FINAL REPORT
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Stability of High-Level Radioactive Waste Forms[*]

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Executive Summary

High-level waste (HLW) glass compositions, processing schemes, limits on waste content, and corrosion/dissolution release models are dependent on an accurate knowledge of melting temperatures and thermochemical values. Unfortunately, existing models for predicting these temperatures are empirically-based, depending on extrapolations of experimental information. In addition, present models of leaching behavior of glass waste forms use simplistic assumptions or experimentally measured values obtained under non-realistic conditions. There is thus a critical need for both more accurate and more widely applicable models for HLW glass behavior, which this project addressed.

Significant progress was made in this project on modeling HLW glass. Borosilicate glass was accurately represented along with the additional important components that contain iron, lithium, potassium, magnesium, and calcium. The formation of crystalline inclusions in the glass, an issue in Hanford HLW formulations, was modeled and shown to be predictive. Thus the results of this work have already demonstrated practical benefits with the ability to map compositional regions where crystalline material forms, and therefore avoid that detrimental effect. With regard to a fundamental understanding, added insights on the behavior of the components of glass have been obtained, including the potential formation of molecular clusters.

The EMSP project had very significant effects beyond the confines of Environmental Management. The models developed for glass have been used to solve a very costly problem in the corrosion of refractories for glass production. The effort resulted in another laboratory, Sandia National Laboratories – Livermore, to become

conversant in the techniques and to apply those through a DOE Office of Industrial Technologies project joint with PPG Industries. The glass industry as a whole is now cognizant of these capabilities, and there is a Glass Manufacturer’s Research Institute proposal in this area that will likely be supported. In addition, individual glass companies are inquiring as to modeling work at ORNL.

Research Objectives

The objective of the proposed effort was 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 was to yield thermodynamic values for waste components that are fundamentally required to predict the melting/crystallization behavior during processing and leaching/corrosion behavior of waste glass in repository environments. The waste glass systems consist of dozens of chemical elements present within a limited number of phases, and thus many elements will be "dissolved" in the host phase(s). The nature of the chemical potential of the constituent elements is determined by their solid solution behavior. And that solid solution behavior will be governed by the energetics of interactions between species, crystalline state, site occupancy, and oxidation state of the elements. Yet, unlike metallic systems, oxide solution thermodynamic relationships are not well established as they are extremely complex with no generally accepted solution models for multiple oxide species as solutes in a solvent phase, especially in the non-equilibrium glass phase.

The production of nuclear materials for defense applications at several sites in the United States has resulted in the accumulation over almost six decades of a substantial quantity of radionuclides. These materials are currently stored in a variety of forms including liquids, sludges, and solids. In addition, there are similar wastes that have resulted from the reprocessing of commercial spent fuel, although this has occurred to a much smaller extent. While the composition and characteristics of the various wastes differ, their behavior is similar in many respects. The focus of current U. S. Department of Energy (DOE) efforts with regard to permanent disposal of these materials is that they will be incorporated in a stable, insoluble host solid (a glass or specific crystalline phase).

Components such as Fe, Cr, Zr, and Al have limited solubility in HLW glasses (Hrma, et al. 1994, Peeler and Vienna 1998, Kim and Hrma 1994, and Mika, et al. 1997). These components precipitate as oxide minerals such as spinel, zircon, and nepheline once their solubility in glass is exceeded. Precipitated minerals may cause melter failure (Bickford, et al. 1990) and can alter the physical properties such as the leach resistance of the glass (Kim, et al. 1995). To avoid these problems, current HLW glasses are formulated to assure oxide minerals do not precipitate in the melter (Hrma, et al. 1996, Vienna, et al. 1995, Bickford, et al. 1990, and Peeler and Vienna 1998). Most often, this is accomplished by dilution of the problematic components in the glass leading to increased glass volume production. The solubility of these components currently dictate HLW glass volume produced at the Savannah River Site (Hrma, et al. 1998) and West Valley and to be produced at Hanford (Lambert, et al. 1996 and Hrma, et al. 1996) and Idaho National Engineering and Environmental Laboratory (INEEL) (Peeler and Vienna 1998).

The solubilities of problematic components in the melt are strongly related to the concentrations of other components. Thus there is a need for better understanding of the solution thermodynamics in multicomponent borosilicate melts (DOE-RL 1997). For example, the solubility of Cr in an alkali-borosilicate melt is strongly dependent upon the concentration of Al, Ni, and Na (Vienna, et al. 1996). The ability to understand and predict compositional effects on component solubilities in HLW glasses is needed in order to maximize the loading of waste in glass and thereby reduce cleanup costs. For example, to meet a need at the Hanford site it was demonstrated in the project that such a representation can be used, with appropriate quasi-equilibrium constraints, to accurately predict the compositional region for precipitation of a crystalline phase within the glass (Besmann et al., 2000).

The requirement to assure the sequestration of HLW for the order of ten thousand years is unprecedented. The limited artifacts which have survived such periods of time allow us to believe that we can safely accomplish this task, however, the level of uncertainty is substantial. Thus, understanding the metastable state of waste forms such as glasses can provide guidance as to the driving forces for chemical and physical changes in the waste forms and to their dissolution behavior. Such metastable state materials can be well-described using thermodynamic equilibrium techniques. Resulting insights into relationships between composition and chemical activity are critical to improving glass durability.

The current interest in the hot repository concept increases the importance for understanding the thermochemical states of these materials. The elevated temperatures (>100°C) of such a repository will result in more significant thermal gradients, more rapid mass transport via diffusion and other mechanisms, and enhanced chemical kinetic rates. It is expected that such elevated temperatures will, for example, cause chemical thermodynamics to predominate over kinetic mechanisms in governing reaction paths for leaching species from glass. The current progress has resulted in an ability to predict activities of species in glass and therefore the ability to determine the driving forces for reactions and transport.

The results of a substantially more accurate model of solution behavior of the constituents of waste glass or spent fuel can be directly input to geochemical models of glass durability, and similarly for codes for the dissolution of spent fuel (Li et al., 1999; Pickett et al., 1998; Jantzen and Plodinec, 1984; Jantzen 1992; Grambow, 1992; Wolery, 1983; Geldart and Kindle, 1988). The ability to model these materials can provide a sound theoretical basis for our confidence in their stability and durability over the necessary long time periods. It will also allow more realistic worst-case prediction of transport and negative chemical reactions between waste forms and container or barrier materials, particularly by the more aggressive constituents such as the alkali metals, cesium, tellurium, and iodine. The result of a more complete understanding of these systems will be significantly less uncertainty in the potential for release from a repository.

Methods and Results

The current EMSP project has been substantially successful in modeling the base glass composition of envisioned HLW glasses. Sub-models having a total of 11 components have been created that accurately represent thermochemical state and phase equilibria of the systems. Significant efforts were required to estimate and modify data for a number of systems where current information failed to be internally consistent. The project, therefore, has also provided basic scientific information on a set of important chemical systems. The model of the Na_2O-Al_2O_3-B_2O_3-SiO_2 system has been used to predict liquidus and other critical information. It has also demonstrated that it can aid in solving problems such as the precipitation of crystalline nepheline on cooling of HLW glass, which was addressed at the request of a group in the TFA program and has been the subject of a TFA Highlight. Lastly, experimental studies have provided important information on the phase equilibria of the Na_2O-B_2O_3-UO_3 system, for which little appears in the literature.

Thermodynamic Data Set Development

The focus of the EMSP project has been on developing accurate thermodynamic data for liquids in binary and ternary subsystems of HLW glass. Interactions of oxide species in a complex, multicomponent liquid solution phase primarily involve two, or at the most three different constituent metal oxides. Thus, the thermodynamic properties of liquid (glass) solutions in a four-component system such as Na_2O-Al_2O_3-B_2O_3-SiO_2 are represented by combining the interaction energies in the binary and ternary subsystems: 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, B_2O_3-SiO_2, 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.

The approach has involved adjusting thermodynamic data of fictive constituents so as to reproduce 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 fitting of phase diagrams can always be performed to yield numbers that can be used to back-calculate a phase diagram. However, it is only when the equations used in the fitting model have a sound thermodynamic basis can the values produced be confidently utilized for calculating unstudied regions of the diagram, predicting equilibrium partial pressures and species activities in a system, and modeling more complex chemical systems.

The computer program ChemSage™ (Eriksson and Hack, 1990) is the primary tool used 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 (1996), our estimates, and simultaneously comparing and optimizing sets of phase equilibria and thermodynamic data. The primary source of phase diagram information is the set of volumes Phase Diagrams for Ceramists plus literature reports, which includes previously optimized thermochemical data; typical examples are seen in Eriksson, Wu, and Pelton (1993). Since a different liquid solution model is used in the assessments and calculations of this work (Spear et al., 1998) than those of most reported studies, the literature information for liquid solutions is used only for comparison purposes.

A large fraction of the needed thermochemical information has not been measured or reported, so a set of procedures has been developed for estimating or calculating the values. In all cases, the complete set of thermochemical information for a system is refined and tested to give reasonable thermodynamic and phase diagram results over wide ranges of temperature and compositions.

The thermodynamic information needed for each solid, liquid, and gaseous species in high-level nuclear waste glass systems includes:

- 298 K enthalpy of formation, $\Delta H^\circ_{f,298}$
- 298 K absolute entropy, S°_{298}
- Heat capacity relations from 298 K to the highest temperature of interest:
  $C_p(298\text{-}T_{tr1})$, with phase transformation temperature T_{tr1} and enthalpy ΔH_{Ttr1},
  $C_p(T_{tr1}\text{-}T_{tr2})$, with phase transformation temperature T_{tr2}, and enthalpy ΔH_{Ttr2},
  etc. . . . .

If data are not available from published sources, or are incomplete, needed values are estimated to obtain an internally consistent dataset by reconciliation with the phase diagram. The optimization process for a chemical system tests the total set of system data for internal consistency. Due to the extreme sensitivity of the phase equilibria to the thermochemical values, a phase diagram places very restrictive limits on the relative thermodynamic stabilities of phases in a system.

