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Lead Principal Investigator:

Dr. Mari Lou Balmer
Pacific Northwest National Laboratory
MSIN K8-93
P. O. Box 999
Richland, Washington 99352
Telephone: 509-376-2006
e-mail: lou.balmer@pnl.gov

Co Principal Investigators:

Dr. Tina Nenoff
Sandia National Laboratories - Albuquerque
P.O. Box 5800
Albuquerque New Mexico 87185 -0709
Telephone: 505-844-0340
e-mail: tmnenof@sandia.gov

Dr. Alexandria Navrotsky
Professor
Department of Chemical Engineering and Materials Science
University of California at Davis
Davis California 95616
Telephone: 916-752-3292
e-mail:anavrotsky@ucdavis.edu

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Principal Investigator

Dr. Mari Lou Balmer
Pacific Northwest National Laboratory
P.O. Box 999, MSIN K8-93
Battelle Blvd., Richland, WA 99352
(509) 376-2006 (phone)
lou.balmer@pnl.gov

Co-Investigators

Dr. Tina Nenoff
Sandia National Laboratories
P.O. Box 5800
Albuquerque, NM 87185-0709
(505) 844-0340 (phone)
tmnenof@sandia.gov

Prof. Alexandra Navrotsky
Department of Chemical Engineering and Material Science
University of California-Davis, Davis, CA 95616
(916) 752-3292 (phone)
anavrotsky@ucdavis.edu

Dr. Yali Su
Pacific Northwest National Laboratory
P.O. Box 999, MSIN K8-93
Battelle Blvd., Richland, WA 99352
(509) 376-5290 (phone)
ya.su@pnl.gov

Contributors and Collaborators

Bob Roth (NIST)
Hongwu Xu (UC Davis)
May Nyman (SNL)
Eric Bitten (PNNL)
Dave McCready (PNNL)
Bruce Bunker (SNL)

Research Objective

The objective of this program is to identify new waste forms and disposal strategies specific to crystalline silicotitanate (CST) secondary waste that is generated from cesium and strontium ion exchange processes. In particular, in situ heat treatment of CSTs to produce an alternative waste form is being examined. Waste forms that are developed in this work will offer an alternative to current disposal plans, which call for recombining the separated cesium, strontium-loaded CST into the high-activity waste (HAW) streams, then dissolving it in borosilicate glass. The goals of the program are to reduce the costs associated with CST waste disposal, minimize the risk of contamination to the environment during CST processing, and provide DOE with technical alternatives for CST disposal. Because there is uncertainty in repository availability and in waste acceptance criteria, it is likely that cesium and strontium-loaded ion exchangers will require short-term storage at Hanford or that new scenarios for long-term storage or disposal of nuclides with relatively short half-lives (such as ^{137}Cs and ^{90}Sr) will arise. Research activities in this program will generate information on the durabilities and stabilities of thermally consolidated CSTs so that the potential of these options as viable storage or disposal scenarios can be evaluated. The technical objectives of the proposed work are to fully characterize the phase relationships, structures, and thermodynamic and kinetic stabilities of crystalline silicotitanate waste forms and to establish a sound technical basis for understanding key waste form properties, such as melting temperatures and aqueous durability, based on an in-depth understanding of waste form structures and thermochemistry.

Research Statement

Plans are in place to retrieve, separate, and immobilize radioactive waste contained in 177 underground storage tanks at the Hanford Site. Likewise, nuclear wastes at other DOE sites across the country must be immobilized in a stable waste form for storage in underground repositories. A viable waste form must be chemically durable under environmental storage conditions (aqueous environments are of primary concern) and thermally stable under repository conditions over a geologic time scale. In addition, an adequate waste form should be capable of incorporating specific waste feeds to form a stable glass or ceramic material with a minimum of waste dilution (to minimize waste volumes) and be easy to process under remote handling conditions. Relatively low processing temperatures are desirable, as are simple heat-treatment cycles.

