Plains CO_2 Reduction (PCOR) Partnership
Practical, Environmentally Sound CO_2 Sequestration

FACTORS AFFECTING THE POTENTIAL FOR CO_2 LEAKAGE FROM GEOLOGIC SINKS

Charles R. Nelson, Energy & Environmental Research Center
James M. Evans, Energy & Environmental Research Center
James A. Sorensen, Energy & Environmental Research Center
Edward N. Steadman, Energy & Environmental Research Center
John A. Harju, Energy & Environmental Research Center

October 2005

EXECUTIVE SUMMARY

The success of geologic carbon dioxide (CO_2) sequestration as a large-scale carbon management strategy is critically dependent on the ability of the geologic sinks and trapping mechanisms to confine the injected CO_2 for hundreds to thousands of years. Leakage of CO_2 from geologic sinks could result in significant release of the CO_2 back to the atmosphere, potentially reducing, if not negating altogether, the benefits of geologic CO_2 sequestration. For example, a leakage rate of 1% per year from 1 billion tons of geologically stored CO_2 (10 million tons) would exceed the current annual CO_2 emissions from all the power plants in North Dakota (4 million tons). Further, leakage could have negative ecological effects and present the potential for health problems other than global warming.

Clearly, the more CO_2 that is stored, the greater the potential that leakage from geologic sinks could result in adverse environmental and atmospheric impacts. It has recently been proposed that leakage rates of 0.01% per year be established as a performance requirement for geologically sequestered CO_2 (White et al., 2003).

This report provides an analysis of how the physicochemical properties of CO_2 would affect its trapping potential and mobility in various types of geologic environments. Analog studies of geologic environments containing large, concentrated amounts of CO_2 or hydrocarbons gas were also used to derive insight regarding the leakage processes that would be inherent in geologic CO_2 sequestration. The analogs included a) naturally occurring deposits of high-purity CO_2, b) a mature CO_2 flood enhanced oil recovery (EOR) project, c) an aquifer natural gas storage reservoir, and d) coalbed natural gas deposits.

Injected CO_2 can be trapped in geologic sinks by four types of mechanisms. Different types of geologic sinks in combination with their site-specific properties would trap CO_2 by different mechanisms. More than one type of trapping mechanism would typically be present in a single geologic sink. Most trapping mechanisms do not permanently immobilize CO_2. Thus leakage of CO_2 to the surface can potentially occur from all types of geologic sinks.

In the right types of geologic settings, a large, concentrated amount of CO_2 could be stored for a geologically long time period without the risk of significant CO_2 leakage

to the surface. The dominant, but by no means sole, barrier to CO_2 leakage to the surface from geologic sinks is not the trapping mechanism(s) but rather the permeability characteristics of the rock layers overlying or adjacent to the geologic sinks. The hydrologic properties of the formations containing the geologic sinks would also affect the potential for CO_2 leakage. Geologic settings with relatively static hydrology, i.e., low formation water velocity, would be preferable.

ACKNOWLEDGMENTS

The Plains CO_2 Reduction (PCOR) Partnership is a collaborative effort of public and private sector stakeholders working toward a better understanding of the technical and economic feasibility of capturing and storing (sequestering) anthropogenic CO_2 emissions from stationary sources in the central interior of North America. It is one of seven regional partnerships funded by the U.S. Department of Energy's (DOE's) National Energy Technology Laboratory (NETL) Regional Carbon Sequestration Partnership (RCSP) Program. The Energy & Environmental Research Center (EERC) would like to thank the following partners who provided funding, data, guidance, and/or experience to support the PCOR Partnership:

- Alberta Department of Environment
- Alberta Energy and Utilities Board
- Alberta Energy Research Institute
- Amerada Hess Corporation
- Basin Electric Power Cooperative
- Bechtel Corporation
- Center for Energy and Economic Development (CEED)
- Chicago Climate Exchange
- Dakota Gasification Company
- Ducks Unlimited Canada
- Eagle Operating, Inc.
- Encore Acquisition Company
- Environment Canada
- Excelsior Energy Inc.
- Fischer Oil and Gas, Inc.
- Great Northern Power Development, LP
- Great River Energy
- Interstate Oil and Gas Compact Commission
- Kiewit Mining Group Inc.
- Lignite Energy Council
- Manitoba Hydro
- Minnesota Pollution Control Agency
- Minnesota Power
- Minnkota Power Cooperative, Inc.
- Montana–Dakota Utilities Co.
- Montana Department of Environmental Quality
- Montana Public Service Commission
- Murex Petroleum Corporation
- Nexant, Inc.
- North Dakota Department of Health
- North Dakota Geological Survey
- North Dakota Industrial Commission Lignite Research, Development and Marketing Program
- North Dakota Industrial Commission Oil and Gas Division
- North Dakota Natural Resources Trust
- North Dakota Petroleum Council
- North Dakota State University
- Otter Tail Power Company
- Petroleum Technology Research Centre
- Petroleum Technology Transfer Council
- Prairie Public Television
- Saskatchewan Industry and Resources
- SaskPower
- Tesoro Refinery (Mandan)
- University of Regina
- U.S. Department of Energy
- U.S. Geological Survey Northern Prairie Wildlife Research Center
- Western Governors' Association
- Xcel Energy

The EERC also acknowledges the following individuals who assisted in the review of this document:

Kim M. Dickman, EERC
Stephanie L. Wolfe, EERC

INTRODUCTION

As one of seven Regional Carbon Sequestration Partnerships (RCSPs), the Plains CO_2 Reduction (PCOR) Partnership is working to identify cost-effective carbon dioxide (CO_2) sequestration systems for the PCOR Partnership region and, in future efforts, to facilitate and manage the demonstration and deployment of these technologies. In this phase of the project, the PCOR Partnership is characterizing the technical issues, enhancing the public's understanding of CO_2 sequestration, identifying the most promising opportunities for sequestration in the region, and detailing an action plan for the demonstration of regional CO_2 sequestration opportunities. This report provides an overview of current knowledge of the factors affecting the potential for CO_2 leakage from geologic sinks.

Carbon management, specifically the separation and capture of CO_2 at fossil energy-fueled electric power plants followed by geological sequestration, is viewed as the most important near-term strategy for achieving deep reductions in global atmospheric CO_2 emissions (Bachu and Stewart, 2002; Bruant et al., 2002; White et al., 2003; Pacala and Socolow, 2004). The technology for transporting and pumping CO_2 into geologic formations is well developed and has been used commercially by the petroleum industry for enhanced oil recovery (EOR) for many decades (Jarrell et al., 2002). However, it is not expected that all potential geologic sinks in a given region will be suitable for CO_2 sequestration. Among the issues that must be addressed is the potential for CO_2 leakage from the geologic sinks back to the atmosphere (Allis et al., 2001; Stevens et al., 2001).

Potential sites for geologic CO_2 sequestration are depleted petroleum reservoirs, deep saline aquifers, deep unminable coal seams, and mined salt caverns (White et al., 2003; Dusseault et al., 2004). At this time, the permanence of CO_2 sequestration in these potential geologic sinks has not been demonstrated. If large volumes of CO_2 are geologically sequestered, small but widespread leakage of CO_2 from the subsurface could result in significant release of the CO_2 back to the atmosphere, potentially reducing, if not negating altogether, the benefits of geologic CO_2 sequestration (Allis et al., 2001). For example, a leakage rate of 1% per year from 1 billion tons of geologically stored CO_2 (10 million tons) would exceed the current annual CO_2 emissions from all the power plants in North Dakota (4 million tons). Further, leakage could have negative ecological effects and present the potential for health problems other than global warming (Pacala, 2002; Celia et al., 2002a).

Clearly, the more CO_2 that is stored the greater the potential that leakage from geologic sinks could result in adverse environmental and atmospheric impacts. It has recently been proposed that leakage rates of 0.01% per year be established as a performance requirement for geologically sequestered CO_2 (White et al., 2003).

To ensure safe and effective geologic CO_2 sequestration, assessment of the potential for CO_2 leakage from geologic sinks must lead technology implementation. Projects must also actively monitor geologic storage sites to detect CO_2 leakage and be prepared to take remedial action in the event that leakage occurs. This report provides an overview of current knowledge of the factors affecting the potential for CO_2 leakage from geologic sinks. This information will serve as guidance for the development of future demonstration projects in the PCOR Partnership region. As development of potential geologic CO_2 sequestration projects is further explored, site-specific assessments of CO_2 leakage potential will need to be performed as part of the site characterization efforts.

PHYSICOCHEMICAL PROPERTIES OF CO_2

The physicochemical properties of CO_2 affect its storage behavior and leakage potential when injected into geologic sinks as well as its potential for causing adverse ecological or human health problems. CO_2 is a colorless, odorless, noncombustible, and relatively nonreactive compound that is a gas under ambient temperature and pressure conditions. CO_2 is a natural component of the earth's atmosphere. The current atmospheric concentration of CO_2 is about 375 ppm (White et al., 2003).

Water Solubility

CO_2 is soluble in water and brine, which are commonly present in soil and sedimentary rocks. The solubility of CO_2 in water and brine progressively increases as pressure increases but decreases sharply as temperature and salinity increase (Wiebe and Gaddy, 1939, 1940; Prutton and Savage, 1945; Jarrell et al., 2002).

The salinity of soil and formation water is affected by numerous variables. These variables include temperature, pressure, pH, and soil or rock lithology. In general, formation water salinity in sedimentary basins progressively increases as depth increases. In normally pressured geologic settings where the formation water is static, i.e., not hydrodynamically connected to outcrops, and the dominant anion is chloride, salinity typically increases at a linear rate between 25,000 and 75,000 ppm/1000 ft (Dickey, 1966, 1969).

The effects of temperature and pressure on the solubility of CO_2 in water are illustrated in Figure 1 (Wiebe and Gaddy, 1939, 1940). In the earth's crust, temperature and pressure progressively increase with depth. Common geothermal gradient values are 1.2° to 2.6°F/100 ft (4.0° to 29.5°C/km) (Bradley, 1975). The normal hydrostatic pressure gradient is 0.43 psi/ft (9.8 kPa/m) (Hunt, 1990).

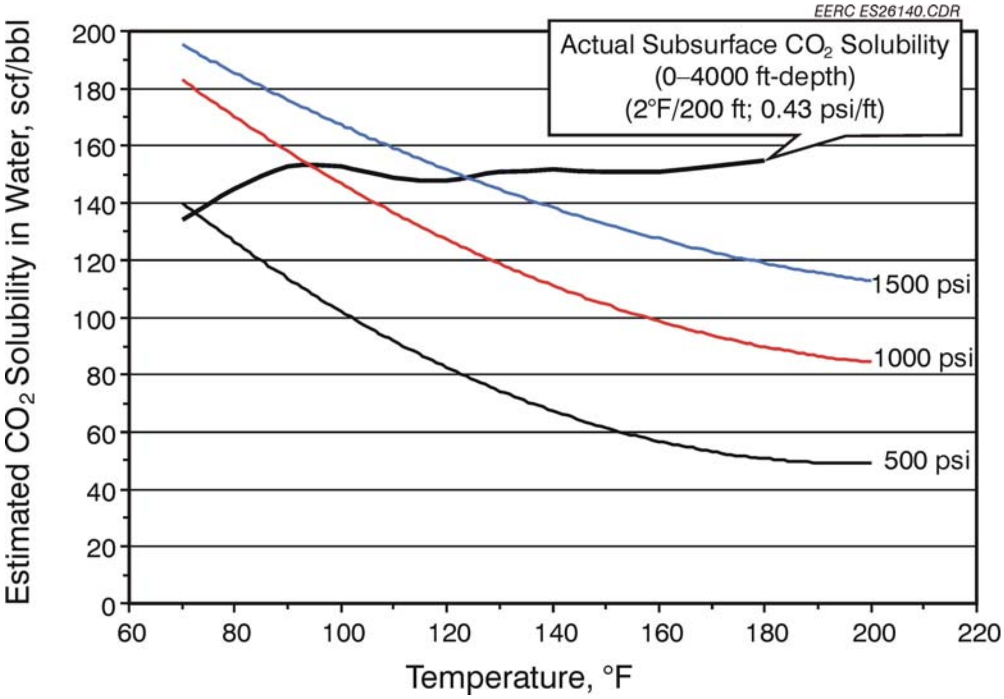

Figure 1. Variation of CO_2 solubility in water as a function of temperature and pressure.

Temperature and pressure have compensating effects on the solubility of CO_2 in water and brine. For a geothermal gradient of 2°F/100 ft (18.6°C/km) and a normal hydrostatic pressure gradient, this compensation phenomenon can be modeled by fitting the experimental data in Figure 1 to a fourth-order polynomial expression (see Equation 1).

$$CO_2 \text{ Solubility (scf/bbl)} =$$

$$(a + b\times + c\times^2 + d\times^3 + e\times^4) \qquad \text{[Eq. 1]}$$

Where:

$\times$ = Temperature (°F)
a = −406
b = 17.6
c = −0.203
d = 0.001
e = −0.000002

The net effect of this compensation phenomenon over a depth interval from the surface to 4000 ft (1220 m) is illustrated by the heavy black line in Figure 1. Because of the compensation effect, the solubility of CO_2 in water exhibits only a small change as a function of this large depth variation.

Formation of Carbonic Acid

When CO_2 dissolves in water, carbonic acid forms, which lowers the pH of the solution. As the partial pressure of CO_2 increases, the concentration of carbonic acid will also increase, and the pH will decrease. The pore water present in naturally occurring CO_2 reservoirs is very acidic and rapidly corrodes steel production casing (Allis et al., 2001).

Low-pH conditions promote the leaching and mobilization of toxic heavy metals such as lead (Pb) and arsenic (As) from minerals. A brine solution containing 20% sodium chloride (NaCl) and dissolved CO_2 under 880 psi (6.1 MPa) pressure at 113°F (45°C) has a pH value of around 3. At this low pH, the solution will be capable of leaching minerals from and weakening the host formations used for geologic sequestration (White et al., 2003). This very acidic solution can also readily destroy the cements used to seal injection well casing (Duguid et al., 2004).

Density and Viscosity

Figure 2 shows the phase diagram for CO_2. Above its critical point temperature of 88°F (31°C) and pressure of 1074 psi (7.4 MPa), CO_2 is a dense, supercritical fluid. In an area with a 1.5°F/100 ft (9.5°C/km) geothermal gradient and a 0.43-psi/ft (9.8-kPa/m) hydrostatic pressure gradient, the injected CO_2 would be in a dense, supercritical phase when the geologic sink was at a depth greater than approximately 2600 ft (790 m).

Gaseous CO_2 at atmospheric temperature and pressure is 1.9 times denser than air. In its supercritical state, CO_2 has a density and viscosity less than that of water. Most of the CO_2 injected into deep geologic sinks saturated with formation water will remain in this dense phase. After CO_2 injection ends, buoyancy would drive its mobility. Its buoyancy will cause the CO_2 to migrate to the top of the injection zone. Only a portion of the injected supercritical CO_2 will dissolve in the aqueous phase. The net result will be a two-phase system of lower-density CO_2-rich fluid, which will flow upward, and a higher-density aqueous phase containing dissolved CO_2, which will flow downward (Oldenburg et al., 2002; Tsang et al., 2001; White et al., 2003).

The mobility of dissolved CO_2 is controlled by the rate of the bulk water flow through the geologic sink. As CO_2-saturated water migrates upward toward the surface, the temperature and pressure will decrease, and the CO_2 will begin to come out of solution, resulting in the formation of bubbles of CO_2 gas that will rise quickly under buoyancy forces (Oldenburg et al., 2002; Tsang et al., 2001; White et al., 2003).

