Figure 11. Numerical simulation of lateral displacement of a well in the South Belridge reservoir.

Large lateral displacements at about 1,000 feet depth occur due to slip on an interface with a friction angle of 6°. Lateral displacements reverse between the years of 1987 and 1992 Hilbert at al, 1996).

An example of the development of shear displacements near the interface between the reservoir and overburden when  $CO_2$  is injected is shown in Figure 12. The figure shows results of a numerical simulation of injection of  $CO_2$  from a single well into a brine-saturated layer. The shaded region in part b of the figure shows where shear stresses develop. The blue outline shows the extent of the  $CO_2$  plume. The volumetric expansion of coal with  $CO_2$  will have an additional component due to swelling associated with gas sorption. Experimental work indicates that  $CO_2$  causes more volumetric changes than methane. This will further alter the distribution of volumetric expansion resulting from repressurization.







- a) The model
- b) Outline of plume and region where shear stresses could cause slip on discontinuities

b)

If a pre-existing discontinuity cuts across the coal seam, model results show that slip can occur in the overburden, outside of the region of pore pressure change. Figure 13a shows a model in which there is a pressurized region between two discontinuities ("faults") dipping at 45°. Calculations were carried out using the coupled hydrologic/geomechanical simulator TOUGH-FLAC (Rutqvist et al, 2002). The faults were represented by "slip lines" with a friction angle of 25°. Figure 13b shows the shear slip on the faults as a function of depth. Due to the symmetry of the problem, the sense of motion is in one direction on one fault and in the opposite direction on the other fault. It is seen that the magnitude of the slip is greatest within the region of pressure increase and tails off quickly outside the region.



a) The model, showing a maximum pressure increase in the region of 2.6 times original pressure

#### Figure 13. Numerical simulation of slip on discontinuities resulting from a pressurized region

b) Shear slip on the faults

Slip on pre-existing faults and other discontinuities which intersect the coal seam are viewed as a likely scenario for generation of possible leakage paths for  $CO_2$ . Numerical sensitivity studies should be performed to evaluate the effects the dip and frictional properties of faults for representative coal seam pressure changes. It is important to capture coal volumetric changes due to sorption and desorption as part of these models.

While slip on pre-existing discontinuities creates a potential leakage path, further analysis is required to evaluate whether or not fluid flow will occur in conjunction with the slip. The risk of leakage will be increased if the magnitude of the slip is on the order of bed thickness. Geologic studies of fault seals have shown that fault movement which brings sand layers into contact can lead to fluid flow across faults from higher to lower pressure sands.

The degree to which slip will increase the potential for flow along faults and discontinuities is much less well understood. Laboratory tests have shown that shearing a rock fracture in rock will increase its permeability as a result of dilatancy. Since fracture surfaces are rough, shear displacements can lead to an opening of the fracture and an increase in permeability. Less dilatancy would be expected for faults or discontinuities filled with clay gouge. The relationship between stress state, slip magnitude, fault and fracture surface geometry and changes in hydrologic properties of infilling materials is an area requiring substantial additional basic research.

### 2.1.2.7 Predictive Quantitative Modeling (Task 2)

Quantitative risk assessment of  $CO_2$  sequestration in coal formations is fundamentally linked to predictive reservoir models. These models are necessary to estimate storage capacity, *in-situ* concentration, transport velocity, contacted volume, and the timeframe for filling, monitoring, and storage. The actual  $CO_2$  sequestration capacity of coal is largely dictated by how effectively injected gases contact and interact with the reservoir over the active project lifetime. The economic limit for methane recovery and  $CO_2$  storage is usually dictated by  $CO_2$  breakthrough, poor injectivity or a variety of other factors that make further operation economically prohibitive. Obvious factors, which may control contact and interaction, include the  $CO_2$ -coal capacity curve (isotherm), reservoir heterogeneity, the respective roles of convective and diffusive transport in a fractured medium,  $CO_2$  dissolution in water, and the effect of  $CO_2$  on reservoir permeability. In this study, the focus of quantitative modeling was placed on an actual field case (Tiffany field), the sensitivity study of key coal reservoir properties, and  $CO_2$  seepage from outcrops. This approach establishes a linkage between the first-hand knowledge of the actual field performance and a more realistic  $CO_2$  seepage forecast. For comparison and validation purpose, two reservoir simulators were used, the BP-Amoco GCOMP and the COMET2, developed by Advanced Resources International.

### 2.1.2.7.1 CO<sub>2</sub> Sequestration Modeling in Coal Formation – Tiffany Field

To date, BP-Amoco's Tiffany project in the San Juan Basin, Colorado is one of a few commercial demonstrations of enhanced methane recovery by gas injection. The Tiffany Field consists of 38 producer and 10 injector wells, Figure 14. Previously, a full-field simulation model has been developed by BP-Amoco's engineers, which incorporates the full geologic description. The description consists of five coal layers, some of which do not extend throughout the unit. Coal continuity and thickness are greatest in the northern portion of the field. The model provided good historical matches of the field performance during the primary production period. During the subsequent enhanced recovery phase, N<sub>2</sub> was injected into the field to accelerate methane recovery. The field model was proven inadequate in many aspects to accurately match field performance during the enhanced recovery phase. Most importantly, it failed to predict nitrogen breakthrough times and nitrogen cut responses at the majority of the responding producers. The actual  $N_2$  breakthrough times were much earlier than that predicted by the field model. For the field model to better match the  $N_2$  breakthrough times and  $N_2$  cut responses, the nitrogen injection would have to be restricted into one geological layer, which accounts for only 25% of the total pay. However, this would violate production-log data from the injectors, which showed nearly uniform injection into most perforated intervals. With BP-Amoco's proposal to supplement the nitrogen injection with the  $CO_2$  captured from its gas processing plant, it is vital that the field model be modified to reflect the actual field performance during gas injection so that the reservoir's true potential for enhanced recovery and CO<sub>2</sub> sequestration can be determined. For a more meaningful history match of the gas injection phase, instead, we developed a mechanistic model specific to CO<sub>2</sub> sequestration in the Fruitland coal of the Tiffany field.

### 2.1.2.7.1.1 Reservoir Performance Modeling

The validity of a particular model description will be determined from its ability to predict injected gas breakthrough times, cumulative production (methane, nitrogen, and carbon dioxide), and methane cut. The desired outcome of the process is an estimate of actual  $CO_2$  sequestration capability and project lifetime, which is in part dictated by the  $CO_2$  breakthrough time and the  $CO_2$  production cut with time. The amount of  $CO_2$  reprocessed will determine the economic limit for the project. Here we focus on a five-spot pattern in the northern part of the field where BP-Amoco plans to conduct a micro-pilot test in the near future. Figure 14 shows that the pattern consists of one in-pattern and three off-pattern injectors as well as four in-pattern and one off-pattern producers.

**Model Description.** To match the field performance during the enhanced recovery phase, we assumed that the high permeability streaks or conduits such as fractured and well-cleated coal within each geologic

layer contributed to the early nitrogen breakthrough. Although the high permeability pay dominates early production response, the long-term response is in large dictated by the amount of gas exchanged between high and low permeability packages. Instead of dividing each geologic layer into a fast and a slow component, we modified the model to include a high-permeability fast layer sandwiched between two low-permeability slow layers. In this mechanistic model, the fast layer represents well-cleated and fractured coal from all geological layers while the slow layers represent coal with little or no fracture development from the same geological layers. Also, the horizontal permeability ( $k_h$ ) in every grid block was rotated 45° counter clockwise to match the field permeability trend (north-south) in the simulation area.



Figure 14. 5-spot pattern area of the simulation study.

History Matching. During history matching, layer thickness and permeability were adjusted to control gas breakthrough. Vertical transmissibility between layers was manipulated to match late time response. Figure 15 shows that the mechanistic model matched the nitrogen breakthrough times and nitrogen cut reasonably well for all in-pattern producers. As shown in Figure 16, the model also did a good job matching the total gas production for all in-pattern producers. However, in order to match nitrogen breakthrough times and nitrogen cut, the vertical transmissibility had to be set to zero. This means that there was no communication between the fast and the slow layers. In this model, nitrogen was allowed to enter all three layers, not just the high-permeability fast layer. However, because the permeabilities of the slow layers were low and there is no communication between the fast and the slow layers, most of the injected nitrogen entered the high-permeability fast layer. Figs. 17, 18, 19 show the nitrogen saturations at the end of the nitrogen injection for the high-permeability fast layer (Layer 2) and the two lowpermeability slow layers (Layers 1 and 3), respectively. From Figure 17, we can clearly see the preferred permeability trends between the injectors and the producers. A comparison between Figure 17 and Figs. 18, 19 shows that at the end of the nitrogen injection, the nitrogen saturations were very high in the fast layer (Layer 2) and very low in the slow layers (Layers 1 and 3). This implies that the nitrogen in jection and enhanced methane recovery were mostly restricted to only about one third of the available pay.



Figure 20 shows that the mechanistic model did a reasonable job matching the bottomhole flowing pressures of all in-pattern producers during the enhanced recovery phase. However, it overestimated the bottomhole flowing pressures during the primary production period for all but one producer. As shown in Figure 20, the mechanistic model matched the pressure responses of Well 6644 reasonably well during both the primary and the enhanced recovery phases. Figure 17 shows that unlike other producers, this well is not linked to any



Figure 17. N<sub>2</sub> saturation at the end of history matching (Layer 2).



Figure 18.  $N_2$  saturation at the end of history matching (Layer 1).



Figure 19. N<sub>2</sub> saturation at the end of history matching (Layer 3).



Figure 20. Bottomhole flowing pressure.

injector on the preferred permeability trends in the simulation area. In other words, the well is least affected by the pressure increase during the gas injection. These findings suggest that the coal formation along the preferred permeability trends in the simulation area reacted differently to pressure depletion during the primary production period and gas injection during the enhanced recovery phase. During nitrogen injection, the elevated pressure caused coal fractures along the preferred permeability trends not only to expand but also to extend from injectors to producers. Even in the low-pressure regions near the producers, the permeabilities were higher than expected. This permeability enhancement may be additionally supported by matrix shrinkage caused by a lower equilibrium adsorbed nitrogen concentration (phase volume) versus methane. One possible way to satisfactory simulate both the primary and enhanced recovery phases is to apply negative skin factors to wells on the preferred permeability trends but not during the primary production period. Another way is to use one

stress-permeability relationship during primary production and a different one during enhanced recovery with gas injection. Also, different stress-permeability relationships might be required for different injector/producer pairs with different degrees of connectivity. Unfortunately, no such specific experimental data are available. Since the mechanistic model is based on field performance during the enhanced recovery phase with N<sub>2</sub> injection, it should be adequate in predicting the field performance during the subsequent  $CO_2$  and N<sub>2</sub> injections.

#### 2.1.2.7.1.2 Model Predictions

The important factors that control the project lifetime and actual CO<sub>2</sub> sequestration capability are the inert gas (CO<sub>2</sub> and N<sub>2</sub>) production and the inert gas cut with time. While methane production represents the income potential, it is the amount of inert gas reprocessed that actually determines the economic limit for a CO<sub>2</sub> sequestration project. We explored three different injection scenarios to study their effects on inert gas production and inert gas cut. In the first scenario, we simulated a continuous injection of pure CO<sub>2</sub>. In the second scenario, we simulated a continuous injection of the nitrogen processing capability at Tiffany Field. In this case, we alternated the injection between the N<sub>2</sub>-CO<sub>2</sub> mixture (Nov. through April) and pure CO<sub>2</sub> (May through Oct.). In all three scenarios, the simulation of future injections ran from 01/01/2002 to 01/01/2020. The total volume of gas injected is constant between scenarios.

**Daily CO**<sub>2</sub> **Production Rate and CO**<sub>2</sub> **Cut.** Figs. 21 and 22 summarize the daily CO<sub>2</sub> production rate and the CO<sub>2</sub> cut with time for the entire 5-spot pattern (excluding well 7201), respectively. Figure 22 shows that the CO<sub>2</sub> breakthrough occurred within one year after the injection began. After breakthrough, the daily CO<sub>2</sub> production rate for all three gas-injection scenarios increased continuously until the end of simulation period. Figure 21 also shows that the increase in daily CO<sub>2</sub> production rate was most significant for the case of continuous CO<sub>2</sub> injection. The CO<sub>2</sub> cut shown in Figure 22 basically followed the similar trend. For the case of continuous CO<sub>2</sub> injection, the CO<sub>2</sub> production cut increased quickly after breakthrough reaching 50% in less than 5 years. The increase was however, less dramatic for the other two gas-injection scenarios.



Figure 21. Daily total CO<sub>2</sub> production (excluding Well 7201).



**Daily Total Inert Gas Production Rate and Inert Gas Cut.** The amount of daily inert gas production that on-site facilities can handle is a limiting factor that determines the economic limit for a  $CO_2$  sequestration project. Figs. 23 and 24 show that for all three gas-injection scenarios, both the daily total inert gas (N<sub>2</sub> plus CO<sub>2</sub>) production and the inert gas cut rose quickly after the gas-injection began. Figure 24 shows that for the cyclic  $CO_2/N2-CO_2$  and continuous N2-CO<sub>2</sub> cases, the inert gas cut reached 50% in less than 2 years. The case of continuous  $CO_2$  injection however, showed a two-year delay in inert gas breakthrough (Figure 23). Also, in this case, the inert gas cut did not reach 50% until 4 years into the gas injection (Figure 24). This delay in inert gas breakthrough was caused by  $CO_2$  being twice as adsorbing on coal than methane.





Figure 23. Daily total inert gas production (excluding Well 7201).

Figure 24. Daily total inert gas cut (excluding Well 7201).

**Methane Production.** Figure 25 shows that the methane production followed a gradual decline trend during the gas-injection period. For the case of continuous  $CO_2$  injection, the methane production showed an initial jump and then basically followed the same decline trend as in other gas-injection scenarios. Figure 26 shows that the cumulative amount of methane recovered during the gas-injection period was proportional to the  $CO_2$  content in the injection gas. (The higher the  $CO_2$  content in the injection gas, the higher the methane recovery.) This is consistent with the theory that  $CO_2$  is more efficient in displacing methane from coal formation.





Figure 25. Daily total methane production (excluding Well 7201).

Figure 26. Total cumulative methane production (excluding Well 7201).

### 2.1.2.7.1.3 Summary

- 1. A mechanistic field model was developed to match the field performance of a 5-spot pattern in the northern part of the Tiffany Field where BP-AMOCO plans to perform a micro-pilot test.
- 2. The mechanistic model consists of one high-permeability fast layer sandwiched between two lowpermeability slow layers. In this mechanistic model, the fast layer represents well-cleated and fractured coal from all geological layers while the slow layers represent coal with little or no fracture development from the same geological layers.
- 3. The model successfully matched the performance of the 5-spot pattern during the enhanced recovery period ( $N_2$  injection). However, in order to match nitrogen breakthrough times and nitrogen cut the vertical transmissibility had to be set to zero. During gas injection, nitrogen was allowed to enter all three layers, not just the high-permeability fast layer. However, because the permeabilities of the slow layers were low and there is no communication between the fast and the slow layers, most of the injected nitrogen entered the high-permeability fast layer. This suggests that the future gas injection and  $CO_2$  sequestration may be restricted to only one third of the total available pay.
- 4. During nitrogen injection, the elevated pressure caused the coal fractures on the preferred permeability trends not only to expand but also to extend from injectors to producers. Even in the low-pressure regions near the producers, the permeabilities were higher than expected.
- 5. The mechanistic model predicted early  $CO_2$  breakthrough with high  $CO_2$  cut during future gas injections. This suggests that the actual  $CO_2$  sequestration capability of the Tiffany Field may not be as high as originally expected. This is a direct consequence of the reduction of the available pay in the mechanistic model.
- 6. The mechanistic model also predicted early inert gas (N<sub>2</sub> plus CO<sub>2</sub>) breakthrough and high inert gas cut during future gas injections. The high volume of inert gas produced could overwhelm the reprocessing capability resulting in early termination of the project.

### 2.1.2.7.2 Effects of Coal Formation Properties

Methane in a coal reservoir is stored by adsorption, held nearly immoveable against the micropore face and is producible only by reduction of pressure or an increase in temperature, which is quite different and more complex than a conventional sandstone or carbonate reservoir. The porosity of coal is a micropore system, called the cleat system, interconnected throughout the coal matrix. The cleat system is normally described using the Warren and Root concept, wherein the matrix blocks are considered to be rectangular parallelepipeds or cubes, and the fractures are considered to be parallel faces between the matrix blocks. Once the methane desorbs from coal matrix and moves into the cleat system, transport follows Darcy's Law for fluid flow through porous media. As observed in the Tiffany field, coal structure could change dramatically during the enhanced methane recovery by gas injection. The elevated pressure may cause the coal cleats on the preferred permeability trends not only to expand but also to extend from injectors to producers. Even in the low-pressure regions near the producers, the permeabilities appeared higher than expected. This suggests that simulation models that can very well match primary production may not be accurate in forecasting the enhanced methane recovery by  $CO_2$  or  $N_2$  injection. Besides permeability, other reservoir properties can also have significant effects on methane recovery. In this section, we present and discuss the findings of a simulation study in which the sensitivity of each key reservoir parameter to methane recovery was simulated. The strategy is to use the basin-wide Fruitland reservoir description from the 3M project (Applied Hydrology Associates, Inc., 2000 and Questa Engineering Corporation 2000) for the primary production and use the Tiffany field performance as the guideline for gas injection to investigate the effects of key reservoir parameters.

### 2.1.2.7.2.1 Basin-Wide Reservoir Description

**3M Project**. The 3M Project **3 M's** stand for **Mapping**, **Modelling**, and **Monitoring**. The 3M Project has been designed as a continuous, decades-long project to provide tools that will develop a more comprehensive understanding of gas and water production from the Fruitland Formation and potential

impacts on the Frutiland Formation outcrop in the Colorado portion of the San Juan Basin. These tools have progressed to adequately support Colorado Oil and Gas Conservation Commission's regulatory implementation of the referenced 160-acre well density application if it is approved.

