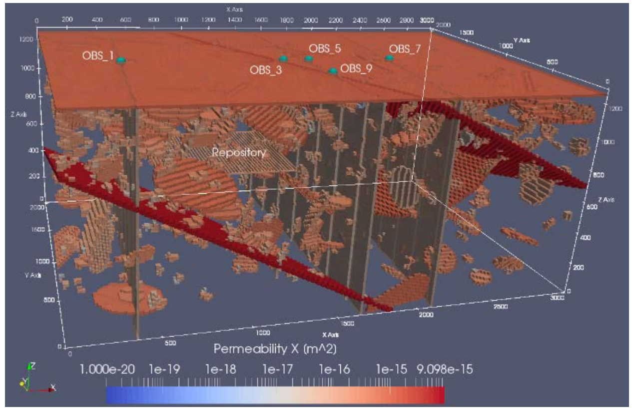

R&D activities to address high temperature and high pH conditions in EB

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Sandia National Laboratories

U.S. Nuclear Waste Technical Review Board
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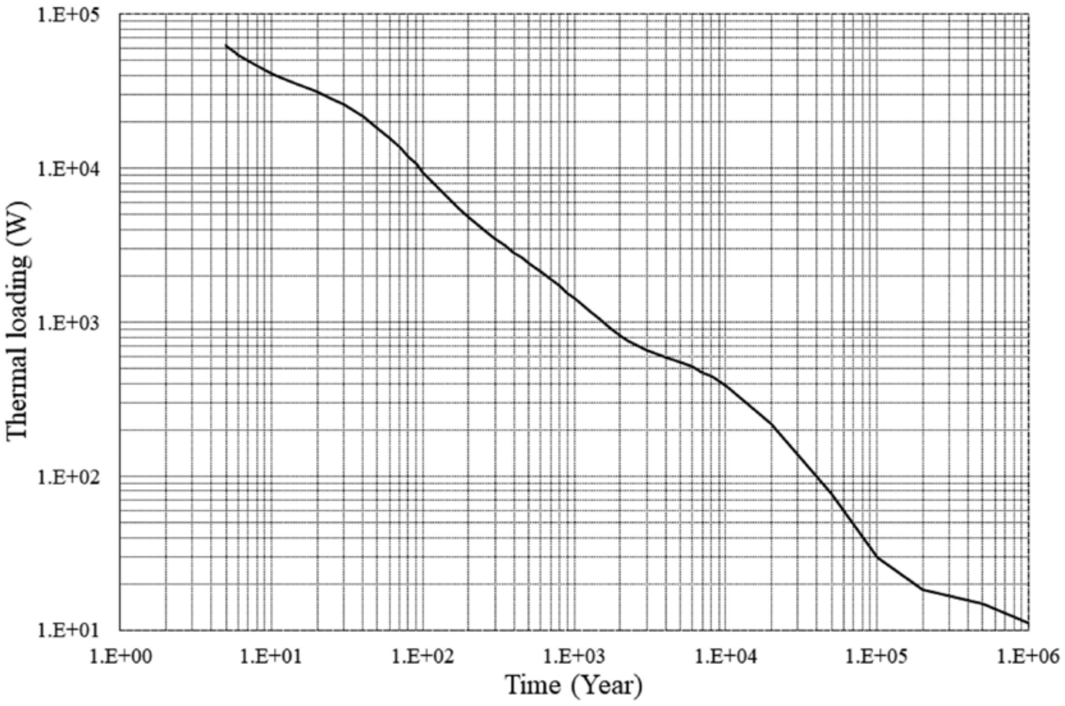
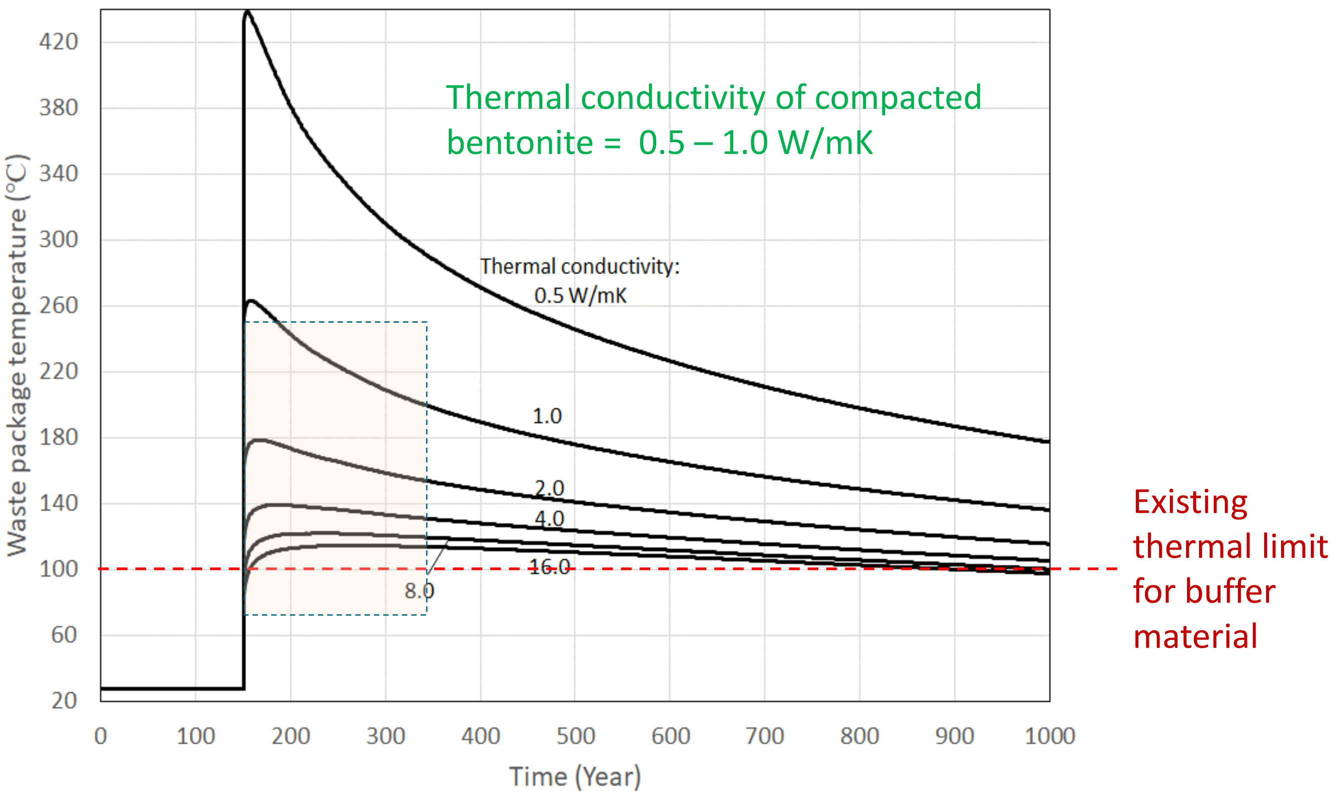
SAND2024-06134O

