

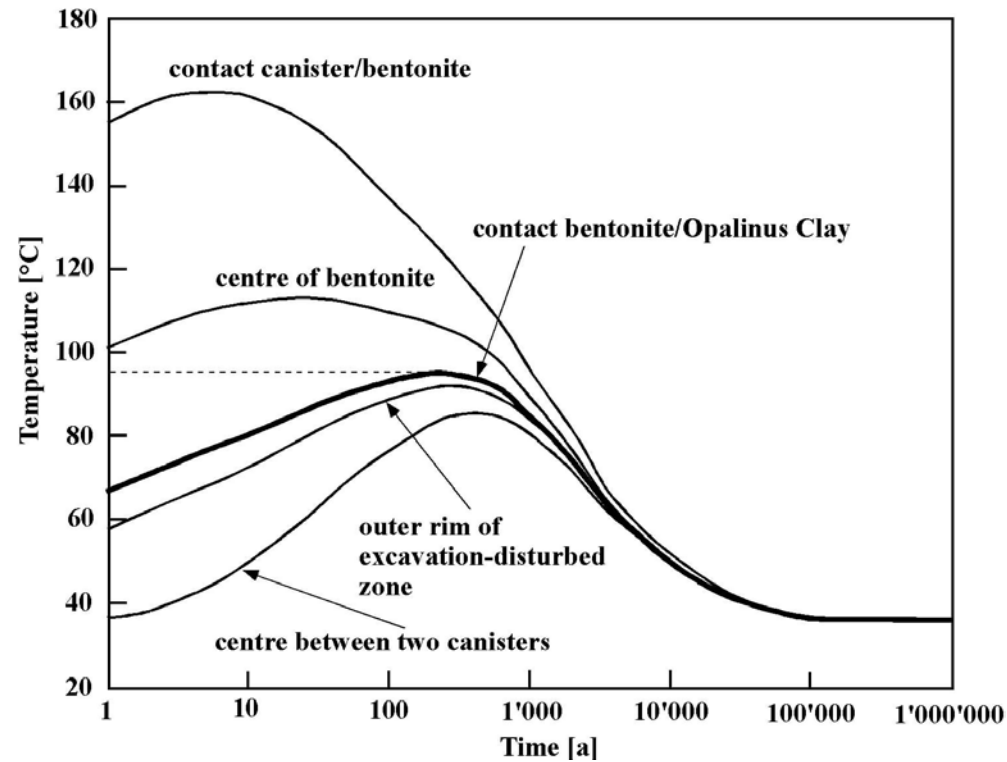
Effects of elevated temperatures on the EBS in crystalline or clay formations

Thorsten Schäfer, Volker Metz, Vanessa Montoya & Andreas Bauer

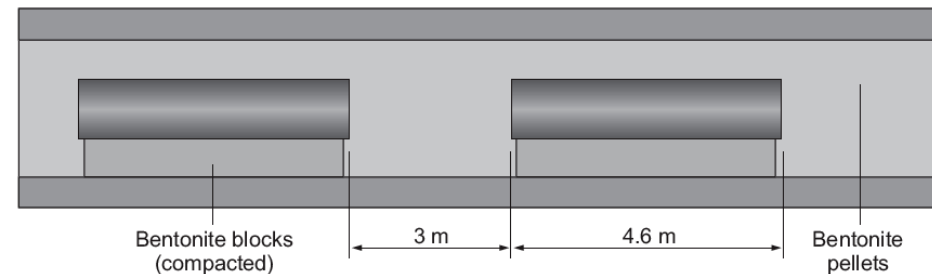
INSTITUT FÜR NUKLEARE ENTSORGUNG (INE)
INSTITUTE FOR NUCLEAR WASTE DISPOSAL (INE)

Thermal pulse in a Swiss SF/HLW repository

- **Opalinus Clay (and other clays/ shales) has a low thermal conductivity (1.3 - 3.2 W/m/K)**
- **Spent MOX fuel is “hot”**
- **Temperature will reach max. 160 °C in bentonite and 95 °C in Opalinus Clay over hundreds of years**



- **Note: In the reference scenario thermal perturbation has decayed before the onset of radionuclide release**



Swedish view (SKB) based on TR-10-47

- *“In addition, all conceivable causes of a canister failure are highly unlikely to occur during the fuel induced thermal transient in the repository.”*
- *“The efficiency of heat transport through the buffer region is important for the performance of the system, since it affects the maximum buffer temperature for which a design threshold ($< 100^{\circ}\text{C}$) has been established.”*
- The most important parameter is thus the **thermal conductivity, λ** , of different parts of the system (density, water saturation & mineral composition).
 - Water-saturated MX-80 bentonite (density of $2,000 \text{ kg/m}^3$) is **$\sim 1.3 \text{ W/(m}\cdot\text{K)}$** .
 - Pellets-filled gap bentonite blocks/ surrounding rock is **$0.3\text{--}0.4 \text{ W/(m}\cdot\text{K)}$** .
 - For the hot air filling the canister-bentonite space, the conductivity is about **$0.03\text{--}0.04 \text{ W/(m}\cdot\text{K)}$** .
- The duration of the temperature pulse:
 - After 2,000 years, the maximum excess temperature in the repository is $15\text{--}20^{\circ}\text{C}$
 - After 5,000 years, the maximum elevation in temperature is about 10°C . The thermal gradients within the buffer are almost zero already after 2,000 years.

