LBNL-56623

GEO-SEQ Best Practices Manual

Geologic Carbon Dioxide Sequestration:

Site Evaluation to Implementation

GEO-SEQ Project Team

Lawrence Berkeley National Laboratory, Lawrence Livermore National Laboratory, Oak Ridge National Laboratory, Stanford University, University of Texas Bureau of Economic Geology, Alberta Research Council

September 30, 2004

Earth Sciences Division
Ernest Orlando Lawrence Berkeley National Laboratory
Berkeley, CA 94720

This work was supported by the Assistant Secretary for Fossil Energy, Office of Coal and Power Systems, of the U.S. Department of Energy (DOE) under Contract No. DE-AC03-76SF00098.

DISCLAIMER

TABLE OF CONTENTS

This page left intentionally blank.

LIST OF TABLES

LIST OF FIGURES

This page left intentionally blank.

EXECUTIVE SUMMARY

The first phase of the GEO-SEQ project supported research in the areas of enhanced hydrocarbon recovery, capacity assessment, code intercomparison, and monitoring to reduce the cost and risk of geologic CO_2 sequestration. Project results were widely published in peer-reviewed journals and in numerous conference proceedings, as well as in a summary report entitled, "The GEO-SEQ Project Results" (Benson et al., 2004a). Although widely disseminated to the scientific community through peer-reviewed articles, the results of the GEO-SEQ project have not been presented in the context of a how-to manual aimed at project managers interested in developing geologic CO_2 sequestration projects. This Best Practices Manual is our attempt to fill this need. The scope of the manual directly reflects the scope of the first phase of the GEO-SEQ project–namely, activities up to, but not including, CO_2 injection, a phase we refer to as the design phase. The design phase encompasses activities such as selecting sites for which enhanced recovery may be possible, evaluating CO_2 capacity and sequestration feasibility, and designing and evaluating monitoring approaches. It is also recognized that the definition of best practices will continue to evolve as experience in geologic sequestration is gained. Of particular value will be the results of field pilot studies, such as the Frio Brine Formation Injection Experiment, which is the current focus of GEO-SEQ project efforts.

A straightforward way to reduce the cost of geologic CO_2 sequestration is to enhance resource recovery through the injection of CO_2. This has been achieved by CO_2 injection into oil reservoirs for over 25 years for the purposes of enhanced oil recovery (EOR). The complementary objective of sequestering CO_2 as cheaply as possible presents the co-optimization problem of getting as much oil out of the ground while leaving as much CO_2 behind. Our work showed that characterization of the reservoir is critical for co-optimizing CO_2-EOR. We recommend that simulations be done using streamline models to study the effect of heterogeneity for trapping CO_2. Based on our simulation studies, we recommend active well control and the use of solvents to co-optimize oil production and CO_2 sequestration.

A process in some ways analogous to CO_2 EOR can be performed in gas reservoirs and is called Carbon Sequestration with Enhanced Gas Recovery (CSEGR). Although CSEGR is a novel concept that has never been tried in the field, our simulations and economic analyses suggest that it can be technically and economically feasible. Favorable conditions for CSEGR exist if the reservoir has a significant thickness, if there is significant gas remaining in the reservoir, and if the reservoir is still under production rather than abandoned. Upon the end of CH_4 production, the reservoir can potentially be used as a gas storage reservoir, with CO_2 as the cushion gas. We recommend that consideration be given to CSEGR when considering gas reservoirs as a target for CO_2 sequestration.

Although hydrocarbon reservoirs are attractive sequestration targets, brine-filled formations are much more widespread and offer the greatest potential capacity. Selection and design of potential CO_2 sequestration sites within a region of brine-filled formations involve estimating capacity. We found that capacity is a function of five factors: (1) intrinsic capacity, controlled by multiphase flow and transport; (2) gravity, controlled by buoyancy forces; (3) heterogeneity of the formation; (4) structures such as folds and fault blocks; and (5) porosity. Numerical simulations using realistic geologic conditions demonstrate the complex nature of the capacity concept, and point out that careful analyses are needed to assess capacity. We recommend that the capacity factor concept be further tested and extended to other geological sequestration target environments.

Because geologic CO_2 sequestration is new, research and development in the field rely heavily on numerical simulation and modeling. The modeling tools being used are typically modifications of codes developed primarily for other purposes. We carried out a code intercomparison study to evaluate how well modelers and their codes could handle relevant geologic CO_2 sequestration problems. Our study showed that overall agreement on a suite of test problems was good. However, some discrepancies were noted and found to be caused by sensitivities to fluid properties and discretization effects. In general, the simulation codes were shown capable of simulating complex phenomena associated with geologic carbon sequestration. We recommend that models consider geomechanical and geochemical coupling effects insofar as these are relevant for CO_2 injection.

Monitoring will be an essential part of geologic CO_2 sequestration to ensure that CO_2 remains in the reservoir and does not cause adverse health, safety, or environmental effects. We have identified a number of different monitoring activities that should be done at different phases over the lifetime of a geologic CO_2 sequestration project. The four main phases of a project are (1) pre-operational, (2) operational, (3) closure, and (4) post-closure. Standard and enhanced monitoring packages can be chosen to achieve specific requirements, depending on the location of the project. We investigated geophysical monitoring by gravity, electromagnetic (EM), and seismic methods. We recommend that modeling be done to identify a suite of methods that will be effective at a particular site, and that geophysical surveys focus on time-lapse and repeat surveys to detect changes in the CO_2 plume. In addition to traditional approaches, crosswell seismic and EM technology, electrical resistance measurements, tilt, and streaming potential measurements should be included in the portfolio of potential geophysical methods.

Surface and near-surface monitoring of soil gas and geochemistry can also potentially be used for monitoring and verification. Surface flux can be measured using accumulation chambers for point measurements, and eddy-correlation towers for aereal measurements. Shallow gas concentrations at different depths can be measured using gas sampling probes to understand the sources of CO_2 and other soil gas components. The natural carbon cycle and its variability will make it difficult to discern any potential leakage or seepage signal. Therefore, careful background measurements should be part of any monitoring program so that natural variability is understood. Carbon isotopes can also be used to distinguish fossil-fuel CO_2 from biogenic sources.

The use of tracers for monitoring has also been investigated under GEO-SEQ. Natural and artificial tracers have the potential to assist in characterizing reservoirs, and calibrating models as well as indicating leakage and seepage.

The lower separation costs associated with using impure CO_2 streams have the potential to greatly reduce the overall cost of geologic CO_2 sequestration. We have investigated by geochemical modeling the effects of impurities such as H_2S and SO_2 in the reservoir. We found that large amounts of co-injected H_2S should not prove problematic for a CO_2 injection process in terms of impact on sequestration. In the case of SO_2, if conditions allow the sulfur to be oxidized to sulfate (and this reaction is thermodynamically favored), only minor amounts of this gas could be tolerated.

This page left intentionally blank.

1. INTRODUCTION

The first phase of the GEO-SEQ project was a multidisciplinary effort focused on investigating ways to lower the cost and risk of geologic carbon sequestration. Through our research in the GEO-SEQ project, we have produced results that may be of interest to the wider geologic carbon sequestration community. However, much of the knowledge developed in GEO-SEQ is not easily accessible because it is dispersed in the peer-reviewed literature and conference proceedings in individual papers on specific topics. The purpose of this report is to present key GEO-SEQ findings relevant to the practical implementation of geologic carbon sequestration in the form of a Best Practices Manual. Because our work in GEO-SEQ focused on the characterization and project development aspects, the scope of this report covers practices prior to injection, referred to as the design phase. The design phase encompasses activities such as selecting sites for which enhanced recovery may be possible, evaluating CO_2 capacity and sequestration feasibility, and designing and evaluating monitoring approaches.

Through this Best Practices Manual, we have endeavored to place our GEO-SEQ findings in a practical context and format that will be useful to readers interested in project implementation. The overall objective of this Manual is to facilitate putting the findings of the GEO-SEQ project into practice.

2. ENHANCED HYDROCARBON RECOVERY

2.1 Enhanced Oil Recovery (EOR)

Selecting successful geologic CO_2 sequestration projects involves optimizing multiple objectives, among which are lowering cost, minimizing risk, and gaining public acceptance. Because hydrocarbon reservoirs are one of the primary subsurface targets for geologic carbon sequestration, enhanced hydrocarbon recovery from these sites is one of the obvious ways to offset CO_2 injection costs at low risk and with demonstrated public acceptance. In this section, we present results and best practice recommendations for enhanced oil recovery (EOR).

Oil reservoirs are attractive early targets as CO_2 sinks because of the potential cost offsets from enhanced oil recovery (EOR) using CO_2. It is estimated that upwards of 80% of oil reservoirs worldwide might be suitable for CO_2, injection based upon oil recovery criteria alone.

There are two fundamentally different scenarios for CO_2 sequestration in oil reservoirs. In the first, anthropogenic CO_2 is provided at a cost competitive with naturally occurring CO_2, but current economic and regulatory drivers remain unchanged. In this case, CO_2 EOR processes are typically designed to obtain maximum oil production while injecting minimum CO_2. This is a mature technology, with established practices for estimating costs.

In the second scenario, storage of CO_2 provides additional revenue through tax credits or emission trading. In this case, the objective will change to one of maximizing the amount of CO_2 left behind at the end of recovery, while also increasing oil production. The GEO-SEQ Project refers to the simultaneous production of oil and maximization of the volume of CO_2 as co-optimization of

EOR and sequestration. The results of work in the GEO-SEQ Project indicate that design of co-optimized EOR and sequestration projects differs considerably from conventional EOR projects. For example, conventional WAG (water after gas) techniques for control of gas mobility appear to be inappropriate. In this section, we present the results and recommendations from our research on co-optimized CO_2 EOR.

2.2 Site Selection and Evaluation for EOR

The first step in a combined sequestration and oil recovery project is to identify potential reservoirs amenable to the process. Aspects to be considered include reservoir depth, storage capacity, formation thickness, permeability, and the state of reservoir seals (Kovscek, 2002). Screening criteria are summarized in Table 2.1.

Once a site has been identified, a workflow for design of a co-optimized process (Kovscek and Wang, 2005) is given by the following steps:

1) Describe the reservoir, including the uncertainty in permeability distribution.
2) Quantify the magnitude of uncertainty with respect to flow prediction and CO_2 retention.
3) Choose an appropriate injection gas composition. Economics dictate either maximization of the injected concentration of CO_2 or minimization of the purchase cost of injectant.
4) Identify reservoir processes that jointly maximize oil production and the volume of CO_2 in place while minimizing the production and cycling of CO_2.
5) Design well placement and completions to reduce the preferential flow of injected gas through high permeability zones.
6) As required and as economics dictate, implement gas mobility control to increase the time required for the transport of injectants to a producer.

