

**FY03 Annual Report for Environmental Management Science Program
- Strategic Design and Optimization of Inorganic Sorbents for Cesium,
Strontium and Actinides**

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

Research Progress

During the second year of the project we continued our focus along two paths: (1) identifying the structure/affinity relationships for crystalline silicotitanate (CST) and (2) synthesis of new sorbents that include derivatives of CST, a titanosilicate analog of the mineral pharmacosiderite, sodium titanates and polyoxoniobates. CST serves as the baseline or alternative technology sorbent for the separation of ^{137}Cs from waste solutions at several of the DOE sites. This material also exhibits a fairly high affinity for strontium, but rather low affinity for plutonium and other actinides. A sodium titanate material,

monosodium titanate (MST), serves as the baseline material at the Savannah River Site for strontium and actinide separations from HLW solutions. Recent work demonstrated that pharmacosiderite materials have strontium and actinide removal characteristics similar to that of MST. A new class of heteropolymetalates, polyoxoniobate, which is comprised principally of niobium, has been synthesized by M. Nyman and colleagues at SNL. These materials have exhibited high selectivity for plutonium under strongly alkaline conditions.

This year project members at Texas A&M completed a detailed structural study of CST and niobium-substituted CST (Nb-CST) sorbents before and after exchange with cesium and strontium. Interestingly, this research found that the CST material exhibits a higher selectivity for strontium, whereas the Nb-CST exhibits higher selectivity for cesium. The differences in the uptake of cesium and strontium result from the different coordination environments of cesium and strontium in the eight-ring channel, that result from various hydration sites in the tunnel (see Figures 1 and 2). The origin of selectivity appears to arise from the higher coordination number of cesium or strontium. Other effects due to niobium substitution are reflected in the increase of both, the *a*- and *c*-dimensions and thus the unit cell volume, and the population of water vs. Na^+ in the channel to charge-balance the $\text{Nb}^{5+} \rightarrow \text{Ti}^{4+}$ substitution. Hence, a handle to fine tune this material based on structure property relationship was established and their exchange capacity for cesium was optimized via niobium substitution.

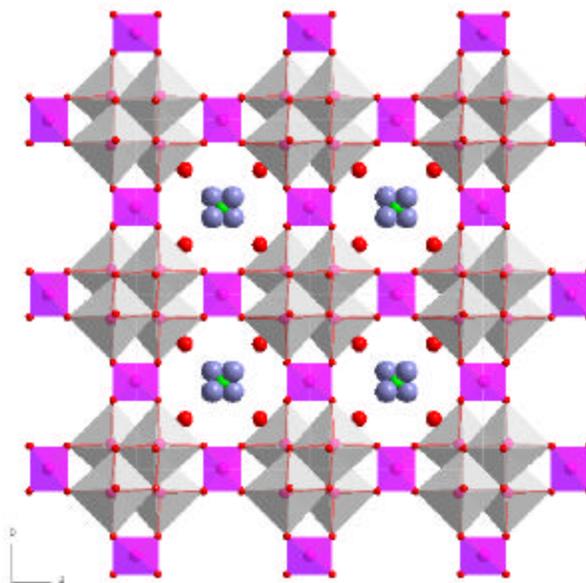


Figure 1. A polyhedral representation (with gray TiO_6 octahedra and purple SiO_4 tetrahedra) of CST along [001], sodium (Blue spheres), cesium (green spheres) and water (red spheres) were located in the 8-atom ring tunnels. In the Nb-CST less sodium and more water molecules are located in the tunnel.

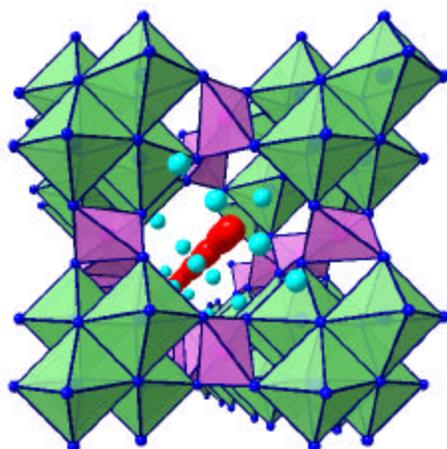


Figure 2. A polyhedral perspective representation of Nb-CST along the [001] plane. Water (blue spheres) and cesium (red spheres) are located in the 8-atom ring tunnels. TiO_6 octahedra are shown in green and SiO_4 tetrahedra in purple.

Team members at Notre Dame have taken the structural data from the CST studies and completed development of a computational model of the CST and Nb-CST sorbents. 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. 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.

