

**Final Report for Environmental Management Science Program -
Strategic Design and Optimization of Inorganic Sorbents for Cesium,
Strontium and Actinides: Activities at the University of Notre Dame**

DE-FG07-01ER63292

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Strategic Design and Optimization of Inorganic Sorbents for Cesium, Strontium and Actinides
Project #81949
January, 2005

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Research Objective:

The basic science goal in this project identifies structure/affinity relationships for selected radionuclides and existing sorbents. The task will apply this knowledge to the design and synthesis of new sorbents that will exhibit increased cesium, strontium and actinide removal. The target problem focuses on the treatment of high-level nuclear wastes. The general approach can likewise be applied to non-radioactive separations. The project involves a collaboration among four organizations, with each focused on a different aspect of the problem. This document is the final report on the three years of activities conducted at the University of

Notre Dame, where the research focus was on the use of molecular modeling to understand ion exchange selectivity in titanosilicates and polyoxoniobate materials.

Research Progress

During the three years of the project our studies focused along the following paths: (1) development of accurate forcefields that can be used to simulate crystalline silicotitanate (CST) and polyoxoniobate (Keggin chain) materials, (2) performing simulations to predict the location of Na^+ cations in CST and Keggin chain materials, (3) simulating the location of Cs^+ in CST materials, and (4) simulating water in these materials to determine its location and role in the ion exchange process. The results of these studies were shared with our experimental collaborators, which helped shed light on the detailed mechanism of ion exchange in these materials.

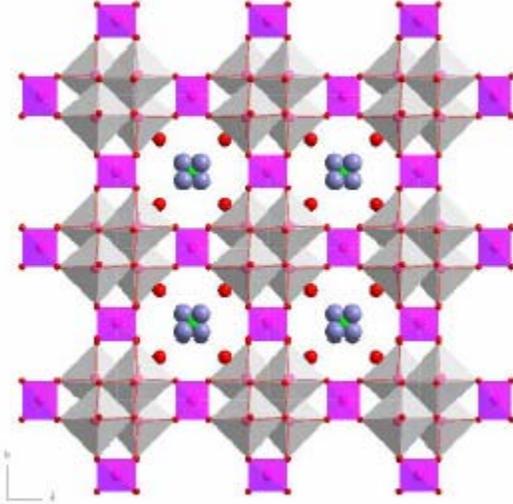


Figure 1. A polyhedral representation (with gray TiO_6 octahedra and purple SiO_4 tetrahedra) of CST along [001], sodium (Blue spheres) and water (red spheres) were located in the 8-atom ring tunnels. In the Nb-CST less sodium and more water molecules are located in the tunnel.

The first step in the project was the development of a computational model for the CST family of ion-exchange materials. Simulations were performed to locate the positions of Na^+ , Cs^+ and H_2O in the base CST materials. The reliability of the calculations hinges on the accuracy of the force field used to represent the interactions of the exchangeable species with the lattice. We used a so-called Born model in which ions interact with a Coulombic potential, while a Buckingham pair potential was used to represent the effects of overlap repulsion and dispersion. The total energy for species i and j at a distance of r_{ij} is thus given by:

$$E_{total} = \frac{1}{2} \sum_{ij} \frac{q_i q_j}{r_{ij}} + \frac{1}{2} \sum_{ij} A_{ij} \exp\left(\frac{-r_{ij}}{\rho_{ij}}\right) + \frac{1}{2} \sum_{ij} C_{ij} \frac{1}{r_{ij}^6} \quad (1)$$

where q is the charge of the species, and A , ρ , and C are Buckingham parameters. Water-water interactions were modeled using a Lennard-Jones potential of the following form:

$$E_{LJ} = \frac{1}{2} \sum_{ij} 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] \quad (2)$$

To capture electronic polarizability of the lattice oxygen atoms, we initially used a shell model potential¹ in which each oxygen atom is treated as a core tethered to a massless shell by a harmonic spring. The polarizability can then be related to the harmonic spring constant and the charges of the shell and core. Parameterization of the forcefield involves determining numerical values for the variables in equations 1 and 2, as well as the core-shell spring constants. Many of these parameters were taken from the literature²⁻¹⁰, where they have been validated against experimentally measurable quantities such as crystal structure and elastic constants. Other parameters did not exist, or were inappropriate for the materials examined in this work. Thus we developed new parameters for Cs^+ as well as for water interactions with Si, Ti, and Nb. While the shell model potential yielded accurate results for cation siting in CST, the computational cost of tracking the fast-moving shells prevents its use for large systems. To overcome this, we also developed a simpler fixed charge model that was as accurate as the shell model but resulted in a *several-fold reduction*

in computer time to perform a given calculation¹¹. This enabled us to study larger systems and probe more conditions without sacrificing accuracy. These parameters enabled us to accurately compute Na⁺, Cs⁺ and water siting and coordination in a well-characterized CST material. Using the same parameters, we also determined the siting of Na⁺, Cs⁺ and water in Nb-substituted CST as well as the Keggin chain materials, as described below.