Typical methods for quantifying uncertainty (step 2, above) employ exhaustive flow simulations of multiple stochastic realizations of the geological architecture of a reservoir. Such approaches are computationally intensive, time consuming, and costly. Based on development work carried out as part of the GEO-SEQ Project (Kovscek and Wang, 2005), it is recommended that an analytical streamline-based proxy for full reservoir simulation be employed, which allows rational selection of a representative subset of equally probable reservoir models that encompass the uncertainty. Unit mobility ratio streamlines correlate approximately with results from non-unit mobility ratio reservoir simulation, but require much less time to compute. Streamlines also provide important information about the connectivity, or lack thereof, among injectors and producers and the distribution of heterogeneities within a reservoir.

It is also recommended that active well control using the producing GOR (gas-oil ratio) and injection pressure as control parameters should be considered as a means of increasing the fraction of the reservoir holding CO_2. At the same time, results indicate that ultimate oil recovery is the same as that from an optimized WAG recovery process. This recommendation derives from studies in the GEO-SEQ Project on approaches to maximize both field-wide oil recovery and sequestration of CO_2 (Jessen et al., 2005; Kovscek and Cakici, 2005). Figure 2.1 indicates an essential problem when conventional WAG recovery techniques are applied for sequestration. Figure 2.1(a) shows the fraction of the reservoir volume filled with CO_2, illustrating that water employed to reduce the tendency of CO_2 to channel selectively through the reservoir fills a substantial volume of pore space, blocking the access of CO_2. By way of background, the figure presents fully compositional numerical simulation results for fieldwide CO_2 sequestration for the reservoir model described above. Scenarios have used pure CO_2 as an immiscible injection gas and a solvent gas composed of about 2/3 by mole CO_2.

Figure 2.1 compares WAG drive mode with immiscible and miscible gas injection, gas injection after waterflood (GAW), and a scheme employing active well control (WC) based on the producing gas-oil ratio (GOR). The first two scenarios are designed so that the mobilities of the injected phases in the reservoir are reduced. In the last scenario, production wells are actively controlled to limit the amount of produced gas and increase the contact of gas with reservoir volume. Control parameters are the producing GOR and the injection pressure. In all cases, oil production is discounted by the equivalent amount of energy needed to compress produced gas. Schemes that incur excessive gas cycling pay a penalty with respect to oil production.

Figure 2.1(a) illustrates that the well control scheme with immisible CO_2 injection sequesters roughly 2.5 times the CO_2 of an optimized WAG process. Further, Figure 2.1(b) demonstrates that oil production obtained from pure CO_2 injection with well control is on par with that obtained in an optimized WAG process. In general, gas-controlled production of pure CO_2 appears to limit gas cycling and maximize CO_2 storage, while allowing identical ultimate oil recovery compared to WAG. Figure 2.1(b) shows, additionally, that oil recovery is greatest as a result of miscible gas injection. With miscible gas injection, the local displacement efficiency approaches unity, and recovery is maximized. Among the scenarios with miscible gas injection, well-controlled injection resulted in oil recovery 7 to 12 % greater than the other cases and approaches 80% of the oil in place. Compared to cases employing pure CO_2, recovery from schemes using solvent is over 30% greater.

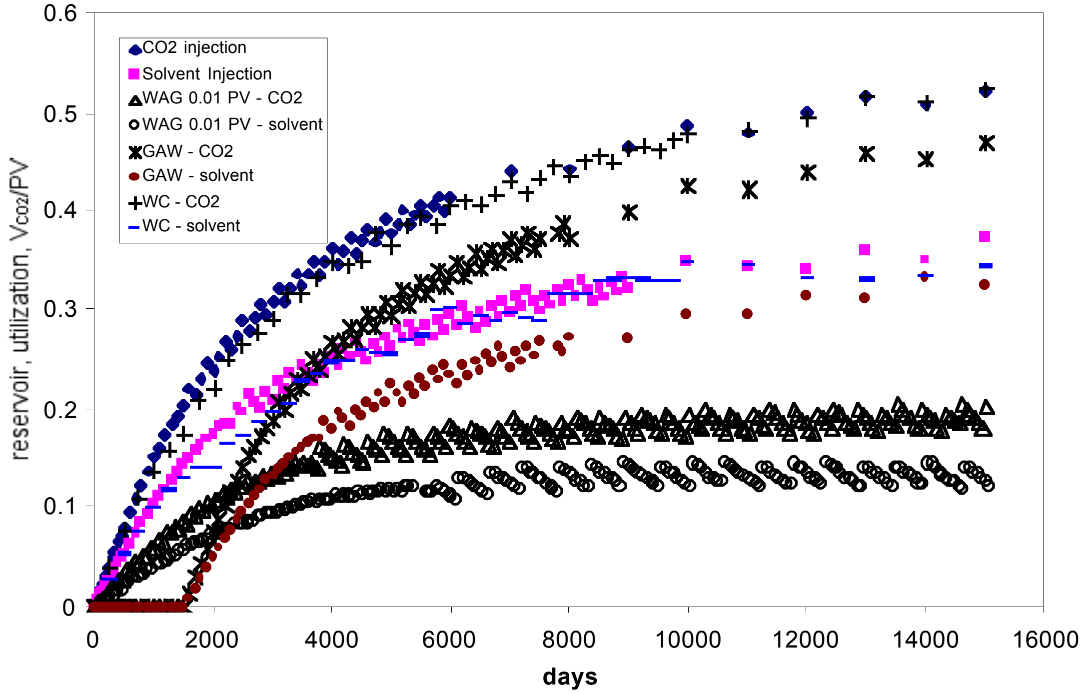
2.3 Summary EOR Recommendations

To carry out a successful CO_2-EOR co-optimization, we recommend characterization and reservoir evaluation tailored to meet the dual objectives of maximizing both recovery of oil and storage of CO_2. Streamline modeling should be used to study the effects of reservoir heterogeneity. Our simulations showed that co-optimization was best achieved if active well control, based on the producing GOR, is employed. Use of solvent also enhances oil recovery.

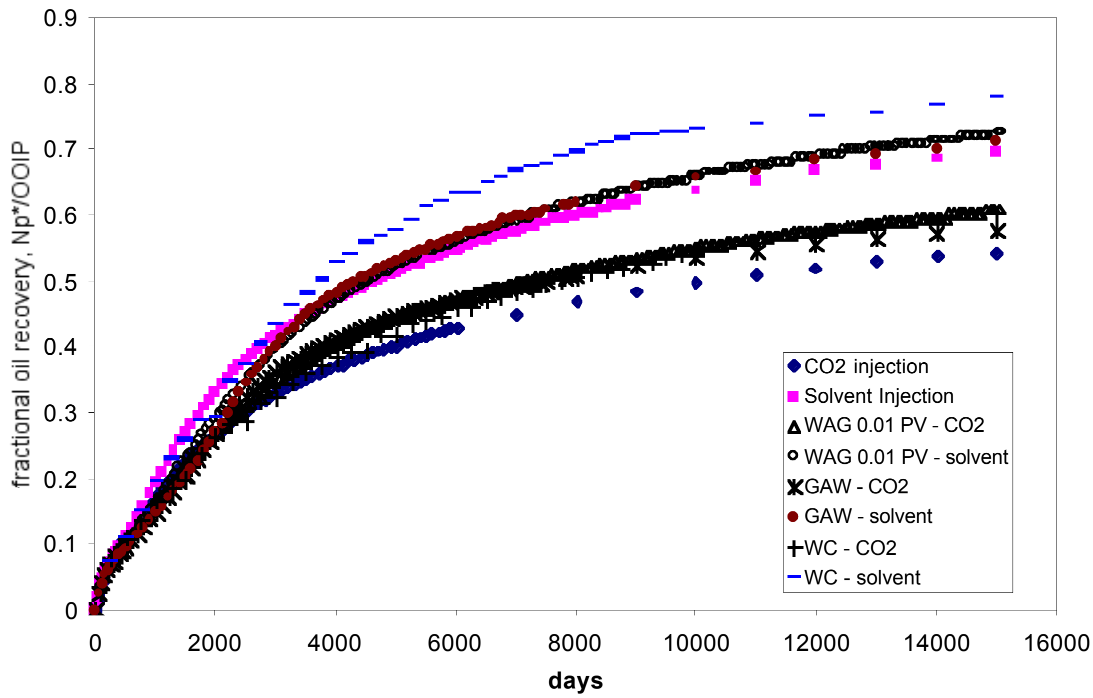
Table 2.1. Screening criteria for anthropogenic CO_2-EOR and CO_2 sequestration.

	Positive Indicators	**Cautionary Indicators**
Reservoir Properties		
$S_o\phi$	≥ 0.05	< 0.05 Consider filling reservoir voidage if capacity is large
kh (m^3)	≥ 10^{-14} - 10^{-13}	< 10^{-14} If kh is less, consider whether injectivity will be sufficient
Capacity (kg/m^3)	> 10	< 10
seals	Adequate characterization of caprock, minimal formation damage,	Areas prone to fault slippage
Oil Properties		
ρ (°API, kg/m^3)	> 22, 900	< 22 Consider immiscible CO_2 EOR, fill reservior voidage if capacity is large
μ (mPa s)	< 10	> 10 Consider immiscible CO_2 EOR
composition	High concentration of C_5 to C_{12}, relatively few aromatics	n/a
Surface Facilities		
corrosion	CO_2 can be separated to 90% purity; development of epoxy coated pipe and corrosion inhibitors	H_2O and H_2S concentration above 500 ppm each
pipelines	Anthropogenic CO_2 source is within 500 km of a CO_2 pipeline or oil field	Source to sink distance is greater than 500 km
synergy	Pre-existing oil production and surface facilities expertise	Little or no expertise in CO_2-EOR within a geographic region

ρ = density
°API = degrees API gravity (measure of density)
μ = viscosity
ϕ = porosity
S_o = oil saturation
kh = permeability-thickness product



(a)



(b)

Figure 2.1. (a) Reservoir utilization and (b) oil recovery performance of different gas injection processes from a 3D, heterogeneous, compositional reservoir example (PV = pore volume).

2.4 Enhanced Gas Recovery (EGR)

Depleted natural gas reservoirs are a promising CO_2 injection target by virtue of their proven long-term containment of natural gas, history of land use, and generally well-characterized nature (Oldenburg et al., 2001). An additional benefit of CO_2 injection into depleted or depleting gas reservoirs is the possibility of enhancing or accelerating methane (CH_4) recovery. Depending on the type of reservoir, a significant amount of CH_4 is often left unproduced in the gas reservoir (Laherrere, 1997). Enhancing or accelerating CH_4 recovery would offer obvious economic advantages to offset the cost of CO_2 injection. EGR differs from CO_2-EOR in that it has never been tested nor used, and thus our analyses to date rely entirely on modeling.

