

Project ID: **60020**

Project Title: **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: A major focus of our efforts to thermochemically describe high-level waste (HLW) glass systems has been to develop internally consistent sets of thermochemical information for major binary and ternary subsystems of the glass. Our approach has involved the “thermodynamic fitting of equilibrium phase diagrams” as a means of testing and generating thermodynamic information for glass forming oxide systems. Since a phase diagram graphically depicts the equilibrium chemistry and thermodynamic properties of a system, the diagram can be calculated if the thermodynamic properties are known for all chemical species/phases that can form in the system.

The computer program ChemSage™ is our primary tool for developing an assessed, internally consistent thermodynamic database, and for subsequent calculations of the equilibrium chemical behavior of the glass systems. The needed thermodynamic data are obtained from the literature and sources such as the assessed SGTE database, our estimates, and simultaneously comparing and optimizing sets of phase equilibria and thermodynamic data. Since we use a different liquid solution model in our assessments and calculations than those used in most reported studies, the literature information for liquid solutions is used only for comparison with our assessments.

A large fraction of the needed thermochemical information has not been measured or reported, so we have developed a set of procedures for estimating or calculating the information. As an example, we have developed what we believe is a reliable set of data for the Na₂O-Al₂O₃-SiO₂ system. A search of the SGTE database and other sources for the Na₂O-Al₂O₃ system revealed a lack of values for the fusion of NaAlO₂, and no thermodynamic data for β-Al₂O₃ [Na₂O•6·Al₂O₃] and β-Al₂O₃ [Na₂O•11·Al₂O₃]. We estimated fusion enthalpies and entropies, absolute entropies at 298K, and heat capacity (C_p) equations for temperatures from 298-3000 K, and calculated enthalpies of formation at 298 K by developing an internally consistent set of phase diagram and thermodynamic data.

An assessed model for the Na₂O-Al₂O₃-SiO₂ system developed in this work was used to predict nepheline precipitation in the glass. This is a significant issue for the Tanks Focus Area as nepheline substantially reduces glass stability. By assuming that nepheline and the glass phase are the only allowable, equilibrium condensed phases that might form, it was possible to overlay a predominance area for both the glass and nepheline on the ternary oxide phase diagram. Not surprisingly, the computed area was discovered to be substantially wider than the phase diagram region for nepheline. An important conclusion was that the computed area also included regions where nepheline was observed by researchers at PNNL to precipitate in the glass, but that were also outside the phase diagram region for nepheline. This ability to predict crystalline phase formation in the glass should allow for the design of more stable glass compositions with minimal experimentation.

Waste in the underground storage tanks at Hanford contains ~1000 metric tons of uranium. Immobilization of uranium and the other actinides is one of the main reasons for vitrification of this waste. Experimental phase studies of the $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{UO}_3$ system are being performed because of the lack of data in the literature. This data is needed to model the behavior of actinides in glass. Differential thermal analysis is being used to determine phase and crystalline transitions and X-ray diffraction is being used to identify the phases.

In previous work, reported in FY 1998, we ran a series of tests on the $\text{B}_2\text{O}_3-\text{UO}_3$ system. In those tests uranyl borate, $\text{UO}_2(\text{BO}_2)_2$ or $\text{UO}_3\cdot\text{B}_2\text{O}_3$, formed slowly at temperatures $>1000^\circ\text{C}$, but decomposed at temperatures near 1100°C . In addition, the solubility of uranyl borate in B_2O_3 was found to be ~5 mol %. In contrast to this, the studies in FY 1999 with Na_2O , in addition to B_2O_3 and UO_3 , have shown that the uranium oxide readily dissolves at temperatures $<1000^\circ\text{C}$.

Samples of sodium uranyl borate, $\text{Na}_2\text{O}\cdot 2\text{UO}_3\cdot\text{B}_2\text{O}_3$, were prepared by heating triuranium octoxide, boric acid, and sodium carbonate. The sodium uranyl borate sample was predominately yellow with a trace amount of an orange compound at the surface of the sample. When the sodium uranyl borate sample was heated to 985°C , the orange compound was no longer present. X-ray diffraction of this sample indicated that the product was sodium uranyl borate. The decomposition of the sodium uranyl borate begins at approximately 1048°C . The melting point of the decomposition product(s) was observed at 1160°C . When the decomposition products were removed from the platinum crucible their primary color was olive green with a trace of black. It should be noted that the color of the triuranium octoxide ranges from olive green to black. X-ray diffraction of the decomposition products showed that they contained sodium uranate $\text{Na}_2\text{O}\cdot 2\text{UO}_2$ and uranium oxide.

In contrast to the limited solubility of uranyl borate in B_2O_3 , 50 mol % $\text{UO}_3\cdot\text{B}_2\text{O}_3$ dissolved in $\text{Na}_2\text{O}\cdot\text{B}_2\text{O}_3$ at 940°C , illustrating the ability to significantly load the Na_2O -containing system

PLANNED ACTIVITIES: The final quarter of FY 1999 will involve modeling the $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{B}_2\text{O}_3-\text{SiO}_2$ system to further refine the region of nepheline precipitation. Continuing experimental work will measure the liquidus temperatures at compositions in the $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{UO}_3$ ternary and look for ternary compounds other than $\text{Na}_2\text{O}\cdot 2\text{UO}_3\cdot\text{B}_2\text{O}_3$. Beginning with FY 2000 efforts will be made to include other relevant species in the model to begin to address the issue of spinel formation in glass melter, another important Tanks Focus Area issue. Phase equilibria and thermochemical values will be assessed and subsystems will be modeled. The global model will be enlarged to include all the important species and will be used to predict spinel formation. The latter part of FY 2000 will see the addition of other important species to the global model so that it will closely follow the composition of waste glass formulations of interest. The model will be assessed against observations of the chemistry of these glasses.

INFORMATION ACCESS – PUBLICATIONS

T. M. Besmann, E. C. Beahm, K. E. Spear, "An Approach to Thermochemical Modeling of Nuclear Waste Glass," *Environmental Issues and Waste Management Technologies IV*, pp. 277-87, eds. J. C. Marra and G. T. Chandler, *Ceramic Transactions Vol. 93*, American Ceramic Society, Westerville, OH, 1999.

K. E. Spear, T. M. Besmann, E. C. Beahm, "Thermochemical Modeling of Glass: Application to High-Level Nuclear Waste Glass," *MRS Bulletin*, April 1999, pp. 37-44.