Stability of High-Level Waste Forms

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RESEARCH OBJECTIVE: The objective of the proposed effort is to use a new approach to develop solution models of complex waste glass systems and spent fuel that are predictive with regard to composition, phase separation, and volatility. The effort will also yield thermodynamic values for waste components that are fundamentally required for corrosion models used to predict the leaching/corrosion behavior for waste glass and spent fuel material. This basic information and understanding of chemical behavior can subsequently be used directly in computational models of leaching and transport in geologic media, in designing and engineering waste forms and barrier systems, and in prediction of chemical interactions.

RESEARCH PROGRESS AND IMPLICATIONS: As of the end of the first year of this project, which is a continuation of two related previous three-year EMSP efforts, thermochemical datafiles with oxide contents critical to HLW and , containing Na-Ca-Fe-Al-B-Si-O has been developed which is a major refinement over all previous efforts.

Na_2O-Al_2O_3-B_2O_3-SiO_2 Quaternary System

The database for the Na_2O-Al_2O_3-B_2O_3-SiO_2 quaternary system was in excellent condition for the data available in the literature. The ternary Na_2O-Al_2O_3-SiO_2 system was reproduced with our database much better than could be done with any other known database. A few precipitation experiments by PNNL on nepheline ($NaAlSiO_4$) plus B_2O_3 and on ($NaAlSiO_4$ + x SiO_2) plus B_2O_3 gave significantly lower precipitation temperatures than we obtained from

modeling calculations. PNNL checked their experimental results, and found their data were reproducible. Checking our data for B_2O_3-containing binary and ternary systems against what was available in the literature did not reveal discrepancies, but the amount of data in the literature is sparse.

With little experimental data to use, it was assumed that some strong liquid interactions between borate species and those in liquid Na_2O-Al_2O_3-SiO_2 species could readily explain the disagreement (more careful thermochemical studies of borate systems would reveal the influence of such interactions). Some reasonable complex liquid associate species ($NaAlSiO_4$ plus B_2O_3 and $NaAlSi_2O_6$ plus B_2O_3) were added along with thermodynamic information using techniques described in earlier papers, and thus it was possible to accurately reproduce the PNNL experimental data for both the ternary Na_2O-Al_2O_3-SiO_2 system.

The database, however, must be reliable for adding boria to compositions off of the $NaAlSiO_4$ - SiO_2 join, so PNNL ran new precipitation experiments adding boria to compositions on both the Na_2O-SiO_2 and Al_2O_3-SiO_2 sides nepheline. The modeling calculations relevant to these new experiments revealed more problems with available borate data. The Al-Si rich side of nepheline was giving problems with Al_2O_3/mullite precipitation when nepheline melted (peritectic melting of nepheline to give Na-Si rich liquid plus Al_2O_3/mullite solids). Increasing nepheline solid and liquid stabilities helped to avoid Al_2O_3/mullite precipitation.

Li_2O-B_2O_3 System

A thermochemical optimization of the Li_2O-B_2O_3 system is mostly complete. With the other work on the Li_2O-Al_2O_3 and Li_2O-SiO_2 systems, the ternary systems within the Li_2O-Al_2O_3-B_2O_3-SiO_2 quaternary will be addressed. Much of the work on the Li_2O-B_2O_3 system was completed using ChemSage software and techniques we have described previously. As ChemSage has been combined with the FACT software to create FactSage, all of our assessment work and calculations are being transferred to the new software. New optimization procedures using FactSage are being developed using Li_2O-B_2O_3 as an example system.

CaO-Al_2O_3-B_2O_3-SiO_2 Quaternary System

A recently developed database for the CaO-Al_2O_3-SiO_2 ternary system is being combined with available boria-containing data so that testing of a quaternary CaO-Al_2O_3-B_2O_3-SiO_2 database can be performed with experimental data being produced at PNNL. These comparisons will help determine what portions of this system need to be refined to create a more reliable thermochemical database.

Li_2O - Al_2O_3 Modeling

In the optimization effort, the initial set of thermodynamic parameters for the solid compounds, and the pure Li_2O and Al_2O_3 solids and liquids were obtained from the available databases. An associate species model for the liquid phase was initially constructed for the desired mix of liquid species in this system. The relevant thermodynamic data for the liquid associate species were estimated using the melting temperatures, the enthalpies of fusion and the standard enthalpies and entropies of formation for the corresponding solid species. Along with this thermodynamic data, experimental phase boundary data and information regarding the important transformation temperatures were input to the FactSage Optimizer for the purpose of obtaining a

suitable set of thermodynamic parameters for the intermediate liquid associates and line compounds which could adequately fit the experimental phase diagram. Based on this process, a successful set of values were obtained that would reproduce the experimental phase diagram.

