



CHALMERS
UNIVERSITY OF TECHNOLOGY

Experimental insight into the thermal nanometric response of clays

Downloaded from: <https://research.chalmers.se>, 2026-04-06 00:42 UTC

Citation for the original published paper (version of record):

Casarella, A., Birmipilis, G., Dijkstra, J. (2023). Experimental insight into the thermal nanometric response of clays. Symposium on Energy Geotechnics, 1-3. <http://dx.doi.org/10.59490/seg.2023.647>

N.B. When citing this work, cite the original published paper.

Peer-reviewed Conference Contribution

Experimental insight into the thermal nanometric response of clays

Angela Casarella^{1,*}, Georgios Birmopilis² and Jelke Dijkstra³

¹ Chalmers University of Technology

² Ramboll Denmark

³ Chalmers University of Technology

* Corresponding author: angela.casarella@chalmers.se

The effect of temperature on the mechanical behaviour of clay-based geomaterials is relevant in several geotechnical applications (e.g., low enthalpy geothermal systems, energy geostructures and nuclear waste disposal). The mechanical response of (saturated) normally consolidated (NC) clay to temperature variation is not intuitive as the material irreversibly contracts upon heating. Since the thermal contraction observed at the engineering scale does not correspond to the thermal expansion of the clay constituents, both in sign and amplitude, the thermo-mechanical response is usually attributed to temperature-induced changes in the arrangement of clay particles/aggregates (changes in the inter-particle/aggregate porosity) [4] or to the nano-scale thermo-mechanical behaviour of the adsorbed water between clay unit layers (changes in the intra-particle porosity) [3].

Especially for clay minerals with a large amount of adsorbed water, such as swelling clays (tens of % of the total water is absorbed in saturated swelling clay samples), the latter hypothesis has been investigated numerically by molecular dynamics modelling of a layer-water-layer system in non-isothermal conditions [3,8] and experimentally through X-ray diffraction and scattering experiments (XRD, SAXS) [5,6,7].

According to the numerical simulations in [3,8], the free energy barrier between stable system states (the number of adsorbed water layers surrounding a clay particle) decreases with temperature, inducing a possible transition between mobile and immobile water. This nanometric phenomenon may result in a macroscopic volumetric thermal contraction.

A similar picture comes from the in-situ diffraction and scattering experiments [5,6,7], where a slight decrease in clay basal spacing (distance between two consecutive clay's aluminosilicate layers) is measured for increasing temperature. However, the experiments reported are performed in unsaturated conditions at controlled humidity and cannot be confronted with the fully saturated samples usually employed in geomechanical testing.

Measurements for monitoring nano-scale changes of fine-grained soils in their natural wet states are needed to prove the nano-scale origin of the thermo-mechanical behaviour of clays. Small-angle X-ray scattering (SAXS) has often been used to study particle orientation in compacted saturated clay [1]. Smaller features of the mineralogy and sub-particle behaviour of clays can be instead accessed by X-ray diffraction (XRD) and wide-angle X-ray scattering (WAXS) [2]. In principle, SAXS/WAXS measurements capture the inter-particle and intra-particle distances by measuring the scattered intensity of an X-ray beam hitting a sample.

This research uses combined SAXS/WAXS measurements to monitor nano-scale changes induced in the clay basal distances of several fine-grained natural soils in their saturated state by temperature variations. The experiments were performed with a SAXSLAB Mat:Nordic Instrument at the Chalmers Material Analysis Laboratory on reconstituted samples of natural sensitive clay (refer to [1]) and remoulded samples of swelling (bentonite) and non-swelling (kaolin) clays.

Figure 1 shows the absolute scattering intensities I [a.U.] as functions of the scattering vector q [\AA^{-1}] recorded at different temperatures for remoulded kaolin clay (Figure 1a) and bentonite (Figure 1b) samples (both remoulded at 0 kPa). The kaolinite ($q=0.898 \text{ \AA}^{-1}$) and montmorillonite ($q=0.312 \text{ \AA}^{-1}$) peaks are clearly visible in Figure 1a and Figure 1b, respectively. In the q -intensity plot, a change of the peak width, or a shift of the peak, indicates nano-scale strain in the material. However, no significant differences

in the two peaks are recorded after a temperature increase of $\Delta T=+45^\circ\text{C}$ and $\Delta T=+95^\circ\text{C}$, respectively; therefore, temperature variations, within the range considered for most thermal applications, do not affect both kaolinite and montmorillonite basal spacings.

