CO₂ Storage by Sorption on Organic Matter and Clay in Gas Shale

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Abstract

In the work described in this paper, we developed simulations of methane production and supercritical carbon dioxide injection that consider competitive sorption of methane (CH₄) and carbon dioxide (CO₂) on both organic matter and the clay mineral montmorillonite. We used the results of these simulations to assess the potential for storage of CO₂ in a hydraulically fractured shale gas reservoir and for enhanced recovery of CH₄. Assuming equal volume fractions of organic matter and montmorillonite, amounts of CO₂ adsorbed on both materials were comparable, while methane desorption from clays was greater than desorption from organic material. CO₂ injection simultaneous to CH₄ production in two separate wells enhanced the contribution of methane desorption from 3,535 to 6,401 metric tons, while storing 82 metric kilotons of CO₂.

Key Words: carbon storage; simulation; adsorption; sorption; enhanced gas recovery; clay

Introduction

Natural gas is considered a cleaner and lower-emission fuel than coal (U.S. Energy Information Administration), and the abundance emerging from advanced drilling techniques has provided an alternative energy source for the United States. However, burning natural gas still increases global atmospheric concentrations of carbon dioxide (CO₂). One approach to reducing anthropogenic CO₂ emissions involves coupling CO₂-based enhanced gas recovery (EGR) operations in depleted shale gas reservoirs with long-term, permanent CO₂ storage operations (Busch et al., 2008, Liu et al., 2013, Ma et al., 2013).

Shale gas reservoirs generally have lower recovery factors (<5 to 20 percent) than conventional gas reservoirs (~50 to 90 percent), although the naturally well-fractured Antrim Shale may have a recovery factor as high as 50 to 60 percent, and the Haynesville Shale in Louisiana may have a recovery factor as high as 30 percent (Rokosh et al., 2009). In general, shale gas projects involve drilling many low-flow-rate wells (560 to 8,400 m³/d; 20 to 300 mcf/d) that decline slowly and produce for two to four decades or more (Curtis, 2002). More rarely, the initial flow rate may be very high (28,000 to 280,000 m³/d; ~1 to 10 mmcf/d); however, this rate generally declines to a low flow rate within a few months or years (Bowker, 2003).

Although initial desorption of methane (CH₄) occurs during depressurization of shale reservoirs, significant amounts remain un-recoverable, retained through interactions with organic content and clay minerals. Many studies have focused on CH₄ adsorption in the organic matter of shale, and the results have revealed a positive correlation between the organic content and the CH₄ adsorption capacity in raw shale samples (Lu et al., 1995, Cui et al., 2009). The mechanism of CH₄ adsorption in organic matter has been well documented, illustrating that the surface

functional groups and micro-pores provided adsorption sites for CH_4 (Ross and Bustin, 2007, Ross and Bustin, 2008, Loucks et al., 2009, Ross and Bustin, 2009, Zhang et al., 2012). Zhang et al. (2012) found the Langmuir maximum CH_4 adsorption capacities for Green River kerogen, Woodford kerogen, and Cameo coal to be 0.78, 1.02, and 1.01 mmol/g, respectively.

Compared with extensive studies of CH_4 adsorption in organic matter, less attention has been paid to CH_4 adsorption to clay minerals. Liu et al. (2013) studied the respective CH_4 adsorption capacity and mechanism of montmorillonite, kaolinite, and illite at 60°C and pressures up to 18.0 MPa. Montmorillonite, kaolinite, and illite showed different CH_4 adsorption capacities, with Langmuir maximum adsorption capacities of 0.268, 0.173, and 0.099 mmol/g, respectively, indicating a significant contribution of clay minerals to CH_4 adsorption in shale. Rother et al. (2013) studied interactions of supercritical CO_2 (scCO_2) with sodium (Na)-saturated montmorillonite clay containing a sub-single layer of water in the interlayer region using sorption and neutron diffraction techniques. They found that swelling clays may interact with CO_2 leading to volume changes and potential impacts to permeability. However, Lahann et al. (2013) found that the New Albany Shale, with illite as the major clay, displayed no changes in pore structure due to sorbed CO_2 .

Recent laboratory research has found that competitive sorption of gases on organic matter is a function of the organic matter and clay content. Based on the differences in CH_4 and CO_2 sorption capacity on coals of different maturities as a function of moisture content, Gensterblum et al. (2014) inferred that oxygen-containing functional groups represent the primary sorption sites for which CO_2 or CH_4 compete with water molecules, where the competitive interaction was a volumetric displacement independent of the gas type. They found that the excess sorption capacity of coals is always higher for CO_2 than for CH_4 , with at least a 2:1 ratio for CO_2 to CH_4 .