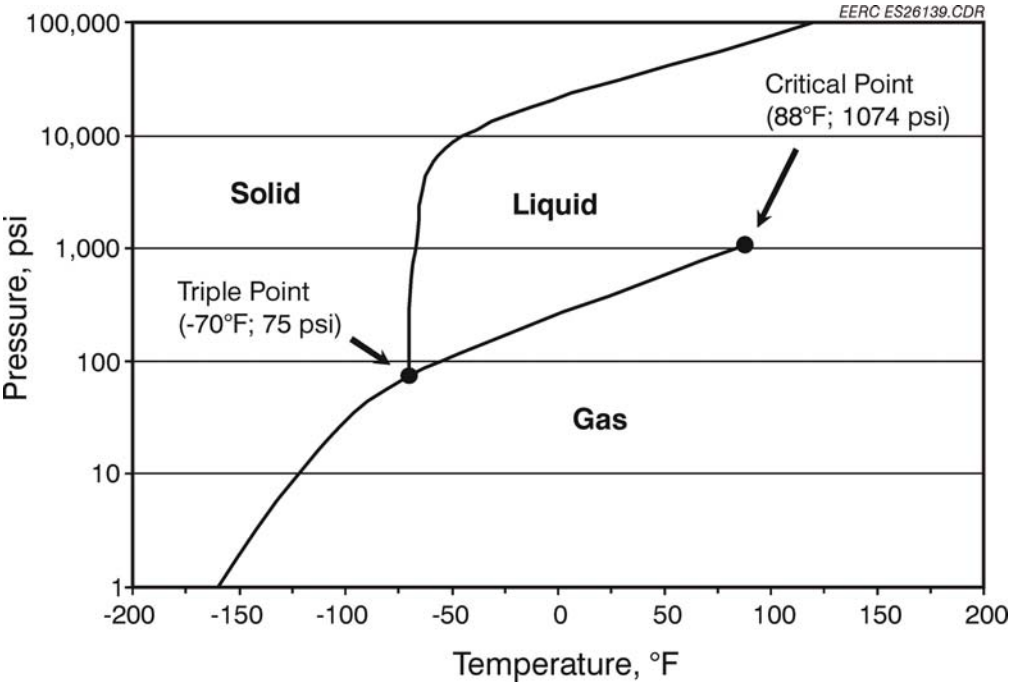

Figure 2. CO_2 phase diagram.

Fluid mobility in porous media is inversely proportional to viscosity. The viscosity of CO_2 (Table 1) is less than that of air at atmospheric pressure, and it will flow faster than air under all comparable circumstances. Further, the viscosity of supercritical CO_2 under all comparable circumstances is about one-tenth that of water. Therefore, CO_2 viscosity remains gaslike in the presence of water. CO_2 gas will always be buoyant in the saturated subsurface and will have the mobility characteristics of a gas, even at very high pressures (Oldenburg et al., 2002).

The shallow subsurface, for example, near the water table and within the vadose zone, is characterized by pressures and temperatures approximately equal to those at the ground surface. CO_2 is a dense gas relative to dry air and behaves approximately ideally at atmospheric pressure. Note that the contrast in density between CO_2 and actual soil gas will be even larger because soil gas is humid and humid air is less dense than dry air. This is because of the relatively smaller molecular weight of water (18 g/mole) compared to dry air (28.96 g/mole). As stated above, CO_2 is less viscous than air (Table 1), a somewhat nonintuitive relation given the contrast in density.

Diffusivity

In addition to density and viscosity, the transport of CO_2, especially in the shallow subsurface, may be controlled by molecular diffusivity. The molecular diffusivity of CO_2 in air is comparable to other gases and is approximately 1.65×10^{-5} m^2 s^{-1} at 77°F (25°C) and 1 atm (0.1 MPa) (Vargaftik et al., 1996). Molecular diffusivity decreases as CO_2 becomes denser and more liquidlike as pressure increases. As with solubility, pressure and temperature are compensating effects; i.e., increasing pressure tends to decrease diffusivity, while increasing temperature increases it (Oldenberg et al., 2002).

Table 1. Viscosity of Gases and Liquids (Perry, 1950; Lide, 2004)

Substance	Viscosity, centipoise	Viscosity, centipoise
CO_2 (supercritical)	0.025 40°C, 80 bar	0.0205 100°C, 80 bar
Water	0.7523 33°C,1 bar	0.2838 100°C, 1 bar
Methane	0.0112 27°C, 1 bar	
CO_2 (gas)	0.015 27°C, 1 bar	
Air	0.0186 27°C, 1 bar	
Nitrogen	0.0179 27°C, 1 bar	
Oxygen	0.0208 27°C, 1 bar	

Health and Ecological Effects

Humans, flora, and fauna experience virtually no adverse effects when exposed to concentrations of CO_2 below 1% (10,000 ppm). While CO_2 is essential for plant photosynthesis processes, it can pose adverse health effects for humans when exposure concentrations are elevated (Benson et al., 2002; Vendrig et al., 2003).

When humans are exposed to atmospheric concentrations of CO_2 between 3% and 5%, they experience respiratory rate increase, and physical discomfort such as headache and dizziness may occur. When the CO_2 concentration is above 5%, physical and mental capacities are impaired, and loss of consciousness can occur. Exposure to more than 10% CO_2 can result in rapid loss of consciousness, possible coma, or death. Plants, insects, and soil organisms have a higher tolerance than humans to elevated CO_2 concentrations. In general, only a few microbes, invertebrates, insects, and fungi can survive in CO_2 concentrations in excess of 20% (Jarrell et al., 2002; Benson et al., 2002; Vendrig et al., 2003).

GEOLOGIC CO_2 TRAPPING MECHANISMS

The geological sequestration of CO_2 can occur by either physical or chemical trapping mechanisms. Four types of trapping mechanisms control the storage density and leakage potential of the CO_2 injected into geologic sinks (White et al., 2003). These four trapping mechanisms are described in the following sections.

Solubility Trapping

In solubility trapping, the CO_2 simply dissolves in the formation water or reacts with the water to form carbonic acid and other aqueous carbonate species. The geologic sink for solubility trapping is a water-filled porous rock layer capped by an essentially impermeable rock layer (White et al., 2003). Solubility trapping also occurs during CO_2 flooding EOR. In this type of geologic sink, the injected CO_2 dissolves in the crude oil contained in the reservoir. The immobile, nonrecoverable fraction of the crude oil is the geologic sink for the CO_2 (Shaw and Bachu, 2002).

Hydrodynamic Trapping

In hydrodynamic trapping, CO_2 occupies the pore space of the rock comprising the geologic sink. The geologic sink for hydrodynamic trapping is a porous rock layer capped by an essentially impermeable rock layer. Other terms that are sometimes used to describe this type of trapping mechanism are structural and stratigraphic trapping (White et al., 2003).

Hydrodynamic trapping can occur even if the rock's pore space is initially 100% saturated with formation water. When the pressure of the injected CO_2 is greater than that of the initial water pressure in the formation, the water compresses, creating free pore space for gaseous CO_2 storage. Although water is a very incompressible fluid, when the total water and injected gas volumes are both very large, water compression can allow a large gas bubble to form (Katz and Tek, 1981)

Adsorption Trapping

In physical adsorption, CO_2 molecules are immobilized or trapped at near liquidlike densities on micropore wall surfaces of coal organic matter, kerogen, or minerals. The hydrostatic pressure in the formation controls the gas adsorption process. Coal seams and shales are types of geologic sinks where physical adsorption trapping occurs (White et al., 2003).

Mineral Trapping

In mineral trapping, dissolved CO_2 undergoes chemical reactions with silicate minerals rich in Ca, Mg, and Fe, resulting in the formation of a solid carbonate mineral phase. Sandstone aquifers rich in glauconite, illite, anorthite, chlorite, or smectite minerals and low in carbonates are the most favorable geologic sinks for mineral trapping of CO_2. Mineral trapping results in the most stable, permanent form of geologic CO_2 sequestration. Although the chemical reactions that generate the solid carbonate mineral phase are reversible, the kinetics of the reverse reactions are very slow (White et al., 2003).

CO_2 LEAKAGE MECHANISMS

Three basic types of mechanisms could result in CO_2 leakage from geologic sinks. The first mechanism is fast-flow path leakage which would primarily involve CO_2 movement up poorly sealed or failed injection well casings and improperly abandoned wellbores and through transmissive faults or fractures in the cap rock above the geologic sink. The second mechanism is slow leakage, which would primarily involve gas transport by diffusion processes and loss of dissolved CO_2 because of the hydrodynamic flow of formation water out of the geologic sink. The third mechanism is leakage due to desorption of adsorbed-phase CO_2.

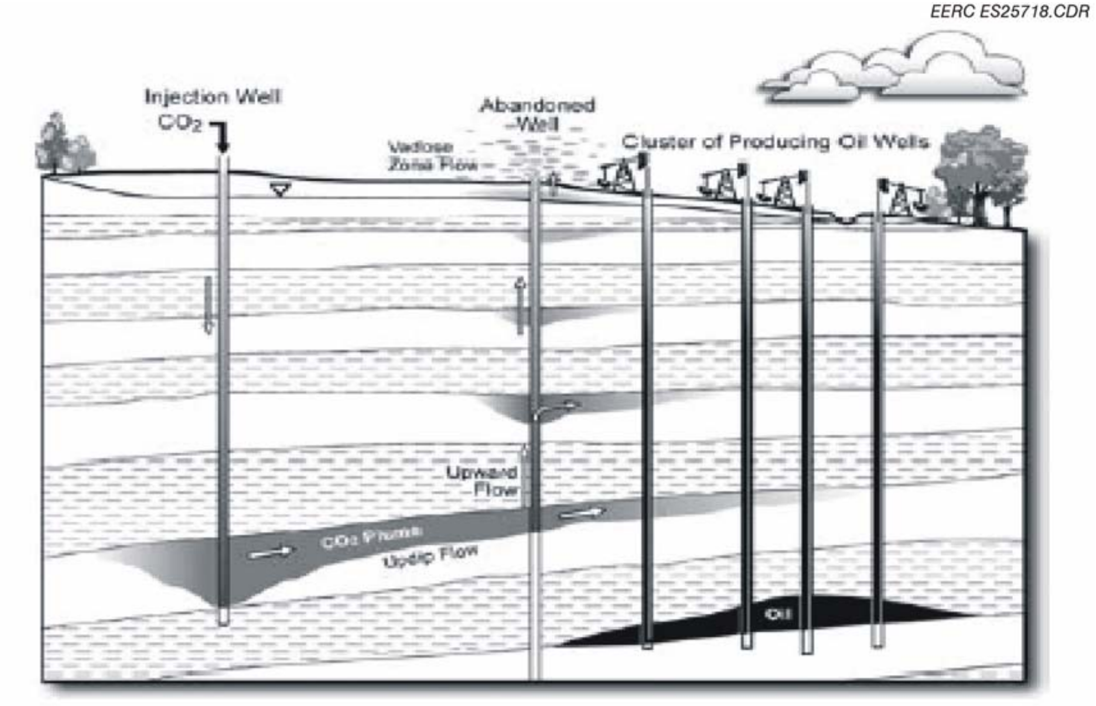

Figure 3. Schematic of CO_2 injection, migration, and leakage along abandoned wells (Celia et al., 2004).

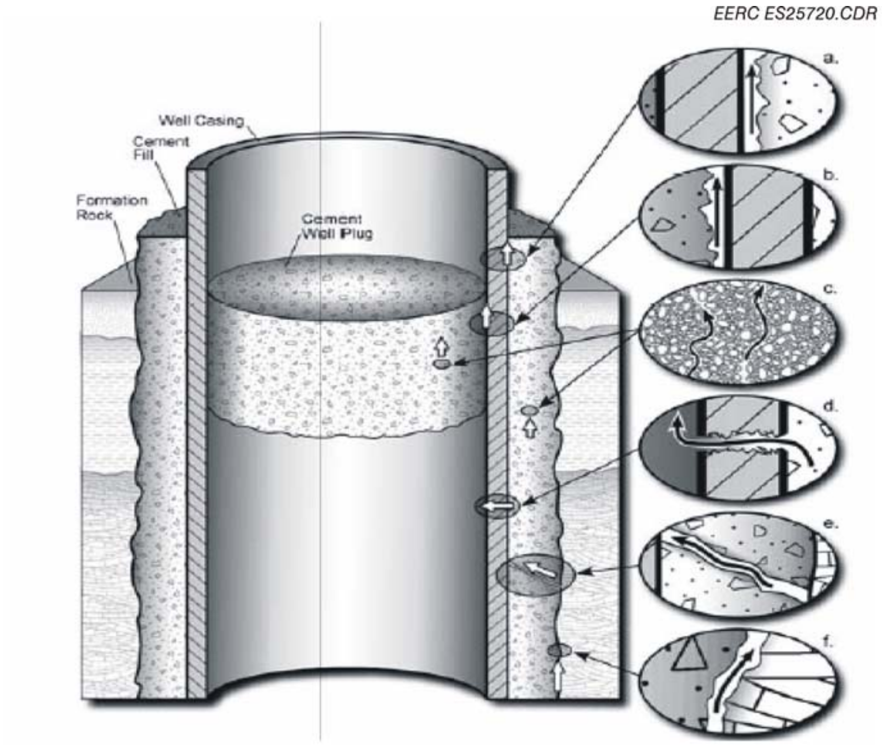

Figure 4. Potential leakage pathways along an existing well: between cement and casing (Paths a and b), through the cement (c), through the casing (d), through fractures (e), and between cement and formation (f) (Celia et al., 2004).

Fast CO_2 Leakage

In the case of leakage up a poorly sealed or failed injection well casing, the CO_2 could leak through a corroded casing wall and travel upward along the outside of the casing or through the adjacent formations to the surface (see Figure 3). In the case of leakage up an improperly abandoned wellbore, the CO_2 could leak through a corroded casing wall and travel upward through the casing to the surface (see Figure 4).

Slow CO_2 Leakage

With both solubility and hydrodynamic trapping, there is potential for vertical or lateral migration of dissolved or gas-phase CO_2 out of geologic sinks. The flow velocity of the formation water would affect the rate of dissolved CO_2 migration out of a geologic sink. A formation with active hydrologic flow would be undesirable, whereas a formation with essentially static hydrology would be a more suitable long-term sink.

Figures 5 and 6 are conceptual models of hydrodynamic traps (Bruant et al., 2002; Celia et al., 2002b). Buoyancy forces drive upward (Figure 5) or upgradient (Figure 6) migration of the CO_2 plume. The upward migration is restricted by permeability and capillary barriers in the overlying cap rock layer. At the top of the trap, the buoyant, upwardly migrating CO_2 plume tends to spread out laterally against the cap rock layer. As the area of contact between the buoyant CO_2 plume and cap rock increases, the probability that the CO_2 plume will encounter transmissive faults where fast-flow path leakage or smaller fractures where slower diffusive leakage can occur increases. If 298 million short tons (2.7×10^{11} kg) of CO_2 were injected into a 328-ft (100-m)-thick aquifer, the

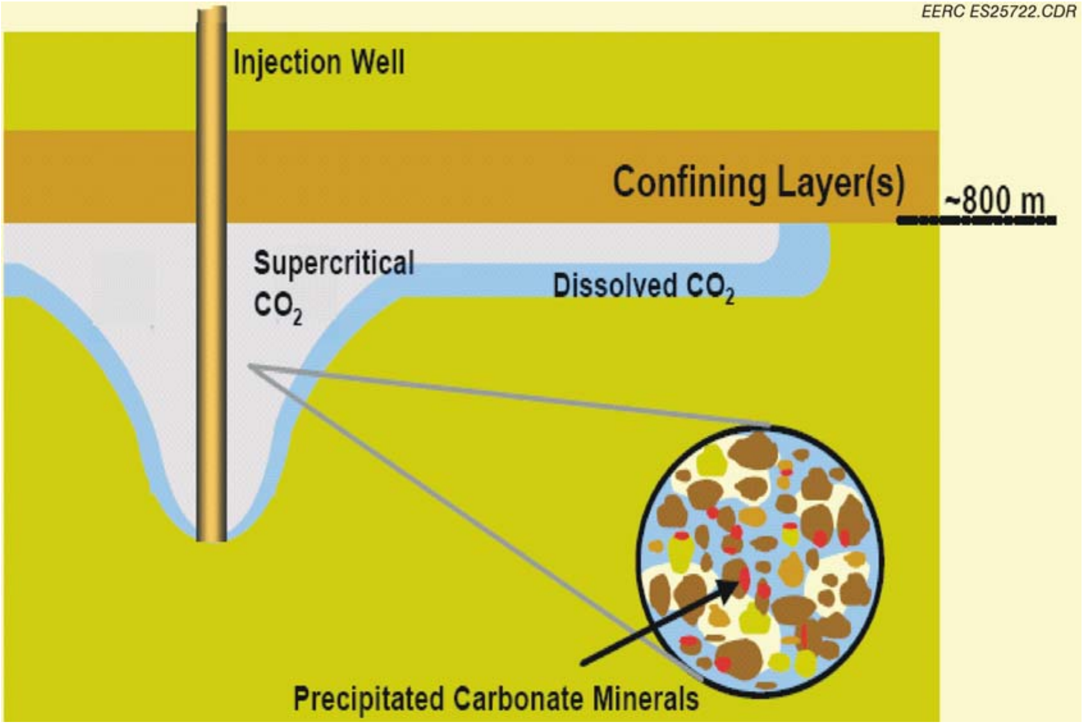

Figure 5. Simulation of CO$_2$ injection into a deep aquifer (modified from Bruant et al., 2002; Celia et al., 2002b).