2.5 Evaluating EGR Potential

2.5.1 Technical Feasibility

The injection of CO_2 for the joint purpose of CO_2 sequestration with enhanced gas recovery is referred to by its acronym CSEGR. The basic idea is to inject CO_2 into a depleted or depleting natural gas reservoir at locations far away from CH_4 production wells. The CO_2 serves two purposes: (1) it displaces CH_4 toward production wells, and (2) it repressurizes the reservoir, thereby accelerating CH_4 production and discouraging water entry into the reservoir. The large density and viscosity of CO_2 relative to CH_4 tend to limit the degree to which the two gases will intermingle and mix, especially when the reservoir has significant vertical extent (e.g., > 20 m) and the dense CO_2 can be injected at the bottom of the reservoir while CH_4 is produced from the top. An example simulation of CSEGR in a three-dimensional quarter five-spot geometry is shown in Figure 2.2. As shown, CO_2 is injected at a low elevation in the reservoir and tends to fill the reservoir from the bottom up as CH_4 is produced from higher up in the reservoir.

The potential for successful CSEGR depends on the nature of the reservoir. Gas reservoir production can be of two end-member types: (1) depletion drive, and (2) water drive. In depletion drive reservoirs, the gas flows out of the wells under its own pressure, as it would flow out of a small hole in a large pressurized tank. In a depletion-drive reservoir, the pressure decline is a direct function of the gas removed. In water-drive reservoirs, water in surrounding rock formations enters the reservoir as natural gas is produced, causing a smaller pressure decrease than would be expected from the rate of gas production from a pure depletion-drive reservoir. Depletion-drive reservoirs are ideal in that the well can conduct the gas out of the reservoir as long as there is a driving force. In contrast, water drive reservoirs fill up with water as the gas is removed, and the water kills the wells, preventing recovery of a substantial portion of the total gas in the reservoir.

The world-wide average recovery factor (ratio of gas produced to gas in place) is approximately 75% (Laherrere, 1997). Depletion-drive reservoirs can have recovery factors of 75–90%, while water-drive reservoirs usually have recovery factors of 50–75%. Even a reservoir with only 10% gas remaining may be a good candidate for CSEGR if it were a very large reservoir to begin with.

Water-drive reservoirs are best exploited through CSEGR while still under production. In this way, pressure can be maintained throughout the production process, thereby keeping water from coning upward into wells.

Another characteristic that aids the feasibility of CSEGR is a large vertical extent of the reservoir. Our simulations have shown that if there is a large vertical extent of the reservoir, greater than 20 m or so, CO_2 can be injected into the lower parts of the reservoir while CH_4 is produced from the higher parts. The vertical extent allows the density contrast between CO_2 and CH_4 to help diminish mixing.

Reservoirs with significant fracture porosity (as opposed to matrix porosity) are thought to be less desirable for CSEGR. Nevertheless, this aspect has not been specifically investigated and therefore remains an open question.

2.5.2 Economic Feasibility

The final and key characteristics of the reservoir are related to economics. First, one needs to know how much gas is left. If significant gas remains, there obviously is greater potential for both gas recovery and CO_2 sequestration. Second, the prices of CH_4 and CO_2 are critical external factors that will control the feasibility of CSEGR. Other costs include the need for additional wells and modifications to existing wells to handle CO_2 injection, and the need for monitoring wells and/or other monitoring infrastructure.

Regarding the economics of CSEGR, we have found that feasibility is critically dependent on three factors: (1) the cost of CO_2, (2) the price of CH_4, and (3) the ratio of CO_2 injected to incremental CH_4 produced. Implicit in the economic analysis is the existence of a significant amount of additional gas that can be recovered. As reflected in Figure 2.3, our analysis showed that CSEGR could be economical with no subsidy at a CO_2 cost of approximately \$10/ton CO_2 (Oldenburg et al., 2004). This is well below current capture costs, but approximately equal to the cost of natural CO_2 as it is used currently in EOR. Note in Figure 2.3 the dependence on the ratio of CO_2 injected to incremental CH_4 produced. It is obviously economically beneficial to produce as much CH_4 as possible for a given amount of CO_2.

There are potential secondary benefits beyond enhanced recovery associated with CSEGR, particularly for reservoirs still in active production, i.e., depleting but not depleted. For example, injecting CO_2 during the normal operation of a gas reservoir can maintain reservoir pressure, and thereby reduce water entry. The pressure support provided by injected CO_2 can also be used to prevent land subsidence, a serious problem in some gas fields. In general, CSEGR is recommended for depleting gas reservoirs (as opposed to abandoned reservoirs) because the infrastructure is in place, and the ongoing history of gas production at the site will be more acceptable to neighbors than a startup of CO_2 injection at an abandoned site. A final possible benefit of CSEGR is that the fully CO_2-charged reservoir may have potential use as a gas storage reservoir, as discussed below.

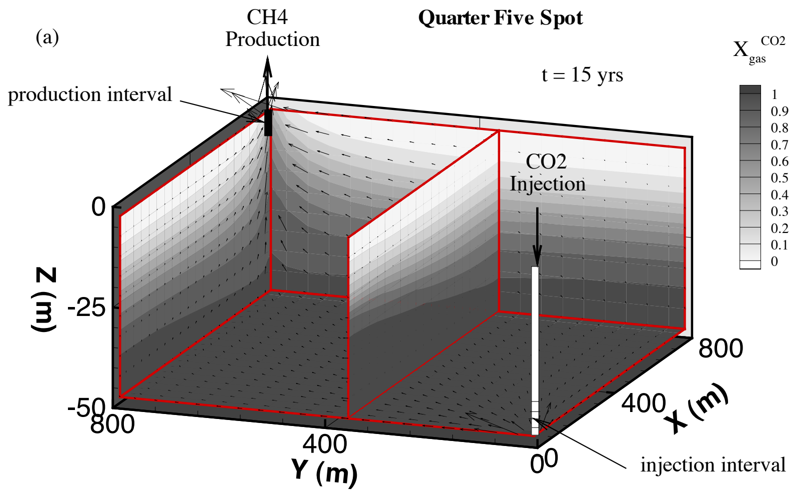


Figure 2.2. Mass fraction of CO_2 for injection into a CH_4 reservoir for the case in which CO_2 is injected low in the reservoir and CH_4 is produced from high in the reservoir.

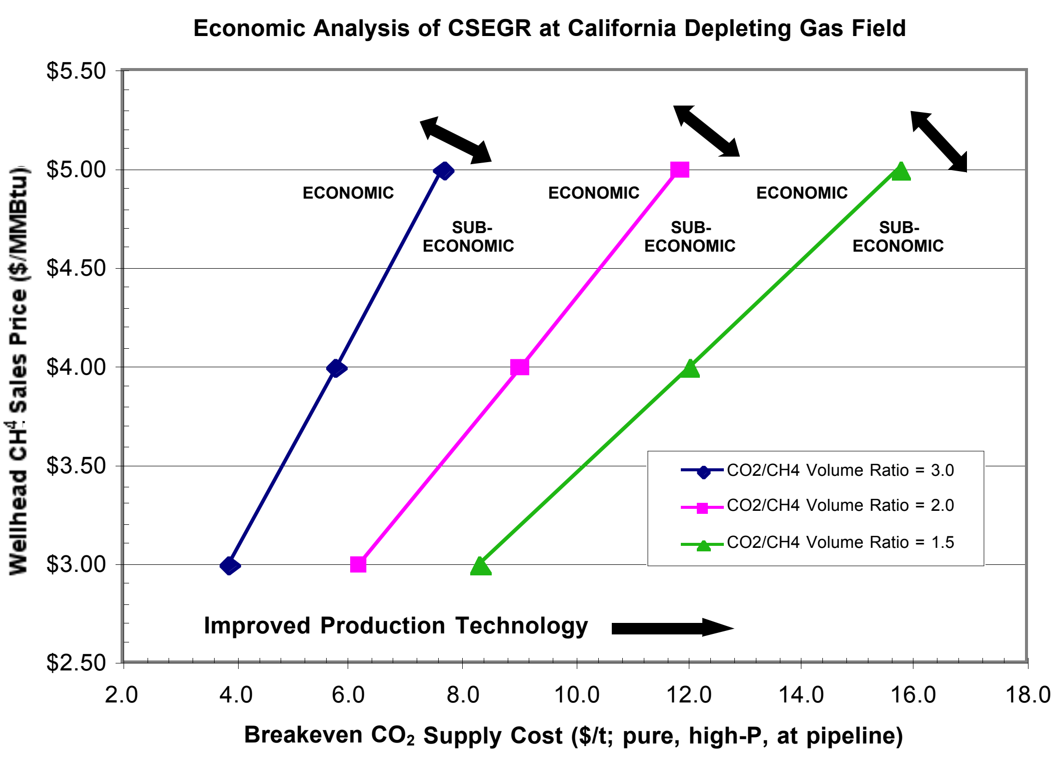


Figure 2.3. Break-even costs of CO_2 as a function of CH_4 sales price for three different injection volume ratios.

2.6 Evaluating Gas Storage Potential

The end-stage of a CSEGR project will be a reservoir filled largely with CO_2. Our simulation studies suggest that 5–10 years of CSEGR may be a typical time scale over which relatively pure CH_4 can be produced during CO_2 injection. After this time, CO_2 separation from the produced gas may have to be done before selling the gas. At some point, the reservoir will become uneconomical as a hydrocarbon resource, and benefit will be derived solely for its role as a CO_2 sink. However, CO_2 has some properties that allow it to be a very effective cushion gas, making the final CO_2-charged reservoir at a mature CSEGR site a potentially effective gas storage reservoir (Oldenburg, 2003).

To achieve the conditions under which CO_2 can be an effective cushion gas, the gas storage reservoir needs to operate between subcritical and supercritical pressures of CO_2 (e.g., between 50 and 100 bars), and the temperature should be on the low side, e.g., 40–50 ˚C. The reason for this is to exploit the large change in CO_2 density that occurs between subcritical and supercritical pressures (P_c = 74 bars) near the critical temperature (T_c = 31 ˚C). Operating the reservoir between these pressures allows the CO_2 gas to act as a super cushion, compressing more than a native CH_4 cushion would during the CH_4 injection season, and expanding more during the withdrawal season.

Our simulations of a model system suggest approximately 30% more gas can be stored for a given volume if CO_2 is the cushion gas relative to the case of a native CH_4 cushion (Oldenburg, 2003).

2.7 EGR Recommendations

We recommend that CSEGR be applied to depleting as opposed to depleted reservoirs because the infrastructure present, working operator knowledge of the field, and land-use history are all favorable for continued gas production. Whether the reservoir is water-drive or depletion drive, promising candidate reservoirs for CSEGR must have significant gas remaining in the reservoir. Reservoirs with large vertical extent are especially favorable for CSEGR, because CO_2 can be injected in the lower regions while CH_4 is produced from the upper regions. Upon filling of the reservoir with CO_2, it may be feasible to use the reservoir as a gas storage reservoir with CO_2 as the cushion gas, although this novel concept will require much more investigation and testing before it can be recommended.