Outline

- Relevant disposal environments
- Related R&D activities
- Stability of bentonite
- Saponite as an alternative buffer material
- Update on HotBENT field experiment
- Concluding remark

Disposal environments: Elevated temperatures





Dual Purpose Canister (DPC):

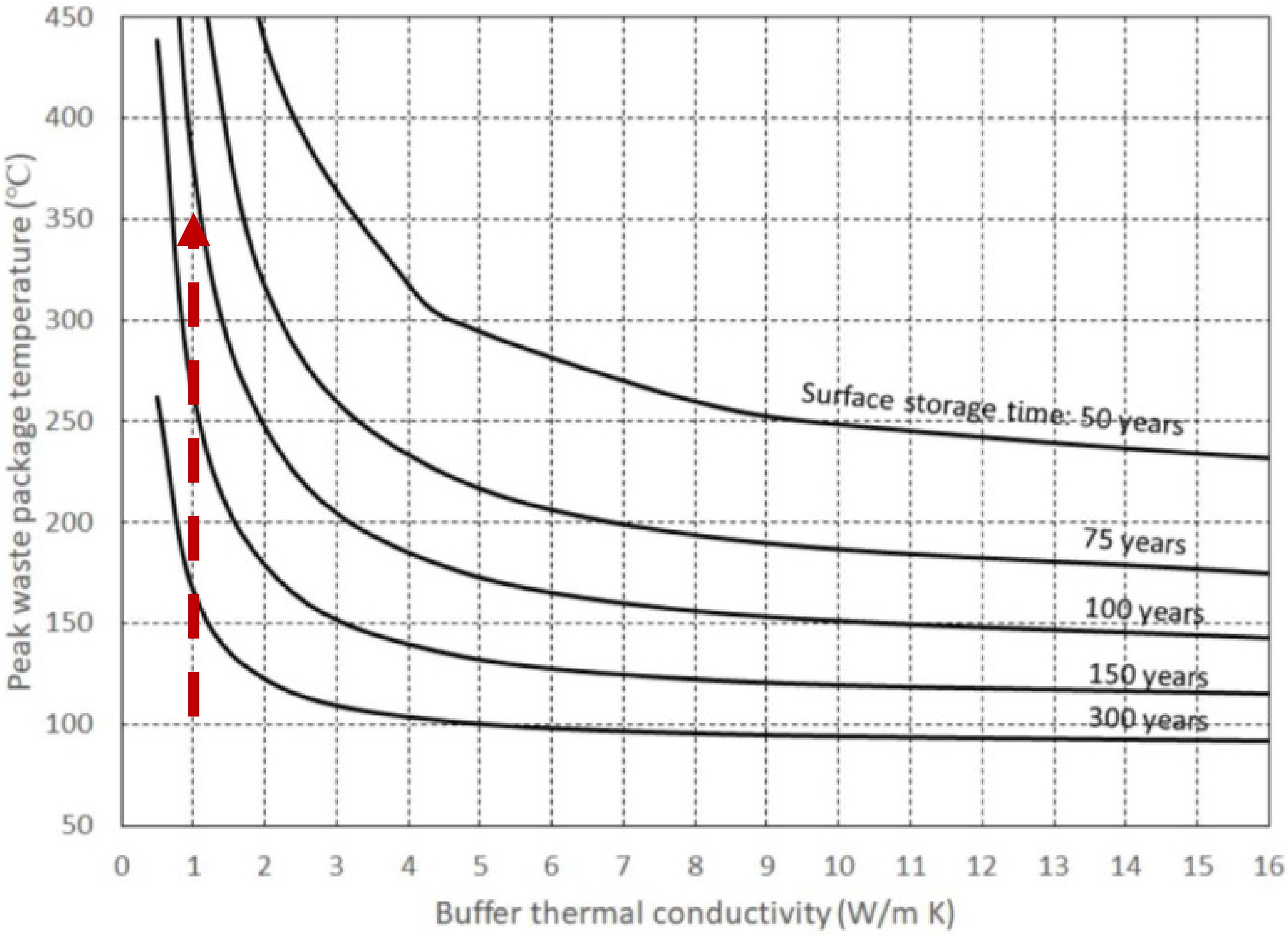
- 37 PWR assemblies
- 60 GWd/metric tonne burnup
- In crystalline rock
- Drift spacing: 60 m
- Canister spacing: 20 m (center to center)

- High temperature can attain on waste package surface.
- Thermal impact on bentonite performance as a barrier for T > 100 ℃ is largely unknown.
- If there is any impact, it must be evaluated over a limited time interval.

Wang and Hadgu (2020)

Why to raise the thermal limit of buffer materials?

- Maximizing repository capacity
- Facilitate earlier disposal
- Demonstrating barrier capability
  - Mineral phase change?
  - To what degree?
  - Swelling capability
  - Sorption capability

