

ASSESSMENT OF NEPHELINE PRECIPITATION IN NUCLEAR WASTE GLASS VIA THERMOCHEMICAL MODELING

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ABSTRACT

A thermochemical representation of the Na-Al-Si-B-O system relevant for nuclear waste glass has been developed based on the associate species approach for the glass solution phase. Thermochemical data were assessed and associate species data determined for binary and ternary subsystems in the Na₂O-Al₂O₃-B₂O₃-SiO₂ system. Computed binary and ternary phase diagrams were compared to published diagrams during this process, with adjustments in data made as necessary to obtain consistent thermodynamic values. The resulting representation for the four oxide system was used to help understand the problem of nepheline precipitation in certain waste glass formulations.

INTRODUCTION

High-level nuclear and transuranic wastes are currently foreseen as being incorporated in a host glass for permanent disposal. A large number of glasses have been explored, with borosilicate glass as the typical base composition. Glass compositions are under development at Pacific Northwest National Laboratory (PNNL) and Savannah River Laboratory that will allow dissolution of the waste species in a glass matrix. Issues of glass stability are important in that the glass must remain mechanically intact and retain a low leach rate on exposure to moisture. A somewhat opposing goal is to maximize waste loading of the glass, with a significant economic gain associated with incremental increases in waste content.

A problem identified at PNNL is the precipitation of a nepheline phase (Na₂O•Al₂O₃•2SiO₂) within certain compositions during the cooling of glass, which weakens the network structure by removing the glass formers Al₂O₃ and SiO₂. The result is that nepheline precipitation in high-level waste glass limits waste species loading. It has been observed that compositions rich in Al₂O₃ and Na₂O are particularly prone to precipitating nepheline[1].

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 [1]. Currently, there are limited thermochemical models for complex glass compositions, with much of the guidance for glass chemistry based on empirical or semi-empirical approaches. In the work reported in this paper, a thermochemical model for the Na₂O-Al₂O₃-B₂O₃-SiO₂ crystalline and glass system has been developed and applied to the problem of nepheline precipitation.

SOLUTION MODEL

An associate model developed in the 1980s was used to represent the thermochemical behavior of liquid oxide solutions. With an accurate model of the liquid solution, the supercooled liquid therefore represents the chemically complex nuclear waste glass. The model was initially utilized for complex solutions by Hastie, Bonnell, and co-workers [2-5]. Other thermodynamic models have been used to represent nuclear waste glass, most notably the

modified quasichemical model of Pelton, Blander and co-workers [6-7] who initially used it to represent molten slag phases, and later, nuclear materials, including waste glass [8]. The associate model, however, is substantially easier to understand and use, and yet the model still accurately represents the limiting thermodynamic activities of components in these metastable glass phases.

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 simply embodied in additional species in the solution. For example, in using the associate model for the $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3$ binary oxide system, an ideal liquid solution phase was created from the liquid components $\text{Na}_2\text{O}(\text{l})$ and $\text{Al}_2\text{O}_3(\text{l})$, along with a $\text{NaAlO}_2(\text{l})$ associate liquid species. In calculating the equilibrium state of the liquid phase containing the three species, the minimization of the total free energy determines the relative mole fractions of the species. This is conveniently accomplished using the thermochemical computational software ChemSage™ [9]. Since the system that includes the associate species is treated as an ideal solution, the activities are by definition equivalent to the species mole fraction. A more detailed description of the approach can be found in a recent review paper [10].

