Combining chemistry and physics

Effect of temperature on geochemical reactions in the vicinity of heat producing radioactive waste repository

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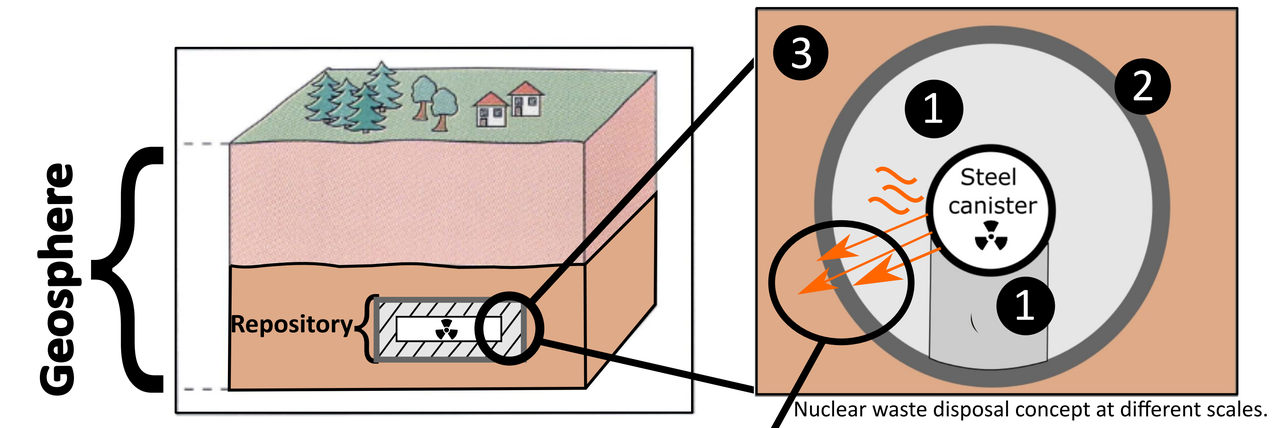
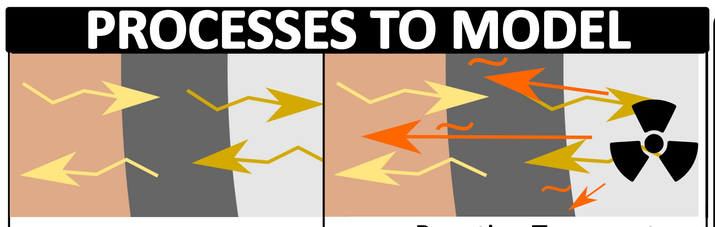
Background

Nuclear Waste Disposal Concept



Nuclear waste disposal concept at different scales. source: Fries et al. (2008) (modified).

PROCESSES TO MODEL



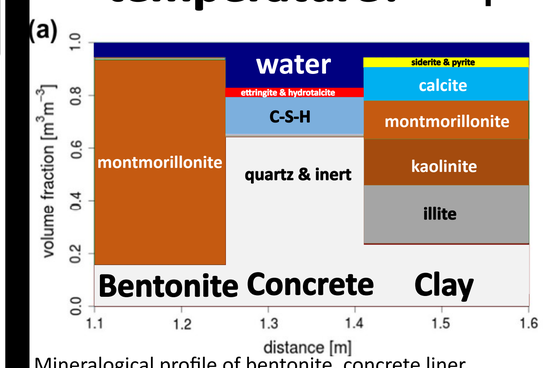
1) Reactive Transport

2) Reactive Transport + Influence of Temperature

AIMS

1) Reproducing Marty et al. (2015) & Berner et al. (2013) thermodynamic setup of reactive transport across interface.
2) Addition of elevated temperature (heat pulse emerging from steel canister).

