

Advanced Aqueous Separation Systems for Actinide Partitioning: Develop Fundamental Understanding of An(III)/Ln(III) Separation

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ABSTRACT

A challenging aspect of advanced processing of used nuclear fuel is the separation of transplutonium actinides from fission-product lanthanides. This separation is essential if actinide transmutation options are to be pursued in advanced fuel cycles, as lanthanides compete with actinides for neutrons in both thermal and fast reactors, thus limiting efficiency. The separation is difficult because the chemistry of Am^{3+} and Cm^{3+} is nearly identical with that of the trivalent lanthanides (Ln^{3+}). Prior literature teaches that two approaches offer the greatest probability of devising a successful group separation process based on aqueous processes: the application of complexing agents containing ligand donor atoms that are softer than oxygen (N, S, Cl) or changing the oxidation state of Am to the IV, V, or VI state to increase the essential differences between Am and lanthanide chemistry. For soft donor extraction systems, process design limitations arise from the overall weakness of the metal-ligand interaction, the tendency of the soft donor complexants to partition into the aqueous phase, the susceptibility to hydrolytic and radiolytic degradation, and slow complexation/phase transfer kinetics. The upper oxidation states of Am are all moderately strong oxidants and hence of only transient stability in media representative of conventional aqueous separations systems. Improved understanding of the underpinning science is needed to develop more effective options for accomplishing these separations.

An existing research program at Washington State University (WSU) has for the past five years investigated both of these approaches to partitioning Am^{3+} from lanthanides. To build on the results of the previous and ongoing research, the following avenues of investigation will be pursued (focusing on fortifying the scientific basis for advanced separations): (a) the basic underlying chemistry of the TALSPEAK process, emphasizing studies of the apparent supramolecular organization of solutes in the organic phase impacting both mass transfer kinetics and pH control, (b) the separation potential and thermal/hydrolytic/radiolytic stability of new varieties of poly-amino extractant molecules for selective extraction of trivalent, and (c) the possibility of selectively stabilizing pentavalent actinide ions (targeting Am(V) in particular) through the formation of intermetallic complexes that encapsulate the unstable AmO_2^+ to either increase its thermodynamic stability or impart adequate kinetic stability (or both) to allow its selective partitioning from Cm^{3+} and fission product lanthanides. Each of these studies promises to increase scientific understanding of phenomena central to developing advanced actinide/lanthanide separations methods. Some explicit advances expected are: improved understanding of TALSPEAK chemistry and solute-solvent interactions in complex systems, the development of new information to support simplification of the UREX + process suite, and improved understanding of the potential effects of supramolecular organization on phase transfer kinetics and basic information on intermetallic actinyl(V) ions to support possible separations applications.