Karlsruhe Institute of Technology

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Solubility and hydrolysis of $NpO_2(am)$ and $PuO_2(am)$ in dilute to concentrated NaCl solutions

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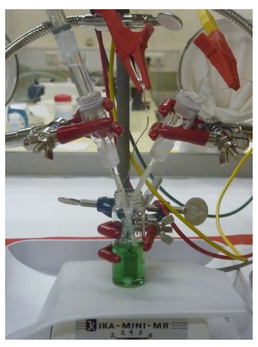
Introduction

- Water intrusion into nuclear waste repository: aquatic radionuclide chemistry and thermodynamics highly relevant for reliable safety assessment.
- Impact of various solution conditions have to be considered, e.g. pH_m, ionic strength I_m, ligands, etc.
- Actinide elements (Pu, Np):
  - highly relevant contribution to radiotoxicity for > 10^5 a
  - complex redox chemistry: An(III / IV / V / VI) redox-neutral + reduc. cond.: An(IV), An(III)
- Studies on the solubility and speciation of An mandatory to understand the redox chemistry
- Previous studies on solubility and hydrolysis of $NpO_2(am)$ and $PuO_2(am)$:
  - comprehensive studies over a wide range of I_m and pH_m values not available
  - data missing for pH_m 3 - 6
  - large uncertainty in reported data for Np(IV) for pH_m > 6

Experimental

- **Synthesis of $NpO_2(am)$:**
  - Pure Np(IV) stock solution prepared by electrolysis
  - $NpO_2(am)$ precipitation with NaOH
- **Synthesis of $PuO_2(am)$:**
  - Pure Pu(VI) stock solution prepared by electrolysis
  - Slow reduction with hydroquinone to Pu(IV) at pH_m = 8 ($E_h \approx$ 50 mV)
  - XRD characterization of the resulting solid phase
- **Batch solubility samples:**
  - Ar glove box: very low O_2 and CO_2 levels
  - 1-3 mg $NpO_2(am)$ or $PuO_2(am)$ per sample
  - [NaCl] = 0.1, 0.5, 2, 4, 5 mol/L
  - $pH_m = -\log[H^+]$ = 2 – 13 (partly stabilized by pH buffers MES and PIPES)
  - Redox buffer (Np exp.): Sn(II), NaS_2O_4, AH_2QDS
  - Redox buffer (Pu exp.): H_2Q, AH_2QDS
  - Equilibration time (Np exp.) 0-60 days (on-going)
- **Measurements:**
  - ^{237}Np and ^{242}Pu determined by liquid scintillation counting after ultrafiltration (10kD)
  - pH_m with combined glass electrodes (Ross)
  - E_h with Metrohm combination platinum electrodes



Electrochemical cell

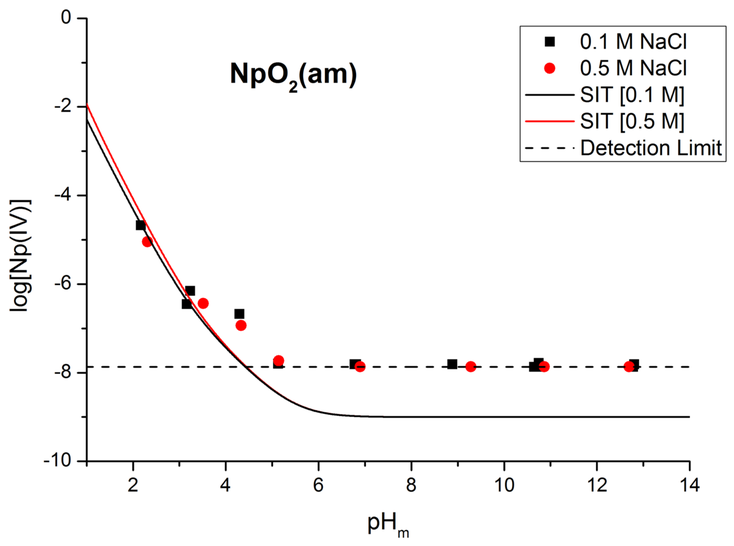
References

[2001NEC/KIM] V. Neck, J. I. Kim, *Radiochimica Acta,* **2001**, *89*, 1–16.

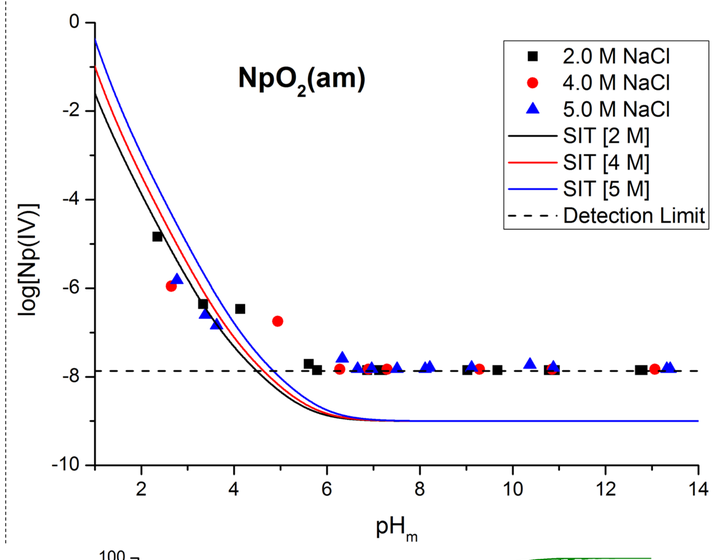
[2003GUI/FAN] Guillaumont, R., Fanghänel, J., Neck, V., Fuger, J., Palmer, D.A., Grenthe, I., Rand, M.H. (2003) Chemical Thermodynamics 5. Update on the Chemical Thermodynamics

