

**FY04 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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National Synchrotron Light Source (NSLS) at the Brookhaven National Laboratory
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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 third year of the project our studies focused along the following paths: (1) identifying the structure/affinity relationships for crystalline silicotitanate (CST) and polyoxoniobate (Keggin chain) materials, (2) synthesis of new sorbents that include a titanasilicate analog of the mineral pharmacosiderite, sodium titanates and polyoxoniobates, (3) in-situ crystal growth and ion exchange studies with CST materials and (4) computational models of the CST and polyoxoniobate materials. 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 no affinity for plutonium, neptunium and uranium. 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. Performance testing at SRNL demonstrated that titanasilicates, sodium nonatitanates and polyoxometalates effectively adsorb strontium and actinides from high ionic strength salt solutions.

Project members at Texas A&M completed two detailed structural characterizations of CST materials and studied the in-situ crystallization process during the synthesis of CST. Structural studies included CST and niobium-substituted CST (Nb-CST)

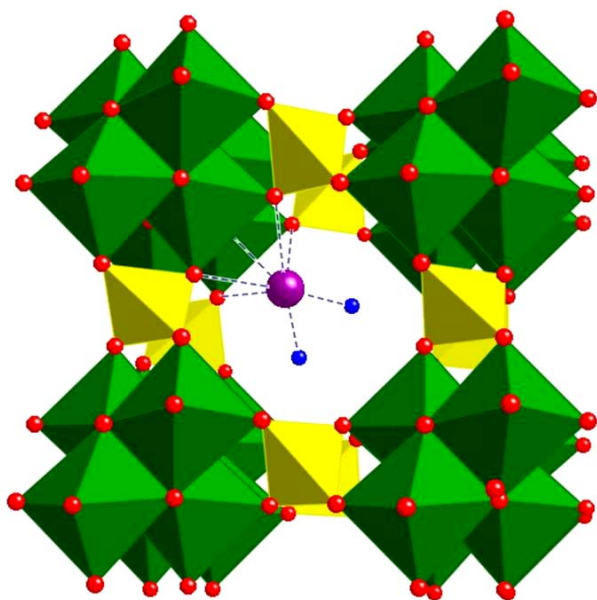


Figure 1. A polyhedral representation (with green TiO_6 octahedra and yellow SiO_4 tetrahedra) of Nb-CST along [001], strontium (purple spheres) and water (blue spheres) were located in the 8-atom ring tunnels. In Nb-CST strontium is seven coordinate, but in CST strontium is ten coordinate.

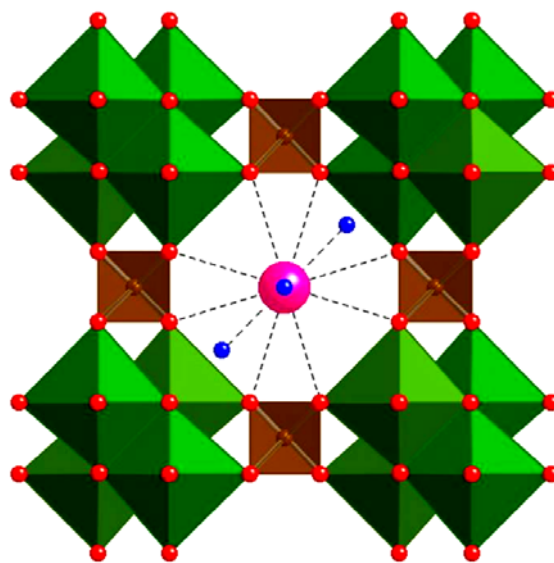


Figure 2. A polyhedral perspective representation of TSP along the [001] plane. Water (blue spheres) and cesium (pink spheres) are located in the 8-atom ring tunnels. TiO_6 octahedra are shown in green and SiO_4 tetrahedra in brown. The coordination of Cs was found to be directly correlated to the observed exchange capacity.

sorbents before and after exchange with strontium and another closely related titanasilicate material with the mineral pharmacosiderite topology (TSP). A complete or partial substitution of elements Ge or Nb was carried out in the framework and the consequent change in the ion exchange properties towards Cs were studied for Ti/Ge/Si, Ti/Si, Nb/Ti/Si and pure Ge phases. This research found that substitution of Ge and Nb into the framework modifies the structure of CST and TSP materials,

which results in changes in the affinity of the material for cesium and strontium. The differences in the uptake of cesium and strontium result from the different coordination environments of these ions in the tunnels (see Figures 1 and 2). Higher selectivity arises from a higher coordination number for cesium or strontium in the occupied tunnel site.

