

## JOULE-THOMSON COOLING DUE TO CO<sub>2</sub> INJECTION INTO NATURAL GAS RESERVOIRS

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### **ABSTRACT**

Depleted natural gas reservoirs are a promising target for Carbon Sequestration with Enhanced Gas Recovery (CSEGR). The focus of this study is on evaluating the importance of Joule-Thomson cooling during CO<sub>2</sub> injection into depleted natural gas reservoirs. Joule-Thomson cooling is the adiabatic cooling that accompanies the expansion of a real gas. If Joule-Thomson cooling were extreme, injectivity and formation permeability could be altered by the freezing of residual water, formation of hydrates, and fracturing due to thermal stresses. The TOUGH2/EOS7C module for CO<sub>2</sub>-CH<sub>4</sub>-H<sub>2</sub>O mixtures is used as the simulation analysis tool. For verification of EOS7C, the classic Joule-Thomson expansion experiment is modeled for pure CO<sub>2</sub> resulting in Joule-Thomson coefficients in agreement with standard references to within 5-7%. For demonstration purposes, CO<sub>2</sub> injection at constant pressure and with a large pressure drop (~50 bars) is presented in order to show that cooling by more than 20 °C can occur by this effect. Two more-realistic constant-rate injection cases show that for typical systems in the Sacramento Valley, California, the Joule-Thomson cooling effect is minimal. This simulation study shows that for constant-rate injections into high-permeability reservoirs, the Joule-Thomson cooling effect is not expected to create significant problems for CSEGR.

### **INTRODUCTION**

Depleted natural gas reservoirs are a promising target for the storage of anthropogenic CO<sub>2</sub> as a climate change mitigation strategy. The benefits of injecting CO<sub>2</sub> into depleted natural gas reservoirs include, among others, the potential for enhanced natural gas (CH<sub>4</sub>) recovery, the sale of which can be used to subsidize the cost of CO<sub>2</sub> injection (van der Burgt et al., 1992; Koide et al., 1993; Blok et al., 1997, Oldenburg et al., 2001; Oldenburg et al., 2004). This process is known as Carbon Sequestration with Enhanced Gas Recovery (CSEGR). Upon completion of the enhanced gas recovery phase of CSEGR, the nearly pure CO<sub>2</sub> filling the reservoir has the potential to serve as a super-cushion gas for natural gas storage (Oldenburg, 2003).

While the general benefits of CSEGR have been pointed out in prior publications, the potential problems and challenges of the process have received less attention. Potential problems that could arise from Joule-Thomson cooling include the freezing of residual water or the formation of hydrates in the reservoir and associated reduction in injectivity. Another effect of extreme cold in the subsurface is the generation of thermal stresses that could fracture the formation. The purpose of this study is to use numerical simulation to investigate the magnitude of Joule-Thomson cooling that may arise during CO<sub>2</sub> injection into depleted CH<sub>4</sub> reservoirs.

### **BACKGROUND**

#### **Joule-Thomson Expansion**

Joule-Thomson cooling is the name given to the drop in temperature that occurs when a real gas such as CO<sub>2</sub> or N<sub>2</sub> expands from high pressure to low pressure at constant enthalpy (i.e., adiabatic expansion). The classic Joule-Thomson expansion experiment consists of a thermally insulated system with gas on one side initially at  $p_1$ ,  $V_1$ , and  $T_1$  that flows through a porous plug and out the other side at  $p_2$ ,  $V_2$ , and  $T_2$ . In the absence of heat exchange with the surroundings, the total work equals the change in internal energy which is

$$w = \Delta U = p_1 V_1 - p_2 V_2 \quad (1).$$

For an ideal gas,  $p_1 V_1 = p_2 V_2$  and the Joule-Thomson expansion would be at constant internal energy. However, our interest is in CO<sub>2</sub> which will be highly non-ideal during injection into natural gas reservoirs. The change in enthalpy of the system in the Joule-Thomson expansion is given by