Questa Engineering Corporation has prepared a basin-wide coalbed methane reservoir model of the Colorado portion of the San Juan Basin for the Southern Ute Indian Tribe, the Colorado Oil and Gas Conservation Commission, and the Bureau of Land Management. This model, called the 3M CBM MODEL, simulates the effects of production from all existing and proposed Fruitland coal wells in Colorado. Figure 27 shows the grid system of 369 by 137 used by the 3M Model. The effects of dewatering, gas adsorption and desorption, and historical production are included in the model. The 3M Model includes up to 20 years of production data from 1,060 wells, 4,870 pressures from 591 wells, thickness data from 742 wells, and water chemistry from 572 wells. The model builds on information from a groundwater or hydrologic model, prepared by Applied Hydrology Associates, covering the entire basin. The groundwater model simulates pre-production conditions for the reservoir model and provides estimates of the amount of groundwater flowing through the Fruitland Coal hydrologic system. The description of the Fruitland outcrop was included in the 3M project. A detailed discussion will be given in the next section.



Figure 27. Outline of the 3M Model grid compared to a township and range grid (Questa Engine ering Corporation, 2000).

**Reservoir Property Probability Distributions.** A database has been created to store the basin-wide reservoir property data from the 3M Model, which includes the coal thickness, initial pressure, initial water saturation, temperature, permeability, and porosity distributions on a grid system of 369 by 137 using one-sixth of a mile grid blocks. It covers the Colorado portion of the San Juan Basin. These data can be used, for any selected region, to estimate the original methane in place and the maximum  $CO_2$  sequestration capacity. Reservoir properties from the 3M Model were generally estimated through analysis of historical production from wells. Permeabilities were estimated from peak gas or water rates, with assumed completion effic iencies based on completion type. Porosities were estimated from extrapolation of produced water trends. Coal thickness and structure were determined from well logs. Gas contents were compiled from public information where available, and through matching performance in some areas where sufficient data are available to allow gas content to be reliably determined. Figure 28 and Figure 29 are the probability distributions of the six reservoir parameters from the Fruitland coal in the Colorado portion of the San Juan Basin and in Tiffany field, respectively. The probability distributions are essential information in quantifying how much  $CO_2$  could be sequestrated in any selected region and in risk analysis related Monte Carlo simulation.



Figure 28. The probability distributions of Fruitland reservoir properties in Colorado portion of the San Juan Basin.



Figure 29. The probability distributions of Fruitland reservoir properties in Tiffany field.

#### 2.1.2.7.2.2 Effects of Key Reservoir Parameters

**Isotherms**. The capacity of the coal matrix to store gas as a function of pressure is described by the Langmuir adsorption isotherm. The gas content adsorbed at a specified pressure is defined by Eq. (1):

$$C_m = \frac{V_L p}{p_L + p} \qquad (1)$$

where  $C_m$  is the matrix gas concentration (scf/ton coal),  $V_L$  is the Langmuir volume constant, (scf/ton),  $p_L$  is the Langmuir pressure constant (psia), and p is the coal formation pressure (psia).  $V_L$  is the maximum volume of gas a coal can adsorb into the matrix surface area.  $P_L$  is the pressure at which the storage capacity of the coal is equal to one-half the Langmuir volume  $V_L$ . The constants in the Langmuir adsorption isotherm equation are determined by fitting desorption data obtained in the laboratory and are specific for any given coal. Figure 30 shows a typical sorption isotherm for coal from the San Juan Basin.

Methane production from coal beds can be enhanced by injection  $CO_2$  to displace or N2 to strip the methane from the coal and accelerate methane production at higher pressures. The mechanism by which  $CO_2$  or  $N_2$  can enhance the coalbed methane recovery process, and  $CO_2$  is sequestered, is a complex mix of physical and chemical interactions that strive to achieve equilibrium simultaneously in the sorbed state and in the gaseous state. Coal has the capacity to hold considerably more  $CO_2$  than either methane or nitrogen in the adsorbed state (in an approximate ratio of 4:2:1). This is because stronger forces of attraction exist between coal and  $CO_2$  than between coal and methane or nitrogen. As a result, in the presence of multiple gases (e.g.,  $CO_2$ ,  $CH_4$  and  $N_2$ ), the amount of each in the adsorbed state would be in approximately these proportions. However, since any injected gas for ECBM is unlikely to be of exactly that composition, a partial-pressure *dis*equilibrium will be created in the gaseous phase (i.e., in the coal cleat system). Adsorption/desorption of individual components will occur until the gases in both the sorbed and gaseous states are each in equilibrium, and are in equilibrium with each other.



Figure 30. San Juan Basin Fruitland coal sorption isotherms.

Both GCOMP and COMET2 use the extended Langmuir approach to model multi-component sorption behavior. Some research suggests that the extended Langmuir model may not be as accurate as expected when water is also present. From our simulation experience, attention should be placed on 1) isotherms measured in laboratory are usually from dry coals. The gas content is much higher than that in actual reservoir conditions; 2) The best way to estimate the actual formation isotherms is to estimate the methane isotherm by history matching the primary methane production and then to rescale the laboratory measured  $CO_2$  and  $N_2$  isotherms according to the ratio of the field and measured methane isotherms; and 3) water saturation in coal matrix could be significant to the adsorption/desorption process and is not considered in the extended Langmuir model.

**Initial Reservoir Pressure and Gas Content.** The initial methane in place consists of free gas in the cleat system and the adsorbed gas on coal matrix. If the methane isotherm is available, from laboratory or field history matching, the adsorbed gas (initial gas content) can be calculated from the initial reservoir pressure by Eq. 1. Initial reservoir pressure data are generally considered as reliable data. As shown in Fig. 30, the initial gas content is usually not very sensitive to the initial pressure if the pressure is high enough, greater than 1200 psi in the Tiffany field, for example. Therefore, the estimation of initial gas content is largely determined by the methane isotherm.

**Porosity and Permeability.** During the primary production, the gas to water production ratio is very sensitive to cleat porosity because the cleat porosity is usually very small and initially filled with water, such as in Tiffany field. About 80 percent of Fruitland coal porosity, in the Colorado portion San Juan basin, is less than 0.03% as shown in Fig. 28 while the coal porosity is almost entirely less than 0.01% in Tiffany field. As demonstrated by history matching the five production wells in the Tiffany pilot area, the permeability aspect ratio of face cleat permeability to butt cleat permeability could have significant effect on gas and water production rates. Fig. 31 shows that using the permeability data from the 3M project,

provided only by a single permeability value, of the face cleat permeability, an acceptable history match can be achieved by adjusting the butt cleat permeability (and therefore the permeability aspect ratio.)



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Figure 31. Effect of the permeability aspect ratio to gas and water production rates.

**Relative Permeabilities.** For conventional oil and gas reservoirs, relative permeabilities are among the most important parameters. A change in relative permeabilities could dramatically affect the simulation prediction. But for coalbeds, injected  $CO_2$  could be entirely adsorbed by the coal before reaching a production well if a large  $CO_2$ -coal contact volume, i.e. a large coal thickness, is assumed. To verify this, a dual model with one injection well and one production well on a 160-acre well spacing was used for simulating nitrogen injections. When a net pay thickness of 50 ft was placed (the average coal thickness in Tiffany field) Fig. 32 shows that little difference was observed even with a large variety of gas relative permeability sets. In Fig. 32, Ng is the parameter used to define a gas relative permeability curve by Eq. (2).

 $k_{rg} = \left(1 - s_w\right)^{N_g} \quad (2)$ 



Figure 32. Nitrogen production cuts (left) simulated with different relative permeability curves (right).

 $CO_2/N_2$  Contacted Volume in Coal. The early N<sub>2</sub> breakthrough and high N<sub>2</sub> cut observed in the Tiffany field suggest that the elevated pressure during gas injection caused the coal fractures on the preferred permeability trends not only to expand but also to extend from injectors to producers. Consequently, the injected inert gas (CO<sub>2</sub> or N<sub>2</sub>) may only contact a small portion of the entire pay volume. A dual model with one injection well and one production well on a 160-acre well spacing was used to simulate the effect of coal net pay thickness here the coal volume on the inert gas production cut. In comparison with the actual field performance, it suggests that only about one tenth to one fifth of the total pay interval may be contacted by injected inert gas (CO<sub>2</sub> or N<sub>2</sub>).



Figure 33. Nitrogen production cuts simulated with different coal net pay thicknesses (left). The comparison between nitrogen and CO<sub>2</sub> breakthrough times (right).

#### 2.1.2.7.2.3 Summary

- 1. A database has been created to store the basin-wide reservoir property data from the 3M Model, which includes the coal thickness, initial pressure, initial water saturation, temperature, permeability, and porosity distributions on a grid system of 369 by 137 using one-sixth of a mile grid blocks. It covers the Colorado portion of the San Juan Basin. Base-wide and regional probability distributions can be obtained from the database.
- 2. Laboratory measured isotherms on dry coals should be rescaled by matching field history performance. Without rescaling, the simulation forecast of  $CO_2$  or  $N_2$  injection may be not accurate.
- 3. Initial reservoir pressure data are generally reliable and the initial gas content is not very sensitive to the initial pressure if the pressure is high enough, greater than 1200 psi in the Tiffany field. Therefore, the estimation of initial gas content is largely determined by the methane isotherm.
- 4. In history matching the CO<sub>2</sub> production cut, the gas relative permeability may not be significant if a large CO<sub>2</sub>-coal contact volume, i.e. a large coal thickness, is assumed.
- 5. During the primary production, the gas to water production ratio is very sensitive to cleat porosity because the cleat porosity is usually very small and initially filled with water, such as in the Tiffany field.
- 6. As demonstrated by history matching the five production wells in the Tiffany pilot area, the permeability aspect ratio (face cleat permeability to butt cleat permeability) could have a significant effect on gas and water production rates. Using the permeability data from the 3M project, provided only a single value, of the face cleat permeability, an acceptable history match can be achieved by adjusting the butt cleat permeability (and therefore the permeability aspect ratio.)
- 7. The early  $N_2$  breakthrough and high  $N_2$  cut observed in the Tiffany field suggest that the elevated pressure during gas injection caused the coal fractures on the preferred permeability trends not only to expand but also to extend from injectors to producers. Consequently, the injected inert gas  $(CO_2 \text{ or } N_2)$  may only contact a small portion of the entire pay volume. A dual model with one injection well and one production well on a 160-acre well spacing was used to simulate the effect of coal net pay thickness (here the coal volume) on the inert gas production cut. In comparison with the actual field performance, it suggests that only about one tenth to one fifth of the total pay interval may be contacted by injected inert gas  $(CO_2 \text{ or } N_2)$ .

### 2.1.2.7.3 Assessment of CO<sub>2</sub> Seepage from Outcrop

Methane seepage has already been observed from many locations along the north and west Fruitland outcrops (Advanced Resources International, Inc., 1994, Amoco 1994 and Oldaker, P. 1999). The concern is that injected  $CO_2$  could likely follow the methane seepage paths and seeps from the outcrop. In this section, a representative seepage model was developed. The model represents a simplified geological setting of the north and west Fruitland outcrops. The 3M Model predicted methane seepage rates were used as the seepage boundary conditions when no  $CO_2$  injection occurs. The nitrogen injection performance in Tiffany field suggests that only a small portion of the coal net pay volume may have been contacted with the injected gas. This guideline was used in creating some extreme seepage scenarios.

#### 2.1.2.7.3.1 Fruitland Outcrop

Geologic surface mapping of the Fruitland Formation outcrop is available (Wray, L.L. 2000). Prior to the initiation of the 3M Project approximately 22 miles of the Fruitland Formation outcrop was mapped from the New Mexico state border northeastward to the northern boundary of the Southern Ute Indian Tribe (SUIT) Reservation. The 3M Project extended outcrop mapped approximately 26 more miles northeastward to the eastern edge of the developed portion of the basin near the La Plata County – Archuleta County line. The Colorado Geologic Survey performed the outcrop geologic surface mapping and published the maps, measured sections, and stratigraphic cross sections in an open-file report. The location of the Fruitland outcrop was obtained from AHA, who digitized available USGS base maps.

**Methane Seepage Sites.** The 3M Model predicted that methane seepage has occurred, and will continue to occur, in areas where it has already been observed: the Pine River area, South Texas Creek, and along the west side (Valencia Canyon and Soda Springs areas), Fig. 34. Additional seeps may start east of the Pine River and in other areas to be determined, but most of the seepage in the model occurs near existing seep locations. When the outcrop was modeled with a perfect connection to the basin, the simulated methane seepage was 10 to 100 times higher than observed levels of seepage. These results indicate that such a perfect connection does not exist; otherwise, there would be much higher seepage. This restricted connection may be related to the structural hingeline between the coals in the basin versus the outcrop, stratigraphic changes in the coal, coalbed geometry, capillary pressure or relative permeability effects, multi-layer effects, high absorptive capacity in the shallow coals, or other unidentified causes. By modifying the simulated connection of the outcrop to the basin, the 3M Model has been calibrated to match observed gas seepage locations and rates. Fig. 34 shows the seepage sites and their rates by 2030 predicted by the 3M Model. Fig. 35 provides statistical distributions of methane seepage rates by seepage sites and by mile.



Figure 34. 3M Model predicted methane seepage sites and rates along the Fruitland coal outcrop (Questa Engineering Corporation, 2000).



Figure 35. Statistical distributions of methane seepage rates.

**Groundwater Recharge.** The annual precipitation in the Colorado portion of San Juan basin varies from 10 inches per year to 30 inches per year. Along the Fruitland outcrop, an average precipitation of 22 inches per year was used in this study. Previous researchers have shown that the recharge rate is only about one percent of the precipitation. Most recharge water migrates to adjacent rivers and creeks. An estimated 15 percent of the recharge water actually enters the basin. Based on above statistics, an estimated outcrop recharge rate of about one hundred barrels per mile per day was calculated and used in a representative seepage model.

**Flow Barriers and Baffles.** A number of flow barriers or baffles were known to be present in the basin, based on previous work by numerous investigators and operators. Other barriers or baffles were

introduced based on the presence or absence of water or gas seepage in particular areas. Fig. 36 shows the identified flow barriers and baffles that are included in the 3M Model.



### 2.1.2.7.3.2 A Representative Seepage Model

**Model Configuration.** Fig. 37 shows the configuration of the representative seepage model. The model is a two-layer, 1.25 mile by 12 mile strip with a down dip of 2.92 degree from the outcrop to the bottom of the basin. There is a total of 240 (5 by 48) grids in each layer with a grid size of 0.25 mile (1320 ft). The model consists of two seepage wells to represent the 1.25 mile outcrop and three water recharge wells placed just below the water table. A total of 28 production wells were placed in the strip with a 160-acre well spacing. Production wells were only perforated in the top layer and water recharge wells were only perforated in the bottom layer. The thickness ratio between top and bottom layers was set to 10:1.



### 2.1.2.7.3.3 Seepage Simulation

**Preferable Scenarios.** Because of the capillary pressure force, a water saturated zone above injected  $CO_2$  could help to prevent  $CO_2$  migrating up to outcrops. Illustrated in Fig. 37, 28 production wells were placed on a 160-acre well spacing where the top two wells were more than 2 miles away from the water table because the grid size is 0.25 mile (1320 ft). Various  $CO_2$  injection schemes have been simulated, which includes alternated 2 to 14 production wells to  $CO_2$  injection wells. A total thickness of 52 ft, about the average for Fruitland coal, was used for all cases. Under all cases, no  $CO_2$  seepage was predicted from the outcrop. As shown in Fig. 38, also no significant change in methane seepage was predicted by simulations even when the coalbed has a 2~5 ft pay interval (the  $CO_2$ -coal contact volume is very small.)



Figure 38. Simulated methane seepage under preferable CO<sub>2</sub> injection scenarios.

**Extreme Scenarios.** To simulate the worst case scenarios,  $CO_2$  injection wells were placed above the water table. Two  $CO_2$ -injection wells were placed with a rate of 3200 Mcf/day for each one. All simulations started with 30 year injection of  $CO_2$  then simulated for another 200 year without  $CO_2$  injection. Fig. 39 and Fig. 40 show that a large  $CO_2$  and methane breakthrough could happen if the  $CO_2$  injection wells are too close to the outcrop, within 2 miles. Fig. 41 and Fig. 42 show that  $CO_2$  and methane seepage rates reduced significantly when the injection wells were located more than 2 miles away from the outcrop. If the rescaled isotherms of  $CO_2$  and methane are proper then injecting  $CO_2$  from at least 3 miles away of the outcrop should be required.



Figure 39. Methane and CO<sub>2</sub> seepage rates vs. coal net pay thicknesses where the injection is one mile from the outcrop.



Figure 40. Methane and CO<sub>2</sub> seepage rates vs. coal net pay thicknesses where the injection is 1.5 mile from the outcrop.



Figure 41. Methane and CO<sub>2</sub> seepage rates vs. injection distances and 2 ft net pay.



Figure 42. Methane and CO<sub>2</sub> seepage rates vs. injection distances and 5 ft net pay.

#### 2.1.2.7.3.4 Summary

1. A representative seepage model was developed. The model is a two-layer, 1.25 mile by 12 mile strip with a down dip of 2.92 degree from the outcrop to the bottom of the basin. The model consists of two seepage wells to represent the 1.25 mile outcrop and three water recharge wells placed just below the water table. A total of 28 production/CO<sub>2</sub>-injection wells are included on a 160-acre well spacing.

- 2. Under preferable scenarios, if CO<sub>2</sub> injection wells are placed below and at least 2 miles away from the water table, no significant change in methane seepage has been predicted by simulations even under an assumption of 2~5 ft pay interval thereby the CO<sub>2</sub>-coal contact volume is very small.
- 3. To simulate the worst case scenarios,  $CO_2$  injection wells have been placed above the water table. The results show that a large  $CO_2$  and methane breakthrough could happen if the  $CO_2$  injection wells are too close to the outcrop, within 2 miles. If the rescaled isotherms of  $CO_2$  and methane are proper then injecting  $CO_2$  from at least 3 miles away of the outcrop will be safe. All simulations runs were started one hundred year stabilization followed by 30 year injection of  $CO_2$ in two wells at a rate of 3200 Mcf/day. After  $CO_2$  injection been stopped we simulated for another 200 year.

