Multicomponent Thermochemistry of Complex Chloride Salts for Sustainable Fuel Cycle Technologies

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ABSTRACT:

Pyrochemical reprocessing based on molten salt electrolysis is a viable method to recover uranium from spent nuclear fuels and produce high assay low enriched uranium (HALEU) ingots. It involves electrometallurgical methods with LiCl-KCl eutectic salt at 500°C as an electrolyte. As the spent fuel is reprocessed, there is an increase in the concentration of fission product chlorides of alkali, alkaline earth, lanthanides, and transuranics, which alters the thermodynamic properties. Efforts to develop a thermodynamic database to estimate the solubilities of chloride salts are essential for improving the process efficiencies. Hence, this project aims to develop a comprehensive thermodynamic database for multicomponent chloride salt system, KCl-LiCl-NaCl-UCl_3-$LnCl_3$ (Ln: La, Pr, Nd). CALPHAD (Calculation of Phase Diagrams) method coupled with critical experiments and Density Functional Theory (DFT) calculations will be applied for this purpose. The following objectives are proposed: (1) Develop a multicomponent thermodynamic database for the chloride salt system using CALPHAD method supported by DFT calculations and key experiments; (2) Determine phase equilibria for the unknown binary and ternary systems through experimental measurement of the phase transitions; (3) Model calibration using experimental inputs from complex simulant chloride salts for predicting solubilities using the CALPHAD database; (4) Perform sensitivity analysis of the developed database using the high-throughput CALPHAD modeling.

The proposed research will be conducted jointly by University of Pittsburgh (Pitt), University of Texas at San Antonio (UTSA), and Idaho National Laboratory (INL). The thermodynamic database of the multicomponent chloride system will be built using the CALPHAD method at Pitt. The following relevant constituent ternary systems (including their binaries), namely, KCl-NaCl-UCl_3, KCl-LiCl-$LaCl_3$, KCl-LiCl-$PrCl_3$, and KCl-LiCl-$NdCl_3$ will be considered. Enthalpies of formation of the intermediate compounds in the binary systems will be estimated using DFT calculations at Pitt. Certain constituent binary and ternary systems such as LiCl-$LaCl_3$, LiCl-KCl-$LaCl_3$, and NaCl-KCl-UCl_3 are unknown without any experimental and theoretical data in the literature. Measurement of phase transition temperatures will be performed at UTSA using a simultaneous thermal analyzer, to aid the thermodynamic modeling of such systems. The inputs required for database calibration, such as the solubilities and transition temperatures, will be measured using differential scanning calorimetry for the complex simulant salt systems at INL. These quantities will be compared with the values calculated using the thermodynamic database at Pitt, and the parameters will be further refined accordingly. Sensitivity analysis of the database model-prediction will be performed through a high-throughput CALPHAD modeling at Pitt. The in-house high-throughput modeling code will be developed using TC-Python for predicting phase equilibria and properties to evaluate the quality of the developed database by comparing with the existing data from experiments for the studied salt systems.

Through this project, a high-fidelity thermodynamic database developed for the multicomponent chloride system will be employed to predict thermodynamic properties as well as multicomponent solubility. These fundamental understandings will help minimize the salt wastes that will be generated from spent fuel treatment operations and estimate the properties that are essential for HALEU production.