# Clay interactions at high temperature by molecular dynamics, thermodynamic modelling and laboratory experiments and analysis

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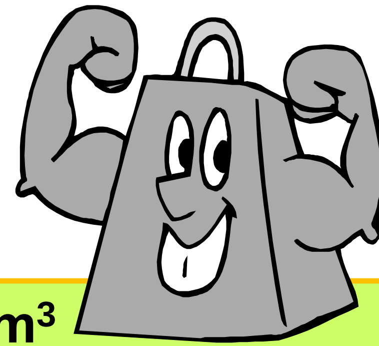
- Temperature compared to other conditions and processes
- KBS-3 method and temperature limitations therein
- Earlier studies at elevated temperatures
- New research ideas

# Temperature compared to other conditions and processes

# Thermodynamics of bentonite in KBS3 method

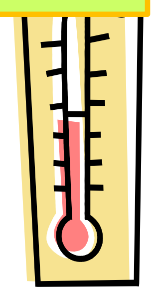
**Thermodynamic variables**

- Temperature, *T*
- Pressure, *P*
- Chemical composition
  - Saturation, *S*
  - Density, *ρ*
  - Ionic strength, *I*



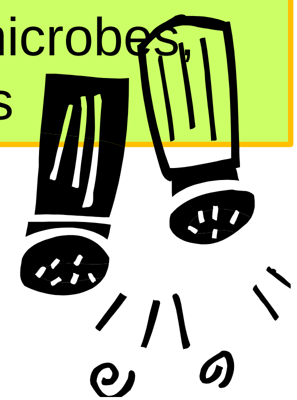
**ρ: 1…1 700 kg/$m^3$**
Montmorillonite, exchangeable cations, accessory minerals

***S*: 0.3…1**
Dry to totally wetted



***T*: -10…100 ºC**

***P*: 0.1…4 MPa +**
ice cover



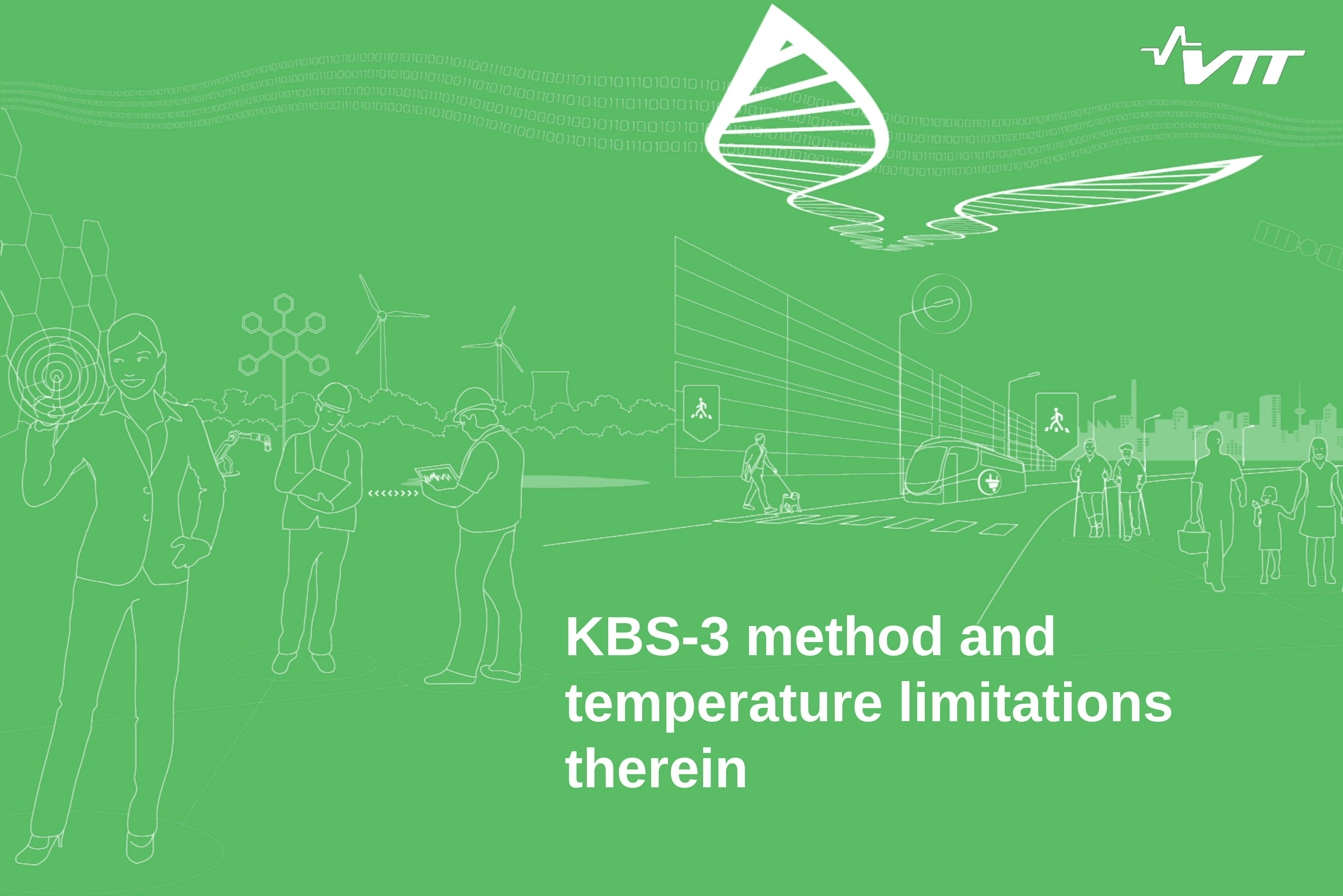
***I*: 0.01 mM…1 M**
1 mg/L…100 g/L Na-Ca-Cl + other ions, microbes, colloids