### 2.1.2.8 Conclusion

### 2.1.2.8.1 Geomechanical Study (Task 1.0.3)

Geomechanical processes lead to risks of developing leakage paths for  $CO_2$  at each step in the process of developing a coal bed methane project for methane production and eventual  $CO_2$  sequestration. Though each of the risks identified in this study needs to be evaluated for specific sites, the following general conclusions have been drawn from this review:

- Conventional techniques are available to minimize risk of leaks in new well construction though additional study should be devoted to establishing best practices for the height of cement behind production casing; risk of leakage is higher for old wells converted to injectors.
- Risks of leakage is much higher for open cavity completions than for cased well completions.
- Coal properties and available technology should minimize the risk that hydrofractures, used as part of completion, will grow out of interval; techniques to monitor fracture height need further development.
- The processes of depressurization during dewatering and methane production, followed by repressurization during CO<sub>2</sub> injection, lead to risks of leakage path formation by failure of the coal and slip on discontinuities in the coal and overburden.
- The most likely mechanism for leakage path formation is slip on pre-existing discontinuities which cut across the coal seam. Sensitivity studies need to be performed to better evaluate this risk.
- Relationships between the amount of slip and the increase in flow (if any) along a discontinuity need to be developed.

### 2.1.2.8.2 Predictive Quantitative Modeling (Task 2)

The mechanism by which  $CO_2$  can enhance the coalbed methane recovery and at the same time sequester  $CO_2$  in coal matrix, is a complex mix of physical and chemical interaction process. More research in both laboratory experiments and field demonstrations are needed before  $CO_2$  sequestration in coal can become an applicable industry practice. Consequently, future improvements to simulation models are also needed, especially in modeling coal structure reactions to gas injection and the multiple component adsorption/desorption processes. The main conclusions from this simulation study are:

- Reservoir models that match the primary production history may not be accurate in forecasting CO<sub>2</sub> or N<sub>2</sub> injection because of the reaction of coal structure to gas injection.
- The simulated early inert gas (N<sub>2</sub> plus CO<sub>2</sub>) breakthrough and high inert gas cut during future gas injections suggests that the future gas injection and CO<sub>2</sub> sequestration may be restricted to only one third of the total available pay. Therefore the actual CO<sub>2</sub> sequestration capability of the Tiffany Field may not be as high as originally expected.
- Isotherm data are the most important data in coalbed methane related simulations. Laboratory measured isotherms on dry coals should be rescaled by matching field history performance. Without rescaling, the simulation forecast of CO<sub>2</sub> or N<sub>2</sub> injection may not be accurate.
- No significant change in methane seepage from outcrop has been predicted by simulations if CO<sub>2</sub> injection wells are placed below and at least 2 miles away from the water table. However, under certain conditions, simulation predicted that a large CO<sub>2</sub> and methane breakthrough could happen if the CO<sub>2</sub> injection wells are too close, within 2 miles, to the outcrop. Consequently, any CO<sub>2</sub> injection within a distance of 3 miles from outcrop should be considered with high risk.

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# 2.1.3 HSE Risk Assessment of Deep Geological Storage Sites

Report Title CO<sub>2</sub> Capture Project - An Integrated, Collaborative Technology Development Project for Next Generation CO<sub>2</sub> Separation, Capture and Geologic Sequestration

### Lawrence Berkeley National Laboratory HSE Risk Assessment of Deep Geological Storage Sites

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Address:	One Cyclotron Road, MS 90-1116 Berkeley, CA 94720, USA

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### 2.1.3.1 Abstract

We describe here a coupled modeling framework for simulating carbon dioxide (CO<sub>2</sub>) leakage and seepage in the subsurface and in the atmospheric surface layer for risk characterization. The results of model simulations can be used to quantify the two key health, safety, and environmental (HSE) risk drivers, namely seepage flux and near-surface concentrations. The methodology and structure of the coupled modeling framework are based on the key concepts that (1) the primary HSE risk is in the nearsurface environment where humans, animals, and plants live, (2) leakage and seepage flow processes are coupled, and (3) the main risk drivers are  $CO_2$  flux and concentration. The coupled modeling framework is built on the integral finite difference multiphase and multicomponent reservoir simulator TOUGH2 and models CO<sub>2</sub> and air in both subsurface and atmospheric surface-layer regions simultaneously. The surface-layer modeling assumes CO<sub>2</sub> dispersion is passive and uses the logarithmic wind profile assumption and advective-dispersive transport equation. Surface-layer dispersivities are calculated from the Pasquill-Gifford curves and Smagorinski Model. We have tested the coupled modeling framework for gas-mixture physical property prediction, surface-layer transport and dispersion, and transition from passive to active flow. We demonstrate the model for a coupled subsurface-surface-layer system and show the large dispersion and dilution expected in the atmospheric surface layer. Whereas  $CO_2$ concentrations in the subsurface can be extremely high, surface layer winds easily reduce  $CO_2$ concentrations to trace levels for the fluxes investigated. Even for calm conditions, density-driven CO<sub>2</sub> flow appears capable of preventing  $CO_2$  concentrations from reaching significant levels over flat and horizontal ground surfaces. We also observe in the demonstration problem the reflux of  $CO_2$  by infiltrating rainwater containing dissolved CO<sub>2</sub>, a process that shows the importance of using a coupled modeling framework. Finally, we compared downwind concentrations for 2-D and 3-D simulations of surface-layer dispersion and observed approximately a factor of two decrease in CO<sub>2</sub> concentration for the 3-D simulation relative to the 2-D simulation.

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### 2.1.3.4 Introduction

The assessment of health, safety, and environmental (HSE) risks is an essential part of planning and permitting for geologic carbon sequestration projects. Risk assessment in general has been described as a three-part process involving the following: (1) definition of scenarios of what can go wrong; (2) assessment of the likelihood of those scenarios; and (3) assignment of a measure of severity to the consequences arising from a given scenario. When applying this approach to substances that pose a hazard to human health and ecosystems, the risk assessment process includes hazard identification and risk characterization. For geologic carbon sequestration, a primary HSE hazard is  $CO_2$  leakage and seepage from the storage site leading to exposure by humans, plants, and animals to elevated  $CO_2$  concentrations in air and water. The fundamental challenge of risk characterization is the estimation or calculation of elevated  $CO_2$  concentrations to which humans, plants, and animals may be exposed in the given failure scenarios.

In Figure 2.1.3.4(1), we present a schematic of some of the important features that may affect HSE risk characterization for  $CO_2$  leakage and seepage in the shallow subsurface and atmospheric surface layer. These features include a house with a basement and cracked floor through which  $CO_2$  can seep, and a water well which could produce water with high dissolved  $CO_2$  content if  $CO_2$  bubbled up through the aquifer. Also shown are plants, a tree, and roots that may be sensitive to elevated  $CO_2$  concentrations in the shallow subsurface. We also show animals that live in the ground and therefore may be susceptible to elevated  $CO_2$  concentrations, along with their burrows that may provide fast flow paths and enhance mixing by barometric pumping of soil gas and ambient atmosphere. In addition, we show in Figure 2.1.3.4(1) the saturated zone, unsaturated zone, surface water, and wind in the atmospheric surface layer which may be capable of diluting and attenuating leaking and seeping  $CO_2$ .

The objective of our research is to demonstrate a coupled modeling framework for risk characterization applicable to the leakage and seepage of  $CO_2$  from geologic carbon sequestration sites. The purpose of the coupled model is to estimate  $CO_2$  fluxes and concentrations in the near-surface environment where risk to humans, plants, and animals is highest. The  $CO_2$  concentration estimates obtained using the coupled model will feed to exposure models already developed for other soil-gas contaminants. The underlying premise of our approach is that the fundamental drivers of the HSE risk are the  $CO_2$  flux and near-surface  $CO_2$  concentrations, and that a rigorous capability to estimate these quantities is essential for a defensible HSE risk assessment. A new coupled model is required because to our knowledge there is no existing model that handles both subsurface and atmospheric surface-layer transport and dispersion along with the coupling at the subsurface–surface-layer interface at the appropriate scale, although model development at smaller scales is currently underway (e.g., Webb and Phelan, 2003).

The purpose of this report is to describe the coupled modeling framework. First, we summarize the background points made in prior project deliverables that are critical to motivating the approach we have taken. In Section 6, we present the methodology and structure of the coupled model with emphasis on the new atmospheric surface-layer flow and dispersion methods. In Section 7, we present results of testing to verify and demonstrate the model.

### 2.1.3.4.1 Background

### 2.1.3.4.1.1 Task 1 Report

Relevant information and research results have already been presented in prior project deliverables in this project (Oldenburg et al., 2002a; 2002b; 2002c). For example, in the Task 1 report (Oldenburg et al., 2002a), we clarified terminology by defining *leakage* as migration away from the primary sequestration target, whereas *seepage* is  $CO_2$  migration through an interface such as the ground surface or a concrete
basement floor or wall. We also presented in the Task 1 report figures showing the high density and low viscosity of  $CO_2$  relative to air, and we discussed how decompression and spreading bebw low-permeability layers during upward flow from the deep subsurface will tend to promote vertical migration along preferential flow paths while solubility trapping will tend to limit upward migration. We also discussed several well-known cases of natural gas storage-related leakage and seepage demonstrating that gases can escape from deep in the subsurface and seep out of the ground. Finally, in the Task 1 report we presented numerical simulations of  $CO_2$  transport through the unsaturated zone that showed the limited capability of the unsaturated zone to attenuate leaking  $CO_2$  (see also Oldenburg and Unger, 2003b).

### 2.1.3.4.1.2 Task 2 Report

In the Task 2 report (Oldenburg et al., 2002b), we discussed risk assessment in general and how it can be applied to HSE risk assessment of geologic carbon sequestration. We discussed human health and ecological effects of elevated  $CO_2$  concentrations, and we noted that if health risks to humans are minimized, minimal risk to the environment is generally assured. We described in general the methods we use to model a coupled subsurface-atmospheric surface-layer system to estimate  $CO_2$  fluxes and concentrations for  $CO_2$  risk characterization under different failure scenarios. Note that our scope at the time of the Task 2 report included calculation of indoor-air  $CO_2$  concentrations as a result of  $CO_2$  leakage and seepage, for example into the house in Figure 2.1.3.4(1). Due to a subsequent mid-project budget cut, we re-scoped the project to focus on the fundamental  $CO_2$  flux and near-surface concentrations alone.

## 2.1.3.4.1.3 Task 3 Report

The Task 3 report (Oldenburg et al., 2002c) focused on atmospheric dispersion of  $CO_2$  where our concern is for the lowest part of the atmospheric boundary layer, here called the surface layer, because this is where humans, plants, and other animals live. We discussed evidence from natural analog releases and from large-scale experiments of dense gas dispersion. We presented extensive correlations used for industrial risk assessment of dense gases, and used these correlations to show that generally atmospheric dispersion will be effective at diluting seeping  $CO_2$ . We also presented the approach we are using for modeling atmospheric transport and dispersion. The presentation of our atmospheric dispersion methods and structure will be updated below in Section 6, and test simulations and demonstrations from the coupled model will be presented in Section 7.



Figure 2.1.3.4(1). Sketch of shallow subsurface and atmospheric surface layer with accompanying features relevant to HSE risk associated with  $CO_2$  leakage and seepage

# 2.1.3.5 Executive Summary

Hazard identification and risk characterization are essential components of health, safety, and environmental (HSE) risk assessment of geologic carbon sequestration. The hazard of concern is exposure to elevated carbon dioxide  $(CO_2)$  concentrations resulting from leakage and seepage of  $CO_2$ from the target geologic sequestration site. Risk characterization is the quantification of the significance of this hazard, including estimating source strength and environmental concentrations in media through which exposure to CO<sub>2</sub> by humans, plants, and animals may occur. We describe here a coupled modeling framework for simulating CO<sub>2</sub> leakage and seepage, including transport and dispersion in the subsurface and in the atmospheric surface layer, for risk characterization. The results of model simulations can be used to quantify the two key HSE risk drivers, namely seepage flux and near-surface concentrations. Our prior work in the area of HSE risk assessment has been reported in three project reports. In the Task 1 report, we defined the terms *leakage* to refer to  $CO_2$  migration away from the target sequestration formation, and *seepage* to refer to CO<sub>2</sub> flowing from the subsurface to the atmosphere, e.g., through the ground surface. We also described the physical properties of  $CO_2$  and air and noted the larger density of CO<sub>2</sub> will cause it to tend to accumulate in the unsaturated zone and hug the ground in the surface layer. We summarized some actual cases of gas leakage and seepage from natural gas storage facilities. Finally, we presented a sensitivity analysis for CO<sub>2</sub> leakage through the unsaturated zone. In the Task 2 report, we discussed HSE risk assessment and described the broad outline of our coupled modeling framework which includes coupled simulation of the subsurface and atmospheric surface layer. In the Task 3 report, we focused on atmospheric dispersion of  $CO_2$  near the ground surface and presented estimates of  $CO_2$ dispersion using extensive correlations developed for industrial gas risk assessment. These correlationbased estimated suggest CO<sub>2</sub> will disperse rapidly in the surface layer.

The methodology and structure of the coupled modeling framework are based on the key concepts that (1) the primary HSE risk is in the near-surface environment where humans, animals, and plants live, (2) leakage and seepage flow processes are coupled, and (3) the main risk drivers are  $CO_2$  flux and concentration. Given these concepts, a rigorous coupled modeling framework is needed to make defensible estimates of  $CO_2$  flux and concentration for potential leakage and seepage scenarios. The relevant time and length scales for HSE risk assessment that we consider are between 1 month and 10 years, and from 10 m to 1 km, respectively. Over these scales, temporal and spatial averaging of surface-layer properties such as temperature, pressure, and precipitation is defensible.

The coupled modeling framework is built on the integral finite difference multiphase and multicomponent reservoir simulator TOUGH2. We describe the new module called T2CA that models  $CO_2$  and air in both subsurface and atmospheric surface-layer regions simultaneously. The surface-layer modeling assumes  $CO_2$  dispersion is passive and uses the logarithmic wind profile assumption and advective-dispersive transport equation. The logarithmic wind profile is generated by suitable choice of boundary conditions and medium properties in the surface layer. Surface-layer dispersivities are calculated from the Pasquill-Gifford curves and Smagorinski Model, for large scale and sub-grid scale atmospheric dispersion, respectively.

We have tested the coupled modeling framework in terms of physical property estimates and observed very good agreement against independent gas-mixture predictions. We have also tested the surface-layer transport and dispersion simulations against the Navier-Stokes fluid dynamics code FLUENT and observed good agreement for low CO<sub>2</sub> seepage fluxes and diminishing agreement, as expected, as the CO<sub>2</sub> seepage flux is increased. Good agreement was also observed for the transition from passive to active flow when compared to correlations developed from experiments and field trials of dense gas dispersion. Demonstrations of the model for full subsurface–surface-layer coupling show the large dispersion and dilution expected in the atmospheric surface layer. Whereas CO<sub>2</sub> concentrations in the subsurface can be extremely high, in the surface layer the wind easily overwhelms the seepage flux and reduces CO<sub>2</sub> concentrations to trace levels. Even for calm conditions, density-driven CO<sub>2</sub> flow appears capable of preventing CO<sub>2</sub> concentrations from reaching significant levels over flat and hor izontal ground surfaces.

We have also observed the reflux of  $CO_2$  by infiltrating rainwater containing dissolved  $CO_2$ , a process that shows the importance of using a coupled modeling framework. Finally, we compared downwind concentrations for 2-D and 3-D simulations of surface-layer dispersion and observed approximately a factor of two decrease in  $CO_2$  concentration for the 3-D simulation relative to the 2-D simulation.

# 2.1.3.6 Experimental

# 2.1.3.6.1 Key Concepts

The methodology and structure of the coupled modeling framework that we are using is based on the following key concepts: (1) the human, plant, and animal receptors span the interface between the subsurface and surface layer; (2) the flow processes involved in leakage and seepage are coupled; and (3) the main risk drivers are  $CO_2$  flux and concentration. Before describing the methods and structure in detail, we elaborate on these three key concepts and discuss the time and length scales appropriate to our approach.

First, HSE risk assessment applies to humans, plants, and animals. These environmental receptors live generally near the ground surface but may be entirely below, entirely above, or in both regions at different times. As examples of the importance of the subsurface, surface-layer, and in-between environments, consider the house and basement and the burrowing animals of Figure 2.1.3.4(1). Clearly the house and the burrow are open to gas flow from both the subsurface and surface layers and therefore  $CO_2$  in either the subsurface or surface layer has the potential to affect the environment in which people or animals live. The plants and trees and their roots similarly will be affected by  $CO_2$  leakage and seepage in both the subsurface and surface-layer environments. Because exposure to  $CO_2$  in the near-surface environment is the main risk of  $CO_2$  leakage and seepage, we have developed a coupled modeling framework that focuses on this region.

Second,  $CO_2$  leakage and seepage are coupled transport processes. Specifically,  $CO_2$  gas in the nearsurface environment will flow by advection and diffusion as controlled by pressure, density, and concentration gradients. For example, seeping  $CO_2$  will be strongly advected by surface winds above the ground surface, and leaking  $CO_2$  will tend to sink in the unsaturated zone by density effects. Similarly, atmospheric pressure variations (i.e., barometric pumping) will cause  $CO_2$  to move in the gas phase in the subsurface. Conversely, the low permeability of the subsurface will tend to dampen advective transport driven by wind in the surface layer. Rainfall and associated infiltration containing dissolved  $CO_2$  can be another mechanism for  $CO_2$  to return from the surface layer to the subsurface. Because of these apparent coupled processes occurring between the surface layer and subsurface, a coupled modeling framework capable of modeling these interactions is required.

