MODELING THE DISPLACEMENT OF GASES IN COAL BEDS

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By
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I certify that I have read this report and that in my opinion it is fully adequate, in scope and in quality, as partial fulfillment of the degree of Master of Science in Petroleum Engineering.

________________________________________

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Abstract

Enhanced Coal Bed Methane (ECBM) recovery can be done by injecting gases to displace methane that is initially adsorbed on the coal surface. The chromatographic partitioning of each gas occurs due to the difference in sorption affinity. To model this process accurately, sorption characteristics including hysteresis need to be known because the flow involves not only adsorption, but also desorption. A nonlinear convection-dispersion equation for each component for one-dimensional flow can be written, and a numerical simulator can then be used to solve the system of equations.

In this report, a detailed formulation for the ECBM simulator is presented. The simulator is then used to perform sensitivity studies of factors that affect the displacement behavior. Adjusting porosity, coal density, and sorption affinity cause significant changes to the volume loss of adsorbing gases, and the volume gain from desorbing gases. These three parameters, therefore, strongly affect volume change on mixing, and have the largest effects on flow performance.

After that, simulations for the binary and ternary systems are investigated, and the results are compared with results of slimtube experiments. A systematic approach for tuning up the parameters is described. Analytical solutions are used to help matching, and the parameters are adjusted based on the knowledge from sensitivity studies.

The simulator is applied for acid gas injection problems in which the system has up to 5 components. A solution for CH₄, CO₂, N₂, H₂S with other gases system is presented as a series of shocks and rarefactions. Their separations depend on how strongly each component adsorbs. Gases that have stronger sorption affinity move slower, and vice versa. H₂S which adsorbs stronger than CO₂ can then be stored in coal along with CO₂. The results from this study also establish the basic understanding of multicomponent gas displacement in coal beds.
Acknowledgements

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I am so grateful to Sameer Parakh, Margot Gerritsen, and Anthony Kovcek for providing me the experimental data, and discussing the results. I would like to give a special thank to Kristian Jessen for letting me use and modify his simulator code in this study. Financial support from the Department of Energy Resources Engineering, and Global Climate and Energy Project are also acknowledged.

I would also like to thank my parents, my grandparents, my brother, and my beloved friends in Thailand for their loves and encouragement. Last but not least, I should extend thanks to my friends here. I shall never forget every second that we have spent together. From the bottom of my heart, I will really miss all of you. Take care and goodbye for now.
Contents

Abstract .............................................................................................................................................. v
Acknowledgements .......................................................................................................................... vii
Contents ........................................................................................................................................... ix
List of Tables ..................................................................................................................................... xi
List of Figures .................................................................................................................................. xiii
1. Introduction ................................................................................................................................... 1
2. Modeling of Gas Flow through Coal Beds ............................................................................. 3
   2.1 Governing Equation .............................................................................................................. 3
   2.2 Adsorption Model ................................................................................................................ 5
      2.2.1 Extended Langmuir approach .................................................................................... 5
      2.2.2 Ideal Adsorbate Solution (IAS) ................................................................................ 7
   2.3 Numerical Simulation ........................................................................................................... 9
      2.3.1 General Assumptions .................................................................................................. 9
      2.3.2 Volume of Adsorbed Phase ...................................................................................... 9
      2.3.3 Volume Change on Mixing ..................................................................................... 10
      2.3.4 Hysteresis Model ..................................................................................................... 11
      2.3.5 Numerical Dispersion ............................................................................................. 12
      2.3.6 Time Step Selection .................................................................................................. 12
3. Sensitivity Study ......................................................................................................................... 13
   3.1 Base Case ............................................................................................................................. 13
   3.2 Pure CO₂ injection for CH₄ displacement ........................................................................... 15
      3.2.1 Coal density ............................................................................................................. 15
      3.2.2 Total porosity .......................................................................................................... 17
      3.2.3 Secondary porosity .................................................................................................. 18
      3.2.4 Physical dispersion ................................................................................................. 18
      3.2.5 CH₄ adsorption ...................................................................................................... 19
      3.2.6 CO₂ adsorption ...................................................................................................... 21
      3.2.7 Pressure .................................................................................................................. 22
      3.2.8 Volume of adsorbed phase .................................................................................... 23
List of Tables

Table 3-1: Parameters for the base case................................................................. 13
Table 3-2: Langmuir adsorption constants for the base case............................... 14
Table 3-3: Variation of normalized eigenvalue, local flow velocity, and characteristic wave velocity for the sensitivity cases of CH₄-CO₂ binary system....................... 28

Table 4-1: Material balance calculation for the case of CO₂ displaces CH₄, N₂ displaces CH₄, and 55/45 CO₂/N₂ mixture displaces CH₄ (before tuning). ......................... 42
Table 4-2: Material balance calculation for the case of CO₂ displaces CH₄, N₂ displaces CH₄, and displacement of CH₄ by a 55/45 CO₂/N₂ mixture (after tuning)................. 44
Table 4-3: Langmuir adsorption constants based on material balance calculations.... 45

Table 5-1: Gas composition in Weyburn pipeline.................................................... 47
Table 5-2: Langmuir adsorption constants for acid gas components. ...................... 48
List of Figures

Figure 3-1: Sorption characteristics of Powder River Basin coal measured at 22 °C........ 14
Figure 3-2: Comparison between the base case of pure CO₂ displacing CH₄ and the case of increased coal density .......................................................................................... 16
Figure 3-3: Amount of volume changes for the base case, increased coal density, and increased total porosity cases .................................................................................................. 16
Figure 3-4: Comparison between the base case of pure CO₂ displacing CH₄ and the case of increased total porosity .................................................................................................. 17
Figure 3-5: Comparison between the base case of pure CO₂ displacing CH₄ and the case of decreased secondary porosity ...................................................................................... 18
Figure 3-6: Comparison between the base case of pure CO₂ displacing CH₄ and the case of increased physical dispersion ........................................................................................ 19
Figure 3-7: Comparison between the base case of pure CO₂ displacing CH₄ and the case of decreased CH₄ adsorption .......................................................................................... 20
Figure 3-8: Amount of volume changes for the base case, decreased CH₄ adsorption, and decreased CO₂ adsorption cases .......................................................................................... 20
Figure 3-9: Comparison between the base case of pure CO₂ displacing CH₄ and the case of decreased CO₂ adsorption .......................................................................................... 21
Figure 3-10: Comparison between the base case of pure CO₂ displacing CH₄ and the case of increased pressure from 450 to 600 psia ................................................................. 23
Figure 3-11: Comparison between the base case of pure CO₂ displacing CH₄ and the case of increased volume of adsorbed phase ................................................................. 24
Figure 3-12: Comparison between the base case of pure CO₂ displacing CH₄ and the case of excluding sorption hysteresis .................................................................................. 25
Figure 3-13: Molar concentration of CH₄ and CO₂ in adsorbate phase at 450 psia and 22°C predicted by the IAS and Langmuir models ......................................................... 26
Figure 3-14: Comparison between the base case of pure CO₂ displacing CH₄ and the case of changing adsorption model to IAS ............................................................................. 26
Figure 3-15: Effect of the difference between upstream and downstream velocity on sharpening of the shock front .................................................................
Figure 3-16: Comparison between the base case of pure CO$_2$ displacing CH$_4$ and the case of decreased total porosity from 44% to 22% ................................................................. 29
Figure 3-17: Comparison between the base case of pure N$_2$ displaces CH$_4$ and the case of increased coal density ................................................................. 30
Figure 3-18: Comparison between the base case of pure N$_2$ displaces CH$_4$ and the case of increased total porosity ................................................................. 31
Figure 3-19: Comparison between the base case of pure N$_2$ displaces CH$_4$ and the case of increased physical dispersion ................................................................. 31
Figure 3-20: Comparison between the base case of pure N$_2$ displaces CH$_4$ and the case of decreased CH$_4$ adsorption ................................................................. 32
Figure 3-21: Comparison between the base case of pure N$_2$ displaces CH$_4$ and the case of decreased N$_2$ adsorption ................................................................. 32
Figure 3-22: Comparison between the base case of pure N$_2$ displaces CH$_4$ and the case of changing adsorption model to IAS ................................................................. 33
Figure 3-23: Molar concentration of CH$_4$ and N$_2$ in adsorbate phase at 500 psia and 22$^\circ$C predicted by the IAS and Langmuir models ................................................................. 34
Figure 3-24: Comparison between the base case of mixture of CO$_2$ and N$_2$ (55:45) displacement of CH$_4$ and the case of increased total porosity ................................................................. 35
Figure 3-25: Comparison between the base case of mixture of CO$_2$ and N$_2$ (55:45) displacement of CH$_4$ and the case of increased physical dispersion ................................................................. 36
Figure 3-26: Comparison between the base case of mixture of CO$_2$ and N$_2$ (55:45) displacement of CH$_4$ and the case of decreased CH$_4$ adsorption ................................................................. 36
Figure 3-27: Comparison between the base case of mixture of CO$_2$ and N$_2$ (55:45) displacement of CH$_4$ and the case of decrease CO$_2$ adsorption ................................................................. 37
Figure 3-28: Comparison between the base case of mixture of CO$_2$ and N$_2$ (55:45) displacement of CH$_4$ and the case of decreased N$_2$ adsorption ................................................................. 38
Figure 3-29: Comparison between the base case of mixture of CO$_2$ and N$_2$ (55:45) displacement of CH$_4$ and the case of changing adsorption model to IAS ................................................................. 38
Figure 3-30: Molar concentration of CH$_4$, CO$_2$, and N$_2$ in adsorbate phase at 475 psia and 22$^\circ$C predicted by the IAS and Langmuir models ................................................................. 39
Figure 4-1: Comparison of experimental and simulated results for pure CO$_2$ displaces CH$_4$ at 450 psia, pure N$_2$ displaces CH$_4$ at 500 psia, and mixture of CO$_2$ and N$_2$ (55:45) displaces CH$_4$ at 475 psia (before tuning)......................................................................... 41

