SOLUBILITY AND REDOX BEHAVIOUR OF PLUTONIUM UNDER HYPERALKALINE REDUCING CONDITIONS

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Background

- Disposal of radioactive waste: repositories in deep geological formations:
  Anoxic corrosion of Fe → reducing conditions
- Disposal of low and intermediate level wastes (L/ILW) → presence of cementitious materials:
  $10 \leq pH \leq 13.3$
- Knowledge of the aquatic chemistry of actinides within the given boundary conditions (pH, E_h): fundamental input in Safety Assessment of repositories for radioactive waste disposal

Pu chemistry

Alkaline, reducing conditions:

- $pH_m \leq 9$ - Pu(III) and Pu(IV) [1]
- $pH_m > 9$ – $Pu(IV)_{aq,s}$ (only?)
- Relevant uncertainties associated to Pu(III) thermodynamic data [2]
- Ill-defined Pu(IV) / Pu(III) redox border under alkaline conditions
- Key input for the prediction of Pu chemical behaviour

Objectives

- Determination of PuO_2(am,hyd) solubility under alkaline to hyperalkaline reducing conditions
- Investigation of the redox behaviour of Pu in the aqueous and solid phase → use of advanced characterization methods
- Reduction of uncertainties for the Pu(IV) / Pu(III) thermodynamic data in the hyperalkaline pH range
- Setting the basis for investigating the impact of ISA on Pu chemistry under hyperalkaline reducing conditions

Experimental

Solubility experiments

- Three series of samples, prepared and stored at 22 ± 2 °C in Ar-gloveboxes (O_2 content < 2 ppm)
- Undersaturation solubility experiments with aged $^{242}PuO_2$(am,hyd), I = 0.10 M (HCl/NaCl/NaOH)
- Acidic series: pH_m = 3 – 6, unbuffered system
  30 mg of Pu solid; equilibration time: ~8 years
- Alkaline series: pH_m = 8 (TRIS), 9 (CHES) to 12.8
  - Redox conditions buffered by:
    2 mM **hydroquinone (pe + pH_m = 9.5 ± 1)**
    (*"reference system" → predominance of Pu(IV)*)
    2 mM **$SnCl_2$ (pe + pH_m = 2 ± 1)**
    (*strongly reducing conditions → Pu(IV) + Pu(III)?*)
  - 0.2-1 mg ^{242}Pu per sample(→ from acidic series)
  - equilibration time ≤ 173 days
- m_{Pu}, pH_m and E_h values regularly monitored

Aqueous phase characterization

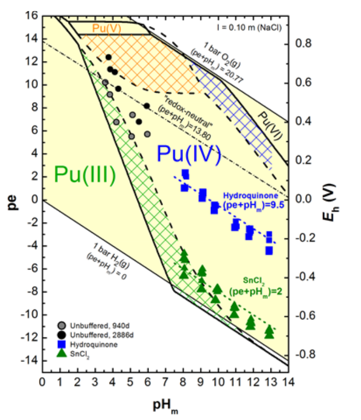
- Phase separation: 10 kD ultrafiltration (LSC) or ultra-centrifugation at 90000 rpm (SF-ICP-MS)
- $[Pu]_{tot}$ determined by LSC or (SF-)ICP-MS
- Pu redox state analysis:
  Liquid-liquid extraction (described in [1])
  PMBP and HDEHP (+ oxidation step with $K_2Cr_2O_7$)
  Capillary Electrophoresis (CE) coupled SF-ICP-MS
  730 mm - fused silica capillary, 75 µm inner diam., CE-BGE: 1.00 M acetic acid, separation voltage of 30 kV, EOF marker: 2-bromo-ethanol

Solid phase characterization

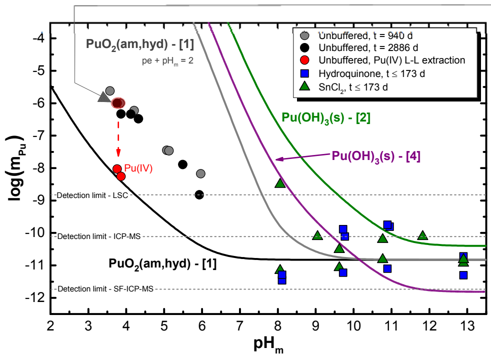
- conventional XRD
- XANES and (synchrotron-based) in-situ XRD → INE-Beamline for Actinide Research at ANKA [3]

