

## **CARBON SEQUESTRATION IN NATURAL GAS RESERVOIRS: ENHANCED GAS RECOVERY AND NATURAL GAS STORAGE**

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### **ABSTRACT**

Natural gas reservoirs are obvious targets for carbon sequestration by direct carbon dioxide (CO<sub>2</sub>) injection by virtue of their proven record of gas production and integrity against gas escape. Carbon sequestration in depleted natural gas reservoirs can be coupled with enhanced gas production by injecting CO<sub>2</sub> into the reservoir as it is being produced, a process called Carbon Sequestration with Enhanced Gas Recovery (CSEGR). In this process, supercritical CO<sub>2</sub> is injected deep in the reservoir while methane (CH<sub>4</sub>) is produced at wells some distance away. The active injection of CO<sub>2</sub> causes repressurization and CH<sub>4</sub> displacement to allow the control and enhancement of gas recovery relative to water-drive or depletion-drive reservoir operations. Carbon dioxide undergoes a large change in density as CO<sub>2</sub> gas passes through the critical pressure at temperatures near the critical temperature. This feature makes CO<sub>2</sub> a potentially effective cushion gas for gas storage reservoirs. Thus at the end of the CSEGR process when the reservoir is filled with CO<sub>2</sub>, additional benefit of the reservoir may be obtained through its operation as a natural gas storage reservoir. In this paper, we present discussion and simulation results from TOUGH2/EOS7C of gas mixture property prediction, gas injection, repressurization, migration, and mixing processes that occur in gas reservoirs under active CO<sub>2</sub> injection.

### **INTRODUCTION**

Depleted natural gas reservoirs are promising sites for geologic carbon sequestration by direct carbon dioxide (CO<sub>2</sub>) injection. First and foremost, natural gas reservoirs have a demonstrated integrity against gas escape shown by their long term containment of methane (CH<sub>4</sub>) and capacity estimated at 140 GtC worldwide (IEA, 1997) and 10 to 25 GtC in the U.S. alone (Reichle et al., 1999). Second, past production activity has allowed them to be relatively well characterized and well understood. Third, there is an existing infrastructure of wells and pipelines and associated land use history amenable to an industrial process such as direct CO<sub>2</sub> injection. These positive

aspects of natural gas reservoirs are further complemented by the fact that recovery factors for gas reservoirs average approximately 75% (Laherrere, 1997), meaning that even when they are considered depleted, many natural gas reservoirs contain significant natural gas that can be potentially recovered by enhanced gas recovery processes associated with injecting CO<sub>2</sub> for carbon sequestration. This additional gas recovery can be used to offset the cost of CO<sub>2</sub> injection. These many aspects of depleted natural gas reservoirs have led to the idea that carbon sequestration with enhanced gas recovery (CSEGR) could be a potentially important process to sequester CO<sub>2</sub> and enhance CH<sub>4</sub> production from depleting gas reservoirs.

Although the concept of CSEGR has been discussed for more than ten years (e.g., van der Burgt et al., 1992; Blok et al., 1997), CSEGR has never actually been tested in any gas reservoir. The main reason for this is that CO<sub>2</sub> is today still an expensive commodity and geologic carbon sequestration is not yet widely practiced. The other reason for resistance to CSEGR is the concern that injected CO<sub>2</sub> will rapidly mix with existing CH<sub>4</sub> thus degrading the natural gas resource.

Recently, we have been carrying out numerical simulations of CSEGR that suggest the process is technically feasible and that mixing between the injected CO<sub>2</sub> and existing CH<sub>4</sub> may not be extensive and that it can potentially be controlled by operational strategies (Oldenburg et al., 2001; Oldenburg and Benson, 2002; Oldenburg et al., 2003). These numerical simulation studies have been complemented by independent laboratory studies that also suggest that CSEGR is technical feasible (Mamora and Seo, 2002).

One strategy that can be used in CSEGR to avoid extensive mixing between injected CO<sub>2</sub> and existing CH<sub>4</sub> is to take advantage the much greater density of CO<sub>2</sub> relative to CH<sub>4</sub> at reservoir conditions and inject CO<sub>2</sub> deep in the reservoir while producing gas from high in the reservoir. In this strategy, CH<sub>4</sub> could be swept from the reservoir both laterally and from the bottom up. At the end of the CSEGR operation, the reservoir would contain mostly CO<sub>2</sub>.

