Final Technical Report

Strategic Design and Optimization of Inorganic Sorbents for
Cesium, Strontium and Actinides

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Edward J. Maginn

Department of Chemical and Biomolecular Engineering

University of Notre Dame

Notre Dame IN 46556 USA

Ph: (574) 631-5687

Email: ed@nd.edu

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Abstract

Background

This project was a collaborative research project involving Savannah River National Laboratory (D. Hobbs), Texas A&M (A. Clearfield), Sandia National Laboratory (M. Nyman) and the University of Notre Dame (E. Maginn). This report only describes activities that occurred at Notre Dame in support of the overall project.

Summary of Research Accomplishments

The primary objective of the Notre Dame component of the project was computational in nature. The goal was to provide a design tool for the synthesis of optimized sorbents for the removal of cesium, strontium and actinides from nuclear waste solutions. Molecular modeling enables us to observe and better understand the molecular level interactions that govern the selectivity of specific radionuclides in a particular sorbent. The research focused on the development and validation of a suitable and transferable model for all the cations and ion exchangers of interest, and then subsequent simulations which determined the siting and mobility of water and cations. Specific accomplishments include:

- improving existing intermolecular force fields to accurately model the sorbents of interest
- utilizing energy-minimizations and molecular dynamics simulations for structural prediction of CST and niobium-substituted CST materials
- determining Na⁺/water positions in polyoxoniobate materials using molecular dynamics simulations
- developing Hybrid Monte Carlo methods for improved structural prediction

Details of Technical Accomplishments

Force Fields

A large number of potential models are available for solids in the literature. One way which solids have been modeled is based on the Born model of solids which assumes that ions interact via long-range electrostatic forces and short-range forces that include both repulsions and the van der Waals attractions between neighboring

e
i

ij

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

where E_{total} is the total potential energy, q is the charge of the ion, and A , ρ , and C are Buckingham parameters. The first term of Equation 1 represents the long-range electrostatic interactions, while the remaining two terms represent the Buckingham form of the short-range repulsion and van der Waals attraction interactions. Short range water-water interactions were modeled using a simple Lennard-Jones potential. The functional form of the potential is given by equation 2.

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

Many of the potential parameters used in our model are taken from the literature¹⁻⁹, where these parameters have been tested and compared to experimentally measurable quantities such as crystal structure and elastic constants. In order to account for polarizability in the lattice, a shell model potential¹⁰ was added to all oxygen atoms. The shell model treats each oxygen atom as a core and a massless shell, where the shell represents the electronic charge cloud of the ion. In addition, the core and shell are connected by a harmonic spring. The polarizability can then be related to the harmonic spring constant and the charges of the shell and core.

A few modifications of the force field were required in order to attain more accurate predictions of structural quantities of the CST materials. The Cs^+ cation short-range repulsive parameters were modified to correctly predict the experimentally determined position in Cs^+ -exchanged CST. In addition, modifications to the framework-water interactions ($\text{Si-O}_{\text{water}}$, $\text{Ti-O}_{\text{water}}$, and $\text{Nb-O}_{\text{water}}$) were made according to Lewis *et al*⁹, where they propose increasing the A parameter of the Buckingham potential in order to avoid the “Buckingham catastrophe”. Modifications of the proton may also be needed in order to achieve better results, as they have been the root cause of the disagreement with experimental studies. A complete listing of all potential parameters is given in Table 1.

Table 1 Potential parameters used for CST and polyoxoniobate structures

Species	Charge/e	Core-shell interaction/ eV Å ⁻²	Species	Charge/e
O (core)	0.86902		Sr ²⁺	2.0
O (shell)	-2.86902	74.92	Cs ⁺	1.0
O _{water} (core)	1.25		Na ⁺	1.0
O _{water} (shell)	-2.05	209.449602	H ⁺	1.0
H _{water}	0.4			
Si	4.0			
Ti	4.0			
Nb	5.0			

Lennard-Jones potential parameters

Ion Pair	A/eV Å ¹²	B/eV Å ⁶
O _{water} -O _{water}	39344.98	42.15

Intermolecular Buckingham Potentials

	A/eV	$\rho/\text{\AA}$	C/eV Å ⁶
O-O	22764.000	0.14900	27.88
O-O _{water}	22764.000	0.14900	28.92
Si-O	1283.907	0.32052	10.66158
Si-O _{water}	1283.907	0.32052	10.66158
Ti-O	760.470	0.38790	0.0
Ti-O _{water}	760.470	0.38790	0.0
Nb-O	3023.184	0.30000	0.0
Nb-O _{water}	3023.184	0.30000	0.0
Sr ²⁺ -O	959.100	0.37210	0.0
Sr ²⁺ -O _{water}	383.640	0.37210	0.0
Cs ⁺ -O	264.354	0.39110	0.0
Cs ⁺ -O _{water}	169.622	0.39110	0.0
Na ⁺ -O	5836.814	0.23870	0.0
Na ⁺ -O _{water}	4088.384	0.23870	0.0
H ⁺ -O	396.270	0.23000	0.0
H ⁺ -O _{water}	396.270	0.25000	0.0

Intramolecular Morse Potential

	D/eV	$a/\text{\AA}^{-1}$	$r_0/\text{\AA}$
H-O _{water}	6.204	2.22003	0.9

Three-body potentials

	k/eV rad ⁻²	θ_0
O-Si-O	2.097	109.47000
H-O _{water} -H	2.097	108.693195

Intra-molecular Coulombic subtraction (%)

H-H	50
O _{water} -H	50

Subsequent to this work a new force field for simulating titanosilicates with sitinakite topology was developed through use of plane wave pseudopotential density functional theory calculations. The Wigner-Seitz charge analysis method enabled us to extract partial charges on the framework atoms without recourse to empirical fitting. We carried out grand canonical Monte Carlo simulations of water in the hydrogen-exchanged form of this material, and computed the isotherm, binding energies, and preferred siting of water. The results agreed quantitatively with the experimental data from Prof. Clearfield's lab, and are superior to our earlier results that relied on empirical charge estimation. This new method is a powerful tool for enabling us to develop reliable and predictive potential models for other materials.

We also investigated the way in which the charge on the proton is smeared over the framework. Figure 1a show the hydrogen bonding network computed by smearing the proton charge over all framework oxygen atoms and Figure 1b is the result when the charge is smeared only over framework O2 oxygen atoms. The structure with proton smearing over all framework O2 oxygen atoms is consistent with experimental observations.