Figure 4-2: Comparison of analytical solution, experimental, and simulated results for pure CO$_2$ displaces CH$_4$ system................................................................. 43

Figure 4-3: Sorption characteristics based on material balance calculations .............. 44

Figure 4-4: Comparison of experimental and simulated results for pure CO$_2$ displaces CH$_4$ at 450 psia, pure N$_2$ displaces CH$_4$ at 500 psia, and mixture of CO$_2$ and N$_2$ (55:45) displaces CH$_4$ at 475 psia (after tuning) ................................................................. 46

Figure 5-1: Effluent composition of acid-gas injection (5-component displacement). .... 49
Chapter 1

1. Introduction

Gas injection is one of the Enhanced Coal Bed Methane (ECBM) recovery techniques. The benefit is not only to extract methane, but some injected gases, for example CO$_2$, can also be trapped within coal as adsorbed solution on the surface. As a result, coal beds can be considered one of the possible CO$_2$ storage settings to be used to reduce emissions of greenhouse gases to the atmosphere, in addition to deep saline aquifers and hydrocarbon reservoirs.

The transport in coal is complicated. The convection-dominated flow takes place in a network of fractures known as cleats, and at the same time there is adsorption/desorption of gases that diffuse from the fractures through the coal matrix. This exchange increases and/or decreases permeability (Lin, 2007). As gases desorb, the matrix shrinks and there is more fracture area open to flow. Thus, the permeability is higher. By contrast, the matrix swells when adsorption occurs, which results in lower permeability.

Analytical solutions for multicomponent gas injection without adsorption were developed by Dindoruk (1992). Zhu (2003) derived the solutions for single-phase flow with adsorption in coal for systems with up to 3-components; his work also includes the effect of temperature variation. An analytical theory for 2-phase, multicomponent flow in coal was presented by Seto (2007).

Experimental investigation is another way to understand the mechanism. Tang et al. (2005) performed a laboratory investigation of gas injection in coal. Crushed coal was packed in a tube, the coal in the tube was saturated with methane, and then the methane was displaced by various injected gases. Prior to the experiment, Tang et al. studied the characteristics of coal from Powder River Basin and the adsorption parameters were
measured. Parakh (2007) used the same coal to construct his experiments in a similar manner for single-phase and two-phase displacements. He used a longer slim tube also packed with powdered coal. His results for the single-phase systems are examined in some detail in the simulation study described in this report.

While analytical solutions provide insight into important aspects of the interaction of flow and adsorption, they are only available for flow systems in which the effects of dispersion are not included. That assumption in the analytical calculation can be relaxed, and the flow equations can also be solved by numerical simulation. Jessen et al. (2004) studied the effect of numerical dispersion in compositional simulations. If the first order upwinding scheme is used, the grid size must be small to prevent the numerical dispersion that modifies the solution (Orr, 2007). Higher order methods are presented by Mallison et al. (2005) for solving gas injection problems.

The ECBM simulator used in this study was developed by Prof. Kristian Jessen. It was also used by Tang et al. (2005) to model the experimental results. The adsorption model in the simulator at that time is an extended Langmuir model (Yang, 1987). Jessen et al. (2007) included the effect of physical dispersion (Perkins et al., 1963), and sorption hysteresis in the model. Moreover, they introduced Ideal Adsorbed Solution (IAS) approach (Myers et al., 1965) to predict multicomponent sorption. These modifications should make the simulator more accurate to the extent that these effects reflect adsorption behavior more accurately.

In this work, the simulation study is performed in order to understand the physics of gas injection in coal beds and to test the representations offered by the two adsorption models. Chapter 2 gives the detailed formulation of the ECBM simulator. Sensitivity studies of factors that affect the displacement behavior are described in Chapter 3. Chapter 4 compares simulated and experimental results. Application of this ECBM simulator is demonstrated in Chapter 5 to predict the behavior of acid gas injection projects. Chapter 6 concludes the study.
Chapter 2

2. Modeling of Gas Flow through Coal Beds

2.1 Governing Equation

Coal is a complex porous medium that consists of multiple porosity systems. The primary porosity is the high permeability fracture network, which provides the flow conduits for production. The secondary porosity is the coal matrix that has low permeability. The majority of gases (> 95%) stored in coal are in this part as they adsorb onto the coal surface (Seto, 2007). The overall porosity of coal can then be written as

\[ \phi = \phi_1 + \phi_2, \quad (2-1) \]

where

\[ \phi \] = porosity of coal,
\[ \phi_1 \] = primary (fracture) porosity, and
\[ \phi_2 \] = secondary (grain) porosity.

The transport in the fracture system is dominated by convection, while diffusion is the main mechanism of transport in the matrix system. The convection-dispersion equations for an isothermal, one-dimensional, single-phase flow in a porous medium with sorption for each component are:

\[ \frac{\partial C_i}{\partial t} + \frac{(1 - \phi)}{\phi} \frac{\partial a_i}{\partial t} + v \frac{\partial C_i}{\partial x} - K \frac{\partial^2 C_i}{\partial x^2} = 0, \quad i = 1, n_c, \quad (2-2) \]
where

\[ C_i = y_i \rho_g. \]  \hspace{1cm} (2-3)

The parameters in Eq. 2-2 and Eq. 2-3 are described as follows:

\[ C_i = \text{molar concentration of component } i \text{ in the gas phase}, \]

\[ y_i = \text{mole fraction of component } i \text{ in the gas phase}, \]

\[ \rho_g = \text{molar density of the gas phase}, \]

\[ a_i = \text{molar concentration of component } i \text{ adsorbed/desorbed on the coal surface}, \]

\[ v = \text{average flow velocity of the gas phase (interstitial velocity), and} \]

\[ K_l = \text{longitudinal dispersion coefficient}. \]

Substituting the following dimensionless variables into Eq. 2-2

\[ \tau = \frac{v_{inj} t}{\phi L}, \]  \hspace{1cm} (2-4)

\[ \xi = \frac{x}{L}, \]  \hspace{1cm} (2-5)

\[ v_p = \frac{v}{v_{inj}} \left( \frac{\phi}{\phi_i} \right), \text{ and} \]

\[ Pe = \frac{L v_{inj}}{K_l}, \]  \hspace{1cm} (2-7)

where

\[ \tau = \text{dimensionless time}, \]

\[ \xi = \text{dimensionless distance}, \]
\[ v_D = \text{dimensionless flow velocity,} \]
\[ v_{inj} = \text{injection velocity,} \]
\[ Pe = \text{Peclet number, and} \]
\[ L = \text{system length,} \]

the transport equations become

\[
\frac{\partial}{\partial \tau} \left( C_i + \frac{1 - \phi}{\phi} a_i \right) + \frac{\partial}{\partial \xi} \left( v_D C_i - \frac{1}{Pe} \frac{\partial C_i}{\partial \xi} \right) = 0 \quad i = 1, n_c. \tag{2-8}
\]

Initial and boundary conditions are

\[
C_i(\xi,0) = \begin{cases} 
C_i^{\text{inj}}, & \xi = 0 \\
C_i^{\text{init}}, & \xi > 0
\end{cases}, \quad \text{and} \tag{2-9}
\]

\[
v_D(\xi,\tau) = \begin{cases} 
0, & \xi = 0, \tau = 0 \\
1, & \xi = 0, \tau > 0
\end{cases}. \tag{2-10}
\]

### 2.2 Adsorption Model

#### 2.2.1 Extended Langmuir approach

This model is extended from the Langmuir isotherm for single-gas adsorption to predict \( n_c \)-component mixture. The adsorbed amount \( n_i \) (scf of gas/ton of coal) of component \( i \) in the mixture is

\[
n_i = \frac{V_{m,i} B_i y_i p}{1 + \sum_{j=1}^{n_c} B_j y_j p}, \tag{2-11}
\]
where:

\[ V_{m,i} = \text{maximum amount of adsorption of component } i, \]
\[ B_i = \text{Langmuir constant at a specified temperature for component } i, \]
\[ y_i = \text{mole fraction of component } i \text{ in the gas phase, and} \]
\[ p = \text{pressure}. \]

