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CO₂ Utilization and Storage in Shale Gas Reservoirs: Experimental Results and Economic Impacts

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Abstract

Natural gas is considered a cleaner and lower-emission fuel than coal, and its high abundance from advanced drilling techniques has positioned natural gas as a major alternative energy source for the U.S. However, each ton of CO₂ emitted from any type of fossil fuel combustion will continue to increase global atmospheric concentrations. One unique approach to reducing anthropogenic CO₂ emissions involves coupling CO₂ based enhanced gas recovery (EGR) operations in depleted shale gas reservoirs with long-term CO₂ storage operations. In this paper, we report unique findings about the interactions between important shale minerals and sorbing gases (CH₄ and CO₂) and associated economic consequences. Where enhanced condensation of CO₂ followed by desorption on clay surface is observed under supercritical conditions, a linear sorption profile emerges for CH₄. Volumetric changes to montmorillonites occur during exposure to CO₂. Theory-based simulations identify interactions with interlayer cations as energetically favorable for CO₂ intercalation. In contrast, experimental evidence suggests CH₄ does not occupy the interlayer and has only the propensity for surface adsorption. Mixed CH₄:CO₂ gas systems, where CH₄ concentrations prevail, indicate preferential CO₂ sorption as determined by *in situ* infrared spectroscopy and X-ray diffraction techniques. Collectively, these laboratory studies combined with a cost-based economic analysis provide a basis for identifying favorable CO₂-EOR opportunities in previously fractured shale gas reservoirs approaching final stages of primary gas production. Moreover, utilization of site-specific laboratory measurements in reservoir simulators provides insight into optimum injection strategies for maximizing CH₄/CO₂ exchange rates to obtain peak natural gas production.

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1. Introduction

Rising energy prices and a move toward highly effective extrication techniques have led to an increase in natural gas production from low-permeability shales. Primarily initiated in North America, this phenomenon has global growth expectations. Advanced drilling techniques and developments in hydraulic fracturing technologies have unlocked these shale gas reservoirs and enabled countries such as the U.S. to significantly increase their estimated reserves of natural gas and decrease their reliance on imported supplies. This has also led to a decrease in natural gas prices in the U.S., adding another disincentive to invest in new coal-fired power plants. However, while natural gas is considered a cleaner and lower-emission fuel than coal, each ton of CO₂ emitted from any type of fossil fuel combustion will continue to increase global atmospheric concentrations. One unique approach to reducing anthropogenic CO₂ emissions involves coupling enhanced gas recovery (EGR) operations in depleted shale gas reservoirs with long-term CO₂ storage operations. Approximately half of the large, stationary CO₂ emission sources in the U.S. are located within 50 miles of a potential shale gas play. With nearly \$1T worth of additional gas recovery possible as a result of CO₂ injection [1], combined operations could provide significant incentives for early carbon capture and sequestration (CCS) deployment.

Although initial desorption of methane (CH₄) readily occurs during depressurization of shale reservoirs, significant amounts remain unrecoverable, retained through interactions with organic content and clay minerals. Releasing trapped CH₄ through an exchange process with CO₂ requires advanced injection strategies designed to maximize CH₄ production, maintain fluid transmissivity throughout the reservoir, and ultimately lead to permanent retention of CO₂. Relative adsorption of gases (i.e., CO₂, CH₄) is not well understood and appears to vary by clay mineral type. To help address this knowledge gap, a unique set of *in situ* experimental techniques has been developed to identify dominant sorption and geochemical processes occurring with clay minerals typically found in shales. Together, through a combination of laboratory studies and atomistic modeling, interactions between clay minerals, CO₂, and CH₄ were observed that could have profound impacts to CO₂-EGR based operations. Studies undertaken in this work were designed to investigate interactions occurring between gases (CO₂ and CH₄) and a common impurity (SO₂) on model clay minerals and elucidate impacts of water content and cation constituents on sorptive capacity, structural changes (swelling/shrinkage), and differential gas adsorptions.

