# **Carbon Dioxide as Cushion Gas for Natural Gas Storage**

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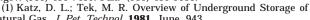
Natural gas storage is used to smooth the natural gas supply to meet high peak demand. In natural gas storage, the working gas (methane) is injected and produced seasonally while a cushion gas that is not extracted is used to provide pressure support. In the case of depleted gas reservoirs being used for gas storage, the cushion gas is commonly leftover native gas (methane). Another approach is to produce most of the methane from the reservoir since it can be sold for profit and inject a cheap inert gas for use as the cushion gas. Carbon dioxide injection during carbon sequestration with enhanced gas recovery can be carried out to produce the methane while simultaneously filling the reservoir with carbon dioxide. Carbon dioxide undergoes a large change in density near its critical pressure, an advantageous feature if used as a cushion gas. Furthermore, the injection of carbon dioxide into the ground may in the future be economically favorable through carbon credits or tax advantages offerred to encourage carbon sequestration. Reservoir simulations of methane injection into a model gas storage reservoir with carbon dioxide as cushion gas demonstrate that 30% more methane can be stored relative to a native gas cushion. Along with economic considerations of carbon dioxide and natural gas prices, the critical issue for the use of carbon dioxide as a cushion gas is limiting the rate of mixing between methane and carbon dioxide through careful reservoir selection and operations.

#### Introduction

Underground natural gas storage is relied upon to smooth the natural gas supply to meet high peak gas demands. The key to smoothing the supply is to be able to store during periods of low demand large quantities of gas that can be produced quickly to meet peak demand. To this end, excess natural gas (methane) delivered by pipelines to metropolitan areas is injected into large underground reservoirs. These are most commonly depleted natural gas reservoirs, but natural gas storage reservoirs can also be developed in aquifers and in mined caverns, e.g., produced by solution mining. When demand for gas exceeds supply, for example, during cold weather when household heating peaks or during hot weather when large amounts of electricity must be generated for air conditioning, gas is withdrawn from the gas storage reservoir to supplement the pipeline supply and meet the peak demand. When demand for natural gas is low, gas is taken from the pipeline and injected into the gas storage reservoir.

A cross-section schematic of an idealized gas storage reservoir developed in a depleted gas reservoir is shown in Figure 1 where the working gas is methane (CH<sub>4</sub>) from the pipeline. Critical to the operation of gas storage reservoirs is the use of a cushion gas, i.e., a gas that compresses and expands as the working gas is injected or withdrawn but which is itself not produced. In the U. S., there are 415 underground natural gas storage

Natural Gas. J. Pet. Technol. 1981, June, 943.



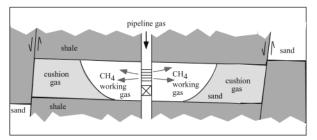


Figure 1. Idealized single-well natural gas storage schematic showing working gas and cushion gas.

sites, of which 348 are in depleted gas reservoirs, with total working gas capacity of 3900 Bcf (7.4  $\times$  10<sup>10</sup> kg) of CH<sub>4</sub> of which 86% is in depleted gas reservoirs.<sup>2</sup> As such, the cushion gas in the U.S. is most commonly the native gas left over after the reservoir was depleted. However, inert cushion gases such as nitrogen (N2) that are injected specifically for use as cushion gas have been used successfully in France for more than 20 years.<sup>3,4</sup> The advantage of using an inert gas cushion is that more of the existing native gas can be sold to generate revenue in the case of depleted gas reservoirs, and the operator will not have to buy expensive methane to use

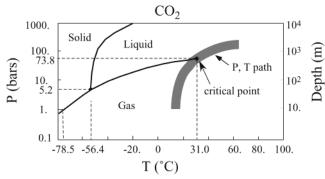
<sup>\*</sup> To whom correspondence should be addressed. cmoldenburg@ lbl.gov. (510) 486-7419. Fax: (510) 486-5686.
(1) Katz, D. L.; Tek, M. R. Overview of Underground Storage of

<sup>(2)</sup> Tobin, J.; Thompson, J. Natural Gas Storage in the United States in 2001: A Current Assessment and near-Term Outlook. U. S. DOE Energy Information Administration: Washington, DC, 2001.

