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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 $\Rightarrow 2 \text{ nm} < \text{Pore radius} < 50 \text{ nm}$ (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 $\text{Li}^+$, $\text{Na}^+$, $\text{K}^+$, $\text{Cs}^+$ and $\text{Ca}^{2+}$ cations & different RH investigated
  - Common practice: DSC on saturated non-swelling samples $\Rightarrow$ 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):

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

HR = 75%

- 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

➢ No free water at RH < 90%

Osmotic swelling
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%
Interpretation (2)

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

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

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

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

\[ \text{Thermoporometry} + \text{XRD} \]

- RH > 80\% + XRD
- 20 < RH < 80\%
- RH > 60\%

**Adsorption isotherms**

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

**XRD**

- \( \text{Li} \)
- \( \text{Na} \)

RH ~ 0\% → RH < 10\% → RH < 20\%
Interpretation (4): hydration sequence

Water adsorption isotherms

RH~0%

RH<10%

RH<20%

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

Thermoporometry + XRD

RH>90%

20<RH<60%

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:

$$m_{\text{theoretical interlayer water}} = d_{001} * (S_{H2O} - S_{N2})$$

where $S_{H2O}$ and $S_{N2}$ 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
The interlayer spaces are never completely filled in montmorillonites, except for Cs-sample.

*Maximal water amount in interlayer space*
- Water present in interlayer space
- Water present in mesopore space

Salles et al., Langmuir, 2010
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 → 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

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

• Simplified equation (Brun et al. 1977)

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

• Na-mont (purified and exchanged MX80 Wyoming) \(\rightarrow\) 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 \(\approx\) 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)