Molar concentration of the adsorbed components \( a_i \) can be calculated from

\[ a_i = \rho_{i,\text{std}} \rho_r n_i, \quad (2-12) \]

where:

\[ \rho_{i,\text{std}} = \text{molar density of component } i \text{ at standard conditions, and} \]
\[ \rho_r = \text{density of coal}. \]

Although the Extended Langmuir model provides explicit calculation, the results are reasonably accurate only for binary gas adsorption systems (Wei et al., 2005). Tang et al. (2005) applied this isotherm to fit their experimental data for ternary gas mixtures, but their simulation results using that isotherm did not match the experimental observations closely. They suggested that the model could be improved by including hysteresis and the effects of multicomponent sorption.
2.2.2 Ideal Adsorbate Solution (IAS)

For multicomponent systems, the equilibrium involves mixed-gas adsorption, and thus the effects of interference by multiple components should be considered. Myers et al. (1965) proposed a technique based on the Gibbs approach. The idea is derived from the equilibrium criterion that for the isothermal conditions the partial fugacity of a component in the adsorbed phase is equal to the partial fugacity of that component in the gas phase. The equation of equilibrium can be written as

\[ py_i \varphi_i = f_i^0 (\Pi) \gamma_i x_i, \]

where

- \( \varphi_i \) = fugacity coefficient of component \( i \) in the gas phase,
- \( f_i^0 \) = fugacity of pure component \( i \) in the adsorbed mixture evaluated at the spreading pressure \( (\Pi) \),
- \( \gamma_i \) = activity coefficient of component \( i \), and
- \( x_i \) = mole fraction of component \( i \) in the adsorbed phase.

At low pressure, the assumption of an ideal gas can be made, and the IAS model also assumes that the adsorbed mixture behaves like an ideal solution (see Talu et al., 1993 for nonideal mixture). Eq. 2-13 simplifies to

\[ py_i = p_i^0 x_i, \]

where

- \( p_i^0 \) = equilibrium gas-phase pressure for the adsorption of pure component \( i \).
The IAS model used in this study is based on the extended Langmuir isotherm. Jessen et al. (2007) suggested that the spreading pressure can be evaluated by

$$\Pi_i^* = V_{m,i} \ln \left(1 + B_i p_i^0 \right).$$

(2-15)

At equilibrium, the spreading pressure of each component must be equal. It can be written as

$$\Pi_i^* = \Pi_j^*. \quad (2-16)$$

Using the procedure explained in Jessen et al. (2007), at given $p$ and $y_i$, start by guessing $x_i$ and then solve Eq. 2-14 and Eq. 2-16 iteratively. The adsorbed amount in $n_i$ is finally found from

$$n_i = x_i n_i^o, \quad (2-17)$$

where

$$n_i = \left(\sum_{i=1}^{n} x_i \right)^{-1}, \quad \text{and} \quad (2-18)$$

$$n_i^o = \text{adsorbed amount of pure component } i.$$  

Once the adsorbed amount $n_i$ is known, molar concentrations of the adsorbed components $a_i$ can be calculated from Eq. 2-12.

The prediction of multicomponent sorption from IAS model is more computationally expensive, but it is more accurate. The improvement of work from Tang et al. (2005) for ternary system can be seen in Jessen et al. (2007).
2.3 Numerical Simulation

2.3.1 General Assumptions

The Enhanced Coal Bed Methane (ECBM) simulator used in this study is a 1-D finite-difference model. The grid type is Cartesian and every block has equal cell width. The simulator can handle a dual porosity system within the coal porous medium. The nonlinear system of transport equation (Eq. 2-8) is solved and gas properties within those equations are described by the Peng-Robinson EOS. Additional assumptions are

- The pressure used to evaluated the amount of adsorption is assumed to be constant (use \( p = p^{\text{init}} \) throughout the domain)
- Local thermodynamic equilibrium is assumed to occur instantaneously (in other words, the kinetics of adsorption is not modeled).

The assumption of constant pressure is made for simplicity in calculating sorption and phase behavior. It also corresponds reasonably well to the experiment of Parakh (2007) in that he tried to keep constant pressure during the displacement through use of a back pressure regulator.

2.3.2 Volume of Adsorbed Phase

The volume of adsorbed gases on coal surfaces is calculated by multiplying the moles of adsorption of each gas with the volume of that gas molecule in the adsorbed state (Lin et al., 2007). In this simulator the volume of the adsorbed phase \( V_{\text{ads}} \) is approximated by

\[
V_{\text{ads}} = \sum_{i=1}^{n} z_i b_i, \tag{2-19}
\]

where

\[
z_i = \frac{a_i}{\sum_{k=1}^{n} a_k}, \tag{2-20}
\]
This procedure is the same as that recommended by Hall et al. (1990). In this model the volume of gas molecules is equal to $b_i$, the hard-sphere co-volume of component $i$ in the PR EOS.

2.3.3 Volume Change on Mixing

With the assumption of constant pressure during the displacement, pressure equation, which is volume balance, is not solved at each time step; only the transport equations (Eq. 2-8) are solved. There may be a volume increase or decrease due to component transfer (volume change on mixing). An explicit correction for the volume discrepancy is suggested by Gerritsen et al. (2005). The local flow velocity at the right interface of a grid cell $k$ is corrected by

$$v_{D,k+\frac{1}{2}} = v_{D,k-\frac{1}{2}} + \varepsilon \frac{\Delta \xi}{\Delta \tau} (q_{vc} - 1),$$  \hspace{1cm} (2-21)

where

$$q_{vc} = \frac{V_{fluid}}{V_{cell}}, \text{ and}$$  \hspace{1cm} (2-22)

$$V_{fluid} = V_{gas} + V_{ads}.$$  \hspace{1cm} (2-23)

The coefficient $\varepsilon$ is a relaxation parameter which controls how fast of volume adjustment. Its value is selected to be less than 1 in order to ensure stability. Note that this treatment can roughly correct the small volume change as the discrepancy is carried forward in time.
2.3.4 Hysteresis Model

The effect of sorption hysteresis is also captured in this simulator. Jessen et al. (2007) proposed the idea of using scanning curves to represent the behavior of gas desorption. This technique arises from the relation that the adsorbed amount at $p_{max}$ predicted by the scanning curve and the adsorption curve must be equal.

$$n_s(p_{max}) = n_a(p_{max}), \quad (2-24)$$

or it can be written as

$$V_{m,s} B_s p_{max} \frac{V_{m,a} B_a p_{max}}{1 + B_s p_{max}} = V_{m,a} B_a p_{max}. \quad (2-25)$$

The other relation is that the slope of the scanning curve should be between the slopes of the bounding curves

$$\left. \frac{\partial n_s}{\partial p} \right|_{p_{max}} = \alpha \left. \frac{\partial n_a}{\partial p} \right|_{p_{max}} + (1 - \alpha) \left. \frac{\partial n_a}{\partial p} \right|_{p_{max}}, \quad (2-26)$$

where $\alpha$ is a weighing parameter for interpolation, which can be expressed as

$$\alpha = \frac{n_d(p_{max})}{n_a(p_{max})}. \quad (2-27)$$

By solving Eq. 2-25 and Eq. 2-26, the parameters of the Langmuir isotherm for the scanning curve ($V_{m,s}$ and $B_s$) can be determined. The scanning curve can be constructed and can be used to describe the desorption behavior.

In the simulator the scanning curves are evaluated for every component except the one that adsorbs strongest. This representation is equivalent to the assumption that weaker
adsorbing gases first adsorb on coal surface, and then some of them are desorbed by more strongly adsorbing gases that come from behind.

2.3.5 Numerical Dispersion

The transport equations (Eq. 2-8) are solved with a fully explicit (forward time), and first order single-point upstream weighting. Lantz (1971) developed the approximation of the numerical dispersion (truncation error) for the finite difference formulation of the purely convective equation for single-phase flow as

\[
P_{e_{num}}^{-1} = \frac{\Delta \xi}{2} \left(1 - \frac{\Delta \tau}{\Delta \xi}\right).
\]  

(2-28)

2.3.6 Time Step Selection

In order to have a stable solution, the time step \( \Delta \tau \) must be chosen to satisfy the CFL condition

\[
\Delta \tau = CFL \frac{\Delta \xi}{v_{\text{max}}}.
\]  

(2-29)

where

- \( v_{\text{max}} \) = maximum propagation speed for a displacement, and
- CFL = Courant-Friedrichs-Lewy number (0<CFL<1).
Chapter 3

3. Sensitivity Study

A series of numerical simulations was carried out to investigate the effect of each parameter that affects the displacement of gases in coal beds. Sensitivity studies start with binary systems in which pure CO\textsubscript{2} displaces CH\textsubscript{4}, and pure N\textsubscript{2} displaces CO\textsubscript{2}, and then move on to ternary displacements in which a mixture of CO\textsubscript{2} and N\textsubscript{2} displace CH\textsubscript{4}.

