Solubility and TRLFS study of Nd(III) and Cm(III) in dilute to concentrated NaCl–$NaNO_3$ and $MgCl_2$–$Mg(NO_3)_2$ solutions

Karlsruhe Institute of Technology

M. Herm[1,*], X. Gaona[1], Th. Rabung[1], D. Fellhauer[1], C. Crepin[2], V. Metz[1], M. Altmaier[1], H. Geckeis[1]

[1] Karlsruhe Institute of Technology, Institute for Nuclear Waste Disposal, P.O. Box 3640, 76021 Karlsruhe, Germany

[2] Ecole National Supérieure de Chimie de Montpellier, 8 Rue de l'Ecole Normale, 34296 Montpellier CEDEX 5, France

[*] michel.herm@kit.edu

Introduction

- Long–term performance assessment of deep geological nuclear waste repositories → prediction of chemical behavior of An and long lived FP in aqueous solutions needed.
- Waste disposal in rock–salt formations in USA; option under consideration in Germany → high [Na^+], [Mg^{2+}] and [Cl^-] expected in water intrusion scenarios.
- Nitrate can be found in high concentrations (≥ 1 M) as part of certain waste forms → waste originated from reprocessing facilities.
- Previous complexation studies with nitrate focused on acidic conditions; no $MgCl_2$ systems considered.

Objectives of this work

- **Assessment of NO_3^- effect on Ln(III)/An(III) solubility under repository relevant conditions.**
- **Development of chemical, thermodynamic and activity models for the system Ln(III)/An(III) in NaCl–$NaNO_3$ and $MgCl_2$–$Mg(NO_3)_2$ solutions.**

Experimental

Solubility experiments

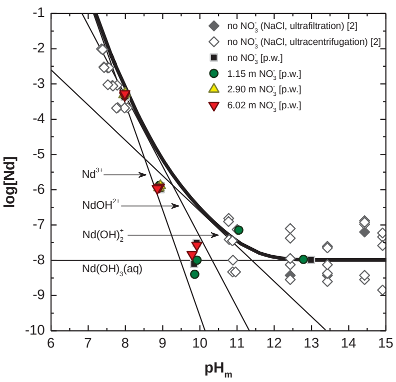
- Batch experiments in Ar atmosphere (22 ± 2°C)
- Undersaturation approach in 0.1–5.0 M NaCl–$NaNO_3$ and 0.25–4.5 M $MgCl_2$–$Mg(NO_3)_2$ mixtures → **up to 7 M NO_3^-**
- pH range: 7.5 ≤ pH_m ≤ 13.0
- 6–12 mg $Nd(OH)_3$(am) solid phase used in each experiment
- Equilibration time: t ≤ 500 days
- pH measurements: $pH_m = -\log m_{H^+} = pH_{exp} + A_m$ [1]; A_m for Cl^-–NO_3^- mixtures determined in this study
- [Nd(III)] measured by ICP–MS after 10 kD (2-3 nm) ultrafiltration
- Solid phase characterization: XRD, SEM–EDX

Cm(III)–TRLFS

- Sample preparation in Ar atmosphere (22 ± 2°C)
- TRLFS studies in 5.0 M NaCl–$NaNO_3$, 0.25 and 3.5 M $MgCl_2$–$Mg(NO_3)_2$ mixtures → **up to 7 M NO_3^-**
- pH range: 1 ≤ pH_m ≤ 9
- [Cm(III)] ~1×10^{-7} M per sample

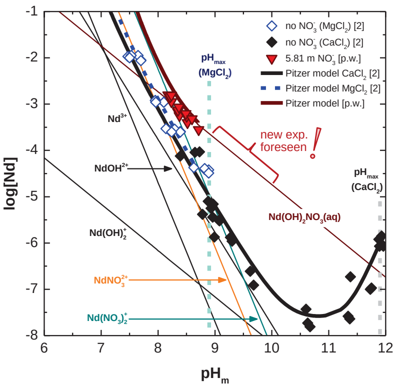
Results and discussion

Solubility of Nd(III) in 5.0 M NaCl–$NaNO_3$



- Very good agreement with nitrate–free solubility data reported in [2].
- No effect of NO_3^- on $Nd(OH)_3$(am) solubility in NaCl–$NaNO_3$ systems **(even in 5 M $NaNO_3$)**.

