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## Building Quantitative Relationships between Ligand Structure and Its Reactivity with Organic Radical Species

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**Program:** Fuel Cycle

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**ABSTRACT:**

In the area of hydrometallurgical recovery of actinides from mixtures of dissolved used nuclear fuel the damaging effect of radiolysis is of major concern. The deposition of the energy of radioactive decay in matter produces highly reactive free radicals, solvent radical cations, nitrate radicals from entrained nitric acid, and peroxy radicals, which impose molecular changes upon everything in their path. All components of any operating recovery process (typically based on solvent extraction) are at risk from such damaging reactivity. Radiolytic degradation has been linked to changes in separation efficiency and physical properties of solution mixtures, solvent-recycle longevity, crud formation, and other unexpected outcomes.

While considerable work has been reported on the kinetics and performance impacts of radiation-induced ligand damage for acidic water radiolysis species far less kinetic and mechanistic data is available for the radiation-induced degradation of extraction ligands in the organic phase. Some recent reports of radiolysis-induced degradation of ligands in organic diluents such as dodecane and octanol have shown vastly different degradation kinetics dependent upon environment. For example, when ligands such as CMPO (octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide) in dodecane are irradiated after pre-equilibration with 3.0 M HNO<sub>3</sub> significantly slower degradation occurs. Nearly a complete preservation of this ligand occurs when it is initially pre-equilibrated with aqueous mixtures of moderate acidities. Similar behavior has been observed for nitrogen heterocyclic reagent, CyMe<sub>4</sub>BTBP, in octanol, but not for acid contacted TODGA in dodecane.

The very disparate response of these three ligands to acidic aqueous phase equilibration points out the existence of a relationship between ligand structure and its radiolytically-induced degradation. It is clear that the ligand-based extraction design process may benefit from the elucidation of such relationships. This proposal offers the opportunity to discover a quantitative connection between the molecular features of extraction reagents and their natural predisposition to reduce radiation-induced damage by radical reactions in the organic phase through simple equilibration with acidic water. To accomplish this we propose to study the reactivity of radiolytically-induced radical organic species for a mono-functional family of organophosphorus-based extraction reagents, CMPO, diglycomides, and BTP's/BTBPs. For diglycolamides, multiple structural variations of TODGA will be investigated in order to establish structure-reactivity relationships.

The major objective of this proposal is to establish global structure-activity correlations between the reaction kinetics for these three organic-phase radicals and the physicochemical properties of extraction ligands determined by their structural features. The understanding of the observed differences in the response to aqueous equilibration could identify promising clues to ligand preservation via "self-protecting" mechanism. This will obviate the need for future phenomenological studies of these systems by providing a quantitative/predictive capability for determining the extent of radiolytically-induced degradation for these, and future solvent systems.