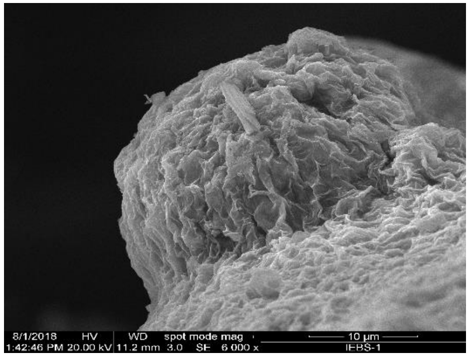
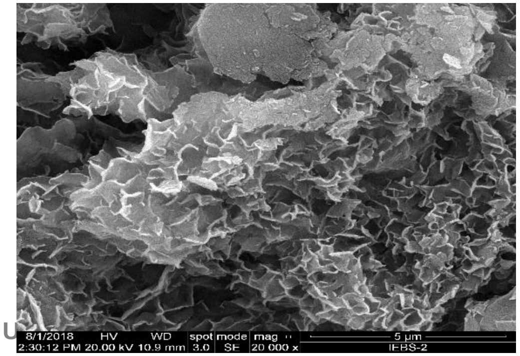
NWTRB – Albuquerque 2022

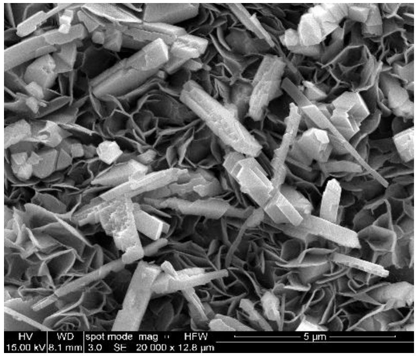
Summary of High Temperature Engineered Barrier Systems Experiments (Los Alamos National Laboratory)

Modeling and Testing Activities of Bentonite Barrier Behavior (Sandia National Laboratories)

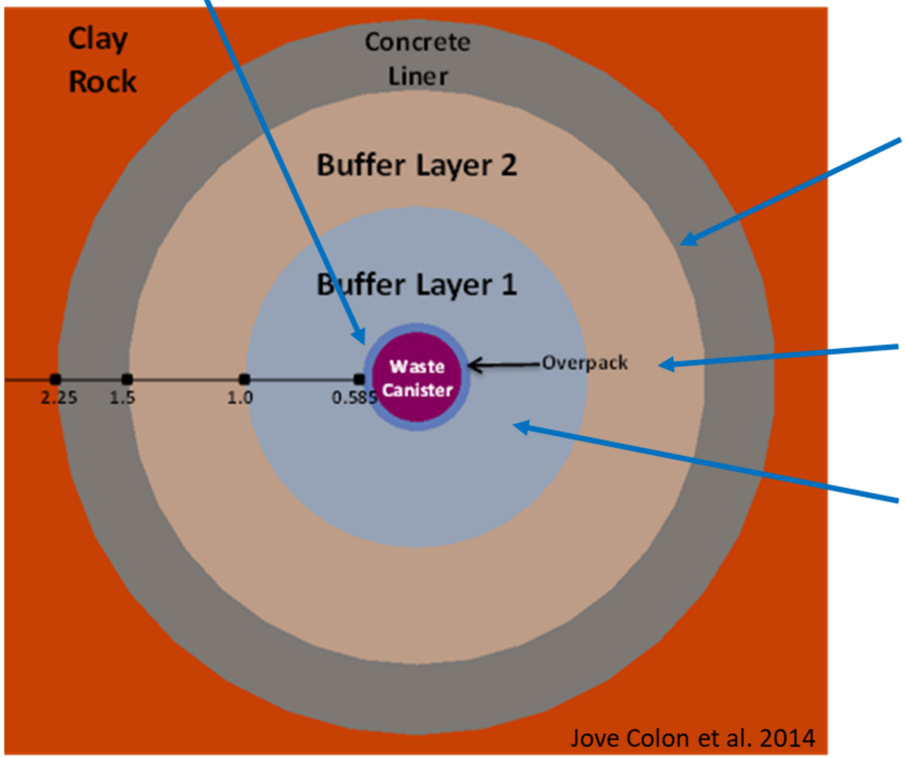
Caporuscio, F.A. (LANL); Jové Colón, C.F. (SNL)







Schematic of clay barrier configuration the Engineered Barrier System



Jove Colon et al. 2014

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?

Stein (2019), NWTRB presentation.

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

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 °C, 150 bar**).
- **Mineral phase changes**

$$\mathbf{Fe_{1.22}Cr_{0.37}Ni_{0.22} + 1.32/2\ H_2O + Na_{0.33}(Al_{1.67},Fe^{3+}_{0.20},Mg_{0.13})Si_4O_{10}(OH)_2 \rightarrow}$$

