Consortium for Processes in Porous Media
23rd Annual Meeting

Rice University, Houston, TX
April 19th, 2019
# Meeting Agenda: Morning Session

**Friday, April 19th**

<table>
<thead>
<tr>
<th>Time</th>
<th>Session</th>
<th>Speaker/Presenter</th>
</tr>
</thead>
<tbody>
<tr>
<td>8:15 am</td>
<td>Opening Speech</td>
<td>Dr. George Hirasaki</td>
</tr>
<tr>
<td>8:30 am</td>
<td>Multiscale Analysis of Reservoir Rock Correlating Pore Scale Information to Reservoir Scale Inputs</td>
<td>Dr. Mark Knackstedt</td>
</tr>
<tr>
<td>9:00 am</td>
<td>Influence of Asphaltene Structure on Deposition</td>
<td>Dr. Sibani Lisa Biswal</td>
</tr>
<tr>
<td>9:20 am</td>
<td>Extended Surface Complexation Model for both Synthetic Calcite and Natural Carbonates in Mixed Electrolytes in A Wide Salinity Range for Wettability Study</td>
<td>Mr. Jin Song</td>
</tr>
<tr>
<td>9:40 am</td>
<td>Retention of AOS1416 Surfactant in Berea Sandstone Rock</td>
<td>Mr. Reza Amirmoshiri</td>
</tr>
<tr>
<td>10:00 am</td>
<td>CO2 Foam Mobility Control Pilot Test in East Seminole Reservoir</td>
<td>Mr. Michael (Guoqing) Jian</td>
</tr>
<tr>
<td>10:20 am</td>
<td>Coffee Break &amp; Poster Session</td>
<td></td>
</tr>
<tr>
<td>10:45 am</td>
<td>CO2 Foam Mobility Control Process for High Temperature, Ultrahigh Salinity, High Pressure Carbonate Reservoir</td>
<td>Mr. Leilei Zhang</td>
</tr>
<tr>
<td>11:05 am</td>
<td>Capillary Pressure Probe to Investigate Foam Stability in Porous Media</td>
<td>Mr. Eric Vavra</td>
</tr>
<tr>
<td>11:25 am</td>
<td>Alkali-Surfactant Foam EOR Process for Heavy Oil Recovery: Phase Behavior and Pore-Scale Experiments</td>
<td>Ms. Eric Vavra</td>
</tr>
<tr>
<td>11:45 am</td>
<td>Lunch</td>
<td></td>
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<tr>
<td>12:30 pm</td>
<td>Poster Session</td>
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<tr>
<td>Time</td>
<td>Session</td>
<td></td>
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<tr>
<td>1:00 pm—1:20 pm</td>
<td>Estimation of the Permeability of an Unconventional Formation Core by History Matching the Saturation with CO₂ Mr. Zeliang Chen</td>
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<tr>
<td>1:20 pm—1:40 pm</td>
<td>Frequency Dependence of NMR Relaxation of Polymers and Bitumen Dr. Phillip Singer</td>
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<tr>
<td>1:40 pm—2:00 pm</td>
<td>Evaluation of Light Hydrocarbon Composition and Pore Size in Organic Rich Chalks Mr. Xinglin Wang using NMR Core-Log Integration</td>
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<tr>
<td>2:00 pm—2:20 pm</td>
<td>EOR Evaluation and NMR Characterization for Unconventional Formation (Bakken) Mr. Mohamed Mohamed</td>
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<tr>
<td>2:20 pm—2:40 pm</td>
<td>Molecular Simulation of NMR Relaxation Behavior of Fluids in Polymer-Alkane Mixtures and Model Nano-porous Systems: Implication for Understanding Fluids in Shale Dr. Dilipkumar Asthagiri</td>
<td></td>
</tr>
<tr>
<td>2:40 pm—3:00 pm</td>
<td>Apolar Behavior of Hydrated Calcite Surface Assists in Naphthenic Acid Adsorption Mr. Arjun Parambathu</td>
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<tr>
<td>3:00 pm—3:20 pm</td>
<td>Molecular Dynamics Simulations of Oil and Brine in a Calcium Carbonate Nano-pore: Toward Predicting Wettability Alteration Mr. Mohamed Al Hosani</td>
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<tr>
<td>3:40 pm—4:00 pm</td>
<td>Comments and Recommendations from Consortium Members Dr. George Hirasaki</td>
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<tr>
<td>4:00 pm—4:30 pm</td>
<td>Lab Tour</td>
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</tbody>
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Introduction