In parallel with the synthesis and ion exchange studies, Notre Dame team members completed development of a computational model for the CST family of ion-exchange materials. To confirm the accuracy of the model, comparison was made to the experimental results of the Texas A&M group on the position of the cations and water in the base CST material. Excellent agreement between the experimental and simulated positions was observed. In addition, the simulations provided additional insight into the mechanisms of cation binding in these systems. 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 3). 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.

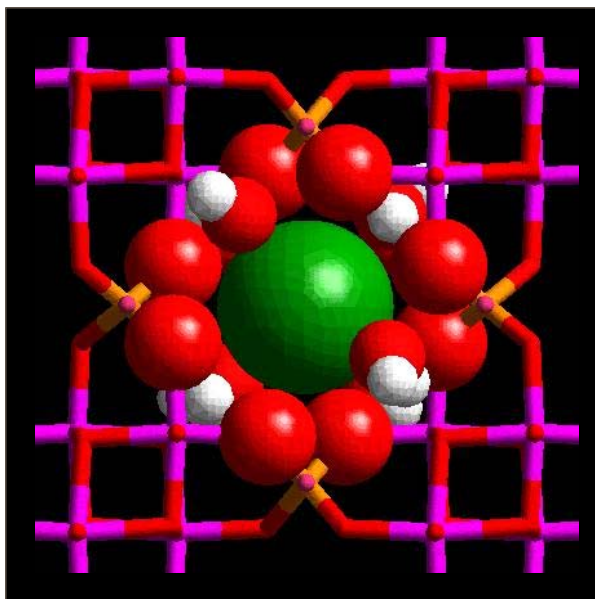


Figure 3: Calculated position of Cs^+ (green) in Nb-CST material. Note the high degree of coordination with the framework oxygen atoms (red) and water (red-white). The addition of Nb to the framework enables water to hydrate the Cs^+ in the tunnel, thereby providing additional stability and hence selectivity.

Texas A& M team members also carried out a series of ex-situ and in-situ crystallization experiments to study crystal growth during the hydrothermal synthesis of CST. Ex-situ experiments identified those parameters that are most influential in determining product composition. In-situ studies were then carried out using the synchrotron radiation facility at BNL to collect dynamic X-ray powder diffraction spectra. In situ studies represent a unique way to optimize the synthesis toward producing more crystalline materials via understanding of the pathway, kinetics and mechanism of the crystallization process.

Figure 4 shows a 3D plot of the X-ray diffraction spectra as a function of time during the titanositic gel heating. As can be seen from the figure the process of CST crystallization starts with the formation of a phase having a broad peak at about 9.5-10 Å, which is identified as sodium nonatitanate (SNT). SNT is an effective material for the removal Sr and actinides from alkaline waste solutions. After heating at 220 °C for 3 hours, the SNT phase begins to transform into the CST phase. The transformation process lasted about 45 minutes.