Through the study of CO<sub>2</sub> properties at a range of reservoir conditions, a related use of the post-CSEGR reservoir became apparent. Namely, the post-CSEGR reservoir could be used as a gas storage reservoir with CO<sub>2</sub> playing the role of a cushion gas. It turns out that the same density changes in CO<sub>2</sub> that occur around the critical pressure and that can be used to inhibit mixing during the process of CSEGR can be exploited in a gas storage reservoir operated around the critical pressure (Oldenburg, 2003). This potential post-CSEGR option provides further potential benefit to applying the CSEGR process in depleting natural gas reservoirs.

This paper presents a review of the CSEGR process and the potential post-CSEGR use of the reservoir as a natural gas storage reservoir. Briefly, the scenario we envision involves CO<sub>2</sub> injection into a depleted gas reservoir for CSEGR. Following the nearly complete removal of CH<sub>4</sub> from the reservoir, say over 5–10 years, the CO<sub>2</sub>-filled reservoir can be used for gas storage.

To test these concepts, numerical experiments are carried out using a new TOUGH2 module called TOUGH2/EOS7C. The key to simulating gas reservoir processes is accurate gas mixture property prediction. We present a review of the properties of CO<sub>2</sub> and CH<sub>4</sub> gas mixtures. This is followed by conceptual descriptions of the processes of CSEGR and gas storage with CO<sub>2</sub> as a cushion gas. Next we present a summary of the methods we use to simulate these processes, along with a summary of the verification of our property predictions. In the last parts of the paper, we present simulation results that illustrate the processes. Finally, we discuss limitations and outstanding issues that need to be addressed in research to make progress in these areas.

## GAS PROPERTIES

### Phase Diagram

The phase diagram for CO<sub>2</sub> is shown in Figure 1, along with a typical  $P, T$  path assuming hydrostatic pressure and 25 °C km<sup>-1</sup> gradients with depth in the earth. As shown, CO<sub>2</sub> will be supercritical ( $P_{crit} = 73.8$  bar,  $T_{crit} = 31.0$  °C (Vargaftik, 1975)) in gas reservoirs that are typically at depths greater than 1 km and hotter than 35 °C. In depleted reservoirs, pressures can be below hydrostatic and subcritical conditions may exist. Therefore, the simulation capability must treat both supercritical and gaseous states of CO<sub>2</sub>.

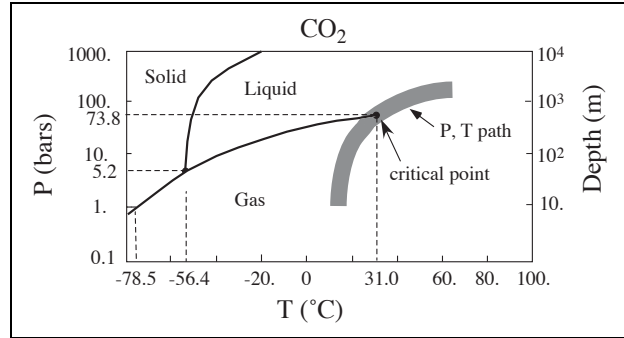


Figure 1. Phase diagram of CO<sub>2</sub> showing typical  $P, T$  path assuming hydrostatic pressure and 25 °C km<sup>-1</sup> geothermal gradient.

### Density and Compressibility Factor

At temperatures near the critical temperature, increasing pressure causes CO<sub>2</sub> to transition from gaseous conditions to supercritical conditions with an associated large change in density. Pure CH<sub>4</sub> exhibits no such drastic change in this same range of pressure and temperature and shows nearly ideal gas behavior. The degree of non-ideality shown by CO<sub>2</sub> can be expressed by the compressibility factor,  $Z$ , where

$$Z = \frac{PV}{nRT} \quad (1)$$

where  $Z = 1.0$  for ideal gases,  $P$  is pressure (Pa),  $V$  is volume (m<sup>3</sup>),  $n$  is moles,  $R$  is the universal gas constant (J mol<sup>-1</sup> K<sup>-1</sup>), and  $T$  is temperature (K). Plotted in Figure 2 are density and compressibility factor ( $Z$ ) of CO<sub>2</sub>-CH<sub>4</sub> mixtures as a function of pressure at  $T = 40$  °C as calculated by the NIST14 database (NIST, 1992; Magee et al., 1994). As shown, the density of supercritical CO<sub>2</sub> can be very high, and is much larger than the density of CH<sub>4</sub> at all relevant gas reservoir conditions.