2. Experimental and Computational Methods

Clay minerals used in this study (SWy-2, STx-1, KGa-1) were purchased from The Source Clays Repository, which is managed by the Clay Mineral Society (Purdue University, West Lafayette, IN) and have been previously characterized in the literature [2-5]. Hydration of and gas sorption by cation saturated montmorillonites (Ca, Mg, and Na) was investigated as a function of dissolved water content in the presence of pressurized CO₂ and CH₄ using an *in situ* infrared spectroscopic titration technique [6-8]. Quantification of sorbed gases on identical clays was accomplished with a quartz crystal microbalance (QCM), that has a typical resolution of 2 ng and a pressure rating of 125 bar at 50 °C [9, 10]. Structural changes (swelling/shrinkage) associated with intercalation of gases into the clays were tracked *in situ* with a high-pressure X-ray diffraction capability [11, 12]. Static pressure tests were conducted in a 25 ml Parr pressure vessel with 25 g clay at 50 °C. Gas samples from these reactors were analysed according to Glezakou et al [13]. Molecular modeling was conducted on montmorillonite analogs to enhance understanding of mechanistic processes dominating the gas-rich environments [9, 14].

Reservoir simulations were developed using a two-phase, nonisothermal, multicomponent simulator, STOMP-COMP [15]. Phase and component flexibility are handled numerically using EOS-COMP, an implementation of the Peng-Robinson cubic equation of state with a two-phase flash equilibrium model in which phase composition is defined through fugacity equilibria. In STOMP-COMP, the multiphase system is assumed to be composed of non-condensable gases (NCGs), water, and salt. The user can specify the number of NCGs; currently, the database consists of ten NCGs (CO₂, O₂, N₂, Ar, CH₄, C₂H₆, C₃H₈, C₄H₁₀, H₂S, and SO₂). The solubility of gas mixtures is calculated using a Peng-Robinson equation of state [16] with distinct binary interaction coefficients for each phase [17], calibrated to observed gas solubilities in pure water and brine. Components of the coupled flow and transport

equations (e.g., water, CO₂, H₂S) may be linked to species in the reactive transport solver, ECKEChem, via source/sink terms. Other species concentrations are calculated with respect to designated equilibrium and kinetic reactions. Porosity changes due to mineral or salt precipitation and dissolution are calculated according to user-specified mineral densities, and permeability changes may be calculated using the method of Verma and Pruess [18].

3. Results and Discussion

3.1. Gas Sorption

Experimental studies by Schaefer et al. [10] describe adsorption behavior of CO₂ onto kaolinite, a common constituent of shale formations [19]. The study concluded that while gas-phase CO₂ adsorbed linearly with pressure, the transition to supercritical CO₂ resulted in surface condensation that increased adsorption significantly before CO₂ began desorbing with further increases in pressure. Adsorption steps, determined by periodic boundary conditions (PBC) density functional theory calculations, showed energetic favorability during the initial CO₂ layer formation. These conditions were consistent until the first CO₂ layer formed, corresponding to approximately the same experimental derived density of ~0.35 g/cm³. Further increases in CO₂ pressure resulted in the adsorbed layer becoming more bulk-like, leading to CO₂ desorption from the mineral surface [10]. Similarly derived adsorption isotherms are observed for other clay minerals including montmorillonite (SWy-2). In this study, we measured the adsorption of N₂, CH₄, and CO₂ on a dehydrated sodium saturated montmorillonite (Na-SWy-2) at 50 °C (Figure 1). The sorption of N₂ and CH₄ are nearly linear throughout the pressure interval and obtain maximum concentrations of 0.4 and 0.6 mmol/g of clay, respectively. In contrast, CO₂ sorption is distinctive with a more pronounced adsorption rate at higher pressures (60-80 bar), resulting in a maximum concentration of 0.6 mmol/g of clay before desorption ensues. The CO₂ sorption behavior is similar to that observed for kaolinite [10] under identical conditions and points towards an instability of the condensed supercritical CO₂ (scCO₂) layer at the higher pressures. Moreover, our recent findings [9] included a theory-based analysis identifying an energy minimum as the driving force for the enhanced sorption of scCO₂ on montmorillonites. At pressures beyond where this energy minimum occurs, interactions between the condensed scCO₂ layer and bulk scCO₂ are greater and therefore drive the desorption process. These findings suggest an ideal pressure window to maximize CO₂ adsorption onto clays, which carries implications for methane recovery, reservoir storage capacity, and project cost.

