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Actinides and Environmental Interfaces: Striving for Molecular-Level Understanding

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Actinides can undergo a variety of complex chemical reactions in the environment. In addition to the formation of solid precipitates, colloids and dissolved solution species common to aqueous systems, actinide ions can interact with the surrounding geo and biomedia to change oxidation states or sorb on surfaces and colloids. The rate of migration is determined by aqueous solubility, and interactions with solid surfaces such as minerals, soils, natural organic matter, and soil microorganisms

Sorption of aqueous actinide species on biological and geological matrices can be quantitatively described by a surface complexation or site-binding model. The disadvantage of this model is the difficulty in the experimental determination of the model parameters and surface reaction constants. Usually, a set of surface reactions and species are proposed based on knowledge of the solution speciation of the solute, and the reaction constants are usually derived by fitting computer-calculated absorption curves to experimental data. Because this process typically involves a large number of potentially adjustable parameters, it is likely to lead to non-unique parameter fitting and does not always result in a consistent set of parameters for the same systems.

A fundamental molecular-level understanding of sorption processes of actinides on environmental surfaces is required to better understand and predict their transport behavior in nature. Several different surface spectroscopic techniques have been applied to the characterization of the adsorbed species and surface reactions and a direct determination of the sorbed species and surface reactions has become possible.

The non-linear optical techniques of second harmonic and sum frequency generation (SHG and SFG) are ideally suited to study surfaces and interfaces of mineral oxides, biosurfactants and biopolymers, organic adlayers adsorbed on solid/mineral surfaces and soil organic matter, including humic and fulvic acids. Resonant enhanced second harmonic generation can probe the electronic (UV-vis region) structure of metal species adsorbed at a surface or interface. Infrared-visible sum frequency generation spectroscopy probes the infrared vibrational spectrum of molecules adsorbed at the interface. SHG/SFG studies will greatly assist with understanding reactivity at interfaces of oxides and soil organic matter with heavy metals and radionuclides/actinides.

Time-resolved Laser-fluorescence spectroscopy (TRLFS) is a highly sensitive tool for actinides that absorb light and de-excite by fluorescence emission, e.g., U(VI) and Cm(III), to probe changes in actinide speciation and coordination environment in solution. This method can also be used to differentiate whether adsorbed species form surface complexes or surface precipitates. Recently, it was shown that the intense synchrotron radiation can change the oxidation states of redox-sensitive actinide samples which may cause erroneous results, and low temperature measurements are now used to alleviate this shortcoming.

X-ray Absorption Fine Structure (XAFS) Spectroscopy is composed of two component spectroscopies, X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) which provide element specific oxidation state and local structure information, respectively. EXAFS (Extended X-ray Absorption Fine Structure Spectroscopy) provides information on the chemical environment of particular actinide, in particular bond lengths and the number of neighboring atoms. Combining both methods, detailed knowledge of the different processes resulting from the interaction of the selected actinides with environmental interfaces can be gained.

XANES and EXAFS measurements and TRLFS studies to obtain molecular-level mechanistic details of actinide interaction with common environmental solutions and interfaces will be presented together with first SHG/SFG characterization results of model systems for environmental interfaces. Areas will be outlined where integrated interdisciplinary research is needed to provide a more comprehensive understanding of these processes.