Molecular Mechanisms of Clay Swelling by CO_2 adsorption

PAUL SPIERING[1,2] , RICK WENTINCK[2], ANDREAS BUSCH[2], JOHANNES G.E.M. FRAAIJE[1] AND TIM J. TAMBACH[2]

[1]Leiden Institute of Chemistry, University of Leiden, Einsteinweg 55, 2333 CC Leiden, The Netherlands
[2]Shell Global Solutions International BV, Kesslerpark 1, 2288 GS Rijswijk, The Netherlands

In geological reservoirs CO_2 can be used for permanent storage or to enhance the production of hydrocarbons. Most of these reservoirs are sealed by tight, argillaceous rocks high in clay content (e.g. kaolinite, illite, smectite). Injected CO_2 will, by buoyancy, move upwards in the reservoir until it reaches the clay-rich seal. The high capillary forces of such a seal will prevent viscous flow, however, aqueous diffusion of CO_2 through the pore network will take place. As shown earlier, clays are able to significantly adsorb CO_2, and, in the case of expandable clays such as montmorillonite this can cause clay swelling and the build-up of swelling pressures. We consider this an important aspect for the long-term containment of injected CO_2. Experimental data on the influence of CO_2 in swelling clays is challenging to interpret due to the lack of a validated molecular model. Therefore the main focus of our work is to use molecular simulations for gaining better insights in molecular configurations and mechanisms present in Na-exchanged Wyoming montmorillonite exposed to CO_2. This is done under in-situ hydration states, typically between zero and one (0W-1W) water layers, in the interlayer space.

We used a hybrid scheme of molecular dynamics – Monte Carlo simulations with the ClayFF force field to model CO_2 adsorption in Na-montmorillonite. The simulations reproduce experimentally measured basal spacings demonstrating partially filled water layer states instead of discrete layers. Strain experiments of CO_2 adsorption in montmorillonite indicate no swelling at these discrete states, but up to 10% swelling strain for hydration states between those. This is qualitatively reproduced with molecular simulations by adding CO_2 molecules in the interlayer of montmorillonite. Radial distribution functions and density profiles show that CO_2 is able to coordinate around the Na-cations, and increasing coordination causes increasing swelling strain.

In summary, molecular simulations provide evidence that CO_2 is able to cause swelling strain in swelling clays by coordination of cations.