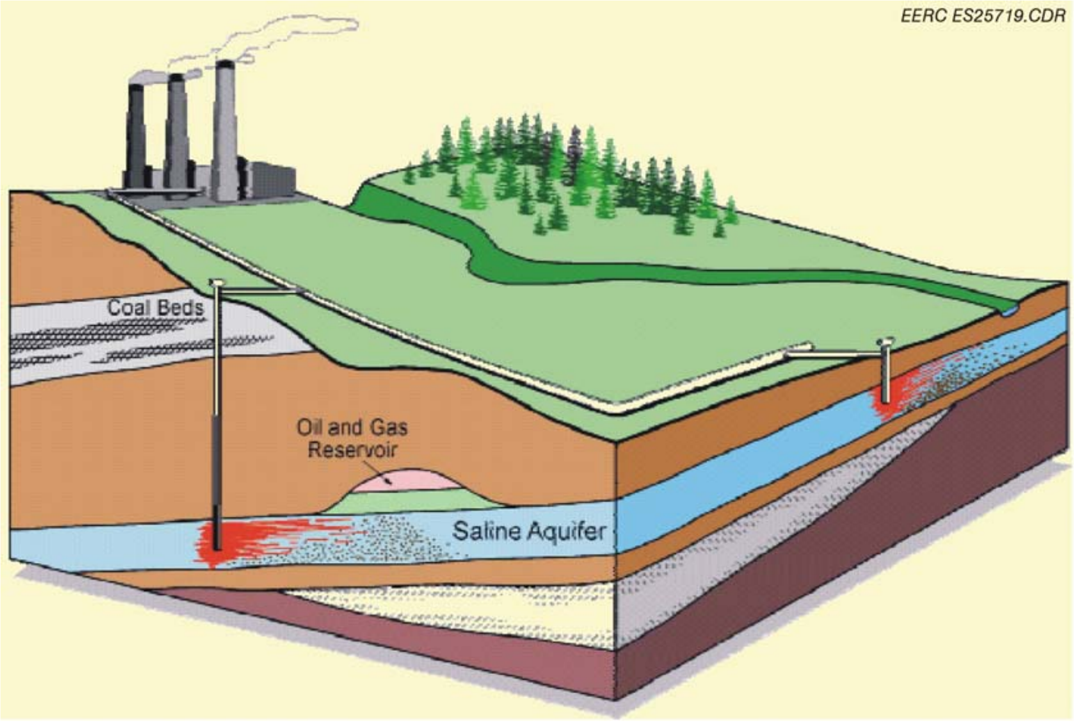

Figure 6. Simulation of a CO$_2$ injection operation after several years (modified from Bruant et al., 2002; Celia et al., 2002b).

aerial extent of the CO_2 plume in contact with the cap rock at the top of the injection zone could be as much as roughly 46 mi^2 (120 km^2) (Tsang et al., 2001). The movement of the plume of supercritical CO_2 and that of the water will be counter to each other. With respect to lateral migration (see Figure 6), the buoyant CO_2 plume will flow upgradient, and the CO_2-laden water will flow downgradient (Pruess and Garcia, 2002; Garcia, 2001; Tsang et al, 2001; Oldenburg et al., 2002; White et al., 2003).

Gas Desorption

With physical adsorption, the adsorbed CO_2 is essentially immobile. However, the intermolecular attraction forces between a CO_2 molecule and a solid surface are relatively weak, and the adsorption process is reversible. Thus pressure must be maintained at or above the gas desorption pressure in order for the adsorbed CO_2 molecules to remain immobile. Buoyancy would drive the upward or upgradient migration of desorbed CO_2. Natural leakage pathways would be through faults, fractures, or outcrops that connect the geologic sink with the surface. Gas desorption and leakage to the surface is a potential risk because the hydrologic pressure in formations can undergo natural variation over geologically long time periods. In order to minimize the risk of leakage, the injected CO_2 volume must be less than the current CO_2 storage capacity of the adsorptive rock in the geologic sink (Pashin and McIntyre, 2003).

LEAKAGE FROM PETROLEUM RESERVOIRS

Concern about the potential for CO_2 leakage from geologic sinks arises because natural pathways and mechanisms exist which permit the hydrocarbon liquids and gases present in petroleum reservoirs to reach the earth’s surface. Petroleum leakage to the surface is presently occurring in roughly 50% of the 370 basins worldwide (both onshore and offshore) with known petroleum reserves (Clarke and Cleverly, 1991). Visible evidence of petroleum leakage includes asphalt and tar deposits or areas where oil or natural gas is actively seeping onto the ground surface, into mines or water wells, or in springs, lakes, and marine coastal areas. Surface sites containing visible evidence that liquid or gaseous hydrocarbons are actively leaking or have previously leaked from a subsurface region are called macroseeps (Link, 1952; Hunt, 1979; Weber, 1997).

Most of the important oil- and natural gas-producing areas around the world were first discovered based on field observations of active or past petroleum macroseeps. The first successful oil well in the United States, the Drake oil well, which was completed in 1859 in Pennsylvania, and the first successful oil well in Texas, which was completed in 1865, were both drilled on or near active oil seeps. The hill near Beaumont, Texas, where the historic Spindletop oil field discovery was made in 1901 was identified as a promising drilling site, in part, because there was a gas seep in a nearby spring (Link, 1952; Hunt, 1979; Weber, 1997).

Petroleum macroseeps are most prevalent in areas underlain with rock layers that are folded, faulted, or exposed at the surface (see Figure 7). The migrating hydrocarbons follow the most permeable pathways to the surface, which are commonly faults and fractures. The migration mechanisms resulting in macroseeps are not well understood, but the driving force for hydrocarbon migration is buoyancy. Macroseeps are not found in areas underlain with very flat-lying rock layers without major faulting or fracturing (Link, 1952; Hunt, 1979; Grunau, 1987).

A second type of leakage is microseepage, which is oil or gas leakage to the surface that is not visible but which is detectable by analytical methods. Microseepage is

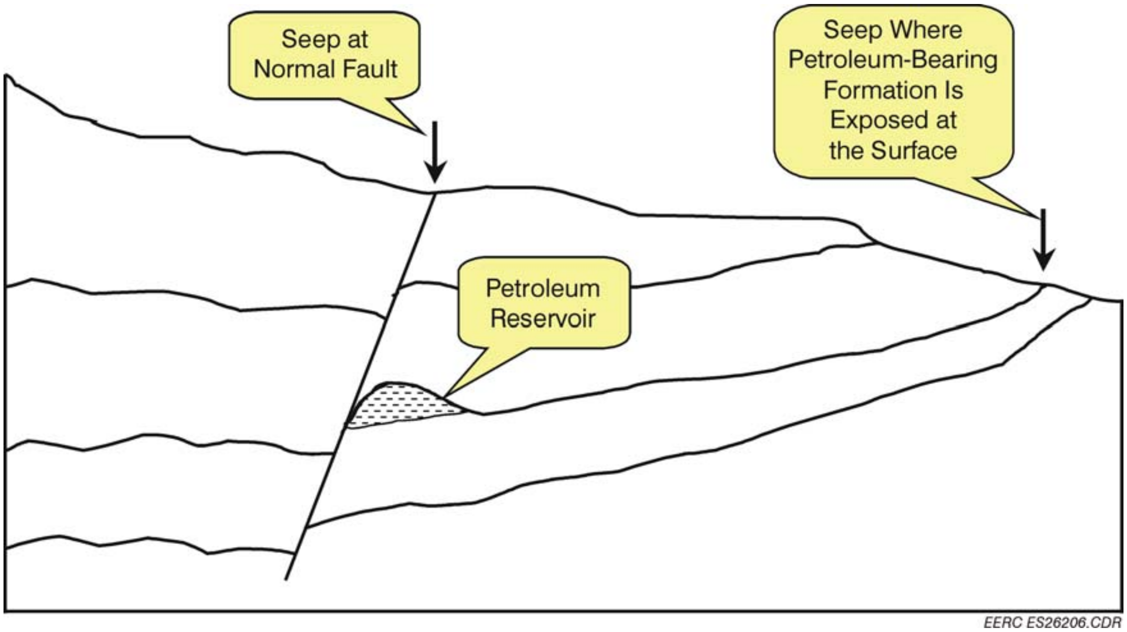

Figure 7. Generalized stratigraphic cross section showing locations of seeps associated with faults and beds exposed at the surface.

detectable above subsurface petroleum reservoirs and also above natural gas storage reservoirs when the cap rock is not an effective seal for the reservoir fluids. A variety of analytical procedures have been developed for detecting petroleum microseeps. The mechanisms by which microseepage occurs are not well understood but the driving force for hydrocarbon migration is buoyancy (Hunt, 1979; Klusman, 1993; Tadesco, 1995; Saunders et al., 1999; Brown, 2000).

CAP ROCKS AND SEALS

Cap rocks are an essential but also the least understood geologic element of petroleum reservoirs. A cap rock is a lithologic unit capable of impeding hydrocarbon movement. Effective cap rocks for liquid and gaseous hydrocarbon accumulations are typically thick, laterally continuous, ductile rocks with high capillary entry pressures. The most common cap rock lithologies over commercial petroleum reservoirs are evaporates and shales. Evaporites seal about 50% of the world's largest oil fields and 36% of the world's 25 largest natural gas fields (Wilhelm, 1945; Hubbert, 1953; Berg, 1975; Downey, 1984; Grunau, 1987; Sales, 1997).

Cap rocks act as valves that control the amount of liquid or gaseous hydrocarbons that reservoir rocks retain or leak. Hydrocarbon leakage through cap rocks is a common phenomenon. Leakage can occur either through preexisting pores or fractures in the cap rock lithology. A cap rock has a membrane seal if leakage is through preexisting pores and has a hydraulic seal if leakage is through fractures opened by pressure in the reservoir. Mercury injection tests, performed in a laboratory using cap rock core samples, are commonly used to determine the capillary entry pressure, the pressure at which membrane seals start to leak. Leak-off tests, performed in wells, are commonly used to determine the pressure at which hydraulic seals start to leak (Watts, 1987; Sales, 1997).

Membrane Seals

Fundamentally, the ability of a cap rock to act as an effective membrane seal is determined by the minimum pressure required to displace connate water from pores or fractures in the cap rock, thereby allowing leakage. For membrane seals, the sealing layer thickness is not important because the rock property that controls seal strength is the capillary entry pressure of the largest interconnected pore throat. Under hydrostatic conditions, the main driving and resistant forces affecting hydrocarbon migration in water wet, porous rocks are buoyancy and capillary pressure, respectively. The factor determining the magnitude of the buoyant force is the density difference between the water phase and the hydrocarbon phase. The greater the density difference, the greater the buoyant force for a given vertical hydrocarbon column length. The factors determining the magnitude of the resistant force are the rock wettability, the largest connected pore throat radius, and the hydrocarbon–water interfacial tension. The sealing capacity of a cap rock increases as the rock wettability and throat radius of the largest connected pores decreases and as the hydrocarbon–water interfacial tension increases (Hubbert, 1953; Berg, 1975; Schowalter, 1979; Downey, 1984; Watts, 1987; Sales, 1997).

Within a petroleum reservoir the fluid properties such as density and interfacial tension and rock properties such as pore throat radius are relatively constant. The variable reservoir property that determines whether leakage occurs is the buoyant force exerted by the vertical height of the hydrocarbon column in the reservoir. Membrane seal strength corresponds to the height of a hydrocarbon column that can be retained before leakage occurs. The expression for calculating the critical hydrocarbon column height in a subsurface reservoir under hydrostatic conditions is shown in Equation 2 (Berg, 1975).

$$\text{Critical height (cm)} = (2\gamma \times [1/r_t - 1/r_p])/(g \times [\rho_w - \rho_o]) \quad \text{[Eq. 2]}$$

Where:

γ = Interfacial tension
r_t = Radius of pore throats (cm)
r_p = Radius of pores (cm)
g = Acceleration of gravity
ρ_w = Water density
ρ_o = Oil density

Figure 8 show the results of calculations of the critical heights of oil or gas columns made using Equation 2. The pore throat radius (r_t) of the finer-grained particles comprising the cap rock and the pore radius (r_p) of the coarser-grained particles comprising the reservoir rock were estimated using Equations 3 and 4, respectively (Berg, 1975).

$$r_t = (0.5 \times [0.154D]) \quad \text{[Eq. 3]}$$

$$r_p = (0.5 \times [0.414D]) \quad \text{[Eq. 4]}$$

Where:

D = Grain diameter (cm)

For illustrative purposes, consider a sandstone reservoir rock with a grain diameter of 0.2 mm. The interfacial tension is assumed to be 35 dynes/cm. The water–oil density difference ($\delta\rho_{w\text{-}o}$) is commonly 0.1 to 0.3 cm^3/g. The water–gas density difference ($\delta\rho_{w\text{-}g}$) approaches 1.0 cm^3/g. If the cap rock is a coarse siltstone with a grain diameter of 0.05 mm, then a 55-ft (17-m) column of low-gravity oil ($\delta\rho_{w\text{-}o} = 0.1$ cm^3/g) but only a 5-ft (1.5-m) column of gas ($\delta\rho_{w\text{-}g} = 1.0$ cm^3/g) could be held in the reservoir before leakage occurs. By contrast, if the cap rock is a fine siltstone with a grain diameter of only 0.01 mm, then a 300-ft (91-m) column of low-gravity oil and a 30-ft (9-m) column of gas could be held in the reservoir before leakage occurs (Berg, 1975; Schowalter, 1979).

