CO₂ leakage in shallow aquifers: A benchmark modeling study of CO₂ gas evolution in heterogeneous porous media

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Abstract

The physicochemical processes associated with CO₂ leakage into shallow aquifer systems are complex and span multiple spatial and time scales. Continuum-scale numerical models that faithfully represent the underlying pore-scale physics are required to predict the long-term behavior and aid in risk analysis regarding regulatory and management decisions. This study focuses on benchmarking the numerical simulator, FEHM, with intermediate-scale column experiments of CO₂ gas evolution in homogeneous and heterogeneous sand configurations. Inverse modeling was conducted to calibrate model parameters and determine model sensitivity to the observed steady-state saturation profiles. It is shown that FEHM is a powerful tool that is capable of capturing the experimentally observed outflow rates and saturation profiles. Moreover, FEHM captures the transition from single- to multi-phase flow and CO₂ gas accumulation at interfaces separating sands. We also derive a simple expression, based on Darcy's law, for the pressure at which CO₂ free phase gas is observed and show that it reliably predicts the location at which single-phase flow transitions to multi-phase flow.

Keywords: Carbon Sequestration, CO₂ Leakage, Exsolution, Multiphase Flow, FEHM

1. Introduction

Long-term storage of CO₂ in geologic formations is one of the most promising technologies aimed at significantly reducing anthropogenic carbon emissions (Pacala and Socolow, 2004). Substantial reductions in emissions will require large quantities of injected CO₂, resulting in CO₂ plumes that could occupy areas of 100 km², or more, which will likely intersect leakage pathways out of intended storage formations (Pruess, 2008). Moreover, the injected CO₂ will displace large quantities of brine, some of which is CO₂-saturated. Thus, the potential for leaked CO₂ or displaced brine to migrate into shallow groundwater aquifers is a concern that must be addressed. This requires knowledge of the physicochemical processes associated with

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CO₂ flow and transport, as well as tools (i.e., numerical models) that can capture these processes and predict long-term behavior.

Possible leakage scenarios and their associated physicochemical processes have been described in the literature (e.g., Pruess, 2008; Plampin et al., 2014a). In this work, we focus on CO₂ gas evolution through shallow aquifers, where evolution refers to the combined processes of CO₂ gas exsolution, accumulation, and free phase migration. These processes are complex and span multiple spatial and time scales. In this leakage scenario CO₂ is initially dissolved in displaced brine that migrates through the aquifer where CO₂ bubbles can exsolve out of solution due, in part, to decreases in pore pressure. These bubbles may either rise individually through the pore space due to buoyant forces (e.g., Corapcioglu et al., 2004; Oldenburg and Lewicki, 2006) or expand while trapped, forming gas clusters that invade pores through invasion-percolation (e.g., Li and Yortsos, 1995a,b; Dominguez et al., 2000). As more gas exsolves, the bubbles and gas clusters coalesce to form a continuous CO₂ gas phase capable of migrating throughout the aquifer. The minimum gas saturation at which a continuous free phase gas forms and becomes mobile is known as the critical gas saturation, S_{gc} . This parameter is important for describing CO₂ gas evolution with continuum models since they rely on the concept of a representative elementary volume (REV), and therefore cannot account for bubble nucleation and exsolution dynamics at the pore scale. Although S_{gc} is a parameter of significant importance, ambiguity still exists regarding its definition, and reported experimental values vary widely (e.g. Du and Yortsos, 1999; Sheng et al., 1999; Tsimpanogiannis and Yortsos, 2004, and references therein).

Heterogeneities are ubiquitous in the subsurface and are expected to affect the evolution of CO₂ gas. However, most laboratory studies have focused on bubble and cluster dynamics in homogeneous micromodels (e.g., Li and Yortsos, 1995b; Du and Yortsos, 1999; Tsimpanogiannis and Yortsos, 2004; Zuo et al., 2013) or free phase migration in homogeneous sands and rocks (e.g., Fry et al., 1997; Enouy et al., 2011; Zuo et al., 2012; Krevor et al., 2012; Falta et al., 2013; Zuo and Benson, 2014). Recently, Sakaki et al. (2013) and Plampin et al. (2014a,b) conducted intermediate-scale CO₂ gas evolution experiments in homogeneous and heterogeneous sand configurations. They showed that simple heterogeneities had significant effects on CO₂ gas evolution, especially at interfaces between coarse and fine sands where they observed increased accumulation of CO₂ in coarse sands when located underneath a layer of fine sand. In addition, they observed values for S_{gc} ranging from 0.2 to 0.4 within their sands.