Third, if high CO<sub>2</sub> concentrations are the fundamental adverse condition for HSE risk, then CO<sub>2</sub> seepage flux and near-surface CO<sub>2</sub> concentration are the main risk drivers. Seepage flux in terms of mass has units of kg CO<sub>2</sub> m<sup>-2</sup> s<sup>-1</sup> and is a measure of the rate at which CO<sub>2</sub> is passing out of the ground per unit area. If CO<sub>2</sub> is the only component of the gas stream seeping out of the ground, then flux and concentration are directly correlated. However, if the CO<sub>2</sub> is contained within a stream of another component (e.g., with steam in a geothermal system vent or geyser), then there can be a high CO<sub>2</sub> flux with low CO<sub>2</sub> concentrations. In this sense, flux and CO<sub>2</sub> concentration must be considered independently. In the case where the only component in the seeping gas is CO<sub>2</sub>, the seepage flux is a good indicator of whether given winds, surface water flows, or plant uptake rates are capable of reducing CO<sub>2</sub> concentrations strongly affects the attendant risk. For example, high CO<sub>2</sub> concentrations at a depth of 2 m in the ground may cause negligible risk to humans because they are living on the ground surface. On the other hand, high CO<sub>2</sub> concentrations in the basement of a building can be a significant health risk since people in the basement will be exposed to air with elevated CO<sub>2</sub> concentrations.

Given these key concepts, it is apparent that a rigorous coupled modeling capability is required to make defensible estimates of  $CO_2$  flux and concentration for various expected leakage and seepage scenarios. Simplified models of the subsurface or surface layer alone may not stand up to public and scientific scrutiny. We have used a methodology and structure that is based on sound principles of multiphase and multicomponent reservoir simulation. The fluxes and concentrations calculated by the coupled

framework can be used as inputs to exposure models to calculate defensible HSE risks. The direct output from the present coupled modeling framework is also useful by itself since  $CO_2$  flux and concentration are primary risk drivers. The approach we have taken can be used to model the whole leakage pathway from deep sequestration site to the surface, but here we focus the model description on the region where the main HSE hazards occur, namely the unsaturated zone and surface layer.

### 2.1.3.6.2 Length and Time Scales

With  $CO_2$  storage and sequestration operations potentially occurring on a large and widespread industrial scale, the length and time scales of interest to  $CO_2$  risk characterization are quite large. Because broad and diffuse  $CO_2$  seepage may occur over large areas for long periods of time, such leakage and seepage may be hard to detect and difficult to mitigate. As such, diffuse seepage is an important focus for risk assessment and risk management. Catastrophic events such as well failures are also relevant, but such events are obviously serious HSE risks and everything possible will be done to stop such events. We have focused on the 10 m to  $10^3$  m length scale, and the 1 month to 10 year time scale. Over these length and time scales, averaging is defensible. For example, constant wind speed, pressure, infiltration, and other weather-related processes can be used since the time scale is relatively long. On shorter time scales, one would want to use variable weather and seasonal conditions. While the coupled model is capable of nonisothermal simulations, we have considered only isothermal situations to date and we make use of a stability class parameterization to model temperature-related instability and its effect on atmospheric dispersion as described in Section 6.4.

### 2.1.3.6.3 Subsurface Flow and Transport

The coupled modeling framework we are using is built on the TOUGH2 code (Pruess et al., 1999), a multiphase and multicomponent integral finite difference reservoir simulator. Briefly, TOUGH2 uses a multiphase version of Darcy's law for fluid flow and the advective dispersive model for component transport. Readers interested in greater detail and information on the theory or practical implementation of TOUGH2 should consult the users guide (Pruess et al., 1999) and the website (<u>http://www-esd.lbl.gov/TOUGH2</u>). The coupled model is based on an extension of the EOS7R module (Oldenburg and Pruess, 1995; Pruess et al., 1999), and handles five components (H<sub>2</sub>O, brine, CO<sub>2</sub>, a gas tracer, air) and heat. Air is a pseudocomponent that is approximated as a mixture of 21% oxygen and 79% nitrogen by volume. Real gas mixture properties are calculated so the full range from high-pressure sequestration-site conditions to low-pressure ambient surface-layer conditions can be modeled. We refer to the coupled model as T2CA, for TOUGH2 CO<sub>2</sub> and <u>A</u>ir. While the discussion below focuses on the CO<sub>2</sub> transport, all of the gas-phase components are modeled in the TOUGH2 multicomponent framework, and an analogous treatment can be developed for heat.

## 2.1.3.6.4 Atmospheric Dispersion

## 2.1.3.6.4.1 Introduction

The approach we use for atmospheric surface-layer transport and dispersion was described in our Task 2 and Task 3 reports (Oldenburg et al., 2002b; 2002c). Because of its importance to  $CO_2$  leakage and seepage risk characterization, we present below an updated description of this approach with illustrative figures similar to that in the recent TOUGH Symposium Proceedings paper (Oldenburg and Unger, 2003a).

### 2.1.3.6.4.2 Defining the Surface Layer

The atmospheric surface layer, often referred to simply as the surface layer, in the coupled modeling framework is defined by setting porosity to unity and permeability to values orders of magnitude larger than the subsurface parts of the domain. Furthermore, the surface-layer boundary conditions and permeabilities should be set to specify the desired wind profile. The wind must be unidirectional and aligned with the *x*-axis. The entire coupled subsurface–surface-layer calculation is carried out using a single grid. Hence, the model regions are implicitly coupled. Full multiphase and multicomponent flow and transport are used throughout the domain. Depending on how the user defines the properties of the domain, the model can be run as subsurface only, surface layer only, or coupled subsurface–surface-layer. Additional layers and materials can be added to represent details such as plants, leaf litter, and soils as information about the effects of these materials becomes known.

### 2.1.3.6.4.3 Passive Mixing Assumption

Field experiments of dense gas dispersion have been used to develop correlations involving the most important parameters controlling atmospheric dispersion such as wind speed, density of released gas, and release flux (Britter, 1989; Britter and McQuaid, 1988). These correlations were developed based on simple scale and dimensional analyses. One of these correlations relates the seepage flux and average wind speed at an elevation of 10 m to the form of the dispersion process, i.e., whether it is active (density-dependent) or passive as appropriate for a gas tracer. In Figure 2.1.3.6.4.3(1), we have plotted this correlation with values appropriate for CO<sub>2</sub>-air mixtures for various source area length scales along with the typical flux of CO<sub>2</sub> emitted and taken up by plants, soil, and roots known as the net ecosystem exchange (NEE) (e.g., Baldocchi and Wilson, 2001). As shown in Figure 2.1.3.6.4.3(1), seepage fluxes have to be quite high (note logarithmic scale) for windy situations for the resulting dispersive mixing process to be active. Note that wind conditions are averages over a period of 10 minutes.

In prior work (Oldenburg et al., 2002a; Oldenburg and Unger, 2003b), we have simulated subsurface migration of leaking  $CO_2$  through the unsaturated zone with rainwater infiltration for various leakage rates specified at the water table. These leakage rates were given as annual mass leakage percentages of the total stored  $CO_2$ . Typical seepage fluxes for the 0.1% yr<sup>-1</sup> leakage rate were on the order of  $10^{5}-10^{-6}$  kg m<sup>-2</sup> s<sup>-1</sup>. As shown in Figure 2.1.3.6.4.3(1), seepage fluxes of this magnitude lead to passive dispersion for all but the calmest wind conditions.

#### 2.1.3.6.4.4 Passive Dispersion and the Logarithmic Wind Profile

Under the assumption of passive flow and dispersion, we can use an ambient wind profile and advectivedispersive models as developed in the atmospheric transport literature (e.g., Slade, 1968; Pasquill, 1974; Stull, 1988; Arya, 1999). The ambient time-averaged wind profile near the ground surface has been shown theoretically to follow a logarithmic profile as shown in Figure 2.1.3.6.4.4(1). The logarithmic wind profile is given as:

$$u_x(z) = \frac{u_*}{k^*} \ln\left(\frac{z}{z_0}\right) \tag{3.1}$$

where  $u_x(z)$  is the ambient wind speed as a function of height,  $u_*$  is the friction velocity (a parameter that governs the shape of the wind profile near the ground surface for various surface types (Slade, 1968)),  $k^*$  is von Karman's constant ( $k^* = 0.4$ ), z is the elevation, and  $z_0$  is a roughness height such that  $u_x(z) = 0$  at  $z = z_0$  and is also a function of various surface types. An excellent review of the assumptions involved in

the logarithmic profile, as well as experimentally derived parameters obtained from calibration to field data, are provided in Slade (1968).

### 2.1.3.6.4.5 Advective-Dispersive Transport

Atmospheric transport and dispersion of  $CO_2$  as a passive gas follows the linear advective-dispersive transport equation. General background and assumptions in the formulation of this transport equation can be found in Slade (1968) and Arya (1999). In short, dispersive transport can be simplified to the following partial differential equation for the three-dimensional (*x*, *y*, *z*) transport of a low-concentration component (such as  $CO_2$ ) at concentration *c*:

$$\frac{\partial c}{\partial t} + u_x \frac{\partial c}{\partial x} + u_y \frac{\partial c}{\partial y} + u_z \frac{\partial c}{\partial z} - D_{xx} \frac{\partial^2 c}{\partial x^2} - D_{yy} \frac{\partial^2 c}{\partial y^2} - D_{zz} \frac{\partial^2 c}{\partial z^2} = 0$$
(3.2)

For atmospheric transport modeling, the coordinate system is arranged so that the positive x-direction is aligned in the downwind direction. Advection is generated by the velocity terms so that with the coordinate system transformation,  $u_y = u_z = 0$ , and  $u_x$  is the ambient wind. The dispersion is governed by local dispersion coefficients  $D_{xx}$ ,  $D_{yy}$ , and  $D_{zz}$  that are the diagonal elements of a dispersion tensor related to the standard deviations ( $s_x$ ,  $s_y$ ,  $s_z$ ) in the concentration distribution by

$$D_{xx} = \frac{\mathbf{s}_x^2}{2t}$$

$$D_{yy} = \frac{\mathbf{s}_y^2}{2t}$$

$$D_{zz} = \frac{\mathbf{s}_z^2}{2t}$$
(3.3)

where *t* is time (e.g., Arya, 1999). With this formulation, the local dispersion coefficients  $(D_{xx}, D_{yy})$ , and  $D_{zz}$  will be a function of location through the *t* term, where *t* is the travel time from the source to the given location, and through *s* from the Pasquill-Gifford dispersion curves discussed below.

#### 2.1.3.6.4.6 Pasquill-Gifford Dispersivities

The empirically derived Pasquill-Gifford (P-G) dispersion curves provide a commonly accepted and practical means of determining large-scale atmospheric dispersion (Slade, 1968; Arya, 1999). Large-scale eddies in the convective motion of the lower atmospheric layers are assumed to result in dispersion of passive constituents that can be mathematically represented as a Fickian diffusion process. The P-G scheme was developed from experiments conducted over a wide variety of terrain (e.g., project Prairie Grass and British diffusion experiments (Pasquill, 1961; Gifford, 1961)) and atmospheric conditions (ranging from class A-extremely unstable, class B-moderately unstable, class C-slightly unstable, class D-neutral, class E-slightly stable, to class F-moderately stable). The P-G curves are shown on Figure 2.1.3.6.4.6(1) and provide a value of  $s_y$  and  $s_z$  as a function of downwind distance under a specific atmospheric condition (classes A–F), with  $s_x$  set equal to zero since advection dominates in the *x*-direction. The empirically derived P-G dispersion scheme is valid for large-scale eddies in the lowest 100 m of the atmosphere evolving over length scales ranging from 100 m to 10,000 m down to 1 m, for reasons that will be discussed below.

#### 2.1.3.6.4.7 Smagorinski Model Dispersion

In the context of  $CO_2$  leakage and seepage, the source zone will often be a surface seep. Health and environmental risks due to  $CO_2$  seepage may need to be resolved at smaller distances from the source than are strictly applicable for the P-G dispersion curves discussed above. On the scale of 100 m or less, small-scale eddies in the convective motion of the near-surface atmospheric layers are assumed to result in dispersion of passive constituents within these layers (Arya, 1999). These eddies arise from the shear stress of the air in contact with the ground surface. Note that this identical mechanism is responsible for the logarithmic wind profile discussed earlier, in which wind velocities approach zero near the ground surface.

The Smagorinski Model is the simplest and most widely used small-scale eddy dispersion model (Arya, 1999). In general, the Smagorinski Model provides a methodology to define a dispersion tensor for use in the conservation of momentum equation when using the Navier-Stokes equations to model air flow near the ground surface. Briefly, the Smagorinski Model assumes that dispersion of momentum (D) is proportional to the vertical (z) and horizontal (x) gradients in air velocity as given by:

$$D = \frac{l^2}{\sqrt{2}} \left( \frac{\partial u_x}{\partial z} + \frac{\partial u_z}{\partial x} \right) = \frac{l^2}{\sqrt{2}} \frac{u_*}{k^* z}$$
(3.4)

where *l* is a grid-related length scale, and  $u_x$  is obtained from the logarithmic wind profile given by Eq. 3.1, while  $u_z$  is zero in the logarithmic wind profile. Scalars such as a passive tracer or heat (energy) are assumed to undergo Fickian dispersion where the diagonal elements of the dispersion tensor are given by the momentum diffusivity in Eq. 3.4 multiplied by a constant ranging from 2.0 to 3.0 (Arya, 1999).

#### 2.1.3.6.4.8 Specification of the Logarithmic Wind Profile

The simulation of atmospheric advection and dispersion by the above methods begins by creating a logarithmic wind profile within the TOUGH2 framework. This step involves generating a grid with sufficient layers parallel to the ground surface to discretize the wind profile to the desired accuracy. Next, a static gas-phase pressure profile in the *z*-direction is used along with a constant pressure difference between the upstream and downstream boundaries of the surface layer

$$\Delta P = P_2 - P_1, \quad P_1 > P_2 \tag{3.5}$$

where  $P_1$  and  $P_2$  are the upstream and downstream pressures, respectively, within a layer. TOUGH2 computes the phase velocity using Darcy's equation

$$u = -\frac{k_D}{fm}\nabla(P - rgz)$$
(3.6)

where  $k_D$  is the intrinsic (Darcy) permeability, f is the porosity, m is the gas viscosity, r is the mass density of the gas phase, g is the gravitational acceleration and z is height. Assuming horizontal layers, constant gas density and viscosity, and porosity of the surface-layer materials equal to unity, the velocity of the atmospheric air in a given layer will be proportional to the permeability of the layer and the pressure difference,  $\Delta P$ . Given that  $\Delta P$  is a constant for all layers, the individual permeability variations of the layers will combine to produce the logarithmic wind profile with  $u_z = u_y = 0$ . Note that the thickness of each layer must be constant to ensure a constant air velocity within the layer across the length of the domain. Note further that the permeability is a pseudo-permeability with no physical significance; its purpose is simply to create the desired velocity profile.

## 2.1.3.6.4.9 Calculating Atmospheric Dispersion

Within the T2CA framework, transport of CO<sub>2</sub> as a passive gas will follow the linear advective-dispersive transport equations. Ambient atmospheric dispersion of CO<sub>2</sub> using either P-G dispersion curves or the Smagorinski Model modified for the dispersion of a scalar is implemented by using a variable effective molecular diffusivity in the surface-layer region. With this approach, the diagonal of the tensor representing Fickian diffusion of CO<sub>2</sub> is modified to be the sum of molecular diffusion, as well as  $D_{yy}$  and  $D_{zz}$  from the P-G curves, as well as a contribution from the Smagorinski Model. This enables T2CA to include the dispersion of the CO<sub>2</sub> plume due to molecular diffusion and both small- and large-scale eddies in the convective motion in the surface layer.

In order to compute values of  $D_{yy}$  and  $D_{zz}$  from the P-G curves at the interface between two nodes within the mesh, the distance from the source to the interface must be computed internally. This distance is then used to interpolate values  $s_y$  and  $s_z$  from the curves given in Figure 2.1.3.6.4.6(1). Note that values of  $s_y$ and  $s_z$  are extrapolated from a downwind distance of 100 m to 1 m in order to prevent a jump in the value of the dispersion tensor as the plume moves a downwind distance of 100 m. Next, the time *t* required for the CO<sub>2</sub> plume to travel to the interface is estimated as the travel distance divided by the wind speed at a specified height. This assumes that the centroid of the plume advects at a constant elevation above the ground surface, i.e., under neutral stability conditions. Finally, values of  $s_y$ ,  $s_z$  and *t* are used in Eq. 3.3 to compute values of  $D_{yy}$  and  $D_{zz}$ . These parameters are specified in the T2CA input file by means of the SELEC data block as discussed below.

### 2.1.3.6.4.10 New Parameters for T2CA

Surface-layer dispersion parameters are specified in the T2CA input file by means of the SELEC data block as follows.

