

THERMOCHEMICAL MODELS FOR NUCLEAR WASTE GLASS SUBSYSTEMS – MgO-CaO and MgO-Al₂O₃

T. M. BESMANN*, K. E. SPEAR**, E. C. BEAHM*

*Oak Ridge National Laboratory, P. O. Box 2008, Oak Ridge, TN 37831-6063

**Materials Science and Engineering Department, Pennsylvania State University, 118 Steidle Building, University Park, PA 16802-5005

ABSTRACT

A relatively simple model, the associate species model, is being applied to nuclear waste glass compositions in order to accurately predict behavior and thermodynamic activities in the material. In the model, the glass is treated as a supercooled liquid, with the liquid species allowed to exist below their melting point. The approach requires an initial assembly of binary and ternary oxide liquid solution data that sufficiently reproduce the equilibrium phase diagrams. Two binary oxide subsystems, MgO-CaO and MgO-Al₂O₃, have been modeled and results compared to published phase diagrams. Computed activities of the glass constituent species are plotted as a function of composition at 1200°C.

INTRODUCTION

A large number of glasses have been explored as hosts for high-level nuclear and transuranic wastes, with borosilicate glass as the typical base composition. Prediction of the long-term stability of these waste forms requires an accurate understanding of the chemical activities of the constituent species.[1] These are necessary for determining volatility, leaching behavior, and corrosion reactions. However, accurate thermochemical values for the constituents of glasses require a global model for the glass phase. To date, such a model is lacking, requiring the use of experimental simulation or oversimplistic assumptions.

It is apparent that any assumption regarding the activity of a constituent in a waste glass will directly influence the predicted behavior with regard to interactions with the environment (e.g., concentration in a leachate). Unfortunately, because of the lack of a suitable model for the thermochemistry of glasses, it has been necessary to either assume a metal oxide is present at unit activity or that it has an activity equal to the overall concentration of the metal in the glass. These approaches can lead to highly misleading results. Accurate thermodynamic activities of its component oxides would help interpret leaching data and provide for more rigorous models.

This paper presents initial efforts in developing a comprehensive model for waste glass compositions. The work is focussed on producing an accurate, easy to understand and use thermochemical representation for describing the stability of waste glasses. The model must be able to generate accurate values for thermodynamic activities of glass components as a function of temperature and glass composition.

The current approach utilizes the common description of a glass as a supercooled liquid solution phase. It therefore requires developing an accurate model for the species activities in the complex oxide liquid phase. This requires a critically assessed thermodynamic database consistent with the model for binary and ternary combinations of the major components in a typical waste glass. These systems can then be combined to represent the thermodynamic behavior of complex, multicomponent glass systems.

SOLUTION MODEL

An associate model developed for complex slags 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]. A review of much of their research incorporating this model is given in Bonnell and Hastie [5]. Pantano, Spear and co-workers also used the model for predicting and explaining interface reactions in fiber-reinforced glass-matrix composite systems [6-8], and the behavior of tin and iron in float glass systems [9-10]. Other thermodynamic models have been used to represent nuclear waste glass, most notably the modified quasichemical model of Pelton, Blander and co-workers [11-12] who initially used it to represent molten slag phases, and later nuclear materials, including subsystems of waste glass [13]. The associate model can include essentially all components and is substantially easier for non-specialists 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. These are considered explicitly in representations such as the quasichemical model [14]. The large-scale use of interaction energies in such an approach can result in a significant multiplication of terms making it cumbersome to develop relationships for complex systems. In the associate model these energies are included 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 MgO-Al₂O₃ binary oxide system examined in this paper, an ideal liquid solution phase was created from the liquid components MgO(l) and Al₂O₃(l) along with a MgAl₂O₄(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. As the system is treated as an ideal solution, the activities are by definition equivalent to the species mole fraction. The resulting activities of these species can be correlated with leaching behavior, corrosion reactions, and other important phenomena.

THERMOCHEMICAL CALCULATIONS

The thermodynamic computer program ChemSage™ [15], thermodynamic data from the SGTE database, 1996 update [16], and phase diagrams from Phase Diagrams for Ceramists [17] were used in our assessments and calculations.