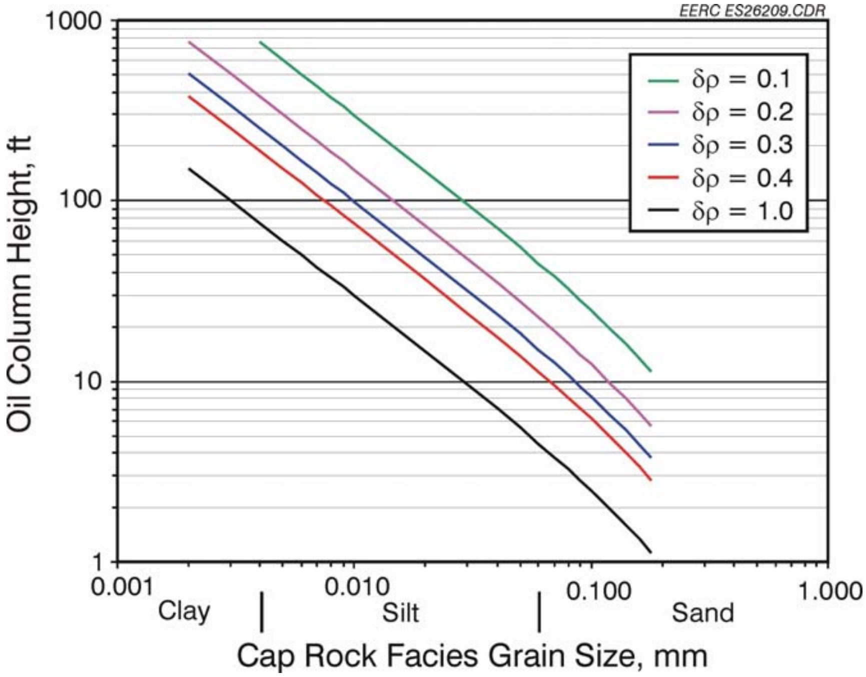

Figure 8. Estimated heights of oil and gas columns that could be trapped by capillary pressure forces in cap rocks of varying grain size when the reservoir rock has a mean grain size of 0.2 mm.

Hydraulic Seals

In the situation where the capillary entry pressure is essentially infinite, seal failure occurs by the development or wedging open of fractures in the cap rock. The hydraulic seal capacity of a cap rock is related to such factors as its thickness and tensile strength, the magnitude of the minimum effective stress in the sealing layer, and the degree of overpressure development in the reservoir system (Watts, 1987).

ABNORMAL PRESSURE SYSTEMS IN SEDIMENTARY BASINS

Pressure measurements indicate that many sedimentary basins contain layers of two or more superimposed hydrogeological systems that are not in hydrologic communication with each other. The shallow system, which is typically basinwide, usually exhibits a normal hydrostatic pressure/depth gradient which frequently extends from the surface down to a depth of about 10,000 ft (3048 m). Below this depth, the deeper systems, which are typically not basinwide, are frequently abnormally pressured and are not in hydrologic pressure communication with the overlying hydrodynamic regime (Bradley, 1975; Hunt, 1990).

The pressure/depth gradients of freestanding columns of freshwater and saturated salt solutions are 0.43 psi/ft (9.8 kPa/m) and 0.53 psi/ft (11.9 kPa/m), respectively. Any pressure/depth gradients outside these limits are considered abnormal. The terms “overpressured” and “underpressured” refer to pressure/depth gradient values above and below these limits, respectively. Abnormal pressure systems, which are mostly overpressured, have been identified in about 180 basins worldwide (Bradley, 1975; Hunt, 1990).

The mechanisms by which overpressured systems are formed and maintained are not well understood. An essential requirement for the existence of an abnormal pressure system is a pressure seal capable of preventing the flow of oil, gas, and water across its boundaries over substantial intervals of geologic time. Most pressure seals are evaporites, shales, or sandstones. The widespread existence of abnormal pressure systems in sedimentary basins is an indication that natural mechanisms exist which can prevent the liquids and gases present in deeply buried areas of sedimentary basins from reaching the earth's surface (Bradley, 1975; Hunt, 1990; Deming, 1994; Osborne and Swarbrick, 1997; Muggeridge et al., 2005).

The Cook Inlet Basin in Alaska is an example of a sedimentary basin that contains an overpressured hydrogeological system. Figure 9 shows the measured pressure/depth gradients for the normally pressured and overpressured systems in the Cook Inlet Basin. Pressure measurements show that there is a sudden pressure/depth gradient discontinuity at a depth of 10,600 ft (3,231 m). The pressure increase is 7534 psi (52 MPa) across the 3280-ft (1000-m)-thick pressure seal. The pressure seal forms a planar top, which extends across geologic structure, facies, formations, and time intervals. This variation suggests that the seal formed along a thermocline. The pressure seal covers about one-third of the 15,440-mi^2 (40,000-km^2) basin area and is believed to represent an interval where bands of calcite precipitation have plugged the porosity and permeability of the rock (Hunt, 1990).

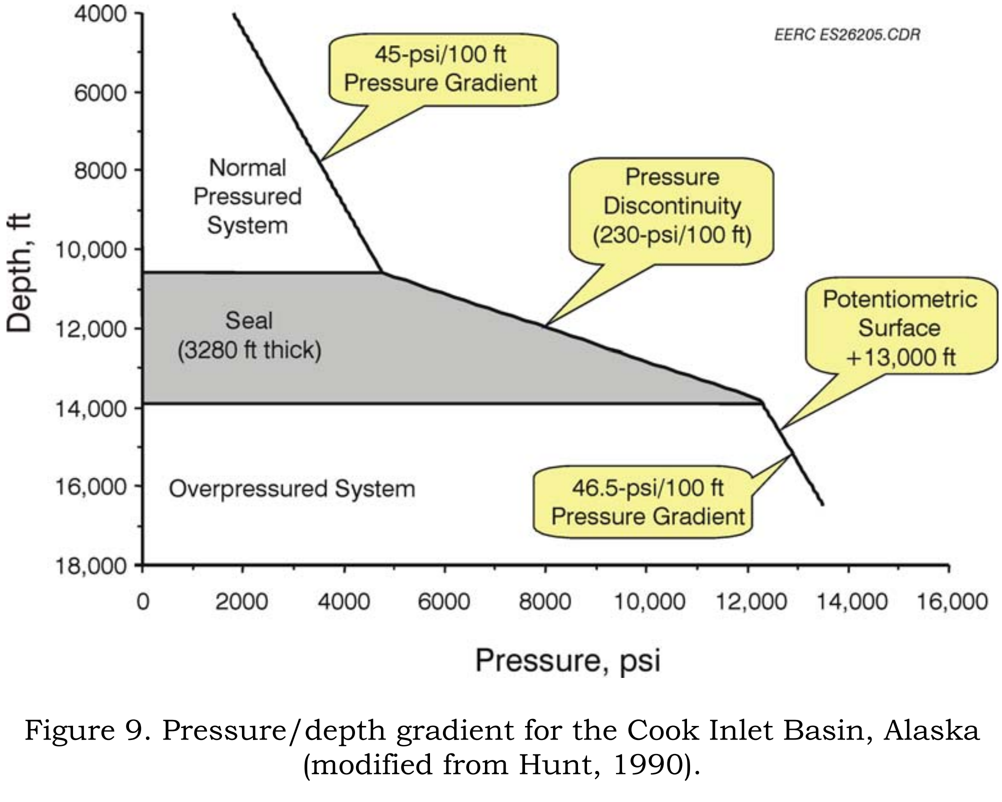

Figure 9. Pressure/depth gradient for the Cook Inlet Basin, Alaska (modified from Hunt, 1990).

UNDERGROUND NATURAL GAS STORAGE

Underground natural gas storage reservoirs are useful analogs for identifying factors that might affect CO_2 leakage from geologic sinks. In 1998, there were more than 466 underground natural gas storage projects in the United States and Canada. The natural gas is stored in depleted oil and gas reservoirs, aquifers, and mined salt caverns. The depleted oil, gas, and aquifer reservoirs used for natural gas storage are anticline structures, which are folded layers of porous rock capped by an essentially impermeable rock layer (Katz and Tek, 1981; American Gas Association, 1999).

A key difference between underground natural gas storage and geologic CO_2 sequestration is that in the former, the gas storage is temporary, with the time interval between gas injection and withdrawal typically being on the order of weeks to months. Currently, the United States natural gas industry injects and withdraws roughly 4 Tcf (1.1×10^{11} m^3) of natural gas into and out of geologic storage annually (Pacala and Socolow, 2004).

The natural gas industry also has recent experience with geologic storage of CO_2. For example, since 1989, the Canadian natural gas industry has been separating CO_2 and H_2S from natural gas and successfully disposing of the acid gas mixture by reinjecting it into subsurface aquifer zones or depleted reservoirs (Wichert and Royan, 1997). Additionally, since 1996, Statoil, Norway's largest oil company, has been separating CO_2 from natural gas produced at the Sleipner Field in the North Sea and reinjecting it at a rate of about 1 million tons (907.2×10^6 kg) per year into brine aquifer formations located 1800 to 4900 ft (550 to 1500 m) beneath the ocean floor. Results from monitoring the aquifers being used for geologic CO_2 sequestration at the Sleipner Field with seismic and other tools suggest that the CO_2 is remaining in the injection zones (Service, 2004; Hansen et al., 2005).

With geologic CO_2 sequestration, the goal is safe and reliable storage of the injected CO_2 over time intervals of hundreds to thousands of years. Despite the enormous storage time interval difference, some of the geologic criteria used for identifying reservoirs suitable for underground natural gas storage are also applicable to geologic sinks proposed for CO_2 sequestration. The criteria that specifically relate to gas leakage potential are described in the following sections.

Vertically Isolated Reservoir

Out-of-zone gas migration is undesirable. Methane (CH_4), the chief component of natural gas, like CO_2, is buoyant and tends to migrate upward to the top of an injection zone. Vertical isolation of the gas storage rock interval by an impermeable cap rock layer is essential for preventing out-of-zone migration of the injected gas (Seidle, 2000; Bruant et al., 2002).

Simple Structure

The cap rock layer should have minimal folds, faults, and fractures. Folding can result in fracture formation. Open, transmissive faults and fractures provide migration pathways for escape of the injected gas (Seidle, 2000).

Static Hydrology

This characteristic is not typically considered critical with respect to natural gas storage because the water solubility of CH_4 is very low (Price, 1979). However, CO_2 is considerably more soluble in water and brine (Wiebe and Gaddy, 1939, 1940; Prutton and Savage, 1945). Thus static hydrology, i.e., low-formation water flow velocity, would be critical for minimizing lateral migration of dense solution-phase CO_2 out geologic traps (Seidle, 2000; Bruant et al., 2002).

GAS LEAKAGE FROM AN AQUIFER STORAGE RESERVOIR

A concern in any underground natural gas storage project is the potential for gas loss through leakage into adjacent formations and to the surface. Gas leakage is an economic burden to the storage operation and can result in an environmental hazard for surface landowners. The leakage may be the result of problems with improperly plugged abandoned wells, imperfect cementing or corrosion of preexisting or newly drilled wells, gas migration along faults or fractures, or cap rock seal failure (Katz and Tek, 1981).

The Leroy aquifer natural gas storage facility in Uinta County, Wyoming, is a site where gas migration out of the storage horizon and leakage to the surface have been recurring problems. The reservoir is an anticline bounded on its west side by a fault. The gas is injected into a coarse grained, porous, and permeable aquifer sandstone at a depth of roughly 3000 ft (900 m) in the lower Thaynes Formation. The middle Thaynes Formation contains shale, siltstone, and anhydrate, which form the cap rock for the storage reservoir. The storage reservoir infrastructure includes preexisting and newly drilled wells (Araktingi et al., 1984).

In 1973 when the natural gas inventory was 3.7 Bcf (110×10^6 m^3) and the bottomhole pressure was 1740 psia (12 MPa) gas began blowing out around the surface casing of Leroy Well 3. This was an old, preexisting exploration well originally drilled in 1951. Log surveys showed that the gas leakage originated at a depth of 1360 ft (415 m) from a corroded well casing in the adjacent Leroy Well 4, with subsequent gas migration through the Twin Creek limestone to the Leroy Well 3, where it then migrated along the side of well pipe to the surface. This type of leakage path is shown in Figure 3. Repairs were attempted but were unsuccessful and the Leroy Well 4 was eventually plugged and abandoned (Araktingi et al., 1984).

Aquifer storage reservoirs require gas injection at pressures higher than the initial value to compress and displace water from the pores (Katz and Tek, 1981). Overpressuring increases the risk of gas leakage to overlying strata and the surface. The initial reservoir pressure in the Thaynes Formation sandstone aquifer was 1500 psig (10.3 MPa). In 1978, the natural gas inventory was 8.7 Bcf (246×10^6 m^3) and the reservoir pressure was 1830 psia (12.6 MPa). During 1978, a surface survey revealed natural gas bubbling in a creek and pond above the storage reservoir site. Several types of tracer gases were injected into the aquifer storage reservoir and all were subsequently detected on the surface within days or weeks of injection. This indicated direct reservoir-to-surface gas leakage (Araktingi et al., 1984).

Some of the gas bubbling was observed to be dependent on the storage reservoir operations and to cease altogether during the summer when the reservoir was flooded and did not contain gas. Some of gas bubbling was observed to be independent of the storage reservoir operations, indicating that some of the leaking gas was migrating to a shallow gas collection zone from which seepage to the surface then occurred. Figure 10 is a cross-sectional view of the Leroy aquifer storage reservoir showing the two proposed gas migration pathways (Araktingi et al., 1984).

Analysis of the reservoir pressure (p/z) versus injected natural gas inventory data showed that the slope of the data plot would begin to flatten whenever p/z exceeded 1800 psia (12.4 MPa). This strongly suggests a pressure-triggered leakage mechanism involving hydraulic seal failure in the reservoir cap rock. From analysis of the p/z versus injected natural

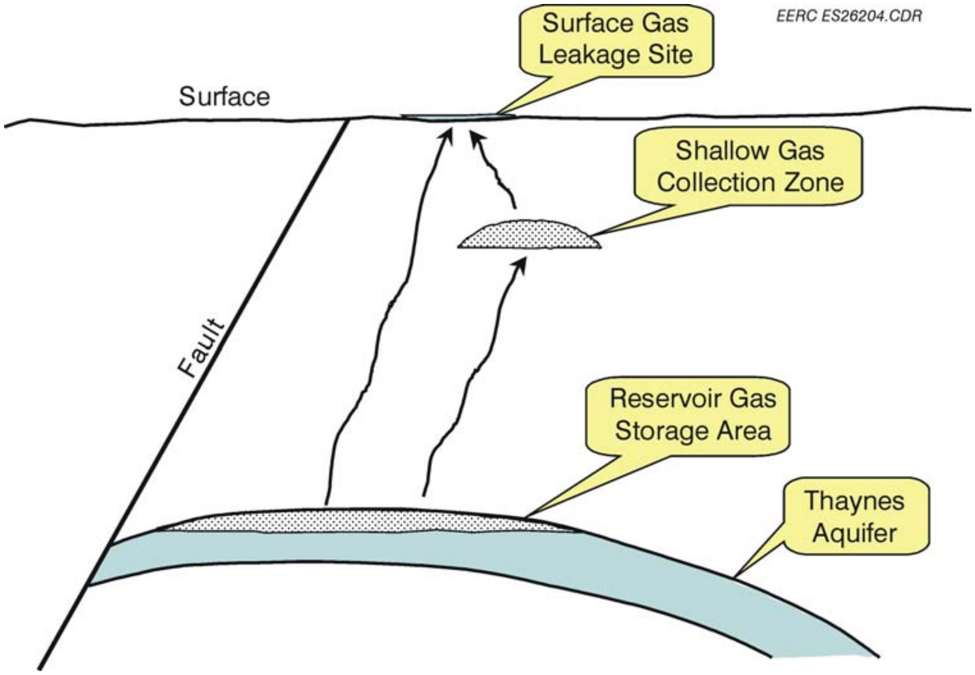

Figure 10. Cross-sectional view of the Leroy aquifer gas storage reservoir showing the two proposed gas migration pathways (modified from Araktingi et al., 1984).

gas inventory data the cumulative natural gas loss over 130 months of storage reservoir operation was estimated to total 0.6 Bcf (17 × 10^6 m^3). Gas loss from the storage reservoir could not be eliminated, but the leakage rate could be controlled by limiting the maximum pressure in the reservoir (Araktingi et al., 1984). The gas leakage rate from the Leroy storage reservoir totaled about 0.7% per year. This greatly exceeded the recently proposed leakage rate performance requirement of 0.01% per year for geologically sequestered CO_2 (White et al., 2003).

