

## **Quarterly Report**

# **Fundamental Understanding of Methane-Carbon Dioxide-Water (CH<sub>4</sub>-CO<sub>2</sub>-H<sub>2</sub>O) 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<sub>2</sub> and H<sub>2</sub>O, either preexisting or introduced, are two major components that coexist with shale gas (predominately CH<sub>4</sub>) during hydrofracturing and gas extraction. Note that liquid or supercritical CO<sub>2</sub> has been suggested as an alternative fluid for subsurface fracturing such that CO<sub>2</sub> enhanced gas recovery can also serve as a CO<sub>2</sub> sequestration process. Limited data indicate that CO<sub>2</sub> may preferentially adsorb in nanopores (particularly those in kerogen) and therefore displace CH<sub>4</sub> in shale. Similarly, the presence of water moisture seems able to displace or trap CH<sub>4</sub> in shale matrix. Therefore, fundamental understanding of CH<sub>4</sub>-CO<sub>2</sub>-H<sub>2</sub>O behavior and their interactions in shale nanopores is of great importance for gas production and the related CO<sub>2</sub> sequestration. This project focuses on the systematic study of CH<sub>4</sub>-CO<sub>2</sub>-H<sub>2</sub>O 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**

We finalized the project management plan and obtained the approval from the NETL Project manager. The project was started on October 1, 2014. The kick-off meeting was held on November 18, 2014.

### **Task 2.0 - Material Preparation & Characterization**

We have obtained four shale core samples through purchasing or from the collaboration with Texas A&M University (TAMU). Professor Yucel Akkutlu visited Sandia in the last December on Sandia-TAMU collaboration on nanogeochemical study of shale gas. One of the shale samples has been sent to Los Alamos National Laboratory for a neutron scattering study. An abstract on neutron scattering results was accepted for presentation at GeoProc 2015 in Salt Lake City in Feb.

We have developed a procedure for the isolation and concentration of kerogen from shale samples. Two kerogen concentrates were obtained. We have also synthesized (or purchased) a number of model materials for studying gas sorption-desorption in nanopores. The model materials include nanoporous silica (specific surface area > 100 m<sup>2</sup>/g), nanoporous alumina (specific surface area > 250 m<sup>2</sup>/g), activated carbon (as analog to kerogen), and clay minerals (smectite, illite, and smectite-illite mixed layers). The nanoporous metal oxides were synthesized using sol-gel methods. Structural characterization of the model materials has been completed.

### 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 CH<sub>4</sub>-CO<sub>2</sub> mixtures with CH<sub>4</sub> 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.

The P-V-T-X properties obtained in this study will be used to establish a high precision equation of state (EOS) applicable to shale gas recovery in confined nano-pore environments. An equation of state (EOS) that can accurately describe interactions in the CH<sub>4</sub>-CO<sub>2</sub>-H<sub>2</sub>O system for a wide range of physico-chemical conditions in a confined environment is an important and essential tool that enables efficient resource recovery from fewer and less environmentally impactful wells. However, such an EOS does not exist at present. For the bulk properties, Duan et al. (1992) proposed an EOS for the CH<sub>4</sub>-CO<sub>2</sub>-H<sub>2</sub>O system. Their EOS was based almost solely on experimental data for the following binary systems, i.e., CH<sub>4</sub>-H<sub>2</sub>O, CO<sub>2</sub>-H<sub>2</sub>O, and CH<sub>4</sub>-CO<sub>2</sub>. As they pointed out, “ternary data are almost nonexistent.” In their parameterization, there were two experimental investigations addressing the ternary system. Price (1981) measured solubility of CH<sub>4</sub> and CO<sub>2</sub> in brine containing 5 wt% NaCl at 150°C and 345 bars. Ramboz et al. (1985) investigated the CH<sub>4</sub>-CO<sub>2</sub>-H<sub>2</sub>O system at temperatures above 370°C, which is not applicable to the conditions for shale gas recovery. After the publication of Duan et al. (1992), a number of studies on the CH<sub>4</sub>-CO<sub>2</sub>-H<sub>2</sub>O system at temperatures below room temperature were initiated. The aim of these studies was to determine the hydrate equilibrium (e.g., Bruusgaard et al., 2010), but again these studies are not relevant to the conditions applicable for shale gas recovery.

