

## Interaction of An(III/IV/V/VI) with borate in dilute to concentrated alkaline NaCl, CaCl<sub>2</sub> and MgCl<sub>2</sub> solutions

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### Abstract

The assessment of the long term safety of a nuclear waste repository requires reliable information about the chemistry and migration behavior of actinides. Boron may be present in repositories for radioactive waste as a component of the emplaced waste. In repositories in rock-salt formations, boron can further be a component of the intruding brine solutions.

In the present work, the interaction of An(III/IV/V/VI) with borate in dilute to concentrated NaCl, MgCl<sub>2</sub> and CaCl<sub>2</sub> solutions was investigated by a comprehensive series of solubility experiments combined with solid phase characterization and aqueous speciation techniques.

Experiments were performed under inert gas (Ar) atmosphere at 22 ± 2°C. Samples were prepared in 0.1–5.0 M NaCl and 0.25–3.5 M CaCl<sub>2</sub> / MgCl<sub>2</sub> with 0.004 M ≤ [B]<sub>tot</sub> ≤ 0.4 M and 7 ≤ pH<sub>c</sub> ≤ 13. Nd(III), <sup>232</sup>Th(IV), <sup>237</sup>Np(V) and <sup>238</sup>U(VI) solubility was investigated in independent batch experiments from undersaturation using Nd(OH)<sub>3</sub>(am), Th(OH)<sub>4</sub>(am), NpO<sub>2</sub>OH(am,fresh), UO<sub>3</sub>·2H<sub>2</sub>O(cr) and Na<sub>2</sub>U<sub>2</sub>O<sub>7</sub>·1.6H<sub>2</sub>O(cr) as solubility-controlling phases. A synthetic, hydrothermally prepared and well-characterized Nd[B<sub>4</sub>O<sub>13</sub>(OH)<sub>4</sub>](cr) solid phase was also investigated from undersaturation and used to define a reference solubility concentration. Samples were equilibrated for up to 142 days; pH<sub>c</sub> and metal concentration were monitored at regular time intervals with ICP–MS (Nd, Th, U) and LSC (Np). After reaching equilibrium conditions, selected solid phases were characterized by XPS and XRD. Aqueous speciation was investigated by TRLFS and UV–vis/NIR for Cm(III) and Np(V), respectively.

A clear red-shift of the Cm(III) fluorescence peak with increasing borate concentrations indicate complex formation for [B]<sub>tot</sub> ≥ 0.04 M and 6 ≤ pH<sub>c</sub> ≤ 9. In spite of this, no significant increase in Nd(III) solubility occurred in any of the investigated systems in the presence of [B]<sub>tot</sub> ≤ 0.4 M, compared to borate-free systems. On the contrary, a significant decrease in Nd(III) concentration was observed at pH<sub>c</sub> ≤ 9 in NaCl and MgCl<sub>2</sub> systems with [B]<sub>tot</sub> ≥ 0.16 M. This observation, together with a clear change in the slope of the solubility curve and the further confirmation by XPS analyses confirms the transformation of Nd(OH)<sub>3</sub>(am) into a so far unknown Nd(III)-borate solid phase. Similar Nd(III) solubility data and XPS spectra are obtained in undersaturation experiments conducted with the hydrothermally prepared phase Nd[B<sub>4</sub>O<sub>13</sub>(OH)<sub>4</sub>](cr). The observed formation of a An(III)–borate phase with lower solubility than the corresponding pure hydroxide constitutes a new and potentially relevant retention mechanism for An(III) under repository-relevant conditions. The solubility of Th(OH)<sub>4</sub>(am) remains largely unaffected by borate within 7 ≤ pH<sub>c</sub> ≤ 11 in dilute to concentrated NaCl and MgCl<sub>2</sub> solutions. UV–vis /NIR of the supernatant solution in equilibrium with NpO<sub>2</sub>OH(am,fresh) shows a clear red shift of the NpO<sub>2</sub><sup>+</sup> peak (λ = 981 nm) for [B]<sub>tot</sub> ≥ 0.16 M. Analogously with the Nd(III) case, a decrease in solubility accompanied with a change in the color of the Np(V) solid phase takes place in some of the samples with the highest borate concentration. Additional solubility experiments with UO<sub>3</sub>·2H<sub>2</sub>O(cr) and Na<sub>2</sub>U<sub>2</sub>O<sub>7</sub>·1.6H<sub>2</sub>O(cr) are currently on-going to complete the relevant oxidation states within the actinide series with the final aim of establishing robust upper solubility limits and evaluate possible transformation processes into less soluble, repository-relevant, borate-bearing actinide phases.