It has been frequently necessary to estimate fusion enthalpies and entropies, enthalpies of formation at 298 K, absolute entropies at 298 K, and C_p equations for temperatures from 298-3000 K and higher. Trends in chemical reaction values as described by Spear (1976) for entropies and heat capacities are used to obtain those values, and then fitting of phase diagrams is used for obtaining enthalpy of formation values. As an example, in this manner a reliable set of data has been developed for the Na_2O-Al_2O_3 system (Table 1). The values shown in *italics and underlined* were estimated or calculated during the optimization process. As noted above, in general, entropies are estimated and enthalpies of reaction are derived from the phase equilibria. The previously published review (Spear et al., 1999) provides details of assumptions and techniques typically used to develop complete sets of assessed thermodynamic data for specific systems.

Table 1. Optimized Thermodynamic Data Set for the Condensed Na_2O-Al_2O_3 System.*

(a) Crystalline Species Formulae Written with the Moles of (Na + Al) = 2

	n(Na_2O)	n(Al_2O_3)	-$\Delta H_{f,298}$(J/mol)	S_{298}(J/K-mol)	T_{fus}(K)	ΔH_{fus}(J/mol)	ΔS_{fus}(J/K-mol)
Na_2O	1.000	0.000	417,982	75.04	1405	47,698	33.95
$NaAlO_2$	0.500	0.500	1,133,090	70.40	1923	*78,543*	*40.84*
$Na_2Al_{12}O_{19}$:/7	0.143	0.857	*1,528,335*	*56.31*	1833	peritectoid decomposition	
$Na_2Al_{22}O_{34}$:/12	0.083	0.917	*1,593,800*	*54.18*	2273	*105,901*	*46.59*
Al_2O_3	0.000	1.000	1,675,690	50.94	2325	111,085	47.74

(b) Liquid Species Formulae Written with the Moles of (Na + Al) = 2

	n(Na_2O)	n(Al_2O_3)	-$\Delta H_{f,298}$(J/mol)	S_{298}(J/K-mol)
Na_2O(l)	1.000	0.000	370,284	108.99
$NaAlO_2$(l)	0.500	0.500	*1,054,547*	*111.24*
Al_2O_3(l)	0.000	1.000	1,564,605	98.68

(c) Heat Capacity Coefficients: $C_p = a + b \cdot T + c \cdot T^2 + d/T^2$ ***(J/K-mol)***

Crystal Species	**a**	**b**	**c**	**d**	**T_{trans}(K)**	**DH$^o_{trans}$(J/mol)**
Na_2O(s)	55.480	7.021E-2	-3.054E-5	-414,000	1023	1,757.3
	82.563	1.235E-2	0	0	1243	11,924.4
	82.563	1.235E-2	0	0	2500	---
$NaAlO_2$(s)	*86.485*	*4.030E-2*	*-1.527E-5*	*-2,062,500*	*1000*	*0***
	100.027	*1.127E-2*	*0*	*-1,855,500*	*2500*	---
$Na_2Al_{12}O_{19}$:/7	*108.631*	*1.893E-2*	*-4.363E-6*	*-3,240,000*	*1000*	*0*
	112.500	*1.066E-2*	*0*	*-3,180,857*	*3000*	---
$Na_2Al_{22}O_{34}$:/12	*112.323*	*1.537E-2*	*-2.546E-6*	*-3,436,250*	*1000*	*0*
	114.579	*1.054E-2*	*0*	*-3,401,750*	*3000*	---
Al_2O_3(s)	117.490	1.038E-2	0	-3,711,000	3000	---
Liquid Species	**a**	**b**	**c**	**d**	**T_{trans}(K)**	**DH$^o_{trans}$(J/mol)**
Na_2O(l)	55.480	7.021E-2	-3.054E-5	-414,000	1023	1,757.3
	82.563	1.235E-2	0	0	1243	11,924.4
	82.563	1.235E-2	0	0	1405	fusion
	104.600	0	0	0	3000	---
$NaAlO_2$(l)	*86.485*	*4.030E-2*	*-1.527E-5*	*-2,062,500*	*1000*	*0*
	100.027	*1.127E-2*	*0*	*-1,855,500*	*1923*	*fusion*
	148.532	*0*	*0*	*0*	*3000*	---
Al_2O_3(l)	117.490	1.038E-2	0	-3,711,000	2325	fusion
	192.464	0	0	0	3000	---

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* Values in *italics and underlined* were estimated, or calculated during the optimization process.

** A value of zero for the enthalpy of transition indicates no transition occurs, but a new Cp equation is used for the next temperature range.

Solution Model

A modified associate species approach was used to model liquid solutions because it (a) accurately represents the thermodynamic behavior of very complex chemical systems over wide temperature and composition ranges, (b) accurately predicts the activities of components in metastable equilibrium glass phases, (c) allows logical estimation of unknown thermodynamic values with an accuracy much greater than that required for predicting useful engineering limits on thermodynamic activities in solutions, and (d) is relatively easy for non-specialists in thermochemistry to understand and use. The modification to the associate species model is the incorporation of positive regular solution constants to represent any positive interaction energies in a solution. It is thus possible to accurately represent reported immiscibility in solution phases. Ideally mixing associate species accurately represent the solution energies in which end member components exhibit attractive forces. The result is simple, well-behaved equations for free energies that can be confidently extrapolated and interpolated into unstudied temperature and composition ranges.

In oxide systems containing stable intermediate compounds, negative nonideal energies usually exist when mixing end-member component species to form a liquid solution. Such energies are included in the associate species model by adding associated liquid species with their respective formation energies to the solution. For example, in using the modified associate model for the Na_2O-B_2O_3 binary oxide system, associate species $Na_2O(l)$ and $B_2O_3(l)$ along with four intermediate $Na_aB_bO_c(l)$ associate species: $(1/3)Na_4B_2O_5$, $NaBO_2$, $(1/3)Na_2B_4O_7$, and $(1/5)Na_2B_8O_{13}$ are used. The formation energies for these liquid associate species provide the negative excess free energy of solution that would be needed if only components $Na_2O(l)$ and $B_2O_3(l)$ made up the liquid solution. However, liquid immiscibility is also reported for the Na_2O-B_2O_3 system. This positive interaction energy is represented in the modified associate species model by utilizing a regular solution constant for interaction between the liquid associate species that bound the composition region exhibiting immiscibility. In the case of the Na_2O-B_2O_3 system, these liquid species are $(1/5)Na_2B_8O_{13}$ and B_2O_3.

Note that all liquid associate species given above are written with formulae to have Na+B=2, which equally weights each species with regard to its ideal mixing contribution. This procedure was adopted during the optimization process when phase diagram information was being mathematically compared with thermodynamic data to obtain internally consistent sets of data for a given chemical system. It was determined that for all systems (aluminates, borates, silicates, aluminosilicates, etc.), the thermochemical data could more easily be optimized when liquid associate species contained two non-oxygen atoms per species rather than one. This procedure influences the ideal mixing energy of the solution phase, but the implications of its use are not yet fully understand. However, for very stable liquid associate species, no ideal mixing energy (ideal mixing entropy) exists at the composition of that associate since one single species makes up the entire liquid solution at that composition. This aspect of our modified associate species model produces mixing behavior identical to that of the quasi-chemical model of Pelton and Blander (Pelton and Blander, 1986; Blander and Pelton, 1987) at the composition of the one intermediate liquid species used in the latter model.

Binary and Ternary Oxide System Models

A listing of the chemical systems in which all thermodynamic and phase equilibria data have been assessed and sub-models developed are listed in Table 2. The first emphasis was on the subsystems of the Na_2O-Al_2O_3-B_2O_3-SiO_2. This system is the basis for essentially all waste glass formulations. As mentioned above, the solution energies and behavior of four-component and higher order systems are represented by combining the interaction terms for the binary and ternary subsystems since the simultaneous interaction of more than three species is unlikely to have a significant influence on this energy. Thus, the Na_2O-Al_2O_3-B_2O_3-SiO_2 solution energies are represented by interaction terms for the binary and ternary subsystems: 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, B_2O_3-SiO_2, 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.

In order to determine the effects of other oxide components, systems containing Li_2O, K_2O, MgO, and CaO have been modeled. The primary focus has been on completing the CaO-containing systems so that the generic effect of alkaline earth oxides can be determined. The Na_2O-component represents generic effects of alkali metal oxides.

Na_2O-Al_2O_3-B_2O_3-SiO_2 System Model

Utilizing the developed sub-models, an internally consistent thermodynamic and phase diagram equilibria model for the four-component Na_2O-Al_2O_3-B_2O_3-SiO_2 system has been developed. The solution data for the four-component system are represented by combining the interaction terms for the binary and ternary subsystems: 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, B_2O_3-SiO_2, 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.

The complex ternary Na_2O-Al_2O_3-SiO_2 system and its binary subsystems were focused on first. There are no previously published set of thermodynamic data that would reproduce the phase equilibria in this ternary system. In order to reproduce the binary portion of the ternary system between $NaAlSiO_4$ and SiO_2, as shown in Fig. 1, ternary associate liquid species of $(2/3)NaAlSiO_4$ (nepheline/carnegieite composition) and $(1/2)NaAlSi_2O_6$ (jadeite composition) had to be used, and the thermodynamic data for these liquid species determined. An associate liquid species with the composition of albite [$(2/5)NaAlSi_3O_8$] was not needed in the liquid solution. The nepheline/carnegieite solid state phase transition is included for the $NaAlSiO_4$ crystalline phase.

Table 2. Current Status of Model Development.

