

## Solubility and spectroscopic study of An<sup>III</sup>/Ln<sup>III</sup> in dilute to concentrated Na–Mg–Ca–Cl–NO<sub>3</sub> solutions

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### Abstract

In long-term safety analyses for deep geological nuclear waste repositories a reliable prediction of the chemical behavior of actinides in aqueous solutions is necessary. Although geological or geotechnical barriers may prevent formation water from contacting the waste, intrusion of aqueous solutions into a repository has to be taken into account. Porewater in certain sedimentary bedrocks as well as water potentially intruding salt rock repositories will be characterized by high ionic strength and high Na<sup>+</sup>, Mg<sup>2+</sup> and Cl<sup>-</sup> concentrations. An(III) and An(IV) are the most relevant actinide redox states under the reducing conditions which develop after the closure of deep underground repositories for nuclear waste. In repositories containing waste from nuclear fuel reprocessing, high concentrations of nitrate ( $\geq 1.0$  M) and slow nitrate reduction kinetics may affect the aqueous speciation of radionuclides and thus impact their mobilization into the biosphere. In this study, the solubility and speciation of trivalent actinides and lanthanides in dilute to concentrated NaCl–NaNO<sub>3</sub>, MgCl<sub>2</sub>–Mg(NO<sub>3</sub>)<sub>2</sub> and CaCl<sub>2</sub>–Ca(NO<sub>3</sub>)<sub>2</sub> mixed solutions are investigated at repository relevant pH conditions and  $22 \pm 2^\circ\text{C}$ .

All samples were prepared and stored in Ar glove boxes. Batch solubility experiments were performed from under-saturation with Nd(OH)<sub>3</sub>(am). Solid phases were characterized using XRD and SEM-EDX. Nd–L<sub>III</sub> EXAFS spectra were recorded at the INE beamline at ANKA. Cm(III)–TRLFS measurements were performed with  $\sim 10^{-7}$  M Cm(III) per sample.

No significant enhancement in Nd(OH)<sub>3</sub>(am) solubility occurs in NaCl–NaNO<sub>3</sub> and CaCl<sub>2</sub>–Ca(NO<sub>3</sub>)<sub>2</sub> mixtures compared to nitrate-free systems [1]. A clear increase in solubility occurs for MgCl<sub>2</sub>–Mg(NO<sub>3</sub>)<sub>2</sub> mixtures with  $m_{\text{Mg}^{2+}} \geq 2.83$  m,  $m_{\text{NO}_3^-} \geq 1.13$  m and pH<sub>m</sub> 8–9. Provided the solubility control exerted by Nd(OH)<sub>3</sub>(am) (confirmed by XRD and SEM-EDX in all systems with  $m_{\text{Cl}^-} \leq 5.82$  m), the slope analysis of the experimental data in MgCl<sub>2</sub>–Mg(NO<sub>3</sub>)<sub>2</sub> mixtures indicates the formation of aqueous species Mg–Nd–OH–NO<sub>3</sub> with stoichiometries Nd:OH 1:1 (pH<sub>m</sub>  $\leq 8.3$ ) and Nd:OH 1:2 (pH<sub>m</sub>  $> 8.3$ ). Cm(III)–TRLFS data reveals the formation of aquatic “Cm(III)–OH–NO<sub>3</sub>” species with pH<sub>m</sub>  $\geq 4.94$  only in MgCl<sub>2</sub>–Mg(NO<sub>3</sub>)<sub>2</sub> systems, thus hinting towards the participation of Mg in the complex formation. Moreover confirmed by EXAFS, where the peak at  $\sim 4 \text{ \AA}$  is properly fitted with Mg as backscatterer. Slope analysis, solid phase characterization, Cm(III)–TRLFS and Nd–L<sub>III</sub> EXAFS observations confirms the relevance of the equilibrium reactions  $\text{An}^{\text{III}}/\text{Ln}^{\text{III}}(\text{OH})_3(\text{am}) + \text{H}^+ + \text{NO}_3^- + \text{Mg}^{2+} \leftrightarrow \text{Mg}[\text{An}^{\text{III}}/\text{Ln}^{\text{III}}(\text{OH})_2\text{NO}_3]^{2+} + \text{H}_2\text{O}$  and  $\text{An}^{\text{III}}/\text{Ln}^{\text{III}}(\text{OH})_3(\text{am}) + 2\text{H}^+ + \text{NO}_3^- + \text{Mg}^{2+} \leftrightarrow \text{Mg}[\text{An}^{\text{III}}/\text{Ln}^{\text{III}}\text{OHNO}_3]^{3+} + 2\text{H}_2\text{O}$  in concentrated nitrate-bearing Mg–systems and permits to further extend the chemical, thermodynamic and activity models described in [1] for Ln(III) and An(III) to  $\text{Ln}^{3+}/\text{An}^{3+} - \text{H}^+ - \text{Na}^+ - \text{Mg}^{2+} - \text{Ca}^{2+} - \text{OH}^- - \text{Cl}^- - \text{NO}_3^-$  systems.

### References:

[1] Neck V., Altmaier M., Rabung Th., Lützenkirchen J., Fanghänel Th., *Pure Appl. Chem.*, **81**, (2009) 1555–1568.