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Solubility and Speciation of Cm(III) and Nd(III)
in borate rich NaCl and CaCl2 solutions

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Introduction

• Nuclear waste disposal in deep underground facilities requires detailed understanding of aqueous actinide (geo)chemistry in order to assess the long-term performance of a repository. Considering waste disposal in rock salt formations, dedicated studies at high ionic strength conditions are mandatory.
• Batch solubility studies allow robust predictions on radionuclide solubility limits as function of key geochemical parameters (pH, Eh, I) and potentially complexing ligands like borate. Nd(III) is used as a well-established analog for trivalent actinides.
• Detailed analysis of actinide speciation using advanced spectroscopic tools like TRLFS (Time Resolved Laser Fluorescence Spectroscopy) is advised as basis for correct and trustworthy chemical and thermodynamic models.
• Actinide–borate complexation has recently become a focus of research attention following the pioneering study of Borkowski et al. [10BOR/RIC]. Boron can be present a salt-based repository as a component of salt formations, dedicated studies at high ionic strength conditions are mandatory.
• Part of the studies on Cm(III)-TRLFS in NaCl performed in cooperation with LANL-CO.
• Focus of the present study is to:
  1. Derive experimental solubility data for Nd(OH)3(am) in dilute to concentrated NaCl at 7 < pHc < 13 and total boron concentrations from 4 mM < [B]tot < 40 mM.
  2. Derive experimental solubility data for Nd(OH)3(am) in dilute to concentrated CaCl2 at 8 < pHc < 12 and total boron concentrations from 4 mM < [B]tot < 40 mM.
  3. Perform systematic Cm(III)-TRLFS studies in the NaCl- and CaCl2 - borate system.
  4. Get information about the speciation of boron in solution by 11B-NMR studies in NaCl and CaCl2 solutions.

Experimental

Solubility experiments with Nd(III)
• Experiments conducted in Ar-glovebox
  - ca. 10 mg Nd(OH)3(am) per experiment (characterized by XRD)
  - [B4O7]3− = 1 mM and 10 mM
  - [Nd] = 1·10−7 M per sample
  - Background electrolytes: NaCl 0.1 M to 5.0 M
  - Equilibration time: 7d - 140 d
  - Phase separation: 10 kD (2-3 nm) ultrafiltration
  - Reference system without borate [GNSEC/ALT]

TRLFS experiments with Cm(III)
• Samples prepared in Ar-glovebox
  - [Cm] = 1·10−7 M per sample
  - [B4O7]3− = 1 mM and 10 mM, 4·10−3 M and 4·10−2 M
  - Background electrolytes: NaCl 0.1 M to 5.0 M
  - Equilibration time: spectra taken at 1 1 d
  - TRLFS data collection: single emission spectra
  - Reference system for TRLFS without borate [08RAB/ALT]

11B-NMR experiments
• Background electrolytes: NaCl 0.1 M to 5.0 M
  - [B]tot = 40 mM
  - Equilibration time: > 1 month

References


Conclusions

• The speciation of boron in aqueous systems is highly complicated and potentially affected by pH, ionic strength and total boron concentration — mandatory information required for comprehensive thermodynamic description of An-borate complexation.
• 11B-NMR studies only give limited information on the boron speciation in solution.
• Nd(OH)3(am) solubility studies in NaCl or CaCl2 solution at the investigated pHc and boron concentrations do not indicate a pronounced solubility enhancement due to strong boron complexation.
• TRLFS-studies in NaCl or CaCl2 solutions with trace amounts of Cm(III) indicate weak borate complexation at pHc = 8-9 and no borate complexation at high pHc (>10).
• Borate complexation seems to compete with hydrolysis of pHc > 8-9 and is out-competed at higher pH conditions. Evaluation of TRLFS data affected by uncertainties regarding Cm-hydrolysis scheme.
• Following the evaluation of the Nd(III) solubility data and TRLFS in NaCl and CaCl2 solution we conclude that the contribution from An(III)-borate complexation to a solubility based An(III) source term at the investigated borate concentrations is limited.
• Studies are currently being extended to (i) even higher borate concentrations (100 mM) in NaCl solution, (ii) investigations of An(III)-borate interactions in MgCl2 solutions and (iii) similar studies on Th(IV) solubility in borate systems. Studies aim at a comprehensive assessment of borate complexation for tri- and tetravalent Actinides in dilute to concentrated NaCl, MgCl2, and CaCl2 solutions.