Uptake of Radium by barite under repository relevant conditions

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Radium in nuclear waste repositories

- In some scenarios of direct disposal of spent fuel, as a result of the $^{238}\text{U}$ decay chain $^{226}\text{Ra}$ dominates the dose during the late stages.
- Possible Ba release during spent fuel corrosion $\rightarrow$ crystallization of barite (BaSO$_4$).
- Ra may be introduced into a system of barite in equilibrium with Ba$^{2+}$ and SO$_4^{2-}$.

Relevance of solid solution formation

Example: 0.1 n NaCl background electrolyte, 25 °C

Solubility of pure RaSO$_4$ $\approx 2 \cdot 10^{-5}$ mol/L

Solid solution (0.5 g/L barite $a_0 = 0$)

Calculated Ra-solubility $\approx 4 \cdot 10^{-8}$ mol/L
Status of WP 2.1

- Details about solid solution formation and barite recrystallization in the presence of Ra to be determined

- Status November 2013: experiments finished; results delivered to WP 4
Ra uptake by BaSO$_4$: open questions

- Does barite take up Ra during recrystallization?
- Does barite completely recrystallize into a Ba$_{1-x}$Ra$_x$SO$_4$ solid solution in the presence of Ra?
- Spatial distribution of Ra within the solid?
- Influence of the presence of Ra on the recrystallization of barite?
- Influence of barite morphology and particle size distribution (PSD)?
Experimental setup

- Experiment: batch experiments with $V = 20$ mL
  $5 \cdot 10^{-6}$ mol/L $^{226}$Ra$^{2+}$
- Ionic strength: 0.1 n NaCl
- Solid/Liquid: 0.5 g/L, 5 g/L
- Variation of barite type Aldrich (AL) and Sachtleben (SL)
- Room temperature
Ra uptake by barite – 5 g/L and 0.5 g/L at RT

- Mass balance calculations give a final $\text{Ra}/\text{Ba}$ ratio of
  - $\sim 2.5 \times 10^{-4}$ for 5 g/L barite at RT
  - $\sim 2.5 \times 10^{-3}$ for 0.5 g/L barite at RT
Does barite take up Ra?

- Determination of Ba and Ra content and distribution
- Time of flight secondary ion mass spectroscopy (ToF-SIMS)
- Sachtleben barite 0.5 g/L
- Analysis of complete grains

Before measurement

After measurement
Does barite take up Ra?

- **Optimization** of the spatial resolution ➔ Identification of individual barite grains

- Integrated intensity distribution of the Ba and Ra signal

- All grains contain Ra
Compositional homogeneity of radiobarite?

- Spatial distribution of Ra within the barite particles
- Depth resolution: ~0.1 µm
- All particles contain Ra
- Indication of a complete recrystallization of barite into a $\text{Ba}_{1-x}\text{Ra}_x\text{SO}_4$ solid solution

**Depth profiles of integrated Ra signals**

- **grain 1**
  - X-Z Slice of Ra+
  - MC: 13; TC: 1.710e+003

- **grain 2**
  - X-Z Slice of Ra+
  - MC: 3; TC: 4.180e+002

- **grain 3**
  - X-Z Slice of Ra+
  - MC: 24; TC: 6.115e+003

- **grain 4**
  - X-Z Slice of Ra+
  - MC: 6; TC: 5.970e+002
Ra/Ba ratio derived from ToF - SIMS measurements

Mass balance calculations give a final Ra/Ba ratio of $2.5 \times 10^{-3}$ for 0.5 g/L barite at RT.
Evolution of the morphology of AL barite

- Newly formed idiomorphous, large particles
- Particle coarsening
- Ostwald ripening
- Shape: less round, sharp edges, less pores on the surface
- Effects more distinct with Ra
Evolution of the particle size distribution of AL barite

- Statistical information by image analysis
- Wide PSD
- Particle coarsening
- Additional influence of Ra
Evolution of the morphology of SL barite

- No significant change of the morphology
- Smoother crystal faces
- Grains are grown together and form large aggregates
Evolution of the particle size distribution of SL barite

- Narrow PSD
- Slight increase of coarse particles
Evolution of morphology and grain size distribution

- Particle coarsening due to Ostwald ripening after recrystallization
- Significant additional effect due to the presence of Ra

Ra enhances the recrystallization of barite

<table>
<thead>
<tr>
<th></th>
<th>Frequency based [µm]</th>
<th>Equ. mass based [µm]</th>
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</thead>
<tbody>
<tr>
<td>AL Reference at the beginning</td>
<td>0.50</td>
<td>0.69</td>
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<tr>
<td>AL Reference 5 g/L after 443 days</td>
<td>0.58</td>
<td>0.82</td>
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<td>AL 5 g/L after 443 days</td>
<td>0.80</td>
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<td>AL 0.5 g/L after 443 days</td>
<td>0.86</td>
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<td>SL Reference at the beginning</td>
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<td>SL 5 g/L after 443 days</td>
<td>15.28</td>
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<tr>
<td>SL 0.5 g/L after 443 days</td>
<td>14.99</td>
<td>18.33</td>
</tr>
</tbody>
</table>
Conclusion

• Efficient Ra uptake by barite

• Ra could be found in all barite particles after recrystallization

• Complete recrystallization of barite into $\text{Ba}_{1-x}\text{Ra}_x\text{SO}_4$ solid solution

$\Rightarrow$ Ra enhances the recrystallization

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Thank you for your attention!