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Modeling of Cation Binding in Hydrated 2:1 Clay Minerals

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Research Objective

The primary focus of our research is the development of molecular theories of ion exchange on clay minerals, with a view toward understanding the mechanism of radionuclide transport through soils. The specific scientific goals of the study involve using molecular simulation methods to correlate clay-ion binding strengths with interlayer structure and swelling properties. This should build upon our fundamental understanding of clay behavior and allow for improvement in transport modeling of radionuclides in clay-rich soils

Research Progress and Implications

This report summarizes work after 1.75 years of a 3-year project.

Code Development: A computer simulation code for investigating hydrated smectite and vermiculite clays has been developed and validated. The code provides the ability to simulate clay minerals of varying composition (layer charge magnitude and location) and with either alkali or alkaline-earth interlayer ions. Simulations may be performed at fixed pressure or volume, and with either water content or water chemical potential held constant. A structure analysis module allows for a graphical display of average ion-clay binding geometries. Hydration (swelling) thermodynamics can be determined through calculations of isosteric adsorption energies, immersion energies, or P versus V data at fixed water chemical potential. The code also has the capability to calculate ion exchange free energies between like-valent ions.

Hydrated Clay Structure: The molecular structures of Cs- and Na-montmorillonite have been determined as a function of clay water content and layer charge location. The observed layer spacings agree well with experimental swelling curves.¹ Analysis of calculated structures indicates that cesium preferentially forms inner-sphere complexes with the clay surface, except for ions located proximally to tetrahedral-layer substitution sites. Near these sites, both sodium and cesium ions are bound to the clay surface, with sodium residing above the substitution site and cesium occupying a hexagonal hole adjacent to the site. At other locations, cesium lies directly above the tetrahedral-layer silicon atoms.

Swelling Thermodynamics: Adsorption of cesium onto clay minerals is accompanied by dehydration, which in turn limits cesium diffusion.² Clay swelling should thus play an important role in both the thermodynamics and kinetics of ion binding in soils. Experimental water adsorption isotherms indicate that Na-montmorillonites will form multilayer hydrates while Cs-montmorillonites swell maximally to a monolayer.¹ We have calculated immersion energy curves for a Na-montmorillonite and for two Cs-montmorillonites. The simulations reveal oscillatory behavior, indicating that a discrete rather than continuous swelling process is energetically favored out to several water monolayers. To our knowledge, these calculations provide unique evidence of the energetic origin of discrete swelling in clay minerals. The global immersion energy minimum occurs at a monolayer water content for all clays studied. For Cs-substituted clays, this is in agreement with the known swelling behavior. In contrast, the data for sodium are not consistent with the expected formation of multilayer hydrates. This suggests that entropic effects also play a significant role in determining swelling extent in clays.

Monovalent Ion Exchange: Monovalent ion exchange calculations are being performed in two steps, with the first step involving ion mutation at fixed volume and water content, and the second

using constant water chemical potential methods to determine the swelling contribution to the exchange free energy. We have completed Na to Cs mutation calculations for a montmorillonite clay at several water contents. Calculations of the swelling contributions to the exchange process are presently underway. It is known that sodium is favorably exchanged with cesium on most clay minerals.³ Our results for the monolayer hydrate (at fixed water content) show favorable exchange free energies for ions associated with octahedral layer charges. In contrast, simulations predict an incorrect, unfavorable exchange for ions associated with tetrahedral layer charges. This result may indicate a model flaw at the tetrahedral substitution sites. The exchange free energy for the two-layer hydrate is larger than for the monolayer hydrate by about 2 kcal mol⁻¹. This indicates correctly that Na-montmorillonite swells more readily than Cs-montmorillonite, and that the swelling contribution to ion exchange is significant. The decomposition of exchange free energies into ‘mutation’ and ‘swelling’ contributions is a unique and potentially powerful feature of the simulation approach used in this project.

Planned Activities

Improvement in the current model representation of tetrahedral substitution sites will be addressed (next 3 months) with density functional theory methods via collaboration with Dr. Randy Cygan (Sandia). A grand canonical molecular dynamics method⁴ will be applied (next 3 months) in order to improve efficiency of the swelling calculations.

Calculations of monovalent ion exchange free energies for several clay compositions should be completed shortly (6 months), allowing for comparison of data with existing exchange theories. Investigations of Sr-substituted clay structure, swelling, and exchange will be initiated within 1 month and performed over the duration of the project period. A ‘uranium phase’ of the project will also be addressed in the final year of the project.

References

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Other Access To Information

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