

# 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

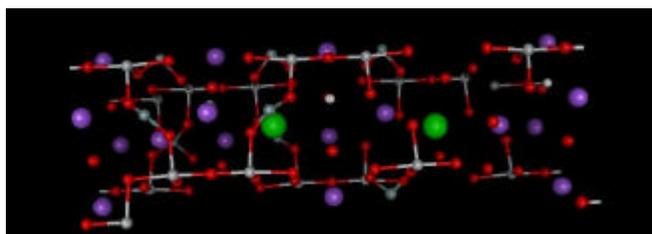
During the first year of the project we focused our efforts along two paths: (1) identifying the structure/affinity relationships for crystalline silicotitanate (CST) and (2) synthesis of new sorbents that include derivatives of CST, sodium titanates and pharmacosiderites. CST serves as the baseline or

alternative technology sorbent for the separation of  $^{137}\text{Cs}$  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 by the authors demonstrated that pharmacosiderite materials have strontium and actinide removal characteristics similar to that of MST.

The CST is a zeolite-like inorganic sorbent with extremely high selectivity for cesium in both acidic and basic environments in the presence of high sodium ion concentrations. Niobium (Nb) substitution for titanium in the CST framework significantly improves cesium selectivity. On the other hand, germanium (Ge) substitution for silicon decreased cesium selectivity. We are currently investigating how the Nb and Ge substitution changes the sorption behavior of the CST framework using data from ion exchange studies, solid state MAS NMR (magic angle spinning nuclear magnetic resonance) spectroscopy, structure determination from X-ray powder data and infrared spectroscopy and molecular modeling utilizing the various spectroscopic data. Preliminary results suggest that Nb substitution depopulates tunnel sites in sodium allowing for increased cesium sorption. Germanium substitution increases the unit cell dimensions which may be decreasing the selectivity by weakening the bonds between cesium and the framework oxygens. Similar studies are in progress to assess the affects of substitution into the CST framework on strontium selectivity.

During this first year we initiated experiments at the National Synchrotron Light Source located at the Brookhaven National Laboratory studying in-situ crystal growth and ion exchange. This testing provides continuous structural information about the crystalline phases as a function of temperature, concentration, sorbate addition and time. This data enables us to monitor growth of crystalline phases such as CST during synthesis as well as the changes in crystal structure during ion exchange. For example, we can monitor the growth of crystalline CST to detect the optimal conditions for synthesis. Preliminary results with ion exchange tests showed measurable changes in the size of the crystal lattice upon exchange of cesium and strontium into the CST and pharmacosiderite materials, respectively.

During this first year we also developed a molecular modeling framework for simulating ion exchange in the crystalline CST materials. This effort included construction of the base framework structures and simulation of the ion exchange process for sodium, cesium and strontium. Validation of the molecular model involves calculating cation locations and energetics and comparing the calculated values with those measured experimentally. Results to date indicate qualitative agreement between the calculated and measured cation locations as determined by X-ray diffraction and energetics as measured by infrared spectra before and after ion exchange with cesium. Figure 1 shows the predicted structure of CST partially exchanged with cesium.



**Figure 1. A single tunnel of the CST material. White spheres are  $\text{H}^+$ , purple spheres are  $\text{Na}^+$  and green spheres are  $\text{Cs}^+$ .**

MST is an amorphous material that exhibits good affinities for strontium and actinides under alkaline conditions. Sodium nonatitanate (SNT) is chemically very similar to MST. Unlike the amorphous MST, SNT is a poorly crystalline layered material with an interlayer spacing of around 9.6 Å. It has been observed that the portion of MST onto which strontium sorbs are microcrystalline regions, that appear morphologically similar to SNT. Therefore we are investigating the role of crystallinity and structural modifications to SNT and other sorbents (e.g., CST) on strontium and actinide sorption characteristics.

Initial work has focused on structural modifications induced by the substitution of transition metals into the SNT framework similar to that studied for the CST materials. To date Nb<sup>5+</sup> has proven to be the best metal to substitute into a Ti<sup>4+</sup> framework: Ti<sup>4+</sup> and Nb<sup>5+</sup> have essentially the same ionic radius and form solid solutions in a number of oxide phases. Similar to CST, we are hoping to open up the interlayer space by exclusion of H<sup>+</sup> or Na<sup>+</sup> to maintain charge-balance of this framework with Nb-substitution. An additional reason we expect niobium to improve the sorption behavior of SNT is that where titanium prefers edge and corner sharing all its bonded oxygens in octahedral coordination; niobium prefers distorted octahedral coordination with one terminal oxygen. These terminal oxygens create sites of concentrated negative charge; and thus excellent binding sites for positively charged radionuclides such as strontium and the actinides.

Results from this year's testing indicate the following: 1) up to 40% titanium in the SNT framework can be substituted with Nb while maintaining the poorly crystalline layered structure, 2) strontium selectivity increases with increasing Nb-substitution into the SNT framework, 3) distinct 35 Å pores are observed by BET surface analysis of Nb-substituted SNT, and 4) a 'coral-like' morphology featuring tunnels and ridges (thus increased surface area) results from Nb-substitution into the SNT framework.

A second class of sorbents we are investigating for strontium/actinide sorption are heteropolyniobates. These materials, synthesized recently for the first time at SNL are close cousins of the heteropolymolybdates, heteropolytungstates and heteropolyvanadates; collectively known as heteropolymetalates. The earlier-known heteropolymetalates have in fact been investigated previously for nuclear waste processing (EMSP project #54716, Polyoxometalates for radioactive waste treatment, Michael T. Pope, 1996) due to their ability to coordinate large metals such as actinides. In contrast to the earlier known heteropolymetalates, these heteropolyniobates are stable in basic solutions. Also, initial results indicate that these materials exhibit higher affinities for strontium than the MST.

A third class of materials we are investigating are materials having the crystal structure of the mineral phase, pharmacosiderite. Two samples of the silicotitanate form M<sub>3</sub>HTi<sub>2</sub>(SiO)<sub>4</sub>·4H<sub>2</sub>O, where M = Na or K were synthesized and shown to exhibit selectivity for cesium, strontium and actinides. Germanium substitution appears to increase cesium selectivity. These materials have a more open structure than CST and, therefore, may exhibit more rapid ion exchange and higher affinity for the larger actinide ions.

### **Planned Activities**

Activities planned for the future include a refinement of the molecular model for that enables substitution of niobium into the CST framework structure and an improved methodology for performing ion exchange calculations including those for strontium in addition to that for cesium. Once we can make these calculations reliably, 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 FY02 we will determine the cesium and actinide separation characteristics of the niobium substituted SNT, heteropolyniobates and pharmacosiderites. If the cesium and actinide removal characteristics appear promising, we plan to characterize the nature of the interaction between the cesium/strontium/actinide and these materials by transmission electron microscopy, X-ray diffraction and extended X-ray absorption spectroscopy during the second year of the project. We also plan to continue the in-situ crystal growth and ion exchange studies at the National Synchrotron Light Source by extending measurements with other sorbent materials including the pharmacosiderites and substituted nonatitanate materials. This data in concert with molecular modeling will guide the synthesis of improved derivatives of these materials.

### **Publications**

"A General Synthetic Procedure for Heteropolyniobates", M. Nyman, F. Bonhomme, T. M. Alam, M. A. Rodriguez, B. R. Rodriguez, B. R. Cherry, J. L. Krumhansl, T. M. Nenoff, A. M. Sattler, *Science*, **2002**, accepted for publication.