate. In the recent development toward the advanced aqueous separation process, the CoDCon flowsheet uses tetravalent uranium to reduce the extracted Pu(IV) to the non-extractable Pu(III) oxidation state and strip Pu from the loaded TBP solvent. To reduce the attractiveness level of the Pu, the CoDCon flowsheet is designed to allow some of the U(IV) to partition to the aqueous phase during Pu stripping. However, the management of other metal ions in the process can be challenging. For example, there are a number of options that might be considered for directing Np within the CoDCon flowsheet. The Np could be (1) routed to the raffinate by reducing it to Np(V), for example, by adding $NaNO_2$, (2) co-extracted with U(VI) and Pu(IV), followed by selective Np stripping flowsheet, or (3) intentionally directed to the U/Pu product stream. A comprehensive understanding of Np chemistry within the framework of the CoDCon system is required to make informed decisions on which Np option to pursue. Zirconium and technetium present similar challenges in developing and demonstrating the CoDCon flowsheet. The proposed objectives of our project are (to):

- Quantify the rates of redox reactions of Np, Tc, Pu with U(IV) and hydrazine, in the absence and presence of the complexing agents and degradation products, applying a variety of spectroscopic and electrochemical techniques to investigate the metal speciation and its changes upon reduction and radiation in both extraction phases. Calculate the time sufficient for complete reduction of Np(VI) to Np(IV), determine the distribution ratios of Np, Pu, Tc and Zr in the absence of CDTA and at various CDTA concentrations, and verify the use of CDTA to suppress Zr extraction.
- For given concentration conditions, quantify the speciation diagram of zirconium, considering all the molecular, colloidal and supramolecular species, in the absence and presence the masking ligand. Apply computational methods (DFT and/or Monte Carlo) and estimate molecular structures of the observed metal complex species. Evaluate formation of the two-metal complexes between two actinides, Zr-actinides and Zr-Tc in systems with higher metals concentrations. Apply computational methods (DFT) to calculate molecular structures of species.
- Estimate the radiation effect on all studied species and their reactions: speciation of metals, the CDTA ligand molecule and on its complexes with metals present in in studied separation systems.
- Compare the collected data with the previously publish data and propose alteration of the flowsheet. Verify the proposed alteration in the counter-current contactors test.