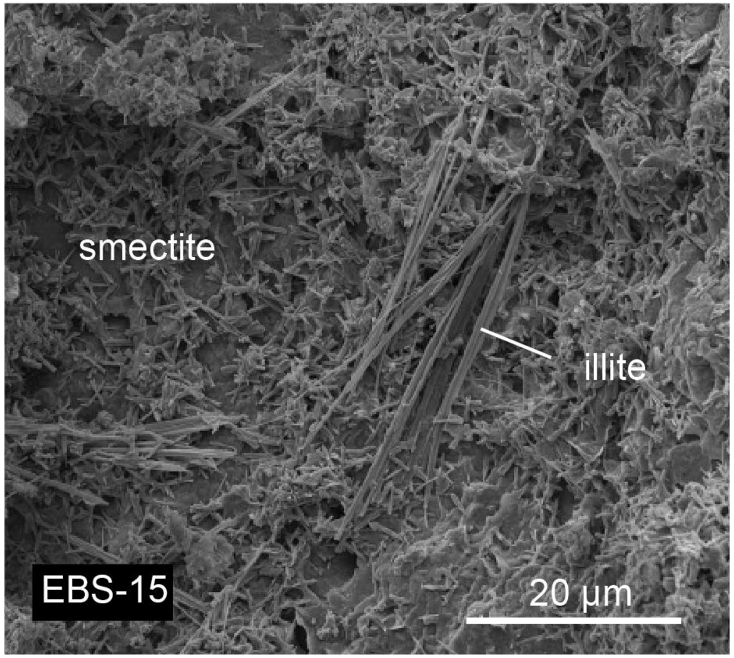
Stainless-steel + water + Montmorillonite

$$\mathbf{Na_{0.33}Fe_3(Si_{3.67},Al_{0.33})O_{10}(OH)_2 + 0.13Mg^{++} + 1.34Al^{+++} + 0.33SiO_2}$$

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



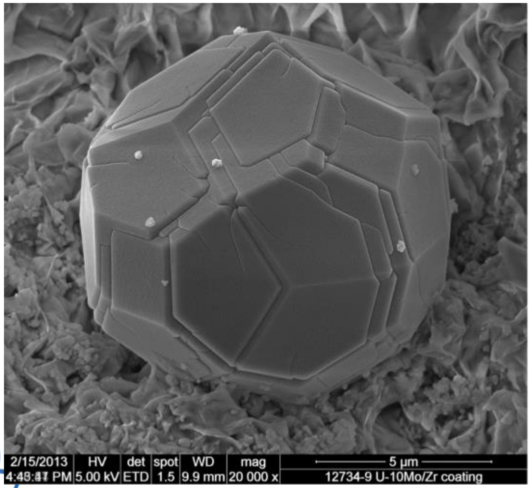
Zeolite and silicate mineral reaction products

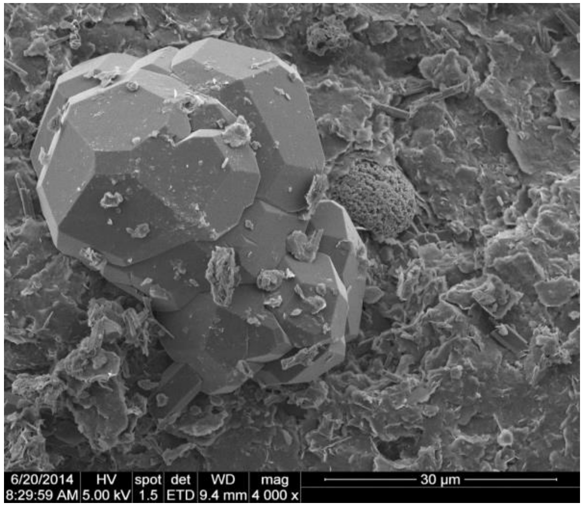
- WY bentonite + Stripa GW → clinoptilolite (cpt) + analcime
- WY bentonite + Opalinus Clay + Opalinus Clay GW → cpt + analcime-wairakite
- WY bentonite + Opalinus Clay + Cement + Opalinus Clay GW → cpt + tobermorite + garronite + analcime
- WY bentonite + **Grimsel Granodiorite + Grimsel GW→ Al-tobermorite (no zeolite minerals observed)**