### Viscosity

The viscosity of CO<sub>2</sub> also increases as pressure rises through the critical pressure. Shown in Figure 3 are density and viscosity of CO<sub>2</sub>-CH<sub>4</sub> mixtures at several different pressures from subcritical to supercritical for CO<sub>2</sub> (NIST14, 1992; Magee et al., 1994). Even though the density of supercritical CO<sub>2</sub> can approach that of liquid water, the viscosities of CO<sub>2</sub>-CH<sub>4</sub> mixtures across the range of compositions are always gas-like. Thus supercritical CO<sub>2</sub> is a highly mobile (low viscosity) fluid with very high density. Note further that CO<sub>2</sub> viscosity is always larger than CH<sub>4</sub> viscosity.

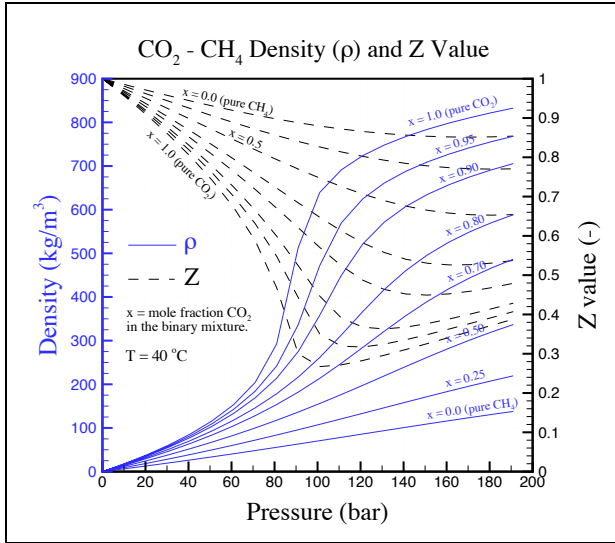


Figure 2. Density and Z factor for  $CO_2$ - $CH_4$  mixtures showing strongly non-ideal behavior of  $CO_2$ -rich gas.

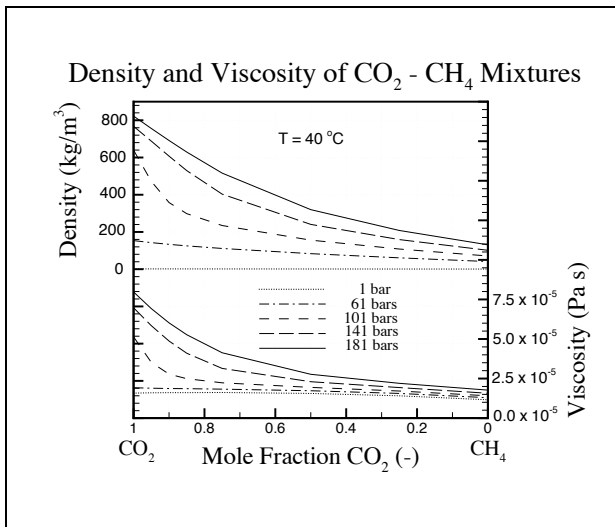


Figure 3. Density and viscosity of  $CO_2$ - $CH_4$  mixtures at several pressures at 40 °C.

**ENHANCED GAS RECOVERY**

Figure 4 shows a schematic of one scenario for CSEGR. In this scenario,  $CH_4$  produced from a depleting gas reservoir is used to generate electricity. The flue gases from power generation and industrial activities are scrubbed and  $CO_2$  is captured, compressed, and transported back to the  $CH_4$  reservoir where it is reinjected at some distance from production wells. In this process, the injection of  $CO_2$  raises the reservoir pressure and displaces  $CH_4$  toward the production wells, thereby enhancing  $CH_4$  production. Because of the pressure maintenance effected by the  $CO_2$  injection, the  $CH_4$  production can

be controlled and water entry avoided in the case of water-drive reservoirs.