Borosilicate glass has been chosen as the baseline host for immobilization of HAW present at the Hanford Site. However, CST, the most promising candidate for removal of cesium and strontium from tank wastes, has been identified as a risk to the borosilicate vitrification process. TiO_2 in the CST promotes crystallization and immiscible phase separation, and affects the redox state and solubility of uranium in glass (Ewest et al. 1987; Galakhov et al. 1988; Bickford et al. 1990; Plodinec 1980). Because of this, a TiO_2 limit of 1 wt% is set for borosilicate waste glass at the Savannah River Defense Waste Processing Facility (DWPF) (Plodinec 1980). If these high levels of waste dilution are required to stabilize CST waste, the volume of expensive high-activity borosilicate waste glass produced for subsequent storage will be substantially increased. Dissolution of the CST in borosilicate glass (as opposed to direct thermal conversion) necessitates removal and transfer of the CST from the column, mixing with glass frit, and melting. Each of these steps significantly increases the risk of contamination to workers and/or the environment. The volume of HAW can be minimized and the process can be simplified by converting the separated, compositionally homogenous loaded exchanger into an alternate waste form rather than recombining it with the HAW for dissolution in glass.

Cesium-loaded silicotitanate ion exchangers contain the basic ingredients that can form a ceramic or glass at high temperature. The premise of this work is that for CST ion exchange waste, waste forms can be tailored to specific waste feeds rather than attempting to tailor waste feeds for accommodation by a single waste form. Direct in situ, thermal conversion of the CST will consolidate and immobilize the loaded ion exchange particulate, minimize handling risks, and remove water and hydroxyl groups thus eliminating radiolytic hydrogen generation during storage.

The research strategy for developing an alternate waste form for CSTs is based on an understanding of ceramic and glass structures and phase stabilities. The key components of the research include

- determining stable and metastable phases that form from heat treatment of the CST and development of phase diagrams for the component systems

- characterizing the structures of ceramic and glass waste form candidates

- developing structure-property relationships that will provide predictive capabilities regarding key performance parameters, including aqueous leach resistance, melt temperatures, melt viscosities, and ease of crystallization for select waste forms

- determining the enthalpies and free energies of formation of key compounds by high-temperature oxide melt solution calorimetry.
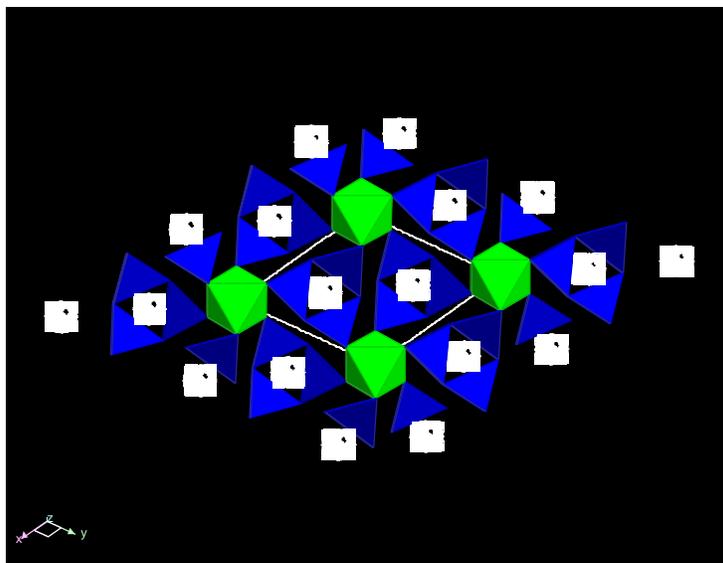
Research Progress

Work during the first year of the program showed that thermally converted CSTs have very high aqueous durablity (Su et al. 1998). These thermally converted waste forms are several orders of magnitude more durable than borosilicate glass. For example, standard engineering assessment (EA) borosilicate glass shows a seven-day leached concentration of alkali of 13.3 g/L (there is no cesium in this standard, only sodium) (Ferrara et al. 1997). In comparison, IE-911 heat-treated to 900°C has a seven-day cesium concentration of 0.008 g/L, or in the worst case for the 700°C heat-treatment, the seven-day cesium concentration is 0.175 g/L. Heat treatments of 900 and 500°C yielded the most durable ceramics; however, all residual water and hydroxy groups are not removed until 800°C. Therefore, 900°C is the optimum heat treatment because the possibility of hydrogen formation from radiolytic decay of physisorbed or chemisorbed water is eliminated.

This early, positive result fulfilled the milestone of defining the chemical durability of thermally converted waste forms. This year we have focused on defining the phase selection, especially the cesium-containing phases and thermodynamic stabilities of compounds related to the ion-exchanged CST and the thermally converted oxides.