Influence of temperature? +

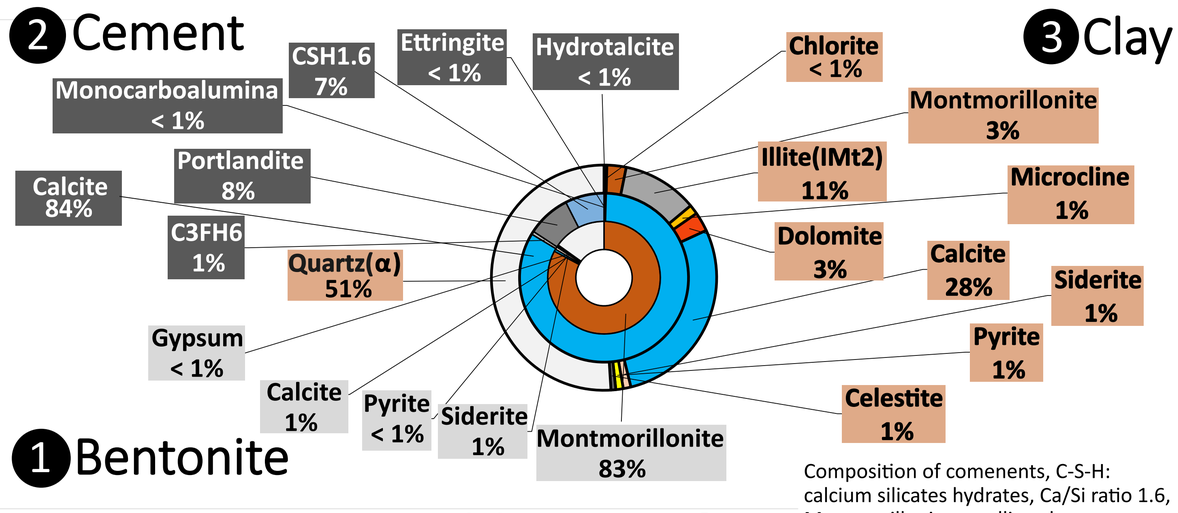


Mineralogical profile of bentonite, concrete liner, and Opalinus clay. source: Marty et al. (2015) (modified).

Materials

2 Cement

3 Clay



1 Bentonite

Composition of comenents, C-S-H: calcium silicates hydrates, Ca/Si ratio 1.6, Montmorillonite: swelling clay.

Pore water composition at 25 °C

[mol/L]	Bentonite	Direction due to chemical gradient	Cement	Direction due to chemical gradient	Clay
Al	6.64E-08	←	2.91E-05	→	8.87E-08
C	6.15E-03	→	2.60E-05	←	4.61E-03
Ca	1.35E-02	→	3.21E-03	←	8.02E-03
Cl	5.61E-02	→	1.41E-06	←	4.30E-02
K	2.16E-08	←	9.90E-02	→	4.90E-04
Mg	7.46E-03	→	2.07E-09	←	5.49E-03
Na	2.34E-01	→	4.24E-02	→	3.92E-02
S	1.07E-01	→	5.55E-04	←	1.02E-02
Si	1.75E-04	→	1.75E-07	←	1.77E-04
OH^-	1.55E-07	←	1.42E-01	→	1.23E-07
pH	7.06		13.04		6.999

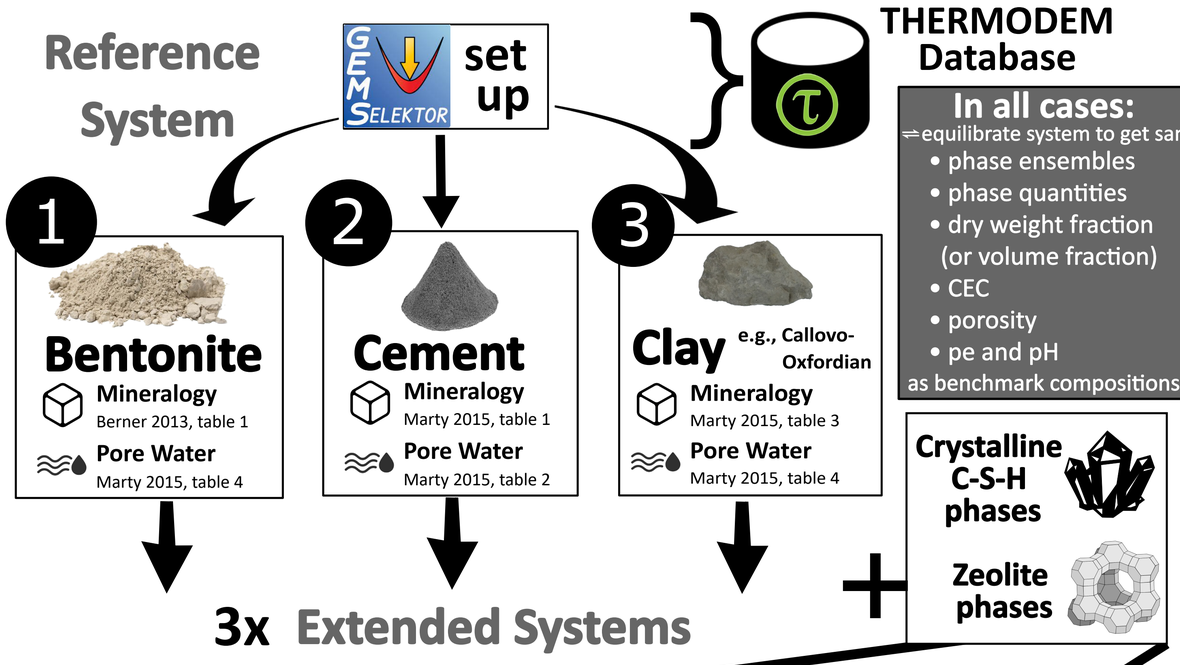
Table: Concentration of materials with chemical gradients after GEMS equilibration, e.g., OH^- gradient serves as pH proxy. Movement from high concentration to lower (chemical gradient).

