Global Climate and Energy Project

Rapid Prediction of CO$_2$ Movement in Aquifers, Coal Beds, and Oil and Gas Reservoirs

Final Report 2006

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Abstract

This report examines the physical mechanisms of processes designed to store CO\textsubscript{2} in subsurface porous media as well as the time scales associated with those mechanisms. Computational tools available for prediction of the performance of CO\textsubscript{2} sequestration projects are reviewed. Two studies demonstrate the use of compositional simulation for design of CO\textsubscript{2} storage projects in oil and gas reservoir settings. Conventional finite-difference compositional simulation is used to examine co-optimization of enhanced oil recovery and CO\textsubscript{2} storage. Streamline compositional simulation is used to predict performance of combined storage of CO\textsubscript{2} and enhanced gas recovery.

The time scales associated with CO\textsubscript{2} storage in deep formations that contain salt water are considered in three ways. The impact of convective mixing of brine-saturated CO\textsubscript{2} (which is slightly denser than brine alone) on the time scale for dissolution of CO\textsubscript{2} is considered using linear stability theory and high order simulation. Those studies show that convective overturn speeds dissolution over diffusion alone, but the time for onset of convective overturn is quite long unless the permeability is quite high. The interplay of gravity segregation and capillary trapping of CO\textsubscript{2} as an immobile residual phase is examined using conventional finite-difference simulation. That study indicates that significant trapping of CO\textsubscript{2} as a residual phase happens on the time scale of a few multiples of the time period in which CO\textsubscript{2} is injected. More CO\textsubscript{2} is trapped when viscous forces dominate than when gravity forces dominate the flow. Compositional streamline simulation with gravity is used to demonstrate that high resolution simulation is practical and much more efficient computationally for large aquifer systems in comparison to conventional finite-difference simulation.

Combined CO\textsubscript{2} storage and coal bed methane recovery is investigated through experiments and theoretical investigations. Time scales for diffusional equilibrium are estimated. For coal beds with small fracture spacing, the assumption of fast local equilibrium of injected CO\textsubscript{2} with the coal is reasonable. Measured adsorption isotherms are reported for dry and moist pulverized coal samples. In these samples, considerably more CO\textsubscript{2} adsorbs than does methane. Reductions in permeability of pulverized coals are reported for mixtures of nitrogen and CO\textsubscript{2}. While reductions in permeability occur when CO\textsubscript{2} is adsorbed, the presence of nitrogen in the injection gas limits the reduction. Wetting behavior of coals is considered with experiments and theory. Both approaches suggest that wetting behavior is sensitive to pH. Results of displacement experiments with pure CO\textsubscript{2} and mixed gases are reported, and detailed numerical simulations are used to interpret the experiments. Experimental and calculational results both indicate that representation of hysteresis is important for accurate prediction of flow behavior. Finally, an analytical theory of flow of water and gas in a coal bed with adsorption of the gas components is presented.

The results presented in this report add to the growing literature suggesting that CO\textsubscript{2} storage in oil and gas settings is best understood, while there is more to be done to characterize fully mechanisms and the time and spatial scales of storage in aquifers and coal beds. Coal bed storage is the least well delineated of the three.
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GCEP Technical Report 2006
1 Introduction

Three primary options are being considered for large-scale storage of CO$_2$ in subsurface formations: oil and gas reservoirs, deep saline aquifers, and coal beds. In each setting a collection of physical mechanisms will act on a variety of time scales to distribute the injected CO$_2$ within the formation and determine its fate in the long term. A key part of putting in place a CO$_2$ storage project will be predicting the movement of CO$_2$ in the subsurface. Modeling the most important of those mechanisms is an essential part of accurate prediction of the distribution of injected CO$_2$ during and after injection of CO$_2$. This report examines the impacts of the various mechanisms, considers the time scales on which they operate, and investigates the suitability of various reservoir simulation tools for prediction of flow behavior in CO$_2$ storage projects.

Some mechanisms will be more important during the injection period than they will be after injection ceases. In an oil reservoir, for example, the flow pathway taken by the CO$_2$ is the result of the pressure gradients established between injection and production wells, gravity segregation of CO$_2$ that is less dense than oil or water, and reservoir heterogeneity that creates preferential flow of low viscosity CO$_2$ in high permeability paths between wells. In a gas reservoir setting, on the other hand, the CO$_2$ is likely to be more dense and more viscous than the gas. In both settings, CO$_2$ will dissolve in oil and water, and components in the oil or in a condensate phase in a gas reservoir will vaporize into the CO$_2$. For enhanced oil recovery applications of CO$_2$ injection and for displacement of condensate in a gas reservoir, these component transfers can have quite significant impact on the fraction of oil or condensate displaced in the zone swept by the CO$_2$.

In a deep saline aquifer, many of the same mechanisms will also operate. The solubility of CO$_2$ in brine is an order of magnitude lower than CO$_2$ solubility in a typical oil, and relatively high capillary forces will mean that CO$_2$ will again flow first through high permeability regions. In many settings well-to-well flow will not occur, and hence pressure gradients will be determined primarily by injection well pressures and flow rates and aquifer permeability. Gravity segregation will still be important.

In coal beds, where the flow takes place primarily in fractures, gravity segregation of CO$_2$ in water-filled fractures will be important, as will the adsorption of CO$_2$ in the coal. Here the time scale for flow in the fractures may or may not differ significantly from that of diffusion, adsorption, and desorption of components within the coal matrix.

A different, but overlapping, set of mechanisms will be most important in the period after injection ends. In all three settings, there will be a period during which the pressure gradients relax and gravity segregation continues to move a separate CO$_2$ phase upward in oil reservoirs, aquifers and coal beds. In many settings, this upward movement of CO$_2$ will create a thin zone with high CO$_2$ saturations below barriers to vertical flow. That zone will extend laterally, possibly over long distances. In gas reservoirs, gravity will drive CO$_2$ downward, though mixing of previously injected CO$_2$ will reduce density differences over time. In all three settings, slow diffusion of CO$_2$ in all the phases in
which it appears will distribute CO$_2$. Dissolution of CO$_2$ in undisplaced oil or brine will take place. As that happens, saturations of CO$_2$ in some zones will decrease, which can lead to capillary trapping of the CO$_2$ as a residual phase. Once trapped, the residual CO$_2$ is essentially immobilized, except for further slow dissolution. Brine containing dissolved CO$_2$ is slightly more dense than brine alone, and hence CO$_2$ dissolving high in a formation will make possible a gravity overturn within the water phase. In aquifers, it may be possible to dissolve all the injected CO$_2$ on some time scale. In oil and gas reservoirs, it is likely that a free CO$_2$ phase will continue to exist indefinitely.

In this report, we examine the time scales associated with various mechanisms, and we report results of analytical analyses, simulations with various computational approaches, and experimental results that test the ability of the various simulation tools to capture the effects of the physical mechanisms and to describe the time scales on which the various mechanisms act. In Section 2, we review briefly the main computational tools available for investigation of CO$_2$ storage projects. In Section 3, we consider two examples of applications of simulation tools to combined CO$_2$ storage and enhanced oil recovery and to combined condensate recovery and CO$_2$ storage in a gas reservoir. Section 4 examines time scales for dissolution of CO$_2$ in brine in an aquifer and considers the impact of convective overturn of brine saturated with CO$_2$ on the rate of dissolution. Section 4 also includes estimates of how efficiently CO$_2$ displaces brine using conventional reservoir simulation tools and more efficient streamline simulation tools. Section 5 reports analyses of time scales for coal bed storage and analytical solutions for flow of a two-component gas mixture (nitrogen and CO$_2$ or methane and CO$_2$, for example) along with water in a coal bed. Also reported in Section 5 are results of adsorption measurements and flow experiments along with simulations of those experiments.
2 Review of Available Simulation Technology

Considerable effort has been devoted to the development of reservoir simulation tools for the oil industry, and there are high quality simulators available that handle effectively many of the flow problems appropriate to oil and gas reservoirs. One area where simulator development is continuing, however, is in the simulation of processes in which multiple components transfer between whatever phases are present in the porous medium. Injection of CO\textsubscript{2} into geologic reservoirs inevitably involves such component transfers, as the injected CO\textsubscript{2} dissolves in any water or oil present, as hydrocarbons transfer to the relatively dense CO\textsubscript{2}-rich phase, or as CO\textsubscript{2}, methane, and possibly N\textsubscript{2} adsorb and desorb in coal.

Because the most important physical mechanisms of storage differ for the three geologic systems, it is appropriate to consider the current state of predictive models for each setting. Compositional simulation tools are best developed for oil and gas reservoir settings, for which several fully capable finite-difference compositional simulators are available. ECLIPSE 300 and GEM are examples. These codes use an equation of state to represent equilibrium partitioning of components between oil and gas phases, and they handle the effects of capillary pressure and gravity well. The principle limitations of these simulation tools are computation speed and the adverse effects of numerical dispersion on computed composition path. For aquifer and coalbed settings there are also several simulation tools available. The capabilities of some of them are reviewed in the paragraphs that follow.

2.1 CO\textsubscript{2} Injection in Saline Aquifers

2.1.1 TOUGH2

TOUGH2 is a numerical simulator for non-isothermal flows of multicomponent, multiphase fluids in one, two and three-dimensional porous and fractured media [77]. TOUGH2 was originally developed for geothermal reservoir engineering, nuclear waste disposal and hydrology. There are several simulators in the TOUGH2 family that include physical mechanisms appropriate to CO\textsubscript{2} sequestration in aquifers, including TOUGHREACT/ECO2 (includes transport of aqueous liquid and vapor phases by advection, chemical reactions for dissolved species and minerals, and molecular diffusion in both liquid and gas phases), ChemTOUGH (implicit formulation that allows larger time steps but requires substantially more memory), and TOUGH2-FLAC3D (coupled TOUGH2/ECO2 with FLAC3D which models rock and soil mechanics). This family of simulators generally makes use of the equilibrium assumption: components equilibrate rapidly among whatever phases are present. An exception is made for mineral dissolution and precipitation, which can be modeled as in local equilibrium or subject to a kinetic model.

2.1.2 NUFT

NUFT [70] is an integrated software package containing five application specific modules, for the simulation of multiphase and multicomponent flow and reactive transport within a wide range of subsurface environments. The code can model
multiphase advection, diffusion, dispersion, relative permeability, and kinetically controlled fluid-mineral reactions. The feedback between transport and geochemical reactions can be modeled by dependence of the permeability on porosity changes due to reactions. PVT properties of CO$_2$ and water are calculated from equation of state formulations. The SUPCRT92 software package is used for calculation of fluid mineral equilibria [31]. It provides standard state thermodynamic data and equilibrium constants for a wide range of minerals, gases, and aqueous species over a wide range of temperatures and pressures.

2.1.3 **FLOTRAN**

FLOTRAN [62] describes coupled thermal-hydrologic-chemical processes in variably saturated, nonisothermal, porous media in three dimensions. FLOTRAN describes systems involving two-phase fluid flow and multicomponent reactive chemical transport involving aqueous, gaseous and mineral species. FLOTRAN includes separate modules that handle the mass and energy transport and the reactive transport. FLOW solves the mass conservation equations for water and gas and energy. TRANS solves mass conservation equations for a multicomponent geochemical system. Effects of capillary, gravity, and viscous forces are included, as are energy transport by convection and conduction. The equilibrium assumption is made for chemical reactions, with kinetic representations available for mineral dissolution and reaction. Changes in porosity and permeability can be represented.

2.1.4 **STOMP**

STOMP [107] is a computer model for simulating subsurface flow and transport. Solute transport, radioactive decay, and first-order chemical reactions modeled, following the solution of the coupled flow equations. Reactions and transport are coupled to the flow by accounting for changes in host rock porosity and permeability. An equation of state for CO$_2$ is included that handles a wide range of temperatures and pressures to 800 bar. Options appropriate to sequestration include H$_2$O-CO$_2$-NaCl, H$_2$O-CO$_2$-NaCl-Energy, H$_2$O-CO$_2$-CH$_4$-NaCl, and H$_2$O-CO$_2$-CH$_4$-NaCl-Energy. Extension to account for other geochemical reactions are planned.

2.1.5 **UTCOMP**

The UTCOMP simulator is a three-dimensional, isothermal, equation-of-state compositional simulator [8]. The simulator can be used to study the effects of physical dispersion, gravity, reservoir heterogeneity, phase behavior, fingering, relative permeability and capillary pressure effects including capillary number, and reactive and partitioning tracers. A maximum of four phases is permitted to co-exist, including one aqueous phase and three hydrocarbon phases. Local thermodynamic equilibrium between hydrocarbon phases is assumed with the exception of rate-limited mass transfer of surfactant between phases, rate-limited mass transfer of hydrocarbons into a flowing gas phase and reactive tracers. UTCOMP was written to simulate enhanced oil recovery and several modifications are needed in order to simulate CO$_2$ sequestration. For CO$_2$ injection into aquifers, phase 2 was used for the aqueous phase and phase 3 was the gas phase (supercritical CO$_2$ plus some H$_2$O as a dense fluid phase). Phase equilibrium in the binary CO$_2$-H$_2$O mixtures in each grid block is calculated using the Peng-Robinson equation of state [76]. The effect of salinity on the solubility of CO$_2$ in brine is modeled...
by adjusting the binary interaction coefficients in the Peng-Robinson equation. Henry’s law is used to model the solubility of CO$_2$ in water, including a correction for salinity of the brine.

### 2.2 CO$_2$ Injection in Coal Beds

Coalbed methane (CBM) simulators also model physical mechanisms thought to be important in CBE recovery and CO$_2$ storage processes: the dual porosity structure of the coal bed, adsorption/desorption of CH$_4$ at the coal surface, coal matrix shrinkage due to CH$_4$ desorption, and diffusion of gas from the matrix to the fracture system. Additional physical mechanisms that may play a role in CO$_2$ storage on coalbeds include: coal matrix swelling due to CO$_2$ adsorption onto the coal surface, mixed gas adsorption, and diffusion of multiple gas components.

Enhanced CBM simulators that are applicable to CO$_2$ storage can be divided into two groups: those that use a compositional framework and those that adopt a black oil framework. In the compositional framework, fluid properties are rigorously modeled based on an equation of state. In the black oil framework, fluid properties are supplied by lookup tables, obtained through laboratory work or correlations.

#### 2.2.1 PSU-COALCOMP

PSU-COALCOMP [85] is a compositional, dual porosity coal bed methane simulator that accounts for multi-component sorption and transport phenomena. Multicomponent sorption is modeled via an ideal adsorbed solution theory and the Peng-Robinson equation of state. Mass transfer between the matrix and fracture system is defined via a sorption time constant, a lumped parameter that incorporates diffusion time, rate or sorption/desorption and cleat spacing of the coal. GCOMP a simulator that assumes instantaneous diffusion between the matrix and the fracture systems, allowing reduction of the system to a single porosity system [90]. Mixed gas adsorption is modeled via an extended Langmuir model. In this approach, the concentration of each gas component is a function of its partial pressure. Geomechanical effects on permeability and porosity are modeled, as are coal matrix shrinkage and swelling due to adsorption/desorption of gases on the coal surface.

#### 2.2.2 SIMED

SIMED II is a two phase multicomponent single or dual porosity coal bed reservoir simulator [100]. The Peng-Robinson equation of state is used to calculate fluid properties. Water phase properties are evaluated internally. Multiphase gas adsorption can be modeled via an extended Langmuir isotherm or an ideal adsorbed solution model. Stress dependent permeability and porosity can be accounted for through a choice of one of five models. SIMED II also accounts for geomechanical effects associated with injection. A dynamic fracture model represents the initiation and growth of injection induced hydraulic fractures.

#### 2.2.3 CMG-GEM

CMG-GEM [12] is another multiphase, multicomponent single of dual porosity coal bed reservoir simulator. Phase behavior can be described by either the Peng-Robinson or Soave-Redlich-Kwong equation of state. Shape factors can be used to account for flow
between porosities and additional transfer enhancements can be used to account for fluid placement in the fractures. Mixed gas adsorption is modeled via an extended Langmuir isotherm, and the corresponding diffusion model can be selected based on either concentrations calculated from adsorption characteristics or based on free gas properties. Stress dependent relative permeability changes and matrix swelling and shrinkage can be included.

2.2.4 METSIM2

METSIM2 [88, 89] is a 3D multicomponent, triple porosity coal bed reservoir simulator. This formulation assumes that there is no water present in macropore system, only free gas exists, and its transport is diffusion controlled. This formulation allows for the competitive desorption in coal by specifying different diffusion time constants for the macropore and the micropore systems. Gas properties are calculated using an equation of state. Multicomponent adsorption is described using an extended Langmuir model. METSIM2 is also coupled to a wellbore and rock mechanics simulator, allowing pore pressure dependent permeability functionality.

2.2.5 COMET3

COMET3 is an extension of COMET and COMET2, developed to model low-rank coal and water saturated gas-shale reservoirs [78]. It can model single, dual and triple porosity approximation of the coal bed system. In the triple porosity system, gas desorbs from the internal matrix, and migrates to the microporosity matrix and finally to the cleat system where it flows to the wellbore. In this formulation, the microporosity matrix system also models multiphase effects. This accounts for the establishment of a critical gas saturation in the matrix, which may be responsible for a delay in early time gas production observed in some fields. Desorption and diffusion are explicitly modeled. COMET3 can model multiple gas components, and accounts for different diffusion rates of the components. An extended Langmuir isotherm is used to model mixed gas adsorption. Pore volume compressibility accounts for stress dependent porosity and permeability changes. A differential swelling model based on laboratory experiments accounts for swelling attributed to non-CH₄ components of the gas.

2.2.6 ECLIPSE-100

ECLIPSE-100 [86] is a black oil simulator with additional features for modeling CBM. A dual porosity system is used to model the coal bed system. This simulator is only able to handle two gas components, and therefore it is not able to model an ECBM process with flue gas injection. Compositional effects between CO₂ and CH₄ are handled by introducing a “solvent” phase. Adsorption is described by the Langmuir isotherm. Eclipse-100 can account for coal shrinkage and compaction effects.

2.3 Summary: Simulation technology

The simulators currently available for aquifer and coalbed storage of CO₂ are very capable, with many physical mechanisms represented. They will continue to be very useful for exploring the interplay of physical mechanisms for computational grids of limited size, but they are subject to significant limitations for application at field scale. Conventional finite-difference compositional simulations, even with relatively small numbers of components, are too slow to handle high resolution representation of the
spatial distribution of permeability at field scale, and when coarse computational grids are used instead, they are badly affected by numerical diffusion, which can alter calculated composition paths in a way that affects calculated performance significantly. Hence, they are probably not suitable for routine simulation of field-scale flows at grid resolutions sufficient to capture the effects of preferential flow paths created by reservoir heterogeneity, especially if the impact of variability in the permeability distribution is to be assessed. For screening of sites, assessment of areas invaded by CO$_2$, or rapid exploration of the impact of injection well placement, simulation tools that are significantly more efficient, but necessarily more limited in the mechanisms represented, are appropriate. One approach, the use of streamline methods, is demonstrated in the following sections for two of the geologic settings, gas reservoirs and aquifers.
3  CO$_2$ Sequestration in Depleted Oil and Gas Reservoirs

Geologic sequestration of carbon dioxide CO$_2$ in oil and gas reservoirs is one possibility to reduce the amount of CO$_2$ released to the atmosphere. Carbon dioxide injection has been used in enhanced oil recovery (EOR) processes since the 1970s; the traditional approach is to attempt to reduce the amount of CO$_2$ injected per barrel of oil produced. For a sequestration process, however, the aim is to maximize both the amount of oil produced and the amount of CO$_2$ stored. It is not readily apparent how this aim is achieved in practice. In this section, we use two compositional reservoir simulation approaches to consider several strategies for increasing CO$_2$ storage. In particular, we investigate injection and production procedures that optimize both hydrocarbon recovery and CO$_2$ storage. The reservoir settings are “nontraditional” for CO$_2$. The first setting is a moderately dense (910 kg/m$^3$) and viscous oil. Pure CO$_2$ and the reservoir fluid do not develop miscibility at any pressure that can be attained in the reservoir. The second setting is a gas condensate reservoir with significant drop out of a condensate liquid phase within the reservoir.

In both settings, simulations are conducted on realistic, three dimensional, heterogeneous reservoir models. The reservoir descriptions are stochastic in that multiple realizations of the reservoir model are available. Reservoir fluids are described compositionally and incorporate multiple distinct components. A major difference in approach between the two settings is the reservoir simulation technique that is found suitable. In the viscous oil setting, a conventional finite difference and fully compositional approach is found adequate. In the condensate setting, however, the coupling of flow through heterogeneous media with the details of the phase behavior of condensate/CO$_2$ mixtures proves to be best represented with a streamline-based approach.

It has been observed elsewhere [74] that oil and gas reservoirs are good initial candidates for sequestration because physical and legal infrastructure already exists for CO$_2$ injection. The main factor setting the efficiency of oil recovery with CO$_2$ injection is the miscibility of CO$_2$ in the hydrocarbon phase [72, 73, 5]. At pressures greater than the minimum miscibility pressure (MMP), the dynamics of the displacement process create mixtures of oil and CO$_2$ are mutually soluble. The dissolved CO$_2$ reduces the viscosity of the oil and also causes swelling of the oil phase. Thus, CO$_2$ injection projects are preferred for oil with densities ranging from 29 to 48 °API (882 to 788 kg/m$^3$) and reservoir depths from 760 to 3700 m below ground surface [95]. If the only considerations are depth and gravity, 80% of the world’s reservoirs qualify for EOR with CO$_2$ [96]. To date, injection processes have been designed to minimize the amount of CO$_2$ injected per barrel of oil produced thereby minimizing the purchase cost of CO$_2$. However, when the aim is to store carbon dioxide, the design question changes significantly [57]. Oil recovery processes need to be modified to leave the maximum amount of CO$_2$ in the reservoir at the completion of operations as well as maximizing the oil recovery.

In some gas reservoirs, condensation of heavier hydrocarbon component occurs with pressure depletion. This liquid often condenses around wells and is immobile. It thereby
blocks gas flow into wells. Further, valuable hydrocarbons are left behind in the reservoir as liquid. Injection of CO$_2$ provides an opportunity to maintain reservoir pressure and, importantly, vaporize and displace the liquid fraction for recovery purposes.

### 3.1 Cooptimization of CO$_2$ Storage and Enhanced Oil Recovery

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Oil reservoirs have considerable appeal as storage locations because they are known to have a geologic seal that trapped the hydrocarbons. Thus, as long as operations during oil production have not damaged that seal, the reservoir should be able to hold injected CO$_2$ indefinitely. Storage of CO$_2$ can take place in zones in which CO$_2$ replaces reservoir oil or water. CO$_2$ is soluble in water, and it is about ten times more soluble in unsaturated oil. A separate CO$_2$-rich phase can also occupy significant pore volume. Movement of oil and gas in a reservoir is dominated by the pressure gradient created between injection and production wells and by the heterogeneity of the rocks. The viscosity of CO$_2$, a few hundredths of a centipoise over a wide range of pressures and typical reservoir temperatures, is low compared to most oils and any water present in the reservoir. The injected CO$_2$ invades high permeability flow paths as it makes its way to production wells. Accurate prediction of the timing of breakthrough of injected CO$_2$ at production wells and the amount of CO$_2$ produced with the oil requires detailed description of the permeability distribution in the reservoir. Those predictions are important because they forecast the amount of subsequent production, recompression, and recycling of CO$_2$ that is produced with oil.

With respect to EOR combined with sequestration, the design question is significantly different in comparison to EOR alone. For pure EOR, one attempts to maximize oil recovery while injecting minimum CO$_2$ and this is accomplished by injecting a significant amount of water in a water-alternating-gas fashion. In combined sequestration and EOR one maximizes both oil recovery and the amount of reservoir volume filled with CO$_2$. This is so-called cooptimization. Our cooptimization efforts focused on (1) exploring injection-production techniques that meet the new design criteria and produce at least as much oil as conventional recovery efforts and (2) expanding the range of candidate reservoirs considered for CO$_2$ injection.

The synthetic reservoir description known as PUNQ3 [24] is chosen. Our implementation of PUNQ3 is as described elsewhere [58]. The reservoir is roughly 28 m thick with a pore (i.e., void) volume of $30 \times 10^6$ m$^3$. Initially, 60% of the pore space is filled with oil. Reservoir shape is anticlinal (i.e., dome shaped) and it is bounded by faults and underlain by an aquifer, as shown in Figure 3.1. Darkly shaded portions of Figure 3.1 locate the regions of the greatest absolute rock permeability, where permeability is a quantitative measure of the conductivity of the rock to fluid. The average horizontal permeability is about 100 md (1 md = $10^{-15}$ m$^2$) and the average porosity (void fraction) is 0.20. Fault location on Figure 3.1 is called out by a thick dotted line. There are four injectors near the flanks of the reservoir and 4 producers near the crest. Arrows indicate the location of injection (down) and production (up) wells. For most simulations in this work, we employ the “truth” model as described in Kovseck and Wang [58] and illustrated in Figure 3.1.
The reservoir fluid, represented by 14 distinct chemical components, is moderately dense (910 kg/m$^3$) and viscous [58]. Pure CO$_2$ and the reservoir fluid are not mutually miscible at reservoir pressure. The minimum pressure for achieving miscibility (MMP) of pure CO$_2$ is in excess of 600 atm (60.8 MPa), whereas the initial reservoir pressure is 250 atm (25.3 MPa). Thus, the reservoir is not a prototypical candidate for CO$_2$–EOR because the oil is heavy and CO$_2$ does not develop miscibility with the oil at reservoir pressure. Because microscopic displacement efficiency approaches unity when the injection gas and oil are miscible, we also explore solvent injection as a means of oil recovery. Table 3.1 lists the compositions of the two injection gases. The solvent is designed to contain a large percentage of CO$_2$ with lesser amounts of ethane (C$_2$), propane (C$_3$), and butane (C$_4$) that allow miscibility to develop at pressures below 250 atm.

Figure 3.1: Reservoir architecture: distribution of horizontal permeability.

Flow within the reservoir is described by the multiphase extension of Darcy's law [3]. The specific relative permeability functions employed in this work are shown in Figure 3.2. The subscripts “w” and “o” refer to the flow of oil and water, respectively, in a water-oil system, whereas the subscripts “g” and “og” refer to the flow of gas and oil, respectively, in an oil-gas system. The Stone II model is used to obtain three-phase relative permeability functions from two-phase data [94].
Figure 3.2: Two-phase relative permeability relationships: (a) water-oil and (b) oil-gas.

Table 3.1: Composition (mole fraction) of injection gases.

<table>
<thead>
<tr>
<th></th>
<th>Lean Gas</th>
<th>Solvent Gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon dioxide, CO₂</td>
<td>1.000</td>
<td>0.667</td>
</tr>
<tr>
<td>Ethane, C₂</td>
<td>0.125</td>
<td></td>
</tr>
<tr>
<td>Propane, C₃</td>
<td></td>
<td>0.125</td>
</tr>
<tr>
<td>Butane, C₄</td>
<td></td>
<td>0.083</td>
</tr>
</tbody>
</table>

3.1.1 Injection Scenarios

Our main goal is to find injection scenarios leading to maximum oil recovery and maximum emplacement of CO₂ in the reservoir. To achieve this goal, we performed
reservoir flow simulations with Eclipse300 [29], a fully-compositional, three-dimensional finite-difference based reservoir simulator.

One of the most important factors affecting the performance of the numerical reservoir simulator is the number and size of the grid blocks in the reservoir model. In order to check the effect of the grid-block size on our results, we have performed reservoir simulations of a water-alternating-gas (WAG) process for three different grid block sizes. In simulations, identical well conditions are used: producer BHP is fixed at 175 bars, and oil and gas injection rates per injection well are 400,000 and 1,000 m$^3$/day, respectively. Alternating water and gas slugs injected are of 0.01 pore volume in size. The WAG ratio is taken as 1.0. Two finer models were created by dividing each grid block of the original model by 4 and 16 on the horizontal plane (i.e. division by 4 and 16 creates $38 \times 56 \times 5$ and $76 \times 112 \times 5$ grid blocks, respectively). Figure 3.3 shows a comparison of the WAG recovery predicted from the three models. When CO$_2$ is used as the injection gas, simulation results show that 61% and 60% of the OOIP is recovered after 15,000 days for the original model and the model that is four times finer. In addition, simulation of WAG with CO$_2$ using the finest model showed recovery performance almost equal to the $38 \times 56 \times 5$ grid block case. When the same simulations are performed by substituting solvent gas for CO$_2$, it is seen that the sensitivity of the recovery performance with respect to grid block size is similar to the case of WAG with CO$_2$. Both of the finer models performed almost equally and performance of the coarsest model is slightly greater than the fine models (73% and 70% of OOIP produced after 15,000 days, respectively). Because, down-gridding does not create significant difference of the simulation results; the original coarse model was used throughout this study.