3. CHARACTERIZING BRINE FORMATIONS

3.1 Introduction

Site characterization has two primary objectives for geologic sequestration of CO_2 in brine-bearing formations. First, it provides the input necessary for estimating the sequestration capacity of the site, and second, it provides information needed to design an effective sequestration operation. In this section, we discuss the basis for brine-formation sequestration, and the use of capacity factor to evaluate the potential capacity of a given brine-bearing formation. Details of this and related work can be found in Doughty et al. (2001, 2002), Doughty and Pruess (2004), and Hovorka et al. (2001, 2004a,b).

3.2 Basis for Brine-Formation Sequestration

Deep brine formations generally have few or no competing uses, and may be well-characterized if they occur in conjunction with oil- or gas-producing formations. Depths greater than about 800 m below the ground surface are generally considered suitable for CO_2 sequestration for at least two reasons. First, deep sequestration sites are far from the biosphere, with a long potential flow path capable of mitigating potential leakage effects. Second, at depths greater than 800 m, CO_2 does not form distinct gas and liquid phases, but primarily exists as an immiscible supercritical phase with a high density, enabling more efficient storage. Although supercritical CO_2 is very dense compared to CO_2 at atmospheric conditions, it is less dense and less viscous than the surrounding brine, making it behave as a gas-like phase in the subsurface relative to brine. In addition to the plume of supercritical CO_2 that will form upon injection, a fraction of the injected CO_2 will dissolve in the brine, creating a small increase in overall brine density.

3.3 Capacity Factor

The capacity factor is a fundamental measure of how much CO_2 a given subsurface formation can hold. We define capacity factor C as the volume fraction of the subsurface within a defined stratigraphic interval available for CO_2 sequestration. C is the sum of terms for the immiscible supercritical (gas-like) phase, C^{gas}, and the CO_2 dissolved in the brine, C^{liq}. We have $C^{gas} = \langle\phi S_g\rangle$ and $C^{liq} = \langle\phi S_l X_l^{CO2}\rho_l/\rho_g\rangle$, where ϕ is porosity, S_g and S_l are the volume fractions of the pore space containing supercritical CO_2 and liquid, respectively, X_l^{CO2} is the mass fraction of CO_2 dissolved in the brine, ρ_l and ρ_g are the densities of the supercritical and liquid phases, respectively, and the angle brackets represent an average over the spatial domain of sequestration.

We conceptualize C as the product of five factors: (1) the intrinsic capacity, controlled by multiphase flow and transport phenomena; (2) a gravity capacity factor, controlled by buoyancy forces; (3) a heterogeneity capacity factor, controlled by local geologic variability such as sand channels and shale lenses; (4) a structural capacity factor, controlled by larger-scale geological structures such as anticlines or fault blocks; and (5) the formation porosity ϕ, the fraction of void space within the formation. These five factors are illustrated schematically in Figure 3.1.

Analytical solutions are available for studying multiphase flow phenomena (e.g., Buckley and Leverett, 1942) and buoyancy flow (e.g., Sorey, 1975) for simple flow geometries, but for more realistic situations involving heterogeneous media, a numerical approach is needed. To investigate CO_2 sequestration capacity, we use a version of the numerical simulator TOUGH2 (Pruess et al., 1999), which was enhanced to accurately represent supercritical CO_2 (Pruess and García, 2002) and considers all flow and transport processes relevant to a two-phase (liquid-gas), three-component (CO_2, water, dissolved NaCl) system.

A three-dimensional numerical model is developed of a 1 km x 1 km x 100 m region of a fluvial-deltaic sedimentary formation. Permeability varies by nearly five orders of magnitude in the model, making preferential flow a significant effect. Our hypothetical sequestration problem specifies that CO_2 is injected at a rate of 0.75 million tonnes per year for a period of 20 years into a well at the center of the model. This injection rate is roughly one-third the rate at which CO_2 is produced by a 1,200 MW gas-fired power plant.

Through a suite of numerical simulations, we have studied how the five components of C shown in Figure 3.1 depend on multiphase flow parameters, formation and injection well configuration, and geologic heterogeneity. Maximum capacity corresponds to a highly idealized case in which purely radial flow occurs through a homogeneous medium ($C_g = C_h = C_s = 1$), whereas for a highly buoyant plume that reaches the spill point of the storage volume rapidly ($C_g << 1$, $C_h = 1$, $C_s << 1$), capacity is much smaller. Adding heterogeneity ($C_h < 1$) generally counteracts buoyancy flow, increasing C_g and C_s, and ultimately C itself.

Based on our conceptualization of the capacity factor as a product of five terms and the supporting simulation results, we can assess and optimize sequestration capacity:

Intrinsic Capacity Factor:

C_i depends on the relative permeability to CO_2 and the viscosity ratio between brine and CO_2. A high C_i means the supercritical CO_2 fills up a large fraction of the pore space compared to the brine (large S_g), leading to a compact CO_2 plume. Conversely, a low C_i describes a more diffuse plume (small S_g). Although a larger subsurface volume is required to store a given amount of CO_2 in the latter case, more brine is in contact with immiscible CO_2, leading to more CO_2 dissolution. Because dissolved CO_2 is not buoyant, it may represent more securely stored CO_2. Two particular factors that have a large impact on C_i are the residual phase saturations S_{lr} and S_{gr}, the saturations below which the liquid and gas-like phases, respectively, are immobile. For the case with large S_{gr} and small S_{lr}, the gas-like phase is only mobile at high values of S_g, thus creating a high S_g plume. For the opposite case with small S_{gr} and large S_{lr}, the reverse is true. Furthermore, for large values of S_{gr}, more CO_2 is trapped in the pore space, hampering the long-term migration of the CO_2 plume away from its injection site.

Gravity Capacity Factor:

C_g increases as intrinsic permeability decreases or medium anisotropy increases (i.e., vertical permeability decreases).

Heterogeneity Capacity Factor:

C_h increases as the quantity of shale or other low-permeability material bypassed by flow decreases; however, layered-type low-permeability features enhance C_g by diminishing buoyancy flow.

Structural Capacity Factor:

C_s reflects large-scale geologic features, and may be optimized by careful placement of injection wells.

Porosity:

A large value of ϕ signifies that a large pore volume is available for sequestration. However, insofar as permeability is usually correlated to porosity, larger ϕ tends to reduce C_g.

3.4 Recommendations

The first step in designing an effective sequestration operation is to do a capacity assessment, and compare the results of that assessment to the magnitude of the CO_2 source. Next, more detailed investigation of the sequestration boundaries must be carried out. The integrity of the top seal is most critical, owing to the buoyant nature of the supercritical CO_2. In specific circumstances, bottom seal integrity may be required to isolate CO_2 from deeper petroleum resources. Depending on the geologic structure, lateral boundaries may be crucial to trapping sequestered CO_2, for example, the updip limit of a tilted formation. Isolated fault blocks may provide good natural traps, but compartmentalization has the disadvantage of increasing pressures accompanying CO_2 injection.

In general, a series of successive numerical models should be developed as knowledge about the target sequestration site increases:

1) Geologically constrained probabilistic model (during site selection process; use for capacity assessment)
2) Same model adapted to test a specific site (incorporating local structure; begin to scope out required number, spacing, and injection rates of wells, expected evolution of CO_2 plume)
3) Site data from detailed reservoir model (based on existing well logs, 3D seismic, literature properties of target formation; investigate the impact of poorly constrained model parameters such as boundary conditions, integrity of seals, two-phase flow properties)
4) Fully deterministic reservoir model (based on new well logs, core analyses, pressure-transient testing, tracer testing; simulate well-tests to determine flow properties and validate model, simulate CO_2 injection to optimize operational conditions)
5) Generalized regional model (to study the far-field impact of the sequestration process, both under ideal conditions and in the event of a leak)

This comprehensive series of steps will be an important element of early sequestration projects. As experience is gained in carrying out storage projects, it may be possible, under some circumstances, to adopt less rigorous approaches.

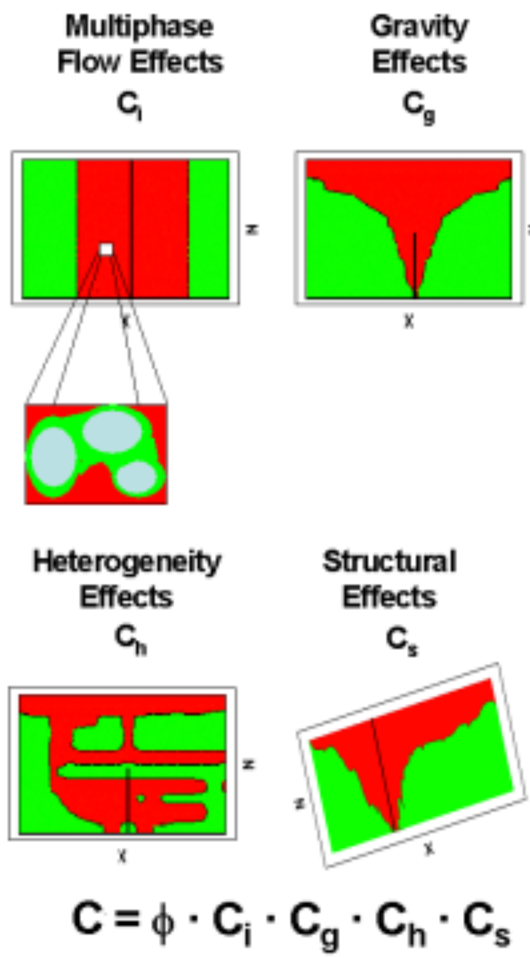


Figure 3.1. Schematic views of the CO_2 distribution (red) in a brine-saturated formation for increasingly complex model assumptions, and the component of the total capacity factor C *that describes the corresponding effects.*

4. MODELING AND SIMULATION

4.1 Introduction

Modeling and simulation are an intrinsic part of the design phase of a CO_2 injection project. From capacity assessments to estimating travel times for potential leakage routes, multiphase and multicomponent reservoir simulation provides the basis for defensible decisions and understanding of the system. However, it is essential that simulation tools are used by competent engineers and scientists who understand the pitfalls and complexities of subsurface reservoir simulation. Furthermore, the practice of CO_2 injection is immature; there is little field experience in the physical processes involved, and therefore extra scrutiny must be given to simulation results.

4.2 Code Intercomparison

Because of the need to demonstrate the effectiveness of numerical simulation of geologic carbon sequestration before it is relied upon for design and performance in actual projects, we conducted a code intercomparison study. The objective of the code intercomparison study was to test and evaluate numerical simulation codes to establish their ability to model complex processes related to CO_2 injection and migration. The approach of the study was to have a group of scientists and engineers from around the world submit test problems, which they and others then solved using different simulation codes. Results were submitted and compiled to provide a direct comparison. There were eight test problems and ten groups from six countries participating.