Phase Selection of Thermally Converted CST

Phase stability and crystal chemistry studies for compositions related to the exchanger are vital to predicting long- and short-term performance of waste forms. In the first year of the program, several phases in the heat-treated waste form were identified; however, the cesium-containing phases were not obvious from x-ray diffraction (XRD) and nuclear magnetic resonance (NMR) studies. This year, transmission electron microscopy (TEM) and further XRD studies were performed. Figure 1 shows a micrograph of a thin section of 12 wt% cesium-exchanged IE-911 heat treated to 900°C. Energy dispersive spectroscopy on individual grains revealed that several oxide phases with unique compositions exist in the sample.

Figure 1. TEM Micrograph of a Thin Section of IE-911 that Was Treated in NaOH, Exchanged with 12 wt% Cesium, then Heat-Treated to 900°C. Energy dispersive spectroscopy of individual grains revealed the approximate compositions of the phases in this proposed waste form.

Among these were Cs, X1, Si oxide, Na, Ti oxide, Na, Ti, X2 oxide, and very minor Na, Cs, Ti, Si, X1 oxide, where X1 and X2 are proprietary components of the ion exchanger. Of these four phases, positive identification by XRD had already been achieved for the sodium titanate phase, $Na_2Ti_6O_{13}$. This structure is a layered structure. While there are known isomorphs for potassium and rubidium substitutions on this structure, cesium substitution had not been documented. The structure of the pure cesium analog, $Cs_2Ti_6O_{13}$, has a different structure than the sodium, potassium, or rubidium forms. To determine whether small amounts of cesium could reside in the $Na_2Ti_6O_{13}$ structure, a solid substitution series of $(Na, Cs)_2Ti_6O_{13}$ was synthesized and the lattice parameters were measured by XRD. This study surprisingly revealed that there is no measurable substitution of cesium for sodium on the $Na_2Ti_6O_{13}$ lattice, eliminating the possibility that small amounts of cesium could reside in this phase in heat-treated IE-911.

TEM revealed that the majority of the cesium is contained in a Cs, X1, Si oxide. This phase could not be synthesized by solid-state reaction; however, it was successfully synthesized using sol gel and hydrothermal reactions. The stoichiometry of the phase is $Cs_2X1Si_3O_9$. While a similar phase is reported in the literature, the crystal structure of this compound is unknown and the powder XRD data are incomplete. We attempted to grow single crystals of this compound; however, due to the refractory nature of the proprietary component, no suitable crystals have been synthesized to date. A search of the powder diffraction database revealed a compound that is a structural isomorph to $Cs_2X1Si_3O_9$. From this it was determined that the new cesium compound is hexagonal with a lattice parameter of a=7.23 Å and c=10.271 Å (space group P63/m). Efforts are under way to refine the structure to obtain the exact atomic positions. The simulated crystal structure based on the atomic positions of the isomorph and the lattice parameters of $Cs_2X1Si_3O_9$ is shown in Figure 2. It consists of silica tetrahedra and X1 octahedra that form three-membered and six-membered rings. The largest free aperture of the rings is approximately 2.2x2.6 Å, which is smaller than a cesium atom (~3.5 Å). Therefore, the cesium in this phase will be immobile. Removal of cesium from the structure will require the cleavage of the strong, covalent Si-O

Figure 2. View of $Cs_2X1Si_3O_9$ Structure Down the [001] Directions. This is the major cesium-containing phase in thermally converted (900°C) IE-911.

and X1-O bonds. This structural feature in part explains the high resistance to leaching of cesium in thermally converted IE-911 that is exposed to aqueous solutions.

A second new phase discovered in TEM (Na, Ti, X2, oxide) has a structure similar to $NaX2O_3$. To determine the extent of titanium substitution in the mixed phase, a series of compounds with up to 20% titanium substituted for X2 were synthesized using a sol gel technique. A systematic shift of the lattice parameter as a function of titanium substitution could clearly be observed. Comparison of the heat-treated IE-911 with the synthesized compounds revealed that the phase in IE-911 has 15% titanium substitution on the lattice. The structure of the new compound is related to a perovskite; however the distribution of the cations in the structure is unknown.