![Figure 3.3: Comparison of the simulation results for WAG schemes with different grid block sizes. WAG ratio is 1.0 and slug size is 0.01 PV.](image)

Four injection strategies were tested including

- gas injection after waterflooding (GAW)
- water alternating gas drive (WAG)
- gas injection with active production and injection well constraints (well control)
- switch from solvent gas injection to pure CO\textsubscript{2} injection

Pure CO\textsubscript{2} and the solvent gas are used in each of the scenarios, Table 3.1. The first two schemes resemble conventional oil recovery methods. Gas injection after waterflooding represents a project where water is used to maintain pressure and drive oil from the reservoir. After some volume of water injection, the project is converted to gas injection as a means of sequestering CO\textsubscript{2}.

For simulation, production wells operate at a fixed pressure of 175 bars. This pressure is the bottomhole pressure (BHP) within the portion of the well just adjacent to the producing formation. Water is injected at a rate of 1000 m\textsuperscript{3}/day per well until injection is switched to CO\textsubscript{2} at 400,000 m\textsuperscript{3}/day (volumes at standard conditions). The size of the initial water injection was varied from 0.1 to 1.0 PV in steps of 0.1 PV. Here, PV (short for pore volume) is a dimensionless quantity referring to the volume of fluid injected (at reservoir conditions) divided by the pore (void) volume of the reservoir. Hence, 0.1 PV signifies injection of a fluid volume equal to 10\% of the reservoir volume.

The WAG scheme injects water and CO\textsubscript{2} in alternating slugs. The water helps to reduce the mobility of CO\textsubscript{2} within the reservoir, making CO\textsubscript{2} a more effective displacement agent. In situations where gravity is significant, the more-dense water sweeps the lower portions of the reservoir while the more buoyant gas sweeps upper portions. Again, production wells operate at a fixed pressure of 175 bars. The injection rate of water is 1000 m\textsuperscript{3}/day, whereas that of CO\textsubscript{2} or solvent is 400,000 m\textsuperscript{3}/day (at standard conditions). Equal volumes of water and gas (at reservoir conditions) are injected during each slug because the optimal WAG ratio (volume of water to that of gas in a slug) is approximately 1 for the combination of relative permeability curves and phase viscosities [7]. Slug sizes of 0.001, 0.01, 0.1, and 1 PV are employed.

The third scheme aims to maximize the mass of CO\textsubscript{2} injected while not reducing oil recovery. The well control parameters are the producing gas-oil ratio (GOR) and the injection pressure, where the producing GOR is the volumetric flow rate of gas produced upon the oil production rate. Table 3.2 summarizes the three well-control schemes that were tested. Producer GOR refers to the GOR threshold that causes a well to be shut in. The pressure columns are the injection or reservoir pressure where production wells are opened to avoid over-pressurizing and thereby damaging the reservoir.

Table 3.2: Well constraints used in optimization study.

<table>
<thead>
<tr>
<th></th>
<th>Producer GOR (m\textsuperscript{3}/m\textsuperscript{3})</th>
<th>Injector BHP (bars)</th>
<th>Average reservoir pressure (bars)</th>
<th>Increment to GOR (m\textsuperscript{3}/m\textsuperscript{3})</th>
</tr>
</thead>
<tbody>
<tr>
<td>WC-1</td>
<td>500</td>
<td>350</td>
<td>n/a</td>
<td>250</td>
</tr>
<tr>
<td>WC-2</td>
<td>500</td>
<td>300</td>
<td>n/a</td>
<td>100</td>
</tr>
<tr>
<td>WC-3</td>
<td>500</td>
<td>n/a</td>
<td>300</td>
<td>100</td>
</tr>
</tbody>
</table>
Every time a production well is opened, the threshold GOR for shutting in a well is increased by the increment indicated. Numerical experimentation showed that no or small increments in the threshold GOR caused wells to turn off rather frequently, and this reduced oil production significantly. The various scenarios are simulated with both pure CO₂ injection and miscible solvent gas injection.

The final scheme employs initially a solvent gas that is rich in light hydrocarbon components. Miscibility of the injection gas with the oil leads to excellent recovery. Later during injection, the solvent gas is switched to pure CO₂. This helps to reduce the volume of relatively expensive solvent required, promotes recovery of the hydrocarbon gas components, as well as leads to maximum concentration of CO₂ in gas-filled pore space. Wells are operated as in the well control scenario. The time for the switching from solvent gas injection to pure CO₂ is the main parameter examined.

3.1.2 Evaluation of Scenarios

In a cooptimization scheme, it may be appropriate to allow some volume of gas to cycle through the reservoir as a means of obtaining maximum CO₂ storage. Any produced gas, however, must be recompressed to injection pressure before it can be recycled to the reservoir. That is, there is an energy penalty associated with gas cycling. To allow the possibility of gas cycling but to also account for the energy penalty, the net cumulative oil recovery, \( N_p^* \), is defined as

\[
N_p^* = N_p - E
\]  

where \( N_p \) is the cumulative oil recovery. The second term on the right is the energy needed, in oil equivalent units, to compress the produced injection gas to injection pressure. It is expressed as [19]

\[
E = \frac{3.1815X^{-7}}{\gamma} P_{in} Q_{in} \left[ \left( \frac{P_{out}}{P_{in}} \right)^{\gamma} - 1 \right] t
\]  

where \( \gamma \) is the compressibility factor (0.23 CO₂), \( P \) is pressure (lb/ft²), \( Q \) is flow rate (ft³/min), and the subscripts in and out refer to the low and high pressure sides of the compressor. In Eq. 3.2, \( E \) has units of barrels of oil and \( t \) is in days. Thus, \( N_p^* \) is the net production of oil discounted by the amount of energy needed to cycle gas through the reservoir.

3.1.3 Results

Figure 3.4 compares the performance of the various reservoir development scenarios that might be used during CO₂ sequestration. The WAG scenarios are designed so that the mobilities of the injected phases in the reservoir are reduced. In the well control scenario, production wells are actively controlled to limit the amount of produced gas and increase the contact of gas with reservoir volume. Control parameters are the producing gas-oil ratio (GOR) and the injection pressure. As Figure 3.4(a) shows, oil recovery is greatest as a result of miscible gas injection. With miscible gas injection, the local
displacement efficiency approaches unity and recovery is maximized. Among the scenarios with miscible gas injection, well-controlled injection resulted in oil recovery 7 to 12% greater than the other cases and approaches 80% of the oil in place. In the case of pure CO$_2$ injection, WAG with small equal-sized slugs (0.01 pore volume) of water and CO$_2$ performs the best, however ultimate recovery is nearly the same as well-controlled CO$_2$ injection. The main differences between these two scenarios are found during intermediate portions of the recovery lying between 3000 and 7000 days.

In Figure 3.4(b), the injection scenarios are compared with respect to the reservoir volume utilized for CO$_2$ storage. In this case, immiscible CO$_2$ injection cases perform better than miscible solvent injection because only two thirds of the solvent gas is CO$_2$. All cases illustrate that injection of water for mobility control frustrates sequestration. Pore space becomes filled with water when it otherwise could be filled with CO$_2$. Gas-controlled production appears promising. Oil production obtained from pure CO$_2$ injection with well control is on par with that obtained in an optimized WAG process while the utilization of reservoir volume to store CO$_2$ is about 2.5 times that of a WAG scheme. In general, gas-controlled production appears to limit gas cycling while increasing oil production and CO$_2$ storage by 12 to 20% as compared to injecting pure CO$_2$ or solvent gas.
To examine further the cooptimization question, the well control scheme was implemented in the simulator that actively shuts in producers with large gas to liquid producing ratios. This scheme allows gas injection without any water injection. Water injection frustrates cooptimization efforts by filling pore space that could otherwise be utilized for sequestration. Control of wells in this fashion allows the same amount of oil to be produced as in an optimized WAG process (with pure CO$_2$ as the injectant) while simultaneously storing about 2.5 times as much CO$_2$ as compared to the WAG.

Despite these promising results, questions existed as to whether the well-control scheme was robust and whether the results obtained with well control were overly sensitive to the distribution of heterogeneities in the reservoir model. The parameters used to operate the production well are producing gas-oil ratio, injection pressure, and an increase in the allowed producing gas-oil ratio each time a producer is allowed to flow. The initial producing gas-oil ratio and the increment to the gas-oil ratio were chosen in an ad hoc fashion. The sensitivity of performance to values of the allowed gas-oil ratio and its increment were examined through further simulation.

Figure 3.5 presents the results for the sensitivity analysis of pure CO$_2$ injection by plotting the variation in the net cumulative recovery, Figure 3.5a, and reservoir utilization functions, Figure 3.5b. The y-axis is the producing gas-oil ratio where the production well is first shut in, whereas the x-axis is the increment made to the producing gas-oil ratio each time an injection well reaches maximum pressure (350 bar) and producers must be opened to prevent overpressurization of the reservoir. Gray shading represents relatively low values of recovery or utilization and white represents relatively greater values.
On the one hand, Figure 3.5 teaches that optimal well control is obtained when the gas oil ratio where the well is first shut in is set to just slightly above the solution gas oil ratio (that is the solubility of gas in the oil). This allows control of gas flow at just about
the time that gas breaks through to the injection well. Similarly, the results show that the increment to the producing gas oil ratio should be made as small as practical to obtain the best performance. On the other hand, these results also show that performance of the well control scheme does not depend critically on control parameters. Note the variations in maximum and minimum values. Differences in recovery and utilization among "best" and "worst" parameters settings differ by 6 to 14%. Thus, the sensitivity analysis indicates that producing gas-oil ratio and injection pressure are robust control parameters. This well control strategy does not appear to require a high degree of parameter tuning to obtain beneficial results.

Similarly, the sensitivity of results obtained with the well-control scheme was examined as a function of the distribution of permeability within the 3D reservoir model. The injection scenarios include: pure CO$_2$ injection, WAG with 0.01 PV slugs of CO$_2$ and water, CO$_2$ injection with well control, and solvent gas (2/3 CO$_2$ and 1/3 C$_2$) injection with well control. Results showed that the oil recovery increased or decreased from model to model, but the best performing production scenario for any given reservoir model is well-controlled injection of solvent. With respect to reservoir utilization, well control with pure CO$_2$ injection sequesters the most CO$_2$. WAG does lead to different sorting of the performances among the reservoir models; however, these deviations from the reference case do not change the conclusion that the well-controlled cases are preferred for cooptimization.

3.2 Combined CO$_2$ Storage and Condensate Vaporization

Carolyn J. Seto, Kristian Jessen and Franklin M. Orr Jr.

CO$_2$ injection into gas reservoirs has been proposed but not yet been attempted. CO$_2$ could be used for pressure maintenance or for condensate vaporization, but the cost of purchasing CO$_2$ has so far prevented these applications in the absence of incentives for CO$_2$ storage. In fields that contain some condensate saturation, CO$_2$ can vaporize the light hydrocarbons that make up the condensate quite efficiently (see below), and it is even possible for CO$_2$ to develop multicontact miscibility with two-phase gas and condensate mixtures [42]. If CO$_2$ sequestration were undertaken in a substantial way, gas reservoirs would be candidate storage locations, again with a known geologic seal capable of holding gas indefinitely.

3.2.1 Storage potential

Storage of CO$_2$ in a gas reservoir would have the advantage that all CO$_2$ that results from oxidation of CH$_4$ produced from the reservoir could be stored in the same reservoir, at the same temperature and pressure, with volume left over. One mole of CO$_2$ is produced for each mole of CH$_4$ oxidized, and the molar density of CO$_2$ is always larger than that of CH$_4$ at a given temperature and pressure. Figure 3.6 shows molar densities of CH$_4$ and CO$_2$ calculated with the Peng-Robinson [76] equation of state with volume translation [46]. The greater molar density of CO$_2$ means that the volume of CH$_4$ produced from a gas reservoir could be replaced by a mixture of N$_2$ and CO$_2$. In other words separation of all of the N$_2$ from a flue gas, for example, would not be required to match injection and withdrawal volumes, though there would be additional cost associated with compression of the N$_2$/CO$_2$ mixture over that for CO$_2$ alone. Figure 3.7
shows that a mixture of 60% N$_2$ and 40% CO$_2$ has approximately the same density as pure CH$_4$ at 50, 75, and 100°C.

![Figure 3.6: Molar density of CH$_4$ and CO$_2$.](image)

![Figure 3.7: Molar density of CH$_4$ and a mixture containing 60% N$_2$ and 40% CO$_2$.](image)

3.2.2 Simulation approach

CO$_2$ injection into a gas reservoir is a process that can be modeled well by a streamline calculation. The viscosity contrast between injected gas and the gas and condensate in place in the reservoir is small (and the mobility ratio is favorable), and density differences are also relatively small, so streamlines change location slowly compared to the rate at which composition fronts move. The local equilibrium assumption (that fluid phases present at a given location are in chemical equilibrium) is also reasonable for this setting.
Gas cycling schemes for enhanced condensate recovery are inherently compositional because condensate moves primarily by vaporization, and hence, compositional simulation is appropriate. The efficiency of a condensate and gas recovery scheme depends on two factors:

- local displacement efficiency that is controlled by phase behavior of mixtures of injection gas and fluid in the reservoir. The fluid characterization must adequately capture fluid PVT and dilution behavior. Condensate behavior is sensitive to small fractions of heavy components. To model retrograde behavior in a gas injection scheme with reasonable accuracy, therefore, sufficient resolution of the heavy components of the condensate is required.

- global sweep efficiency that is controlled by reservoir heterogeneity. High mobility injection gas flows preferentially through high permeability paths in the reservoir, efficiently displacing condensate in these regions while bypassing condensate in low permeability zones. Extremes in permeability have significant impact in determining fluid flow. Hence accurate prediction of process performance and CO$_2$ storage also requires good resolution of permeability heterogeneity in the reservoir.

Compositional finite difference (FD) simulation is the conventional way to model these systems. In this method, a material balance for each component, over each block, must be calculated. Included in this calculation is at least one flash calculation per grid block per time step. For large models or complex fluid descriptions, computation times are prohibitively long. In order to obtain results in a reasonable time, simplifications in fluid description and reservoir heterogeneity are necessary, potentially rendering results inaccurate. An alternative to FD simulation is compositional SL simulation [99, 14, 40]. In this method, compositions are propagated as 1D displacements along streamlines. Coupling streamlines with the fast analytical solutions of the displacement reduces simulation times by orders of magnitude.

In the simulations of fluid displacements along streamlines, the following assumptions are made:

- No gravity or viscous crossflow: In condensate systems, the density difference between injected gas and reservoir gas is small. As a result, mobility differences are also small, and it can be assumed that the location of streamlines remain fixed as fluids propagate through the reservoir.

- No capillary forces: Pressures and temperatures in condensate systems are close enough to critical conditions that interfacial tensions are expected to be low. During gas injection in condensate systems, much of the displacement occurs as gas displaces gas, with vaporization of immobile condensate.

- No physical dispersion: On the reservoir scale, convective velocities are orders of magnitude larger than those due to dispersion. Convection is the dominant mechanism propagating gas from injector to producer.
Zhou et al. [113] discuss the scaling of multiphase flow in heterogeneous porous media and use gravity numbers ($N_{gv}$) defined by

$$N_{gv} = \frac{\Delta \rho g L K_{ave}}{H \mu v}, \quad (3.3)$$

where $\Delta \rho$ is the density difference between the fluid in place and the injected fluid, $g$ is the gravity, $L$ is the length of the system, $K_{ave}$ is the average permeability in, $H$ is the height of the system, $v$ the flow velocity and $\mu$ the viscosity of the fluid in place. Zhou et al. [113] classify the flow to be dominated by gravity forces if

$$\frac{N_{gv} M}{M + 1} >> 1, \quad (3.4)$$

where $M$ is the endpoint mobility ratio. Based on estimates of the properties of fluids and formation given in Table 3.3, $N_{gv}$ is evaluated to $= 13.2$, and $M = 0.84$, and hence, the left-hand side of Eq. 3.4 equals 6.0. Thus, these displacements lie in the transition region between viscous-dominated and gravity dominated flows.

<table>
<thead>
<tr>
<th>Table 3.3: Properties used in scaling analysis ($N_{gv}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscosity of CO$_2$ (cp)</td>
</tr>
<tr>
<td>Viscosity of mobile gas phase (cp)</td>
</tr>
<tr>
<td>Density difference, $\Delta \rho$ (kg/m$^3$)</td>
</tr>
<tr>
<td>Formation thickness (m)</td>
</tr>
<tr>
<td>Formation length (m)</td>
</tr>
<tr>
<td>Flow velocity (m/d)</td>
</tr>
<tr>
<td>Average permeability (md)</td>
</tr>
<tr>
<td>Interfacial tension, $\sigma$ (mN/m)</td>
</tr>
</tbody>
</table>

Gravity effects can be accounted for explicitly in compositional streamline simulation by an operator splitting technique [14, 44]. However, since gravity effects due to variations in phase densities along the displacement path are modest, these effects are neglected in the following calculations.

Streamline methods have also been developed to account for capillary forces [4]. In critical fluid systems such as gas condensates, interfacial tensions are low. Hamon and Vidal [34] use the Bond number classify ($N_B$) to classify capillary dominated displacements. $N_B$ is defined as

$$N_B = \frac{\Delta \rho g L^2}{\sigma}, \quad (3.5)$$

where $\sigma$ is the interfacial tension. A displacement is considered capillary dominated if $N_B < 0.05$. Using displacement properties listed in Table 3.3, $N_B$ for this system ranges from $1.25 \times 10^{12}$-$1.86 \times 10^{13}$, an indication that the flow is far from a capillary-dominated regime.
Analysis of the scaling of these crossflow phenomena suggested that capillary effects are small enough to be neglected, while gravity effects are somewhat larger but still small enough that testing the use of the streamline in the absence of a representation of gravity segregation was reasonable.

### 3.2.3 Results

To test the use of streamline simulation for CO$_2$ injection in a gas reservoir in which condensate dropout had occurred, we compared streamline simulations with results of ECLIPSE-300 simulations for the same system.

Displacement of a 13-component system was considered. Fluid properties and equation-of-state characterization for the fluid system are reported by [42]. The analytical solution for one-dimensional displacement of this fluid system by pure CO$_2$ is shown in Figure 3.8.

![Figure 3.8: Comparison of analytical solution for 1D displacement of a 13-component gas condensate system by pure CO$_2$.](image)

As the injected CO$_2$ propagates through the porous medium, it vaporizes condensate, creating a bank of hydrocarbon liquid at the leading edge of the transition zone. The analytical solution is compared in Figure 3.8 with a series of finite difference simulations for the same problem, with grid resolutions of 100, 500, 1000, and 5000 grid blocks. Comparison of the numerical and analytical solutions indicates that for this compositional problem, the numerical dispersion present in the FD solutions does not resolve the
condensate bank unless a very fine grid is used. It is unlikely that use of such fine grids would be attempted in field-scale compositional simulations because the computation times required would be unacceptably large.

To investigate the magnitude of gravitational effects and to validate the deduction of the scaling group analysis, FD simulations were performed for the same permeability distribution (Figure 3.9) oriented vertically (xz) and horizontally (xy).

![Figure 3.9: 2D permeability field used to investigate effects of gravity](image)

For gas cycling in this condensate system, heterogeneity dominates flow, and ultimately controls recovery. Comparison of the gas saturation in the formation after 2000 days of injection, shown in Figure 3.10 illustrates the modest effect of gravity.

![Figure 3.10: Gas saturation after 2000 days of high-rate injection: a) FD simulation of xy oriented permeability, b) FD simulation of xz oriented permeability, c) FD simulation of xz oriented permeability at low rate (4000 days) and d) SL simulation of xy (or xz) oriented permeability.](image)

At reservoir conditions, CO₂ is has a higher density thane the mobile vapor phase ($\rho_{\text{CO}_2} = 250.04 \text{ kg/m}^3$, $\rho_{\text{gas}} = 183.64 \text{ kg/m}^3$). Figure 3.10(a) shows the distribution of gas
saturation obtained by FD simulation for horizontal orientation of the 2D porous medium. Figure 3.10b and c show similar results for vertical orientations. The injection rate for the simulation shown in Figure 3.10c is half that of Figure 3.10b. At the lower rate, some evidence of segregation of the heavier CO$_2$ can be seen at the lower edge of the cross section. Figure 3.11, which reports recovery and producing GOR, shows that gravity and injection rate have almost no effect on recovery.

The corresponding plot of the gas saturation for the 2D streamline simulation is shown in Figure 3.10d. Because effects of gravity are neglected in the streamline simulation, there is no difference between the vertical and horizontal simulations for the streamline approach. The produced gas-oil ratios (GOR) for all 2D simulations are compared in Figure 3.11.

Between 0.9 PVI and 1.95 PVI, there is a separation between recovery predicted by the streamline approach and the finite difference simulations. The maximum separation occurs near 1.4 PVI. This difference is due to the production of the condensate bank resolved in the analytical solution but not in the finite difference computations. In this grid, the resolution between injector and producer is 200 grid blocks.

![Figure 3.11: Recovery and GOR predictions for 2D displacement simulations.](image)

In the finite difference simulations of the 1D displacement (Figure 3.8), this resolution was inadequate to capture the effect of the condensate bank. As injection continues, the difference in recovery between the two methods converges to a similar value. Once breakthrough occurs in the streamline method, injection gas cycles through
the reservoir, making the displacement increasingly inefficient. Numerical dispersion in the finite difference method smears the front of the displacement, artificially increasing the sweep efficiency in low permeability regions. The velocity of the front is also reduced, delaying breakthrough, as indicated by the difference in GOR between the two methods at later times.

The saturation maps shown in Figure 3.10 confirm the results of the scaling analysis given above in that some impact of gravity are observed, but the overall effect of gravity on the displacement performance is moderate.

Next, a 3D sector model representing a multiwell gas injection scheme was simulated with E300 and the compositional streamline approach. The permeability field and well locations for this displacement are shown in Figure 3.12.

![Figure 3.12: Permeability field and well locations for a 3D sector displacement.](image)

Gas saturation distributions as predicted by the FD simulation and the SL simulation are compared after 2500 days of injection in Figure 3.13.
Corresponding recovery and total CO$_2$ storage curves for the sector model are shown in Figure 3.14. Breakthrough occurs slightly earlier when the displacement is simulated using streamlines. Again, this is related to formation of high flow zones once the displacement front reaches a producer. CO$_2$ bypasses condensate in the unswept areas resulting in a lower recovery, but high local displacement efficiency in the swept zones. In the FD simulation dispersion creates a larger area reservoir area contacted by the injected CO$_2$ while the local displacement efficiency in parts of the swept zones is fairly low. The trade off between sweep efficiency and local displacement efficiency results, for this case, in a higher recovery prediction by the FD simulation, which may very well be artificially optimistic. While the finite difference method and streamline method represent two end members of process recovery (due to low dispersion effects in a condensate displacement), it is likely that the dispersion-free solution used in the streamline calculation more accurately predicts process recovery. The lower sequestration capacity (Figure 3.14) predicted by the streamline approach is again due to the lower sweep efficiency, a conservative estimate in this example.
Two full-field models were constructed based on the geological information and the well locations shown in Figure 3.15. Initially, a coarse-grid model with only 5774 active grid cells was investigated to compare FD simulation with SL simulation in a more complex geometry with multiple wells. The results were found to be in excellent agreement with the SL approach offering a significant speed-up over the FD approach.

For field scale simulation, where the number of gridblocks can be on the order of millions, streamline simulation is the only method currently fast enough to simulate a sequestration project in a reasonable amount of time. To demonstrate the efficiency of compositional streamline simulation when applied to large models, a full-field model with ~ 600,000 active cells was simulated. The aim of the simulations was to investigate an optimal injection strategy based on existing wells in terms of recovery and CO$_2$ storage. Four different scenarios were investigated.
Figure 3.15: Full-field model with well locations

Figure 3.16 shows the results of an optimization study to increase sequestration capacity of a field scale CO$_2$ injection scheme. Sequestration capacity was optimized by changing injection well location and the number of injector wells. The reservoir model contained ~ 600K active grid blocks. Injection of 1 PV was simulated. Run time of each streamline simulation was less than 10 minutes.

Figure 3.16: Recovery and sequestration predictions for a field scale optimization study to maximize production and sequestration capacity. In a reservoir model with ~ 600K grid blocks, alternative operating scenarios are quickly assessed.

Simulation times of compositional finite difference and streamline simulations are summarized in Table 3.4. Speed up factors observed were on the order of $10^2$-$10^3$. These are dependent on system size. Computational time in a streamline simulation scales approximately linearly with model size, while that of a finite difference method scales approximately as the third power of the number of grid blocks. Therefore, the ratio of
times is approximately the square of the number of grid blocks. As the number of active grid blocks simulated increases, speed up factors increase approximately quadratically.

<table>
<thead>
<tr>
<th>Model Size</th>
<th>FD (s)</th>
<th>SL (s)</th>
<th>Speed Up Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>2D: 5,000</td>
<td>7406</td>
<td>14</td>
<td>499</td>
</tr>
<tr>
<td>Sector: 13,500</td>
<td>38991</td>
<td>24</td>
<td>1624</td>
</tr>
<tr>
<td>Full field A: 5,774</td>
<td>4446</td>
<td>19</td>
<td>234</td>
</tr>
<tr>
<td>Full field B: ~600K</td>
<td>N/A</td>
<td>1914 (for 1 PVI)</td>
<td>N/A</td>
</tr>
</tbody>
</table>

### 3.3 Summary: Depleted oil and gas reservoirs

The examples considered in this section demonstrate that the compositional simulation tools available for modeling of displacements in oil and gas reservoirs are sufficiently capable that a reasonable range of design and optimization problems can be attacked. For example, the displacement of a relatively heavy oil considered in Section 3.1 is one in which calculated displacement performance is relatively insensitive to adverse effects of numerical dispersion. In that case, conventional finite difference simulation is fast enough to permit detailed examination of injection and well control strategies for maximizing both recovery of oil and storage of CO₂.

The example of Section 3.2, which considers condensate vaporization in a depleting gas reservoir, is one in which the number of components required to represent condensate drop-out adequately is relatively large, and in contrast with the heavy oil displacement, local displacement efficiency of the condensate is quite sensitive to the effects of numerical dispersion. As a result, conventional finite difference compositional simulation is too slow to be useful for large-scale computations. The condensate vaporization problem can be attacked, however, with compositional streamline simulation. In this example, effects of gravity are negligible (though they can be handled with streamline methods as discussed by Jessen and Orr [44]), the viscosity ratio of the injected and in-place fluid is close to one, and hence streamlines change location only slightly during the course of the displacement process. As a result, a very efficient and accurate compositional simulation can be performed using an analytical one-dimensional solution for the compositional part of the displacement mechanism, with streamlines used to capture the effects of well locations and heterogeneity. That approach is orders of magnitude faster than conventional compositional simulation, and it is much less subject to adverse effects of numerical dispersion.

Thus, careful selection of a computational tool that reflects the dominant physical mechanisms operating in a displacement process is an essential part of design and optimization of a process that combines enhanced oil or gas recovery with storage of CO₂.
4 CO₂ Sequestration in Saline Aquifers

The ultimate goal of injection of CO₂ into deep formations that contain salt water is to dissolve the CO₂ in the water. When that has happened, the driving force for upward migration of the CO₂ out of the formation is gone. Prior to that time, pressure gradients created by injection will drive flow, and gravity segregation will occur. After injection ceases, gravity forces will redistribute injected CO₂, and capillary forces will trap some CO₂ as a residual phase. These mechanisms will act, on a variety of time scales, to determine the distance CO₂ travels from the injection well and the time period during which the CO₂ has the potential to leak upward to another formation above. In this chapter, we use several approaches to quantify these time scales and to examine how convection, dissolution, and capillary trapping interact to determine the fate of the injected CO₂.

In Section 4.1, we use linear stability theory and high order numerical solutions to study how the unstable convection that arises from the fact that brine containing dissolved CO₂ is slightly more dense than brine alone affects the rate of dissolution of CO₂. In section 4.2, we use conventional finite difference reservoir simulation to examine the interplay of gravity and viscous forces to determine the amount of CO₂ that can be trapped as a residual phase and the time scale for that trapping. Finally in Section 4.3, we demonstrate how compositional streamline simulation can be used to predict flow performance very efficiently for large-scale aquifer settings. The results of these analyses and simulations indicate that for many systems, capillary trapping will immobilize CO₂ on time scales that are shorter than those required for dissolution of the CO₂.