The conclusion of the intercomparison study was that most simulation codes in the hands of the experienced analysts who participated in the study, yielded similar results on the various test problems. However, some discrepancies were noted and found to result from sensitivities to fluid properties and discretization effects. In general, the simulation codes were shown capable of simulating complex phenomena associated with geologic carbon sequestration. The details of the test problems and results of the study can be found in Pruess et al. (2004).

4.3 Recommendations

In general, CO_2 injection problems involve a high degree of coupling between geochemical, geomechanical, and hydrologic processes. For this reason, coupled simulation capabilities are often needed. In some cases, multiple codes may be needed to model different scales and time frames. For example, compositional well-bore simulators are needed to model well-bore flow, while reservoir simulators are needed for larger-scale flow processes. Analysts working closely with earth scientists will be in the best position to recommend which codes are to be used. Because the field of geologic carbon sequestration is new, we recommend that analysts use simulators for which the source code is available, so that minor code changes can be made by the analyst when the need for new scenarios or processes arises.

5. MONITORING

5.1 Introduction

Monitoring of geologic CO_2 sequestration sites will be used to demonstrate that geologic storage is successful at keeping injected CO_2 from entering the atmosphere. There are three overarching purposes for monitoring:

1) Ensure that CO_2 sequestration is safe from a human-health perspective;
2) Ensure that CO_2 sequestration does not create adverse local environmental impacts;
3) Ensure sequestration effectiveness, i.e., ensure that CO_2 is not being released to the atmosphere.

While a broad range of safety and environmental issues must be addressed to ensure safe and effective sequestration, the majority of these issues hinge on two primary factors; namely, (1) implementation of effective controls on injection well completion, injection rates, and wellhead and formation pressures; and (2) assurance that the CO_2 remains trapped and does not leak out of the intended storage reservoir(s). The relationship between these factors and the overarching purposes for monitoring are illustrated in Figure 5.1 (Benson et al., 2004b).

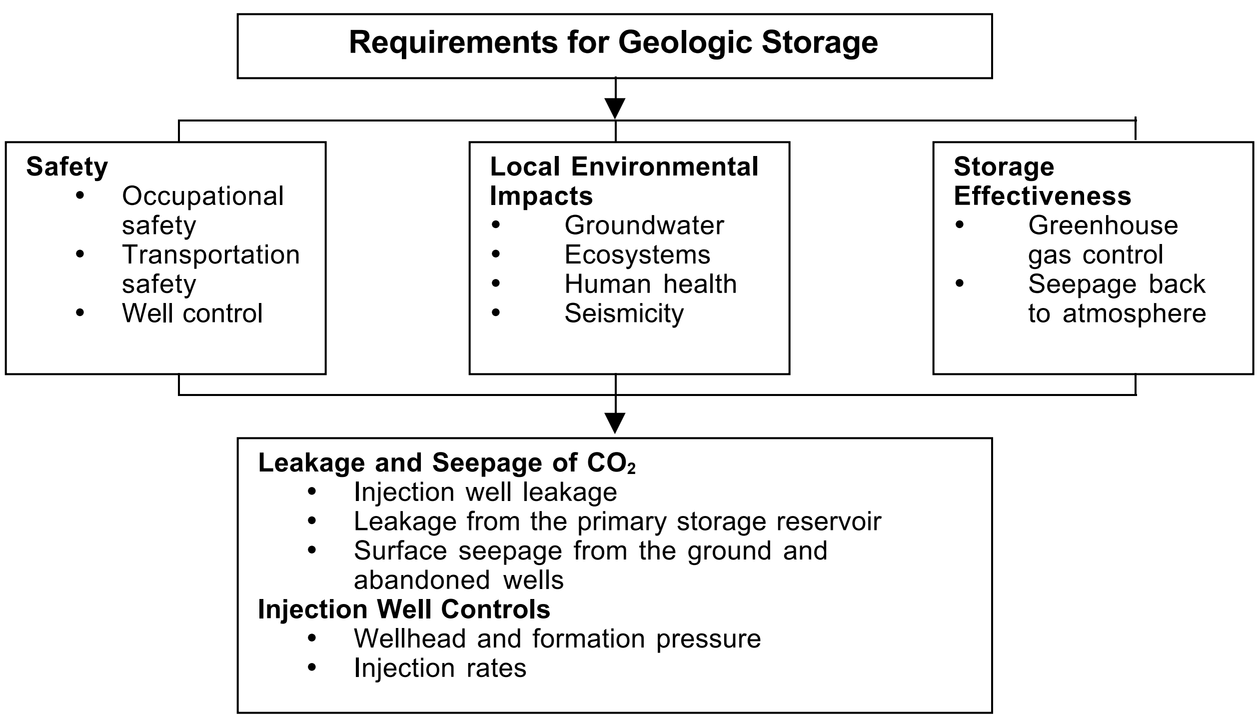


Figure 5.1. Schematic showing requirements for safe and effective geologic storage of CO_2.

5.2 Monitoring Activities

5.2.1 Phasing

Benson et al. (2004b) identified a number of specific monitoring activities that are recommended in order to achieve the objectives identified in Figure 5.1. These activities are:

- Establishing baseline conditions from which the impacts of CO_2 storage can be assessed
- Monitoring to ensure effective injection controls
- Monitoring to detect the location of the injected CO_2 plume
- Assessing the integrity of shut-in, plugged, or abandoned wells
- Monitoring to identify and confirm storage efficiency and processes
- Monitoring for model calibration and performance confirmation–comparing model predictions to monitoring
- Monitoring to detect and quantify surface seepage
- Monitoring to assess health, safety, and environmental impacts of leakage
- Monitoring micro-seismicity associated with CO_2 injection
- Monitoring to design and evaluate remediation efforts, if needed
- Provide assurance and accounting for monetary transactions
- Evaluating interactions with or impacts on other geological resources
- Settling of legal disputes due to leaks, seismic events, or ground movement
- Assuring the public when visibility and transparency is of prime importance

Benson et al. (2004b) also introduced the concept of four distinct phases in the life-cycle of a geologic storage project. Monitoring activities will vary between these phases. The four phases are:

1) Pre-operation phase, in which project design is carried out, base-line conditions are established, geology is characterized, and risks are identified;
2) Operation phase, corresponding to periods of 30 to 50 years during which CO_2 will be injected into the storage reservoir;
3) Closure phase, beginning after injection has stopped, during which ongoing monitoring is used to demonstrate that the storage project is performing as expected and that it is safe to discontinue further monitoring;
4) Post-closure phase, during which monitoring will no longer be required except in the event of ongoing leakage, legal disputes, or other matters that may require new information about the status of the storage project.

Table 5.2 provides suggestions for the monitoring activities that would be appropriate for the different phases in the life-cycle of a storage project.

Table 5.2. Summary of the purposes for monitoring during the phases of a storage project.

Monitoring Activity	Pre-Operation Phase	Operational Phase	Closure Phase	Post-Closure Phase
Establishing baseline conditions from which the impacts of CO_2 storage can be assessed	Yes			
Ensure effective injection controls		Yes		
Detect the location of the CO_2 plume		Yes	Yes	
Assessing the integrity of shut-in, plugged or abandoned wells	Yes	If leakage detected	If leakage not stopped	If leakage not stopped
Identify and confirm storage efficiency and processes	Yes	Yes		
Model calibration and performance confirmation – comparing model predictions to monitoring data		Yes	Yes	
Detect and quantify surface seepage		If leakage detected	If leakage not stopped	If leakage not stopped
Assess environmental, health and safety impacts of leakage		If leakage detected	If leakage not stopped	If leakage not stopped
Monitoring micro-seismicity associated with CO_2 injection	Yes	If micro-seismicity detected		
Monitoring to design and evaluate remediation efforts		If leakage detected	If leakage detected	
Provide assurance and accounting where monetary transactions are involved such as with carbon trading and emission tax or emission reduction incentives		Yes	Yes	
Evaluating interactions or impacts with other geological resources: for example nearby water, coal, oil & gas, mineral reserves or other geological waste disposal operations.		If interactions are possible	If interactions are possible	If interactions are possible
Settling of legal disputes for example due to leaks, seismic events, ground movement		If leakage, seismicity or ground movement detected	If leakage, seismicity or ground movement detected	If leakage, seismicity or ground movement detected
Assuring the public where visibility and transparency is of prime importance		Yes	Yes	

Finally, Benson et al. (2004b) have recommended generic monitoring packages that would be appropriate for each phase in the life-cycle of a storage project. As will be discussed in a later section, the monitoring packages recommended for a particular storage project will depend on site-specific objectives. The first package, called the "basic monitoring package," is designed primarily to provide assurance that the CO_2 is staying within the intended storage formation. The second monitoring package, called the "enhanced monitoring package," includes groundwater sampling, surface CO_2 flux monitoring and a geophysical monitoring program includes gravity and electromagnetic measurements. Table 5.3 lists the components of both monitoring packages.

Table 5.3. Components of the basic and enhanced monitoring packages.

Basic Monitoring Package	Enhanced Monitoring Package
Pre-Operational Monitoring	**Pre-Operational Monitoring**
Well Logs	Well Logs
Wellhead Pressure	Wellhead Pressure
Formation Pressure	Formation Pressure
Injection and Production Rate Testing	Injection and Production Rate Testing
Seismic Survey	Seismic Survey
Atmospheric CO_2 Monitoring	Gravity Survey
	Electromagnetic Survey
	Atmospheric CO_2 Monitoring
	CO_2 Flux Monitoring
	Pressure and Water Quality Above the Storage Formation
Operational Monitoring	**Operational Monitoring**
Wellhead Pressure	Well Logs
Injection and Production Rates	Wellhead Pressure
Wellhead Atmospheric CO_2 Monitoring	Injection and Production Rates
Microseismicity	Wellhead Atmospheric CO_2 Monitoring
Seismic Surveys	Microseismicity
	Seismic Survey
	Gravity Survey
	Electromagnetic Survey
	Continuous CO_2 Flux Monitoring at 10 Stations
	Pressure and Water Quality Above the Storage Formation
Closure Monitoring	**Closure Monitoring**
Seismic Survey	Seismic Survey
	Gravity Survey
	Electromagnetic Survey
	Continuous CO_2 Flux monitoring at 10 stations
	Pressure and Water Quality Above the Storage Formation
	Wellhead Pressure Monitoring for 5 years, After Which Time the Wells Will Be Abandoned

5.2.2 Tailored Monitoring Approach

Monitoring for CO_2 storage projects should be tailored to the specific conditions and risks at the storage site. For example, if the storage project is in a depleted oil reservoir with a well-defined cap rock and storage trap, the most likely pathway for leakage is the injection well itself or (perhaps) abandoned wells from former reservoir operations. In this case, the monitoring program should focus on detecting leakage from injection wells, locating any abandoned wells in the area and ensuring that they are not leaking CO_2 to the land surface or shallow aquifers. On the other hand, if a project is in a brine-filled reservoir where the cap rock is less well defined or lacks a local structural trap, the monitoring program should focus on tracking the migration of the plume and ensuring that it does not leak through discontinuities in the cap rock. Similar arguments can be made about projects where solubility or mineral trapping is a critical component of the storage security. Here it would be necessary to demonstrate that the geochemical interactions were effective and progressing as predicted.