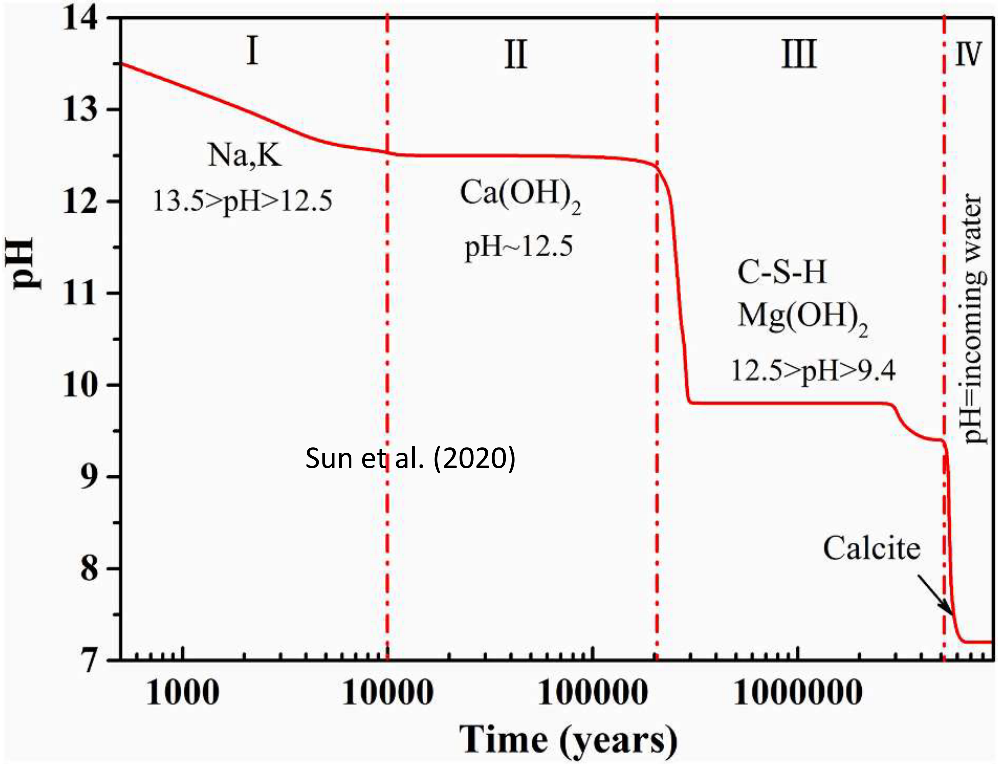


Wang and Hadgu (2020)

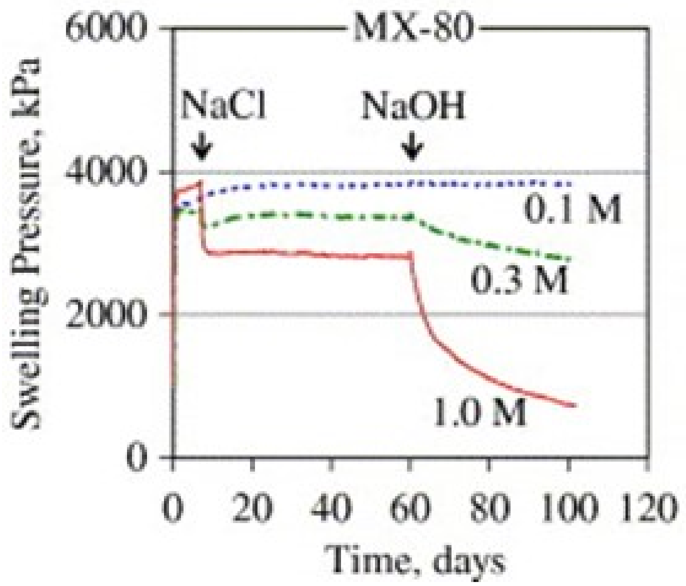
Disposal environments: High pH

Cementitious materials

- Rock support
- Liner
- Tunnel plug



Sun et al. (2020)



Karnland et al. (2007)

Alkaline plume from a cementitious material may impact swelling capability of a bentonite buffer material.

Raising the thermal limit of buffer materials: A joint effort

Objectives

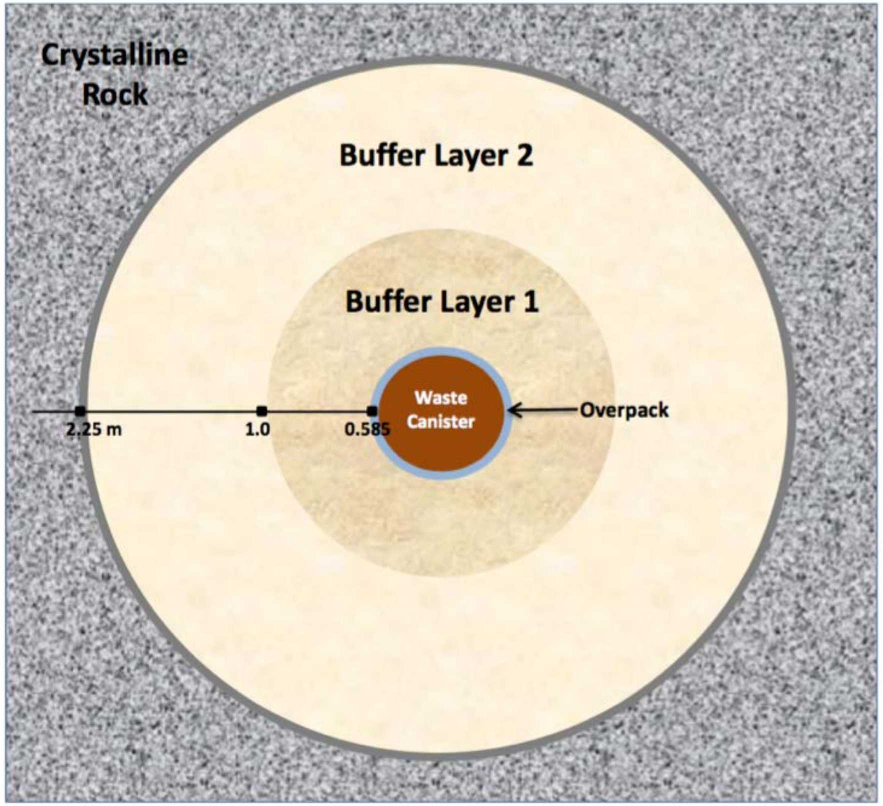
- Clarify limiting factors for smectite-to-illite transformation.
- Demonstrate the stability of bentonite materials at elevated temperature
- Develop new buffer materials for harsh environments

Related R&D activities

- Hydrothermal stability study of Na smectite (SNL).
- Radionuclide sorption study of hydrothermally altered bentonite (LLNL).
- Feasibility study of saponite as a new buffer material for harsh environments (SNL)
- Thermal-hydrologic-mechanical-chemical (THMC) modeling (LBNL)

Related International programs:

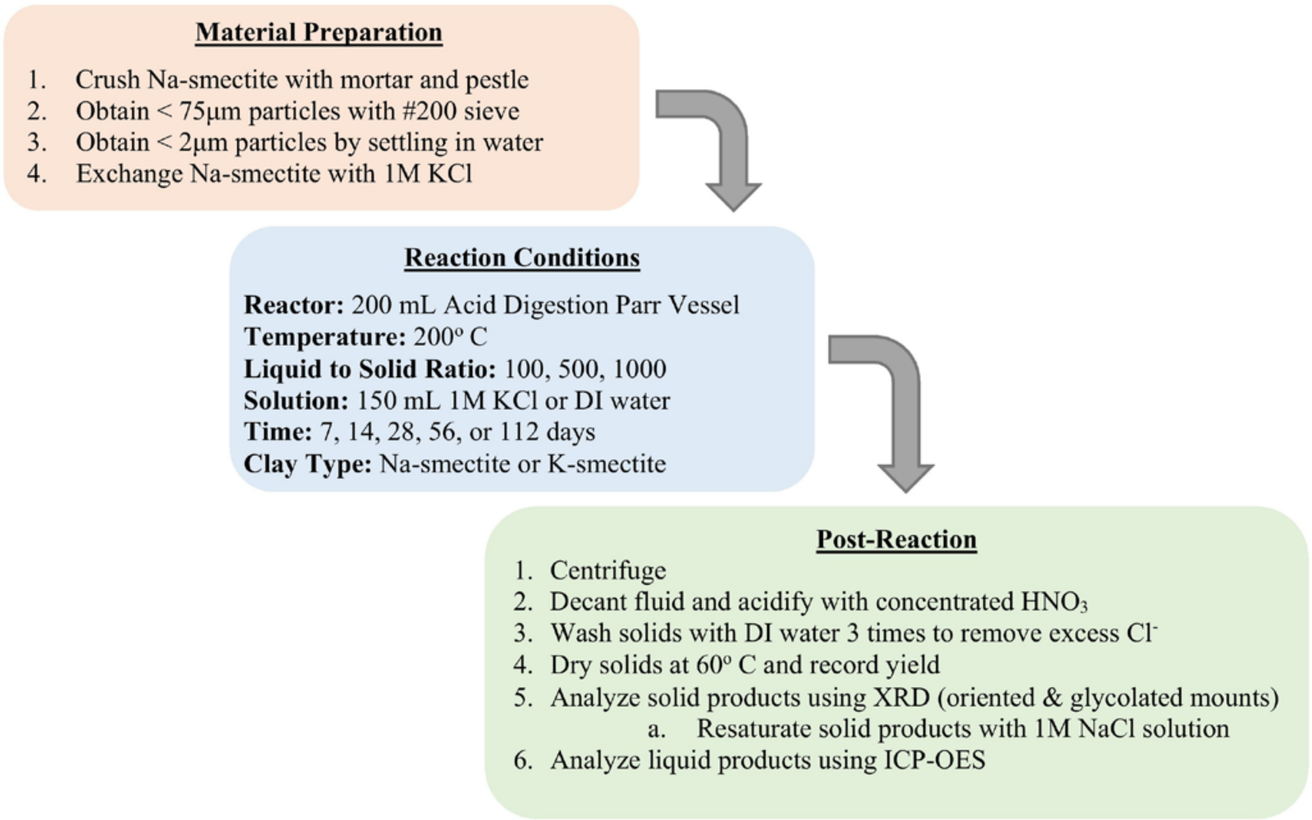
- HotBENT: T= 175, 200 ℃; materials = Wyoming (MX-80), BCV (Czech Republic bentonite)
- HE-E: T = 140 ℃; material = MX-80
- EURAD-HITEC: T = 100 - 150 ℃; materials = bentonite, host rock



Reference case: Double layer configuration with two clay buffer materials for a 12-PWR canister

Clarifying limiting factors for smectite-to-illite transformation: Accelerated experiments

Approach: (1) Create optimal conditions to make illite, and then (2) find out which factors can effectively inhibit the transformation.



Potential controlling factors:

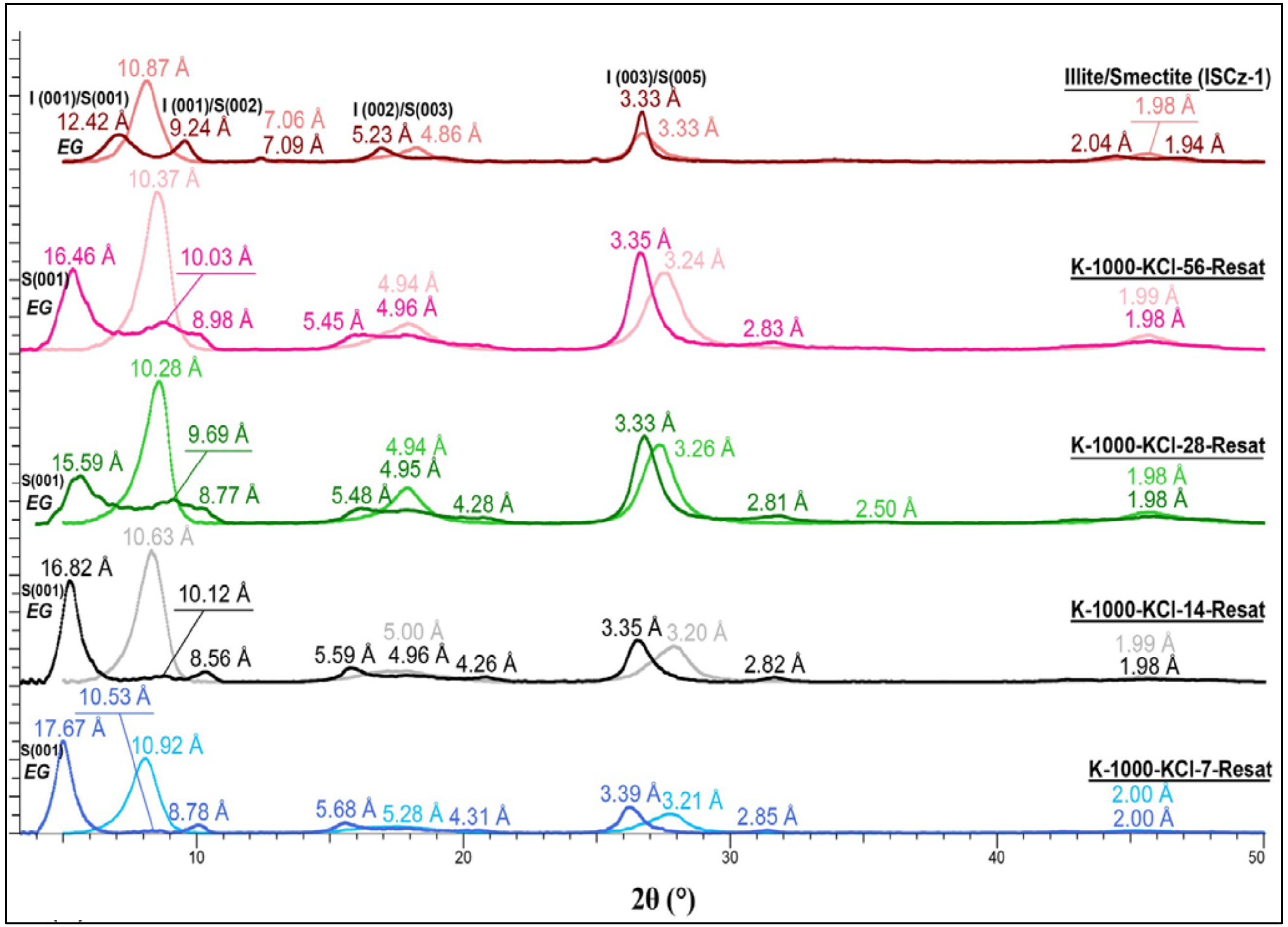
- Temperature
- Water/solid ratio (SiO_2 concentration)
- Duration
- Cations (Na, K)
- Solution chemistry (DI, KCl solution)