Dr. George J. Hirasaki
A.J. Hartsook Chair Professor in Chemical Engineering (gjh@rice.edu)

Abstract
Welcome to the 23rd annual meeting of the Consortium on Processes in Porous Media. We had our first meeting in 1996. This was a year after Shell and Schlumberger purchased a MARAN II NMR spectrometer and donated it to us, so we could measure NMR properties of fluids in rock samples. We have now expanded to include enhanced oil recovery. In the past we have also done research on methane hydrates and asphaltene deposition. Hear what we have done over the past year. We hope to hear from you about the directions that you think we should be doing going into the future.

Notes
Presentations

Friday, April 19th: 8:30 am — 9:00 am

Multiscale Analysis of Reservoir Rock
Correlating Pore Scale Information to Reservoir Scale Inputs

Dr. Mark Knackstedt
Professor, Applied Mathematics
Australian National University
(mark.knackstedt@anu.edu.au)

Abstract

3D pore scale imaging and computation, allows an unprecedented quantitative understanding of the pore scale at which all reservoir processes operate. Projects have historically focused on applications to laboratory core analysis – characterizing experimental details at the pore scale and used to explain uncertainties and trends from laboratory measurements (e.g., issues with heterogeneity, wettability, distribution of remaining oil saturation, EOR processes). We describe the predictive capabilities of modelling by comparing, on a pore by pore basis, the simulated fluid distributions with the corresponding micro-CT imaged distributions. Simulated and experimental fluid distributions are in good agreement for both drainage and imbibition. Models enable sensitivity studies of the impact of wettability and on the magnitude of recovery.

We describe the extension of 3D imaging technology to reliably derive and predict properties along continuous lengths of core material and to integrate the data with other forms of data at increasingly larger scales (log characterization, geomodels and ultimately reservoir simulators). We describe further steps being undertaken to create value via methods to image larger quantities of core– defining appropriate representative scales for different rock types and developing methods to efficiently make continuous calculations of properties – from the pore to the reservoir scale.

Notes
Abstract
I will elucidate the deposition dynamics of various asphaltene sub-fractions in a porous media microfluidic model. Fractionation of crude oil samples report a mixture of abundant island and archipelago motifs. Deposition rate increases when the compositional ratio archipelago/island motif increases, whereas asphaltenes appear to exhibit stronger aggregation for fractions which composition is uniformly island-type. In general, the deposition rate is consistent with the amount of precipitated asphaltenes. However, the correlation is not merely a linear one and the pore-scale morphology changes even with similar deposition rates. Estimated diffusivity, the relative ratio of convection and diffusion, and fluid flow profiles are used to explain the dynamic growth of the deposit at the pore scale.
Presentations

Friday, April 19th: 9:20 am — 9:40 am

Extended Surface Complexation Model for both Synthetic Calcite and Natural Carbonates in Mixed Electrolytes in A Wide Salinity Range for Wettability Study

Mr. Jin Song
PhD Graduate Student, 4th Year (js110@rice.edu)

Abstract
In this work we developed an extended Surface Complexation Model (SCM) that successfully fits all tested zeta potential data (63 in total) of synthetic calcite and three natural carbonates in brines with divalent ions at a wide range of ionic strengths (0.001M~0.5M). To develop this extended model, our previous reported SCM is first optimized by incorporating zeta potential of synthetic calcite in a wide range of ionic strength (0.001M to 0.5M) along with previously published data for parameter refitting. Then the model is extended to fit the zeta potential of natural carbonates by adding surface reactions for impurities such as silica and organic-based carboxylic acids. The coverage of the organic impurities is found to be essential for explaining why the zeta potential of natural carbonates is more negative compared to synthetic calcite. Naphthenic acid (assumed to have 1 carboxylic group) and humic/fulvic acid (assumed to have 6 carboxylic groups) are tested in the model calculation as possible sources of surface impurities to demonstrate the effect of the number of carboxylic groups in the acid molecule. Finally, the effect of a humic acid pre-treatment on the zeta potential of synthetic calcite is investigated experimentally to verify the assumption.