Analcime – wairakite solid solution formation

Formation of analcime from dissolution of clinoptilolite in bentonite buffer

Formation of analcime–wairakite from precursor kaolinite in Opalinus Clay

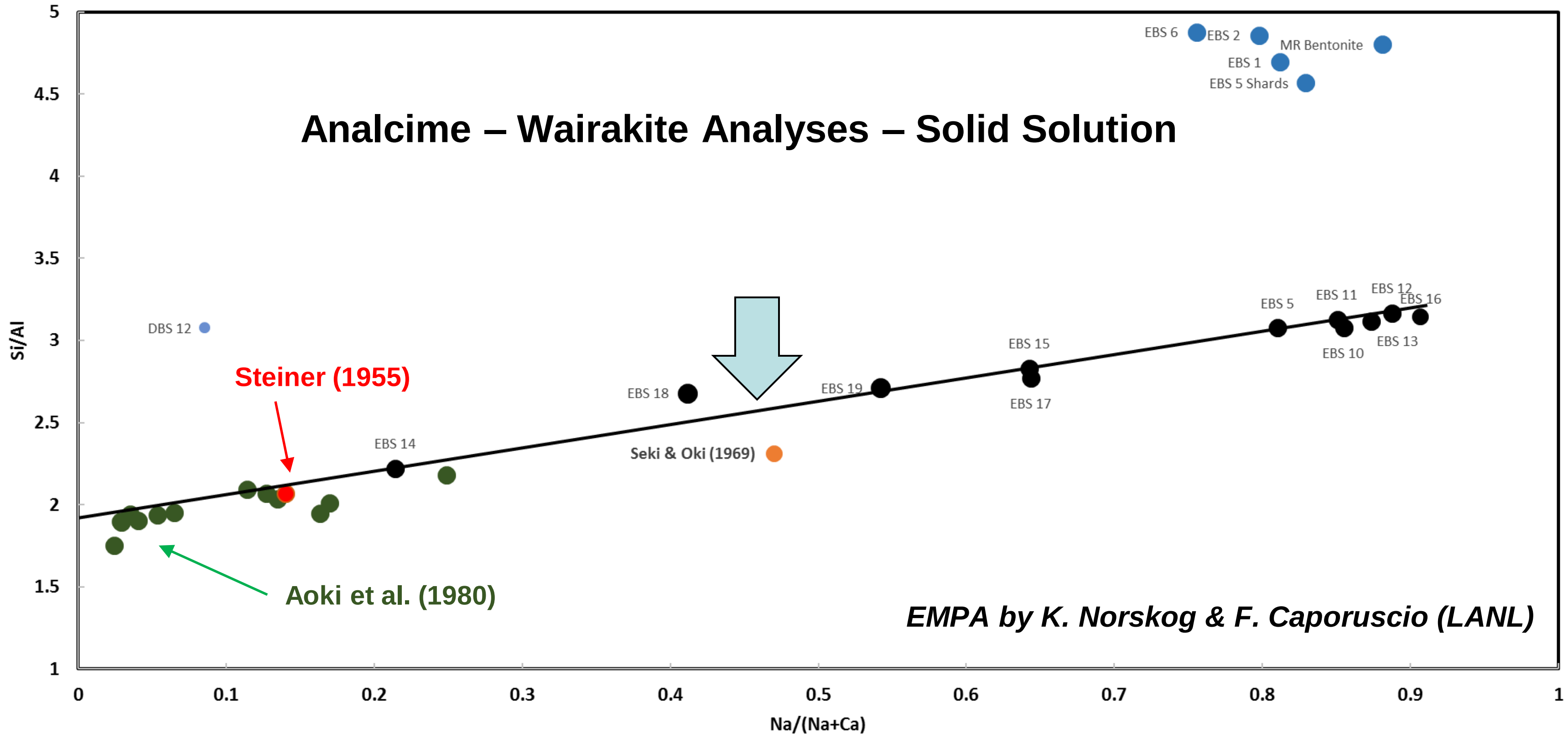




Zeolite formation mechanisms

Glass in Bent → Clinoptilolite → Analcime

Kaolinite in OPA → Wairakite


Analcime – Wairakite Analyses – Solid Solution

Steiner (1955)

Aoki et al. (1980)

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

Jové Colón et al. (2017)

Stability of CASH minerals - summary

With the addition of Ordinary Portland Cement at 200°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 → 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 → interaction of other phases (i.e., calcite, clay) form zeolites

Comparison of Wyoming Bentonite to Opalinus Clay ± Wyoming Bentonite ± Portland Cement

- **Wyoming Bentonite only:**
  - Smectite stable (no illite)
  - Clinoptilolite/glass → analcime at 300°C
- **Bentonite + Opalinus Clay:**
  - Smectite → 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 → 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

Opalinus Clay

- Temperature = 300°C
- NaCl rich brine
- Analcime – wairakite_{ss}
- Minor illite-smectite, discrete illite

Summary

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 Al^{3+} 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.**

Summary – Opalinus wall rock

- 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)

Acknowledgements

This project was funded by U.S. Department of Energy, Office of Nuclear Energy, Spent Fuel & Waste Science and Technology Campaign

Special Thanks to Carlos Jove Colon, Kirsten Sauer, Marley Rock, Amber Zandanel, Kate Norskog, Michael Cheshire, Steve Chipera, George Morgan, Lindsey Hunt, George Perkins, Emily Kluk and Oana Marina provided assistance in the laboratories.

LA-UR-22- 25776

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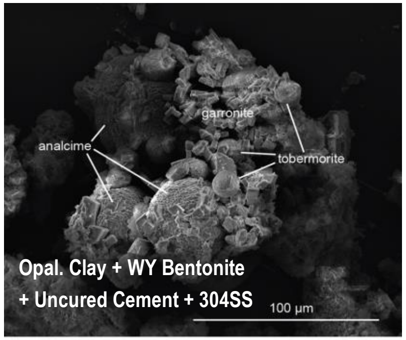
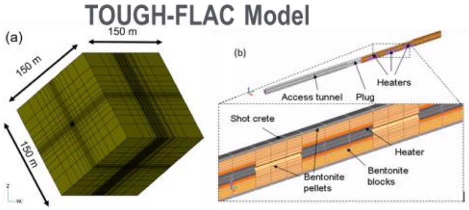
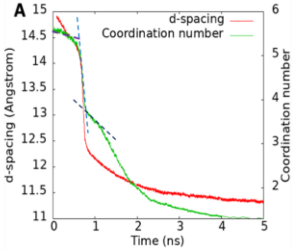
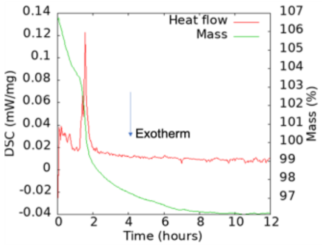
Highlights – Disposal in Argillite R&D: Experimental & Modeling Activities

- **Experimental Activities: Barrier Material Interactions at high temperatures (LANL)**
- **International Collaborations & Disposal R&D (SNL):**
  - **DECOVALEX2023: Modeling of THC processes in bentonite**
  - **SKB Task Force (TF): cement-bentonite interactions (Task 12; subtask A)**
  - **HotBENT (Grimsel site): Material characterization of column test bentonite**
- **Molecular dynamics (MD) simulation of water transport phenomena in smectite (SNL)**
- **Modeling of Ordinary Portland Cement (OPC) leaching experiments (SNL, Vanderbilt Univ.)**
- **Modeling of coupled THMC processes & shale creep in argillite repository (Int. Collaborations – LBNL)**
- **Machine-Learning (ML) approach for radionuclide-mineral interactions & surface complexation database development (LLNL)**
- **Thermodynamic database development (LLNL, SNL)**