Solubility of Nd(III) in 3.5 M $MgCl_2$–$Mg(NO_3)_2$



- Significant effect of [NO_3^-] on $Nd(OH)_3$(am) solubility.
- Slope of solubility curve increases at pH_m ≥ 8.44 → change in number of OH^- involved in solubility reaction.
- Additional experiments in $CaCl_2$–$Ca(NO_3)_2$ (pH_{max} ~12) planned to confirm this trend.
- *Handouts with experimental data at other ionic strength can be shown upon request.*

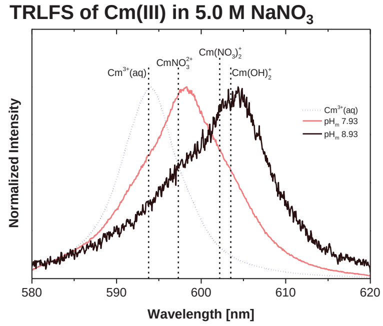
Chemical and thermodynamic model for the system Nd^{3+}/Cm^{3+}–H^+–Mg^{2+}–OH^-–Cl^-–NO_3^-

(preliminary Pitzer model available upon request)

- Solid phase controlling solubility: $Nd(OH)_3$(am) (XRD, SEM–EDX).
- Slope −1 in presence of NO_3^- and pH_m ≥ 8.44 → 1 Nd(III) : 2 OH^- (solubility).
- Binary Cm(III)–NO_3 species relevant for pH_m ≤ 8.14 (TRLFS).
- Formation of $Cm(OH)_2NO_3$(aq) indicated by TRLFS at pH_m ≥ 8.44.

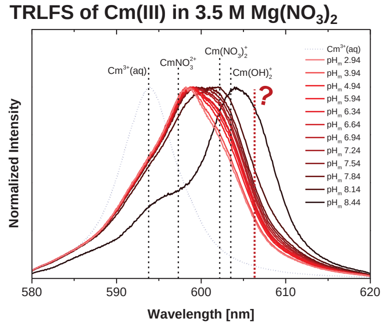
$$Nd(OH)_3(am) + H^+ + NO_3^- \Leftrightarrow Nd(OH)_2NO_3(aq) + H_2O$$

TRLFS of Cm(III) in 5.0 M $NaNO_3$



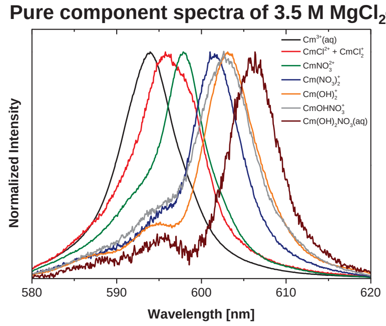
- $CmNO_3^{2+}$ prevails in 5 M $NaNO_3$ and pH_m < 8.93.
- $Cm(OH)_2^+$ dominates at pH_m ≥ 8.93.
- No clear evidence of relevant ternary Cm–OH–NO_3 species in 5 M $NaNO_3$.

TRLFS of Cm(III) in 3.5 M $Mg(NO_3)_2$



- $CmNO_3^{2+}$ and $Cm(NO_3)_2^+$ forming at pH_m ≤ 8.14, in good agreement with thermodynamic calculations based upon [3].
- New (ternary) species arising at pH_m ≥ 8.44.
- Three ligands complexing Cm(III) based upon red shift: 1 Cm(III) : 2 OH^- : 1 NO_3^-.

Pure component spectra of 3.5 M $MgCl_2$–$Mg(NO_3)_2$



- Nitrate effect → genuine complexation reaction!
- Very complex Cm(III) speciation found in $MgCl_2$–$Mg(NO_3)_2$ mixtures → two ternary Cm–OH–NO_3 species forming.

Conclusion and outlook

- **Nitrate significantly influences solubility of $Nd(OH)_3$(am) in concentrated and weakly alkaline $MgCl_2$–$Mg(NO_3)_2$ solutions at [Mg^{2+}] ≥ 2.5 M and [NO_3^-] ≥ 1 M.**
- **TRLFS data confirm that the effect of NO_3^- on solubility is resulting from complex formation reactions and not related to matrix effects (presence of NO_3^- instead of Cl^-).**
- **A chemical model has been proposed including the formation of the ternary aqueous species $Nd(OH)_2NO_3$(aq) in equilibrium with solid $Nd(OH)_3$(am).**
- **Thermodynamic and activity models (Pitzer) for Nd^{3+}/Cm^{3+}–H^+–Mg^{2+}–OH^-–Cl^-–NO_3^- system are currently derived, based upon the proposed chemical model.**
- **Additional solubility experiments in $CaCl_2$–$Ca(NO_3)_2$ and use of advanced spectroscopic techniques (EXAFS/XANES) foreseen to confirm aqueous speciation.**

References

[1] M. Altmaier, V. Metz, V. Neck, R. Müller, Th. Fanghänel. *Geochim. Cosmochim. Acta* **67**, 3595 (2003).

[2] V. Neck, M. Altmaier, Th. Rabung, J. Lützenkirchen, Th. Fanghänel. *Pure Appl. Chem.* **81**, 1555 (2009).

[3] A. Skerencak, P. J. Panak, W. Hauser, V. Neck, R. Klenze, P. Lindqvist-Reis, Th. Fanghänel. *Radiochim. Acta* **97**, 385 (2009).

Acknowledgements: M. Böttle, F. Geyer and E. Soballa are kindly acknowledged for their technical support during this study.