Figure 1: Snapshots of water adsorbed inside the CST tunnel.

Energy-minimizations and molecular dynamics simulations

The pure CST and Nb-substituted CST structures have been well characterized through the use of X-ray powder diffraction techniques^{11,12}. This important experimental data enabled us to test and fine tune our models in order to achieve an optimum model that is transferable across all sorbates and sorbents of interest.

Initially, energy minimization was used to predict structural characteristics such as the location of cation and water sites within the materials and the coordinating

environment of the cations. Energy minimizations were conducted on hundreds of different initial configurations and lowest energy structures were taken as representative of the equilibrium structure. Comparison of these results against experimental data for the well-characterized CST materials enabled the accuracy of the force field to be tested. The results demonstrated the ability of the calculations to provide a reasonable estimation of Cs^+ , Na^+ and water positions within the various CST materials.

Although energy minimizations give a reasonable estimate to the crystal structure, it only provides a snapshot of where cations and water molecules reside. Experimentally, X-ray diffraction gives an averaged position of cations and water sites, which may be a reason for some of the observed discrepancies between energy minimization results and experiment. Molecular dynamics, on the other hand, enables one to obtain a time-averaged position of the cations and water molecules. In addition, molecular dynamics allows us to compute dynamic properties of the materials.

All energy-minimizations and molecular dynamics simulations for the CST materials were carried out under the following conditions:

1. All experimental symmetry constraints were removed for the model structure
2. The lattice constants were held fixed to their experimentally determined, crystallographic coordinates
3. All framework atoms (O, Si, Ti, and Framework Na^+) were held fixed to their experimentally determined, crystallographic coordinates
4. All tunnel atoms (H_2O , Cs^+ , Exchangeable Na^+ , and H^+) were free to move

Na^+ -CST

For Na-CST (see Figure 2 and Table 2), it is observed that the exchangeable Na^+ cations are located $\sim 0.4 \text{ \AA}$ farther from the center of the tunnel than the experimentally determined position, but at nearly the same z-coordinate distance down the tunnel axis as the experimentally determined position. The water molecules are predicted to be located over 3 sites. Two of the sites agree quite well with the experimentally determined O(W1) and O(W2) sites. However, the third computed water site is not observed experimentally. We believe the proton is the primary reason for the discrepancy. The simulations indicate that the proton is located very near to the O(W2) site. It interacts with water, thereby preventing additional water molecules from locating at the O(W2) site. This gives rise to the third predicted water site. The potential parameters for the proton may need to be adjusted to prevent this interaction.

Figure 2. A polyhedral representation (with purple TiO_6 octahedra and yellow SiO_4 tetrahedra) of the lowest energy Na^+ -exchanged CST along [001], sodium cations (pink spheres) and water (red spheres with white hydrogen spheres) were located in the tunnels. The sodium cations are located $\sim 0.4 \text{ \AA}$ farther off center than seen experimentally.

Table 2. A comparison with experiment of the Na-CST atomic coordinates obtained through energy-minimizations and molecular dynamics simulations. The framework atoms (Si, Ti, O, and Na-frame) were held fixed to the experimentally determined, crystallographic coordinates. The predicted coordinates were averaged and folded into the experimental symmetry. The lattice constants and partial occupancies are also provided.

Na-CST Experimental				
Lattice Constants				
	a	b	c	
	7.8082	7.8082	11.9735	
	x	y	z	Occ.
Na+	0.435	0.435	0.060	0.320
H+	????	????	????	????
O(W1)	0.264	0.264	0.500	1.000
O(W2)	0.431	0.431	0.310	0.420
Symmetry P42/mcm				

Na-CST (Energy-minimization)				
Lattice Constants				
	a	b	c	
	7.8082	7.8082	11.9735	
	x	y	z	Occ.
Na+(1)	0.400	0.400	0.069	0.250
Na+(2)	0.400	0.400	0.179	0.125
H+	0.290	0.460	0.190	0.063
O(W1)	0.279	0.279	0.500	1.000
O(W2)	0.465	0.465	0.300	0.250
O(W3)	0.409	0.409	0.037	0.125
Symmetry P42/mcm				

Na-CST (Molecular Dynamics)				
Lattice Constants				
	a	b	c	
	7.8082	7.8082	11.9735	
	x	y	z	Occ.
Na+	0.356	0.356	0.150	0.750
H+	0.390	0.440	0.190	0.063
O(W1)	0.270	0.270	0.000	1.000
O(W2)	0.450	0.450	0.310	0.250
O(W3)	0.450	0.450	0.090	0.125
Symmetry P42/mcm				

In performing molecular dynamics simulation of the Na-CST material (Figure 3), it was observed that the exchangeable sodium cations agree quite well with the positions determined in the energy-minimized structure, but still showed some discrepancy with experiment. The exchangeable Na^+ cations are located $\sim 0.6 \text{ \AA}$ farther from the center of the tunnel as compared to the experimental position. The water was again found to be located at 3 sites, just as it was in the energy minimized structure. Again, two of the sites agreed very well with the experimental O(W1) and O(W2) positions, while the third water site is not observed experimentally. The

proton was found at the same general position as in the case of the energy minimized structure, which is located in the general vicinity of the experimentally determined O(W2) position, thereby leading to a third water site.

Figure 3. A distribution cloud of the sodium cations along [100]. This representation depicts the trajectories of Na⁺ cations as they progress in a molecular dynamics simulation. A more intense color represents a higher frequency in which the Na⁺ cations were located at a particular XY coordinate. The Na⁺ cations are seen to localize around a specific site. An averaged position of the site is calculated and compared to experiment.

Cs⁺-CST

For the Cs⁺-exchanged CST (see Figure 4 and Table 3), the lowest energy configuration snapshot shows the Cs⁺ cation to be located slightly off-center by ~0.1 Å with respect to the tunnel axis, and its z-coordinate deviating by ~0.3 Å from experiment. The partial occupancies are calculated for the simulated structure. Note that for the Cs⁺ cations, an “apparent occupancy” is reported. This arises in the simulated results due to the Cs⁺ cation being off center. In folding the simulated atomic positions into the experimental symmetry, there are an increased number of possible Cs⁺ sites (8 sites) that arise as compared to experiment (2 sites). For comparison purposes, the apparent occupancy of Cs⁺ is calculated with respect to the possible number of experimental sites. The simulated occupancy is greater than the experimental occupancy due to the fact that we are approximating the structural formula with a slightly higher Cs⁺ content as compared to the experimental structure.

