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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

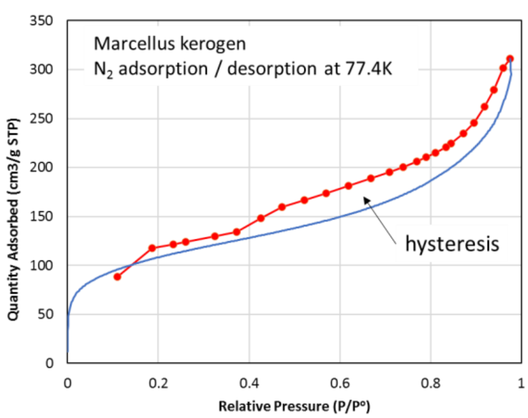
Shale is characterized by the predominant presence of nanometer-scale (1-100 nm) pores. The behavior of fluids in those pores directly controls shale gas storage and release in shale matrix and ultimately the wellbore production in unconventional reservoirs. Recently, it has been recognized that a fluid 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 to develop new stimulation strategies to enable efficient resource recovery from fewer and less environmentally impactful wells.

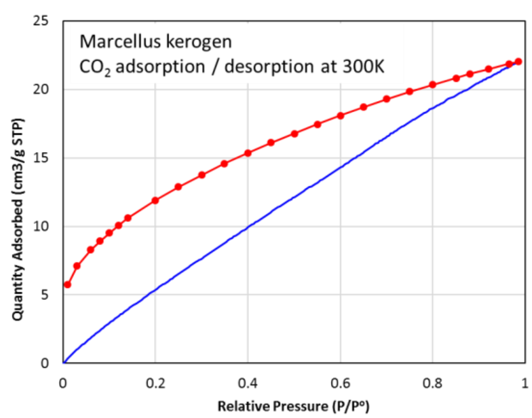
2.0 ACCOMPLISHMENTS

Experimental:

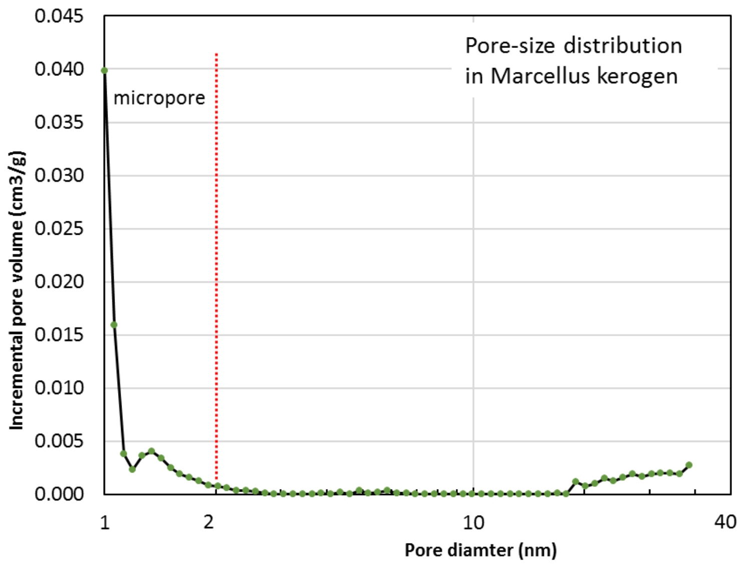
Kerogen extracted from Woodford shale and Marcellus shale have been characterized using ATR-FTIR and BET. CO_2 adsorption and desorption isotherms for extracted kerogen were measured at 273 K and 300 K. The specific surface area for kerogen from Woodford shale is 50 cm^2/g and 357 cm^2/g for Marcellus kerogen which are consistent with maturity measurement by vitrinite reflectance with Wood shale being immature and Marcellus shale being mature.

For Marcellus kerogen, the hysteresis exists until very low pressure ($P/P^0 < 0.2$) and a drop in the desorption curve (red color) at P/P^0 of 0.45. Molecular dynamics (MD) modeling together with the measured pore-size distribution will help to explain what controls the hysteresis loop.