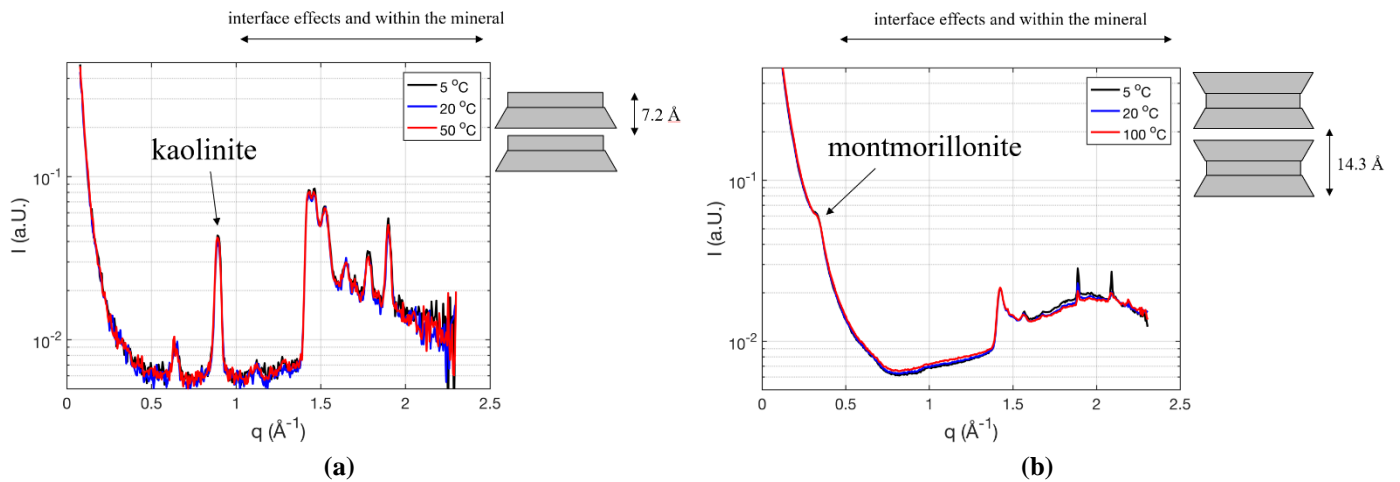


Figure 1: q -intensity plots for (a) remoulded kaolin clay (0 kPa) and (b) remoulded bentonite (0 kPa).

The results in Figure 1a (kaolin clay) are consistent with the idea that the amount of adsorbed water in the intra-particle porosity is significantly low in non-swelling clay minerals. As a result, the kaolinite macroscopic thermomechanical response cannot be associated with nanometric changes in the intra-particle absorbed water.

On the other hand, a significantly similar scattering response is recorded for bentonite in Figure 1b. Therefore, the activity (swelling capability) of the clay mineral and, thus, the amount of the sample absorbed water seems not to affect the response of the basal spacing to temperature, which stays constant upon heating.

Differently from what has been observed by [5,6,7] in unsaturated conditions, the current SAXS/WAXS measurements show that, for modest temperature changes, intra-particle changes upon heating in saturated samples do not play a major role in the macroscopic thermo-mechanical response of clay within the temperature range considered for most thermal applications, and this is independent by clay mineralogy. Therefore, thermo-mechanical strains must be investigated at a scale beyond what is accessible for a laboratory WAXS/SAXS instrument ($> 200 \text{ nm}$), focusing on temperature-induced particle/aggregate rearrangement.

Contributor statement

AC – drafting manuscript, data analysis; GB – experiments, data processing; JD – review of draft, supervision, funding acquisition

Acknowledgments

The funding from Vetenskapsrådet from grants 2020-03982 & 2022-03809 is greatly acknowledged.

References

- [1] Birmipilis, G., Ahmadi-Naghadeh, R., & Dijkstra, J. (2019). Macroscopic interpretation of nano-scale scattering data in clay. *Géotechnique Letters*, 9(4), 355-360.
- [2] Birmipilis, G., Hall, S. A., Lages, S., & Dijkstra, J. (2019). Monitoring of the nano-structure response of natural clay under mechanical perturbation using small angle X-ray scattering and digital image correlation. *Acta Geotechnica*, 14, 1965-1975.
- [3] Brochard, L., Honório, T., Vandamme, M., Bornert, M., & Peigney, M. (2017). Nanoscale origin of the thermo-mechanical behavior of clays. *Acta Geotechnica*, 12, 1261-1279.
- [4] Casarella, A., Tarantino, A., & Di Donna, A. (2020). Micromechanical interpretation of thermo-plastic behaviour of clays. In *E3S Web of Conferences* (Vol. 205, p. 09003). EDP Sciences.
- [5] Da Silva, G. J., Fossum, J. O., DiMasi, E., & Måløy, K. J. (2003). Hydration transitions in a nanolayered synthetic silicate: A synchrotron x-ray scattering study. *Physical review B*, 67(9), 094114.
- [6] Ferrage, E., Lanson, B., Michot, L. J., & Robert, J. L. (2010). Hydration properties and interlayer organization of water and ions in synthetic Na-smectite with tetrahedral layer charge. Part 1. Results from X-ray diffraction profile modeling. *The Journal of Physical Chemistry C*, 114(10), 4515-4526.
- [7] Morodome, S., & Kawamura, K. (2009). Swelling behavior of Na-and Ca-montmorillonite up to 150 C by in situ X-ray diffraction experiments. *Clays and Clay Minerals*, 57(2), 150-160.

- [8] Smith, D. E., Wang, Y., Chaturvedi, A., & Whitley, H. D. (2006). Molecular simulations of the pressure, temperature, and chemical potential dependencies of clay swelling. *The Journal of Physical Chemistry B*, 110(40), 20046-20054.