# SELECTION

Record SELEC.7

	Format(8E10.4) XSOURCE, YSOURCE, ZSOURCE, CLASS, LSCALE, FRICVEL, ZO, ZPLUME
XSOURCE	<i>x</i> -coordinate of the source centroid, m
YSOURCE	note: the mesh must be oriented such that wind advects along the $x$ axis only v-coordinate of the source centroid. m
ZSOURCE	<i>z</i> -coordinate of the source centroid, m
	note: dispersion due to both the P-G curves and the Smagorinski Model is computed only in the region: $z > ZSOURCE$ , $x > XSOURCE$
	while the downwind distance <i>l</i> is given as : $l = ((x - XSOURCE)^2 + (y - YSOURCE)^2 + (z - ZSOURCE)^2)^{1/2}$
CLASS	atmospheric stability class (A = 1.0, B = 2.0, C = 3.0, D = 4.0, E = 5.0, F = 6.0) note: to active dispersion due to both the P-G curves and the Smagorinski Model, set $MOP(24) = 1$ and $1.0 \le CLASS \le 6.0$
LSCALE	length scale used in the Smagorinski Model, m
FRICVEL	friction velocity from Eq. 3.1, m s <sup>-1</sup>
ZO	regression parameter from Eq. 3.1, m
ZPLUME	height at which the centroid of the plume travels, m

## 2.1.3.6.4.11 Note on Magnitudes of Dispersion Terms

As described above, the dispersion terms are added together and enter the advective-dispersive transport equation analogous to a molecular diffusion term. Note that the P-G dispersivities are functions of distance and travel time from the source, and the Smagorinksi Model dispersion term is a function of height above the ground surface. Because these terms may vary with time and position, the relative magnitude of the overall dispersion term will vary within the domain. Typically the Smagorinski Model term will be large near the ground surface and become negligible with height, while the P-G term becomes larger with distance from the source. We plot in Figure 2.1.3.6.4.11(1) an example of the variation of the various dispersion terms for the sample problem shown in Figure 2.1.3.7.4(1). In Figure 2.1.3.6.4.11(1), we observe first that the difference between the extremely unstable class A and the moderately stable class F is approximately a factor of 100 in terms of P-G dispersivity, and that this difference gets larger with distance from the source. The second thing to note is the factor of five or so difference in P-G dispersivity between the 1 and 5 m s<sup>-1</sup> wind speed. As for Smagorinski Model dispersivity, we note that it is independent of distance from the source, but inversely proportional to height above the source. For wind at 5 m s<sup>-1</sup>, the Smagorinski Model dispersivity is always larger than the P-G class F dispersivity. On the other hand for P-G class A, the P-G dispersivity is larger than the Smagorinski Model dispersivity except when less than 50 m or so from the source. In general, Smagorinski Model dispersion is most important near the ground surface and when the atmosphere is stable, while P-G dispersion dominates under unstable conditions and at some significant height above the ground surface. In general, molecular diffusion is orders of magnitude smaller than either the P-G or Smagorinski Model dispersion terms.

## 2.1.3.6.4.12 Numerical Dispersion

In any approach involving the numerical solution of the advective-dispersive transport equation using single-point upstream weighting, numerical dispersion will be a significant effect. For the case of large length scales and fast wind speeds, it is particularly significant. For example, dispersivity due to numerical dispersion in the integral finite difference method of T2CA can be approximated as being equal to velocity multiplied by one-half of the grid dimension. Specifically, for a case with 10 m grid blocks and 1 m s<sup>-1</sup> winds, the numerical dispersion is on the order of 5 m<sup>2</sup> s<sup>-1</sup>. This is large relative to our usual experience in subsurface hydrology where the flow velocities are usually not larger than  $10^{-5}$  m s<sup>-1</sup>. This issue is moderated by (1) the fact that we are not interested in resolving the behavior of the plume front, but rather we are interested in the maximum concentrations in the plume body, and (2) the fact that P-G and Smagorinski Model dispersivities are also large. Furthermore, the largest numerical dispersion occurs in the direction of flow. With the logarithmic wind profile assumption, the flow is unidirectional, and over the relatively long time scales of interest for risk characterization, advection is the dominant transport mechanism in the flow direction. Because the focus of our approach is on quasi-steady-state concentrations within the plume body and not on the plume front, the coupled model results are not strongly affected by numerical dispersion.

## 2.1.3.6.4.13 Summary

An effective means of modeling large-scale atmospheric transport of CO<sub>2</sub> as a passive gas involves solving the advection-dispersion equation for various flux or concentration source conditions with advection obtained from the logarithmic wind profile and dispersion obtained using the P-G dispersion curves. Within the immediate vicinity of the source zone, the same approach can be used with the dispersion coefficient estimated by the Smagorinski Model. The extrapolation of the P-G curves to smaller length scales is done so the transition from small-scale (i.e., Smagorinski Model) to large-scale (i.e., P-G) dispersion will be smooth. Because Fickian diffusion is a linear flux operator in the context of the advection-dispersion equation, the P-G curves and the Smagorinski Model can be applied

simultaneously along with pure molecular diffusion with the largest term controlling dispersion. What is new in our approach is the coupling of the atmospheric surface layer to the subsurface region. This coupling is important because  $CO_2$  is a dense gas that may seep out of—but also possibly back into—the subsurface.

While our approach in the surface layer is strictly correct only for passive mixing, it may also prove to be acceptable in calm conditions for active (density-dependent)  $CO_2$  transport and dispersion. Specifically, the density gradient term is retained in the flow equation so that if density effects become important, the density field will affect the flow equations. However, inertia and viscous stress terms are not present in the T2CA flow equations. Viscosity dependence is also present in the flow equation, although this contrast is only 20% or so for air and  $CO_2$  in the surface layer and does not strongly affect the flow field. If significant active flow effects ever arise, the surface-layer velocity will be affected and will deviate from the presumed constant logarithmic velocity profile. If this occurs, it is an indication that the atmospheric dispersion process is active as opposed to passive, and the user should proceed carefully to assess whether other methods should be applied to model active dense gas dispersion.



Figure 2.1.3.6.4.3(1) Correlation for active (i.e., density-dependent) and passive dispersion in the surface layer as a function of seepage flux and wind speed.



Figure 2.1.3.6.4.4(1) Schematic of the logarithmic velocity profile used to approximate time-averaged winds in the surface layer.



Figure 2.1.3.6.4.6(1) Pasquill-Gifford (P-G) dispersion curves for deriving atmospheric dispersivities in the transverse (y) and vertical (z) directions for the five different atmospheric stability classes: A-extremely unstable; B-moderately unstable; C-slightly unstable; D-neutral; E-slightly stable; F-moderately stable.



Figure 2.1.3.6.4.11(1) Comparison of Pasquill-Gifford (P-G) and Smagorinski Model (SM) dispersivities for two different wind speeds and P-G stability classes.

# 2.1.3.7 Results and Discussion

In this section, we present results from our testing and verification studies of the coupled subsurfacesurface-layer model. Because of the lack of available experimental or numerical results for coupled subsurface-surface-layer CO<sub>2</sub> flow and transport, we have compared results of various aspects of the model against available independent data and simulation results. For example, we have compared physical properties of the gas mixtures in T2CA against independent predictions from a database of the National Institute of Science and Technology (NIST). The subsurface flow and transport part of T2CA uses the same approach as another module (TOUGH2/EOS7C) with a change in the components modeled. Specifically, we substitute air for methane ( $CH_4$ ) in T2CA. The TOUGH2/EOS7C code was part of a code intercomparison study that demonstrated broad agreement with three other numerical simulators for gas reservoir processes (Oldenburg et al., 2002d) and therefore serves as verification of the subsurface part of T2CA. We have also compared our results against a commercial fluid dynamics code called FLUENT (http://www.fluent.com/) that solves the complete Navier-Stokes equations for densitydependent gas flow. And finally we have compared our model against the experimental correlations of Britter and McQuaid (1988) with respect to the transition from passive to active flow. Taken together, the agreement of our model with other data and models for its various components provides a significant level of confidence of the coupled model. Validation of the approach will have to await field experience with  $CO_2$  leakage and seepage.

# 2.1.3.7.1 Physical Property Verification

The physical properties density and viscosity play a key role in  $CO_2$  flow and transport. In order to verify the approach used in T2CA for predicting gas mixture properties, we have compared property estimates against values produced by the NIST14 Database (NIST, 1992). Shown in Figure 2.1.3.7.1(1) are densities of air- $CO_2$  gas mixtures at 20 °C and 1 bar pressure, appropriate for the shallow subsurface environment. As shown, the densities produced by T2CA agree very closely with the NIST14 results. In short, T2CA produces very accurate density estimates for gas mixtures. Shown in Figure 2.1.3.7.1(2) are the analogous comparisons of viscosity estimates produced by T2CA and by the NIST14 Database (NIST, 1992). Although there are systematic differences, the estimated viscosities agree to within 5%. The NIST14 Database was developed with an emphasis on gas density prediction at the expense of other properties such as viscosity (NIST, 1992; Magee et al., 1994). T2CA uses the method of Chung et al., 1988) and is considered a very accurate approach for gas mixtures.

## 2.1.3.7.2 Surface-Layer Dispersion

In this section we present results showing comparisons of T2CA against the commercial fluid dynamics code FLUENT. The purpose of this comparison is to demonstrate that the approach we are using in T2CA is equivalent to the more complete description of the flow process used in FLUENT under the conditions of passive gas flow. Specifically, FLUENT solves for the flow field using the full Navier-Stokes equations which contain terms accounting for fluid inertia and viscous stresses. In contrast, T2CA uses a simplified flow equation without inertia or viscous stress terms. Both FLUENT and T2CA solve an advective-dispersive transport equation for transport and dispersion of the gas components. To compare results of these two approaches, we defined a simplified test problem as shown in Figure 2.1.3.7.2(1). In the test problem, wind with a logarithmic velocity profile sweeps past a source of CO<sub>2</sub> specified by a mass flux uniformly distributed over 5 m along the bottom of the flow domain. This CO<sub>2</sub> will then be transported and dispersed by the flowing wind until it is carried out of the domain on the right-hand side. The dispersion is specified in a simple way to guarantee a direct comparison from two independent simulation approaches by specifying a constant molecular diffusion coefficient of  $10^2 \text{ m}^2 \text{ s}^{-1}$ .

Results are shown in Figure 2.1.3.7.2(2)-2.1.3.7.2(4) where we plot mass fraction of CO<sub>2</sub> in the gas phase along with gas velocity vectors. As shown in Figure 2.1.3.7.2(2)a and b, agreement between T2CA (a) and FLUENT (b) is quite good for a source flux of  $10^{-5}$  kg m<sup>-2</sup> s<sup>-1</sup>. Figure 2.1.3.7.2(3)a and b show results for a flux of  $10^{-4}$  kg m<sup>-2</sup> s<sup>-1</sup>, and Figure 2.1.3.7.2(4)a and b show results for CO<sub>2</sub> flux of  $10^{-3}$  kg m<sup>-2</sup> s<sup>-1</sup>. Note the overall good agreement in  $CO_2$  gas mass fraction in Figure 2.1.3.7.2(2) and 2.1.3.7.2(3). Note in Figure 2.1.3.7.2(4)a, and b the differences in the flow field near the upwind edge of the seepage plume, and the mass fraction field near the outflow boundary on the right-hand side. The T2CA result is showing a small recirculation due to density effects at the upwind edge of the source, and boundary condition effects at the downwind side. As expected, the results of FLUENT and T2CA agree well for small CO<sub>2</sub> fluxes and deviate from one another as the flux becomes larger. The reason for this is that the transport and dispersion become increasingly density-coupled as the  $O_2$  flux gets larger and, accordingly, the  $O_2$ concentrations become larger. FLUENT models strongly coupled flow because it solves the full Navier-Stokes equations, whereas T2CA is restriced to passive flow and dispersion in the surface layer for its approach to be formally applicable. Nevertheless, T2CA retains a density term in its flow equation (see Eq. 3.6), and therefore when density coupling becomes significant the flow field will change in obvious ways. Such an occurrence should be a signal to the user that a full Navier-Stokes approach is needed.

Property	Value	
Surface Layer		
2-D domain size $(x \times y \times z)$	55 m x 1 m x 5 m	
Discretization ( $Nx \ge Ny \ge Nz$ )	110 x 1 x 50 gridblocks	
Pressure	1 bar	
Temperature	15 ℃	
Effective diffusivity	$10^{-2} \text{ m}^2 \text{ s}^{-1}$	
$CO_2$ flux region	25  m < x < 30  m	
CO <sub>2</sub> mass flux	$10^{-5}$ , $10^{-4}$ , $10^{-3}$ kg m <sup>-2</sup> s <sup>-1</sup>	
Wind Profile	logarithmic	
Reference velocity at $z = 2$ m	$2 \text{ m s}^{-1}$	
Friction velocity for $u_x = 2 \text{ m s}^{-1}$	$0.267 \text{ m s}^{-1}$	
Reference height $(z_0)$	0.10 m	

Table 2.1.3.7.2(1)	) Properties	of the	surface-lay	ver dis	persion test	problem.
				/		

## 2.1.3.7.3 Passive vs. Active Flow

Using the obvious changes in the flow field that occur when flow becomes strongly coupled to  $CO_2$  transport as indicators of active flow, we have compared the transition point estimated by Britter and McQuaid (1988) on the basis of field and laboratory experiments of dense gas dispersion against the transition observed in T2CA simulations for a test problem. The test problem here is similar to the prior one except it is larger and has a 100 m long source area. Results are shown in Figure 2.1.3.7.3(1) where we plot an "A" for active and a "P" for passive directly over the transition curve derived by Britter and McQuaid (1988) as a function of wind speed (*x*-axis) and seepage flux (*y*-axis). The tests were carried out by changing the fluxes for simulations using two different logarithmic velocity profiles as shown by the dashed lines indicating constant velocity in Figure 2.1.3.7.3(1). As shown in Figure 2.1.3.7.3(1), the results agree well with the experimental curve showing that our approach is sensitive to the potential strong density-dependent flow and that users will be able to observe when the flow field becomes strongly coupled by density effects.

#### 2.1.3.7.4 Subsurface–Surface-Layer Coupling

In this section, we present preliminary results of the coupled subsurface–surface-layer flow and transport of  $CO_2$  as a demonstration of the coupled model capabilities. The first demonstration problem is 2-D, a schematic of which is shown in Figure 2.1.3.7.4(1) along with the discretization used. This problem is intended to engage the fundamental capabilities of coupled subsurface–surface-layer flow and transport. It is important to note that in all of the simulations we have assumed a zero background  $CO_2$  concentration to emphasize the additional  $CO_2$  that seeps from the ground in the various scenarios.

Property	Value
Subsurface	
Subsurface region extent $(x \times y \times z)$	1  km x  1  m, 0  m < z < 35  m
Discretization ( $Nx \ge Ny \ge Nz$ )	100 x 1 x 35
Permeability ( $k_X = k_Z$	$1 \times 10^{-12} m^2$
Porosity $(f)$	0.2
Infiltration rate ( <i>i</i> )	10. cm yr <sup>-1</sup>
$CO_2$ flux region	450  m < x < 550  m
$CO_2$ mass flux	$4.04 \times 10^{-6} \text{ kg m}^2 \text{ s}^{-1}$
Residual water sat. $(S_{lr})$	0.1
Residual gas sat. $(S_{gr})$	0.01
van Genuchten (1980) a	$1 \ge 10^{-4} \text{ Pa}^{-1}$
van Genuchten (1980) m	0.2
Surface Layer	
Surface-layer region extent $(x \times y \times z)$	1 km x 1 m, 35 m < <i>z</i> < 45 m
Discretization ( $Nx \ge Ny \ge Nz$ )	100 x 1 x 20
Pressure in surface layer	1 bar
Temperature (isothermal)	15 ℃
Pasquill-Gifford stability class	F
Velocity profile	logarithmic
Reference velocity at $z = 10$ m	0, 1, or 5 m s <sup>-1</sup>
Friction velocity for $u_x = 1 \text{ m s}^{-1}$	$0.0868 \text{ m s}^{-1}$
Friction velocity for $u_x = 5 \text{ m s}^{-1}$	$0.434 \text{ m s}^{-1}$
Reference height $(z_0)$	0.10 m

Table 2.1.3.7.2(2) Properties of the coupled subsurface–surface-layer model system.

The first test involved a case of zero surface-layer wind. In this case, results of which are shown in Figure 2.1.3.7.4(2), the flow of  $CO_2$  in the surface layer is driven entirely by density effects, and dispersion is by molecular diffusion. As shown, the  $CO_2$  seeps out of the ground and spreads symmetrically to the right and left along the ground surface. Concentrations in the surface layer reach mass fractions of approximately 0.001, or approximately 1.6 times current atmospheric concentration. Note the downward migration of  $CO_2$  back into the subsurface on the left- and right-hand sides of the plume. This reflux of  $CO_2$  is caused by dissolution of  $CO_2$  into the infiltrating rainwater specified at the ground surface. This kind of effect points out the importance of coupled subsurface–surface-layer coupling.

In the second test, we have imposed a logarithmic velocity profile with winds of 1 m s<sup>-1</sup> at an elevation of 5 m and Pasquill-Gifford stability class F (most stable) as shown in Figure 2.1.3.7.4(3). Note that even for a stable stability class, there is a large amount of dispersion and CO<sub>2</sub> concentrations in the surface layer are very small (note countour interval on the low end). Such low CO<sub>2</sub> concentrations would be a challenge to detect in the presence of natural variations and ecological processes that affect CO<sub>2</sub> concentrations more strongly. For less stable conditions, CO<sub>2</sub> dispersion and dilution would be even stronger and CO<sub>2</sub> concentrations correspondingly smaller.

To demonstrate the effect of wind speed, we increased the wind to 5 m s<sup>-1</sup> keeping all other variables constant. These results are shown in Figure 2.1.3.7.4(4) where we observe even lower  $CO_2$  concentrations in the surface layer than for the 1 m s<sup>-1</sup> wind case of Figure 2.1.3.7.4(3). Note again the reflux of  $CO_2$  into the subsurface caused by the rainwater infiltration.

Given that HSE risks will be calculated based on exposures at certain locations in the flow field, we have made a preliminary analysis of the dependence of downwind  $CO_2$  concentrations as a function of wind speed and height above the ground surface. Shown in Figure 2.1.3.7.4(5) are values of  $CO_2$  mass fraction in the surface-layer gas phase as a function of Pasquill-Gifford stability class for two different average ambient winds. As shown, the downwind concentrations depend mostly on wind speed and stability class. Wind speed increasing by a factor of five causes  $CO_2$  mass fractions to decline by approximately a factor of seven. With increasing atmospheric stability, the downwind concentration can be expected to increase by approximately a factor of five. Because dispersion is strong in all cases, the concentrations depend less strongly on height above the ground.