By comparison with the X-ray diffraction studies carried out by our collaborators at Texas A&M, we were able to confirm the accuracy of the model; excellent agreement between the experimental and simulated positions was observed. In addition, the simulations provided insight into the mechanisms of cation binding in these systems. Using the base material as a benchmark, we went on to predict the location of Na⁺ and H₂O in the Nb-substituted and H-form of the material. Upon substitution of Nb into the CST framework, the simulations showed that the stability of Cs⁺ was enhanced in the tunnel by additional water coordination (see Figure 2). This was the same mechanism proposed experimentally to explain the increased selectivity that the Nb-substituted materials has for Cs⁺ over the base CST. These independent results appear to confirm the mechanism for why Nb substitution enhances selectivity. In addition, the simulations predicted where residual Na⁺ locates for the Cs-exchanged material. X-ray data was not able to locate these sites.

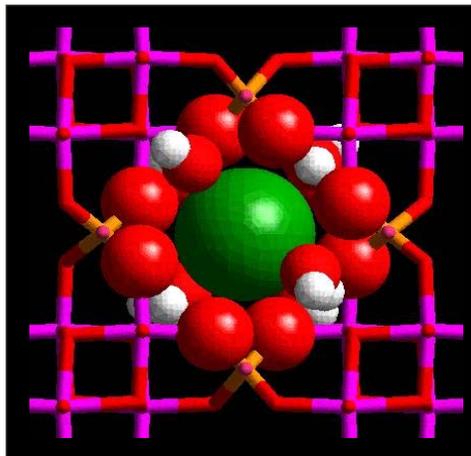


Figure 2: Calculated position of Cs⁺ (green) in Nb-CST material. Note the high degree of coordination with the framework oxygen atoms (red) and water (red-white). The addition of Nb to the framework enables water to hydrate the Cs⁺ in the tunnel, thereby

During FY04 team members at Sandia National Laboratory focused efforts on the synthesis of new Keggin-chain materials and obtaining a better understanding of the structure of the Na-Keggin chain materials with