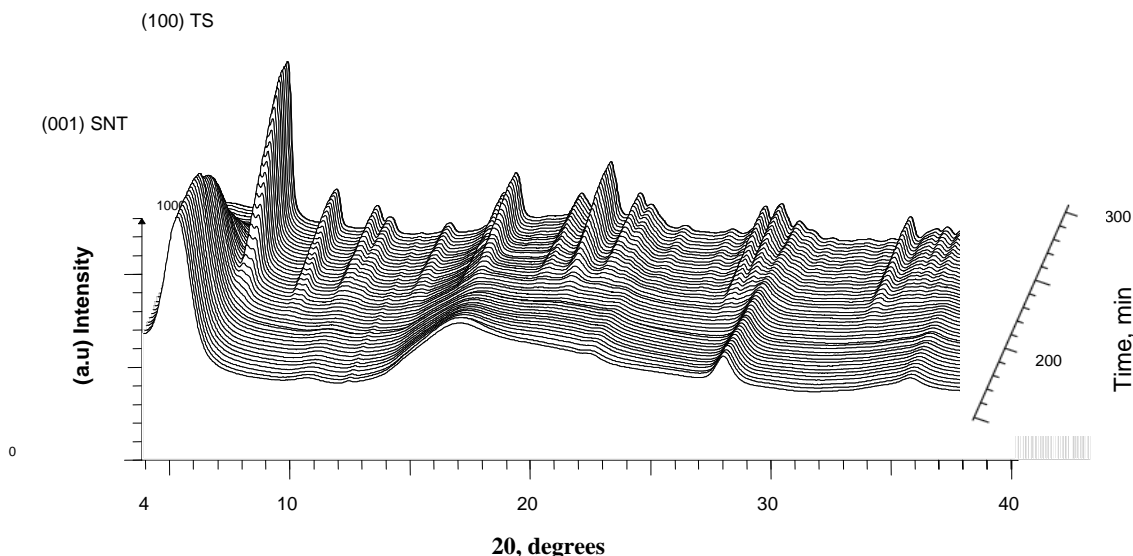


Figure 4. Time-resolved X-ray powder diffraction spectra of SNT- CST transformation for the gel with composition: 1.0TiO₂:1.98SiO₂:6.77Na₂O:218 H₂O. Powder patterns are collected in 2.5 min interval.

The discovery of the CST reaction pathway provides a method to produce a mixed phase material, SNT-CST, which is selective both for Cs, Sr and actinides. During FY04, SRNL team members tested several SNT and SNT-CST samples prepared at Texas A&M for strontium and actinide removal performance with simulated SRS waste solutions. Overall, the performance of the H-SNT and the SNT-CST samples showed evidence of enhanced affinities for strontium and actinides and increased strontium removal kinetics for the H-SNT sample. Figure 5 provides a plot of plutonium concentration versus time upon contact of the sorbent with the simulated waste solution. The SNT-CST material exhibited slower strontium removal kinetics compared to the other pure SNT and MST samples. Plutonium and neptunium removal characteristics were similar to those of the other SNT materials, which is remarkable. Previous testing with commercially prepared CST materials showed that this sorbent exhibits very little affinity for actinides. Given the reduced SNT content in the SNT-CST material, the relatively good plutonium and neptunium removal performance reflects either increased actinide removal characteristics of the SNT or the CST phase. We believe that the SNT-CST mixed phase material exhibits promise for one-step treatment process to remove cesium, strontium and actinides from HLW solutions. We plan to pursue further development of this material.

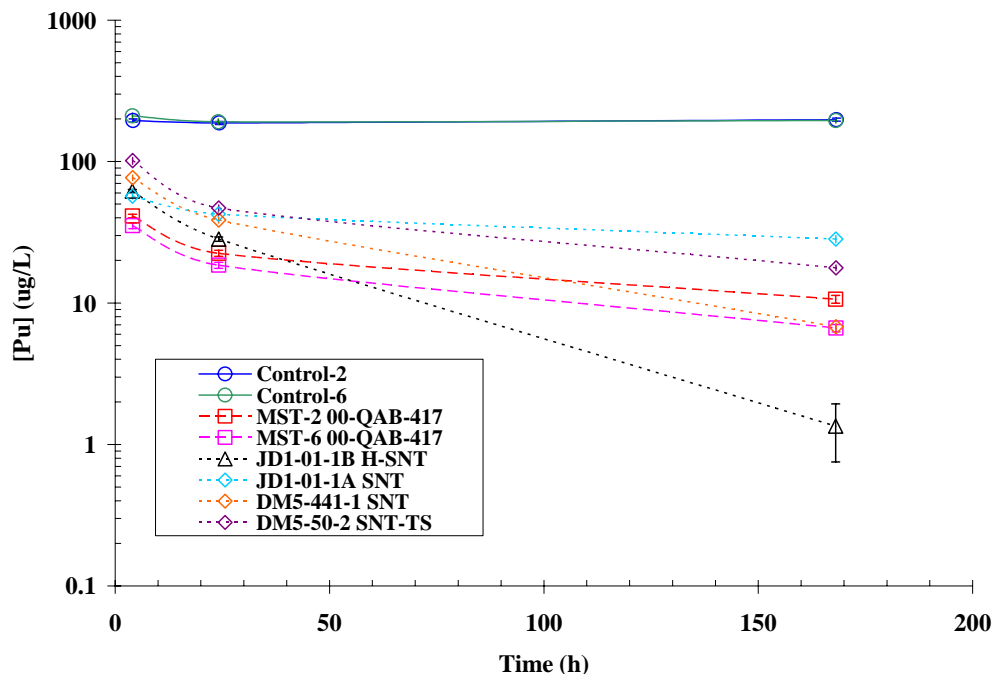


Figure 5. Plot of plutonium concentration versus time upon contact of TAMU prepared SNT and SNT-CST materials with simulated SRS waste solution.

