The Role of Zeolite Phase Transformations in Deep Borehole Seals

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Repository Program Objectives

U.S. Used Fuel Disposition Campaign Deep boreholes Program

• Use mine-run, unpurified bentonite and highly saline brines

• Investigate chemical evolution in a bentonite buffer at deep borehole temperature and pressure.
  - Silica generation and cation exchange

Zeolites – recognize significance of their growth

Previous EBS work identified clinoptilolite, analcime, wairakite

Scenarios – Base of Seals, Bottom of Hole

Base of Seals: 150 – 175 C, 300 bar, 8 week (hydrostatic) - ongoing

Bottom of Borehole: 400 C, 1 Kbar, 2 week (lithostatic) - results
Experimental conditions for bottom of borehole

Experimental Reactants

• Unprocessed Wyoming bentonite
• $f(O_2)$ buffered at $\approx$ IM (iron-magnetite) univariant line
• Cs-Na-Ca-Cl-based solution: loaded at 2:1 W/R ratio
  • NaCl, CaCl, Cs/Ca/NaCl brines, 2molal
  • 400°C, 1 Kbar

![Image of experimental setup]
Clinoptilolite SEM Images

Clinoptilolite after glass shard – WY bentonite

Clinoptilolite dissolution - EBS12- low water content
Zeolite transformation at high temperature

- clinoptilolite → analcime + SiO₂ + H₂O

- (Na,K,Ca)₂₋₃Al₃(Al,Si)₂Si₁₃O₃₆ · 2H₂O → Na₆Al₆Si₁₂O₃₆ + SiO₂ + 2H₂O

- Phase change as low as 100 °C (Smyth, 1982, Masuda, et al., 1996)) however most occurred between 200-300 °C in our experiments
EBS5 - Analcime reaction product
### Opalminus Clay Experiments

#### Three experiments

**EBS-14 Opalminus Clay (O.C.) only** – 300 °C isothermal, 6 week, O.C. groundwater

**EBS-15** – As above + WY bentonite + 316 S.S.

**EBS-17** - As above + WY bentonite + Cu

#### Opalminus Clay Brine

<table>
<thead>
<tr>
<th>Species</th>
<th>Type Solution</th>
<th>Actual Solution</th>
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<tbody>
<tr>
<td>Ca²⁺</td>
<td>421</td>
<td>426</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>5672</td>
<td>6470</td>
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<tr>
<td>CO₃²⁻</td>
<td>162</td>
<td>n.m.</td>
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<tr>
<td>K⁺</td>
<td>221</td>
<td>225</td>
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<tr>
<td>Na⁺</td>
<td>3885</td>
<td>3846</td>
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<tr>
<td>Si</td>
<td>5</td>
<td>1</td>
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<tr>
<td>SO₄²⁻</td>
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<td>998</td>
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<tr>
<td>Sr²⁺</td>
<td>27</td>
<td>0.16</td>
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<tr>
<td>TDS</td>
<td>11502</td>
<td>12153</td>
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<tr>
<td>pH</td>
<td>7.24</td>
<td>7.50</td>
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</tbody>
</table>

| Experiment Used | EBS 14, 15, 17 |
EBS-14 – Wairakite produced as reaction product
Mixed clay experiments – Opalinus + WY Bentonite

- Experiments EBS-15 (316 SS) and EBS-17 (Cu)
- Brine: Opalinus Clay groundwater
- Analcime in early experiments
- Wairakite in Opalinus Clay experiment

One would expect a high temperature zeolite somewhere in the Analcime – Wairakite solid solution join

\[ \text{Na}_3\text{Al}_6\text{Si}_{12}\text{O}_{36} \leftrightarrow \text{Ca}_3\text{Al}_6\text{Si}_{12}\text{O}_{36} \]
EBS15  Analcime$_{64}$--Wairakite$_{36}$
Analcime – Wairakite Solid Solution Determinations

Si / Al ratio to % Analcime

EBS 1
EBS 2
EBS 5 Shards
EBS 10
EBS 11
EBS 12
EBS 13
EBS 15
EBS 16
EBS 17
MR Bentonite

0.000 0.100 0.200 0.300 0.400 0.500 0.600 0.700 0.800 0.900 1.000

2.0 2.5 3.0 3.5 4.0 4.5 5.0

Na/(Na+Ca)

[SERIES NAME]
Pollucite Generation from Cs waste forms

- Further experimental system – Explore the tertiary portion of this zeolite group.
- Cesium may be a waste stream disposed of in Deep Boreholes
- Would Cs be readily incorporated into analcime structure if canister failed post emplacement?

\[
\text{Analcime} \leftrightarrow \text{Pollucite} \leftrightarrow \text{Wairakite}
\]

\[
\text{Na}_6\text{Al}_6\text{Si}_{12}\text{O}_{36} \leftrightarrow \text{Cs}_6\text{Al}_6\text{Si}_{12}\text{O}_{36} \leftrightarrow \text{Ca}_3\text{Al}_6\text{Si}_{12}\text{O}_{36}
\]
Pollucite created from bentonite clay at high P,T

Average of 30 EMP analyses

\[ \text{An}_{18.3} \text{ Wrk}_{39} \text{ Pol}_{42.7} \]

<table>
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<tr>
<th>Element</th>
<th>Composition</th>
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<tbody>
<tr>
<td>SiO₂</td>
<td>56.64</td>
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<tr>
<td>Al₂O₃</td>
<td>18.63</td>
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<tr>
<td>FeO</td>
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<tr>
<td>MnO</td>
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<td>MgO</td>
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<tr>
<td>CaO</td>
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<tr>
<td>Na₂O</td>
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<tr>
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<tr>
<td>Cs₂O</td>
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<td>Cl</td>
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<tr>
<td>O=Hal</td>
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<tr>
<td>TOTAL</td>
<td>96.01</td>
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Conclusions

- Engineered Barrier Systems using bentonite backfill /buffer in a high temperature repository must be aware of system bulk chemistry.
- Na-rich / Ca-poor clays (WY bentonite) produces Analcime
- Ca-rich / Na-poor clay rock (Opalinus Clay) produces Wairakite
- Mixed system (Opalinus Clay + WY bentonite) generates Analcime – Wairakite SS
- Created Cs bearing zeolite (Pollucite) from bentonite and Cs/Ca/NaCl brine at high P,T
- This zeolite may be critical to isolating Cs contamination
- Need to now investigate stability field
Acknowledgements

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