$$\Delta H = \Delta U + \Delta(pV) \quad (2).$$

Upon substitution of Eq. 1 into Eq. 2, we have

$$\Delta H = 0. \quad (3)$$

i.e., the Joule-Thomson expansion is at constant enthalpy. If the Joule-Thomson expansion is carried out at a number of different pressure drops ( $\Delta P$ )

across the porous plug for which different  $\Delta T$ 's would be measured, the points when plotted as  $\Delta T$  vs.  $\Delta P$  would be approximately linear with a slope equal to the Joule-Thomson coefficient ( $\mu_{JT}$ ):

$$\frac{\Delta T}{\Delta P} \approx \left( \frac{\partial T}{\partial P} \right)_H = \mu_{JT} \quad (4).$$

So far this discussion has assumed that  $\mu_{JT}$  is positive (i.e., expansion leads to cooling). However, the sign of  $\mu_{JT}$  can also be negative (i.e., causing the gas to heat upon expansion) depending on the Joule-Thomson inversion temperature of the particular gas and the temperature of the process. Above the Joule-Thomson inversion temperature, gases heat upon expansion. At room temperature, common gases such as CO<sub>2</sub>, N<sub>2</sub>, and O<sub>2</sub> cool upon expansion while He and Ne warm upon expansion. The Joule-Thomson inversion temperatures at 1 atm for CO<sub>2</sub> and CH<sub>4</sub> are 1500 K (1227 °C) and 968 K (695 °C), respectively (Atkins, 1990, p. 949), meaning CO<sub>2</sub> and CH<sub>4</sub> will cool upon expansion for conditions relevant to hydrocarbon reservoirs.

The main concerns in the CSEGR process relative to Joule-Thomson cooling are that (1) CO<sub>2</sub> will cool so much upon injection into a depleted reservoir that residual water could freeze and/or form hydrates with CO<sub>2</sub> (or CH<sub>4</sub>) and potentially limit injectivity, and (2) thermal stresses due to cooling could fracture reservoir rocks changing the permeability structure.

### **Depleted Reservoirs**

Natural gas reservoirs span the range in type from water-drive to depletion-drive. In water-drive reservoirs, gas remains in near-hydrostatic pressure as water flows into the reservoir from surrounding aquifers continuously while gas is produced. In such reservoirs, much of the gas present cannot be produced because gas wells “water out,” a process by which water cones upward to the well preventing gas from entering the well thereby “killing” production. Such reservoirs typically only produce 60% or less of the original gas in place (e.g., Laherrère, 1997). As such, these reservoirs are good candidates for CSEGR, but may require innovative approaches for implementation, such as the idea of syn-production-CSEGR in which CO<sub>2</sub> is injected at the same time as CH<sub>4</sub> is produced over the life of the reservoir thereby maintaining reservoir pressure and preventing water intrusion from ever happening. These strategies are beyond the scope of the present paper.

The other end member of reservoir types is the depletion-drive reservoir, in which reservoir pressure declines with gas production due to the lack of ingress of water from surrounding aquifers. In depletion-drive reservoirs, 90% or more of the gas

can be produced because there is no invading water to kill the wells (e.g., Laherrère, 1997). Despite the high production potential, even 10% remaining gas in a large gas reservoir can be an attractive target for CSEGR. Syn-production-style CSEGR over the life of the reservoir could also work for depletion-drive reservoirs to maintain reservoir pressure and accelerate production when market forces are attractive through increased CO<sub>2</sub> injection rate. However, such methods have not been used in the past, and the challenge today is to store anthropogenic CO<sub>2</sub> indefinitely while enhancing gas recovery from largely depleted reservoirs.

Regardless of whether a given reservoir is one of the end-member types or falls somewhere in between, CO<sub>2</sub> injection will always involve a pressure drop ( $\Delta P$ ) from the well to the reservoir. The magnitude of  $\Delta P$  depends on the rate at which CO<sub>2</sub> is injected and the injectivity of the formation and will typically be on the order of 5-10 bars (75-150 psi) for high-quality gas reservoirs. Such pressure changes can result in Joule-Thomson cooling of injected CO<sub>2</sub>. We focus the study on depletion-drive reservoirs such as those in the Sacramento Valley (e.g., Rio Vista area), California, because injection will be easier (no water to displace) and the low reservoir pressure creates the possibility of a large pressure drop between injection well and the reservoir.