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 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 a computational modeling approach with Notre Dame team members 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.

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 6). 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 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 6a and 6b, 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 Nb_2O_2 unit repelling the positively charged sodium ions.

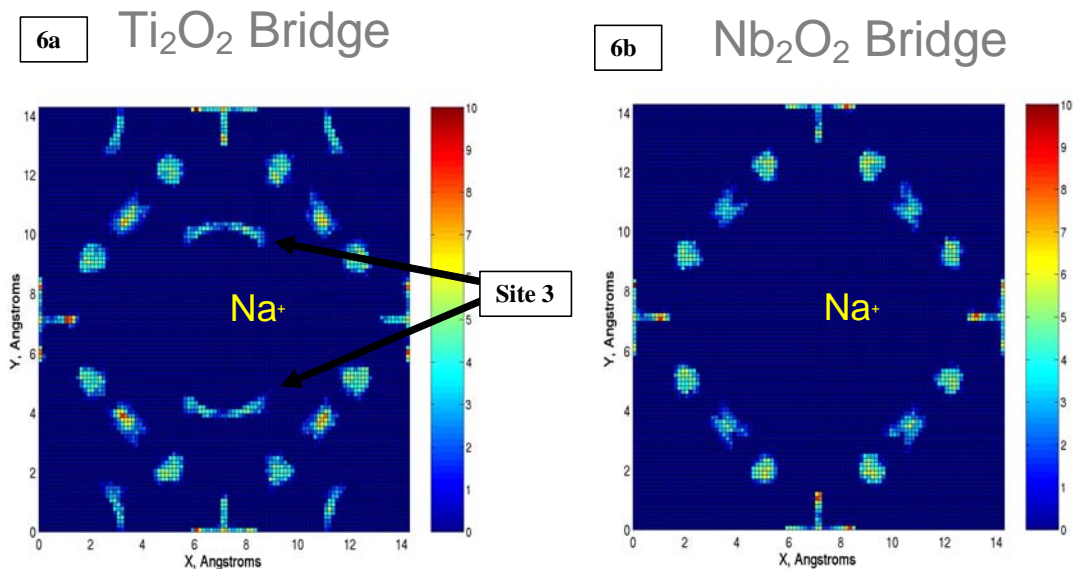


Figure 6: Probability distributions of Na^+ in the polyoxoniobate material. In Figure 6a (left) the distribution of Na^+ in the base material is shown. Intensity levels indicate the relative probability of observing a cation in a given site. These sites agree very well with the experimentally observed sites by X-ray diffraction analysis. In Figure 6b (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.

The Na Keggin-chain phases easily undergo Sr exchange. All the Sr is exchangeable in a single exchange step at room temperature, with an expansion in the unit cell of around 7-8% for each phase. Figure 7 shows the X-ray powder diffraction patterns of $\text{Na}_{12}[\text{Ti}_2\text{O}_2][\text{SiNb}_{12}\text{O}_{40}] \cdot 4\text{H}_2\text{O}$ and the Sr-exchanged analogue. There is a distinct shift to smaller 2-theta (larger unit cell) with Sr exchange, and the structure is well-preserved.