3.1 Base Case

Table 3-1 shows the input parameters for the base case. The data are based on the coal pack in the slim tube experiments done by Parakh (2007). Total porosity data was averaged from several sets of measurements with helium. Matrix porosity was not directly measured in his work, so it is a free variable that can be tuned to match the experimental results. In the numerical issue, the number of gridblocks was set so that the effect of numerical dispersion was small compared to the physical dispersion. In order to have a stable solution, the time step was selected to satisfy the CFL condition.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coal density, $\rho_r$ (kg/m$^3$)</td>
<td>1466</td>
</tr>
<tr>
<td>Total porosity of coal, $\phi$</td>
<td>0.44</td>
</tr>
<tr>
<td>Primary porosity, $\phi_1$</td>
<td>0.34</td>
</tr>
<tr>
<td>Secondary (matrix) porosity, $\phi_2$</td>
<td>0.10</td>
</tr>
<tr>
<td>Physical Peclet number, $Pe_{phys}$</td>
<td>300</td>
</tr>
<tr>
<td>Number of gridblocks</td>
<td>1000</td>
</tr>
<tr>
<td>CFL number</td>
<td>0.9</td>
</tr>
</tbody>
</table>
The extended Langmuir model is used in the simulator to predict the adsorption of gases on coal. The effect of sorption hysteresis is also included in the base case. Langmuir adsorption constants are reported in Table 3-2. These values are based on the experiments of Tang et al. (2005). Measured adsorption/desorption curves versus pressure at zero initial water saturation are presented in Figure 3-1.

Table 3-2: Langmuir adsorption constants for the base case.

<table>
<thead>
<tr>
<th></th>
<th>Adsorption</th>
<th></th>
<th>Desorption</th>
<th></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>
</tr>
<tr>
<td>CH$_4$</td>
<td>811</td>
<td>0.00237</td>
<td>543</td>
<td>0.0382</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>1760</td>
<td>0.00521</td>
<td>1560</td>
<td>0.0158</td>
</tr>
<tr>
<td>N$_2$</td>
<td>272</td>
<td>0.00242</td>
<td>226</td>
<td>0.00574</td>
</tr>
</tbody>
</table>

Figure 3-1: Sorption characteristics of Powder River Basin coal measured at 22°C (Tang et al., 2005).
3.2 Pure $CO_2$ injection for $CH_4$ displacement

$CH_4$ saturated coal was the initial condition for this system. Pure $CO_2$ was injected to displace $CH_4$ at 450 psia and 22°C. Comparison of the effluent concentration is shown for various cases of changing each of the parameters in Table 3-1 and Table 3-2 in turn.

3.2.1 Coal density

Figure 3-2 shows the results of numerical simulations for the base case and the case of increased coal density. The result of increasing coal density by 20% is a delayed breakthrough of $CO_2$ shock front. This slower recovery is mainly due to the change in flow velocity through the effect of volume change on adsorption/desorption. The calculation of the amount of volume change for this sensitivity case compared to the base case is shown in Figure 3-3. Once $CO_2$ adsorbs on coal surface, the flowing gas loses some of its volume (130.76 cm$^3$). At the same time it has the volume gains back from $CH_4$ desorption (51.49 cm$^3$). However, the $CH_4$ volume that comes out is less than the volume of $CO_2$ adsorbed, because less $CH_4$ is adsorbed on the coal than $CO_2$. This volume change (79.27 cm$^3$ loss compared to 66.06 cm$^3$ in the base case) reduces the flow velocity. When the coal density increases, according to Eq. 2-12, the molar concentration of the adsorbed component increases; it is as if the coal has more coal particles to adsorb more $CO_2$. More adsorbed $CO_2$ causes more volume loss resulting in slower flow velocity.
Figure 3-2: Comparison between the base case of pure CO₂ displacing CH₄ and the case of increased coal density.

Figure 3-3: Amount of volume changes for the base case, increased coal density, and increased total porosity cases.
### 3.2.2 Total porosity

When gases flow through fracture networks, only primary porosity is involved in this convection-dominated flow. The secondary (matrix) porosity just takes part in adsorption process. At the same bulk volume of coal, an increase in total porosity without changing the primary porosity makes the coal have less grain volume compared to the base case; this change is opposite to when the coal density increases. From Figure 3-3, the amount of CO$_2$ adsorbed in this case is lower (100.41 cm$^3$ compared to the base case 108.97 cm$^3$). The volume gain from CH$_4$ desorption is also lower (3 cm$^3$ decreases from the base case), but this volume is relatively small. The flowing gas, therefore, has a faster breakthrough time, which is mainly due to a smaller volume loss of CO$_2$. Figure 3-4 shows the effect of increasing total porosity by 10% (from 0.44 to 0.484); the primary porosity remains at 0.34.

![Figure 3-4: Comparison between the base case of pure CO$_2$ displacing CH$_4$ and the case of increased total porosity.](image)

Figure 3-4: Comparison between the base case of pure CO$_2$ displacing CH$_4$ and the case of increased total porosity.
### 3.2.3 Secondary porosity

Keeping the total porosity constant and decreasing the secondary porosity by 50% (from 0.10 to 0.05) causes the volume of flow path to increase due to higher primary porosity. The flow velocity is then reduced, and the shock front travels more slowly (Figure 3-5). Eq. 2-6 shows the relation between the primary porosity and the flow velocity. If the primary porosity, in the denominator, increases, the flow velocity decreases.

![Figure 3-5: Comparison between the base case of pure CO\textsubscript{2} displacing CH\textsubscript{4} and the case of decreased secondary porosity.](image)

### 3.2.4 Physical dispersion

An increase in the physical dispersion is simply done by decreasing the physical Peclet number. Figure 3-6 shows the case where the Peclet number of 300 is reduced to 100. The flow velocity is not affected by this change; thus the breakthrough time is the same. However, after breakthrough it takes longer for CH\textsubscript{4} to completely come out because dispersion enhances CH\textsubscript{4} to mix back with CO\textsubscript{2} that flows behind. This smearing shock front is as expected when increasing dispersion.

---

18
Figure 3-6: Comparison between the base case of pure CO$_2$ displacing CH$_4$ and the case of increased physical dispersion.

3.2.5 CH$_4$ adsorption

The results of decreasing 30% of CH$_4$ adsorption can be seen from Figure 3-7. The calculations of the amount of volume change are shown in Figure 3-8. In this case, CH$_4$ has less volume that desorbs from coal (from 42.91 to 30.04 cm$^3$); the flow velocity is slightly lower. However, the volume of CH$_4$ from desorption is much smaller than the volume loss of CO$_2$ (108.97 cm$^3$) that adsorbed on to the coal surfaces. Thus, decreasing CH$_4$ adsorption does not significantly delay the breakthrough time, but, interestingly, a more self-sharpening shock front is observed.
Figure 3-7: Comparison between the base case of pure CO₂ displacing CH₄ and the case of decreased CH₄ adsorption.

Figure 3-8: Amount of volume changes for the base case, decreased CH₄ adsorption, and decreased CO₂ adsorption cases.
This result is corresponding to the analytical solution of that stronger adsorption gas displaces gas that has weaker sorption affinity. In this case CO₂ adsorption compared to those of CH₄ is even stronger. The solution is, as expected, closer to the shock solution. The more quantitative discussion on sharpening of the shock front will be presented later in this section.

3.2.6 CO₂ adsorption

Reducing sorption affinity of CO₂ by 30% (Figure 3-9) directly results in less volume loss of CO₂ due to adsorption (from 108.97 to 76.28 cm³) as shown in Figure 3-8. The flowing gas has more CO₂ volume (33.37 cm³ loss instead of 66.06 cm³) when compared to the base case; the flow velocity increases and causes an earlier breakthrough. It is obvious that adjusting the CO₂ adsorption causes a stronger effect than varying CH₄ adsorption (due to higher volume change). The flow velocity is, therefore, mostly controlled by the volume loss of CO₂. As opposite to the decreasing CH₄ adsorption case, decreasing adsorption of CO₂ affects in a less self-sharpening shock front.

![Figure 3-9: Comparison between the base case of pure CO₂ displacing CH₄ and the case of decreased CO₂ adsorption.](image-url)
3.2.7 Pressure

Increasing pressure causes three effects: higher density of flowing gas, and stronger sorption affinity of both CO₂ and CH₄. Increasing adsorption of CO₂ causes more volume loss of flowing CO₂. Meanwhile the volume gain from CH₄ increases due to stronger desorption. As discussed in the previous case, the effect of changing CO₂ adsorption is much more significant than adjusting sorption of CH₄. The flowing gas has less volume from effect of these sorption changes, which results in lower flow velocity and delayed breakthrough time.

However, when the density is higher, the volume of flowing gas decreases; this makes less difference in the volume of flowing CO₂ before and after adsorbing on coal surface. The flowing gas has less volume of CO₂ loss, and the flow velocity is then higher when compared to the base case. Thus, the effect of increasing density is faster breakthrough time.

