SAND2018-13468R

Quarterly Report

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

October 31, 2018

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). 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

Understanding gas sorption-desorption hysteresis: Additional gas sorption experiments were conducted on kerogen samples with different maturities at 27°C and 57°C. Both mature kerogen and overmature kerogen materials adsorb CO_2 more than twice as much as immature kerogen. However, after normalization to their corresponding surface areas, immature kerogen adsorbs more CO_2 and CH_4 compared to mature and over-mature kerogen per unit surface area. Both surface area and function groups are important factors controlling gas sorption. It is important to notice the existence of significant hysteresis in gas sorption-desorption measurements (Figure 1). To quantify the effect of hysteresis, we have calculated the percentages of hysteresis for each measurement as shown in Figure 2 and Table 1. It has been found that the hysteresis percentage increases with temperature and CO_2 has a higher hysteresis percentage that CH_4. The results seem contradictory to the existing capillary condensation and pore neck snapping mechanism. An alternative explanation is that this hysteresis is probably caused by "plastic" swelling of kerogen pores due to gas sorption (Figure 3).

Table 1. Hysteresis percentages

Hysteresis loop %		BET surface area (m^2/g)	Pressure from 0 to 1 atmosphere					Pressure: 0 to 100 bar	
			N_2 77K	27 °C CO_2	57 °C CO_2	27 °C CH_4	57 °C CH_4	27 °C CH_4	57 °C CH_4
Marcellus	immature	54	21.3%	18.6%		4.8%			
	mature	205	38.1%	9.5%		0.9%			
	overmature	301.5	14.0%	27.1%	44.8%	6.2%	11.8%	2.8%	3.5% / 5.6%*
Woodford	immature	50	12.6%	16.2%	23.0%	2.9%	4.3%		
Carbon Black		31	7.9%	74.9%		9.5%			
Activated carbon		474	9.6%	5.2%		3.1%			

* from 0 to 72.5 bar and curves overlap from 72.5 to 100 bar

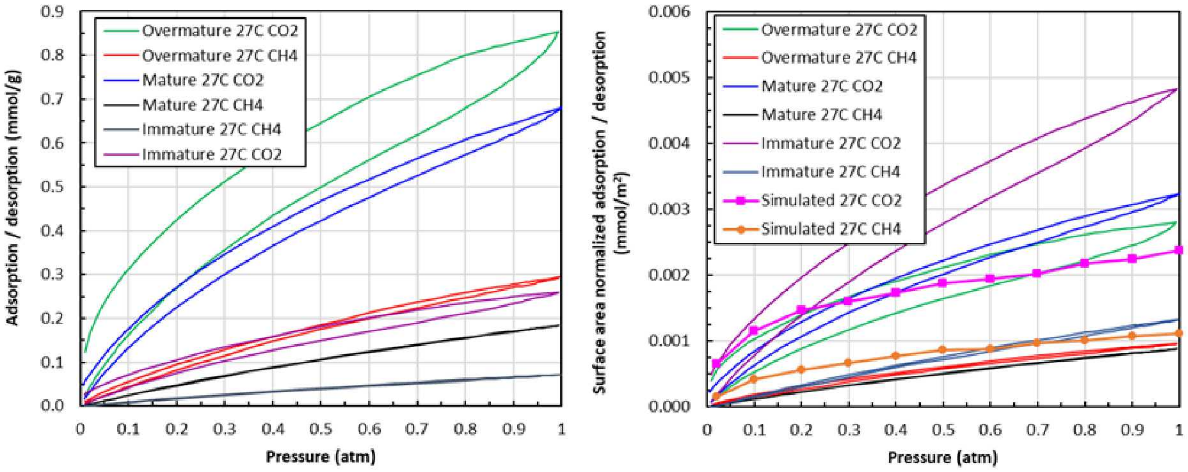

Figure 1. Adsorption and desorption curves for CO_2 and CH_4 at 27 °C for Marcellus shale kerogen with different maturity (immature, mature and over-mature). In the right panel, the adsorption / desorption is normalized by their corresponding surface areas. The curves with dots are the gas sorption isotherms predicted from molecular dynamics (MD) simulations. Note that the predicted sorption isotherms are in good agreement with the measurements.