### **Injection Mechanics**

The injection mechanics of CO<sub>2</sub> into depleted hydrocarbon reservoirs depend strongly on the source of CO<sub>2</sub>. For recent and near-future pilot studies such as the Frio test in Texas, CO<sub>2</sub> typically arrives by truck as a cold liquid at approximately 20 bar pressure (Hovorka et al., 2006). This form of CO<sub>2</sub>, referred to as cryogenic CO<sub>2</sub>, is warmed prior to injection to avoid detrimental thermal stresses in the well and formation, and may need to be compressed depending on reservoir pressure, injectivity, and desired flow rate. For the future large-scale deployment of CSEGR, CO<sub>2</sub> will arrive by way of pipelines such as those used today for CO<sub>2</sub>-enhanced oil recovery. Pipeline CO<sub>2</sub> is at high pressure (100-200 bars) and ambient temperature. Therefore pipeline CO<sub>2</sub> may be injected without heating but will likely be throttled down prior to directing into the well to control the injection rate into the formation.

In this study, idealized scenarios of injection mechanics including constant pressure and temperature as well as constant flow rate and temperature will be presented to examine the potential significance of Joule-Thomson cooling for these end-member injection scenarios.

**METHODS**

**EOS7C**

The TOUGH2 module called EOS7C (Oldenburg et al., 2004) is used in this study. EOS7C models five components (water, brine, non-condensable gas, tracer, and methane) under isothermal or non-isothermal conditions. The non-condensable gas can be chosen by the user as either CO<sub>2</sub> or N<sub>2</sub>. In the simulations presented here, EOS7C calls the Peng-Robinson equation of state as implemented in the GasEOS subroutines (<http://lnx.lbl.gov/GasEOS>) for calculating properties of gas mixtures in the system H<sub>2</sub>O-CO<sub>2</sub>-CH<sub>4</sub>. Extensive verification of EOS7C and test problems are provided in the User Guide (Oldenburg et al., 2004).

**Verification**

In order to verify the methods used in EOS7C for expansion-related cooling, the Joule-Thomson experiment is simulated by constructing a simple four-gridblock mesh consisting of two constant-property gridblocks (infinite volume) on either side of a low-permeability block and a monitoring block (Figure 1). The block on the left-hand side (A11 1) remains at constant pressure and temperature such that gas flows from left to right into the right-hand-side gridblock (A14 1) that also remains at constant pressure and temperature. The pressure drop in the system occurs almost entirely across the low-permeability gridblock (A12 1) which plays the role of the porous plug in the Joule-Thomson experiment. The temperature drop is recorded in the monitoring gridblock (A13 1) just downstream. Note the problem as constructed is entirely artificial to approach the assumptions of the Joule-Thomson expansion experiment, with thermal conductivity set to zero, porosity set to one, and Darcy's Law assumed for flow between all gridblocks.

Results for single-phase CO<sub>2</sub> gas at several different pressures and 75 °C, and a single point at 27 °C, are shown in Table 1. As shown, EOS7C using the Peng-Robinson equation of state agrees with reference values to within approximately 5-7%. This is considered acceptable for the approximate equations of state used in GasEOS. Although results are shown only for pure CO<sub>2</sub> for which we can compare results to those of authoritative sources, EOS7C can handle gas mixtures of CO<sub>2</sub>-CH<sub>4</sub>-H<sub>2</sub>O and N<sub>2</sub>-CH<sub>4</sub>-H<sub>2</sub>O.

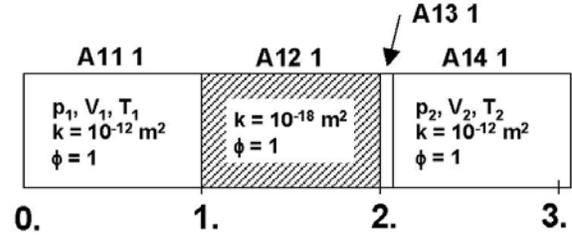


Figure 1. Four gridblocks used for the Joule-Thomson isenthalpic expansion verification problem. Gridblock A13 1 has the same properties as A14 1 and A11 1.

