Prediction, scale-up, and optimization of used nuclear fuel processes using hydroxypyridinone-based hold-back reagents for actinide and fission product recovery

PI: Rebecca J. Abergel
University of California, Berkeley

Collaborators: Gregory P. Holmbeck
Idaho National Laboratory

Program: Nuclear Fuel Cycle Chemistry

ABSTRACT:

High level waste, such as Plutonium Uranium Redox Extraction (PUREX) raffinate, generates much heat and remains highly radiotoxic for thousands of years, mainly due to long-lived fission products (some of which are lanthanides, Ln) and minor actinides (minor An, mostly Np, Am, and Cm). Among the many radionuclides existing in used nuclear fuel (UNF), separating the trivalent Ln and minor An from each other is of particular interest. The separation of Am^{3+} and Cm^{3+} from Ln^{3+} is very challenging because they exhibit the same oxidation state, comparable charge densities, and similar hydrated ionic radii. Discrimination primarily relies on the fact that Ln^{3+} ions are slightly harder than An^{3+} ions. One approach for effecting this separation is the use of water-soluble soft donor chelators to hold back Am^{3+} and Cm^{3+} in the aqueous phase, while Ln^{3+} are extracted into an organic phase by hard donor extractants. Our team has developed water-soluble hydroxypyridinone-based (HOPO-) chelators for complexation of An^{3+} and Ln^{3+} elements for fundamental chemistry studies, and various medical applications. We determined that some of these chelators present a unique set of properties highly suitable for UNF separation technologies: *(i)* unprecedented charge-based selectivity; *(ii)* formation of highly stable complexes even at high acidity (up to 10 M H_{aq}^+); *(iii)* ability to change the oxidation state of metal ions (Sn, Ce, Pu, and Bk) without adding redox active species; *(iv)* simple and controllable speciation over a broad pH range; *(v)* fast complexation kinetic; and *(vi)*, as part of Phase I, HOPO was found to also possess significant alpha irradiation robustness (up to 100 kGy) and no change in radiation-induced reaction kinetics upon metal ion complexation. These properties are un-equaled by other contemporary chelating structures, namely the polyaminocarboxylates, and could be the cornerstone of new UNF separation strategies.

Studies performed under Phase I demonstrated the applicability of leveraging HOPO-based ligand architectures to drive the efficient separation of target elements and operate under the extreme conditions of a multi-component (alpha, beta, and gamma) radiation field. We performed a combination of speciation and spectroscopic measurements with liquid-liquid extraction and irradiation experiments that provided a clear phenomenological understanding of Ln^{3+}/An^{3+} ion complexation with HOPO-based ligands, demonstrating their potential as new reagents for UNF separations.

The continuation project seeks to optimize and scale-up and optimize this new approach, combined with multi-scale modeling for the prediction of radiolytic ligand longevity and degradation product formation over time, so as to augment at-scale engineering models in support of future process-scale implementation. Additionally, with growing interest in direct dissolution reprocessing technologies, Phase II of our work will also seek to develop HOPO-based ligand strategies for direct dissolution scenarios.