<sup>(3)</sup> Laille, J.-P.; Molinard, J.-E.; A. Wents, A. Inert Gas Injection as Part of the Cushion of the Underground Storage of Saint-Clair-Sur-Epte, France. Presented at the Gas Technology Symposium, Dallas, Texas, June 13–15, 1988. In *Soc. Pet. Eng.*, SPE-17740

<sup>(4)</sup> Misra, B. R.; Foh, S. E.; Shikari, Y. A.; Berry, R. M.; Labaune, F. The Use of Inert Base Gas in Underground Natural Gas Storage. Presented at the Gas Technology Symposium, Dallas, Texas, June 13–15, 1988. In *Soc. Pet. Eng.*, SPE-17741.





**Figure 2.** Semilog plot phase diagram for CO<sub>2</sub> showing CO<sub>2</sub> will be supercritical in typical natural gas reservoirs.

as a cushion in the case of aguifer and solution-mined cavern storage reservoirs. Although the use of inert cushion gases in the U. S. has been considered, 5,6 they are not used at this time in North America.

As the working gas is injected against the cushion gas, pressure in the reservoir increases. Care must be taken not to overpressurize the gas reservoir due to the potential for leakage and for compromising the integrity of the formation cap if the reservoir is over pressurized. Similarly, as gas is withdrawn and the pressure becomes low, there is a point when it is no longer economically feasible to produce gas. As indicated by the name "cushion," compressibility is the key property of cushion gases. Because all gases are compressible, just about any gas can be used as a cushion gas. However, the efficiency of gas storage operations can be increased if the cushion gas has greater effective compressibility.

The purpose of this paper is to discuss the physical properties of carbon dioxide (CO2) and CH4 and show by way of numerical simulations that CO2 may be a good choice for a cushion gas because of its high effective compressibility near its critical pressure. There may also be economic incentive for using CO<sub>2</sub> through carbon credits and tax advantages created to encourage carbon sequestration. Gas storage with CO2 as cushion gas may be a logical choice for further use of gas reservoirs that have been filled with CO<sub>2</sub> during the proposed process of carbon sequestration with enhanced gas recovery (CSEGR).7

# Physical Properties of CO<sub>2</sub> and CH<sub>4</sub>

Figure 2 shows the phase diagram of CO<sub>2</sub> with a typical subsurface P-T path assuming hydrostatic pressure and a geothermal gradient of 25 °C/km. Because of the geothermal gradient and typical depth of gas storage reservoirs, CO2 will normally be supercritical by virtue of temperature, and may be supercritical in terms of pressure depending on the depth and stage in the annual storage cycle. The density of CO<sub>2</sub> changes drastically around its critical point of 31.0 °C

and 73.8 bar. The nonideality of real gases can be expressed by the compressibility factor Z, where

$$Z = \frac{PV}{nRT} \tag{1}$$

and where Z = 1.0 for ideal gases, P is pressure (Pa), Vis volume  $(m^3)$ , n is moles, R is the universal gas constant (J mol $^{-1}$  K $^{-1}$ ), and T is temperature (K). Shown in Figure 3 are real gas density ( $\rho$ ) and Z of various CO<sub>2</sub>-CH<sub>4</sub> mixtures as a function of pressure at 40 °C calculated from the NIST14 database.<sup>8,9</sup> Note from the figure that for pure CH<sub>4</sub> Z varies from 1.0 to approximately 0.85, while Z for CO<sub>2</sub> varies from 1.0 to less than 0.3. As shown in Figure 3, when the pressure changes from 60 to 130 bar, the density of pure CO<sub>2</sub> increases by a factor of 5, whereas pure CH<sub>4</sub> density increases by just over a factor of 2. If CO<sub>2</sub> were used as a cushion gas within the pressure range of 60–130 bar, it would allow significantly larger quantities of working gas to be injected with less increase in pressure relative to using a cushion gas consisting of native gas or inert gas (e.g., nitrogen, N<sub>2</sub>). Furthermore, when the working gas is withdrawn and the reservoir pressure decreases, there will be a corresponding larger gas drive due to the rapid decrease in density (i.e., increase in volume) of the CO<sub>2</sub> cushion gas.