The partitioning of water (H_2O) and CO_2 into a Na-saturated montmorillonite (Na-SWy-2) has been characterized and linked to the structural layer spacings within the clay as a function of the percent H_2O saturation in scCO_2 at 50°C and 90 bar (Loring et al., 2014). Schaef et al. (2014) found the sorption of nitrogen and CH_4 to be linear at pressures up to 120 bar, and obtained maximum concentrations of 0.4 and 0.6 mmol/g of clay, respectively. In contrast, sorbed CO_2 was distinctive with a more pronounced sorption rate at higher pressures (60 to 80 bar), resulting in a maximum concentration of 0.6 mmol/g of clay before desorption ensues (Schaef et al., 2014). The CO_2 sorption behavior is similar to that observed for kaolinite (Schaef et al., 2013) under identical conditions and points towards an instability of the condensed scCO_2 layer at the higher pressures. Here, the term “sorption” includes both adsorption and intercalation. This is important to note, as Schaef et al. (2014, 2015) showed that montmorillonite will readily intercalate scCO_2 to variable extents depending on its hydration state. At 50°C and 90 bar, montmorillonite expanded by 5.8 percent in the presence of scCO_2 (Schaef et al., 2014). Interestingly, Schaef et al. (2014) found no evidence of CH_4 intercalation at these conditions.

Releasing trapped CH_4 through an exchange process with CO_2 requires advanced injection strategies designed to maximize CH_4 production, maintain fluid transmissivity throughout the reservoir, and ultimately lead to permanently retained CO_2 . As Liu et al. (2013) notes, clay minerals in shales could provide additional sites for adsorption; although CO_2 storage by this mechanism has not been considered in any field-scale modeling efforts to date. The objective of this paper is to integrate laboratory-derived measurements of competitive CO_2 and CH_4 sorption on organic matter and clay into a reservoir simulation, providing a quantitative approach for

estimating recoverable amounts of CH₄ and sequestered amounts of CO₂ in a hydraulically fractured depleted shale gas formation through scCO₂ injection.

Methods

Reservoir simulations have been developed using STOMP-EOR, a new numerical simulator (http://stomp.pnnl.gov/user_guide/STOMP_guide.stm). STOMP (Subsurface Transport Over Multiple Phases) is a suite of numerical simulators (White and Oostrom, 2006) and the name extension EOR signifies enhanced oil recovery. STOMP-EOR is designed to solve problems involving the production of oil and gas from petroleum reservoirs through the three stages of production: primary, secondary, and tertiary recovery, where tertiary recovery is principally by injection of CO₂ or flue gases with the potential for alternating water floods (White et al., 2014). The simulator is founded on conservation equations for energy, water mass, salt mass, CO₂ mass, CH₄ mass, and a number of user-defined petroleum component masses that describe the transport of components through fluids and energy through geologic media. Three mobile fluids are possible: 1) aqueous, 2) non-aqueous-liquid, and 3) gaseous. Phase equilibria and properties are computed using cubic equations of state. Either Peng-Robinson (Peng and Robinson, 1976) or Soave-Redlich-Kwong (Redlich and Kwong, 1949, Soave, 1972) equations may be specified, both implemented with a Peneloux volume correction (Peneloux et al., 1982). CO₂, CH₄, and other components may be linked to species in the reactive transport solver, ECKEChem (White and McGrail, 2005), via source/sink terms. Other species concentrations are calculated with respect to designated equilibrium and kinetic reactions.

Model Setup

Emerging shale gas reservoirs in the United States have average depths ranging from 1,400 ft (~427 m) to 15,250 ft (~4,648 m) (U.S. Energy Information Administration (EIA), 2011). For the simulations in this paper, we considered an injection depth of approximately 850 m. To calculate the ambient pressure and temperature at this depth, a geothermal gradient of 0.032°C/m and a hydrostatic gradient of 10.5 kPa/m were assumed, yielding a formation pressure of 9 MPa and a formation temperature of 47.5°C (assuming the surface is at 20°C). CO₂ is supercritical at pressures and temperatures above its critical point of 31.1°C and 7.39 MPa. A fracture pressure gradient of 12.78 kPa/m was assumed, limiting injection pressures at this depth to 10.95 MPa. Simulations are conducted at this depth because the availability of sorption data for CO₂ and CH₄ on clays is limited. Fluid phase equilibria and properties were computed using the Peng-Robinson equation of state with a Peneloux volume correction.

