SAND2019-13223R

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

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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

Development of New Kerogen Structural Models: As we pointed out early, the existing kerogen structural models are not adequate to capture the both chemical and structural properties of kerogens from different geochemical environments and maturities (Weck et al., 2017). As part of this year work scope, we are starting to construct new kerogen structure models using detailed chemical and spectroscopic measurements assisted with molecular modeling. Based on the data provided by West Virginia University (WVU), we have completed the construction of the first new structural model for a mature kerogen from the Marcellus formation. We first constructed a candidate molecular structure (Figure 1) and then used Ab Initio molecular dynamics (AIMD) to check if the constructed structure is physically feasible and consequently optimized the structure.

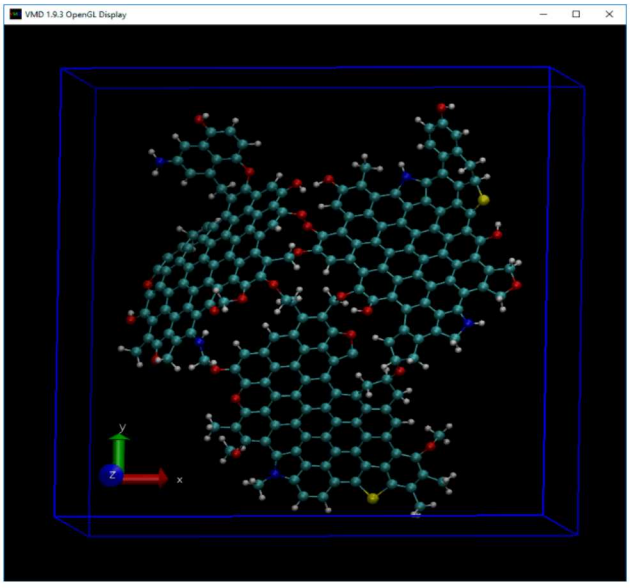

Figure 1. Ball-and-stick representation of candidate structure for 3D-periodic MarK-type model build from classical force-field simulations, based on structural kerogen cluster parameters provided by UWV collaborators.

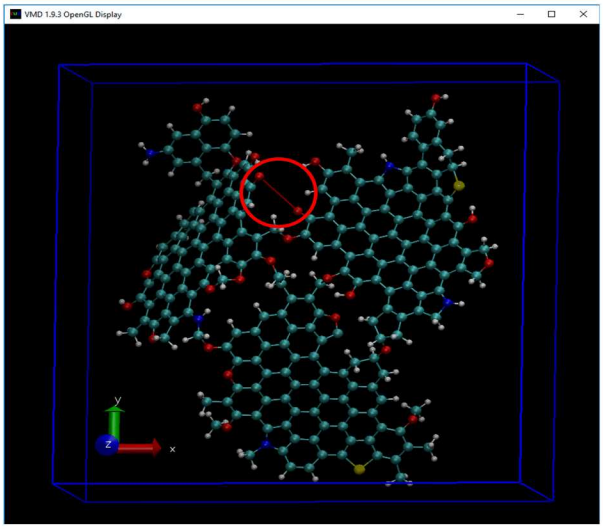

Figure 2. Ball-and-stick representation of candidate structure for 3D-periodic MarK-type model built from classical force-field simulations, after reoptimization at 300 K with Ab Initio Molecular Dynamics (AIMD) simulations. The red circle indicates the presence of an unphysical O-O bond in the initial model.

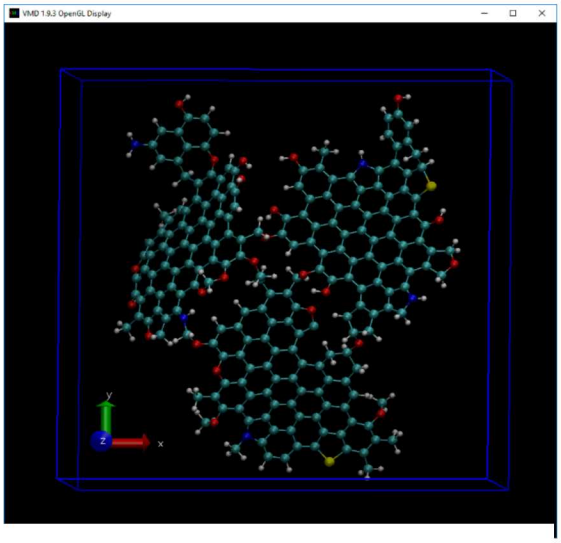

Figure 3. Ball-and-stick representation of the optimized structure for 3D-periodic MarK-type model after modification and reoptimization with Ab Initio Molecular Dynamics (AIMD)

we carried out Ab Initio Molecular Dynamics (AIMD) simulations using the VASP density functional theory code to test the stability of an initial MarK-type model built from classical force-field simulations, based on structural kerogen cluster parameters provided by UWV collaborators (cf. Figure 1). AIMD simulations at 300 K indicated that an unphysical O-O bond was present in the initial model, resulting in a kerogen structure with non-zero magnetic moment due to the creation of C-O dangling bonds (cf. Figure 2). Using these findings from AIMD simulations, a new corrected model was proposed, where this unphysical O-O bond in the initial model was replaced with O-H bonds and reoptimized at 300 K with AIMD. The new candidate structure was reoptimized (see Figure 3) and will be used as a chemically correct building-block in large scale classical force-field MD simulations to be performed with the LAMMPS code. Our result thus demonstrates a new approach to constructing kerogen structures by integrating chemical/spectrocopic analyses with molecular simulations.

With the approach we have developed and by leveraging the comprehensive data set collected at the WVU, we are now in a process to build a suite of representative molecular structures for kerogens from diverse environments. We will then use these molecular structures to evaluate their capabilities for shale gas/oil disposition and transport, to clarify a potential control of kerogen structure on field production. Such a control seems to exist based on existing field observations.

3.0 OUTLOOK

The next steps will include:

- With the developed approach, additional molecular structures will be constructed and evaluated for their gas sorption/transport capacities.
- 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.
- More MD simulations will be performed on different hydrocarbon fluids and their phase separation in nanopores.
- Based on the existing experimental and modeling results to formulate new gas disposition and release model for well production.

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References:

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