$2Na_{0.4}(Al_{1.47}Mg_{0.29}Fe_{0.18})Si_4O_{10}(OH)_2$ (Na-smectite) $+ 0.85K^+ + 1.07H^+ \rightarrow$
$1.065K_{0.8}(Al_{1.98}Mg_{0.02})(Si_{3.22}Al_{0.78})O_{10}(OH)_2$(illite) $+ 4.6SiO_2 + 0.36Fe(OH)_3 + 0.56Mg^{2+} + 0.8Na^+ + 0.9H_2O$

Mills et al. (2023)

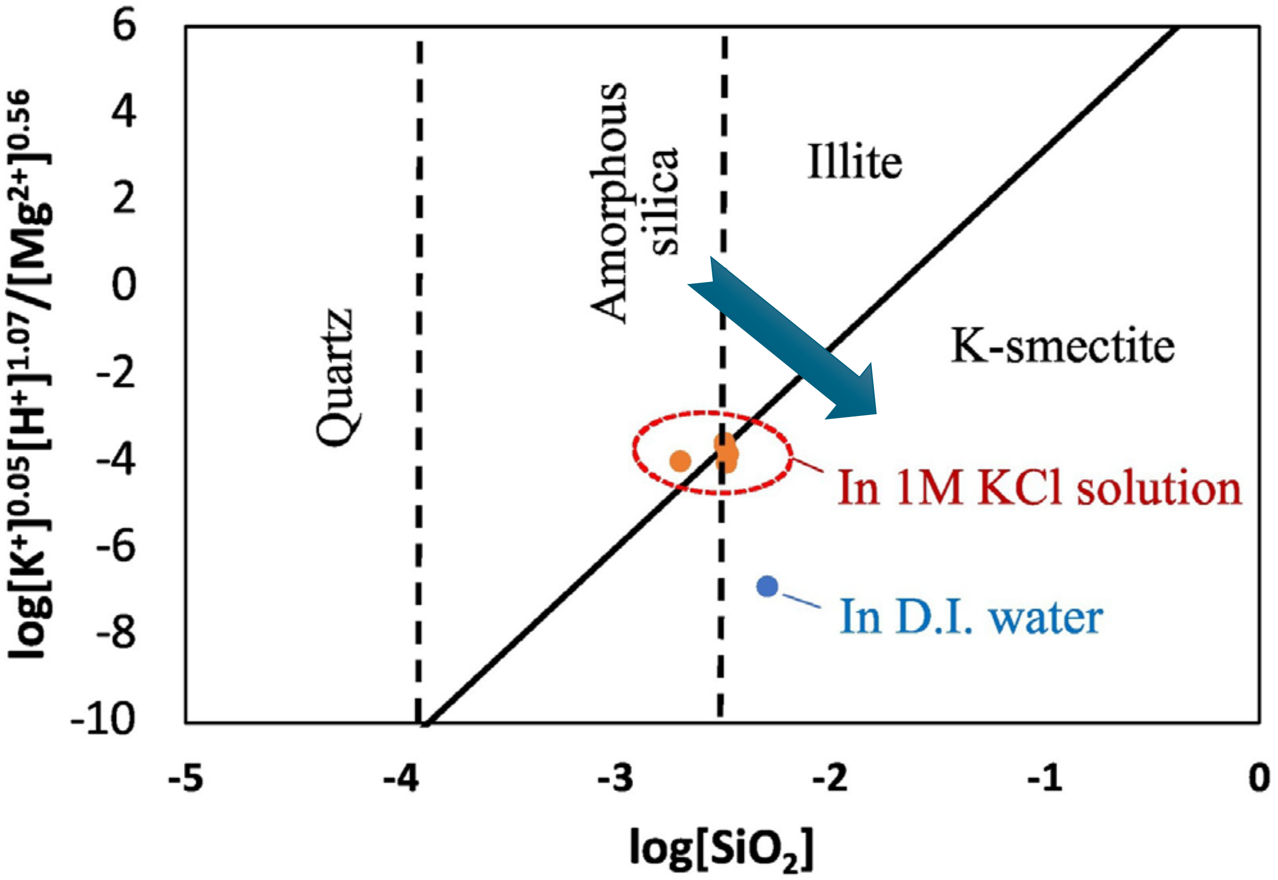
Findings: It is possible to raise the thermal limit of bentonite beyond the existing limit

- Under optimal conditions, smectite-to-illite transformation can happen relatively fast (within weeks).
- Transformation requires a large external K^+ source. K-exchanged smectite in DI water is still deficient in K^+ to convert smectite to illite at 200 °C.
- Transformation requires an extremely high water/solid ratio for SiO_2 dissolution.
- The required optimal conditions can hardly be met in an actual barrier system.
- If happening, the transformation would be limited.