Al_2O_3-B_2O_3-SiO_2 Systems	**completed**
Al_2O_3-B_2O_3	yes
B_2O_3-SiO_2	yes
Al_2O_3-SiO_2	yes
Al_2O_3-B_2O_3-SiO_2	yes

Na_2O-(Al_2O_3-B_2O_3-SiO_2) Systems	**completed**
Na_2O-Al_2O_3	yes
Na_2O-B_2O_3	yes
Na_2O-SiO_2	yes
Na_2O-Al_2O_3-B_2O_3	yes
Na_2O-B_2O_3-SiO_2	yes
Na_2O-Al_2O_3-SiO_2	yes

K_2O-(Al_2O_3-B_2O_3-SiO_2) Systems	**completed**
K_2O-Al_2O_3	partial
K_2O-SiO_2	yes

Li_2O-(Al_2O_3-B_2O_3-SiO_2) Systems	**completed**
Li_2O-Al_2O_3	partial
Li_2O-SiO_2	partial

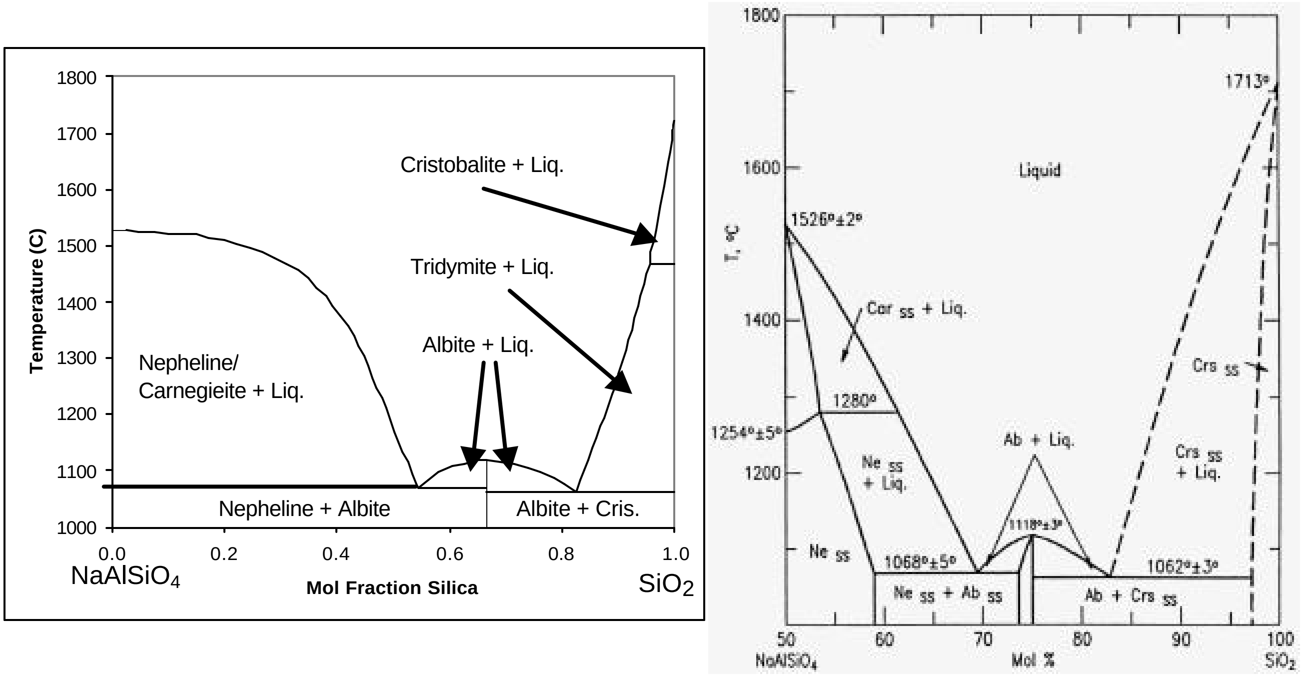
CaO-(Al_2O_3-B_2O_3-SiO_2) Systems	**completed**
CaO-SiO_2	yes
CaO-Al_2O_3	yes
CaO-Al_2O_3-SiO_2	yes

MgO-(Al_2O_3-B_2O_3-SiO_2) Systems	**completed**
MgO-SiO_2	partial
MgO-Al_2O_3	yes

(CaO-MgO)-(Al_2O_3-B_2O_3-SiO_2) Systems	**completed**
CaO-MgO	yes

(FeO-Fe_2O_3)-(Al_2O_3-B_2O_3-SiO_2) Systems	**completed**
Fe-Fe_2O_3	yes
(FeO-Fe_2O_3)-SiO_2	partial

NiO-(Al_2O_3-B_2O_3-SiO_2) Systems	**completed**
Ni-NiO	yes
NiO-Al_2O_3	yes
NiO-B_2O_3	partial
NiO-SiO_2	partial



(a) (b)

Fig. 1. (a) Computed and (b) published pseudo-binary phase diagram for the nepheline/carnegeite-albite-silica system (No. 10013 in Phase Diagrams for Ceramists).

The critical sodium borosilicate glass system, Na_2O-B_2O_3-SiO_2, has not previously been well defined in terms of thermodynamic properties. More than half of the thermodynamic data for the binary subsystems and ternary system had to be estimated and/or calculated with the use of partial phase equilibria information. The calculated binary diagram for the Na_2O-SiO_2 systems, and the activities (a_i) of liquid species at 1500°C are shown in Figs. 2 and 3. Liquid immiscibility is reported for each of the binary systems Na_2O-SiO_2, Na_2O-B_2O_3, and SiO_2-B_2O_3, and this immiscibility extends into the ternary system. The positive interaction energy is represented in the solution model by utilizing a regular solution constant for interactions between the liquid associate species that bound the composition region exhibiting immiscibility. For the Na_2O-SiO_2 system, these liquid species are (1/2)$Na_2Si_2O_5$ and Si_2O_4; for Na_2O-B_2O_3, these liquid species are (1/5)$Na_2B_8O_{13}$ and B_2O_3; for SiO_2-B_2O_3, these liquid species are B_2O_3 and Si_2O_4.

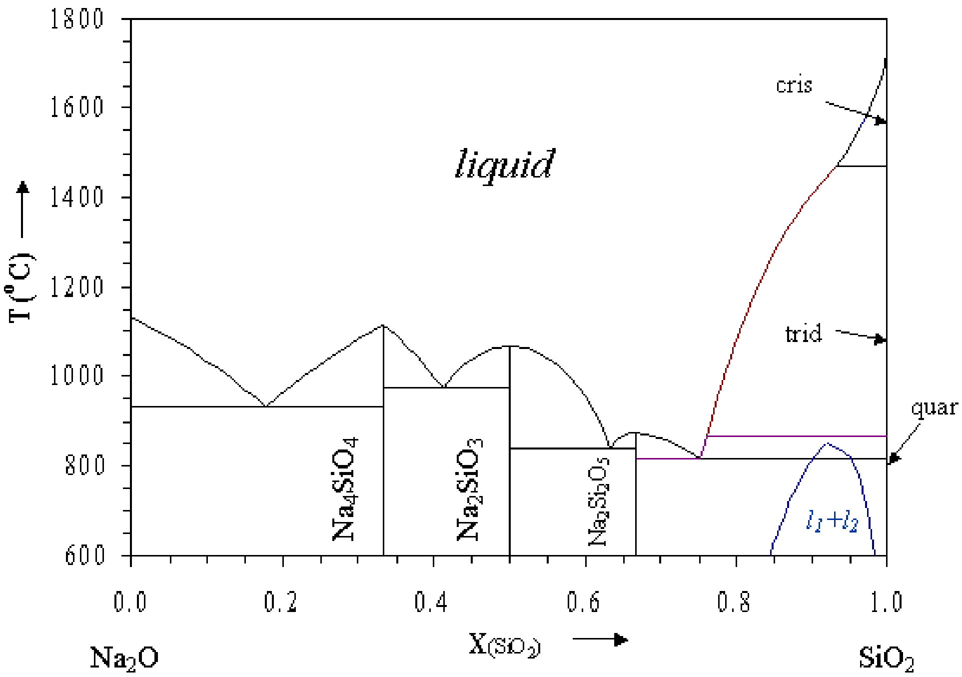


Fig. 2. Calculated Na_2O-SiO_2 phase diagram using the optimized data for this system.

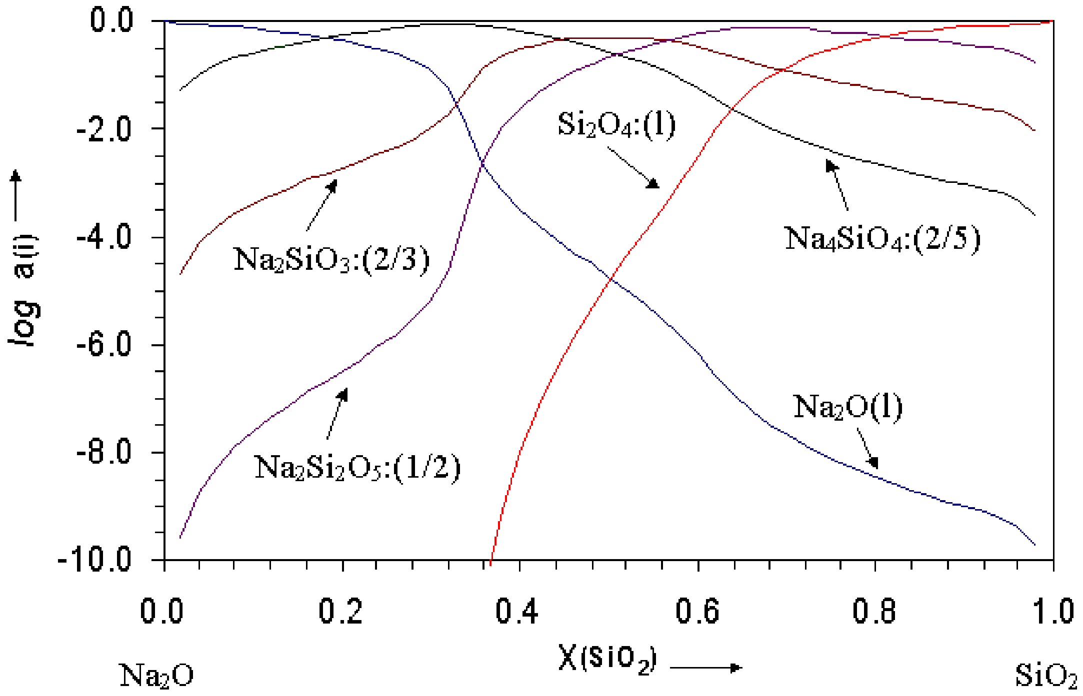


Fig. 3. Calculated Na_2O-SiO_2 liquid species activities (a_i) at 1500°C using the optimized data for this system.