When the effects of increasing sorption affinity and increasing gas density are combined, in this case (pressure increases from 450 psia to 600 psia), the effect of higher density is stronger. The effluent curves, therefore, show an earlier breakthrough time as in Figure 3-10. In addition, there is a change in sharpening of the shock front as observed in the cases of adjusting CH₄ and CO₂ adsorption.

Note that Figure 3-10 only demonstrates the simulation results at 600 psia compared to 450 psia. When selecting other pressures, the effects of sorption change and density change must be compared so that the final result can be predicted.
3.2.8 Volume of adsorbed phase

Figure 3-11 shows the result when the volume of adsorbed phased increases (Eq. 2-19). The hard sphere co-volume ($b_i$) is the only parameter that was adjusted in this case. When the values of $b_i$ for CO$_2$ and CH$_4$ are 100% higher, the volume of adsorbed gas is higher. The volume of flowing gas is lower, which results in less volume loss of CO$_2$. However, this adsorbed volume is small when compared to the volume of flowing gas. The flow velocity, thus, is only slightly faster than the base case.
3.2.9 Sorption hysteresis

In the case of neglecting the effects of sorption hysteresis, only the information from adsorption curves is used. From Figure 3-1, not having desorption curves in the model leads to lower CH₄ desorption (the simulator does not consider the effect of CO₂ hysteresis because it is the strongest adsorbing gas in this system). The flow velocity then slightly decreases due to the smaller volume gain from CH₄ that comes out of the coal surface. This smaller volume not only delays the breakthrough time, but it also sharpens the shock front as in the case of decreasing CH₄ adsorption. Figure 3-12 shows the later breakthrough time and more sharpening shock front when excluding sorption hysteresis.
Figure 3-12: Comparison between the base case of pure CO₂ displacing CH₄ and the case of excluding sorption hysteresis.

3.2.10 IAS model

Figure 3-13 shows the plot of molar concentration of adsorbate phase versus CH₄ mole fraction at 450 psia and 22 °C. The IAS model predicts slightly stronger CO₂ adsorption, and smaller CH₄ adsorption than the Langmuir model. The effluent result is then the combination of increasing CO₂ adsorption, and decreasing CH₄ adsorption as discussed earlier. The breakthrough time is delayed, and the shock front is more self-sharpening as seen in Figure 3-14.
Figure 3-13: Molar concentration of CH$_4$ and CO$_2$ in adsorbate phase at 450 psia and 22$^\circ$C predicted by the IAS and Langmuir models.

Figure 3-14: Comparison between the base case of pure CO$_2$ displacing CH$_4$ and the case of changing adsorption model to IAS.
3.2.11 Detailed discussion of sharpening of the shock front

In the numerical simulation, shocks are smeared by the effects of physical and numerical dispersion. On the other hand, from the analytical solution, the difference between upstream and downstream velocity tends to sharpen the front. In order for a shock to be stable, the propagation velocity upstream of the shock must be greater than or equal to the shock velocity, and the propagation velocity downstream of the shock must be lower than the shock velocity. If the difference in velocity across the shock is large, then the shock is strongly self-sharpening. Any smearing due to dispersion is opposed by the velocity difference. The sharpening and smearing effects from these three factors compete with each other and make the solution profile of each case look different. If the physical and numerical dispersion are fixed, the sharpening behavior should depend on the velocity difference. In binary systems, Zhu (2003) derived the expression for normalized eigenvalues in one-dimensional flow as

\[
\lambda^* = \frac{\phi \rho}{\phi \rho + (1 - \phi) \left( z_2 \frac{\partial a_1}{\partial z_1} - z_1 \frac{\partial a_2}{\partial z_1} \right)}.
\]

From Eq. 3-1, the component velocity is a function of porosity, gas density, coal density, and sorption of each gas. Normalized eigenvalue, local flow velocity, and characteristic wave velocity for each sensitivity case can be calculated as shown in Table 3-3. The last three rows contain the simulation results that show the spreading behavior of the shock wave. The parameter \( \Delta L \) is the difference (in PVI) between 90% and 10% concentrations on the CH\(_4\) effluent curve.

Figure 3-15 shows the plot of \( \Delta L \) versus \( \Delta \lambda \) for all the cases displayed in Table 3-3. It is evident that the larger the difference in characteristic wave velocity upstream and downstream (\( \Delta \lambda \)), the more self-sharpening the shock front is (smaller \( \Delta L \)).

It is important to note here that the changes in coal density and porosity also affect sharpening of the shock front, although in the sensitivity cases shown previously that
their effects are very small. For example, in the case of 20% increase in coal density it is quite difficult to distinguish between $\Delta L = 0.1867$ PVI and $\Delta L = 0.1946$ PVI. To demonstrate that coal density and porosity really affect sharpening of the front, the analytical calculation of the case that the effect of these parameters can be seen is made before running the simulation. Figure 3-16 shows that case where the total porosity is reduced to 22%.

Table 3-3: Variation of normalized eigenvalue, local flow velocity, and characteristic wave velocity for the sensitivity cases of CH$_4$-CO$_2$ binary system.

<table>
<thead>
<tr>
<th></th>
<th>Base Case</th>
<th>$\rho_{\text{coal}} + 20%$</th>
<th>$\Phi = 48.4%$</th>
<th>$\Phi = 22%$</th>
<th>CH$_4\text{ads} - 30%$</th>
<th>CO$_2\text{ads} - 30%$</th>
<th>$p = 600$ psia</th>
<th>$P_{\text{phys}} = 100$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\lambda^*_u$</td>
<td>0.6296</td>
<td>0.5862</td>
<td>0.6699</td>
<td>0.3789</td>
<td>0.7083</td>
<td>0.6296</td>
<td>0.6892</td>
<td>0.6296</td>
</tr>
<tr>
<td>$u_u$</td>
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<td>1.4171</td>
<td>1.4171</td>
<td>1.4171</td>
<td>1.4171</td>
<td>1.4171</td>
<td>0.9549</td>
<td>1.4171</td>
</tr>
<tr>
<td>$\lambda_u$</td>
<td>0.8922</td>
<td>0.8307</td>
<td>0.9493</td>
<td>0.5370</td>
<td>1.0038</td>
<td>0.8922</td>
<td>0.6581</td>
<td>0.8922</td>
</tr>
<tr>
<td>$\lambda^*_d$</td>
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<td>0.2912</td>
<td>0.3705</td>
<td>0.1504</td>
<td>0.3302</td>
<td>0.4133</td>
<td>0.3830</td>
<td>0.3302</td>
</tr>
<tr>
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<td>0.8715</td>
<td>0.8362</td>
<td>0.9075</td>
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<td>0.7652</td>
<td>1.0767</td>
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<td>0.8715</td>
</tr>
<tr>
<td>$\lambda_d$</td>
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<td>0.3363</td>
<td>0.1060</td>
<td>0.2527</td>
<td>0.4449</td>
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</tr>
<tr>
<td>$\Delta \lambda$</td>
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<td>0.5872</td>
<td>0.6131</td>
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<td>0.7511</td>
<td>0.4473</td>
<td>0.4044</td>
<td>0.6044</td>
</tr>
<tr>
<td>$P_{\text{e,numerical}}$</td>
<td>2222.22</td>
<td>2222.22</td>
<td>2222.22</td>
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<td>$P_{\text{e,physical}}$</td>
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<td>300</td>
<td>300</td>
<td>300</td>
<td>100</td>
</tr>
<tr>
<td>PVI @ 90% effluent conc.</td>
<td>1.9409</td>
<td>2.1924</td>
<td>1.5785</td>
<td>4.1800</td>
<td>1.9949</td>
<td>1.4544</td>
<td>1.4008</td>
<td>1.8940</td>
</tr>
<tr>
<td>PVI @ 10% effluent conc.</td>
<td>2.1276</td>
<td>2.3871</td>
<td>1.7430</td>
<td>4.4550</td>
<td>2.0950</td>
<td>1.8347</td>
<td>1.8709</td>
<td>2.1518</td>
</tr>
<tr>
<td>$\Delta L$ (PVI)</td>
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<td>0.1946</td>
<td>0.1645</td>
<td>0.2750</td>
<td>0.1000</td>
<td>0.3804</td>
<td>0.4700</td>
<td>0.2578</td>
</tr>
</tbody>
</table>
Figure 3-15: Effect of the difference between upstream and downstream velocity on sharpening of the shock front.

Figure 3-16: Comparison between the base case of pure CO$_2$ displacing CH$_4$ and the case of decreased total porosity from 44% to 22%.
3.3 Pure \( N_2 \) injection for \( CH_4 \) displacement

In this section the injection of \( N_2 \) through a coal saturated with \( CH_4 \) is examined. The production condition is 500 psia and 22°C. The parameters that affect the effluent curves are described as in the case of pure \( CO_2 \) displacement of \( CH_4 \).