3.2. Intercalation

Transmissivity of gases through a shale gas reservoir often exhibits unexplained variations and deviations from numerical modeling predictions [20]. Potential impacts to CH₄ productivity and CO₂ injectivity have recently been identified with reported volumetric changes to montmorillonite clays in contact with scCO₂ fluids [11, 12, 21, 22]. With this in mind, experiments were designed to examine conditions influencing expansion of montmorillonites, including the roles that interlayer cation types (Ca, Mg, or Na) and water play in controlling sorbed gas concentrations (adsorbed and intercalated) in these swelling clays. Measurements by *in situ* infrared spectroscopic and X-ray diffraction techniques demonstrate limited CO₂ diffusion into a dehydrated Na-montmorillonite interlayer but increased access with exposure to wet scCO₂ [6, 9]. Loring et al. [6] conducted titrations of Na-SWy-2 that tracked CO₂ sorption as a function of dissolved H₂O in the scCO₂. When initially exposed to anhydrous scCO₂, the clay remained volumetrically stable at a d₀₀₁ value of 10 Å with CO₂ sorbing predominantly on external surfaces. As water was titrated into the scCO₂, the clay sorbed H₂O and additional CO₂ into the interlayer. A maximum concentration of sorbed CO₂ occurred at the sorbed H₂O concentration required to increase the basal spacing from 10Å to ~12.3Å, which corresponds to a fully hydrated 1W clay [23]. Further increases in sorbed H₂O lead to a

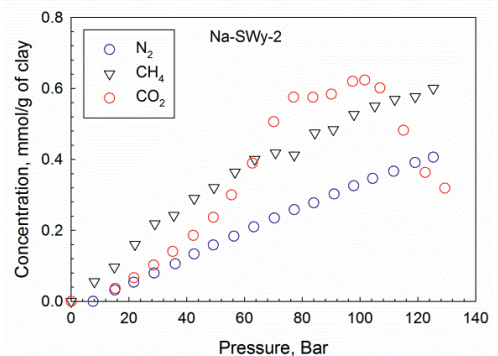


Figure 1. Gas adsorption measurements (N₂, CH₄, and CO₂) obtained from sodium saturated montmorillonite (Na-SWy-2) at 50 °C with a quartz crystal microbalance.

decrease in sorbed CO_2 . Similarly, Ca-SWy-2 initially in the <1 layer of water in the interlayer (sub 1W) hydration state expands due to CO_2 uptake in the interlayer when exposed to scCO_2 , but the clay undergoes a decrease in intercalated CO_2 concentrations with further sorption of water [9]. Structural changes related to increased dissolved water content in the scCO_2 and subsequent clay hydration suggest that water content significantly impacts the degree to which CO_2 can move into the interlayer for storage.

Figure 2 illustrates the expansion of a calcium saturated SWy-2 montmorillonite (Ca-SWy-2) during contact with scCO_2 at 50 °C and 90 bar. Initially, the clay was exposed to vacuum (50 °C) to remove water, which reduced the hydration state of the clay to a sub 1W [23]. The basal d_{001} value increases from 11.90 Å under vacuum to 12.41 Å during contact with scCO_2 (90 bar). In contrast, no measurable expansion was observed in the presence of CH_4 with the same clay (Figure 2). Minor peak differences in the d_{004} reflections were noted between the CH_4 and vacuum conditions, but are likely explainable through a minor reordering of variably hydrated clay particles within the sample; montmorillonites are known to be heterogeneously hydrated [23]. Similar experiments were carried out on a completely dehydrated Na-SWy-2. During exposure to vacuum, the d_{001} basal value of this clay measured ~ 10 Å. This value did not deviate following exposure to either CH_4 or CO_2 , indicating little or no expansion and no evidence for intercalation. Based on these studies, montmorillonites will readily intercalate CO_2 to variable extents depending on hydration state (adequate expansion is required for montmorillonites to intercalate CO_2), but there is no XRD evidence of CH_4 intercalation.

