Research Objective

The objective of the proposed effort is to expand the development of solution models of complex waste glass systems that are predictive with regard to composition, phase separation, chemical activity, and volatility. The effort will also yield thermodynamic values for waste components that are fundamentally required to predict the leaching/corrosion behavior of waste glass in repository environments.

Research Progress and Implications

This work represents the results of the first 10 months of a three project that is a renewal of a previous project that spanned four years. A 13-element ChemSage® datafile containing Na-K-Ca-Mg-Fe-Al-B-Si-O-H-S-C-N has been created. The glass contains primarily Na-K-Ca-Mg-Fe-Al-B-Si-O, with minor components of H (water and hydroxide species), and S (sulfate, sulfite, and sulfide species), while gaseous species and/or stoichiometric solids may also contain C and N. Therefore, the influence of gaseous and or crystalline phases on the HLW glass might also be calculated.

The self-consistent heat capacity equations have been derived for 298 – 3000 K for the 19 condensed ternary species in the systems: $CaO-Al_2O_3-SiO_2$, $MgO-Al_2O_3-SiO_2$, $CaO-MgO-SiO_2$, $Na_2O-CaO-SiO_2$, $Na_2O-MgO-SiO_2$, $K_2O-Al_2O_3-SiO_2$, $Na_2O-K_2O-SiO_2$, $K_2O-CaO-SiO_2$, $K_2O-MgO-SiO_2$. It is anticipated that values for the 298 K enthalpies of formation and the absolute entropies for these crystalline ternary species, and for the needed ternary liquid species in these systems will be ready for inclusion into the above glass database by July 1, 2002.

This large 13-element datafile development for ChemSage is cumbersome, so it will be soon converted (after July 2002) into a database for use with FactSage, the new Windows-based thermodynamic program that is a merging and enhancement of features in both Win-FACT and ChemSage. This FactSage database can then be added to and edited in a relatively easy manner as elements such as Li and Ni are added to it.

The liquidus temperature (T_L) of several glass melts along the $NaAlSiO_4$ – SiO_2 join in the $Al_2O_3 \cdot Na_2O \cdot SiO_2 \cdot B_2O_3 \cdot CaO$ system were measured. This system represents the basis for most waste glasses in that waste glasses are typically composed of 70% or more of those five components. This preliminary dataset will be augmented and used to improve/validate the associate species model and the data will be published in a peer-reviewed journal.

A study of the solubility of chromium in a typical waste glass was measured as a function of temperature. The results of this study showed that melts with a reasonably small concentration of NiO and Fe_2O_3 (e.g., within the eskolaite primary phase field) can contain over two mass percent chromium (on a Cr_2O_3 basis). This finding will have a significant effect on the expected loading of many Hanford waste compositions in glass. The solubility of chromium in glasses within the spinel primary phase field was also studied. This study resulted in a Ph.D. dissertation completed at Washington State University.

A literature review of glass melt structure is underway. Specifically the study focuses on the second nearest neighbor interactions of components in silicate melts. The results of this literature study will be used to support corroborate the predictions of prominent associate species determined by thermodynamic modeling.

Planned Activities

The second year of the project will continue expansion of the model to include more relevant elements/species. These will include Cr, P, Ni, Fe, Cr, and Zn. Experimental results with regard to liquidus behavior will be used to refine the model and model-predicted phase equilibria. The third year will be devoted to further refinements based on greater amounts of experimental data and will culminate in the development of a global model or set of models for waste glasses that will be available in a user-friendly format.

Publications

K. E. Spear and Mark D. Allendorf, "Thermodynamic Analysis of Alumina Refractory Corrosion by Sodium or Potassium Hydroxide in Glass Melting Furnaces," J. Electrochem. Soc. *Accepted for publication May 2002.*

K. E. Spear and Mark D. Allendorf, " Thermodynamic Analysis of the Corrosion of Alumina-Based Refractories Alkali Hydroxides," High Temperature Corrosion and Materials Chemistry III (M. McNallan and E. Opila, eds.), Proc. Vol. 2001-12, The Electrochemical Society, Pennington, NJ, (2001), pp. 274-284.

J. D. Vienna. *The Effects of Temperature and Composition on the Solubility of Chromium in Multi-Component Alkali-Borosilicate Glass Melts*, a Ph.D. Dissertation, Washington State University, Pullman, Washington (2002).