Notes
Abstract

In this study, we investigate the retention of AOS$_{1416}$ surfactant in Berea sandstone cores under different wettability states and surface redox potentials. Surfactant adsorption levels are determined by analyzing the effluent history data with a dynamic adsorption model assuming Langmuir isotherm. We demonstrate that changing the surface wettability from water-wet to neutral-wet increases the surfactant adsorption significantly. Surfactant adsorption in the neutral-wet core takes place in parallel with the extraction of the adsorbed crude oil components from the rock surface, as a sign of wettability alteration. We further show that changing the surface redox potential from an oxidized to a reduced state decreases the adsorption levels to some extent. This is attributed to the removal of ferric ions, as a potential surfactant adsorption sites, from sandstone surface during core reduction. Findings from this study suggest that laboratory surfactant adsorption tests need to be conducted under controlled surface wettability and redox state. This is crucial for obtaining adsorption levels that would be more representative of reservoir conditions.
CO₂ Foam Mobility Control for Pilot Test in East Seminole Carbonate Reservoir

Mr. Michael (Guoqing) Jian
PhD Graduate Student, 6th Year (gj4@rice.edu)

Abstract
This presentation describes the laboratory investigation of a nonionic surfactant C_{12-14}E_{22} (L24-22) for CO₂ foam mobility control pilot test in East Seminole carbonate reservoir.

An HPLC-ELSD method was developed for characterizing the surfactant adsorption and stability. The surfactant was found to have low adsorption on carbonate minerals. Adsorption amount of L24-22 on dolomite materials does not change in the presence of ES Brine and CO₂.

L24-22 degrades at high temperature in the oxidizing environment. An oxygen scavenger called carbohydrazide (rather than sulfite) was found to be effective to control the stability of L24-22 at elevated temperature. A phosphonate scale inhibitor was studied and found to be compatible with the oxygen scavenger and surfactant.

Foam transport process in the absence and presence of crude oil was studied. Foam parameters based on the STARS foam model were obtained based on the steady-state experiments. Results show strong CO₂ foam forms in the absence and the presence of East Seminole crude oil in the bulk foam and core flooding tests. Emulsion was found during oil fractional flow test, but there is no core plugging observed.

Notes
CO₂ Foam Mobility Control Process for High Temperature, Ultrahigh Salinity, High Pressure Carbonate Reservoir

Mr. Leilei Zhang
PhD Graduate Student, 5th Year (lz34@rice.edu)

Abstract
An amine-based foaming agent, Duomeen CTM (C₁₂₋₁₄N(CH₃)C₃N(CH₃)₂), and oil effect on supercritical CO₂ foam transport are evaluated for high pressure, high temperature, and ultrahigh salinity carbonate reservoir. The CTM solubility in the ultrahigh salinity formation brine (FB) is evaluated as a function of temperature and pH. When CTM surfactant is directly added to FB, it is not fully soluble, but CTM is soluble when the pH is adjusted to or below the critical pH. The thermal stability of CTM at pH 4 was demonstrated at 120 °C in the presence of oxygen scavenger. The adsorption of CTM was evaluated on pure calcite and reservoir material. The adsorption on calcite was low but was moderate on reservoir carbonate, possibly caused by the presence of siliceous minerals. The phase behavior of CTM solution with crude oil was Winsor Type I, indicating that the surfactant is preferentially propagate with aqueous phase in the presence of oil. The CTM foamability was evaluated in Indiana limestone cores: (1) in the absence oil in water wet core, (2) in presence of residual oil in water wet cores, and (3) in the presence of residual oil in oil wet cores. Only slight impairment in foam strength was observed in the presence of 13% residual oil under water-wet condition without observing minimum pressure gradient (MPG). Interestingly, with 42% residual oil saturation in oil-wet core, an MPG of 3 psi/ft was observed for foam generation, and foam strength at steady state was impaired.

