Project ID: **54823**

Project Title: Modeling of Cation Binding in Hydrated 2:1 Clay Minerals
Award Number: DE-FG07-96ER14697
Publication Date: 06/15/99

Principle Investigator: David E. Smith
Department of Chemistry and Biochemistry
New Mexico State University
Las Cruces, NM 88003-8001
Phone: (505) 646-5210 Fax: (505) 646-2649
E-mail: davsmith@nmsu.edu

Technical Progress Report:

RESEARCH OBJECTIVE

The primary objective of our research is the development of molecular models of ion exchange on 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. These goals will, in general, facilitate the development structure-function relationships in clays.

RESEARCH PROGRESS AND IMPLICATIONS

This report summarizes work completed in the first 2.75 years of the 3-year project period, with emphasis placed on the most recent accomplishments.

Method and Code Development: This phase of the project was essentially completed with the recent 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 by us.

Swelling Free Energy: The GMD method has been applied to investigations of the swelling of Cs-montmorillonite[2] and Na-montmorillonite[3] in contact with bulk water. Disjoining pressures at constant water chemical potential were calculated as a function of clay layer spacing over a region encompassing the one- and two-layer hydrates. The pressures show oscillations that are indicative of crystalline-swelling phase transitions. Integration of the disjoining pressures yielded free-energy curves with minima at approximately 12.5 (Cs only) and 15.5 Å, representative of the one-layer and two-layer hydrates. These are displayed in Fig. 1. Results for Cs-montmorillonite indicate incor-

rectly that the two-layer hydrate is more stable than the one-layer hydrate.[4] The simulation model may therefore require some adjustment for quantitative treatment of clay swelling. Decomposition of the free energy into its entropic and energetic components indicates that the one-layer hydrate is favored energetically, but disfavored entropically. The dependence of the swelling free energy upon ion size is qualitatively correct. While results for sodium-montmorillonite should be considered preliminary, decreasing the interlayer ion size clearly results in stabilization of the two-layer

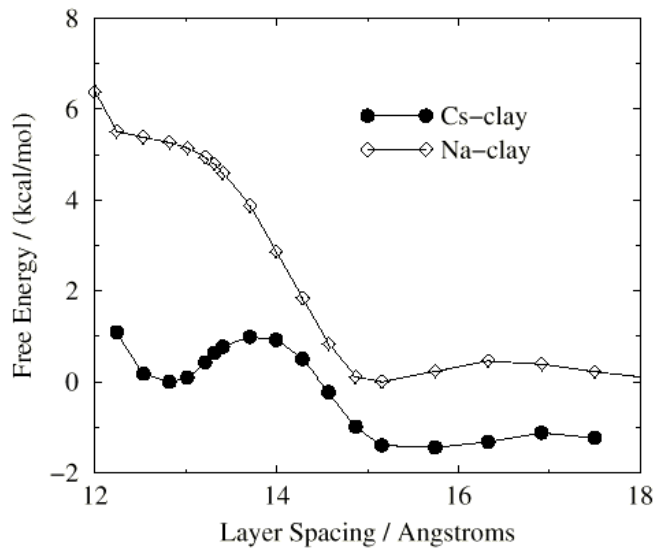

Figure 1: Swelling free energies. Curves are displaced for clarity.

hydrate relative to the one-layer hydrate.

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. Sodium to cesium exchange free energies, calculated at constant layer spacing for a montmorillonite clay, have been determined at several water contents. These results were discussed in a previous report. The swelling contribution to exchange may be calculated from the GMD swelling free energies displayed in Fig. 1. Exchange of sodium with cesium 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 cesium is accompanied by dehydration to the one-layer hydrate. [4] The overall exchange free energy is also qualitatively consistent with experimental measurements.[5]