Spinel-Forming Systems

Spinel precipitation (AB_2O_4 phases where A is a transition metal) has been a major problem area in HLW glass processing and storage. Thus, recent emphasis has been placed on examining FeO_x- and NiO-containing systems, with Cr_2O_3 included in future envisioned work. The influence on, for example, FeO_x activity of various composition changes in the Na_2O-CaO-Al_2O_3-B_2O_3-SiO_2-(Fe-Fe_2O_3) system can be determined only with reliable thermochemical data for the various binary and ternary combinations of oxides in this system. Critical to this is reliable data for the Fe- Fe_2O_3 system. A set of data has been developed which will calculate the basic phase equilibria for the Fe-Fe_2O_3 system, except for the FeO solid solution range, which was not modeled. This now provides the necessary reliable data for the liquid Fe-Fe_2O_3 compositions for the glass solution phases. Critical to the accuracy of the model of this system was that calculated oxygen partial pressures as a function of temperature for the Fe-FeO, FeO-Fe_3O_4, and Fe_3O_4-Fe_2O_3 two-phase regions were in agreement with the well-established values.

Experimental Studies of the B_2O_3-U(VI) Oxide System

Experimental studies have been conducted on the uranium oxide-boron oxide (B_2O_3) system. The region of interest for waste glass is the boron oxide-rich side of mixtures with U(VI) oxide. Little is known about this system, with one compound known to exist: uranyl borate, $UO_2(BO_2)_2$, which may also be expressed as $UO_3 \bullet B_2O_3$. Differential thermal analysis (DTA) was used to determine phase and crystalline transitions for samples in this system.

The initial components were B_2O_3 and U_3O_8. These react in air to form uranyl borate:

$$U_3O_8 + 3\,B_2O_3 + \tfrac{1}{2}\,O_2 \rightarrow 3\,UO_2(BO_2)_2$$

Table 3 gives the heating schedule used in the DTA studies and Table 4 lists the transitions above 450°C, the melting point of B_2O_3. The first transition is at 795°C and most likely represents a crystalline transformation of $UO_2(BO_2)_2$, and the second transition near 1100°C is its decomposition temperature.

Table 3. Differential thermal analysis heating schedule.

Step	Ramp Rate
1st step	300°C/h from 50 to 350°C, with a 1 h hold at 350°C
2nd step	120°C/h from 350 to 1260°C
3rd step	500°C/h from 1260 to 90°C, with a 24 h hold at 90°C

Table 4. Transition Temperatures (^{o}C) for B_2O_3 - UO_3 System

Mol % UO_3	1st Transition	2nd Transition
0.75	770 ?	1100
1.34	800 ?	n/o*
8.1	795	1096
13.9	795	1097
35.8	795	1105
39.7	795	1105

*Not observable

At the lowest concentrations, transitions became difficult to determine accurately; those indicated by "?" being particularly uncertain.

The standard free energy of formation (ΔG^{o}_{T} in kJ/mol) for $UO_2(BO_2)_2$ was estimated from its decomposition temperature and its hydrolysis as:

$$\Delta G^{o}_{T} = 2.52 \times 10^{3} + 5.17 \times 10^{-1} T$$

Uranyl borate forms slowly at temperatures below ~ 1000^{o}C. Tests with bulk samples heated at 930^{o}C for a day failed to produce the compound. In the DTA studies, a yellow-green product formed after the samples were cycled through a heating-cooling cycle. Thus, the transitions reported in Table 4 were obtained on the second or third heating-cooling cycle. Some weight loss was observed during these cycles. This is attributed to volatilization of B_2O_3. The mol % figures in Table 4 are corrected for this loss. Figure 4 depicts the partial phase diagram that can be derived from this data. The position of the liquidus is conjectural, and included for illustrative purposes.

For waste applications involving sequestration of uranium, a wide range of solubility of UO_X is desirable, and the transition to a two-phase region (i.e, liquid + crystal) should occur at a sufficiently low temperature such that the liquid transitions to glass before entering the two-phase region. That is not the case in this system, where the liquidus boundary (sketched as a dashed line at the left of the diagram) lies somewhere below 0.75 mol% UO_3. Alternatively, if the kinetics of crystal formation is sufficiently slow, the liquid may solidify to a glass before crystal formation occurs. The kinetics of formation of the crystalline phase were fairly slow in the composition region explored, but on balance, the low solubility limit and limited stability region made this system appear unpromising. For this reason, the system was extended to include Na_2O.

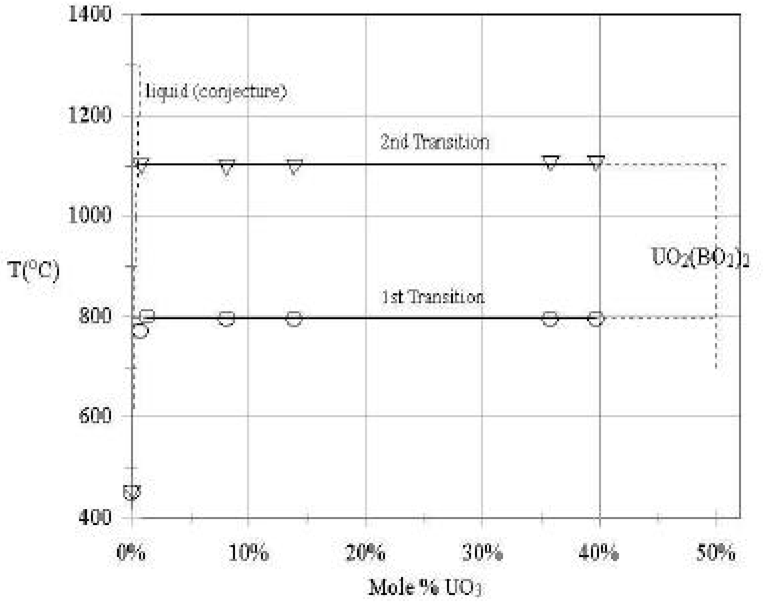


Fig. 4. Experimentally determined partial phase diagram for the UO_3-B_2O_3 system.

Experimental Studies of the $Na_2B_4O_7$ - U(VI) Oxide System

Thermodynamic calculations indicated that the addition of Na_2O to the system would lead to stabilization of uranium oxides. In the calculations, this took the form of formation of more stable adducts of Na_2O, B_2O_3, and UO_3 from an initial mixture of Na_2O and those compounds stable in the B_2O_3 - UO_3 system. It was considered plausible that the same trend would carry over into liquid or glass phases.

There is very little information in the literature on the Na_2O - B_2O_3 - UO_3 system. One compound has been reported ($Na_2B_2U_2O_{10}$) which decomposes at 1100°C. Infrared, visible and Raman spectroscopy has been performed on a glass with the composition 2 mol % UO_3, 98% $Na_2B_4O_7$ (Hoekstra, 1967). Ciric (1961) mapped composition regions observed to form glasses, mixed glass and crystalline solids, and pure crystalline phases from melts composed of Na_2O, B_2O_3, and UO_2 (Culea et al, 1971). Figure 5 shows the known compounds in this system, as well as the approximate boundary of Ciric's glass-forming region. Also indicated are four compositions examined in the experiments reported here.

Ciric's report (1961) suggests that in a UO_2 / $Na_2B_4O_7$ mixture, UO_2 loadings up to about 40 wt % (31 mole % UO_2) may be possible without the precipitation of crystalline phases on cooling. Since higher uranium loadings are of greater technological interest, compositions between about 15 and 45 mole% UO_3, (the balance being $Na_2B_4O_7$) were targeted for examination. In the presence of oxygen, the initial uranium oxide is likely, on thermodynamic grounds, to convert to its stable form during sample preparation, probably UO_3.

Preliminary experiments were performed on two compositions (15 and 25 mol %). This was extended to three further sets of samples at compositions of 25, 35 and 45 mole %. Samples were characterized by DTA and by XRD. Scoping tests were done with the goal of examining the solubility of the higher-loaded compositions in aqueous media of widely varying pH. Sample preparation details are contained in Table 5. After preparation, the samples from both series visually appeared to be glassy and homogeneous.

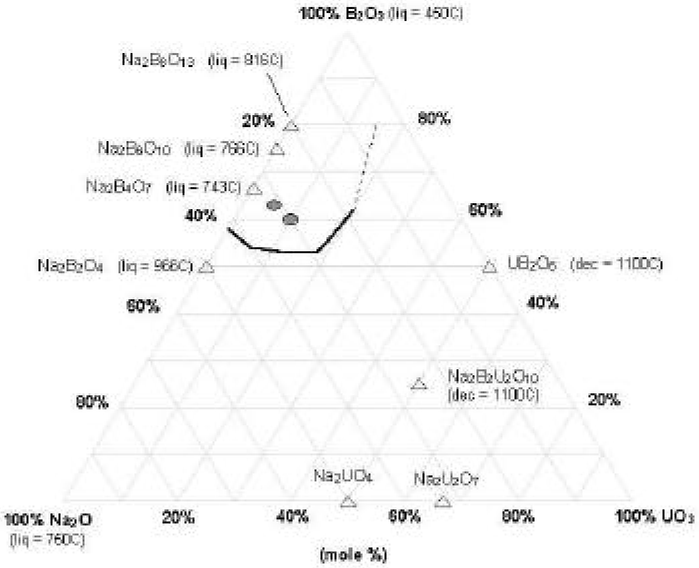


Fig. 5. Circles represent glass samples prepared in this work and triangles are known crystalline phases. The line encloses the region determined by Ciric (1961) in which glass forms during cooling.

Table 5. Aqueous test sample series description

Mix No.	Sample numbers	UO_3	$Na_2B_4O_7$	UO_3	$Na_2B_4O_7$
		mol %	mol %	gm	gm
I	1,2,3,4	25.1%	74.9%	0.3234	0.6784
II	5,6,7,8	35.0%	65.0%	0.4337	0.5666
III	9,10,11,12	45.0%	55.0%	0.3997	0.3436

Following sample preparation, a third heat-up was conducted on samples 99-a, 99-b, and 99-c, this time to 1262°C at 120°C/h, during which a DTA study was conducted. The 15% sample appeared to exhibit transitions at 410 and 1130°C, plus a strong transition of indistinct onset between 800 and 850°C; the 25% samples indicated transitions at 660, 880, and 1155°C.

One sample of each of mixtures I, II and III was examined by TGA and DTA. TGA/DTA scans were done in a 20% O_2 / 80% N_2 mixture. The samples were heated at approximately 140 $^oC/h$ up to 1265^{o}C. TGA traces showed that all samples experienced a slight weight loss in the temperature range 100 to 250^{o}C and again above 1100^{o}C. The DTA traces showed a modest endothermic response to the higher temperature weight loss (as one might expect). In addition to that response, several transitions were observed in the DTA trace. The temperatures of these transitions are listed in Table 6. Meaningful interpretation of these transitions will require further observations and characterization.

