Determination of Local Structure and Phase Stability of Uranium Species in Molten Halide Salts: Linking Microscopic Structure with Macroscopic Thermodynamics

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ABSTRACT:

The goal is to determine the local structure and thermodynamic stability of uranium species in molten halide salt mixtures at high temperatures using a combination of experimental and modeling methods. We will investigate both chloride- and fluoride-based salts: UCl_3 or UCl_4 – NaCl or KCl or LiCl or $MgCl_2$, UF_3 or UF_4 – LiF or NaF or KF or $BeCl_2$, and their ternary phases (particularly the eutectics), where the molar ratios will be varied systematically. Valence state, coordination configuration and medium-range structure of molten U salt species will be determined by *in situ* Raman spectroscopy, X-ray absorption spectroscopy and synchrotron X-ray total scattering using a specialized diamond anvil cell coupled with density functional theory and *ab initio* molecular dynamics (AIMD) calculations. Thermodynamic properties, especially enthalpies of mixing, of molten salts will be measured and calculated using high temperature melt calorimetry and AIMD, respectively. The results will reveal the relations between the local structure and thermodynamic stability of uranium-bearing molten halide salts and develop acid-base scales to determine the solubility of uranium in molten halide salts.

This research will fill critical knowledge gaps in the local structures and thermochemical properties of uranium species in molten halide salt mixtures and establish systematic structure – stability relationships based on spectroscopic, scattering and calorimetric data as well as first-principles calculations for predicting their thermodynamic and other macroscopic properties at relevant reactor operating conditions. The following two key questions will be addressed:

• What are the local structures (short-range, coordination structures; medium-range configurations) of uranium species in molten halide salt mixtures, and how do they change as a function of temperature and composition? What are the principles that control solubility and stability of these species in molten halide salts? Are there distinct systematics between molten chloride and fluoride salts?

• What are the systematic changes in the enthalpy interaction parameter (closely tied to complexation) in halide molten salts, from binary to ternary, and with changing cation species? What is an accurate thermodynamic mixing model to describe their far-from-ideal thermodynamic properties? Under what conditions is solubility limited, leading to precipitation of new solid impurity phases?

Specific deliverables include: 1) Determination of short- and medium-range structures of binary and ternary molten halide salt mixtures; 2) Measurements of their thermodynamic properties especially enthalpies of mixing; 3) Establishment of structure-stability relationship; and 4) Development of acid-base scale. Through linking the microscopic structures at atomic/molecular levels with the macroscopic thermodynamic properties of uranium-bearing molten halide salts, the obtained results will have important applications for predicting their thermodynamic and other macroscopic properties at reactor operating conditions and for optimization and development of MSR technologies.