Experimentally, it is not known where the exchangeable Na⁺ cations are located. This study has allowed us to characterize a position and determine the coordination environment of the exchangeable Na⁺ cations. The water molecules are observed to populate 2 sites within the Cs-CST material. Seventy-five percent of the water in the system agrees very well with the fully occupied, experimental position O(W1). The remaining water is located closer to the center of the tunnel. This water position is not

observed experimentally. It is observed that this extra water site arises again due to the proton in the system. The proton tends to interact with the water molecule in such a way where it prevents the water from filling the fully occupied, experimental O(W1) water site. The proton is located near the framework atoms, and pushes the water molecule away from the framework atoms and towards the center of the tunnel, thus giving rise to a second water site.

Figure 4. A polyhedral representation (with purple TiO_6 octahedra and yellow SiO_4 tetrahedra) of the lowest energy Cs^+ -exchanged CST along [001], sodium cations (pink spheres), cesium cations (green spheres) and water (red spheres with white hydrogen spheres) were located in the tunnels. Cesium cations are found slightly off-center, while there are two distinct water sites. The first site is 75% occupied and is observed experimentally, while the second site (located closer to the tunnel axis) is 25% occupied and is not observed experimentally.

Table 3. A comparison with experiment of the Cs-CST atomic coordinates obtained through energy-minimizations and molecular dynamics simulations. The framework atoms (Si, Ti, O, and Na-frame) were held fixed to the experimentally determined, crystallographic coordinates. The predicted coordinates were averaged and folded into the experimental symmetry. The lattice constants and partial occupancies are also provided. **An “apparent occupancy” is reported for Cs⁺ for comparison puposes.

Cs-CST Experimental				
Lattice Constants				
	a	b	c	
	7.8258	7.8258	11.9815	
	x	y	z	Occ.
Cs1	0.5	0.5	0.25	0.2
Cs2	0.5	0.5	0.131	0.1
Na+	????	????	????	????
H+	????	????	????	????
O(W1)	0.274	0.274	0.500	1.000
Symmetry P42/mcm				

Cs-CST (Energy-minimization)				
Lattice Constants				
	a	b	c	
	7.8258	7.8258	11.9815	
	x	y	z	Occ.
Cs+	0.49	0.49	0.22	0.5**
Na+(1)	0.390	0.390	0.310	0.125
Na+(2)	0.390	0.390	0.050	0.125
H+	0.060	0.060	0.500	0.125
O(W1)	0.290	0.290	0.500	0.750
O(W2)	0.420	0.420	0.390	0.250
Symmetry P42/mcm				

Cs-CST (Molecular Dynamics)				
Lattice Constants				
	a	b	c	
	7.8258	7.8258	11.9815	
	x	y	z	Occ.
Cs+	0.5	0.5	0.23	0.5**
Na+(1)	0.390	0.390	0.310	0.125
Na+(2)	0.390	0.390	0.000	0.125
H+	0.150	0.150	0.500	0.125
O(W1)	0.270	0.270	0.500	0.750
O(W2)	0.460	0.460	0.170	0.250
Symmetry P42/mcm				

In using molecular dynamics for the Cs⁺-exchanged CST case (see Figure 5), one cesium position is located at ~ 0.05 Å off-center and ~ 0.735 fractional units down the c-axis, as compared to the experimental location of cesium at the center and at 0.75 fractional units down the c-axis. This is very near to the experimentally determined, 8-coordinated Cs⁺ site, and gives a more accurate predicted position as compared to the energy-minimized structure. The second experimentally observed cesium site is not seen in the simulations. The exchangeable sodium cations obtained through molecular dynamics simulations agree very well with the energy minimized locations. Both simulations (MD and energy-minimizations) predict the experimental O(W1) site very well, but only seventy-five percent of the simulated water is found in this site. The remaining water gives rise to a second water site, O(W2). This site is not seen experimentally. Again, we believe that the reason that this extra water site arises is due to the proton. The proton locates very near to the framework oxygen atoms, thereby blocking the water from completing the experimental O(W1) full occupancy.

Figure 5. A distribution cloud of the cesium cation along [100]. This representation depicts the trajectory of the Cs^+ cation as it progresses in a molecular dynamics simulation. The Cs^+ cation is localized around the center of the CST tunnel. The averaged position shows the Cs^+ cation to be located almost exactly at the center.

Niobium-substituted CST

A similar analysis was performed for the Na^+ and Cs^+ exchanged niobium-substituted CST ion exchangers (see Table 4). The Na^+ -exchanged Nb-CST agrees extremely well with experimental results. The Na^+ sites and water sites are located very close to the experimentally determined positions. This gives us a good indication that we have a good model for Nb^{5+} . The Cs^+ -exchanged case yields some discrepancy with experiment. As in the previous case, only one Cs^+ is observed in the simulations, while two sites are seen experimentally. The simulated position agrees well with the experimentally determined Cs1 site, although the simulated position is slightly off the center of the axis and shifted down the tunnel axis by 0.03 fractional units relative to the experimental position. The use of a larger simulation box, where additional water configurations with different neighboring environments could arise, may allow the Cs2 site to be observed. We believe the major reason for the dislocation of Cs^+ in the simulations is the presence of niobium in the framework. In substituting Nb^{5+} for Ti^{4+} , there is more charge introduced into the framework. This extra charge for Nb^{5+} is believed to have an effect on the Cs^+ cation, where it pushes the Cs^+ cation away, thereby causing Cs^+ to be located off-center and further down the z-axis. In addition, there are two water sites that are observed through modeling. The first simulated water site agrees well with the experimental O(W1) site, while the second simulated water site is located close to a vacant Cs^+ site. There is indication that the second simulated water site is observed experimentally at this site. Tripathi *et al.* mention the following:

“In the absence of Cs^+ an electron density was also observed at ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{4}$) in the difference Fourier. This can be attributed to water or minor amounts of Na^+ .”

Finally, we note that the experimental O(W2) site is not observed through simulation. Once again, a larger simulation box may be needed to observe this site, as it may arise in the presence of a Cs2 site.

Table 4. A comparison with experiment of the Nb-substituted CST atomic coordinates obtained through molecular dynamics simulations. The framework atoms (Si, Ti, Nb, O, and Na-frame) were held fixed to the experimentally determined, crystallographic coordinates. The predicted coordinates were averaged and folded into the experimental symmetry. The lattice constants and partial occupancies are also provided.