During FY2003 the Notre Dame researchers conducted molecular dynamic calculations of the CST materials. Compared to energy minimization, molecular dynamics enables one to obtain a time-averaged position of the cations and water molecules. In addition, molecular dynamics allows one to compute dynamic properties of the materials. Figure 3 provides plots of the cesium ion (Cs^+) positions from the molecular dynamic simulations as viewed from two different faces of the CST molecule. In the ab-face, the cesium positions cluster around the center of the tunnel. However, as viewed from the bc-face, the location of the Cs^+ is off-center. Overall the results indicate good agreement with positions determined experimentally by X-ray diffraction.

Cs^+ positions in Cs-exchanged CST

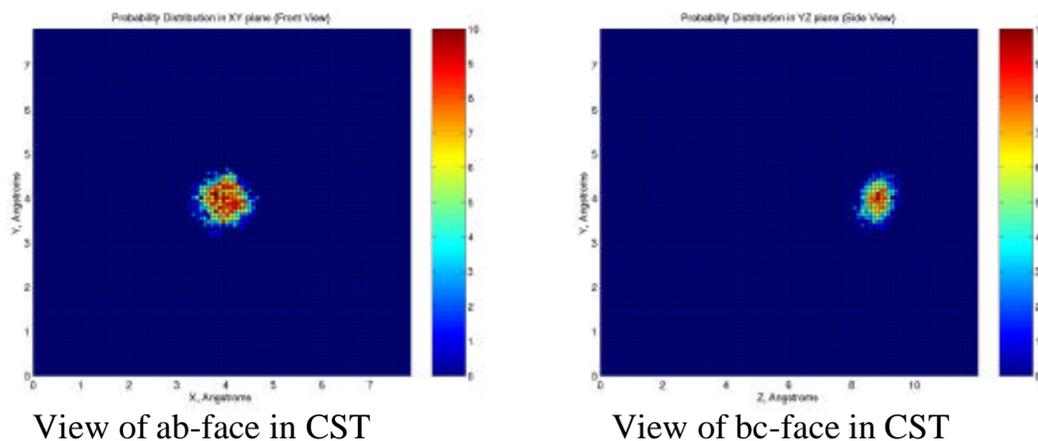


Figure 3. Molecular dynamic simulation of cesium exchanged CST from two different faces of the CST molecule. In the ab-face, the Cs^+ clusters about the tunnel center. In the bc-face, the Cs^+ positions are off-center.

Synthesis efforts at Sandia during FY03 focused primarily on niobium-substituted sodium nonatitanates and polyoxoniobate-based materials. We are interested in niobium-based materials because NbO_6 octahedra in the solid-state are distorted in a way that is conducive to binding metals such as radionuclides. Scanning electron micrographs of the niobium-substituted sodium nonatitanates reveal an interesting coral-like structure (see Figure 4), which is significantly different than that of sodium nonatitanate.

The polyoxoniobate-based materials belong to a larger class of materials called polyoxometalates. Polyoxometalates are known for their metal-binding properties and it has been suggested that they would be useful for selective radionuclide binding. Previously reported polyoxometalates have shown ion-exchange properties under acidic conditions, but proved unstable in alkaline conditions. The polyoxoniobate materials prepared in this project are the first polyoxometalates that are stable in basic solution and, therefore, can actually be utilized in very basic tank wastes. Figures 5a and b provide a representation of the structure of the polyoxoniobate. Unlike CST, the polyoxoniobate material features a chain-like structure. The chains are composed of $[\text{XNb}_{12}\text{O}_{40}]^{16-}$ ($\text{X}=\text{Si}, \text{Ge}$) Keggin ions and are linked by $[\text{M}_2\text{O}_2]$ bridges where $\text{M} = \text{Ti}$ or Nb . The chains are charge-balanced by 12 Na^+ or K^+ in the case of $\text{M}=\text{Ti}$; and 10 Na^+ or K^+ in the case of $\text{M}=\text{Nb}$.

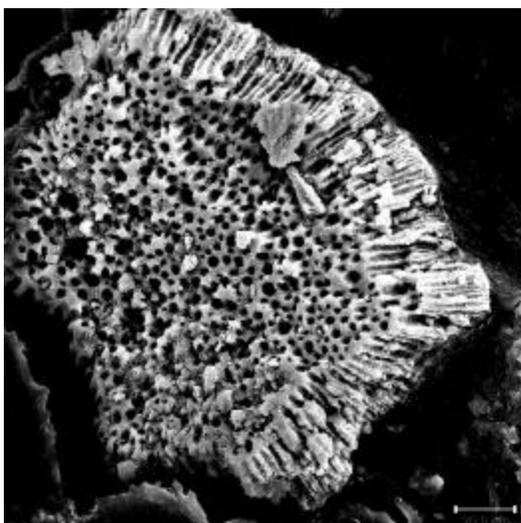


Figure 4. Scanning electron micrograph of niobium-substituted sodium nonatitanate