- Temperature effect on **host rock**
- Temperature effect on **bentonite buffer**

Temperature effect on **host rock**

- The in-situ observations of the **Heated Failure Tests** with temperature up to 85°C in the AECL's URL (Canada) showed no changes in the host rock stability and no increase in the EDZ (excavation damage zone) through the temperature increase (Ohata & Chandler, 1997).
- In Posiva's Olkiluoto Spalling Experiment (POSE) in Olkiluoto (Finland) an increase of the EDZ via temperature increase has been observed (Valli et al., 2014)
- Ongoing characterization of samples from the FEBEX dismantling project. Bentonite under natural re-saturation in Crystalline rock (Grimsel Test Site).

- Temperature effect on **host rock**
- Temperature effect on **bentonite buffer**

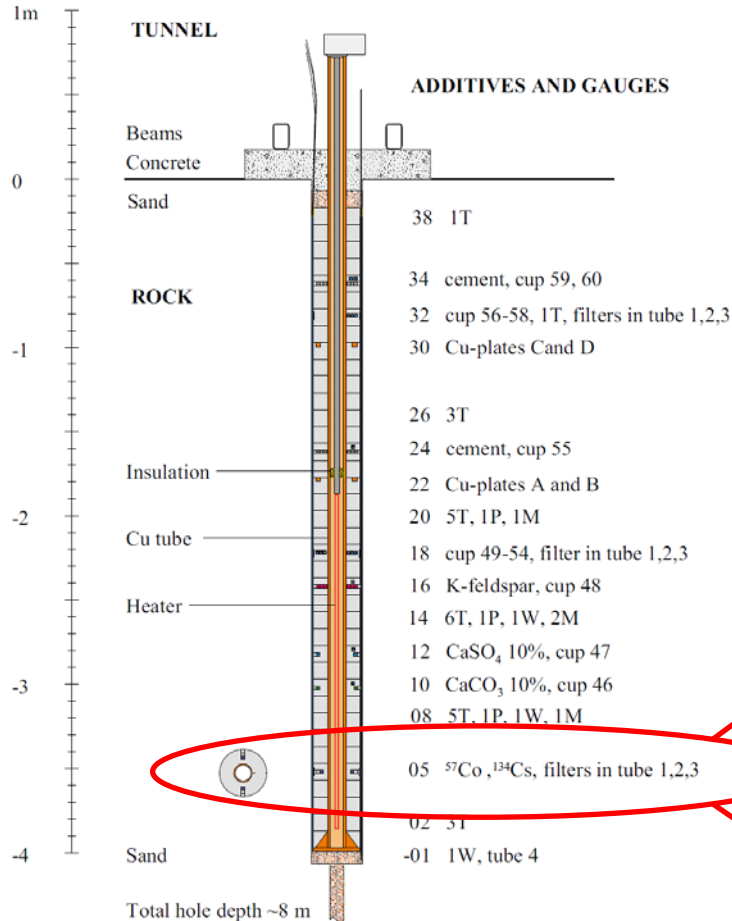
High Temperature Tests (TR-10-47)

- Hydrothermal tests with purified standard bentonite (SWy-1) heated to 150–200°C have shown that cooling leads to **precipitation of silicon compounds** in various forms.
 - The precipitation is assumed to cause cementation effects, including a ***strength increase***, which has been demonstrated in several laboratory investigations (e.g. Pusch and Karnland, 1988).
 - At the highest temperature in the buffer (**90°C**), **cementation was not of such a great extent.**
 - Precipitation of sulphate and carbonate could be observed in one-year experiments with hydrothermal treatment of MX-80. XRD analyses indicated that **sulphates and calcite had gone into solution and had been transported to the hot iron surface, where they had precipitated.**
- ✓ **Specific isotope experiments to better elucidate the coupled processes!**

ABM-II test (Kumpulainen et al. *Clay Min.* 2016, 51(2),129-44.)

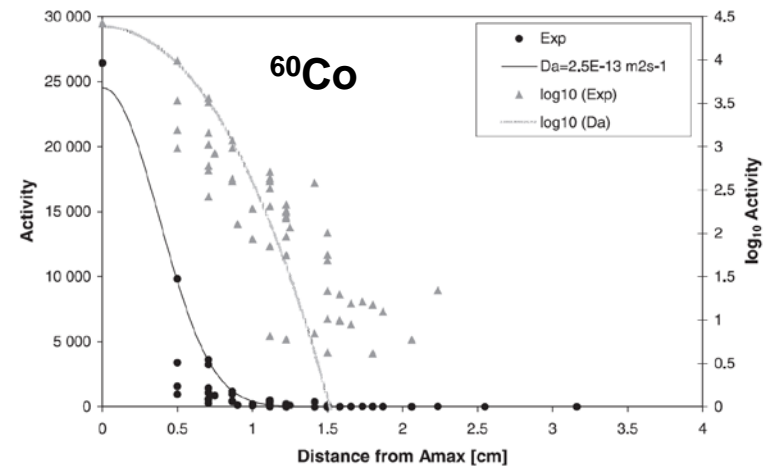
- The chemical/mineralogical effects observed in the ABM2 test were more pronounced than those in the ABM1 (5 y heating at 130°C in ABM2 compared to 2.5 y in ABM1). In ABM2, three types of chemical effects were recorded:
 - uniform changes occurred in blocks
 - rising or falling trends in horizontal profiles of the blocks, and
 - changes occurring only at the boundary with the iron heater.
- Compared to the reference samples, the exchangeable **cation populations changed uniformly in all blocks**. Increases in water-soluble Ca, Mg, K and SO₄, decreases in poorly crystalline Fe oxides, **increase in the total amounts of Mg, Ca, S** and **decreases in the total amounts of Na and K** were noted in horizontal profiles **towards the heater**.
- At the **boundary with the heater**, **increase in Fe** and decreases in the amounts of Si and Al, the **precipitation of gypsum and anhydrite**, indications of the formation of **trioctahedral clay minerals** (saponite), and the dissolution of cristobalite and feldspars were observed.
- A decrease in the swelling pressure of core-drilled samples of Friedland clay was observed that was recovered after grinding and re-compaction.
- After Svensson (2015) in the ABM-II experiment **indications are given that boiling has occurred leading to a loss of barrier integrity**.