# Thermodynamics

- Temperature, pressure (stress) and chemical composition define the (equilibrium) state of any system
- Thermal-Hydraulic-Mechanic-Chemical or THMC approach is well known also for clays
- Chemical composition and reactions are known to control diffusion, adsorption and swelling of bentonite
- Temperature affects mainly chemical kinetics and equilibrium
  - Mechanical properties?

# The effect of temperature change on molecular level phenomena

- Electronic movement accelerates
- New chemical bonds form, and old chemical bonds are broken
- New chemical species form (the activation energy barriers of reactions can be exceeded more easily because of rising temperature)
  - What species? Stable or highly reactive?
  - Are the chemical and physical properties of new species same as those of species at the lower temperatures?
  - How much reaction kinetics accelerates?

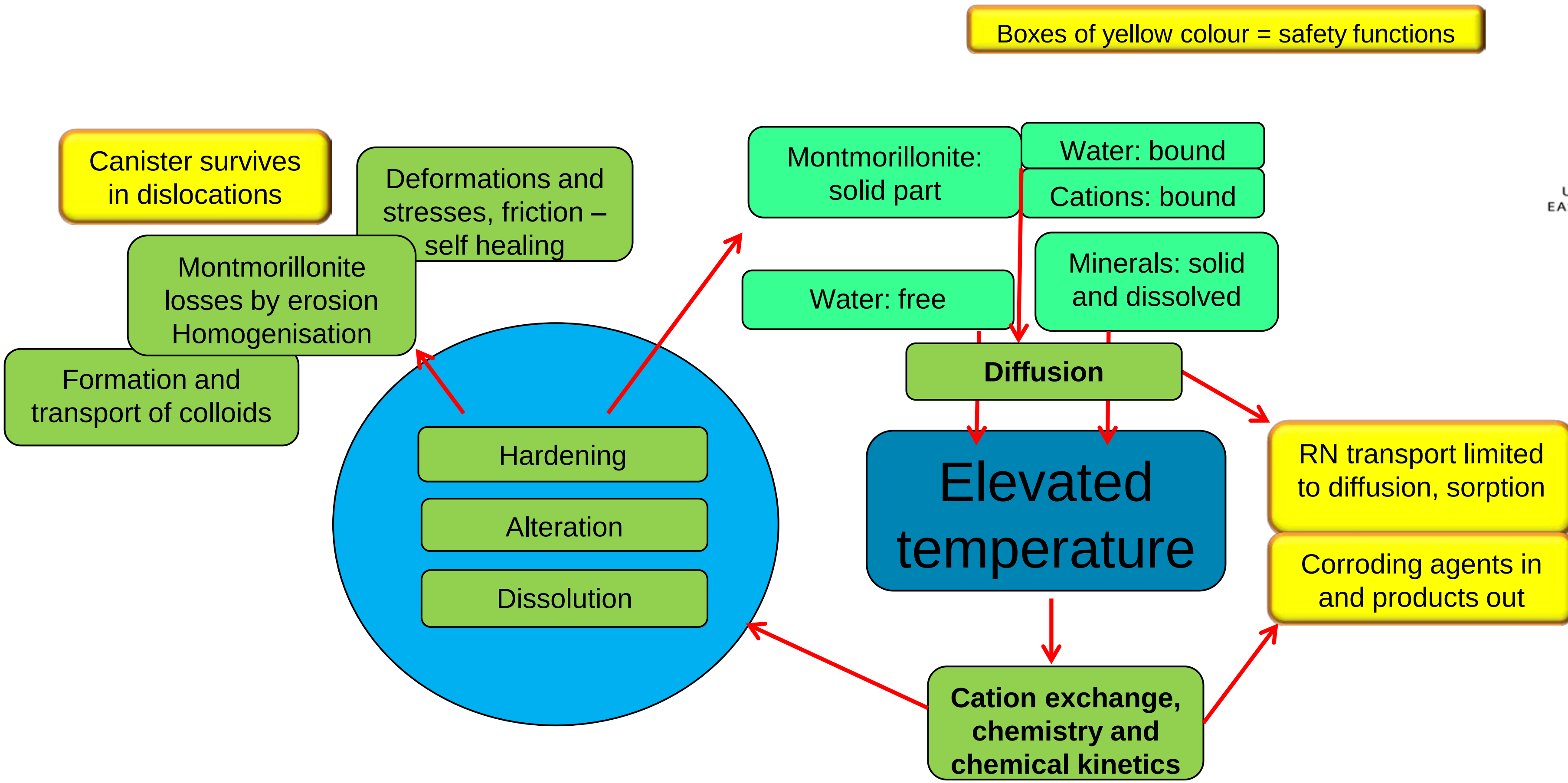


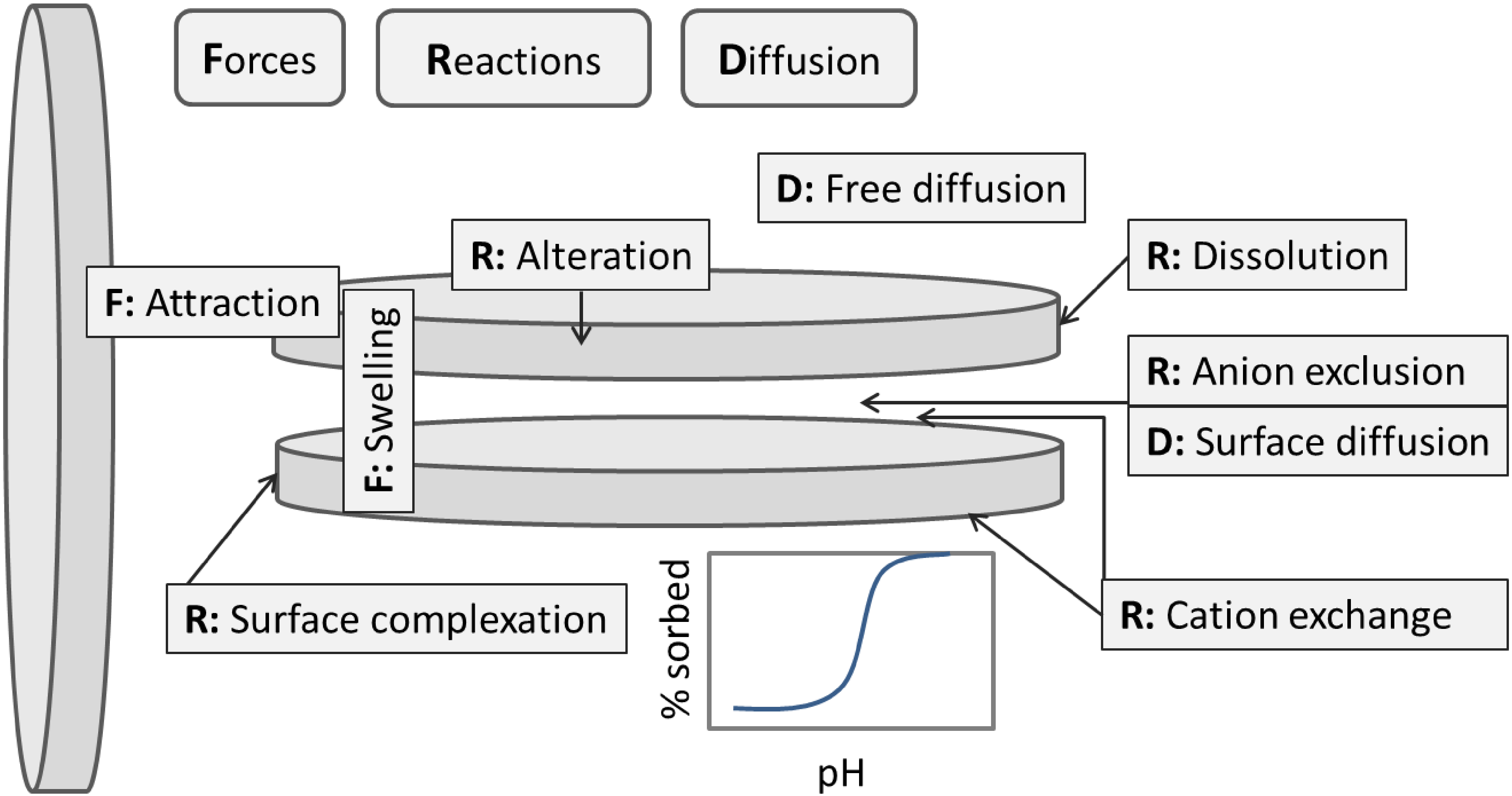
# KBS-3 method and temperature limitations therein

