Pu(VI) HYDROLYSIS IN AQUEOUS NaCl-NaOH SOLUTIONS

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Abstract The hydrolysis behavior of Pu(VI) in aqueous solution shows some unique features amongst the An(VI) series. One example is the observation that U(VI) and Np(VI) readily form sparingly soluble An(VI)-(hydr)oxide solid phases in neutral to alkaline solutions, whereas the hydrolytic behavior of Pu(VI) is dominated by the formation of dissolved polynuclear hydrolysis species $(PuO_2)_y(OH)_x^{2y-x}(aq)$. The latter are metastable, even at relatively high $[Pu(VI)]_{tot}$, which becomes evident in the kinetically unfavored formation of Pu(VI)-(hydr)oxides. Most of the available experimental studies on Pu(VI)-OH speciation focus on systems with acidic and near-neutral pH_c values [1], fewer also covered alkaline pH_c conditions, *e.g.*, [2, 3]. Still, a (halfway) clear pictures of the polynuclear $(PuO_2)_y(OH)_x^{2y-x}(aq)$ speciation arises only for acidic to neutral conditions, leaving clear gaps in the chemical understanding and thermodynamic description. In this work we have evaluated the Pu(VI)-OH speciation in 1.0 M NaCl-NaOH up to high alkalinity by Vis/NIR spectroscopy, and highlight the great importance of polynuclear Pu(VI)-OH species.

All experiments were performed under inert Ar atmosphere at T = 23±3°C. Oxidation state pure $^{242}PuO_2^{2+}$ stock solutions were used as Pu starting material. About 200 independent Pu(VI) samples with V = 1.5-5.0 mL and I = 1.0 M (aqueous NaCl-NaOH) were prepared and analysed by UV-Vis/NIR absorption spectroscopy (Agilent Cary 6000i, Perkin Elmer Lambda 1050+), pH_c (glass combination electrode or, for highly alkaline samples, calculated from the analytical $[OH^-]$), and [Pu(VI)] after equilibration (liquid extraction, LSC). These samples were implemented in a systematic experimental framework, namely i) two pH_c dependent series where [Pu(VI)] was kept (approx.) constant at $2.2\cdot10^{-4}$ M and $5.0\cdot10^{-4}$ M with pH_c varied between 2.0 and 13.7, and ii) 14 concentration dependent series where [Pu(VI)] was typically varied from $\approx 10^{-5}$-10^{-3} M at fixed pH_c between 5.3 to 13.7. All data were systematically evaluated including the use of model-based and model-free fitting tools. An additional set of four samples with high [Pu(VI)] and selected pH_c values were investigated by Pu L_3-edge XANES and EXAFS at the *INE Beamline for Radionuclide Research at the Karlsruhe Research Accelerator (KARA)* to determine structural parameters of the predominant Pu(VI)-OH species. Crystalline precipitates that occasionally formed in some of the most alkaline samples were analyzed by SEM-EDX, solid state Vis/NIR, Raman, single crystal XRD (at *JRC Karlsruhe*) and Pu L_3-edge XAFS.