LOT experiment (Long term buffer material test at Äspö HRL)



■ After KARNLAND et al. (2009):

- Due to water saturation of bentonite and the temperature up to 130°C only minor mineralogical changes (1-5 a observation) are recorded.
- These changes have not changed the material properties, nor the integrity of the bentonite buffer concerning sealing.



Jansson et al. (2003) *Appl Clay Sci.* 23(1–4):77-85.

Bentonite high temperature experiments in crystalline environments (partly adapted from Patrik Sellin)

- **Clay mineral alteration is unlikely to be detected in the 5-10a experiments**
 - No observations of formation of non-swelling minerals
- **Dissolution/ Precipitation reactions of sulphates/ carbonates observed**
- **Mg-accumulation towards heaters have been observed; reasoning?**
- **Tri-octahedral smectite formation has been observed (Fe- saponite), at least with an iron heater**
 - Process: Neo-formation or alteration? What parameter triggers the process?
- **Boiling in the near-field (=> HotBent?)**
 - Pressure control is important to avoid boiling in the repository
 - Integrity issue?

✓ Geochemistry:

- Maturation reactions in organic material
- Illitisation of smectite - loss of swelling
- Saponite formation – Fe speciation

✓ Cementation reactions, secondary phase formation

- Precipitation/dissolution reactions
- Shift of geochemical equilibria

✓ Hydrogeology:

- Build-up of pore pressure (thermal expansion), fracturing
- Change in transport parameters

✗ **Mechanics: embrittlement, etc.**

Not our competence but open to joint experimental program

Handling of model variables influencing the buffer, backfill and closure process (from TR 10-47)

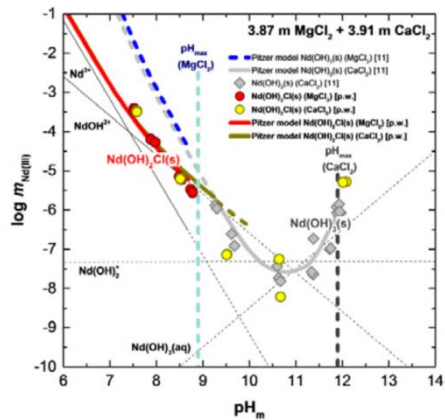
The process is coupled to the water saturation process which is difficult to model in detail, especially the evolution of gaps. Also, the water saturation process is highly dependent on the uncertain hydraulic conditions in the rock around the deposition hole.

- **The influences of varying hydraulic conditions in the saturating buffer, including porosity variations, are conservatively neglected.**
- **The gap between the canister and the buffer will conservatively be assumed to be open until the peak temperature has been reached.**
- Critical uncertain input data for use in determining the peak canister temperature include
 - The heat power of the fuel, the thermal conductivity of the partly saturated buffer material and of the host rock.
 - Also uncertainties of the emissivities of the inner buffer and in particular the outer copper surfaces are decisive in determining the peak canister temperature.

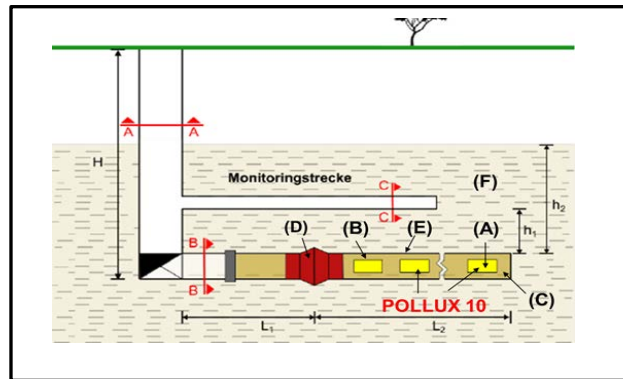
Tools and parameters for RTM

Geochemical information and databases

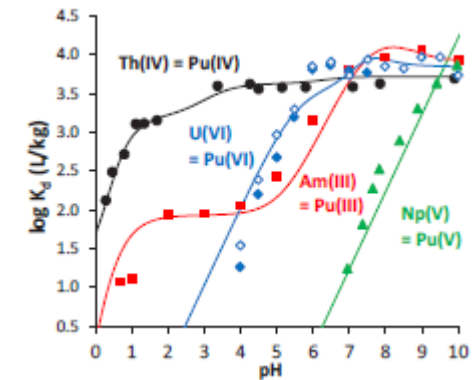
Thermodynamics (TDB)



Reactive transport modelling (RTM)



Sorption (TDB)



(user, not code developer):

- PHREEQC v.3.
- COMSOL Multiphysics v.5
- iMaGe-ICP „Interface to couple Comsol-Phreeqc“



Comsol
Comsol API working
over Comsol server



➤ Deriving geochemical boundary conditions for different generic SNF/HAW glass repository systems

Thank you
for your kind attention!