Nb-CST Experimental					Nb-CST (Molecular Dynamics)				
Lattice Constants					Lattice Constants				
	a	b	c			a	b	c	
	7.8331	7.8331	12.0074			7.8331	7.8331	12.0074	
	x	y	z	Occ.		x	y	z	Occ.
H+	????	????	????	????	H+	0.410	0.470	0.260	0.125
O(W1)	0.2744	0.2744	0.500	1.000	O(W1)	0.263	0.263	0.500	1.000
O(W2)	0.4479	0.4479	0.1117	0.5000	O(W2)	0.450	0.450	0.120	0.500
Symmetry P42/mcm					Symmetry P42/mcm				

Table 5. A comparison with experiment of the Cs-exchanged Nb-CST atomic coordinates obtained through molecular dynamics simulations. The framework atoms (Si, Ti, Nb, O, and Na-frame) were held fixed to the experimentally determined, crystallographic coordinates. The predicted coordinates were averaged and folded into the experimental symmetry. The lattice constants and partial occupancies are also provided. **An “apparent occupancy” is reported for Cs⁺ for comparison purposes.

Cs-exchanged Nb-CST Experimental					Cs-exchanged Nb-CST (Molecular Dynamics)				
Lattice Constants					Lattice Constants				
	a	b	c			a	b	c	
	7.8331	7.8331	12.0074			7.8331	7.8331	12.0074	
	x	y	z	Occ.		x	y	z	Occ.
Cs1	0.500	0.500	0.250	0.300	Cs+	0.485	0.485	0.280	0.5**
Cs2	0.500	0.500	0.126	0.100					
H+	????	????	????	????	H+	0.410	0.480	0.200	0.063
O(W1)	0.2824	0.2824	0.5000	0.5000	O(W1)	0.287	0.287	0.500	0.750
O(W2)	0.5916	0.5916	0.5000	0.5000	O(W2)	0.500	0.530	0.310	0.250
Symmetry P42/mcm					Symmetry P42/mcm				

Overall, in the CST family of structures, good agreement with the experimental data is obtained. Some disagreement is observed with a small amount of water and some cations being displaced relative to their experimental coordinates. This gives rise to the additional sites for water and cations. It is noted that the proton has played a major role in causing the discrepancy, and may indicate problems with the potential model used for it. Future work will include refining the parameters of the proton to see if the effects can be diminished.

Earlier it was stated that a refined force field was developed for CST materials. Table 6 shows the greater accuracy of the new forcefield (FF2) compared to the original FF1. It shows the location of water in two different sites (O5 and O6). The first row is raw data, and the second accounts for moving the water to special crystallographic positions. “Dev.” represents the average deviation from experiment.

Std. Dev. is the standard deviation of the atom about the average position, and is a measure of mobility. Notice that FF2 gets the occupancies of the sites much more accurately than FF1.

Table 6: predicted positions of water in CST using two force fields (FF1 and FF2).

Atom	X	Y	Z	Dev. (Å)	Std. Dev. (Å)	Pop. Frac.	Exptl. Occ.
Water (O5) FF1	0.313	0.045	0.500	0.46	0.65	80.3%	100.0%
	0.313	0.045	0.500	0.46			
Water (O6) FF1	0.498	-0.001	0.101	0.25	0.71	44.2%	50.0%
	0.500	0.000	0.101	0.25			
Water (O5) FF2	0.307	0.052	0.499	0.37	0.23	95.5%	100.0%
	0.307	0.052	0.500	0.37			
Water (O6) FF2	0.502	0.002	0.099	0.23	0.64	46.7%	50.0%
	0.500	0.000	0.099	0.23			

Polyoxometallate Structures

Another potentially important class of ion exchangers are polyoxoniobate structures¹³ (see Figure 6). These materials have shown selectivity towards specific radionuclides and are currently being synthesized and tested for their ion exchange capabilities. Unfortunately, X-ray powder diffraction is not able to differentiate between the identity of Na⁺ cations and water sites. This presents a formidable problem for molecular modeling. Molecular dynamics simulations were used to determine where the Na⁺ cations and water molecules tend to reside in the Na-analogue polyoxoniobate material, which will lead to a better understanding of the origins of selectivity. From X-ray diffraction, it has been determined that the water and Na⁺ cations are located over 4 possible sites (Na1, Na2, Na3, and Na4). Preliminary modeling results show that some of the sodium sites are highly mobile, while there are some that are quite a bit less mobile. Furthermore, these low mobility positions seem to be located very close to the experimentally determined Na1 and Na3 sites, which give indication that these sites may always be filled with Na⁺ cations. The cause of this low mobility is seen when observing the coordination environment of these particular sites. At ~2.5 to 3.0 Å, the Na⁺ cations become highly coordinated with framework oxygen atoms in the material. The extra coordination leads to a more favorable site for Na⁺ cations to locate and also leads to the lower mobility observed. The Na2 and Na4 sites have less framework oxygen around to bind to the Na⁺ cations, thus leading to the higher mobility observed.

Figure 6. A polyhedral representation (with purple TiO_6 octahedra and yellow SiO_4 tetrahedra) of the polyoxoniobate structure along [001], sodium cations (pink spheres), water (red spheres with white hydrogen spheres) after 300 ps in a molecular dynamics simulation. The Na^+ cations are found to locate in the experimentally determined Na1 and Na3 sites. The water and remaining Na^+ sites have shown a high mobility, which makes it difficult to determine which sites they prefer. Further simulations are being conducted to resolve the water and remaining Na^+ positions.

Experimentally, the Na^+ -analogue polyoxoniobate structure was solved from powder x-ray diffraction data and refined by the Rietveld method. The refined structure was characterized into two different models. The first model has space group symmetry of I-4mmm, while the second model has I-4m2 space group symmetry.

The initial configuration of the Na^+ -analogue polyoxoniobate structure was generated according to the experimentally determined, crystallographic atom coordinates. The I-4m2 model was used in this work to characterize the positions of the atoms. The lattice constants ($a, b, c, \alpha, \beta, \gamma$) were constrained to the crystallographic data. The Keggin $\text{Nb}_{12}\text{SiO}_{40}$ clusters and the linking Ti_2O_2 units were also constrained to their crystallographic coordinates, while only the counterbalancing Na^+ cations and water molecules were permitted to move. In the simulations, all symmetry constraints were removed.