NATURAL CO_2 RESERVOIRS

Large deposits of high-purity (typically 98+%) CO_2 occur in many sedimentary basins in the United States and in other countries (Dobbin, 1935; Miller, 1938; Germann, 1938; Picard and Holland, 1962; Irwin and Barnes, 1982; Dai et al., 1996). Many of these CO_2 deposits are being exploited to provide CO_2 for EOR projects, dry ice manufacture, and other uses. Table 2 summarizes the characteristics of major CO_2 deposits in the United States. The most common reservoir lithologies are sandstone and dolomite. The predominant sealing cap rock lithologies are anhydrite and shale (Miller, 1938; Carpen, 1957; Lang, 1959; Foster and Jensen, 1972; Gerling, 1983; Johnson, 1983; Roth, 1983; Jenden and Kaplan, 1989; Jenden et al., 1993; Allis et al., 2001; Stevens et al., 2001; Jarrell et al., 2002; Hughes, 2004).

The examples of large, naturally occurring CO_2 reservoirs listed in Table 2 clearly suggest that in the right type of geologic setting CO_2 sequestration would be possible. By analogy with conventional natural gas deposit formation, these naturally occurring CO_2 reservoirs were formed as a result of the geologic trapping of CO_2 during its upward migration from a more deeply buried source location. The sources for naturally occurring CO_2 deposits include volcanic gas and thermal

Table 2. Large Naturally Occurring CO_2 Deposits in the United States

Field	State	Reservoir Area	Reservoir Depth	Trap Type	Reservoir Lithology	Seal Lithology	CO_2 Reserves
Big Piney – La Barge	WY	3500 km^2	~45000 m	Anticline	Dolomitized limestone	Sandstone	134 Tcf
McElmo Dome	CO	800 km^2	1800–2600 m	Anticline	Dolomitic carbonate	Salt	17 Tcf
Bravo Dome	NM	2000 km^2	600–700 m	Anticline	Arkosic to conglomeratic sandstone	Anhydrite and mudstone	16 Tcf
St. Johns-Springerville Dome	AZ NM	1800 km^2	200–700 m	Anticline	Sandstone intercalated with siltstone, anhydrate, and dolomite	Multiple Anhydrite beds	15.8 Tcf
Jackson Dome	MS	NA*	>5000 m	NA	Sandstone	NA	10 Tcf
Farnham Dome	UT	10 km^2	~900 m	Anticline	Sandstone	Interbedded limestone, shale, and siltstone	2.2 Tcf
Gordon Creek	UT	34 km^2	3300–3900 m	Anticline	Sandstone	Dolomite	0.14 Tcf
Escalante	UT	150 km^2	400–960 m	Anticline	Sandstone	Shale	4 Tcf
Sheep Mountain	CO	20 km^2	1000–1800 m	Anticline	Sandstone	Marine sediments capped by a laccolith	2.5 Tcf
North McCallum	CO	~10 km^2	~1500 m	Anticline	Sandstone	Shale	NA
Des Moines	NM	NA	~610 m	Anticline	Arkosic to conglomeratic sandstone	Mudstone	NA
Indian Creek	WV	NA	~2060 m	NA	Sandstone	NA	NA

NA = Not available.

decomposition of marine carbonates (Germann and Ayers, 1942; Lang, 1959; Zartman et al., 1961; Farmer, 1965; Hunt, 1996; Allis et al., 2001).

The large deposits of high-purity CO_2 found in the Rocky Mountain region of the United States occur in areas containing both marine carbonate rocks and basaltic intrusives and lavas. Geologic and geochemical studies indicate that the CO_2 found in these deposits was formed by the thermal decomposition of marine carbonate rocks (Lang, 1959; Zartman et al., 1961). For example, the probable source for the CO_2 in the McElmo Dome anticline was igneous intrusion into the Mississippian Leadville Formation limestone, which caused the thermal decomposition of this carbonate rock. The released CO_2 then migrated up-dip through the Leadville Formation limestone until it accumulated in the McElmo Dome anticline (Hunt, 1996).

Helium Content Differences

The naturally occurring CO_2 deposits at the Big Piney-La Barge, Escalante, North McCallum, St. Johns-Springerville, and Indian Creek anticlines contain significant amounts (0.1%–0.8%) of helium. Only trace (ppm) amounts of helium are present in the other CO_2 deposits. The observed differences in the helium contents of these naturally occurring CO_2 deposits could be due either to cap rock permeability differences or, alternatively, to other types of site-specific geologic factors related to helium origin.

Helium has two sources: disintegration of radioactive elements such as uranium, which yields crustal helium (^{4}He), and the earth's mantle, which yields primordial helium (^{3}He). Helium isotope studies indicate that the helium found in most continental areas of the United States is crustal helium (Jenden et al., 1993).

Helium is a very buoyant gas, has an effective molecular diameter of 0.2 nm, and is relatively insoluble in water. As a consequence of these properties, helium migrates very readily through most rocks and preferentially partitions into the gas phase if it comes into contact with water. Because of its mobility characteristics, only very impermeable reservoir cap rocks can retain helium for geologically long time periods (Zartman et al., 1961; Jenden et al., 1993; Hunt, 1996).

The scatter plot shown in Figure 11 indicates that the helium and nitrogen (N_2) contents of naturally occurring CO_2 deposits strongly covary. This type of correlation is found for helium in conventional natural gas deposits; i.e., helium-rich natural gas deposits are consistently nitrogen-rich. By contrast, the inverse relationship, i.e., that nitrogen-rich natural gas deposits are also helium-rich is not consistently found (Picard and Holland, 1962; Jenden et al., 1988; Jenden et al., 1993).

The correlation shown in Figure 11 suggests that the observed differences in the helium contents of the naturally occurring CO_2 deposits are probably due to site-specific geologic factors related to the helium origin as opposed to cap rock permeability differences. Additionally, both helium and nitrogen clearly have a separate origin from that of the CO_2.

CO_2 LEAKAGE FROM A FAULT IN EASTERN UTAH

Geologic and geochemical studies suggest that CO_2 leakage to the surface has been

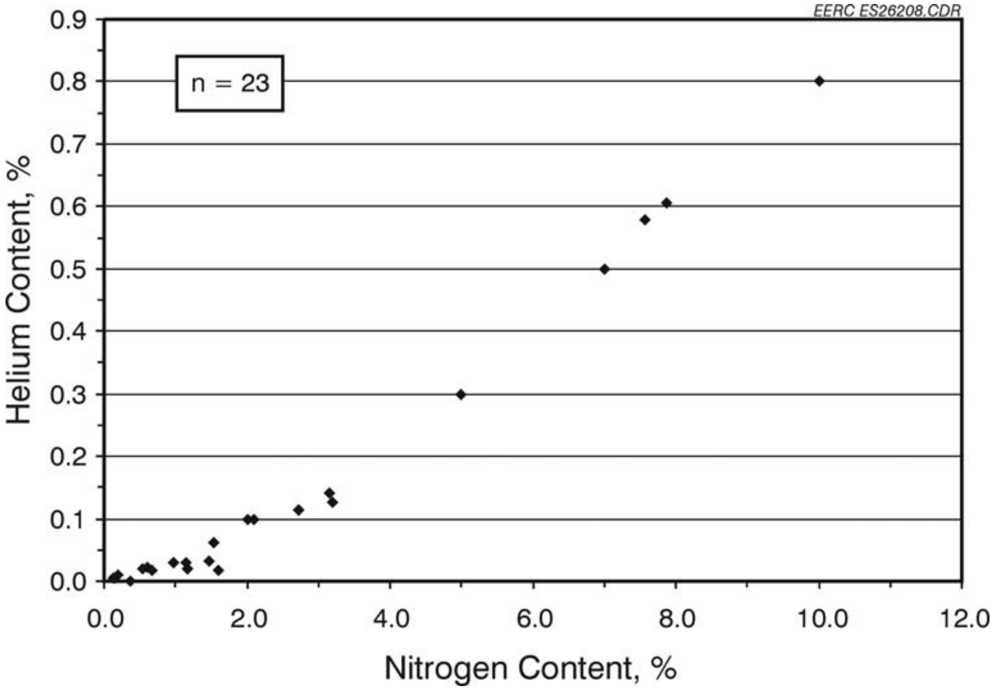

Figure 11. He–N_2 scatter plot for CO_2-rich gas deposits.

occurring for at least the past several hundred thousand years at the Little Grand Wash Fault near Green River, Utah. CO_2-saturated and mineral-laden water flows to the surface from springs along the fault trace and from Crystal Geyser located next to the fault. The geyser and fault are located 52 miles (84 km) southwest of the large, naturally occurring CO_2 deposit at the Farnham Dome anticline (Baer and Rigby, 1978; Shipton et al., 2001; Heath et al., 2002, 2003).

CO_2-saturated water also flows from geysers and springs at many other sites in the United States. Examples include Saratoga Springs, New York; Soda Spring, Idaho; and Yellowstone National Park, Wyoming (Irwin and Barnes, 1982). The stable carbon isotope abundance ratios of CO_2 samples obtained from the geysers and springs at these sites all fall within the range representative of carbon derived from marine carbonate rocks (Lang, 1959; Hunt, 1996). The stable carbon isotope abundance ratios of the CO_2 in the Farnham Dome anticline and that flowing from Crystal Geyser and the springs along the Little Grand Wash Fault also fall within the range representative of carbon derived from marine carbonate rocks (Zartman et al., 1961; Shipton et al., 2001; Heath et al., 2002, 2003).

Deposits of travertine and tufa, which are forms of calcium carbonate rock, are found along a 1.5-mi (2.4-km) section of the Little Grand Wash Fault. The travertine and tufa deposits are being actively built by the CO_2-saturated and mineral-laden water that flows from the fault trace springs and Crystal Geyser. The carbon isotope abundance ratio data for the carbon in the travertine falls within the range representative of carbon derived from marine carbonate rocks. The stratigraphic geology of the tufa deposits indicates that CO_2-saturated and mineral-laden springs have been active along the Little Grand Wash Fault for several hundred thousand years (Baer and Rigby, 1978; Heath et al., 2002).

Crystal Geyser and the springs along the Little Grand Wash Fault discharge significant amounts of CO_2-rich (96+% purity) gas. Crystal Geyser flows out of an unplugged, abandoned oil and gas exploration well, which crosses the Little Grand Wash Fault and penetrates the Navajo Sandstone, which is the reservoir for the large CO_2 deposit at the Farnham Dome anticline. Crystal Geyser erupts at irregular 4- to 6-hr intervals. The eruptions average 7 minutes in duration and reach heights of 70 to 90 ft (21 to 27 m). In addition to the emission to the atmosphere of CO_2, each eruption discharges roughly 0.1 acre-ft (123 m^3) of mineral-laden water, some of which eventually flows into the nearby Green River. Annually, Crystal Geyser and the springs along the Little Grand Wash Fault discharge roughly 3000 short tons (2730 metric tons) of bicarbonate, carbonate, sulfate, and chloride salts into the Green River (Baer and Rigby, 1978).

CO_2 Leakage Process Models

The source of the CO_2-saturated and mineral-laden water that flows from Crystal Geyser and the springs along the Little Grand Wash Fault has not been identified. It was suggested that the source could be the Navajo Sandstone (Baer and Rigby, 1978). Figure 12 is a generalized stratigraphic cross section showing the elevations from sea level of the Navajo Sandstone at the Farnham Dome anticline and at the Little Grand Wash Fault. The elevation from sea level of the Navajo Sandstone is roughly 600 ft (183 m) lower at the Farnham Dome anticline than at the Little Grand Wash Fault (see Figure 12). Thus the Navajo Sandstone in the anticline

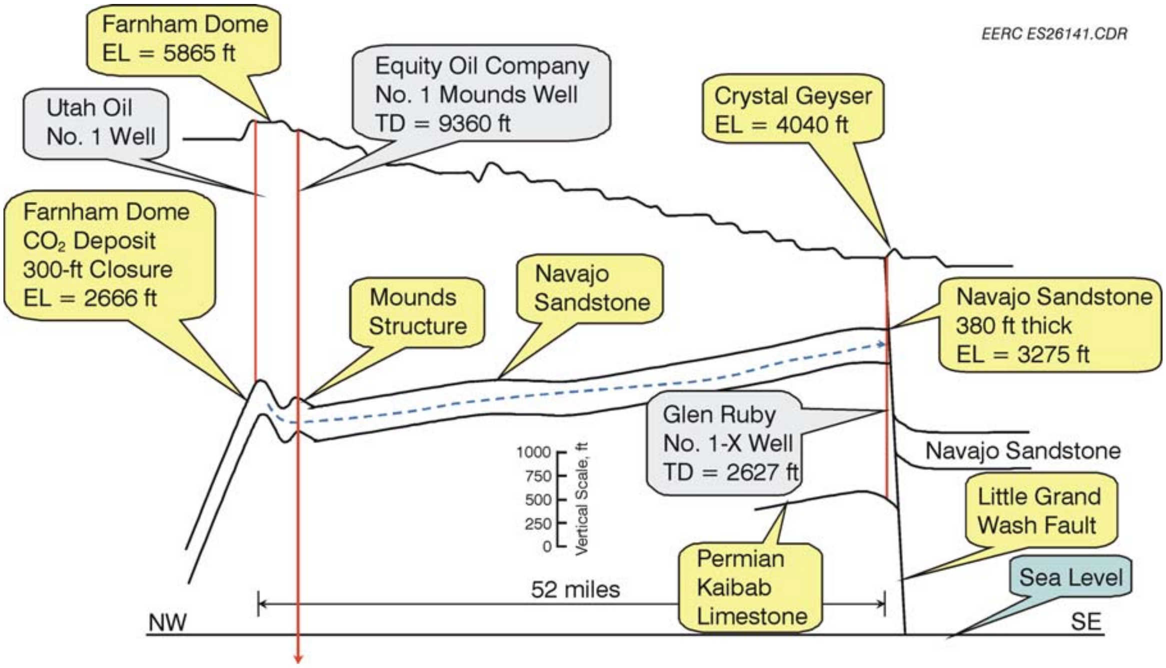

Figure 12. Generalized stratigraphic cross section showing the elevations of the Navajo Sandstone at the Farnham Dome anticline and at the Little Grand Wash Fault.

containing the CO_2 deposit is downgradient from the site where it is intersected by the Little Grand Wash Fault (Calvert, 1923; Mahoney and Kunkel, 1963; Baer and Rigby, 1978; Gloyn et al., 2003).

The depth of the Navajo Sandstone at the Farnham Dome anticline is roughly 3100 ft (944 m). At this depth, the CO_2 would be partitioned into an upper, buoyant supercritical CO_2 layer and a lower, dense CO_2-saturated brine layer (Miller, 1938). If the dense CO_2-saturated brine escaped from the anticline trap, its negative buoyancy would inhibit its upgradient migration through the Navajo Sandstone toward the Little Grand Wash Fault.

At Farnham Dome, the supercritical CO_2 gas–water contact is lower on the northwest side of the structure (Morgan et al., 2005). This indicates that the supercritical CO_2 gas cap in the anticline is being hydrodynamically displaced by water that is flowing toward the northwest (Hubbert, 1953). This is the opposite flow direction needed for the CO_2-saturated brine to reach the Little Grand Wash Fault.

If the supercritical CO_2 escapes from the structural closure of the anticline trap, its buoyancy should favor its lateral upgradient migration through the Navajo Sandstone toward the Little Grand Wash Fault (see dashed line in Figure 12). Lateral hydrologic continuity would be needed within the Navajo Sandstone for such long-distance migration. The 52-mi (84-km) distance from the Farnham Dome anticline to the Little Grand Wash Fault is not excessive for lateral migration of a buoyant gas. Geologic interpretations of the lateral migration of petroleum over distances of 60 to 90 mi (97 to 145 km) have been suggested for the Illinois, Williston, Denver, Big Horn, Powder River, and Alberta Basins. Both hydrodynamic and buoyant forces contribute to long-distance lateral migration (Hubbert, 1953; Gussow, 1954; Bethke et al., 1991).