Table 6. DTA transitions

Sample	mole % UO_3	Transition temperatures (^{o}C)
99-c	15%	410, 800-850(broad), 1130
99-a	25%	660, 880, 1155
I-4	25%	720 , 950 (weak) , 1210
II-8	35%	730 , 987 (weak) , 1140
III-12	45%	738 , 950 (weak) , 1211

X-ray diffraction was performed on a subsample of 99-a (one of the 25% samples) prior to the high-temperature heat-up and again after the high-temperature exposure. An automated spectral library search of the results both before and after the high temperature exposure suggested the presence of $Na_2U_2O_5$, $NaUBO_5$, and possibly UO_2, UO_3, and U_3O_8. Post heat-up samples showed increased $Na_2U_2O_5$ and uranium oxide content. The XRD identifications suggest both U(IV) and U(VI) compounds in the material as well as the presence of at least some crystalline phase, in spite of the overall glassy appearance of the material. This may indicate that the overall formula was outside the glass-forming region for the temperature program used or, alternatively, it could simply reflect dissolution kinetics.

One sample from each composition of the later series was also examined by X-ray diffraction. The diffraction data was obtained with a Siemens D5005 XRD unit. The X-ray source utilized the Cu Kα line (0.154 nm). Samples examined were those numbered I-4, II-8, and III-12 (nominally 25, 35 and 45 mole % UO_3). XRD was performed after they had been subjected to TGA/DTA, during which they which reached temperatures of 1265^{o}C. Samples I-4 (25%) and II-12 (45%) showed only very weak diffraction patterns, indicative of largely amorphous samples with possibly very minor crystalline inclusions. Sample II-8 (35%) showed no diffraction lines. Diffraction lines observed for I-4 and III-12 are indicated in Table 7. Relative intensities of the lines observed are also listed, but it should be noted that in an absolute sense, all these lines were very weak, some barely above the background noise level of the XRD spectra. Interferences from considerably stronger lines from the sample holder were removed by spectral subtraction. The strongest line in both samples fell in the vicinity of such a background line, but seemed to be present after subtraction. The other lines listed in Table 7 did not have such interferences. Comparison of these lines with reference patterns for plausible oxide compounds of uranium, boron, and sodium showed resemblances, but no definitive match. The conclusion to be drawn from the X-ray diffraction analysis is that samples 4 and 12 had only minimal crystalline content and 8 appeared completely amorphous.

Table 7. X-ray diffraction data for samples I-4 and III-12.

Sample number	d (Å)	relative intensity	note
I-4 (25% UO_3)	4.436	0.2	
	4.168	0.3	
	3.517	1.0	a
III-12 (45% UO_3)	3.517	1.0	a
	2.665	0.8	
	1.932	0.4	

[a] a peak due to the sample container interfered; value shown is the residual after spectral subtraction.

Scoping tests were performed on the solubility in aqueous media of the later set of glasses. The solution was analyzed by ICP to determine the quantity of B and U that had gone into solution. Results for each sample are listed in Table 8.

Table 8 - Solubility test results. The fraction in the solvent is the fraction in the sample that appeared in the solution phase.

Formula (note 1,2)	**Sample ID**	**Sample mass** (g)	**Solvent**	**Conc. in solvent**		**Fraction in solvent**	
				U (wt. ppm)	**B** (wt. ppm)	**U**	**B**
I	1	0.1975	1M HNO_3	1627	6783	1.53%	11.80%
II	5	0.2003	1M HNO_3	5690	2188	3.94%	4.49%
III	9	0.2064	1M HNO_3	4111	3711	2.23%	9.05%
I	3	0.1936	water		(note 3)		
I	4	0.0533	water	1067	8636	3.73%	55.67%
I - h	4-hb	0.0372	water	383	164	1.91%	1.51%
II	7	0.204	water	665	5812	0.45%	11.70%
II - h	8-h	0.064	water	0	384	0.00%	2.46%
III	11	0.2082	water	1178	11324	0.63%	27.38%
III - h	12-h	0.0363	water	29	356	0.09%	4.94%
I	2	0.2079	1M NaOH	69	5379	0.06%	8.89%
I - h	4-ha	0.0611	1M NaOH	0	7658	0.00%	43.07%
II	6	0.2049	1M NaOH	82	5611	0.06%	11.25%
III	12	0.1033	1M NaOH	42	13398	0.05%	65.28%

(note 1) Types I, II, and III are nominally 25, 35 and 45 mol % UO_3, respectively
(note 2) "h" indicates sample used after TGA heat treatment (1260°C)
(note 3) Formed a 3-part gel -- not further analyzed

These solubility tests were intended to very roughly scope the solubility behavior of some of the higher U-loaded glasses. Some general observations to be drawn from the solubility tests are:

(1) Most samples did not dissolve congruently. That is, a larger proportion of B ended up in solution compared to U. This could lead to elemental separation during solution and concentration of U in the undissolved residue. This was particularly true of solubility in alkaline solution, in which at least two orders of magnitude separated the U and B fractions dissolved.

(2) U-Solubility (not surprisingly) decreases in going from acid to neutral to basic solution.

(3) The as-prepared samples exhibited solubilities in the thousands of ppm (U/solvent) in acid; generally less in water; and under 100 in alkaline solution. B-solubility did not vary a great deal with pH among the as-prepared samples, being in the high thousands of ppm.

(4) Samples exposed to the higher temperatures during TGA (up to 1260° C) were less soluble, U in two cases being undetectable in the solvent and considerably reduced in the other two cases. B-solubility in the high temperature-exposed samples was lower by more than an order of magnitude when compared to the corresponding lower-temperature prepared samples.

(5) There did not appear to be a striking difference in the solution behavior across the three compositions examined, though the highest U-concentration set (III, 45 mole % UO_3) tended to yield the largest solubility of boron in neutral or alkaline media.

Modeling Nepheline Precipitation in HLW Glass

A problem identified at PNNL is the precipitation within certain compositions during the cooling of glass of a nepheline phase ($NaAlSiO_4$), which weakens the network structure by removing the glass formers Al_2O_3 and SiO_2. The result is that nepheline precipitation in HLW glass limits waste species loading. It has been observed that compositions rich in Al_2O_3 and Na_2O are particularly prone to precipitating nepheline (Li et al., 1997). Based on a request from TFA researchers at PNNL this issue was addressed using the modeling capability.

The rapid kinetics of nepheline formation in the cooling glass suggests that an equilibrium thermodynamic model may provide useful insights with regard to the compositional parameters governing its precipitation. As a result, the thermochemical model for the Na_2O-Al_2O_3-B_2O_3-SiO_2 crystalline and glass system developed in the current work was applied to the assessment of this problem.

It has been observed that the precipitation of nepheline occurs during glass cooling in the absence of other crystalline phases (Li et al., 1997). It is thus possible to model this behavior utilizing pseudo-equilibrium calculations in which nepheline and the glass/liquid phase are the only phases allowed to form, with all other crystalline phases prevented from being present. The thermochemical computations, therefore, would indicate either the glass alone is present, or the glass is present in equilibrium with nepheline.

Utilizing the ChemSage™ 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. 6 with the binary oxides and the nepheline compositions indicated.

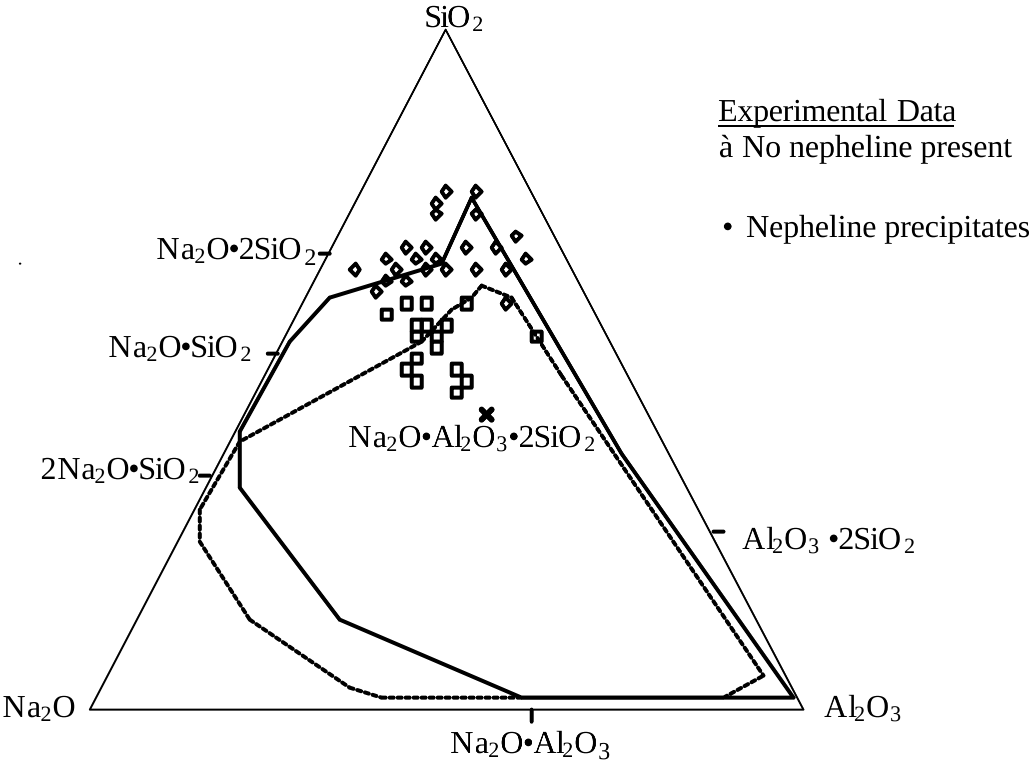


Fig. 6. Ternary Na_2O-Al_2O_3-SiO_2 phase space (wt. %) showing the computed stability region for nepheline plus the glass phase at 800°C with no boria (━━) and 30 wt.% boria (╍╍╍) along with experimentally determined precipitation data (Li et al., 1997).

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 are also shown on the diagram, and agree reasonably with the results of the calculations. In the experimental work a variety of boria contents were used which span the 0-30 wt.% range, however, the Na_2O-Al_2O_3-B_2O_3-SiO_2 system also contained other components representative of practical waste compositions such as Li_2O, K_2O, CaO, and Fe_2O_3. Similar calculations were performed for the system at 600°C, and in that case the stability range for nepheline moved to higher silica contents, having a maximum on the ternary diagram of 90 wt.% silica without boria and 75 wt.% silica with 30 wt.% boria.