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.

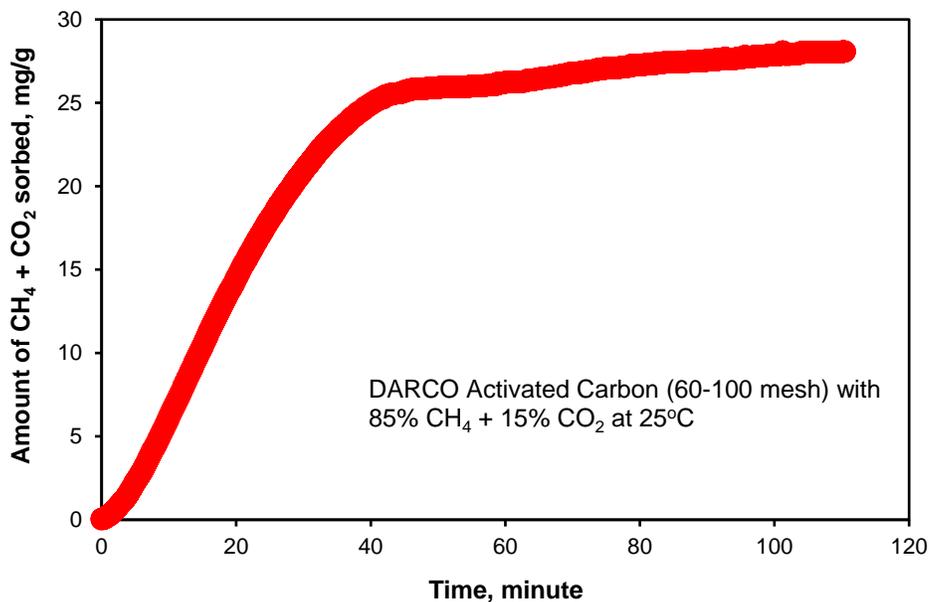
The low pressure sorption measurements were performed using a thermal gravimetric analyzer (TGA). The TGA analysis was conducted using a Netzsch STA 409 thermal gravimetric analyzer with differential scanning calorimeter (DSC) and Differential temperature analyzer (DTA) that is adapted for measurements of adsorption capacities and kinetics of the three types of materials at reservoir relevant temperatures up to 125°C and constant pressures up to 1 bar. We studied the adsorption kinetics by monitoring the evolution of the weight change as a function of time after a mixture of CO<sub>2</sub> and CH<sub>4</sub> was introduced into the sorption vessel and until sorption saturation equilibrium was reached.

A typical sorption curve is shown in Figure 1. The linear portion of the curve is used for determination of sorption kinetics. The portion that indicates the sorption saturation has been attained is used for the determination of sorption capacities. For illustration, Figure 2 shows the

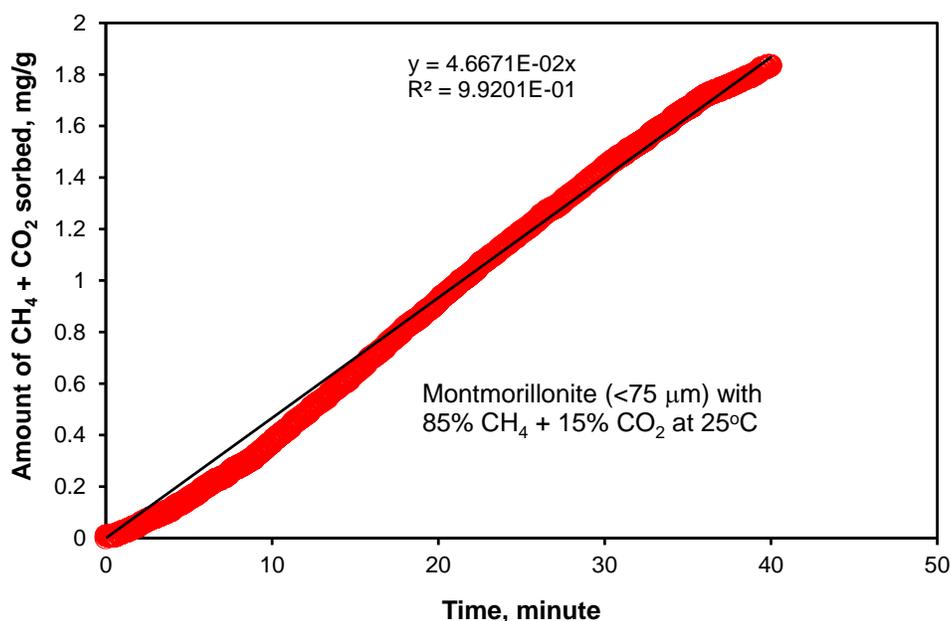
determination of sorption rate for montmorillonite. We have used this methodology to determine the sorption capacities and kinetics for activated carbon, crushed shale, illite and montmorillonite. We have obtained raw data for these model materials up to 125°C. The sorption capacities and sorption rates that have been processed so far are listed in Table 1. More results will be reported in the next quarter.

