

The modelling of the dissolution of actinide compounds – the use of ab initio methods to calculate thermodynamic data from first principles

Sophie Cooper^{1*}, Matthew Mckenzie¹, Claire Utton¹, Mark Bankhead¹

¹UKNNL, Warrington, UK; *sophie.cooper@uknnl.com

Understanding the dissolution and aqueous speciation of actinide compounds with a range of different acid media is important for decommissioning activities. A chemical thermodynamic model (Pitzer) was developed to describe the dissolution of actinide compounds in concentrated nitric/hydrofluoric acid (HNO₃/HF) solutions at high temperatures (<120°C).

A critical review of the literature identified several gaps relating to the description of species e.g. actinide fluoride and nitride species were poorly described missing Log K and/or enthalpy values. Where data existed, the literature review identified inconsistencies in the reported thermodynamic data e.g. for the fluorides.

To fill the data gap on speciation, Density Functional Theory (DFT) calculations were performed. DFT outcomes were 2-fold - 1) to validate literature data, 2) to generate missing data. Implicit solvation models were generated to calculate Gibbs energy of formation for aqueous actinide fluoride species. Gibbs energy was used to calculate Log K and enthalpy values using the van't Hoff equation. The DFT results showed a strong correlation with experimental Log K's but overpredicted the stability of the formed complex, agreeing with similar published work. Using the developed DFT solvation models and predicted correlations, literature Log K values were validated for the fluorides and enthalpy calculated from first principles.