With the discovery of the two new oxide phases in heat-treated CST, the phase identification is nearly complete. Figure 3 shows the XRD pattern of cesium-exchanged heat-treated IE-911 compared with a simulated x-ray pattern, which is a combination of the patterns of the three phases identified in this program, $Na_2Ti_6O_{13}$, $Cs_2X1Si_3O_9$, and $Na(Ti, X2)O_3$. It can be seen that all of the major peaks have been identified. Several very small peaks that appear in the thermally converted IE-911 pattern are not present in the simulated pattern. The intensity of these peaks decreases significantly with longer heat treatment at 900°C or with heat treatment to 1000°C, indicating that this phase is metastable. Some of these minor peaks may also correspond to the minor Cs, Na, Si, Ti, X1 oxide identified with TEM. Work will continue to determine the structure of this minor phase.
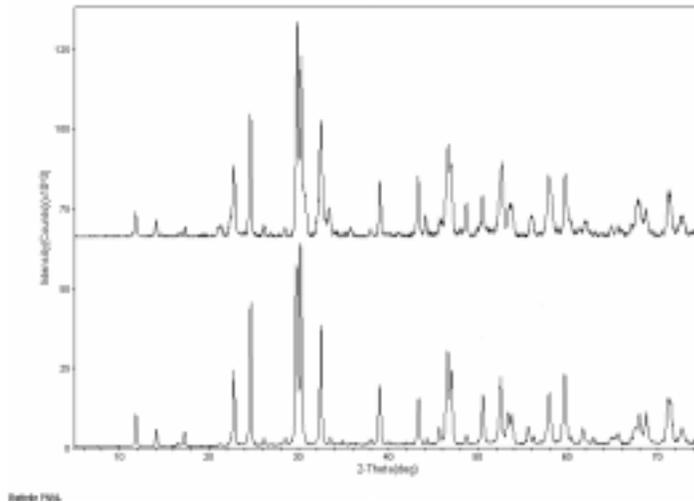
Figure 3. Comparison of the Experimental XRD Pattern of Mixed-Phase Cesium-Exchanged IE-911 Heat-Treated to 900°C (upper pattern) with a Simulated Pattern that Is a Compilation of the X-Ray Patterns from Synthesized Compounds $Na_2Ti_6O_{13}$, $Cs_2X1Si_3O_9$, and $Na(Ti, X2)O_3$ (lower pattern). The excellent match between the two patterns suggests that these compounds represent the major phases in the waste form.

Hydrothermal Synthesis of Metastable Phases

Cs_2O-TiO_2-SiO_2 Phases

Researchers at Sandia National Laboratory are studying the metastable phase development in the component systems that represent the cesium-loaded ion exchanger. This work complements the stable phase development studies at PNNL and allows for a complete understanding of the phase development from the metastable ion exchanger to the stable ceramic waste form. Hydrothermal Cs_2O-TiO_2-SiO_2 ternary phase searches have produced two novel phases, which we have designated SNL-A and SNL-B. The stability regions of these phases as a function of Cs_2O:TiO_2:SiO_2 precursor ratio (and pH) are plotted on the ternary diagram in Figure 4 for five days at 170°C (left) and 120°C (right). These experiments show a distinct relationship between SNL-B and SNL-A. At 170°C, SNL-B is formed in a mixture with SNL-A. With increased time at temperature, only SNL-A is formed. For example, at 120°C for 5–20 days, only SNL-B is formed, while at 120°C for 28 days, only SNL-A is formed. Also shown on the ternary plot is the stability region for TiO_2 and pharmacosiderite (a known microporous Cs_2O-TiO_2-SiO_2 ion exchanger).
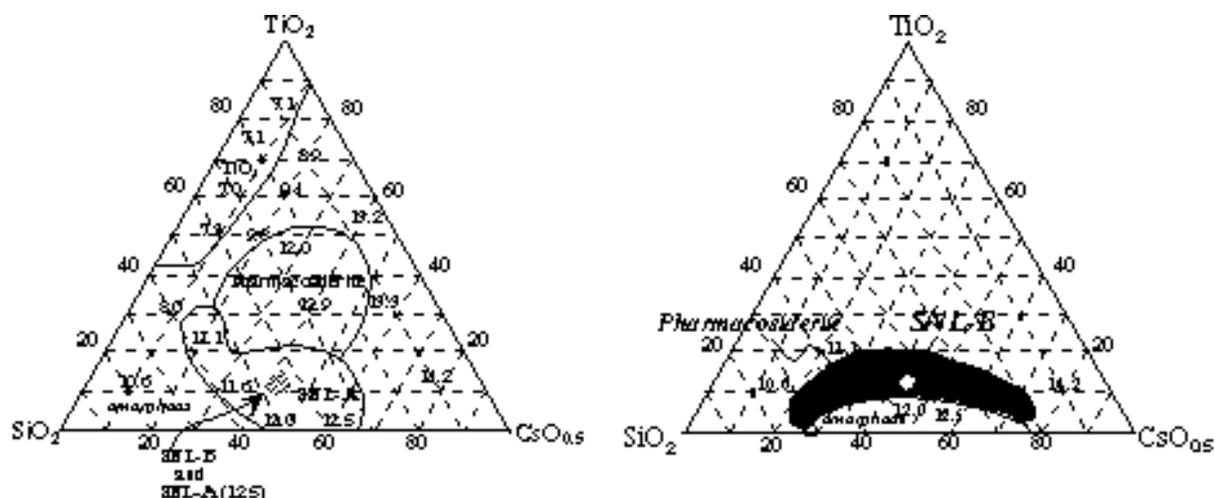
Figure 4. Stability of Hydrothermally Synthesized Cs_2O-TiO_2-SiO_2 Ternary Phases at 170°C (left) and 120°C (right)

