Project Title: Effect of Radiolysis on Pertechnetate under Solvent Extraction Conditions, including Tributyl Phosphate

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Program: Nuclear Fuel Cycle Chemistry FC-1.2

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ABSTRACT:

This project directly addresses FC-1.2 of the FOA: nuclear fuel cycle chemical separations of important elements. The overarching objective of the research is to assess the impact of radiolysis on pertechnetate ($^{99}TcO_4^-$) speciation during tributyl phosphate (TBP) extractions from the molecular level to macroscale. ^{99}Tc is a high yield fission product and there is a gap in understanding radiation-induced speciation under fuel cycle conditions, specifically upon extraction with TBP in the presence of other metals.

Deliverables: 1) determination of ^{99}Tc speciation during solvent extractions using TBP under radiation fields and including other high yield fission products and uranium. 2) Development of an innovative approach to use TiO_2 nanoparticles under UV irradiation as a surrogate for gamma irradiation. This strategy will allow convenient and quick prioritization of samples to choose those that will be sent forward to gamma irradiation at Brookhaven (BNL) using their ^{60}Co irradiation system.

Impact: This work will address outstanding fundamental knowledge gaps regarding redox and extraction behavior of ^{99}Tc in the HNO_3/ TBP/dodecane system. Moreover, a detailed knowledge of the redox chemistry and speciation of Tc under these separation conditions can improve the understanding of early actinide (U, Np, Pu) behavior when they are together in separations matrices. This study also provides a new approach that mimics irradiation that can be used broadly by others to study other valuable metals.

We have assembled a team of experienced senior and junior researchers that can uniquely take on the challenges of this project. Hunter is the lead; all ^{99}Tc samples will be prepared in Hunter facilities. Lehman will lead the effort in theoretical chemistry to inform on stability of Tc-phosphate complexes. Gamma irradiation of Tc solvent extraction samples will use the ^{60}Co irradiator in the BNL ACER facility. After gamma irradiation, separations will be performed in the radiological laboratories in the Isotope Program at BNL. X-ray Absorption Spectroscopy (XAS) will be performed at BNL NSLS II.

This project is divided into four tasks:

Task 1) measure distribution coefficients for Tc in extractions using reprocessing simulants based on TBP and its degradation products and metals (Ce, Zr, U) that are in PUREX process relevant concentrations. XAS will reveal oxidation state and coordination environment. Multinuclear NMR (^{99}Tc, ^{31}P, ^{1}H) and FT-IR will inform on Tc and phosphate speciation.

Task 2) Use a surrogate method to mimic radiolysis (TiO_2 photocatalysis) to determine Tc distribution ratios, oxidation state speciation and coordination environment of Tc upon irradiating TcO_4^- (in the presence of Ce, Zr, U) plus TBP under reprocessing conditions. As in Task 1, XAS, multinuclear NMR, and FT-IR can further inform on Tc oxidation state and speciation. This Task will screen conditions to prepare samples for Task 3.

Task 3) Use conditions generated from Task 2 to determine Tc distribution ratios, oxidation state speciation and coordination of Tc upon irradiating TcO_4^- (in the presence of Ce, Zr, U) plus TBP under reprocessing conditions using ^{60}Co gamma irradiation. As in Tasks 1 and 2, XAS, multinuclear NMR, and FT-IR can further inform on Tc oxidation state and speciation.

Task 4) Computations will provide an evaluation of formation of Tc phosphate species.