Typical U.S. shale gas formations have less than 10 percent total porosity (Curtis, 2002, Hayden and Pursell, 2005, Rokosh et al., 2009, U.S. EIA, 2011, U.S. DOE, 2013); correspondingly, permeabilities are low ($<10^{-3}$ mD) compared to other gas bearing sedimentary formations (Rokosh et al., 2009, Ma et al., 2013). The presence of multiple fluid phases and adsorbed phase gases reduces the average free-gas filled porosity between 1 and 5 percent (Hayden and Pursell, 2005). In these simulations, the un-fractured shale is assumed to have a diffusive porosity of 5 percent and a permeability of 10^{-3} mD. The diffusive porosity refers to the interconnected pore spaces and is used to calculate diffusive fluxes, while the permeability is used to calculate advective flux terms. The porosity and permeability are higher when fractures are present; for these simulations, the naturally fractured shale was assigned 14 percent diffusive porosity and 1 mD permeability (Liu et al., 2013, Ma et al., 2013).

Capillary pressure characteristics are based on measurements for CO₂-water systems at reservoir conditions. The Brooks and Corey (1964) function for aqueous-gas systems relates the gas-aqueous capillary pressure to the effective aqueous saturation with two correlation parameters. The first parameter, ψ , is referred to as the entry head and equals the minimum drainage capillary head for which a continuous non-wetting phase (e.g., gas phase) exits. The second parameter, λ , is related to the pore-size distribution within the porous media. Brooks-Corey parameters (Table 2) for the Colorado Fm. Shale (Bachu and Bennion, 2007) were used for the un-fractured shale, and parameters for the more easily drained Viking Sandstone (Bennion and Bachu, 2006) were used for the hydraulic fracture and for the surrounding enhanced fracture network. Relative permeability for the gas and water are based on the power law (Corey, 1954) correlation; relative permeability parameters for the shale and hydraulic fractures (Table 3) also are based on the Colorado Fm. Shale and Viking Sandstone and are taken from Bennion and Bachu (2008).

Horizontal wells and hydraulic fracturing have been employed to increase gas production rates in these low-permeability formations (White et al., 2013). Two models were developed for simulations. The first model was used for a set of production-only scenarios and a huff-n-puff strategy (Figure 1). The second model employed two horizontal wells—one for CO₂ injection and one for production (Figure 2). The horizontal wells each had four stages of hydraulic fracturing. Like Liu et al. (2013), hydraulic fracture conductivity is assumed to be 100 mD-ft (30 mD-m), with a hydraulic fracture width of 2 ft (0.6 m) and a fracture half-length of 450 ft (137 m). The hydraulic fracture is modeled discretely, with an enhanced fracture network extending from the hydraulic fracture assumed to have a porosity of 30 percent and a permeability of 50 mD).

Shale gas reservoirs in the United States have total organic contents ranging from 2 to 14 percent by weight (U.S. Energy Information Administration, 2011). Clay contents of “average” shales range from 48 to 69 percent by weight, with illite, smectite, and kaolinite being the most abundant clay minerals (Yaalon, 1962). With increasing burial depth and temperature, smectite is transformed into illite, making montmorillonite less likely to be abundant in thermally mature shales. The Pierre Shale contains 20 percent by weight smectite (Metwally and Chesnokov, 2012), but the New Albany Shale contains mostly illite (Lahann et al., 2013). To compare the relative effects of sorption on organic matter and montmorillonite, we assume the shale consists of 10 percent (by volume) organic matter and 10 percent (by volume) montmorillonite.

Competitive Adsorption

Competitive adsorption of two different gases was accounted for by the use of a modified Langmuir adsorption model. Under equilibrium conditions, and assuming (1) all sites are equivalent, (2) each site can hold one molecule of A or B , but not both, and (3) there are no interactions between adsorbates on adjacent sites, the equilibrium constants can be expressed as

$$K_{eq}^A = \frac{[A_{ad}]}{P_A[S]} \quad K_{eq}^B = \frac{[B_{ad}]}{P_B[S]} \quad (1)$$

where A_{ad} and B_{ad} are the surface concentrations (moles/m²), P_A and P_B are the partial pressures over the surface (Pa), and S is the concentration of bare adsorption sites (number of sites/m²) (Masel, 1996). The site balance is given by

$$[S] = [S_0] - [A_{ad}] - [B_{ad}] \quad (2)$$

where S_0 is the concentration of all sites (Masel, 1996). The fractional occupancies are given by

$$\theta_A = \frac{K_{eq}^A P_A}{1 + K_{eq}^A P_A + K_{eq}^B P_B} \quad (3)$$

$$\theta_B = \frac{K_{eq}^B P_B}{1 + K_{eq}^A P_A + K_{eq}^B P_B} \quad (4)$$

To include this behavior in models, we empirically define K_{eq} values from fitting experimental measurements of pure CH_4 and pure CO_2 sorption onto organic matter and calcium saturation montmorillonite clay. Sorption data for CO_2 and CH_4 on dry organic matter at $45^\circ C$ was taken from Gensterblum et al. (2013). Sorption data for CO_2 and CH_4 on dry montmorillonite at $50^\circ C$ was taken from Schaef et al. (2014, 2015).

