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Hydration sequence for swelling clays exchanged with mixed alkali/alkali-earth cations

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Context of the study

• Disposal of radioactive wastes in deep geological repositories and multi-barriers concept

• Role of clays:
  – limiting water fluxes in the repository
  – swelling and filling up technical gaps
  – adsorbing RNs (in the interlayer space and onto surfaces)
Outline plan

• Objectives and experimental approach

• Multi-scale structure of clays

• Thermoporometry results for Montmorillonites samples saturated by alkaline cations: pore size distribution

• Consequences for the hydration sequence in clays as a function of the interlayer cation nature

• Diffusion of the interlayer cation as a function of the hydration state

• Conclusions
Objectives and experimental approach

- Study the “clay-water” system by looking at the modifications of water properties
  → “water in clays” is different from liquid water (or free water)!

- **Thermoporometry** = calorimetric technique sensitive to phase transitions of fluid confined in the porosity  
  → 2 nm < Pore radius < 50 nm (mesoporosity)
  → Hypothesis: Pore size is the major parameter which influences the properties of the confined fluid

- Originality of these experiments: swelling material (homoionic Wyoming montmorillonite saturated by Li$^+$, Na$^+$, K$^+$, Cs$^+$ and Ca$^{2+}$ cations & different RH investigated
  → Common practice : DSC on **saturated** non-swelling samples
    = all pores are filled
  → Saturation of studied porosity is necessary

- Quantify the evolution of the mesopore size as a function of RH
- Discuss these results in terms of the sequence of clay hydration
Pore size distribution (PSD)

- Pore size distribution obtained with Brun equations (parameters result from fit with various materials):
  
  \[ R_p = \frac{A}{\Delta T} + B \]

  ![Graph showing fusion and solidification with peak at 75% HR]

  - 2 peaks = 2 well-defined families of pore size
Multi-scale structure of clays

- Multi-scale aspect
- Focus on mesoporosity
Results for RH ≤ 54%

- Na-mont (purified and exchanged MX80 Wyoming) → powder

- RH < 54% → no interpretable signal (pores not filled with water? not enough water?)

- Results for RH = 54%:
  - Thermoporometry not conclusive alone but same results as BJH: pores filled at 54%
  - We verify that the effect of Rp is dominant
Results for RH > 54%

- Results for RH ranging from 75% to saturation

HR = 75%
- No free water

HR = 90%
- FREE WATER

HR sat
- Osmotic swelling

- No free water at RH < 90%
Interpretation(1): evidence for osmotic swelling in mesopores

- Pore size in mesopores (for the 2 families)

- Osmotic swelling in the mesopores occurs starting at RH ~ 54%
Evolution of interlamellar space

- Comparison with interlayer space (d001) measurements with XRD (Ferrage, 2005)

Interpretation (2)

- Osmotic swelling in interlayer space occurs at RH > 80% compared to RH ~ 54% in mesopores

Crystalline swelling (2 layers of water)

Salles et al., Appl. Clay Sci., 2008
Interpretation (3): hydration sequence

... towards a step-by-step model for the hydration

**Thermoporometry** + XRD

- RH < 10%
- RH < 20%
- RH > 80%
- RH > 60%
- 20 < RH < 80%

**Adsorption isotherms**
Interpretation (4): hydration sequence

- RH~0%
- RH<10%
- RH<20%

Water adsorption isotherms

Thermoporometry + XRD

Salles et al., Langmuir, 2010
Coherence with the driving forces of hydration

For Li and Na-samples: Cation Hydration is the driving force
For K, Rb and Cs-samples: Surface Hydration is the driving force
Changes of leading driving forces in agreement with the experimental behavior varying with the interlayer cation

Towards the distinction between interlayer or mesopore water

- From experimental data: it is possible to estimate
  - $m_{\text{water in clay}} \rightarrow$ from water adsorption isotherm
  - $m_{\text{water in mesopore}} \rightarrow$ from thermoporometry data

- It follows:

$$m_{\text{interlayer water}} = m_{\text{water in clay}} - m_{\text{water in mesopore}}$$

- The theoretical quantity of water (=maximal amount) present in interlayer space can be determined from the following equation:

$$m_{\text{theoretical interlayer water}} = d_{001} \times (S_{\text{H}_2\text{O}} - S_{\text{N}_2})$$

where $S_{\text{H}_2\text{O}}$ and $S_{\text{N}_2}$ are the specific surface area as a function of RH* and $d_{001}$ is related to the interlayer space opening

* Salles et al., J. Colloid Interf. Sci., 2009
Distinction of interlayer and mesopore water

The interlayer spaces are never completely filled in montmorillonites, except for Cs-sample

Salles et al., Langmuir, 2010
Diffusion of Cations in swelling clays

For Li and Na-samples: Cation diffusion reaches values for bulk water
For K, Rb and Cs-samples: Slow diffusion
Diffusion behavior is varying with the interlayer cation \(\rightarrow\) osmotic swelling

Case of Montmorillonites with mixture Na/Ca

- For Na/Ca-samples: Na$^+$ diffusion reaches values lower than bulk water
- Influence of Ca$^{2+}$ and repartition of cations?
Conclusions

• Summary:
  – Osmotic swelling in mesopores evidenced by original use of thermoporometry
  – Free water is observed in mesopores only starting at RH > 90%
  – Osmotic swelling occurs in mesopores before crystalline swelling is finished in the interlayer space (2nd layer of water)
  – Sequence of hydration is depending on the interlayer cation nature
  – Interlayer space water > mesopore water for all cations
  – Interlayer space is never completely filled by water at RH<97% for all samples except Cs⁺-montmorillonite
  – Impact of Na⁺ in the Na/Ca-sample
Thank you for your attention!
Thermoporometry equations

• Theoretical equation

\[
\frac{1}{(R_p - t)} = - \frac{1}{2\gamma_{sl}} \int_{T_o}^{T} \Delta S_f \frac{dT}{\nu}
\]

• Simplified equation (Brun et al. 1977)

\[
R_p = A + \frac{B}{\Delta T}
\]
Material and method

• Na-mont (purified and exchanged MX80 Wyoming) → powder

• Thermoporometry:
  – fusion-solidification-fusion cycles (2°C/min for a range of temperatures between -80°C and 0°C)
  – RH conditions: 11%, 33%, 54%, 75%, 90% (for each RH sample: equilibration for 1 month with saline solutions), saturated material (97% < RH < 99%)
  – Study of hysteresis between adsorption-desorption
  – Hydration with liquid water or with water vapour for saturated samples

• Experiments: samples mass ≈ 10mg
Influence of hydration method

- Liquid water vs. vapour hydration process

2 fusion cycles are identical
2 solidification cycles slightly different = no significant modification of pore structure
No influence between the two modes of hydration
PSD: hysteresis between adsorption and desorption

- No notable differences for the first peak < 0.05 nm (experimental error)
- Difference for the second peak: hysteresis (observed also in water adsorption isotherms)