Table 1. Results from the simulated Joule-Thomson experiment.

T (°C)	P (bar)	EOS7C	NIST	Atkins
		$\mu_{JT}$ (K/bar)	Webbook $\mu_{JT}$ (K/bar)	(1990) $\mu_{JT}$ (K/bar)
75	1	0.770	0.742	-
75	10	0.773	0.742	-
75	20	0.771	0.740	-
75	30	0.768	.736	-
75	40	0.761	0.730	-
75	70	0.715	0.694	-
75	90	0.651	0.645	-
27	1	1.030	1.075	1.095

**Complications of Porous Media**

In an isenthalpic expansion in a porous medium, the temperature drop given by Eq. 4 can be thought of in terms of temperature gradient and associated heat flow. By this reasoning, the temperature gradient produced by Joule-Thomson cooling is equal to the Joule-Thomson coefficient multiplied by the corresponding pressure gradient. Hence, the pressure gradient can be thought of as controlling the heat flow and therefore the cooling rate. The complicating factor in a porous medium is that the cooling rate will be diminished by heat provided by the matrix grains of the rock ( $\sim(1-\phi) \rho_R C_R$ ). This is a transient effect, and eventually the matrix grains will lose all of their heat during a prolonged expansion-related cooling process. In summary, transient Joule-Thomson cooling in dry gas reservoirs depends not only on pressure drop but also on formation thermal properties such as porosity, rock grain heat capacity, and thermal conductivity.

## RESULTS

To investigate potential Joule-Thomson effects associated with CO<sub>2</sub> injection into natural gas reservoirs in horizontally bedded sandstones and shales, a simple one-dimensional radial geometry was chosen to represent a depleted gas reservoir. The geometry and properties of the system were chosen to match those used in the economic feasibility study that examined the economics of CSEGR in the Rio Vista Gas Field, California (Oldenburg et al., 2004). A highly refined mesh with gridblocks as small as 5 cm in radius was designed to capture the area around the injection well where Joule-Thomson effects are expected to be largest (Figure 2). Production is idealized as being from the outer-most (right-most) gridblock to represent production from four surrounding wells in a five-spot pattern. Reservoir properties are given in Table 2.

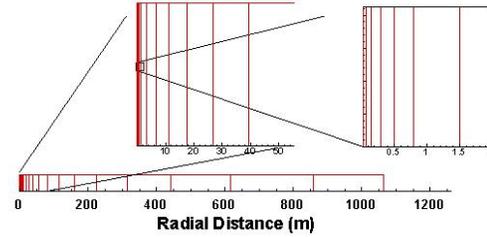


Figure 2. Geometry and gridblock interfaces at three different magnifications for the 1-D radial gas reservoir problem.

Table 2. Properties of the 1-D radial gas reservoir.

Property	Value	Alt. Units
Radius	1130 m	0.70 mi
Thickness	50 m	164 ft
Porosity	0.30	0.30
Permeability	10 <sup>-12</sup> m <sup>2</sup> (base case) 2 x 10 <sup>-14</sup> m <sup>2</sup> (low-k case)	1 Darcy 20 mD
Rock density ( $\rho_R$ )	2600 kg m <sup>-3</sup>	-
Rock heat capacity ( $C_R$ )	1000 J kg <sup>-1</sup> °C <sup>-1</sup>	-
Formation thermal conductivity	2.51 W m <sup>-1</sup> °C <sup>-1</sup>	-
Relative Permeability	Corey curves <sup>1</sup>	-
Capillary Pressure	$S_{lr} = 0.2, S_{gr} = 0.01$ van Genuchten <sup>1</sup> $\lambda = 0.2, S_{lr} = 0.25,$ $\alpha = 8.2, P_{max} = 10^5$ Pa, $S_{ls} = 1.$	-
Molec. diffusivity (1 bar, 0 °C)	Liquid: 10 <sup>-10</sup> m <sup>2</sup> s <sup>-1</sup> , Gas: 10 <sup>-5</sup> m <sup>2</sup> s <sup>-1</sup>	-
$T$ at $t = 0$	75 °C	167 °F
$P$ at $t = 0$	50 bars	725 psi
CO <sub>2</sub> injection rate	3 kg s <sup>-1</sup>	280 t/day
CH <sub>4</sub> production rate	0.56 kg s <sup>-1</sup>	2514 Mcf/day
Final reservoir pressure after 15 yrs (base case)	55.6 bars	817 psi