### 2.1.3.7.4.1 Three-Dimensional Effects

All of the results shown above have been for 2-D systems. The coupled modeling framework is a fully 3-D capability, limited only by computer resources and other practical data handling issues insofar as problem size is concerned. To demonstrate 3-D dispersion, we have defined a test problem that considers only  $CO_2$  transport and dispersion in the surface layer. We have calculated dispersion results for the two end-member stability classes (A-extremely unstable, and F-moderately stable) at steady state for a seepage flux of 4.04 x 10<sup>-6</sup> kg m<sup>-2</sup> s<sup>-1</sup> out of an area 100 m x 100 m (1 hectare) with wind speed of 5 m s<sup>-1</sup>. We exploit the symmetry of the problem and only simulate one-half of the domain. The results for class A are shown in Figure 2.1.3.7.4.1(1) and reveal the highly dispersive nature of the system. Note the contour scale which shows that  $CO_2$  concentrations due to seepage at the specified rate into the highly unstable flow field result in at most increases of a few percent above background  $CO_2$  concentrations. The difference between the extremely unstable and moderately stable conditions are apparent by comparing Figure 2.1.3.7.4.1(1) and 2.1.3.7.4.1(2). Clearly, atmospheric stability decreases potential  $CO_2$ dispersion and will be a key factor in risk characterization for  $CO_2$  leakage and seepage risk assessment.

In order to quantify the differences between 3-D and 2-D dispersion results for similar systems, we have plotted the  $CO_2$  mass fraction at a point 100 m downwind from the seepage source for similar 2-D and 3-D simulations with wind velocity of 5 m s<sup>-1</sup>. The issue here is how much dispersion occurs in the transverse direction not modeled in the 2-D system. The calculated concentrations show that 2-D results overpredict  $CO_2$  concentrations by approximately a factor of two at this location.

Table 2.1.5.7.4.1(1) Properties of the 3-D sufface-fayer model system.			
Property	Value		
Surface Layer			
Domain size $(x \ge y \le z)$	700 m x 500 m x 10 m		
Discretization ( $Nx \ge Ny \ge Nz$ )	28 x 20 x 20		
Seepage source location (center)	x = 100 m, y = 0 m, z = 0 m		
Seepage flux area	100 m by 100 m (1 hectare)		
Seepage mass flux	$4.04 \text{ x} 10^{-6} \text{ kg m}^2 \text{ s}^{-1}$		
Pressure	1 bar		
Temperature	15 ℃		
Pasquill-Gifford stability class	A (extrem. unstable) or F (mod. stable)		
Wind profile	logarithmic		
Reference velocity at $z = 2$ m	0, 1, or 5 m s <sup>-1</sup>		
Friction velocity for $u_x = 1 \text{ m s}^{-1}$	$0.1335 \text{ m s}^{-1}$		
Reference height $(z_0)$	0.10 m		

Table 2.1.3.7.4.1(1) Properties of the 3-D surface-layer model system.



Figure 2.1.3.7.1(1) Comparison of density of  $CO_2$ -air mixtures as calculated by the NIST14 Database and by T2CA.



Figure 2.1.3.7.1(2) Comparison of viscosity of  $CO_2$ -air mixtures as calculated by the NIST14 Database and by T2CA.



Figure 2.1.3.7.2(1) Schematic of the 2-D surface layer dispersion test problem.



Figure 2.1.3.7.2(2) Simulated CO<sub>2</sub> mass fractions from (a) T2CA and (b) FLUENT for atmospheric dispersion for seepage flux equal to 1. x  $10^{-5}$  kg m<sup>-2</sup> s<sup>-1</sup>.



Figure 2.1.3.7.2(3) Simulated CO<sub>2</sub> mass fractions from (a) T2CA and (b) FLUENT for atmospheric dispersion for seepage flux equal to  $1. \times 10^{-4} \text{ kg m}^2 \text{ s}^{-1}$ .



Figure 2.1.3.7.2(4) Simulated CO<sub>2</sub> mass fractions from (a) T2CA and (b) FLUENT for atmospheric dispersion for seepage flux equal to 1.  $\times 10^{-3}$  kg m<sup>2</sup> s<sup>-1</sup>.



Figure 2.1.3.7.3(1) Verification of passive (P) and active (A) atmospheric dispersion of  $CO_2$  as simulated in 2-D.



Figure 2.1.3.7.4(1) Domain and discretization used in the coupled subsurface–surface-layer test problem.



Figure 2.1.3.7.4(2) Simulated  $CO_2$  mass fractions and gas velocity vectors for coupled subsurface and surface-layer dispersion for calm conditions (no wind).



Figure 2.1.3.7.4(3) Simulated  $CO_2$  mass fractions and gas velocity vectors for coupled subsurface and surface-layer dispersion for wind speed equal to 1 m s<sup>-1</sup>.



Figure 2.1.3.7.4(4)  $CO_2$  mass fractions and gas velocity vectors for coupled subsurface and surface-layer dispersion for wind speed equal to 5 m s<sup>-1</sup>.



Figure 2.1.3.7.4(5) Concentration ( $CO_2$  mass fraction) at a point 100 m downwind from the seepage source for various atmospheric and wind conditions.



Figure 2.1.3.7.4.1(1) Simulated  $CO_2$  mass fractions and gas velocity vectors for 3-D atmospheric dispersion for atmospheric stability class A (extremely unstable) showing lateral, vertical, and downwind dispersion.



Figure 2.1.3.7.4.1(2) Simulated  $CO_2$  mass fractions and gas velocity vectors for 3-D atmospheric dispersion for atmospheric stability class F (moderately stable) showing lateral, vertical, and downwind dispersion.



Figure 2.1.3.7.4.1(3) Concentration (CO<sub>2</sub> mass fraction) at a point 100 m downwind from the seepage source for 2-D and 3-D models.

# 2.1.3.8 Conclusion

We have demonstrated a coupled modeling framework for risk characterization. The coupled model handles subsurface and atmospheric surface-layer flow and transport assuming that dispersion in the surface-layer is passive and that the wind is described using a logarithmic wind profile. The coupled model shows good agreement with a commercial fluid dynamics code FLUENT for surface-layer dispersion, and agrees with empirical correlations for the transition from passive to active (i.e., density-dependent) flow. Coupled subsurface–surface-layer demonstration simulations show the large degree of dilution that occurs in the surface layer, and the possible reflux of  $CO_2$  to the subsurface that occurs when  $CO_2$  dissolves in infiltrating rainwater. Simulations show that dilution of  $CO_2$  by atmospheric dispersion is approximately two times larger in 3-D than for similar 2-D results. This coupled modeling framework can be used to estimate  $CO_2$  fluxes and concentrations for risk characterization of various leakage and seepage scenarios.

# 2.1.3.9 References

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# 2.1.3.10 Publications

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# 2.1.3.11 Bibliography

See references.

# 2.1.3.12 List of Acronyms and Abbreviations

2–D	Two-dimensional
3–D	Three-dimensional
$CH_4$	Methane
$CO_2$	Carbon dioxide
EOS7C	Equation of State 7 for CO <sub>2</sub>
FLUENT	A commercial fluid dynamics code.
HSE	Health, safety and environmental (risks)
NEE	Net ecosystem exchange (for CO <sub>2</sub> )
NIST	National Institute for Science and Technology
P–G	Pasquill-Gifford
SM	Smagorinski Model
TOUGH2	Reservoir simulator, Transport of Unsaturated Groundwater and Heat 2.
T2CA	for <u>TOUGH2 CO<sub>2</sub> and Air</u>

2.1.5 Reactive Transport Modeling to Predict Long-Term Cap-Rock Integrity
## Report Title CO<sub>2</sub> Capture Project - An Integrated, Collaborative Technology Development Project for Next Generation CO<sub>2</sub> Separation, Capture and Geologic Sequestration

# **Reactive Transport Modeling to Predict Long-Term Cap-Rock Integrity**

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Address:	Environmental Sciences Division, L-221 7000 East Ave. Livermore, CA 94550

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## 2.1.5.1 Abstract

Long-term cap rock integrity represents the single most important constraint on the long-term isolation performance of natural and engineered geologic  $CO_2$  storage sites.  $CO_2$  influx that forms natural accumulations and  $CO_2$  injection for EOR or saline-aquifer disposal both lead to concomitant geochemical alteration and geomechanical deformation of the cap rock, enhancing or degrading its seal integrity depending on the relative effectiveness of these interdependent processes. Influx-triggered mineral dissolution/precipitation reactions within typical shales continuously reduce microfracture apertures, while pressure and effective-stress evolution first rapidly increase then slowly constrict them. Using our reactive transport simulator (NUFT), supporting geochemical databases and software (SUPCRT92), and distinct-element geomechanical model (LDEC), we have evaluated the net effect of these initially opposing contributions to cap-rock integrity for both natural and engineered  $CO_2$  influx. The extent of geochemical alteration is nearly independent of filling mode. In contrast, geomechanical deformation—which invariably results in net aperture opening for compartmentalized reservoirs—is significantly more pronounced during engineered influx. These results limit the extent to which natural and engineered storage sites are analogous, and suggest that in both settings shale cap rocks may evolve into effective seals.

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## 2.1.5.3 Executive Summary

Long-term cap rock integrity represents the single most important constraint on the long-term isolation performance of natural and engineered geologic CO<sub>2</sub> storage sites. CO<sub>2</sub> influx that forms natural accumulations and CO<sub>2</sub> injection for EOR/sequestration or saline-aquifer disposal both lead to concomitant geochemical alteration and geomechanical deformation of the cap rock, enhancing or degrading its seal integrity depending on the relative effectiveness of these interdependent processes. Using our reactive transport simulator (NUFT), supporting geochemical databases and software (SUPCRT92), and distinct-element geomechanical model (LDEC), we have shown that influx-triggered mineral dissolution/precipitation reactions within typical shale cap rocks continuously reduce microfracture apertures, while pressure and effective-stress evolution first rapidly increase then slowly constrict them. For a given shale composition, the extent of geochemical enhancement is nearly independent of key reservoir properties (permeability and lateral continuity) that distinguish saline aquifer and EOR/sequestration settings and CO<sub>2</sub> influx parameters (rate, focality, and duration) that distinguish engineered disposal sites and natural accumulations. In contrast, the extent of geomechanical degradation is highly dependent on these reservoir properties and influx parameters because they effectively dictate magnitude of the pressure perturbation; specifically, initial geomechanical degradation has been shown inversely proportional to reservoir permeability and lateral continuity and proportional to influx rate. Hence, while the extent of geochemical alteration is nearly independent of filling mode, that of geomechanical deformation—which invariably results in net aperture opening for compartmentalized reservoirs—is significantly more pronounced during engineered injection. These results limit the extent to which natural CO<sub>2</sub> accumulations and engineered disposal sites can be considered analogous. A new conceptual framework that permits inter-comparison of geochemical and geomechanical contributions to long-term cap rock integrity has been introduced. This framework reveals that ultimate counterbalancing of geochemical and geomechanical effects is feasible, which suggests that shale cap rocks may *evolve* into effective seals—in both natural and engineered storage sites.

Abstracts focusing on relevant subsets of the research described in this report have been presented at three technical conferences: the Offshore Technology Conference, the Second National Conference on Carbon Sequestration, and the AAPG annual meeting. A fourth abstract has been accepted for presentation at the upcoming national meeting of the American Chemical Society. A paper was prepared for and included in the proceedings volume for the Offshore Technology Conference (Johnson et al., 2003a). For our abstract entitled "CO<sub>2</sub> reservoirs: are they natural analogs to engineered geologic storage sites?", which was presented at the AAPG annual meeting, we received the 2003 AAPG DEG (Division of Environmental Geosciences) "Best Paper—Oral Presentation" award.

This being the first semi-annual report requested of CRADA-funded participants within the  $CO_2$  Capture Project (CCP), we have been instructed (by Stuart Green, CCP Control Engineer) to describe all technical work completed to date in this inaugural report. We received initial funding in late May 2002, and began work in June 2002.

# 2.1.5.4 Introduction

This project encompasses both model development and application. The development phase has two components: (1) to interface our existing reactive transport and geomechanical modeling capabilities to facilitate assessment of stress-strain evolution along and above the reservoir/cap-rock interface for both engineered and natural  $CO_2$  influx scenarios, and (2) to develop a new conceptual framework for evaluating the relative impact on long-term cap rock integrity of concomitant geochemical alteration and geomechanical deformation processes in these environments.

In the application phase, our augmented modeling capabilities are used to address two fundamental questions associated with geologic  $CO_2$  sequestration. First, what is the evolution of cap-rock integrity during engineered disposal as a function of integrated hydrological, geochemical, and geomechanical processes? This work builds directly upon our earlier modeling studies, which demonstrated enhanced integrity of shale cap rocks as a function of injection-triggered hydrological and geochemical processes during saline aquifer storage (Johnson et al., 2001, 2002a-b, 2003e). Here, we expand our earlier analyses to include explicit account of geomechanical processes and evaluate the relative effect on cap-rock integrity of concomitant geochemical alteration and geomechanical deformation.

We then address a closely related and equally fundamental issue: is the predicted evolution of cap-rock integrity for engineered  $CO_2$  disposal sites similar to or appreciably different from that of natural  $CO_2$  accumulations; i.e., what is the dependence of this evolution on the rate, duration, and focality of  $CO_2$  influx? The widely espoused natural analog concept implicitly assumes a dearth of such dependence. This assumption—on which strict validity of the concept hinges—may be invalid in some cases. For example, a given reservoir/cap rock system that now holds a natural  $CO_2$  accumulation may be incapable of doing so in the context of an engineered injection owing to significant differences in the magnitude and style of  $CO_2$  influx. Further, the currently secure cap rock of a given natural accumulation may have evolved into an effective hydrodynamic seal following geochemical alteration that attended some degree of  $CO_2$  migration through it. To address these issues, we conduct and compare reactive transport simulations of a generic natural  $CO_2$  reservoir for both natural and engineered "filling" modes.

Because long-term cap-rock integrity is the ultimate constraint on long-term isolation performance for geologic  $CO_2$  storage sites, it is not surprising that our reactive transport modeling analysis of this constraint is linked to a number of currently funded CCP projects. Specifically, there are potential direct links to three projects:

- "Influence of CO<sub>2</sub> injection on the physical properties of reservoir and cap rocks" (Borm et al.). A coordinated effort with this project might provide laboratory-scale "proof of concept" for our modeling capabilities.
- "Safety assessment methodology for carbon dioxide sequestration (SAMCARDS)" (Wildenberg et al.). Results of our work could feed directly into this study.
- "Natural analogs for geologic CO<sub>2</sub> sequestration" (Stevens et al.). A coordinated effort with this project might provide field-scale "proof of concept" for our modeling capabilities.

In addition, our work is indirectly linked to three additional projects:

- "Noble isotopes for screening, verification, and monitoring at CO<sub>2</sub> storage sites" (Nimz and Bryant). Our modeling capabilities could be augmented to address subsurface migration and diffusion of imposed anomalies in noble gas isotope ratios.
- "Novel geophysical techniques for monitoring of CO<sub>2</sub> migration" (Hoversten). Our reactive transport simulation results could be interfaced with software used in this project to generate the dependent geophysical properties.

• "Analysis of CO<sub>2</sub>-charged fluid migration along faults in naturally occurring gas systems" (Evans et al.). Our modeling capability could potentially be used to evaluate the migration paths inferred from field measurements of this system.

# 2.1.5.5 Experimental

Reactive transport modeling is an advanced computational method for quantitatively predicting the longterm consequences of natural or engineered perturbations to the subsurface environment (Johnson et al., 1999). Because these predictions typically involve space, time, and system complexity scales that preclude development of direct analytical or experimental analogs, they often represent a unique forecasting tool. The necessary point of departure for predictive investigations of this kind is established by successful application of the method to simulate well-constrained laboratory experiments (e.g., Johnson et al., 1998).

The method is based on mathematical models of the integrated thermal, hydrological, geochemical, and geomechanical processes that redistribute mass and energy in response to the disequilibrium state imposed by perturbation events such as magmatic intrusion or  $CO_2$  influx (Figure 1). Traditionally, such models have been developed as separate entities and applied as such to address specific issues relevant their individual scope. The fundamental advance embodied in reactive transport modeling is its explicit integration of these conceptually distinct process models. In practice, however, present-day simulators address various subsets of these models, while the ultimate simulation tool—one that implements and explicitly couples all of the relevant processes—remains on the horizon.





We have developed a unique computational package that integrates a state-of-the-art reactive transport simulator (NUFT: Nitao, 1998a,b, 2003), supporting geochemical software and databases (SUPCRT92: Johnson et al., 1992; GEMBOCHS: Johnson and Lundeen, 1994a,b), and a dedicated graphics package (Xtool: Daveler, 1998). In a series of recent studies, we have used this package, which treats coupled thermal, hydrological, and geochemical—but not geomechanical—processes, to address a number of key technical issues regarding  $CO_2$  storage in saline aquifers (Johnson et al., 2001; 2002a,b; 2003e). Paramount among these is the issue of long-term cap rock integrity, which represents the most important risk-assessment concern when evaluating potential sites (i.e., forecasting their long-term isolation performance).

However, because cap-rock integrity evolves as a function of the concomitant geochemical alteration and geomechanical deformation triggered by  $CO_2$  injection, accurate prediction of its long-term evolution requires extending our earlier analyses to explicitly incorporate treatment of geomechanical effects. In the present study, we have accomplished this extension by developing an interface between NUFT and LDEC, a distinct-element geomechanical model developed by Morris et al. (2002, 2003). This interface facilitates mapping the injection-induced pressure perturbation along and above the reservoir/cap-rock contact into the corresponding evolution of effective stress and microfracture apertures.

Finally, we introduce a new conceptual model that depicts geochemical counterbalancing of geomechanical aperture evolution as a function of effective diffusion distance and reaction progress. This model provides a theoretical framework for assessing the extent to which cap-rock integrity will ultimately be enhanced or degraded in specific reservoir/cap-rock systems in the context of specific injection scenarios.