Solubility of $NpO_2(am)$

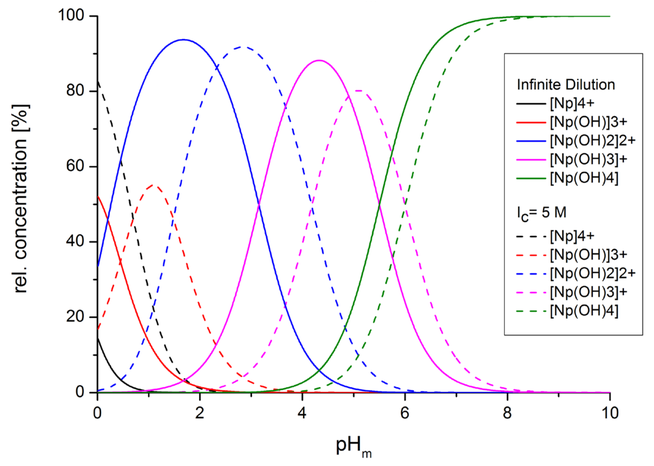
Low ionic strength (I_m < 1)



High ionic strength (I_m > 1)



- Exp. E_h values ca. -20 mV (low pH_m) to -700 mV (high pH_m) → effective stabilisation of An(IV) by redox buffers
- **pH_m < 6:**
  - First systematic solubility data for $NpO_2(am)$
  - Exp. data for I_m = 0.1 + 0.5 M in good agreement with SIT calculations
  - I_m > 0.5 M: slight deviations between exp. data and model → data not yet in equilibrium (?)
- **pH_m > 6:**
  - Exp [Np(IV)] at/below LSC det. lim. (in line with literature data).
  - HR-ICPMS analysis ongoing to quantify Np(IV) equilibrium concentration

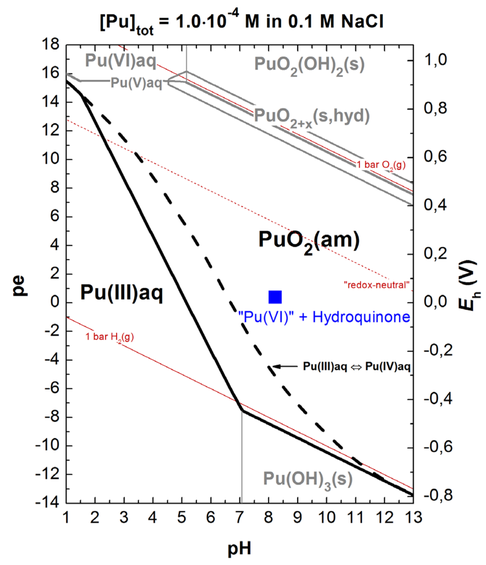


Thermodynamic calculations

- log $*\beta^\circ_{(1,x)}$ and log $*K_{s,0}$ taken from [2001NEC/KIM] and [2003GUI/FAN]
- SIT ion interaction coefficients estimated in [2001NEC/KIM]

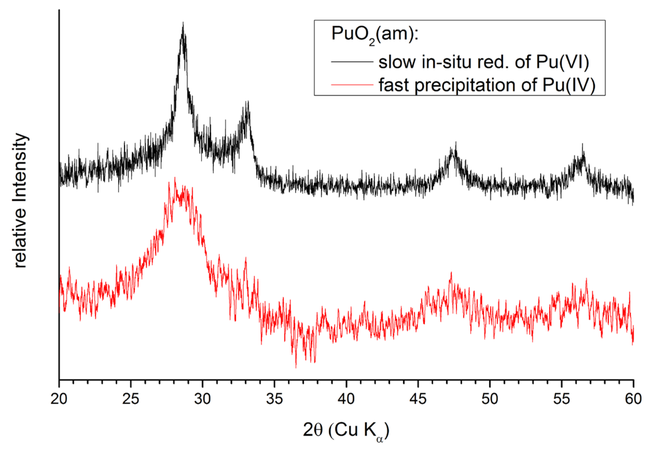
Solubility of $PuO_2(am)$ *(in preparation)*

Predominance diagram: pH_m and E_h measurements



- Experimental pH_m and E_h in the stability field of Pu(IV) → conditions chosen to favor the slow in-situ reduction of Pu(VI) and precipitation of $PuO_2(am)$

Powder X-ray diffraction



- XRD spectra shows sharper peaks than prepared with electrolysis → $PuO_2(am)$ more crystalline
- Solid phase to be used in batch solubility samples *(in preparation)*

Summary and outlook

- First systematic study of the solubility and hydrolysis of $NpO_2(am)$ in dilute to concentrated NaCl solutions over the entire pH_m range
  - Np(IV) solubility data at I_m < 0.5 in good agreement with thermodynamic calculations.
  - Data at I_m > 0.5 not yet in equilibrium (after 60 days)
  - Np(IV) solubility experiments to be complemented with accurate solid phase characterizaton (XRD, SEM–EDX, TEM), liquid-liquid extraction and UV-vis investigations (for samples with higher [Np])
- $PuO_2(am)$ solid phase prepared and ready to start solubility experiments
- Np(IV) and Pu(IV) investigations will be extended to *carbonate containing solutions:* investigation of An(IV)-OH-CO_3 complexes
- Pu investigations will be extended to strongly reducing solutions in the absence and presence of carbonate