Nanoscopic OM functional group heterogeneity

Beamline:

X1A1 & X1A2 (NSLS)
Pollux (SLS)
10ID-1-STXM (CLS)

Technique: Soft X-Ray Spectro-Microscopy

Publication(s):

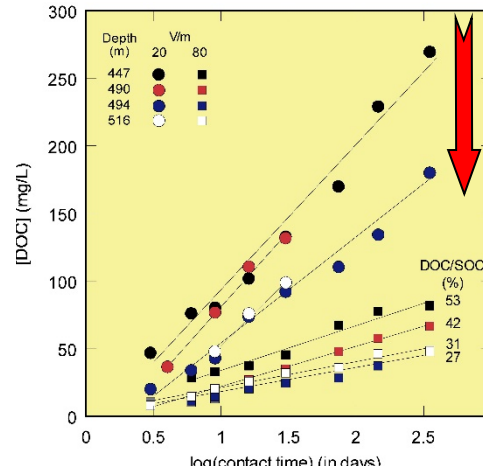
1. Claret, Bauer, Schäfer, Griffault, Lanson (2002) *Clays Clay Min.*, 50(5), 633-646.
2. Claret, Schäfer, Bauer, Buckau, (2003) *Sci. Total Environ.*, 317 (1-3), 189-200.
3. Lerotic, Jacobsen, Schäfer, Vogt (2004) *Ultramicroscopy* 100, 35-57.
4. Schäfer, Claret, Beetz, Lerotic, Wirick, Jacobsen, Smith, Miller *J. Electron Spectrosc. Relat. Phenomena* 2009; 170: 49-56.
5. Schäfer, Claret, Bauer, Griffault, Ferrage, Lanson (2003) *J. Phys. IV*, 104, 413-416.

Motivation:

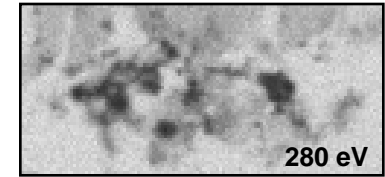
- DOC release of Callovo-Oxfordian argillite clay fraction shows depth dependence (see Fig.).
- The simultaneous change in clay mineralogy (smectite presence in the upper part; 447m depth) suggests a mineralogy dependent OM functionality.
- Sulfur embedded 100nm thick whole rock microtome (447m) were analyzed. Post-processing by PCA and cluster analysis was used to retrieve spectral differences.

Results:

- OM functionality varies significantly with mineral type (Ca and π^* -transition at 290.2eV for carbonate, potassium for illite type clay minerals; Ca for smectite). Mineralogy confirmed by infrared spectro-microscopy (U10B, NSLS).
- Expected for young soils, but here diagenetically overprinted Jurassic sediments.

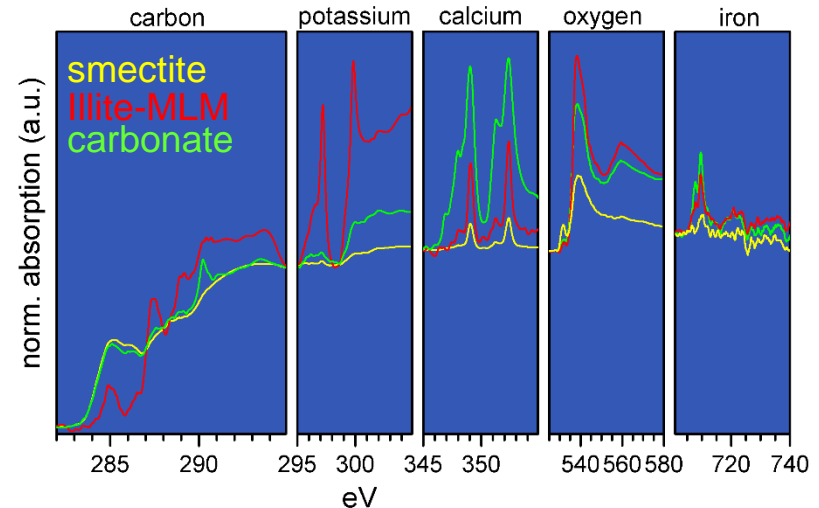
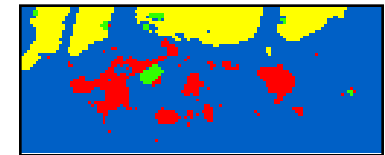