Further characterization of the CH_4 -montmorillonite system was accomplished through *in situ* IR spectroscopic experiments where Na-SWy-2 was titrated with water in methane at 50 °C and 90 bar. With increasing adsorbed water concentrations, no significant changes were observed in the CH stretching (3014 cm^{-1}) or bending (1303 cm^{-1}) modes of CH_4 . This is in contrast to IR results for CO_2 , which showed specific changes in the asymmetric CO stretching band, indicative of CO_2 intercalation [6, 9]. It should be noted, however, that the CH stretching and bending modes of CH_4 are about 20 times less intense than the asymmetric CO stretching band at experimental pressure and temperature, which makes detection of CH_4 intercalation more difficult than for CO_2 . These results are consistent with those obtained from *in situ* XRD as illustrated in Figure 2.

3.3. CH_4 : CO_2 System

To probe the effects of CO_2 content in methane-dominated environments, *in situ* IR spectroscopic titrations of montmorillonites with water were carried out in a mixture of 3% (mole percent) CO_2 in methane at 50 °C and 90 bar. These initial studies were conducted with Na-SWy-2 and show an increase in the absorbance of the asymmetric CO stretching band of CO_2 sorbed to the clay (2343 cm^{-1}) as water is first titrated into the mixture (starting from anhydrous conditions). A maximum in the absorbance of this band is eventually reached with increasing dissolved H_2O concentrations, but the absorbance decreases thereafter. Pressurized XRD experiments conducted with a sub 1W Ca-SWy-2 clay indicate a structural change in the montmorillonite did not occur with pure CH_4 gas. Figure 3 shows the Ca-SWy-2 clay in the vacuum state, which produces an 11.59 Å d_{001} value, consistent with a sub 1W hydration state [23]. After exposure to anhydrous CH_4 containing 3% CO_2 , the d_{001} value expands to 12.27 Å, and the higher-order d_{004} reflection increases

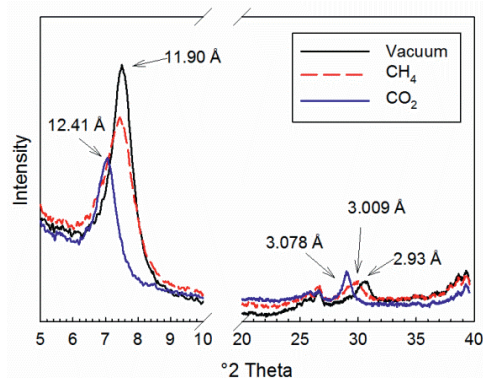


Figure 2. Results from XRD analysis showing a stable calcium montmorillonite structure exposed to CH_4 , but expanded in the presence of scCO_2 (50 °C, 90 bar).

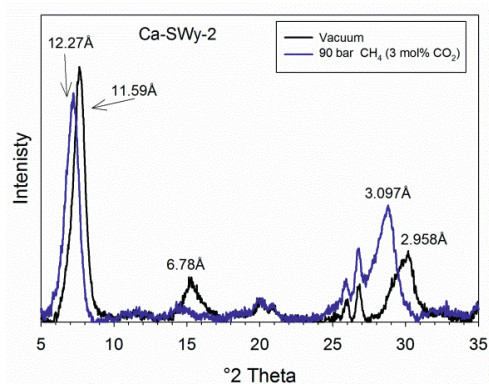


Figure 3. Results from *in situ* XRD analysis showing a montmorillonite under vacuum and then during exposure to CH_4 containing 3 mol % CO_2 (50°C, 90 bar).

from 2.958 to 3.097 Å. To further characterize the mixed-gas system, a series of experiments are underway to obtain sorbed H₂O concentrations and d_{001} structural values as a function of percent H₂O saturation for a broader range of CO₂ concentrations in CH₄. However, based on these limited measurements, preliminary results point towards similar behaviour of CO₂ towards intercalation, even in CO₂/CH₄ mixtures with low CO₂ content.