Al_2O_3-Cr_2O_3-SiO_2 System

Ideal, regular, or subregular models for solid solutions and ideal solution models for the oxide liquids of the Al_2O_3-Cr_2O_3-SiO_2 system were found to well-represent activities and phase equilibria where they are known for the binary oxide systems Al_2O_3-Cr_2O_3 and Cr_2O_3-SiO_2. The higher temperature regions of the phase equilibria for these systems could be well-reproduced. The current disagreement with regard to the compositional symmetry of the corundum solid solution miscibility gap in the Al_2O_3-Cr_2O_3 system and its critical temperature appears to be resolved with the reproduction of the asymmetrical gap and its higher critical temperature through direct optimization with only activity data and solidus-liquidus phase equilibria. The Al_2O_3-SiO_2 system previously modeled was combined with the other binary oxide systems to produce a reasonable model for the ternary oxide Al_2O_3-Cr_2O_3-SiO_2 system. An important observation is that consistency in the assumption of solution species stoichiometry may be important when modeling both liquid and solid oxide solutions in a system.

Experimental Efforts

The addition of components to the thermochemical model of waste glass becomes increasingly more complex as the total number of components in the model increases. The model expansion requires a significant amount of experimental work for model optimization. The progress on the third project phase to-date, includes:

- the fabrication and measurement of over 100 unique multi-component melt compositions the development of a binary FeO_x-MnO_x phase diagram
- development of experimental techniques and measurement of both CrO_x and SO_x in multi-component glass melts

The impacts of this testing includes a solid contribution to the understanding of multi-component silicate melt chemistry and thermodynamics as evidenced by the publications listed below. The testing work on Cr_2O_3 solubility in waste glass melts led to the development of a high Cr waste glass melt (<1.5 wt% as Cr_2O_3). The results of this melt have led to a change in the Hanford waste cleanup system planning and have cut an estimated 35% of the projected high-level waste glass volume to be produced at Hanford.

PLANNED ACTIVITIES: In the coming period we will be engaged in further refining and expanding the model for high-level nuclear waste glass. The base systems will be reconciled with experiment. The experimental data from PNNL on the Na-Si rich side of nepheline is very difficult to reproduce. Various new liquid complex species were produced, but did not help in reaching agreement. Very low precipitation temperatures, and several Na-borate and Na-silicate precipitates are a problem that cannot seem to be alleviated with current database species. This has led to a reevaluation of the Na-B-Si-O system. The Na_2O-B_2O_3 system will be tested more thoroughly, based on the above results. The ternary Na_2O-B_2O_3-SiO_2 system will then be re-assessed, using new nepheline-types $NaBSiO_4$(s,l) species in the dataset. Such a nepheline-type

boria containing solid phase has been reported, but not confirmed in the literature. The $NaBSiO_4$(s,l) (B-nepheline) species will be made "metastable" – solid won't quite form as a stable phase in system ($Na_2B_2O_4 + 2\ SiO_2 = 2\ NaBSiO_4$). Having a liquid species of $NaBSiO_4$(l) in the NABS-system may help eliminate the Na-borate/Na-silicate precipitates in the Na-Si rich side of nepheline. Also, the nepheline solid solution will now be made up of [$NaAlSiO_4$(s)+ $NaBSiO_4$(s)+ $NaAlSi_2O_6$(s)+ $NaAlO_2$(s)].

A recently developed new database for the Na_2O-CaO-SiO_2 ternary system has been completed. These data are being combined with available boria-containing data so that testing of a quaternary Na_2O-CaO-B_2O_3-SiO_2 database with experimental data being produced at PNNL can be started. However, the above-discussed re-examination of the Na_2O-B_2O_3-SiO_2 ternary system must be completed before a reliable quaternary database can be put together. These comparisons will help determine what portions of this system need to be re-examined to create a more reliable thermochemical database.

Ternary immiscibility has also not been carefully included in our ternary diagram fitting because of the very limited available data. The binary immiscibility data for the Na_2O-B_2O_3 system is also quite uncertain. Inconsistencies between the Na_2O-B_2O_3 metastable immiscibility gap and liquidus data for the binary are also apparent. These will be further examined based on our problems with fitting quaternary precipitation data. The other two binary systems Na_2O-SiO_2 and B_2O_3-SiO_2 are in excellent shape and will not be adjusted.

Spinel components will be continually added to the model, with MgO nearing completion and MnO and iron being evaluated. Zirconium-containing systems are also nearing completion and these too will be added to the base system.

The experimental portion of the study will focus on 1) developing additional phase diagrams for systems not adequately covered in literature, but, critical to continued model development, and 2) addition of new components to the ternary, quaternary, and higher-order systems currently modeled. The data generated will be used to help develop and validate the models.

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INFORMATION ACCESS:

PUBLICATIONS

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WEBSITE

www.ca.sandia.gov/HiTempThermo/index.html