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Quarterly Report

Fundamental Understanding of Methane-Carbon Dioxide-Water (CH_4-CO_2-H_2O) Interactions in Shale Nanopores under Reservoir Conditions

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WORK PERFORMED UNDER

Field Work Proposal 14-017608

PRINCIPAL INVESTIGATOR

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1.0 GOALS OF PROJECT

Shale is characterized by the predominant presence of nanometer-scale (1-100 nm) pores. The behavior of fluids in those pores directly controls shale gas storage and release in shale matrix and ultimately the wellbore production in unconventional reservoirs. Recently, it has been recognized that a fluid confined in nanopores can behave dramatically differently from the corresponding bulk phase due to nanopore confinement (Wang, 2014). CO_2 and H_2O, either preexisting or introduced, are two major components that coexist with shale gas (predominately CH_4) during hydrofracturing and gas extraction. Note that liquid or supercritical CO_2 has been suggested as an alternative fluid for subsurface fracturing such that CO_2 enhanced gas recovery can also serve as a CO_2 sequestration process. Limited data indicate that CO_2 may preferentially adsorb in nanopores (particularly those in kerogen) and therefore displace CH_4 in shale. Similarly, the presence of water moisture seems able to displace or trap CH_4 in shale matrix. Therefore, fundamental understanding of CH_4-CO_2-H_2O behavior and their interactions in shale nanopores is of great importance for gas production and the related CO_2 sequestration. This project focuses on the systematic study of CH_4-CO_2-H_2O interactions in shale nanopores under high-pressure and high temperature reservoir conditions. The proposed work will help develop new stimulation strategies to enable efficient resource recovery from fewer and less environmentally impactful wells**.**

2.0 ACCOMPLISHMENTS

Publication: Manuscript entitled "Fast Advective Water Flow through Nanochannels in Clay Interlayers: Implications for Moisture Transport in Soils and Unconventional Oil/Gas Production" was accepted by *ACS Applied Nano Materials.* Here is the abstract:

Water flow in nanometer or sub-nanometer hydrophilic channels bears special importance for diverse fields of science and engineering. However, the nature of such water flow remains elusive. Here we report our molecular modeling results on water flow in a sub-nanometer clay interlayer between two montmorillonite layers. We show that a fast advective flow can be induced by evaporation at one end of the interlayer channel, i.e., a large suction pressure created by evaporation (~818 MPa) is able to drive the fast water flow through the channel (~ 0.88 m/s for a 46 Å long channel). Scaled up for the pressure gradient to a 2 μm particle, the velocity of water is estimated to be about 95 μm/s, indicating that water can quickly flow through a μm-sized clay particle within seconds. The prediction seems to be confirmed by our thermo-gravimetric analysis of bentonite hydration and dehydration processes, which indicates that water transport at the early stage of the dehydration is a fast advective process, followed by a slow diffusion process. The possible occurrence of fast advective water flow in clay interlayers prompts us to reassess water transport in a broad set of natural and engineered systems such as clay swelling/shrinking, moisture transport in soils, water uptake by plants, water imbibition/release in unconventional hydrocarbon reservoirs, and cap rock integrity of supercritical CO_2 storage.

Effects of gas extraction and injection on water-kerogen contact angle: Molecular dynamics simulations were carried out to investigate the wettability alteration of kerogen and mineral upon shale gas extraction and CO_2 injection. The results indicate that contact angle of a water droplet changes significantly with a changing gas pressure for kerogen and pyrophyllite surfaces (Fig. 1). At the same gas pressure, CO_2 causes a more significant change in the wettability compared to CH_4 (comparison between Fig. 2A vs. 2B for 50 atm gas pressure, and between Fig. 2C and 2D for 100 atm gas pressure).

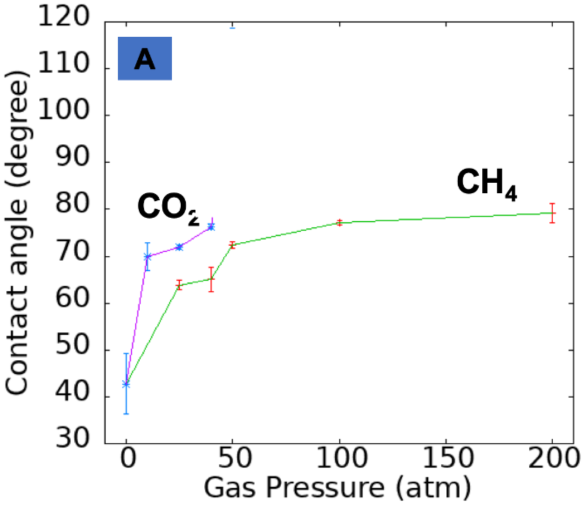

Figure 1. Contact angle of water droplet on kerogen II-D surface as a function of CH_4 and CO_2 gas pressure

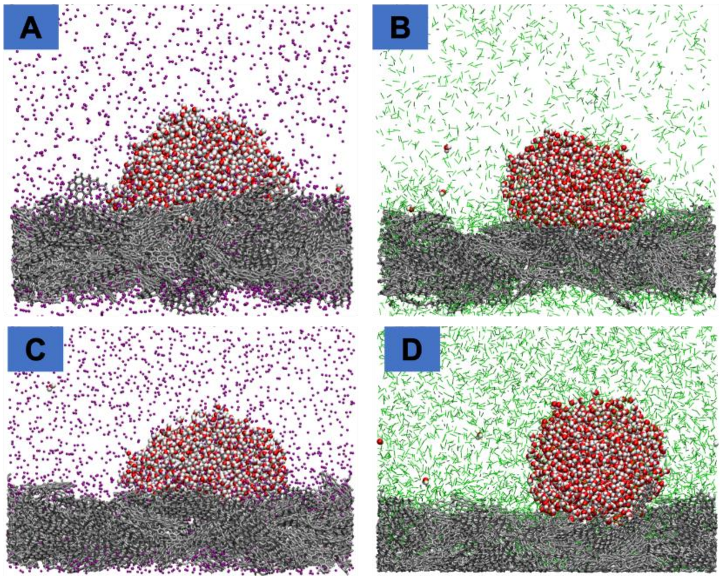

Figure 2 Comparing contact angles of a water droplet on II-D kerogen surface at 50 atm CH_4 (A) and CO_2 (B), and at 100 atm CH_4 (C) and CO_2 (D).

The results indicate that, upon CH_4 extraction, the gas pressure decreases and so does the contact angle of water droplet, suggesting that more water can move into the kerogen matrix during the gas extraction process. However, during CO_2 injection, the CO_2 gas pressure increases upon injection. The surface becomes more hydrophobic, indicating that water would move away from the kerogen surface and make the surface available for CO_2 gas adsorption. The results have a significant implication to reservoir-scale simulations for shale gas extraction and CO_2 injection.

3.0 OUTLOOK

The next steps will include:

- With the developed approach, additional molecular structures will be constructed and evaluated for their gas sorption/transport capacities.
- Perform additional sorption measurements on crushed shale samples.
- Perform sorption measurements more on multicomponent systems to clarify the interactions among different components (CH_4-CO_2-H_2O).
- Understand the underlying mechanism for the observed gas sorption-desorption hysteresis.
- More MD simulations will be performed on different hydrocarbon fluids and their phase separation in nanopores.
- Use the existing experimental and modeling results to formulate new gas disposition and release models for well production.

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