Atomistic simulations, based on Ca-montmorillonite models [14], were used to compare CO₂ and CH₄ sorption potentials as a function of pressure. Figure 4 shows estimates of CH₄ (red) and CO₂ (blue) adsorption energies over hydrated Ca-montmorillonite (~1W). In agreement with experimental observations previously published for Ca-SWy-2 [9] and described in section 3.1 for Na-SWy-2 where CO₂ adsorption reaches a maximum at ~90-100 bar, the simulated adsorption curve shows an energy minimum, indicating increased stabilization. Continued increases in pressure results in desorption as the condensed layer becomes bulk-like. Unlike CO₂, the methane adsorption energy is favorable (negative) throughout the range of pressures. Molecular trajectories were also generated to quantify the difference in sorption behavior between CO₂ and CH₄. The analysis identifies enhanced CH₄ sorption occurring at low hydration states (sub-1W to 1W), where interaction of CH₄ with sorbed Ca cations is most favorable. Based on DFT calculations, estimated interaction energies between Ca²⁺/CH₄ are ~50% lower compared to Ca²⁺/H₂O; Ca²⁺/CO₂ interactions are ~70% of Ca²⁺/H₂O. Results from these calculations suggest interactions between cations, H₂O, and CO₂ are enhanced compared to those predicted for CH₄. Deconvoluting interactive forces influencing CH₄:CO₂ exchange mechanisms provide value for estimating CO₂ reservoir storage capacities.

3.4. SO₂:CO₂ System

Impacts of trace impurities such as SO₂ on the sorption of CO₂ onto clay minerals were investigated. In our earlier work [13], extraction of gaseous sulfur (SO₂) from a mixed gas stream (CO₂, SO₂) was achieved by contacting hydrated dolomite with scCO₂ containing 1 wt% SO₂. Gaseous SO₂ was permanently converted into a solid through the formation of sulfite minerals, resulting in a nearly pure scCO₂ fluid. In this study, we expanded on our previous work by investigating the behavior of important shale minerals, such as kaolinite and montmorillonites. As-received powdered clay standards (KGa-1, STx-1, and SWy-2) were exposed to anhydrous scCO₂ containing 1 wt% SO₂ and allowed to equilibrate at 50°C, 90 bar for 16 days. Figure 5 shows the measured SO₂/CO₂ ratio determined for each clay as a function of time. The SWy-2 clay removes SO₂ during the first 48 hours. This trend continues over the next 14 days until nearly all detectable SO₂ is sequestered. In contrast, the kaolinite (KGa-1) and Texas montmorillonite (STx-1) show little propensity to sorb SO₂. Upon conclusion of the 16-day study, ~75% of the measurable SO₂ remained in the gaseous form for the KGa-1 and STx-1 clays. Post characterization by XRD did not detect sulfur containing minerals on the reacted samples. Although distinguishing the types of interactions occurring between the clay and SO₂ (i.e. sorption, intercalation) is not possible with these types of measurements, theory-based simulations suggest intercalation of SO₂ is energetically favorable [14]. Immobilizing trace contaminants and predicting mineral stability during exposure to mixed acid gas fluids has implications for long-term reservoir stability.