One critical issue in this process is the degree to which the injected  $CO_2$  will mix with the  $CH_4$ , degrading the quality of the produced gas. The physical properties of  $CO_2$  and  $CH_4$  at reservoir conditions appear to discourage mixing. Specifically, the high density of  $CO_2$  can be exploited by injecting the  $CO_2$  in the lower parts of the reservoir while producing from higher parts. The lower mobility of  $CO_2$  (higher viscosity) relative to  $CH_4$  produces a stable displacement process. Furthermore, the nearly gas-like viscosity of supercritical  $CO_2$  means that it can be injected easily. Together, the properties of  $CO_2$  and  $CH_4$  including density, viscosity, and viscosity ratio promote downward migration, injectibility, and stable displacements, respectively. These effects work in favor of CSEGR and will be demonstrated in numerical simulations below.

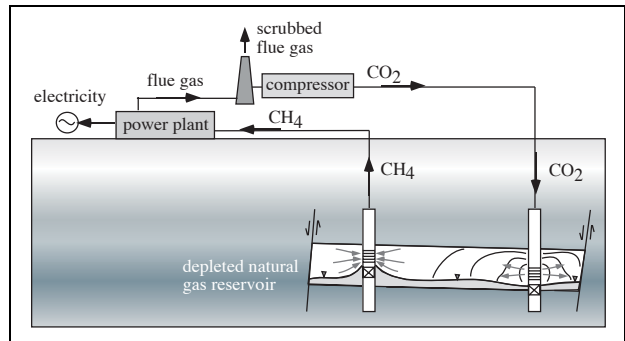


Figure 4. Schematic of CSEGR.

**GAS STORAGE WITH  $CO_2$  AS CUSHION GAS**

Once the reservoir is filled largely with  $CO_2$ , it will serve as an effective carbon sequestration site. Such a reservoir may have additional potential uses, specifically as a natural gas storage reservoir (Oldenburg, 2003). Natural gas storage is used to smooth the natural gas supply (Katz and Tek, 1981). The approach allows storage in reservoirs near metropolitan areas of natural gas ( $CH_4$ ) delivered by pipeline from far-off production fields during periods of low demand, and rapid  $CH_4$  production from the storage reservoir during periods of high demand.

Critical to the use of gas storage reservoirs is the idea of a cushion gas, i.e., a gas whose compression allows additional storage of working gas, and whose expansion helps drive production of the working gas. A schematic showing a gas storage reservoir is shown in Figure 5. Often, the cushion gas is remnant  $CH_4$  in a depleted gas reservoir, although inert cushion gases such as nitrogen have also been used (Laille et al., 1988). Just about any gas will work as

Table 1. Properties of CO<sub>2</sub>-CH<sub>4</sub> gas mixtures and aqueous solubility at 40 and 100 bars, 40 °C.

$P = 40 \text{ bars}, T = 40 \text{ }^\circ\text{C}$		gas phase			aqueous phase	
Prediction Source	$x_g^{\text{CH}_4}$	$x_g^{\text{CO}_2}$	$\rho \text{ (kg m}^{-3}\text{)}$	$\mu \text{ (Pa s)}$	$x_1^{\text{CH}_4}$	$x_1^{\text{CO}_2}$
TOUGH2/EOS7C	0.	1.	85.45	$1.70 \times 10^{-5}$	0.	$1.62 \times 10^{-2}$
Reference Values	0.	1.	83.79 [1]	$1.73 \times 10^{-5}$ [1]	0.	$1.37 \times 10^{-2}$ [2]
TOUGH2/EOS7C	0.5	0.5	51.97	$1.44 \times 10^{-5}$	$3.73 \times 10^{-4}$	$8.07 \times 10^{-3}$
Reference Values	0.5	0.5	51.33 [1]	$1.67 \times 10^{-5}$ [1]	$3.66 \times 10^{-4}$ [3,4,5,6]	$6.74 \times 10^{-3}$ [3,4,5,6]
TOUGH2/EOS7C	1.	0.	26.42	$1.21 \times 10^{-5}$	$7.43 \times 10^{-4}$	0.
Reference Values	1.	0.	26.10 [1]	$1.23 \times 10^{-5}$ [1]	$7.22 \times 10^{-4}$ [3,4,5,6]	0.
$P = 100 \text{ bars}, T = 40 \text{ }^\circ\text{C}$		gas phase			aqueous phase	
TOUGH2/EOS7C	0.	1.	566.00	$4.35 \times 10^{-5}$	0.	$4.03 \times 10^{-2}$
Reference Values	0.	1.	631.90[1]	$5.04 \times 10^{-5}$ [1]	0.	$2.19 \times 10^{-2}$ [2]
TOUGH2/EOS7C	0.5	0.5	155.16	$1.81 \times 10^{-5}$	$9.43 \times 10^{-4}$	$2.00 \times 10^{-2}$
Reference Values	0.5	0.5	153.97 [1]	$1.94 \times 10^{-5}$ [1]	$7.95 \times 10^{-4}$ [3,4,5,6]	$1.21 \times 10^{-2}$ [3,4,5,6]
TOUGH2/EOS7C	1.	0.	71.57	$1.41 \times 10^{-5}$	$1.86 \times 10^{-3}$	0.
Reference Values	1.	0.	70.03 [1]	$1.41 \times 10^{-5}$ [1]	$1.54 \times 10^{-3}$ [3,4,5,6]	0.