## 2.1.5.6 Results and Discussion

Long-term cap rock integrity represents the single most important constraint on the long-term isolation performance and geohazard potential of engineered (or natural)  $CO_2$  storage sites. Predicting long-term permeability evolution within the cap-rock environment requires first identifying and then quantifying its functional dependence on key system parameters and dynamic processes. The most important factors influencing this evolution are conveniently subdivided into three groups: intrinsic cap rock properties, chemical conditions at the reservoir/cap-rock interface, and the injection-triggered pressure perturbation.

Relevant cap-rock properties include geomechanical parameters, such as fracture normal stiffness, and geochemical characteristics, such as bulk concentrations of carbonate-forming cations, principally Fe, Mg, Ca, Na, and Al. These cation concentrations represent the primary control on geochemical alteration processes, while chemical conditions at the reservoir/cap-rock interface, which are determined by reservoir compositions and  $CO_2$  waste-stream impurities (e.g.,  $SO_x$  and  $NO_x$  concentrations), exert a secondary control. The magnitude, duration, and focality of the injection-induced pressure perturbation, which depend on these same characteristics of  $CO_2$  influx as well as on reservoir permeability, lateral continuity, compartment height (for laterally confined settings), depth, and thickness, represent the fundamental control on geomechanical deformation processes.

Long-term enhancement or degradation of cap rock integrity hinges on the relative contributions of geochemical alteration, which tends to reduce microfracture apertures in shale, and geomechanical deformation, which—on balance—tends to widen them (Figure 2). As a result, long-term performance forecasting of potential storage sites requires a predictive capability that quantifies this pivotal interplay of geochemical and geomechanical processes. As an initial step toward achieving this capability, we have previously modeled the geochemical contribution within a full system analysis of coupled hydrological and geochemical processes. In this project, we are assessing the geomechanical contribution through an independent analysis of its dependencies on hydrological processes and key reservoir properties, then



Figure 2: Schematic depiction of concomitant injection-induced geochemical and geomechanical processes within shale cap rock microfractures. Mineral dissolution/precipitation reactions tend to continuously reduce fracture apertures while pressure evolution tends to first widen then reduce them (net widening). From Johnson et al. (2003a). developing a conceptual model that facilitates comparison of these two contributions within a common reference frame.

In describing this work, we begin with a brief review of subsurface  $CO_2$  migration and sequestration processes, which provides not only the geochemical contribution to long-term cap rock integrity, but also full-system context for the subsequent analysis, which focuses on the cap rock environment.

### 2.1.5.6.1 Subsurface CO<sub>2</sub> migration and sequestration processes

Our previous modeling studies (Johnson et al., 2001; 2002a,b; 2003) have been largely based on simulating  $CO_2$  injection at Statoil's North-Sea Sleipner facility—the world's first commercial saline-aquifer storage site. Here,  $CO_2$ -rich natural gas is produced from 3500 m below the seabed. Excess  $CO_2$  is removed by amine absorption on the platform, then stripped from the amine, and finally injected—at the rate of one million tons per year since 1996—into the Utsira formation 2500 m above the hydrocarbon reservoir (Torp and Gale, 2002). The 200-m-thick Utsira is a highly permeable fluid-saturated sandstone capped by the Nordland Shale. Hydrologic and compositional properties of the Utsira are relatively well constrained (Gregersen et al., 1998), while those of the Nordland Shale are virtually unknown, and must be estimated (Johnson et al., 2001, 2003e).

All of our Sleipner simulations have been carried out within a common 600x250 m spatial domain, which represents the near-field disposal environment, and over a single 20-year time frame, which encompasses equal-duration prograde (active-injection) and retrograde (post-injection) phases. The domain includes a 200-m-thick saline aquifer (35% porosity, 3-darcy permeability), 25-m-thick shale cap rock (5% porosity, 3-microdarcy permeability), and an overlying 25-m-thick saline aquifer. Its lateral boundaries are open to multiphase flow, while its top and bottom boundaries are not. During the prograde phase, pure  $CO_2$  is injected at a rate of 10,000 tons/yr into the basal center of this domain (37°C, 111 bars), which therefore corresponds to a one-m-thick cross-section though the actual 100-m screen length at Sleipner. Within the common domain, we have evaluated three distinct injection scenarios—models XSH, CSH, and DSH. Model XSH examines CO<sub>2</sub> injection into a shale-capped homogeneous sandstone aquifer. Models CSH and DSH impose into XSH four thin (3-m thick) intra-aquifer shales, which are separated from the cap rock and each other by 25 m. Model CSH examines the effect of imposing laterally continuous microfractured shales having assigned permeability (3 md) that equates to a continuum representation of 100-um fractures spaced roughly 30 m apart. Model DSH examines the effect of imposing laterally discontinuous shales, which are bridged by lateral facies change to sandstone. Assigned permeability of these shales (3 µd; same as the cap rock) reflects typical shale integrity.

Compositionally, the saline aquifers are represented as impure quartz sand (80% quartz, 10% K-feldspar, 5% plag-ab<sub>80</sub>, 3% muscovite, 2% phlogopite), while the shale cap rock is represented as 60% clay minerals (50% muscovite, 10% Mg-chlorite), 35% quartz, and 5% K-feldspar. Mg end-member components are used to represent Fe/Mg solid solutions because *in situ* oxidation states are unknown. The saline aquifers and shale are all saturated with an aqueous phase of near-seawater composition.

Our Sleipner simulations suggest that the ultimate fate of  $CO_2$  injected into saline aquifers is governed by three interdependent yet conceptually distinct processes:  $CO_2$  migration as a buoyant immiscible fluid phase, direct chemical interaction of this rising plume with ambient saline waters, and its indirect chemical interaction with aquifer and cap-rock minerals through the aqueous wetting phase. Each process is directly linked to a corresponding trapping mechanism: immiscible plume migration to hydrodynamic trapping, plume-water interaction to solubility trapping, and plume-mineral interaction to mineral trapping.

#### 2.1.5.6.1.1 Immiscible Plume Migration and Hydrodynamic Trapping

Intra-aquifer permeability structure controls the path of prograde immiscible CO<sub>2</sub> migration, thereby establishing the spatial framework of plume-aquifer interaction and the potential effectiveness of solubility and mineral trapping. Actual efficacy of these trapping mechanisms is determined by compositional characteristics of the aquifer and cap rock (Johnson et al., 2001, 2003e). By retarding vertical and promoting lateral plume mobility, inter-bedded thin shales significantly expand this framework (i.e., CO<sub>2</sub> storage capacity), enhance this potential, and delay outward migration of the plume from the near-field environment (Figure 3). Seismic data strongly suggest that the Utsira formation combines elements of models CSH and DSH (Johnson et al., 2001, 2003e).

In all three models, steady-state configuration of the immiscible  $CO_2$  plume is realized within one year. During the prograde phase, a residual saturation zone marks the wake of initial plume ascent to the cap rock or deepest inter-bedded shale (e.g., Figure 3A, left insets). During the retrograde phase, this zone encompasses virtually the entire prograde steady-state plume (e.g., Figure 3A, right inset)—effectively maintaining the prograde extent of solubility trapping and continually enhancing that of mineral trapping, as described below for model DSH. In the near-field environment of Sleipner-like settings, 80-85% by mass of injected  $CO_2$  remains and migrates as an immiscible fluid phase ultimately subject to hydrodynamic trapping beneath the cap rock, which represents an effective seal in these models.

#### 2.1.5.6.1.2 Geochemical Trapping Mechanisms

As the immiscible plume equilibrates with saline formation waters, intra-plume aqueous  $CO_2$  concentrations (primarily as  $CO_2(aq)$  and  $HCO_3$ ) rapidly achieve their solubility limit, while pH decreases:

$$CO_2(g) + H_2O = CO_2(aq) + H_2O = HCO_3^{-} + H^+$$
 (1)





For the chemical system and P-T conditions that characterize the Utsira formation at Sleipner, equilibrium aqueous  $CO_2$  solubility is 1.1-1.2 molal, accounting for 15-20% by mass of injected  $CO_2$  (Figure 4A).

Owing to residual saturation of immiscible CO<sub>2</sub>, this degree of solubility trapping is virtually constant throughout the prograde and retrograde phases. The initial pH drop caused by solubility trapping—from 7.1 to 3.4—catalyzes silicate dissolution, which after 20 years has increased pH from 3.4 to 5.3. This dissolution hydrolyzes potential carbonate-forming cations (here, primarily Na, Al, and Mg) within the immiscible -plume source region, and thus represents the critical forerunner of all mineral-trapping mechanisms.

We have identified four distinct mechanisms whereby  $CO_2$  precipitates as carbonate minerals. Intraplume dawsonite cementation (Figure 4B) is catalyzed by high ambient Na<sup>+</sup> concentration,  $CO_2$  influx, and acid-induced K-feldspar dissolution:

$$\frac{\text{KAlSi}_{3}\text{O}_{8}}{\text{K-feldspar}} + \text{Na}^{+} + \text{CO}_{2}(\text{aq}) + \text{H}_{2}\text{O} \quad \bigstar \quad \underline{\text{NaAlCO}_{3}(\text{OH})_{2}}{\text{dawsonite}} + 3 \frac{\text{SiO}_{2}}{\text{silica}} + \text{K}^{+} \quad (2)$$

The volume of co-precipitating dawsonite and silica polymorphs slightly exceeds that of dissolving K-feldspar. Hence, this kinetic dissolution/precipitation reaction effectively maintains initial  $CO_2$  injectivity; after 20 years, porosity has decreased by a factor of less than 0.1% (Figure 5A). Pervasive dawsonite cementation will likely be characteristic of saline aquifer storage in any feldspathic sandstone. In fact, there is a natural analog for this process: widespread dawsonite cement in the Bowen-Gunnedah-Sydney basin of Eastern Australia, which has been interpreted to reflect magmatic  $CO_2$  seepage on a continental scale (Baker et al., 1995).



Figure 4: Geochemical trapping mechanisms after 20 years in model DSH: (A) solubility trapping (composite molality of all carbon-bearing aqueous species), (B) intra-plume dawsonite cementation, (C) plume-bounding magnesite precipitation (shales shown in white [off-scale high]), and (D) intra-shale magnesite precipitation. From Johnson et al. (2003a).

Calcite-group carbonate rind (here, magnesite) forms along—and therefore effectively delineates—both lateral and upper plume boundaries (Figure 4C). Genetically distinct, these two processes can be described by:

$$Mg^{+2} + CO_2(aq) + H_2O \iff MgCO_3 + 2 H^+$$
(3)  
magnesite

As intra-plume formation waters, progressively enriched in  $Mg^{+2}$  from phlogopite dissolution, migrate outward across lateral plume boundaries, they traverse steep gradients in  $CO_2(aq)$  and pH; the net effect strongly promotes magnesite precipitation. Along upper plume boundaries,  $CO_2(aq)$  concentration and pH are nearly constant, but aqueous  $Mg^{+2}$  concentration increases most rapidly here because formation-water saturation is minimized; this leads to magnesite cementation from the reservoir/cap-rock interface downward.

However, magnesite precipitation is most extensive from this interface *upwards* (cf. Figures 4C and 4D), owing to the relatively high concentration of Mg in clay-rich shales. The coupled intra-shale mineral dissolution/precipitation reaction can be expressed as:

 $\frac{KAlSi_{3}O_{8}}{K-feldspar} + 2.5 \frac{Mg_{5}Al_{2}Si_{3}O_{10}(OH)_{8}}{Mg-chlorite} + 12.5 CO_{2}(aq)$ 

#### ←→

$$\frac{\text{KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2}{\text{muscovite}} + 1.5 \frac{\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4}{\text{kaolinite}} + 12.5 \frac{\text{MgCO}_3}{\text{magnesite}} + 4.5 \frac{\text{SiO}_2}{\text{SiO}_2} + 6 \text{H}_2\text{O}$$
(4)

This kinetic reaction proceeds to the right with an increase in solid-phase volume of 18.5% (magnesite accounting for 47 vol.% of the product assemblage). After 20 years, porosity and permeability of the 5m-thick cap-rock base have been reduced by 8% and 22%, respectively, by this process (Figure 5B), which upon hypothetical completion at 130 years would reduce initial porosity by half and initial permeability by an order of magnitude (Figure 5C), thereby significantly improving cap-rock integrity. A natural analog to reaction (4) has recently been documented in the Ladbroke Grove natural gas field, where post-accumulation  $CO_2$  influx has converted Fe-rich chlorite to Fe-rich dolomite (ankerite), kaolinite, and silica (Watson et al., 2002).



Figure 5: Porosity and permeability reduction in model DSH due to mineral trapping (A) after 20 years in the reservoir (initial porosity:35%; shales shown in white [off-scale low]) and (B-C) after 20 and 130 years in the cap rock. From Johnson et al. (2003a).

Although composite mineral trapping accounts for less than 1% by mass of injected  $CO_2$  in the near-field disposal environment, it has enormous strategic significance: it maintains initial  $CO_2$  injectivity (reaction 2), delineates and may partially self-seal plume boundaries (reaction 3), and—most importantly—reduces cap-rock permeability (reaction 4), thereby enhancing hydrodynamic containment of immiscible and solubility-trapped  $CO_2$ .

The  $CO_2$  migration and sequestration processes reviewed above in the context of saline-aquifer storage are equally applicable to (1)  $CO_2$ -flood EOR operations in shale-capped water-wet oil reservoirs, which are primarily distinguished by the presence of a hydrocarbon phase and lateral confinement, and (2) the formation of natural  $CO_2$  reservoirs, which are fundamentally distinguished in by the rate, focality, and duration of  $CO_2$  influx. However, in all of these settings the effect of geochemical alteration to improve cap-rock integrity may be counterbalanced or even overwhelmed by concomitant geomechanical deformation, which initially acts in opposition. Hence, in evaluating long-term cap rock integrity, explicit account must be taken of both processes.

#### 2.1.5.6.2 Pressure evolution and geomechanical deformation

A first-order assessment of cap-rock geomechanical deformation can be obtained from evaluating the dependence of microfracture aperture evolution on the influx-triggered pressure perturbation at and above the reservoir/cap-rock interface. In a new series of NUFT simulations, we have assessed this dependence, first as a function of reservoir permeability and lateral continuity—two key parameters that typically distinguish saline-aquifer disposal sites and oil reservoirs, and second, as a function of  $CO_2$  influx rate—the fundamental parameter that distinguishes engineered storage and natural accumulation settings. Within these new models, the values adopted for other important parameters that influence geomechanical response to  $CO_2$  injection (e.g., reservoir depth and thickness as well as influx duration) are those used in the Sleipner simulations described above.

In the Sleipner models, we addressed coupled hydrological and geochemical processes. In the following simulations, we explicitly address only the effect of hydrological (multiphase flow) processes. However, this approximation has negligible impact for impure sandstone reservoirs (such as the Utsira formation), where reservoir porosity and permeability—and thus the injection-induced pressure perturbation—are not modified appreciably by geochemical alteration, as demonstrated above (Figure 5A).



#### 2.1.5.6.2.1 Dependence on Reservoir Properties: saline aquifer versus EOR settings

Figure 6: Schematic depiction of the laterally unconfined and laterally confined simulation domains used for models UHP/ULP and CHP/CLP, respectively. The pre-injection hydrostatic gradient is identical in the two systems. Illustrated domain cells are not drawn to scale. From Johnson et al. (2003a).

In this study, four distinct simulations have been carried within two spatial domains (Figure 6). Reservoir permeability and lateral continuity are varied from 3000 md and infinite in model UHP (laterally-Unconfined, High Permeability), which represents desirable saline-aquifer storage sites, to 300 md and 2000 m in model CLP (laterally-Confined, Low Permeability), which represents a typical compartmentalized EOR setting. Models ULP and CHP represent cross-combinations of these values, which facilitate evaluation of specific dependence on reservoir permeability and lateral confinement. In both laterally confined models, compartment height—itself a parameter that exerts second-order influence on the injection-induced pressure perturbation—is 150 m. In all four models, supercritical  $CO_2$  is injected at the rate of  $10^4$  tons/yr during the prograde event.

Magnitude of the influx-triggered pressure perturbation at the reservoir/cap rock interface varies significantly with (and inversely proportional to) reservoir permeability and lateral continuity (Figures 7-10), although its general evolution during prograde and retrograde phases of the influx event does not (Figure 11). For highly permeable, laterally extensive reservoirs (model UHP), this perturbation follows a characteristic three-stage evolution: (1) initial rapid increase to maximum pressure as the aqueous phase is displaced upwards during ascent of the immiscible  $CO_2$  plume to the cap rock, (2) rapid asymptotic decrease to a near steady-state value intermediate to ambient and maximum pressures that is maintained thereafter during the prograde regime; and (3) a second rapid asymptotic decrease towards the ambient value, which is triggered by onset of the retrograde regime (Figure 7). This pressure evolution suggests that the potential for dependent geomechanical deformation events is maximized during three very brief, distinct episodes that occur during the earliest stages of prograde and retrograde disposal. Note that for this Sleipner-like setting, the range of injection-induced pressure variation is small—on the order of 3 bars.





Decreasing reservoir permeability from 3000 to 300 md without imposing lateral confinement (i.e., model ULP) significantly increases magnitude of the pressure perturbation—from roughly 3 to nearly 22 bars—without altering the three-stage evolution described above (cf. Figures 7 and 8). Also noteworthy from this comparison is the inverse dependence of  $CO_2$  storage capacity on reservoir permeability, which suggests that for pure-sequestration scenarios the addit ional energy cost of exploiting less permeable reservoirs—which require higher injection pressures—may be partially offset by the benefit of increased storage and delayed migration into the far-field environment, providing cap-rock performance is not significantly compromised.



Figure 8. NUFT simulation of immiscible CO<sub>2</sub> migration and the associated pressure perturbation at the reservoir/ cap rock interface for the laterally unconfined 300 md reservoir.

The influence of reservoir compartmentalization on the influx-induced pressure perturbation at the reservoir/cap rock interface is examined in models CHP and CLP (Figures 9-10).



Figure 9. NUFT simulation of immiscible CO<sub>2</sub> migration and the associated pressure perturbation at the reservoir/ cap rock interface for the laterally confined 3000 md reservoir.