3.5. Economics

Of crucial importance in assessing the theoretical potential for additional methane recovery and CO₂ storage is a

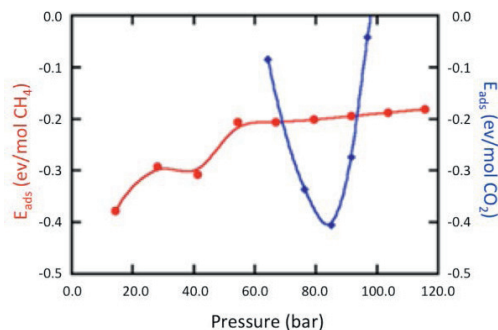


Figure 4. CH₄ and CO₂ adsorption energy variation as a function of pressure at 50 °C.

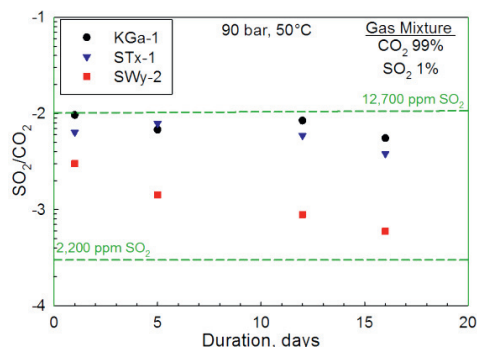


Figure 5. Adsorption of SO₂ onto clay minerals as a function of time at 50°C and 90 bar (99% CO₂, 1% SO₂).

deep understanding of the physical and chemical processes by which these gases interact with each other and the mineral and organic components of various shales. Figure 1 illustrates relative sorption capacities of methane and CO₂ for Na-SWy-2. Methane sorption data for Ca-SWy-2 is provided in Figure 6 along with the CO₂ sorption data [9]. As expected and based on published experimental and simulation work on gas sorption in shales [19, 24], the preference of important clay minerals for CO₂ sorption over methane is clear throughout most of the range of pressures evaluated. However, depending on the clay mineral, affinity for CO₂ exceeds the pressure-dependent increase in methane adsorption by more than twice what the trend from 0 to 75 bar would suggest. This indicates what may be a meaningful “sweet spot” for CO₂ storage in shales, allowing more CO₂ to be adsorbed onto clays of this type relative to the amount of methane displaced, subject to physical constraints on volumetric expansion. Understanding this behavior for each of the important constituents of gas-bearing shales will enable a more nuanced understanding of amenability to CO₂ storage. This can be used to inform not only reservoir simulation, but also resource estimates and economic valuation.

For example, of the 27 assessment units evaluated by Davidson & McGrail [1], only two are at average depths that fall within the pressure range of elevated CO₂ affinity shown in Figure 6. The Niobrara Chalk and New Albany shales, both of which are relatively shallow shale reservoirs, are expected to have pressures in this range, suggesting that they may be able to serve as better-than-average targets for CO₂ storage. However, it is also worth noting that the other assessment units evaluated in that study are at depths where pressures are expected to exceed the range of pressures evaluated in this paper and by Schaefer et al. [9]. This understanding is being used to guide future experimental and simulation work, to ensure that laboratory and computational research is addressing the conditions likely to be encountered in the field.

3.6. Reservoir Modeling

Integration of laboratory-derived measurements into reservoir simulators provides a more robust approach to estimating recoverable amounts of CH₄ in fractured depleted shale gas formations through CO₂ based injection technologies. As an example of how simulators such as STOMP-COMP may be used to optimize injection/extraction scenarios to maximize sequestration of CO₂ and SO₂ (simulate post- and oxy-combustion flue gas streams), simulations of EGR in a formation with hydraulic properties based on the New Albany Shale [25] were developed. The model includes a CO₂ injection well and a CH₄ production well, each with four stages of hydraulic fracturing. The initial formation pressure was 28.56 bar; the well-bottom pressure of the producing well was set to 26.56 bar, and the well-top pressure of the injecting well was limited to 30.56 bar. The injection or extraction rate varied according to the pressure differential between the well and the formation, which varied with time. A simple linear isotherm for methane adsorption was assumed, based on experimental data at the reservoir pressure [26]. Competitive adsorption by CO₂ and SO₂ is assumed in proportion to the partial pressures of each of the gases. Symmetry was invoked to focus on a sub-model encompassing only the third stages connected to each well. It was assumed that the hydraulic fracture conductivity is 100 mD-ft with a hydraulic fracture width of 2 ft, and that the natural fracture conductivity is 20 μD-ft. The hydraulic fracture half-length was 450 ft. The reservoir porosity was 14% with an initial water saturation of 40%.