The depth of the Navajo Sandstone at the Little Grand Wash Fault is 765 ft (233 m), which means that at some point during upgradient migration, the pressure conditions in the sandstone would no longer enable CO_2 to be a buoyant supercritical fluid. The CO_2 would then have to migrate either as a normal gas or in a dissolved state. The fault would be a structural barrier to further lateral migration of the CO_2 and provide a transmissive pathway enabling it to reach the surface.

A possible escape route for the buoyant supercritical CO_2 in the Farnham Dome anticline might be through corroded well casings of abandoned oil and gas exploration wells (see Figures 3 and 4). Three wells produced CO_2 that was utilized for manufacturing dry ice from the Navajo Sandstone at this anticline from 1931 through 1979. These wells are now abandoned. Other wells passed through the Navajo Sandstone in this anticline to test the oil and gas potential of deeper formations. Several wells were also drilled through the Mounds structure located 4 mi (6.5 km) southeast of Farnham Dome (see Figure 12). Oil and gas shows were encountered in the deeper wells at Farnham Dome and the Mounds structure sites. Attempts to complete the wells as commercial producers failed because of low-permeability problems. The wells were plugged and abandoned. Fracture pathways for lateral CO_2 migration away from the wells may exist since operators tried to stimulate oil and gas production by shooting the wells with nitroglycerine explosives (Walton, 1955; Mahoney and Kunkel, 1963; Gloyn et al., 2003).

Leakage of CO_2 from the Farnham Dome anticline is not a necessary or unique explanation for the CO_2-saturated water at Crystal Geyser and the springs along the Little Grand Wash Fault. Although a leakage pathway could exist, the geologic and geochemical data do not establish the Farnham Dome anticline CO_2 deposit as the source of the CO_2-saturated water at Crystal Geyser and the springs along the Little Grand Wash Fault. The Navajo Sandstone is known to be saturated with CO_2 at other sites such as the Gordon Creek anticline, which is roughly 25 mi (40 km) west of the Farnham Dome anticline (Walton, 1955). Since there is also a minor structure on the west side of the Little Grand Wash Fault (Campbell and Baer, 1978), the Navajo Sandstone in the structure near the fault could contain a CO_2 deposit which, in turn, could be the source for the CO_2-saturated water being discharged by Crystal Geyser and the springs along the fault trace.

Alternatively, the Little Grand Wash Fault extends downward 1.5 mi (2.4 km) into Pennsylvanian-age rocks. These deeper formations could be the source for CO_2 that migrates up the fault. CO_2-rich gas (50+%) has been encountered in numerous deep formations in Carbon and Emery Counties, Utah (Dobbin, 1935; Miller, 1938; Mahoney and Kunkel, 1963; Campbell and Baer, 1978; Shipton et al., 2001; Gloyn et al., 2003).

CO_2 LEAKAGE FROM A MATURE EOR FIELD IN WESTERN COLORADO

During the 1980s, CO_2 flooding EOR became an important commercial technique for tertiary oil recovery. CO_2 flooding EOR results in a dual benefit. The injected CO_2 dissolves in the oil, lowering its interfacial tension and viscosity, which enhance the oil's recoverability. CO_2 flooding EOR facilitates recovery of an additional 7% to 25% of the original-oil-in-place. The second benefit is that a fraction of the injected CO_2 becomes geologically sequestered in the reservoir (Jarrell et al., 2002; Shaw and Bachu, 2002).

A large-scale CO_2 flood EOR operation has been under way since 1986 at the Rangely oil field in western Colorado. Data from a recent geochemical study indicate that CO_2 sequestration and a small amount of CO_2 leakage to the surface are occurring at the Rangely EOR field. This EOR field extends over a 29.7-mi^2 (78-km^2) area. The reservoir is an anticline bounded on the west side by the Mellon Hill Fault. Oil production is from the Weber Sandstone at an average depth of 6500 ft (1980 m). The Moenkopi Formation shale is the cap rock for the reservoir. Primary oil recovery at Rangely began in the 1940s, secondary water flood oil recovery began in 1957–1958, and CO_2 flood EOR began in 1986 (Bowker and Shuler, 1991; Klusman, 2003a).

The CO_2 is injected in water-alternating-gas (WAG) cycles. Figure 13 is a schematic diagram depicting the WAG process. Currently, about 80% of the injected CO_2 returns to the surface along with oil, natural gas, and brine. The CO_2, natural gas, and brine are separated from the oil and reinjected into the reservoir. At the reservoir temperature and pressure conditions, the injected CO_2 is a dense, supercritical fluid. Hydrostatic pressure is roughly 3000 psi (20.7 MPa). The downhole pressure is 4500 psi (30.5 MPa) when water is being injected and 5000 psi (34.5 MPa) when the CH_4 and CO_2 are being injected. The CO_2 flooding process results in reservoir overpressuring, which increases the potential for CH_4 and CO_2 leakage through the cap rock (Bowker and Shuler, 1991; Klusman, 2003a, 2003b).

CO_2 Leakage Evaluation

An evaluation of whether CO_2 leakage to the surface occurs above the Rangely EOR field was made by analyzing CO_2 concentrations in shallow and deep soil horizons and CO_2 flux into the atmosphere. These analyses were made during 2000–2002 at locations over the field, the Mellon Hill Fault, and a nearby control area having similar geology, soils, and climate. The data yielded a lower limit estimate for CO_2 leakage to the surface above the Rangely EOR field of roughly 170 tons/year (154×10^3 kg/year) (Klusman, 2003a).

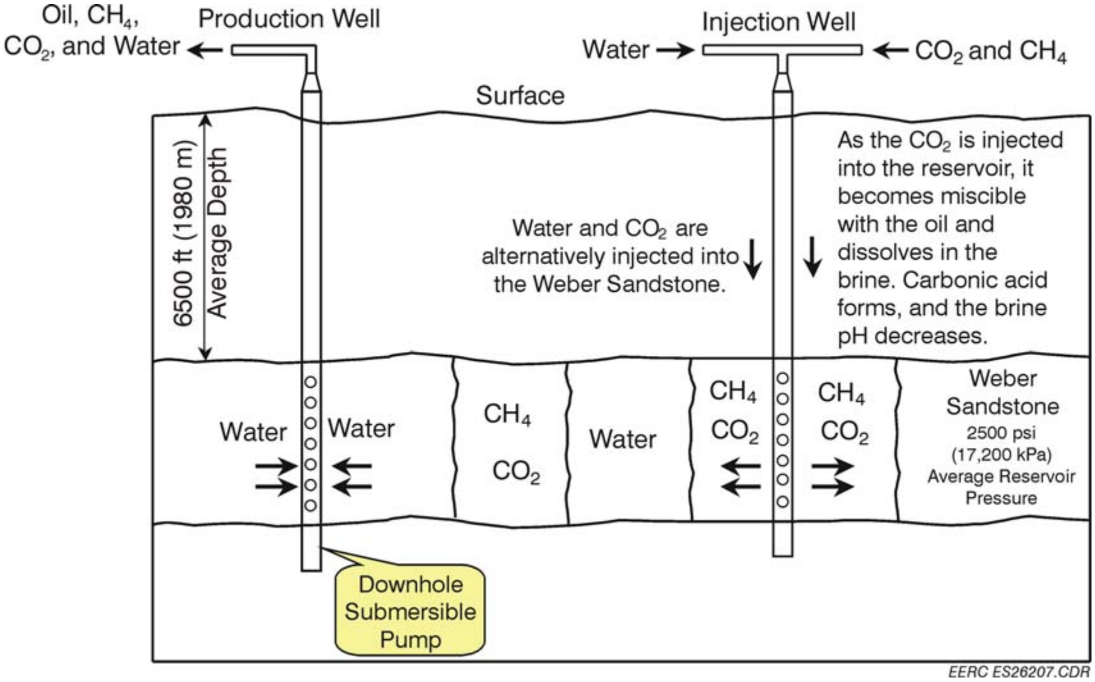

Figure 13. Schematic diagram of the WAG process at the Rangely EOR field (modified from Bowker and Shuler, 1991).

Currently, 160 million scf/day (9283 tons/day) of CO_2 is being injected at the Rangely EOR field (Klusman, 2003a). The soil gas flux data indicate that the annual amount of CO_2 leaking to the surface above this EOR field is roughly 0.005% of the annual injected CO_2 volume. If reliable, this CO_2 leakage rate estimate suggests that the sealing properties of the shale cap rock above the Weber Sandstone reservoir at this CO_2 flood EOR field meet the recently proposed leakage rate performance requirement of 0.01% per year for geologically sequestered CO_2 (White et al., 2003).

CH_4 Leakage Evaluation

The Weber Sandstone at the Rangely oil field originally contained a 900-ft (270-m) hydrocarbon column, which included a 150-ft (45-m) gas cap (Bowker and Shuler, 1991). The reservoir depth and the size of the gas cap indicate that initially the oil would have contained a large quantity of dissolved natural gas. An evaluation of whether CH_4 leakage to the surface occurs above the Rangely field was made by analyzing CH_4 and light hydrocarbon gas concentrations in shallow and deep soil horizons and direct transport of CH_4 into the atmosphere. These analyses were made during 2000–2002 at the same times and locations as the CO_2 leakage analyses. The data yield an estimate for CH_4 leakage to the surface above the Rangely EOR field of roughly 400 tons/year (363×10^3 kg/year) (Klusman, 2003a).

Gas Leakage Pathway

The evidence from the geochemical studies indicates that CO_2 and CH_4 leakage to overlying strata and the surface are occurring at the Rangely EOR field. Because the reservoir is very overpressured, the CO_2 and CH_4 leakage could be evidence of seal failure in the reservoir cap rock. However, this is not a unique or necessary explanation for the gas leakage. There also are numerous gas injection and production wells at the Rangely EOR field. These wellbores penetrate the reservoir cap rock, and the gas leakage pathway could be through the wellbore cement layer (see Figure 4).

CO_2 and CH_4 Migration Processes

Buoyancy forces would drive the upward migration of the CO_2 and CH_4. The estimated CH_4 leakage rate is more than twice as large as that of the CO_2. If these leakage rate estimates are accurate and if the source of the CH_4 and CO_2 is the Weber Sandstone EOR reservoir, then either the two gases are leaking through the cap rock at different rates or, alternatively, the migration processes of the two gases are different. The two gases could be migrating to the surface independently of one another or, alternatively, the CO_2 could be acting as a carrier gas for the CH_4. The leakage rate difference does not uniquely distinguish between these two processes.

The migration rate difference could be due, at least in part, to the relative solubility differences of the two gases. The Navajo Sandstone and Entrada Sandstone aquifers overlie the Rangely EOR field (Bowker and Shuler, 1991). CH_4 is relatively insoluble in water (Price, 1979) and, thus, it would preferentially partition into the gas phase when it encountered these aquifers. By contrast, CO_2 is soluble in water, and it would partition into a dissolved phase when it encountered these aquifers (Wiebe and Gaddy, 1939, 1940; Prutton and Savage, 1945). Thus all other factors being equal, CH_4 would migrate faster as a gas through the Navajo and Entrada aquifers than CO_2, which would be slowed by partitioning into a dissolved phase during migration through these aquifers. Alternatively, if CO_2 were acting as a carrier gas for CH_4, then the CH_4-to-CO_2 ratio could become enriched during migration through the sandstone aquifers because of the preferential aqueous-phase partitioning of the CO_2.

CO_2 Sequestration Assessment

An analysis of the variation of formation water chemistry from prior to the start of the water and CO_2 floods through 1999 was used to determine the fate of the CO_2 injected at the Rangely EOR field. These data indicate that most of the sequestered CO_2 is stored as dissolved CO_2, and only a small amount is stored as bicarbonate. Based on the estimated volume of water in the reservoir, the reservoir currently contains 16.2 million tons (14.7×10^9 kg) of dissolved CO_2. This estimated amount of sequestered CO_2 was described as being roughly equal to the total amount of CO_2 purchased for injection at the Rangely field through 1999 (Klusman, 2003a).

CO_2 that is sequestered by solution trapping is potentially susceptible to leakage. The Mellon Hill Fault is located about 1 mi (1.6 km) from the western edge of the Rangely oil field (Klusman, 2003a). Over a geologically long time interval, the dense, CO_2-saturated formation water could potentially migrate downgradient through the Weber Sandstone until it intersected the Mellon Hill Fault. The fault would be a structural barrier to further lateral migration of the CO_2-saturated brine but could provide a transmissive pathway for its leakage to the surface.

By contrast, CO_2 that is sequestered by mineral trapping would not be susceptible to leakage. It is noteworthy that although Rangely is a mature CO_2 flood EOR project, little if any of the injected CO_2 has been sequestered by mineral trapping (Klusman, 2003a). Sandstone aquifers rich in clay minerals and low in carbonates would be the most favorable geologic sinks for mineral trapping of CO_2 (White et al., 2003). The Weber Sandstone is partially cemented with carbonate minerals (average 10 vol%) but contains only an average of 5 vol% clay minerals, which are mostly illite and mixed-layer smectite/illite (Bowker and Shuler, 1991). From a compositional perspective, the carbonate-to-clay mineral ratio in the Weber Sandstone would not be a favorable chemical environment for mineral trapping of CO_2.

Water Chemistry Changes

The water flood and CO_2 flood EOR operations at the Rangely field altered the chemistry of the formation water in the Weber Sandstone. Before the start of the water flood in 1957, the total dissolved solids (TDS) content of the formation water in the Weber Sandstone was 100,000 ppm, but the TDS was only 33,000 ppm at the start of CO_2 flood in 1986. This TDS decrease occurred because water obtained from the Navajo Sandstone (20,000 ppm TDS) and Entrada Sandstone (5500 ppm TDS) aquifers was used in making up the injection water for the water flood (Bowker and Shuler, 1991). Ten years after the initiation of the CO_2 flood, the bicarbonate concentration of the produced water had increased 900% and the TDS had increased to 49,700 ppm (Klusman, 2003a).

Before the start of CO_2 injection in 1986, the pH of the formation water was roughly 7.5. At the typical downhole injection pressure of 5000 psi (34.5 MPa), the pH in the reservoir at the CO_2 injection wells is roughly 3.5, but increases to 4.5 near the production wells. This pH increase occurs because as the injected CO_2 moves through the reservoir, the carbonic acid formed by its reaction with the formation water is partially consumed through dissolution of carbonate cement in the Weber Sandstone. Because of the pH decrease, the calcium, magnesium, and iron content of the produced water also increased after the start of CO_2 injection. The pH decrease reduced the magnitude of carbonate scale problems in downhole sections of producing wells, but this benefit was offset by an increase in wellbore sulfate scale problems (Bowker and Shuler, 1991).

COALBED NATURAL GAS DEPOSITS

Subsurface coal seams are a geologic environment where naturally occurring, concentrated accumulations of natural gas are found. The natural gas components are primarily stored by physical adsorption. The composition of the gases found in coal seams is quite variable. The dominant hydrocarbon component is CH_4, and CO_2 is the other major component (Rice et al., 1993). Coalbed natural gas resources in the continental U.S. total roughly 750 Tcf (Nelson, 2001). If the average CO_2 content of these resources is 10%, then the coals would contain an estimated 75 Tcf of geologically sequestered CO_2.

The leakage to the atmosphere of CH_4 and CO_2 occurs naturally at coal outcrops and surface-penetrating faults that intersect subsurface coal seams. Coal mining also results in the release of CH_4 and CO_2 to the atmosphere. In 1995, CH_4 emissions to the atmosphere from all major coal-mining operations in the United States totaled an estimated 4.67 million tons (4.2×10^9 kg) (Rice et al., 1993; Clayton et al., 1993; Kirchgessner et al., 2000).

