Environmental Management Science Program

Project ID Number 60020

Stability of High-Level Waste Forms

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June 1, 1998

New Silicotitanate Waste Forms: Development and Characterization

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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 Cs and Sr ion exchange processes. In particular, in-situ heat treatment of CSTs to produce an alternate 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 Cs, Sr-loaded CST into the high activity waste streams then dissolving it in borosilicate glass. The goals of the program are to reduce the costs associated with CST waste disposal, to minimize the risk of contamination to the environment during CST processing, and to provide DOE with technical alternatives for CST disposal. Because there is uncertainty in repository availability and in waste acceptance criteria, it is likely that Cs and Sr 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 Progress and Implications

This report summarizes work after seven months of a three year program. To date studies have been performed to: 1.) determine the durability of waste forms synthesized by heat treating the UOP CST IE-911, 2.) investigate the stable and metastable phase formation from heat treated CST and from model 3-component systems, and 3.) measure the heat of formation for the CST without proprietary components. Leach tests have shown that waste forms with durabilities orders of magnitude higher than baseline borosilicate glass can be achieved by a simple heat treatment of the Cs-loaded ion exchanger with no additives. Optimum durabilities are achieved at heat treatment temperatures in the range of 800-1000°C. Direct thermal conversion reduces the total volume of waste generated from the ion exchanger by about 40% and dramatically simplifies processing. In addition, heat treatment of the ion exchanger coarsens fines, reducing inhalation risk, and completely removes molecular water and hydroxyl groups, eliminating the possibility of radiolytic hydrogen production during storage. The IE-911 CST ion-exchanger is compositionally complex. There are a number of phases that appear when the ion exchanger is heat treated, several of which are new. After heat treatment between 800-1000°C (where the best durability is obtained), a mixture of crystalline phases precipitates that are different from the structure of the ion exchanger. Preliminary NMR and x-ray diffraction simulation results indicate that the Cs resides in solid solution in a crystalline sodium titanate. Phase equilibria and single crystal growth experiments on the three component $\text{Cs}_2\text{O-TiO}_2\text{-SiO}_2$ system have revealed two new stable compounds. One of these compounds is

related to a silicotitanate pollucite compound discovered at PNNL that encapsulates Cs in a covalently bonded silicotitanate cage. In addition, two new (potentially metastable) phases have been synthesized in the $\text{Cs}_2\text{O-TiO}_2\text{-SiO}_2$ system using hydrothermal techniques.

Planned Activities

Future work will concentrate on identifying all Cs-containing phases in the heat treated waste forms and determining their thermodynamic stabilities so that long term predictions of durability can be made. A solid solution series of $(\text{Cs,Na}) \text{ } ^2\text{Ti}_6\text{O}_{13}$ compounds will be synthesized for analysis by X-ray diffraction, NMR, and solution drop calorimetry. The stability of Cs-containing compounds when it radioactively decays to Barium-137 is of concern. When Cs-containing phases have been identified and characterized, solid solutions such as $(\text{Ba, Cs, Na}) \text{ } ^2\text{Ti}_6\text{O}_{13}$ will be synthesized and analyzed for stability, chemical durability, crystal structure type and Cs environment. Crystal growth studies revealed that there is a tetragonal phase with composition near the cubic pollucite phase. Diffraction and DSC studies will be performed on this phase to determine if there is a low temperature cubic to tetragonal transition. Variations in reaction conditions will be attempted in order to synthesize phase pure samples for XRD and thermochemical analysis.

Other Access To Information

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