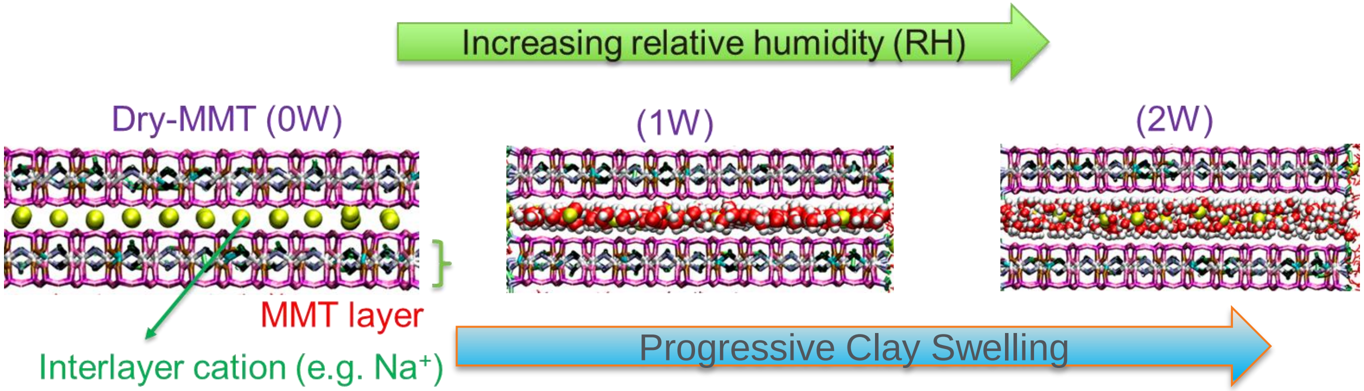
Bentonite (De)hydration Phenomena

Research Questions:

Water transport in smectite clay interlayers during clay dehydration?

Thermal stability of bentonite and effects on swelling performance?

Molecular Dynamics (MD) Simulations



Increasing relative humidity (RH)

Dry-MMT (0W)

(1W)

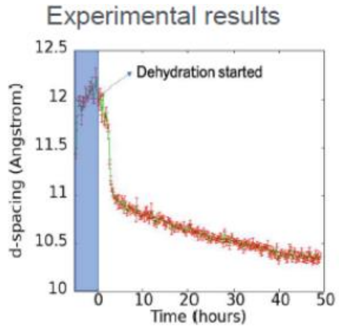
(2W)

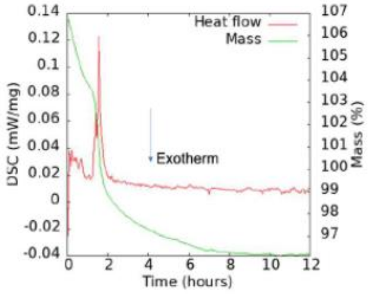
MMT layer

Interlayer cation (e.g. Na⁺)

Progressive Clay Swelling

Thermal (TGA/DSC)
and *in situ* XRD (RH, T)


Experimental results



Objectives

- **Elucidate mechanisms of bentonite (de)hydration at elevated temperatures**
- **Moisture transport and bentonite behavior under unsaturated conditions**
- **Model comparisons with experimental observations**

DECOVALEX2023: Task D Experiment S1-3

International Collaboration Activity

Problem Overview

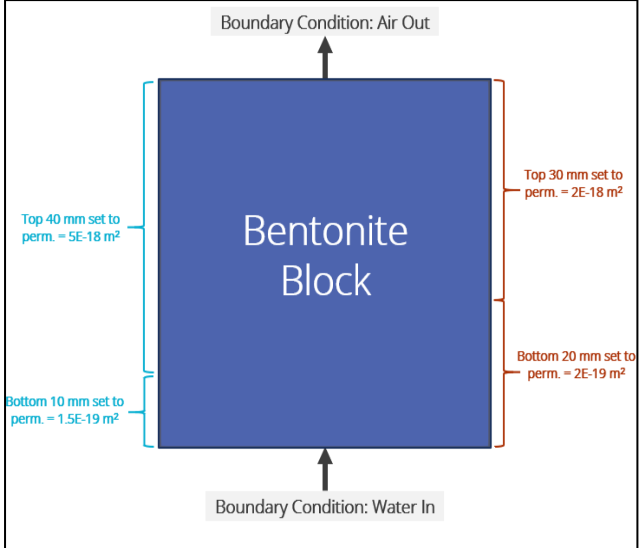
- A bentonite block is saturated vertically (from bottom to top) over 30 days
- Block is wetted with either deionized water (DW) or dilute groundwater (GW)