# KBS-3 method

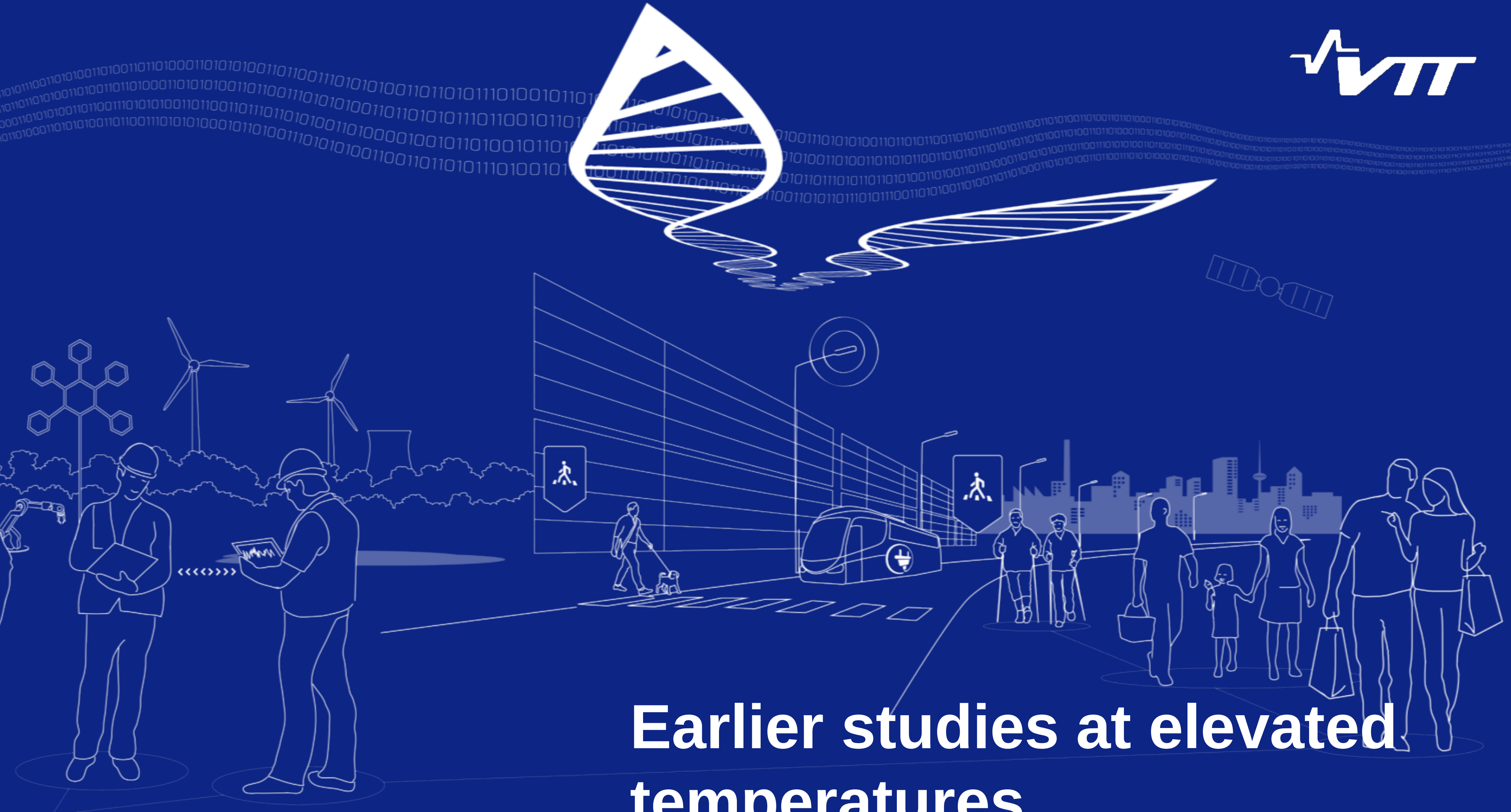
- Bentonite is applied as
  - buffering material around copper canister (min 35 cm)
  - backfilling in deposition holes
- Temperature is limited below 100 $^{o}$C, but planned to be clearly lower (80 – 85)
  - Mineral alteration slower
- Temperature limitation define the minimum distance between deposition holes and length of deposition tunnels
  - Temperature defines the packing density and much of the cost of construction and backfilling

