

Quarterly Report

Fundamental Understanding of Methane-Carbon Dioxide-Water (CH₄-CO₂-H₂O) Interactions in Shale Nanopores under Reservoir Conditions

April 21, 2015

WORK PERFORMED UNDER

Field Work Proposal 14-017608

PRINCIPAL INVESTIGATOR

Yifeng Wang

Sandia National Laboratories, 1515 Eubank SE, Mail Stop 0779, Albuquerque, NM 87123;
telephone: (505)844-8271; fax: (505)844-2348; e-mail: ywang@sandia.gov

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). CO₂ and H₂O, either preexisting or introduced, are two major components that coexist with shale gas (predominately CH₄) during hydrofracturing and gas extraction. Note that liquid or supercritical CO₂ has been suggested as an alternative fluid for subsurface fracturing such that CO₂ enhanced gas recovery can also serve as a CO₂ sequestration process. Limited data indicate that CO₂ may preferentially adsorb in nanopores (particularly those in kerogen) and therefore displace CH₄ in shale. Similarly, the presence of water moisture seems able to displace or trap CH₄ in shale matrix. Therefore, fundamental understanding of CH₄-CO₂-H₂O behavior and their interactions in shale nanopores is of great importance for gas production and the related CO₂ sequestration. This project focuses on the systematic study of CH₄-CO₂-H₂O 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

Task 1.0 - Project Management

The 1st quarterly report was submitted on January 30, 2015. The allocation of the second segment of funding was discussed. P.I. Yifeng Wang visited Texas A&M University and explored a possibility for forming a shale gas research consortium.

Task 2.0 - Material Preparation & Characterization

We have obtained about 10 shale core samples through purchasing or from the collaboration with Texas A&M University (TAMU). We have tried to isolate kerogen from Mancos shale using a procedure we developed, but the result is mixed. The resulting isolates still contain a significant portion of inorganic components. For this reason, about 200 grams of Mancos shale was sent out to GeoMark Research, Ltd. for kerogen isolation. ~ 1 gram of pure



Figure 1. Kerogen isolated from Mancos shale

kerogen was obtained (Figure 1). The BET surface area of the kerogen was determined to be $\sim 2 \text{ m}^2/\text{g}$.

Mancos shale sample was sent to Los Alamos National Laboratory for a neutron scattering study, and the analysis result was received. The result shows a relatively low organic carbon content in this shale. The pore size of the shale is dominated by 1-100 nm (Figure 2).

Task 3.0 Full Cycle Sorption-Desorption Experiments

We have designed and constructed a unique high temperature and pressure experimental system that can measure both of the P-V-T-X properties and adsorption kinetics sequentially. We plan to measure the P-V-T-X properties of $\text{CH}_4\text{-CO}_2$ mixtures with CH_4 up to 95 vol. %, and adsorption kinetics of various materials, under the conditions relevant to shale gas reservoir. Three types of materials will be used: (I) model materials, (II) single solid phases separated from shale samples, and (III) crushed bulk shale samples. The model materials are well characterized in terms of pore sizes. Therefore, the results obtained for the model materials serve as benchmarks for our model development.

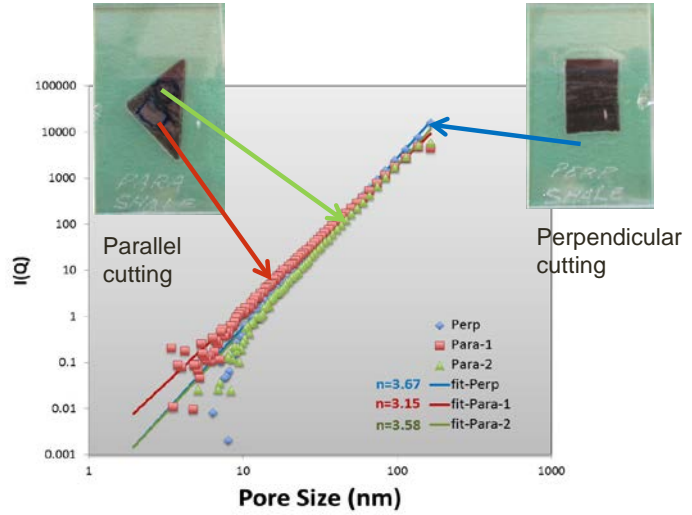


Figure 2. Small angle neutron scattering analysis of Mancos shale

Table 1. Experimental measurements of sorption capacities and sorption rates for the model substances at 1 bar total pressure