Computational Approach

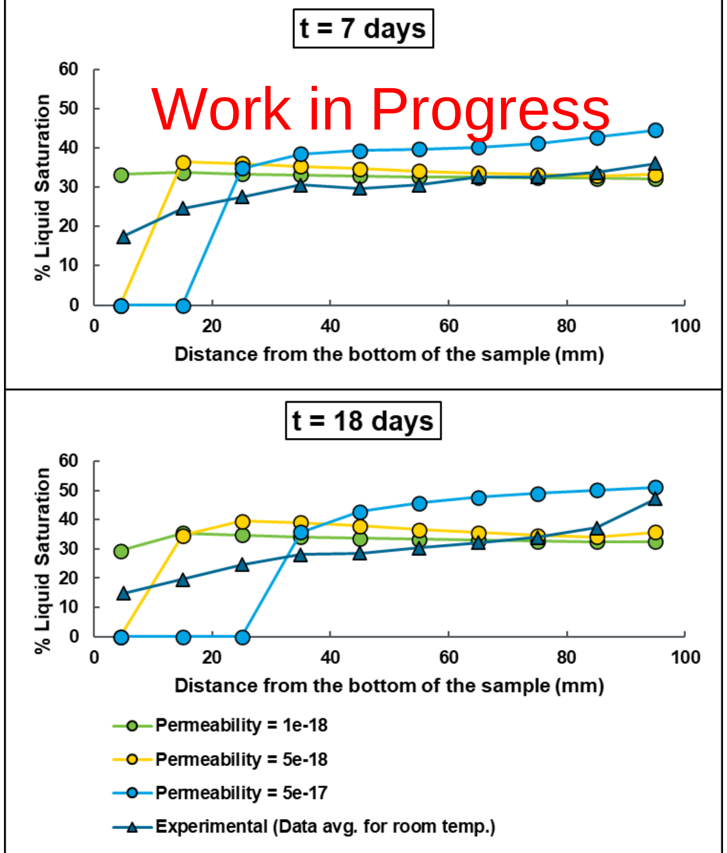
- Used PLFOTRAN to model laboratory experiments performed by JAEA
- 1D, saturation-driven, two-phase transport; chemistry off
- Permeability treated as variable input; heterogeneous
- Tested heterogeneous and homogeneous initial saturation profiles

Findings

- General trends are well-represented by PFLOTRAN models
- Effects of initial saturation profile decrease with time



PFLOTRAN model inputs, including permeability structures for DW/GW cases.



Work in Progress

DECOVALEX2023: Task D Experiment S1-4

International Collaboration Activity

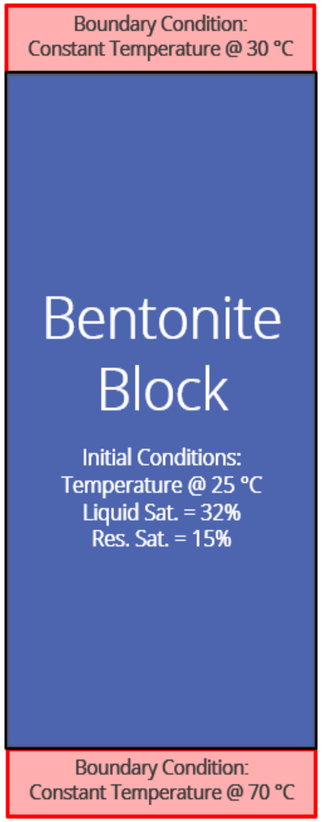
WORK IN PROGRESS

Problem Overview

- A temperature gradient is imposed on a bentonite block over 18 days
- Looking at evolution of saturation profile over time
- Constant temperature boundary conditions

Computational Approach

- Used PLFOTRAN to model laboratory experiments performed by JAEA
- 1D, saturation-driven, two-phase transport; chemistry off
- Permeability treated as variable input; homogeneous
- Uniform initial saturation
- Swelling not simulated
- Boundary conditions impose temperature gradient