To aid in controlling nepheline precipitation it is useful to know the temperature at which the phase will form. Figure 7 is a plot of the calculated formation temperatures in the presence of the glass phase over the nepheline-albite ($NaAlSi_3O_8$) compositional range. The calculations were performed with no boria present and with 30 wt% boria, with and without other phases allowed to form. The boria content can be seen to substantially reduce the formation temperature, with the potential presence of other phases not having a significant effect.

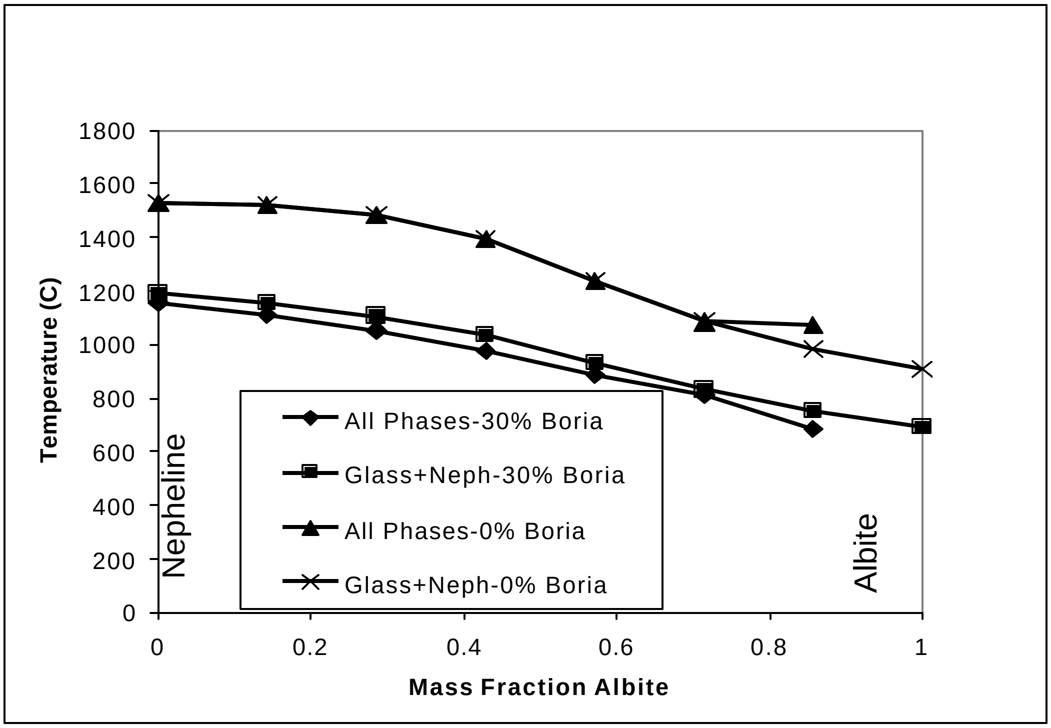


Fig. 7. Formation temperature for nepheline with no boria and 30 wt% boria, assuming all phases can form or only the glass and nepheline.

The amount of nepheline expected to form under the pseudo-equilibrium conditions also varies with composition. Utilizing the thermochemical computations the amount of the glass and nepheline phases predicted can be determined under any set of conditions. Figure 8 contains plots of the phase amounts at 800°C with no boria present and with 30 wt% boria for a low silica (55 wt%) and a high silica (65 wt%) content. Note that for simplicity in presentation the non-boria constituents are fixed to add to 100 wt%, and the Na_2O content is thus the difference of the sum of the Al_2O_3 and SiO_2. As expected from the phase relations, both higher boria and higher silica results in lower nepheline amounts.

The liquidus curves for waste compositions have a direct influence on glass processing and the likelihood of second phase precipitation, such as that of nepheline. Equilibrium calculations were performed over the compositional region between nepheline and albite assuming all phases in the system can form. The resulting liquidus temperatures were plotted for compositions with 10 wt% and 30 wt% boria (Fig. 9). Over this region the effect of boria content is small, with the liquidus temperature varying smoothly from the nepheline melting point to that for the albite. At melting in the 10 wt% boria system the phase present with the liquid is nepheline at low albite compositions and the $Al_6B_{1.33}O_{11}\bullet Al_6Si_2O_{13}$ solid solution at high albite compositions. In the 30 wt% boria system the solid solution phase is in equilibrium with the liquid over the entire compositional range.

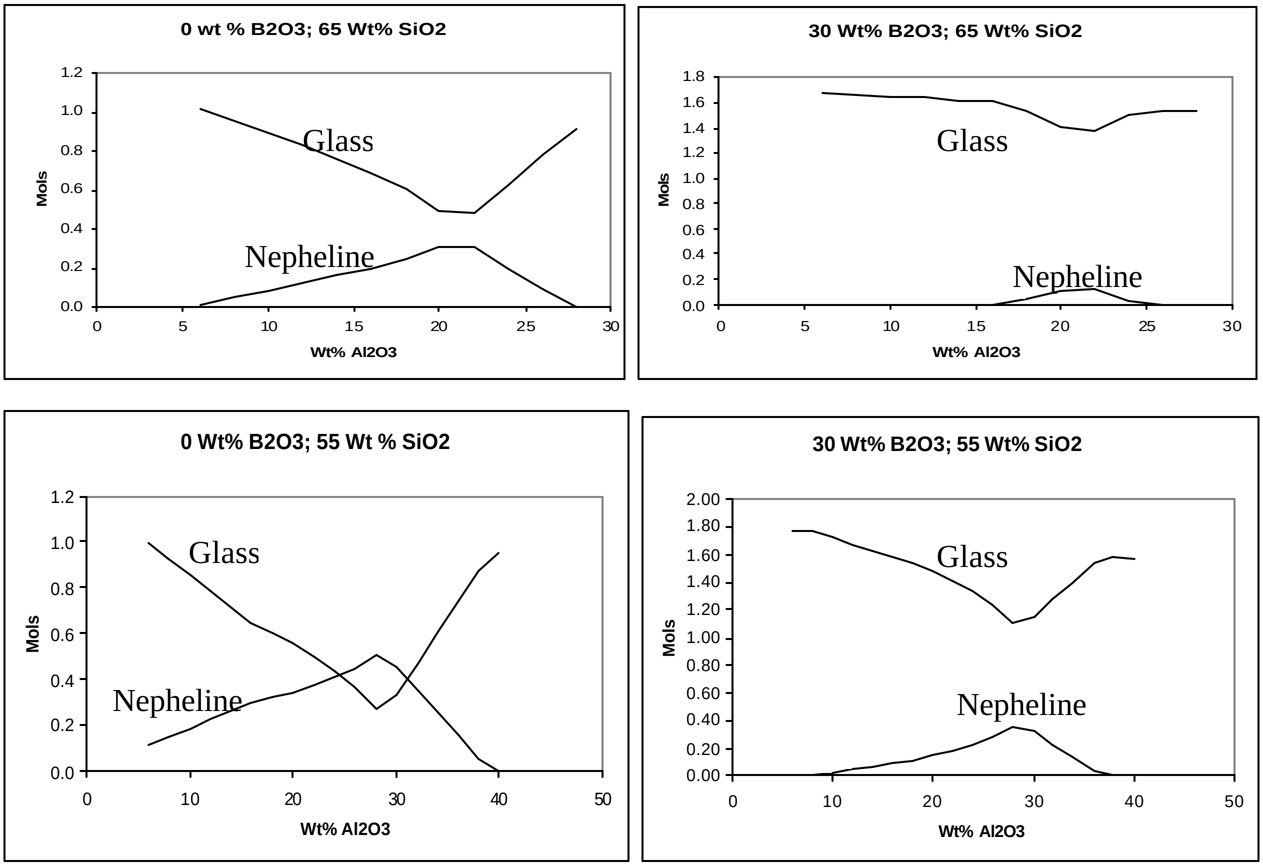
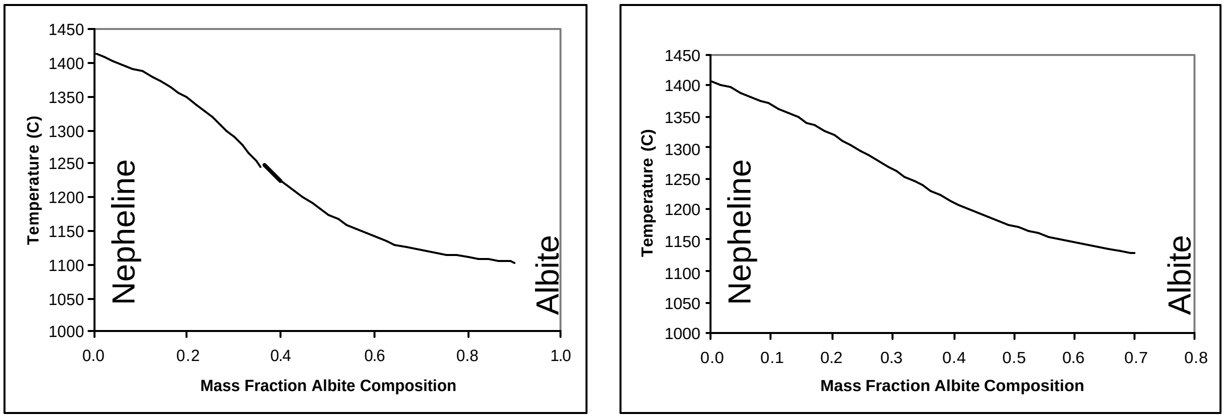


Fig. 8. Amount of nepheline and glass computed to form at 800°C as a function of composition.

The predicted stability region for the formation of nepheline can have a significant influence on waste glass compositions. From the current work it is apparent that nepheline formation can be avoided by utilizing compositions high in silica and boria. In addition, even within the nepheline formation region, the amount of nepheline can be suppressed by higher silica and boria contents. The effect of these components on nepheline formation is directly related to lowering the activity of Na_2O in the glass phase, restricting the sodium available to form nepheline.



(a) (b)

Fig. 9. Liquidus curves for (a) 10 wt% boria and (b) 30 wt% boria.

