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Solubility and thermodynamics of the U(VI)-Na/Mg-NO_3-H_2O systems

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Understanding the solubility and speciation of long-lived actinides like uranium(VI) contributes to the long-term safety assessment of radioactive waste repositories. Considerable quantities of nitrates will be part of the waste inventory in some repository concepts (ILW-LL in cementitious environment), and accordingly necessitates the investigation of the chemical behavior of U(VI) under these conditions. The solubility, complexation and ion interaction processes in the U(VI)-NO_3 system are addressed in the present study by a combination of experimental solubility investigations and thermodynamic model development.

Solubility experiments within the systems U(VI)-Na-NO_3-H_2O and U(VI)-Mg-NO_3-H_2O were conducted from undersaturation conditions with $UO_2(NO_3)_2{\cdot}6H_2O$(cr) in $NaNO_3$ (0-9 mol/kg H_2O) and $Mg(NO_3)_2$ (0−5 mol/kg H_2O) solutions. Batch experiments were performed at T = (22 ± 2) °C under weakly acidic conditions to prevent U(VI) hydrolysis. Regular sampling and analysis via ICP-OES were executed for all samples to ensure thermodynamic equilibrium. X-ray powder diffraction is used for solid phase analysis.

First thermodynamic SIT[1] and Pitzer[2] models were deduced based on solubility data, isopiestic investigations on the U(VI)-Na-NO_3-H_2O system, and osmotic coefficients in the binary subsystems. Full and partial dissociation approaches were comparatively used, in the later case including the formation of at least two uranyl nitrate complexes, i.e., $UO_2NO_3^+$ and $UO_2(NO_3)_2$(aq). Geochemical calculation codes PhreeqC and PhreeSCALE combined with the PEST parameter estimation software were used in the parametrization routine, with the databases ThermoChimie[3] for SIT and PhreeSCALE[4] for Pitzer modeling. The parameter sets obtained enable a satisfying description of solubility and isopiestic datasets. Further improvements are expected with the consideration of results from spectroscopic techniques like time resolved laser fluorescence, UV/Vis and Raman spectroscopy for a better description of concentration-dependent aqueous species distribution.

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References

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