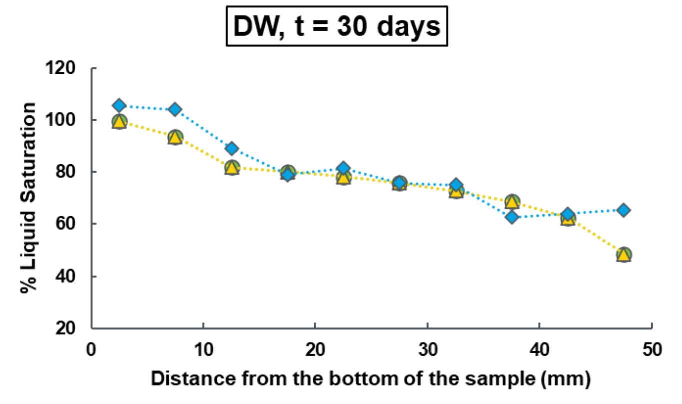


Boundary Condition:
Constant Temperature @ 30 °C

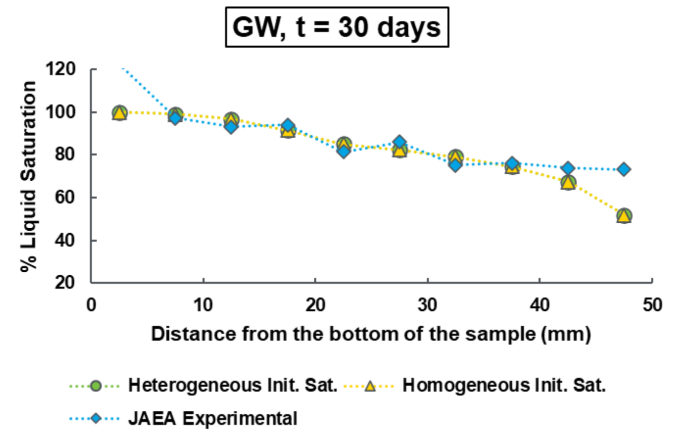
Bentonite Block

Initial Conditions:
Temperature @ 25 °C
Liquid Sat. = 32%
Res. Sat. = 15%

Boundary Condition:
Constant Temperature @ 70 °C



DW, t = 30 days



GW, t = 30 days

Findings

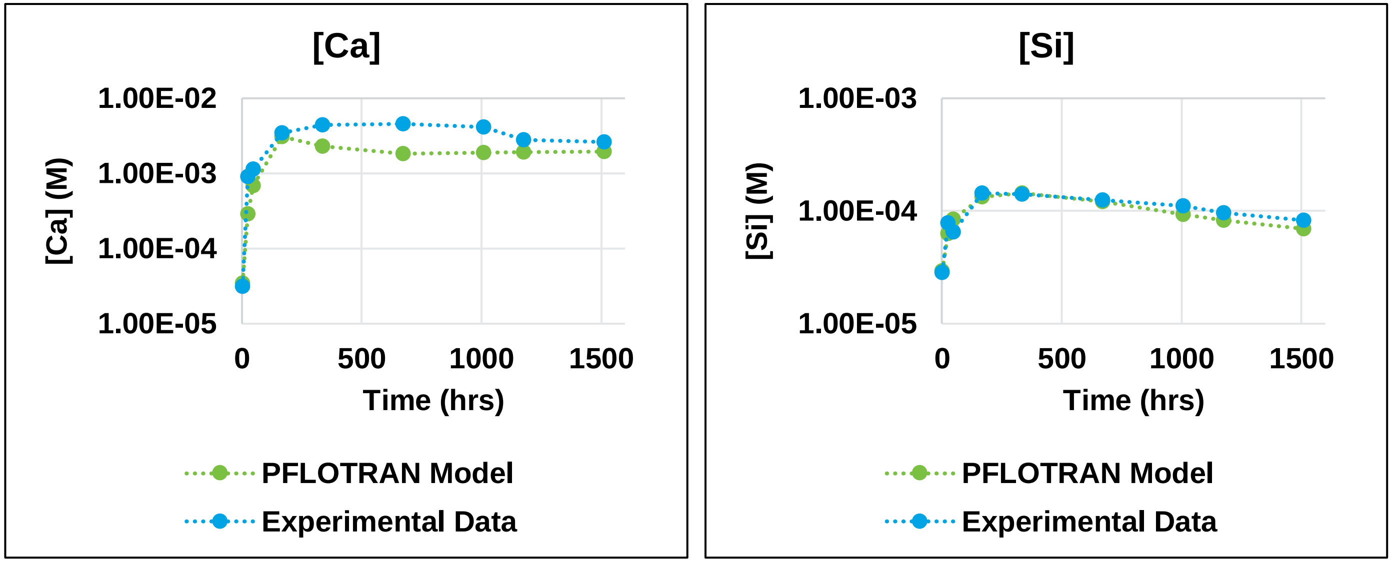
- The model does not yet capture the trends of the experimental data.
- Results are very sensitive to permeability.

Modeling of OPC Leaching

Modeling leaching of OPC using PFLOTRAN, for comparison against experimental leaching data obtained by Vanderbilt University

- Diffusion-only 1D reactive transport model; isothermal (25°C)
- Reacting OPC with water over 1500+ hours.
- Experiments following EPA Method 1315: leaching solution replenished with fresh water at specific time intervals.
- Initial cement composition uses prediction made by Vanderbilt's ORCHESTRA leaching model as a baseline.
- Anhydrous cement and sulfate salts are added to fit experimental data.

WORK IN PROGRESS



Ongoing and Futrure R&D Activities (SNL)

- PFLOTRAN THC modeling:
  - Variably saturated bentonite (TH) (isothermal / non-isothermal)
  - Reactive-transport modeling (HC) of OPC leaching experiments to evaluate chemical interactions at interfaces
    - Parameter evaluation, sensitivity analyses, mesh refinement
    - Reduced order model – development and implementation (e.g., swelling
- LBNL HotBENT Heated/Unheated Column Experiments
  - Thermal analyses of bentonites from column experiments
- Cyclical thermal analyses at higher temperatures and controlled moisture conditions
  - In situ XRD analyses under controlled moisture and temperature conditions
  - Close examination of calorimetric data
- MD simulations on dehydration phenomena of the clay interlayer
  - Exploratory studies of H_2(gas) adsorption and transport/mobility at the clay interlayer
  - Analysis of thermodynamic parameters of clay dehydration from MD simulations
- Thermodynamic database evaluation / expansion / development

*** Lothenbach et al. (2019) Cemdata18: A chemical thermodynamic database for hydrated Portland cements and alkali-activated materials. Cement Concrete Res 115, 472-506.**

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QUESTIONS?

EXTRA SLIDES

Bentonite hydrothermal experiment mineral changes - outline

- **Background**
- **Experiment parameters** (Use mine-run, unpurified bentonite, steel/copper, and K-Ca-Na-Cl brines).
- Investigate chemical evolution of clay mineralogy at repository temperature and pressure (**300-250-200 °C, 150 bar)**
- **Number and range of experiments**

Experimental Results:

  - Copper alteration- Steel alteration-Clay reaction products-Zeolite reaction products-CASH mineral reaction products