Thermodynamic data for crystalline phases in the MgO-CaO and MgO-Al₂O₃ systems were available from the SGTE database [16], but a liquid solution phase had to be developed for each system and the data refined by manually optimizing liquid species values to match the best available binary temperature-composition phase diagrams [17]. Species assumed in the liquid solution for the MgO-CaO system were Mg₂O₂(l) and Ca₂O₂(l). Note that the formulae Mg₂O₂ and Ca₂O₂ have the same atom ratio as the typically denoted crystalline phase formulae: MgO and CaO. Each species in the liquid phase was written so that



where M and M' are dissimilar metals, i.e., the number of metals per formula unit equals 2. This general rule was followed for each system studied since it gives equal weight to all liquid species in the solution with regard to the entropy of mixing, and resulted in the best fits of the phase

diagrams. The fundamental reasons for why better phase diagram fits were obtained when the sum of the non-oxygen atoms equaled 2/formula unit rather than 1/formula unit is not understood

The MgO-Al₂O₃ liquid was modeled as a solution containing the species Mg₂O₂(l), Al₂O₃(l), and Mg_{2/3}Al_{4/3}O_{8/3}(l). In this case the binary oxide phase MgAl₂O₄ is congruently melting and the liquid species was thus considered as an associate in the melt.

The liquid species thermodynamic values were initially estimated from those of the crystalline phases. This was done for each species by simply adding the heat of fusion to the 25°C enthalpy and by adding the entropy change (computed from the heat of fusion by dividing it by the absolute melting temperature) to the 25°C entropy. The heat capacity values of the crystalline phases were retained for the liquid species up to their respective melting points.

PHASE EQUILIBRIA

The computed phase diagram for the MgO-CaO system of Fig. 1 was obtained using the thermochemical assumptions described in the previous section with the ChemSage™ software package [15]. The melting points of the end members are correct, however, the eutectic composition is too MgO-rich as compared to the diagram derived from an early phase equilibria study [17]. That work also has the melting temperature for CaO too low by 200°C. Based on the limited information on this system currently available, Fig. 1 is a very good reproduction of the high temperature MgO-CaO phase diagram. The only the exception is that there is no provision for the inter-solution of the end members.

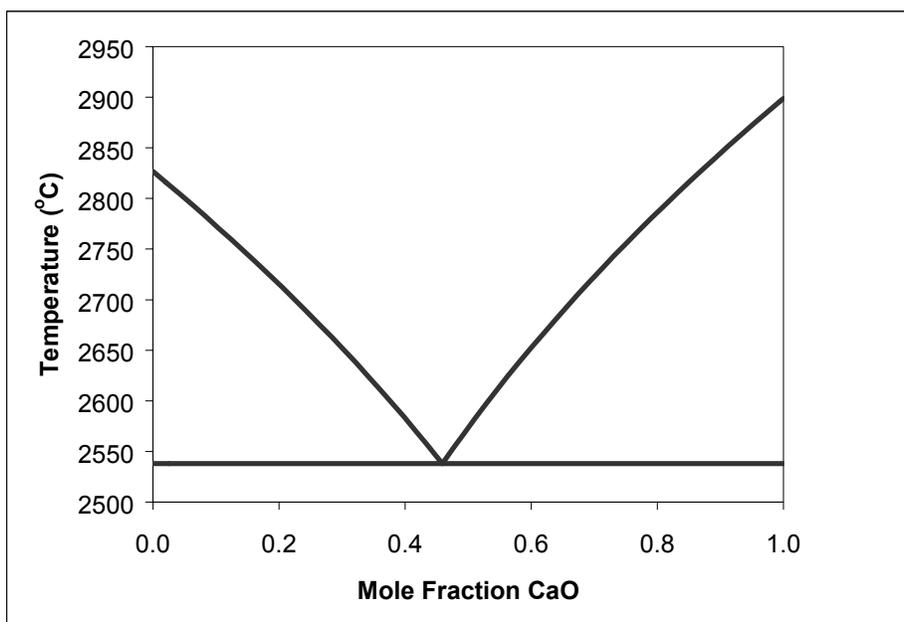


Figure 1. Computed phase diagram for the MgO-CaO system.