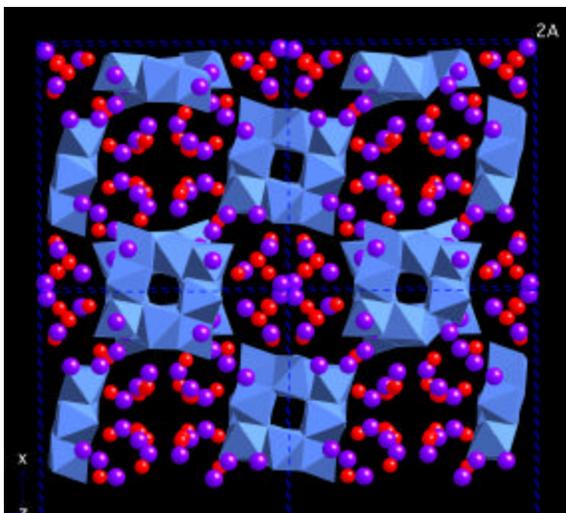


Figure 5a. Structure representation of polyoxoniobate looking down the z-axis. Blue octahedra represent niobate Keggin ions, red spheres are water molecules and purple spheres are potassium or sodium atoms.

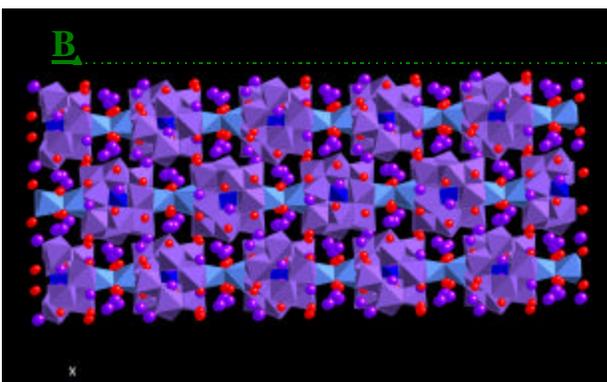


Figure 5b. A view of the Keggin ion materials looking parallel to the chains. The light blue octahedral linking the Keggin ions (purple) contains either Ti or Nb.

New material syntheses at Texas A&M during FY03 have focused on a titanasilicate (TSP) material with a pharmacosiderite type structure. The pharmacosiderite structure has a similar tunnel structure to that CST. Unlike CST, which has a 2-dimensional tunnel structure, the cubic structure of this material requires that the tunnels in which ion exchange occurs are 3-dimensional. A 3-dimensional tunnel structure opens the material more, which should increase the effective number of exchange sites and facilitate mass transfer to the ion-exchange sites. We have prepared several TSP phases containing varying amounts of germanium. Germanium substitution occurs in both octahedral and tetrahedral sites. The substitution of germanium into these sites changes in the unit cell dimensions. We are currently investigating the structure and ion exchange properties of these new materials.

During FY03, SRTC team members evaluated 9 new materials prepared by the Sandia and Texas A&M team members for cesium, strontium and actinide removal performance with simulated and actual tank waste solutions. Materials tested included sodium nonatitanate, niobium-substituted sodium nonatitanate, TSP pharmacosiderites and polyoxoniobates. The results indicated that several of these materials exhibited a higher affinity for plutonium relative to strontium than the baseline material used at the Savannah River Site. Although, the overall performance proved lower than that of the baseline material, monosodium titanate, the increased affinity for plutonium suggests structural modification of titanates, titanasilicates and new polyoxoniobate materials offers binding sites more conducive to interactions with plutonium.

The progress made in new materials development under this EMSP project resulted in the award of a Phase I grant by the DOE in April, 2003 to accelerate development efforts on producing optimized sodium titanate and titanosilicate materials for strontium and actinide separation from SRS waste solutions. D. Hobbs of SRTC serves as the principal investigator for this project with M. Nyman of SNL and A. Clearfield of Texas A&M University serving as the leads for synthesis of optimized materials.

Planned Activities

Modeling activities will extend to Sr^{2+} exchanged CST as well as to the development of models for the titanosilicate pharmacosiderite and polyoxoniobate materials. Enhancements to the molecular dynamic simulations will investigate the use of a Hybrid Monte Carlo approach for cation exchange. Upon validation of the model, we will compute thermodynamic properties of the various ion exchange materials. Upon completion of this phase of the project, we will conduct "exploratory" simulations to see how different structural factors might change ion selectivity. This information will guide the synthesis of new materials exhibiting greater affinities for cesium, strontium and actinides.

During the remainder of FY03 we will determine the cesium, strontium and actinide separation characteristics of the recently prepared sodium titanate, heteropolyniobates and pharmacosiderite materials. We will also characterize the nature of the interaction between the cesium/strontium/actinide elements and these materials by a variety of techniques including transmission electron microscopy, X-ray diffraction and extended X-ray absorption spectroscopy. Synthesis of new materials will continue into FY04 building on strontium/actinide removal performance characteristics as measured with existing materials and results obtained from modeling simulations.