Gensterblum et al. (2013) reported excess sorption data for CO_2 and CH_4 on dry sub-bituminous coal at $45^\circ C$ collected using the manometric method. Density changes in the gas phase must be accounted for when fitting these measurements at high pressures. Our fitting methodology follows from Gensterblum et al. (2013), where measured excess sorption data are fit using Eq. (5).

$$n_{excess} = n_{absolute} \left(1 - \frac{\rho_{gas}(T)}{\rho_{ads}} \right) \quad (5)$$

where $n_{absolute}$ is the absolute sorption, ρ_{gas} is the free gas density, ρ_{ads} is the sorbed phase density, and the terms are a function of gas partial pressure or gas concentration of the component and temperature (T). The Langmuir sorption model was then substituted in for absolute sorption to derive Eq. (6).

$$n_{absolute} = n_{max} \left(\frac{K_{eq} C_g}{1 + K_{eq} C_g} \right) \quad (6)$$

where n_{max} is the maximum number of sorption sites available, K_{eq} is the equilibrium constant, and C_g is the gas concentration (or partial pressure) of the component. At low pressures, the ratio of gas density to adsorbed phase density is low and the Langmuir model fits experimentally derived sorption data well; however, as pressure increases, the increasing density ratio leads to a reduction in perceived sorption from common sorption isotherm measurement methods (e.g., volumetric, manometric, gravimetric) (Gensterblum et al., 2013). This apparent phenomenon is

199 termed “excess sorption”. Fitting parameters for excess sorption of CO₂ and CH₄ on sub-
200 bituminous coal were provided by Gensterblum et al. (2013); however, we recalculated these
201 parameters using densities produced from the Peng-Robinson Equation of State with Perneloux
202 volume correction, as is employed by STOMP-EOR (Table 1). The densities of the adsorbed
203 phases were taken as constants with values of 373 and 1027 kg/m³ for CH₄ and CO₂,
204 respectively, corresponding to the inverse of the “van der Waals volumes” (Gensterblum, 2013).
205 Measured data with new excess sorption fits are given in Figure 3 and the corresponding absolute
206 sorption isotherms are given in Figure 4.

207 It is important to note that the solution sets of Langmuir parameters are not unique, and
208 excellent fits to experimental data can be obtained by two or more slightly different sets
209 (Gensterblum, 2013). For the purposes of these models, the solution sets were of sufficient
210 accuracy to describe the competitive adsorption/desorption behavior of CO₂ and CH₄ on organic
211 matter.

212 Schaefer et al. (2014, 2015) used a quartz crystal microbalance (QCM) method to measure
213 the change in mass of the crystal per active surface area while the clay was exposed to pure CO₂
214 and pure CH₄ under reservoir conditions. Measurements from this method do not require a
215 density correction like those from volumetric methods, and can be taken as absolute sorption
216 measurements. This allows for a direct sorption isotherm fit to the data. Due to the nature of the
217 Langmuir isotherm being a monotonic function, it is not possible to fit the desorption behavior at
218 high pressures. To avoid a poor fit across all the data, the isotherm fit was weighted between 6
219 and 11 MPa and simulations were kept within that range. The fitted Langmuir isotherm
220 parameters are given in Table 1 and the corresponding fits to data are shown in Figure 5.
221 Additional measurements of CO₂ sorption onto a Ca⁺ montmorillonite collected using the

manometric method (Romanov, 2013) were been plotted for comparison. These measurements were collected during an investigation into the hysteretic sorption behavior of CO₂ on clays and show both adsorption and desorption measurements.

As a first attempt, the Langmuir model provides reasonably good fits to the trends of experimental data. It is noteworthy that the Langmuir isotherm does not fit CO₂ sorption behavior measured by Schaef et al (2015) at high pressures or at low pressures. Schaef et al. (2014, 2015) observed CO₂ desorption at high pressures due to a decrease in adsorption energy beyond the stabilization energy of the supercritical phase. For the purposes of this study, this misfit is not of importance because simulations remained within a 6 to 11 Mpa pressure range. In order to perform simulations at higher pressures, a more sophisticated isotherm would have to be derived which accounts for desorption. The Langmuir isotherm does not appear to fit CH₄ data at high pressures either; however, this difference is attributed to slight errors in corrections applied to obtain the delta frequency from raw data.

The ratio of sorption capacities for CO₂ to CH₄ on montmorillonite and sub-bituminous coal were plotted to directly compare the sorption behavior of each gas on each adsorbent (Figure 6). Within the pressure range of interest, the ratio of adsorbed CO₂ to CH₄ is 2.7 for sub-bituminous coal and 1.6 for Ca⁺ montmorillonite. To account for these relationships, simulations were setup to allow for 2.7 moles of CO₂ to occupy each site that a single molecule of CH₄ could occupy on organic matter and, consistently, 1.6 moles CO₂ to 1 mole CH₄ on montmorillonite clay.

