Modeling Molten Salt Performance in MSRs: Using Thermochemical Behavior

Theodore M. Besmann,[a] Johnathan C. Ard,[a] Jacob W. McMurray[b]

[a] *University of South Carolina, 541 Main St., Columbia, SC 29208, besmann@cec.sc.edu*
[b] *ORNL, P.O. Box 2008, Oak Ridge, TN 37831, mcmurrayjw1@ornl.gov*

INTRODUCTION

The utilization of molten salts as fuel in a reactor was demonstrated between 1965 and 1969 by the Molten Salt Reactor Experiment, which was an 8 MW critical reactor operating with LiF-BeF2-ZrF4-UF4 flowing through a graphite moderator at ~650°C [Ref. 1]. Molten salt fueled, or simply molten salt cooled reactors are now part of the Generation IV concepts offering variants that can be fast or thermal, and with the advantages of a low pressure coolant loop with a high thermal conductivity fluid and high outlet temperatures.

For liquid fueled molten salt systems it is particularly necessary to deal with time and spatial evolution behavior due to temperature and compositional variations from

- Burnup-generated fission products and transuranics;
- Addition of fresh fuel salt ;
- Evolving composition due to isotopic decay/neutron absorption;
- Graphite pickup (systems where salt directly contacts graphite moderator);
- Corrosion product dissolution/deposition;
- In-leakage of atmospheric oxygen and nitrogen;
- Adjustment of redox with fluorine addition;
- Removal of fission and corrosion products, and transuranic elements; and
- Off-gas removal.

Given the high temperatures and nature of the phases (largely ionic liquids and solids together with gases/vapors, metals, and graphite), it is expected that chemical and phase behavior approach equilibrium, and thus are governed by their thermodynamic properties, i.e., free energies. Computed equilibria in the molten salts thus can provide

- Local composition/speciation;
- Precipitating solid phases;
- Liquid-liquid immiscibility;
- State of dislodged graphite or alloy material;
- Chemical potentials/redox for determining/controlling corrosion and transport;
- Vapor pressures;
- Thermal expansion/specific volume; and
- Input for phase field calculations: Modeling nucleation and grain growth.

In the current work the overall goal is to create a predictive thermochemical database and demonstrate its use in representing complex fluoride and chloride salt systems in equilibrium calculations. These in turn are to be used in reactor performance modeling, providing the chemical activity and phase state of the system. An approach to developing such capability will be presented.

CHEMICAL THERMODYNAMIC MODELING

The development of simulation capability relies on a thermochemical database that consists of models for the free energies of the molten salts as well as other phases such as any solids that can precipitate and vapor species. The solids, if not strictly stoichiometric compounds, are treated as solid solutions. For crystalline phases, sublattice solid solution models are required that assign elements to site positions on either cation or anion lattices. For molten salts, the most widely accepted model is the modified quasi-chemical in the quadruplet approximation [Ref. 2]. Vapor species are treated as ideal (or non-ideal as necessary) gases whose partial pressures depend on the chemical activity of the systems.

To solve the equilibria for such complex systems requires having thermodynamic values for the solid and liquid solution models along with free energies for the stoichiometric compounds and vapor species. These need to be available from a qualified database. It is the objective of this work to develop such a database utilizing the ASC-II format for exported data files generated using the FactSage equilibrium software. A database of fluoride salt compositions with Li, Na, K, Rb, Cs, Be, Ca, La, Th, U, and Pu has already been developed by the Joint Research Center-Karlsruhe, with values reported in the literature. In the current work, demonstration databases are being prepared for initial evaluation with thermodynamic, and eventually reactor modeling codes.

The early work has resulted in the generation of an initial fuel salt composition database which is allowing computation of composition-temperature properties. Figure 1 is an example of computed thermochemical properties, the numerical values of which can be directly provided for assessing fuel systems and for representing properties in reactor performance codes. The nature and composition of precipitating phases are obtained as well.

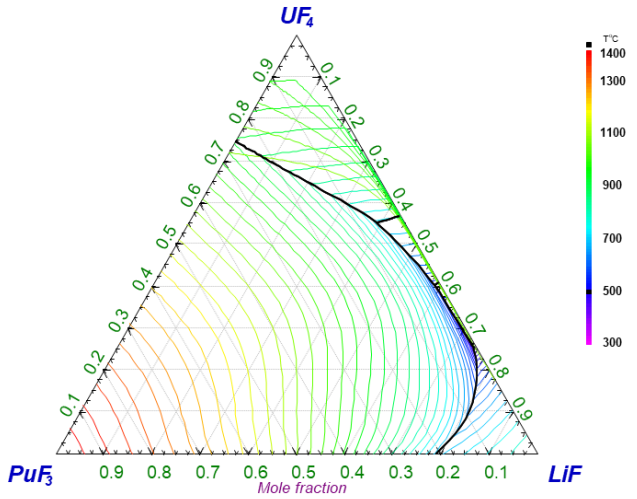

Fig. 1. Computed liquidus projections and invariant points for the UF_4-PuF_3-LiF system using the FactSage code.

REACTOR MODELING

The results of chemical thermodynamic calculations can inform reactor simulations through coupled calculations. For example, the code Thermochimica [Ref. 3] can compute equilibrium compositions and chemical activities from local composition of the salt that is obtained from reactor physics codes, with temperature provided by fission rates from the physics codes together with thermal hydraulics models. That chemical and phase state information can then be passed to transport simulations, again interacting with thermal hydraulics determinations. And in turn new local compositions can be computed that are needed for reactor physics calculations. The system can thus iteratively determine local chemical, transport, thermal, and nuclear behavior. Although not considered in the current presentation, such reactor performance simulations are the ultimate application of the database and attendant thermochemical equilibrium calculations.

SUMMARY

This presentation reports on the approach to development of a validated, consistent database of fluoride and chloride salts containing initial fuel compositions, FPs, TRUs, and potential corrosion products for likely MSR systems. The database will be structured to allow commercial and open source codes to search for and generate subset data files to compute equilibrium states, and thus the various characteristics listed above over desired ranges of temperature, composition, and pressure. A prototypical database developed in this work will be used to demonstrate applicable calculations for use in MSR performance simulations.

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