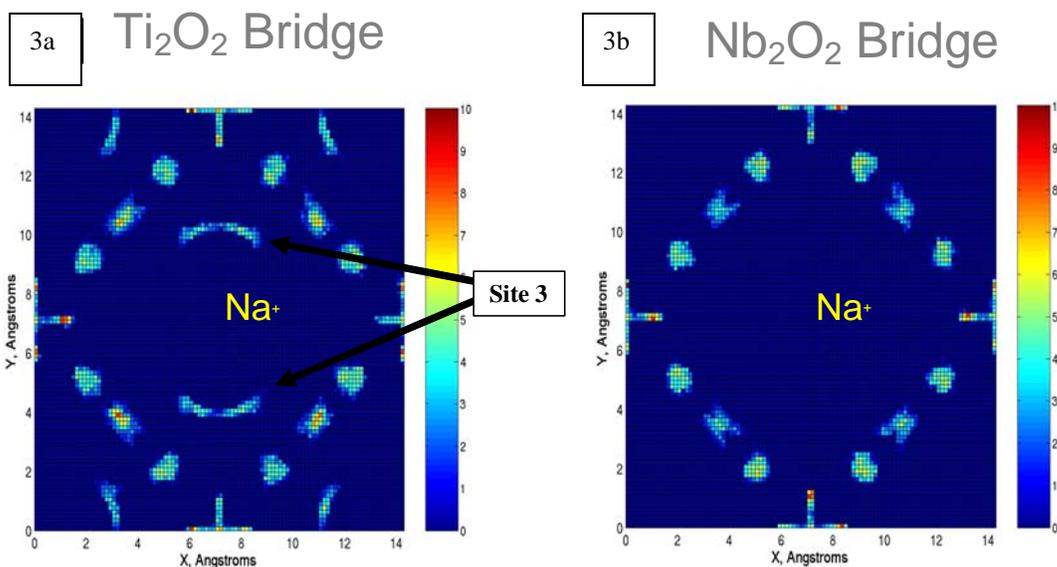


Figure 3: Probability distributions of Na⁺ in the polyoxoniobate material. In Figure 3a (left) the distribution of Na⁺ in the base material is shown. Intensity levels indicate the relative probability of observing a cation in a given site. These sites agree very well with the experimentally observed sites by X-ray diffraction analysis. In Figure 3b (right) the distribution when Nb is substituted for Ti in the bridging structure is shown. Notice the depopulation of intensity of site 3 for the Nb-substituted case is reduced compared to the other Na⁺ sites.

regards to sodium and water positions. It is difficult to distinguish between sodium and water in this structure because: (1) the structure was solved from X-ray powder diffraction (XRD) data rather than single-crystal data which reduces the quality and quantity of information that can be extracted, (2) the Na atoms and water molecules are highly mobile and therefore difficult to locate precisely, (3) there may be mixed occupancy of sodium and water on the inter-chain sites, (4) Na and water look very similar by XRD and (5) metal substitutions in the Keggin-chain structure result different amounts of water and Na due to charge-balancing requirements. It is important to determine these sodium and water positions more precisely than the XRD data allows to provide a more complete picture of the structure and chemistry of these Keggin chain materials and the ease of exchange of cations and water. For these reasons, we used our simulations to identify the optimum Na/H₂O positions and bonding in the inter-chain sites of the Na-Keggin chain materials. The computational approach used the same modeling strategy developed for CST materials to examine the location of Na⁺ and water in the polyoxoniobate materials.

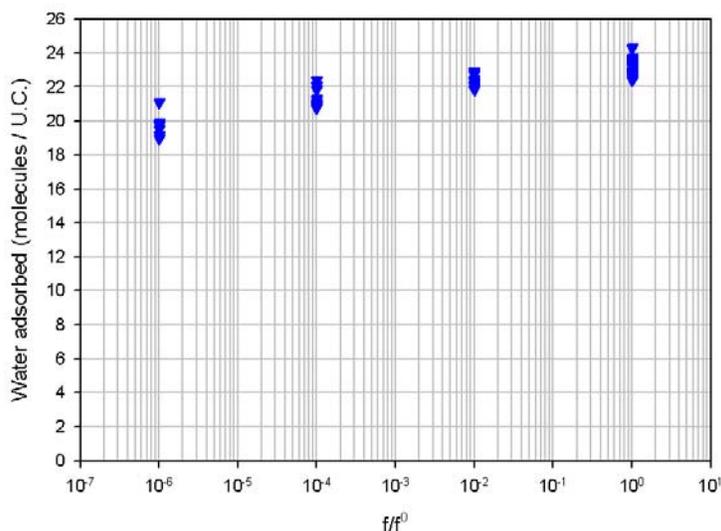


Figure 4: Water isotherms calculated for Na⁺ form of the Keggin chain material. Note that the saturation loading is about 23 water molecules per unit cell.

Ti₂O₂ bridging unit. Interestingly, when Nb is substituted for Ti in these bridging units, the distribution of Na⁺ changes. As can be observed in the in Figures 3a and 3b, the simulations show that site 3 becomes depopulated of Na⁺ upon substitution of Nb for Ti, while the population of Na⁺ in the other sites increases. This is due to the greater positive charge on the Nb₂O₂ unit repelling the positively charged sodium ions.

Another interesting result emerged from the calculations on the Keggin chain materials. Using powder X-ray data, it was determined that there were roughly 8 water molecules per formula unit. When we performed isotherm calculations using a newly developed Grand Canonical Monte Carlo method, however, we discovered that nearly three times as much water adsorbed in these materials as what was thought experimentally. Figure 4 shows one such isotherm. This was puzzling initially, until it was discovered that the experimental thermal gravimetric analysis data was consistent with the much higher water loading found in the simulations. Moreover, the computed X-ray diffraction patterns from simulations containing 8 and 24 water molecules are nearly indistinguishable, due to the disorder of water (see Figure 5). It was thus concluded that the experimental water loadings originally determined were incorrect, and that the values found in the simulations were much more likely.

