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

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To cite this version:
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 electostatic 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

Purified and exchanged powders of montmorillonites (Mont) from the MX80 bentonite (octahedral substitutions - saturated with a large majority of Na as interlayer cations)


Conductivity is measured in the frequency range (10^4 Hz – 10^8 Hz) at different temperatures (200°C-50°C for dry state and -120°C-20°C for hydrated state) with a Novocontrol impedancemeter

• 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 → 2 nm < Pore radius < 50 nm (mesoporosity)

→ Originality of these experiments: investigation of swelling material & various RH

Introduction and Principle

Material and Method

Experiments

Results and Interpretation

Hydration Sequence

• 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

Osmotic swelling in mesopores

Free water is observed in mesopores only starting at RH > 90% in Li- and Na-montmorillonites

Sequence of hydration is depending on the interlayer cation nature

Interlayer space is never completely filled by water at RH<97% for all samples except Cs+ montmorillonite

Diffusion coefficients at 20°C

D = σkT/(z²e²c)

D is the diffusion coefficient
σ 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

Comparison between evolution of \( \Delta u_r \), 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⁺⁺ is hydrated at lower RH than the Na⁺ cation as confirmed by adsorption calorimetry