It should be noted that STOMP-EOR does not currently take into account changes to effective porosity and permeability due to the adsorption or desorption of gases. Therefore, the initial porosities and permeabilities assigned to these simulations were treated as effective

properties in the presence of adsorbed CH₄ gas. Using the adsorption models discussed and assuming the adsorbed phase density of CH₄ is 373 k/m³, the adsorbed phase volume was initially 492,753mt while the fluid filled volume was 2,393,083mt. The adsorbed phase accounted for 1.2 percent of the total volume and 17.1 percent of the total porosity, where the average total porosity of all materials is 7.2 percent.

Results

Three different pumping scenarios were run: 1) production only base case, 2) CO₂ injection and production in two separate wells, and 3) CO₂ injection followed by production in a single well (the huff-n-puff strategy). Scenarios integrate laboratory-derived measurements of CO₂ and CH₄ sorption on organic matter and clay. Sub-scenarios account for variations in key parameters specific to shale gas formations. A summary of results is given in Table 4.

Case 1: Production Only

This pumping scenario was used to develop a set of reference models in which CH₄ was produced via depressurization and CO₂ was not injected. Case 1 has two sub-cases in which the initial water saturation is varied between a “dry” formation ($S_w=0.10$) and a “wet” formation ($S_w=0.40$). While neither case is strictly dry nor wet (fully saturated), these values are relative to the range of typical saturations found in targeted shales (Curtis, 2002, Liu et al., 2013, Yu and Sepehrnoori, 2014).

CASE 1A: CH₄ PRODUCTION IN A DRY FORMATION

There were originally 322,707 metric tons (mt) of CH₄ gas in place, where the original gas-in-place was determined based on the sum of all free-gas and adsorbed gas present. Of the original gas-in-place, 44 percent was adsorbed to montmorillonite and 13 percent was adsorbed to organic

material. The bottomhole pressure of the producing well (horizontal well #1) was limited to a minimum of 6.0 MPa, and production continued for 30 years. After 30 years, 30,634 m³ of CH₄ gas and 708 m³ of water were produced (Figure 7). In relation to the amount of CH₄ produced, 8 percent can be accounted for as being desorbed from montmorillonite and 4 percent from organic matter (Figure 8). This relatively low percentage of desorption is consistent with the CH₄ sorption isotherms for this high pressure range (Figure 4 and Figure 5).

Half of the total CH₄ was produced 4.5 years into simulations, an equivalent energy of 850 TJ at standard conditions. Water accumulation on the interfaces between the fractured zones and the un-fractured shale (Figure 9) led to reduced rate of gas production. From 4.5 years on, flow to the well was limited by the effective permeabilities of the un-fractured material.

CASE 1B: CH₄ PRODUCTION IN A WET FORMATION

While a dryer formation is favorable for gas production, Case 1b simulations were run to provide a scope for gas production across the range of expected water saturations in shale formations. The presence of higher water saturations reduced the initial mass of CH₄ in place to 286,131 m³, where 51 percent was adsorbed to montmorillonite and 15 percent was adsorbed to organic material. Higher initial water saturations will exacerbate the aqueous buildup discussed in Case 1a and lead to pressure buildup at the interface between fractured and unfractured materials. All else left the same, simulation results showed a production duration of less than a year before the formation was over-pressurized (Figure 10). To avoid unwanted fracturing or formation collapse, production must not lead to pressure buildup in excess of the fracture pressure (10.95 MPa). To mitigate this effect, this simulation case was run with a bottomhole pressure of 8.5 MPa. Using this method, 30 years of production were achieved without the formation becoming over-pressurized (Figure 11).

Methane gas production was reduced to 7,143mt (Figure 12), 77 percent less than Case 1a at the same 30 year mark. Half of the total produced CH₄ was produced in the first 5.25 years. This is similar behavior to the previous “dry” case. Relative to the total mass of gas produced, 19 percent can be accounted for desorbed from montmorillonite and 10 percent from organic matter (Figure 13). While the proportion of desorbed CH₄ was increased, it should be taken in context of the total mass of desorbed CH₄, which was decreased by 1500 mt.

In both cases, the contribution of CH₄ due to desorption from montmorillonite was twice as much as that of the organic matter. These simple depressurization cases alone show CH₄ desorption from clay minerals may be on the same order of magnitude as desorption from organic matter and should *not* be neglected.