4.1 Time/Length Scales during Convective Mixing of Dissolved CO₂

Marc Hesse, Amir Riaz, and Hamdi Tchelepi

Because brine containing dissolved CO₂ is denser than brine alone, the driving force for upward vertical migration of CO₂ disappears when all the injected CO₂ has dissolved. This effect is often referred to as solution or dissolution trapping [64, 20]. Gravity forces will cause the injected CO₂ to move upward to the top of the reservoir or to intermediate flow barriers such as shales with low permeability. To analyze the time scales for dissolution, we assume that the CO₂ forms a layer that is separated from the brine below by a relatively sharp horizontal interface, as is illustrated schematically in Figure 4.1.
Across the interface CO$_2$ will dissolve into the brine to form a diffusive boundary layer that grows with time [64]. The CO$_2$-rich brine in this boundary layer is denser than the underlying brine, and hence the geometric arrangement of dense fluid above less dense fluid will eventually become unstable. Fingers of dense CO$_2$-rich brine will propagate downward and transport the dissolved CO$_2$ away from the interface. This density-driven convection increases the rate of mass transport from the CO$_2$-rich vapor into the brine, and therefore reduces the time required for the total dissolution of the CO$_2$-rich vapor plume several orders of magnitude [20]. Increased mass transport due to convection in the brine has been observed experimentally by Yang and Gu [110]. If the CO$_2$ has collected in a hydrodynamic trap like that shown in Figure 4.1, CO$_2$ dissolution is an important trapping mechanism. It moves CO$_2$ from a buoyant phase to a gravitationally stable phase, and it creates the possibility of capillary snap-off of residual CO$_2$, as brine moves upward to fill the volume previously occupied by the CO$_2$ (residual trapping). Hence, gravity-driven convection is an important mechanism that enhances solution trapping and residual trapping.

The stability analysis has been extended and significantly improved compared to the project report for 2004 [35]. See also Riaz et al. [82] for a detailed discussion of the analysis. Here, we summarize the main results concerning time scales.

In a closed aquifer, three dynamic regimes of mass transport can be identified from the evolution of the total concentration $\bar{C}$ in the aquifer (Figure 4.2).
During the initial period of diffusive transport the amount of dissolved CO$_2$ is proportional to $t^{1/2}$. After some time convection begins and fingers of CO$_2$-saturated brine sink to the bottom of the reservoir and the amount of dissolved CO$_2$ increases linearly with $t$. As the total concentration of CO$_2$ rises, the effectiveness of convective mass transport decreases and in the long term limit dissolved CO$_2$ increases proportional to $t^{1/2}$.

The timing of the second regime of vigorous convection determines the importance of dissolution trapping in a particular reservoir. The time of transition from the first to the second regime is well defined by the onset of increased mass transport and will be referred to as the onset time $t_{on}$. The transition from the second to the third regime is marked by the fingers reaching the bottom of the domain, is less sharp and will be referred to as the slow-down time $t_{slow}$. We will also distinguish the critical time $t_c$ after which the system becomes unstable and fingers can form. The critical time is distinct from the onset time, but the two are strongly correlated. Finally we have the time necessary for the brine in the reservoir to become completely saturated with dissolved CO$_2$ $t_{sat}$. For practical purposes $t_{sat}$ is reached when the reservoir is 95% saturated.

4.1.1 Analysis of Hydrodynamic Instability

The hydrodynamic stability of the diffusive boundary layer has in CO$_2$-brine systems has attracted considerable interest in the last two years [21, 82, 108, 37]. Convection in porous media is governed by the Rayleigh number $Ra = k\Delta \rho g H/\mu D$, defined by average properties of the porous medium, where $k$ is the permeability, $\Delta \rho$ is the density difference, $H$ is the height of the reservoir, $\mu$ is the viscosity, and $D$ is the diffusion/dispersion coefficient. In the context of a diffusive boundary layer it is useful to think of the non-dimensional time as an additional parameter, because all systems above the critical $Ra$ number are initially stable and become unstable after a critical time.

This critical time is the only time scale that can be investigated analytically, because the equations can be linearized at early times. The linearized equations give the following expression for the growth rate $\sigma$ of a disturbance
\[ \sigma(\tau; k) = -\frac{1}{\tau} - \frac{s^2}{Ra} + \frac{k}{\sqrt{\pi}} F(\tau; s), \]

(4.1)

where \( F(\tau, s) \geq 0 \), and \( s \) is the wavenumber of the disturbance [82]. The dimensionless critical time \( \tau_c \) is obtained by solving the scalar algebraic equation \( \sigma(\tau_c; s) = 0 \). The equation clearly shows the stabilizing effect of short times and small \( Ra \) numbers. The theoretical results agree very well with a high accuracy numerical simulation of the full non-linear problem. The theory predicts the critical time \( t_c \) and the critical wavelength \( \lambda_c \),

\[ t_c = \frac{146 \phi \mu^2 D}{(k\Delta \rho g)^2}, \quad \lambda_c = \frac{2\pi \mu D}{0.07k\Delta \rho g}, \]

(4.2)

in terms of the average aquifer parameters. The permeability \( k \) has the largest variability between different injection sites, and will therefore control the convective transport.

The critical time and wavelength decrease rapidly with increasing \( k \), suggesting that the effects of convection will be much more important in high-\( k \) aquifers. In the discussion that follows, we illustrate the differences between high-\( k \) and low-\( k \) aquifers by calculating the time scales for two hypothetical aquifers shown in Table 4.1.

In terms of \( CO_2 \) sequestration we are interested in the timing of the second dynamic regime where the dissolved \( CO_2 \) increases proportional to \( t \). Since \( t_c \) is a lower bound for the onset time \( t_{on} \), the theoretical results have direct implications for the effectiveness of dissolution trapping. The theory predicts that high-\( k \) aquifers will have very short critical times \( t_c \ll 1 \text{yr} \). Low-\( k \) aquifers on the other hand have longer critical times \( t_c > 1 \text{yr} \), about 2 orders of magnitude higher than the high-\( k \) case.

The theory also predicts the critical wavelength \( \lambda_c \) that becomes unstable first and starts growing. In high-\( k \) aquifers these wavelength are very short \( \lambda_c < 1 \text{m} \), and again about two orders of magnitude higher in the low-\( k \) case. Resolving these short length scales is a challenge for numerical methods currently used for reservoir simulation. This is another example where the linear stability analysis complements numerical analysis, because it has no resolution problems, and it can be used to guide the design of numerical methods.

### 4.1.2 Long Term Evolution

To be able to resolve these small physical length scales, we used a high accuracy research code to simulate the long term behavior of the convecting system [82]. These numerical simulations allow us to determine the remaining time scales. Figure 4.3 shows numerical results for the concentration evolution at \( Ra = 1000 \).
Figure 4.3: Evolution of the concentration contours of dissolved CO₂ in the storage aquifer.

The concentration field during the second regime with high mass transfer is shown in the top graph. All other pictures show the decay of convective motion during the third regime. The onset time $t_{on}$ and the slow down time $t_{slow}$ can be determined from the graphs of $dC/d\tau$ vs. $\tau$ shown on the right in Figure 4.2. For $Ra > 500$ the onset time scales with a slightly different exponent and a larger constant compared to $t_c$.

$$t_{on} = 6215 \frac{\phi \mu^{1/5} D^{6/5}}{(k\Delta \rho g)^{1/5} H^{1/5}}.$$  \hspace{1cm} (4.3)

The dimensionless times for slow down and for full saturation are constant for all $Ra > 500$ and in dimensional form they are given by

$$t_{slow} = 15 \frac{\phi \mu H}{k\Delta \rho g}; \quad t_{sat} = 230 \frac{\phi \mu H}{k\Delta \rho g} \approx 15 \cdot t_{slow}.$$  \hspace{1cm} (4.4)

Note that both the critical time $t_c$ is independent of the height $H$ of the domain, and the onset time $t_{on}$ is only a weak function of $H$. The two later time scales are positive functions of $H$. Table 4.1 shows values calculated for the high-k and low-k aquifers.
Table 4.1: Aquifer properties, time scales, and length scales.

<table>
<thead>
<tr>
<th>Aquifer Properties</th>
<th>high perm</th>
<th>low perm</th>
</tr>
</thead>
<tbody>
<tr>
<td>permeability $k$</td>
<td>3400 mD</td>
<td>100 mD</td>
</tr>
<tr>
<td>height $H$</td>
<td>200 m</td>
<td>200 m</td>
</tr>
<tr>
<td>diffusivity $D$</td>
<td>$10^{-9}$ m$^2$s$^{-1}$</td>
<td>$10^{-9}$ m$^2$s$^{-1}$</td>
</tr>
<tr>
<td>viscosity $\mu$</td>
<td>$5\cdot10^{-4}$ Pa s</td>
<td>$5\cdot10^{-4}$ Pa s</td>
</tr>
<tr>
<td>porosity $\phi$</td>
<td>0.3</td>
<td>0.1</td>
</tr>
<tr>
<td>density difference $\Delta \rho$</td>
<td>5 kg m$^{-3}$</td>
<td>5 kg m$^{-3}$</td>
</tr>
<tr>
<td>Rayleigh number $Ra$</td>
<td>58860</td>
<td>1962</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Time Scales</th>
<th>high perm</th>
<th>low perm</th>
</tr>
</thead>
<tbody>
<tr>
<td>critical time $t_c$</td>
<td>0.02 yrs</td>
<td>5 yrs</td>
</tr>
<tr>
<td>onset time $t_{on}$</td>
<td>0.08 yrs</td>
<td>208 yrs</td>
</tr>
<tr>
<td>slow down time $t_{slow}$</td>
<td>97 yrs</td>
<td>970 yrs</td>
</tr>
<tr>
<td>time for saturation $t_{sat}$</td>
<td>1487 yrs</td>
<td>14867 yrs</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Length Scales</th>
<th>high perm</th>
<th>low perm</th>
</tr>
</thead>
<tbody>
<tr>
<td>crit. wavelength $\lambda_c$</td>
<td>0.2 m</td>
<td>10 m</td>
</tr>
<tr>
<td>final wavelength $\lambda_{sat}$</td>
<td>$O(H)$</td>
<td>$O(H)$</td>
</tr>
</tbody>
</table>

A high-k aquifer will experience vigorous convection in the first 100 yrs, and dissolution trapping will be enhanced significantly. Convection will saturate the aquifer with dissolved CO$_2$ in the first 2000 yrs, assuming enough CO$_2$ has been supplied by the CO$_2$ vapor plume. On the other hand in a low-k aquifer the time scales are much longer and convection may not occur for the first few hundred years. Note that the vigorous part of the convection is already over in the high permeability aquifer, before it even starts in the low perm reservoir.

Initially the dimensionless wavelength is a linear function of the $Ra$ number, later it increases with time for all $Ra$ numbers until it equals the domain height $H$. Generally the wavelength is a function of the $Ra$ number of the system in the first two regimes for $t < t_{slow}$ and only a weak function of Ra at later times. The wavelength at very early times can be predicted from linear theory (see above), at late time it is determined by the geometry, but in the highly non-linear regime between $t_{on}$ and $t_{slow}$ high accuracy numerical simulations are necessary.

4.1.3 Implications for CO$_2$ Sequestration

We can therefore conclude that dissolution trapping will be enhanced by gravity driven convection in high permeability aquifers. Whether the same process is considered important in low permeability aquifers will depend on the length of the overall storage time that is necessary. Given that convection enhanced dissolution is an important process in high permeability aquifers, numerical methods should be able to represent the physical length scales. Theory predicts a very short the critical wavelength $\lambda_c$ for high-permeability aquifers, i.e. for Sleipner type aquifers $\lambda_c \sim 1$m. These short length scales represent a challenge for the numerical simulation of this process on the field scale and over long times. The work by Lindeberg and Bergmo [63] illustrates the effect of insufficient numerical resolution on the evolution of the convective mass transport. Using the Eclipse simulator, they determined that 3 cm by 4 cm grid blocks were
necessary to resolve the onset of convection. As they coarsened the numerical grid to a more realistic size for field scale simulation of 100m by 100m, they observed a delay of the onset of convection from 2 yrs to 100 yrs, a change of two orders of magnitude. They studied the Sleipner injection site, which is very similar in properties to the high-k aquifer described in Table 4.1. We can see that the coarsening of the grid causes a shift in the time scales that makes the high-k case to look more like the low-k case. Given that convection enhanced dissolution is one of the important trapping mechanisms at the Sleipner site, the issue of numerical resolution has to be addressed.

4.1.4 Summary: Time and length scales

We have identified four convective time scales, from linear theory and high accuracy numerical simulations:

- The critical time $t_c \propto K^{-2}$, is the time after which small perturbations grow. The critical time is important because it gives an analytic lower bound on the onset of convection.
- The onset time $t_{on} \propto K^{-2.2}$, marks the transition from a diffusive to a convective regime of mass transfer, and corresponds to the appearance of the first fingers in the concentration profile.
- The slow down time $t_{slow} \propto H/K$, marks the transition to a less efficient regime of decaying convection, and corresponds to the first fingers reaching the bottom of the domain.
- The saturation time $t_{sat} \propto H/K$, is defined as the time when the normalized total concentration of dissolved CO$_2$ in the aquifer has reached 95%.

These time scales separate the convective evolution into three dynamic regimes, characterized by different rates of mass transfer. The three regimes may be characterized as:

- In the diffusive regime ($t < t_{on}$) the total concentration increases proportional to $t^{1/2}$, and the flux of CO$_2$ decreases rapidly as $t^{-1/2}$. In the absence of the gravitational instability this would be the only regime.
- In the infinite acting regime ($t_{on} < t < t_{slow}$) the dynamics are independent of the domain size. In this regime the total concentration increases linearly with $t$, and the flux of CO$_2$ stabilizes around a plateau. This is the most effective regime of mass transfer, and characterized by rapidly growing fingers with strong non-linear interactions.
- The finite acting regime ($t > t_{slow}$), where the finite size of the aquifer influences the dynamics of convection. This regime is characterized by large, slow convective cells.
- Finally we have determined two important length scales of the convective motion:
  - The critical wavelength $\lambda_c$ of the first growing perturbations in the stability analysis. To resolve the evolution of the convective flow a numerical method needs to be able to resolve the critical wavelength.

In the long term systems of all $Ra$ numbers tend to the same convection pattern of large cells determined by the aquifer height.
We have also demonstrated that the combination of linear theory and non-linear numerical simulations is very successful at identifying important physical processes and the associated length and time scales.

The simplifications necessary to treat the problem theoretically may introduce significant errors when such results are applied to real aquifers. The important assumptions are the homogeneity and isotropy of the porous medium, as well as the assumption of the single phase flow and the absence of velocity induced dispersion. The assumption of single phase flow will break down if capillary forces are significant. Additionally, physical mechanisms related to dissolution, precipitation and geochemical reactions, which are not accounted for in our analysis, can be expected to play a role in the long term evolution. Some of these processes may be incorporated in the linear stability analysis, while others can only be investigated with high resolution non-linear simulations. The results for the basic gravitational fingering instability presented here, form the basis to investigate the effect and importance of these additional processes.

4.2 Capillary Trapping of CO\textsubscript{2} in an Aquifer

S. Ide, K. Jessen, and F.M. Orr, Jr.

In the previous section, the focus was on the time scales of dissolution, and the effects of capillary trapping were not considered. In this section, we investigate the role of capillary trapping but ignore effects of solubility of CO\textsubscript{2} in brine. Capillary trapping occur when the saturation of a nonwetting gas phase is decreasing and the saturation of a wetting phase is increasing. Imbibition of brine can cause the necks of bubbles of gas in pore throats to become unstable, and the resulting snap-off [83] isolates bubbles of gas in a pore body or multiple pore bodies immobilizes the gas unless the local pressure gradient due to flow is very large or the interfacial tension between the gas and brine is reduced. It is this mechanism that leads to the formation of a residual oil saturation during waterflooding, for example. In CO\textsubscript{2} storage projects, capillary trapping can be used to reduce the amount of mobile CO\textsubscript{2}, and hence to limit the volume of CO\textsubscript{2} that could leak from the aquifer. Kumar et al. [59] examined many of these mechanisms for a heterogeneous aquifer and concluded that a significant fraction of injected CO\textsubscript{2} could be immobilized by capillary trapping. Spiteri et al. [92] investigated the effects of hysteresis in relative permeability functions and showed that residual trapping can limit significantly the movement of injected CO\textsubscript{2}. In this work we focus on the impact of the balance of viscous and gravity forces on the amount of CO\textsubscript{2} that can be trapped and the rate at which it is immobilized by trapping. The effects of gravitational and viscous forces on CO\textsubscript{2} trapping were investigated through simulations over a wide range of ratios of gravity to viscous forces using the simulator, Eclipse 100.

4.2.1 Fluid and Aquifer Properties

Figure 4.4 shows the relative permeability functions used in the simulations. Those functions approximate the measured data of Oak et al. [71]. The irreducible water saturation was assumed to be 0.2, and the residual gas saturation, 0.35. Relative permeability hysteresis was represented by Killough’s model [55], which makes use of Land’s formulation [60] to obtain a trapped gas saturation that is a function of the
maximum gas saturation reached in a grid block prior to a decline in gas saturation. The Land trapping coefficient was 1.24.

![Figure 4.4](image1.png)

**Figure 4.4:** Wetting and nonwetting phase relative permeability functions.

Some simulations included the effects of capillary pressure. The capillary pressure curves used are reported in Figure 4.5. The drainage curve is that of van Genuchten [101]. The imbibition curve was estimated with a residual gas saturation consistent with the value of 0.35 used for the residual gas saturation in the relative permeability functions.

![Figure 4.5](image2.png)

**Figure 4.5:** Capillary pressure functions.

In the simulations described here, the aquifer depth was taken to be 2500 m, the salinity, 100,000 ppm, and the temperature 65°C. Fluid properties were estimated with
the correlation of Ennis-King [22]. Figure 4.6 shows the ratio of brine viscosity to CO₂ viscosity assuming a hydrostatic pressure gradient (0.1 atm/m), a surface temperature of 15°C, and geothermal gradients of 20, 25, and 30 °C/km.

![Figure 4.6: Ratio of brine viscosity to CO₂ viscosity for a hydrostatic pressure gradient and geothermal gradients of 20, 25, and 30 °C/km and a surface temperature of 15°C.](image)

Figure 4.6 shows that for depths below about 1500 m, the viscosity ratio is nearly independent of the temperature gradient, but it does depend on depth. Brine viscosity decreases with depth, because brine viscosity depends more strongly on temperature than on pressure [53]. CO₂ viscosity increases with depth, however, because it depends more strongly on pressure than on temperature [103, 23]. That ratio, along with the relative permeability functions appropriate to the porous medium determines local efficiency of displacement of brine by CO₂. Figure 4.6 shows that viscosity ratios typically from about 6 to about 15 for depths between 1000 and 2800 m, with a value of about 7 at a depth of 2500 m.

Figure 4.7 shows the ratio of CO₂ density to brine density, again as a function of depth and the geothermal gradient. At depths below 1000m, where the pressure is high enough for the CO₂ to form a dense supercritical yet liquid-like phase, the density ratio is seen to vary smoothly with increasing depth. CO₂ is always less dense than brine, and the density difference is large enough to cause significant gravity segregation when the flow is slow.

Simulations were performed for two-dimensional, vertical cross sections of aquifers with four spatial distributions of permeability. One cross section was homogenous, and the other three had differing spatial distributions of permeability shown in Figure 4.8. Aquifer dimensions were held constant.
Figure 4.7: Density ratio (CO$_2$/brine) for a hydrostatic pressure gradient and geothermal gradients of 20, 25, and 30 °C/km and a surface temperature of 15°C.

The aquifer length was 800 $m$, and the aquifer height, 40 $m$. The aquifer was represented by a grid of 400 x 40 = 16,000 grid blocks. Average horizontal permeability was 242 mD. Fluid was injected only through the bottom 10 $m$ of the well at the left end of the cross section. A well at the right end was open over the entire height and was held at constant pressure at the bottom of the well. The top and bottom boundaries were impervious to flow.

Figure 4.8: Heterogeneous aquifers: (top) layered system - red/blue = 267/10 mD, (middle) short correlation length, (bottom) longer correlation length. The y-axis is exaggerated by a factor of 2.

In the simulations described here, the ratio of viscous to gravity forces was varied over several orders of magnitude by adjusting injection rates or the ratio of vertical to horizontal permeability. CO$_2$ was injected for a period, and then the wells were shut in and the gas and brine phases were allowed to redistribute until equilibrium was reached.
Fluid injection rates and the total amount injected were chosen so that the CO\textsubscript{2} did not reach the right boundary during the injection phase.

### 4.2.2 Average Displacement Efficiency

An indication of the relative importance of viscous and gravity forces is given by the gravity to viscous ratio, $N_{gv}$, defined as [112]

$$N_{gv} = \frac{k_v L \Delta \rho g}{H u \mu},$$

(4.5)

where $k_v$ is the vertical permeability, $L$ is the aquifer length, $\Delta \rho$ is the density difference, $g$ is the acceleration of gravity, $H$ is the aquifer height, $u$ is the average flow velocity, and $\mu$ is the viscosity of brine. When $N_{gv}$ is large, gravity forces dominate the flow, which occurs primarily in a thin gravity tongue at the top of the aquifer. When $N_{gv}$ is small, viscous forces are more important, and the permeability distribution controls fluid movement.

Figure 4.9 shows the impact of variations in $N_{gv}$ on the fraction of an aquifer invaded by CO\textsubscript{2}. Capillary pressure was not included in these calculations.

![Figure 4.9: Fraction of the homogeneous aquifer occupied by injected CO\textsubscript{2} when CO\textsubscript{2} reaches the constant-pressure boundary.]

At low $N_{gv}$, the fraction of the aquifer occupied by CO\textsubscript{2} just prior to the time when CO\textsubscript{2} reaches the right boundary is about 4%. That fraction is controlled by the adverse viscosity ratio, heterogeneity, and the injection pattern. As $N_{gv}$ increases, the fraction invaded decreases, due to the formation of a gravity tongue at the top of the aquifer. When the injected gas encounters the top of the aquifer, it is forced to travel in the horizontal direction beneath the cap rock. As more CO\textsubscript{2} rises into the gravity tongue, it becomes the path of least resistance for any subsequent CO\textsubscript{2} injected into the aquifer. Thus in a system with high $N_{gv}$, only a small fraction of the reservoir is contacted before
the injected CO$_2$ reaches the constant pressure boundary. As a result, the volume of undisplaced brine is more than sufficient to dissolve all of the injected CO$_2$.

### 4.2.3 Interplay of Capillary Trapping with Gravity and Viscous Forces

When gas injection ceases, gravity segregation continues for a period whose length depends strongly on vertical permeability. As gas migrates to the top of the aquifer, gas saturations at the top will increase, while those at zones from which gas is migrating will decrease. It is that decrease in saturation that can act to trap CO$_2$ by capillary snap-off. Figure 4.10 and Figure 4.11 illustrate what happens in the layered aquifer at high $N_{gv}$ ($N_{gv} = 214.4$). In these examples, the effects of relative permeability hysteresis were included, but the effects of capillary pressure were not. Figure 4.10 shows the gas saturation at the end of the injection period. A thin gravity tongue occupies the top of the aquifer. Figure 4.11 shows the locations of gas trapped when flow has ceased. Most of the trapping occurs in the near well region, where significant vertical flow takes place and in the zones just below the gravity tongue, where gas saturations reached levels high enough that significant trapped saturations were possible and then the gas saturation declined as gas migrated upward after injection ceased.

![Figure 4.10: Gas Saturation, $S_g$, at the end of the injection period in the layered model with $N_{gv} = 214.4$.](image)

Another example of flow at high $N_{gv}$ is shown in Figure 4.12 and Figure 4.13. The heterogeneity of the permeability field enlarges the region of vertical flow near the well, but otherwise the patterns are similar to those observed for the layered aquifer. Here again, the highest values the trapped saturation occur at the base of the gravity tongue, where gas saturations reached magnitudes large enough that significant trapping could occur. The larger zone of vertical flow near the injection well also permits trapping as that gas segregates. This behavior suggests that injection strategies that create large zones of vertical flow can help trap some CO$_2$ even in flows that are dominated by gravity.

![Figure 4.11: Trapped gas saturation, $S_{gt}$, at the end of the gravity relaxation period for the flow illustrated in Figure 4.10.](image)
In flow at low $N_{gv}$, where viscous forces dominate, trapping occurs in different portions of the aquifer, but the greatest amount of trapping still occurs in areas where the gas saturation was the highest prior to flow reversal. Figure 4.14 and Figure 4.15 show gas saturations at the end of the injection period for flow in the homogeneous aquifer and after equilibration. Because viscous forces dominate in this flow, gravity has relatively small effect during the injection period, moving injected CO$_2$ upward only about half the length of the open section of the injection well, as Figure 4.14 shows for a displacement with $N_{gv} = 0.0555$. After injection ceases, however, trapped the highest saturations of trapped CO$_2$ occur in the inlet region, where gas saturations reached the largest values, and there is an extensive zone of trapping above the full region penetrated by the injected CO$_2$. 

**Figure 4.12:** Gas Saturation, $S_g$, at the end of the injection period in the model with short correlation length with $N_{gv} = 214.4$.

**Figure 4.13:** Trapped gas saturation, $S_{gt}$, at the end of the gravity relaxation period for the flow illustrated in Figure 4.12.

**Figure 4.14:** Gas Saturation, $S_g$, at the end of the injection period in the homogeneous model with $N_{gv} = 0.0555$.

**Figure 4.15:** Trapped gas saturation, $S_{gt}$, at the end of the gravity relaxation period for the flow illustrated in Figure 4.14.
Figure 4.16 and Figure 4.17 show similar results for a low $N_{gv}$ displacement in the aquifer with short correlation length. The presence of heterogeneity provides flow paths that distribute fluid vertically, and there is a larger vertical zone in which trapping occurs. Even so, the basic patterns remain similar. The highest trapped saturations occur where high saturations were created and then subsequently reduced by vertical flow.

Figure 4.16: Gas Saturation, $S_g$, at the end of the injection period in the heterogeneous model with short correlation length and $N_{gv} = 0.0555$.

Figure 4.17: Trapped gas saturation, $S_{gt}$, at the end of the gravity relaxation period for the flow illustrated in Figure 4.16.

The effect of capillary pressure on a high $N_{gv}$ displacement is shown in Figure 4.18 and Figure 4.19. Including capillary pressure decreases the maximum saturation in the gravity tongue significantly and smears all the saturation fronts. Imbibition that occurs after injection ceases traps CO$_2$ over broader zones but the trapped saturations are lower because the maximum saturations reached before imbibition began are lower.

Figure 4.18: Gas Saturation, $S_g$, at the end of the injection period in the layered model with $N_{gv} = 214.4$.

Figure 4.19: Trapped gas saturation, $S_{gt}$, at the end of the gravity relaxation period for the flow illustrated in Figure 4.18.
Effects of the addition of capillary pressure in a low \( N_{gv} \) displacement in the aquifer with longer correlation length are shown in Figure 4.20 and Figure 4.21. Here again, capillary pressure reduces saturation gradients and limits the maximum saturation, which in turn limits the trapped saturation.

![Figure 4.20: Gas Saturation, \( S_g \), at the end of the injection period in the model with longer correlation length including capillary pressure. \( N_{gv} = 0.0555 \).](image)

![Figure 4.21: Trapped gas saturation, \( S_{gt} \), at the end of the gravity relaxation period for the flow illustrated in Figure 4.20.](image)

The effect of variation in \( N_{gv} \) on the total amount of gas trapped is shown in Figure 4.22, which reports trapped volumes for all four permeability distributions and shows results obtained with and without capillary pressure. For consistency, the same amount of gas was injected into each model aquifer. Figure 4.22 shows how increasing \( N_{gv} \) leads to less trapping of the injected gas, while low gravity number systems trap nearly all of the gas injected. Figure 4.22 shows clearly that CO\(_2\) should be injected at the maximum rate consistent with avoidance of fracturing as a way to increase \( N_{gv} \) and therefore increase trapping.
There is much less trapping in high $N_{gv}$ displacements because the gases residing in the gravity tongue cannot be trapped because there is no mechanism to reduce the gas saturation there. Systems with stronger gravitational forces have a higher saturation of CO$_2$ in the uppermost zone, and therefore subsequently have less gas available to trap elsewhere.

The rate of trapping of injected CO$_2$ is also of interest because it is important to establish whether residual trapping will occur on a time scale that is shorter or longer than the time scales of other modes of trapping such as chemical reactions and dissolution. To capture the rate at which trapping occurs, cases with different $N_{gv}$ values were selected. Figure 4.23 reports the rate at which the final value of fraction of gas trapped is attained. The time is made dimensionless with respect to the duration of injection (total time elapsed/total time of gas injected). Systems with strong gravity effects trap less injected gas, but the gas that is trapped is trapped relatively quickly. Systems with strong viscous forces trap a significant fraction of injected gas, but take a longer time to do so.
These results make sense in light of the gas saturation profiles presented in Figure 4.10 - Figure 4.21. In the high $N_{gv}$ examples, the final trapped gas fraction is low because much of the injected gas invades the zone just beneath the upper boundary. The rate at which the final fraction is reached is high, however, because the high saturations of gas that are subject to trapping are concentrated at the lower edge of the gravity tongue. In low $N_{gv}$ flows, the amount of gas that is trapped is very high, but the rate at which this happens is relatively low due to the fact that a larger fraction of the aquifer is contacted.

