

Paramagnetic adsorption on silica as an analogue for actinide adsorption: A solid-state NMR study

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Many previous studies on actinide sorption have been performed at high loading levels to maximize the possibility of observing the behavior with available instrumentation. However, some contaminated sites contain concentrations of actinides such as Pu from 10^{-8} M and lower, and it is unclear if high loading level experimental results are applicable. Therefore, the development of methods to measure relevant reactions at very low loadings is necessary. Here we developed solid state nuclear magnetic resonance (NMR) techniques for analyses of actinide adsorption at low loadings.

The majority of actinides and actinide complexes exhibit paramagnetic electronic structures. The presences of even low amounts of paramagnetic cations can significantly affect the signal observed for other elements such as ^1H or ^{29}Si . These effects include, but are not limited to broadening, shifting, and relaxing the NMR signal. Quantification of these effects can allow indirect observation of actinide sorption.

We investigated the adsorption of paramagnetic cations such as Fe^{3+} , Mn^{2+} , and Ni^{2+} on silica surfaces at a range of low loading levels. The goals of this study were to develop these systems as 'safe' analogues to actinide systems where radiation and acute toxicity are a concern, and to determine the lowest loading level where paramagnetic effects on the NMR signal can be observed.

The loading level limits at pH = 6 were investigated by varying the paramagnetic cation concentration ($<10 \mu\text{M}$) and the silica substrate surface area ($300 \text{ m}^2/\text{g}$ to $\sim 4 \text{ cm}^2/\text{g}$). We measured differences in the ^1H spin-lattice, spin-spin, and rotating frame spin-lattice relaxation rates ($1/T_1$, $1/T_2$, and $1/T_{1\rho}$ respectively) for paramagnetic cations adsorbed to silica. Given that ^1H is the most abundant and sensitive nuclei in these systems, these rates should be influenced greatest by the presence of paramagnetic cations. Measuring differences in ^1H $T_{1\rho}$ by $^{29}\text{Si}\{^1\text{H}\}$ cross-polarization magic angle spinning (CP/MAS) NMR can identify specific surface species which associate with paramagnets the strongest. Preliminary results from $^{29}\text{Si}\{^1\text{H}\}$ CP/MAS indicate that for mesoporous silica, Fe^{3+} adsorbs preferentially to Q³ polymerized surface silanols over Q² and Q⁴ sites.

First principles modeling studies of cation adsorption at oxide-water interfaces

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Hydrated oxide surfaces play key roles in modern technologies such as automotive pollution control, solid oxide fuel cells, and nanoscale biosensors as well as both fundamental and applied environmental chemistry, geochemistry, and even the origins of life. Yet a persistent barrier to solving a wide range of environmental and technological problems is the current lack of molecular-level understanding about reactions at solid-water interfaces.

Modeling interface reactivity offers control over reactivity parameters and system complexity. By separately varying factors such as surface composition or surface structure, the role of each factor on reactivity can be elucidated. Additional complexity can be added systematically to build a framework for understanding which physical properties exert control on reactivity and how these factors compete or cooperate in solid-water interfaces.

Here, we present results of first principles modeling, using density functional theory and ab initio thermodynamics, applied to various environmental interface systems. We focus on structure-reactivity relationships in corundum type oxide-water interfaces and cation sorption. We discuss and give examples of how surface properties (structure, hydroxylation, composition) and cation properties (identity and electronic structure) govern adsorption modes, interaction strength, and reactivity trends.