Publications and Presentations

Peer reviewed publications of work completed in this project include the following:

1. "A General Synthetic Procedure for Heteropolyniobates" May Nyman, François Bonhomme, Todd M. Alam, Mark A. Rodriguez, Brian R. Cherry, James L. Krumhansl, Tina M. Nenoff, Amy M. Sattler. *Science*, August 9, **2002**.
2. "Investigation of Cation Environment Changes in Silicotitanate Exchange Materials using Solid State ^{23}Na , ^{29}Si , and ^{133}Cs MAS NMR" B.R. Cherry, T.M. Alam, M. Nyman: *submitted for publication*.
3. " ^{93}Nb MAS NMR of niobium containing silicotitanate exchange materials", B. R. Cherry, T.M. Alam, M. Nyman, Conference Proceeding of the 104th Annual Meeting of the American Ceramic Society, In Press, 2003.
4. "Selectivity for Cs and Sr in Nb-Substituted Titanosilicate with Sitinakite Topology," Akhilesh Tripathi, Dmitri Medvedev, May Nyman, Abraham Clearfield, **Journal of Solid State Chemistry** (In Press).

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

1. "Optimized and Alternative Sorbents for Sr^{2+} and Actinide Removal from SRS Alkaline Waste Solutions" May Nyman and David T. Hobbs, Fall 2002 Materials Research Society National Meeting, Symposium on Scientific Basis for Nuclear Waste Management.
2. "Investigation of Cation Environment Changes in Silicotitanate Exchange Materials using ^{23}Na , ^{29}Si , ^{93}Nb , and ^{133}Cs MAS NMR", B.R. Cherry, M. Nyman, and T.M. Alam 104th Annual Meeting of the American Ceramic Society, St. Louis, MO, May 2002.
3. "Novel polyoxometalates: Templated synthesis of germanium and transition metal oxide mixed clusters," Akhilesh Tripathi & Abraham Clearfield, Abstracts of Papers, 224th ACS National Meeting, Boston, MA, United States, August 18-22, 2002, INOR-423.
4. "Niobium-substituted silicotitanates: Ion exchangers for nuclear waste remediation," Abraham Clearfield, Akhilesh Tripathi, May Nyman, Dmitri Medvedev, Abstracts of Papers, 224th ACS National Meeting, Boston, MA, United States, August 18-22, 2002, INOR-346.
5. "Optimized and Alternative Sorbents for Sr^{2+} and Actinide Removal from SRS Alkaline Waste Solutions." May Nyman and David T. Hobbs, MRS National Fall Meeting, Boston, MA, November 2002.

6. "Synthesis and Characterization of Heteropolyniobates." May Nyman, Francois Bonhomme, Brian R. Cherry, Todd M. Alam, Mark A. Rodriguez, Louise J. Criscenti, Randall T. Cygan, MRS National Fall Meeting, Boston, MA, November 2002.
7. "Structural Investigation of the Origin of Selectivity for Cs and Sr in the Nb-Substituted Titanosilicate with the Mineral Sitinakite Topology," A. Tripathi, D. Medvedev, A. Clearfield (Texas A & M), A. Celestian, J.B. Parise (SUNY, Stony Brook), and J. Hanson (X7B, BNL/Chem), Beamline(s): Highlight X7B, Abstract No. Trip0299, 1/13/03.
8. "In-situ synchrotron X-ray structural studies of crystal growth and ion exchange in tunnel type silicotitanates," A. Tripathi, D. G. Medvedev, A. Clearfield, A. J. Celestian, J.B. Parise, M. Nyman and J. Hanson, Abstracts of Papers, Division of Inorganic Chemistry, 225th ACS National Meeting, New Orleans, LA, March 23-27, 2003.
9. "Ion-exchange and structural investigation of strontium loaded germanium substituted titanium silicates pharmacosiderites," D. G. Medvedev, A. Tripathi and A. Clearfield, Abstracts of Papers, Division of Inorganic Chemistry, 225th ACS National Meeting, New Orleans, LA, March 23-27, 2003.
10. "Strontium and actinide separations from high-level nuclear waste solutions," Hobbs, D. T., Nyman, M., Medvedev, D., Tripathi, A., Clearfield, A., Savannah River Technology Center, Westinghouse Savannah River Company, Aiken, SC, USA. Abstracts of Papers, 225th ACS National Meeting, New Orleans, LA, United States, March 23-27, 2003 (2003).
11. "Strontium and actinide separations from high-level nuclear waste solutions," Hobbs, D. T., Nyman, M., Medvedev, D., Tripathi, A., Clearfield, A., Savannah River Technology Center, Westinghouse Savannah River Company, Aiken, SC, USA. 27th Actinide Separations Conference, Argonne, IL, United States, June 9-12, 2003.