SNL-B is a microporous ion exchanger with a chemical formula $CsTiSi_4O_{10.5} \cdot xH_2O$ and SNL-A is a condensed phase with a formula $Cs_2TiSi_4O_{11}$. Solid state ^{133}Cs and ^{29}Si MAS-NMR (magic angle spinning nuclear magnetic resonance) and CP (cross polarization) MAS NMR of SNL-A and SNL-B reveal that both phases are structurally complex with multiple silicon and cesium coordination sites. The chemical shifts of these sites are compiled in Table 1. All silicon atoms in both phases are in tetrahedral coordination sites (the "x" of Q^x gives the number of silicon atoms in the second coordination sphere and 4-x is the number of titanium atoms in the second coordination sphere). The CP-MAS NMR experiments show there is internal water in SNL-B and none in SNL-A.

Table 1. MAS-NMR Characterization of SNL-A and SNL-B

| Experiment	Chemical Shifts (ppm)	Comments
SNL-A		
^{29}Si MAS NMR	-88 (Q^1)	Chemical shifts typical of silicotitanates
	-96, -97 (Q^2)	
	-100, -102 (Q^3)	
	-107, -110 (Q^4)	
^{29}Si CP-MAS NMR	None	Indicative of no hydrogen associated with silicon in the crystal lattice (no OH⁻ or H_2O)
^{133}Cs MAS NMR	+65, +86	
SNL-B		
^{29}Si MAS NMR	-87 (Q^0)	Chemical shifts typical of silicotitanates
	-97 (Q^1 - Q^2)	
	-103, -105 (Q^4)	
^{29}Si CP-MAS NMR	-97 (Q^3)	The silicon associated with this chemical shift is near H_2O
^{133}Cs MAS NMR	+8, +23, +57	

This is confirmed by thermogravimetry experiments. The structural complexity of SNL-A, which is suggested by the multiple NMR chemical shifts (7 for silicon, 2 for cesium), is also seen by TEM analysis. These preliminary structural analyses reveal that SNL-A has a unit cell of low symmetry (either monoclinic or triclinic).

In situ TEM-monitored electron irradiation studies of SNL-A and SNL-B were also carried out (in collaboration with Dr. Rod Ewing at the University of Michigan) to determine the stability of these new phases in radioactive environments. The irradiation-induced transformation of microporous crystalline SNL-B to amorphous material is observed by fading Bragg-diffraction spots in the electron diffraction pattern. The irradiation dose needed for amorphization of SNL-B is inversely dependent on temperature. This corresponds to heat accelerated cesium and/or water loss, and finally a thermally induced phase change at 500°C (which is also observed by differential thermal analysis). This amorphization behavior is typical of other zeolite materials studied by Dr. Ewing. The condensed phase SNL-A, on the other hand, is very irradiation-resistant. It does not undergo any irradiation damage with very high dose rates. Ongoing and future work in characterization of SNL-A and SNL-B includes crystal growth experiments for structural characterization of these novel phases.

