

## **FINAL REPORT**

**Award Number:** DE-FG07-97ER45674

**Project Title:** New Metal Niobate and Silicotitanate Ion Exchangers: Development and Characterization

**Covering Period:** September 15, 1997 – September 14, 2003

**Report by:** Alexandra Navrotsky, University of California at Davis  
anavrotsky@ucdavis.edu

### **EXECUTIVE SUMMARY TO INCLUDE (one of the three below – minimum one paragraph)**

How Does the Research Add to the Understanding of the Area Investigated?

New materials for ion exchange and cleanup of radioactive waste have been synthesized, characterized, and their thermodynamic properties investigated.

The Technical Effectiveness and Economic Feasibility of the Methods or Techniques investigated or demonstrated:

Some technically very promising materials have been found

How the Project is Otherwise of Benefit to the Public:

It educates scientists who join the nation's technical workforce

### **COMPARISON OF ACTUAL ACCOMPLISHMENTS WITH THE GOALS AND OBJECTIVES OF THE PROJECT:**

We have adhered to the project plan and accomplished the goals and even more than planned.

**SUMMARIZE PROJECT ACTIVITIES FOR THE ENTIRE PERIOD OF FUNDING** including original hypotheses, approaches used, problems encountered and departure from planned methodology.

Due to the extreme complexity of DOE mixed wastes (i.e. Hanford tank solutions), a variety of advanced processes are necessary to separate out hazardous radioactive and RCRA metals so that these wastes may be processed and disposed with minimal cost and maximum efficiency. Therefore, there is an ongoing effort to produce and test new phases with novel ion exchange properties for waste cleanup applications. The Sandia and PNNL, parts of this EMSP, synthesized a novel class of thermally and chemically stable, microporous, niobate-based, ion exchanger materials. Ion exchanged studies show these new phases are highly selective for

$\text{Sr}^{2+}$  and other bivalent metals. Additionally, the Sr-loaded ion exchangers undergo direct thermal conversion to perovskite, a highly durable phase with potential waste form applications.

The enthalpies of formation from constituent oxides for two series of silicotitanates at 298 K have been determined by drop-solution calorimetry into molten  $2\text{PbO}\cdot\text{B}_2\text{O}_3$  at 974 K: the  $(\text{Na}_{1-x}\text{Cs}_x)_3\text{Ti}_4\text{Si}_3\text{O}_{15}(\text{OH})\cdot n\text{H}_2\text{O}$  ( $n=4$  to 5) phases with a cubic structure ( $P43m$ ), and the  $(\text{Na}_{1-x}\text{Cs}_x)_3\text{Ti}_4\text{Si}_2\text{O}_{13}(\text{OH})\cdot n\text{H}_2\text{O}$  ( $n=4$  to 5) phases with a tetragonal structure ( $P4_2/mcm$ ). The enthalpies of formation from the oxides for the cubic series become more exothermic as  $\text{Cs}/(\text{Na} + \text{Cs})$  increases, whereas those for the tetragonal series become less exothermic. This result indicates that the incorporation of Cs in the cubic phase is somewhat thermodynamically favorable, whereas that in the tetragonal phase is thermodynamically unfavorable and kinetically driven. In addition, the cubic phases are more stable than the corresponding tetragonal phases with the same Cs/Na ratios. Those disparities in the energetic behavior between the two series are attributed to their difference in both local bonding configuration and degree of hydration

A suite of perovskites phases with the compositions  $\text{NaTi}_x\text{Nb}_{1-x}\text{O}_{3-0.5x}$ ,  $0 \leq x \leq 0.2$ , has been synthesized for the first time using the sol-gel method. Rietveld analysis of powder XRD data reveals that with increasing Ti content, the orthorhombic perovskite structure becomes more cubic-like, as evidenced by the smaller differences among its three cell parameters. Enthalpies of formation of the synthesized phases from the constituent oxides and from the elements have been determined by drop solution calorimetry into molten  $3\text{Na}_2\text{O}\cdot 4\text{MoO}_3$  solvent at 974 K. As  $\text{Ti}^{4+}$  substitutes for  $\text{Nb}^{5+}$ , the formation enthalpies become less exothermic in a nearly linear manner. This behavior suggests that the  $\text{Ti} \rightarrow \text{Nb}$  substitution destabilizes the perovskite structure, presumably because of the concomitant occurrence of  $\text{O}^{2-}$  vacancies, which compensate the charge imbalance between  $\text{Ti}^{4+}$  and  $\text{Nb}^{5+}$  in the structure.