Notes
Capillary Pressure Probe to Investigate Foam Stability in Porous Media

Mr. Eric Vavra
PhD Graduate Student, 4th Year (edv1@rice.edu)

Abstract
Gas-water capillary pressure $P_{cgw}$ of foam flowing through porous media was first measured in 1987 using a newly invented capillary pressure probe (Khatib et. al.). In the study, foam quality scan experiments were conducted at a constant gas flow rate with increasing foam quality until a characteristic plateau value of $P_{cgw}$ was reached. This value was defined as the limiting capillary pressure, denoted as $P_c^*$. Above this capillary pressure, the foam coarsens significantly which is accompanied by an associated decrease in the pressure gradient. $P_c^*$ depends on gas velocity, permeability, and surfactant formulation, but the mechanisms for these dependencies have yet to be fully explained. A better understanding of $P_c^*$ is important for incorporating this crucial parameter into foam flow simulators.

Recently, we have reconstructed the capillary pressure probe at Rice University. With this one-of-a-kind instrument, the unanswered questions relating of $P_c^*$ will be explored. In this presentation, the preliminary details of the probe construction, validation, and measurements will be discussed.

Notes
Alkali-Surfactant Foam EOR Process for Heavy Oil Recovery: Phase Behavior and Pore-Scale Experiments

Mr. Eric Vavra  
PhD Graduate Student, 4th Year (edv1@rice.edu)

Abstract
Recent works have predicted an increase in the role of heavy oil in the global energy landscape. The highly viscous nature of heavy crude oil poses a challenge for recovery, and EOR methods are typically necessary to reduce to apparent viscosity during production. Alkali Surfactant (AS) flooding is one such method that has been effective at recovering heavy oil. AS involves an alkali component which reacts with the natural naphthenic acid components in the crude oil to produce soaps. A synergistic synthetic surfactant component is also present in this type of chemical flood. Several mechanisms, such as wettability alteration, interfacial tension reduction, and emulsion production, play a role in this EOR method; however, poor mobility control has been identified as the most prominent shortcoming of AS flooding for heavy oil. Foaming the AS solution is one method for improving mobility control. When AS and foam are used together, the process is called alkali surfactant foam (ASF) flooding. A critical component of a successful ASF flood is proper formulation and knowledge of the phase behavior of a particular surfactant system with the specific crude oil to be recovered. Optimal formulation of a chemical system is necessary to achieve the desired phase behavior. This presentation will cover our work in developing a method to characterize the ASF process by phase behavior and micromodel flow studies.
Estimation of the Permeability of an Unconventional Formation Core by History Matching the Saturation with CO$_2$

Mr. Zeliang Chen
PhD Graduate Student, 5th Year (zc24@rice.edu)

Abstract
The ultralow permeability makes the production from unconventional reservoirs challenging. Therefore, the permeability estimation is of vital importance in reservoir engineering. The existing methods, including the steady-state and unsteady-state approaches, are either complicated in terms of set-ups and interpretations or time-consuming. We propose a novel unsteady-state method to determine the permeability by transient-pressure history matching. On the experimental side, the investigated core undergoes 1D constant-pressure CO$_2$-injection and/or production experiments. We monitor the transient pressure for history matching. We also calculate the rock porosity and rock porosity compressibility using independent volume measurements. On the simulation side, the transient pressure history is simulated using real-gas pseudo pressure to deal with non-linear pressure-dependent density and viscosity. The free parameter, permeability, in the simulation is adjusted for history matching to determine the rock permeability. Our simulation is able to generate high-quality transient-pressure history with the capability of handling the phase transition of CO$_2$ for history matching. The permeability estimated by this unsteady-state method is validated by the standard steady-state method. The advantages of this unsteady-state approach are: 1) simple set-ups; 2) no complicated interpretations; 3) short run time; 4) can be conducted in a wide pressure range.

Notes
Abstract

We It was previously shown that at high viscosities, the log-mean of the $^1$H NMR longitudinal relaxation-time ($T_{1LM}$) becomes independent of viscosity and (roughly) proportional to the NMR frequency, for both polymers and bitumen. These observations present significant deviations from the traditional models of NMR relaxation by $^1$H-$^1$H dipole-dipole interactions, where the molecules are treated as mono-dispersed hard-spheres. In order to better understand these deviations, we present NMR measurements of the polymers over a wide range of frequencies using $T_1$ field-cycling relaxometry and $T_{1p}$ relaxation in the rotating frame. We successfully fit the frequency dependence in $T_{1LM}$ over the wide range of frequencies using our new relaxation model, which (1) accounts for a distribution in molecular correlation times for these poly-dispersed polymers, and (2) accounts for internal motions in the non-rigid polymer branches. We also show how our new model successfully fits the frequency dependence of previously reported bitumen data over a wide range of frequencies.