Reducing the liquidus temperature can also aid in controlling nepheline formation and content. Compositions with lower nepheline formation temperatures are less likely to actually form the phase during cooling of the glass since at the lower temperature kinetics will be slower.

These results are in general agreement with experimental observations. It is expected that they will also provide guidance in the development of waste formulations that can avoid or minimize the detrimental formation of crystalline nepheline inclusions in glass that can occur during waste canister cooling.

Relevance, Impact, and Technology Transfer

The research performed in this EMSP project has fundamental importance for the treatment and disposal of both HLW and LAW – two major EM mission areas. This research serves at least three U.S. DOE sites: Hanford, Savannah River, and INEEL.

For HLW treatment and disposal, the results of the research will aid in optimizing waste glass compositions, increasing waste loading, improving models for plant operation and waste form acceptance, and possibly decreasing testing requirements. A number of published site needs refer to the necessity for a better understanding of the effects of composition, temperature, and oxygen partial pressure on key glass properties such as liquidus temperature, component solubilities, and glass durability.

The project has helped fulfill the need for improved models for liquidus temperature due to the current high level of uncertainty of liquidus temperature models, which is also a TFA need. (Supports EM Need ID: SR00-2032, “Optimize Melter Glass Chemistry and Increase Waste Loading.") An application of the model to investigate crystalline phase formation in HLW glass was the subject of a TFA Highlight. The HLW glass model was also applied to the issue of nepheline phase precipitation in PNNL glass formulations and has indicated compositional and temperature regimes which minimize the problem (Besmann et al., 2000). A second area is related to constraints on durability models which can cause acceptable glasses to be rejected. The applicability of current models is uncertain leaving durability indeterminate. (Supports EM Need ID: ID-2.1.58, “HAW Immobilization,” and Need ID: RL-WT066, “Compositional Dependence of the Long Term Performance of Glass as a Low-Activity Waste Form.”) This is, in part, the impetus for the expressed EM need for investigations of the fundamental chemistry of key waste components. Of perhaps lesser importance are issues of species volatility during melter operations and corrosion of melter components and related equipment. Accurate models of waste glass can be a major contributor to resolving all of these issues.

The model and methodologies can also be extended to other, similar problems identified in TFA, such as determination of immiscibility boundaries in many-component glasses. “These have been looming problems for many years in waste glass development” (Vienna, 2000). According to Marra (2000) of the Savannah River Site, the main issue for DWPF glass waste is the limited operating region and the need to maximize waste loading. For example, the current homogeneity constraint is designed to avoid regions of phase-separated glass. The constraint, however, is believed to be overly conservative and limits the design of waste glass formulations and waste loading. The EMSP effort included consideration of immiscible liquids, and therefore should be helpful in predicting phase-separated glass formation.

A significant contribution of the project also lies in substantially improving the reaction path information for codes such as ESP used in modeling geochemical behavior and transport of leached species.(Rafal et al., 1994) The current approach is to assume the waste components are simple oxides having unit activity (i.e., present as the individual oxide material undissolved in the host material) or, at best, an ideal solution. Such assumptions can lead to gross overestimates of leaching behavior since radionuclides dissolved in glass are almost certainly effected by the energetics of interactions between dissolved components. The lack of realistic reaction path information and subsequent overestimates of leaching behavior for specific waste glass systems can lead to the discarding of promising formulations that would have substantial advantages (e.g., higher loading).

A number of waste form constituents are relatively volatile at elevated temperature, including cesium and other alkali metals. Although the waste form, after processing, is not expected to experience temperatures that would volatilize significant amounts, understanding the composition-vapor pressure relationships would provide base-line safety analysis information. In addition, such information may allow processing temperature profiles to be profitably modified to accomplish similar goals with reduced loss of the volatile metals, thus requiring a lower capacity recovery system.

The associate species model has important implications for the crystal and defect chemistry of ceramic systems. The associate model assumes that complex oxide species containing two or more metals can represent the strong interactions of the binary end members. Equilibrium, ideal solution calculations which include these complex species will give an indication as to their importance through their computed activities. Complex species with higher activities may provide indications of strong binary interactions, and thus the possible precipitation of new phases. This, in turn, provides insight with regard to bonding in glass systems. Such information can provide direction for study of the association and bonding of these binary, glass constituents. These studies add to the understanding of glass bonding and stability, which remains largely inadequate, and to the crystal chemistry of complex ceramic systems with a number of dissolved constituents.

The research on complex waste glass forms can have many technological spinoff benefits for other government and industrial materials programs. Chemical interactions at interfaces in glass matrix composites critically determine their properties and usage lifetimes. These interactions can be tailored by "alloying" the glass. Thermochemical modeling of the interactions has proven very effective in designing optimum glass compositions.(Qi et al., 1993; Pantano et al., 1993; Spear et al., 1987a,b) An example of a problem to which the model has already been applied is the corrosion of refractories in glass melting tanks (Allendorf and Spear, 2001). As glass compositions become more and more complex, like alloy systems, understanding and predicting the chemical interactions between the glass and its container and environment becomes much more difficult. The use of complex associate species to represent the thermodynamic properties of the glass will greatly enhance the ability to model these interactions.

A good foundation has been established by the development of the solution model for the alkali-alumino-borosilicate glass system, which forms the basis of the glasses proposed for immobilization of Hanford low activity waste (LAW) and HLW, INEEL sodium-bearing waste (SBW) and calcine waste, and Savannah River HLW. This basic model showed good correlation with experimental data from multi-component waste glasses. What truly hindered initial progress was the surprising inability of existing thermochemical data for the basic Na_2O-Al_2O_3-B_2O_3-SiO_2 system to properly reproduce experimental phase equilibria. Thus, although much effort was therefore expended on remedying this situation, the result is now a very accurate model for this very important system.

Technology transfer to EM activities has been through interactions with PNNL staff. Periodic teleconferences and meetings at conferences, plus a meeting at PNNL, has resulted in PNNL acquiring an thorough understanding of the EMSP activity. In addition, PNNL staff have provided guidance with regard to problems of particular interest, such as nepheline precipitation.

The EMSP project had very significant effects beyond the confines of the program. The models developed for glass were subsequently used to solve a very costly problem in the corrosion of refractories for glass production (Allendorf and Spear, 2000). The effort resulted in another laboratory, Sandia National Laboratories – Livermore, to become conversant in the techniques and to apply those through a DOE Office of Industrial Technologies project. The glass industry as a whole is now cognizant of these capabilities, and there is a Glass Manufacturer’s Research Institute proposal in this area that will likely be supported. In addition, individual glass companies are inquiring as to modeling work at ORNL.

Project Productivity

The EMSP project has been substantially successful in modeling the base glass composition of envisioned HLW glass. Sub-models having a total of 11 components have been created that accurately represent the thermochemical and phase equilibria of the systems. Significant efforts were required to estimate and modify data for a number of systems where current information failed to be internally consistent. The project, therefore, has also provided basic scientific information on a set of important chemical systems. The model of the Na_2O-Al_2O_3-B_2O_3-SiO_2 system has been used to predict liquidus and other critical information. It has also demonstrated that it can aid in solving problems such as the precipitation of crystalline nepheline in cooling HLW glass, which was addressed at the request of a group in the TFA program and has been the subject of a TFA Highlight. Lastly, experimental studies have provided important information on the phase equilibria of the Na_2O-B_2O_3-UO_3 system, for which little appears in the literature.

Work that remains to be performed, and which it was hoped could have been performed in the project, includes the expansion and extension of the model to allow for the prediction of key glass/melt properties. The loading of waste in glass is typically determined by the solution behavior of a few, relatively minor, components, the modeling of which could not be accomplished under the current program due to lack of time and resources. For example, the loading of Savannah River HLW in glass is ultimately determined by model constraints for homogeneity and liquidus temperature, the loading of Hanford LAW in glass will be determined by sulfur solubility and resultant durability, the loading of Hanford HLW in glass will be determined by chromium, zirconium, manganese, nickel, and phosphorus species solubilities (roughly in that order), the loading of SBW in glass will be determined by sulfur and phosphorus solubilities and durability, the loading of INEEL calcine HLW in glass will be determined by the solubilities of fluorine, phosphorus, zirconium, calcium, and molybdenum species. The solubilities of these key components in the basic alkali-alumino-borosilicate melt/glass are functions of glass compositions, temperature, and oxygen partial pressure. The associate species model needs to be expanded to include these key waste components thereby yielding a tool to relate the state functions (composition, pressure, and temperature) to the activity of components in solution.

TFA Highlight

Accomplishments of the EMSP project were recognized as a "highlight" for the Tanks Focus Area.

TANKS FOCUS AREA (TFA) TECHNICAL HIGHLIGHTS
PERIOD ENDING OCTOBER 31, 1999

TFA/EMSP MODELING EFFORTS CONFIRM GLASS EXPERIMENTS (TMS 2009)
Throughout the DOE complex, vitrification is the preferred method for immobilizing high-level waste (HLW) in a form suitable for final disposal. One of the goals of TFA's immobilization activities is to increase the amount of waste that is loaded into HLW glasses, thereby reducing the number of storage

canisters needed, leading to reduced life-cycle treatment and disposal costs.

At Oak Ridge Reservation (ORR), the Environmental Management Science Program (EMSP) project "Stability of High-Level Nuclear Waste Forms" is developing a thermochemical model of waste glass formulations. Recent modeling efforts at Oak Ridge National Laboratory (ORNL) focused on the effect of boron oxide on the formation of a crystalline phase nepheline (NaAlSiO4) in HLW glasses. A thermochemical model of glass was exercised to determine the phases over which nepheline would co-exist with the glass, using compositions with no boron oxide and those with 30 wt% boron oxide. A significant trend in the computations, confirmed by previous observations at Pacific Northwest National Laboratory, indicated the stability region for nepheline shifted to lower silica contents with the presence of boron oxide. Additionally, increased boron oxide content in the glass substantially reduced the amount of nepheline formation, even in thermochemically stable regions. Thus, the model results are consistent with experimental observations, and explain those observations.