<sup>1</sup>NIST, 1992. <sup>2</sup>Wiebe and Gaddy, 1940. <sup>3</sup>Spycher and Reed, 1988. <sup>4</sup>Johnson et al., 1992. <sup>5</sup>Shock et al., 1989. <sup>6</sup>Wagman et al., 1982.

a cushion gas. However, CO<sub>2</sub> that is compressed through its critical pressure near the critical temperature is a very effective cushion gas because of its large compressibility. This can be seen in Figure 2 by the large change in density or corresponding small value of Z. Thus the use of a CO<sub>2</sub> cushion gas will allow more gas to be stored for a given pressure rise than is possible with a native gas or nitrogen cushion (Oldenburg, 2003). This process will be demonstrated by numerical simulation below.

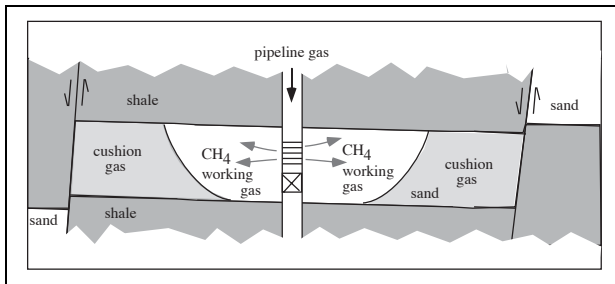


Figure 5. Schematic of gas storage showing cushion gas that is never produced.

### SIMULATION METHODS

For the simulation of CSEGR and gas storage with CO<sub>2</sub> as a cushion gas, we are using a new module called TOUGH2/EOS7C. This module was developed by extending EOS7R (Oldenburg and Pruess, 1995; Pruess et al., 1999) by changing one of the volatile components to CO<sub>2</sub>, and by changing the air to CH<sub>4</sub>. Thus, EOS7C considers five mass components (water, brine, CO<sub>2</sub>, gas tracer, CH<sub>4</sub>) and heat. Solubility subroutines for CO<sub>2</sub> and CH<sub>4</sub> were

taken from EWASG (Battistelli et al., 1997; Cramer, 1982). For the key gas mixture properties, new real gas mixture subroutines were developed to calculate density and enthalpy departure in the system H<sub>2</sub>O-CO<sub>2</sub>-CH<sub>4</sub> using the Peng-Robinson equation of state (e.g., Poling et al., 2001). Accurate gas mixture viscosities are calculated using the method of Chung et al. (1988). A summary of gas mixture properties is presented in Table 1 for verification of the gas properties module. As shown, TOUGH2/EOS7C predicts density and viscosity very well, but overpredicts gas solubility. Current efforts are underway to improve the solubility model. Future effort is needed to test and verify the non-isothermal capabilities of TOUGH2/EOS7C.

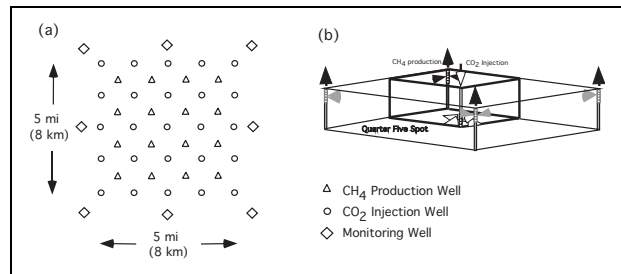


Figure 6. Schematic of model gas reservoir well pattern and quarter five-spot simulation domain.

