

# Macroscopic characteristics of montmorillonite from its nanoscale components – Insights from molecular dynamics simulations

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Bentonite clay is proposed as buffer material in several concepts of High Level Radioactive Waste (HLRW) repositories, and a truthful description of this material is of utter importance given that the expected operational time is up to one million years. The desirable properties of bentonite emerge from the clay mineral montmorillonite, which is a nanoporous material that exhibit swelling-shrinking behavior owing to osmosis. Montmorillonite particles are plate shaped with thickness of 1 nm and lateral dimensions of 100-1000 nm. Further, the particles are negatively charged and this charge is compensated by cations residing in the interlayer space between clay layers.

The swelling-shrinking behavior of montmorillonite was studied using molecular dynamics simulations where external force was applied to a stack of montmorillonite layers. Due to explicit water in the simulation, the resulting relationship between osmotic pressure and basal distance differs from continuum models. In agreement with experiment, basal distances change abruptly between hydration states at certain pressures. Within a given hydration state, the basal distances were found to vary with applied pressure also seen experimentally.

Another aspect of importance for HLRW repositories is the diffusion of corroding agents that may harm the waste canisters. A significant factor governing the in-diffusion of corrosives is the partition coefficient between the external aqueous solution and the montmorillonite interlayer solution.

We investigated the partition coefficient using molecular dynamics simulations of compacted montmorillonite with two hydration layers of water in the interlayer. The montmorillonite was contacted to an electrolyte reservoir, and the calculations were performed at different concentrations.

The calculations showed that excess salt, i.e., both anions and cations enter interlayer space to the extent predicted by general Donnan equilibrium that includes free-energy corrections (activities). Thus the excess salt concentration is reduced in the interlayer in comparison to the external electrolyte but not totally excluded. This draws attention to a misconception, often seen in the literature, stating that anions cannot enter interlayer space due to electrostatic repulsion forces.

The present study highlights the importance of the montmorillonite interlayer as a common denominator for seemingly unrelated macroscopic phenomena, namely the swelling-shrinking of montmorillonite and the salt partition between interlayer and external solution.