Stability of High-Level Waste Forms

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RESEARCH OBJECTIVE: The objective of the proposed effort is to use a new approach to develop solution models of complex waste glass systems and spent fuel that are predictive with regard to composition, phase separation, and volatility. The effort will also yield thermodynamic values for waste components that are fundamentally required for corrosion models used to predict the leaching/corrosion behavior for waste glass and spent fuel material. This basic information and understanding of chemical behavior can subsequently be used directly in computational models of leaching and transport in geologic media, in designing and engineering waste forms and barrier systems, and in prediction of chemical interactions.

RESEARCH PROGRESS AND IMPLICATIONS: As of the end of the third year of this project, which is a continuation of a previous three-year EMSP effort, a ChemSage datafile containing Na-Ca-Fe-Al-B-Si-O has been developed which is a major refinement over all previous efforts. This file has been converted into FactSage databases (one for compounds, and one for each solution phase). The FactSage program is particularly useful for calculating and displaying isothermal ternary sections that can be compared with reported literature data.

Zirconia is present in small, but important amounts in waste glasses (< 5 wt %). Optimized models based on the modified associate species approach for a few representative binary ZrO_2-based systems, the ZrO_2-Al_2O_3, ZrO_2-SiO_2, ZrO_2- CaO and ZrO_2- Cr_2O_3 systems, were used to obtain phase diagrams that compare well with published phase diagrams.

There is substantial concern with regard to spinel formation in glass melters. The current project has made considerable progress in modeling the liquid/glass systems with related spinel phases.

Specifically, the goal is to fully represent (Mn, Fe, Ni)(Al, Cr, Mn, Fe)$_2$O$_4$ together with other relevant crystalline oxides and the liquid/glass. The modified associate species model, while well-suited for representing the liquid/glass phase, is inappropriate for crystalline spinel phases. The two-sublattice model has proven to work well for spinel phases. Other, crystalline binary oxide solutions have been treated as ideal mixtures or by applying the Redlich-Kister formalism to mixtures of the end-member oxides.

The experimental phase of this project has focused primarily on liquidus temperature measurement in simplified melt compositions appropriate for waste vitrification. As the study continued, more components were added to the glass melts and the liquidus surface was experimentally mapped. These data were used to directly support the modeling efforts and to generate data directly useful to the waste glass producers.

The liquidus surface was mapped over a relatively large fraction of the five-component system: Al_2O_3-B_2O_3-CaO-Na_2O-SiO_2. To map this surface, 63 melts with systematic variation in component concentrations were fabricated and the liquidus temperature was measured for each composition. The ranges of composition are slightly larger than those considered to be applicable to current DOE waste glasses. Liquidus measurements were made on 63 compositions, 19 of which were aborted, primarily due to the inability to achieve equilibrium or to exceedingly high melting temperatures required to fabricate the glass.

PLANNED ACTIVITIES: This is the last year of the current project, and thus remaining activities will cover only the last few weeks of the fiscal year. In the coming period we will be engaged in further refining and expanding the model for high-level nuclear waste glass. The zirconia and spinel-forming constituents will be integrated into a global model of HLW glass.

A test matrix of glasses has been developed to experimentally explore the liquidus surface in an expanded composition region which includes the previous composition region and adds Li_2O, Cr_2O_3, NiO, and Fe_2O_3, and ZrO_2. These oxides include the oxides most important to the formation of crystals in HLW glasses and accounts for more than 90% of typical HLW glass melts. The matrix was developed to cover the appropriate concentration ranges. Experiments determining liquidus temperatures will be performed per the test matrix.

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INFORMATION ACCESS:

PUBLICATIONS

T. M. Besmann and K. E. Spear, “Thermochemical Modeling of Oxide Glasses,” *J. Am. Ceram. Soc.* **85,** 2887 (2002).

T. M. Besmann, K. E. Spear, and J. D. Vienna, “Extension Of The Modified Associate Species Thermochemical Model For High-Level Nuclear Waste Glass,” Proc. Fall Meeting of the MRS, 2002, in press.

T. M. Besmann, N. S. Kulkarni, and K. E. Spear, "Thermochemical And Phase Equilibria Property Prediction For Oxide Glass Systems Based On The Modified Associate Species Approach," Proc., 103rd Meeting of the Electrochemical Society, 2003, in press.

T. M. Besmann, N. S. Kulkarni, and K. E. Spear, "Thermochemical And Phase Equilibria Property Prediction For Oxide Glass Systems Based On The Modified Associate Species Approach," *High Temperature Corrosion and Materials Technology IV*, The Electrochemical Society, Pennington, NJ 2004, in press.

T**.** M. Besman**n**, K**.** E. Spear, and J**.** D. Vienna**, "**Extension of the Modified Associate Species Thermochemical Model for High-Level Nuclear Waste: Inclusion of Chromia**,"** II5.12.1, *Scientific Basis for Nuclear Waste Management XXVI***,** R. Finch and D. Bullen, eds., MRS Proc. Vol. 757, Materials Research Society, Warrendale, PA, 2004.

P. Hrma, P. Izak, J. D. Vienna, G. M. Irwin, and M. L. Thomas, "Partial Molar Liquidus Temperatures of Multivalent Elements in Multicomponent Borosilicate Glass," *Phys. Chem. Glasses* 43 [2] 128-136 (2002).

P. Izak, P. Hrma, B. K. Wilson, and J. D. Vienna, "The Effect of Oxygen Partial Pressure on Liquidus Temperature of a High-Level Waste Glass with Spinel as the Primary Phase," in *Ceramic Transactions 119*, pp. 309-316, American Ceramic Society, Westerville, Ohio 2001.

B. K. Wilson, P. Hrma, J. Alton, T. J. Plaisted, and J. D. Vienna, "The Effect of Composition on Spinel Equilibrium and Crystal Size in High-Level Waste Glass," in *J. Matl. Sci.*, **37** [24], 5327-5331 (2002).

WEBSITE

www.ca.sandia.gov/HiTempThermo/index.html