

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-96SR18500 with the U.S. Department of Energy.

This work was prepared under an agreement with and funded by the U.S. Government. Neither the U. S. Government or its employees, nor any of its contractors, subcontractors or their employees, makes any express or implied: 1. warranty or assumes any legal liability for the accuracy, completeness, or for the use or results of such use of any information, product, or process disclosed; or 2. representation that such use or results of such use would not infringe privately owned rights; or 3. endorsement or recommendation of any specifically identified commercial product, process, or service. Any views and opinions of authors expressed in this work do not necessarily state or reflect those of the United States Government, or its contractors, or subcontractors.

**FY06 Annual Report for Environmental Management Science Program
Project #95061
Strategic Design and Optimization of Inorganic Sorbents
For Cesium, Strontium and Actinides**

**D. Hobbs, Savannah River National Laboratory
M. Nyman, Sandia National Laboratories
A. Clearfield, Texas A&M University
E. Maginn, University of Notre Dame**

Investigators

Dr. David Hobbs
Savannah River National Laboratory
Westinghouse Savannah River Company
773-A, B-117
Aiken, SC 29808
803-725-2838
david.hobbs@srs.gov

Dr. May Nyman
Sandia National Laboratories
P. O. Box 5800 Mailstop 0755
Albuquerque, NM 87185-0755
505-284-4484
mdnyman@sandia.gov

Dr. Abraham Clearfield
Department of Chemistry
Texas A&M University
College Station, TX 77842
979-845-2936
clearfield@mail.chem.tamu.edu

Dr. Edward Maginn
Department of Chemical Engineering
University of Notre Dame
Notre Dame, IN 46556
574-631-5687
ed@nd.edu

Other Participants:

Dr. Martine Duff (SRNL)
Dr. Douglas Hunter (SRNL)
Dr. Francois Bonhomme (SNL – Postdoctoral Research Associate)
Dr. Margaret Welk (SNL – Postdoctoral Research Associate)
Mr. Joel Bixler (SNL – Undergraduate Student)
Dr. Akhilesh Tripathi (TAMU – Postdoctoral Research Associate))
Mr. Chris Fewox (TAMU – Graduate Student)
Mr. Houston Perry, (TAMU – Graduate Student)
Mr. Jose Delgado (TAMU – Undergraduate Student (Hispanic), received BS in Chemistry May 2006, graduate student starting September 2006)
Mr. Steven Kerlegon, (TAMU – Undergraduate student (African-American), received BS in Chemistry May 2006, employed by Celanese Corporation)
Dr. James Larentzos (ND – Graduate Student) – graduated December 2005
Mr. Craig Powers (ND – Graduate Student)
Dr. Wei Shi (ND – postdoctoral researcher)

Collaborators:

Professor John Parise, Professor of Geology and Chemistry, SUNY Stonybrook, New York
Aaron Celestian, (SUNY Stonybrook – graduate student)
National Synchrotron Light Source (NSLS) at the Brookhaven National Laboratory

Advanced Photon Source (APS) at the Argonne National Laboratory

Dr. Karl Mueller, Pennsylvania State University

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 affinity for cesium, strontium and actinide separations. The target problem focuses on the treatment of high-level nuclear wastes. The general approach can likewise be applied to non-radioactive separations.

Research Progress

During the fifth year of the project our studies focused along the following paths: (1) determination of Cs⁺ ion exchange mechanism in sodium titanium silicates with sitinikite topology and the influence of crystallinity on ion exchange, (2) synthesis and characterization of novel peroxy-titanate materials for strontium and actinide separations, and (3) further refinements in computational models for the CST and polyoxoniobate materials.