**Table 1.** Experimental measurements of sorption capacities and sorption rates for the model substances

Model Substances	Temp, °C	Gas Mixture, volume percent	Pressure, bar	Sorption Capacity, mg/g	Sorption Rate, mg/g min <sup>-1</sup>
DARCO activated carbon	25	85% CH <sub>4</sub> + 15% CO <sub>2</sub>	1	28	0.68
	75	85% CH <sub>4</sub> + 15% CO <sub>2</sub>	1	9.0	0.31
Montmorillonite, <75 μm	25	85% CH <sub>4</sub> + 15% CO <sub>2</sub>	1	2.8	4.7 × 10 <sup>-2</sup>



**Figure 1.** Sorption of CH<sub>4</sub> + CO<sub>2</sub> on activated carbon at 25°C and 1 bar



**Figure 2.** Sorption kinetics of CH<sub>4</sub> + CO<sub>2</sub> on montmorillonite at 25°C and 1 bar. Note that only linear part of the sorption curve is used.

As shown in Table 1, activated carbon (as an analog to kerogen) has a high sorption capacity for CH<sub>4</sub> and CO<sub>2</sub>. Interestingly, our data show that a significant fraction of CH<sub>4</sub> and CO<sub>2</sub> can be adsorbed onto montmorillonite. Although the sorption capacity of montmorillonite is much less than that for activated carbon, our data indicate that methane adsorbed on clay minerals could contribute a significant portion of gas-in-place in an unconventional reservoir, considering that clay minerals constitute a major part of a shale gas reservoir.