4.2.4 Summary: Capillary trapping

The simulation results presented here establish that there is a significant interaction of gravity and viscous forces that determines in large part how much CO$_2$ can be trapped by capillary forces. Trapping requires that gas saturations decrease, either at the trailing edge of gas that is migrating upward, or because redistribution of water causes it to flow into an area with high gas saturations, and the amount that can be trapped is larger if the gas saturation reaches a high value than it is for lower peak gas saturations. More gas is trapped when high gas saturations are subsequently reduced. When gravity dominates the flow, a thin tongue of injected gas flows just under the top boundary of the aquifer. Gas saturations reach high levels there, but in the absence of dissolution, there is no mechanism that acts during the post-injection period to reduce those high gas saturations. When viscous forces dominate, in the other hand, the long period of post-injection redistribution of gas by gravity-driven flow allows significant trapping.

The time scales for trapping also depend on the interplay of viscous and gravity forces. When gravity forces dominate, less gas is trapped, but the gas that becomes trapped does so relatively quickly. When viscous forces dominate, more gas is trapped eventually, but the rate of trapping is lower.
4.3 Compositional Streamline Simulation of CO₂ Injection into Saline Aquifers

K. Jessen, and F.M. Orr, Jr.

Considerable effort has been devoted to the development of reservoir simulation tools for the oil industry, and high quality simulators are available that handle effectively many of the flow problems appropriate to oil and gas reservoirs. One area where simulator development is continuing, however, is in the simulation of processes in which components transfer between the phases present in the porous medium. Injection of CO₂ into saline aquifers involves such component transfers, as the injected CO₂ dissolves in any undisplaced brine. An overview of available technology for simulation of CO₂ flows in aquifers, including contributions from the groundwater community as well as the oil and gas community, is reported in Section 2. These methods are all based on Eulerian finite difference/volume/element methods.

Up to this point, no investigation of the efficiency of compositional streamline simulation (a Lagrangian approach) has been reported for CO₂ injection in saline aquifers. A large literature describes the development and application of streamline simulation to prediction of flow in three-dimensional heterogeneous reservoirs. See the papers of King and Datta-Gupta [56] and Crane et al. [14] for many references to the full range of work on streamlines. The use of compositional streamline simulation for gas injection processes was demonstrated by Thiele and coworkers [97, 98]. Jessen and Orr [40] showed how to combine the streamline approach with multicomponent analytical solutions for three-dimensional gas displacement problems, and Seto et al. [87] applied that approach to the simulation of a gas condensate recovery process. Several investigators have shown that effects of gravity can be represented by operator splitting [14, 41]. Thus, there is considerable evidence that compositional streamline methods can be applied to describe the interaction of compositional effects associated with component transfers and dissolution that occur in CO₂ sequestration processes.

We begin by describing how to improve the computational efficiency of streamline simulation when applied to CO₂/brine systems. Then we report a comparison of streamline simulations with equivalent black-oil formulations to assess the efficiency and accuracy of existing technology relative to that of compositional streamline simulation. The comparison of the streamline approach with a black-oil finite volume approach was chosen due to the simplicity and efficiency of the black-oil models over finite volume compositional models. Finally, we discuss the limitations of the streamline approach.

4.3.1 Compositional effects

For given temperature, pressure and salinity, the solubility of CO₂ in the aquifer and the amount of water vapor that is present in a CO₂-rich gas phase in equilibrium with CO₂ saturated brine can be predicted by a standard equation of state, e.g. Peng-Robinson, using a non-symmetric binary interaction coefficient matrix [109, 59]. The densities and viscosities of the equilibrated phases can also be predicted quite accurately using an appropriate set of temperature dependent volume translation parameters.

Given that the system in question is a binary system with only one independent phase mole fraction (x₂ = 1-x₁), very efficient calculation of the phase behavior in
compositional simulation can be performed using a K-factor lookup table generated prior to performing the streamline calculation. During the initialization of a given injection calculation, temperature, salinity and expected pressure range are estimated and a one dimensional table (pressure as independent variable) is generated for the equilibrium K-factors, phase densities and viscosities. During the actual simulation, mole fractions of vapor and phase compositions can be calculated explicitly given the pressure (K-factors) and an overall composition ($\tilde{z}$) from

$$\beta = -\frac{z_i \alpha_i + z_j \alpha_j}{\alpha_i \alpha_j}, \quad \alpha'_j = \tilde{z}_j (K_i - 1),$$

\hspace{1cm} (4.6)

and

$$x_j = \frac{z_j}{1 - \beta + \beta K_j}, \quad y_j = K_j x_j.$$ \hspace{1cm} (4.7)

Eq. (4.6) is used to test if an overall composition is in the two-phase region at a given pressure. For values of $\beta$ between 0 and 1, equilibrium phase compositions are evaluated from Eq. (4.7) whereas the corresponding phase densities and viscosities are evaluated from look-up tables using an appropriate interpolation scheme. For single phase mixtures ($\beta < 0$ or $\beta > 1$), density and viscosity is evaluated directly the equation of state. Figure 4.24 shows the variation of equilibrium K-factors as a function of pressure for the CO$_2$-brine system at 298K.

![Figure 4.24: Equilibrium K-factors for CO$_2$ – Brine (250000 ppm) at 298K.](image)

The CPU time for performing $10^6$ equilibrium calculations at random pressures between 1 and 500 bar and random feed compositions, was found to be an order of magnitude less for the look-up table approach than that of a general state of the art flash algorithm.

4.3.2 Calculation examples

The lookup-table approach described above has been implemented in the compositional streamline simulator CSLS [26] and tested for a range of displacement calculations. To compare the compositional streamline approach with a commercial black-oil simulator, an equivalent black-oil representation of the phase behavior was generated by simulating a differential depletion experiment (DDE) with the thermodynamic module of CSLS. Throughout the comparison, the temperature of the
aquifer in question is assumed to be constant at 323K. The black-oil properties at this temperature along with relative permeability functions used in the reported calculation examples are shown in Figure 4.25. In a black-oil formulation, the solubility of CO$_2$ in the brine is modeled by a solution gas-water ratio ($R_S$).

![Figure 4.25: Black oil properties (left) and saturation functions (right) used in calculation examples.](image)

Initial calculations were performed for a one-dimensional (1D) domain to gauge the impact of capillary forces on the displacement behavior. The saturation profile predicted by the streamline calculation (CSLS) is compared in Figure 4.26 with fully implicit (FIM) black-oil calculations, with and without inclusion of effects of capillary pressure.

![Figure 4.26: 1D displacement calculations using CSLS and FIM: Impact of capillarity.](image)

Figure 4.26 suggests that capillarity plays a more significant role near the injection point than around the leading edge of the displacement. In this drainage process capillarity opposes a reduction in the brine saturation towards the residual near the injection boundary. The overall effect of capillarity on the displacement characteristics, however, is seen to be minor. Additional considerations about the impact of capillarity in 3D displacements are given in the discussion section.
To illustrate the efficiency of compositional streamline simulation, two three-dimensional (3D) models were investigated:

- Model A; a 1250m by 1250m by 100m section of a heterogeneous aquifer was represented by a 50x50x10 computational grid (25000 active cells).

- Model b; a 4500m by 4500m by 160m section of a heterogeneous aquifer was represented by a 180x180x16 computational grid (518400 active cells).

The permeability variation within the computational domain of Model B is shown in Figure 4.27.

![Figure 4.27: Permeability heterogeneity of Model B](image)

The average permeability of Model B is 100mD, and the average porosity is 0.3. The initial pressure at the top of the aquifer is 90 bars, and CO$_2$ is injected at 150 bars in the center of the domain for 10 years corresponding to approximately 2.5% of the aquifer pore volume. Production wells were placed at the outer edges of the model and operated at a fixed bottom-hole pressure of 90 bar to mimic a constant pressure boundary condition. Figure 4.28 compares the saturation distribution at the end of the injection period for the two simulation approaches. The two approaches are seen to be in good agreement.
In this setting, the flow of the injected CO\textsubscript{2} is strongly affected by gravity and permeability heterogeneity. The injected CO\textsubscript{2} rises to the top of the formation where the flow of the plume is then restricted to high permeability zones.

The CPU time for the streamline simulation was 21 min, whereas the time for running the equivalent black-oil simulation was 232 min. The modest computation time clearly demonstrates the potential of compositional streamline simulation to allow for uncertainty assessment through multiple realizations of the model parameters in a reasonable time frame. An equivalent compositional finite difference calculation is not currently feasible due to the global time step restriction in IMPES models or the more diffusive nature of fully implicit (FIM) that may render the displacement calculations less accurate. These example computations demonstrate, therefore, that high resolution, three-dimensional, field-scale streamline simulations can be performed with quite reasonable computation times. A summary of CPU requirements for the flow settings investigated is given in Table 4.2.

**Table 4.2:** Comparison of CPU requirements for 3D calculations: 2.8GHz

<table>
<thead>
<tr>
<th>Model</th>
<th>(N_{\text{cells}})</th>
<th>CSLS</th>
<th>FD-FIM</th>
<th>Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>25000</td>
<td>0.7 min</td>
<td>6 min</td>
<td>9</td>
</tr>
<tr>
<td>B</td>
<td>518400</td>
<td>21 min</td>
<td>232 min</td>
<td>11</td>
</tr>
</tbody>
</table>
Speed-up factors for 3D displacement calculations were found to be in the range of an order of magnitude. Additional increase in the speed-up factors is expected for larger computational domains where the pressure solves become increasingly CPU-time consuming. In the comparison presented, no effort was put towards optimization of the time-step control parameters of the FIM scheme that was run with the default parameter set. We emphasize, also, that the compositional streamline simulator used in this work is a research code that has not yet been fully optimized.

4.3.3 Discussion

We have demonstrated that the proposed streamline formulation is significantly less CPU intensive than existing methods for the flow settings typically encountered during the injection phase of CO$_2$ sequestration in saline aquifers. For larger scale problems with more than 500K active grid cells, the run times for the proposed formulation are more than an order of magnitude lower than those for conventional numerical approaches.

Effects of capillarity are not included in the streamline approach but can be included in conventional approaches. To gauge the impact of capillarity on CO$_2$ plume development, black-oil simulations of Model A were performed including and excluding capillary pressure. Standard Leverett J-scaling was used to represent capillarity in the heterogeneous permeability field. The average permeability of the computational domain of Model A is 90mD with an average porosity is 0.3. CO$_2$ was injected at a constant rate of 2000 Rm$^3$/day for a period of 3 years corresponding to ~5% of the pore volume. The results of the three simulations are compared in Figure 4.29, which shows the CO$_2$ distribution (gas saturation) within the computational domain at the end of the injection period.

Differences between the three simulations are quite small, which suggests that gravity and viscous forces dominate the displacement process. This, in turn, suggests that capillarity may be neglected, as in compositional streamline simulation, for a range of sequestration projects. Capillary forces resist invasion of non-wetting phase (CO$_2$) in low permeability zones. This, in turn, acts to reduce the amount that locations of streamlines will change as the simulation progresses. Reduced movement of streamlines during the injection period works in favor of the accuracy of the streamline approach, where streamlines are updated only periodically to account for effects of mobility changes and gravity segregation. However, a more detailed study is required to fully understand and map out the limitations of the streamline approach for this type of displacements. An initial investigation of the limitations of streamline methods, covering a full range of capillary to viscous forces, is reported for displacements in layered 2D systems by Sam-Olibale [84].
4.3.4 Summary: Compositional streamline simulation

Based on the results presented we conclude that:

- Compositional streamline simulation is an efficient and accurate technique for predicting the injection phase of CO₂ injection in saline aquifers.

- CPU requirements for the streamline approach are an order of magnitude less than fully implicit black-oil modeling. The speed-up factor is expected to increase with increasing size of aquifer model.

- Compositional streamline simulation is efficient enough to allow its use in uncertainty assessment frameworks in which a large number of realizations must be run within a reasonable timeframe.
4.4 Summary: Saline aquifers

In this section we have examined how the interplay of viscous, gravity, and capillary forces acts to determine the fate of injected CO\textsubscript{2}. During the injection period, pressure gradients in the aquifer are created by the injection well and the density difference between CO\textsubscript{2} and brine, and convection induced by those gradients determines the distribution of injected CO\textsubscript{2}. Both conventional finite difference simulation and streamline simulation approaches can be used to predict the movement of CO\textsubscript{2} during the injection period, as the examples presented here show. However, streamline simulation is much more efficient, with computation times an order of magnitude lower than those of a fully implicit finite difference computation.

Conventional finite difference simulations as well as streamline simulations demonstrate conclusively that the ratio of gravity to viscous forces is important in aquifer injection. CO\textsubscript{2} is less dense than brine, and it is much less viscous, and hence average local displacement efficiency will be low. When gravity forces dominate, a relatively thin tongue of CO\textsubscript{2} forms at the top of the aquifer. After CO\textsubscript{2} injection ceases, that CO\textsubscript{2} will dissolve at a rate that is affected significantly by the vertical permeability of the aquifer. In high permeability aquifers, the dissolution rate is increased significantly by the unstable convection that occurs when dissolved CO\textsubscript{2} makes a brine mixture that is slightly more dense than brine alone. After an initial period of diffusion, density-driven fingers form that increase the rate of dissolution, especially for the period before the fingers reach the base of the aquifer. At Sleipner, for example, the onset of vertical convection occurs rapidly (on the order of months), and the mixing that results from the vertical fingering of the dense brine through less dense brine speeds dissolution for about 100 years. But Sleipner has very high permeability (Darcies), and in aquifers with lower permeability (say one hundred millidarcies) vertical convection speeds dissolution over diffusion alone, but the onset of convection is delayed by two centuries, and the rates are sufficiently low that good containment of the injected CO\textsubscript{2} will be required for long periods. That result suggests that the use of capillary trapping of a residual CO\textsubscript{2} phase should be explored in detail.

Conventional finite difference simulations indicate that capillary trapping can act on relatively short time scales, however, to immobilize a portion of the injected CO\textsubscript{2}. How much is trapped depends strongly on the ratio of viscous to gravity forces. When gravity forces dominate, less CO\textsubscript{2} is trapped, but most of the CO\textsubscript{2} that is trapped as a residual phase is trapped on the time scale of a few injection periods. When gravity forces dominate, on the other hand, much more CO\textsubscript{2} can be trapped, and significant quantities trap quickly, but many injection periods are required to trap the remaining undissolved CO\textsubscript{2}. These results suggest that CO\textsubscript{2} should be injected at the highest feasible rates (consistent with avoiding fracturing of the aquifer formation) should be used to reduce the gravity to viscous ratio. They also suggest that the use of water injection should be considered as a way to reduce gas saturations and increase trapped saturations on even shorter time scales.
5 CO₂ Storage and Coalbed Methane Recovery

Enhanced coal bed methane (ECBM) recovery combined with carbon dioxide (CO₂) storage is also an option for sequestration of CO₂. As with storage in oil and gas reservoirs, coal beds provide the opportunity for enhanced recovery of energy resources simultaneous with greenhouse gas storage. Coal bed methane has grown in importance as an energy source in recent years and now accounts for about 10% of U.S. natural gas production. Coal beds have large internal surface area and strong affinity for gases such as methane (CH₄) and CO₂. Coal beds, however, are the least understood setting for geological storage of carbon dioxide. The fundamental mechanisms of emplacement and containment of CO₂ are not well elucidated. Hence, potential volumes of storage in coal beds are smaller and estimated with less reliability in comparison to the other geological settings.

Effective methods to release CH₄ from tight coal bed resources are still being developed. Coal bed CH₄ exploitation occurs, typically, through primary recovery using cavity-completed wells [75]. This completion technique is akin to hydraulic fracturing [13]. The coal bed is then dewatered to reduce pressure so that CH₄ desorbs from coal surfaces. Dewatering generally involves the pumping of significant quantities of water to the surface for disposal. Unfortunately, such primary methods typically recover less than half of the CH₄ in a coal bed [93]. Injection of CO₂, or possibly nitrogen (N₂), so-called enhanced coal bed CH₄ recovery (ECBM), is a possible means to increase the ultimate recovery. Field test results are reported elsewhere [79, 67].

Gas injection can maintain overall coal bed pressure and perhaps reduce the total volume of water that must be lifted to the surface. Injecting a second gas, or a mixture of gases, can reduce the partial pressure of CH₄ in the free gas and thereby enhance desorption from coal surfaces. Gas injectants can also sweep desorbed CH₄ through the reservoir.

Nitrogen is a natural choice for ECBM due to its availability and the fact that it tends to yield incremental recovery response relatively rapidly [114]. Carbon dioxide injection also has advantages in that CO₂ tends to adsorb to coal surfaces more strongly than either CH₄ or N₂ (adsorption results follow). The strong adsorption characteristics of CO₂ tend to impede premature breakthrough of injectant and result in more rapid complete displacement of CH₄ [114]. Moreover, CH₄ emits about half as much CO₂ when combusted, as compared to coal; there is synergy among ECBM and carbon sequestration.

Whereas equilibrium gas adsorption on coals is relatively well studied because the topic is related to mine safety [50], the process model for ECBM and its numerical representation is not well elucidated. Modeling attempts of note are well summarized in a recent review [106] that finds a general lack of understanding of the physical mechanisms occurring as CO₂ is injected into coal seams. This lack of understanding motivated us to begin a simultaneous experimental, analytical modeling and numerical modeling study that builds upon our previous analytical modeling effort [114].
ultimate goals are to (i) generate a suite of laboratory data that probes the transport of multicomponent, adsorbing gas mixtures through coal as well as sorption induced permeability changes of coal, (ii) develop an understanding of the critical processes that control the time scales for gas emplacement and displacement from coal beds, and (iii) translate the understanding of process physics engendered into practical and accurate quantitative models for sequestration in coal beds.

Our previous analytical study of the flow of multicomponent gases through coal [114] predicted interesting interplay between the adsorption properties of coal surfaces and the advance of individual gas species. For instance, injection of pure CO$_2$ into a linear coal pack leads to virtually 100% production of the original CH$_4$ in place prior to the breakthrough of CO$_2$. Injection of mixtures of N$_2$ and CO$_2$ into a CH$_4$ filled pack are predicted to be separated by the coal bed as CO$_2$ adsorbs more strongly to coal surfaces and is preferentially retained by the coal bed.

Subsequent sections present exploration of the unsteady flow of pure gas and gas mixtures through one-dimensional coal systems. We begin with an exploration of the timescales for gas transport in fractured coal bed systems. Then we turn to measurement of coal bed properties such as adsorption of various gases, permeability to pure gases and gas mixtures, and wettability. This is followed by further measurements of gas transport in coal beds. Analytical and numerical modeling efforts follow. A discussion and conclusions complete the section.

5.1 Time Scales for Coal Bed Sequestration

Flow through coal bed reservoirs occurs in a network of subparallel face cleats orthogonally intersected by butt cleats. For a mature, high rank coal, typical cleat aperture is approximately 0.1 mm, and typical cleat spacing is 1-2 cm [25]. When CO$_2$ is injected, it flows through the cleat system and diffuses into the matrix. Preferential adsorption of CO$_2$ causes adsorbed CH$_4$ to desorb. The desorbed CH$_4$ then diffuses through the matrix to the cleat system, where it flows to the production well and is produced. Diffusion through the matrix is controlled by concentration gradients, while flow through the cleat system is controlled by pressure gradients. The rate of production from coal bed reservoirs is controlled by the slower of these two processes. In this section we consider the question of whether it is appropriate to model field-scale flow in a coal bed with an assumption of local chemical equilibrium between coal and gas or whether some more complex model is required.

The following simple scaling analysis examines the effect of diffusion transport in the cleat and matrix systems. In cases where convection dominates, the local equilibrium assumption is reasonable. If the local equilibrium assumption can be made, then the cleat network controls flow through coal bed reservoirs and the details of matrix diffusion effects need not be represented explicitly.

5.1.1 Cleat System

Flow in the cleat system can be described by the convection-dispersion equation shown in Eq. (5.1), which describes the concentration of injected gas in the fracture
system, $C_f$. The Peclet number ($Pe$), defined in Eq. (5.2), is a ratio of the characteristic time for diffusion to the characteristic time for convection.

$$\frac{\partial C_f}{\partial \tau} + \nabla \cdot C_f - \frac{1}{Pe} \nabla^2 C_f = 0,$$  \hspace{1cm} (5.1)

where

$$Pe = \frac{vL_f}{\phi_f D_f},$$  \hspace{1cm} (5.2)

and $\tau$ is dimensionless time, $v$ is the average flow velocity in the fractures, $L_f$ is the displacement length, $\phi$ is the fracture porosity, and $D_f$ is the diffusion coefficient in the gas phase in the fractures. Large values of $Pe$ characterize convection-dominated flows. For typical ECBM displacements, $Pe$ is very large. For a flow velocity of 0.33 m/d, a flow length of 400 m, fracture porosity of 0.01, and a diffusion coefficient in the gas of $10^{-4}$ cm$^2$/s, for example, the resulting Peclet number is $1.5 \times 10^7$. Even for a flow velocity two orders of magnitude larger, the Peclet number would still exceed $10^3$. Those values are large enough that it is quite reasonable to neglect the effects of longitudinal diffusion in a flow calculation.

5.1.2 Matrix System

In the coal matrix system, we assume that diffusion is the only mechanism of transport. The conservation equation is

$$\frac{\partial C_m}{\partial t} = \nabla \cdot D_m \nabla C_m,$$  \hspace{1cm} (5.3)

where $C_m$ is the concentration of injection gas in the matrix and $D_m$ is the diffusion coefficient in the matrix. Diffusional transport was considered for a dry matrix and a wet matrix. For the dry matrix, diffusion through a single matrix block was considered. The system was reduced to an equivalent spherical system, and a constant diffusion coefficient was assumed. For a spherical coordinate system assuming that $D_m$ is constant, Eq. (5.3) becomes

$$\frac{\partial C}{\partial t} = \frac{D_m}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial C}{\partial r} \right),$$  \hspace{1cm} (5.4)

with boundary conditions

$$C(r = R, t) = 1,$$  \hspace{1cm} (5.5)

$$C(r, t = 0) = 0.$$  \hspace{1cm} (5.6)

The time required for the average concentration in the sphere to reach 95% was calculated. The resulting diffusion time as a function of effective diffusion coefficient and radius of the sphere is shown in Figure 5.1. The time required for equilibration depends fairly strongly on the assumed diffusion coefficient. Shi and Durucan [89] report values, estimated by fitting effluent composition data for pulverized coals, of $5 \times$
$10^8$ to $5 \times 10^{-6}$ cm$^2$/s for micropores and $2 \times 10^{-5}$ to $7 \times 10^{-4}$ cm$^2$/s for macropores. Thus, for large diffusion coefficients, equilibration time for all radii of sphere considered is on the order of days.

![Figure 5.1: Time required for the average concentration to reach 95% in a sphere of dry coal. Typical matrix size for a mature coal is 1-2 cm.](image)

For small diffusion coefficients, the equilibration times for larger fractures spacings are significant. Hence, the equilibrium assumptions for high velocity flow in systems with large fracture spacing may not be justified. For a high rank coal, where fracture spacing is small, equilibration time is on the order of tens of days for a typical solid phase diffusion coefficient of $10^{-7}$ cm$^2$/s. In such settings, equilibrium assumptions during flow simulation seems reasonable.

Coal reservoirs are typically water saturated, and the coal surface is water wet [68]. In this system, for mass transfer between matrix and fracture systems, we assume that gas must diffuse through a thin film of water. The presence of water creates extra resistance to mass transfer. The concentration gradient driving mass transfer in the water phase is relatively low, because the solubility of gas in the water limits the concentration gradient in that phase.

![Figure 5.2: Schematic of a simplified wet matrix system.](image)
For this calculation, the wet matrix was approximated as a spherical film of constant thickness, surrounding the matrix (Figure 5.2). The time to reach the 99% of the solubility concentration at \( r_a \) is presented as a function of diffusion coefficient and film thickness in Figure 5.3. For the range of thicknesses and diffusion coefficients considered, film equilibration times are very short (on the order of minutes) compared to matrix equilibration times. Diffusion coefficients for \( \text{CO}_2 \) in water at high pressure are on the order of \( 10^{-5} \text{ cm}^2/\text{s} \) (Grogan, 1988). Hence, we conclude that for a typical cleat aperture of 0.1 mm, the time required for diffusion through a water film with similar thickness is small compared to the other characteristic times for flow and equilibration.

![Figure 5.3](image_url)

\textbf{Figure 5.3:} Time required for wet film to reach solubility concentration.

\subsection*{5.1.3 Summary: Time Scales}

This simple analysis of diffusion in the cleat and matrix system suggests that for coal beds in which fracture spacing is small (< 2 cm) with diffusion coefficients of \( 10^{-6} \text{ cm}^2/\text{s} \) or larger, diffusion times are short enough that for flow at field scale, it is a reasonable approximation to assume that the fluid in the cleat system is in equilibrium with the solid. If so, then the problem of representing adsorption of \( \text{CO}_2 \) and other gases in a coal bed revolves around accurate representation of the multicomponent adsorption. If a suitable model of that adsorption is available, it should be possible to take advantage of the speed of streamline simulation techniques for this system.

\subsection*{5.2 Adsorption Isotherms}

All measurements reported in this work have been conducted with a single, large sample of coal from the Powder River Basin, WY. The coal sample originates from a coal bed at a depth of 900-1200 ft. The coal sample as received was extensively fractured and broken into small pieces, filled with formation water, and contained some clay or shale. The small size of intact pieces precluded the use of core samples. The coal was ground to a particle size of about 60 mesh and the internal surface area of the coal was exposed. The ground samples were preserved in desiccators under vacuum to avoid
The mean size of the coal particles is 0.25 mm. The ground coal material was relatively easy to use. Coal particles were formed into a coal pack by pressing the ground coal into cylindrical shapes.

A schematic of the experimental component is shown in Figure 5.4. The centerpiece of these studies is the coal pack of 25 cm length and 4.25 cm diameter. Porosity and permeability of each pack are measured with helium as reported in Table 5.1. It is assumed that helium does not adsorb to the coal surface. For adsorption and displacement studies, the coal was packed directly into an aluminum tube. This tube contains sampling ports along its length to provide measurements of flowing gas composition along the length of the apparatus.

Figure 5.4: Schematic of experimental components for adsorption, permeability, and displacement tests.

Table 5.1: Coal pack data

<table>
<thead>
<tr>
<th></th>
<th>#1 adsorption-displacement</th>
<th>#2 adsorption-displacement</th>
<th>#3 steady-state permeability</th>
</tr>
</thead>
<tbody>
<tr>
<td>Size of coal particle, cm</td>
<td>0.025</td>
<td>0.025</td>
<td>0.025</td>
</tr>
<tr>
<td>Length, cm</td>
<td>25.0</td>
<td>25.0</td>
<td>30.5</td>
</tr>
<tr>
<td>Diameter, cm</td>
<td>4.25</td>
<td>4.25</td>
<td>2.54</td>
</tr>
<tr>
<td>Porosity, %</td>
<td>44</td>
<td>37</td>
<td>19</td>
</tr>
<tr>
<td>Permeability (helium), mD</td>
<td>144</td>
<td>43</td>
<td>36</td>
</tr>
<tr>
<td>Weight of coal, g</td>
<td>218</td>
<td>231</td>
<td>114</td>
</tr>
</tbody>
</table>

For measurement of steady-state permeability, coal was first packed into a viton rubber sleeve and this sleeve placed inside of a support sleeve made from a stainless steel tube with numerous perforations. The rubber-sleeve stainless steel assembly was placed within an outer holder so that various confining pressures could be applied to the coal pack, as illustrated in Figure 5.5. This second holder allows us to separate the affect of
permeability reduction in the coal pack from that of the confining pressure. Steady-state measurements were conducted at a constant difference between confining and pore pressure.

![Figure 5.5: Photograph of inner stainless steel supporting coreholder (lower) and outer pressure vessel (upper). A viton sleeve packed with coal is placed within the supporting coreholder.](image)

At the inlet of the coal pack holder, either a gas flow rate controller for constant-rate gas injection rate at test pressure, or a pressure regulator is used. The pressure drop across the coal pack is measured via pressure transducer to the nearest 0.1 psi (0.7 kPa). A back-pressure regulator at the coal pack outlet elevates the test pressure to the desired level. Downstream of the back-pressure regulator, a gas-flow rate meter measures the gas production rate at standard conditions. The effluent gas from the flow meter is then sent to a gas analyzer to measure the fraction of each gas species in the mixture.