$\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{B}_2\text{O}_3-\text{SiO}_2$ MODEL

In developing the thermodynamic data file for the quaternary $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{B}_2\text{O}_3-\text{SiO}_2$ system, the thermodynamic and phase diagram data for six binary ($\text{Na}_2\text{O}-\text{Al}_2\text{O}_3$, $\text{Na}_2\text{O}-\text{B}_2\text{O}_3$, $\text{Na}_2\text{O}-\text{SiO}_2$, $\text{Al}_2\text{O}_3-\text{B}_2\text{O}_3$, $\text{Al}_2\text{O}_3-\text{SiO}_2$, and $\text{B}_2\text{O}_3-\text{SiO}_2$) and four ternary ($\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{B}_2\text{O}_3$, $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$, $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$, and $\text{Al}_2\text{O}_3-\text{B}_2\text{O}_3-\text{SiO}_2$) subsystems were assessed and optimized. The approach involved adjusting thermodynamic data 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. A large fraction of the needed thermochemical information has not been measured or reported, so a set of procedures for estimating or calculating the information was developed [10]. In all cases, the complete set of thermochemical information for a system is refined and tested to give reasonable thermodynamic and phase diagram information over wide ranges of temperature and composition.

ChemSage™ [9] was the 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 substance database associated with ChemSage™, our estimates, and simultaneously comparing and optimizing sets of phase equilibria and thermodynamic data. A primary source of phase diagram information is the set of volumes Phase Diagrams for Ceramists [11], plus literature that includes reports of previously optimized thermochemical data.

Several liquid associate species were used in modeling the quaternary $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{B}_2\text{O}_3-\text{SiO}_2$ system. As a means of providing equal weighting to each liquid associate species, each species was adjusted to have a total of two non-oxygen atoms in its formula. A listing of the species is given below:

Single oxide liquid species

Na₂O Al₂O₃ B₂O₃ Si₂O₄

Binary oxide liquid species

(1/4)Al₆Si₂O₁₃ NaAlO₂
(1/3)Na₄B₂O₅ NaBO₂ (1/3)Na₂B₄O₇ (1/5)Na₂B₈O₁₃
(2/5)Na₄SiO₄ (2/3)Na₂SiO₃ (1/2)Na₂Si₂O₅

Ternary oxide liquid species

(2/3)NaAlSiO₄ (1/2)NaAlSi₂O₆

An example of the computed phase relations compared with that experimentally determined [12] can be seen in the pseudo-binary diagrams for the nepheline/carnegeite-albite-silica system (Fig. 1). Although the homogeneity ranges for the crystalline phases were not modeled, the computed phase diagram reproduces the observed phase relations remarkably well given the simplicity of the model.