Absorption image



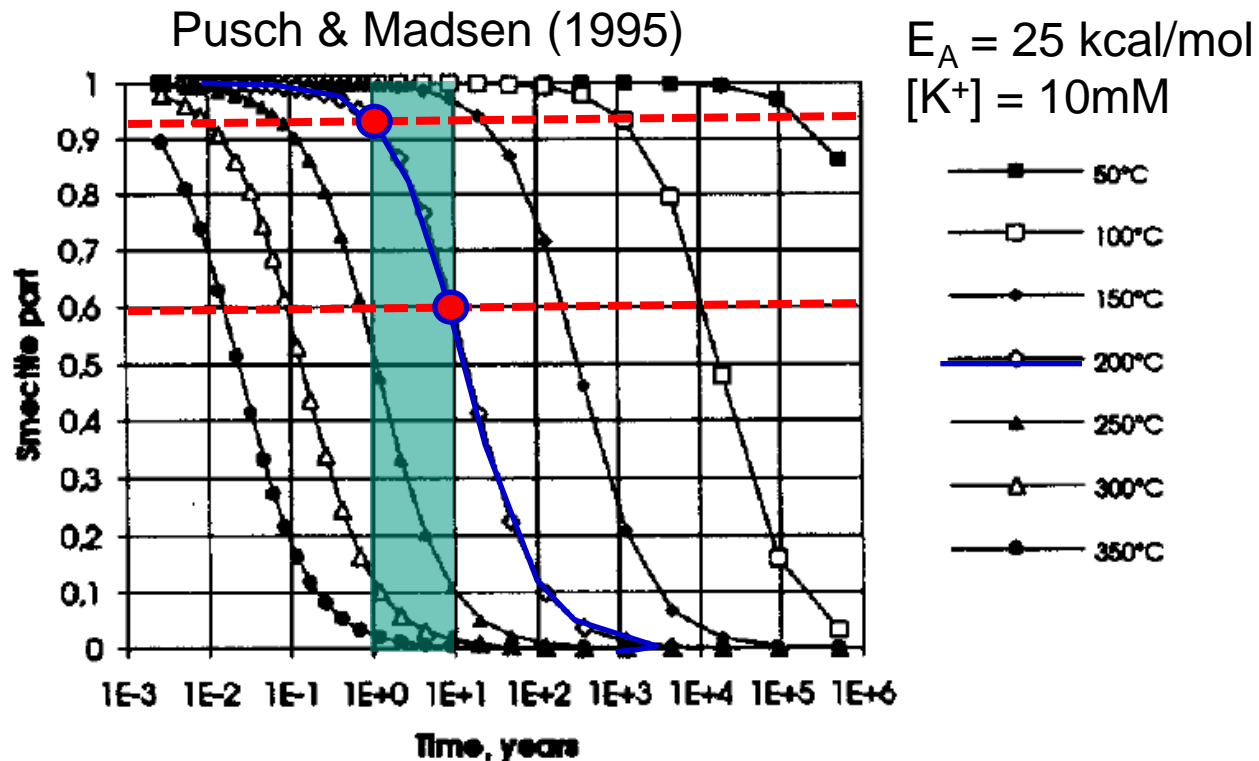
3µm

Cluster analysis



(Top, left) Depth dependent DOC release from Callovo-Oxfordian argillite clay fraction <2µm. (Bottom) C, K, Ca, O and Fe-edge spectra of the three clusters found (red, yellow, green).

Effect of mineral transformation as $f(T)$ on buffer integrity

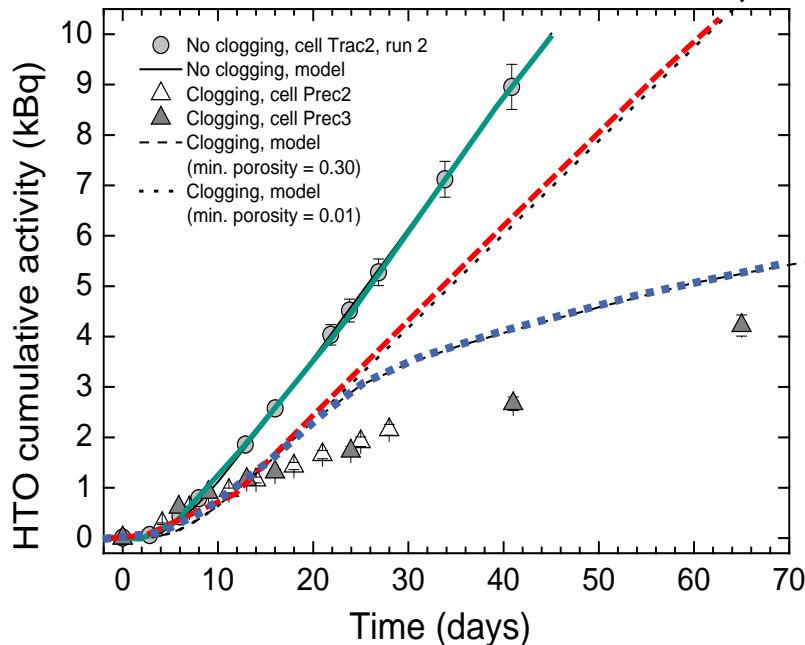
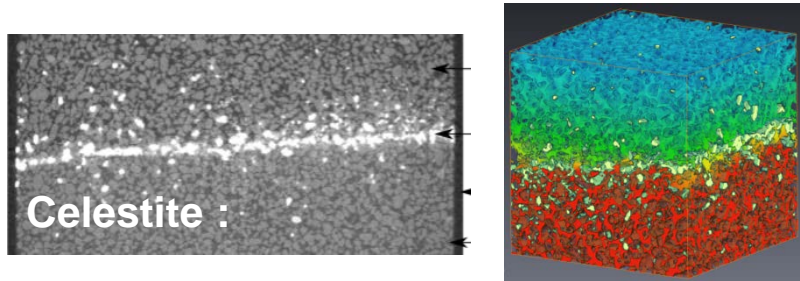


- Temperature $\sim 200^\circ\text{C}$ for potential illite formation in reasonable time frame
- AND/OR „Simulation“ by physical mixing with illite? => as done with other materials in LOT
- In situ diffusion tests (D_a) via pore water labeling (AMS see: Quinto et al. (2015) *Anal Chem.* 87(11):5766-73.)

