Verhalten von Actiniden unter endlagerrelevanten Bedingungen

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Introduction

Nuclear waste disposal in deep geological formations:

• Actinides (Plutonium) responsible for long-term radiotoxicity of HLW / spent fuel.
• Aquatic actinide chemistry relevant in the case of water intrusion into a repository.
  ⇒ For reliable assessment of long-term safety of nuclear waste repositories:
    prediction of actinide solubility and speciation basic requirement.

Actinide redox properties

• Actinides known to exist/coexist in different oxidation states, e.g. U(IV,VI), Np(IV,V,VI), Pu(III,IV,V,VI).
• Chemical behavior depends strongly on redox state.
• Understanding of actinide redox behavior mandatory for prediction of actinide solubility.
Aqueous Plutonium chemistry is complex due to:
- coexistence of up to four oxidation states,
- polymeric and colloidal species,
- complex solid phases.

Topics of PhD work:
- solubility of Pu(IV) in alkaline CaCl₂ solutions.
- solubility of Pu(VI) in alkaline CaCl₂ solutions.
- Pu redox behavior under reducing conditions: Pu(III) ⇌ Pu(IV) equilibrium.
Topics of PhD work:
- **solubility of Np(IV)** in alkaline CaCl₂ solutions.
- **solubility of Np(V)** in alkaline CaCl₂ solutions.
- **solubility of Np(VI)** in alkaline CaCl₂ solutions.
- **Np redox behavior:** thermodynamics and kinetics of Np(V) reduction
A) Redox experiments: Np(V) → Np(IV) reduction

Addition of Np(V)$_{aq}$ to various reducing systems (0.1 M NaCl, pH 4 - 10): reduction YES / NO ?

$$[\text{Np}]_{\text{tot}} = 3.4 \times 10^{-5} \text{ M in 0.1 M NaCl}$$
B) Solubility experiments: Np in CaCl₂ solutions

Results of redox experiments:
$E_h$ and pH conditions to stabilize the different Np oxidation states → solubility experiments.

$[\text{Np}]_{\text{tot}} = 3.4 \times 10^{-5}$ M in 0.1 M NaCl
B) Solubility experiments: Np in CaCl$_2$ solutions

Results of redox experiments:

$E_h$ and pH conditions to stabilize the different Np oxidation states $\rightarrow$ solubility experiments.

$[\text{Np}]_{\text{tot}} = 3.4 \times 10^{-5}$ M in 0.1 M NaCl

- **Np(V) solubility**
  - Reducing conditions
  - Open symbol: Np(V) $\rightarrow$ Np(IV)

- **Np(IV) solubility**
  - Filled symbol: Np(V) stable

![Graph showing solubility of Np(V) and Np(IV) in CaCl$_2$ solutions with pH and $E_h$ conditions.](image)