Project ID number: 54823
Project Title: Modeling of Cation Binding in Hydrated 2:1 Clay Minerals
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DOE PROBLEM AREAS: This basic research may impact the prediction of subsurface contaminant transport in clay-rich media through the development of improved molecular models for clay swelling and ion exchange. The research should also yield an improved understanding of the performance of clay-based containment materials.

RESEARCH OBJECTIVE: The primary objective of our research is the development of molecular models of swelling and ion exchange in clay minerals with a view toward understanding the mechanisms of radionuclide transport through clay-rich soils. Specific scientific goals include using molecular computer simulations to calculate the thermodynamics of clay swelling and ion exchange, and to evaluate the dependence of clay properties upon interlayer ion identity and clay composition. The realization of these goals will, in general, improve our understanding of structure-function relationships in clays.

RESEARCH PROGRESS AND IMPLICATIONS: This report summarizes work completed during 3.5 years of the 4-year project period.

Method and Code Development. This phase of the project was completed with the development of a grand-canonical ensemble molecular dynamics (GMD) simulation method.[1,2] Ion exchange and clay swelling processes in the environment typically take place under conditions of constant water chemical potential. These conditions are reproduced in the GMD simulations. Particle insertion and deletion processes, made difficult by the constrained clay interlayer environment, are catalyzed using a bias potential method developed in our group.

Hydration and Swelling. Immersion energy simulations at fixed water content have revealed an energetic origin to both step-wise swelling and the formation of mixed-layer hydrates in Cs-, Na-, and Sr-montmorillonites.[3,4] The extent of swelling predicted by these simulations is in good agreement with experimental measurements. Cs^+ forms inner-sphere complexes with the clay surface and acts as a swelling inhibitor, while both Na^+ and Sr^{2+} favor outer-sphere complexes and swollen states. Registry motions of adjacent clay layers are restricted most significantly in Sr-clays, indicative of strong interactions between the hydrated ions and the clay surface. The simulations predict that the clay swelling mechanism varies with the interlayer ion charge. For monovalent substituted clays, swelling and hydration occur simultaneously. For Sr-montmorillonite, in contrast, the initial hydration of the interlayer ions results in formation of a partially-hydrated, expanded state. Filling of the remaining interlammelar space occurs as a separate process. Swelling transitions leading to the formation of these states have been characterized using pressure versus layer spacing isotherms. Results indicate that strong Sr-water interactions are responsible for the formation of partially-filled expanded states.

Entropy and Free Energy of Swelling. The GMD method has been used to determine swelling entropies and free energies for Cs- and Na-montmorillonites in contact with bulk water.[2,5] The free energy curves, displayed in Fig. 1, exhibit minima at approximately 12.5 and 15.5 Å, representative of the one- and two-

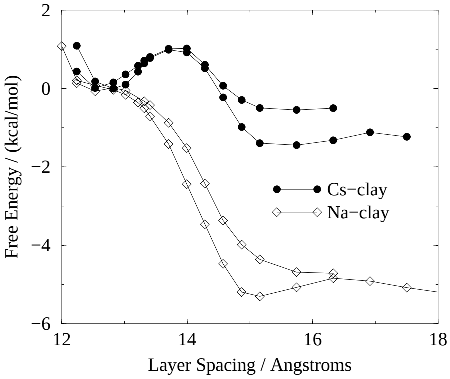

Figure 1: Swelling free energies. Curves are displaced for clarity.

layer hydrates. The two curves for each clay were calculated at different registry positions. Results for Cs-montmorillonite indicate incorrectly that the two-layer hydrate is most stable, suggesting that some adjustment of the simulation model may still be required. Decomposition of the free energies into entropic and energetic components indicates that swelling is entropically driven for both clays.

Ion Exchange. Ion exchange calculations are being performed using a method that isolates the constant-volume exchange and swelling contributions to the overall exchange process.[5] Na^+ to Cs^+ exchange free energies, calculated at constant layer spacing for a montmorillonite clay, have been determined at several water contents. The swelling contribution to exchange may be calculated from the GMD swelling free energies displayed in Fig. 1. Exchange of Na^+ with Cs^+ is much more favorable for the one-layer hydrate than for the two-layer hydrate. This is in agreement with the experimental observation that exchange with Cs^+ leads to dehydration.

Swelling and Ion Exchange Models. Current models for swelling and ion exchange in clay minerals are based upon macroscopic experimental measurements. Our simulation results provide input for the development of new, molecular models of these processes that, in turn, may improve the prediction of subsurface contaminant transport.

PLANNED ACTIVITIES: Completion of the ion exchange calculations is scheduled for the final six months of the project. Initial work toward the development of a molecular model for clay swelling is also planned.

References:

[1] R.M. Shroll and D.E. Smith, J. Chem. Phys. **110**, 8295 (1999).
[2] R.M. Shroll and D.E. Smith, J. Chem. Phys. **111**, 9025 (1999).
[3] D.E. Smith, Langmuir **14**, 5959 (1998).
[4] D.A. Young and D.E. Smith, “Simulations of Clay Mineral Swelling and Hydration: Dependence upon Interlayer Ion Size and Charge” J. Phys. Chem. (submitted).
[5] R.M. Shroll, D.A. Young, R.W. Waymire, H. Whitley, C. Del Rio, and D.E. Smith, “Computer Simulations of Ion Exchange in Clay Minerals” (in preparation).

INFORMATION ACCESS: References [1-3] above are in print. Reference [4] has been submitted and reference [5] is in preparation.