Figure 1a shows exemplarily the 40 absorption spectra of the pH dependent series with [Pu(VI)] = $2.2\cdot10^{-4}$ M and pH_c = 2.0-13.7 in the region of the prominent Pu(VI) NIR absorption band at λ = 820-900 nm. Under the experimental boundary conditions, unhydrolyzed Pu(VI), *i.e.*, the aquo ion PuO_2^{2+} with $\lambda_{max} \approx 830$ nm and minor contributions from PuO_2Cl^+ with $\lambda_{max} \approx 836$ nm, is predominant for $pH_c \approx$ 2-5. The onset of Pu(VI) hydrolysis occurring at $pH_c \geq \approx 5$ is apparent from the decrease of the aquo ion absorbance and the formation of new peaks at λ = 840-900 nm. Systematic evaluation of all data provided a comprehensive chemical model for the Pu(VI) hydrolysis. The initial Pu(VI)-OH species is the dimer $(PuO_2)_2(OH)_2^{2+}$. While its stability field is rather small, we can show that four trimeric species of the type $(PuO_2)_3(O)(OH)_x^{4+-x}$ with x = 3-6, briefly (3,5), (3,6), (3,7), (3,8), are dominating the aqueous Pu(VI) over wide ranges of $pH_c \approx 6$-13 and [Pu(VI)]. Finally, the mononuclear complex $PuO_2(OH)_4^{2-}$ (1,4) starts forming at $pH_c > 12$ representing the limiting complex for the present system. The chemical speciation and the corresponding equilibrium constants evaluated in the present work significantly enhance the present NEA-TDB model [1]. Structural parameters of the trimeric solution species were derived from the results of Pu L_3-edge EXAFS measurements. Brownish needle-like crystals formed in certain samples with very high [Pu(VI)] and most alkaline pH_c values. The results from single crystal analysis reveals that this material is exclusively built from Na-$(PuO_2)_{60}$-O(H) cage-clusters, see Figure 1b. The formation of the latter can be understood as a self-assembly (condensation) of twenty trimers of the type $(PuO_2)_3(O)(OH)_6^{2-}$(aq) which are the predominant species under the building conditions of these crystals. Additional results from SEM-EDX, solid state Vis/NIR and Raman are discussed in the presentation.

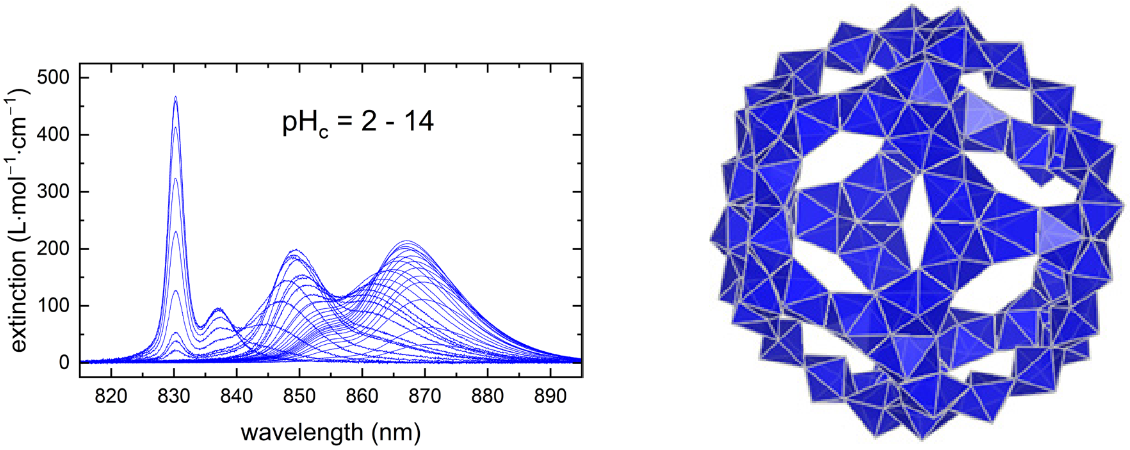

Figure 1. a) NIR spectra of $2.2 \cdot 10^{-4}$ M Pu(VI) in 1.0 M NaCl-NaOH with $pH_c = 2.0$-13.7, b) depiction of the Na-$(PuO_2)_{60}$-O(H) buckyball building up needle-like Na-Pu(VI)-O(H) crystals.

The present work provides for the first time a comprehensive picture of the Pu(VI) hydrolysis and thermodynamics in aqueous solutions valid over the entire pH range, and describes a novel structural type of M-Pu(VI)-O(H) compounds. It also closes a cold case tracing back to the Manhattan project reports from 1949 where formation of the same type of crystal was initially reported without revealing its chemical nature [4].

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