Figure 2 is the high temperature computed phase diagram of the MgO-Al₂O₃ system. The best fit was obtained without modification of the thermochemical values. An apparent discrepancy is seen in the Al₂O₃-MgAl₂O₄ eutectic whose Al₂O₃ content is too low (70 mol % instead of 90 mol %) and whose melting point is ~100°C too low [17]. This is understandable since the large solubility of Al₂O₃ in both MgO and MgAl₂O₄ is not included.

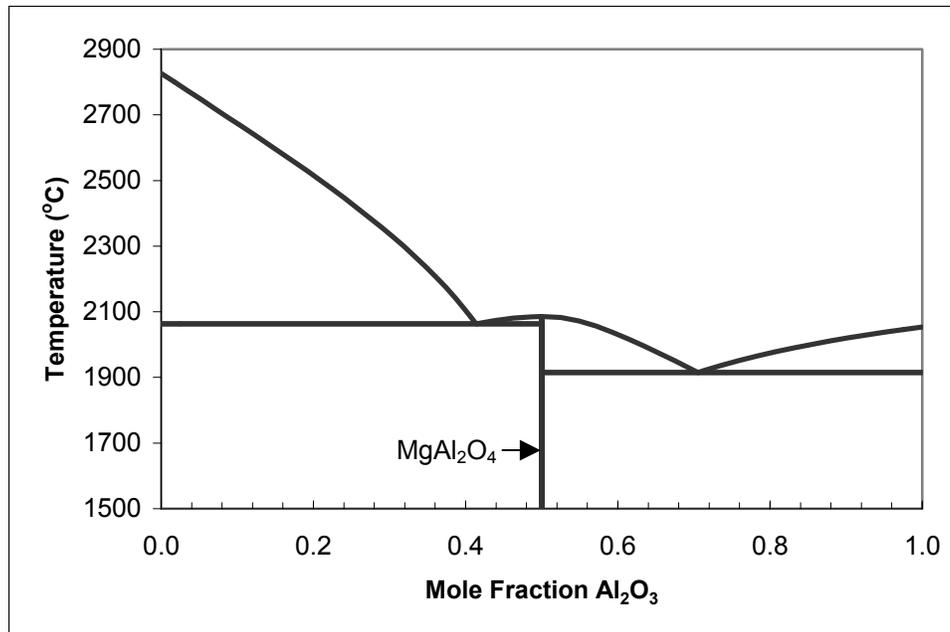


Figure 2. Computed phase diagram for the MgO-Al₂O₃ system.

CHEMICAL ACTIVITIES IN THE GLASS

The 1200°C chemical activities of the species in the supercooled liquid were obtained by computing the phase equilibria assuming the crystalline species were not present. Figure 3 displays the chemical activity of the species Mg₂O₂(l) and Ca₂O₂(l). Because of the lack of associate species, end member constituents are the only relevant species, and thus the activities default to simply the end member mole fractions in the solution.

Figure 4 is a plot of the 1200°C activities of the species Mg₂O₂(l), Al₂O₃(l), and Mg_{2/3}Al_{4/3}O_{8/3}(l) in the supercooled liquid obtained assuming no crystalline phases present. In this case the presence of the associate species Mg_{2/3}Al_{4/3}O_{8/3}(l) has a significant effect on the activities. While the end member species predominate near the terminal compositions, the associate species Al_{4/3}Mg_{2/3}O_{8/3}(l) has the highest activity of the three species over most of the rest of the compositional space. Thus any accurate calculation of the activity of magnesia and alumina must consider the interactions between the constituents as described by the thermochemistry of the associate species.

CONCLUSIONS

As demonstrated in the current work, as well as in previous studies, the associate model is a simple and accurate means for representing the activities of the constituent species of oxide melts and glasses. The approach of developing a critically assessed thermodynamic database for binary and ternary combinations of the major components in a typical waste glass is continuing