Mills et al. (2023)

Enhancing smectite stability with chemical additives



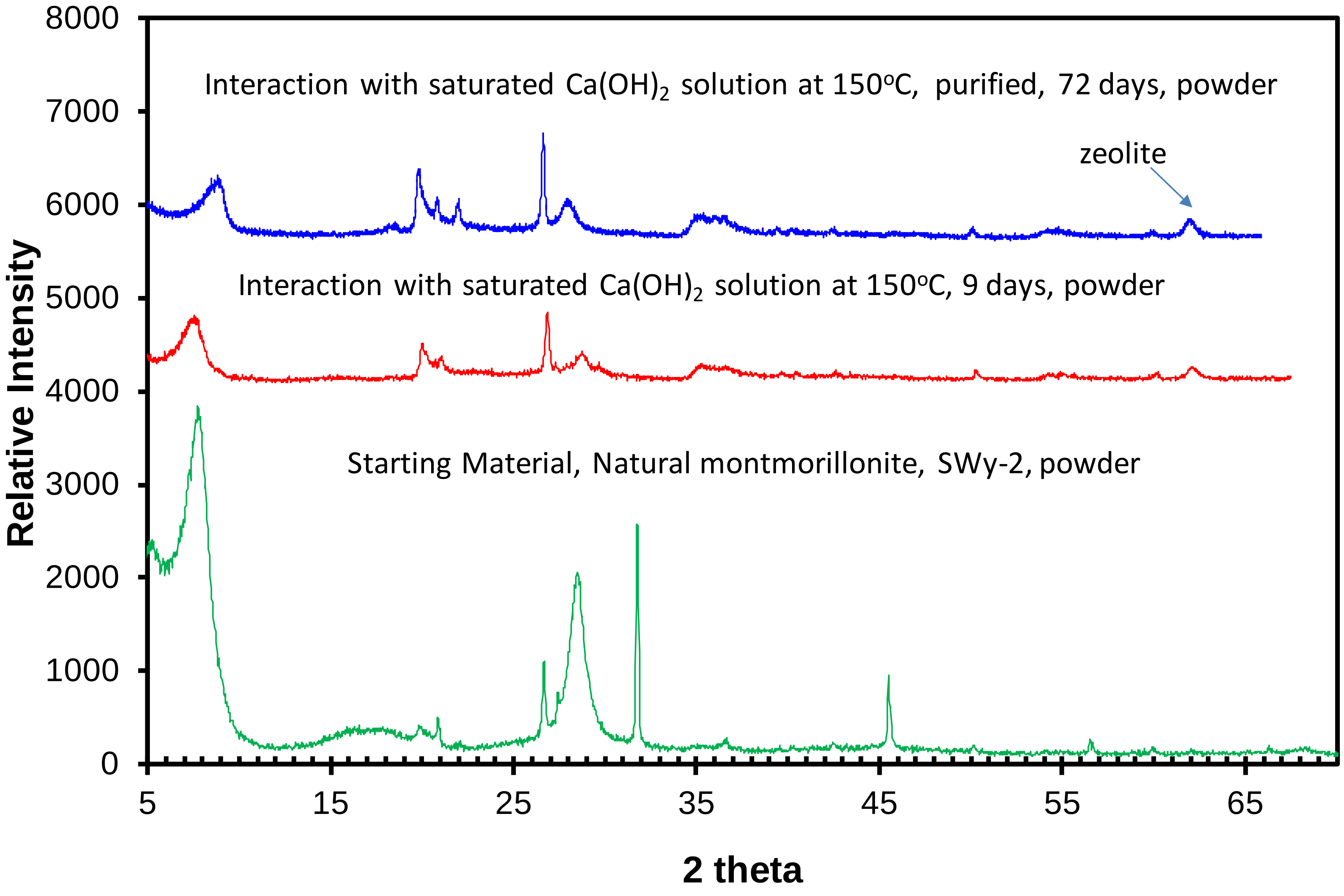
Chemical additives to inhibit smectite-to-illite transformation:

$Mg(OH)_2$ (brucite) → Mg^{2+} + OH^-

SiO_2 (am) → SiO_2 (aq)

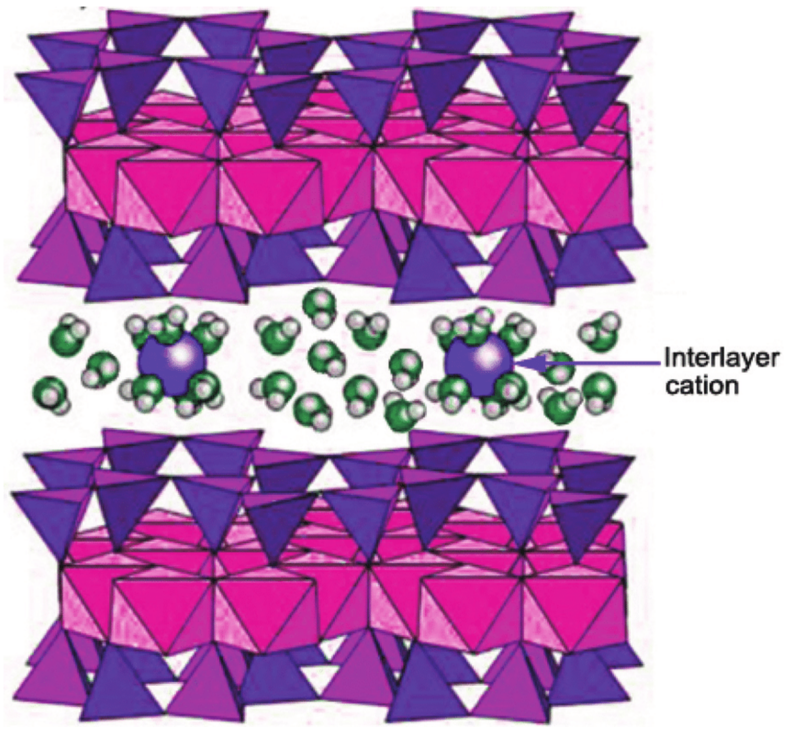
Mills et al. (2023)