We also find semi-quantitative agreement between the polymer measurements and molecular dynamics simulations, which further supports our proposition that at high viscosities, the NMR relaxation for both polymers and bitumen is dominated by $^1$H-$^1$H dipole-dipole interactions, without the need to invoke paramagnetism. Finally, we reflect on the observation that at high viscosities, the (log-mean) transverse relaxation-time $T_{2LM}$ is (roughly) inversely-proportional to the square-root of viscosity, for both polymers and bitumen, again indicating significant deviations from traditional NMR models.

Notes
Evaluation of Light Hydrocarbon Composition and Pore Size in Organic Rich Chalks using NMR Core-Log Integration

Mr. Xinglin Wang
PhD Graduate Student, 2nd Year (xw51@rice.edu)

Abstract
The objective of this study is to integrate laboratory and downhole NMR measurements to estimate the hydrocarbon composition and pore size in an organic-rich-chalk reservoir. The study consists of pressure saturation of the as-received reservoir core plugs, followed by NMR $T_1$, $T_2$ and $D-T_2$ measurements. The saturating fluids include water and light hydrocarbons ($C_1$, $C_2$, $C_3$, $C_4$, $C_5$ and $C_{10}$). The laboratory-measured $T_2$ is converted to the downhole condition by using the known magnetic-field gradients of the NMR logging tool. The downhole hydrocarbon composition is estimated by comparing the apparent $T_2$ distributions between laboratory and log data. We also observe a contrast of $T_1/T_2$ between light hydrocarbons and water. Methane and natural gas liquids (NGLs) yield higher $T_1/T_2$ compared to water and $C_{10}$ under downhole condition. The pore size and tortuosity can be calculated by applying the Padé approximation to fit the restricted diffusivity of light hydrocarbons with respect to the diffusion length.

Notes
EOR Evaluation and NMR Characterization for Unconventional Formation (Bakken)

Mr. Mohamed M.A. Mohamed
Visiting Student from University of North Dakota; Fulbright student
(mohamed.awad91990@yahoo.com)

Abstract
Bakken is considered one of the largest unconventional reservoirs in the world. The new Bakken wells have high decline rate from the initial production rate, sometimes as high as 85% per year, this high decline rate is because of low porosity and low permeability. In this study, NMR response for Bakken cores was measured after saturation of twin cores with octane and formation brine. The NMR measurements were performed using two different radio frequencies (2.3&22MHz) and under ambient and high temperature (~100°C). EOR potential was evaluated by screening several thermally stable surfactants. Phase behavior analysis, interfacial tension measurements, and spontaneous imbibition test were conducted. The main challenges in this study were high reservoir temperature (105°C), high formation brine salinity (~309,612 ppm), low porosity (4-6%), and low permeability of the Bakken rocks (0.001-0.01md).

Notes
Molecular simulation of NMR relaxation behavior of fluids in polymer-alkane mixtures and model nano-porous systems: implications for understanding fluids in shale

Dr. Dilipkumar Asthagiri
Lecturer, MChE Program Director (dna6@rice.edu)

Abstract
We have initiated a program to use atomistic molecular dynamics simulations to enhance the understanding and interpretation of NMR relaxation in confined systems. In this presentation, we outline the foundational ideas of both NMR and how we can use the atomistic simulations to obtain insights into NMR $^1$H-$^1$H dipole-dipole relaxation, which is of foremost interest in the context of hydrocarbons and water present in unconventional reservoirs.

We will first briefly summarize our earlier work on modeling the NMR relaxation dynamics and diffusion in bulk methane, the C5-to-C17 normal alkanes, and water.