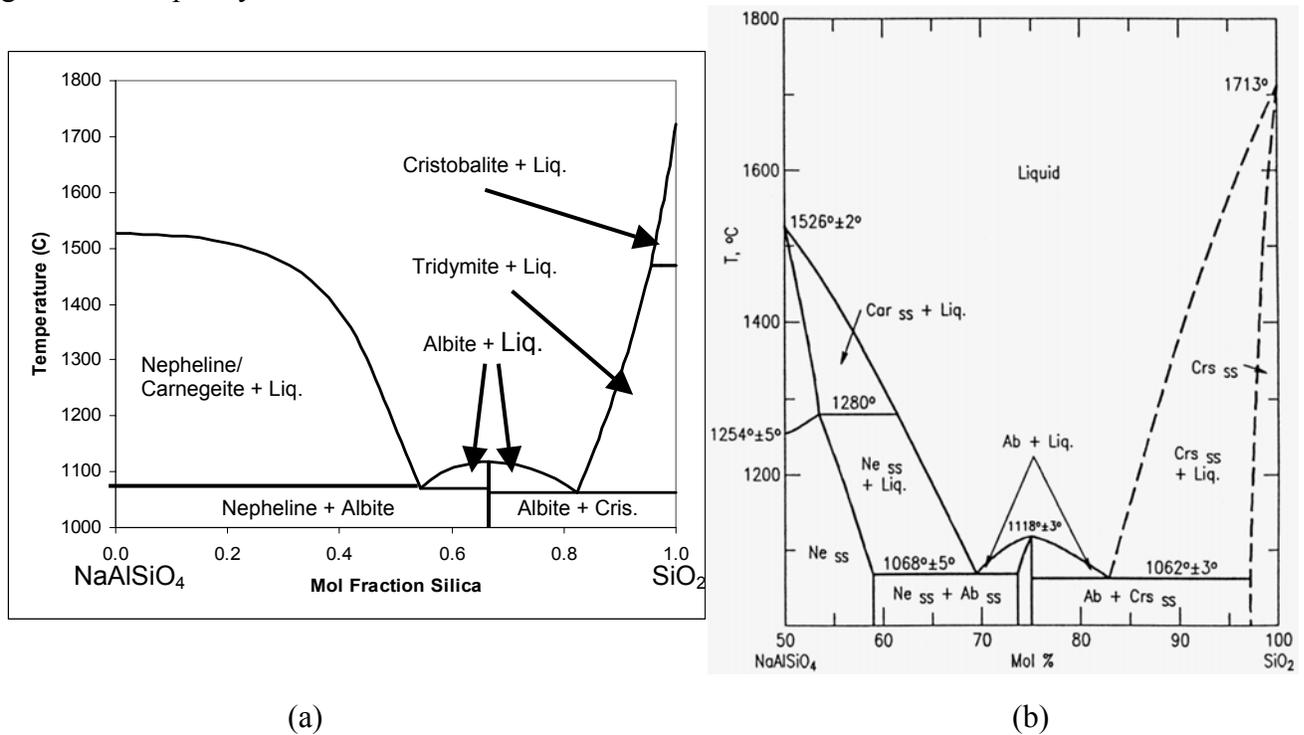


Fig. 1. (a) Computed and (b) published pseudo-binary phase diagram for the nepheline/carnegeite-albite-silica system (No. 10013 in ref. [12]).

NEPHELINE-GLASS PSEUDO-EQUILIBRIUM

As has been observed, the precipitation of nepheline occurs during glass cooling in the absence of other crystalline phases [1]. 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.

Stability Region

Utilizing the ChemSage™ software and the thermochemical data file for the $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ system, the composition space of the ternary oxide $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ 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. 2 with the binary oxides and the nepheline composition indicated.

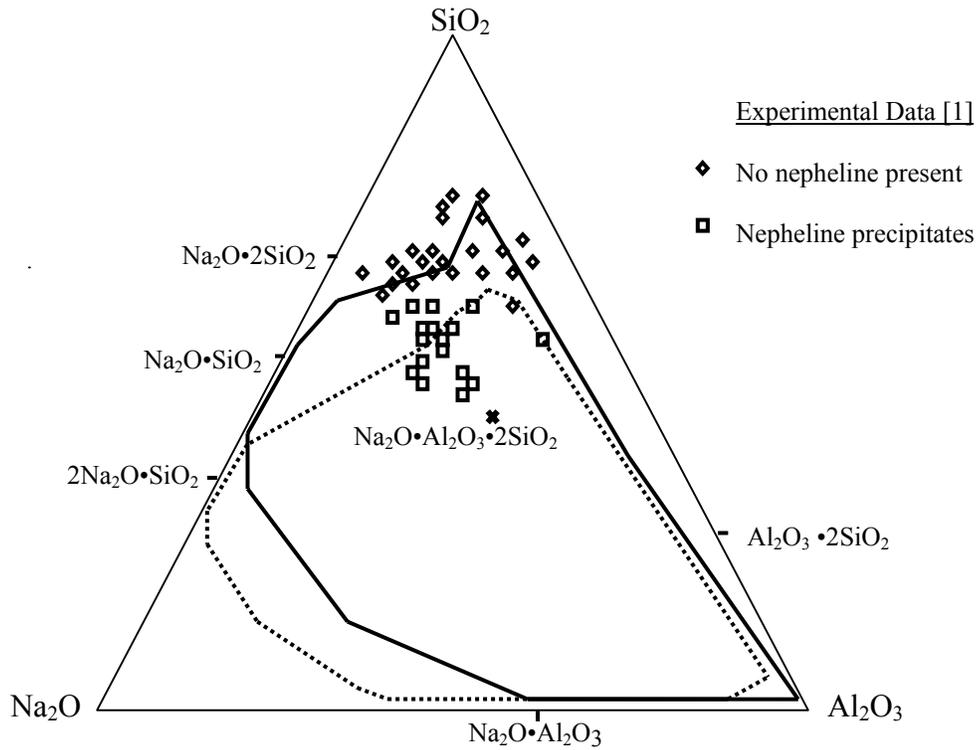


Fig. 2. Ternary $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ phase space (wt. %) showing the computed stability region for nepheline plus the glass phase at 800°C with no boria (—) and 30 wt.% boria (.....) along with experimentally determined precipitation data [1].