Experimentally, it is determined that the O6 oxygen atoms in the linking Ti_2O_2 units are half-occupied, therefore leading to four possible O6 oxygen sites. In order to account for this, random configurations of the O6 atoms across the four possible sites were used in the simulations. Finally, the positions of the Na^+ cations and water molecules were randomly placed across the possible sites that were solved experimentally. The possible sites are labeled experimentally as Na1, Na2, Na3, and

Na4. By charge neutrality, there are 12 Na⁺ cations for every Nb₁₂SiO₄₀ cluster. In addition, there are 4 water molecules for every Nb₁₂SiO₄₀ cluster, giving a total of 16 occupied sites for every Nb₁₂SiO₄₀ cluster.

The interatomic potentials used to model the interactions between atoms in the polyoxoniobate structure are the same as those used in modeling the crystalline silicotitanate (CST) structures. Previous simulations of CST materials have shown the interatomic potential parameters to predict structural characteristics that agree with experiment very well. The model assumes that ions interact via long-range electrostatic forces and short-range forces that include both repulsions and the van der Waals attractions between neighboring electron charge clouds. The functional form of the potential model for the interaction of ions *i* and *j* at a distance of *r_{ij}* is given by the expression:

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

where *E_{total}* is the total potential energy, *q* is the charge of the ion, and *A*, *ρ*, and *C* are Buckingham parameters. The first term of Equation 1 represents the long-range electrostatic interactions, while the remaining two terms represent the Buckingham form of the short-range repulsion and van der Waals attraction interactions. Short range water-water interactions were modeled using a simple Lennard-Jones potential.

In order to account for polarizability in the lattice, a shell model potential was added to all oxygen atoms. The shell model treats each oxygen atom as a core and a massless shell, where the shell represents the electronic charge cloud of the ion. In addition, the core and shell are connected by a harmonic spring. The polarizability can then be related to the harmonic spring constant and the charges of the shell and core. A complete listing of all potential parameters is given in Table 1.

The simulations were performed using the shell model molecular dynamics algorithm available in the GULP code. Molecular dynamics simulations were carried out for 500 picoseconds in each simulation. In this time, the Na⁺ cations and water molecules have the opportunity to move out of their original sites, and eventually locate themselves in the most stable configuration that they can find. The simulations were carried out at high temperatures (~700 K) in order to be sure that the cations/water will sample all important regions of phase space and not become trapped in less important regions.

Energy minimizations were carried out on ~1500 different initial configurations of Na⁺ cations and water molecules. Each configuration was minimized and the lowest energy configuration was analyzed in this work. The lowest energy configuration is considered to be the most stable of all the minimized configurations; therefore it is assumed that its structure will be closely related to the equilibrium structure.

Although the molecular dynamics simulations were carried out at very high temperatures, it is observed that the Na^+ cations eventually find very stable configurations and lose their initially high mobility. This gives a good indication that these atomic positions are stable configurations and most likely to occur naturally. In order to better understand the dominant influences for these equilibrium positions, a number of properties of the system were calculated, such as coordination number and mean square displacements. Figure 7 shows the mean square displacement of water and Na^+ as the molecular dynamics simulation progresses. It can be seen that water is more mobile as compared to the Na^+ cations in the system. For this reason, it is difficult to assign a particular site to the water molecules. Additional simulations are being performed at lower temperatures in order to better understand the water behavior.

Figure 7: Mean square displacement of Na^+ and water in Na-Keggin system

In all the molecular dynamics simulations conducted, it is observed that the Na^+ cations fully occupy the Na1 and Na3 sites. A comparison between averaged atomic coordinates calculated through molecular dynamics and the experimental atomic coordinates is given in Table 7. In addition, the energy minimizations also support the argument that the Na1 and Na3 sites are fully occupied. For the Na1 site, there is an average deviation from experiment of $\sim 0.27 \text{ \AA}$. Likewise, for the Na3 site, there is an average deviation of $\sim 0.81 \text{ \AA}$ from experiment. Comparison with experiment is given in Table 8.

In looking at the coordinating environments (see Table 9), it is observed that the Na1 and Na3 sites are located very close to $\text{Nb}_{12}\text{SiO}_{40}$ clusters, which allows the Na^+ cations to become highly coordinated, thereby giving them additional stability. Experimentally, the

Na1 sites coordinate with four oxygen atoms from the neighboring $\text{Nb}_{12}\text{SiO}_{40}$ clusters at distances ranging from 2.4 Å to 2.9 Å. It cannot be determined experimentally the role water plays in adding to the coordinating environment. Simulations also show four coordinating oxygen atoms from the neighboring $\text{Nb}_{12}\text{SiO}_{40}$ clusters at a distance of ~2.7 Å. Minimal amounts of water are observed in the neighborhood of the Na1 sites. The high coordinating environment of the Na1 sites causes the Na^+ cations to be rigidly held into place and to fully occupy the Na1 sites.

The Na3 sites are also fully occupied by Na^+ cations. Experimentally, there are two oxygen atoms from the neighboring $\text{Nb}_{12}\text{SiO}_{40}$ clusters that coordinate with the Na3 sites from 2.4 Å to 2.9 Å (see Table 7). Computationally, it is observed that the Na3 site coordinates with between 2 and 3 oxygen atoms from the $\text{Nb}_{12}\text{SiO}_{40}$ clusters at distances ranging from 2.4 Å to 2.9 Å. In addition, it is observed that the Na3 site gains extra coordination from a neighboring water molecule at these distances. Again, this high coordination environment provides a favorable environment for Na^+ cations to reside, which gives good indication that the Na3 sites are fully occupied with Na^+ cations.

The remaining Na^+ cations are observed to occupy 50% of the Na2 sites and 25% of the Na4 sites. In order to determine which of the Na2 sites were occupied by Na^+ cations, the 50% occupied O6 oxygen atoms must be examined closer. It is observed that the Na2 sites that are occupied by Na^+ cations are dependent upon which O6 oxygen sites are occupied. Furthermore, the Na^+ occupied Na2 sites are always located in such a way that it gains extra-coordination with one O6 oxygen atom. An illustration is shown in Figure 8 demonstrating the dependence of Na2 on the 50% occupied O6 oxygen atoms.

Figure 8 -- Depiction of the dependence of the Na²⁺ on the O₆ oxygen site. These are views down the c-axis of the crystal, where Na²⁺ cations are pink, and the O₆ oxygen atoms are red. Figure3(a) (TOP) shows all the possible sites of the O₆ and Na²⁺ cations. In Figure3(b) (BOTTOM LEFT), one scenario of the 50% occupied O₆ configuration is shown. The Na²⁺ cations seek to coordinate with one of the O₆ linking oxygen atoms, thereby making the cations dependent upon the orientation of the O₆ oxygen atoms. Likewise, in Figure3(c) (BOTTOM RIGHT), the Na²⁺ cations are oriented in line with the O₆ oxygen atoms.

