Sorption behavior of Np(V) onto clays from Russian and Indian deposits

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Clays samples

Khakassia  Rajasthan  Kutch

[Map showing locations of Khakassia, Rajasthan, and Kutch]
Characterization of clays
## Characterization of clays
### XRF: Elemental composition

<table>
<thead>
<tr>
<th>Sample</th>
<th>LOI</th>
<th>Na₂O</th>
<th>MgO</th>
<th>Al₂O₃</th>
<th>SiO₂</th>
<th>K₂O</th>
<th>CaO</th>
<th>TiO₂</th>
<th>MnO</th>
<th>Fe₂O₃</th>
<th>P₂O₅</th>
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<tbody>
<tr>
<td>Rajastan clay</td>
<td>20.06</td>
<td>1.15</td>
<td>4.64</td>
<td>16.28</td>
<td>35.12</td>
<td>0.30</td>
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</table>
### Characterization of clays

#### XRD: Phase composition

<table>
<thead>
<tr>
<th>Clay Type</th>
<th>Smectite</th>
<th>Kaolinite</th>
<th>Quartz</th>
<th>Albite</th>
<th>Microcline</th>
<th>Orthoclase</th>
<th>Calcite</th>
<th>Dolomite</th>
<th>Gypsum</th>
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<tbody>
<tr>
<td>Khakassia clay</td>
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<td>1.3</td>
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<td>6.6</td>
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</table>

#### Clay minerals:

- **Khakassia clay**: 67%
- **Rajasthan clay**: 69%
- **Kutch clay**: 76%
Characterization of clays
Mössbauer spectroscopy: Iron speciation

Khakassia clay

Rajasthan clay

Kutch clay

Fe(II): structural iron
Fe(III): structural iron and nanoparticles of goethite

Only Fe(III):
- structural iron,
- hematite (around 5%)
- Nanoparticles of goethite

$T = 77K$
Summary of characterization

Khakassia
- Na-Montmorillonite – 66%
- Goethite – around 1.5%
- No anatase
- SA=15 m²/g

Rajasthan
- Na-Montmorillonite – 47%
- Illite-smectite MLM – 8%
- Kaolinite – 14%
- nanoparticles of Goethite – 12%
- Hematite – 0.5%
- Anatase – 1.7%
- SA=50 m²/g

Kutch
- Ca-Montmorillonite – 76%
- nanoparticles of Goethite – 15%
- Hematite – 0.5%
- Anatase – 0.5%
- SA=115 m²/g
Sorption study
Kinetics of Np(V) sorption onto clay

- **I = 0.01 M NaClO₄**
  - **Kutch**
  - **Rajasthan**
  - **Khakassia**

- Steady state for Np(V) sorption onto clay in ~24 hours

- **I = 1 M NaClO₄**
  - **Kutch**
  - **Rajasthan**
  - **Khakassia**

✓ Sorption of Np(V) onto Khakassia clay is lower but faster
Np(V) sorption pH-edge
Khakassia clay

At pH > 6.5 sorption is not dependent on ionic strength – surface complexation is predominant mechanism of sorption

At pH < 6.5 sorption increase with decreasing ionic strength – ion exchange is predominant mechanism

[solid phase] = 0.5 g/L
[Np] = 4 \cdot 10^{-14} \text{ M}
Np(V) sorption pH-edge

Rajasthan clay

- In all pH range sorption is not dependent on ionic strength – surface complexation is predominant mechanism of sorption

- Sorption is higher than on Khakassia clay

[solid phase] = 0.5 g/L
[Np] = 4 \cdot 10^{-14} M
Np(V) sorption pH-edge
Kutch clay

Sorption is higher at I = 1M NaClO4

Ca-Montmorillonite influence???

[solid phase] = 0.5 g/L
[Np] = 4 \cdot 10^{-14} M
Kutch bentonite at 1M NaClO₄

Tubes were capped
Shaken for 1 day
Centrifuge for 20 min.
Separate the two phases

Modified Kutch bentonite

Further studies

- Characterization by XRD
- Np(V) sorption profile

Modified Kutch bentonite

Aqueous

Clay Colloids in Aqueous Systems, February 2016
Clay Colloids in Aqueous Systems, February 2016

XRD of Kutch and Modified bentonite

Kutch

- d : 15.2 Å

- d : 12.7 Å

Modified
Ca-form demonstrate lower sorption
Summary of sorption data

- Khakassia clay
- Rajasthan clay
- Kutch clay

![Sorption data graph](image)
Modeling
Thermodynamic modeling

- Mineral composition
- Surface properties for each component
- Equilibrium constant for sorption onto pure mineral

Component Additivity

NEA Sorption Project Phase II, 2005
Thermodynamic modeling

Component Additivity

Literature data

<table>
<thead>
<tr>
<th>Reaction</th>
<th>logK</th>
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<tbody>
<tr>
<td>$\equiv\text{AIOH} + \text{NpO}_2^+ \rightarrow \equiv\text{AlONpO}_2 + \text{H}^+$</td>
<td>-4,55</td>
</tr>
<tr>
<td>$\equiv\text{AIOH} + \text{NpO}_2^+ + \text{H}_2\text{O} \rightarrow \equiv\text{AlONpO}_2\text{OH}^- + 2\text{H}^+$</td>
<td>-13,8</td>
</tr>
<tr>
<td>$\equiv\text{FeOH} + \text{NpO}_2^+ \rightarrow \equiv\text{FeONpO}_2 + \text{H}^+$</td>
<td>-3,32</td>
</tr>
<tr>
<td>$\equiv\text{TiOH} + \text{NpO}_2^+ \rightarrow \equiv\text{TiONpO}_2 + \text{H}^+$</td>
<td>-2,89</td>
</tr>
<tr>
<td>$\text{NpO}_2^+ + \text{X}^- \rightarrow \text{XNpO}_2$</td>
<td>-0,26</td>
</tr>
</tbody>
</table>
The same set of the equilibrium constants for different clays
[Np] $10^{-6}$ M

“Light” fraction

“Dark” fraction
α-track analysis images

Rajasthan clay
Summary

• Non-clay minerals can dramatically affect on radionuclides sorption onto clay
• Thermodynamic modeling with CA-approach can be used for modeling sorption onto clays

Thank you for your attention!
Mössbauer spectroscopy

Rajasthan clay

\( T = 300K \)

\( T = 77K \)