### CSEGR

We have used TOUGH2/EOS7C to carry out a number of CSEGR simulation studies over the last several years (e.g., Oldenburg et al., 2001; Oldenburg

and Benson, 2002; Oldenburg et al., 2003). Here we present a representative result that demonstrates the concept of injecting CO<sub>2</sub> deep in the reservoir while producing from higher in the reservoir.

A schematic of the model well pattern and five-spot reservoir geometry are shown in Figure. 6, while properties of the model reservoir are presented in Table 2. The reservoir properties and injection and production rates are based loosely on the Rio Vista gas field in California (Cummings, 1999; Johnson, 1990). Someday carbon dioxide could be sent by pipeline from electricity generation and industrial sources in the San Francisco Bay Area to the Rio Vista gas field.

Table 2. Properties of the quarter five-spot domain.

Property	Value
Quarter five spot size (21 x 21 gridblocks in X-, Y-dir.)	6.4 x 10 <sup>5</sup> m <sup>2</sup> (160 acres)
Reservoir thickness (10 gridblocks in Z-dir.)	50 m (160 ft)
Porosity	0.30
Permeability (isotropic)	1 x 10 <sup>-12</sup> m <sup>2</sup>
Residual liquid saturation	0.20
<i>Relative permeability</i>	
Liquid	Immobile.
Gas	Equal to gas saturation.
Diffusivity in gas and liquid	1.0 x 10 <sup>-5</sup> m <sup>2</sup> s <sup>-1</sup> , 1.0 x 10 <sup>-10</sup> m <sup>2</sup> s <sup>-1</sup>
Temperature (isothermal)	75 °C (167 °F)
Pressure at start of CSEGR	50 bars (725 psi)
CO <sub>2</sub> inj. rate (per full well)	3 kg s <sup>-1</sup> (260 t/day)
CH <sub>4</sub> prod. rate (per full well)	0.56 kg s <sup>-1</sup> (48 t/day)
Pressure (after 15 years)	60 bars (870 psi)

Simulation results are shown in Figure 7 for the 3-D quarter five-spot domain in which CO<sub>2</sub> is injected in the lower 10 m of a 50 m thick reservoir while CH<sub>4</sub> is produced from the top 10 m. In this configuration, the high density of CO<sub>2</sub> makes it remain in the lower parts of the reservoir, and CH<sub>4</sub> displacement is to some degree from the bottom up. As shown in Figure 7, the CO<sub>2</sub> breakthrough occurs after approximately 15 years, before which time high CH<sub>4</sub> production rates could be maintained by means of CO<sub>2</sub> injection and sustaining high pressure in the reservoir. Although not modeled specifically in this study, pressure maintenance would help prevent water from entering the reservoir and discourage land subsidence that is observed at some gas fields.

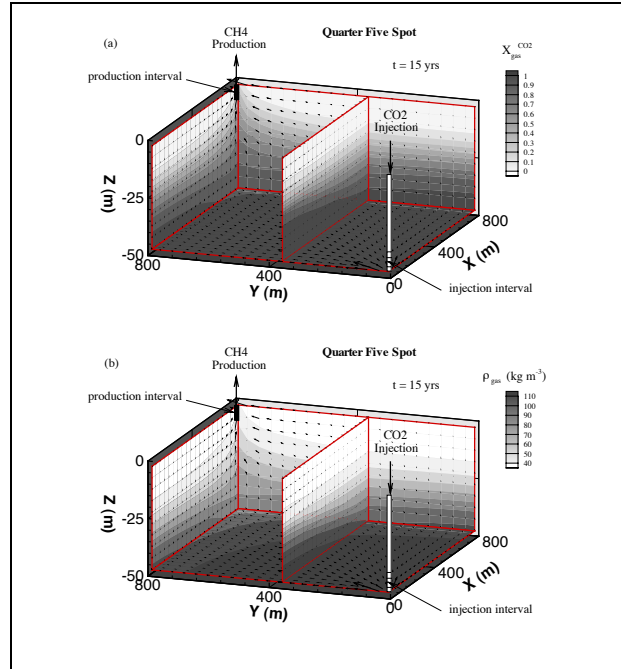


Figure 7. Simulation results of mass fraction CO<sub>2</sub> and gas-phase density.