New Sr-Selective Microporous Ion Exchanger

In the course of Na_2O-TiO_2 hydrothermal phase searches, researchers at SNL discovered a class of Na_2O-TiO_2-X (X = transition metals) novel ion exchanger phases. One phase of this class, designated SNL-C, demonstrates extreme selectivity for divalent cations, especially strontium. The selectivity for strontium is demonstrated in a plot of K_d (mL/g) vs. concentration of a competitive cation (Na) in solution (Figure 5).

Table 2 gives distribution coefficients of a variety of RCRA metals, monovalent alkali metal, and divalent alkaline earth metals for SNL-C. This data shows the selectivity of SNL-C for divalent cations. Heating strontium-loaded SNL-C results in alteration to a perovskite, a very durable phase that has waste form applications. Structural characterization of SNL-C is under way.
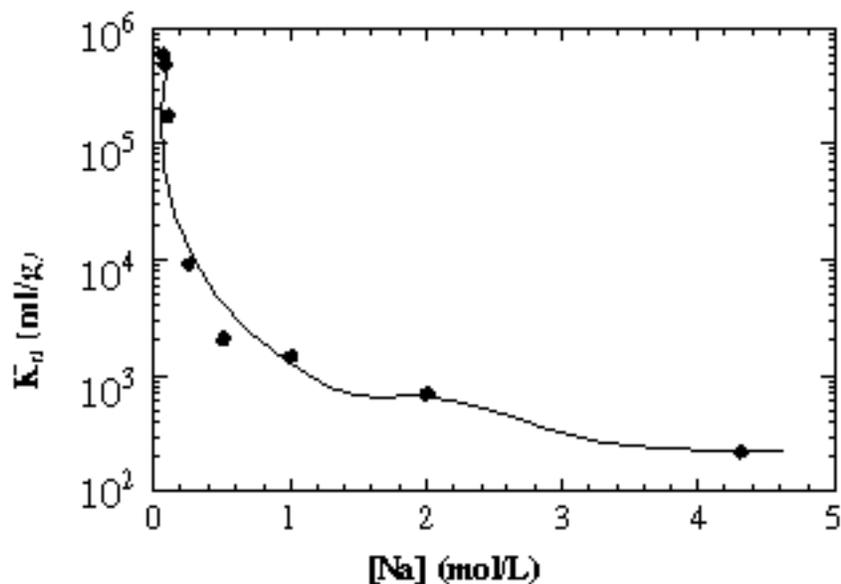
**Figure 5**. Selectivity of Strontium (50 ppm) as a Function of $NaNO_3$ Concentration in Solution

Table 2. Distribution Coefficients for Metals on SNL-C

Cation	Radius in pm (6-coordinate)	K_d (ml/g)[a]
La^{3+}	117	>199,800[b]
Sr^{2+}	132	>99,800[c]
Pb^{2+}	133	>99,800[c]
Ba^{2+}	149	>499,800[d]
Zn^{2+}	88	>99,800[c]
Cd^{2+}	109	>99,800[c]
Ni^{2+}	83	6,467
Cr^{2+}	94	3,371
Co^{2+}	89	1,208
Li^+	90	276
Mg^{2+}	86	467
Cd^{2+}	109	>99,800[c]
Cs^+	181	13
K^+	152	22
(a) Calculated for detection limit of metal.		
(b) 0.05 ppm.		
(c) 0.1 ppm.		
(d) 0.02 ppm.		