Figure 4 shows density and viscosity at various pressures as a function of composition at 40 °C. Although the density of supercritical CO<sub>2</sub> approaches that of liquid water, the viscosity is always gaslike, i.e., on the order of  $10^{-5}$  Pa s. The relative mobility of the two gases will be controlled by the term

$$M = \frac{k_{\rm r}}{\mu} \tag{2}$$

where M is the mobility ratio,  $k_r$  is gas relative permeability, and  $\mu$  is gas viscosity. As can be seen in Figure 4, the mobility of CH<sub>4</sub> is larger than the mobility of CO<sub>2</sub> due to the lower viscosity of CH<sub>4</sub>. This will tend to make the interface between CH<sub>4</sub> and CO<sub>2</sub> unstable as working gas is injected against the CO<sub>2</sub> cushion. However, the opposite situation will arise during the production cycle, as relatively viscous CO<sub>2</sub> pushes against CH<sub>4</sub>. The coefficient multiplying the pressure gradient to give the mass flux of gas in a porous medium is  $\rho Mk$ , where *k* is the permeability of the medium. Note from Figure 4 that variations in the density and viscosity of the two gases and their mixtures are strongly correlated. This correlation will make the flow term  $\rho Mk$  relatively constant as a function of pressure for the two gases. The compensating effects of density and viscosity imply that the displacement processes between the two gases will not change significantly as pressure changes.

### **Modeling Approach**

Because CO<sub>2</sub> has not yet been used as a cushion gas for gas storage, the analysis approach used here is numerical simula-

(9) NIST (National Institute of Science and Technology). NIST Database 14 Mixture Property Database, version 9.08; U.S. Department of Commerce: Washington, DC, Oct 1992.

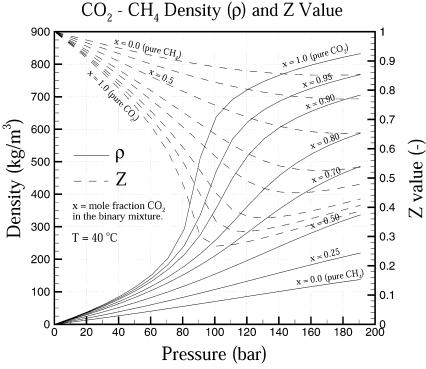
<sup>(5)</sup> Walker, C. J.; Huff, R. V. Feasibility of Inert-Gas Cushions in Gas Storages. Bureau of Mines Report of Investigations 6534; U. S.

Department of the Interior: Washington, DC, 1964; 25 pp.

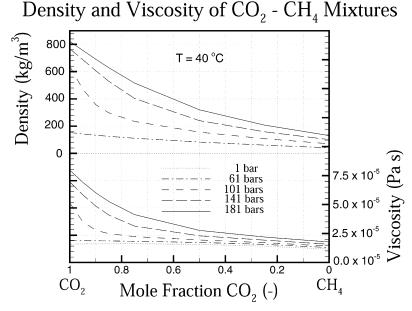
(6) Department of Energy (U. S. DOE). Economic Feasibility of Inert Cushions in Underground Gas Storage; DOE/FE/33008-1, Sept 1980.

(7) Oldenburg, C. M.; Benson, S. M.; Pruess, K. Process Modeling of CO<sub>2</sub> Injection into Natural Gas Reservoirs for Carbon Sequestration and Enhanced Gas Recovery. Energy Fuels 2001, 15, 293-298.