Table 3. Properties of the model gas storage reservoir.

Property	Value
Area (X-, Y-direction)	4 km x 1 km (1.5 mi <sup>2</sup> )
Thickness (Z-direction)	22 m
Gridblocks in X-, Y-dir.	1 x 200
Gridblocks in Z-dir.	11
Porosity	0.30
Permeability (isotropic)	1.0 x 10 <sup>-12</sup> m <sup>2</sup>
Relative permeability	Van Genuchten (1980)
$m, S_{lr}, S_{ls}, S_{gr}$	0.2, 0.27, 1, 0.01
Liquid is immobile	$S_l \approx 0.26 < S_{lr}$
Diffusivity gas, liquid	1.0 x 10 <sup>-6</sup> , 1.0 x 10 <sup>-10</sup>
Temperature	40 °C (isothermal)
Initial pressure	60 bars
CH <sub>4</sub> injection rate	73.5 kg s <sup>-1</sup>

### SIMULATIONS OF CO<sub>2</sub> AS CUSHION GAS

Simulations of an idealized two-dimensional gas storage reservoir with CO<sub>2</sub> as a cushion gas have also been carried out (Oldenburg, 2003). The idea here is that after CSEGR is completed, the reservoir could be used for gas storage. We present in Table 3 properties of the model gas storage reservoir idealized to represent a reservoir that is an elongated dome structure with a line of wells along the axis. Note that the reservoir starts at 60 bars and will exceed the CO<sub>2</sub> critical pressure (73.8 bars) during the storage cycle.. Shown in Figure 8 are contours of CO<sub>2</sub> mass fraction in the gas at three times during the storage cycle. The working gas is injected in the

upper left-hand corner of the model domain. Figure 9 shows the corresponding gas density for the same simulation. Note that the CO<sub>2</sub> cushion gas density increases from just below 200 kg m<sup>-3</sup> to just below 600 kg m<sup>-3</sup>. As shown, the CO<sub>2</sub> cushion drastically compresses, allowing more volume for CH<sub>4</sub> for a given pressure increase.

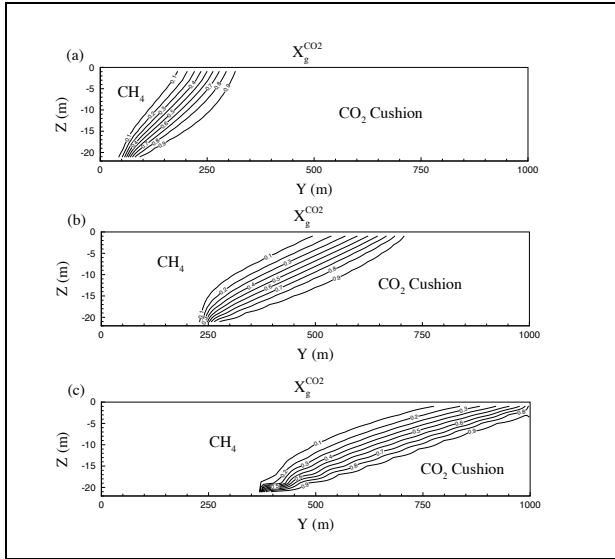


Figure 8. Two-dimensional simulation results of CO<sub>2</sub> mass fraction where CO<sub>2</sub> is the cushion gas: (a) 30 days; (b) 90 days, and (c) 180 days.

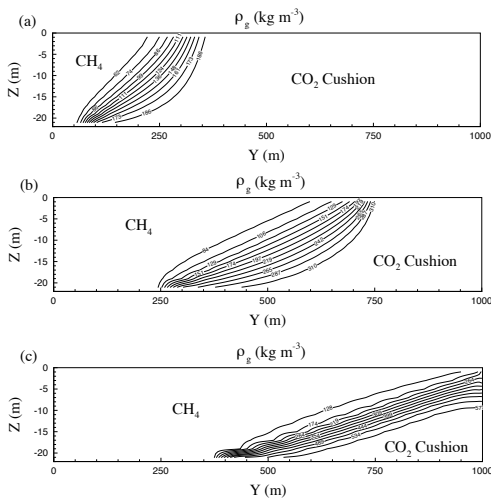


Figure 9. Two-dimensional simulation results of gas-phase density where CO<sub>2</sub> is the cushion gas: (a) 30 days; (b) 90 days, and (c) 180 days.