Black Warrior Basin, Alabama

Natural gas is commonly but not always present in subsurface coal deposits. In the Black Warrior Basin, Alabama, there are areas with very-low-gas-content coal surrounded by areas with very-high-gas-content coal. The geologic explanation for the low-gas-content anomalies is that the gas desorbed and leaked to the atmosphere through faults as a result of local decreases in the hydrostatic pressure of the coal seams (Malone et al., 1987).

Powder River Basin, Wyoming

In the Gillette, Wyoming, area of the Powder River Basin, surface coal mining activities reduced the hydrostatic pressure gradient across a broad area downgradient from the surface mines. This, in turn, resulted in the desorption of CH_4 from the coal, which then migrated upward through faults into surface soils. The presence of high concentrations of CH_4 in the surface soils became an environmental hazard to local home owners (Clayton et al., 1993).

Coalbed Natural Gas Production

During the early 1990s, the large-scale commercial recovery of coalbed natural gas became established in several areas of the United States (Nelson, 1999, 2000, 2001). U.S. coalbed natural gas production in 2002 totaled 1.65 Tcf (4.7×10^{10} m^3) and accounted for roughly 9% of the total U.S. natural gas production (Wood et al., 2004). Coalbed natural gas production operations often result in the release of significant amounts of CO_2 into the atmosphere (Nelson, 1999).

Many coalbed reservoirs such as those in the Black Warrior and Appalachian Basins contain high-purity (98+%) CH_4. By contrast, coalbed reservoirs in the San Juan, Piceance, Uinta, and Powder River Basins have CO_2 contents of from 5% to 40% (Rice et al., 1993; Nelson, 1999).

Primary recovery of coalbed natural gas is accomplished by reducing the hydrostatic pressure in the formation. Depressuring the formation promotes gas desorption. Table 3 compares heat of adsorption values for CH_4 and CO_2 on bituminous coal and carbon black (Glass and Larsen, 1993, 1994). The magnitude of the heat of adsorption value reflects the strength of the attractive force between the gas and adsorbent. On both types of adsorbents, CO_2 has a higher heat of adsorption value, which means that the physical attraction is stronger and, therefore, more stable.

Because CO_2 is more strongly adsorbed than CH_4, the latter preferentially desorbs when the pressure in coalbed reservoirs is reduced, and initially, the produced gas stream consists of high-purity CH_4. Eventually, however, as the reservoir pressure is progressively decreased, the

Table 3. Heat of Adsorption Values for CH_4 and CO_2 on Bituminous Coal and Carbon Black

Adsorbent	CH_4	CO_2
Bituminous Coal	3.1 kcal/mol	6.6 kcal/mol
Carbon Black	3.0 kcal/mol	4.3 kcal/mol

CO_2 content of the produced gas stream begins to increase. Figure 14 shows how the CO_2 content of the raw gas stream from a coalbed reservoir in the San Juan Basin varies as a function of reservoir pressure drawdown (Nelson, 1999).

Coalbed natural gas resources containing CO_2 have considerable economic value. Through 2003, the cumulative coalbed natural gas production from the San Juan Basin totaled 10.2 Tcf (2.9×10^{11} m^3), which was 71% of total cumulative U.S. coalbed natural gas production (Wood et al., 2004). In 1999, over 0.16 Bcf (4.5×10^6 m^3) per day of CO_2 was being separated from produced coalbed natural gas in the San Juan Basin and vented to the atmosphere (Nelson, 1999). Clearly, the adsorbed-phase CO_2 in coalbed reservoirs is not permanently immobile.

Geologic CO_2 Sequestration

A pilot study conducted by industry in the San Juan Basin indicates that geologic CO_2 sequestration can be achieved by injecting CO_2 into a coalbed gas reservoir (Nelson, 2000; White et al., 2003). Only, deep unminable coal would be suitable for geologic CO_2 sequestration since subsequent mining of the coal would result in release of the CO_2 back into the atmosphere. Because the gas adsorption process is reversible, the hydrostatic pressure in the coalbed reservoir used for geologic CO_2 sequestration must be maintained at or above the CO_2 desorption pressure in order for the adsorbed-phase CO_2 to remain immobile (Pashin and McIntyre, 2003). Clearly, geologic settings with relatively static hydrology, i.e., low-formation water flow velocity, would be preferable.

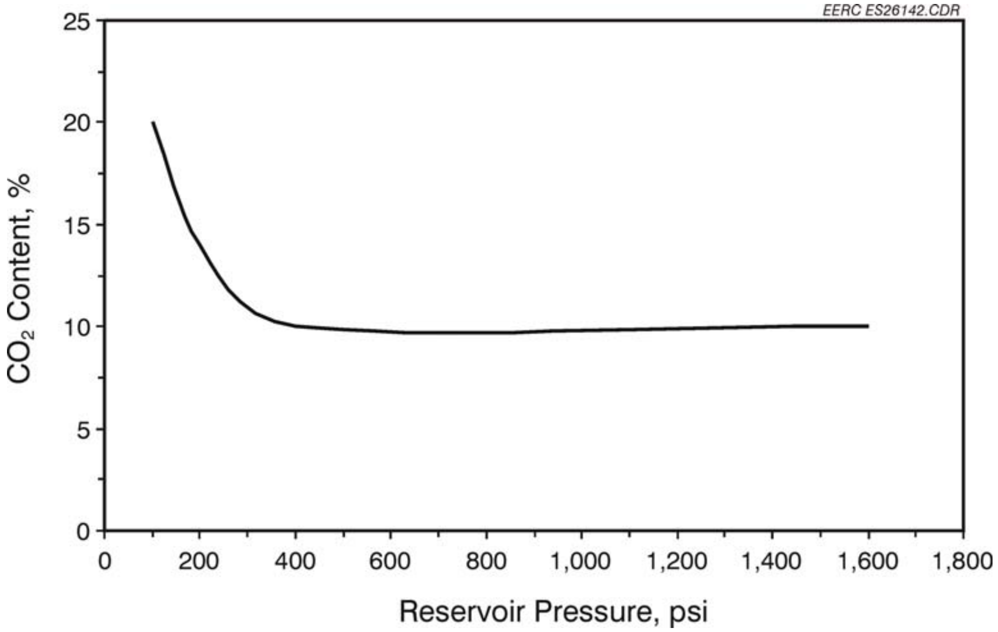

Figure 14. CO_2 content variation of raw produced gas stream as a function of coalbed reservoir pressure decrease.

SUMMARY

The success of geologic CO_2 sequestration as a large-scale carbon management strategy is critically dependent on the ability of the geologic sinks and trapping mechanisms to confine the injected CO_2 for hundreds to thousands of years. Leakage of CO_2 from geologic sinks could result in significant release of the CO_2 back to the atmosphere, potentially reducing, if not negating altogether, the benefits of geologic CO_2 sequestration.

Injected CO_2 can be trapped in geologic sinks by four types of mechanisms. Different types of geologic sinks in combination with their site-specific properties would trap CO_2 by different mechanisms. More than one type of trapping mechanism would typically be present in a single geologic sink. Most trapping mechanisms do not permanently immobilize CO_2. Thus leakage of CO_2 to the surface can potentially occur from all types of geologic sinks.

In the right types of geologic settings, a large, concentrated amount of CO_2 could be stored for a geologically long time period without the risk of significant CO_2 leakage to the surface. The dominant, but by no means sole, barrier to CO_2 leakage to the surface from geologic sinks is not the trapping mechanism(s) but rather the permeability characteristics of the rock layers overlying or adjacent to the geologic sink. The hydrologic properties of the formations containing the geologic sinks would also affect the potential for CO_2 leakage. Geologic settings with relatively static hydrology, i.e., low-formation water velocity, would be preferable.

REFERENCES

American Gas Association, 1999, Survey of underground storage of natural gas in the United States and Canada: AGA Catalog No. SU9901C, 1998.

Allis, R., Chidsey, T., Gwynn, W., Morgan, C., White, S., Adams, M., and Moore, J., 2001, Natural CO_2 reservoirs on the Colorado Plateau and Southern Rocky Mountains—candidates for CO_2 sequestration, First National Conference on Carbon Sequestration, Washington, D.C., May 14–17, 2001, Proceedings: p. 19.

Araktingi, R.E., Benefield, M.E., Bessenyei, Z., Coats, K.H., and Tek, M.R., 1984, Leroy storage facility, Uinta County, Wyoming—a case history of attempted gas migration control: Journal of Petroleum Technology, v. 36, no. 1, p. 132–140.

Bachu, S., and Stewart, S., 2002, Geological sequestration of anthropogenic carbon dioxide in the Western Canadian Sedimentary Basin—suitability analysis, Journal of Canadian Petroleum Technology, v. 41, no. 2, p. 32–40.

Baer, J.L., and Rigby, J.K., 1978, Geology of the Crystal Geyser and environmental implications of its effluent, Grand County, Utah: Utah Geology, v. 5, no. 2, p. 125–130.

Benson, S.M., Hepple, R., Apps, J., Tsang, C.F., and Lippmann, M., 2002, Lessons learned from natural and industrial analogues for storage of carbon dioxide in deep geological formations: Report No. LBNL-51170, Berkeley, California, Lawrence Berkeley National Laboratory, p. 135.

Berg, R.R., 1975, Capillary pressures in stratigraphic traps: AAPG Bulletin, v. 59, no. 6, p. 939–956.

Bethke, C.M., Reed, J.D., and Oltz, D.F., 1991, Long-range petroleum migration in the Illinois Basin: AAPG Bulletin, v. 75, no. 5, p. 925–945.

Bowker, K.A., and Shuler, P.J., 1991, Carbon dioxide injection and resultant alteration of the Weber Sandstone, Rangely Field, Colorado: AAPG Bulletin, v. 75, no. 9, p. 1489–1499.

Bradley, J.S., 1975, Abnormal formation pressure: AAPG Bulletin, v. 59, no. 6, p. 957–973.

Brown, A., 2000, Evaluation of possible gas microseepage mechanisms: AAPG Bulletin, v. 84, no. 11, p. 1775–1789.

Bruant, R.G., Jr., Guswa, A.J., Celia, M.A., and Peters, C.A., 2002, Safe storage of CO_2 in deep saline aquifers: Environmental Science and Technology, v. 36, no. 11, p. 240A–245A.

Calvert, W.R., 1923, Gas at Farnham, Utah: AAPG Bulletin, v. 7, p. 293–295.

Campbell, J.A., and Baer, J.L., 1978, Little Grand Wash Fault-Crystal Geyser area, *in* Fassett, J.E., (ed.), Oil and gas fields of the four corners area, Four Corners Geological Society: p. 666–669.

Carpen, T.R., 1957, North McCallum field, Jackson County, Colorado, *in* Finch, W.C., (ed.), Ninth annual field conference guidebook to the geology of North and Middle Park Basin, Colorado, Denver, Colorado, Rocky Mountain Association of Geologists: p. 109–112.

Celia, M.A., Bachu, S., Nordbotten, J.M. Gasda, S.E. and Dahle, H.K., 2004, Quantitative estimation of CO_2 leakage from geological storage—analytical models numerical models, and data needs: Princeton Environmental Institute, The Princeton papers at Vancouver GHGT-7, Paper ID #228 www.princeton.edu/%7Ecmi/research/Vancouver04/pprlist.shtml (accessed May 2004).

Celia, M.A., Peters, C.A., and Bachu, S., 2002a, Geologic storage of CO_2—leakage pathways and environmental risks: Princeton University and Alberta Geological Survey, www.princeton.edu/%7Ecmi/research/Storage/storageprt.shtml (accessed May 2004).

Celia, M.A., Peters, C.A., and Bachu, S., 2002b, Geologic storage of CO_2—leakage pathways and environmental risks, American Geophysical Union 2002 Spring Meeting, Washington, D.C., Eos. Trans. AGU, 83(19), Spring Meet. Suppl., Abstract GC32A-03, www.princeton.edu/%7Ecmi/research/Storage/storageppr.shtml (accessed May 2004).

Clarke, R.H., and Cleverly, R.W., 1991, Petroleum seepage and post-accumulation migration, *in* England, W.A., and Fleet, A.J., (eds.), Petroleum migration, London, The Geological Society: p. 265–271.

Clayton, J.L., Leventhal, J.S., Rice, D.D., Pashin, J.C., Mosher, B., and Czepiel, P., 1993, Atmospheric methane flux from coals—preliminary investigation of coal mines and geologic structures in the Black Warrior Basin, Alabama, *in* Howell, D.G., (ed.), The future of energy gases, U.S. Geological Survey Professional Paper 1570, Washington, D.C., U.S. Government Printing Office, p. 471–492.

Dai, J., Song, Y., Dai, C., and Wang, D., 1996, Geochemistry and accumulation of carbon dioxide gases in China: AAPG Bulletin, v. 80, no. 10, p. 1615–1626.

Deming, D., 1994, Factors necessary to define a pressure seal, AAPG Bulletin, v. 78, no. 6, p. 1005–1009.

Dickey, P.A., 1966, Patterns of chemical composition in deep subsurface waters:

AAPG Bulletin, v. 50, no. 11, p. 2472–2478.

Dickey, P.A., 1969, Increasing concentration of subsurface brines with depth: Chemical Geology, v. 4, p. 361–370.

Dobbin, C.E., 1935, Geology of natural gases rich in helium, nitrogen, carbon dioxide, and hydrogen sulfide, *in* Ley, H.A., (ed.), Geology of natural gas, Tulsa, Oklahoma, The American Association of Petroleum Geologists, p. 1053–1072.

Downey, M.W., 1984, Evaluating seals for hydrocarbon accumulations: AAPG Bulletin, v. 68, no. 11, p. 1752–1763.

Duguid, A.M., Radonjic, R., Bruant, T., Mandecki, G., Scherer, M., and Celia, M.A., 2004, The effect of CO_2 sequestration on oil well cements, Princeton Environmental Institute, The Princeton papers at Vancouver GHGT-7, www.princeton.edu/%7Ecmi/research/Vancouver04/pprlist.shtml (accessed May 2004).

Dusseault, M.B., Bachu, S., and Rothenburg, L., 2004, Sequestration of CO_2 in salt caverns; Journal of the Canadian Petroleum Technology, v. 43, no. 11, p. 49–55.

Farmer, R.E., 1965, Genesis of subsurface carbon dioxide, *in* Young, A., and Galley, J.E., (eds.), Fluids in subsurface environments, The American Association of Petroleum Geologists, Tulsa, Oklahoma, p. 378–385.

Foster, R.W., and Jensen, J.G., 1972, Carbon dioxide in northeastern New Mexico, *in* Kelley, V.C. and Trauger, F.D., (eds.), Twenty-third field conference guidebook of east-central New Mexico, September 28–30, 1972: New Mexico Geological Society: p. 192–200.

Garcia, J.E., 2001, Density of aqueous solutions of CO_2: Earth Sciences Division, Lawrence Berkeley National Laboratory, October 1, 2001.

Gerling, C.R., 1983, McElmo Dome Leadville carbon dioxide field, Colorado, *in* Fassett, J.E., (ed.), Oil and gas fields of the four corners area, Four Corners Geological Society: p. 735–739.

Germann, F.E.E., 1938, The occurrence of carbon dioxide with notes on the origin and relative importance of subterranean carbon dioxide: Science, v. 87, no. 2267, p. 513–521.

Germann, F.E.E., and Ayers, H.W., 1942, The origin of underground carbon dioxide: Journal of Physical Chemistry, v. 46, p. 61–68.

Glass, A.S., and Larsen, J.W., 1993, Surface thermodynamics for nonpolar adsorbates on Illinois No. 6 coal by inverse gas chromatography: Energy & Fuels, v. 7, p. 994–1000.