We will next discuss our studies on NMR relaxation in heptane-polymer mixtures, where the highly viscous polymer matrix mimics kerogen. We find that surface relaxation times for heptane ($T_{1S}$ and $T_{2S}$) in the polymer matrix decrease dramatically with decreasing heptane concentration, where the polymer acts as the “surface”. We find that for nano-pores, $T_{1S}$ is dispersive, similar to previously reported measurements for hydrocarbons confined in organic matter such as bitumen and kerogen. For larger, more conventional pores, $T_{1S}$ is not dispersive. These findings imply that $^1$H-$^1$H dipole-dipole interactions enhanced by nanopore confinement dominate $T_{1S}$ and $T_{2S}$ relaxation, without the need to invoke paramagnetism.

To understand better the role of nano-confinement, we studied relaxation behavior in alkanes in idealized graphitic cavities. Our results point to the importance of surface-interactions in addition to nano-confinement as being important in recovering the dispersive $T_{1S}$ behavior.

Notes
Presentations
Friday, April 19th: 2:40 pm — 3:00 pm

Apolar behavior of hydrated calcite surface assists in naphthenic acid adsorption

Mr. Arjun Parambathu
PhD Graduate Student, 3rd Year (av42@rice.edu)

Abstract
Water molecules bind strongly to the polar calcite surface and form a surface adsorbed layer that has properties akin to an apolar surface. This has important implications for understanding the thermodynamic driving forces underlying the adsorption of acid groups from crude oil, in particular naphthenic acid, onto calcite. Free energy calculations show that naphthenic acid binds favorably to the water mono-layer adsorbed on the calcite surface. But to bond directly to the calcite, a free energy barrier has to be overcome to expel the intervening layer of water. Further, naphthenic acids with longer alkyl chains bind with lower free energy to the calcite surface than those with shorter alkyl chains, and, for the same chain length, branching also enhances adsorption. To better understand this behavior, for a specified alkyl chain length we study adsorption at different temperatures. Consistent with experiments, we find that adsorption is enhanced at higher temperatures. Examining the enthalpic and entropic contributions to adsorption shows that adsorption of naphthenic acid is entropically favored.

Notes
Abstract
Low-salinity water flooding can alter the rock surface wettability of a reservoir from oil-wet to water-wet. In such scenarios, oil flows through the rock pores mostly as droplets known as snap-off oil, but these droplets may be re-trapped in the pores. Recently, it has been reported that ion concentration and the presence of nonionic surfactant can influence the elasticity of oil/water interface, which may have important implications on the oil snap-off and/or re-trapping phenomena. In this work, we studied the molecular behavior of oil flowing through calcite nano-pore during low salinity flooding. More specifically, we used molecular dynamics (MD) simulations to investigate the effects of salt concentrations on oil snap-off, and correlate our findings with calcium carbonate wettability alteration based on contact angles predicted by MD simulations. Our simulations successfully captured the influence of the ions at molecular level. In our next work, we will be focusing on the combined effect of salt concentrations and surfactant.

Ms. Jinlu Liu
PhD Graduate Student, 6$^{th}$ Year (jinlu.liu1990@gmail.com)

Abstract
A molecular density functional theory (DFT) which reduces to perturbed chain- statistical associating fluid theory (PC-SAFT) in bulk fluid region is applied to study CO$_2$ competitive sorption with shale gas under various conditions from simple to complex pore characteristics. The DFT model is first verified by grand canonical Monte Carlo (GCMC) simulation in graphite slit pores for pure and binary component systems at different temperatures, pressures, pore sizes and bulk gas compositions for methane/ethane with CO$_2$. Then the model is utilized in multicomponent systems which include CH$_4$, C$_2$H$_6$, and C$_3$+ components of different compositions. It is shown that selectivity of CO$_2$ decreases as temperature / pressure/ nanopore size/ average molecular weight of shale gas increase. Extending the model to more realistic situations, we consider the pore as either moisturized with water preloaded in the pore or being permeable to gas molecules with organic matter kerogen formed pore walls. The water-graphite interactions is calibrated with molecular simulation data from the literature. The kerogen pore model prediction on gas absolute sorption is compared with experimental and molecular simulation values in the literature. It is shown that the presence of water reduces the CO$_2$adsorption but improves the CO$_2$ selectivity and the dissolution of gases to kerogen matrix also leads to increase of CO$_2$ selectivity. The effect of kerogen type and maturity on the gas sorption amount and CO$_2$ selectivity is also studied. The associated mechanisms are discussed to provide fundamental understandings for gas recovery by CO$_2$. 

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