
Elucidation of the kinetics of Advanced Separation systems

PI: Stephen Mezyk CSULB

Collaborators: Leigh R. Martin, Idaho National Laboratory

Program: Fuel Cycle R&D FC1.2

ABSTRACT:

The separation of transuranic elements from used nuclear fuel is predominantly performed using solvent extraction technologies. The only industrial scale process deployed globally is the PUREX process for the separation of uranium and plutonium from used fuel. It is a significantly greater challenge to remove the minor actinides (americium) from the fission product lanthanides due to their almost identical physical and chemical properties. Separation systems have been developed based upon the thermodynamics of these processes, but only tested at the laboratory scale. A fundamental understanding of the chemical kinetics relevant to separation of transuranic elements from used fuel is needed to create an optimized approach that could provide a simplified, single-step recovery process with minimal waste generation.

Of the many proposed schemes to for actinide-lanthanide separation significant success has been found by utilizing separations reagents with soft donor atoms. One of the most studied approaches for this separation is the TALSPEAK (Trivalent Actinide Lanthanide Separations by Phosphorus-reagent Extraction from Aqueous Komplexes) process that utilizes an aqueous phase complexant (DTPA) to hold back the actinides with the lanthanides extracted using a ligand such as HDEHP into an organic phase. This research has been the inspiration for new techniques such as Advanced TALSPEAK and ALSEP processes that have slightly improved performance agreement between empirical thermodynamic models and the experimentally measured distribution data.

While research continues to determine thermodynamic stability constants for lanthanide-DTPA complexes there is still considerable disagreement about the absolute kinetics involved. For example, there have only been three studies that have specifically investigated the absolute kinetics for DTPA-complexation of lanthanides. The rate constant data reported are inconsistent, with both mono-exponential and bi-exponential kinetics observed, and elucidated rate constants differing by orders of magnitude. Even less kinetic data is available for ligand (notably diglycolamides such as TODGA) complexation with lanthanides and actinides in the SANEX, GANEX and ALSEP extraction systems.

The major objective of this proposal is to quantitatively establish the kinetics of ligand complexation with both lanthanides and actinides in the organic and aqueous phases. By elucidating and quantifying the important factors in the rates at which ligands complex these metal ions, and especially how fast decomplexation of metal-ligand species occurs, a general computer model of this chemistry can be constructed that will allow quantitative prediction of this chemistry under process conditions. This type of model is essential for operations of a large, complex chemical process and therefore this work is directly supportive of current DOE efforts to understand both the fundamental chemistry and of the scaling of a process for the efficient separation of actinides and lanthanides.