Glass, A.S., and Larsen, J.W., 1994, Coal surface properties—specific and nonspecific interactions for polar molecules and surface tensions for hydrocarbons at the surface of Illinois No. 6 coal: Energy & Fuels, v. 8, p. 629–634.

Gloyn, R.W., Tabet, D.E., Tripp, B.T., Bishop, C.E., Morgan, C.D., Gwynn, J.W., and Blackett, R.E., 2003, Energy, mineral, and ground-water resources of Carbon and Emery Counties, Utah; Bulletin 132, Utah Geological Survey, p. 26–27.

Grunau, H.R., 1987, A worldwide look at the cap-rock problem: Journal of

Petroleum Geology, v. 10, no. 3, p. 245–266.

Gussow, W.C., 1954, Differential entrapment of oil and gas: a fundamental principle: AAPG Bulletin, v. 38, no. 5, p. 816–853.

Hansen, H., Eiken, O., and Aasum, T.O., 2005, Tracing the path of carbon dioxide from a gas/condensate reservoir, through an amine plant and back into a subsurface aquifer-case study: the Sleipner area, Norwegian North Sea, Paper SPE 96742, *in* Offshore Europe 2005, Aberdeen, Scotland, UK, September 6–9, 2005, Proceedings.

Heath, J.E., Williams, A.P., Evans, J.P., and Shipton, Z., 2002, Structural and geochemical analysis of the Little Grand and Salt Wash faults to investigate the leakage of CO_2 from a natural reservoir: AAPG Bulletin, v. 86, no. 13 (supplement), Abstract, AAPG Annual Meeting, Houston, Texas, March 10–13, 2003.

Heath, J.A., Evans, J.P., and Lachmar, T.F., 2003, Hydrogeochemical characterization of leaking CO_2-charged, low net-to-gross fault zones—the Little Grand and Salt Wash fault zones, Emery and Grand Counties, Utah: AAPG Bulletin, v. 87, no. 13 (supplement), AAPG International Conference, Barcelona, Spain, September 21–24, 2003.

Hubbert, M.K., 1953, Entrapment of petroleum under hydrodynamic conditions: AAPG Bulletin, v. 37, no. 8, p. 1954–2026.

Hughes, A., 2004, Using the Indian Creek natural gas field as a potential analog for CO_2 storage: AAPG Bulletin, v. 88, no. 13 (supplement).

Hunt, J.M., 1979, Petroleum geochemistry and geology: W.H. Freedman and Company, New York, p. 617.

Hunt, J.M., 1990, Generation and migration of petroleum from abnormally pressured fluid compartments: AAPG Bulletin, v. 74, no. 1, p. 1–12.

Hunt, J.M., 1996, Petroleum geochemistry and geology: W.H. Freedman and Company, New York, p. 743.

Irwin, W.P., and Barnes, I., 1982, Carbon dioxide rich springs and gas wells in the conterminous United States, Miscellaneous Investigations Series I-1301, U.S. Geological Survey, p. 1–9.

Jarrell, P.M., Fox. C.E., Stein, M.H., and Well, S.L., 2002, Practical aspects of CO_2 flooding: SPE Monograph, v. 22, Richardson, Texas, Society of Petroleum Engineers, p. 220.

Jenden, P.D., Newell, K.D., Kaplan, I.R., and Watney, W.L., 1988, Composition and stable-isotope geochemistry of natural gases from Kansas, mid-continent, U.S.A.: Chemical Geology, v. 71, p. 117–147.

Jenden, P.D., and Kaplan, I.R., 1989, Analysis of gases in the earth's crust: Report GRI-88/0262, Gas Research Institute, Chicago, Illinois. National Technical Information Service, Accession Number PB91-104273/XAB.

Jenden, P.D., Hilton, D.R., Kaplan, I.R., and Craig, H., 1993, Abiogenic hydrocarbons and mantle helium in oil and gas fields, *in* The future of energy gases: Howell, D.G., ed., U.S. Geological Survey Professional Paper 1570, Washington, D.C., U.S. Government Printing Office, p. 31–56.

Johnson, R.E., 1983, Bravo dome carbon dioxide area, Northeast New Mexico, *in*

Fassett, J.E., (ed.), Oil and gas fields of the four corners area, Four Corners Geological Society, p. 745–748.

Katz, D.L., and Tek, M.R., 1981, Overview on underground storage of natural gas: Journal of Petroleum Technology, June 1981, p. 943–951.

Kirchgessner, D.A., Piccot, S.D., and Masemore, S.S., 2000, An improved inventory of methane emissions from coal mining in the United States: Journal of the Air & Waste Management Association, v. 50, p. 1904–1919.

Klusman, R.W., 1993, Soil gas and related methods for natural resource exploration, New York, John Wiley & Sons, p. 483.

Klusman, R.W., 2003a, A geochemical perspective and assessment of leakage potential for a mature carbon dioxide-enhanced oil recovery project and as a prototype for carbon dioxide sequestration—Rangely field, Colorado: AAPG Bulletin, v. 87, no. 9, p. 1485–1507.

Klusman, R.W., 2003b, Possible vertical migration of CO_2 associated with large-scale injection into subsurface geologic formations: Final report for DOE Grant DE-FG03-00ER15090 to Colorado School of Mines, June 2003, p. 152.

Lang, W.B., 1959, The origin of some natural carbon dioxide gases: Journal of Geophysical Research, v. 64, no. 1, p. 127–131.

Lide, D.R., Ed., 2004, Handbook of chemistry and physics, 85th Ed., 2002–2005, CRC Press.

Link, W.K., 1952, Significance of oil and gas seeps in world oil exploration: AAPG bulletin, v. 36, no. 8, p. 1505–1540.

Mahoney, S.R., and Kunkel, R.P., 1963, Geology and oil and gas possibilities of east-central Utah, *in* Crawford, A.L., (ed.), Oil and gas possibilities of Utah, reevaluated, Bulletin 54, Utah Geological and Mineralogical Survey, p. 353–380.

Malone, P.G., Briscoe, F.H., Camp, B.S., and Boyer, C.M., 1987, Discovery and explanation of low gas contents encountered in coalbeds at the GRI/USSC Big Indiana Creek site, Warrior Basin, Alabama, Paper 8715, *in* 1987 International Coalbed Methane Symposium, Tuscaloosa, Alabama, The University of Alabama, May 16–19, 1987, Proceeding: p. 63–72.

Miller, J.C., 1938, Carbon dioxide accumulations in geologic structures, Transactions of the American Institute of Mining and Metallurgical Engineers, v. 129, p. 439–468.

Morgan, C.D., McClure, K., Chidsey, T.C., Jr., and Allis, R., 2005, Structure and reservoir characterization of Farnham Dome field, Carbon County, Utah, Technical Program Abstracts, Rocky Mountain Section – AAPG Annual Meeting, Jackson, Wyoming, September 24–26, 2005.

Muggeridge, A., Abacioglu, Y., England, W., and Smalley, C., 2005, The rate of pressure dissipation from abnormally pressured compartments: AAPG Bulletin, v. 89, no. 1, p. 61–80.

Nelson, C.R., 1999, Gem in the rough-technology, economics putting new shine on coalbed methane: The American Oil & Gas Reporter, v. 42, no. 3, p. 85–92.

Nelson, C.R., 2000, Coalbed methane resource potential of the U.S. Rocky Mountain Region; GasTIPS, v. 6, no. 3. Chicago, Illinois, Gas Research Institute, p. 4–11.

Nelson, C.R., 2001, North American coalbed methane resource map, GTI-01/0165, Gas Technology Institute, Des Plains, Illinois.

Oldenburg, C.M., Unger, A.J.A., Hepple, R.P., and Jordan, P.D., 2002, On leakage and seepage from geological carbon sequestration sites: Lawrence Berkeley National Laboratory, Berkeley, California, U.S. Department of Energy Contract Number AC03-76SF00098, www.osti. gov/bridge/product. biblio.jsp?osti_id=806116 (accessed May 2004).

Osborne, M.J., and Swarbrick, R.E., 1997, Mechanisms for generating overpressure in sedimentary basins—a reevaluation: AAPG Bulletin, v. 81, no. 6, p. 1023–1041.

Pacala, S.W., 2002, Global constraints on reservoir leakage carbon mitigation initiative: Princeton, New Jersey, www.princeton.edu/~cmi/research/kyoto02/pacala%20kyoto%2002.pdf (accessed May 2004).

Pacala, S. and Socolow, R., 2004, Stabilization wedges—solving the climate problem for the next 50 years with current technologies: Science, v. 305, p. 968–972.

Pashin, J.C., and McIntyre, M.R., 2003, Defining the supercritical phase window for CO_2 in coalbed methane reservoirs of the Black Warrior Basin—implications for CO_2 sequestration and enhanced coalbed methane recovery, Paper 0316, Proceedings 2003 International Coalbed Methane Symposium, Tuscaloosa, Alabama, the University of Alabama, May 5–9, 2003, p. 12.

Perry, John H., ed., 1950, Chemical engineer's handbook, Third Edition. New York, New York, McGraw-Hill, 1950.

Picard, M.D., and Holland, H.D., 1962, Occurrence and origin of Mississippian gas in four corners region: AAPG Bulletin, v. 46, no. 9, p. 1681–1700.

Price, L.C., 1979, Aqueous solubility of methane at elevated pressures and temperatures: AAPG Bulletin, v. 63, no. 9, p. 1527–1533.

Pruess, K., and Garcia, J., 2002, Multiphase flow dynamics during CO_2 Injection into saline aquifers: Environmental Geology, v. 42, p. 282–295.

Prutton, C.F., and Savage, R.L., 1945, The solubilities of carbon dioxide in calcium chloride-water solutions at 75°, 100°, 120° and high pressure: Journal of American Chemical Society, v. 67, p. 1550–1554.

Rice, D.D., Law, B.E., and Clayton, J.L., 1993, Coalbed gas—an undeveloped resource, *in* The future of energy gases, in Howell, D.G., (ed.), U.S. Geological Survey Professional Paper 1570, Washington, D.C, U.S. Government Printing Office, p. 389–404.

Roth, G., 1983, Sheep Mountain and Dike Mountain fields, Huerfano County, Colorado—a source of CO_2 for enhanced oil recovery, *in* Fassett, J.E., (ed.), Oil and gas fields of the four corners area, Four Corners Geological Society: p. 740–744.

Sales, J.K., 1997, Seal strength vs. trap closure–a fundamental control on the distribution of oil and gas, *in* Surdam, R.C., (ed.), Seals, traps, and petroleum systems: Tulsa, Oklahoma, American Association of Petroleum Geologists, p. 57–83.

Saunders, D.F., Burson, K.R., and Thompson, C.K., 1999, Model for hydrocarbon microseepage and related near-surface alterations: AAPG Bulletin, v. 83, no. 1, p. 170–185.

Schowalter, T.T., 1979, Mechanics of secondary hydrocarbon migration and entrapment: AAPB Bulletin, v. 63, no. 5, p. 723–760.

Seidle, J.P., 2000, Reservoir engineering aspects of CO_2 sequestration in coals, Paper SPE 59788, 2000 SPE/CERI Gas Technology Symposium, Calgary, Alberta, Canada, May 3–5, 2000, Proceedings: p. 657–666.

Service, R.F., 2004, The carbon conundrum: Science, v. 305, p. 962–963.

Shaw, J., and Bachu, S., 2002, Screening, evaluation, and ranking of oil reservoirs suitable for CO_2-flood EOR and carbon dioxide sequestration: Journal of Canadian Petroleum Technology, v. 41, no. 9, p. 51–61.

Shipton, Z.K., Evans, J.P., and Kolesar, P.T., 2001, Analysis of CO_2-charged fluid migration along faults in naturally occurring gas systems: AAPG Bulletin, v. 85, no. 13 (supplement), Abstract, AAPG Annual Meeting, Denver, Colorado, June 3–6, 2001.

Stevens, S.H., Pearce, J.M., and Rigg, A.A.J., 2001, Natural analogs for geologic storage of CO_2—an integrated global research program, First National Conference on Carbon Sequestration, Washington, D.C., May 14–17, 2001, Proceedings: p. 12.

Tadesco, S.A., 1995, Surface geochemistry in petroleum exploration, New York, Chapman & Hall: p. 256.

Tsang, C.F., Benson, S.M., Kobelski, B., and Smith, R., 2001, Scientific considerations related to development for CO_2 sequestration in brine aquifers: www.esd.lbl.gov/GEOSEQ/pdf/tsang_netl.pdf (accessed May 2004).

Vargaftik, N.B., Vinogradov, Y.K., and Yargin, V.S., 1996, Handbook of physical properties of liquids and gases, Third Ed., New York, Begell House, p. 1359.

Vendrig, M., Spouge, J., Bird, A., Daycock, J., and Johnsen, O., 2003, Risk analysis of the geological sequestration of carbon dioxide: No. R DTI/pub., prepared for Department of Trade and Industry's Cleaner Coal Technology Transfer Programme.

Walton, P.T., 1955, Wasatch plateau gas fields, Utah: AAPG Bulletin, v. 39, no. 4, p. 385–421.

Watts, N.L., 1987, Theoretical aspects of cap-rock and fault seals for single- and two-phase hydrocarbon columns: Marine and Petroleum Geology, v. 4, no. 11, p. 274–307.

Weber, K.J., 1997, A historical overview of the efforts to predict and quantify hydrocarbon trapping features in the exploration phase and in field development planning, *in* Moller-Pedersen, P., and Koestler, A.G., (eds.), Hydrocarbon seals importance for exploration and production: Norwegian Petroleum Society (NPF), Special Publication No. 7, Elsevier Science (Singapore) Pte Ltd., p. 1–13.

White, C.M., Straziser, B.R., Granite, E.J., Hoffman, J.S., and Pennline, H.W., 2003, Separation and capture of CO_2

from large stationary sources and sequestration in geological formations—coalbeds and deep saline aquifers: Journal of the Air & Waste Management Association, v. 53, p. 645–715.

Wichert, E., and Royan, T., 1997, Acid gas injection eliminates sulfur recovery expense: Oil & Gas Journal, v. 95, p. 67–72.

Wiebe, R., and Gaddy, V.L., 1939, The solubilities in water of carbon dioxide at 50°, 75° and 100°, at pressures to 700 atmospheres: Journal of American Chemical Society, v. 61, p. 315–318.

Wiebe, R., and Gaddy, V.L., 1940, The solubilities of carbon dioxide in water at various temperatures from 12° to 40° and at pressures to 500 atmospheres—critical phenomena: Journal of American Chemical Society, v. 62, p. 815–817.

Wilhelm, O., 1945, Classification of petroleum reservoirs: AAPG Bulletin, v. 29, no. 11, p. 1537-1580.

Wood, J.H., Grape, S.G., Green, R.S., and Zeinalpour, R.M., 2004, U.S. crude oil, natural gas, and natural gas liquids reserves: 2003 Annual Report, Energy Information Administration, Office of Oil and Gas, Washington, D.C., DOE/EIA-0216 (2003), November 2004, p. 47.

Zartman, R.E., Wasserburg, G.J., and Reynolds, J.H., 1961, Helium, argon, and carbon in some natural gases: Journal of Geophysical Research, v. 66, no. 1, p. 277–306.

For more information on this topic, contact:

Charles R. Nelson, EERC Senior Research Advisor
(701) 777-5000; charles.nelson2@att.net

James M. Evans, EERC Senior Research Advisor
(847) 577-5778; jamesmerrillevans@sbcglobal.net

Edward N. Steadman, EERC Senior Research Advisor
(701) 777-5279; esteadman@undeerc.org

John A. Harju, EERC Associate Director for Research
(701) 777-5157; jharju@undeerc.org

Visit the PCOR Partnership Web site at www.undeerc.org/PCOR.

Sponsored in Part by the
U.S. Department of Energy