Supercritical gas adsorption in clay minerals and shales

RONNY PINI[1]

[1]Department of Chemical Engineering, Imperial College London, London, SW7 2AZ, UK

Clay minerals are ubiquitous in the subsurface: they are found in CO_2 sequestration targets (e.g., sandstones) and in the seals above them, and are major constituents of unconventional shale plays considered for natural gas recovery. A signficant fraction of the porosity in clay-rich systems is occupied by micro- and meso-pores that provide a large surface area for physical and chemical interactions with the surrounding fluids. Of particular interest to this study is the adsorption behaviour of CO_2 and CH_4 that leads to the trapping of these gases in the porous structure at liquid-like densities. From a practical perspective, gas adsorption can lead to (i) an increase of storage capacity in reservoirs having larger clay contents, (ii) an advance in storage safety by limiting gas diffusion through cap rock seals, and (iii) an enhancement of gas production from tight shale formations through an adsorption/desorption (CO_2/CH_4) process.

Supercritical gas adsorption studies on various clay and shale samples that address these aspects are found in the literature, but the picture is still far from being complete. The main reason for this is the intrinsic difficulty in performing these experiments at subsurface conditions (high-pressure and temperature), and in their description, because the interactions between the gases and the rock's constituents (both clays and organic matter) are quite complex, leading to contrasting observations, such as densification and/or depletion phenomena.

We report results from a systematic experimental investigation on the adsorption properties of CO_2 and CH_4 over a wide range of conditions (0-25 MPa and 40-80°C). The systems considered include pure clay minerals (e.g., Na-montmorillonite), shale samples from various (potential) plays (Eagle Ford, Utica and Bowland Shale), as well as reference materials with well defined surface chemistry and pore structure (zeolites and mesoporous adsorbents). Data are interpreted using appropriate quantitative measures, such as the excess adsorption. To support the experimental observations, the measured adsorption isotherms are described using a so-called Lattice Density Functional Theory (LDFT) model that uses as input parameter the pore structure of the material (measured from e.g., conventional cryogenic adsorption experiments). As such, the modelling approach is more rigorous, has predictive capability and represents a significant departure from conventional empirical approaches that use Langmuir- or BET-type of models.