X-RAY STUDIES ON NANO- AND MICROSCALE ORIENTATION IN COMPACTED BENTONITE AND CALCIUM MONTMORILLONITE

Jussi-Petteri Suuronen

Department of Physics, University of Helsinki
Bentonite clay

- Montmorillonite + accessory minerals (e.g. quartz, feldspar)
- Lamellar clay composed of aluminosilicate disks and exchangeable interlayer cations
- Water is absorbed in hydration shells around cations
- Various applications due to good water retention and swelling properties
Microstructural anisotropy of bentonite

- Tactoids have a high aspect ratio (width in the µm range, thickness in nm range)
- Preferred orientation of tactoids can result from uniaxial compaction and purification of montmorillonite

What can we learn with x-rays?

Small-angle scattering (SAXS)
- Scattering angle => lamellar period (12-20 Å)
- Width of reflection => tactoid size
- Azimuthal intensity variation => preferred orientation
- 1-10 nm scale effects

Microtomography (XMT)
- Spatial distribution of accessory minerals and porosities
- Swelling properties
- 1 μm scale effects
Samples and setup

- Uniaxially compacted clay equilibrated with deionized H$_2$O for 4 months
- Dry density 1.5 – 1.6 g/cm$^3$
- Both purified Ca-montmorillonite and MX-80 bentonite studied
- XMT complemented by localized SAXS measurements
- Use XMT image to ‘aim’ SAXS beam at a specific sub-volume of sample
- Humidity control with saturated salt solutions
Wet sample: 100% Relative Humidity (RH)

- No cracks visible in XMT
- SAXS measured from two orientations
- SAXS results show preferred orientation of clay stacks

Width of arrow = width of SAXS beam (200-300 µm)
Sample at ~85% RH for 14 hours, SAXS measurements near a microcrack
Sample at room RH (~30%) for > 48 hours

- Approximately aligned microcracks visible in µCT
- Orientation of tactoids appears to correlate with that of microcracks
Quantification of results (1/2)

1. Segmentation of pore volume within the beam path of SAXS measurement

2. Sum of 2D-autocorrelations of (vertical) slices

3. Comparison with corresponding SAXS pattern
Quantification of results (2/2)

- Decay rate of autocorrelation function vs. azimuthal plot of 001-reflection in SAXS pattern
- Well correlated in calcium montmorillonite, MX-80 not oriented
- Also increasing salinity reduced orientation
SAXS results combined

- Sum of SAXS intensities of all measurements (no background correction => some peaks due to PCR hood)
- Loss of interlamellar water results in smaller d-spacing
- Splitting of 001-peak can also be seen under some conditions => heterogeneous stacking structure
Re-wetting of Ca-montmorillonite sampled parallel or perpendicular to axis of compaction

Initial situation

Video: 1 min to 3 hrs after start of the experiment

Left: perpendicular sampling
Right: parallel sampling
Conclusions

- Multiscale analysis with XMT and SAXS reveals that:
  - Microcrack and tactoid orientation are correlated in purified, uniaxially compacted Ca-montmorillonite
  - The presence of accessory minerals and lack of purification reduces orientation in MX-80

- How does this influence the buffer properties of bentonite?
  - Anisotropy should be considered when using purified montmorillonite as an analogue for bentonite
  - Significant anisotropy observed in drying but not swelling
  - Anisotropic diffusion in the buffer/backfill could be a design consideration in some waste disposal scenarios
Acknowledgements

- Samples prepared by Michal Matusewicz, VTT
- Discussions and analysis of results:
  - Kari Pirkkalainen (now Oxford Instruments)
  - Ritva Serimaa (UH)
  - Markus Olin (VTT)
- Special thanks for help with the experiments:
  - Ville Liljeström (presently Aalto University)
  - Aki Kallonen (UH)
- Financial support: BOA project, NGSMP and Väisälä fund