Stability of Montmorillonite



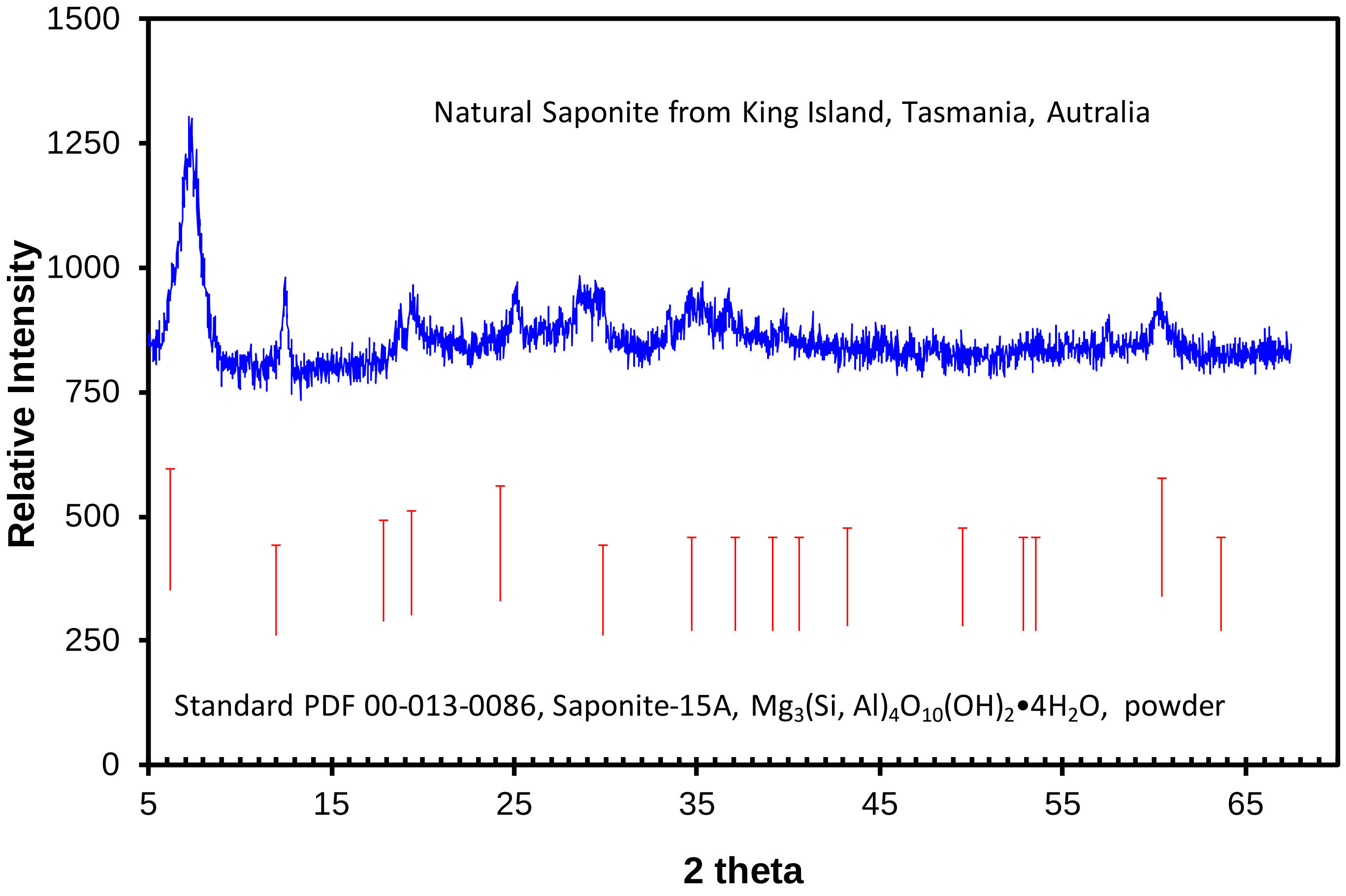
Xiong and Wang (2023)

Saponite: Trioctahedral Mineral of Smectite Group



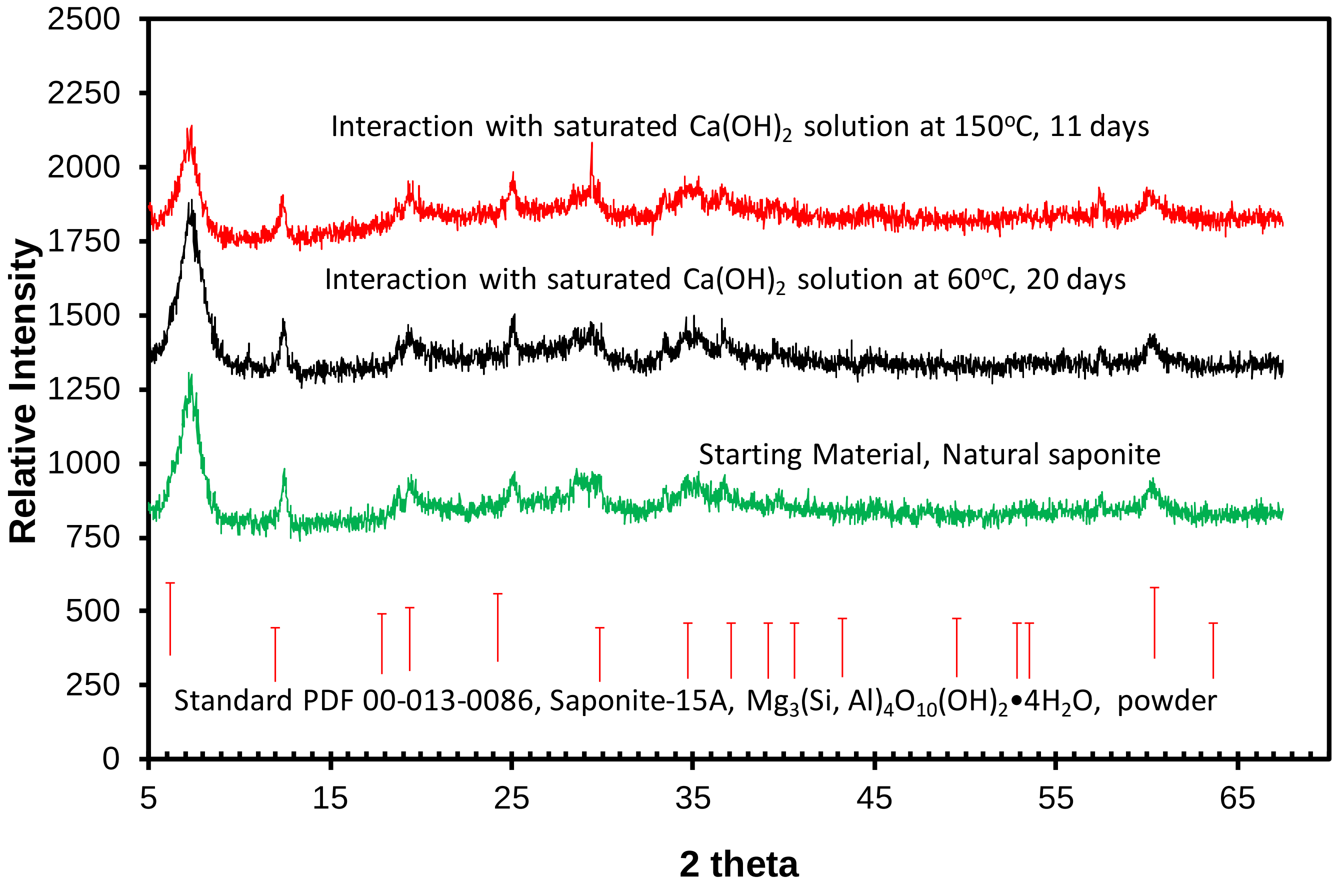
$Na_{0.95}Mg_{5.90}[(Si_{7.07}Al_{0.99})O_{20}](OH)_4$