#### **Task 4.0 Development of Equation of State (EOS) for CH<sub>4</sub>-CO<sub>2</sub>-H<sub>2</sub>O in Nanopores**

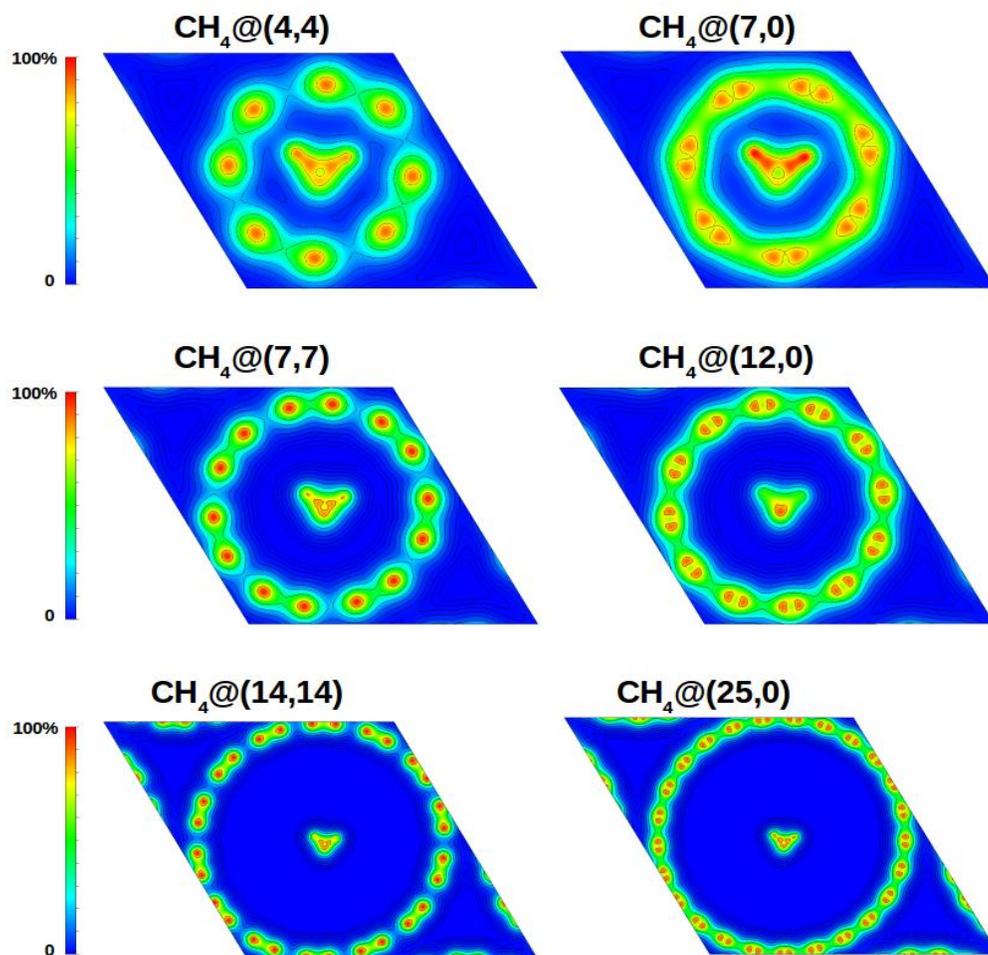
This task focuses on the data interpretation and synthesis using both molecular dynamics simulations and the density functional theory (DFT) (including the classic DFT). The modeling work in the first quarter was aimed to set up appropriate modeling systems and test the modeling methodology to be employed. Some of the results are summarized below.

1) 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 the structural optimization of the following structures:

- **Pristine 3-D periodic single-walled carbon nanotubes (SWCNT):** Calculations were carried out for both armchair- and zigzag-type SWCNTs with similar diameters, i.e. (4,4) (5.42 Å diameter), (7,0) (5.48 Å diameter), (7,7) (9.49 Å diameter), (12,0) (9.39 Å diameter), (14,14) (18.98 Å diameter) and (25,0) (19.57 Å diameter).

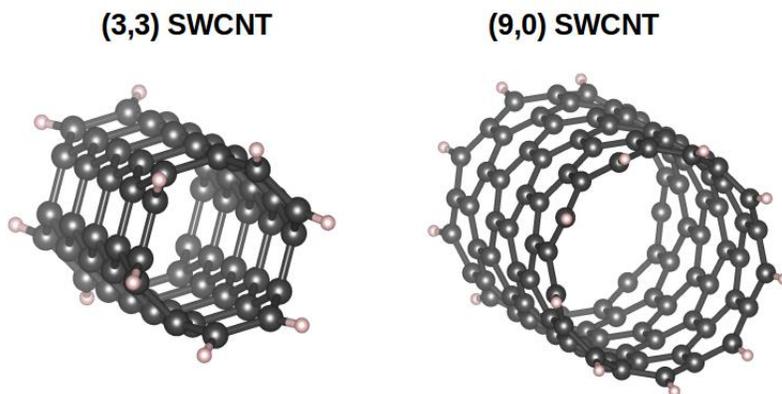
- **CH<sub>4</sub>@SWCNTs**: The structure and interaction of one CH<sub>4</sub> molecule inside (4,4), (7,0), (7,7), (12,0), (14,14) and (25,0) SWCNTs was investigated; charge distribution maps of the CH<sub>4</sub>@SWCNTs were obtained (Figure 3).

These calculations provide valuable information about the interaction of CH<sub>4</sub> and CO<sub>2</sub> with the confining wall of nanopores.