The structure of  $\text{Cs}_2\text{ZrSi}_3\text{O}_9$  synthesized using a sol-gel method was determined from the Rietveld refinement of experimental powder X-ray diffraction data. The refinement confirmed that this compound was isostructural with wadeite: its structure was hexagonal (space group  $P6_3/m$ ), and its lattice parameters were  $a = 7.2303(2) \text{ \AA}$  and  $c = 10.2682(4) \text{ \AA}$ . The aqueous durability of  $\text{Cs}_2\text{ZrSi}_3\text{O}_9$  varied, depending on the solution conditions. In modified leach tests with buffered (pH 7) and unbuffered solutions, the cesium release rates were  $< 1.2 \times 10^{-4} \text{ g}\cdot(\text{m}^2\cdot\text{day})^{-1}$ , which indicated high aqueous durability. However, in unsaturated, unbuffered solutions with a pH of 9-10, the durability was much lower, with 7-d cesium release rates of  $2.2 \times 10^{-3} \text{ g}\cdot(\text{m}^2\cdot\text{day})^{-1}$ . The ability of this material to retain cesium in aqueous environments can be explained by its condensed ring structure, in which the size of the channel openings is smaller than the diameter of  $\text{Cs}^+$  ion. However, dissolution of the network silicate occurred at high pH, which resulted in the release of cesium.

## **IDENTIFY PRODUCTS DEVELOPED UNDER THE AWARD AND TECHNOLOGY TRANSFER ACTIVITIES:**

### **PUBLICATIONS:**

Su, Y., Balmer, M.L., Wang, L., Bunker, B.C., Nyman, M., Nenoff, T., and Navrotsky, A. (1999) Evaluation of Thermally Converted Silicotitanate Waste Forms. *Mat. Res. Soc. Symp. Proc.* 556, 77-84.

Nyman, M., Nenoff, T., Su, Y., Balmer, M.L., Navrotsky, A., and Xu, H. (1999) New Crystalline Silicotitanate (CST) Waste Forms: Hydrothermal Synthesis and Characterization of CS-SI-TI-O Phases. *Mat. Res. Soc. Symp. Proc.* 556, 71-76.

Xu, H., Navrotsky, A., Nyman, M., Nenoff, T. (2000) Thermochemistry of Microporous Silicotitanate Phases in the  $\text{Na}_2\text{O}-\text{Cs}_2\text{O}-\text{SiO}_2-\text{H}_2\text{O}$  System. *J. Mater. Res.* 15, 815-823.

Balmer, M.L., Su, Y., Xu, H., Bitten, E., McCready, D., and Navrotsky, A. (2001) Synthesis, Structure Determination, and Aqueous Durability of  $\text{Cs}_2\text{SrSi}_3\text{O}_9$ . *J. Amer. Ceram. Soc.* 84, 153-160.

Nenoff, T., Nyman, M., Su, Y., Balmer, M.L., Navrotsky, A., and Xu, H. (2001) Synthesis, Characterization and Ion Exchange of Novel Sodium Niobate Phases. *ACS Symposium Series*, 778(Nuclear Site Remediation), 175-186.

Xu, H., Navrotsky, A., Balmer, M.L., and Su, Y. (2002) Thermochemistry of Substituted Perovskites in the  $\text{NaTi}_x\text{Nb}_{1-x}\text{O}_{3-0.5x}$  System. *Mat. Res. Soc. Sympo. Proc.* 718, 65-70.