Although the functional form of pressure evolution in these models is analogous to that described above for laterally unconfined reservoirs, three significant variations are introduced by compartmentalization. First, the magnitude of initial pressure increase during plume ascent to the cap rock is significantly enhanced—reaching 60 bars in model CLP—owing to the restricted lateral flow (increased flow resistance) of displaced formation water. Second, a permeability-dependent fourth stage of pressure evolution—one that bridges cap-rock and spillpoint plume arrival times—is introduced that either causes a secondary pressure increase (CHP) or slows prograde decrease (CLP) of the initial pressure anomaly. Third, owing to presence of the accumulated  $CO_2$  column, during the retrograde phase pressure decays asymptotically toward a steady-state value that exceeds hydrostatic and whose magnitude is proportional to column height. This final variation is extremely significant because it imposes a long-term pressure perturbation upon the cap-rock interface, which does not occur in unconfined reservoirs.



Figure 10. NUFT simulation of immiscible CO<sub>2</sub> migration and the associated pressure perturbation at the reservoir/ cap rock interface for the laterally confined 300 md reservoir.



Figure 11: NUFT simulation of pressure evolution at the reservoir/cap rock interface of models UHP, ULP, CHP, and CLP together with the distance profiles associated with attainment of pressure maxima (inset). From Johnson et al. (2003a).

Direct translation of the injection-induced pressure perturbation from the well to and above the reservoir/cap-rock interface in all four models controls  $CO_2$  migration into the undeformed cap rock through changes in capillary pressure, and controls geomechanical deformation of the cap rock through changes in effective stress and dependent microfracture apertures. Hence, the magnitude and evolution of these migration and deformation processes directly reflect those of the injection-induced pressure perturbation. The capillary pressure effect can be modeled directly with NUFT, while assessment of deformation effects requires developing and implementing a NUFT/DLEC interface.

 $CO_2$  migration into the undeformed 25-m-thick 3-µd cap rock through increased capillary pressure is minimized in model UHP, where penetration distance is only 5 m, and maximized in model CLP, where such migration actually breeches the overlying reservoir (Figure 12).



Figure 12. NUFT simulation of CO<sub>2</sub> migration into geomechanically undeformed cap rock through increased capillary pressure after 20 years in models UHP, ULP, CHP, and CLP, which are shown from left to right.

Pressure evolution at and above the cap rock can be mapped into a corresponding evolution of effective stress and dependent microfracture apertures, yielding a first-order estimate of injection-induced geomechanical deformation. Here, we use a simplified form of the constitutive relationship between effective stress ( $\sigma_E$ ), total stress ( $\sigma_T$ ), and pressure ( $P_f$ ):

$$\sigma_{\rm E} = \sigma_{\rm T} - P_{\rm f} \quad , \tag{5}$$

where  $\sigma_T$  is assumed to be constant ( $\Delta \sigma_E = -\Delta P_f$ ). By further neglecting the nonlinear aperture dependence of fracture normal stiffness (K<sub>N</sub>), normal aperture displacement due to reduced effective normal stress ( $\Delta a_N$ ) can be expressed as:

$$\Delta a_{\rm N} = (\Delta P_{\rm f} / K_{\rm N}) \tag{6}$$

Using equations (5) and (6) together with an estimated normal stiffness for shale fractures at depth (Bilgin, 1990), we first translate the maximum injection-induced pressure perturbation for each of the four models (Figure 11) into the corresponding maximum aperture normal displacement in order to gauge relative scale (Figure 13). As can be seen, the potential maximum aperture increase due to reduced effective normal stress is 50-1100  $\mu$ m. Because attainment of this pressure maximum coincides with arrival of the immiscible plume at the cap rock—after only 15-100 days in all four models—the potential for geomechanical deformation is maximized very early during the prograde phase.





Simulating long-term aperture evolution requires an interface between our reactive transport (NUFT) and geomechanical (LDEC) models, which we developed during the reporting period. This interface facilitates translation of pressure evolution within a given reservoir cap-rock system into the dependent evolution of effective stress and microfracture apertures—here cast within the simplifying context of eqns (5) and (6). In this application, the interface is applied to a representative sub-grid from our NUFT domains: a 60m-by-50m half-space that encompasses the uppermost 10 m of the lower reservoir (2 NUFT grid cells), the 25-m-thick shale cap rock (5 cells), and the 25-m-thick upper reservoir (5 cells). The functional form of aperture evolution at the reservoir/cap rock interface is directly analogous to that described above for pressure, as exemplified by LDEC simulation of such evolution for model CLP (Figure 14). As can be seen, during the prograde phase apertures rapidly increase during initial plume ascent, and then asymptotically decrease to a steady-state value that reflects net widening. During the retrograde phase, they first rapidly decrease from this prograde steady state, then continue to decrease asymptotically towards a steady state value that reflects net widening of about 75  $\mu$ m per the approximate 5-bar net pressure increase associated with CO<sub>2</sub> accumulation. Hence, geomechanical deformation degrades cap-rock integrity only during the earliest stages of the prograde phase, after which it slowly but



Figure 14. LDEC simulation of aperture evolution at the reservoir/cap rock interface of model CLP.

continuously mitigates this initial degradation event. However, unless counterbalanced by geochemical effects, this 75- $\mu$ m net aperture widening could facilitate long-term CO<sub>2</sub> migration into the cap rock. Moreover, although maximum prograde and ultimate net aperture increases (roughly 1100 and 75  $\mu$ m, respectively) occur at the reservoir interface, concomitant increases of 200-1100 and a few 10s of  $\mu$ m are realized throughout the basal 20m of the 25-m-thick shale cap rock (Figure 15). Such pervasiveness suggests the potential development of microfracture continuity sufficient to permit CO<sub>2</sub> migration into and perhaps completely through relatively thin shale cap rocks in certain influx settings.



Figure 15. LDEC simulation of aperture evolution within and immediately surrounding the cap rock in model CLP.

#### Dependence on influx parameters: engineered versus natural storage

In this study, three distinct simulations have been carried within a single spatial domain (Figure 16) that represents a confined sandstone reservoir whose compartment width (10 km), height (100 m), and width:height aspect ratio (100:1) typify natural CO<sub>2</sub> reservoirs (Allis et al., 2001). In all three models, sandstone reservoir and shale cap rock permeability are 300 md and 3  $\mu$ d, respectively. The models are distinguished primarily by prograde CO<sub>2</sub> influx rate, which is varied from 10<sup>4</sup> to 10<sup>3</sup> to 10<sup>2</sup> tons/yr, representing engineered injection, "fast" natural accumulation, and "slow" natural accumulation, respectively. The engineered injection rate is that used in the earlier Sleipner simulations, while the two values adopted for natural accumulation rates—which are presently unknown—are rough estimates. A secondary difference is duration of the prograde and retrograde events, both of which span 10 years for the engineered injection, but are extended to 40 and 20 years in both natural accumulation models.





Because the engineered-injection model adopts the same injection rate used in the preceding set of simulations, it illustrates dependence of the pressure perturbation on compartment width and aspect ratio, while providing a baseline for evaluating its dependence on influx rate per comparison with the two natural accumulation models (Figure 17). Increasing compartment width from 2 to 10 km causes pressure



Figure 17. NUFT simulation of immiscible CO<sub>2</sub> migration and the associated pressure perturbation at the reservoir/ cap rock interface for engineered injection.

to increase even after the plume has reached the cap rock, owing to the increased volume of formation water that must be displaced. Hence, while pressure increases from 90 to 150 during plume ascent in both models CLP and here (cf.. Figures 10 and 17), in this case pressure ultimately reaches 250 bars before declining after the plume reaches the lateral boundary. Subsequent asymptotic pressure decline during the post-spillpoint prograde and retrograde phases is dampened by increased compartment width.

When influx rate is reduced by one and two orders of magnitude, migration of the plume is retarded and the pressure perturbation is reduced proportionately, while its functional form remains unchanged (Figures 18-19). In the "fast" natural accumulation model, the immiscible plume does not reach the lateral compartment boundary until just before termination of the 40-year prograde event, while the maximum pressure perturbation (about 22 bars) is a factor of 7-8 less than that for the engineered injection model. In the "slow" natural accumulation model, the plume has not quite advanced halfway to the compartment boundary after 60 years (which encompasses both the prograde and retrograde events), while the maximum pressure perturbation is less than 3 bars.



Figure 18. NUFT simulation of immiscible CO<sub>2</sub> migration and the associated pressure perturbation at the reservoir/ cap rock interface for "fast" natural accumulation.



60

10

20

10

distance from injection well (m)

20

Figure 19. NUFT simulation of immiscible CO<sub>2</sub> migration and the associated pressure perturbation at the reservoir/ cap rock interface for "slow" natural accumulation.



The extent of  $CO_2$  migration into undeformed shale through increased capillary pressure is strongly dependent on influx rate. Such migration extends halfway through the 25-m-thick shale in the "slow" accumulation model (intra-shale saturations approaching 8%), completely through this shale and halfway through the overlying 25-m-thick reservoir in the "fast" accumulation model (upper reservoir saturations approaching 12%), and completely through this upper reservoir to form a laterally-restricted (see Figure 17) accumulation zone beneath the upper domain boundary (where saturations approach 25%) in the engineered injection model (Figure 20).

10

20 0

The extent of geomechanical cap-rock deformation through changes in effective stress and dependent aperture evolution is also strongly dependent on influx rate. As the maximum pressure perturbation realized at the reservoir/cap rock interface increases from 3 to 22 to 160 bars with a 10- to 100-fold increase in influx rate (Figures 17-19), the dependent aperture opening—evaluated in the context of eqns (5) and (6)—increases from approximately 50 to 350 to 2900 µm.

The three simulations described above address a fundamental question regarding natural  $CO_2$  reservoirs: are they natural analogs to engineered  $CO_2$  storage sites? The models suggest that geomechanical degradation of seal integrity will be characteristic of both natural and engineered  $CO_2$  influx, but significantly more severe during the latter. This result implies that cap-rock isolation performance may

vary considerably as a function of filling mode, which severely limits the extent to which natural  $CO_2$  reservoirs can be considered directly analogous to engineered  $CO_2$  storage sites.

#### 2.1.5.6.3 Geochemical counterbalancing of geomechanical effects

Long-term enhancement or degradation of shale cap-rock integrity ultimately hinges on the relative effectiveness of concomitant geochemical alteration and geomechanical deformation. The analyses presented above offer an opportunity to evaluate an important aspect of this geochemical/geomechanical interplay: the extent to which these initially opposing processes may counterbalance one another.

This cross-comparison requires a common reference frame, the choices for which are changes in porosity or fracture aperture, which have been used above to represent the respective contributions of geochemical and geomechanical effects. Converting aperture change into the corresponding porosity change requires an initial aperture or fracture density (neither of which are known), while the aperture change associated with matrix expansion due to a specific mineral dissolution/precipitation reaction can be represented as a function of the dependent variables. Hence, we adopt the latter approach and translate the geochemical contribution into the aperture-change reference frame.

For a given dissolution/precipitation reaction within the matrix, the associated aperture change (Da) depends on initial volume fraction of the reactant assemblage (VR/VT), standard molal volume change of the reaction (DVro = VPo - VRo), effective diffusion distance (LD, how deep into matrix blocks the reaction occurs), and reaction progress (C, the extent to which the reaction proceeds to completion):

$$\Delta a = -2 \left[ \left( V_{\rm R} / V_{\rm T} \right) \left( \Delta V_{\rm r}^{\rm o} / V_{\rm R}^{\rm o} \right) L_{\rm D} C \right]$$
(7)

All of these variables are typically known or can be closely estimated except for diffusion distance and reaction progress. Hence, it is both appropriate and convenient to plot Da isopleths as a function of these latter two parameters.

We have constructed such a diagram for reaction 4 (Figure 21), where the Da-isopleths plotted span the range of maximum aperture widening due to geomechanical displacement that was predicted for models UHP, ULP, CHP, and CLP (Figure 11). Hence, they can be viewed as geochemical "counterbalance" isopleths; i.e., along any curve, departing to greater diffusion distances or reaction progress equates to net aperture closure (improved cap-rock integrity) as a function of combined geochemical and geomechanical effects, while departing to lesser values equates to net opening (degraded integrity).





This diagram reveals that geochemical counterbalancing of geomechanical deformation over this range of  $\Delta a$  requires diffusion distances of only 3-6.5 cm for reaction progress of 30-60%. These ranges—both of which are commonly observed in natural systems—suggest that early-stage maximum geomechanical deformation may be eventually counterbalanced by geochemic al alteration. This raises the possibility that shale cap rocks in CO<sub>2</sub> reservoirs (so-called natural analogs to engineered disposal sites) may have *evolved* into effective seals following some degree of CO<sub>2</sub> migration through them. Careful mineralogical and petrographic analyses of these shale cap rocks may shed light on this concept.

#### 2.1.5.6.4 Abstracts, papers, and awards

Abstracts focusing on relevant subsets of the research described in this report have been presented at three technical conferences: the Offshore Technology Conference (invited talk in a Special Session on Geohazards), the Second National Conference on Carbon Sequestration, and the AAPG annual meeting (Special Session on Geological Sequestration of  $CO_2$ ). A fourth abstract was submitted to and has been accepted for presentation at the upcoming national meeting of the American Chemical Society (another Special Session on  $CO_2$  sequestration). Finally, a paper was prepared for and included in the proceedings volume for the Offshore Technology Conference (Johnson et al., 2003a). Complete citations for these abstracts and the proceedings article are provided in section 2.1.5.10 ("Publications").

For our abstract entitled " $CO_2$  reservoirs: are they natural analogs to engineered geologic storage sites?", which was presented at the AAPG annual meeting, we received the 2003 AAPG DEG (Division of Environmental Geosciences) "Best Paper—Oral Presentation" award.

### 2.1.5.7 Conclusion

Long-term cap rock integrity represents the single most important constraint on the long-term isolation performance of natural and engineered geologic CO<sub>2</sub> storage sites. CO<sub>2</sub> influx that forms natural accumulations and CO<sub>2</sub> injection for EOR/sequestration or saline-aquifer disposal both lead to concomitant geochemical alteration and geomechanical deformation of the cap rock, enhancing or degrading its seal integrity depending on the relative effectiveness of these interdependent processes. Using our reactive transport simulator (NUFT), supporting geochemical databases and software (SUPCRT92), and distinct-element geomechanical model (LDEC), we have shown that influx-triggered mineral dissolution/precipitation reactions within typical shale cap rocks continuously reduce microfracture apertures, while pressure and effective-stress evolution first rapidly increase then slowly constrict them. For a given shale composition, the extent of geochemical enhancement is nearly independent of key reservoir properties (permeability and lateral continuity) that distinguish saline aquifer and EOR/sequestration settings and CO<sub>2</sub> influx parameters (rate, focality, and duration) that distinguish engineered disposal sites and natural accumulations. In contrast, the extent of geomechanical degradation is highly dependent on these reservoir properties and influx parameters because they effectively dictate magnitude of the pressure perturbation; specifically, initial geomechanical degradation has been shown inversely proportional to reservoir permeability and lateral continuity and proportional to influx rate. Hence, while the extent of geochemical alteration is nearly independent of filling mode, that of geomechanical deformation—which invariably results in net aperture opening for compartmentalized reservoirs—is significantly more pronounced during engineered injection. These results limit the extent to which natural  $CO_2$  accumulations and engineered disposal sites can be considered analogous. A new conceptual framework that permits inter-comparison of geochemical and geomechanical contributions to long-term cap rock integrity has been introduced. This framework reveals that ultimate counterbalancing of geochemical and geomechanical effects is feasible, which suggests that shale cap rocks may *evolve* into effective seals-in both natural and engineered storage sites.

### 2.1.5.8 References

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# 2.1.5.9 Publications

### Papers

Johnson, J.W., Nitao, J.J., Morris, J.P., and Blair, S.C., Reactive transport modeling of geohazards associated with offshore CO<sub>2</sub> injection for EOR and geologic sequestration: *invited paper*, *Proceedings Offshore Technology Conference 2003*, Houston, TX, May 5-8, 2003, 9 p.

### **Abstracts/Presentations**

Johnson, J.W., Nitao, J.J., and Morris, J.P., Reactive transport modeling of cap rock integrity during natural and engineered CO<sub>2</sub> sequestration: American Chemical Society National Meeting, New York, NY, September 7-11, 2003 (abstract submitted May 11, 2003; accepted May 20, 2003; oral presentation).

Johnson, J.W., Nitao, J.J., Blair, S.C., and Morris, J.P., CO<sub>2</sub> reservoirs: are they natural analogs to engineered geologic storage sites?: Special Session on Geological Sequestration of CO<sub>2</sub>, AAPG Annual Meeting, Salt Lake City, UT, May 11-14, 2003 (abstract and oral presentation). *NOTE: we received the 2003 AAPG DEG (Division of Environmental Geosciences)* "Best Paper—Oral Presentation" award for this presentation.

Johnson, J.W., Nitao, J.J., and Morris, J.P., Reactive transport modeling of long-term cap rock integrity during  $CO_2$  injection for EOR or saline-aquifer storage: Second National Conference on Carbon Sequestration, Alexandria, VA, May 5-8, 2003 (abstract and poster presentation).

Johnson, J.W., Nitao, J.J., Blair, S.C., and Morris, J.P., Reactive transport modeling of geohazards associated with offshore CO<sub>2</sub> injection for EOR and geologic sequestration: Special Session on Geohazards (Fred Aminzadeh, organizer), Offshore Technology Conference 2003, Houston, TX, May 5-8, 2003 (invited abstract and oral presentation).

### Presentations

Johnson, J.W., Nitao, J.J., Blair, S.C., and Morris, J.P., Reactive transport modeling to predict long-term cap-rock integrity, JIP CO<sub>2</sub> Capture Project Workshop: "Leveraging the SMV Family of Technology Providers", Santa Cruz, CA, Oct 21-23, 2002 (oral presentation).

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