Alpha Radiolysis of Nuclear Solvent Extraction Ligands Used for An(III) and Ln(III) Separations

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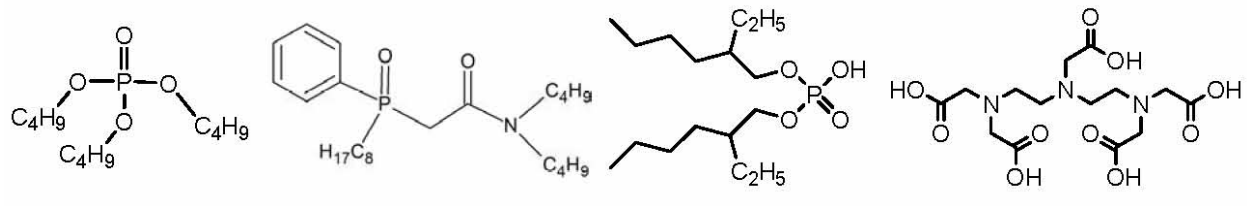
ABSTRACT

In NEUP RFP-910, understanding fundamental chemistry in separations processes is essential for an optimized approach that will allow used nuclear fuel recycling and minimize radioactive waste generation. Current separations are designed to recover fissionable material and minimize the radiotoxicity of nuclear waste destined for geological disposal. One of the more formidable challenges in this regard is the separation of the minor actinides from the lanthanides, which is problematic due to their very similar chemistry.

While multiple separation approaches have been proposed for lanthanide/actinide separation, all of these processes have to be robust under high-radiation conditions. The presence of both gamma and alpha radiation can degrade solvent extraction formulations and result in decreased ligand concentrations and lower extraction efficiency due to the generation of undesired complexing chemicals, precipitates, and increased solution viscosity. As solvent recycling is desirable to minimize ligand loss, an understanding of the major radiation effects is necessary for their successful deployment. Minimizing deleterious effects and proper design of solvent washing steps to remove radiolytic degradation products could result in significant cost savings for large-scale reprocessing.

While some work is currently underway towards this goal, significant gaps in our knowledge remain. The work proposed here will measure and compare the effects of γ and α irradiation on ligands used in separation systems for nuclear material. This will be accomplished by using steady-state irradiations to measure effects on distribution and stripping ratios and decomposition products, and electron pulse radiolysis measurements to determine kinetic parameters for important transient species. The comparison of the α and γ irradiations will allow us to elucidate the mechanisms of ligand decomposition since the respective yields of the major radicals that will degrade the extraction ligands, $^{\cdot}OH$, $NO_3^{\cdot}$ and $H^{\cdot}$, produced by the different radiation sources are known. The kinetics of these radicals do not depend on how they are produced; thus, the data obtained by pulsed radiolysis methods are applicable to both α and γ radiolysis. Three distinctly different methods for alpha radiolysis will be benchmarked on known systems, and the optimal method utilized for our new studies. The major extracting and complexing agents, TBP, CMPO, HDEHP, and DTPA shown below, will be the focus of this work.

A major component of this proposal is the investigation of the radiolytically induced degradation of metal-loaded ligands. Very little information is available for such systems, and much of this information is contradictory. Furthermore, there is no data available for the kinetics of radiolysis reactions in the organic phase. Thus this investigation will fill major current gaps to describe deleterious reactions with importance in a real-world, irradiated, solvent system. The knowledge gained will provide not only a comprehensive understanding of the radiation chemistry of currently proposed processes but also give baseline information and evaluation methods for any future proposed nuclear solvent extraction systems.



Ligands of interest of this study, from left to right: TBP, CMPO, HDEHP, DTPA.