Both molecular dynamics simulations and energy minimizations yield the same positioning for the Na²⁺ cations in the Na₂ sites with respect to the O₆ oxygen atoms. Experimentally, the Na₂ position is located on the unit cell face. The averaged molecular dynamics position agrees well with the experimental results, as would be expected due to the averaging of atomic positions automatically performed by powder X-ray diffraction. Taking a closer look at the computational results, it is observed that the Na₂ is located slightly off the face. Figure 9 shows the trajectories from a molecular dynamics simulation of the Na²⁺ cations as they progress in time.

Figure 9 -- Probability distribution of the positions of all Na⁺ cations obtained from a molecular dynamics trajectory. This view is looking down the c-axis of the crystal. The Na2 sites are circled in red and are observed to be located off the unit cell face, but the averaged position would be located very close to the cell face. The remaining sites are labeled in yellow. For simplicity, only one of the respective sites are labeled. By performing the symmetry operation, the remaining unlabeled sites can be determined.

Clearly, there is a higher probability of finding the Na⁺ cations that are associated with the Na2 sites in positions slightly off of the unit cell face. In addition, energy minimizations show an average deviation from the experimental site of ~ 1.0 Å. These results suggest a higher mobility for Na2 as compared to the Na1 and Na3 sites. It also indicates that Na⁺ cations that are located in the Na2 sites are seeking a more favorable, higher coordinating position. Experimentally, the Na2 site only coordinates with one O6 oxygen atom at distances ranging from 2.4 Å to 2.9 Å. Computationally, the Na2 site is observed to coordinate with between two to three neighboring oxygen atoms from the Nb₁₂SiO₄₀ clusters and Ti₂O₂ linkages, which arises due to the dislocation of Na2 off the unit cell face. In addition, there is also some water present that assists in stabilizing the Na⁺ cations in the Na2 sites.

Finally, it is known experimentally that the Na2 site is a fully occupied site. Since 50% of the sites are occupied by Na⁺ cations, the remaining sites must be occupied by water. Water is observed to be very mobile (see Figure 10) as compared to the Na⁺ cations, therefore it is difficult to determine a particular site in which water is associated with. Further simulations performed at lower temperatures may give some insight into the

water locations. In general, it is observed that water coordinates with the Na2 and Na4 sites to give extra stability to these cations.

Figure 10 -- Probability distribution of water in a molecular dynamics trajectory. It can be seen that water is more mobile as compared to the Na⁺ cations, thereby making it difficult to determine a specific site. We can see that water is in the neighborhood of the Na2 and Na4 sites.

The remaining Na⁺ cations are located in the Na4 sites, where the Na⁺ cations occupy 25% of the sites. It cannot be determined which of the particular Na4 sites are occupied, but rather it is thought that the Na⁺ are able to jump from one neighboring Na4 site to another. Once again, energy minimizations agree well with molecular dynamics simulations in determining the Na⁺ cations that are located in the Na4 sites. An average deviation from experiment of ~ 1.5 Å is observed, which gives further indication of the higher mobility of the Na4 cations and also the notion that the Na⁺ cations are located in the region of all the Na4 sites, not in one specific Na4 site. Water occupies 25% of the Na4 sites, thereby giving Na4 a partial occupancy of 50%. In addition, water is observed to be in the neighborhood of the Na4 sites, where it aids in coordinating with the Na⁺ cations occupying these sites. Again, water is observed to be highly mobile, thereby giving it the ability to jump from one Na4 site to another.

Finally, a simulated diffraction pattern of the energy minimized structure is given in Figure 11.

Figure 11 -- Powder x-ray diffraction pattern of the energy minimized structure.

Table 7 – Comparison of atomic coordinates obtained through molecular dynamics simulations with experimental X-ray diffraction determined atomic coordinates. The distance in which the simulated results deviate from experiment are also reported along with the average and standard deviation.

Site	Molecular Dynamics			Experimental					
	Averaged Coordinates			Coordinates of Sites			Deviation	Average	Std. Dev.
Na1	10.76	3.98	-0.02	10.71	3.69	0.00	0.298644		
Na1	3.60	3.95	-0.01	3.69	3.69	0.00	0.272424		
Na1	3.60	10.35	-0.01	3.69	10.71	0.00	0.366483		
Na1	11.10	3.62	5.67	10.89	3.51	5.65	0.236369	0.323385	0.103534
Na1	3.27	10.81	5.64	3.51	10.89	5.65	0.252146		
Na1	10.84	10.22	-0.05	10.71	10.71	0.00	0.508457		
Na1	11.04	10.74	5.67	10.89	10.89	5.65	0.218918		
Na1	3.11	3.68	5.67	3.51	3.51	5.65	0.433641		
Na2	3.07	0.57	5.65	3.62	0.00	5.34	0.850543		
Na2	11.18	0.05	5.72	10.78	0.00	5.34	0.54978	0.733633	0.177045
Na2	7.42	4.03	-0.06	7.20	3.58	0.31	0.618235		
Na2	7.79	10.21	-0.03	7.20	10.82	0.31	0.915974		
Na3	5.15	2.11	2.68	5.66	1.54	2.83	0.783818		
Na3	2.01	9.16	8.44	1.53	8.74	8.48	0.636292		
Na3	9.21	12.28	2.92	8.74	12.86	2.85	0.74274		
Na3	12.33	5.20	8.48	12.86	5.66	8.48	0.698696	0.716583	0.089209
Na3	9.22	2.04	2.88	8.74	1.54	2.83	0.69516		
Na3	12.37	9.13	8.36	12.86	8.74	8.48	0.638939		
Na3	5.08	12.18	2.76	5.66	12.86	2.83	0.894718		
Na3	1.99	5.21	8.55	1.54	5.66	8.48	0.642305		
Na4	14.32	7.42	4.64	13.95	5.69	3.98	1.884762		
Na4	0.08	7.42	4.64	0.45	8.71	3.98	1.500102		
Na4	0.08	7.42	4.64	0.45	5.69	3.98	1.88406		
Na4	14.32	7.42	4.64	13.95	8.71	3.98	1.500983		
Na4	7.14	14.11	10.30	6.75	12.89	9.63	1.443309		
Na4	7.14	-0.13	10.30	7.65	1.51	9.63	1.843711		
Na4	7.14	14.11	10.30	7.65	12.89	9.63	1.482728		
Na4	7.14	-0.13	10.30	6.75	1.51	9.63	1.812161	1.659433	0.185476
Na4	6.95	14.23	6.73	8.71	13.95	7.32	1.878497		
Na4	6.95	-0.01	6.73	5.69	0.45	7.32	1.462011		
Na4	6.95	14.23	6.73	5.69	13.95	7.32	1.41784		
Na4	6.95	-0.01	6.73	8.71	0.45	7.32	1.912056		
Na4	0.15	7.14	1.03	1.51	6.75	1.67	1.551734		
Na4	14.39	7.14	1.03	12.89	7.65	1.67	1.711315		
Na4	14.39	7.14	1.03	12.89	6.75	1.67	1.678775		
Na4	0.15	7.14	1.03	1.51	7.65	1.67	1.586882		

