A Review of High Temperature Engineered Barrier Systems Experiments

Part 2 _Summary of High Temperature Engineered Barrier System Experiments (Los Alamos National Laboratory)
Schematic of clay barrier configuration - the Engineered Barrier System

Mineralogical changes at the steel/bentonite interface

Waste package corrosion rate
- How does it evolve with time?
- What are the most important dependencies?

Reactions at the cement/bentonite interface

Major element chemistry controlling U speciation and surface complexation

Bentonite illitization

Radionuclide solubility and sorption
- Spatial heterogeneity?
- Temporal evolution?
- Most important dependencies?
Investigate chemical and mineralogical changes at repository temperature and pressure (300-250-200 °C, 150 bar)

**Wyoming Bentonite**
- 16 experiments, 300°C, 4 weeks to 6 months
- Ramped and isothermal temperature profiles
- Cu, LCS, 304 SS, 316 SS, graphite, or quartz sand added

**Opalinus Clay only**
- 1 experiment, 300°C, 6 weeks

**Wyoming Bentonite + Opalinus Clay**
- 5 experiments, 300°C, 6 weeks to 6 months
- 2 experiments, 200°C, 8 weeks
- Cu, LCS, 304SS, or 316 SS added

**Wyoming Bentonite + Opalinus Clay + Ordinary Portland Cement (or low pH cement)**
- 14 experiments, 200°C, 8 weeks (including 6 month experiment)
- LCS, 304SS, or 316 SS added

**Wyoming Bentonite + Grimsel Granodiorite + low pH cement**
- 10 experiments, 250°C, 6–8 weeks
- LCS, 304SS, or 316 SS added

Over 50 Experiments
Formation of Fe-rich clay at the steel interface

- Use mine-run, bentonite, steel, and K-Ca-Na-Cl brines
- Investigate chemical evolution of steel clay interface at repository temperature and pressure ($300 ^\circ$ C, 150 bar).

**Mineral phase changes**

- Fe$_{1.22}$Cr$_{0.37}$Ni$_{0.22}$+ 1.32/2 H$_2$O + Na$_{0.33}$(Al$_{1.67}$,Fe$_{3+0.20}$,Mg$_{0.13}$)Si$_{4}$O$_{10}$(OH)$_{2}$ → Stainless-steel + water + Montmorillonite
- Na$_{0.33}$Fe$_3$(Si$_{3.67}$,Al$_{0.33}$)O$_{10}$(OH)$_2$+ 0.13Mg+++ 1.34Al++++ 0.33SiO$_2$
  - Fe-saponite
  - Opal
Clay Mineral & Argillite rock Summary

- **Opalinus Clay + Wyoming Bentonite**
  - Smectite structure most affected in:
    - 6 month/300° C experiment
    - 8 week/200° C saline experiment
  - Minor interlayered illite-smectite
  - Illite nucleation on pre-existing illite in Opalinus Clay
  - QXRD: increase in wt.% of clay fraction

- **Portland Cement**
  - Swelling decrease
  - Clay degradation
  - Montmorillonite → tobermorite
Zeolite and silicate mineral reaction products

- WY bentonite + Stripa GW $\rightarrow$ clinoptilolite (cpt) + analcime
- WY bentonite + Opalinus Clay + Opalinus Clay GW $\rightarrow$ cpt+ analcime-wairakite
- WY bentonite + Opalinus Clay + Cement+ Opalinus Clay GW $\rightarrow$ cpt+ tobermorite+ garronite + analcime
- WY bentonite + Grimsel Granodiorite + Grimsel GW $\rightarrow$ Al-tobermorite (no zeolite minerals observed)
• Formation of analcime from dissolution of clinoptilolite in bentonite buffer

• Formation of analcime–wairakite from precursor kaolinite in Opalinus Clay
Zeolite formation mechanisms
Glass in Bent $\rightarrow$ Clinoptilolite $\rightarrow$ Analcime
Kaolinite in OPA $\rightarrow$ Wairakite

Jové Colón et al. (2017)

EMPA by K. Norskog & F. Caporuscio (LANL)

Steiner (1955)

Aoki et al. (1980)
Stability of CASH minerals - summary

- With the addition of Ordinary Portland Cement at 200\(^\circ\) C:
- Montmorillonite in Wyoming Bentonite breaks down to form tobermorite
- CASH phases (such as tobermorite) are precursor phase to analcime/garronite, which are spatially associated/intergrown.
- Tobermorite is interlayered with montmorillonite \(\rightarrow\) tobermorite peaks are significant in the XRD patterns of the clay fraction).

- The change in smectite abundance is significant.
- For example, EBS-26, smectite is reduced by \(~19\) wt\% and zeolites (analcime + garronite) increase by \(~14\) wt\%.

- Estimation of the before and after experiment wt\% clinoptilolite is unchanged or slightly reduced (\(~8\) wt\% to 4–8 wt\%, respectively) in all the experiments with cement \(\rightarrow\) interaction of other phases (i.e., calcite, clay) form zeolites
Wyoming Bentonite only:
• Smectite stable (no illite)
• Clinoptilolite/glass → analcime at 300°C

Bentonite + Opalinus Clay:
• Smectite $\rightarrow$ illite/smectite, some discrete illite formation
• Analcime/wairakite formation at 300°C

Bentonite + Opalinus Clay + Portland Cement:
• Significant smectite loss, illite-smectite and discrete illite formation
• CASH mineral generation
• Montmorillonite $\rightarrow$ tobermorite, garronite + analcime observed at 200°C
Comparison of crystalline to argillite host rock experiments

**Grimsel Granodiorite**
- Temperature = 250°C
- Carbonate rich brine
- Al-tobermorite
- Accessory chlorite and gypsum
- No illite or illite-smectite observed
- Bentonite colloids (not stable in experiment, formed during quench, Garcia-Garcia et.al. 2009)

**Opalinus Clay**
- Temperature = 300°C
- NaCl-rich brine
- Analcime –wairakitess
- Minor illite-smectite, discrete illite
Engineered Barrier Systems using bentonite backfill / buffer in a high temperature, pressure repository must consider system bulk chemistry.

**Bentonite alteration**

- High Na+ activity and restricted K+ supply inhibit/retarding illitization.
- Clinoptilolite to analcime highly sensitive to reaction conditions
- Very slow kinetics, with sequestered Al3+ inhibiting illitization.

**Steel Corrosion**

- Metal acts as a mineral growth substrate: Fe-saponite created at steel / clay interface, minor chlorite.
- Growth of Fe-rich clays increase waste canister’s active surface area, providing increased actinide retention.
Opalinus Clay + Wyoming Bentonite
• Smectite structure most affected in:
  — 6 month/300° C experiment
  — 8 week/200° C saline experiment
• Minor interlayered illite-smectite
• Illite nucleation on pre-existing illite in Opalinus Clay
• QXRD: increase in wt.% of clay fraction

+ Portland Cement
• Swelling decrease
• Clay degradation
• Montmorillonite → tobermorite
• Significant authigenic silicate phases (analcime, garronite)
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REFERENCES