Case 2: Injection and Production in Separate Wells

To investigate competitive sorption processes, CO₂ was injected simultaneous to CH₄ production in two different wells. The bottomhole pressure of the producing well (horizontal well #1) was limited to a minimum of 6 MPa and the wellhead pressure of the injecting well (horizontal well #2) was limited to a maximum of 10 MPa. A key feature of this strategy was that the fracture networks between wells were connected, allowing for the CH₄ desorbed by CO₂ replacement (Figure 5) to flow to the production well. The increased porosity in the enhanced fractures led to a higher initial mass of gas-in-place (322,875 mt). The wells operated simultaneously for 30 years.

This method enhanced CH₄ production (Figure 14) while storing the majority of injected CO₂ (Figure 15). Methane production was increased over the base depressurization case (1a) from 3 years on. At the end of the 30 year simulation, 10 percent more CH₄ had been produced compared to Case 1a; however, 12 mole percent of the produced fluid was reproduced

CO₂. Natural gas pipeline specifications limit the CO₂ concentration to 2 mole percent. Carbon dioxide breakthrough at well #1 began 5 years into simulations; the concentration of CO₂ in the produced gas increased from this point until the end of simulation. The 2 mole percent limit was reached 13.15 years into simulation.

These results present two options: either end the EGR operation at 13.15 years or employ a gas separation technology to the produced fluids and continue production. Ending the EGR operation 13.15 years into the simulations would have resulted in 81,900 mt CO₂ stored in the formation with 27 percent adsorbed to organic matter and 19 percent adsorbed to montmorillonite (Figure 16). This strategy would have led to 24,773 mt CH₄ and 335 mt water produced. Competitive CO₂ sorption increased CH₄ desorption from 3,535 mt to 6,401 mt, where 18 percent of the produced gas can be accounted for by CH₄ desorbed from montmorillonite and 8 percent from organic matter (Figure 17).

CASE 2B: REDUCED PERMEABILITY DUE TO CO₂ INTERCALATION

Schaef et al. (2014, 2015) showed that montmorillonite will readily intercalate scCO₂ to variable extents depending on its hydration state. This structural change reduces the porosity and permeability of the material and will effectively impede the flow of fluids. To demonstrate this process, a second set of simulations were run with appropriately reduced permeabilities in the fractured materials.

The shale material is composed of 10 percent montmorillonite, which leads to a swelling of 0.58 percent of the total solid material. In the naturally fractured material, the porosity is reduced from 14 to 13.5 percent. In the hydraulically fractured material, the porosity is reduced from 30 to 29.6 percent. The corresponding permeabilities were then calculated using the

Kozeny-Carman relationship. The original gas-in-place was slightly reduced due to these changes in porosity (321,816 mt). It is worth noting changes in porosity due to adsorption and desorption of gases were neglected here. Preliminary results showed the exchange of CH₄ and CO₂ molecules at the grain surface had a lesser impact on porosity than reduction due to clay swelling. For instance, in these simulations the initial volume of adsorbed phase accounted for 1.2 percent of the total volume, while the final volume of combined CO₂ and CH₄ adsorbed molecules accounted for 1.3 percent of the total volume.

Gas production was reduced by 4 percent (Figure 18) and CO₂ storage was reduced by 7 percent (Figure 19) compared to Case 2a at 30 years. The reduction in permeability had an insignificant effect on the adsorption or desorption behavior of CO₂ and CH₄. The reduced flow rate prolonged the duration before 2 percent CO₂ mole fraction was reached in the produced fluids by a year (14.1 yrs) and reduced the amount of CO₂ stored at this time by nearly 3,000 mt. Results from this case and Case 2a bound the expected fluid flow between initial permeability and minimum permeability due to fully swollen clay minerals.

Case 3: Injection and Production in a Single Well (huff-n-puff)

A huff-n-puff strategy was performed in horizontal well #1 during which CH₄ was produced for 3 years followed by CO₂ injection for 1 year and a second cycle of CH₄ production for 3 years. This process was performed to investigate enhanced gas production in a single well using CO₂ exchange to desorb immobile CH₄. The bottomhole pressure during production was initially limited to a minimum of 6 MPa, but the second cycle of production required a slightly higher minimum to maintain supercritical conditions for the injected CO₂ and was set at 7.43 MPa. The wellhead pressure during injection was limited to a maximum of 9.5 MPa.

Results showed CO₂ injection from the same well did not improve CH₄ production. While injected CO₂ sorbed to the clay and organic matter and desorbed CH₄, the bulk phase CH₄ was pushed away from the well, and the displaced gas was not recovered during secondary production (Figure 20). Overall, the withdrawal of CH₄ decreased by 25 percent compared to Case 1a at the same time (7 years) (Figure 21). In addition to decreased CH₄ production, the CH₄ that was produced would have to be separated from a large amount of re-produced CO₂. Forty percent of the injected CO₂ was recovered during cycles, leaving 22,250 mt stored in the formation (Figure 22). Ultimately, a third of the stored CO₂ remained in the gas phase, 45 percent was adsorbed to organic matter, and 22 percent was adsorbed to montmorillonite.