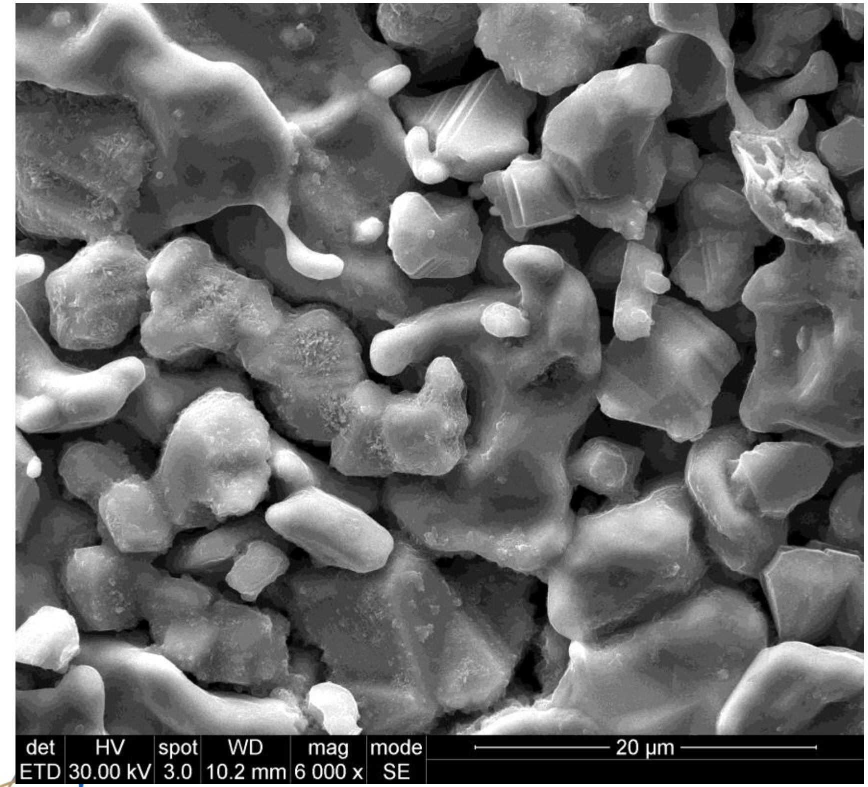
- **Comparison of results from crystalline and argillite experiments**
- **Conclusions**
- **Summary**
- **References**

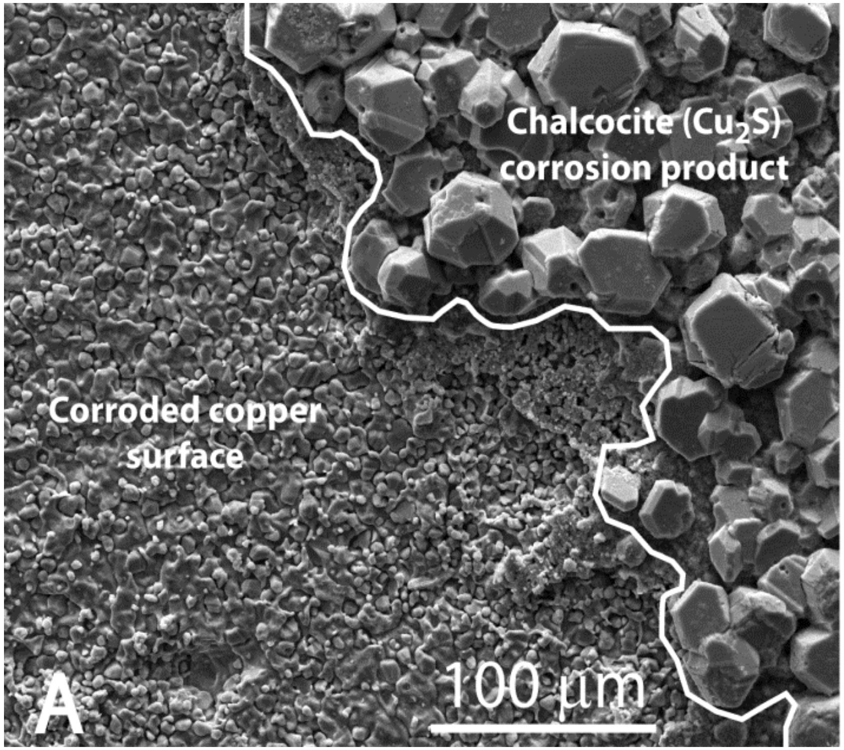
$2Cu° + H_2S \rightarrow Cu_2S_{(s)} + 2e^- + 2H^+$

