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**Adsorption and Reduction of Uranium in Engineered Barrier Systems:  
Effects of Iron and Heat**

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**ABSTRACT:**

Most future nuclear waste repositories will include compacted bentonite, mainly consisting of montmorillonite clay, as part of an engineered barrier system to minimize contaminant mobility. Engineered barrier systems are expected to provide iron-rich environments, due to the anaerobic corrosion of steel canisters, the dissolution of pyrite and siderite impurities in bentonite, and the fact that montmorillonite clay naturally contains 2-3% of structural Fe(III). Uranium (U) is the primary element in spent nuclear fuel, and from an environmental perspective, a potential contaminant of water resources. In bentonite barriers, U(VI) mobility is expected to be strongly controlled by its adsorption onto montmorillonite surfaces, which will affect contaminant retardation, diffusive fluxes and uranium concentrations in pore water solutions. In addition, with increasingly reducing conditions after repository closure, chemical reduction processes involving the Fe(II)/Fe(III) redox couple will provide a highly important ancillary mechanism to further limit the source term and transport of uranium, since the solubility and mobility of U(IV) are expected to be low.

With the proposed research, we aim to reduce current uncertainties in nuclear repository performance assessment models with regard to the source term and mobility of uranium in engineered barrier systems. In particular, we plan to investigate the chemical reduction and adsorption of uranium on montmorillonite clay surfaces in the presence of iron and at elevated temperatures due to decay heat. Our primary goal is to develop a new uranium-montmorillonite surface complexation/reduction model that can include these processes based on: (1) a new, comprehensive, experimental dataset describing uranium adsorption/reduction in Fe-rich montmorillonite systems; (2) the spectroscopic characterization of uranium surface speciation and oxidation states; and (3) the results from quantum chemical cluster modeling evaluating the role of U(V) surface intermediates. Our new uranium adsorption/reduction model will allow us to calculate “smart uranium  $K_d$  values”, which can then be incorporated into large-scale reactive transport models. In addition, we will characterize the effects of elevated temperatures on uranium adsorption/reduction processes experimentally, and assess the potential access of relevant uranium solution complexes to clay nanopores, which is considered another important process limiting contaminant mobility in compacted bentonite systems.

Overall, this project will allow us to gain a better understanding of the source term and mobility of uranium in engineered barrier systems, and to develop modeling tools to predict uranium sorption and transport behavior as a function of changing chemical conditions over time.