Conclusion

This study provided results from the first field-scale modeling effort to include sorption properties of clays applied to CH₄ production and CO₂ storage in fractured shale. Laboratory-derived measurements of competitive CO₂ and CH₄ sorption on organic matter and clay were incorporated into reservoir simulations, providing a quantitative approach for estimating recoverable amounts of CH₄ and sequestered amounts of CO₂ in hydraulically fractured depleted shale gas formations through scCO₂ injection. Three different pumping scenarios were simulated: 1) production only, 2) CO₂ injection and production in two separate wells, and 3) CO₂ injection followed by production in a single well (huff-n-puff). Sub-scenarios account for variations in formation water saturation and swelling caused by CO₂ intercalation.

Cases 1a and 1b provided an understanding of the system without CO₂ injection. Results showed the water saturation and the pressure at the un-fractured shale interface were key parameters. Production rates for both cases decreased with time, coinciding with aqueous buildup

around the well. In both cases, a 5-year production period may be optimal in terms of maximizing the rate of CH₄ recovery. Methane production was highly sensitive to the initial water saturation, with outputs ranging between 30,634 mt for a relatively dry formation and 7,143 mt for a relatively wet formation. Production pressures had to be managed to avoid unwanted fracturing or formation collapse. Neither case resulted in large amounts of desorbed CH₄ as formation pressures were kept relatively high in relation to sorption isotherms. Regardless, these cases exhibited greater CH₄ desorption from montmorillonite than organic matter. This suggests that even in simple cases, the contribution of clay minerals to CH₄ sorption processes in shale is equally important to consider as that of organic matter.

Cases 2a and 2b showed how CO₂ injection could be used to increase CH₄ production while storing CO₂. These cases also considered permeability changes due to CO₂ intercalation. By injecting CO₂ in a nearby well, pipeline quality CH₄ was produced for ~13 years in Case 2a and ~14 years in Case 2b. The success of this strategy depended on the degree of connectivity of fractures between wells. Ironically, flow through the connected fractures also led to the limiting factor of production—CO₂ breakthrough at the production well—as CO₂ storage would be reduced and gas separation may be uneconomical. Both Case 2a and 2b resulted in recovery of ~25,000 mt CH₄ and storage of ~80,000 mt CO₂. Case 2a showed methane desorption increased from 3,535 to 6,401 metric tons, where the majority of desorption was from montmorillonite clay. Carbon dioxide sorption to both materials was comparable, with 18 percent adsorbed to montmorillonite and 27 percent adsorbed to organic matter.

In Case 3, we used a huff-n-puff strategy to produce CH₄ and inject CO₂ through the same horizontal well. In contrast to the previous cases, Case 3 did not improve CH₄ production and resulted in considerably less CO₂ storage. A comparison of production rates to Case 1a showed

the majority of CH_4 was recovered prior to CO_2 injection, followed by an immediate decrease in CH_4 production that was not recovered. As the partial pressures of CO_2 decreased, CO_2 desorbed from organic matter and clay. This method may be worth re-visiting in future models at higher pressures, where the behavior of CO_2 does not follow the Langmuir sorption model.

The purpose of this study was to include clay sorption behavior in a series of shale gas production models as a first step towards more accurate predictions of these systems. The production models provide examples of how experimental measurements can be integrated into calculations of field scale operations and ultimately, be used to design enhanced production schemes. Results suggest that CO_2 injection from a separate well can increase the productivity of CH_4 recovery operations in fractured shale formations. The amount of desorbed CH_4 was increased an order of magnitude by employing this CO_2 injection strategy and taking into account clay sorption behavior. This demonstrates that CH_4 and CO_2 sorption behavior on clay is important to consider and has the potential to enhance these types of EGR operations. Future studies will focus on the inclusion of a more sophisticated sorption isotherm that captures CO_2 desorption at high pressures in order to accurately predict behavior across the range of shale gas reservoir pressures, particularly those higher than 11 MPa.

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553

554 Table 1. Langmuir parameters for excess sorption models of methane and carbon dioxide at
 555 elevated pressures.

Fluid	Solid	K_{eq} (MPa ⁻¹)	Nmax (mmol/g)	T (°C)	Reference
CH ₄	Sub-bituminous Coal	0.162	1.17	45	(Gensterblum et al., 2013)
CO ₂	Sub-bituminous Coal	0.259	4.30	45	(Gensterblum et al., 2013)
CH ₄	Ca+Montmorillonite	0.493	0.92	50	(Schaefer et al., 2014)
CO ₂	Ca+Montmorillonite	0.135	2.2	50	(Schaefer et al., 2015)

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559 Table 2. Brooks and Corey (1964) capillary pressure function parameters.