Results obtained from reservoir modeling are shown in Figure 7 and include the cumulative amount of CO₂ and SO₂ injected and the amounts of CH₄, CO₂, and SO₂ produced over a period of 10 years. Following hydraulic fracturing, the reservoir produced methane for five years with a fixed well-bottom pressure of 26.56 bar, resulting in a cumulative methane production of 2.14×10^5 kg. Injection of a CO₂ based fluid containing 1 wt% SO₂ was initiated at year 5 at a fixed well-top pressure of 30.56 bar and allowed to run for 5 years total. Simulation of the reservoir with CO₂ provided an additional 3.3×10^5 kg of methane production. Cumulatively, 1.28×10^7 kg of CO₂ and 1.3×10^5 kg of SO₂ was injected, of which 72% remained in the reservoir after 10 years with 97% of the SO₂ being immobilized.

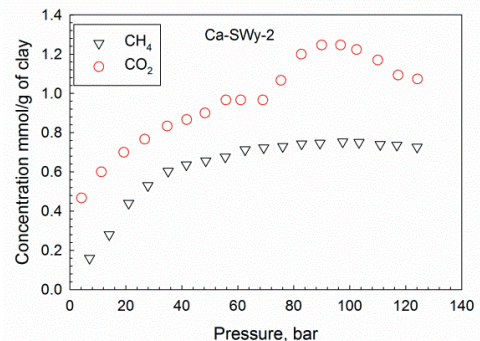


Figure 6. Relative sorption capacities for CO₂ and CH₄ on calcium montmorillonite (Ca-SWy-2) 50°C and 90 bar.

Impacts of clay swelling due to CO₂ were considered to examine changes in reservoir properties during CO₂-EGR. An increase of interlayer thickness from 11.59 Å to 12.27 Å indicates an estimated montmorillonite volume increase of 5.8%. A formation consisting of 20% montmorillonite would undergo a 1% increase in solid volume fraction which translates into a decrease in porosity from 14% to 13%. Shale gas diffuses from micro-pores in the shale matrix, traveling into the large pores and fractures, following Darcy's law [27]. If CO₂ induced swelling occurs, micro-porosity and fluid flow rates into the primary fracture network are most vulnerable.

4. Conclusion

Development of economic models for identifying early CO₂-EGR opportunities requires accurate methane recovery estimates and CO₂ storage capacities. Integration of laboratory derived measurements into cost simulators allows a robust comparison of reservoir characteristics alongside a consideration of capital resources and existing infrastructure. Through a series of *in situ* experiments and theory based calculations, phase behavior of sorbed gases (CO₂, CH₄, and SO₂) onto important clay minerals has provided new insights into gas-mineral interactions. Moreover, after identification of suitable targets, obtaining key experimental data for specific shale mineralogy reservoirs for inclusion in reservoir models is strategic to optimizing injection rates and volumes for maximum CH₄ desorption and CO₂ retention at a field-scale level.

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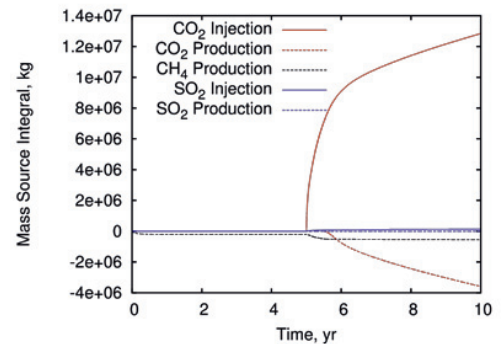


Figure 7. Amount of CO₂ and SO₂ injected compared with amount of CH₄, CO₂ and SO₂ produced.

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