When \( N_2 \) is injected, the partial pressure of \( CH_4 \) in the flowing gas decreases, and methane desorbs from the coal surface. The desorbed \( CH_4 \) is then driven by the flowing gas and reaches the outlet. Figure 3-17 shows the sensitivity study of this binary \( CH_4\)-\( N_2 \) case. Increasing coal density increases the amount of coal grain that initially adsorbs \( CH_4 \). Thus, it takes longer time for more \( CH_4 \) volume to completely come out after it reaches the outlet. This case is opposite to the case of increasing porosity Figure 3-18 which makes less coal grain to adsorb gases and results in faster recovery of all \( CH_4 \). Increasing physical dispersion (Figure 3-19), as expected, spreads the wave; however, its effect is quite small.

![Figure 3-17](image)

Figure 3-17: Comparison between the base case of pure \( N_2 \) displaces \( CH_4 \) and the case of increased 20% coal density.
Figure 3-18: Comparison between the base case of pure N\textsubscript{2} displaces CH\textsubscript{4} and the case of increased 10\% total porosity.

Figure 3-19: Comparison between the base case of pure N\textsubscript{2} displaces CH\textsubscript{4} and the case of increased physical dispersion by reducing Peclet number to 100.
Figure 3-20: Comparison between the base case of pure N\textsubscript{2} displaces CH\textsubscript{4} and the case of decreased 30\% CH\textsubscript{4} adsorption.

Figure 3-21: Comparison between the base case of pure N\textsubscript{2} displaces CH\textsubscript{4} and the case of decreased 30\% N\textsubscript{2} adsorption.
The parameter that significantly affects the solution is CH₄ adsorption. Decreasing it by 30% (Figure 3-20) reduces the amount of CH₄ adsorbed on coal surfaces, and it takes shorter time for this smaller volume to be recovered. The more sharpening wave is corresponding to the continuous solution of weaker adsorbing gas injection. When the difference of affinity between 2 gases is lower, less spreading occurs in the rarefaction. The opposite case is shown in Figure 3-21 where N₂ adsorption is reduced by 30%. It barely affects the solution because N₂ adsorbs very little compared to CH₄. However, its effect is a slightly faster recovery of CH₄ because the flow velocity increases due to lower N₂ adsorption. The rarefaction is also more spreading because of the greater difference between sorption affinities.

![Figure 3-22: Comparison between the base case of pure N₂ displaces CH₄ and the case of changing adsorption model to IAS.](image)

Figure 3-22 shows the case when using IAS model instead of extended Langmuir. The IAS model predicts stronger CH₄ and weaker N₂ adsorption as shown in the plot of molar concentration of adsorbate phase versus CH₄ mole fraction at 500 psia and 22 °C (Figure 3-23). The behavior in this example is then the result of the effects of increasing CH₄ and
decreasing $N_2$ adsorption. Gases come out faster, and the continuous solution is more spreading.

Figure 3-23: Molar concentration of CH$_4$ and N$_2$ in adsorbate phase at 500 psia and 22$^\circ$C predicted by the IAS and Langmuir models.
3.4 Displacement of CH$_4$ by a mixture of CO$_2$ and N$_2$

In this system, 55% by mole fraction of CO$_2$ and 45% of N$_2$ are injected to displace CH$_4$ at 475 psia and 22°C. The solution is like a superposition of pure CO$_2$ displacement of CH$_4$, and pure N$_2$ displacement of CH$_4$; a series of shocks and rarefactions occurs. CO$_2$ which has strongest affinity among these 3 gases comes out last because it loses volume due to adsorption; a discontinuous solution occurs for that portion of the flow. N$_2$ comes out before CO$_2$ because it adsorbs only weakly; the solution for this portion of the flow is a rarefaction.

![Figure 3-24: Comparison between the base case of mixture of CO$_2$ and N$_2$ (55:45) displacement of CH$_4$ and the case of increased 10% total porosity.](image)

The sensitivity results for this ternary system are similar to the binary cases. When the total porosity increases (Figure 3-24), the flow velocity is faster; the injected gases appears earlier at the outlet. Increasing physical dispersion (Figure 3-25) only smears the solution curves.
Figure 3-25: Comparison between the base case of mixture of CO$_2$ and N$_2$ (55:45) displacement of CH$_4$ and the case of increased physical dispersion by reducing Peclet number to 100.

Figure 3-26: Comparison between the base case of mixture of CO$_2$ and N$_2$ (55:45) displacement of CH$_4$ and the case of decreased 30% CH$_4$ adsorption.
The effects of decreasing CH$_4$ adsorption (Figure 3-26) are less spreading of N$_2$ rarefaction and more sharpening of CO$_2$ shock as in binary systems. The size of the N$_2$ peak depends on how fast the CO$_2$ shock front breaks through. The later time for CO$_2$ to reach the outlet, the larger the hump as the rarefaction continues to spread.

![Graph](image)

**Figure 3-27**: Comparison between the base case of mixture of CO$_2$ and N$_2$ (55:45) displacement of CH$_4$ and the case of decrease 30% CO$_2$ adsorption.

When the CO$_2$ adsorption decreases (Figure 3-27), the injected gases flow faster because there is less volume of CO$_2$ adsorbed; N$_2$ and CO$_2$ come out faster. The N$_2$ peak in this sensitivity case is then smaller, and the CO$_2$ shock front is less self-sharpening. Changing N$_2$ (Figure 3-28) adsorption does not significantly affects the solutions as N$_2$ adsorbs on coal much less when compared to the other gases. Moreover, it can be seen that changing N$_2$ adsorption has less effect on the solution as the injection continues.
Figure 3-28: Comparison between the base case of mixture of CO\textsubscript{2} and N\textsubscript{2} (55:45) displacement of CH\textsubscript{4} and the case of decreased 30\% N\textsubscript{2} adsorption.

Figure 3-29: Comparison between the base case of mixture of CO\textsubscript{2} and N\textsubscript{2} (55:45) displacement of CH\textsubscript{4} and the case of changing adsorption model to IAS.
The IAS model (Figure 3-29), qualitatively, predicts similar behaviors as in the extended Langmuir model. Nonetheless, the adsorption amounts of each gas substantially change as shown in Figure 3-30. The IAS model predicts stronger CO$_2$ adsorption; thus the major difference is the delayed breakthrough time of CO$_2$. The CO$_2$ front is more self-sharpening due to the effects of weaker CH$_4$ and stronger CO$_2$ adsorption. The N$_2$ peak, in this case, is not growing bigger as in the case of decreasing CH$_4$, but continues to spread out instead. This is because from Figure 3-30 the decrease in sorption affinity of N$_2$ (roughly 60%) is much more than the decrease in CH$_4$ adsorption (5-10%). The weaker N$_2$ adsorption, therefore, has a stronger effect on altering the rarefaction behavior.

![Figure 3-30: Molar concentration of CH$_4$, CO$_2$, and N$_2$ in adsorbate phase at 475 psia and 22°C predicted by the IAS and Langmuir models.](image)
Chapter 4

4. Matching the experiments

The results of the systematic study of the sensitivity of displacement behavior to simulation parameters were used to match the single phase displacement experimental results obtained by Parakh (2007). Three systems of interest are pure CO$_2$ displacement of CH$_4$ at 450 psia, pure N$_2$ displacement of CH$_4$ at 500 psia, and displacement of CH$_4$ by a mixture of CO$_2$ and N$_2$ (55:45) at 475 psia. The operating conditions for each system are as presented in the base case of simulation study in Chapter 3. The same coal pack was used in all the experiments. The coal pack data are the same as in the input parameters in Table 3-1. The sorption isotherm is as summarized in Table 3-2 and Figure 3-1. Simple analytical solutions for binary mixture were constructed to help on parameter selection and also to verify the simulation results. Initially, the extended Langmuir isotherm was used in the simulator to fit the adsorption data. Once it gave a reasonable match, the IAS model was used. Finally, the results from both models are compared.

4.1 First Trial

Figure 4-1 shows the matching results for the first attempt. For N$_2$ displacement of CH$_4$ (Figure 4-1b), the effluent composition curves show a big difference between experimental and simulated data. The knowledge from sensitivity studies in Chapter 3 indicates that the total porosity is too low and/or the CH$_4$ adsorption is too strong. In the case of 55/45 CO$_2$/N$_2$ mixture displacing CH$_4$ (Figure 4-1c), when compared to the experiment, the simulated results show a delayed breakthrough time for CO$_2$. The explanations for this unmatched result are that the flow velocity is too slow, which is possibly caused by exaggerated CO$_2$ adsorption and/or too low porosity. Figure 4-1a, which is the system of CO$_2$ displacement of CH$_4$, agrees well with the experimental
results, but tuning some parameters to make a reasonable match in other cases also changes the results for this system.

Figure 4-1: Comparison (before tuning) of experimental (symbols) and simulated (full lines) results for (top panel) pure CO$_2$ displaces CH$_4$ at 450 psia, (middle panel) pure N$_2$ displaces CH$_4$ at 500 psia, and (bottom panel) mixture of CO$_2$ and N$_2$ (55:45) displaces CH$_4$ at 475 psia.
4.2 Tuning the Parameters

The common problem found from the first trial is the stronger sorption affinity used in the simulator than in the experiments. Material balance calculations were performed and the results are shown in Table 4-1. The measurement data are taken from Parakh (2007). It is clear that when using the sorption parameters as in Table 3-2, the calculation is not consistent with the measured values from the experiment. All the three systems show too much adsorption of CH$_4$, CO$_2$, and N$_2$. It is possible that the coal used in the experiments might have been oxidized and the sorption affinity reduced significantly. Hence, the sorption affinity was adjusted to improve the match.

