SOLUBILITY AND TRLFS STUDY OF Nd(III) AND Cm(III) IN DILUTE TO CONCENTRATED ALKALINE NaCl–NaNO₃ AND MgCl₂–Mg(NO₃)₂ SOLUTIONS

M. Herm[1], X. Gaona[1], Th. Rabung[1], C. Crepin[2], V. Metz[1], <u>M. Altmaier</u>[1], H. Geckeis[1]

[1] *Institute for Nuclear Waste Disposal, Karlsruhe Institute of Technology, Karlsruhe, Germany*
[2] *Ecole National Supérieure de Chimie de Montpellier, Montpellier, France*

In long–term performance assessment 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^+, Mg^{2+} and Cl^- concentrations. In repositories with waste from nuclear fuel reprocessing, high nitrate concentrations (≥ 1.0 M) and slow nitrate reduction kinetics have to be taken into account which may impact the mobilization of actinides. 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.

Nitrate complexes of actinides are reported to be weak but clearly more stable than the corresponding chloride counterparts. Accounting for the An(III)–NO_3 system, the last NEA–TDB update [1] selected only thermodynamic data for the complex $AmNO_3^{2+}$. Recent Cm(III)–TRLFS studies in the presence of elevated nitrate concentrations proposed the formation of both $CmNO_3^{2+}$ [2–3] and $Cm(NO_3)_2^+$ [2] complexes. So far, all these studies focus on acidic conditions, leaving aside the assessment of nitrate effects under neutral to alkaline repository–relevant pH conditions.

Solubility experiments were conducted with $Nd(OH)_3(am)$ in 0.1–5.0 M NaCl–NaNO₃ and 0.25–4.5 M MgCl₂–Mg(NO₃)₂ mixtures at $7.5 \leq pH_c \leq 13$ and $0 \leq [NO_3^-] \leq 7.0$ M at $22 \pm 2°C$ under inert gas (Ar) atmosphere. Samples were equilibrated for $t \leq 500$ days, and pH_c and [Nd] (ICP–MS) monitored at regular time intervals. After ensuring equilibrium conditions, solid phases were characterized by XRD and SEM–EDX. Aqueous speciation was further investigated by TRLFS with $\sim 10^{-7}$ M Cm(III) in 5.0 M NaCl–NaNO₃ and 0.25/3.5 M MgCl₂–Mg(NO₃)₂ mixtures as background electrolyte. The original pH_c ($pH_{max} \sim 9$) was titrated to $pH_c = 1$ with HCl of corresponding ionic strength and Cm(III) fluorescence spectra collected at each individual pH_c. The comparison of Nd(III) solubility in MgCl₂–Mg(NO₃)₂ systems with nitrate–free MgCl₂ solutions [4] shows a clear increase of [Nd(III)] for $[Mg^{2+}] \geq 2.5$ M, $[NO_3^-] \geq 1.0$ M and pH_c 8–9. In contrast to Mg–bearing systems, no effect of nitrate on Nd(III) solubility is observed in dilute to concentrated NaCl–NaNO₃ solutions even up to 5.0 M NaNO₃. XRD and SEM–EDX results confirm that $Nd(OH)_3(am)$ is the solubility controlling solid phase in all systems with $[Cl^-] \leq 5.0$ M. TRLFS studies in 3.5 M MgCl₂–Mg(NO₃)₂ with $0 \leq [NO_3^-] \leq 7.0$ M solutions indicate the formation of $CmNO_3^{2+}$ and $Cm(NO_3)_2^+$ complexes in acidic to near neutral pH conditions as previously described in [2]. Peak deconvolution of the complete set of fluorescence spectra further reveals the formation of ternary Cm–OH–NO_3 species under weakly alkaline pH_c conditions, likely $CmOHNO_3^+$ and $Cm(OH)_2NO_3(aq)$. These spectroscopic results confirm that the observed increase in solubility for $Nd(OH)_3(am)$ is not a simple matrix effect but is related to a genuine complexation reaction with nitrate.

The combination of slope analysis, solid phase characterization and TRLFS indicates the equilibrium reaction $Nd(OH)_3(am) + 2H^+ + NO_3^- \Leftrightarrow NdOHNO_3^+ + 2H_2O$ in concentrated nitrate–bearing systems and permits to further extend the chemical and thermodynamic models described in [4] for Ln(III) and An(III) to Ln^{3+}/An^{3+}–H^+–Na^+–Mg^{2+}–Ca^{2+}–OH^-–Cl^-–NO_3^- systems.

[1] R. Guillaumont, Th. Fanghänel, V. Neck, J. Fuger, D.A. Palmer, I. Grenthe, M.H. Rand, Elsevier, Amsterdam (2003).
[2] A. Skerencak, P.J. Panak, W. Hauser, V. Neck, R. Klenze, P. Lindqvist-Reis, Th. Fanghänel, Radiochim. Acta 97, 385–393 (2009).
[3] L. Rao, G. Tian, Dalton Trans. 40, 914–918 (2011).
[4] V. Neck, M. Altmaier, Th. Rabung, J. Lützenkirchen, Th. Fanghänel, Pure Appl. Chem. 81, 1555–1568 (2009).