<sup>(8)</sup> Magee, J. W.; Howley, J. A.; Ely, J. F. A Predictive Model for the Thermophysical Properties of Carbon Dioxide Rich Mixtures. Research Report RR-136; Gas Processors Association: Tulsa, OK, 1994;



**Figure 3.** Density and Z value of  $CO_2$ – $CH_4$  mixtures at T = 40 °C.



**Figure 4.** Density and viscosity of  $CO_2$ – $CH_4$  mixtures at several relevant pressures at T = 40 °C.

tion in a generic storage reservoir. The purpose of this approach is to demonstrate generally the main effect of the large increase in density of  $CO_2$  around the critical region and its role in increasing storage capacity. Simulation results presented below are carried out using EOS7C, a research module of the integral finite difference TOUGH2 code<sup>10</sup> that considers multiphase, multicomponent, and real-gas mixture properties for flow and transport of water, brine,  $CO_2$ , gas tracer,  $CH_4$ , and heat in subsurface systems.

The model system is a two-dimensional slice of a 2 km  $\times$  4 km (1.5 mi²) reservoir typical of depleted gas reservoirs in the unconsolidated sediments of the California San Joaquin-

(10) Pruess, K.; Oldenburg, C.; Moridis, G. *TOUGH2 User's Guide*, version 2.0; Lawrence Berkeley National Laboratory Report LBNL-43134; Lawrence Berkeley National Laboratory: Berkeley, Nov 1999.

Sacramento River Delta area. Properties of the model reservoir are shown in Table 1, where the relative permeability function is based on the models of Mualem and van Genuchten. The model reservoir as shown in Figure 5 is 22 m thick by 1000 m wide by 4 km long with a single injection and production well and models one-half (assuming mirrorplane symmetry) of a 2 km  $\times$  4 km reservoir. This two-dimensional geometry is an approximation of a physical reservoir in which a line of wells exists along the center line of the 4-km-long reservoir. As such, the single-well injection and production rates are representa-

<sup>(11)</sup> Mualem, Y. A New Model for Predicting the Hydraulic Conductivity of Unsaturated Porous Media. *Water Resour. Res.* **1976**, *12*, 513–522.

<sup>(12)</sup> Van Genuchten, M. Th. A Closed Form Equation for Predicting the Hydraulic Conductivity of Unsaturated soils. *Soil Sci. Soc. Am. J.* **1980**, *44*, 892–898.

Table 1. Properties of the Model Gas Storage Reservoir

property	value	units
reservoir area (X- and Y-direction)	4000 × 1000 (1.5 mi²)	m <sup>2</sup>
reservoir thickness (Z-direction)	22	m
porosity	0.30	
permeability (isotropic)	$1.0 imes10^{-12}$	$m^2$
gas relative permeability	Van Genuchten-Mualem <sup>a,b</sup>	
$m$ , $S_{lr}$ , $S_{ls}$ , $S_{gr}$	0.2, 0.27, 1, 0.01	
liquid is immobile	$S_{ m l}\sim 0.26 \le S_{ m lr}$	
molecular diffusivity gas, liquid	$1.0  imes 10^{-6}, 1.0  imes 10^{-10}$	$m^2 \ s^{-1}, \ m^2 \ s^{-1}$
temperature	40	$^{\circ}\mathrm{C}$
initial pressure	60	bars
CH₄ injection rate	73.5	${ m kg~s^{-1}}$

<sup>&</sup>lt;sup>a</sup> Reference 12. <sup>b</sup> Reference 11.