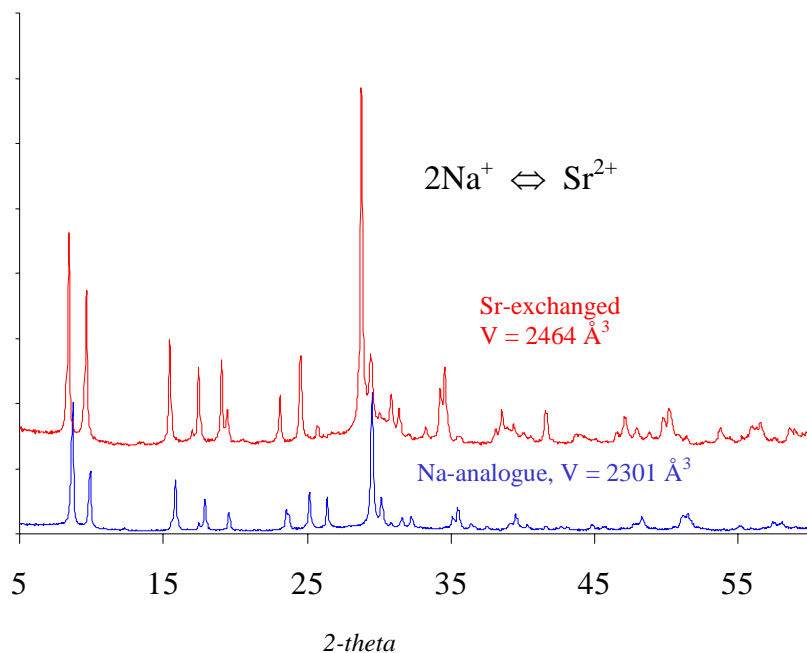


Figure 7. X-ray powder diffraction spectra of $\text{Na}_{12}[\text{Ti}_2\text{O}_2][\text{SiNb}_{12}\text{O}_{40}]\cdot 4\text{H}_2\text{O}$, and its Sr-exchanged version.

SRNL tested several of the Keggin-chain materials for strontium and actinide removal performance in simulated SRS waste solutions. Figure 8 provides a plot of total alpha activity versus time for a series for the Ti/Si Keggin-chain materials of the type $\text{Na}_2[\text{A}_2\text{O}_2][\text{TNb}_{12}\text{O}_{40}]\cdot x\text{H}_2\text{O}$ where A = Ti or Nb and T = Si or Ge. Alpha removal proved lower than the baseline MST material. Testing also indicated that only the titanium bridged materials exhibited significant affinity for actinides.

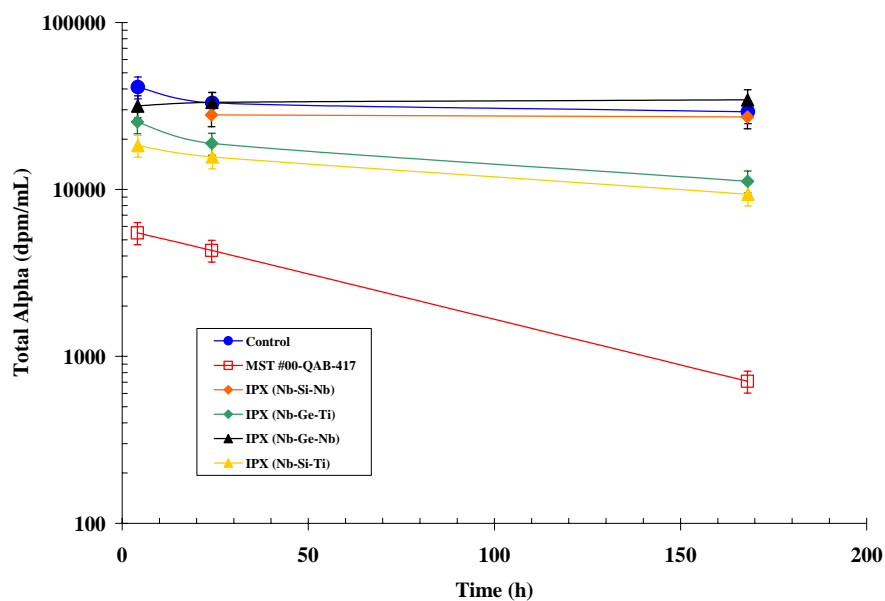


Figure 8. Plot of alpha activity versus time upon contact of SNL prepared Keggin-chain materials and baseline MST material with simulated SRS waste solution. Alpha activity derives almost entirely from plutonium isotopes.

Recently we have synthesized Na Keggin-chain materials with phosphorous in the central tetrahedral position and Ti in the bridging position, which would give an overall charge of 11^+ for the chains, and would therefore require 11 charge balancing Na-cations. This gives a formula of $\text{Na}_{11}[\text{Ti}_2\text{O}_2][\text{PNb}_{12}\text{O}_{40}] \cdot 4\text{H}_2\text{O}$. This particular phase forms larger crystals than the Si-centered and Ge-centered phases and may therefore provide unprecedented opportunity for obtaining a structure from single-crystal X-ray data. This will provide valuable data for helping understand the optimized Na/H₂O positions for the four compositions discussed above.

