

Chemical Controls on Microstructure and Swelling Change in Compacted Montmorillonite

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Understanding the chemical controls on smectite swelling and microstructure change is crucial for predicting the hydro-mechanical-chemical coupling processes in clayey materials found in natural and engineered barriers for surface and subsurface energy applications such as nuclear waste storage, CO₂ sequestration, and hydrogen underground storage. While water chemistry is known to affect clay swelling, in-situ measurements of swelling and microstructure changes on compacted clayey systems as a function of in-flow chemical composition have rarely been explored, particularly in the sub-nanometer to nanometer scale. In this study, we developed a miniaturized μ -oedometer system that allows us to simultaneously measure chemical- and time-resolved swelling pressure using a montmorillonite sample (Kunipia-F) as a function of ionic strength (0.001M – 5M NaCl) and cation types (Na⁺ vs. K⁺). It is equipped with an X-ray transparent custom-made cells that hold compacted clay samples that allows for monitoring of the in-situ change of montmorillonite microstructure using small-angle X-ray scattering (SAXS) techniques at the Advanced Light Source (ALS). We have successfully shown the chemical-resolved SAXS profile changes at both crystalline and osmotic swelling states. The clay interlayer basal spacing increases from 15.5Å to 18.8Å with decreasing ionic strength in response to the interlayer hydration state changing from 2-layer hydrate at 5M NaCl, to a transient mixture of 2- and 3-layer hydrates at 1M NaCl, and 3-layer hydrate at 0.1M and 0.001M NaCl. The basal spacing is 15.6Å (2-layer hydrate) at 1M KCl, which is different from those at 1M NaCl (15.6 – 18.4Å). At 0.001M NaCl, we also observed the osmotic swelling signals with layer-to-layer distance of 41.0 – 47.7Å, an observation unique to compacted clay systems using the SAXS technique. These results are in good agreement with our chemical- and time-resolved swelling pressure measurement where the swelling pressure increases with decreasing ionic strength (5M to 0.001M NaCl). The swelling pressure continuously decreases with increasing K⁺/Na⁺ ratios under a constant ionic strength (1M) indicating the effect of different cations. These observations and more measurements under dynamically changing conditions will provide valuable insight in