Specific experimental procedures are listed prior to reporting results from each type of measurement: adsorption, permeability, displacement efficiency. After completion of an experiment or measurement, a vacuum pump is used to remove gas from the coal pack. The coal pack holder is placed on an electronic balance that measures the weight of the coal pack holder. Gas removal is verified by the attainment of the original mass of the coal pack.

Sorption isotherms have been measured for dry and wet coal systems. The results are reported in the following sections.

### 5.2.1 Dry Coal

All experiments were conducted at 22 °C. The coal pack was connected to the gas-supply cylinder directly through a pressure regulator during measurement of adsorption/desorption properties. The outlet of the coal pack holder was closed. Except for the pressure transducer, all other components were removed to reduce dead volume. The coal pack was subjected to gas from the cylinder at a constant test pressure. When the weight was constant, it was recorded. The pore volume of the coal pack and gas compressibility versus pressure are known. We calculate the weight of free gas in the coal pack \(W_f\). The total weight at an equilibrium state \(W_t\) minus the weight of free gas
is the weight of adsorbed gas \((W_a)\). The coal pack holder was then subjected to a greater pressure to measure adsorption. This continued until a maximum adsorption was attained or in the case of CO\(_2\), the pressure approached the critical pressure of CO\(_2\). For desorption, the process was reversed. The pressure in the coal pack was gradually released and adsorbed gas mass was measured. A minimum of 24 hours was allowed between the stabilization of weight and the establishment of a new equilibrium pressure. The data was processed to obtain a total adsorption isotherm that accounts for the volume of the adsorbed phase \([67, 10]\). The total gas adsorbed was then converted into gas volume at standard conditions.

The Langmuir isotherm is used to correlate results for each gas,

\[
V = \frac{V_m b P}{(1 + b P)},
\]

where \(V\) is the gas adsorption at the test pressure, \(V_m\) is the maximum gas adsorption (a constant), \(b\) is also a constant. \(P\) is the absolute pressure. For some measurements, the coal was made moist by adsorbing water vapor prior to measurements.

Figure 5.6 presents adsorption/desorption curves versus pressure for CH\(_4\), CO\(_2\), and N\(_2\) at zero initial water saturation. Open symbols represent adsorption whereas closed symbols are for desorption. The curves are the best-fit using the Langmuir-isotherm, Table 5.2.

**Table 5.2:** Langmuir adsorption constants.

<table>
<thead>
<tr>
<th></th>
<th>Adsorption</th>
<th></th>
<th></th>
<th>Mixed Gas</th>
<th>selectivity</th>
<th>(\alpha)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(V_m) (SCF/ton)</td>
<td>(b) (1/psia)</td>
<td>(V_m) (SCF/ton)</td>
<td>(b) (1/psia)</td>
<td>(\alpha) (\text{CH}_4/\text{CO}_2)</td>
<td>(\alpha) (\text{CH}_4/\text{N}_2)</td>
</tr>
<tr>
<td>CH(_4)</td>
<td>811</td>
<td>0.00237</td>
<td>543</td>
<td>0.0382</td>
<td>0.2006</td>
<td>3.15</td>
</tr>
<tr>
<td>CH(_4)</td>
<td>scanning loop 2</td>
<td>498</td>
<td>0.0118</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH(_4)</td>
<td>scanning loop 3</td>
<td>510</td>
<td>0.0186</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO(_2)</td>
<td>1760</td>
<td>0.00521</td>
<td>1560</td>
<td>0.0158</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N(_2)</td>
<td>272</td>
<td>0.00242</td>
<td>226</td>
<td>0.00574</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH(_4) + CO(_2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.2006</td>
<td></td>
</tr>
<tr>
<td>CH(_4) + N(_2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3.15</td>
<td></td>
</tr>
<tr>
<td>CO(_2) + N(_2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>15.705</td>
<td></td>
</tr>
</tbody>
</table>

It appears adequate for description of pure gas adsorption/desorption behavior. For CH\(_4\), the maximum adsorption of 811 scf/ton, is reached at a pressure of roughly 1200 psia. There is significant hysteresis between adsorption and desorption curves. During desorption there is little response to pressure decline from 1200 psia to 250 psia. The majority of CH\(_4\) desorbs at pressures below 150 psia. Thus, coal bed reservoirs that display such adsorption behavior must reach quite low pressures to release CH\(_4\) from coal surfaces during depletion.
Carbon dioxide adsorption/desorption curves versus pressure also display significant hysteresis and follow a Langmuir-type relationship. While hysteresis may be detrimental to CH₄ recovery during primary depletion, it has benefit during CO₂ sequestration. Hysteretic CO₂ loading and unloading in Figure 5.6 indicates that coal surfaces retain significant volumes of CO₂ even though they may experience pressure reduction. Moreover, CO₂ adsorption is significantly greater than CH₄ at the same pressure. The maximum pure-component CO₂ adsorption is about 1500 scf/ton at the pressure of 840 psia. That is, roughly 2.5 times the loading of CH₄ at that pressure. Note that the critical pressure for CO₂ is about 1070 psia. Our apparatus is not currently configured for supercritical CO₂, but supercritical adsorption properties are clearly an area for future investigation.

The N₂ adsorption/desorption behavior displays characteristics similar to CH₄ and CO₂. Its adsorption capacity is the least among the three test gases. Nitrogen desorption shows less hysteresis, in an absolute sense, than that observed for CO₂ and CH₄. Comparison of N₂ and CO₂ curves indicates that the coal surface holds nearly 6 times the volume of CO₂ relative to N₂. For strictly enhancing coal bed CH₄ recovery, N₂ injection may be favored owing to lesser loss of the injectant to the coal surface though the price is a separation of CH₄ from N₂.

The adsorption hysteresis displayed by all gases raises several interesting questions. One question is the dependence of the desorption characteristics on the initial pressure of the coal sample. Figure 5.7 illustrates that for CH₄, the desorption isotherm followed by any gas during pressure reduction is a function of the initial pressure of the coal bed.
This is similar to so-called scanning loops measured for capillary pressure as a function of water saturation for rocks and soils. Carbon dioxide and N\textsubscript{2} may display similar scanning loops. This dependence on initial pressure is still to be investigated.

![Figure 5.7: Scanning loops for adsorption and desorption of CH\textsubscript{4} from Powder River Basin coal. Desorption curves depend on the initial pressure (given in parentheses) where depressurization begins.](image)

5.2.2 Mixed Gases on Dry Coal

In our modeling effort, we use the extended Langmuir equation \[65\] to describe the adsorption behavior of multiple gas components. Adsorption characteristics of a N\textsubscript{2}/CO\textsubscript{2} mixture were measured to verify use of the extended Langmuir approach for binary mixtures. The adsorption of component \textit{i} is predicted as

\[
V_i = \frac{V_m b_i P_i}{1 + \sum_j b_j P_j}, \tag{5.8}
\]

where

\[
P_i = P y_i, \tag{5.9}
\]

and the selectivity is

\[
\alpha = \frac{(x / y)_i}{(x / y)_j} = \frac{(V_m b)_i}{(V_m b)_j}. \tag{5.10}
\]

The symbol \textit{V} is gas adsorption, \textit{P} is partial pressure, \textit{V}_m is the saturation adsorption constant, \textit{b} is a constant, \textit{y} is the free gas mole fraction, \textit{\alpha} is the selectivity ratio, and \textit{x} is the adsorbed gas mole fraction.

A mixture of CO\textsubscript{2} and N\textsubscript{2} was injected into the coal pack at a given pressure. After reaching equilibrium, free gas was sampled to measure the gas composition. This yields
the free gas mole fraction and pressure. Thus the partial pressure for each gas in the pore space is known. With the selectivity ratio calculated from Eq. (5.10), we calculate the adsorbed gas mole fraction. With Eq. (5.8), we examine each gas at the test pressure. Figure 5.8 gives the measured adsorption isotherm for the binary system (48% N\textsubscript{2}+52% CO\textsubscript{2}). As expected, N\textsubscript{2} adsorption is much lower than that of CO\textsubscript{2}. This is reasonable because CO\textsubscript{2} has a selectivity ratio, $\alpha$, approximately equal to 15 (CO\textsubscript{2}:N\textsubscript{2}), (Table 5.2).

Compared to pure CO\textsubscript{2}, the CO\textsubscript{2} adsorption for the binary gas system is lower because N\textsubscript{2} occupies some adsorption sites. For example, at 800 psia, CO\textsubscript{2} adsorption is 840 scf/ton for the mixed gas case, but it is about 1600 scf/ton for pure CO\textsubscript{2}. At the same time, N\textsubscript{2} adsorption also decreases from 250 to 80 scf/ton for pure to mixed gas cases. Nevertheless, Figure 5.8 illustrates that predictions from the extended Langmuir equation, given as solid lines, reasonably approximate the measured loadings as a function of pressure, symbols.

![Figure 5.8: Adsorption of a 48% N\textsubscript{2} and 52% CO\textsubscript{2} mixture on Powder River Basin Coal. Symbols are measurements and solid lines are predictions from the extended Langmuir equation.](image)

5.2.3 **Moist Coal**

Moist coal is sometimes reported to have somewhat different adsorption properties than dry coal [50, 10]. Generally, once the moisture content is above some threshold, say 5%, moist coal adsorption properties are constant [50]. In order to study the effect of initial water saturation on gas adsorption, CH\textsubscript{4}, CO\textsubscript{2}, and N\textsubscript{2} adsorption were measured in moist samples. The water phase is 0.5 wt% NaCl. The initial water saturation is about 8-9% and is established by flushing the coal pack with humidified N\textsubscript{2}. When the desired initial water saturation is reached, the coal pack is then evacuated to remove dissolved and adsorbed N\textsubscript{2}. Because N\textsubscript{2} has lower affinity for coal surfaces than water and is only sparingly soluble in water, N\textsubscript{2} is easily removed. The initial water saturation is then established by weighing the coal pack.
Figure 5.9 compares the adsorption curves with and without initial water saturation for CH₄, CO₂, and N₂, respectively. The results show that the presence of an initial water saturation does reduce CH₄, CO₂, and N₂ adsorption. Maximum CH₄ adsorption decreases by 30%, and the CH₄ adsorption approaches maximum at a lower pressure. A similar effect is observed for N₂. The maximum N₂ adsorption also decreases by 33%. The effect of initial water saturation on CO₂ adsorption is markedly smaller. The maximum adsorption only decreases by about 15%. The effect of initial water saturation on gas adsorption may be related to the gas solubility in water. CO₂ has the greatest solubility in water among these gases.

![Figure 5.9: Comparison of the effect of moisture on the adsorption of CO₂(Sₘᵢₐ₉ = 8.47%), CH₄(Sₘᵢₐ₉ = 8.67%), and N₂(Sₘᵢₐ₉ = 8.54%) on coal surfaces.](image)

5.2.4 Summary: Adsorption

Pure CH₄, CO₂, and N₂ adsorption on Wyoming Powder River Basin coal is well represented by the Langmuir equation under both dry and moist conditions. The pure component adsorption capacity of CO₂ is about 2.5 times greater than CH₄ and about 4 times greater than N₂. All of the gases tested appear to display some degree of hysteresis between adsorption and desorption loading of coal surfaces. For desorption of CH₄ from these samples, the specific desorption curve depends on the maximum pressure attained during adsorption.

5.3 Coal Permeability versus Gas Composition

Steady-state coal pack permeability was measured in the adsorption cell and in the sleeved coreholder, shown in Figure 5.5, as a function of the composition of the gas injected. The difference between the overburden and pore pressure was kept fixed at 400 psi. The compositions of the injected gases are as follows: pure CH₄, pure N₂, 25% CO₂+75% N₂, 50% CO₂+50% N₂, 75% CO₂+25% N₂, 85% CO₂+15% N₂, and pure CO₂.
For pure gases, we used bottled laboratory gases. Gas mixtures were prepared in the laboratory from pure gases. Mixtures were made according to partial pressure and the mass of the pressure cell loaded with gas at a total pressure of 800 psi. Permeability is calculated using Darcy’s Law applied to compressible single-phase systems:

\[
k_g = \frac{2000\mu_g q_g P_g L}{A_c (P_1 + P_2) (P_1 - P_2)}, \tag{5.11}
\]

where, \(k_g\) is the absolute permeability (mD) of the coal pack, \(\mu_g\) is gas viscosity (cp), \(q_g\) is gas flow (cm³/s) at atmosphere pressure, \(P_g\) is standard atmospheric pressure, atm, \(L\) is length of the coal pack in cm, \(A_c\) is cross sectional area of the coal pack, cm², and \(P_1, P_2\) are inlet and outlet pressures of the coal holder, atm.

### 5.3.1 Experimental Results

First, measurements are reported where the difference between confining pressure and pore pressure is fixed at 400 psi as the pore pressure is increased. Results are shown in Figure 5.10 that plots permeability versus pore pressure.

![Figure 5.10: Permeability of coal pack versus pore pressure for pure and mixed gases. The confining pressure minus the pore pressure is constant at 400 psi for all measurements.](image)

Figure 5.10 shows that the permeability of the coal pack decreased as the pore pressure increased in all cases. That is, as the amount of gas adsorbed increased, the permeability decreased. The permeability reduction with pressure was small for \(N_2\), somewhat greater for the various mixtures, and greatest for pure \(CO_2\). For the mixed gases, the decrease in permeability with pressure was greatest for mixtures with large fractions of \(CO_2\). Permeability did not decrease substantially for the mixtures where the \(CO_2\) concentration was 25%, 50% and 75%; on the other hand, permeability decreased more significantly for the mixture where \(CO_2\) concentration was 85%. The results in
Figure 5.10 indicate that a small fraction of $N_2$ in the injection gas serves to preserve coal pack permeability.

We have exerted some effort to represent these permeability reduction results via a simple relationship. Preliminary results are encouraging and summarized next. Let permeability reduction be defined as $k_i/k$, where the subscript $i$ denotes the initial helium permeability. The maximum loading of $N_2$ from Figure 5.6 is assumed to define a monolayer of coverage on the coal surface. Next, the fractional coverage of the coal surface at every pressure corresponding to a measurement of $k_i/k$ was calculated. The cross-sectional areas of molecules are set to 16.2 Å$^2$ for $N_2$, 19.5 Å$^2$ for $CO_2$ and 17.7 Å$^2$ for $CH_4$. Figure 5.11 displays the result. A fractional coverage greater than 1 implies that multiple layers of gas molecules, relative to $N_2$, have adsorbed on the surface. For pure gases, it appears that permeability reduction correlates with the fraction of the coal surface covered with adsorbed gas. One implication of Figure 5.11 is that permeability reduction of the coal pack is not a result of swelling of the coal matrix, but occurs because the pore space of the coal available to carry free gas is reduced by the volume of adsorbed gas. These results suggest that mixed gas permeability behavior might be similarly reduced to a characteristic curve.

![Figure 5.11: Fractional coverage of coal surface versus permeability reduction factor for pure gases. The surface area occupied by the maximum loading of $N_2$ defines a coverage ratio of 1.](image)

Displacement experiments are conducted in the same cell as that used for adsorption measurements because it provides the opportunity to sample free gas along the length of the coal pack. Hence, the effect of $CO_2$ pressure on steady-state permeability was also determined for this set up. The experiments are conducted at a constant pressure from low to high. The coal pack is saturated with $CO_2$ for about 12-24 hours and allowed to reach equilibrium. Carbon dioxide was then injected at a constant rate at test pressure. When the displacement reaches steady-state, we record the differential pressure and flow rate. Results are processed according to Eq. (5.11) and presented in Figure 5.12.
As in the constant net confining pressure experiments, the permeability decreases with pressure. The permeability decreases quickly at pressures less than 300 psia. Thereafter, the permeability decreases slowly. Recall the CO$_2$ adsorption curve indicates that adsorption increases most dramatically at pressures less than 300 psi. The permeability reduction is related to the adsorption process. When CO$_2$ is adsorbed, it can be assumed to be in a pseudo-liquid state. Carbon dioxide molecules possibly coat the coal particle surfaces, like a liquid film and do not move. Thus, an increase in the thickness of CO$_2$ blocks flow paths. At 800 psia, CO$_2$ adsorption is about 15 grams. If the liquid CO$_2$ density is used (about 0.7 g/cm$^3$), we estimate that adsorbed CO$_2$ volume is about 21 cm$^3$. Thus, for the test coal pack, the effective porosity reduces by roughly 15%.

5.3.2 Summary: Permeability

Steady-state coal pack permeability varies markedly with the composition of the gas injected. Permeability reduction correlates qualitatively with adsorption. That is, CO$_2$ adsorbs to the greatest degree and the coal packs experience the greatest change in permeability during the flow of pure CO$_2$. The limited results obtained, to date, appear to be consistent with a finite volume of adsorbed gas reducing the pore volume available for flow.

5.4 Wettability of Coal beds

Coal is a heterogeneous mixture of carboniferous plant remains and minerals. These plant remains form coal macerals that are discrete organic entities in the coal with characteristic chemical and physical properties. One such property is wetting behavior, or wettability, as it is commonly termed. Wettability is of interest because it influences...
the affinity of CO$_2$ for coal surfaces, and hence it may affect the rate at which equilibrium adsorption of CO$_2$ takes place.

The wettability of coal is relatively well studied in the literature because of the importance of flotation to coal processing. Measurements of the contact angle, through the water phase, range from 20 to 100° (e.g., Gutierrez-Rodriguez et al. [32]; Arnold and Aplan [2]; Gowiewska et al. [31]). The nonzero contact angle formed on coal surfaces varies with the pH of water and the coal source. On the other hand, some of the inorganic mineral matter in coal, so-called ash, is water wet. On a percentage basis by weight, ash ranges typically from virtually zero to 20%. Thus, while a coal bed may be initially filled with water, the coal bed is largely formed of carbon in the form of coal that is not strongly water wet as evidenced by contact angles that are significantly greater than zero.

Although the literature on coal flotation is not necessarily relevant to gas and water flow properties of coal, these data do indicate that careful consideration of the wettability of coal surfaces as a function of the salinity and pH of water is warranted. Additionally, there is relatively little understanding of the wettability of solid coal surfaces that have gases such as CO$_2$ and CH$_4$ adsorbed to them. This facet of our studies is directed towards understanding wettability of coal surfaces, so that we gain an improved understanding of the interplay of adsorption, wettability, and multiphase flow in coal beds containing CO$_2$. Our first steps are oriented toward developing a mechanistic understanding of coal water wettability as a function of solution pH.

The water in a coalbed may vary from acidic to neutral to basic. Dissolved gases such as CO$_2$ reduce the pH of the water by forming carbonic acid. A typical CO$_2$-saturated water has a pH of 3.5. We have therefore concentrated our efforts on understanding the effect of pH on wettability of coal surfaces. Wettability of porous media, such as coal, is directly proportional to the ease with which the coal imbibes water spontaneously. We quantify wettability experimentally in terms of the rate of imbibition of water by coal. Additionally, wettability is obtained from first principles in terms of the contact angle that is calculated for various pH solutions using the Derjaguin-Frumkin equation [38]. Computations resulting in relatively small contact angles suggest that the liquid spreads readily and that imbibition rate is relatively large, and vice versa. The primary input to the Derjaguin-Frumkin equation is the so-called disjoining pressure isotherm. It is a manifestation of surface forces that allow thin films to coat solids. The disjoining pressure characteristics of many practical systems are calculable from DLVO (Derjaguin, Landau, Verwey, Overbeek) theory [39].

### 5.4.1 Modeling a CO$_2$-Coal Surface

As discussed above, we are most interested in CBM systems in the presence of CO$_2$. A dominant characteristic with respect to wettability, is reduction in the pH of the solution as CO$_2$ dissolves. This is explained by the formation of carbonic acid H$_2$CO$_3$. First, the wettability of coal as a function of pH is estimated. Kelebek et al. [54] reported that contact angles measured on a coal surface go through a maximum at a pH of 4 as pH is varied from 1 to 12. Our calculations to follow seek to reproduce such dependencies.
DLVO theory suggests that the interaction forces between a solid surface and a gas-water interface are either attractive or repulsive. The disjoining forces have three components: (1) structural forces, (2) van der Waals forces, and (3) electrostatic interactions originating from the overlap of ion clouds at each interface. The sum of these forces \( F_h, F_A, F_d \) results in the disjoining pressure, \( \Pi \), between the surfaces.

Structural forces explain repulsion as two molecules come near each other. When the thick film ruptures it forms a thin layer on the coal surface. This thin layer has dimensions of a few water molecule diameters. As the layer cannot be thinner than the diameter of a water molecule, the structural forces are modeled so as to become substantially repulsive at 0.3 nm, which is the diameter of a water molecule. Churaev and Derjaguin [9] have also suggested an attractive component to the structural forces for hydrophobic surfaces. We have, however, retained the conventional purely repulsive picture of structural forces. The forces in general are modeled as exponentially decreasing with increasing thickness of the film, \( h \). These are taken to be of the form

\[
F_h = A_s \exp\left(-\frac{h}{h_o}\right), \quad (5.12)
\]

where \( A_s \) depends upon the type of system and \( h_o \) is the decay length. We have used values as suggested by Hirasaki [38] who states that a typical value of \( h_o \) is 0.05 nm. Van der Waals forces are dependent on the distance between any two surfaces. For thin film interaction, van der Waals forces are given as [6]:

\[
F_A = -\frac{A}{(12\pi h^4)} \left( \frac{15.96 \cdot \frac{h}{A} + 2}{1+5.32 \cdot \frac{h}{A}} \right)^2, \quad (5.13)
\]

where \( h \) is the distance between the gas-water interface and the coal surface, \( A \) is the Hamaker constant, and \( \lambda \) is the London wavelength that is approximately 100 nm for most systems. The Hamaker constant may be measured or calculated by Lifshitz theory as explained in detail later.

The two surfaces of a colloidal thin film may interact as a result of the presence of ionic charge on these surfaces. The forces between the two surfaces are usually calculated by modeling the surfaces as either constant potential or constant surface charge. Mathematical expressions were developed by Gregory [27] for both cases as well as an intermediate case.

The constant potential case, as developed by Gregory, is formulated in terms of surface potentials as:
The constant charge case, as the name suggests, assumes constant charge on the two surfaces.

\[ F_d = n_b^* k^* T \left\{ \frac{2 \varphi_1 \varphi_2 \cosh(kh) + \varphi_1^2 + \varphi_2^2}{\sinh(kh)^2} \right\}, \quad (5.15) \]

where \( \varphi_1 \) and \( \varphi_2 \) are reduced potentials that are written as

\[ \varphi_1 = e^{\frac{\xi_1}{kT}}, \quad (5.16) \]

and

\[ \varphi_2 = e^{\frac{\xi_2}{kT}}. \quad (5.17) \]

In Eqs. (5.15) to (5.17), the symbol \( \kappa \) is the inverse Debye length;

\[ \kappa = \left( \frac{2n_b e^2}{\varepsilon kT} \right)^{\frac{1}{2}}, \quad (5.18) \]

\( \xi \) is the surface potential that is commonly taken as the zeta potential, \( k \) is Boltzmann’s constant \((1.38 \times 10^{-23} \text{ J/K})\), \( n_b \) is the ion density, \( e \) is the electronic charge \((1.6 \times 10^{-19} \text{ C})\), \( \varepsilon \) is the electric permittivity \((1.48 \times 10^{-9} \text{ C}^2/\text{N-m}^2)\), and \( T \) is absolute temperature. Temperature is assumed constant at 300K.

According to Gregory [27] most cases lie somewhere in between the constant potential and constant charge case. He proposed a linear superposition of the two cases giving:

\[ F_d = 64n_b kT \varphi_1 \varphi_2 \exp(-\kappa h), \quad (5.19) \]

with

\[ \varphi_1 = \tanh\left( \frac{\xi_1}{4} \right), \quad (5.20) \]

and

\[ \varphi_2 = \tanh\left( \frac{\xi_2}{4} \right). \quad (5.21) \]

Calculation of the wettability of a surface is accomplished by first summing the individual contributions of thin-film forces to the disjoining pressure:

\[ \Pi(h) = F_b(h) + F_A(h) + F_d(h). \quad (5.22) \]
Direct integration of the augmented Young-Laplace equation of capillarity

\[ P_c = \sigma C_m + \Pi(h), \quad (5.23) \]

where \( C_m \) is the interfacial curvature yields the following relationship between equilibrium contact angle \( \theta \) and disjoining pressure [16]

\[ \cos \theta = 1 + \frac{1}{\sigma} \left( \int_{0}^{a} \pi(h) dh + h \pi(h) \right). \quad (5.24) \]

Again, \( h \) is the equilibrium film thickness of interest.

5.4.2 Model Results

A numerical code was developed to calculate the disjoining pressure curve and the contact angles for the variety of conditions expected. The input parameters are the number of ions formed, molar concentration and the zeta potential values at the two surfaces. Using DLVO theory and the definitions of different forces we calculate the disjoining pressure curve, Eq. (5.22). This is then used to calculate the contact angle, Eq. (5.24).

Calculations assume constant potential. The disjoining pressure isotherm is calculated for \( h \) ranging from 0.01nm to 100nm. Contact angles are calculated based on a limiting thickness of thin film; hence, if the limiting thickness is \( h=a \), the area under the disjoining pressure curve is calculated from \( h=a \) to \( h=100 \)nm. Finally, \( \pi(a)a \) is added to the integral and then \( \cos \theta \) is calculated. For generality, calculations were made for a number of thicknesses assuming the film to be 1 to 4 layers of water molecules.

Several inputs are needed to conduct calculations of wettability using Eq. (5.24). These include zeta potential at different values of pH, the Hamaker constant, and the structural force parameters. The zeta potential data for the vapor-water surface is taken from Karakker and Radke [52]. They developed a model for the interface based on the Gibb’s adsorption isotherm. This model compares well with data collected by Li and Somasundaram [61]. For the coal water surface we used the ionizable surface group model developed by Valverede et al. [102].

Uncertainty exists regarding values of the Hamaker constant and structural forces relevant to the coal-water system. We have modeled these physical quantities for the coal-water-\( \text{CO}_2 \) system based on limited data available in the literature. A sensitivity analysis is summarized to determine and predict the parameters that most influence wettability and to what extent.

The salinity decides the molar ion density and therefore the strength of the electrostatic forces as compared to the other components. For the case of coal and acidic water, it was seen that the forces become more attractive with increasing salinity. Example dependencies are shown in Figure 5.13. The contact angle decreases with increasing salinity, according to Eq. (5.24). Figure 5.13 illustrates an important aspect of
coal surfaces. Consider a film on an uncurved surface, $C_m$ equal to 0. Equation (5.24) then indicates that $P_c$ is equal to $\Pi$. For positive nonzero capillary pressures, all equilibrium films, corresponding to the curves in Figure 5.13 are quite thin and of order 0.4 nm. Thus, water does not form thick wetting films on such surfaces and contact angles are strictly nonzero for such $\Pi$ versus $h$ relationships.

![Figure 5.13: Variation in disjoining pressure with salinity.](image)

Hamaker constants are computed in terms of the refractive index and the dielectric permittivity of the media [39]. The Hamaker constant based on this theory is found as the sum of two terms, the static dielectric term and a second term evaluated on the basis of using dielectric constants at imaginary frequencies. The equation is written as:

$$A = \frac{3}{4k} \left( \frac{(\varepsilon_1 - \varepsilon_3)(\varepsilon_2 - \varepsilon_3)}{(\varepsilon_1 - \varepsilon_3)(\varepsilon_2 - \varepsilon_3)} \right) + \frac{3}{8\sqrt{2}} \left( \frac{n_1^2 - n_3^2}{\sqrt{n_1^2 + n_2^2 + n_3^2}} + \frac{n_2^2 - n_3^2}{\sqrt{n_1^2 + n_2^2 + n_3^2}} \right). \tag{5.25}$$

Here $\varepsilon$ are the dielectric constants and $n$ are the refractive indices. The subscripts 1 and 3 represent the different phases, solid and vapor, and the subscript 2 represents the separating medium, water.

In the literature Hamaker constants are generally assumed to be constant for a given system. However for significant pH variation from 3 to 12, Eq. (5.25) indicates that the Hamaker constant varies because it depends on the dielectric properties of the medium, of the coal surface and the vapor. Amongst these, the dielectric properties of water experience the most significant change with variation of pH [104].

Representative disjoining pressure and contact angle calculations were made assuming firstly a constant Hamaker constant 10-20 J and secondly a linearly varying
Hamaker constant. In the latter case, the linear variation of A is from \(10^{-20}\) J at a pH of 3 to \(2 \times 10^{-20}\) J at a pH of 12. Figure 5.14 summarizes results. For reference, measured contact angle data for two different coals are also presented. A linear variation of A with pH yields contact angle functionality most similar to the experimental data presented in the literature. A maximum contact angle is found at a pH of 4 and coal becomes progressively more water wet as the wetting solution becomes more basic or acidic.

