

Quarterly Report

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

Feb. 2, 2016

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.



Figure 1. Kerogens isolated from Woodford and Marcellus shales.

2.0 ACCOMPLISHMENTS

Experimental Work

In the previous quarter, we purchased two more shale core samples: 2 kg of Marcellus sample and 2 kg of Woodford sample. In this quarter, we isolated kerogens from the additional shale core samples (Figure 1). These two samples plus the previous one represent a wide range of maturity of shale. We performed the Fourier Transform Infrared Spectroscopy (FTIR) analysis of three kerogens isolated. The FTIR data show distinct characteristics for three different maturity kerogens (Figure 2).

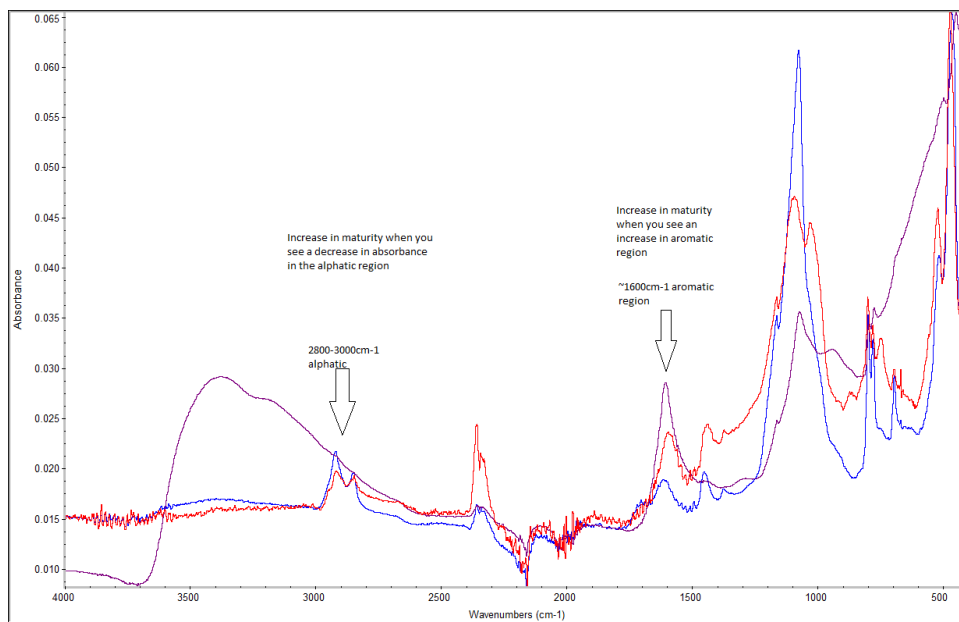


Figure 2. FTIR spectra of kerogens isolated from Mancos, Woodford and Marcellus shales.

Modeling Work

Molecular modeling including Monte Carlo (MC) and molecular dynamics (MD) simulations were implemented to study the adsorption and transport properties of methane within a condensed kerogen phase. The simulated kerogen represents type II-D kerogen (post mature, gas formation zone), which is similar to that found in Barnett shale (Ungerer et al., 2015) (Figure 3). The condensed kerogen consists of 24 kerogen molecules (Figure 3) and can be simulated at different temperature and pressure.

To study the flow of methane in complex kerogen structure we conducted an extraction simulation (Figure 4) mimicking the field production where natural gas is withdrawn from a reservoir. In our simulation, methane was withdrawn from the porous structure by deleting the methane molecules that move into a defined region (large purple sphere). Because of the pressure gradient (due to deleting molecules) and thermal motion methane molecules migrate

