Modeling Speciation and Phase Equilibria in Aqueous Systems Containing Rare Earth Elements in the Presence of Inorganic and Organic Ligands

Gaurav Das, Jiangping Liu, Malgorzata Lencka and Andre Anderko [C, S]
OLI Systems Inc., Parsippany, NJ, U.S.A.
aanderko@olisystems.com

Thermodynamic properties of rare earth elements in complex, multicomponent aqueous solutions are essential for the design and optimization of processes for the recovery and recycling of rare earths. Therefore, a systematic study has been undertaken to develop a comprehensive thermodynamic model for predicting speciation and phase equilibria in mixtures containing rare earth cations and various inorganic and organic anions. For this purpose, the previously developed Mixed-Solvent Electrolyte (MSE) framework has been extended and parametrized for rare earth-containing systems. The framework has been designed for calculating thermodynamic properties over wide ranges of temperature (up to 300 °C) at concentrations extending to solid-liquid saturation. The framework combines an equation of state for standard-state thermochemical properties of aqueous species with an ion-interaction formulation for the excess Gibbs energy. The model has been applied to rare earth hydroxides and fluorides across the lanthanide series. For this purpose, experimental data on solid-liquid equilibria and complexation equilibria have been critically evaluated and used to determine the optimum thermodynamic parameters for the complex species that exist in solutions. Solid-liquid phase diagrams have been constructed to elucidate the solubility of both crystalline and amorphous solid phases. Regularities in the solubility behavior have been identified as a function of the cation radius for both the hydroxides and fluorides. Furthermore, the model has been applied to rare earths in the presence of strongly complexing organic ligands, including citrate and tartrate ions. For such systems, the model makes it possible to reproduce the competitive formation of rare earth hydroxide and citrate or tartrate solids as a function of pH and ligand concentration, which provides a thermodynamic foundation for emerging electrochemical methods for rare earth separation.