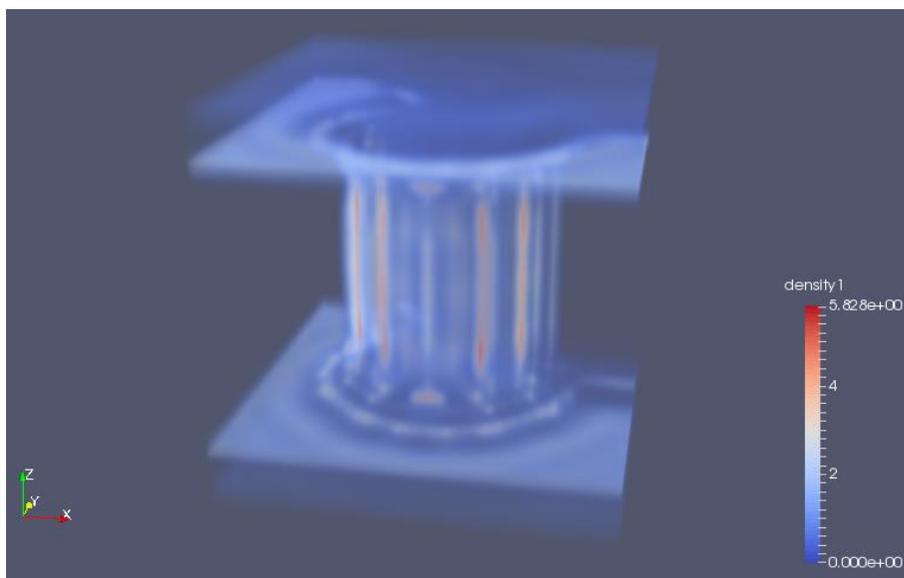
**Figure 3.** Models for Charge density maps of one CH<sub>4</sub> molecule inside (4,4), (7,0), (7,7), (12,0), (14,14) and (25,0) SWCNTs

2) Model structures of finite-size SWCNTs terminated by hydrogen atoms (Figure 4) have been built for armchair SWCNTs from (3,3) to (8,8) and zigzag SWCNTs from (4,0) to (9,0) and corresponding input files have been prepared for DFT calculations using the Gaussian09 software to be carried out at TAMU.



**Figure 4.** Model structures of finite-length (3,3) and (9,0) tubules with terminal dangling bond saturated by hydrogen

3) Test calculations have been carried out with a classic density functional theory (cDFT) as implemented in the Tramonto software for a 3D fluid flow in a cylindrical pore model (Figure 5). The cDFT provides a key formulation to bridge microscopic understanding to macroscopic sorption measurements. Tramonto is a cDFT software package developed at Sandia.



**Figure 5.** Fluid density functional theory (cDFT) calculation of 3D fluid flow in a cylindrical pore model

### 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. Also the measurements will be expanded to the systems with other CH<sub>4</sub>-CO<sub>2</sub> mixture ratios.
- Obtaining a preliminary data set for high pressure and high temperature sorption measurements.
- Starting a cDFT formulation for CH<sub>4</sub>-CO<sub>2</sub> sorption in nanopores and trying to apply the model to low pressure measurement data.

### 4.0 REFERENCES

- Bruusgaard, H., Beltrán J.G., Servio, P., 2010. Solubility measurements for the CH<sub>4</sub> + CO<sub>2</sub> + H<sub>2</sub>O system under hydrate-liquid-vapor equilibrium. *Fluid Phase Equilibria* 296, 106-109.
- Duan, Z.-H., Moller, N., Weare, J.H., 1992. An equation of state for the CO<sub>2</sub>-CH<sub>4</sub>-H<sub>2</sub>O system: II. Mixtures from 50 to 1000°C and 0 to 1000 bar. *Geochimica et Cosmochimica Acta* 56, 2619-2631.
- Price, L. C., 1981. Methane solubility in brines with application to the geopressured resource. *Proceedings of the 5th Geopressured and Geothermal Energy Conference* 5, 205-214.
- Ramboz, C., Schnapperd, D., and Dubessy, J., 1985. The *P-V-T-X-fO<sub>2</sub>* evolution of CO<sub>2</sub>-CH<sub>4</sub>-H<sub>2</sub>O-bearing fluid in a wolframite vein: Reconstruction from fluid inclusion studies. *Geochimica et Cosmochimica Acta* 49, 205-219.
- Wang, Y., 2014. Nanogeochemistry: Nanostructures, emergent properties and their control on geochemical reactions and mass transfers. *Chemical Geology* 378-379, 1-23.