Table 8 – Comparison of the energy minimized atomic coordinates with the experimental coordinates. The distance which the energy minimized coordinates deviate from experiment are also reported, along with the average and standard deviation.

Site	MINIMIZED DATA			EXPERIMENTAL DATA			DEVIATION	AVERAGE	STD. DEV
Na1	10.42	3.50	11.06	10.71	3.69	0.00	0.34		
Na1	3.43	10.78	5.50	3.51	10.89	5.65	0.15		
Na1	3.29	3.73	0.00	3.69	3.69	0.00	0.38		
Na1	10.49	10.44	0.16	10.71	10.71	0.00	0.27	0.27	0.10
Na1	10.81	3.49	5.78	10.89	3.51	5.65	0.14		
Na1	3.71	3.62	5.85	3.51	3.51	5.65	0.34		
Na1	3.55	10.45	0.08	3.69	10.71	0.00	0.22		
Na1	10.78	10.45	5.57	10.89	10.89	5.65	0.36		
Na2	6.70	10.17	0.36	7.20	10.82	0.31	0.71		
Na2	11.76	12.68	5.73	10.78	0.00	5.34	1.96	1.03	0.62
Na2	3.10	0.48	5.14	3.62	0.00	5.34	0.71		
Na2	6.55	3.99	0.35	7.20	3.58	0.31	0.74		
Na3	2.14	9.14	8.73	1.53	8.74	8.48	0.82		
Na3	12.27	5.11	8.48	12.86	5.66	8.48	0.69		
Na3	9.11	2.23	2.70	8.74	1.54	2.83	0.84		
Na3	12.24	9.14	8.39	12.86	8.74	8.48	0.70	0.81	0.11
Na3	8.70	12.20	2.40	8.74	12.86	2.85	0.69		
Na3	2.24	5.08	8.72	1.54	5.66	8.48	0.92		
Na3	5.01	2.07	2.86	5.66	1.54	2.83	0.82		
Na3	4.97	12.03	2.90	5.66	12.86	2.83	0.96		
Na4	14.19	6.85	4.37	13.95	5.69	3.98	1.32		
Na4				0.45	8.71	3.98	1.90		
Na4				0.45	5.69	3.98	1.38		
Na4				13.95	8.71	3.98	1.86		
Na4	7.07	14.13	9.94	6.75	12.89	9.63	1.44		
Na4				7.65	1.51	9.63	1.75	1.51	0.32
Na4				7.65	12.89	9.63	1.48		
Na4				6.75	1.51	9.63	1.72		
Na4	8.66	14.21	5.88	8.71	13.95	7.32	1.48		
Na4				8.71	0.45	7.32	1.52		
Na4	12.91	6.90	0.13	12.89	7.65	1.67	0.69		
Na4				12.89	6.75	1.67	1.56		

Table 9 -- Comparison of the simulated and experimental coordination number as a function of distance for the Na1, Na2, Na3, and Na4 sites.

Na1 Sites (Experimental)				Na1 Sites (Calculated)			
Distance (Å)	Total Coordination	Water Coordination	Nb ₁₂ SiO ₄₀ Coordination	Distance (Å)	Total Coordination	Water Coordination	Nb ₁₂ SiO ₄₀ Coordination
2.07	0.0000	unavailable	0.0000	2.07	0.7740	0.0000	0.7740
2.15	2.0000	unavailable	2.0000	2.15	1.3300	0.0000	1.3300
2.22	2.0000	unavailable	2.0000	2.22	1.8440	0.0010	1.8430
2.30	2.0000	unavailable	2.0000	2.30	2.2630	0.0030	2.2600
2.38	4.0000	unavailable	4.0000	2.38	2.6020	0.0090	2.5940
2.46	4.0000	unavailable	4.0000	2.46	2.9090	0.0200	2.8890
2.54	4.0000	unavailable	4.0000	2.54	3.1960	0.0360	3.1600
2.61	4.0000	unavailable	4.0000	2.61	3.4480	0.0530	3.3950
2.69	4.0000	unavailable	4.0000	2.69	3.7380	0.0700	3.6670
2.77	4.0000	unavailable	4.0000	2.77	4.0300	0.0890	3.9410
2.85	4.0000	unavailable	4.0000	2.85	4.3380	0.1010	4.2370
2.93	4.0000	unavailable	4.0000	2.93	4.6650	0.1190	4.5460
3.00	6.0000	unavailable	6.0000	3.00	4.9890	0.1400	4.8490
3.08	6.0000	unavailable	6.0000	3.08	5.2740	0.1590	5.1140
3.16	6.0000	unavailable	6.0000	3.16	5.5190	0.1930	5.3260