# **Temperature** related to processes and structure





Forces
Reactions
Diffusion
D: Free diffusion
R: Alteration
R: Dissolution
F: Attraction
F: Swelling
R: Anion exclusion
D: Surface diffusion
R: Surface complexation
% sorbed
pH
R: Cation exchange



# Earlier studies at elevated temperatures

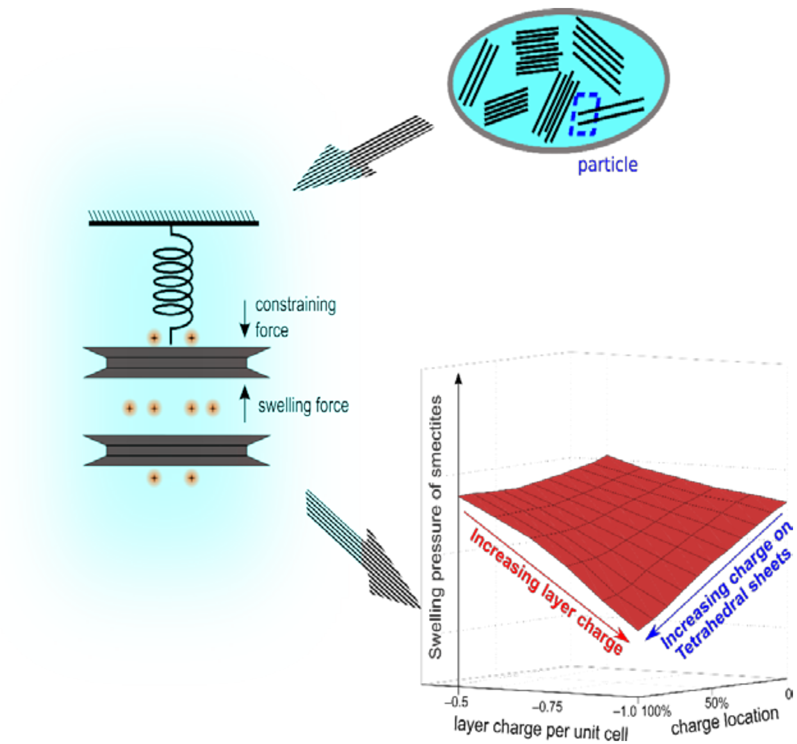
# Experimenting chemistry and diffusion below or at 80 $^{o}C$ (VTT)

- Earlier lab studies in 90s very often carried out maximum temperature of 80 $^{o}C$
- Observations:
  - Nothing really worrying appeared
  - Difficult to maintain high temperature in lab conditions for years (who pays?)