<sup>1</sup>Pruess et al., 1999.

### Constant High-Pressure Injection

We present first for demonstration purposes a case with a large Joule-Thomson effect by specifying a constant-pressure injection with large injection pressure. In this example, a 100-bar large-capacity CO<sub>2</sub> supply pipeline is envisioned to be available for direct connection to an injection well via a heat exchanger that heats the CO<sub>2</sub> to 75 °C, the ambient temperature of the reservoir. Methane is not produced from the reservoir in this example simulation, leading to monotonic reservoir pressure increase. Because the injected CO<sub>2</sub> is initially at the same temperature as the reservoir, all of the variation in temperature during injection is due to Joule-Thomson cooling or other evaporative cooling effects. Shown in Figure 3 are results for this extreme case of a large pressure injection. Note that the pressure drop between the injection well and the reservoir causes strong Joule-Thomson cooling effects of approximately 20 °C. The theoretical maximum temperature drop corresponding to these  $P$ - $T$  conditions but without residual heat from porous media would be approximately 37.5 °C ( $\Delta T = \mu_{JT} \Delta P = 0.75 \text{ °C/bar} * 50 \text{ bar} = 37.5 \text{ °C}$ ). The residual heat provided by the rock grains along with the declining  $\Delta P$  serve to diminish the cooling effect. Joule-Thomson coefficients are temperature-dependent and increase slightly between 75 and 25 °C, meaning that if the initial CO<sub>2</sub> were not heated to 75 °C prior to injection but instead injected at 25 °C, the associated temperature drop could be larger than 20 °C and could lead to freezing conditions in the reservoir resulting potentially in CO<sub>2</sub>-hydrate formation and freezing of residual water.

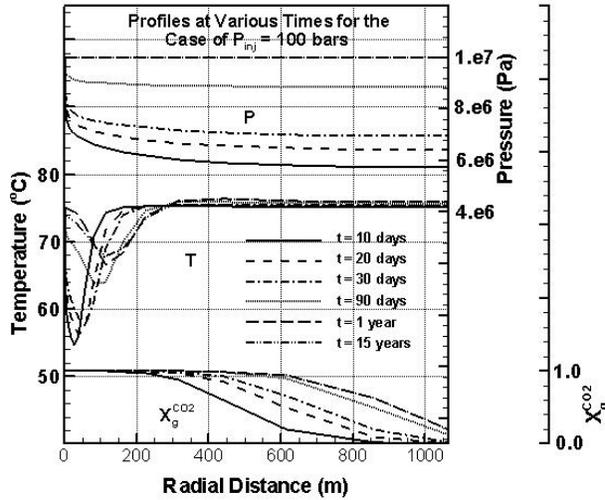


Figure 3. Profiles of pressure, temperature, and mass fraction  $CO_2$  in the gas phase ( $X_g^{CO_2}$ ) at six different times for the high-pressure injection case.

This simulation shows the dramatic potential effect of Joule-Thomson cooling, but overestimates it because the injection pressure is higher than would commonly be applied in a real system with 1 Darcy permeability. Furthermore, injection into an actual reservoir is probably better modeled as a constant-rate injection rather than a constant-pressure injection.