Apparent from the calculational results is the wide compositional range over which nepheline is stable. The maximum silica composition lies along the $\text{SiO}_2-\text{Na}_2\text{O}\cdot\text{Al}_2\text{O}_3$ 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 $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{B}_2\text{O}_3-\text{SiO}_2$ 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.

Formation Temperature

To aid in controlling nepheline precipitation it is useful to know the temperature at which the phase will form. Figure 3 is a plot of the calculated formation temperatures in the presence of the glass phase over the nepheline-albite ($\text{Na}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot 6\text{SiO}_2$) 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.

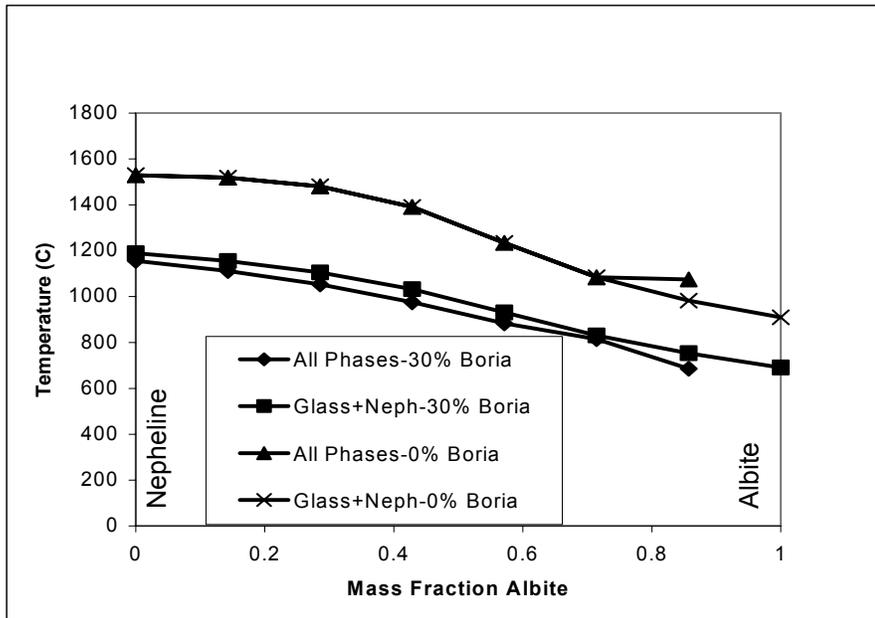


Fig. 3. Formation temperature for nepheline with no boria and 30 wt.% boria, assuming all phases can form or only the glass and nepheline.

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. As expected from the phase relations, both higher boria and higher silica results in lower nepheline amounts.

CONCLUSIONS

A relatively simple thermochemical model for the $\text{Na}_2\text{O}\text{-Al}_2\text{O}_3\text{-B}_2\text{O}_3\text{-SiO}_2$ system has been developed and has been shown to be accurate and predictive. The model can be easily expanded to include other chemical components. Other waste constituents will be added in the future to allow further modeling of high-level nuclear waste forms.

The predicted stability region for the formation of nepheline can have a significant influence on the choice of 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. These effects are directly related to lowering the activity of Na_2O in the glass phase, restricting the sodium available to form nepheline.

Reducing the liquidus temperature or the temperature at which the nepheline phase is computed to form 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 lower temperatures kinetics and mass transport will be slower.

These results are in general agreement with experimental observations [1]. They should 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.

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