One can also imagine that the extent of land surface monitoring would depend on the proximity and size of the local population. If a project were located in an urban area, extra precautions would be put in place to assure the public that the storage project was not causing a safety or human health hazard.

The value of taking a tailored approach to monitoring is two-fold. First, the monitoring program focuses on the largest risks. Second, since monitoring may be expensive, a tailored approach will enable the most cost-effective use of monitoring resources. Having said this, however, it is likely that there will be a minimum set of monitoring requirements that will be based on experience and regulations from related activities such as natural gas storage, CO_2 enhanced oil recovery, and disposal of industrial wastes in deep geologic formations (Benson et al., 2002).

5.2.3 Selecting Geophysical Monitoring Approaches

Considerable effort in the GEO-SEQ project was devoted to assessing and demonstrating the application of geophysical methods for monitoring subsurface processes of interest in geologic sequestration projects. The workflow for application of geophysical methods in a geologic sequestration project involves the following steps:

- Identify subsurface processes or targets relevant to the particular monitoring activity of interest
- Select the suite of geophysical techniques best suited for the subsurface measurements
- Perform a baseline set of measurements before CO_2 injection
- Repeat measurements at intervals during and after injection
- Interpret results, focusing on time-lapse changes

The recommended steps for selection of suitable geophysical techniques include:

- Develop a geologic model for the sequestration site that includes the reservoir, the seals, and overburden;
- Perform reservoir simulations of the sequestration processes of interest, such as prediction of changes and the distribution of fluid phases resulting from CO_2 injection;
- Using the geologic model and results of reservoir simulations, perform numerical simulations to predict the response of candidate geophysical techniques;
- Interpret the results of the geophysical modeling using the same techniques that would be used to interpret field measurements.

An example of this approach is the analysis done of a potential CO_2 flood at the Schrader Bluff field on the North Slope of Alaska (Hoversten and Gasperikova, 2004). In order to compare the spatial resolution and sensitivity of various geophysical techniques being considered for CO_2 sequestration monitoring, a 3D flow simulation model of the reservoir provided by BP was used in conjunction with rock-property relations developed from log data to produce geophysical models from the flow simulations. The Schrader Bluff reservoir is a sandstone unit between 25 and 30 m thick, at a depth of 1,100–1,400 m. Time-lapse snap shots of the reservoir at initial conditions and 5-year increments out to 2035 were used. A water after gas (WAG) injection strategy is considered, which produces complicated spatial variations in fluid (CO_2, brine, oil and gas) saturation within the reservoir over time.

The analysis considered the application of surface and borehole gravity, electromagnetic, and seismic geophysical techniques. The geophysical techniques were modeled in a time-lapse scenario, where baseline measurements were done (prior to CO_2 injection), and then subsequent measurements were made every year or so during injection. Results showed that there would be a clear change in seismic amplitudes associated with changes in water and CO_2 saturation. In addition, there would be changes in the AVO (amplitude versus offset) signature. Both amplitude and AVO effects could be used to make quantitative estimates of saturation changes. The gravity modeling evaluated the change in gravity and gravity gradient resulting from the change in density in the reservoir produced by injection of the CO_2. Results showed that the difference in the vertical component of gravity on the surface caused by CO_2 injection over a 20-year period would be below the level of repeatability of current field techniques. However, if measurements could be made in boreholes just above the reservoir, simulations showed that gravity could be used to map the areas of density changes caused by CO_2 injection. Finally, an electromagnetic (EM) surface technique was evaluated as a method to quantitatively measure changes in brine saturation in the reservoir. The EM configuration consisted of 100 m electric dipoles operating at 1 Hz, with electric field measurements at a separation of 2 km in line with the transmitting dipole. Results showed that the injected CO_2 would result in changes in the electric field of an order of magnitude above the background electric noise at 1 Hz.

The steps outlined above represent a comprehensive approach to assessing the sensitivity of geophysical techniques. This approach is justified in the early projects, when there is little experience in sequestration technology in general, and monitoring in particular. As experience is gained it may be reasonable to adopt less rigorous approaches.

5.2.4 Supplemental Geophysical Techniques

In addition to the geophysical techniques discussed above, work in the GEO-SEQ project showed that crosswell seismic and EM technology, electrical resistance measurements, tilt, and streaming potential measurements should be included in the portfolio of geophysical methods available for storage monitoring.

Crosswell seismic and EM technology has developed over the past two decades to provide high spatial resolution images of the seismic velocities and electrical conductivity of the region between wells. Because of the cost and time involved in conducting surveys, it is not recommended that this technology be considered as a method of monitoring the entire reservoir storage volume. The potential application of these methods is in defining reservoir heterogeneity, leaks, and fluid saturation at higher spatial resolution than can be obtained from surface methods. The GEO-SEQ project field tested crosswell seismic and electromagnetic geophysical techniques for monitoring CO_2 storage at the Lost Hills, California, CO_2 EOR pilot (Hoversten et al., 2003). Results of this work (Figure 5.2) showed that these techniques could provide quantitative information on the saturation of CO_2 within the reservoir for the region between wells. The results also showed that the quantitative interpretation of saturation, particularly in the case of CO_2 EOR in which brine, oil, methane and CO_2 can be present as separate phases, required that the techniques be used jointly. Neither technique alone provides enough information to differentiate between the various phases as they change during a CO_2 EOR operation.

Numerical simulations showed that electrical resistance measurements made between wells could provide low-resolution images of CO_2 migration (Ramirez et al., 2003). In this technique, the steel casings of wells are used as electrodes and the resistance between wells is monitored to detect changes caused by CO_2 migration. Though low resolution, the method has the advantages of being low cost, with measurements made on the surface and with little or no interruption of normal field activities.

Numerical simulations also suggested that measuring the deformation (tilt) of the overburden above a storage project would provide additional information for monitoring purposes (Benson et al., 2004a). Tilt can be measured either on the ground surface or in wells, and it arises from changes in fluid pressure in a reservoir as CO_2 is injected. Inversion of the tilt measurements provides a low-resolution spatial image of where pressure has changed, and CO_2 has moved, in the reservoir.

Finally, numerical simulations indicated that streaming potential (SP) measurements might also provide additional monitoring information (Hoversten and Gasperikova, 2004). This method would measure the electric potential generated by displacement of brine by CO_2 in a storage reservoir. This is also a very low-resolution, but also low-cost form of monitoring measurement.

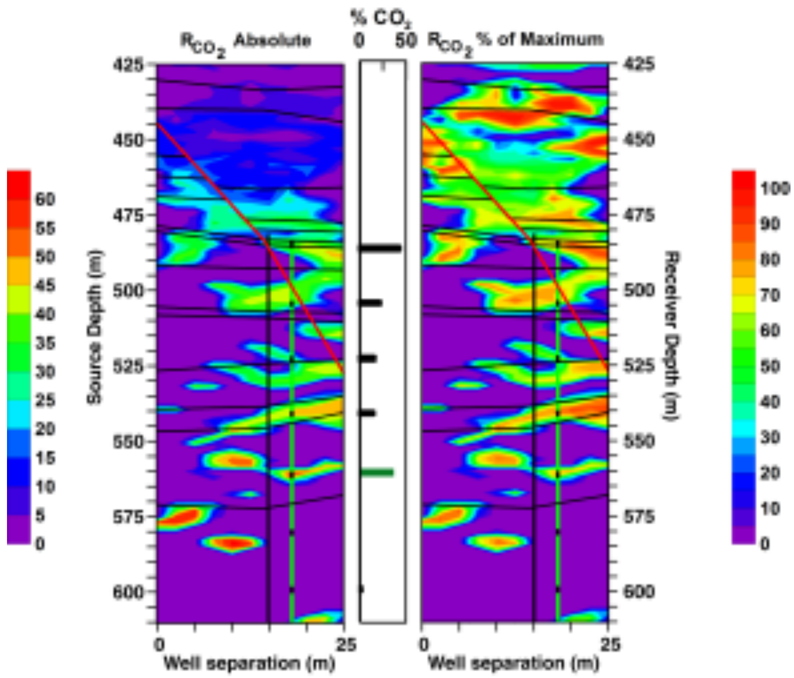


Figure 5.2. Predicted CO_2/oil ratio (R_{CO2}). Left side shows absolute R_{CO2}, right side shows R_{CO2} as a percent of the maximum value for the given pressure and temperature. Major unit boundaries are shown as black subhorizontal lines, estimated location of the previous water injection fracture is shown as a vertical black line, estimated location of the CO_2 injection fracture is shown as a vertical green line, perforation intervals for CO_2 injection are shown as black dots on top of the CO_2 injection fracture, and the mapped location of a fault zone is shown as a red diagonal line.

5.3 Summary of Monitoring Recommendations

Monitoring programs need to be designed for multiple purposes which change over the life cycle of a sequestration project. We recommend an approach in which methods are selected from a portfolio of techniques and tailored to the specific conditions and risks at the storage site. For example, if the storage project is in a depleted oil reservoir with a well-defined cap rock and storage trap, the monitoring program should focus on detecting leakage from the injection well, and locating any abandoned wells in the area to ensure that they are not leaking CO_2 to the land surface or shallow aquifers. On the other hand, if a project is in a brine-filled reservoir, the monitoring program should focus on tracking migration of the plume and ensuring that is does not leak through discontinuities in the cap rock.

We recommend that the portfolio of techniques include a basic and enhanced monitoring package, which can then be tailored to site-specific requirements. Techniques included in these packages reflect a substantial technology base in the petroleum industry that can be directly applied to monitoring of geologic sequestration projects. We recommend using geophysical techniques for imaging and monitoring of processes in the storage reservoir and in the overburden, with seismic methods being a central element of the basic and enhanced monitoring packages. A systematic set of steps should be followed in selecting the most appropriate set of geophysical techniques at a particular site. The basic and enhanced packages can be augmented by other geophysical techniques. We recommend crosswell seismic and EM techniques for applications requiring high resolution imaging. The applicability of other techniques, such as electrical resistance measurements, SP, and surface and borehole tilt measurements, should continue to be explored.