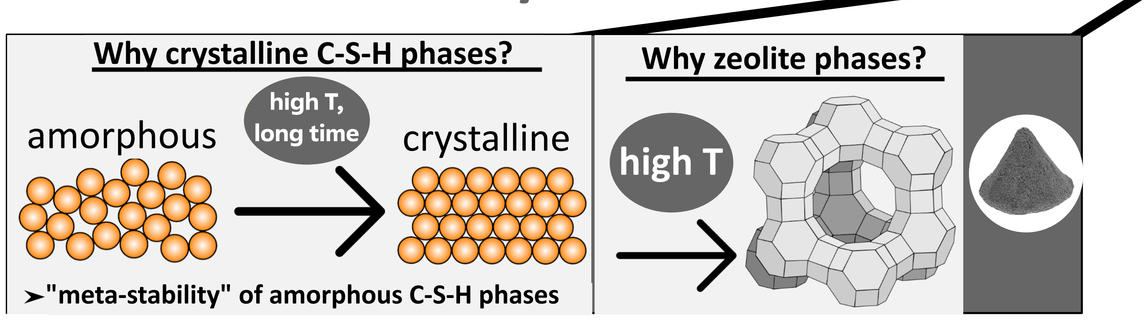
Methods

WHY? **Long-term safety:** predict and quantify the geochemical evolution of the depository components in the future. To replicate benchmark reactive transport model to add temperature effect, **first system set up is required.**

Step 1

GEMS: Gibbs Energy Minimization Software for Geochemical Modeling
➤ Calculation of phase (solid/minerals, gas, liquid) equilibria.



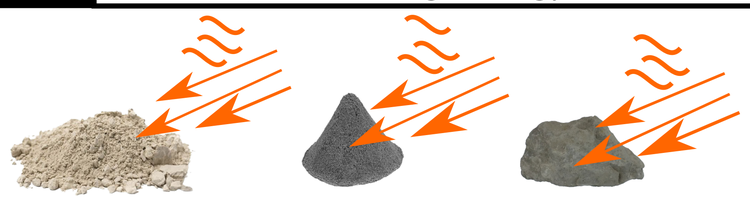


Visual representation of GEMS set up process.

Zeolites and crystalline C-S-H phases are expected in cement compartment, thermodynamic consistency of all phases need to be tested for the reactive transport simulations. Added based on report NAB 18-41.

Step 2

Modeling influence of temperature on each material closed system, i.e., can exchange energy with surroundings but no matter.

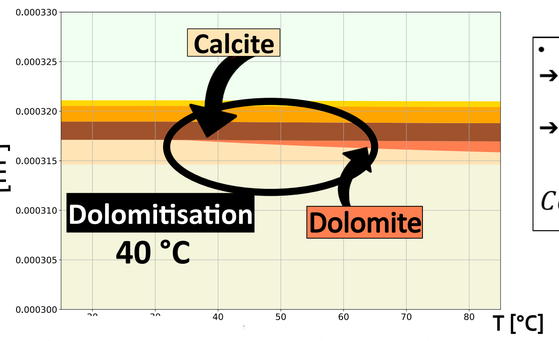


Reference & Extended

- Mineralogical changes and whether they correspond to observations made in nature, e.g., real-life laboratory experiments.
- Temperature source in real-life in our case is nuclear waste canister of repository.