1. Cesium Ion Exchange Mechanism and the Influence of Particle Crystallinity

Sodium titanium silicates with sitinikite topology (CST) feature one-dimensional tunnels that will exchange alkali and alkaline earth ions. In the sodium form (Na-CST), the tunnel is symmetrical. Exchange of cesium ions for sodium ions does not change the shape of the tunnel and the space group remains P4₂/mcm. However, when the sodium form is converted to the proton form (H-CST), there is a change in unit cell dimension and space group. The H-CST features an elliptical tunnel with the ratio of the long to the short distance of the tunnel of 1.28. As a result the large Cs⁺ entering the tunnel cannot diffuse down the tunnel because the framework oxygens are constricted to cut the free tunnel space to below the ionic diameter of Cs⁺. Therefore the Cs⁺ accumulates in a secondary site below the constriction. At a certain level of Cs⁺ uptake the framework changes back to the original Na⁺ space group opening the tunnel to further diffusion of the Cs⁺. The Cs⁺ can then occupy the favored site within the center of the tunnels.

This phase change also explains why the cesium elution from CST by contacting with an acid solution is relatively ineffective. Upon contact with acid the unit cell reverts to the proton phase blocking the movement of Cs⁺ within the tunnels. Currently we are examining the complete removal of Cs⁺ using sodium ion solutions.

We have found that if a small amount of Cs⁺ is added to the reaction mixture, the Nb-CST can be prepared in 10h at 200°C instead of 5-10 days. Even this small amount of Cs⁺ cannot be removed by treatment with acid. It thus appears that the Nb-CST undergoes the same crystallographic rearrangements as the non-niobium phase. The reason for the better performance of Nb-CST in sorption of Cs⁺ is the fact that the increased framework charge reduces the Na⁺ content in the tunnels by 50%. The space is then filled by water molecules. This permits the formation of a twelve coordinated Cs⁺ in the tunnel with four water molecules bonded to Cs⁺ as contrasted to an 8-coordinated species (no water) in the non-niobium phase.

The diffusion of the Cs⁺ through the tunnels is slow. In order to increase the diffusion rate we have reduced the crystallinity of CST by preparing it at temperatures as low as 170°C and for lesser reaction times. Indeed the rate of exchange increases. The less crystalline products have high surface areas (~ 200 m²/g) versus 8 or less m²/g for the crystals. The data were not optimized as we are in the process of carrying out a more systematic study of ion exchange with Nb-CST.

2. Peroxo-titanate Materials

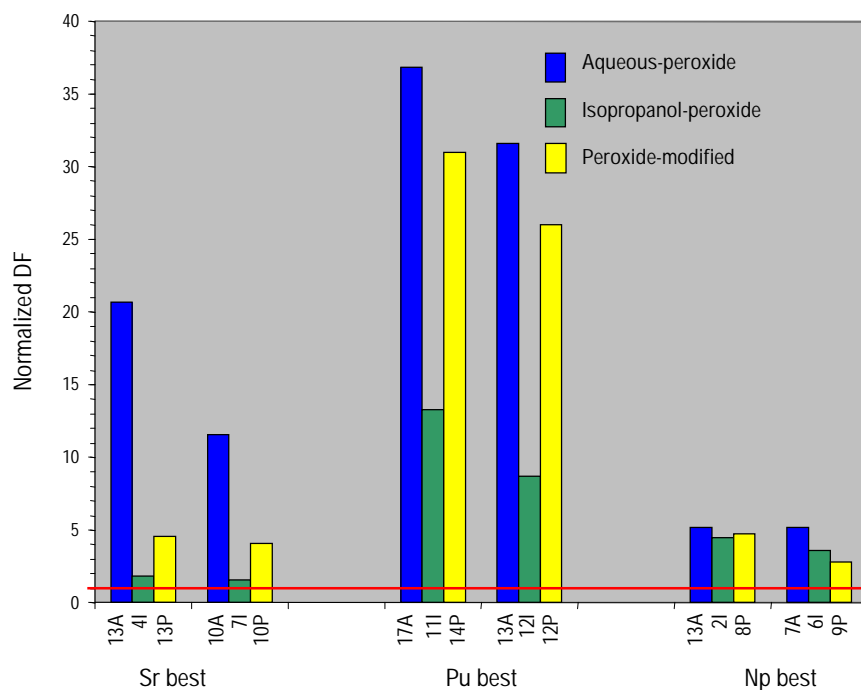
Work at SNL and SRNL for FY06 involved continued preparation and evaluation of peroxy-titanate materials for improved kinetics, selectivity and capacity for Sr and actinide separations. The peroxy-titanates are synthesized by three general routes: 1) from an isopropanol solution, 2) from an aqueous solution, and 3) peroxide treatment of monosodium titanate (MST). Our studies have shown a number of trends of improved sorption behavior with sorbent characteristics. Universally, peroxy-titanates out-perform the related sodium titanates for all metals tested including Sr, Np and Pu predominantly but also Am and Pa.