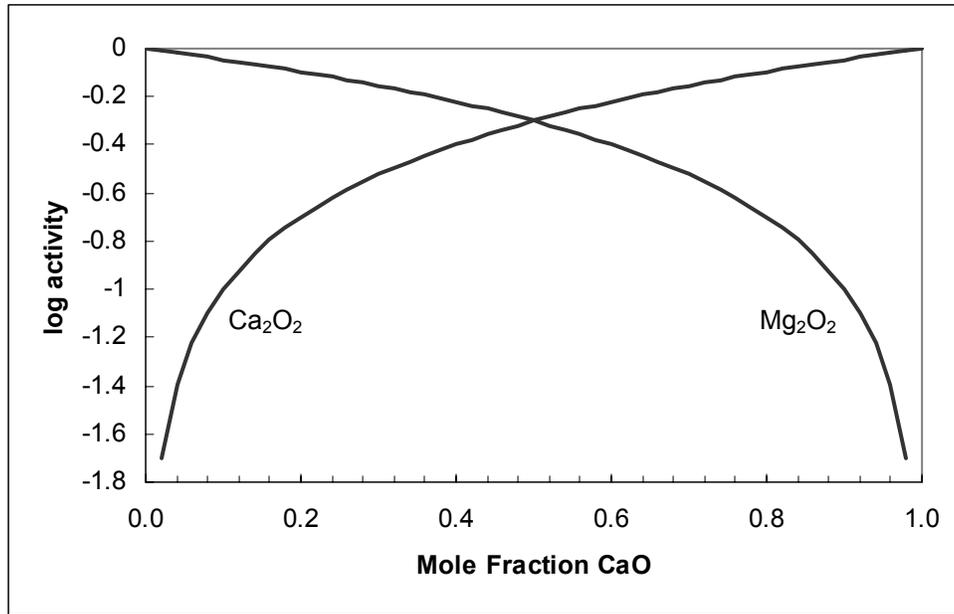


Figure 3. Activity of species in the supercooled MgO-CaO liquid at 1200°C.

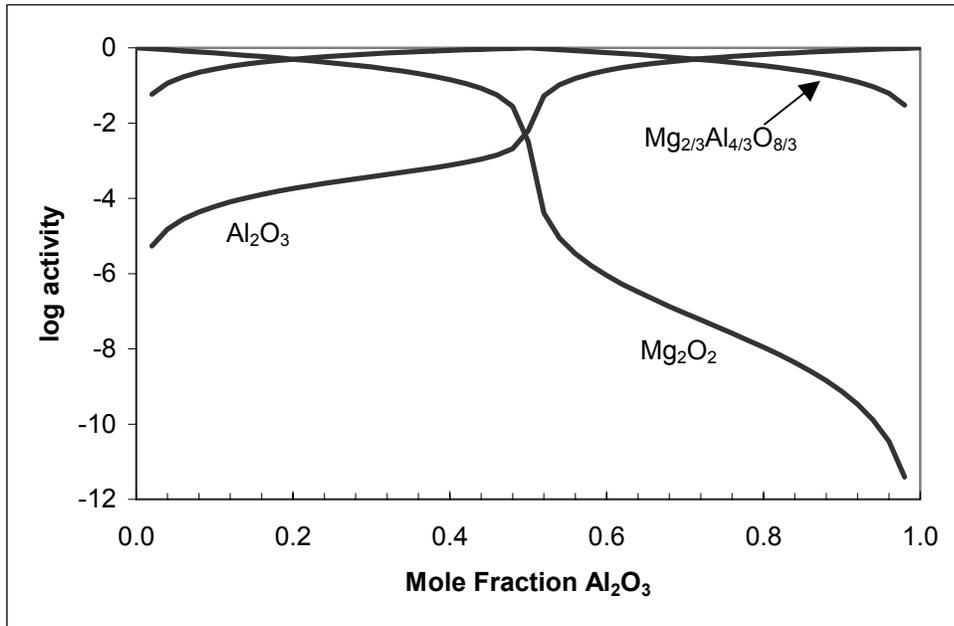


Figure 4. Activity of species in the supercooled MgO-Al₂O₃ liquid at 1200°C.

with assessments of other binary alkali and alkaline earth silicates, aluminates, and borates. At the same time, the database being created will be used for producing data sets for assessments of ternary and higher order systems so that the importance of ternary associate species on the liquid solution stability can be determined. These data will then be combined to predict the thermodynamic behavior of the more complex glass systems used for high-level nuclear and transuranic wastes. In the case of leaching from a waste form, the activity of each of the more important (higher activity) species, whether single oxide or associate species, should be used in the calculation of the equilibrium hydration reaction. This procedure should give the most accurate results with regard to equilibrium concentrations of leaching constituents.

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