Stability of High-Level Radioactive Waste Forms

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Research Objective

The current project is important because of the DOE efforts to increase waste loading of glass waste forms, including the improved understanding of waste components with limited solubility in glass (i.e., phase separation and crystallization) and better models for liquidus temperature due to the current high level of uncertainty. A second area is related to constraints on durability models which can cause acceptable glasses to be rejected. Also considered are issues of species volatility during melter operations and corrosion of melter components and related equipment.

The objective is to develop solution models of complex waste glass systems and spent fuel that are predictive with regard to composition, phase separation, and volatility.

Research Progress and Implications

This report summarizes work after $2^1/_2$ years of the three-year project. An associate model developed in the 1980s was used to represent the thermochemical behavior of liquid/glass oxide solutions. Energies of interaction between end-member component oxides beyond those of ideal mixing often exist and their use in complex systems results in a significant multiplication of terms. These energies are included in the associate model by adding "associate species," with their respective formation energies, to the solution. Thus, the complex interaction terms are embodied in additional species in the solution resulting in a substantially simpler and more easily applied model.

The current work has resulted in the development of a thermodynamic data-file for the quaternary Na_2O-Al_2O_3-B_2O_3-SiO_2 system. The thermodynamic and phase diagram data for six binary (Na_2O-Al_2O_3, Na_2O-B_2O_3, Na_2O-SiO_2, Al_2O_3-B_2O_3, Al_2O_3-SiO_2, and B_2O_3-SiO_2) and four ternary (Na_2O-Al_2O_3-B_2O_3, Na_2O-Al_2O_3-SiO_2, Na_2O-B_2O_3-SiO_2, and Al_2O_3-B_2O_3-SiO_2) subsystems were assessed and optimized. Several liquid associate species were used in modeling the quaternary $Na_2O – Al_2O_3 – B_2O_3 – SiO_2$ system.

At PNNL there has been concern regarding the precipitation of the nepheline ($NaAlSiO_4$) phase during cooling of certain waste glass compositions. Utilizing the thermochemical computational software and the thermochemical data for the Na_2O-Al_2O_3-B_2O_3-SiO_2 system, the composition space of the ternary oxide Na_2O-Al_2O_3-SiO_2 system was explored at 800°C with no boria present and with 30 wt% boria. The results can be seen in the ternary diagram of Fig. 1 with the binary oxides and the nepheline compositions indicated.

Apparent from the calculational results is the wide compositional range over which nepheline is stable. The maximum silica composition lies along the SiO_2-$Na_2O•Al_2O_3$ join. Important for the selection of waste compositions is the observation that the stability region decreases to lower silica content with increasing boria. Experimental results from PNNL at various boria contents are also shown on the diagram, and agree reasonably with the results of the calculations.

Planned Activities

The remainder of the project will be devoted to incorporating the oxides of Fe, Ca, Li, K, Mg, and Ni into the model and its application to the problem of spinel formation in glass melters.

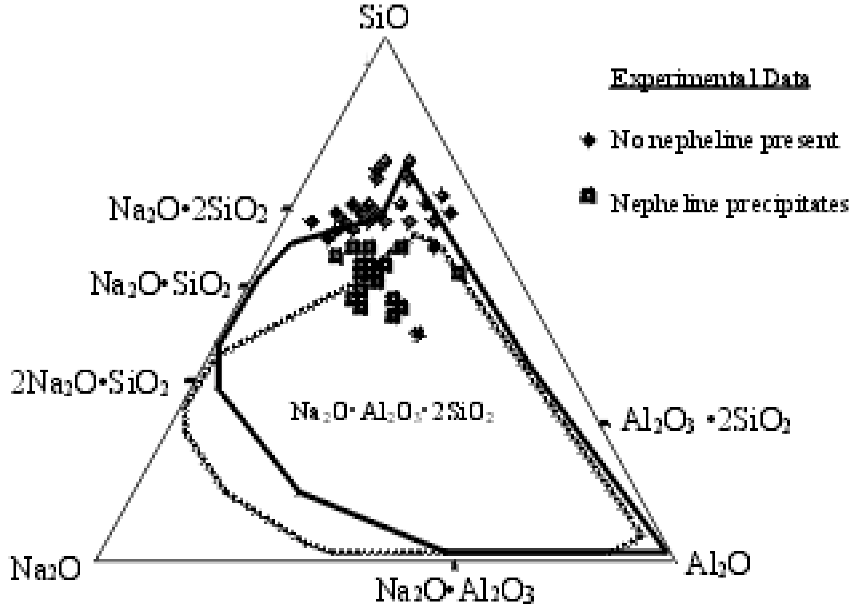

Fig. 1. Ternary Na_2O-Al_2O_3-SiO_2 phase space (wt. %) showing the computed stability region for nepheline plus the glass phase at 800°C with no boria (▬) and 30 wt.% boria (▪▪▪) along with experimentally determined precipitation data.

Publications

T. M. Besmann, K. E. Spear, and E. C. Beahm, "Assessment of Nepheline Precipitation in Nuclear Waste Glass via Thermochemical Modeling," in Scientific Basis for Nuclear Waste Management XXIII, Mater. Res. Soc. Symp. Proc., in press.

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