# Some results: LOT project A2 test parcel, 140°C

- Observations (SKB Technical Report TR-09-29):
  - reorganization of easily dissolved accessory minerals in the bentonite, in particular $CaSO_4$
  - increase in cation exchange capacity of the bentonite in parts exposed to high temperature
  - no formation of illite or other typical montmorillonite alteration minerals
  - decrease in strain at failure of bentonite exposed to high temperature
  - diffusive transport of trace elements in accordance with previous studies
  - corrosion rate of metallic copper in agreement with model predictions and previous tests
  - a minor survival of bacteria.
  - An overarching conclusion is that the observed mineralogical alterations, as a consequence of the water saturation process and the exposure to high temperature, are relatively small and that these alterations did not change the physical properties to such an extent that the buffer function is jeopardized.

# Molecular dynamics prediction of swelling pressure in smectites

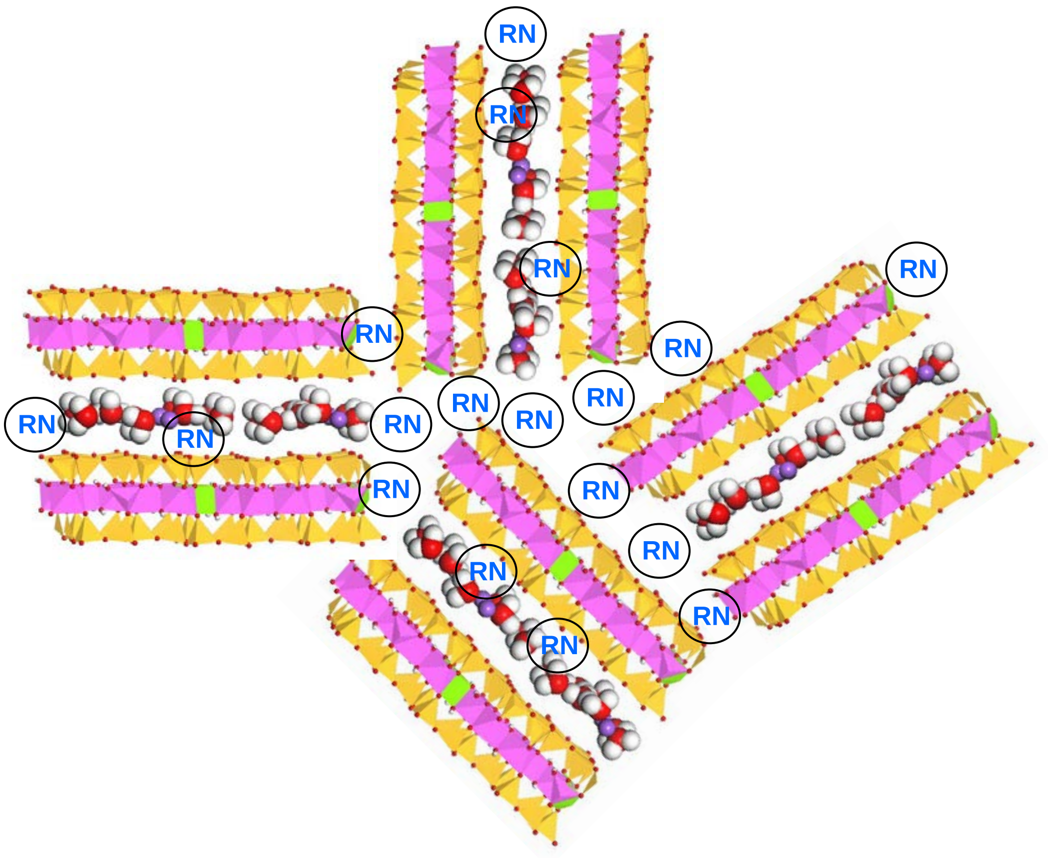



- New MD model has been presented for swelling pressure simulation*
- For swelling pressure the role of layer charge and charge fraction on tetrahedral and octahedral sheet has been presented
- Cation species strongly influence the swelling characteristics as well as them increase salinity of surrounding water
- The simulated swelling pressures are in good agreement with the experimentally reported trends
- Model has been applied as a function of temperature

*Sun, L.; Ling, C. Y.; Lavikainen, L. P.; Hirvi, J. T.; Kasa, S.; Pakkanen, T. A. Influence of Layer Charge and Charge Location on the Swelling Pressure of Dioctahedral Smectites. *Chem Phys* **2016**, *473*, 40–45.