Precipitation/dissolution reactions

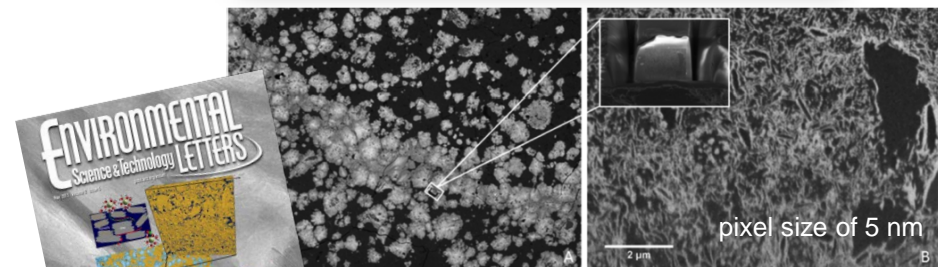
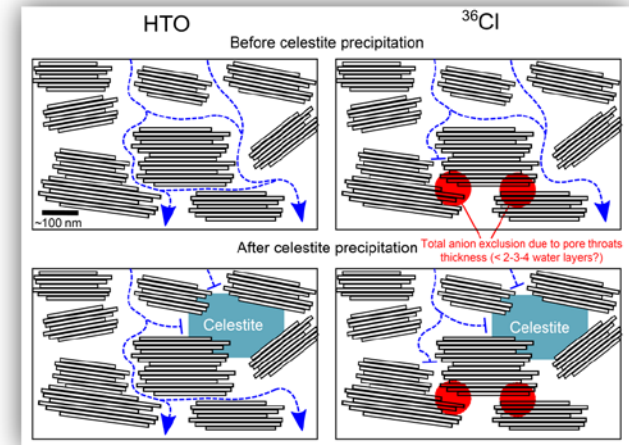
Effect of sulphate precipitation front on transport parameters

Chagneau et al. (2015) *Geochem Trans.* 16, (13), 015-0027.



Microstructure matters concerning anion mobility in compacted clays (example illite)

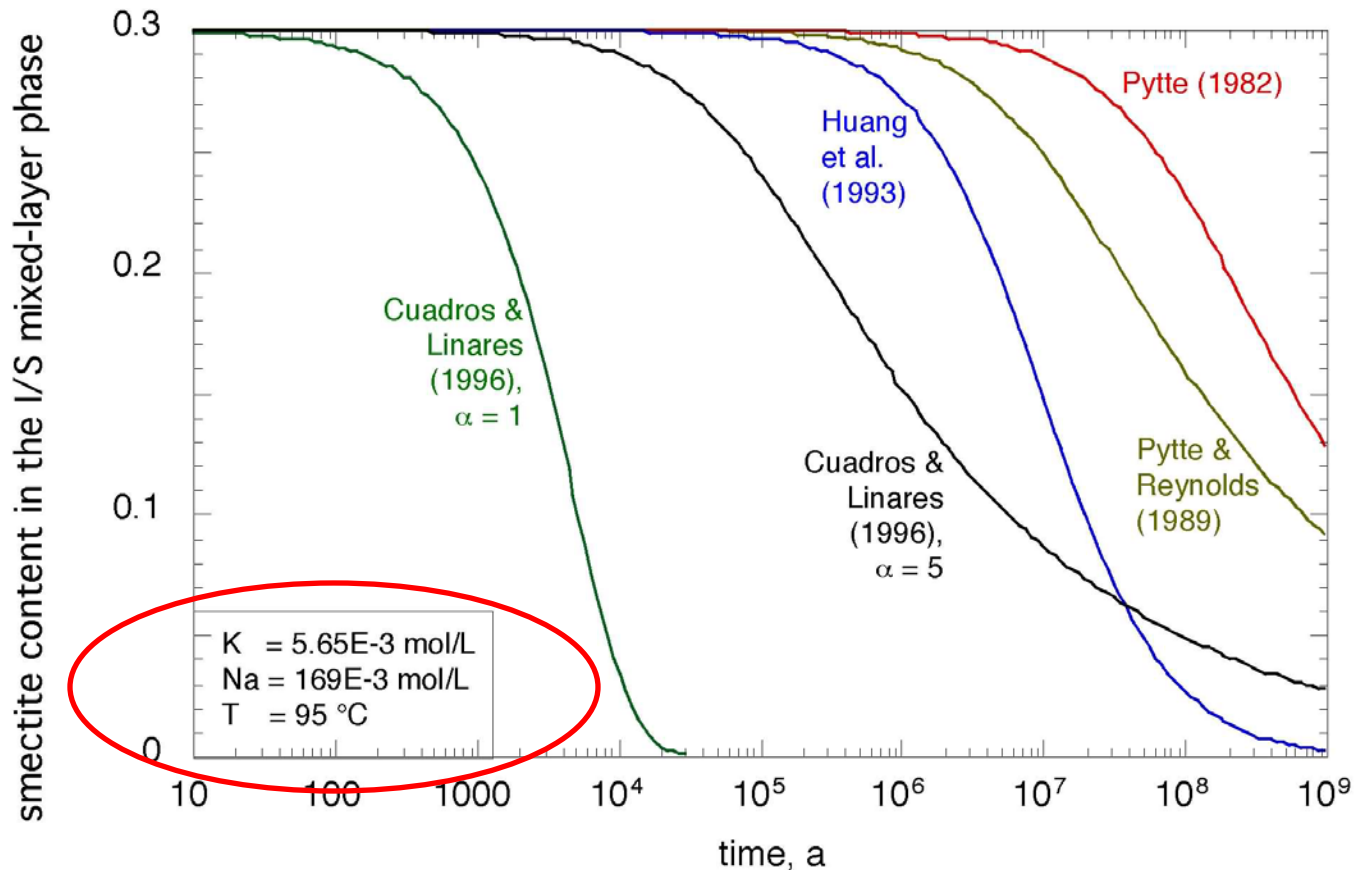
Chagneau et al. (2015) *ES&T Letters* 2(5):139-43.