Mitra et al., Physical Review E
87, 062317 (2013)



Xiong and Wang (2023)

Saponite as a Buffer Material for Harsh Disposal Environments



Xiong and Wang (2023)

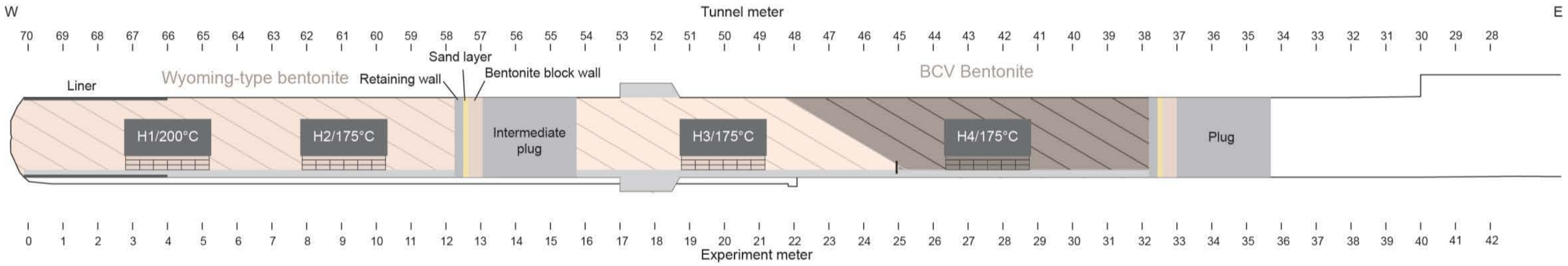
Samples	Density kg/m^3	Dry density kg/m^3	Hydraulic conductivity (K), m/s	Swelling pressure (p_s), kPa
MX-80	1800	1310	E-10	200
MX-80	2000	1175	2E-13	4700
GMZ	1788	1233	E-11	530
Saponite	1800	1175	4E-12	1300
Mixed-layer FIM	1800	1392	4E-11	280
Mixed-layer FIM	2000	1175	2E-11	1000
Mixed-layer Holmehus	1800	1310	2E-11	600
Mixed-layer Holmehus	2000	1175	8E-12	2000

Yang et al. (2014)

Saponite

- Naturally occurring, bulkily available
- Chemical stable at elevated temperature and high pH
- Sufficiently high swelling pressure

HotBENT Field Experiments: Field scale long-term testing of buffer material stability



Design:

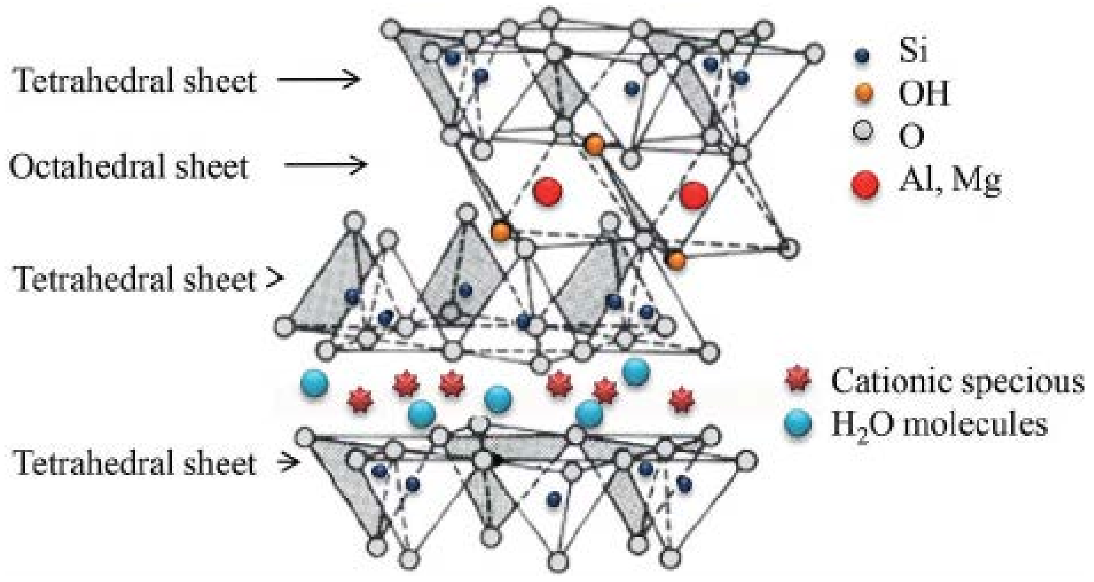
- **Four modules** Differing in heating temperature, bentonite, time length and w/o concrete liner
- **Two experimental time lengths** H3 and H4 will run for 5-10 years; H1 and H2 will run 15-20 years
- **Two bentonites:** Wyoming (MX-80) BCV (Czech Republic bentonite)
- **Two shapes:** Pedestals for the heaters made of highly compacted blocks, dry density > 1.7 g/cm^3; granulated Bentonite Mixture (GBM), dry density >1.45 g/cm^3

Updates

- Heating Started on Sep 9, 2021.
- Heaters have been ramped up in steps.
- By June 2, 2022 all heaters reached their targeted temperature.
- Sensor data have been collected. Many relative humidity sensors are not operational.

Concluding remark

- Raising the thermal limit of buffer material will maximize repository capacity and facilitate earlier disposal.
- Smectite-to-illite transformation is not favorable in an actual repository environment with limited K^+ availability, a low water/solid ratio, and a narrow thermal window for transformation.
- Stability of smectite can be further improved by chemical additives.
- Saponite can be an attractive buffer material for high temperature and high pH environments.
- By combining laboratory studies and long-term field tests, it is possible to raise the thermal limit of buffer materials beyond the existing 100 ℃.



https://www.researchgate.net/figure/Smectite-structure-of-a-2-1-clay-mineral-showing-two-tetrahedral-sheets-sandwiched_fig2_274095227

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Acknowledgment

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