Na2 Sites (Experimental)				Na2 Sites (Calculated)			
Distance (Å)	Total Coordination	Water Coordination	Nb ₁₂ SiO ₄₀ Coordination	Distance (Å)	Total Coordination	Water Coordination	Nb ₁₂ SiO ₄₀ Coordination
2.07	0.0000	unavailable	0.0000	2.07	0.3020	0.0090	0.2930
2.15	0.0000	unavailable	0.0000	2.15	0.6890	0.0170	0.6720
2.22	0.0000	unavailable	0.0000	2.22	1.1660	0.0340	1.1310
2.30	0.0000	unavailable	0.0000	2.30	1.6620	0.0780	1.5840
2.38	0.0000	unavailable	0.0000	2.38	2.1390	0.1190	2.0200
2.46	1.0000	unavailable	1.0000	2.46	2.5430	0.1910	2.3520
2.54	1.0000	unavailable	1.0000	2.54	2.8530	0.2810	2.5730
2.61	1.0000	unavailable	1.0000	2.61	3.0850	0.3550	2.7310
2.69	1.0000	unavailable	1.0000	2.69	3.3050	0.4270	2.8770
2.77	1.0000	unavailable	1.0000	2.77	3.4680	0.4860	2.9820
2.85	1.0000	unavailable	1.0000	2.85	3.6820	0.5360	3.1460
2.93	1.0000	unavailable	1.0000	2.93	3.9950	0.5710	3.4230
3.00	2.0000	unavailable	2.0000	3.00	4.4240	0.6150	3.8100
3.08	2.0000	unavailable	2.0000	3.08	4.8800	0.6530	4.2270
3.16	2.0000	unavailable	2.0000	3.16	5.2650	0.6810	4.5840

Na3 Sites (Experimental)			
Distance (Å)	Total Coordination	Water Coordination	Nb ₁₂ SiO ₄₀ Coordination
2.07	0.0000	unavailable	0.0000
2.15	0.0000	unavailable	0.0000
2.22	0.0000	unavailable	0.0000
2.30	0.0000	unavailable	0.0000
2.38	0.0000	unavailable	0.0000
2.46	2.0000	unavailable	2.0000
2.54	2.0000	unavailable	2.0000
2.61	2.0000	unavailable	2.0000
2.69	2.0000	unavailable	2.0000
2.77	2.0000	unavailable	2.0000
2.85	2.0000	unavailable	2.0000
2.93	2.0000	unavailable	2.0000
3.00	2.0000	unavailable	2.0000
3.08	2.0000	unavailable	2.0000
3.16	2.0000	unavailable	2.0000

Na3 Sites (Calculated)			
Distance (Å)	Total Coordination	Water Coordination	Nb ₁₂ SiO ₄₀ Coordination
2.07	0.2260	0.0010	0.2250
2.15	0.6920	0.0060	0.6860
2.22	1.2750	0.0270	1.2470
2.30	1.7230	0.0710	1.6520
2.38	2.0540	0.1420	1.9120
2.46	2.3400	0.2540	2.0870
2.54	2.6020	0.3720	2.2300
2.61	2.8960	0.5200	2.3760
2.69	3.1850	0.6520	2.5320
2.77	3.4830	0.7780	2.7050
2.85	3.7650	0.8800	2.8850
2.93	4.0770	0.9940	3.0830
3.00	4.3910	1.0830	3.3070
3.08	4.6800	1.1500	3.5300
3.16	5.0110	1.2200	3.7910

Na4 Sites (Experimental)			
Distance (Å)	Total Coordination	Water Coordination	Nb ₁₂ SiO ₄₀ Coordination
2.07	0.0000	unavailable	0.0000
2.15	0.0000	unavailable	0.0000
2.22	0.0000	unavailable	0.0000
2.30	0.0000	unavailable	0.0000
2.38	0.0000	unavailable	0.0000
2.46	0.0000	unavailable	0.0000
2.54	1.0000	unavailable	1.0000
2.61	1.0000	unavailable	1.0000
2.69	1.0000	unavailable	1.0000
2.77	1.0000	unavailable	1.0000
2.85	1.0000	unavailable	1.0000
2.93	1.0000	unavailable	1.0000
3.00	1.0000	unavailable	1.0000
3.08	2.0000	unavailable	2.0000
3.16	2.0000	unavailable	2.0000

Na4 Sites (Calculated)			
Distance (Å)	Total Coordination	Water Coordination	Nb ₁₂ SiO ₄₀ Coordination
2.07	1.0800	0.2290	0.8510
2.15	1.6030	0.2490	1.3540
2.22	1.9440	0.2840	1.6590
2.30	2.1550	0.3250	1.8300
2.38	2.3260	0.4130	1.9130
2.46	2.4930	0.5450	1.9490
2.54	2.6340	0.6640	1.9690
2.61	2.7870	0.8010	1.9860
2.69	2.9500	0.9500	2.0000
2.77	3.1310	1.1150	2.0160
2.85	3.3150	1.2860	2.0290
2.93	3.5290	1.4870	2.0420
3.00	3.6960	1.6530	2.0430
3.08	3.8400	1.7940	2.0460
3.16	3.9540	1.9040	2.0500

Hybrid Monte Carlo

In general, molecular dynamics simulations give rise to a more accurate predicted position than the energy minimized structures. It was suspected that the better accuracy of molecular dynamics arises due to the fact that we are able to obtain an averaged position, just as X-ray diffraction gives averaged cation and water positions. However, in the CST materials, molecular dynamics simulations do have an inherent weakness. Due to the small tunnel sizes, one of the drawbacks of the MD simulations in these systems is that cations may block the pore and retard diffusion of water and other cations. Therefore, the system is no longer able to explore all the important regions of phase space. With this limitation, the molecular dynamics simulations, and furthermore, the structural predictions become highly dependent on the initial configuration used to start the simulation. More elaborate methods are required in order to accurately predict the correct structure. One way to overcome this limitation is to run a large number of energy minimizations to obtain a reasonable initial configuration in which to start the molecular dynamics simulation. Another, and perhaps, more efficient method is to use a Hybrid Monte Carlo (HMC) approach. In this approach, molecular dynamics simulations are run to capture the dynamics of the system. Periodically, a Monte Carlo swap move is proposed to switch the positions of two cations, two water molecules, or a water molecule and cation. Development of the HMC method is underway. It will allow a better sampling of phase space, thereby leading us to a better prediction of the structural properties.

Summary

Force fields have been developed for a broad class of ion exchange materials, including H-, Na- and Cs-forms of CST. Force fields for polyoxometallate ("Keggin chain") materials have also been developed. Advanced molecular simulations including energy minimization, molecular dynamics and hybrid Monte Carlo have been used to understand the siting, energetics and arrangement of cations and water in these materials. When experimental data are available, the agreement between simulations and experiments is good. The simulations have been used to predict the locations of Na⁺ and water in these systems when experimental data was inconclusive. A mechanistic explanation for the increase in selectivity of CST for Cs⁺ over Na⁺ when Nb is substituted into the lattice has been obtained from the simulations.

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Students Supported by this Grant

James P. Larentzos, PhD (now at High Performance Technologies Inc.)
Craig Powers (currentl finishing up his PhD at Notre Dame)