Actinide NMR Research at Lawrence Livermore National Laboratory

LLNL SFA (Laboratory Research Manager: Annie B. Kersting)

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As a part of the Transuranic Subsurface Transport Scientific Focus Area at LLNL, we are developing nuclear magnetic resonance (NMR) techniques focused on investigating geochemical and biogechemical reactions with actinide species. The program builds upon the combined expertise of the group and has two major thrusts: *1) The development of surface specific solid-state NMR techniques to investigate the sorption of actinide species to mineral surfaces; 2) The measurement of reaction rates of actinide solution species, and comparing these to rates calculated from ab-initio atomistic modeling.* The current status of this program has been benchmarking these techniques by investigating systems which allow safe technique development over a larger range of experimental conditions. This benchmarking has yielded results that will allow us to confidently extend these methods to systems containing low concentrations of actinide species. These goals are within reach at LLNL due to new capabilities in the NMR facility which allow us to investigate samples containing up to 10 μCi of ionizing radiation.

Many actinide species (e.g. Pu^{4+}, Pu^{5+}, and Np^{5+}) exhibit paramagnetic electronic ordering which can have a substantial effect on the NMR signal. Therefore, we have developed solid-state cross-polarization magic angle spinning (CP/MAS) NMR as a surface specific technique to probe the sorption of low loadings (1.6 - 54 nmol/m^2) of paramagnetic species (Cu^{2+} and Ni^{2+}) to mineral surfaces. We used statistical methods to provide model-free analysis of the results from variable contact time $^{29}Si\{^1H\}$ CP/MAS NMR spectra on amorphous silica which identified protonated and deprotonated silanol sites. These experiments established the deprotonated surface species as the preferential metal sorption site at pH 8, and show the ability to discern between precipitation of a separate phase and surface sorption. Additional experiments also proved the same results can be obtained under static (non-spinning) conditions, and can, therefore, be safely extended to systems containing low concentrations of paramagnetic actinide species such as Pu^{4+}. Experiments with trivalent lanthanide species (Sm^{3+} and Eu^{3+}) are on-going to further constrain the effective concentration and pH range over which this method is valid.

We also are building on existing expertise in measuring ligand exchange and reaction rates of actinide species using solution state NMR spectroscopy. This work extends previous work in uranyl systems where both the apical oxygen and carbonate counter ion exchange mechanisms were investigated as a function of hydrostatic pressure and temperature. These types of measurements allow for the determination of the activation volume for the exchange process where the magnitude of this value elucidates the mechanism by which the transition state occurs. This is one of the few techniques that allows for direct observation of associative vs. dissociative exchange mechanisms. Further, the unique electronic environment of actinide systems allows for a wide range of NMR techniques to monitor exchange rates. In diamagnetic systems magnetization exchange through the use of tailored excitation allows for the direct detection of exchange rates. In paramagnetic systems it is more difficult to directly monitor exchange; however, the effect of exchange on line widths is well understood and will allow for quantifiable rate determination. Therefore we have accumulated the expertise required to investigate actinide exchange processes at LLNL, and we are moving forward with similar experiments designed to measure the exchange rates for actinide species such as Np^{5+}, Pu^{4+}, Pu^{5+}, and Th^{4+}. By analyzing such reaction rates we gain insight into the limiting reactions which may govern the reactions of these species with minerals surfaces, and complex organic species.