Material	Entry Pressure, MPa	Pore-Size Distribution Index
Un-fractured shale	4.66	1.484
Hydraulic fracture and fractured shale	0.109	1.124

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561

562 Table 3. Gas and aqueous relative permeability Corey correlation parameters.

Parameter	Un-Fractured Shale	Hydraulic Fracture and Fractured Shale
$K_{r-water} \text{ at } S_{g-irreducible}$	0.0024	0.365
$S_{g-irreducible}$	0.349	0.297
$K_{g-CO_2} \text{ at } S_{w-irreducible}$	0.0148	0.2638
$S_{w-irreducible}$	0.605	0.423
Corey Parameter for Water	6.5	1.7
Core Parameter for CO_2	2.6	2.8

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566 Table 4.Cumulative mass injected or produced (mt) from each well for each case at 30 years and
 567 at recommended end times where applicable.

		Well #2	Well #1			
Case	End Year	CO ₂ Injected	CO ₂ Injected	CO ₂ Produced	H ₂ O Produced	CH ₄ Produced
1a	30	-	-	-	708	30,634
1b	30	-	-	-	134	7,143
2a	30	148,815	-	12,047	540	33,520
2a	13.15	82,939	-	1,387	335	24,773
2b	30	137,381	-	10,302	752	32,079
2b	14.12	80,318	-	1,378	518	24,225
3a		-				

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570 Figure 1. Model Grid #1, well and material zones.

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573 Figure 2. Model Grid #2, wells and material zones.

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Figure 3. Excess sorption of CO₂ and CH₄ on sub-bituminous coal at 45 °C. Fitting parameters in Table 1.

¹Gensterblum et al., 2013

Figure 4. Absolute sorption isotherms for CO₂ and CH₄ on sub-bituminous coal at 45 °C. (2013). Fitting parameters in Table 1.

Figure 5. Sorption isotherms for CO₂ and CH₄ on Ca+ montmorillonite clay at 50 °C. Fitting parameters in Table 1.

²Schaefer et al., 2014

³Schaefer et al., 2015

⁴Romanov, 2013

Figure 6. Sorption capacity ratios of CO₂ to CH₄ for each adsorbent.

Figure 7. Case 1a cumulative production results in metric tonnes (mt).

Figure 8. Case 1a: Fraction of produced CH_4 from the gaseous and sorbed phases for the “dry” case.

Figure 9. Case 1a: Aqueous saturation increasing around the production well. Contours at 4, 5, and 30 years.

Figure 10. Pressure contours at 1 year after production began in the “wet” formation. Bottom-hole pressure set to 6 MPa. The fracture pressure (10.95 MPa) was set as a contour cut-off; therefore, any white elements represent over-pressurized areas.

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Figure 11. Case 1b: Pressure contours with the adjusted production rate (8.5 MPa bottom-hole pressure) at 1 year and at end of production.

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617 Figure 12. Case 1b: Cumulative production results for CH₄ and water in metric tonnes (mt) in the
618 “wet” formation. Case 1a shown in gray for comparison.
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Figure 13. Case 1b: Fraction of produced CH₄ from the gaseous and sorbed phases for the “wet” case.

Figure 14. Case 2a: Fluids produced under a CO₂ injection/CH₄ production scheme. The base case (1a) is shown for comparison to CH₄ production under simple depressurization circumstances.

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631 Figure 15. Case 2a: CO₂ stored in the shale gas formation throughout a 30 year injection. This plot
632 corrects for injected CO₂ reproduced from the production well. The CH₄ produced from the
633 production well is shown for reference.

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638 Figure 16.Case 2a: Fraction of stored CO₂ in the gaseous and sorbed phases.

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Figure 17. Case 2a: Fraction of produced CH₄ from the gaseous and sorbed phases.

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Figure 18. Case 2b: Fluids produced under a CO₂ injection/CH₄ production scheme with reduced permeability. Case 2a is shown for comparison.

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651 Figure 19. Case 2b: CO₂ stored in the shale gas formation throughout a 30 year injection with
 652 reduced permeability due to clay swelling. This plot corrects for injected CO₂ reproduced from
 653 the production well. Case 2a and the CH₄ produced from the production well are shown for
 654 reference.

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658 Figure 20. Case 3: CH₄ gas pushed away from the well during CO₂ injection is not recovered

659 during production. This contour plot shows the CH₄ distribution at the end of the secondary

660 recovery period (7 years). The areas around the production screens have relatively low

661 CH₄gaseous mole fractions.

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665 Figure 21. Case 3: Cumulative production results in comparison with Case 1a results (gray-scale).

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668 Figure 22.Case 3:Net CO₂storage. Flat or decreasing time periods represent production periods.