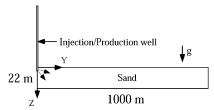


Figure 5. Schematic of two-dimensional half-reservoir model domain.

tive of multiple wells. The purpose of this simple geometry is to emphasize the general behavior of CO2 gas, rather than particular behavior that may arise in specific reservoirs with different geometry, hydrology, and heterogeneity. The domain is discretized into 2200 uniform gridblocks (11 imes 200 gridblocks in Z- and Y-directions, respectively) and injection and production occur on the left-hand side at Z = -3 m. All of the boundaries are closed, and the initial condition is gas-static at approximately 60 bar with residual water saturation of approximately 0.26. Depending on the case studied, the reservoir is filled initially with either CO2 or native CH4 cushion gas at 60 bar. This scenario does not consider the replacement of the native gas by the cushion gas, although this process can be part of CSEGR,7 where CO<sub>2</sub> injection is used for enhanced gas recovery, and natural gas storage could be carried out as a post-CSEGR beneficial use of the reservoir. With porosity of 0.30 and residual liquid saturation of 0.26, this half-size reservoir could hold  $1.4 \times 10^9$  kg (89 Bcf) of CH<sub>4</sub> at 40 °C and 100 bar. Assuming the storage reservoir receives through the injection/production well  $1.14 \times 10^9$  kg (60 Bcf) of CH<sub>4</sub> over a six-month storage period, the constant CH<sub>4</sub> injection rate is  $73.5 \text{ kg s}^{-1}$  (330 MMcf day<sup>-1</sup>). All simulations are isothermal at T = 40 °C.

#### **Results**

Shown in Figures 6 and 7 are simulated gas composition and density at three times (30, 90, and 180 days) during the injection of CH<sub>4</sub> into the storage reservoir.

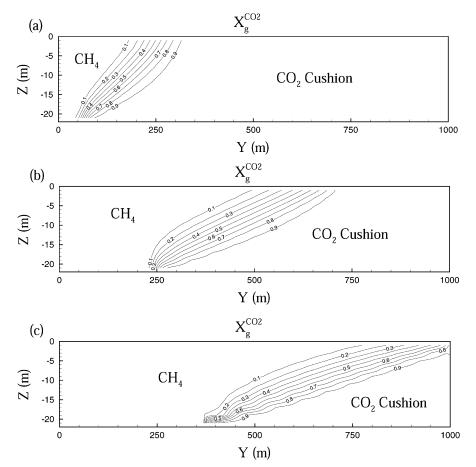


Figure 6. CO<sub>2</sub> mass fraction in the gas after 30, 90, and 180 days of injection.

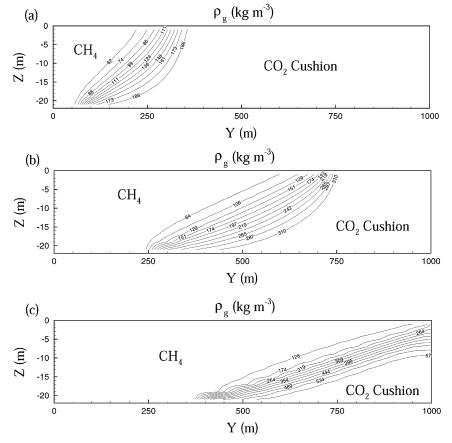
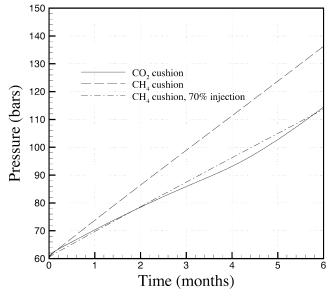


Figure 7. Gas density after 30, 90, and 180 days of injection.

As the pressure increases through the critical pressure,  $CO_2$  undergoes its large compression and occupies a smaller and smaller volume. The final pressure after 6 months is approximately 114 bar. As shown, the strong density contrast and shallow injection interval lead to  $CH_4$  overriding the  $CO_2$  cushion to some degree. This effect is large in the thin reservoir (22 m thick) considered here, but would be much less significant in a thicker (vertically oriented) reservoir (e.g., a solution-mined cavity) where the primary direction of displacement of the cushion would be up-and-down rather than side-to-side.

