Technical Progress Report

Title: Modeling of Cation Binding in Hydrated 2:1 Clay Minerals
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Overall Aims

The primary focus of our research is the development of molecular theories of ion binding to clay minerals, with a view toward understanding the mechanism of radionuclide transport through soils. The overall aim of the research and the computational methods employed are essentially unchanged from those originally proposed. The research is split conceptually into three phases, based on the radionuclides considered. The first, 'cesium' phase has an estimated completion time of 1.5 years from the project initiation. This phase is ongoing at this time. The second, 'strontium' and third, 'uranium' phases will be addressed in the second half of the project period.

Phase 1 Accomplishments

Code Development: A computer simulation code for the treatment of hydrated smectite and vermiculite clays with varying water content has been developed. This version of the code enables calculations under conditions of constant interlayer spacing or constant applied pressure, and for the complete series of interlayer alkali-metal ions. Final development of the code for (i), calculations of exchange free energies, and (ii), calculations at constant water chemical potential should be completed within the next month. This will allow the most important scientific issues of phase 1 to be fully addressed.

Hydrated Clay Structure: The molecular structures of Cs^+- and Na^+-montmorillonite (a common swelling clay) have been investigated. The observed layer spacings versus water content of both clays agree well with experimental swelling curves.[1,2] This has provided validation of the simulation models. Comparison of cesium and sodium structures indicate that cesium preferentially forms inner-sphere complexes with the clay surface. The relationship of this structural observation to $Na^+ \rightarrow$ (Cs+ exchange thermodynamics is presently under investigation.

Dry Cs^+-Montmorillonite Structure: It is thought that dry, cesium-substituted montmorillonites exist as mixed-layer structures with both symmetrical (hexagonal cavities overlapping) and non-symmetrical (hexagonal cavities shifted) stacking configurations.[3,4] We have

observed both types of structures in our calculations and confirmed that they are energetically comparable.

Swelling Thermodynamics: Adsorption of cesium onto clay minerals is often accompanied by dehydration, which in turn limits cesium diffusion.[5] Water adsorption isotherms are consistent with this behavior in that Na^+-montmorillonites will form two- or three-layer hydrates under conditions where Cs^+-montmorillonites form one-layer hydrates. Our calculations have revealed an energetic preference for the one-layer hydrate in Cs^+-montmorillonite. This is illustrated in Figure 1, where the system immersion energy (relative to the highest calculated water content) is plotted versus water content. The data clearly indicate an energetic preference for a water content of $\approx$ 0.12 g/g clay, corresponding to the monolayer hydrate.

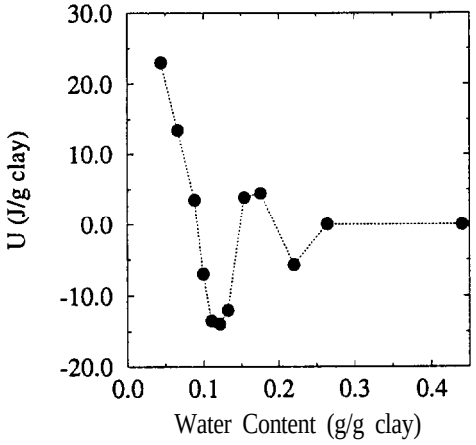

Figure 1: Calculated clay internal energy versus water content.

References

[1] M.H. Fu, Z.Z. Zhang, and P.F. Low, Clays & Clay Miner. **38,** 485 (1990).
[2] R. Calvet, Ann. Agron. **24,** 77 (1973).
[3] C.A. Weiss Jr., R.J. Kirkpatrick, and S.P. Altaner, Geochim. et Cosmochim. Acta **54,** 1655 (1990).
[4] I. Beŕend, J.-M. Cases, M. Francois, J.-P. Uriot, L. Michot, A. Masion, and F. Thomas, Clay & Clay Miner. **43,** 324 (1995).
[5] R.M. Cornell, J. Radioanal. Nucl. Chem. **171,** 483 (1993).

Presentations

An oral presentation titled 'Computer Simulations of Cesium Adsorption on Hydrated Clay Minerals' was given at the American Chemical Society Fall National Meeting in Las Vegas, September 7-11, 1997.

Publications

In Preparation: 'Computer Simulations of Cesium Adsorption on Hydrated Clay Minerals', by David E. Smith. Expect submission to the Journal of Physical Chemistry by November, 1997.