Copper **Chalcocite**

Pit corrosion on Cu foil

Cu surface with Chalcocite alteration





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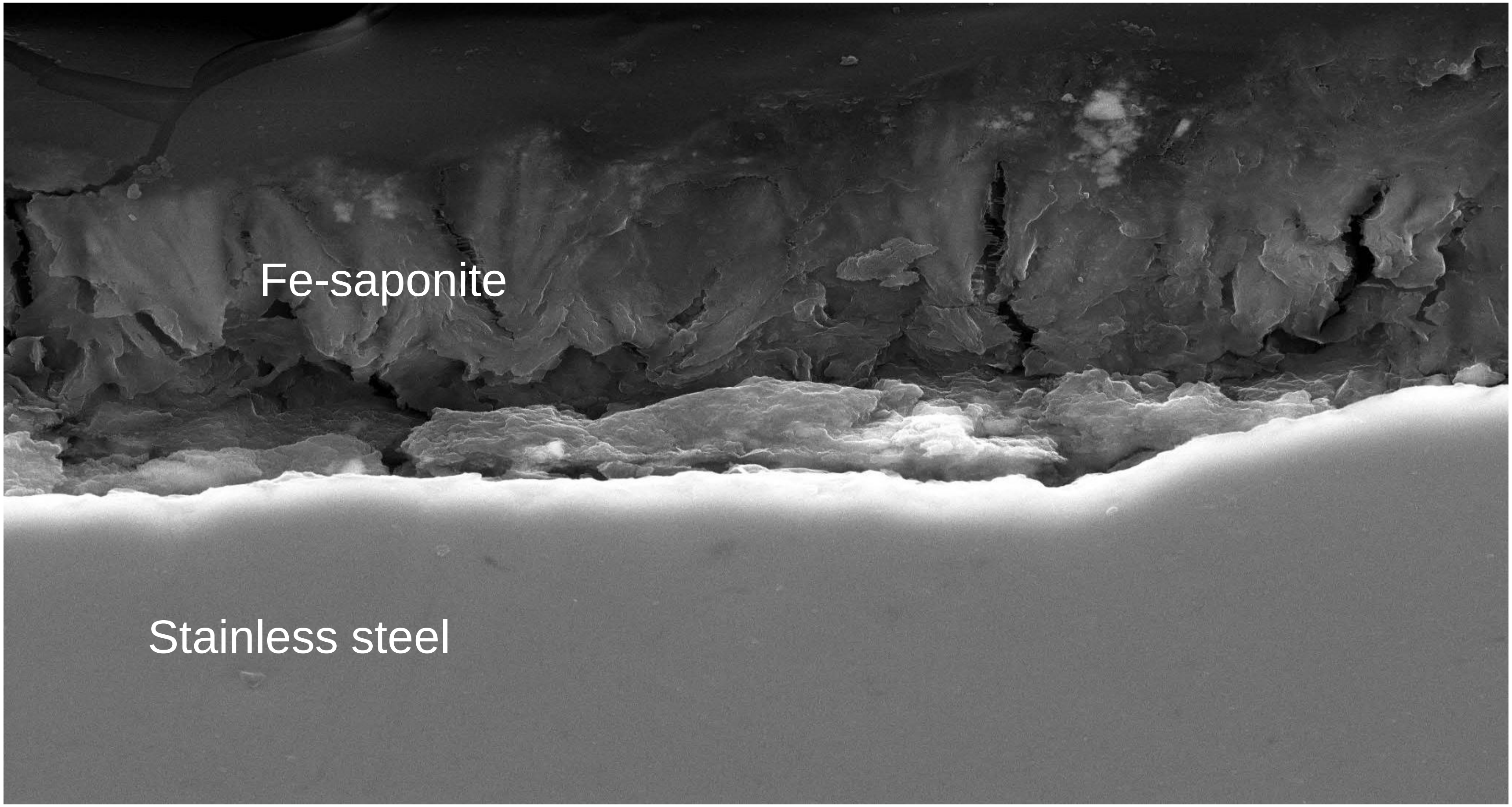
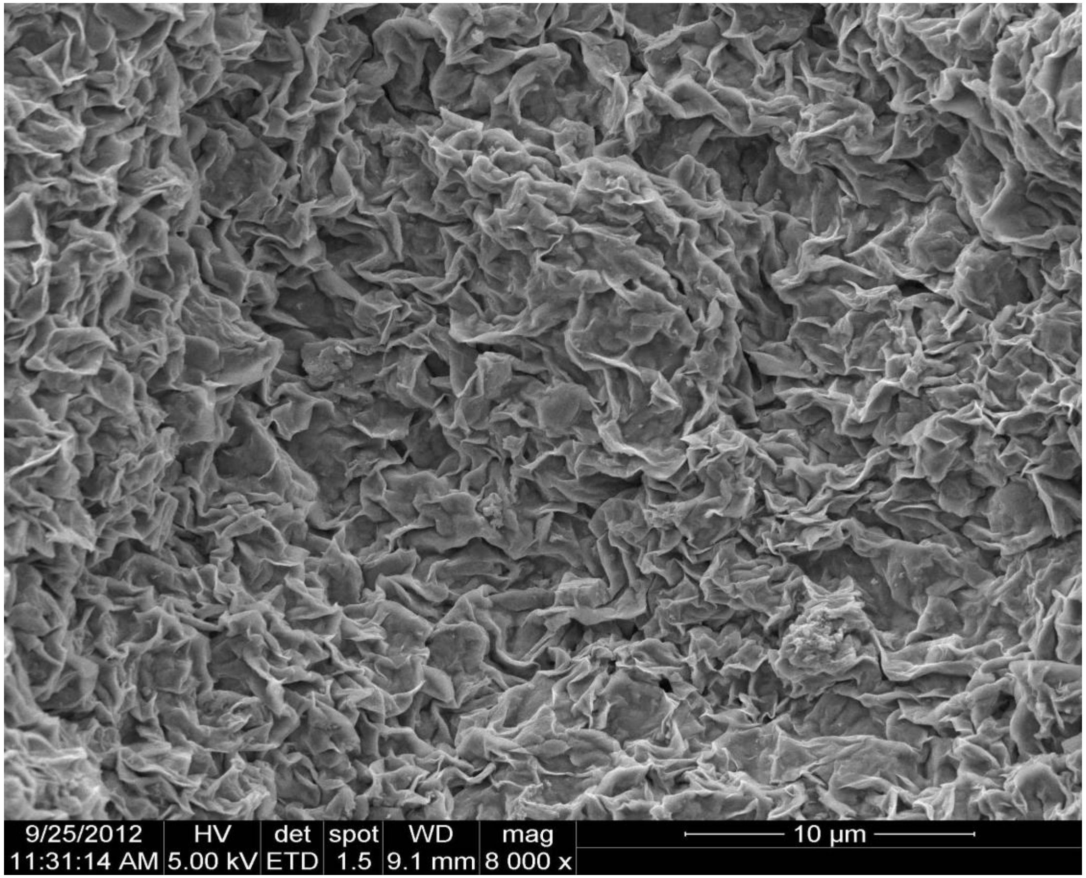
Fe-saponite perpendicular to steel (field of view - 40µm)



Foily "Corn flake" Smectite morphology



Bentonite only, 100 -300°C, 4 weeks