EMSP work on glass formulations relates to TFA's "Waste Loading Optimization" task, which identified that precipitation of nepheline during the cooling of waste glass is a significant problem (nepheline precipitators within the glass decrease glass stability, leading to high leach rates). The model described above may be predictive with regard to nepheline effects, and also aid in identifying optimal glass compositions for waste glass. This has significant consequences for maximizing waste loading at the Hanford Site. (Contact: Bill Holtzscheiter, WSRC, 803-725-2170)

Personnel Supported

Theodore M. Besmann, Oak Ridge National Laboratory

Lee D. Trowbridge, Oak Ridge National Laboratory

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William Wolf, Pennsylvania State University

Publications

All articles were in peer-reviewed journals or peer-reviewed proceedings.

T. M. Besmann, K. E. Spear, and E. C. Beahm, “Assessment of Nepheline Precipitation in Nuclear Waste Glass via Thermochemical Modeling,” pp. 715-720 in Scientific Basis for Nuclear Waste Management XXIII, ed. R. W. Smith and D. W. Shoesmith, Mater. Res. Soc. Symp. Proc. Vol. 608, Materials Research Society, Pittsburgh, PA (2000).

K. E. Spear, M. N. Palmisiano, C. G. Pantano, T. M. Besmann, and E. C. Beahm, “Surface Modification of Glass by Vaporization Reactions,” Proc. Vol. 98-23, Fundamental Gas-Phase and Surface Chemistry of Vapor-Phase Materials Synthesis, (T. J. Mountziaris, M. D. Allendorf, K. F. Jensen, R. K. Ulrich, M. R. Zachariah and M. Meyyappan, eds.), The Electrochemical Society, 65 South Main St., Pennington, NJ (1999).

K. E. Spear, T. M. Besmann, and E. C. Beahm, “Thermochemical Modeling of Glass: Application to High-Level Nuclear Waste Glass,” 10th International Conference on High Temperature Materials Chemistry (HTMC X), Julich, Germany, April 11, 2000.

K. E. Spear and Mark D. Allendorf , "Mechanisms of Silica Refractory Corrosion in Glass-Melting Furnaces: Equilibrium Predictions," High Temperature Corrosion and Materials Chemistry: Per Kofstad Memorial Symposium (M. McNallan, E. Opila, T. Maruyama, and T. Narita, eds.), Proc. Vol. 99-38, The Electrochemical Society, Pennington, NJ, (2000), pp. 439-448.

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B. S. Thesis – Pennsylvania State University

William Wolf (advisor: Karl E. Spear), B. S. Thesis in Ceramic Science and Engineering, May 1999, “Thermodynamic Analysis of the Phase Equilibria in the CaO-Al_2O_3 and CaO-SiO_2 Systems.”

Interactions:

Presentations

“Thermochemical Modeling of High-Level Nuclear Waste Glass and Related Solid Solutions,” T. M. Besmann, L. D. Trowbridge, and K. E. Spear, 103rd Annual Meeting and Exposition of the American Ceramic Society, April 22-25, 2001, Indianapolis, Indiana.

“Prediction of Crystalline Phase Precipitation in High-Level Nuclear Waste Glass,” T. M. Besmann, L. D. Trowbridge, and K. E. Spear, 102nd Annual Meeting and Exposition of the American Ceramic Society, April 30- May 3, 2000, St. Louis, Missouri.

“Thermochemical Modeling of High-Level Waste Glass and Application to Waste Form Stability,” T. M. Besmann, E. C. Beahm, L. D. Trowbridge, and K. E. Spear EMSP National Workshop, April 24-27, Atlanta, Georgia.

“Assessment of Nepheline Precipitation in Nuclear Waste Glass via Thermochemical Modeling,” T. M. Besmann, E. C. Beahm, and K. E. Spear**,** Materials Research Society, Nov. 29- Dec. 3, 1999, Boston, Massachusetts.

“Solid Solution Thermochemical Models for Phase Systems in High-Level Nuclear Waste Glass,” T. M. Besmann, E. C. Beahm, and K. E. Spear, 101st Annual Meeting and Exposition of the American Ceramic Society, April 25-28, 1999, Indianapolis, Indiana.

“Thermochemical Models for Liquid Solutions in Nuclear Waste Glass Subsystems,” T. M. Besmann, E. C. Beahm, and K. E. Spear**,** Materials Research Society, Nov. 30- Dec. 4, 1998, Boston, Massachusetts.

“Thermodynamic Approach for Modeling High Temperature Interface reactions with Glass,” Annual Meeting of the Society of Glass Technology, North American Section, Penn State, University Park, PA, Karl E. Spear and Carlo G. Pantano, Sept. 12, 1997.

“An Approach to Thermochemical Modeling of High-Level Nuclear Waste Glass,” 100th Annual American Ceramic Society, Cincinnati, OH, T. M. Besmann, E. C. Beahm, and K. E. Spear, May 6, 1998.

“A Thermochemical Modeling of Nuclear Waste Glass,” 193rd Meeting of The Electrochemical Society, San Diego, CA, K.E. Spear, T. M. Besmann, and E. C. Beahm, May 7, 1998.

“Thermochemical Modeling Applied to Advanced Materials Behavior,” Seminar, Physical and Chemical Properties Division, National Institute of Standards and Technology, Gaithersburg, MD, Karl E. Spear, May 20, 1998.

“Thermodynamic Analysis of the Tin Penetration Profile in High-Iron Float Glass,” The International Congress on Glass, San Francisco, CA, Thomas E. Paulson, Karl E. Spear and Carlo G. Pantano, July 1998.

“A Thermochemical Modeling of Nuclear Waste Glass,” Symposium on High Temperature Corrosion and Materials Chemistry, The Electrochemical Society Meeting, San Diego, Karl E. Spear, T. M. Besmann, and E. Beahm, May 6, 1998.

"Thermochemical Modeling Applied to Glass Processes in Industry and Nuclear Waste Processes," Chemistry Division Seminar, NIST, Karl E. Spear, May 20, 1998. (invited)

“Thermodynamic Analysis of the Tin Penetration Profile in High-Iron Float Glass,” The International Congress on Glass, San Francisco, CA, Thomas E. Paulson, Karl E. Spear and Carlo G. Pantano, July 8, 1998.

“Thermodynamic Modeling of Nuclear Waste Glass,” Gordon Research Conference on High Temperature Materials Chemistry and Diagnostics, Plymouth, NH, Karl E. Spear, T. M. Besmann, and E. Beahm, July 22, 1998.

“Thermodynamic and Kinetic Modeling Capabilities,” 75 Years of Ceramics at Penn State, and 53rd Annual PCA Forum. Penn State, University Park, PA, Karl E. Spear, Oct. 15, 1998.

“Surface Modification of Glass by Vaporization Reactions,” Sympos. Fundamental Gas-Phase and Surface Chemistry of Vapor-Phase Materials Synthesis, The Electrochemical Society Meeting, Boston, K. E. Spear, M. N. Palmisiano, C. G. Pantano, T. M. Besmann, and E. C. Beahm, Nov. 6, 1998.

"Thermodynamic Models for Nuclear Waste Subsystems - MgO-CaO and MgO-Al_2O_3," MRS Symposium, Boston, T. M. Besmann, K. E. Spear, and E. C. Beahm, Dec. 2, 1998.

"Solid Solution Thermochemical Models for Phase Systems in High-Level Nuclear Waste Glass," Symposium on Waste Management Science and Technology in the Ceramic and Nuclear Industries, American Ceramic Society Annual Meeting, Indianapolis, IN, T. M. Besmann, K. E. Spear, and E. C. Beahm, April 27, 1999.

"Mechanisms of Silica Refractory Corrosion in Glass-Melting Furnaces: Equilibrium Predictions," Honolula, Hawaii, Kopfstad Memorial Symposium on High Temperature Corrosion and Materials Chemistry, Electrochemical Society Meeting, Karl E. Spear and Mark Allendorf, Oct. 15, 1999.

"High Temperature Chemistry: A Key to Understanding Interface Reactions," Seminar at Northeastern University, New England Local Section of ECS, Karl E. Spear, Dec. 21, 1999.

"A Predictive Thermodynamic Model for Glass: Applications to High-Level Radioactive Waste, Corrosion in Glass Furnaces, and Float Glass Processing," Seminar at IIT, Chicago (Local Section of ECS), Karl E. Spear, Feb. 23, 2000.

“Thermochemical Modeling of Glass: Application to High-Level Nuclear Waste Glass,” HTMC-X, Juelich, Germany, 10th International Conference on High Temperature Materials Chemistry (HTMC X), K. E. Spear, T. M. Besmann, and E. C. Beahm, April 11, 2000.

"Theory and Applications of a Predictive Thermodynamic Model for Glass," Georgia Tech, Materials Seminar, Karl E. Spear, May 2, 2000.

"Thermodynamic Analysis of Alumina Refractory Corrosion in Glass-Melting Furnaces," The Electrochemical Society Meeting, Washington DC, K. E. Spear and Mark D. Allendorf, March 27, 2001.

"Theory and Applications of a Thermodynamic Model for Glass," Seminar at University of Minnesota, Minneapolis (Local Section of ECS) Karl E. Spear, April 12, 2001.

Consultative and Advisory Functions

T. M. Besmann presented research results and obtained feedback from staff at the Pacific Northwest National Laboratory, June 7, 2000, at PNNL. Staff involved included PNNL Principal Investigators John Vienna and Pavel Hrma.

T. M. Besmann, E. C. Beahm, L. D. Trowbridge, and K. E. Spear, have provided teleconference and e-mail support to efforts at PNNL on a periodic basis.

K. E. Spear and T. M. Besmann have provided periodic contact and consultation to M. D. Allendorf at Sandia National Laboratories – Livermore.

Collaborations

K. E. Spear has collaborated with M. D. Allendorf of Sandia National Laboratories (SNL) – Livermore on a DOE-OIT project to understand and design mitigation for corrosion of refractories in glass remelt furnaces.

Transitions

Thermochemical understanding of nepheline precipitation in nuclear waste glass has provided guidance with regard to selection of compositions. Confirming experiment, it was determined that increasing silica and boria contents suppress nepheline precipitation, and therefore can increase waste loading. This was applied by PNNL – John Vienna and Pavel Hrma.

Information was used through a DOE-OIT project, described above, to understand refractories corrosion in a glass remelt furnace. This knowledge has allowed glass manufacturers to select refractories compositions that will be less susceptible to corrosion. This was applied by SNL, M. D. Allendorf, to their analysis, and is being adopted by the glass industry.

Patents – None

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