Results & Discussion (STEP 2)

1 Bentonite

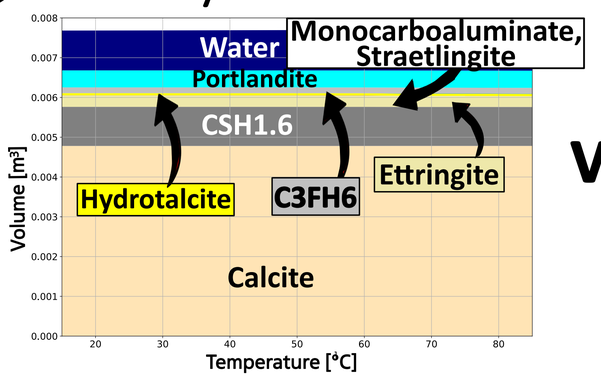


- **Dolomitisation:**
  → Mg^{2+} ions (from pore water and on the exchanger) replace calcium ions
  → increase in Ca^{2+} ions in solution

$$2CaCO_{3(Calcite)} + Mg^{2+} \leftrightarrow CaMg(CO_3)_{2(Dolomite)} + Ca^{2+}$$

Temperature-dependent evolution of mineralogical composition of bentonite (zoomed in).

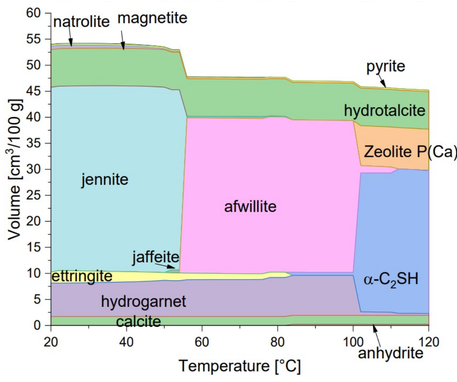
2 Ordinary Portland Cement



Temperature-dependent evolution of mineralogical composition of OPC.

VS.

Blended Cement

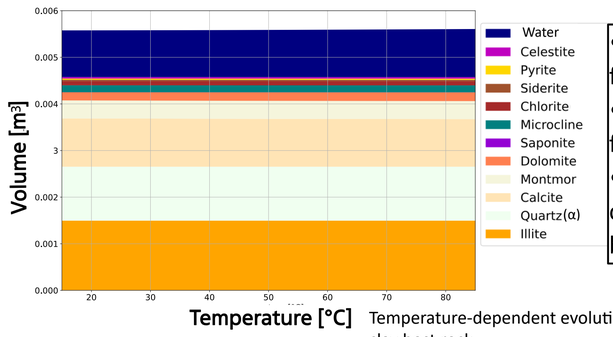


OPC with SiO_2, crystalline C-S-H phases. source: NAB 18-41.

Comparison: NAB 18-41 set up got other mineral phases
(A) → they did not use Ordinary Portland Cement (OPC) but blended cement: OPC + SiO_2.

Consequence: set up a blended cement with their same cement paste (3.1 kg, of which 3 kg SiO_2) to H_2O (2 kg) ratio
(B) → adding SiO_2 dissolves portlandite, cryst. C-S-H phases appear.

3 Clay (Callovo-Oxfordian)



Temperature-dependent evolution of mineralogical composition of clay host rock.

Summary of Results

- **Extended systems look the same as reference,** apart from cement,where C3FH6 completely replaces CSH1.6.
- The temperature-dependent plots display the phase formations that would be expected, e.g., dolomitisation.
- The set up of a blended cement has also been completed, generally showing the phase formations to be expected according to NAB 18-41 report.

Outlook

Step 3 & 4

References:

- Berner, U., Kulik, D. A. and Kosakowski, G. (2013) Geochemical impact of a low-pH cement liner on the near field of a repository for spent fuel and high-level radioactive waste. Physics and Chemistry of the Earth, 64, pp. 46–56. doi: 10.1016/j.pce.2013.03.007.
- Cloet, V., Curti, E., Kosakowski, G., Lura, P., Lothenbach, B., Wieland, E., (2018) Cementitious backfill for a high-level waste repository: impact of repository induced effects. Nagra Arbeitsbericht NAB 18-41, Nagra, Wettingen, Switzerland.
- Fries, T. et al. (2008) THE SWISS CONCEPT FOR THE DISPOSAL OF SPENT FUEL AND VITRIFIED HLW.
- Marty, N. C. M. et al. (2015) Benchmarks for multicomponent reactive transport across a cement/clay interface. Computational Geosciences, 19(3), pp. 635–653. doi: 10.1007/s10596-014-9463-6.