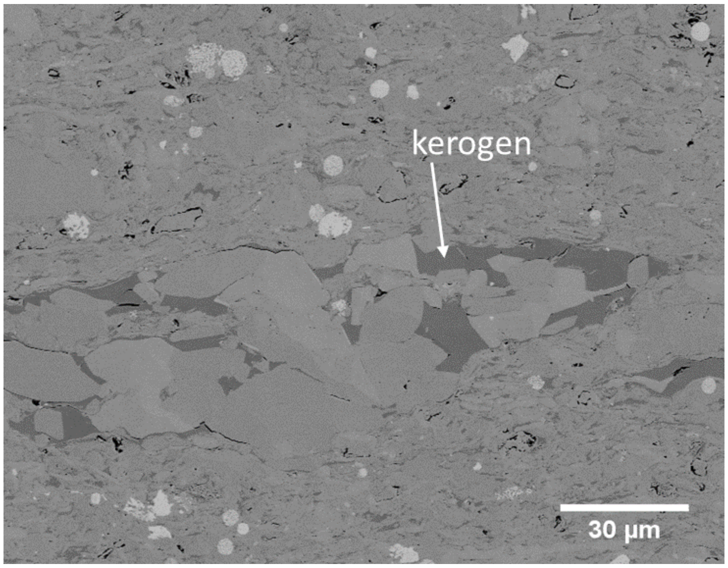




Marcellus kerogen pore-size distributions, obtained using classic Density functional theory (DFT) model from liquid nitrogen adsorption, shows bimodal distributions with micropore (2 nm or less) accounting more than 75% of the total pore volume and the rest 25% pore volume from pores with 20 – 30 nm diameter. There are no pores between 3 to 20 nm, which is confirmed by scanning electron microscope (SEM) images from Marcellus shale, which is very unusual for mature shale with maturity of 2.2 (VRo). Kerogen spatial heterogeneity in maturity is being analyzed using FTIR microscope and Raman microscope.



SEM images were obtained for Marcellus shale. There are only a few visible large pores/cracks inside the kerogen. Microspores with 2 nm or less diameters cannot be detected with current SEM settings.



Modeling:

Kerogen may swell upon gas sorption (per communication with Drew Pomerantz at Schlumberger). This swelling may affect the porosity and permeability of shale. Using a hybrid molecular dynamics/Monte Carlo simulation technique, we have investigated the swelling properties of kerogen upon helium (He), methane (CH_4), and carbon dioxide (CO_2) adsorption. The results indicate that kerogen insignificantly swells under helium adsorption. However, kerogen volume increases up to 5.4% and 11% upon methane and carbon dioxide adsorption at 192 atm, respectively. The kerogen volume increases when gas pressure increases, and at the same gas pressure it increases more in carbon dioxide than in methane. Because of the swelling nanostructural properties of kerogen including porosity, surface area, and pore size distribution change significantly. Our results illustrate the necessity of including kerogen swelling in the porosity, permeability, and adsorption data interpretation, and provide a mechanistic understanding of the interaction between kerogen and gas that is useful for shale gas and carbon sequestration applications. A manuscript on this work is ready for submission.

Publications:

- Model representations of kerogen structures: An insight from density functional theory calculations and spectroscopic measurements, Scientific Reports 7:7068 (2017). DOI:10.1038/s41598-017-07310-9.
- Atomistic structure of mineral nano-aggregates from simulated compaction and dewatering, Scientific Reports 7:15286 (2017). DOI:10.1038/s41598-017-15639-4.
- Natural indices for the chemical hardness/softness of metal cations and ligands, ACS Omega, 2, 7185-7193 (2017).
- Mechanistic understanding of CO_2, CH_4 and H_2O retention, release and interactions in natural organic matter, submitted to Energy & Fuels (resubmitted after revision).
- Kerogen swelling in gas: A hybrid molecular dynamics/Monte Carlo simulation study (to be submitted).

3.0 OUTLOOK

The next step will include:

- Characterize physical and chemical properties of newly isolated kerogen.
- Performing additional high pressure and high temperature 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).
- Based on the existing experimental and modeling results to formulate new gas disposition and release model for well-borehole production.

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