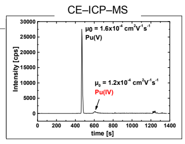
Pourbaix-diagram

Experimentally measured (pe + pH_m) values



Solubility and redox speciation





Acidic region

- Consistent values after 940d and 2886d,
- Solvent extraction and CE–ICP–MS: Pu(V) - predominant aqueous species

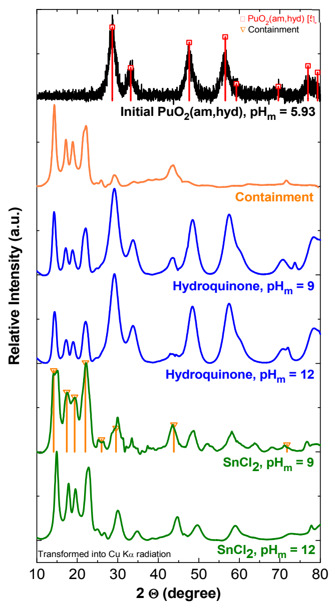
PuO_2(am,hyd) solubility-controlling phase; $m_{Pu(IV)}$ known:
$\log^*K°_{s,0}$= –58.12 ± 0.30 (excellent agreement with [1])

Alkaline region

- Hydroquinone system: very low m_{Pu} (–9.9 ≤ $\log(m_{Pu})$ ≤ –11.4) within $8 \leq pH_m \leq 12.8$ → $Pu(IV)_s \leftrightarrow Pu(IV)_{aq}$
- $SnCl_2$ system: very low m_{Pu} at $pH_m \geq 9$. Behaviour at pH_m = 8 under evaluation → formation of $Pu(III)_s$ and/or $Pu(III)_{aq}$? [4]

Solid phase characterization

Conventional / in-situ XRD



Diffraction patterns

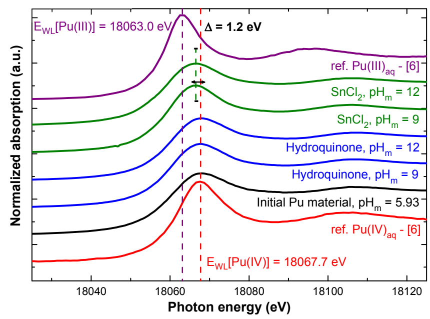
- Initial Pu solid from acidic solubility series, pH_m = 5.93
- solid phases from HQ–syst.:
  – perfect match with patterns of PuO_2(cr) reported in [5]

PuO_2(am,hyd) confirmed as solubility controlling phase

- $SnCl_2$–buffered system:
  – weaker signal of PuO_2(cr), additional reflections related to $Sn_3O_2(OH)_2$(s) at pH_m = 9

Expected predominance of PuO_2(am,hyd), however the presence of Pu_2O_3(cr) and PuO_{2-x}(cr) cannot be ruled out → similar XRD patterns

XANES



Pu L_{III}-edge spectra

- HQ–buffered systems and initial solid material:
  – identical edge energies with the reference value of $Pu(IV)_{aq}$ reported in [6]
- $SnCl_2$–buffered systems:
  – shift in the white line position: ΔE = 1.2 eV

Significant contribution of Pu(III) → 30 ± 5 % by LC of the reference spectra from [6]

Summary

- A nanocrystalline PuO_2(am,hyd) solid phase was thoroughly characterized using XRD, XPS and XANES analysis. Experimentally determined $\log^*K°_{s,0}$ is in excellent agreement with current NEA–TDB selection [2]
- Solubility of Pu in hydroquinone systems at $8 \leq pH_m \leq 13$ is very low and consistent with the solubility control by PuO_2(am,hyd) ↔ $Pu(IV)_{aq}$
- XANES analyses confirm the presence of a Pu(III) solid phase in $SnCl_2$ systems. However, Pu solubility remains very low (≤ 10^{-10} m) at $pH_m \geq 9$ → $\log^*K°_{s,0}\{Pu(OH)_3(s)\}$ selected in NEA–TDB [2] likely overestimated

Outlook

- Additional experiments on-going in $SnCl_2$ systems at $pH_m \leq 9$ to determine the formation and stability of $Pu(III)_s$ and $Pu(III)_{aq}$
- Optimization of CE–SF–ICP–MS for the redox speciation of Pu at ultra-trace level under hyperalkaline reducing conditions
- Use of the established methodology and experimental approach to investigate Pu–ISA interaction under reducing conditions and its impact on the uptake by cement

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