FIB-nt showing the precipitation of celestite (white) in the illite inter-aggregate porosity.

Rate laws of the smectite -> illite reaction

- Wide spread of rate laws in the literature (at least 8 orders of magnitude!)
- Laboratory data often yield higher reaction rates than data derived from natural observations => REASONING?



Heat conductivity λ (saturation)

■ Heat pulse tests

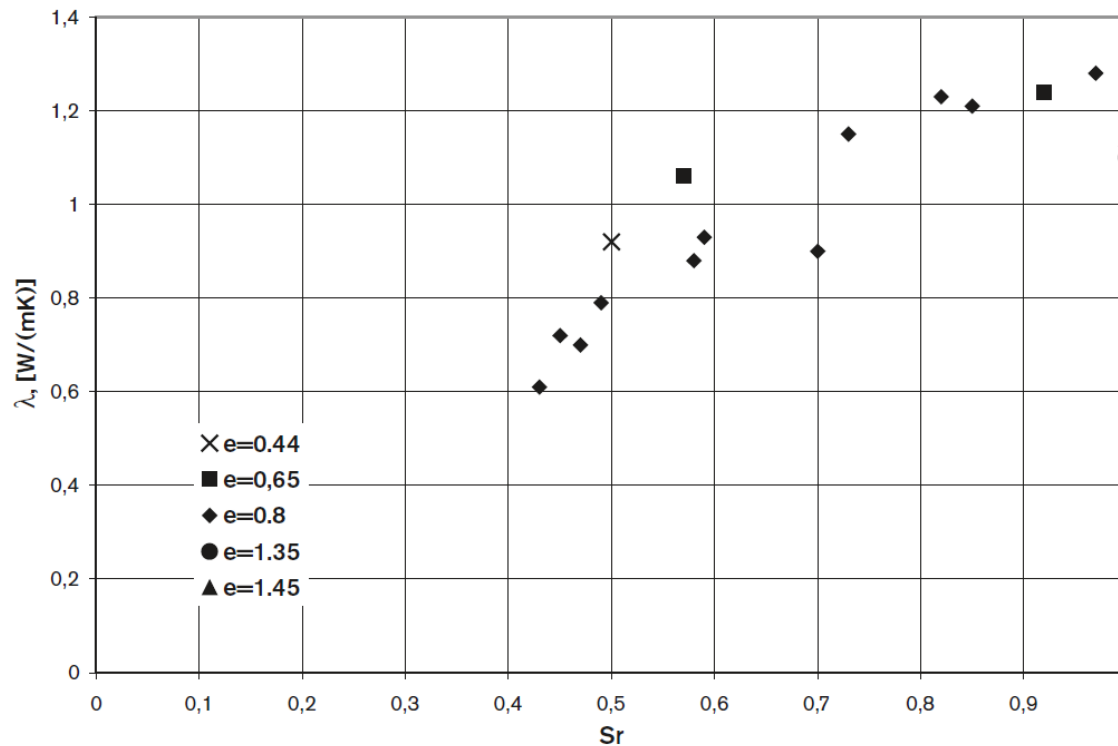


Figure 3-1. Heat conductivity of laboratory-scale bentonite samples as function of saturation for a few values of the void ratio, e /Börgesson et al. 1994/.

Temperature effect on bentonite: boiling

- In the ABM-II experiment (granite-bentonite-iron interaction at 130°C) indications are given that boiling has occurred leading to a loss of barrier integrity (SVENSSON, 2015).
- Based on the risk of boiling in Sweden the standard temperature of 90°C is preferred and in the British reference disposal concept boiling is taken as a criterion of temperature limit (HICKS et al., 2009).

Natural samples with different smectite content

Table 2d. Relative proportions of the different phases contributing to the diffracted intensity in the sampled Callovo-Oxfordian series (EST 104 borehole) as determined from XRD profile fitting using the multi-specimen technique (Sakharov *et al.*, 1999).