Table 4-1: Material balance calculation for the case of CO$_2$ displaces CH$_4$, N$_2$ displaces CH$_4$, and 55/45 CO$_2$/N$_2$ mixture displaces CH$_4$ (before tuning).

<table>
<thead>
<tr>
<th></th>
<th>CO$_2$ displaces CH$_4$</th>
<th>N$_2$ displaces CH$_4$</th>
<th>55/45 CO$_2$/N$_2$ displaces CH$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Gmoles (measured)</td>
<td>Gmoles (calculated)</td>
<td>Gmoles (measured)</td>
</tr>
<tr>
<td>Amount of CH$_4$ injected initially</td>
<td>0.0925</td>
<td>0.1443</td>
<td>0.1</td>
</tr>
<tr>
<td>CH$_4$ present in pore space</td>
<td>-</td>
<td>0.0856</td>
<td>-</td>
</tr>
<tr>
<td>CH$_4$ adsorbed in matrix</td>
<td>-</td>
<td>0.0587</td>
<td>-</td>
</tr>
<tr>
<td>Amount of CH$_4$ produced</td>
<td>0.0918</td>
<td>-</td>
<td>0.097</td>
</tr>
<tr>
<td>Amount of injected gases trapped in coal</td>
<td>0.188</td>
<td>0.2734</td>
<td>0.073</td>
</tr>
</tbody>
</table>

After decreasing sorption affinity of each gas, the effluence curves for the N$_2$ displacement of CH$_4$ match better. However, for CO$_2$ displacement of CH$_4$ and CO$_2$/N$_2$ displacement of CH$_4$, the CO$_2$ front now moves faster, and it breaks through earlier than was observed in the experiments. Thus, porosity, which is another parameter that affects flow velocity, was adjusted.
Analytical calculation for CO\textsubscript{2} displacement of CH\textsubscript{4}, which gives a shock solution, was performed to help in tuning up the parameters. The flow velocity can be varied by adjusting the sorption isotherm and porosity; the breakthrough time calculated from the analytical solution was then compared to the experimental results in order to determine their appropriate values. Figure 4-2 shows one of the adjustments that gives an acceptable match. In this case, the total porosity is reduced from 44\% to 42\%, and the secondary porosity has to be as small as 0\% in order to make the shock front slower. This adjustment is quite reasonable because that 44\% total porosity is averaged from several set of measurements. The value of 42\% is still in the acceptable range. Although a secondary porosity of coal is typically around 2 to 8\% (Resnik \textit{et al.}, 1984), in this experiment coal is crushed into very small powder and packed into a slimtube. It is not a bad assumption to treat it like a single porosity porous medium of 42\% total porosity.

![Figure 4-2: Comparison of analytical solution (dashed lines), experimental (symbols), and simulated results (full lines) for pure CO\textsubscript{2} displaces CH\textsubscript{4} system.](image)

Table 4-2 shows the material balance calculations after the adjustment described above. New Langmuir sorption characteristics compared to the original one are shown in Figure 4-3. New Langmuir constants are summarized in Table 4-3. Note that these values are roughly approximated based on material balance calculations from all 3 experiments.
Table 4-2: Material balance calculation for the case of CO$_2$ displaces CH$_4$, N$_2$ displaces CH$_4$, and displacement of CH$_4$ by a 55/45 CO$_2$/N$_2$ mixture (after tuning).

<table>
<thead>
<tr>
<th></th>
<th>CO$_2$ displaces CH$_4$</th>
<th>N$_2$ displaces CH$_4$</th>
<th>55/45 CO$_2$/N$_2$ displaces CH$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Gmoles (measured)</td>
<td>Gmoles (calculated)</td>
<td>Gmoles (measured)</td>
</tr>
<tr>
<td>Amount of CH$_4$ injected initially</td>
<td>0.0925</td>
<td>0.0925</td>
<td>0.1</td>
</tr>
<tr>
<td>CH$_4$ present in pore space</td>
<td>-</td>
<td>0.0817</td>
<td>-</td>
</tr>
<tr>
<td>CH$_4$ adsorbed in matrix</td>
<td>-</td>
<td>0.0108</td>
<td>-</td>
</tr>
<tr>
<td>Amount of CH$_4$ produced</td>
<td>0.0918</td>
<td>-</td>
<td>0.097</td>
</tr>
<tr>
<td>Amount of injected gases trapped in coal</td>
<td>0.188</td>
<td>0.1883</td>
<td>0.073</td>
</tr>
</tbody>
</table>

Figure 4-3: Sorption characteristics based on material balance calculations (full lines) and their original values (dashed lines).
Table 4-3: Langmuir adsorption constants based on material balance calculations.

<table>
<thead>
<tr>
<th></th>
<th>Adsorption</th>
<th>Desorption</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$V_m$ (SCF/ton)</td>
<td>$b$ (1/psia)</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>310</td>
<td>0.0007</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>1230</td>
<td>0.0024</td>
</tr>
<tr>
<td>N$_2$</td>
<td>100</td>
<td>0.001</td>
</tr>
</tbody>
</table>

4.3 Final Results

Figure 4-4 shows the simulated results after tuning the parameters. Both Langmuir and IAS models are compared to the experiments. Their results are just slightly different. The IAS model predicts stronger adsorption of CO$_2$ than the extended Langmuir isotherm as shown in Figure 3-13 and Figure 3-30, and therefore the CO$_2$ fronts in the CO$_2$ displacement of CH$_4$ (top panel) and the displacement of CH$_4$ by CO$_2$/N$_2$ systems (bottom panel) move slower. The shock is also more self-sharpening in the IAS model. In the N$_2$ displacement of CH$_4$ (middle panel), the simulated results from both models are close to each other, but the IAS predicts more spreading curves mainly due to more CH$_4$ adsorption as in shown Figure 3-23. In the attempt of fitting the simulated results in the ternary case, both models show early breakthrough of CO$_2$ in the binary case.

Note that the matching was first done by using the extended Langmuir isotherm. Once the acceptable matches were achieved, all the same input parameters were used to generate the results predicted by the IAS model. It does not imply that the extended Langmuir is more accurate than the IAS model. In the ternary system (bottom panel of Figure 4-4), the effluent curves from the IAS model can be matched better by a slight decrease in CO$_2$ adsorption and/or increasing porosity. However, these adjustments would slightly affect the solutions in the binary systems.
Figure 4-4: Comparison (after tuning) of experimental (symbols) and simulated results (lines) for (top panel) pure CO$_2$ displaces CH$_4$ at 450 psia, (middle panel) pure N$_2$ displaces CH$_4$ at 500 psia, and (bottom panel) mixture of CO$_2$ and N$_2$ (55:45) displaces CH$_4$ at 475 psia.
Chapter 5

5. Application to Acid Gas Injection

An attempt to reduce atmospheric emissions does not only focus on greenhouse gases (CO$_2$), but in some settings where CO$_2$ is separated (natural gas separations or coal gasification, for example), acid gases, for example H$_2$S and SO$_2$, are necessary to be handled. One alternative is to dispose of these gases underground. In this chapter, the simulator is applied to the case of acid gas injection in which the system is single phase. Table 5-1 shows the composition of gases in the Weyburn pipeline from the Great Plains Synfuels Plant (Beulah, North Dakota), to the Weyburn enhanced oil recovery project in Saskatchewan. CO$_2$ is the main component at a concentration of 97%. The remaining components include 1% H$_2$S which is the acid gas, and small amounts of CH$_4$, C$_2$+ hydrocarbons, CO, O$_2$, and N$_2$.

Table 5-1: Gas composition in Weyburn pipeline (IPCC Special Report on Carbon dioxide Capture and Storage).

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$</td>
<td>96.8%</td>
</tr>
<tr>
<td>H$_2$S</td>
<td>1.1%</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>0.3%</td>
</tr>
<tr>
<td>C$_2$+</td>
<td>1%</td>
</tr>
<tr>
<td>Others (CO, O$_2$, N$_2$)</td>
<td>0.8%</td>
</tr>
</tbody>
</table>

A numerical simulation was performed to investigate how these gas components migrate through coal. CO, O$_2$, and N$_2$ are grouped into together so that the system has total of 5 components. Sorption parameters of each gas used in the simulator are summarized in Table 5-2. These values are not from the laboratory measurement, but are assumed to be reasonable to the characteristics of each gas instead just for the purpose of study.
It can be seen from Table 5-2 that H$_2$S is more strongly adsorbed than CO$_2$. If all these gases are injected together into coal, H$_2$S will propagate slower and can be stored in coal beds as well as CO$_2$.

Table 5-2: Langmuir adsorption constants for acid gas components.

