Molecular simulation studies of H_2O-CO_2-CH_4 complex in swelling clays

QI RAO[1] AND YONGSHENG LENG [1]

[1] Department of Mechanical & Aerospace Engineering, The George Washington University, Washington, DC 20052, USA (leng@gwu.edu)

Shale gas production with water-based hydraulic fracturing may invoke high water consumption and formation damage. Carbon dioxide (CO_2) is a promising candidate for reservoir fracturing and enhanced oil-gas recovery (EOGR), plus benefit from long-term CO_2 sequestration. Swelling clays are important components of shales. Understanding the interaction between water–carbon dioxide–methane (CH_4) ternary mixture and swelling clays is important for CO_2-EOGR and CO_2 sequestration in shale gas reservoirs.

In this study, we employ the grand-canonical Monte Carlo (GCMC) and molecular dynamics (MD) simulations to investigate a H_2O–CO_2–CH_4 ternary mixture in Na-montmorillonite clay interlayer under geological conditions (T = 323 K, P = 90 bar) with relative humidity (RH) in the ranges of 5% – 40%. We studied the effects of RH on the intercalation of different species. The stable clay interlayer distances at different RH values are determined based on the calculated free energy curves of the clay-fluid compex system. Simulation results show that there are two stable hydration states: the monolayer (1W) H_2O–CO_2–CH_4–Na complex with a basal spacing around 12 Å and a bilayer (2W) state with a basal spacing around 14.5 – 15.7 Å. In the range of RH investigated, the 1W state is more stable than the 2W state. Smilar to our early studies, CO_2 and CH_4 intercalation into the clay mineral is strongly influenced by RH. Our simulation results show that the intercalation of CH_4 is strongly outcompeted by CO_2 upon the hydration of interlayer sodium ions by water molecules. However, low RHs do provide opportunities for the co-sorption of CH_4 with CO_2. The competitive sorption between CO_2 and CH_4 in clay interlayers depends on the CO_2/CH_4 ratio in the ternary mixture. MD simulations show that CO_2 and CH_4 molecules are partially hydrated, especially at low RHs, while sodium ions are fully hydrated due to its large hydration energy with water molecules. Further, some CO_2 molecules can migrate into the first hydration shell of sodium ions at low RHs (< 20%). These findings provide better understanding of the behavior of H_2O–CO_2–CH_4 ternary mixture in clay interlayers and demonstrate the potential implementation of CO_2-based EOGR in shale gas reservoirs.