The interface between the two gases shows the effects of mixing due to molecular diffusion and numerical dispersion. Most of the mixing in the simulations is from numerical dispersion due to space discretization, which for a rectangular grid and full upstream weighting is approximately one-half the grid spacing multiplied by the gas velocity. For these simulations, the numerical dispersion is on the order  $10^{-4}~\rm m^2~s^{-1}$  (5 m/2  $\times$  700 m/6 months). This value of numerical dispersion is approximately 2 orders of magnitude larger than molecular diffusion, creating an artificially wide mixed zone for the conditions specified.

Shown in Figure 8 are pressure evolutions for the  $CO_2$  cushion gas case along with the cases of a native gas cushion with original injection rate and with reduced injection rate. As shown, the pressure increases more for the native gas cushion. By reducing the injection rate to 70% of the original rate, and correspondingly storing 70% as much gas, the pressure evolution curve for a case with a native gas cushion approximately matches the  $CO_2$  gas cushion curve. This figure shows the funda-



**Figure 8.** Pressure as a function of time for constant injection rate using  $CO_2$  and native  $CH_4$  as cushion gas.

mental advantage of the  $CO_2$  gas cushion, namely, the ability of the system to store more gas than if a native gas cushion is used.

Shown in Figure 9 are  $CO_2$  mass fraction and gas density after 10 months (after four months of production from the gas storage reservoir at the same rate as the original injection). Note that at this time,  $CO_2$  is upconing and impure  $CH_4$  would be produced if more production were to occur at this high rate. Such upconing and gravity override discussed above would be

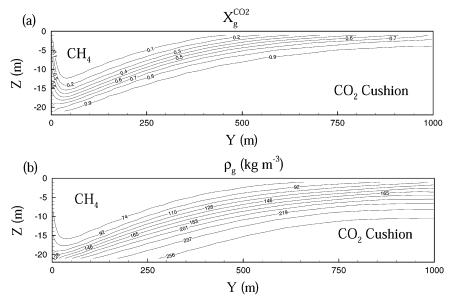


Figure 9. Mass fraction of CO<sub>2</sub> in the gas and density after 120 days of gas production.

greatly reduced in a reservoir with greater thickness, where the cushion gas could be emplaced into the bottom of the reservoir and working gas injected and produced from the top. Nevertheless, this simulation demonstrates that even for the case of a thin reservoir, a large fraction of the working gas can be recovered from a storage reservoir with a CO2 gas cushion prior to CO2 breakthrough. More favorable geometry and reduced production rate would allow more pure working gas to be produced.

# **Discussion and Conclusions**

Simulations of gas storage with CO<sub>2</sub> cushion gas in an idealized model reservoir demonstrate that the density change of CO2 around the critical pressure can be potentially exploited as a way of increasing the storage capacity of a gas storage reservoir. This effect arises because of the large decrease in Z value for CO<sub>2</sub> in the pressure range from 60 to 100 bar at temperatures near 40 °C. As the reservoir temperature increases beyond 40 °C, the Z value of CO<sub>2</sub> is larger and the advantage for gas storage diminishes. Thus depleted natural gas reservoirs with temperatures near 40 °C are favored over hotter reservoirs for using CO<sub>2</sub> as a cushion gas.

While the focus of this paper is on the physical properties of CO<sub>2</sub> and their exploitation for the benefit of gas storage, economic considerations will control ultimate use of the process. Currently, large volumes of CO<sub>2</sub> extracted from natural CO<sub>2</sub> reservoirs are used for enhanced oil recovery (EOR)13 at a cost of approximately \$12/ton CO<sub>2</sub>, or \$0.65/Mcf CO<sub>2</sub>. <sup>14</sup> Recent analysis suggests that at this price, and assuming a natural gas price in the neighborhood of \$4/Mcf CH<sub>4</sub> (\$0.14/m<sup>3</sup> CH<sub>4</sub>), enhanced gas recovery (EGR) using CO<sub>2</sub> may be nearly economically feasible.<sup>15</sup> With future

changes in costs, it is possible that gas reservoirs may someday be filled with CO<sub>2</sub> for EGR. A potential secondary use of such a reservoir after all of the economically recoverable CH4 has been produced may be gas storage, with the CO2 already present serving as the cushion gas. Although economic considerations will dictate whether CO<sub>2</sub> is ever used in gas reservoirs for any purpose, the uncertainty in future economic conditions, for example, with respect to potential future carbon credits for storing CO<sub>2</sub> underground, hinders detailed economic analyses at present.