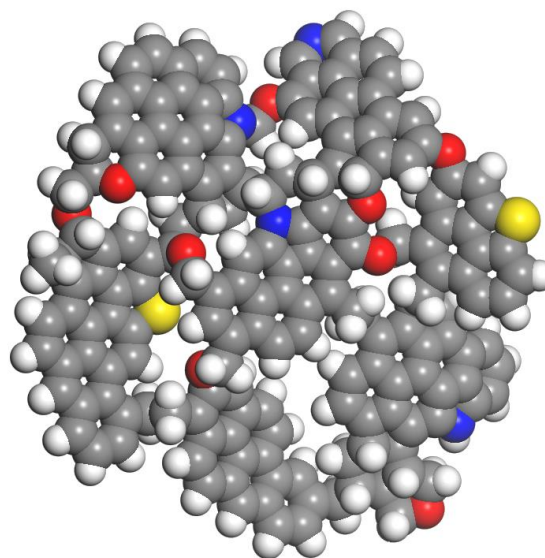
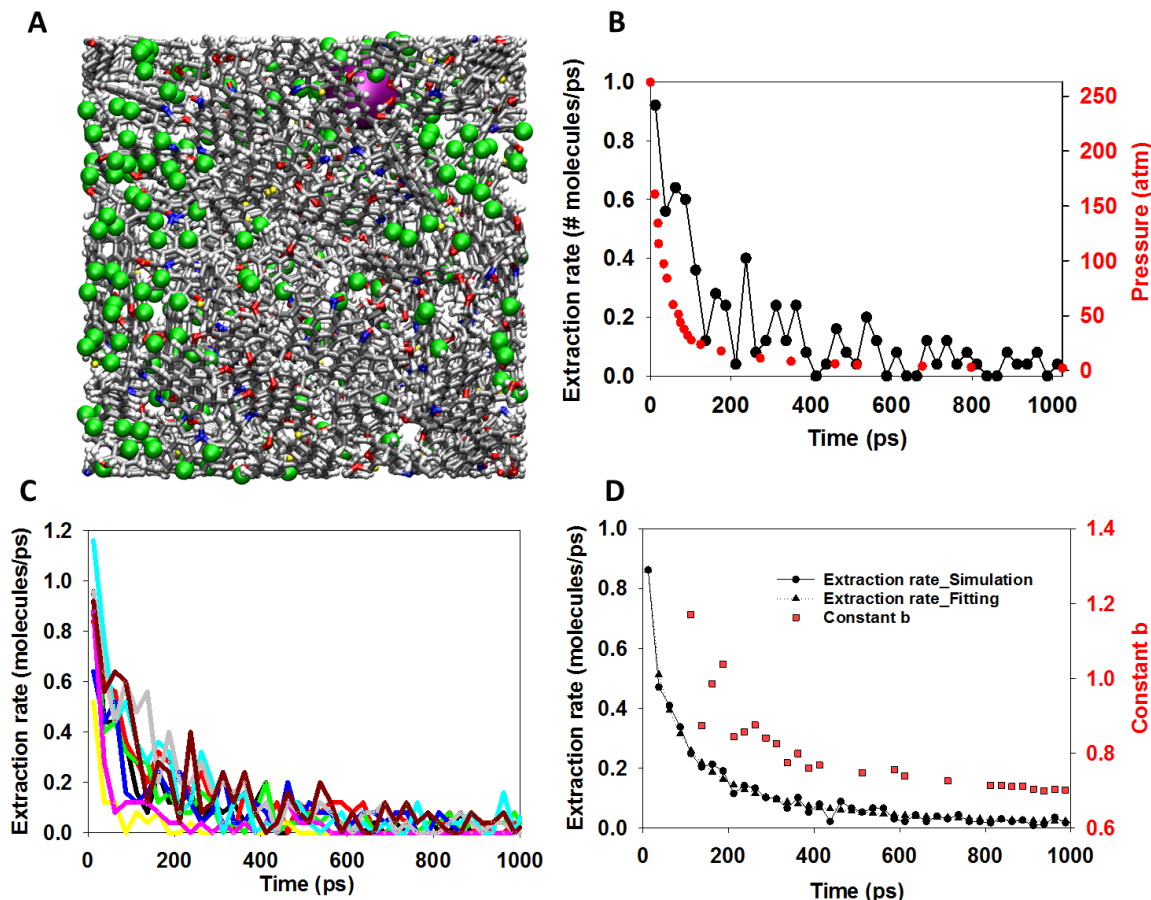


Figure 3. Snapshot illustrating kerogen molecule. Silver, white, red, blue, and yellow spheres represent carbon, hydrogen, oxygen, nitrogen, and sulfur atoms, respectively

into the defined region if the molecule is not trapped in the isolated pore. This method allows us to study (i) flow of methane in porous materials as the system pressure gradually decreases because of extraction, (ii) extraction rate as a function of time, (iii) the effect of adsorption, desorption, diffusion and nanoporous structure on the extraction rate. This method also eliminates one of the most serious troubles encountered in other non-equilibrium MD simulations in which large, unrealistic forces are usually used to induce flow. One set of simulations is shown in Figure 4. The result indicates that the extraction rate significantly reduces in a short period of time after the start of extraction. We are now exploring a possible implication of the result to actual wellbore production decline. One manuscript is completed on



the simulation result.

Figure 4. Molecular dynamics (MD) simulation of methane extraction from kerogen.

3.0 OUTLOOK

The next step will include:

- Expanding the low pressure sorption measurements to a full cycle of adsorption-desorption measurements.

- Performing 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 (CH₄-CO₂-H₂O).
- Starting a cDFT formulation for CH₄-CO₂ sorption in nanopores and trying to apply the model to both low and high pressure measurements.

4.0 REFERENCES

Ungerer et al., 2015. Molecular modeling of the volumetric and thermodynamic properties of Kerogen: Influence of organic type and maturity, *Energy & Fuels*, 29, 91-105.

Wang, Y., 2014, Nanogeochemistry: Nanostructures, emergent properties and their control on geochemical reactions and mass transfers. *Chemical Geology*, 378-379, 1-23.

Acknowledgment: Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000. The work is supported by National Energy Technology Laboratory.