

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:
 $10 \leq \text{pH} \leq 13.3$
- 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:
- $\text{pH}_m \leq 9$ - Pu(III) and Pu(IV) [1]
 - $\text{pH}_m > 9$ - 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 PuO₂(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 (O₂ content < 2 ppm)
- Undersaturation solubility experiments with aged ²⁴²PuO₂(am,hyd), $I = 0.10$ M (HCl/NaCl/NaOH)
- Acidic series: $\text{pH}_m = 3 - 6$, unbuffered system
30 mg of Pu solid; equilibration time: ~8 years
- Alkaline series: $\text{pH}_m = 8$ (TRIS), 9 (CHES) to 12.8
- Redox conditions buffered by:
2 mM hydroquinone ($\text{pe} + \text{pH}_m = 9.5 \pm 1$) ("reference system" → predominance of Pu(IV))
2 mM SnCl₂ ($\text{pe} + \text{pH}_m = 2 \pm 1$) (strongly reducing conditions → Pu(IV) + Pu(III)?)
- 0.2-1 mg ²⁴²Pu per sample (→ from acidic series)
- equilibration time ≤ 173 days
- m_{Pu} , pH_m and E_h values regularly monitored

Aqueous phase characterization

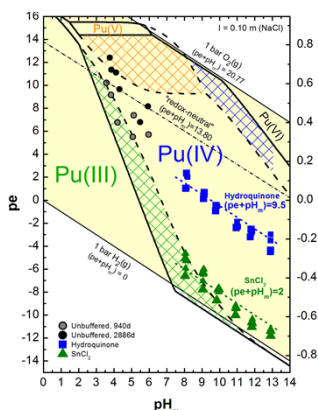
- Phase separation: 10 kD ultrafiltration (LSC) or ultra-centrifugation at 90000 rpm (SF-ICP-MS)
- [Pu]_{tot} determined by LSC or (SF-)ICP-MS
- Pu redox state analysis:
Liquid-liquid extraction (described in [1])
PMBP and HDEHP (+ oxidation step with K₂Cr₂O₇)
Capillary Electrophoresis (CE) coupled SF-ICP-MS
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

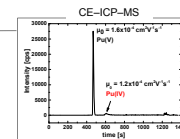
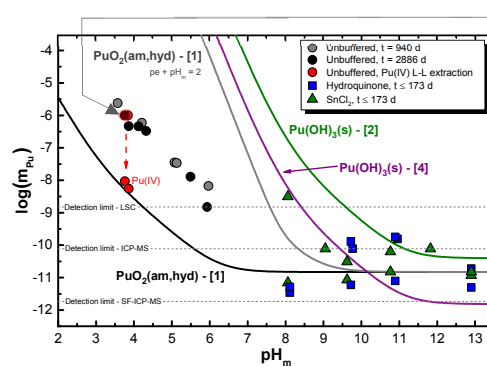
- conventional XRD
- XANES and (synchrotron-based) in-situ XRD → INE-Beamline for Actinide Research at ANKA [3]

Pourbaix-diagram

Experimentally measured ($\text{pe} + \text{pH}_m$) values



Solubility and redox speciation



Acidic region

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

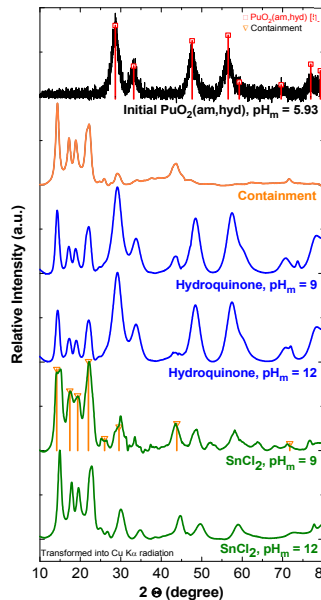
PuO₂(am,hyd) solubility-controlling phase; $m_{\text{Pu(IV)}}$ known:
 $\log^*K^*_{s,0} = -58.12 \pm 0.30$ (excellent agreement with [1])

Alkaline region

- Hydroquinone system: very low m_{Pu} ($-9.9 \leq \log(m_{\text{Pu}}) \leq -11.4$) within $8 \leq \text{pH}_m \leq 12.8$ → Pu(IV)_s ↔ Pu(IV)_{aq}
- SnCl₂ system: very low m_{Pu} at $\text{pH}_m \geq 9$. Behaviour at $\text{pH}_m = 8$ under evaluation → formation of Pu(III)_s and/or Pu(III)_{aq}? [4]

Solid phase characterization

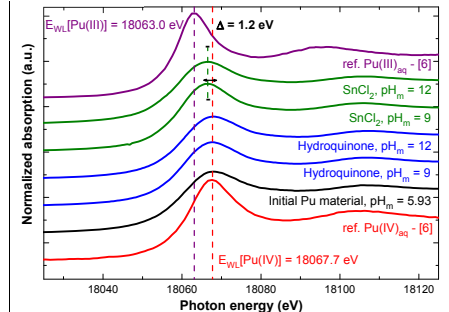
Conventional / in-situ XRD



Diffraction patterns

- Initial Pu solid from acidic solubility series, $\text{pH}_m = 5.93$
- solid phases from HQ-syst.: - perfect match with patterns of PuO₂(cr) reported in [5]
- PuO₂(am,hyd) confirmed as solubility controlling phase
- SnCl₂-buffered system: - weaker signal of PuO₂(cr), additional reflections related to Sn₃O₂(OH)₂(s) at $\text{pH}_m = 9$
- Expected predominance of PuO₂(am,hyd), however the presence of Pu₂O₃(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]
- SnCl₂-buffered systems: - shift in the white line position: $\Delta E = 1.2$ eV

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

Summary

- A nanocrystalline PuO₂(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 $8 \leq \text{pH}_m \leq 13$ is very low and consistent with the solubility control by PuO₂(am,hyd) ↔ Pu(IV)_{aq}
- XANES analyses confirm the presence of a Pu(III) solid phase in SnCl₂ systems. However, Pu solubility remains very low ($\leq 10^{-10}$ M) at $\text{pH}_m \geq 9$ → $\log^*K^*_{s,0}\{\text{Pu(OH)}_3(\text{s})\}$ selected in NEA-TDB [2] likely overestimated

Outlook

- Additional experiments on-going in SnCl₂ systems at $\text{pH}_m \leq 9$ 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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