We have also prepared a novel '2-dimensional' Keggin-chain material with the formula $\text{K}_9[\text{Nb}_2\text{O}_2][\text{K}][\text{TNb}_{12}\text{O}_{40}] \cdot 8\text{H}_2\text{O}$ (T=Si, Ge). This phase crystallizes in the orthorhombic Imm2 space group with unit cell parameters $a=10.9509 \text{ \AA}$, $b=11.6028 \text{ \AA}$, $c=19.9159 \text{ \AA}$, $V=2531 \text{ \AA}^3$. Two views of the layers are shown in Figure 9. These materials are similar to the Keggin chain materials in that they are linked in one dimension by edge sharing NbO_6 octahedra along the b -direction. Along the a -direction, we see a new mode of Keggin ion linkage. In this direction, a K-cation resides between two Keggin ions and has four bonds to each. This structure differs from the other K- and Na- Keggin chain materials in that the Keggin chains are aligned in two directions so that they can be linked in two directions. The 1-dimensional Keggin chain materials are aligned in one crystallographic direction and staggered in the other two directions. The remaining charge-balancing potassium cations are disordered over 14 partially occupied sites (ranging from ~10-40% occupied). The layered Keggin ion material can undergo Sr exchange but not without gross structural change and some structural degradation. This layered material has not yet been tested for its affinity for cesium, strontium or actinides.

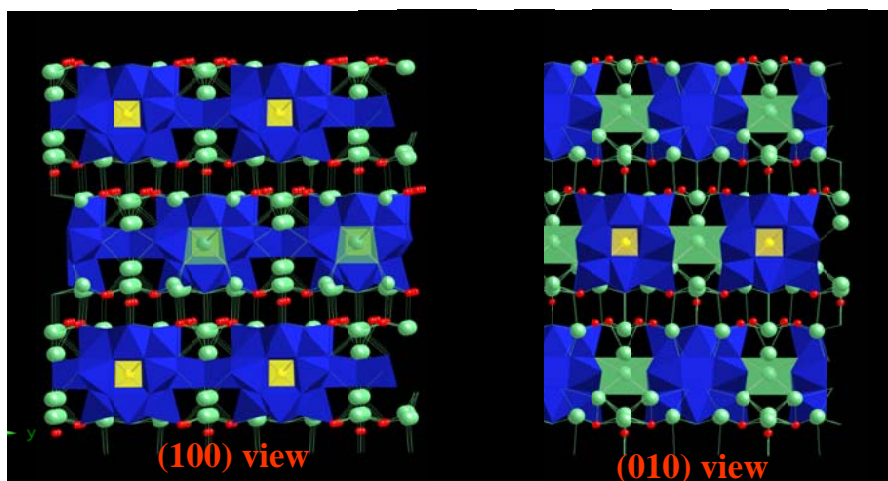


Figure 9. Two views of $\text{K}_9[\text{Nb}_2\text{O}_2][\text{K}][\text{TNb}_{12}\text{O}_{40}] \cdot 8\text{H}_2\text{O}$, the layered Keggin ion material.

Planned Activities

Plans are to continue to investigate compositional variations of the tunnel titanates, Keggin-chain and mixed phase SNT-CST materials including testing the affinity of these materials for cesium, strontium and actinides. Modeling activities will extend to Sr^{2+} exchanged germanium substituted pharmacosiderites as well as to the development of minimum energy models for other pharmacosiderites. Since Sr exchange pharmacosiderites results in mixture of phases we plan to prepare single crystals of Ge form of pharmacosiderites. In situ work at NSLS will include Sr exchange studies in CST and TSPs and crystal growth conditions for mixed niobium substituted SNT-CST phases. We plan to characterize strontium exchanged sorbents

by strontium nuclear magnetic resonance spectroscopy in collaboration with Dr. Karl Mueller at Pennsylvania State University