6. NEAR-SURFACE MONITORING

6.1 Introduction

Carbon dioxide seepage from a storage reservoir may create surface CO_2 fluxes of sufficient magnitude to distinguish from background CO_2 fluxes. The magnitude of CO_2 seepage fluxes will depend on a variety of factors, such as the style of emission (e.g., focused CO_2 flow along a near-surface fault or more diffuse emission through sediments) and wind and density-driven atmospheric dispersion. Anomalous surface CO_2 fluxes may be detected using several well-tested and readily available techniques. Relative to atmospheric gases, subsurface gases are less prone to dilution of the leakage CO_2 signal by background ecological and meteorological processes. As a result, monitoring for CO_2 migration from the storage reservoir should also focus on the shallow subsurface gas geochemistry. Several methods are available to measure surface CO_2 flux and subsurface CO_2 concentration and to determine the origin of CO_2.

6.2 Methods

6.2.1 Accumulation Chamber

The accumulation chamber (AC) method (e.g., Norman et al., 1992) is used to measure soil CO_2 flux at discrete locations. In this technique, an AC with an open bottom (cm^2 scale) is placed either directly on the soil surface or on a collar installed on the ground surface, and the contained air is circulated through the AC and an infrared gas analyzer (IRGA). The rate of change of CO_2 concentration in the chamber is used to derive the flux of CO_2 across the ground surface at the point of measurement. To map the spatial trends in surface CO_2 flux and estimate the total CO_2 emission rate from an area of interest, flux measurements should be made along grids and standard statistical methods should be applied to these data. Repeated measurements or automated systems can be used to characterize the temporal variability.

6.2.2 Eddy Covariance

Eddy covariance (EC), or eddy correlation, is a technique whereby high frequency measurements of atmospheric CO_2 concentrations at a height above the ground are made by an IRGA, along with measurements of micrometeorological variables such as wind velocity, relative humidity, and temperature (e.g., Anderson and Farrar, 2001; Baldocchi et al., 1996). Integration of these measurements allows derivation of the net CO_2 flux over the upwind footprint, typically m^2 to km^2 in area depending on tower height. The primary limitation of the EC method is that it assumes a horizontal and homogeneous surface, which is rarely found in natural systems. Also, the EC measurement should be made under statistically steady meteorologic conditions; morning and evening periods, as well as times of changing weather conditions should be avoided.

6.2.3 Shallow Sub-Surface Gas Geochemistry

Carbon isotopic compositions (carbon-13 and carbon-14) of vadose zone CO_2 reflect the compositions and relative proportions of the contributing sources and therefore can serve as effective tracers of CO_2 origin. Background isotopic compositions of CO_2 in the soil column will be most strongly affected by contributions from root respiration, decay of organic material, and the atmosphere. At subsoil depths, CO_2 can be produced to a lesser extent by groundwater degassing of CO_2 derived from atmospheric and soil-respired sources and decay of organic matter; the carbon-13 and carbon-14 signatures of this CO_2 will depend on the relative proportions of the CO_2 from the different sources and may be close to values measured above in the soil. The average carbon-13 value of CO_2 derived from burning of fossil fuels (e.g., Hoefs, 1987) will distinguish it from CO_2 derived from atmospheric and certain plant-derived (e.g., C_4) sources; however, it is similar to that of CO_2 from C_3 plants, and therefore alone would be problematic in distinguishing these sources. However, fossil-fuel-derived CO_2 is carbon-14 free. Leaking fossil CO_2 will therefore have a carbon-14 signal that is distinct from atmospheric and most biogenic respiration sources.

The bulk chemical composition of gases collected at soil and subsoil depths can also be used to assess whether CO_2 is produced at depth and if so, whether it is derived from nonbiologic respiration sources. In particular, numerical simulations of leakage and seepage show that CO_2 concentrations can reach very high levels in the shallow subsurface even for relatively modest CO_2 leakage fluxes (Oldenburg and Unger, 2003). Therefore, measurement of shallow subsurface CO_2 concentrations at numerous locations within a study area, and contouring of the resulting data, can likely be used to detect leaking CO_2 and delineate the geometry of the anomaly. Measurement of CO_2 concentration with depth will provide information about CO_2 production; an increase in CO_2 concentration below the soil indicates a CO_2 source at depth.

6.3 Recommendations

We recommend baseline studies as described above be carried out prior to CO_2 injection to characterize the background spatial trends and variability. Measurements should also be made repeatedly over time at several fixed "representative" sites to capture diurnal to seasonal variations. Special attention should be paid to making measurements near geologic features that may serve as conduits for gas flow from depth (e.g., geologic structures). Soil temperature and moisture should be monitored contemporaneously with fluxes. Atmospheric temperature, pressure, and wind speed and direction should also be measured at a weather station concurrently with soil CO_2 fluxes by the AC method. Correlation analysis of CO_2 flux and environmental parameters should be performed. Empirical relationships between correlated parameters should be established and used to predict the background CO_2 fluxes expected under a given set of environmental conditions. Gas-sampling profiles should be installed at selected locations within the study area and sampled, along with pre-existing wells within the study area, to characterize background subsoil gas chemistry and isotopic compositions (i.e., CO_2 concentration, O_2 concentration, carbon-13, and carbon-14 profiles with depth). If the study area meets the terrain conditions required by the EC method, then EC instrumentation should be deployed to characterize spatially averaged background CO_2 fluxes.

A range of measurements should be made during and after CO_2 injection into the storage reservoir at frequencies that will likely change with time following injection. During and after CO_2 injection, monitoring for CO_2 leakage and seepage should focus on rapid, economical, low-error measurements of soil CO_2 concentration and surface CO_2 fluxes along the grids established within the study area prior to injection. If terrain conditions allow, EC should be used in conjunction with AC and soil CO_2 concentration measurements. Where anomalously high soil CO_2 concentration and flux are located, gases should be sampled at regular intervals from the surface to the water table for chemical and carbon isotopic compositions. Overall, the observations of CO_2 concentration gradients with depth, CO_2 production distribution, surface CO_2 fluxes, and carbon isotopic compositions should be used together to determine if CO_2 derived from a deep fossil-fuel source consistent with a geologic CO_2 storage site is present. Details of our proposed monitoring strategy can be found in Oldenburg et al. (2003).

6.4 Natural and Artificial Tracers

Chemical tracers, both natural and introduced, can be used for *in situ* subsurface characterization as well as to calibrate and validate models used to (a) estimate CO_2 residence time, reservoir storage capacity, and storage mechanisms, (b) test injection scenarios for process optimization, and (c) assess the potential leakage of CO_2 from the storage reservoir. For example, reservoir characteristics (e.g., effective porosity) and *in situ* mass-transfer coefficients (e.g., diffusion coefficients) used in transport simulations can be constrained by simultaneous injection of multiple tracers.

Naturally occurring chemical constituents such as stable isotopes of O, H, C, S, and N, noble gases (He, Ne, Ar, Kr, Xe) and their isotopes, and radioactive isotopes (e.g., tritium, ^{14}C, ^{36}Cl, ^{125}I, ^{129}I, ^{131}I) can be used to assess fluid origin, migration, and interaction with host rocks along flow paths. For example, by monitoring how stable carbon and oxygen isotopes vary during and after CO_2 injection, geochemical processes involving CO_2 can be quantified (Cole et al., 2004). Introduced tracers (e.g., perfluorocarbon tracers, PFTs) can be injected into a system in different combinations, and at different concentrations and frequencies. By measuring changes in the concentration ratios of these tracers along the transport pathway, losses (e.g., sequestration through diffusion, reaction, or partitioning) and the mechanisms controlling the losses can be investigated (Fisher et al., 2003; McCallum et al., 2004). In particular, processes affecting solute transport such as diffusion into low-permeability materials, sorption, partitioning into nonaqueous phase liquids, partitioning into trapped gas phases, and leakage of the sequestered CO_2 can be constrained (Blencoe et al., 2001).

We investigated both introduced and natural stable isotope tracers in the context of process optimization for CO_2 sequestration. For introduced tracers, (1) the utility of multiple introduced tracers for enhancing and interpreting transport processes and breakthrough behavior was tested using experiments on cores to investigate the relationship between fracture characteristics and the processes of matrix diffusion and sorption, (2) the suitability of various PFTs for use in sequestration field tests was evaluated through assessment of known properties and estimated predictions of their behavior at conditions relevant to subsurface reservoirs, (3) a laboratory dynamic flow system was constructed and used for testing the interactions of tracers with reservoir materials under a range of temperature and pressure conditions relevant for subsurface CO_2 injection and sequestration, and (4) gas chromatograph analytical protocols for separation and detection of PFTs at low concentrations were established.

We recommend that natural stable isotopes be considered for use in concert with multiple injected PFTs as a tool to interpret subsurface CO_2 transport processes, breakthrough behavior, and monitor for possible leakage of CO_2 from the storage reservoir. Multiple gas tracers should be injected with CO_2 in pilot studies to further investigate the utility and sampling protocols of tracers.

7. SEQUESTRATION OF IMPURE CO_2 STREAMS

7.1 Introduction

The cost of geological carbon sequestration is dominated by the costs of separating CO_2 from the flue gas and compressing the separated CO_2. These two processes can account for 75% or more of the total cost. One possible approach to cost reduction is to sequester less-pure CO_2 waste streams that are less expensive or require less energy to separate from, for example, a flue gas or a coal gasification process. Typical co-contaminants in the gas waste stream are the acid-producing gases: H_2S, SO_2, and NO_2. The increased acidity produced by the co-contaminant gases in water could result in adverse effects to carbon sequestration (e.g., well-bore and caprock seal integrity compromised or porosity loss due to clay production or impeding the solubility and mineral CO_2 trapping mechanisms). However, at least one of these acid gases (H_2S, sour gas) is routinely injected for disposal purposes, so this suggests that other gases might also be co-injected.

7.2 Assessing Impacts

The geochemical effects of injecting co-contaminants need to be assessed as a basis for recommendations on the type and amount of these substances which could be tolerated in the injected CO_2 stream. The GEO-SEQ project conducted both equilibrium thermodynamic rock-water-gas-interaction geochemical simulations and chemical kinetic simulations.

In initial simulations, generic sandstone and carbonate reservoir rocks were defined. The feldspathic sandstone reservoir consisted of 88.5% quartz, 9% K-feldspar, 1% calcite, 0.5% siderite, 0.5% pyrite, and 0.5% muscovite. The siderite was added to the mix as a proxy for solid solution of Fe in the calcite. The muscovite was added as a proxy for all clay-like phases, e.g., illite. The carbonate reservoir consisted of: 49.25% calcite, 49.25% dolomite, 0.75% siderite and 0.75% pyrite. Both generic reservoirs were assumed to have 33% porosity. The simplified brine composition consisted of 0.7 m NaCl. The equilibrium thermodynamic and chemical kinetic (no transport) simulations were done using the codes EQ3/6 and REACT. These simulations permitted definition of generic waste-gas phase compositions based on actual field experience (in the case of H_2S) or chemically reasonable gas fugacities that result in aqueous pH values of no less than pH 1 (in the cases of NO_2 and SO_2). Numerous simulations were carried out for the two generic reservoirs assuming four injected gas compositions: CO_2, $CO_2 + H_2S$, $CO_2 + NO_2$ and $CO_2 + SO_2$ (Knauss et al., 2003a).