Sample	State	I-Exp MLM (%)	Smectite (%)	Illite (%)	Kaolinite (%)	Chlorite (%)	R_{wp} (%)
447	Ca-EG	54	24	21	0	1	8.8
	Ca-AD	55	20	25	0	1	11.5
482	Ca-EG	54	20	25	0	1	7.7
	Ca-AD	53	18	28	0	1	9.7
489	Ca-EG	67	10	21	0	2	10.5
	Ca-AD	62	10	27	0	1	11.0
492	Ca-EG	66	4	24	5	1	10.1
	Ca-AD	61	4	29	5	1	10.6
494	Ca-EG	68	1	27	3	1	8.0
	Ca-AD	66	3	27	3	1	10.8
528	Ca-EG	68*	0	21	10	1	12.2
	Ca-AD	68*	0	21	10	1	13.2

Note: Relative proportions are given as weight %. * For sample 528 the contributions of both MLM1 and MLM2 (Table 2c) are summed to determine the relative contribution of the I-Exp MLM phase. R_{wp} is the usual parameter to assess the quality of fit.

Claret et al. (2004) *Clay Clay Miner.* 52(5), 515-32.

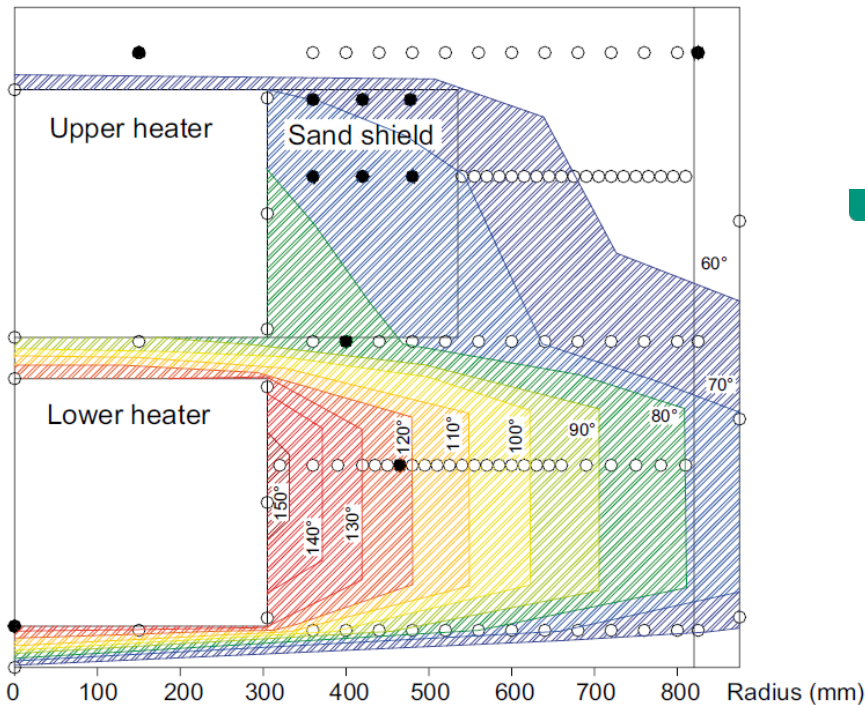
TBT (Temperature Buffer Test)

The hydro-mechanical characterizations of the bentonite resulted in the following observations: i) compared to the reference material no large deviation was seen in the retention curves for the Na converted fine fraction of the material from the innermost positions, and for the bulk material from the same positions a marked deviation was observed for equilibrium with $RH = 97\%$; ii) a reduction in swelling pressure was observed on re-saturated samples from the field experiment, especially on those from the innermost part. Measured hydraulic conductivity values were generally scattered, but displayed a tendency with increased values on re-saturated specimens drilled from the innermost part, and a similar tendency was also observed on ground and re-compacted specimens and specimens prepared from dried material; iii) the triaxial test performed on the one specimen from the inner part demonstrated a brittle behaviour involving high stiffness, high shear strength, and low strain at failure; and iv) the unconfined compression tests demonstrated a reduced strain at failure on all specimens from the field material, and also a reduced maximum deviator stress on the re-saturated specimens from the innermost position.

The chemical/mineralogical characterization indicated that: i) sulfate was redistributed under the thermal and hydration gradients that were prevalent during the test. Anhydrite accumulated at some distance from the heater, whereas gypsum was dissolved in the peripheral parts of the buffer where water was supplied; ii) cristobalite was dissolved at the bentonite/heater contact; iii) calcite was dissolved in the warmest parts of the block; iv) exchangeable sodium was replaced by calcium in the warmest parts, probably as an effect of calcite dissolution, which must have affected the porewater composition; v) at the heater, the iron content of the bentonite had increased due to corrosion of the steel. The excess iron was readily extractable into a citrate-bicarbonate-dithionite solution, which suggests that iron was not incorporated into the smectite structure but existed mainly as free oxides/oxyhydroxides (after oxidation); vi) the distribution of non-exchangeable magnesium displayed a clear gradient with a distinct maximum at the heater, suggesting a transfer of magnesium along the thermal gradient; vii) the Mössbauer spectroscopy with a three component fit and the measurements with lower Doppler-velocity indicated that the amount of Fe^{2+} had increased slightly, but the five component fit didn't support this observation. Hence, the increase in the amount of iron observed with chemical analyses was probably too small to be detected reliably with Mössbauer spectroscopy.

TBT (Temperature Buffer Test) from SKB P12-06

August 16, 2009



Duration 2003-2009/10

- Äspö HRL, high thermal gradients and with maximum buffer temperatures up to 155°C.
- After ÅKESSON et al. (2012) the following observations:
 - No significant changes in the water retention curves of bentonite
 - Small decrease in swelling pressure
 - No tendency of hydraulic conductivity increase, nor the stiffness and the shear strength of bentonite.
 - The failure strain decreased.