Plutonium speciation during sorption on natural clay

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• Motivation

• Characteristics of Opalinus Clay (OPA) and pore water

• Sorption of Pu on OPA
  - Results of batch experiments
  - Synchrotron radiation based speciation

• Conclusions
Motivation

- Plutonium is a major contributor to the radiotoxicity of spent nuclear fuel after a storage time of more than 1,000 years.

- Argillaceous rocks are considered as potential host rocks for the construction of high-level nuclear waste repositories.

- Opalinus Clay (OPA) from the Underground Laboratory Mont Terri, Switzerland, was selected as a reference for a natural clay rock.

- Detailed sorption studies of Pu are needed to predict its migration behaviour in the geological barrier after a leakage of Pu from the repository.

- Our sorption studies are aimed at the determination of
  - $K_d$ values
  - Chemical information about Pu (speciation)
Characteristics of Opalinus Clay (OPA) and pore water

**Average mineralogy of OPA** [1]

- CEC: 9 ± 2 meq/100 g
- spec. surf. area: 38.0 m²/g
- TOC: ≤ 1%

**Pore water composition** [2]

<table>
<thead>
<tr>
<th>Component</th>
<th>mol/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na⁺</td>
<td>0.2404</td>
</tr>
<tr>
<td>K⁺</td>
<td>0.0016</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>0.0169</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>0.0258</td>
</tr>
<tr>
<td>Sr²⁺</td>
<td>0.0005</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>0.2998</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>0.0141</td>
</tr>
<tr>
<td>HCO₃⁻</td>
<td>0.005</td>
</tr>
<tr>
<td>I.S.</td>
<td>0.39</td>
</tr>
<tr>
<td>Eh (SHE)</td>
<td>+ 200 mV</td>
</tr>
<tr>
<td>pH</td>
<td>7.6</td>
</tr>
</tbody>
</table>

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[1] Nagra (2002), NTB 02-03

[An(IV)] = 4×10^{-7} M, S/L = 1 g/L, 0.1 M NaClO$_4$.

**Influence of pH**

![Graph showing Th(IV) or Pu(IV) sorption as a function of pH]

Distribution coefficients $K_d$ for the sorption of Th, U, Np, Pu, Am on OPA in PW (pH = 7.6)

<table>
<thead>
<tr>
<th>Element</th>
<th>$K_d$ (m$^3$/kg)</th>
<th>$K_d$ (m$^3$/kg)</th>
<th>$K_d$ (m$^3$/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Th(IV)</td>
<td>159 ± 37</td>
<td>30 ± 2</td>
<td>Am(III)</td>
</tr>
<tr>
<td>U(VI)</td>
<td>83 ± 34</td>
<td>29 ± 16</td>
<td>Th(IV)</td>
</tr>
<tr>
<td>Np(V)</td>
<td>-</td>
<td>0.03 ± 0.01</td>
<td>Np(V)</td>
</tr>
<tr>
<td>U(VI)</td>
<td>13 ± 3</td>
<td>0.03 ± 0.01</td>
<td>U(VI)</td>
</tr>
</tbody>
</table>

[1] Amayri et al. (in preparation)
**XAFS (X-ray Absorption Fine Structure)**

μ-XAFS
- Actinide speciation

μ-XRF (X-ray fluorescence)
- Elemental distributions

μ-XRD (X-ray diffraction)
- Crystalline phases

Synchrotron radiation based techniques

ESRF, ROBL BM 20

PSI, SLS, microXAS
Samples for XAFS, XRF and XRD measurements

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pu oxidation state</th>
<th>[Pu]$_{tot}$ mol/L</th>
<th>pH</th>
<th>Atmosphere</th>
<th>Eh (SHE) mV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Powder</td>
<td>III</td>
<td>$1 \times 10^{-5}$</td>
<td>7.6</td>
<td>Argon</td>
<td>-58</td>
</tr>
<tr>
<td>Powder</td>
<td>IV</td>
<td>$1 \times 10^{-5}$</td>
<td>7.6</td>
<td>Argon</td>
<td>-59</td>
</tr>
<tr>
<td>Powder</td>
<td>V</td>
<td>$1 \times 10^{-5}$</td>
<td>7.6</td>
<td>Argon</td>
<td>-40</td>
</tr>
<tr>
<td>Thin section</td>
<td>VI</td>
<td>$2 \times 10^{-5}$</td>
<td>7.6</td>
<td>Air</td>
<td>+236</td>
</tr>
</tbody>
</table>
Pu L_{III}-edge EXAFS spectra and corresponding FT

400 ppm Pu sorbed onto OPA at pH 7.6 under Ar atmosphere

Pu(III):
- Exp.
- Fit

Pu(IV):
- Exp.
- Fit

Pu(V):
- Exp.
- Fit

FT:
- R+Δ (Å)
- 8x O
- 2x Al/Si
- 3.14 Å
- 3.17 Å
- 3.20 Å
- 3.78 Å

χ(k)*k^3

k (Å⁻¹)
μ-XRF mapping of OPA thin section

Pu vs. Fe scatterplot
Pu L$_{III}$-edge μ-XANES of OPA thin section

Conradson et al., Polyhedron 17, 599 (1998)

μ-XANES

Pu(IV): 99 %

μ-EXAFS

<table>
<thead>
<tr>
<th>N</th>
<th>R/Å</th>
<th>$\sigma^2$/Å$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pu-O</td>
<td>8</td>
<td>2.38</td>
</tr>
</tbody>
</table>
μ-XRD of OPA thin section (preliminary result)

Pu

Fe

μ-XRD

Siderite

Kaolinite
Conclusions

Pu is retained by OPA in the reduced and less mobile tetravalent oxidation state of Pu.

Pu is localized on or in close vicinity of the Fe(II) mineral siderite and the clay mineral kaolinite.

Chemical information on trace elements in heterogeneous media can be obtained with high spatial resolution using synchrotron radiation based μ-XAFS, μ-XRF and μ-XRD.
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