Model Substances	Temp, °C	Gas Mixture, volume percent	Pressure, bar	Sorption Capacity, mg/g	Sorption Rate, mg/g min ⁻¹
DARCO activated carbon	25	85% CH ₄ + 15% CO ₂	1	28	0.68
	50	85% CH ₄ + 15% CO ₂	1	11	0.59
	75	85% CH ₄ + 15% CO ₂	1	9.0	0.31
	100	85% CH ₄ + 15% CO ₂	1	2.1	0.14
	125	85% CH ₄ + 15% CO ₂	1	1.8	0.10
Montmorillonite, <75 μm	25	85% CH ₄ + 15% CO ₂	1	2.8	4.7 × 10 ⁻²
	50	85% CH ₄ + 15% CO ₂	1	0.30	9.6 × 10 ⁻³
	75	85% CH ₄ + 15% CO ₂	1	0.19	6.7 × 10 ⁻³
	100	85% CH ₄ + 15% CO ₂	1	0.18	5.1 × 10 ⁻³
	125	85% CH ₄ + 15% CO ₂	1	0.12	3.3 × 10 ⁻³

Two sets of gas sorption-desorption experiments were planned: (1) low pressure experiments and high pressure and high temperature experiments. Significant progress has been made in the low pressure experiments. The high pressure and high temperature experiments have been initiated. What is summarized below is a part of low pressure measurements. The result was presented at the fall meeting of American Geophysical Union in San Francisco in the last December.

As reported earlier, the low pressure sorption measurements were performed using a thermal gravimetric analyzer (TGA). Co-P.I. Yongliang Xiong presented the result at the High Temperature Aqueous Chemistry (HiTAC)-II Workshop in Heidelberg. A full set of TGA analyses is shown in Table 1.

We have performed the measurements for CH₄ (90%)-CO₂ (10%) sorption on activated carbon 25, 50, 75 °C and pressures up to 2000 PSI. The analysis of the data is in progress.

Task 4.0 Development of Equation of State (EOS) for CH₄-CO₂-H₂O in Nanopores

This task focuses on the data interpretation and synthesis using both molecular dynamics simulations and the density functional theory (DFT) (including the classic DFT). The modeling work in the first quarter was aimed to set up appropriate modeling systems and test the modeling methodology to be employed. Density functional theory (DFT) calculations have been carried out using the VASP code within the generalized gradient approximation with the Perdew-Burke-Ernzerhof exchange-correlation functional (GGA/PBE) for CH₄-H₂O-CO₂ interactions in a single wall carbon nanotube (Figure 3). These calculations provide valuable information about the interaction of CH₄ and CO₂ with the confining wall of nanopores.

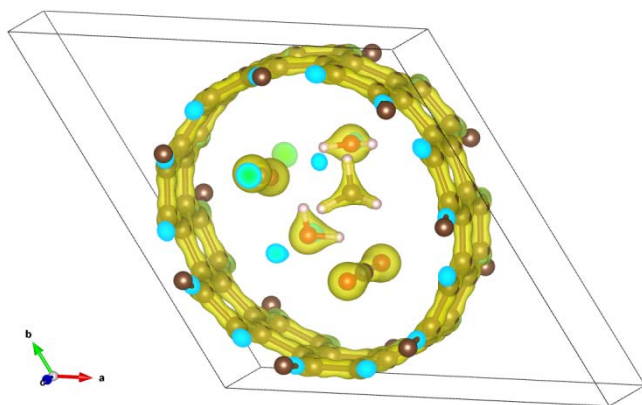


Figure 3. Charge density (yellow) of an optimized periodic (7,7) SWCNT containing one CH₄, two H₂O and two CO₂ molecules calculated with DFT-D2 at the GGA/PBE level of theory.

3.0 OUTLOOK

The next step will include:

- Expanding the low pressure sorption measurements to a full cycle of adsorption-desorption measurements. The data to be obtained will help understand the possible hysteresis behavior of gas sorption in nanopores.
- Continue performing high pressure and high temperature sorption measurements. Develop a highly accurate equation of state (EOS) for CH₄-CO₂ mixtures for data interpretation.
- Starting a cDFT formulation for CH₄-CO₂ sorption in nanopores and trying to apply the model to low pressure measurement data.