<table>
<thead>
<tr>
<th>Component</th>
<th>Adsorption</th>
<th>Desorption</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$V_m$ (SCF/ton)</td>
<td>$b$ (1/psia)</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>1230</td>
<td>0.0024</td>
</tr>
<tr>
<td>H$_2$S</td>
<td>1760</td>
<td>0.00521</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>310</td>
<td>0.0007</td>
</tr>
<tr>
<td>C$_2+$</td>
<td>400</td>
<td>0.0025</td>
</tr>
<tr>
<td>Others</td>
<td>100</td>
<td>0.001</td>
</tr>
</tbody>
</table>

Figure 5-1 shows the composition profile of this 5-component displacement. The difference in breakthrough time indicates that each gas flows at a different velocity, and the components separate from each other. Their separations depend on how strong they adsorb on coal surface. In this case the pseudocomponent of CO, O$_2$, and N$_2$, which is the weakest adsorbing gas, flows fastest because it least strongly adsorbed. The solution profile of this gas is a rarefaction because it has weaker sorption affinity compared to CH$_4$ that is originally adsorbed. The recovery is then followed by the second weakest adsorbing gas, C$_2+$. Because C$_2+$ adsorbs more strongly than CH$_4$, its front is a smeared shock. Next to C$_2+$, CO$_2$, which is the next most strongly adsorbing gas, reaches the outlet. The breakthrough time of H$_2$S is the latest, after 3 PVI. This slowest propagation velocity clearly shows that it is the component with the strongest sorption affinity.

The behaviors predicted by the extended Langmuir isotherm and the IAS model are even more different in this 5-component system. When the number of component increases, the sorption phenomena are more complex. The difference between the simple mathematical model (Langmuir) and the more complicated model that considers
thermodynamic equilibrium (IAS) is more significant. From Figure 5-1, the IAS model predicts different sorption affinity for each gas, and the separations of the results from both models are more distinguish in the components that strongly adsorb on coal.

![Figure 5-1: Effluent composition of acid-gas injection (5-component displacement).](image)

This example suggests that it might be feasible to produce CH₄ from coal beds and store CO₂ and H₂S at the same time. If the injection stops before 1.6 PVI, CO₂ and H₂S can be trapped. CO₂, which flows faster, is stored farther away from the producer, while H₂S is just retained near the injector. This sequestration strategy can also be applied to any other gases that have stronger sorption affinity than CO₂.
Chapter 6

6. Conclusions

6.1 \textit{CH}_4-\textit{CO}_2\,\textit{binary system}

A shock solution occurs when CO\textsubscript{2} displaces CH\textsubscript{4} because CO\textsubscript{2} has higher affinity for coal than that of CH\textsubscript{4}. The difference in effluent curves for the sensitivity cases show changes in the breakthrough time and sharpening of the shock front. The factor that directly affects the breakthrough time is flow velocity. Variation in flow velocity is caused by volume change of flowing gas due to adsorption and desorption. If the flowing gases have more volume, the flow velocity increases, which results in faster breakthrough time, and vice versa.

The sharpening of the shock front is affected by physical dispersion, numerical dispersion, and the difference in upstream and downstream velocity of the shock front. The dispersion can be controlled by adjusting the Peclet number. Smaller Peclet number means the flow is more dispersive; the shock front is more smeared. By contrast, larger Peclet number (less dispersive) makes the shock more self-sharpening.

The composition velocity ($\lambda$) is a complicated function of porosity, coal density, gas density, amount of gas sorption, and molar composition. When the difference between upstream and downstream composition velocity increases, a shock front tends to be more sharpening. The effect of smearing can be seen when these characteristic wave velocities are less different.
6.2 $CH_4$-$N_2$ binary system

For the case of less strongly adsorbing $N_2$ displace $CH_4$, the result is a continuous solution or rarefaction. The main parameters that affect the solution are related to $CH_4$ adsorption: coal density, porosity, adsorption model, and $CH_4$ adsorption itself. Varying coal density and/or porosity change the amount of $CH_4$ adsorbed. For example, if the coal density is higher (this is equivalent to lower porosity), more $CH_4$ adsorbs on coal surfaces, and it takes longer for all $CH_4$ to be recovered at the outlet. The rarefaction is then more spreading. By contrast, if the $CH_4$ adsorption is lower, the solution spreads less.

Other parameters such as $N_2$ adsorption are less significant because $CH_4$ adsorbs much more strongly when compared to $N_2$. The solution for the adjusting $N_2$ adsorption case is almost unchanged.

6.3 $CH_4$-$CO_2$/$N_2$ ternary system

The solution for mixture of $CO_2$/$N_2$ displaces $CH_4$ can be thought of as a combination of $CH_4$-$CO_2$ and $CH_4$-$N_2$ binary systems: $N_2$ rarefaction occurs first followed by the $CO_2$ shock. The size of $N_2$ bank grows larger until the $CO_2$ front breakthrough. Parameters that affect the solution are similar to those described in the binary systems. Increasing porosity speeds up the flow. Varying sorption creates the change in solution profiles that depends on how strong of gas adsorption/desorption. For example, changing the volume loss (due to adsorption) of $CO_2$, which has the strongest sorption affinity among these 3 gases, causes significant change in the flowing gas velocity, while adjusting $N_2$ adsorption, which is smaller than the others, almost has no effect on the solution.
6.4 Recommendations for model matching

1. Based on the experience from this work, the flow velocity is strongly affected by porosity and sorption characteristics of each gas. Small adjustments of these key parameters would change the solution significantly. Hysteresis is also necessary to be included into the model to predict both adsorption and desorption processes accurately.

2. Material balance calculations based on experimental results (Table 4-2) are an effective tool to check whether the measured parameters are consistent or not. It was noticed in this study that sorption affinity might change significantly when coal was kept for a long time and exposed to the atmosphere; this fact makes the prior measurement less accurate.

3. Analytical solutions, as constructed in Figure 4-2, assist in tuning up the simulator. Important parameters can be varied and the results can be quickly estimated in advance before running the simulation.

6.5 Application to multicomponent displacement

In multicomponent displacement each gas flows at different velocities, and separates from other components based on their sorption affinities. Components that adsorb most strongly propagate most slowly, while those that adsorb least strongly move fastest. In acid gas injection, for example, C\textsubscript{1}, C\textsubscript{2+}, and other gases already come out, while CO\textsubscript{2} and H\textsubscript{2}S, which move slower, are still retained in coal.
Nomenclature

\( a_i \) = molar concentration of component \( i \) adsorbed/desorbed on the coal surface

\( b_i \) = the hard-sphere co-volume of component \( i \) in PR-EOS

\( B_i \) = Langmuir constant at a specified temperature for component \( i \)

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

CFL = Courant-Friedrichs-Lewy number

\( f_i^0 \) = fugacity of pure component \( i \) in the adsorbed mixture

\( K_l \) = longitudinal dispersion coefficient

\( L \) = system length

\( n_i \) = adsorbed amount of component \( i \) (scf of gas/ton of coal)

\( n_i^o \) = adsorbed amount of pure component \( i \)

\( n_a \) = adsorbed amount predicted by adsorption curve

\( n_d \) = adsorbed amount predicted by desorption curve

\( n_s \) = adsorbed amount predicted by scanning curve

\( p \) = pressure

\( p_i^0 \) = equilibrium gas-phase pressure for the adsorption of pure component \( i \)

\( Pe \) = Peclet number

\( Pe_{num} \) = numerical Peclet number

\( Pe_{phys} \) = physical Peclet number

\( v \) = average flow velocity of the gas phase (interstitial velocity)

\( v_D \) = dimensionless flow velocity

\( v_{inj} \) = injection velocity

\( v_{max} \) = maximum propagation speed for a displacement
\[ V_{ads} = \text{volume of adsorbed phase} \]
\[ V_{gas} = \text{volume of flowing gas phase} \]
\[ V_{m,i} = \text{maximum amount of adsorption of component } i \]
\[ x_i = \text{mole fraction of component } i \text{ in the adsorbed phase} \]
\[ y_i = \text{mole fraction of component } i \text{ in the gas phase} \]
\[ z_i = \text{mole fraction of component } i \]

**Greek Symbols**

\[ \xi = \text{dimensionless distance} \]
\[ \tau = \text{dimensionless time} \]
\[ \rho_{i,\text{std}} = \text{molar density of component } i \text{ at standard conditions} \]
\[ \rho_r = \text{density of coal} \]
\[ \rho_y = \text{molar density of the gas phase} \]
\[ \phi = \text{porosity of coal} \]
\[ \phi_1 = \text{primary (fracture) porosity} \]
\[ \phi_2 = \text{secondary (grain) porosity} \]
\[ \gamma_i = \text{activity coefficient of component } i \]
\[ \varphi_i = \text{fugacity coefficient of component } i \text{ in the gas phase} \]
\[ \Pi = \text{spreading pressure} \]
\[ \lambda^* = \text{normalized composition velocity} \]
\[ \lambda_d = \text{downstream composition velocity} \]
\[ \lambda_u = \text{upstream composition velocity} \]
References