![Figure 5.14: Summary of example calculations for contact angle on a coal surface. For reference, literature trends (Kelebek, 1982) are also indicated.](image)

The disjoining pressure calculations presented in Figure 5.13 indicate that water films on coal surfaces are quite thin, possibly on the order of one or several layers of water molecules. In this case, short-range structural forces within thin films become important. As stated earlier, the values of \(A_s\) and \(h_0\) are system dependent. For the coal, water, and CO\(_2\) system these values have not been studied. The magnitude of \(A_s\) was varied over 3 orders of magnitude to check impact on contact angle calculations. Sensitivity of the computed contact values is small and the contact angle is always nonzero.

5.4.3 Experimental Investigation

The modeling and literature review presented above suggests that the contact angle of coal surfaces varies with the chemistry of the wetting solution. In terms of spontaneous imbibition of water into coal, the imbibition rate should be a function of solution pH. As the contact angle changes, so does the rate of imbibition. Our experimental effort was aimed at verifying the above predictions.

The coal used was from the Powder River Basin, Wyoming. It was extracted from a well at a depth of 900-1200 ft below ground surface. Unfortunately, samples were broken into small pieces and unsuitable for use as cores. The coal was ground to a size of 60 mesh (mean size 0.25 mm) so that powdered coal could be formed into coal packs for
experiments. The powdered coal was compressed and forced into a polyvinyl core holder. Each end of the core holder is capped with stainless steel mesh of a size small enough to retain coal particles. Two cores were constructed identically to allow dual experiments to be conducted.

The apparatus consisted of the coal pack fixed into a core holder that imbibed water at different pH. The endcaps of the core holder were constructed so as to allow for counter or co-current imbibition. During a countercurrent experiment, water flows through the endcap and across the face of the coal pack. The endcap contains a 5 mm gap through which water flows and provides a supply of fresh water at the face of the coal pack. Figure 5.15 shows the core holder filled with powdered coal and the end caps. Figure 5.16 is a schematic of the assembly of the experimental components. The data collected were the mass of water imbibed versus time and photographs of the position of the imbibition front in the transparent coal pack. Mass versus time was recorded automatically on a PC.

Solution pH was the main parameter examined to date. The pH set studied was 3, 7, and 10. The theoretical model developed suggests that the contact angles should be greater for the more acidic solution. That is, the more acidic the solution, the slower is the rate of water imbibition.

The procedure was relatively simple. The coal pack was dried under vacuum for at least 48 hours until core weight became constant. The system was then assembled as illustrated in Figure 5.15. The valves were set so that flow through the coal pack is countercurrent, the balance was zeroed, data collection begins, and the pump circulates

![Figure 5.15: The core holder, coal pack, and endcaps.](image-url)
water through the endcap and across the face of the coal pack at a rate of 5 cm$^3$/min. The flow through the endcap merely provided water for imbibition into the coal pack. It did not create a pressure gradient to force imbibition into the pack.

Figure 5.16: Schematic of the experimental apparatus.

Figure 5.17: Imbibition of water of pH equal to 3 and 7 in a powdered coal core.

Figure 5.17 presents the results for spontaneous imbibition at pH’s of 3 and 7. The mass imbibed versus the square root of time is plotted consistent with classical imbibition theory [105, 1]. The total time elapsed was about 7 days. The results for a pH of 7 are
linear with respect to the square root of time over virtually the entire period of imbibition until the weight gain plateaus. The experiment at pH equal to 3 encountered some difficulties in data collection at early time and some data are missing. For data analysis, we must, thus, use the later time trends for this pH.

Classical water imbibition theory is used to interpret the data collected. Handy [105] derived an approximate equation correlating the mass of water imbibed, \( m \), with capillarity and wettability that reads

\[
m = \rho_w A \sqrt{2 P_c k \phi S_w} \frac{1}{t^{1/2}} / \mu ,
\]

where \( \rho_w \) is the density of water, \( A \) is the cross sectional area, \( P_c \) is the capillary pressure, \( k \) is the permeability, \( \phi \) is the porosity, \( S_w \) is the saturation, \( \mu_w \) is the viscosity of water and \( t \) is the time. The slope of the lines, with respect to \( t^{1/2} \), is then

\[
\rho_w A \sqrt{2 P_c k \phi S_w} / \mu .
\]

Next, the Leverett J-function, Eq. (5.28), is substituted into Eq. (5.26)

\[
P_c = \sigma \cos \theta \sqrt{\frac{\phi}{k}} J(S_w) .
\]

Among different pH solutions, \( P_c \) differs by a factor of \( \cos \theta \) because \( J(S_w) \) is unique for similar coalpacks and the interfacial tension, \( \sigma \), is sensibly independent of pH. So from imbibition data collected at two different pH’s, we obtain the following ratio of mass imbibed

\[
\frac{m_1}{m_2} = \frac{\cos \theta_1 S_w t_1}{\cos \theta_2 S_w t_2} ,
\]

All quantities, except the ratio \( \cos \theta_1 / \cos \theta_2 \) are measured. These measurements then indicate the relative change of contact angle with pH. For the data reported in Figure 5.17, the ratio of the slopes of the lines representing each pH is 0.7. We equate that ratio to \( \cos \theta_1 / \cos \theta_2 \) and choose a reference contact angle of 37° representing a coal surface at pH equal to 7, as indicated in Figure 5.14. The ratio of cosines then indicates a contact angle of 56 degrees at pH equal to 3. This increase in contact angle as the aqueous solution becomes more acidic agrees with the trend in Figure 5.14 for CB coal.

5.4.4 Summary: Wettability

These first results are encouraging. Fundamental calculations of the wettability of coal surfaces appear to be corroborated by measurements of spontaneous imbibition behavior of coal packs. That is, coal bed wettability is sensitive to solution pH. Further experiments at a variety of pH need to be conducted to ascertain better whether the functionality indicated for contact angle versus pH is found experimentally. Experiments incorporating initial water saturation also need to be conducted.
5.5 Displacement Experiments

Displacement of coal bed CH$_4$ was conducted under a variety of conditions. The coal pack was always 100% saturated with CH$_4$ and allowed to reach equilibrium prior to a displacement test.

5.5.1 Pure CO$_2$

In the first set of experiments, pure CO$_2$ was injected at a variety of pressures. The CO$_2$ was compressed to a pressure equal to pore pressure in a cylinder equipped with a piston. Gas was displaced from the cylinder by injecting water at a fixed volumetric rate using a high pressure syringe pump (ISCO 500D). Tests were conducted at pressures ranging from 200 to 800 psia. The gas composition and outflow rate was measured versus time. Figure 5.18 shows the produced CO$_2$ concentration profile versus injected volume at the four different pressures.

![Figure 5.18: Effect of pressure on CO$_2$ elution from coal pack. Injection rate is 0.5 cm$^3$/min at standard conditions.](image)

The CO$_2$ breakthrough time was similar for all cases; however, after breakthrough, effluent CO$_2$ concentration behaved differently. At high pressure, the effluent concentration increases sharply, indicating that the displacement is more piston-like. When the pressure is lower, the effluent CO$_2$ concentration is more dispersed. As a result, the CH$_4$ production rate at high pressure is greater than that at low pressure. It is difficult to differentiate the effects of adsorption kinetics and longitudinal dispersion. This result may be related to the instantaneous CO$_2$ adsorption rate. The observed behavior is consistent with the idea that at high pressure, the adsorption rate is fast, thereby reducing the time for CO$_2$ to replace CH$_4$ from coal surfaces. On the other hand, as the pressure increases, the mean free path in the gas phase, and correspondingly the
gas-phase diffusion coefficient, decrease. Consequently, the longitudinal dispersion decreases as pressure increases, and the effluent concentration profile becomes more pistonlike.

The sampling ports along the length of the coal pack allow us to measure the composition of the free gas during tests. Figure 5.19 displays a typical result for gas composition measured at fractions of 0.2, 0.4, 0.6, 0.8, and 1 along the length of the core.

![Figure 5.19: CO₂ concentration versus time as sampled from various locations along the length of the coal pack.](image)

In this experiment, the injection pressure was 420 psi, and the coal was free of moisture. Upon reaching a sampling port along the core, the concentration of CO₂ in the free gas increased rapidly and smoothly to the injection composition of 100%. The flow of CO₂ within the coal pack evolved quickly to become nearly piston-like, an indication that CH₄ was displaced efficiently.

5.5.2 Gas Mixtures

All of the following displacement tests were conducted at 600 psia. Again the initial coal pack state was 100% saturated with CH₄. The injected gas composition was varied as 100% N₂, 75% N₂ + 25% CO₂, 50% N₂ + 50% CO₂, 25% N₂ + 25% CO₂, and 100% CO₂, respectively. The binary injection gas (N₂+CO₂) was prepared in the high pressure cylinder equipped with a piston. Pure N₂ was first injected into the cylinder at a given pressure, and thus the total moles were known. Then CO₂ was injected into the cylinder. After the mixing process was completed, the composition of the mixture was checked using a gas analyzer.

Pure N₂ was injected first. Figure 5.20a shows the effluent gas concentration versus the injected gas volume, PVI. At PVI < 0.41, only pure CH₄ was produced. The N₂
broke through to the outlet at PVI = 0.41. Thereafter, both N\textsubscript{2} and CH\textsubscript{4} were produced until 2.9 PVI. Between PVI equal to 0.41 and 0.58, produced CH\textsubscript{4} concentration decreased linearly from 100% to 60%. For injection volumes greater than 0.58 PVI, CH\textsubscript{4} concentration in the effluent gas gradually tailed to zero.

**Figure 5.20:** Elution of CO\textsubscript{2}, N\textsubscript{2}, and CH\textsubscript{4} resulting from the injection of various gas mixtures: (a) pure N\textsubscript{2}, (b) 75% N\textsubscript{2}+25% CO\textsubscript{2}, (c) 46% N\textsubscript{2}+54% CO\textsubscript{2}, (d) 15% N\textsubscript{2}+85% CO\textsubscript{2}, (e) pure CO\textsubscript{2}.

At PVI = 2.9, only N\textsubscript{2} was detected in the effluent gases, and no CH\textsubscript{4} was produced. We injected nearly 3 PV of N\textsubscript{2} to displace all the movable CH\textsubscript{4}. This behavior indicates that CH\textsubscript{4} recovery by injecting N\textsubscript{2} is a slow process.

Results for injection of 75% N\textsubscript{2}+25% CO\textsubscript{2} are presented in Figure 5.20b. Nitrogen broke through at 0.38 PVI, which is about 0.03 PVI earlier than the breakthrough time for
pure N₂. Carbon dioxide, however, broke through at roughly 4 PVI. At the same time, the CH₄ concentration in effluent gases decreased with time and reached zero at 3.4 PVI.

Apparently, the coal surfaces are effective at separating N₂ and CO₂. We offer the following qualitative explanation of the observed behavior. When a N₂/CO₂ mixture is injected, the CO₂ functions mainly to displace CH₄ from coal surfaces, whereas N₂ serves as a displacing agent to drive CH₄ from the coal pack. At greater than 3.5 PVI, CO₂ broke through to the outlet. Note that CH₄ was undetectable in effluent gases at times greater than 3.3 PVI. This phenomenon reveals that the CO₂ adsorption approached a maximum value. At 4.8 PVI (end of test), the produced CO₂ concentration was about 5%, which is still less than the injected concentration, an indication that most of the injected CO₂ adsorbed on the coal surfaces. Material balance verifies this statement.

The CO₂ concentration in the injected gas was next increased to 54%. Results are given in Figure 5.20c. Nitrogen broke through at 0.33 PV, which is 0.05 PV earlier than the breakthrough time for injection of a mixture with 75% N₂ and 25% CO₂. The CO₂ broke through at 2.2 PVI, which is about one pore volume earlier than for injection of the mixture of 75% N₂+25% CO₂. Also the concentration of CO₂ in the effluent increased quickly from 0 to 44%, which is close to the injected value. At 2.7 PVI, CH₄ production was complete. Comparison of the results in Figure 5.20b and Figure 5.20c suggests that increasing the CO₂ concentration in the mixture improves CH₄ production. Carbon dioxide does breakthrough earlier, however. The material balance calculation shows that the total injected CO₂ at 2.2 PVI was about 14.2 grams, which is slightly greater than the equilibrium adsorption value at 600 psi. This indicates that there was some CO₂ gas in pore spaces.

Figure 5.20d gives the effluent gas concentration versus injected gas volume for CH₄ displacement by a mixture with 15% N₂+85% CO₂. For this case, the N₂ broke through at 0.55 PVI, which was later than previous tests. As in the previous cases, the N₂ served primarily as a displacing agent to drive CH₄ from the pore spaces. After N₂ breakthrough, its concentration increased quickly, peaked, and then declined to the steady-state value. This result occurred because the injected CO₂ adsorbs on the coal surfaces, and the volume of CH₄ released is less than the volume of adsorbed CO₂. Note that adsorption of CO₂ is about 2.5 times of that for CH₄ at the same pressure. Thus, the concentration of N₂ in the produced gas was elevated. The greatest N₂ concentration in the effluent gases was about 66% at 1.69 PVI. Thereafter, the produced N₂ concentration decreased to 15% gradually. Carbon dioxide broke through to the outlet at 1.7 PVI. Carbon dioxide concentration in the effluent gases then increased sharply to the injected value of 85%. The total CO₂ injection at breakthrough was about 19.5 grams. This value is much greater than its equilibrium adsorption at 600 psia, indicating that there was CO₂ in the free gas state at breakthrough. Methane production terminated at 2.2 PVI.

Figure 5.20e presents the results for pure CO₂ injection. First, CO₂ broke through at 1.45 PVI. At breakthrough, 19.97 grams of CO₂ had been injected. This value is the similar to that for injection of 15% N₂+85% CO₂. Excluding the free CO₂ in pore spaces, the amount of adsorbed CO₂ was nearly equal to its equilibrium adsorption, verifying that
the displacement of CH$_4$ by pure CO$_2$ is nearly piston-like. Results displayed in Figure 5.19 and Figure 5.20 show that the adsorption of CO$_2$ onto coal surfaces to replace CH$_4$ is very fast and approaches local equilibrium. Methane concentration in the effluent gases reached zero at PVI = 2.0.

5.5.3 Methane Recovery

Figure 5.21 shows the CH$_4$ recovery for all of the tests. Gas injection is effective in enhancing the recovery of CH$_4$ from coal beds, at laboratory scale, at least. When pure N$_2$ is the displacing gas, CH$_4$ production is fast for less than 1 PVI because the majority of injected gas contributes to displacement. However, the CH$_4$ recovery versus gas injected is not linear in all cases. The pressure drop associated with displacement was less than 10 per cent of the system pressure, indicating that compressibility is not a major effect. The nonlinearity in the recovery curves may arise from the hysteresis between adsorption and desorption of N$_2$. As the injection gas moves through the coal pack CO$_2$ is removed from the free gas, which increases the concentration and partial pressure of N$_2$ in the free gas. Nitrogen adsorbs onto coal surfaces at a partial pressure greater than the N$_2$ partial pressure in the injection gas. As the CO$_2$ bank trailing N$_2$ saturates the coal surface, the partial pressure of N$_2$ decreases and N$_2$ desorbs.

![Figure 5.21: Methane recovery for the various tests with different injection gases.](image)

Figure 5.21 shows that the total CH$_4$ recovery was about 92% for injection of pure N$_2$. As CO$_2$ composition increased, the CH$_4$ recovery increased systematically to roughly 96% for pure CO$_2$. Full recovery of CH$_4$ in place is not achieved, presumably due to incomplete sweep of methane from all surfaces of the coal sample.

5.5.4 Summary: Displacement Experiments

The interplay of gas sorption and transport in coal yields a rich set of dynamical behavior. Injection of mixtures with a large fraction of CO$_2$ reduces the initial recovery
rate but increases breakthrough time as well as decreases the total amount of injected needed to sweep out the coal bed. The experimental program verifies that coal beds can be used to separate chromatographically N\textsubscript{2} and CO\textsubscript{2}, while at the same time coal bed CH\textsubscript{4} is recovered.

5.6 Numerical Simulation of Displacement Experiments

A one-dimensional, two-phase (gas and solid) model was employed to interpret the experimental data and trends. Reproduction of binary behavior is characterized as excellent, whereas the dynamics of ternary systems are predicted with less accuracy. For these coals, the most sensitive simulation input were the adsorption-desorption isotherms, including scanning loops. Additionally, the coal exhibited a two porosity matrix that was incorporated numerically.

5.6.1 Mathematical Model and Numerical Approach

Our starting points are the analytical model and concomitant assumptions of Zhu et al. [114]. They are consistent with the initial experimental results reported above. The governing equations for single-phase flow of gas species \( i \) in a porous medium including sorption are written

\[
\frac{\partial C_i}{\partial t} + (1 - \phi) \frac{\partial a_i}{\partial t} + \nabla \cdot (y C_i) = q_i.
\]  

(5.30)

\( C_i \) is the molar concentration of component \( i \) in the gas phase

\[
C_i = y_i \rho_y,
\]  

(5.31)

where \( y_i \) is the mole fraction of component \( i \) in the gas phase and \( \rho_y \) is the molar density of the gas phase. Next, \( a_i \) is the molar concentration of component \( i \) adsorbed on the coal surface. The adsorbed amount is obtained from the extended Langmuir isotherm [65] that employs only pure component isotherm parameters

\[
a_i = \frac{\alpha_i \beta_i y_i}{1 + \sum_k \beta_k y_k}.
\]  

(5.32)

where

\[
\alpha_i = \rho_{i,\text{std}} \rho_{\text{coal}} V_{m,i},
\]  

(5.33a)

\[
\beta_i = b_i p.
\]  

(5.33b)

In Eq. (5.33), \( \rho_{i,\text{std}} \) is the molar density of pure component \( i \) at standard conditions (101.325 kPa, 288.15 K), \( \rho_{\text{coal}} \) is the mass density of the (solid) coal sample, \( V_{m,i} \) and \( b_i \) are Langmuir constants for a pure gas species and \( p \) is the displacement pressure. In the third term on the left of Eq. (5.30), the overall flow velocity is denoted \( \nu \). Additionally, the ground coal particles have internal porosity. A typical matrix porosity for coal is 2 to 8 % [80, 66] and this porosity is exhibited within coal grains. We term the grain porosity secondary porosity, \( \phi_2 \). Secondary porosity is dead-end pore space that does not contribute to the overall flow, but participates in the adsorption of gases. The secondary porosity is assumed to be in instantaneous equilibrium with the bulk phase composition.
of the primary pore porosity ($\phi_i$). Accordingly the overall porosity of the coal packs is written

$$\phi = \phi_1 + \phi_2$$  \hspace{1cm} (5.34)

We do not have direct measurements of the secondary porosity of our coal packs. It is implemented as a single adjustable parameter to match the binary displacement experiments to follow.

Equations (5.30) are rewritten for one-dimensional (1D) flow, the primary/secondary porosity concept is implemented, and time and distance are nondimensionalized as $\tau$ and $\xi$ respectively

$$\frac{\partial C_i}{\partial \tau} + \frac{(1 - \phi)}{\phi} \frac{\partial a_i}{\partial \tau} + \frac{\partial v_d C_i}{\partial \xi} = Q_i,$$ \hspace{1cm} (5.35)

with

$$\tau = \frac{v_{inj} t}{\phi L}$$ \hspace{1cm} (5.36a)

$$\xi = \frac{x}{L}$$ \hspace{1cm} (5.36b)

$$v_d = \left( \frac{v}{v_{inj}} \right) \left( \frac{\phi}{\phi_i} \right).$$ \hspace{1cm} (5.36c)

The conservation equations were solved numerically using explicit time stepping and single-point upstream weighting of component fluxes. The adsorption and desorption of gas molecules on the coal surface during the displacement of CH$_4$ introduces a sharpening behavior of the species concentration within the gas phase that renders the displacement calculations significantly less sensitive to numerical diffusion than traditional convection-dominated flows. We used 200 grid cells in all displacement calculations. The time steps used in the calculation examples corresponded to $\Delta t/\Delta x = 0.18$. Phase properties were predicted by the Peng-Robinson equation of state [76]. For the purpose of evaluating phase behavior, we assumed that the pressure drop along the displacement length is negligible and use the value of the initial pressure throughout the displacement calculation.

As gas is injected into the coal pack and partitions between the coal surface and the free gas phase, new mixtures are formed with partial molar volumes different from the original fluid in place. In addition, gas species adsorb with different affinity to the coal surface, as seen from the sorption measurements. Thus, the porosity is partially filled with immobile adsorbed species. Computationally, the secondary porosity is filled before filling the primary porosity. Accordingly volume change of the adsorbed species on mixing/sorption plays a role and was included in the simulation of the displacement processes. We approximated the volume occupied by the adsorbed phase ($V_{ads}$) using

$$V_{ads} = \sum_i z_i V_{b, i}$$ \hspace{1cm} (5.37)
as recommended by Hall et al. [33], where \( V_{b,i} \) is the hard-sphere, co-volume of component \( i \) predicted by the PR EOS and \( z_i \) is the mole fraction of component \( i \) in the adsorbate \( (z_i = a_i/\sum a_k) \). This is, in fact, identical to the procedure used to obtain volume of the adsorbed phase during adsorption/desorption measurements.

As the pressure equation (volume balance) is not solved at each time step during the simulation, an explicit correction of the local flow velocity is applied to ensure simultaneous volume and mass conservation. In the explicit treatment, we carry any volume discrepancy forward in time [26] and correct the velocities of a grid cell \( k \) by

\[
v_{d,k+\frac{1}{2}} = v_{d,k-\frac{1}{2}} + \varepsilon \frac{\Delta t}{\Delta v} (q_{vc} - 1)
\]

where \( q_{vc} = V_{\text{fluid}}/V_{\text{cell}} \) and the coefficient \( \varepsilon (<1) \) is introduced to ensure stability of the overall numerical scheme.

### 5.6.2 Pure CO\(_2\) and N\(_2\)

The measured sorption isotherms, permeability, and porosity were used as input for calculation of the displacement of pure CH\(_4\) by pure CO\(_2\) and pure CH\(_4\) by pure N\(_2\) at 600 psi. The secondary porosity is unknown. It was adjusted such that simulated breakthrough times matched experimental for binary displacements. The value of \( \phi_1 \) obtained is 7.4% relative to the overall porosity of 37%. This value of the secondary porosity agrees well with coal matrix porosities reported elsewhere [80, 67]. Figure 5.22 and Figure 5.23 present the production profiles resulting from the injection of CO\(_2\) and N\(_2\). In other words, the concentration at the outlet versus is presented as a function of pore volumes of gas injected (PVI). The gas flood results from experiment and simulation are in substantial agreement. The different injection gases yield different production responses as detailed next.

![Figure 5.22: Experimental (symbols) and simulated (lines) production for pure N\(_2\) displacing CH\(_4\) at 600 psi.](image)

Nitrogen injection, presented in Figure 5.22, yields injected fluid breakthrough at the outlet in about 0.55 PVI. Thereafter, both N\(_2\) and CH\(_4\) are produced, with decreasing CH\(_4\) concentration, until 2.9 PVI. For injection volumes greater than 1 PVI, CH\(_4\) concentration in the effluent gas gradually tails to zero. More than 3 PVI of N\(_2\) were
injected to displace movable CH$_4$. This behavior indicates that CH$_4$ recovery by injecting N$_2$ is a slow process with significant mixing of the injected gas and original gas in place.

Figure 5.23 presents the results for pure CO$_2$ injection. Carbon dioxide breaks through to the outlet about 1 PVI later than N$_2$ at 1.5 PVI. At breakthrough, 20.0 grams of CO$_2$ has been injected. Excluding the free CO$_2$ in pore spaces, the amount of adsorbed CO$_2$ is nearly equal to its equilibrium adsorption, verifying that the displacement of CH$_4$ by pure CO$_2$ is nearly piston-like. Methane concentration in the effluent gases reaches zero by 2 PVI. A sharper displacement front was expected for injection of the stronger adsorbing CO$_2$. The observed spreading of the displacement front suggests some multidimensional behavior of the coal pack.

![Figure 5.23: Experimental (symbols) and simulated (lines) production for pure CO$_2$ displacing CH$_4$ at 600 psi.](image)

5.6.3 Gas mixtures

With the exception of the composition of the injection gas, parameters and boundary conditions identical to the binary displacement simulations were used to predict the results of ternary displacements. Figure 5.24 to Figure 5.26 present the comparisons among experimental and simulation results. Qualitatively, similar trends are observed as the fraction of CO$_2$ in the injection gas decreases from 85 to 46 to 24%; however, the agreement is far from exact. The discussion presents some possible explanations for these discrepancies.

Figure 5.24 gives the effluent gas concentration versus injected gas volume for CH$_4$ displacement by a mixture of 85/15 CO$_2$/N$_2$. The N$_2$ breaks through to the outlet at 0.55 PVI. This time is nearly identical to the pure N$_2$ result. Similar to the pure N$_2$ injection, N$_2$ serves primarily as a displacing agent to drive CH$_4$ from the pore spaces. After N$_2$ breakthrough, its concentration increases quickly and is even briefly greater than the injected concentration. Elevated N$_2$ concentration occurs because the injected CO$_2$ is adsorbed more strongly by the coal surfaces, replacing a smaller volume (number of moles) of CH$_4$. This, in turn, creates a N$_2$ bank at the leading edge of the displacement. Note that adsorption of CO$_2$ at a partial pressure of 3.5 MPa (510 psi=0.85x600) is about 2.5 times that for pure CH$_4$ at 600 psi. Thus, the concentration of N$_2$ in the produced gas
is elevated. The experimentally measured concentrations are greater, however, both experiment and simulation display clear banking of N\textsubscript{2}.

![Figure 5.24: Experimental (symbols) and simulated (lines) production for 85/15 CO\textsubscript{2}/N\textsubscript{2} mixture displacing CH\textsubscript{4} at 600 psi](image)

The greatest N\textsubscript{2} concentration in the experimental effluent gases is about 66\% at 1.7 PVI. Thereafter, the produced N\textsubscript{2} concentration decreases to the injected concentration of 15\% by roughly 2 PVI. Carbon dioxide breaks through to the outlet between 1.5 and 1.7 PVI. Carbon dioxide concentration in the effluent gases then increases sharply to the injected value of 85\% indicating piston-like advance. Methane production terminates somewhat later at 2.2 PVI in comparison to pure CO\textsubscript{2} injection.

![Figure 5.25: Experimental (symbols) and simulated (lines) production for 46/54 CO\textsubscript{2}/N\textsubscript{2} mixture displacing CH\textsubscript{4} at 600 psi.](image)

Carbon dioxide concentration in the injected gas was next decreased to 46\%, Figure 5.25. Experimentally, N\textsubscript{2} breaks through at 0.4 PV which is about 0.1 PV earlier than that for injection of a pure N\textsubscript{2} or the 85/15 CO\textsubscript{2}/N\textsubscript{2} mixture. The CO\textsubscript{2} breaks through is in excess of 2 PVI for both experiment and simulation. The concentration of CO\textsubscript{2} in the effluent increases quickly, in both cases, from 0 to 46\% consistent with significant CO\textsubscript{2} retention and piston-like advance. By 2.5 PVI, CH\textsubscript{4} production is essentially complete, although the experiments do exhibit some tailing.
Next consider results for injection of 24/76 CO\textsubscript{2}/N\textsubscript{2}, Figure 5.26. Nitrogen in the experiment breaks through at 0.4 PVI, similar to the previous case. The simulated breakthrough time of N\textsubscript{2} is about 0.6 PVI. Carbon dioxide, however, breaks through at greater than 2 PVI in both experiment and simulation; however, breakthrough times are not in agreement. Simultaneously, the CH\textsubscript{4} concentration in effluent gases decreases with time and reaches zero at roughly 3 PVI.

![Figure 5.26: Experimental (symbols) and simulated (lines) production for 24/76 CO\textsubscript{2}/N\textsubscript{2} mixture displacing CH\textsubscript{4} at 600 psi.](image)

Consistent with results from injection of the previous two gas mixtures, the coal surfaces affect a chromatographic separation of N\textsubscript{2} and CO\textsubscript{2}. In simple terms, CO\textsubscript{2}/N\textsubscript{2} injection gases embody two mechanisms. The CO\textsubscript{2} functions mainly to displace CH\textsubscript{4} from coal surfaces, whereas N\textsubscript{2} serves as a displacing agent to drive CH\textsubscript{4} from the coal pack. For all mixtures and consistent among experiment and theory, the breakthrough of CO\textsubscript{2} signals that the end of CH\textsubscript{4} production is imminent.