Although X-ray diffraction enables four distinct sites to be identified in this material, the identity of the species populating a given site could not be determined, given the similarity in scattering intensity of water and sodium. The simulations observed the same four sites as were seen by XRD (see Figure 3). It was found that two of these sites are populated at nearly 100% with Na⁺. The remaining two sites have smaller amounts of Na⁺ and some water. Most of the water was disordered and highly mobile. Of these two remaining sites, the one designated as “site 3” was most favorable for Na⁺ in the base material. The reason is because Na⁺ is stabilized by the oxygen atoms in the nearby

Summary

An intermolecular forcefield has been developed for simulating ion exchange in CST and Keggin cha materials. The forcefields and methods have been validated by comparing benchmark calculations against experimental results for well-characterized systems. The methods were then applied to less well-characterized materials and several new insights discovered. The mechanism whereby Nb-exchange in the CST framework leads to higher Cs^+ selectivity over Na^+ was elucidated and found to be in excellent agreement with experiment. In the Keggin chain materials, the location of Na^+ and water was determined for the first time. It was also determined through molecular modeling that much more water is present in these systems than originally thought. Given these forcefields and methods, it will now be possible to move on to other more interesting systems. The calculations will continue to provide fundamental insight into the ion exchange mechanism in these materials, thereby greatly assisting in the synthetic efforts directed at finding new ion exchange materials with greater selectivity and capacity.

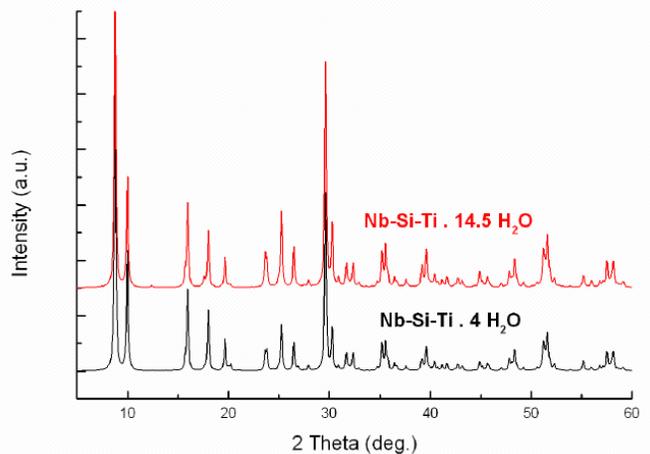


Figure 5: Simulated X-ray diffraction pattern with high water loading (red trace) and low water loading (black trace). The two are nearly indistinguishable, thus suggesting that the simulation results, which predicted high water loading, are likely in accord with TGA data.

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11. James P. Larentzos, Abraham Clearfield, Akilesh Tripathi and Edward J. Maginn, "A Molecular Modeling Investigation of Cation and Water Siting in Crystalline Silicotitanates", *Journal of Physical Chemistry B*, **2004**, 108, 17560-17570.

Publications and Presentations

Peer reviewed publications from this project include the following:

1. James P. Larentzos, Abraham Clearfield, Akilesh Tripathi and Edward J. Maginn, "A Molecular Modeling Investigation of Cation and Water Siting in Crystalline Silicotitanates", *Journal of Physical Chemistry B*, **2004**, 108, 17560-17570.
2. François Bonhomme, James P. Larentzos, Edward J. Maginn and May Nyman, "Synthesis, Structural Characterization, and Molecular Modeling of Dodecaniobate Keggin Chain Materials", in press, *Inorganic Chemistry*, **2005**.

Presentations of work completed in this project at technical conferences include the following:

1. E. J. Maginn and J. Larentzos "Molecular Modeling Investigation of Cation Siting in Crystalline Silicotitanate and Polyoxoniobate Materials", 227th ACS Meeting, Anaheim, CA, March, **2004**.
2. E. J. Maginn and J. P. Larentzos, "Molecular Modeling of the Ion Exchange Process in Crystalline Silicotitanate Materials for Cs, Sr, and Actinide Removal", Plenary Lecture, 8th International Conference on the Fundamentals of Adsorption", Sedona, AZ, May, **2004**.
3. E. J. Maginn and J. P. Larentzos, "Determination of Cation and Water Positions in Crystalline Silicotitanates and Polyoxoniobate Ion Exchange Materials", AIChE Annual Meeting, Austin, TX, November **2004**.
4. J. P. Larentzos and E. J. Maginn, "Molecular Modeling of Ion Exchange in Crystalline Silicotitanate Materials", 10th International Conference on Properties and Phase Equilibria for Product and Process Design", Snowbird, UT, May 2004.