The central issue in the physical processes of using CO2 as a cushion gas is the extent to which working gas will mix with CO<sub>2</sub> and reduce the value of the working gas. Experimental studies have demonstrated that diffusion and dispersion processes are the same for supercritical fluids as for normal gases and liquids, 16 so there should be no unexpected penalty at supercritical conditions in this regard. Recent experimental results focused on CSEGR show limited mixing for CH<sub>4</sub> displaced by CO<sub>2</sub> in carbonate rock cores.<sup>17</sup> Inert (e.g., N<sub>2</sub>) cushion gases have been used with apparently acceptable degrees of mixing in France in aquifer gas storage projects for over 20 years. Furthermore, the higher density and viscosity of CO2 relative to CH4 should limit mixing of the two gases.<sup>7</sup> In the simulations presented here, the reservoir is relatively thin (22 m) and the gas flow is predominantly horizontal. This leads to gravity override and a broadening of the interfacial area between the gases and correspondingly more mixing. In gas reservoirs with a large vertical extent relative to lateral (e.g., a vertically oriented solution-

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<sup>(14)</sup> Bondor, P. L. Applications of Carbon Dioxide in Enhanced Oil Recovery. Energy Convers. Manage. 1992, 33, 579-586.

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<sup>(17)</sup> Mamora, D. D.; Seo, J. G. Enhanced Recovery by Carbon Dioxide Sequestration in Depleted Gas Reservoirs. SPE Annual Technology Conference and Exhibition, San Antonio, TX, 29 Sept-2 Oct 2002. In Soc. Pet. Eng., SPE-77347.

mined cavity), the density effect of  $CO_2$  could be exploited by placing the  $CO_2$  deep in the reservoir and injecting and producing working gas from near the top. In the actual gas storage reservoir, hydrodynamic dispersion will occur which will also lead to mixing, although the degree to which reservoir gases mix is subject to considerable variability depending on reservoir geometry, anisotropy, heterogeneity, fracturing, and other properties. In short, careful reservoir selection and injection and production strategies can be developed that will limit gas mixing in particular gas storage reservoirs under consideration for injection of  $CO_2$  as a cushion gas. But clearly the extent and rate of gas mixing in the subsurface is uncertain and needs to be investigated further.

A second reason for concern about gas mixing is the change in density associated with mixing. In particular, when supercritical  $CO_2$  mixes with even a small amount of  $CH_4$ , the gas density decreases strongly (Figure 3) which will lead to pressurization at constant volume. Thus pressurization of the reservoir simply due to gas mixing is possible, and this effect offsets the advantage of using  $CO_2$ , namely that of small Z value. This points out again the importance of understanding gas mixing in the subsurface, as well as the potential use of monitoring reservoir pressure as a means of assessing mixing.

In conclusion, the properties of  $CO_2$  make it a good candidate for use as a cushion gas. However, the same mixing issues that arise in the use of other inert cushion gases will arise with the use of  $CO_2$ , and thorough analyses of suitability will have to be carried out before  $CO_2$  can be proposed with confidence for use in any particular gas storage reservoir. If it is determined that  $CO_2$  would be a suitable cushion gas in a particular project, then a comprehensive evaluation of costs, including benefits such as carbon sequestration credits, can be considered in the final decision. The opportunity to use  $CO_2$  as a cushion gas may arise as a way of getting additional benefit from a depleted gas reservoir where CSEGR has already been carried out.

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