### 5.6.4 Discussion

Figure 5.27 presents a summary of the recovery of original CH\textsubscript{4} in place versus PVI for the various injection gases. It also compares experiment, Figure 5.27 (a), and simulation, Figure 5.27 (b). The measured, ultimate recovery of CH\textsubscript{4} is greater than 94% in all cases. Recovery is obtained from the measured effluent concentration of CH\textsubscript{4} and the flow rate at the coal pack exit. The measurement of effluent flow rate is subject to considerably more uncertainty than the concentration measurement. The error in the reported recovery is estimated at less than 4% of the original gas in place. There is no residual gas or irreversible adsorption in the simulations and, hence, simulated recovery is 100%. We note that mass is conserved in both experiments and simulations to the accuracy of the measurements and representation of numbers on a standard PC respectively.
In both experiments and simulation, the initial recovery rate decreases as the fraction of CO$_2$ in the injection gas increases. Of all gas species in the system, the adsorption of CO$_2$ onto the coal is the greatest. Injection gases rich in CO$_2$ experience significant volume reduction upon adsorption thereby reducing the flow velocity of the injection gas.

Comparison of Figure 5.24 to Figure 5.27 indicates that in ternary displacements the simulations predict a higher the rate of CH$_4$ recovery as well as the concentration of CH$_4$ in the effluent gas. Additionally, ternary experiments show consistently earlier breakthrough times for N$_2$ and later breakthrough times of CO$_2$ as compared to simulation. Next, we discuss three possibilities for the discrepancy between experimental and simulated behavior of the ternary systems: (i) mass transfer limitations for gas exchange, (ii) geomechanical effects resulting from coal shrinkage and swelling with gas loading, and (iii) prediction of multicomponent sorption.
We do not believe that significant mass transfer resistance is exhibited in our experiments. This assertion is supported by the binary displacement results that present almost exact agreement between experiment and theory without incorporation of rate effects (Figure 5.22 and Figure 5.23). Secondly, the coal particles are 0.25 mm in diameter and, correspondingly, the times for diffusive exchange of gas species from the particle exterior to the center of the particle are quite short. Crank [129] solves the unsteady diffusion equation in spherical coordinates under the conditions of a uniform initial concentration and a constant concentration at the sphere boundary. Refer to his Fig. 6.1 and Eqs. 6.18 to 6.20. For diffusivities from $10^{-7}$ to $10^{-5} \text{m}^2/\text{s}$, the time required for the concentration of a gas species at the center of the spherical grain to increase from 0 to 95% of the concentration of gas on the exterior of the sphere ranges from 0.1 to $10^{-4}$ s, respectively. The time needed for gas to diffuse across a stagnant boundary layer on the particle surface is similarly short.

With respect to geomechanical effects, the discrepancy among experimental and simulation results for ternary systems could be related to shrinkage and swelling of coal particles. Nitrogen consistently breaks through during experiments more quickly than predicted and CO$_2$ breaks through later than predicted. Nevertheless, the exact match of binary displacement behavior for N$_2$/CH$_4$ and CO$_2$/CH$_4$ with identical values of coalpack permeability and no evolution of permeability as CO$_2$ permeates the pack suggests that swelling is not important to the results of these laboratory displacements. Finally, the permeability measurements for these coalpacks, shown in Figure 5.10 indicate that N$_2$ flows across the spectrum of pressure from 100 to 800 psi with no change in permeability of the coalpack. Shrinkage does not appear to be responsible for the more rapid breakthrough of N$_2$ than expected.

The representation of multicomponent sorption phenomena, including scanning loops and hysteresis, is the most likely source of discrepancy. Initial prediction of the binary cases employing the extended Langmuir equation suggested that it approximated sorption adequately for estimation of flow results. The extended Langmuir equation predicts a constant selectivity for CO$_2$ adsorption over CH$_4$, for instance. Some adsorption studies suggest that such selectivity is a function of total gas pressure and gas species concentration [129]. The experimental effluent ternary data suggest that the selectivity of N$_2$ for coal surfaces, relative to the extended Langmuir equation, decreases in the presence of CH$_4$ and CO$_2$. Thus, N$_2$ transits the system more rapidly in reality than predictions. Similarly, the effluent data suggest that CO$_2$ selectivity is enhanced resulting in later actual breakthrough times in comparison to predictions.

To illustrate the sensitivity of flow prediction to the sorption model, an additional simulation was conducted for the 46/54 CO$_2$/N$_2$ injection gas. Figure 5.28 reports two cases. Case 1 was identical to the numerical result in Figure 5.25. Case 2 was obtained using only the desorption isotherm for N$_2$ reported in Figure 5.6. That is there is no hysteresis in N$_2$ sorption in the calculation. The sorption behavior of pure CH$_4$ and CO$_2$ was unchanged and again the extended Langmuir equation is used to predict multicomponent adsorption. With changes to only the N$_2$ sorption characteristics, the breakthrough time for CO$_2$ has been reduced about 0.3 PV, and the elution curve for CH$_4$...
gas changed dramatically. About 0.3 PV less time is required to sweep out all of the CH₄. The breakthrough time for N₂ is virtually unchanged, but the area under the N₂ elution curve has decreased somewhat.

**Figure 5.28:** Comparison of simulation results for a 46/54 CO₂/N₂ mixture displacing CH₄ at 600 psi. Case 1 is the result from Figure 5.25. Case 2 employs slightly modified adsorption behavior for N₂ with no changes to CH₄ and CO₂.

5.6.5 **Summary: Displacement calculations**

Injection of pure CO₂ into a coal pack results in piston-like displacement of CH₄. Pure N₂ injection results in a more dispersed advancing front. In general, breakthrough times for CO₂ are greater than 1.5 PVI, whereas for N₂ they are about 0.5 PVI. Additionally, both N₂ and CO₂ sweep out all moveable CH₄ in about 1.5 PVI. Either gas is an effective displacement agent for coal bed CH₄ from the laboratory perspective.

With respect to gas mixtures, CH₄ production enhanced by the injection of a gas mixture becomes more efficient as the fraction of CO₂ in the injection gas increases.

Clearly, the representation of ternary and greater adsorption phenomena within the framework of gas adsorption, desorption, and transport is an area where continued investigation is needed. Moreover, gas adsorption on coal surfaces should be characterized fully including scanning loops.
5.7 Analytical Theory of Multicomponent Two-Phase Systems with Adsorption

The method of characteristics has been applied to solve problems of flow in porous media problems involving adsorption, adsorption chromatography [81, 17], and polymer flooding of oil reservoirs [47, 48]. Recently, Zhu, et al. [114] applied this method to model recovery in coal beds via gas injection. Adsorption and desorption of gas from the coal played a key role in transport in these systems. This analysis considered only single-phase gas systems; any water present was assumed to be immobile. In many systems under consideration for ECBM (Powder River basin, Wyoming; Ardley Formation, Alberta; Bowen basin, Australia) coals are water-saturated. Transport of the water component must be considered when modeling ECBM in these systems. Since adsorption capacity is a function of pressure (more gas is adsorbed at higher pressures than at lower pressures), coals that have not been dewatered have a greater capacity for sequestration over coals that have been dewatered and are at a lower hydrostatic pressure, though the question of whether presence of water would restrict access of the adsorbing gas to the coal surfaces will have to be resolved. In conventional CBM production of water-saturated coals, depressurization is achieved through large amounts of water production (San Juan: 100-300 bbl/d water/well, Powder River: 200-500 bbl/d/well). In many cases, produced water is saline (San Juan: 14,000-40,000 tds), creating a water disposal issue. Moreover, in active aquifer systems, pressure support from the aquifer maintains reservoir pressure, reducing the desorption efficacy of the dewatering stage. In these settings, ECBM is an alternative recovery process that could reduce the need to produce and dispose water.

In this section, analytical solutions are derived for two phase flow in binary, tertiary and quaternary ECBM systems. In this analysis, the following assumptions are made:

- Flow occurs in one dimension.
- The porous medium is homogeneous.
- Gravity and capillary effects are ignored.
- Dissolution of small amounts of gas in the water phase has a negligible effect on water phase density. A similar assumption is made about the effect of water vapor in the gas phase.
- Adsorption and desorption of gas on the coal surface is described by an extended Langmuir isotherm.
- Water does not adsorb onto the coal surface.
- Temperature is constant.

5.7.1 Mathematical Model

For a system with \( N_c \) components, the conservation equation for component \( i \) is

\[
\frac{\partial G_i}{\partial \tau} + \frac{\partial H_i}{\partial \xi} = 0,
\]

\( G_i = \rho_{DG} y_i S_g + \rho_{DL} x_i (1 - S_g) + \frac{1 - \phi}{\phi} a_i \),

\[
H_i = u_B \left( \rho_{DG} y_i f_g + \rho_{DL} x_i (1 - f_g) \right),
\]
where $G_i$ is the overall molar concentration of species $i$, $H_i$ is the molar flux of species $i$, and $a_{iD}$ is molar concentration of species $i$ adsorbed, and is described by an extended Langmuir isotherm [111]

$$a_{iD} = \frac{1}{\rho_{inj}} \frac{\rho_{i,\text{std}} \rho_{\text{coal}} V_m b_i P_{inj}}{1 + \sum_{i=1}^{N_{\text{std}}} b_i P_{inj}}. \quad (5.42)$$

Eqs. 5.39 through 5.42 are given in dimensionless form with $\rho_{DG}$, $\rho_{DL}$ and $a_{iD}$ denoting the dimensionless molar density of gas, liquid and adsorbed phases respectively. The densities are scaled by the molar density of the injected fluid ($\rho_{inj}$). $u_D$ is the dimensionless total velocity, scaled with respect to the injection velocity and $f_g$ is the fractional flow of gas given, as a function of the gas saturation ($S_g$), by the Corey type relation

$$f_g = \frac{\hat{S}^2}{\hat{S}^2 + M(I - \hat{S})^2}, \quad M = \frac{\mu_g}{\mu_w}, \quad \hat{S} = \frac{S_g - S_{gc} - S_{wc}}{I - S_{gc} - S_{wc}}. \quad (5.43)$$

In this work, the critical gas saturation ($S_{gc}$) and the connate water saturation ($S_{wc}$) are set to zero. The viscosity of gas and liquid phases entering Eq. (5.43) are given by $\mu_g$ and $\mu_w$ respectively. The amount of component $i$ adsorbed depends on the partial pressure ($P_{y_i}$) of the equilibrium gas composition ($y_i$) and the Langmuir parameters $V_m$ and $b_i$. The adsorbed amount (scf/ton of coal) is converted to moles/m$^3$ using pure component molar density at standard conditions ($\rho_{i,\text{std}}$) and the coal mass density ($\rho_{\text{coal}}$).

In the analysis by Johansen and Winther [47, 48], changes in molar density as the injected fluid propagates through the system and mixes with the resident fluid were not considered. Their analysis was for an immiscible polymer-oil system, in which volume change is not significant. In this analysis, changes in molar density are considered, because volume change effects are expected to be significant as gas propagates through and is adsorbed onto the coal. As a result, local flow velocity varies spatially and must be determined as part of the solution. This system can be decomposed into an eigenvalue problem. The eigenvalues are the wave velocities at which the composition propagates, and the corresponding eigenvectors represent the direction of variation in composition space.

The procedure outlined by Dindoruk [18] was used to decouple the system. Two subsystems result: one for unknowns in composition space, and the other for the local flow velocity. The decoupled system is:

$$
\begin{bmatrix}
\frac{\partial a_{i_1}}{\partial t} - \frac{\partial a_{i_1}}{\partial x_1} - L \frac{\partial a_{i_1}}{\partial x_1} - \lambda \frac{\partial a_{i_1}}{\partial x_1} \\
\frac{\partial a_{i_2}}{\partial t} - \frac{\partial a_{i_2}}{\partial x_1} - L \frac{\partial a_{i_2}}{\partial x_1} - \lambda \frac{\partial a_{i_2}}{\partial x_1} \\
\vdots \\
\frac{\partial a_{i_{N-1}}}{\partial t} - \frac{\partial a_{i_{N-1}}}{\partial x_1} - L \frac{\partial a_{i_{N-1}}}{\partial x_1} - \lambda \frac{\partial a_{i_{N-1}}}{\partial x_1} \\
\frac{\partial a_{i_N}}{\partial t} - \frac{\partial a_{i_N}}{\partial x_1} - L \frac{\partial a_{i_N}}{\partial x_1} - \lambda \frac{\partial a_{i_N}}{\partial x_1}
\end{bmatrix}
\begin{bmatrix}
\frac{\partial a_{i_1}}{\partial x_1} \\
\frac{\partial a_{i_2}}{\partial x_1} \\
\vdots \\
\frac{\partial a_{i_{N-1}}}{\partial x_1} \\
\frac{\partial a_{i_N}}{\partial x_1}
\end{bmatrix}
= \lambda
\begin{bmatrix}
\frac{\partial a_{i_1}}{\partial x_1} \\
\frac{\partial a_{i_2}}{\partial x_1} \\
\vdots \\
\frac{\partial a_{i_{N-1}}}{\partial x_1} \\
\frac{\partial a_{i_N}}{\partial x_1}
\end{bmatrix}
$$

$$
\begin{bmatrix}
\frac{1}{a_{i_1}} \frac{\partial a_{i_1}}{\partial x_2} - L \frac{1}{a_{i_1}} \frac{\partial a_{i_1}}{\partial x_2} \\
\frac{1}{a_{i_2}} \frac{\partial a_{i_2}}{\partial x_2} - L \frac{1}{a_{i_2}} \frac{\partial a_{i_2}}{\partial x_2} \\
\vdots \\
\frac{1}{a_{i_{N-1}}} \frac{\partial a_{i_{N-1}}}{\partial x_2} - L \frac{1}{a_{i_{N-1}}} \frac{\partial a_{i_{N-1}}}{\partial x_2} \\
\frac{1}{a_{i_N}} \frac{\partial a_{i_N}}{\partial x_2} - L \frac{1}{a_{i_N}} \frac{\partial a_{i_N}}{\partial x_2}
\end{bmatrix}
\begin{bmatrix}
\frac{\partial a_{i_1}}{\partial x_2} \\
\frac{\partial a_{i_2}}{\partial x_2} \\
\vdots \\
\frac{\partial a_{i_{N-1}}}{\partial x_2} \\
\frac{\partial a_{i_N}}{\partial x_2}
\end{bmatrix}
= \lambda
\begin{bmatrix}
\frac{\partial a_{i_1}}{\partial x_2} \\
\frac{\partial a_{i_2}}{\partial x_2} \\
\vdots \\
\frac{\partial a_{i_{N-1}}}{\partial x_2} \\
\frac{\partial a_{i_N}}{\partial x_2}
\end{bmatrix}
$$

$$
\begin{bmatrix}
\frac{\partial a_{i_1}}{\partial x_1} \\
\frac{\partial a_{i_2}}{\partial x_1} \\
\vdots \\
\frac{\partial a_{i_{N-1}}}{\partial x_1} \\
\frac{\partial a_{i_N}}{\partial x_1}
\end{bmatrix}
= \bar{u}
$$

$$
\begin{bmatrix}
\frac{\partial x_{i_1}}{\partial t} \\
\frac{\partial x_{i_2}}{\partial t} \\
\vdots \\
\frac{\partial x_{i_{N-1}}}{\partial t} \\
\frac{\partial x_{i_N}}{\partial t}
\end{bmatrix}
= \frac{1}{a_{i_1}} \frac{\partial a_{i_1}}{\partial t}
$$

$$
\frac{\partial x_{i_1}}{\partial t}
= \frac{1}{a_{i_1}} \frac{\partial a_{i_1}}{\partial t}
$$

$$
\frac{1}{a_{i_1}} \frac{\partial a_{i_1}}{\partial t}
= \bar{u}
$$
\[ \alpha_i = \rho_{CD} y_i f_g + \rho_{LD} x_i (1 - f_g), \]

\[ \lambda^* = \frac{\lambda}{u_D}, \]

Initial compositions and the injection gas composition are constant. Solutions connecting the injection state to initial state may consist of a series of continuous variations (rarefactions), discontinuous segments (shocks) and zones of constant state. These segments are assembled to yield a unique and physical solution by applying the velocity rule and an entropy condition, as outlined by Johns [49].

### 5.7.2 Binary Systems

In a binary system, the eigenvalue (normalized by the local flow velocity) in the two phase region is given by

\[ \lambda^* = \frac{df}{dS}, \]

and compositions can vary only along tie lines, along which

\[ \frac{dS}{d\eta} = 1. \]

In the single phase region, the normalized eigenvalue is

\[ \lambda^* = \frac{\rho \left( 1 + \frac{z_1}{z_2} \right)}{\rho \left( 1 + \frac{z_1}{z_2} \right) + \frac{1 - \phi}{\phi} \frac{da}{dz}}. \]

Quadratic relative permeabilities were used in this analysis. Figure 5.29 shows the variation of eigenvalues in the two phase region. At phase boundaries, the eigenvalue approaches zero.
Figure 5.29: Variation of eigenvalues as a function of composition. There is a discontinuity in eigenvalues at the two phase boundary.

The adsorption function used in this analysis is a positive, concave down function. As a result, normalized eigenvalues in the single phase region will always be greater than zero. Therefore, a shock must occur as compositions enter and leave the two phase region. The landing point for a shock from the single-phase region to the two-phase region is found through solution of the shock balance,

\[
\Lambda = \frac{H_i^u - H_i^d}{G_i^u - G_i^d} = \frac{H_2^u - H_2^d}{G_2^u - G_2^d},
\]

where \( u \) is the upstream state and \( d \) is the downstream state.

Equilibrium K-values were used to describe partitioning of components between phases. From Henry’s Law we have

\[
y_i P = h_i x_i,
\]

\[
K_i = \frac{h_i}{P},
\]

where \( h_i \) is the Henry’s Law constant. The model parameters used in these examples were chosen to allow better visualization of the features of these displacements. In actual \( \text{N}_2-\text{CH}_4-\text{CO}_2-\text{H}_2\text{O} \) systems, K-values of \( \text{N}_2 \), \( \text{CO}_2 \) and \( \text{CH}_4 \) are much higher, while that of \( \text{H}_2\text{O} \) is much lower than the values used here to illustrate solution structure. This results in even lower solubilities of \( \text{CO}_2 \) and \( \text{CH}_4 \) in the aqueous phase, increasing the size of the two phase region. When more realistic values are used, the features of the displacement (shocks, rarefactions and zones of constant state) remain the same but they are scaled appropriately to the phase behavior of the system. Figure 5.30 shows the solution profile for injection of \( \text{CO}_2 \) into a water-saturated core. Model flow parameters for the solutions presented are summarized in Table 5.3. Table 5.4 summaries adsorption parameters used [114]. A coal density of 0.034 ton/ft\(^3\) (Eq. 5.42) was used.
In the binary displacement, shocks are required to enter and leave the two phase region. The leading shock saturation is low due to the unfavorable mobility ratio between injection gas and reservoir fluid. A slow trailing shock occurs at the upstream end of the displacement. Due to the low solubility of CO$_2$ in H$_2$O, many pore volumes of CO$_2$ must be injection to vaporize the remaining portion of H$_2$O. It should also be noted that there is an approximately 20% decrease in flow velocity between injection conditions and initial conditions. Adsorption of CO$_2$ onto the surface, with the accompanying volume change, slows the leading shock.

**Table 5.3:** Flow parameters used in the displacements presented.

<table>
<thead>
<tr>
<th>M</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\rho_{GD}$</td>
<td>1</td>
</tr>
<tr>
<td>$\rho_{LD}$</td>
<td>2</td>
</tr>
</tbody>
</table>

**Table 5.4.:** Equilibrium model parameters used in the displacements presented.

<table>
<thead>
<tr>
<th>Component</th>
<th>$K_i$</th>
<th>$V_{m,i}$ (scf/ton)</th>
<th>$b_i$ (psi$^{-1}$)</th>
<th>$\rho_{i, std}$ (mol/scf)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N$_2$</td>
<td>5</td>
<td>222</td>
<td>0.0017</td>
<td>0.0390</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>3</td>
<td>444</td>
<td>0.0034</td>
<td>0.0390</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>1.2</td>
<td>707</td>
<td>0.0066</td>
<td>0.0392</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>0.1</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
5.7.3 Ternary Systems

The key features of the binary displacement are preserved when the number of components is increased to three. In the two phase region of the displacement, the eigenvalues and corresponding eigenvectors are:

\[
\lambda_i^* = \frac{df}{dS}, \quad \lambda_{nt}^* = \frac{f - \chi_i}{S - \chi_1 - \chi_2},
\]

and

\[
\bar{\epsilon}_i = \begin{bmatrix} f \\ 0 \end{bmatrix}, \quad \bar{\epsilon}_{nt} = \begin{bmatrix} \lambda_{nt}^* - \lambda_i^* \\ \frac{l}{H_1} \frac{dH_1}{d\eta} \end{bmatrix}.
\]

Where:

\[
\chi_1 = \left( \begin{array}{c} \frac{\partial \beta_1}{\partial y_1} - \frac{\alpha_1}{\alpha_3} \frac{\partial \gamma_1}{\partial y_1} \\ \frac{\partial \gamma_1}{\partial y_1} - \frac{\alpha_1}{\alpha_3} \frac{\partial \gamma_1}{\partial y_1} \end{array} \right) \left( \begin{array}{c} \gamma_2 - \frac{\alpha_2}{\alpha_3} \gamma_3 \\ \gamma_2 - \frac{\alpha_2}{\alpha_3} \gamma_3 \end{array} \right) - \left( \begin{array}{c} \frac{\partial \beta_2}{\partial y_1} - \frac{\alpha_2}{\alpha_3} \frac{\partial \gamma_1}{\partial y_1} \\ \frac{\partial \gamma_2}{\partial y_1} - \frac{\alpha_2}{\alpha_3} \frac{\partial \gamma_1}{\partial y_1} \end{array} \right) \left( \begin{array}{c} \gamma_1 - \frac{\alpha_1}{\alpha_3} \gamma_3 \\ \gamma_1 - \frac{\alpha_1}{\alpha_3} \gamma_3 \end{array} \right),
\]

\[
\chi_2 = \left( \begin{array}{c} \frac{\partial \beta_1}{\partial y_1} - \frac{\alpha_1}{\alpha_3} \frac{\partial \gamma_1}{\partial y_1} \\ \frac{\partial \gamma_1}{\partial y_1} - \frac{\alpha_1}{\alpha_3} \frac{\partial \gamma_1}{\partial y_1} \end{array} \right) \left( \begin{array}{c} \gamma_2 - \frac{\alpha_2}{\alpha_3} \gamma_3 \\ \gamma_2 - \frac{\alpha_2}{\alpha_3} \gamma_3 \end{array} \right) - \left( \begin{array}{c} \frac{\partial \beta_2}{\partial y_1} - \frac{\alpha_2}{\alpha_3} \frac{\partial \gamma_1}{\partial y_1} \\ \frac{\partial \gamma_2}{\partial y_1} - \frac{\alpha_2}{\alpha_3} \frac{\partial \gamma_1}{\partial y_1} \end{array} \right) \left( \begin{array}{c} \gamma_1 - \frac{\alpha_1}{\alpha_3} \gamma_3 \\ \gamma_1 - \frac{\alpha_1}{\alpha_3} \gamma_3 \end{array} \right),
\]

\[
\gamma_i = \rho_{GD} y_i - \rho_{LD} x_i, \quad \beta_i = \rho_{LD} x_i, \quad \delta_i = \frac{l - \phi}{\phi} a_{id}.
\]

\(\chi_i\) describes the variation in composition and \(\chi_2\) describes the variation in adsorption, and along a tie line, these are constant. Continuous solutions are possible along tie-line and nontie-line paths. At the phase boundary, adsorption reduces the nontie-line eigenvalue so that its value is no longer 1. As a result of the \(\chi_2\) term in the denominator of the nontie-line eigenvalue, the phase boundary and equivelocity point are no longer paths (as they are in problems with component partitioning between flowing phases without adsorption). Figure 5.31 and Figure 5.32 show the variation of eigenvalues and eigenvectors in saturation and composition space. Solution paths shown are presented in a normalized mobile composition space.
**Figure 5.31.** Eigenvalue variation as a function of $S_g$.

**Figure 5.32.** Eigenvectors in the two phase region; tie line (black), non-tie line (red). Composition paths are projected onto the mobile phase concentration plane.
**Saturated Initial Composition**

In the two-phase region, solution features are similar to those for corresponding systems without adsorption. In adsorbing systems without mobile water present, solutions also consist of continuous and discontinuous solution segments which satisfy the material balance [114]. Displacements in the ternary system can be classified into two types: Type I, self sharpening; and Type II, spreading. These were compared against numerical solutions obtained from a first-order accurate, fully explicit finite-difference simulator developed by Kristian Jessen.

Type I displacements occur when the injected gas is more strongly adsorbing than the gas present initially. Preferential adsorption of components in the injected gas removes molecules from the mobile phase as it propagates through the system, resulting in self-sharpening behavior. In the example solution presented in Figure 5.33, a CO$_2$-rich gas (10% CH$_4$, 90% CO$_2$) is injected into coal bed containing H$_2$O saturated with CH$_4$ and a small amount of CO$_2$ (29% CH$_4$, 5% CO$_2$, 66% H$_2$O). Injection and initial compositions are reported in mol percent. Compositions paths are plotted in terms of the normalized mobile composition:

\[
G_{i,\text{norm}} = G_i - \frac{1 - \phi}{\phi} a_i / \sum_{j=1}^{N} G_j - \frac{1 - \phi}{\phi} a_j .
\] (5.60)

**Figure 5.33.** Displacement of an aqueous phase saturated with CH$_4$ and a small amount of CO$_2$ by CO$_2$–rich gas in composition space. Analytical solution (red) and a finite-difference solution with, 1000 grid blocks (blue).
The solution path for this displacement in composition space is shown in Figure 5.33. The solution includes a tangent shock from the initial condition (I) into the two phase region (point A), a rarefaction along the injection tie line from A to B, a shock connecting the injection tie line and the initial tie line from B to C, and a genuine shock from C to initial composition O. A comparison of the analytical and numerical composition paths is also shown in Figure 5.33. Figure 5.34 presents the variation in eigenvalues as the path is traced from the injection composition to the initial composition.

![Figure 5.34. Eigenvalue variation between injection and initial states.](image)

As the composition path is traced from upstream to downstream, the velocity rule is violated. Therefore, a shock is required to connect injection and initial states. Compositions upstream and downstream of the shock are found by solving the shock balance, given in Eq. (5.49). For saturated initial conditions, shocks in and out of the two phase region occur along a tie line. The Langmuir adsorption function is a function of the equilibrium composition of the gas phase. Along a tie line, adsorption is constant. If the initial composition is a saturated phase, the adsorption component cancels, and the shock occurs along the tie line. The saturation profile for this displacement is shown in Figure 5.35.

As the composition varies from the injection state to the initial state, local flow velocity decreases by approximately 20%. As the more strongly adsorbing CO₂ propagates through the reservoir, it is removed from the mobile phase, slowing down the leading shock. Replacement of CH₄ by CO₂ on the coal surface creates a bank of CH₄ that propagates downstream. Due to the unfavorable mobility ratio between water and the injection gas, breakthrough occurs at a low gas saturation. A slow, trailing, evaporation shock occurs at the upstream end of the displacement to connect the solution to the injection composition. Due to the low solubility of water in the injected gas phase, a large amount of gas must be injected to evaporate all the water.
Figure 5.35: Saturation, composition, and flow velocity profiles for the type I displacement.

Also shown in Figure 5.35 are results of fine-grid, one-dimensional simulations of the displacement process. The simulation results clearly show the same features as the analytical solutions, the shocks are smeared by numerical dispersion. In this example, the calculated results are relatively sensitive to numerical dispersion. Even with 1000 grid blocks, there is significant smearing of the shocks. CH$_4$ recovery is shown in Figure 5.36.
Type II solutions occur when a weakly adsorbing gas is injected to displace a more strongly adsorbing gas. A decrease in partial pressure is required to displace the gas initially adsorbed, since this is the preferentially adsorbed species. In the example solution presented, N\textsubscript{2} is injected into N\textsubscript{2}-CH\textsubscript{4} saturated water (5.7% N\textsubscript{2}, 21.4% CH\textsubscript{4}, 72.9% H\textsubscript{2}O), modeling an enhanced coal bed CH\textsubscript{4} (ECBM) displacement using N\textsubscript{2}.

The composition path for a type II displacement is shown in Figure 5.37. In this solution, the tie line that extends through the initial composition is connected to the tie line associated with the injection composition by a continuous variation. Figure 5.38 shows that as the composition path is traced from initial state to injection state, eigenvalues decrease, satisfying the velocity rule, and hence, a continuous variation along a nontie-line path is allowed. Solution construction starts at the initial composition.
Figure 5.37: Displacement of an aqueous phase saturated with CH\(_4\) and N\(_2\) by pure N\(_2\).