Energetics of Crystalline Cs_2O-Na_2O-SiO_2-TiO_2-H_2O Phases

Using hydrothermal methods, two series of microporous silicotitanates were synthesized at SNL: 1) $(Na_{1-x}Cs_x)_3Ti_4Si_2O_{13}(OH)\cdot xH_2O$ (x = 4-5) phases with a cubic structure of $P\bar{4}3m$ (analogues of the mineral pharmacosiderite), and 2) $(Na_xCs_{1-x})_3Ti_4Si_3O_{13}(OH)\cdot xH_2O$ (x = 4-5) phases with a tetragonal structure of $P4_2/mcm$. The enthalpies of drop solution in molten $2PbO\cdot B_2O_3$ at 974K were measured at UC Davis by high-temperature reaction calorimetry, and the enthalpies of formation have been determined from constituent oxides using appropriate thermochemical cycles. The enthalpies of formation for the cubic phases become more exothermic as Cs/(Na+Cs) increases (Figure 6a), whereas those for the tetragonal phases become less exothermic (Figure 6b). Therefore, the cesium uptake in the cubic phases is thermodynamically driven, while that in the tetragonal phases is kinetically driven. In addition, the cubic phases appear to be more stable than the corresponding tetragonal phases with the same Cs/Na ratio. We attribute these disparities in the energetic behavior for the two series to their differences in both local bonding configuration and degree of hydration.
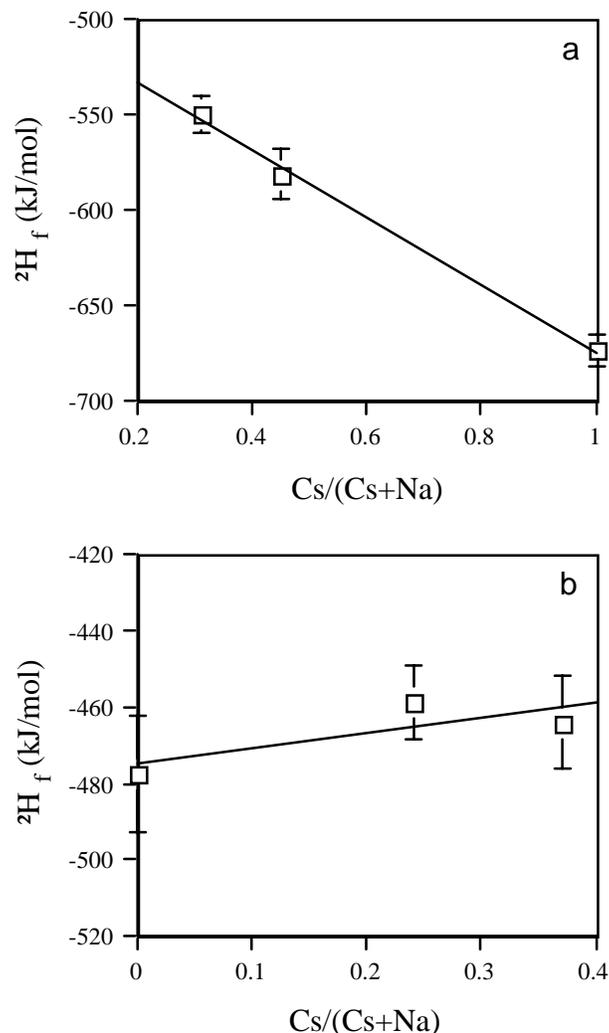
Figure 6. Enthalpies of Formation from Oxides of (a) the Cubic Phases and (b) the Tetragonal Phases as a Function of Composition

Summary

In summary, in the second year of the program, efforts focused on determining the stable and metastable phase development in a heat-treated, cesium-exchanged crystalline silicotitanate ion exchanger (IE-911). Transmission electron microscopy, XRD, and synthesis studies have revealed that the major phases in the ion exchanger are $Na_2Ti_6O_{13}$, $Cs_2X1Si_3O_9$, and $Na(Ti, X2)O_3$. The network structure of the cesium-containing phases precludes facile migration of the cesium ion, resulting in extremely high aqueous durability. Metastable phase-development studies have revealed three new phases. One of these shows extremely good selectivity for divalent ions even in high concentrations of sodium. In addition, the thermodynamic stabilities of metastable and stable compounds have been determined by solution drop calorimetry. This combined information on phase selection as a function of composition, chemical durablity, and thermodynamic stability can be used to determine processing windows and to predict long- and short-term stability of thermally converted CST ion exchangers.

Planned Activities

Future work will concentrate on determining the structures and refining the atomic positions of the two new compounds found in the heat-treated waste form and of the new compounds synthesized hydrothermally. The heat of formation of these compounds and related compounds in the representative ternary and quaternary systems will be measured. In addition, the radiation stability of thermally converted waste forms as well as of the single-phase cesium-containing constituent of the waste form ($Cs_2X1Si_3O_9$) will be measured.

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