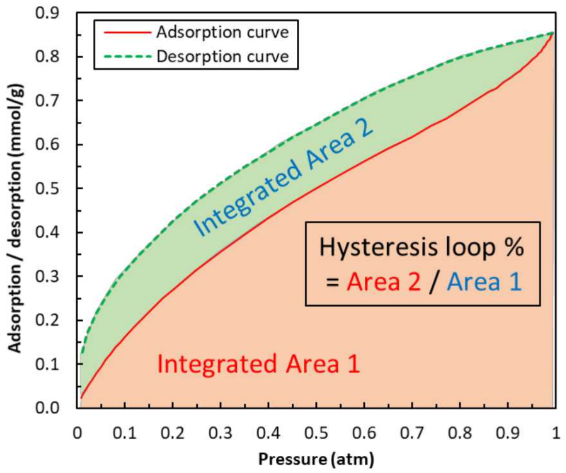

Figure 2. Quantification of sorption-desorption hysteresis.

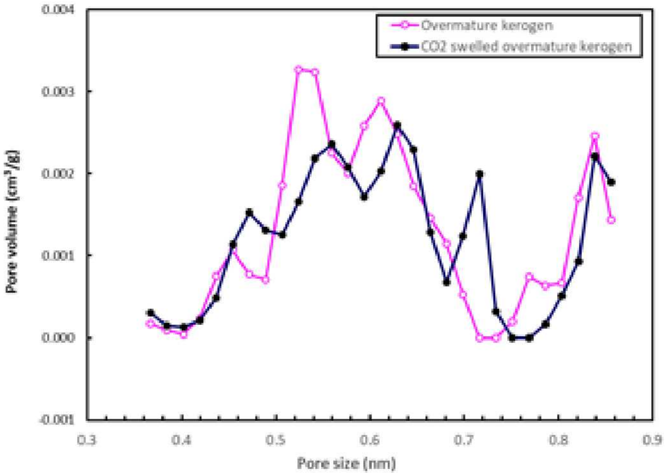

Figure 3. Pore swelling induced by CO_2 sorption. Kerogen pores swelled irreversibly after gas sorption.

Further comparison of calculated FTIR spectra of kerogen with measurements: Using density functional theory (DFT), we previously showed the existing kerogen molecular models might be inadequate in representing actual kerogen molecular structures (Weck et al., 2017). One of the ongoing efforts is to develop new kerogen models that account for all compositional, structural and spectroscopic measurements. We have performed additional DFT and molecular dynamics (MD) simulations to calculate FTIR spectra for different size kerogen clusters for both over-mature (Marcellus) and immature (Woodford) kerogens. The objective of these calculations is twofold: (1) to test if the force field parameters used in MD simulations are consistent with ab-initio DFT calculations, and (2) to further test the adequacy of existing kerogen models. The results are shown in Figure 4. The results indicate that there are some discrepancies between DFT and MD predictions for the same small kerogen cluster, implying that an improvement to the existing force field parameters may be needed. The results also show that there are significant gaps exist between the MD-predicted FTIR and the measurements for both bulk over-mature and immature kerogens, further confirming our earlier assertion that the existing kerogen models may be inadequate in representing actual kerogen molecular structures.