A comparison of the pressure increase during gas storage over a half a year for the case of CO<sub>2</sub> as a

cushion gas, CH<sub>4</sub> as a cushion gas, and for CH<sub>4</sub> as cushion gas using 70% of the CH<sub>4</sub> injection rate, is presented in Figure 10. This figure shows that using CO<sub>2</sub> as a cushion gas allows approximately 30% more gas to be stored for a given pressure increase relative to using a native CH<sub>4</sub> cushion gas.

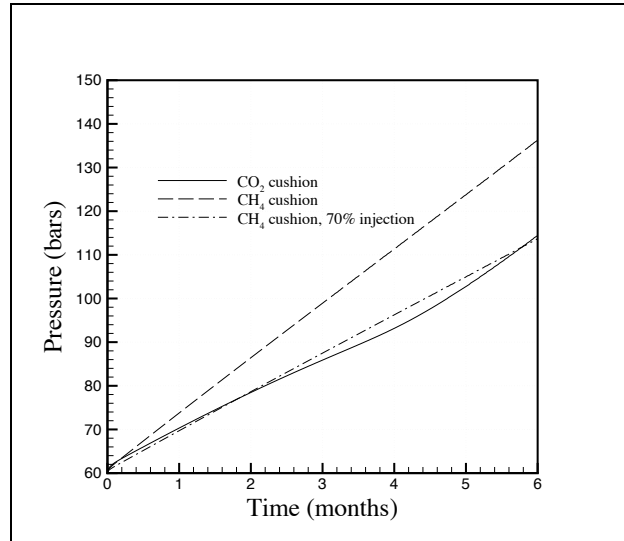


Figure 10. Pressure vs. time for one cycle of CH<sub>4</sub> injection showing the lower pressure rise for CO<sub>2</sub> cushion gas relative to a native gas cushion.

The simulations carried out to date include significant numerical dispersion, making a mixing zone that is artificially large. For a rectangular grid with full upstream weighting, the numerical dispersion is approximately one-half the grid spacing multiplied by the gas velocity. For these simulations, numerical dispersion is on the order 10<sup>-4</sup> m<sup>2</sup> s<sup>-1</sup> (5 m/2 x 700 m/6 months), approximately two orders of magnitude greater than molecular diffusion. Nevertheless, gas mixing will be a concern in actual practice since the injection and production cycle operate repeatedly over the years, unlike CSEGR which is a one-time displacement. Considerable additional research will have to be done before CO<sub>2</sub> can be considered a practical cushion gas. Nevertheless, the unique properties of CO<sub>2</sub> make it an intriguing cushion gas option. Other configurations and applications, for example, for gas storage in an open tank or solution-mined cavity with a physical barrier separating the two gases, are being investigated to avoid the mixing problem.

### CONCLUSIONS

Simulation studies suggest that CSEGR and gas storage with CO<sub>2</sub> as a cushion gas may be technically feasible uses of depleting gas reservoirs. In both processes, the properties of CO<sub>2</sub> and CH<sub>4</sub> favor

limited mixing of the gases. In particular, the large density and viscosity of CO<sub>2</sub> relative to CH<sub>4</sub> favor lack of mixing for CO<sub>2</sub> displacing CH<sub>4</sub> in CSEGR. The large effective compressibility of CO<sub>2</sub> for pressures around the critical pressure favors the use of CO<sub>2</sub> as a cushion gas. We envision a scenario where depleting gas reservoirs near CO<sub>2</sub> sources are first used for approximately a decade for CSEGR, and then after CO<sub>2</sub> breakthrough, they can be used as gas storage reservoirs. Additional simulation capability development to consider nonisothermal effects and further detailed reservoir characterization will have to be carried out to investigate these processes further. In the meantime, a field pilot experiment of CSEGR should be carried out to verify the simulation results and further test the idea.

#### **ACKNOWLEDGMENT**

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