**Constant Injection Rate, High Permeability**

The second example, the base case, considers constant injection at a rate of 3 kg/s into a 1 Darcy reservoir as used in Oldenburg et al. (2002) and at ambient temperature ( $T = 20\text{ }^\circ\text{C}$ ) such as would come from a pipeline supply. Production of  $CH_4$  occurs from the outer perimeter of the radial system at a rate of 0.56 kg/s as used in Oldenburg et al. (2004). Profiles for the first 100 m of the system away from the injection well are shown in Figure 4. As shown, there is very little pressure increase in the well and therefore very little  $\Delta P$  in the reservoir. Therefore, Joule-Thomson expansion is small, and there is little associated Joule-Thomson cooling. The low temperatures in the reservoir are instead due to the low temperature ( $20\text{ }^\circ\text{C}$ ) of the injected  $CO_2$ . As shown, the  $20\text{ }^\circ\text{C}$   $CO_2$  cools the rock and residual liquid to a distance of approximately 40 m from the well at  $t = 1$  year.

**Constant Injection Rate, Low Permeability**

The third example is identical to the second example (base case) except the reservoir permeability is set to  $2 \times 10^{-14}\text{ m}^2$  (20 mD) to generate a larger  $\Delta P$  and associated Joule-Thomson cooling effect. As shown in Figure 5, there is a small Joule-Thomson effect (approximately  $4\text{ }^\circ\text{C}$  of cooling) and a slightly

delayed propagation of injected  $CO_2$  relative to the higher-permeability case due to the associated higher pressure and corresponding higher density. However, in general, the effect of Joule-Thomson cooling is still very small.

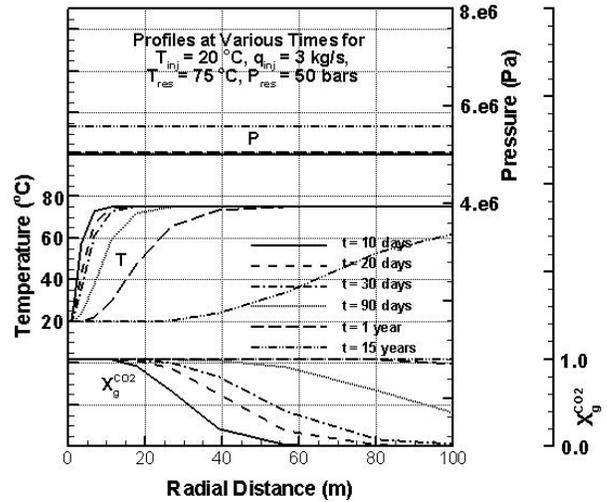


Figure 4. Profiles (0-100 m) of pressure, temperature, and mass fraction  $CO_2$  in the gas phase ( $X_g^{CO_2}$ ) at six different times for the case of constant injection rate into the high-permeability reservoir.

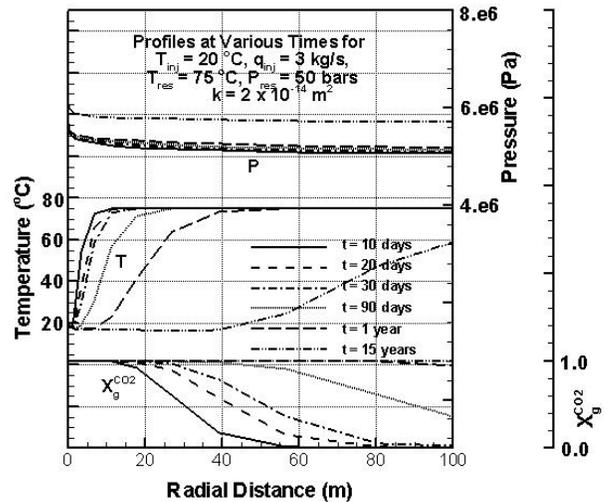


Figure 5. Profiles (0-100 m) of pressure, temperature, and mass fraction  $CO_2$  in the gas phase ( $X_g^{CO_2}$ ) at six different times for the case of constant injection rate into the low-permeability reservoir