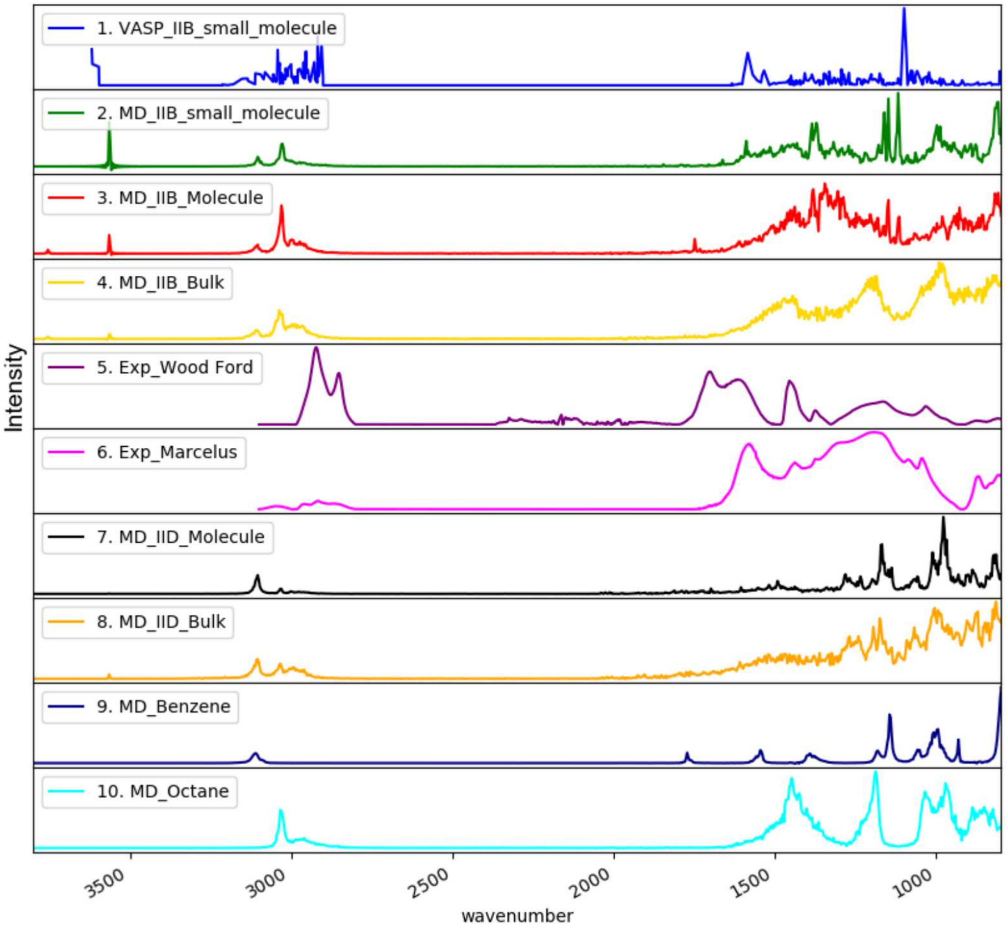

Figure 4. FTIR spectrum calculated from DFT (curve 1) and MD simulations (curves 2, 3, 4, 7 and 8) for different size kerogen clusters as compared to experimental measurements (curves 5 and 6).

Publications since the inception of the project:

Xiong, Y., Wang, Y. & Olivas, T. (2015) Experimental Determination of P-V-T-X Properties and Sorption Kinetics in the CO_2-CH_4-H_2O System under Shale Gas Reservoir Conditions: Part One, P-V-T-X Properties, Sorption Capacities and Kinetics of Model Materials for CO_2-CH_4 Mixtures to 125°C , High Temperature Aqueous Chemistry, HiTAC-II Workshop, Heidelberg, April 16, 2015.

Ho, T. A., Criscenti, L. J. & Wang, Y. (2016) Nanostructural control of methane release in kerogen and its implications to wellbore production decline. Scientific Reports 6, 28053; doi: 10.1038/srep28053.

Weck, P. F., Kim, E. & Wang, Y. (2016) van der Waals forces and confinement in carbon nanopores: Interaction between CH_4, COOH, NH_3, OH, SH and single-walled carbon nanotubes. Chem. Phys. Lett. 62, 22-26.

Cristancho, D., Akkutlu, I.Y., Criscenti, L.J., Wang, Y. (2016) Gas storage in model kerogen pores with surface heterogeneities, SPE-180142-MS, DOI: 10.2118/180142-MS.

Wang, Y. (2017) On subsurface fracture opening and closure. J. Petrol. Eng. 155, 46-53.

Wang, Y. (2018) From nanofluidics to basin-scale flow in shale: Tracer investigations, In: Shale Subsurface Science and Engineering (in press, book chapter)

Weck, P. F. Kim, E., Wang, Y. et al. (2017) Model representation of kerogen structures: An insight from the density functional theory. Scientific Reports, 7, DOI:10.1038/s41598-017-07310-9.

Ho, T. A., Greathouse, J. A., Wang, Y, and Criscenti, L. J. (2017) Atomistic structure of mineral nano-aggregates from simulated compaction and dewatering. Scientific Reports, 7, 15286.

Ho, T. A., Wang, Y., Criscenti, L. J. & Xiong, Y. (2017) Differential retention and release of CO_2 and CH_4 in kerogen nanopores: Implications to gas extraction and carbon sequestration. Fuel, 220, 1-7.

Ho, T. A. Wang, Y. and Criscenti, L. J. (2018) Chemo-mechanical coupling in kerogen gas adsorption/desorption. Phys. Chem. Chem. Phys., 20, 1239.

Ho, T. A, Wang, Y. et al. (2018) Supercritical CO2-induced atomistic lubrication for water in a rough hydrophilic nanochannel. Nanoscale (online now)

Wang, Y. et al. (2019) Nanogeochemistry of unconventional oil/gas reservoirs (invited paper by Chemical Geology).

3.0 OUTLOOK

The next step will include:

- 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.
- Based on the existing experimental and modeling results to formulate new gas disposition and release model for well-borehole production.

4.0 REFERENCES

Weck, P. F., Kim, E., Wang, Y., Kruichak, J. N., Mills, M. M., Matteo, E. N., and Pellenq R. J.-M. (2017) Model representations of kerogen structures: An insight from density functional theory calculations and spectroscopic measurements. *Scientific Reports* **7**, 41598; DOI:10.1038/s41598-017-07310-9.

Acknowledgment: Sandia National Laboratories is a multi-mission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525. This work is supported by National Energy Technology Laboratory.