Ion Size and Charge Dependence: The ion size and charge dependence of clay swelling has been investigated using Na, Cs, and Sr-montmorillonite clays.[6,7] Results suggest a dramatic difference in behavior between monovalent- and divalent-ion substituted clay minerals. Immersion energies for the three clays are displayed in Fig. 2. All three curves

show oscillations consistent with a discrete swelling mechanism. The results indicate, in agreement with experiment,[4] that the one- layer hydrate is energetically favored for Cs-montmorillonite, while the two-layer hydrate is favored for both Na- and Sr-montmorillonite. The immersion energy curve for Sr-montmorillonite shows a discontinuous jump at approximately the one-layer hydrate. The energetic jump is accompanied by signi_cant increases in clay layer spacing and in the strontium coordination number. Metastable states occur along both branches of the immersion energy curve surrounding the discontinuity. This suggests that, for Sr-montmorillonite only, there is a constant water content phase transition between one-layer and two-layer spacings. This transition has been characterized using pressure versus layer spacing isotherms. Integration of the isotherms yields a free-energy curve with min- ima for both one- and two-layer states. This has provided the identification of global free-energy minima for several water contents near the transition point. The discontinuous behavior in Sr- montmorillonite possibly originates from the strong, Sr-water interactions that force the clay to two-layer spacings even with near one-layer water contents.

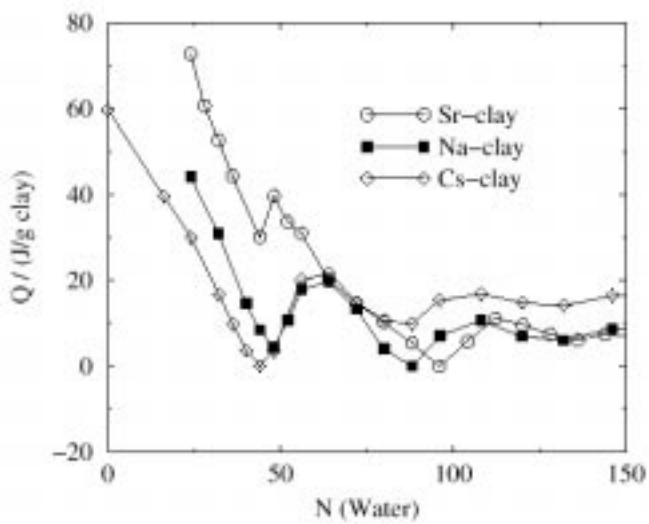

Figure 2: Immersion energies.

PLANNED ACTIVITIES

A one-year, no-cost extension for this project has been requested. This will allow for expansion of the breadth of the ion exchange and swelling calculations discussed above to include a wider range of interlayer ions and clay composition. This is necessary for the evaluation and development of ion exchange models. Efforts to address some simulation model deficiencies will also be made.

<u>References:</u>

[1] R.M. Shroll and D.E. Smith, J. Chem. Phys. **110**, 8295 (1999).

[2] R.M. Shroll and D.E. Smith, “Molecular Dynamics Simulations in the Grand Canonical Ensemble: Application to Clay Minerals" (in preparation).
[3] R.M. Shroll, D.A. Young, R. Waymire, and D.E. Smith, “Computer Simulations of Ion Exchange in Clay Minerals" (in preparation).
[4] I. Bérend, J.-M. Cases, M. Francois, J.-P. Uriot, L. Michot, A. Masion, and F. Thomas, Clay & Clay Miner. **43**, 324 (1995).
[5] S. Xu and J.B. Harsh, Soil. Sci. Soc. Am. J. **54**, 1596 (1990).
[6] D. E. Smith, Langmuir 14 , 5959 (1998).
[7] D.A. Young and D.E. Smith, “Ion Size and Charge Dependence of Clay Mineral Swelling" (in preparation).

INFORMATION ACCESS

References [1] and [6] above are in print. A topical report for each article will be submitted shortly. Reference [2] has a target submission date of June 30th, reference [7] of July 31st, and reference [3] of September 30th.