# New research ideas

# Quantum chemical approach




- Temperature increases
  - Water starts to vaporize → pressure increases
  - Movement of radionuclides (RN) increases → Diffusion increases
  - Possibility to cation exchange reactions increase, but perhaps also probability to opposite reactions increase
  - New surface complexation reactions happen, which are not possible at the lower temperatures → New species are formed, the reactivity of which is unknown
    - $RN(H_2O)_x$, $RN(OH)_x$, $RN(CO_3)_x$, $RN(SO_4)_x$, $Rn(NO_3)_x$, $RN(PO_4)_x$

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# Modelling of high temperature systems based on dynamically swelling clay models

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- The new molecular dynamics swelling pressure model will be applied to phenomena at elevated temperatures.
- Swelling pressure will be studied as a function of temperature. Other variables include clay composition, interlayer cations and the surrounding water media.
- The transfer of interlayer ions to the surrounding water phase and vice versa will be of particular interest.
- The simulated physical quantities will be compared with the experimental data when available.
- The ultimate goal is a comprehensive atomic level picture of the clay behaviour at elevated temperatures.

# Experimental study on the effect of temperature on the clay erosion and interaction

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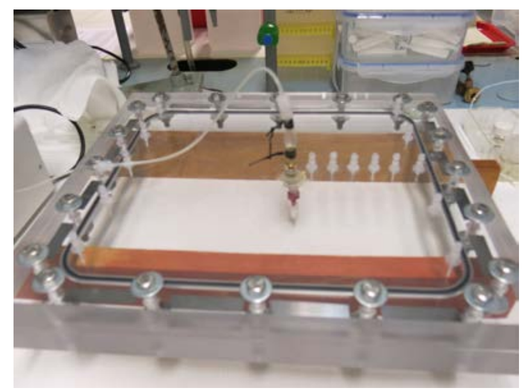
- Static and dynamic erosion experiments in a artificial fracture
- Batch type experiments
- Variation in the parameters (clay composition, density, temperature, salinity, pH)
- Erosion kinetics and mechanisms
- Interaction with the cations in the water phase and interlayers of the clay
- Characterization methods:
  - PCS, Rheology, ICP-MS, ICP-OES, XRD, SAXS, FESEM, FIB, AFM, Digital Beaver autoradiography system
  - Advanced spectroscopy methods (ATR FT-IR, EXAFS, TRLFS)



# Structural experiments at high temperature

- Small angle X-ray scattering (SAXS) or X-ray diffraction (XRD) – monitoring of the basal spacing as a function of temperature
- Nuclear magnetic resonance (NMR) – pulse relaxation techniques can show changes in the behaviour of porewater in connection with the structural changes (the relaxation signal is depending on water mobility and pore sizes)

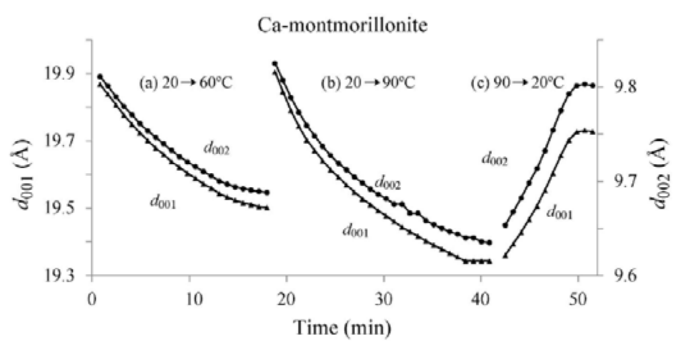



Figure 10. Ca-montmorillonite basal spacing as a function of temperature given as $d_{001}$ (dots) and $d_{002}$ (triangles). Three consecutive series: (a) 20→60°C, (b) 20→90°C, and (c) 90 → 20°C.

Svensson, Per Daniel, and Staffan Hansen. 2013. "Combined Salt and Temperature Impact on Montmorillonite Hydration." *Clays and Clay Minerals* 61 (4). Clay Minerals Soc: 328–41. doi:10.1346/CCMN.2013.0610412
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# Conclusions

- Maximum temperature is an important design requirement
  - Size of the system -> costs
- Earlier studies
  - Many KBS-3 studies has been limited up to 80 $^{o}$C
- New studies and tools
  - Molecular dynamics is new tool to study also temperature
  - It can be combined to microstructural studies (SAXS, NMR)
  - New approaches are also under work in thermodynamic modelling
- Issues
  - Bentonite is hard to study and much work to be done at elevated temperatures


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