Publications and Presentations

Peer reviewed publications from 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. "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*, **2003**, 175, 72-83..
3. "Investigation of Cation Environment and Framework Changes in Silicotitanate Exchange Materials using Solid State ^{23}Na , ^{29}Si , and ^{133}Cs MAS NMR" Brian R. Cherry, May Nyman, and Todd M. Alam, *Journal of Solid State Chemistry*, vol 177(6) pp 2079-2093, **2004**.
4. "Optimizing Cs-exchange in Titanosilicate with the Mineral Pharmacosiderite Topology: Framework Substitution of Nb and Ge" Akhilesh Tripathi, Dmitri G. Medvedev, Jose Delgado, Abraham Clearfield, *Journal of Solid State Chemistry*, **2004**, 177 (8), 2904-2916.
5. "Crystallization of Sodium Titanium Silicate with Sitinakite Topology: Evolution from Sodium Nonatitanate Phase" Dmitri G. Medvedev, Akhilesh Tripathi, Aaron J. Celestian, John B. Parise, John Hanson, Abraham Clearfield, In Press: *Chemistry of Materials*, 2004.
6. "The Crystal Structures of Strontium Exchanged Sodium Titanosilicates in Relation to Selectivity for Nuclear Waste Treatment" Akhilesh Tripathi, Dmitri G. Medvedev, Abraham Clearfield, In Press: *Journal of Solid State Chemistry*, 2004.
7. "A Molecular Modeling Investigation of Cation and Water Siting in Crystalline Silicotitanates" James P. Larentzos, Abraham Clearfield, Akhilesh Tripathi, Edward J. Maginn, *Journal of Physical Chemistry*, submitted.
8. "Dodecaniobate Keggin chain materials: Synthesis, Structural Characterization and Molecular Modeling of $\text{Na}_x[\text{A}_2\text{O}_2][\text{TNb}_{12}\text{O}_{40}]\cdot 4\text{H}_2\text{O}$ (T=Si,Ge; A=Ti,Nb; x=10,12)", M. Nyman, F. Bonhomme, E. Maginn and J. Larentzos., *Inorganic Chemistry*, submitted.

Presentations of work completed in this project at technical conferences during FY04 include the following:

1. A. Clearfield, Presented paper at Pittsburgh Diffraction Conference, Rutgers University on History of Structure Solutions from Powder Data at Texas A&M University, Oct. 30-31, 2003.
2. May Nyman and Francois Bonhomme, "Development of dodecaniobate Keggin chain materials as alternative sorbents for Sr and actinide removal from high-level waste solutions" Abstracts of Papers, 227th ACS National Meeting, Anaheim, CA, March 27-April 1, 2004 (2004).
3. E. J. Maginn and J. Larentzos "Molecular Modeling Investigation of Cation Siting in Crystalline Silicotitanate and Polyoxoniobate Materials", Abstracts of Papers, 227th ACS National Meeting, Anaheim, CA, March 27-April 1, 2004 (2004).
4. "Evaluation on new inorganic sorbent for strontium and actinide removal from high-level nuclear waste solutions," D. T., Nyman, M., Medvedev, D., Tripathi, A., Clearfield, A., Savannah River Technology Center, Westinghouse Savannah River Company, Aiken, SC, USA. Abstracts of Papers, 227th ACS National Meeting, Anaheim, CA, March 27-April 1, 2004 (2004).

5. Aaron J. Celestian, Dmitri Medvedev, Akhilesh Tripathi, John B. Parise, Abraham Clearfield, Jonathan C. Hanson, "Synchrotron time resolved x-ray diffraction of Cs exchange into molecular sieve H-CST" Abstracts of Papers, 227th ACS National Meeting, Anaheim, CA, United States, March 28-April 1, 2004.
6. Dmitri Medvedev, Akhilesh Tripathi, Abraham Clearfield, Aaron J. Celestian, John B. Parise, Jonathan C. Hanson, "Time resolved diffraction studies on titanasilicate with mineral sitinakite topology: From crystallization to ion-exchange" Abstracts of Papers, 227th ACS National Meeting, Anaheim, CA, United States, March 28-April 1, 2004.
7. Akhilesh Tripathi, Dmitri Medvedev, Jose Delgado, Abraham Clearfield, "Optimizing Cs and Sr selectivity in titanasilicate with pharmacosiderite topology: framework substitution of Nb and Ge" Abstracts of Papers, 227th ACS National Meeting, Anaheim, CA, United States, March 28-April 1, 2004.
8. Abraham Clearfield, Akhilesh Tripathi, Dmitri Medvedev, Jose Delgado, May Nyman, "Origin of selectivity in tunnel type inorganic ion exchangers" Abstracts of Papers, 227th ACS National Meeting, Anaheim, CA, United States, March 28-April 1, 2004
9. 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.
10. 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.
11. A. Clearfield, Presented lecture on Porous materials, Chemistry Department, University of San Juan, Puerto Rico, May 21, 2004.
12. "Evaluation on new inorganic sorbent for strontium and actinide removal from high-level nuclear waste solutions," Hobbs, D. T., Nyman, Clearfield, A., Savannah River National Laboratory, Westinghouse Savannah River Company, Aiken, SC, USA., 28th Actinide Separations Conference, Asheville, NC, June 7 – 10, 2004.