Figure 5.38. Variation of eigenvalues in Type II displacement.

The solution includes a shock into the two phase region from O to D, followed by a rarefaction along the initial tie line from D to C. A path switch occurs at the equal eigenvalue point, C, to a nontie-line path. The nontie-line variation from C to B connects the initial and injection tie lines. A second path switch at B to the injection tie line is followed by a rarefaction along the injection tie line from B to A. Finally, there is a
shock from the two phase region to injection conditions from A to I. The corresponding saturation, composition and velocity profiles are presented in Figure 5.39.

As \( \text{N}_2 \) gas propagates through the reservoir, the partial pressure of \( \text{CH}_4 \) is reduced, causing it to desorb. A bank of \( \text{CH}_4 \) at the leading edge of the displacement is created. As the displacement propagates, local flow velocity increases, since volume is added to the flowing gas as \( \text{CH}_4 \) desorbs. \( \text{CH}_4 \) recovery for this displacement is shown in Figure 5.40.
Figure 5.40: Recovery of CH₄. Complete CH₄ recovery is achieved after 1.37 PVI. The preferential existence of N₂ in the gas phase and the additional volume of CH₄ added to the mobile phase as the displacement propagates results in faster recovery of CH₄ than when CO₂ is injected.

Undersaturated Initial Compositions

When the initial aqueous phase is undersaturated, entry from the single phase region into the two phase region no longer occurs along the tie line that extends through the initial composition (see Figure 5.41). Nonlinearities in the adsorption function prevent cancellation of the adsorption terms in the shock balance. Solutions are constructed by determining the tie line to which the injection composition shocks. As in problems without adsorption, the shortest tie line controls displacement, and the procedure for solution construction is similar to that described for flows without adsorption [45].

A Type I solution in the undersaturated region is presented in Figure 5.41. The two phase region is entered via a tangent shock from the injection composition, I to point A. This is followed by a rarefaction along the injection tie line from A to B. Another tangent shock connects point B on the injection tie line to point C on the initial tie line. The displacement is completed with a genuine shock from C to the initial composition, O. Solution profiles for this type of displacement are shown in Figure 5.42 and Figure 5.43.

In the undersaturated system, less CH₄ is available to be recovered than in the saturated case. As a result, the tie line that satisfies the shock balance has a lower equilibrium concentration than that of the tie line extension. The injection tie line is still the shortest tie line. The solution at the trailing edge of the displacement resembles that of the saturated case. A rarefaction still occurs along the injection tie line, and solution construction is initiated at this tie line. The new tie line, to which a tangent shock is constructed, is richer in CO₂ than the extension tie line, resulting in a slower shock at a higher S₉. This is followed by a genuine shock from the landing point on this new tie line...
to the injection composition. The volume change associated with this genuine shock results in a decrease in the wave velocity of the leading shock.

**Figure 5.41:** Type I solution, with undersaturated initial conditions. The injection composition is 10% CH₄, 90% CO₂, and the initial composition is 5% CH₄, 5% CO₂, 90% H₂O by mole. Comparison of analytical solution (red) with finite difference solution, 1000 points (blue).

**Figure 5.42:** Solution profiles for a Type I undersaturated displacement.
Figure 5.43: Solution profiles for a Type I undersaturated displacement.

Figure 5.44 and Figure 5.45 compare the saturated and undersaturated displacements. Since the injection tie line controls the structure of the displacement in these two cases, trailing edge solutions are similar. Initial fractions of CH\textsubscript{4} and CO\textsubscript{2} in the undersaturated case are much lower than in the saturated case. Formation of CH\textsubscript{4} banks are seen in both the undersaturated and the saturated profiles (Figure 5.45).

Figure 5.44. Comparison of saturated (blue) and undersaturated (red) Type I solution. Solution construction starts with the injection tie line. Because this section of the displacement is unaffected by the undersaturated conditions, solution structure is similar.
Figure 5.45. Comparison of solution profiles for saturated (blue) and undersaturated (red) initial condition cases. In the undersaturated case, a large bank of CH$_4$ propagates through the system. CH$_4$ in the injection gas is not preferentially adsorbed, propagating through the system at a higher velocity than CO$_2$.

A comparison of recoveries from displacements of saturated and undersaturated initial compositions is shown in Figure 5.46. Both systems demonstrate complete recovery. Complete recovery for the undersaturated case is slightly delayed compared to the saturated case. At early times, CH$_4$ recovery in the undersaturated case is slower than in the saturated case as additional injection gas is required to saturate the liquid phase. Once the CH$_4$ bank reaches the production outlet, recovery quickly increases.
5.7.4 Quaternary Systems

Addition of a fourth component adds one more eigenvalue and eigenvector to the flow description. An example of variations in eigenvalues along a timeline is shown in Figure 5.47.

As in the ternary system, adsorption reduces the nontie-line eigenvalues, making their values at the phase boundaries less than 1. For the N$_2$-CH$_4$-CO$_2$-H$_2$O system, the
behavior of $\lambda^*_{nt1}$ is controlled by CH$_4$ adsorption and $\lambda^*_{nt2}$ is controlled by CO$_2$ adsorption. Reduction of wave speed is a function of strength of adsorption. For more strongly adsorbing components, there is a greater reduction in wave speed. For the system presented, adsorption of CO$_2$ is strong enough that it completely separates itself from the other nontie-line eigenvalue such that the two nontie-line eigenvalues no longer cross, as they do in nonadsorbing systems. Several integral curves of the eigenvectors in the two phase region are shown in Figure 5.48.

![Figure 5.48: Variation of eigenvectors in the two phase region. Only the upper equal eigenvalue point variation for each non-tie line eigenvalue is shown.](image)

A sample quaternary solution is presented in Figure 5.49 through Figure 5.51 for injection of a mixture containing 90% N$_2$ and 10% CH$_4$ displacing and initial mixture containing 17% N$_2$, 5% CO$_2$, and 78% H$_2$O. The solution for the four-component displacement includes segments that are similar to the ternary displacements. As in the nonadsorbing system, a crossover tie [69] is required to connect initial and injection ternary faces. Solution construction begins on the crossover tie line. The details of the solution structure for this displacement are shown in Figure 5.49. A tangent shock (A-B) connects the crossover tie line to the initial tie line. This is followed by continuous variation (B-C) along the initial tie line and a shock to the initial conditions (C-O). The injection tie line is connected to the crossover tie line from a nontie-line rarefaction (D-E) initiated from the crossover tie line. At point E, a path switch from the nontie-line path to the tie-line path occurs. This is followed by a very short rarefaction along the injection tie line (E-F) and a tangent shock to the injection composition (F-I).
Figure 5.49: Composition path for a quaternary displacement (blue). The injection gas contains 90% N$_2$ and 10% CH$_4$, and the initial composition is 17% N$_2$, 5% CO$_2$, and 78% H$_2$O. Related ternary displacements are displayed in red.

Figure 5.50. Comparison of the analytical solution (red) with a numerical solution obtained with 1000 grid blocks (blue).
Figure 5.51. Solution profiles for quaternary system: injection: 90% N₂, 10% CH₄; initial: 17% N₂, 5% CO₂, 78% H₂O. CO₂ is completely displaced by the injection gas. For the system parameters used, approximately 3 pore volumes are required. A small bank of N₂ is created as it sweeps through the system due to its relatively weak adsorption and preferential tendency to remain in the gas phase.
Preliminary solutions were developed for injection of a flue gas to displace CH₄. Two sets of solutions were constructed for variation of initial compositions and variation of injection compositions. In these sets of solutions, preferential adsorption of CO₂ results in separation via a shock, while the least strongly adsorbing and lightest component N₂ tends to separate through a continuous variation.

In the example that follows, the injection composition was kept constant at 90% N₂, 10% CO₂, while the initial compositions were varied along the N₂-CH₄-H₂O face. Only saturated initial conditions were considered in this analysis. In these systems, the crossover tie line coincides with the N₂-H₂O axis. For these systems, solution construction is started at both the injection and initial points. An example solution is presented in Figure 5.52.

![Composition path for an enriched flue gas injection mixture into a N₂-CH₄ saturated coal bed. Injection composition: 90% N₂, 10% CO₂. Initial composition: 5.7% N₂, 21.4% CH₄, 72.9% H₂O. Initial and injection segments are constructed independently until they intersect the N₂-H₂O boundary. Adsorption removes CO₂ from the system. Phase behavior will tend to keep less soluble components at the leading edge of the displacement.](image)

The initial composition is 5.7% N₂, 21.4% CH₄ and 72.9% H₂O. The injection segment solution starts with a tangent shock into the two phase region (I-F), followed by continuous variation along the injection tie line to E. A tangent shock (E-D) connects the injection tie line with the N₂-H₂O axis. Continuous variation along nontie-line composition paths from the injection tie line violates the velocity rule, and therefore a shock is necessary. The initial segment starts with a tangent shock into the two phase region (O-A). This is followed by a rarefaction along the initial tie line to the equal-eigenvalue point (A-B). At the equal-eigenvalue point, a path switch from the tie line path to the nontie-line path occurs. Continuous variation along the nontie-line path...
connects the initial tie line and the N$_2$-H$_2$O axis (B-C). Application of the concept of intersecting tie-line extensions from the nonadsorbing theory indicates that the expected position of the crossover tie line is the N$_2$-H$_2$O boundary. At the N$_2$-H$_2$O axis, landing points from these segments (C and D) are connected by a shock, because continuous variation violates the velocity rule (Figure 5.53).

Figure 5.53: Landing points of injection and initial segments of displacement on the N$_2$-H$_2$O boundary. Continuous variation from injection segment to initial segment violates the velocity rule, since eigenvalues would decrease. A shock is required to connect the two segments.

This solution structure is similar to the N$_2$-C$_4$H$_{10}$ displacement presented by Dindoruk (1992). Comparison of the analytical solution to a numerical solution obtained with 1000 grid blocks is presented in Figure 5.54 and Figure 5.55.

Figure 5.54: Comparison of analytical (red) and numerical solutions (blue), 1000 points.
Agreement is quite good, though the numerical solution has difficulties resolving the thin banks created when the solution path follows the N\textsubscript{2}-H\textsubscript{2}O axis.

Figure 5.55: Solution profiles for: injection composition: 90% N\textsubscript{2}, 10% CO\textsubscript{2}; initial composition: 5.7% N\textsubscript{2}, 21.4% CH\textsubscript{4}, 72.9% H\textsubscript{2}O. Complete separation of CO\textsubscript{2} from the injection gas mixture is achieved. As N\textsubscript{2} sweeps through the system, CH\textsubscript{4} desorbs and forms a bank.
As injection gas propagates through the system, CO$_2$ is completely separated from N$_2$. N$_2$ is the least adsorbing gas, and it partitions preferentially into the gas phase, so it propagates quickly through the system. CH$_4$ desorbs as N$_2$ sweeps through the system, creating a bank of CH$_4$. This bank reaches a maximum concentration at the equal-eigenvalue point (Figure 5.55). Profiles of adsorbed amounts are presented in Figure 5.56.

Reduction in the partial pressure of CH$_4$ by the N$_2$ bank causes desorption of CH$_4$. At higher CH$_4$ concentrations, the amount of CH$_4$ adsorbed is larger, creating a bank of adsorbed CH$_4$ that corresponds to the bank of CH$_4$ propagating ahead of the N$_2$ bank.

![Figure 5.56: Profiles of adsorbed gases. Along tie lines, the amount of gas adsorbed is constant.](image)

As the initial composition is gradually enriched with CH$_4$, the solution structure remains the same as shown in Figure 5.57. The trailing edge of the displacement is unchanged for all cases listed in Table 5.5.

**Table 5.5: Summary of injection compositions presented in Figure 5.57 to Figure 5.59.**

<table>
<thead>
<tr>
<th>Initial</th>
<th>$z_{N_2}$</th>
<th>$z_{CH_4}$</th>
<th>$z_{CO_2}$</th>
<th>$z_{H_2O}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Init 1</td>
<td>0.144</td>
<td>0.000</td>
<td>0.074</td>
<td>0.786</td>
</tr>
<tr>
<td>Init 2</td>
<td>0.104</td>
<td>0.000</td>
<td>0.135</td>
<td>0.761</td>
</tr>
<tr>
<td>Init 3</td>
<td>0.057</td>
<td>0.000</td>
<td>0.214</td>
<td>0.729</td>
</tr>
<tr>
<td>Init 4</td>
<td>0.036</td>
<td>0.000</td>
<td>0.250</td>
<td>0.1714</td>
</tr>
</tbody>
</table>

As the amount of CH$_4$ in the initial composition is gradually increased, the equal eigenvalue point on the initial tie line appears at lower gas saturations (Figure 5.57). The landing point of the non-tie line path on the N$_2$-H$_2$O line is located at a higher gas saturation as initial compositions are enriched with CH$_4$, making the non-tie-line
rarefaction longer. The N₂-H₂O shock velocity connecting injection and initial segments decreases.


Gas breakthrough occurs earlier as the CH₄ concentration in the initial mixture increases, since there is more gas available to desorb, add volume to the flowing fluid, and increase the local flow velocity, resulting in faster CH₄ recovery (Figure 5.58).

Figure 5.58: Recovery of CH₄ for varying initial compositions. Faster recovery occurs as the initial fraction of CH₄ increases. Larger initial CH₄ concentrations cause larger volume additions due to desorption, accelerating CH₄ production.

Solution profiles are shown for all displacements in Figure 5.59.
Figure 5.59: Solution profiles for variation of initial compositions. Trailing segments remain unchanged.
5.7.5 Summary: Analytical Theory

The analytical theory for two-phase, three- and four-component flow for convection-dominated systems has been extended to include effects of adsorption of one or more gas components on coal surfaces. These solutions provide understanding of the interplay among adsorption and desorption of gas components, phase behavior, and convection in ECBM processes. Systems in which a component that adsorbs more strongly displaces a component that is more weakly adsorbed display a shock, a sharp transition from high concentrations of the displaced component to high concentrations of the injected component. An example of such a displacement is CO$_2$ injection into coal that has CH$_4$ adsorbed initially.

In systems where a weakly adsorbing component displaces a strongly adsorbing component, a rarefaction occurs between tie lines associated with the injection gas and initial composition. N$_2$ injection to displace adsorbed CH$_4$ is an example of such a displacement, in which a gradual increase in N$_2$ concentration is observed as the displacement proceeds. When flue gas, a mixture of N$_2$ and CO$_2$, is injected, the composition profiles exhibit both shock and rarefaction features.

The analytical and numerical solutions reported here demonstrate that the combination of adsorption and desorption and two-phase flow can lead to efficient recovery of CH$_4$, in the zones of a coal bed invaded by the injected gas. Recovery of CH$_4$ is faster when N$_2$ is present in the injection gas due to the volume increase that occurs as CH$_4$ present initially desorbs. However, that faster recovery comes at a price, because produced CH$_4$ would have to be separated from produced N$_2$. When CO$_2$ is present in the injection gas, CH$_4$ recovery is slower due to the volume loss associated with CO$_2$ adsorbing onto the coal, allowing more CO$_2$ to be sequestered per volume of CH$_4$ recovered.

When a mixture of N$_2$ and CO$_2$ is injected, CO$_2$ is chromatographically separated from N$_2$. However, the produced gas is a mixture of CH$_4$ and N$_2$. Again, a separation of produced CH$_4$ from N$_2$ would be required.

When gas is injected into an undersaturated coal bed, an additional volume decrease occurs as components present in the injected gas adsorb. This loss of volume reduces the propagation velocity of the leading edge of the displacement, allowing a longer period of sequestration before gas breakthrough is experienced. The results presented indicate that designers of an ECBM project can adjust injection gas compositions to maximize CO$_2$ sequestration prior to CO$_2$ breakthrough at production wells or to accelerate CH$_4$ production. The analytical solutions provide insight, therefore, into the behavior of gas species during a displacement, and provide a systematic way to adjust the composition of and injection gas mixture to achieve the desired goal.

5.8 Summary: Coal Bed Methane

Our research in the area of coal beds is aimed at increasing significantly the number and volume of potential geologic storage locations for CO$_2$ while expanding simultaneously the potential for additional recovery of coal bed CH$_4$, particularly for
deep coal beds. A combined experimental and mechanistic modeling approach has revealed an interplay of multicomponent gas sorption, phase behavior, and transport in coal that yields dynamical behavior rich in complexity. Sorption and multiphase flow phenomena in coal remain to be described fully in both a conceptual and quantitative sense. Nevertheless several generalizations and conclusions are apparent, as follows.

Measurements of the adsorption and desorption of CO$_2$, CH$_4$, and N$_2$ on a coal sample from the Powder River Basing Wyoming confirm that CO$_2$ is more strongly adsorbed in comparison to the other gases. A result of the strong affinity of CO$_2$ for coal surfaces is that CO$_2$ displaces CH$_4$ relatively efficiently. Experiment and simulation show consistently that CO$_2$ moves through coal in a piston-like fashion. As a result, breakthrough times for CO$_2$ are significantly large. The least measured breakthrough time corresponded to 1.5 PVI. Likewise, both experiments and calculations verify that coal beds are useful to separate chromatographically N$_2$ and CO$_2$. This separation occurs while coal bed CH$_4$ recovery is enhanced.

Calculations from a surface forces perspective and experimental results for water imbibition into coal samples both suggest that coal is not strongly water wet. Hence injected CO$_2$ should be able to contact coal surfaces efficiently. Once CO$_2$ is in place, our initial results suggest that the water wettability of coal surfaces is, at least, a function of the pH of the aqueous phase.

Attempts to reconcile experimental and computed dynamical behavior of gas transport in coal beds suggest that significant work remains to describe multicomponent gas adsorption and transport through coal. While it was found that the adsorption behavior of single and two component systems in samples of Powder River Basin coal are well described by Langmuir adsorption phenomena and instantaneous chemical equilibrium, the quantitative behavior of the transport of ternary gas systems remains to be proven. Numerical representation of the dynamics of multicomponent gas transport through coal beds appears to be quite sensitive to the representation of sorption phenomena. Such phenomena include adsorption/desorption hysteresis, scanning loops, and the selectivity of a gas species for coal surfaces as a function of pressure and free gas composition. Additional research is needed in this area to move beyond such generalizations.

The sensitivity of coal bed permeability to the composition and pressure of gas flowing through the coal is another area where additional research is needed. The experimental results presented indicate that the average permeability of a coal pack increases as CH$_4$ desorbs and decreases as CO$_2$ adsorbs. This is so-called shrinkage and swelling. Mixtures of CO$_2$ and N$_2$ are especially interesting. Coal bed permeability to gas appears to be maintained with the addition of small amounts of N$_2$ to injection gas. In addition to sensitivity of permeability to the composition of the gas, we find that the stress state and magnitude of the confining stress affect the degree of permeability change. The greatest amount of permeability reduction accompanying CO$_2$ injection occurs as the net effective stress (the difference between confining pressure and pore pressure) is held constant as CO$_2$ loading of the coal surface increases. It is clear that a
A combination of detailed measurements of adsorption, strain response to stress with adsorbed gases present, and observations of the physical state of fractures at stress conditions that mimic the subsurface is needed to delineate potential permeability response to injection of CO$_2$ and production of CH$_4$.

Additionally, the experimental results for gas injection into coal reveal displacement physics that appear to be amenable to treatment analytically using the method of characteristics. Here, the geological setting must allow chemical equilibrium to be established quickly between free gas in fractures and gas in the coal matrix. Also, permeability evolution must be mild as CH$_4$ on coal surfaces is replaced by injection gas. Analytical solution for multicomponent, multiphase flow, nevertheless, provides the underpinnings for rapid streamline simulations of flow in heterogeneous coalbeds. Further, method of characteristics solutions also supplement our physical understanding by providing solutions to the governing flow and adsorption equations that are free of numerical artifacts such as dispersion.

In summary, the investigations described here blend experiments, analysis, and simulation to delineate and quantify the physical mechanisms that control flow behavior in the subsurface. The ability to predict such behavior is fundamental to building understanding of the long term containment of the CO$_2$ and to the design of effective processes for sequestration.
6 Summary

In this report, we have considered some of the computational tools available for modeling of CO$_2$ storage processes and projects, and we have examined some of the physical mechanisms that control the migration of CO$_2$ in the subsurface at various stages of a project as well as the time scales that are associated with the various physical mechanisms.

A review of the simulators currently available for aquifer and coal bed storage of CO$_2$ (see Section 2) indicates that they are very capable, with many physical mechanisms represented. They will continue to be very useful for exploring the interplay of physical mechanisms for computational grids of limited size, but they are subject to significant limitations for application at field scale. Conventional finite-difference compositional simulations, even with relatively small numbers of components, are too slow to handle high resolution representation of the spatial distribution of permeability at field scale, and when coarse computational grids are used instead, they are badly affected by numerical diffusion, which can alter calculated composition paths in a way that affects calculated performance significantly. Hence, they are probably not suitable for routine simulation of field-scale flows at grid resolutions sufficient to capture the effects of preferential flow paths created by reservoir heterogeneity, especially if the impact of variability in the permeability distribution is to be assessed. For screening of sites, assessment of areas invaded by CO$_2$, or rapid exploration of the impact of injection well placement, simulation tools that are significantly more efficient, but necessarily more limited in the mechanisms represented, are appropriate. One approach, the use of streamline methods, has been extended to be applicable for two of the geologic settings considered in this report, gas reservoirs and aquifers.

The examples considered in Section 3.1 demonstrate that the compositional simulation tools available for modeling of displacements in oil and gas reservoirs are sufficiently capable that a reasonable range of design and optimization problems can be attacked. For example, the displacement of a relatively heavy oil considered in Section 3.1 is one in which calculated displacement performance is relatively insensitive to adverse effects of numerical dispersion. In that case, conventional finite difference simulation is fast enough to permit detailed examination of injection and well control strategies for maximizing both recovery of oil and storage of CO$_2$.

The example of Section 3.2, which considers condensate vaporization in a depleting gas reservoir, is one in which the number of components required to represent condensate drop-out adequately is relatively large, and in contrast with the heavy oil displacement, local displacement efficiency of the condensate is quite sensitive to the effects of numerical dispersion. As a result, conventional finite difference compositional simulation is too slow to be useful for large-scale computations. The condensate vaporization problem can be attacked, however, with compositional streamline simulation. In this example, effects of gravity are negligible, the viscosity ratio of the injected and in-place fluid is close to one, and hence streamlines change location only slightly during the course of the displacement process. As a result, a very efficient and
accurate compositional simulation can be performed using an analytical one-dimensional solution for the compositional part of the displacement mechanism, with streamlines used to capture the effects of well locations and heterogeneity. That approach is orders of magnitude faster than conventional compositional simulation, and it is much less subject to adverse effects of numerical dispersion.

Computational examples presented in Section 4 demonstrate that the interplay of viscous, gravity, and capillary forces determines the fate of injected CO$_2$. During the injection period, pressure gradients in the aquifer are created by the injection well and the density difference between CO$_2$ and brine, and convection induced by those gradients determines the distribution of injected CO$_2$. Both conventional finite difference simulation and streamline simulation approaches can be used to predict the movement of CO$_2$ during the injection period, as the examples presented here show. However, streamline simulation is much more efficient, with computation times an order of magnitude lower than those of a fully implicit finite difference computation.

Conventional finite difference simulations as well as streamline simulations demonstrate conclusively that the ratio of gravity to viscous forces is important in aquifer injection. CO$_2$ is less dense than brine, and it is much less viscous, and hence average local displacement efficiency will be low. When gravity forces dominate, a relatively thin tongue of CO$_2$ forms at the top of the aquifer. After CO$_2$ injection ceases, that CO$_2$ will dissolve at a rate that is affected significantly by the vertical permeability of the aquifer. In high permeability aquifers, the dissolution rate is increased significantly by the unstable convection that occurs when dissolved CO$_2$ makes a brine mixture that is slightly more dense than brine alone. After an initial period of diffusion, density-driven fingers form that increase the rate of dissolution, especially for the period before the fingers reach the base of the aquifer. At Sleipner, for example, the onset of vertical convection occurs rapidly (on the order of months), and the mixing that results from the vertical fingering of the dense brine through less dense brine speeds dissolution for about 100 years. But Sleipner has very high permeability (Darcies), and in aquifers with lower permeability (say one hundred millidarcies) vertical convection speeds dissolution over diffusion alone, but the onset of convection is delayed by two centuries, and the rates are sufficiently low that good containment of the injected CO$_2$ will be required for long periods. That result suggests that the use of capillary trapping of a residual CO$_2$ phase should be explored in detail.

Conventional finite difference simulations indicate that capillary trapping can act on relatively short time scales, however, to immobilize a portion of the injected CO$_2$. How much is trapped depends strongly on the ratio of viscous to gravity forces. When gravity forces dominate, less CO$_2$ is trapped, but most of the CO$_2$ that is trapped as a residual phase is trapped on the time scale of a few injection periods. When gravity forces dominate, on the other hand, much more CO$_2$ can be trapped, and significant quantities trap quickly, but many injection periods are required to trap the remaining undissolved CO$_2$. These results suggest that CO$_2$ should be injected at the highest feasible rates (consistent with avoiding fracturing of the aquifer formation) should be used to reduce the gravity to viscous ratio. They also suggest that the use of water injection should be
considered as a way to reduce gas saturations and increase trapped saturations on even shorter time scales.

A combined experimental and mechanistic modeling approach described in Section 5 has revealed an interplay of multicomponent gas sorption, phase behavior, and transport in coal that yields dynamical behavior rich in complexity. Sorption and multiphase flow phenomena in coal remain to be described fully in both a conceptual and quantitative sense. The results of the experiments and theory completed to date lead to the following conclusions.

Measurements of the adsorption and desorption of CO$_2$, CH$_4$, and N$_2$ on a coal sample from the Powder River Basing Wyoming confirm that CO$_2$ is more strongly adsorbed in comparison to the other gases. A result of the strong affinity of CO$_2$ for coal surfaces is that CO$_2$ displaces CH$_4$ relatively efficiently. Experiment and simulation show consistently that CO$_2$ moves through coal in a piston-like fashion. As a result, breakthrough times for CO$_2$ are significantly large. The least measured breakthrough time corresponded to 1.5 PVI. Likewise, both experiments and calculations verify that coal beds separate chromatographically N$_2$ and CO$_2$. This separation occurs while coal bed CH$_4$ recovery is enhanced.

Calculations from a surface forces perspective and experimental results for water imbibition into coal samples both suggest that coal is not strongly water wet. Hence injected CO$_2$ should be able to contact coal surfaces relatively efficiently. Once CO$_2$ is in place, our initial results suggest that the water wettability of coal surfaces is, at least, a function of the pH of the aqueous phase.

Our attempts to reconcile experimental and computed dynamical behavior of gas transport in coal beds suggest that significant work remains to describe multicomponent gas adsorption and transport through coal. While it was found that the adsorption behavior of single and two component systems in samples of Powder River Basin coal are well described by Langmuir adsorption phenomena and instantaneous chemical equilibrium, the quantitative behavior of the transport of ternary gas systems remains to be proven. Numerical representation of the dynamics of multicomponent gas transport through coal beds appears to be quite sensitive to the representation of sorption phenomena. Such phenomena include adsorption/desorption hysteresis, scanning loops, and the selectivity of a gas species for coal surfaces as a function of pressure and free gas composition. Additional research is needed in this area to move beyond such generalizations.

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the confining stress affect the degree of permeability change. The greatest amount of permeability reduction accompanying CO₂ injection occurs as the net effective stress (the difference between confining pressure and pore pressure) is held constant as CO₂ loading of the coal surface increases. It is clear that a combination of detailed measurements of adsorption, strain response to stress with adsorbed gases present, and observations of the physical state of fractures at stress conditions that mimic the subsurface is needed to delineate potential permeability response to injection of CO₂ and production of CH₄.

Additionally, the experimental results for gas injection into coal reveal displacement physics that appear to be amenable to treatment analytically using the method of characteristics. Here, the geological setting must allow chemical equilibrium to be established quickly between free gas in fractures and gas in the coal matrix. Also, permeability evolution must be mild as CH₄ on coal surfaces is replaced by injection gas. Analytical solution for multicomponent, multiphase flow, nevertheless, provides the underpinnings for rapid streamline simulations of flow in heterogeneous coalbeds. Further, method of characteristics solutions also supplement our physical understanding by providing solutions to the governing flow and adsorption equations that are free of numerical artifacts such as dispersion.

In summary, the investigations described here blend experiments, analysis, and simulation to delineate and quantify the physical mechanisms that control flow behavior in the subsurface. The ability to predict such behavior is fundamental to building understanding of the long term containment of the CO₂ and to the design of effective processes for sequestration.
7 References


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