Interrogating *f*-element Ligand Interactions by X-ray Absorption Spectroscopy

PI: Christopher Dares, Florida International University

Program: FY 2021 General Scientific Infrastructure Call

Co-PIs: Raphael Raptis, Florida International University

Alexander Mebel, Florida International University

Konstantinos Kavallieratos, Florida International University

Konstantin Bukhryakov, Florida International University

ABSTRACT:

The goal of this project is to answer questions of direct interest to the nuclear fuel cycle by obtaining a better understanding of the nature of inner and outer coordination sphere or actinide complexes and materials of interest. This includes fuel preparation, materials recovery, and wasteform development. We will accomplish this through studies involving *f*-element ligand complexes which will be characterized by spectroscopic techniques currently available at FIU, and new capabilities provided by infrastructure requested in this proposal including multinuclear NMR spectroscopy and by X-ray absorption spectroscopy. This will not only include studies of lanthanides, but also the study of actinides outside of their 'typical' oxidation state, including the study of U, Np, Am, and possibly Cm, in oxidation states ranging from +7 to +3. We are able to handle >10 mCi quantities each of the most common isotopes of these actinides. Our understanding of oxidation state control and the how we can manipulate the relative stability of specific oxidations states for specific actinides is at the heart of PUREX chemistry. This includes investigating ligand interactions with Ln(III) and Am(III) metals to further our development of Am(III) extractants and holdback agents. It also includes our use of simple methods we have developed to quantitatively prepare high valent actinides such as Am(VI) without the addition of any complexing agents. Our methods involve the use of high surface area metal oxide electrodes where the surface may be functionalized with different ligands. The interaction between the ligand and actinide (like Am(III)) at the surface of the electrode is key to their operation. Our understanding is currently limited to in house electrochemical, and visible absorption spectroscopy. We will expand these capabilities through the purchase of a broadband NMR probe for multi-nuclear NMR structure elucidation, and the inclusion of X-ray absorption spectrometer. The data acquired from these instruments will greatly benefit our understanding of these functional materials.

The understanding that we gain from experimentally measuring the X-ray absorption spectra of these *f*-element complexes will provide fundamental details regarding the bonding, valence electron localization, and redox stability. These data can then be used to develop new complexants, new separations schemes, improve existing schemes, and provide more accurate computational models where *f*-elements are currently a challenge. Each of these projects will benefit from the additional infrastructure proposed here, by advancing the state of the art understanding of actinide coordination chemistry. Our expectation is to provide access to the radiological facilities and infrastructure, not only to all researchers at FIU and collaborators, but, to develop it into a Nuclear Science User Facility (NSUF) to provide the tools necessary to answer questions regarding actinide chemistry that will undoubtedly arise in the future.