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

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Swelling clays can absorb/adsorb a great quantity of water inside the interlayer space and the mesoporosity. This adsorbed quantity of water is strongly dependent on the nature of the interlayer cation. In order to probe the hydration sequence in clays as a function of the relative humidity (RH), XRD measurements, water adsorption and calorimetry, thermoporometry and electrical conductivity results are coupled with electrostatic calculations.

**Aim of this study:**
(i) determination of the hydration sequence of swelling clays as a function of the nature of the interlayer cations
(ii) To elucidate the mobility process of the interlayer cations as a function of the hydration state

**Material and Method**

**Experiments**

- Study the “clay-water” system by looking at the modifications of water properties
  - “water inside clays” is different from liquid water (or free water!)
- Thermoporometry + calorimetric technique sensitive to phase transitions of fluid confined in the porosity
  - towards a step-by-step model for the hydration
- Originality of these experiments: investigation of swelling material & various RH

**Introduction and Principle**

- Study the “clay-water” system by looking at the modifications of water properties
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**Results and Interpretation**

- Quantify the evolution of the mesopore size as a function of RH
- Discuss these results in terms of the sequence of clay hydration
- Comprehensive determination of clay hydration sequence for Na-Ca montmorillonite

**Hydration Sequence**

- RH<10%
- RH~0%
- RH<20%
- RH<40%
- RH<60%
- RH<75%
- RH<80%
- RH<90%
- RH>90%

**Diffusion coefficients at 20°C**

- Comparison between evolution of $d_{001}$ from X-ray diffraction (see Ferrage et al., 2005) and evolution of the diffusion coefficients

**Evolution of the mobility is impacted by both the interlayer space opening and the hydration status of the extra-framework cation**

**Conclusion**

- Sequence of hydration is depending on the interlayer cation nature.
- High mobility/diffusion of the smaller cations confirms the weak interactions existing between the hydrated Li$^+$ and Na$^+$ compared to the others cations.
- In the case of the mixture Na/Ca cations, Ca$^{2+}$ is hydrated at lower RH than the Na$^+$ cation as confirmed by adsorption calorimetry

**Diffusion Coefficient (m²/s)**

\[ D = \frac{\sigma k T}{(z^2 e^2 c)} \]

- $D$ is the diffusion coefficient
- $\sigma$ is the conductivity
- $k$ the Boltzmann constant & $T$ the temperature
- $z$ the charge of the species & $e$ the electrical charge
- $c$ the concentration of the species

The concentration of cations is estimated from the specific surface areas calculated from water adsorption isotherm.