Later simulations (Knauss et al., 2003b) focused on the reactive transport processes expected to occur at the CO_2 injection pilot study in the Frio Formation in Texas. In the studies, the actual formation mineralogy and water chemistry was used. To study longer-term effects, simulations were carried out in which CO_2 injection was carried out for 5 years, followed by a 95-year post-injection phase of slow regional groundwater flow. Results suggested that significant amounts of carbon can be sequestered essentially permanently as carbonate minerals in the Frio Formation.

7.3 Recommendations

These preliminary simulations suggest that large amounts of co-injected H_2S should not prove problematic for a CO_2 injection process in terms of impact on sequestration. In the case of SO_2, if conditions allow the sulfur to be oxidized to sulfate (and this reaction is thermodynamically favored), only minor amounts of this gas could be tolerated, because of the extremely low pH generated. Potential for porosity loss resulting from the formation of anhydrite will also need to be assessed. For NO_2 the situation is intermediate between H_2S and SO_2; significantly more NO_2 than SO_2 could be tolerated, but the amount may be similarly limited by the potential for oxidation to nitrate.

ACKNOWLEDGMENTS

This report is based upon the technical contributions of the members of the GEO-SEQ team, including: Sally Benson, Larry Myer, Curt Oldenburg, Chris Doughty, Karsten Pruess, Jennifer Lewicki, Mike Hoversten, Erika Gasperikova, Thomas Daley, Ernie Majer, Marcelo Lippmann, and Chin-Fu Tsang of Lawrence Berkeley National Laboratory; Kevin Knauss, James Johnson, William Foxall, Abe Ramirez, and Robin Newmark of Lawrence Livermore National Laboratory; David Cole, Tommy Phelps, J. Parker, A. Palumbo, J. Horita, S. Fisher, and Gerry Moline of Oak Ridge National Laboratory; Lynn Orr, Tony Kovscek, K. Jessen, Y. Wang, J. Zhu, and M. Cakici of Stanford University; Susan Hovorka, Mark Holtz, and Shinichi Sakurai of Texas Bureau of Economic Geology; Bill Gunter and David Law of Alberta Research Council; and Bert van der Meer of TNO, The Netherlands. Sally Benson is acknowledged for leading the GEO-SEQ project. We thank Kenzi Karasaki and Marcelo Lippmann (LBNL) for constructive comments and reviews of this report. This work was supported by the Assistant Secretary for Fossil Energy, Office of Coal and Power Systems, of the U.S. Department of Energy (DOE) under Contract No. DE-AC03-76SF00098.

REFERENCES

Anderson, D.E. and and C.D. Farrar, Eddy covariance measurement of CO_2 flux to the atmosphere from an area of high volcanogenic emissions, Mammoth Mountain, California, *Chem. Geology, 177*, 31–42, 2001.

Baldocchi, D.D., R. Valentini, S. Running, W. Oechel, and R. Dahlman, Strategies for measuring and modeling carbon dioxide and water vapor fluxes over terrestrial ecosystems, *Global Change Biology*, *2*, 159–168, 1996.

Benson, S. M., R. Hepple, J. Apps, C.-F. Tsang, and M. Lippmann, Lessons Learned from Natural and Industrial Analogues for Storage of Carbon Dioxide in Deep Geological Formations, Lawrence Berkeley Laboratory Berkeley *LBNL-51170*, CA, 2002.

Benson, S.M., et al., The GEO-SEQ Project Results, Lawrence Berkeley National Laboratory, April 26, 2004a.

Benson, S.M., E. Gasperikova, and G.M. Hoversten, Overview of monitoring techniques and protocols for geologic storage projects, IEA Greenhouse Gas R&D Program Report, *in press*, 2004b.

Blencoe, J.G., D.R. Cole, J. Horita, and G.R. Moline, Experimental geochemical studies relevant to carbon sequestration. Proceedings ofthe First National Conference on Carbon Sequestration, Washington, DC, May 15–17, 2001.

Buckley, S.E. and M.C. Leverett, Mechanism of fluid displacement in sands, *Transactions AIME*, *146*, 107–116, 1942.

Cole, D.R., J. Horita, M.C. van Soest, B.M. Kennedy, and M.F. Morea, Gas chemistry and isotopic monitoring during the CO_2 injection test at Lost Hills, CA, *Applied Geochemistry*, submitted, 2004.

Doughty, C., K. Pruess, S.M. Benson, S.D. Hovorka, P.R. Knox, and C.T. Green, Capacity investigation of brine-bearing sands of the Frio Formation for geologic sequestration of CO_2, First National Conference on Carbon Sequestration, May 14-17, Washington DC, National Energy Technology Laboratory, 2001.

Doughty, C., S.M. Benson, and K. Pruess, Capacity investigation of brine-bearing sands for geologic sequestration of CO_2, Presented at GHGT-6 Conference, Kyoto, Japan, September 30–October 4, 2002.

Doughty, C. and K. Pruess, Modeling supercritical CO_2 injection in heterogeneous porous media, *Vadose Zone Journal*, *3*, 837–847, 2004

Fisher, L.S., D.R. Cole, J.G. Blencoe, G.R. Moline, J.C. Parker, and T.J. Phelps, High pressure flow-through column for assessing subsurface carbon sequestration, Proceedings of the Second Annual Conference on Carbon Sequestration, Alexandria, VA, 2003.

Hoefs, J., *Stable Isotope Geochemistry*, Springer-Verlag, New York, NY, 1987.

Hoversten, G.M. and Gasperikova, E., Non-seismic Geophysical Approaches to Monitoring, in *Carbon Dioxide Capture for Storage in Deep Geologic Formations - Results from the CO2 Capture Project, Volume 2: Geologic Storage of Carbon Dioxide with Monitoring and*

Verification; Elsevier Ltd., in press, 2004.

Hoversten, G.M., R. Gritto, J. Washbourne, and T.M. Daley, Pressure and fluid saturation prediction in a multicomponent reservoir using combined seismic and electromagnetic imaging: *Geophysics, 68*, 1580–1591, 2003.

Hovorka, S.D., C. Doughty, P.R. Knox, C.T. Green, K. Pruess, and S.M. Benson, Evaluation of brine-bearing sands of the Frio Formation, upper Texas Gulf Coast for geological sequestration of CO_2, First National Conference on Carbon Sequestration, May 14–17, Washington DC, National Energy Technology Laboratory, 2001.

Hovorka, S. D., C. Doughty, S.M. Benson, K. Pruess, and P.R. Knox, The impact of geological heterogeneity on CO2 storage in brine formations: a case study from the Texas Gulf Coast, In Geological Storage of Carbon Dioxide, S.J. Baines and R.H. Worden, Editors, Geological Society, London, *Special Publications*, *233*, in press, 2004a.

Hovorka, S.D., C. Doughty, and M.H. Holtz, Testing efficiency of storage in the subsurface: Frio Brine Pilot Experiment, Presented at Seventh International Conference on Greenhouse Gas Control Technologies (GHGT-7), IEA Greenhouse Gas R&D Programme, Vancouver, Canada, September 5–9, 2004b.

Jessen, K., A.R. Kovscek, and F.M. Orr, Jr., Increasing CO_2 storage in oil recovery, *Energy Conversion and Management*, *46,* 293–311, 2005.

Knauss, K.G., J.W. Johnson, and C.I. Steefel, Evaluation of the impact of CO_2, co-contaminant gas, aqueous fluid and reservoir rock interactions on the geologic sequestration of CO_2. *Chem. Geol*., submitted, 2003a.

Knauss, K.G., J.W. Johnson, and C.I. Steefel, CO_2 sequestration in the Frio Fm, TX: Evaluation of the impact of CO_2, co-contaminant gas, aqueous fluid and reservoir rock interactions. *Proceedings of the Second National Conference on Carbon Sequestration*, 2003b.

Kovscek, A.R., Screening criteria for CO_2 storage in oil reservoirs, *Petroleum Science and Technology*, *20*(7&8), 841–866, 2002.

Kovscek, A.R., and M.D. Cakici, Geologic storage of carbon dioxide and enhanced oil recovery II: Cooptimization of storage and recovery, *Energy Conversion and Management*, in press, 2005.

Kovscek, A.R. and Y. Wang, Geologic storage of carbon dioxide and enhanced oil recovery I: Uncertainty quantification employing a streamline-based proxy for reservoir flow simulation," *Energy Conversion and Management*, in press, 2005.

Laherrere, J., Distribution and evolution of "recovery factor," Presented at the Oil Reserves Conference, Paris, France, 11 November 1997 (http://www.dieoff.org/page183.htm).

McCallum, S.D., S. Fisher, D.R. Cole, J.G. Blencoe, G.R. Moline, J. Parker, D.E. Riestenberg, and T.J. Phelps, High pressure flow-through column for simulating fluid and gas flow in geologic material, Proceedings of the Third National Conference on Carbon Sequestration, Alexandria, VA, 2004.

Norman, J.M., R. Garcia, and S.B. Verma, Soil surface CO_2 fluxes and the carbon budget of a grassland, *J. Geophys. Res., 97*, 18,845–18,853, 1992.

Oldenburg, C.M., J.L. Lewicki, and R.P. Hepple, Near-surface monitoring strategies for geologic carbon dioxide storage verification, Lawrence Berkeley National Laboratory *LBNL-54089,* October 2003.

Oldenburg, C.M., and A.J.A. Unger, On leakage and seepage from geologic carbon sequestration sites: Unsaturated zone attenuation, *Vadose Zone Journal*, 2(3), 287–296, 2003.

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

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

Oldenburg, C.M., K. Pruess, and S.M. Benson, Process modeling of CO_2 injection into natural gas reservoirs for carbon sequestration and enhanced gas recovery, *Energy&Fuel*, *15*, 293–298, 2001.

Pruess, K, J. Garcia, T. Kovscek, C. Oldenburg, J. Rutqvist, C. Steefel, and T. Xu, Code intercomparison builds confidence in numerical simulation models for geologic disposal of CO_2, *Energy*, 29, 1431–1444, 2004

Pruess, K. and J. García, Multiphase flow dynamics during CO_2 injection into saline aquifers, *Environmental Geology*, *42*, 282–295, 2002.

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

Ramirez, A., R. Newmark, and W. Daily, Geophysical monitoring of carbon dioxide sequestration using electrical resistance tomography (ERT): Sensitity studies, *J. Environmental and Engineering Geophysics*, *8*, 187–208, 2003.

Sorey, M.L., Numerical modeling of liquid geothermal systems, Ph.D. dissertation, Dept. of Civil Engineering, University of California, Berkeley, 65 pp., 1975.