## **DISCUSSION AND CONCLUSIONS**

The simulation results presented here show that Joule-Thomson cooling is a minor effect for low injection rates and for permeabilities in the range expected in the Rio Vista, California, area. In the extreme case of a high-pressure injection scenario into a low-pressure reservoir, approximately 20 °C of Joule-Thomson cooling occurs. If the injection temperature were near ambient such as would prevail for a pipeline source, 20 °C of cooling could bring reservoir rock to temperatures below the freezing point of water and into the CO<sub>2</sub>-hydrate stability field with potentially negative effects on injectivity. However, these conditions are extreme and probably unrealistic. Another possibility is permeability heterogeneity over the length of the screened (perforated) interval and the potential for large  $\Delta P$  in isolated intervals of the well. This could result in locally large cooling and potential freezing. However, for more realistic conditions of constant flow-rate injection into relatively homogeneous sand reservoirs such as those chosen for the base case and which are representative of many CSEGR prospects, the conclusion is that Joule-Thomson cooling is not expected to be a significant obstacle to successful CSEGR in depleted or depleting gas reservoirs. For pilot studies that use cryogenic CO<sub>2</sub> in which the CO<sub>2</sub> is not heated significantly prior to injection, injection rates should be controlled to avoid large pressure drop in the reservoir that could lead to sub-freezing temperatures upon expansion in the reservoir.

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## **REFERENCES**

Atkins, P.W., *Physical Chemistry, 4th Edition*, W.H. Freeman and Company, New York, 1990.

Blok, K., R.H. Williams, R.E. Katofsky, and C.A. Hendricks, Hydrogen production from natural gas, sequestration of recovered CO<sub>2</sub> in depleted gas wells

and enhanced gas recovery, *Energy*, 22(2/3), 161-168, 1997.

Hovorka, S.D., S.M. Benson, C. Doughty, B.M. Freifeld, S. Sakurai, T.M. Daley, Y.K. Kharaka, M.H. Holtz, R.C. Trautz, H.S. Nance, L.R. Myer, and K.G. Knauss, Measuring permanence of CO<sub>2</sub> storage in saline formations: the Frio experiment, *Env. Geosci.*, 13(2), 1-17, 2006.

Koide, H., Y. Tazaki, Y. Noguchi, M. Iijima, K. Ito, and Y. Shindo, Underground storage of carbon dioxide in depleted natural gas reservoirs and in useless aquifers, *Engin. Geol.*, 34, 175-179, 1993.

Laherrère J., Distribution and evolution of “recovery factor”. IEA Oil Reserves Conference, Paris, France, November 11, 1997. <http://dieoff.org/page183.pdf>

Lemmon E.W., McLinden M.O., Friend D.G., Thermophysical Properties of Fluid Systems. In: Linstrom P.J, Mallard W.G. (eds), NIST Chemistry WebBook, *NIST Standard Reference Database Number 69*, National Institute of Standards and Technology, Gaithersburg, Maryland, 2003 (<http://webbook.nist.gov>)

Oldenburg, C.M., Carbon dioxide as cushion gas for natural gas storage, *Energy & Fuels*, 17(1), 240-246, 2003.

Oldenburg, C.M., K. Pruess, and S.M. Benson, Process modeling of CO<sub>2</sub> injection into natural gas reservoirs for carbon sequestration and enhanced gas recovery, *Energy&Fuels*, 15, 293-298, 2001.

Oldenburg, C.M., G.J. Moridis, N. Spycher, and K. Pruess, *EOS7C Version 1.0: TOUGH2 module for Carbon dioxide or Nitrogen in natural gas (methane) reservoirs*, Lawrence Berkeley National Laboratory Report LBNL-56589, March 2004.

Oldenburg, C.M., S.J. Stevens, and S.M. Benson, Economic feasibility of carbon sequestration with enhanced gas recovery (CSEGR), *Energy*, 29, 1413-1422, 2004.

Pruess, K., C. Oldenburg, and G. Moridis, *TOUGH2 User's Guide, Version 2.0*, Report LBNL-43134, Lawrence Berkeley National Laboratory, Berkeley, Calif., 1999.

Van der Burgt, M.J., J. Cantle, and V.K. Boutkan, Carbon dioxide disposal from coal-based IGCC's in depleted gas fields, *Energy Conv. Mgmt.*, 33(5-8), 603-610, 1992.