
Quantification of Cation Sorption to Engineered Barrier Materials Under Extreme Conditions

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Program: Fuel Cycle R&D

ABSTRACT

Objective: The objective of this work is to quantify interactions of risk driving radionuclides with engineered barrier materials used in radioactive waste repositories. The engineered solids to be examined will be iron oxide byproducts of steel corrosion and bentonite clays as representative backfill materials. Data examining sorption and ion exchange of various radionuclides to these materials are available. However, data are lacking for studies at high temperatures and high ionic strengths. The high ionic strength is expected to limit sorption of cations due to competition for a finite number of sorption and/or exchange sites. However, as temperature increases, sorption of actinide ions is hypothesized to increase based on an entropy driven displacement of solvating waters. Therefore studies at extremely high ionic strengths and at high temperatures are necessary. We will use a suite of actinide ions in these experiments to allow for a systematic and quantitative understanding of ion interactions with these materials as a function of ion size, hydration state, and charge. The deliverable will be a qualitative conceptual model and a quantitative thermodynamic aqueous/surface complexation speciation model describing actinide sorption to engineered barrier materials, which is based upon a mechanistic understanding of specific sorption processes as determined from both micro-scale and macro-scale experimental techniques.

Hypotheses: The overarching hypothesis of this research is that strong actinide interactions with metal (oxyhydr)oxide surfaces are manifested by large stability constants for the actinide surface complexes. These large stability constants are due to positive entropies which are mechanistically driven by displacement of solvating water molecules from the actinide ion and the mineral surface during sorption and/or surface precipitation. Such entropies are accessible through measurement of sorption enthalpies and stability constants using surface complexation modeling and calorimetric titration techniques. Additional specific hypotheses that are corollaries to this general hypothesis are:

1. Dehydration of metal ions upon sorption may provide an energetic barrier to desorption.
2. The ability of bentonite clay to sequester radionuclides can be enhanced via amendment of the clay with functionalized or redox active materials such as fly ash or zeolites.

Outcomes: This work directly addresses the expressed need in Technical Work Scope Identifier FC-6 for understanding “*aqueous speciation and surface sorption at high temperature and high ionic strengths anticipated in near field conditions.*” The primary deliverable will be a set of thermodynamically based sorption and ion exchange constants describing radionuclide sorption to engineered barrier materials. These data will provide an understanding of the fundamental reaction mechanisms occurring at the mineral-water interface. A greater understanding of these processes will reduce the uncertainty in strategies for sequestration of radionuclide bearing wastes. Overall this project will increase our understanding of radionuclide interfacial reactions and help to ensure human and environmental health are protected during treatment and disposal of radionuclide bearing wastes.