In general, the aqueous-peroxide synthesis and peroxide-treated MST were the better sorbents for Sr and Pu, and the isopropanol-peroxide synthesis produced sorbents that were more effective for Np. Sr and Pu sorption generally improved with post-synthesis acidic treatment of the sorbent, and storing and utilizing the sorbent as a slurry, without ever converting it to a dry powder. On the other hand, Np sorption was not necessarily improved by either of these parameters.

Improved sorption as a function of acidification and slurried samples could simply be argued as a surface-area effect. However, we believe the Ti-bound peroxy ligands (as indicated by the characteristic yellow color) do indeed play a role in coordinating or stabilizing sorbed radionuclides. Certainly in the case of Np where anomalous sorption behavior is observed that cannot be tied to surface area, we expect the peroxide ligands to contribute significantly to enhanced sorption behavior. Investigations using vibrational spectroscopies and EXAFS are underway.

The top two performing sorbents for each of the three synthesis types and three radionuclides are summarized in Figure 1. The decontamination values (DF) are normalized to the DF for baseline MST, and the red line at unity represents the performance of MST. It is clear from these results that the various peroxo-titanate materials greatly outperform the baseline MST material selected for use at the Savannah River Site.

Figure 1. Decontamination Factors (DF) for Peroxo-titanate Samples Normalized to MST.



3. Computational Models for CST and Polyoxometalates

A new force field potential 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 at TAMU, 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.

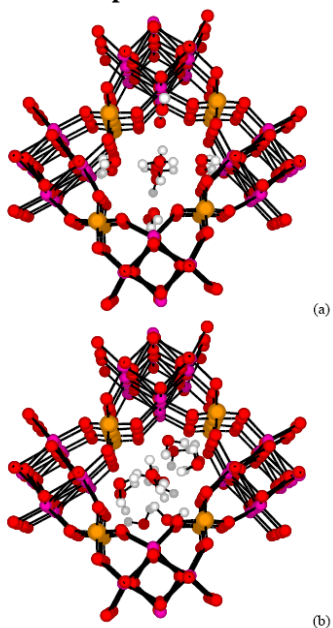
Table 1 shows the greater accuracy of the new force field (FF2) compared to FF1. It shows the location of water in two different sites (O5 and O6). The first row is raw data, and the second accounts for moving the water to special crystallographic positions. "Dev." represents the average deviation from 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.

We have also implemented a new simulation technique known as "replica exchange" Monte Carlo, and applied it to the study of water and ion motion in these materials as well as polyoxoniobate materials synthesized at SNL. The DFT approach for determining framework charges has also been applied to the materials synthesized by M. Nyman (SNL). We are presently writing two papers to describe this work.

| 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 | | | |

We also investigated the way in which the charge on the proton is smeared over the framework. Figure 2a show the hydrogen bonding network computed by smearing the proton charge over all framework oxygen atoms and Figure 2b 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 2. Computed Framework Structures for Polyoxometalate



FY06 Publications:

1. François Bonhomme, James P. Larentzos, Todd M. Alam, Edward J. Maginn and May Nyman, "Synthesis, Structural Characterization, and Molecular Modeling of Dodecaniobate Keggin Chain Materials", *Inorganic Chemistry*, **2005**, 44, 1774-1785.
2. A.J. Celestian, D.G. Medvedev, A. Tripathi, J.B. Parise, A. Clearfield, Optimizing synthesis of $\text{Na}_2\text{Ti}_2\text{SiO}_7 \cdot 2\text{H}_2\text{O}$ (Na-CST) and ion exchange pathways for $\text{Cs}_{0.4}\text{H}_{1.6}\text{Ti}_2\text{SiO}_7 \cdot \text{H}_2\text{O}$ (Cs-CST) determined from in situ synchrotron X-ray powder diffraction, *Nucl. Instrum. Methods. Phys. Res. B* **238**, 61-69 (2005).
3. Clearfield, A. Tripathi, D. Medvedev, A.J. Celestian, J.B. Parise, *In situ* type study of hydrothermally prepared titanates and silicotitanates, *J. Mater. Sci.*, **41**, 1325-1333 (2006).
4. Tripathi, D. G. Medvedev, and A. Clearfield, The Crystal Structures of Strontium Exchanged Sodium Titanosilicates in Relation to Selectivity for Nuclear Waste Treatment, *J. Solid State Chem.* **178**, 253-261 (2005).
5. J. Celestian, J. B. Parise, R. I. Smith, B. H. Toby and A. Clearfield, Role of the hydroxyl-water hydrogen bond and selectivity toward cesium in $\text{Cs}_{0.38}(\text{D}_{1.08}\text{H}_{0.54})\text{SiT}_2\text{O}_7 \cdot (\text{D}_{0.86}\text{H}_{0.14})_0$ crystalline silicotitanate, in press.

FY06 Presentations:

"Strontium and actinide separations from High Level Nuclear waste solutions using monosodium titanate," Hobbs, D. T.; Peters, T. B.; Barnes, M. J.; Walker, D. D.; Fondeur, F. F.; Norato, M. A.; Fink, S. D., Savannah River National Laboratory, Westinghouse Savannah River Company, Aiken, SC, USA., 14th Symposium on Separation Science and Technology for Energy Applications, Gatlinburg, TN, October 23 – 27, 2005.

"Development of an Improved Titanate-Based Sorbent for Strontium and Actinide Removal from High Ionic Strength Waste solutions (D. T. Hobbs*, M. D. Nyman, M. J. Barnes, M. E. Stallings, F. F. Fondeur and S. D. Fink, presented at the Actinide Separations Conference, May 22-25, 2006, Richland, WA.

"Development and Application of Atomistic Simulations to the Study of New Materials: From Ionic Liquids to Crystalline Nanoporous Adsorbents", Edward Maginn, James Larentzos, Cesar Cadena, and David Eike, UOP Research Center, Des Plaines, IL, Sept. 29, 2005.

"Development of New Molecular Dynamics Sampling Methods for Phase Equilibria Calculations", Edward Maginn, James Larentzos, Timothy Morrow, and David Eike, China / USA / Japan Joint Chemical Engineering Conference, Beijing, China, October 13, 2005.

"Atomistic Simulation of Ionic Systems: Application to Ionic Liquids and Nanoporous Ion Exchangers", Chemical Engineering departmental seminar, Purdue University, West Lafayette, IN, March 28, 2006.

"Atomistic Simulation of Ionic Systems: Application to Ionic Liquids and Nanoporous Ion Exchangers", Edward Maginn, James Larentzos, Cesar Cadena, and David Eike, Department of Chemical and Petroleum Engineering seminar, University of Kansas, Lawrence, KS, April 11, 2006.

"Atomistic Modeling of Adsorption and Ion Exchange in Zeolites", Edward Maginn, James Larentzos, Cesar Cadena, and David Eike, Plenary Lecture, 7th International Conference on the Occurrence, Properties and Utilization of Natural Zeolites, Socorro, NM, July 16-21, 2006.