Although several numerical simulators have been developed specifically for CO₂ sequestration and leakage applications (e.g., Class et al., 2009), benchmark studies involving comparisons with laboratory experiments are scarce. In fact, we are aware of only one such study conducted by Enouy et al. (2011), in which they compared their model to CO₂ gas evolution column experiments in homogeneous glass beads and sands. In their model, they assumed rate-limited mass transfer of CO₂ from aqueous to gas phase and showed that advection of the gas phase is adequately modeled with the classical extension of Darcy's law for multi-

phase flow and conventional constitutive relationships. However, recent experimental studies have suggested that non-conventional relative permeability relationships may be required to accurately represent CO₂ gas evolution in porous media (Krevor et al., 2012; Falta et al., 2013; Zuo and Benson, 2014). In fact, Zuo and Benson (2014) conducted microtomography experiments comparing CO₂ gas exsolution and immiscible displacement and concluded that the traditional model parameters and constitutive relationships are process-dependent. Similar observations have been reported in oil- and gas-water systems (e.g. Fishlock et al., 1988; Grattoni et al., 2001). Thus, there is a need to benchmark existing numerical simulators with experimental observations and test conventional parameterization methods for these models, especially in heterogeneous media.

Accordingly, the objective of this work is to assess how well the numerical simulator, FEHM (<https://fehm.lanl.gov>), can capture CO₂ gas evolution in the homogeneous and heterogeneous intermediate-scale CO₂ leakage experiments conducted by Plampin et al. (2014a,b). In Section 2, we provide a brief summary of the experiments followed by a detailed description of FEHM and the simulations. FEHM differs from the model employed by Enouy et al. (2011) in that equilibrium mass transfer of CO₂ from aqueous phase to gas phase is assumed, which is calculated using a variable-switching method Forsyth and Sammon (1984). Based on the lack of model parameter data for CO₂ gas and water, we conducted inverse modeling using PEST (<http://www.pesthomepage.org>) to estimate suitable parameter values and determine model sensitivity. In addition, we developed a simple analytic expression, based on single-phase flow theory, to estimate the critical pressure at which CO₂ can exsolve out of solution to form free phase CO₂ gas. Plampin et al. (2014a, Sec. 3.1 & Fig. 4), developed a similar expression based on Henry’s law and hydrostatic conditions within the column. However, we have extended that relationship to account for the additional pressure drop due to flow, which is applicable to both homogeneous and heterogeneous systems. The results are presented in Section 3, where we compare experimental and simulated outflow rates and steady-state saturation profiles. In addition, we show that there is agreement between experiments, numerical simulations, and theory for the depth at which CO₂ evolution is observed and that FEHM captures CO₂ gas accumulation at interfaces between different sands. We conclude with a summary and discussion regarding the implications of this work for shallow aquifer systems in Section 4.

2. Methods

2.1. Experimental System

Here, we summarize the most important features of the experiments, complete details can be found in Plampin et al. (2014a,b). Figure 1 illustrates the experimental systems and sand configurations, which consisted of two different columns. The first column was 4.5 m tall by 0.06 m diameter (hereafter called the long column) packed with two homogeneous and three heterogeneous sand configurations. The second

column was 1.68 m tall by 0.06 m diameter (hereafter called the short column) packed with two heterogeneous sand configurations and equipped with a water reservoir to allow for different hydrostatic pressures within the column. The properties of the three sands used in the experiments are provided in Table 1. Prior to each experiment, the column was initially saturated with DI water. In each experiment, CO₂-saturated water was injected into the bottom of the column at a constant volumetric flow rate of 4 cm³min⁻¹. The Capillary and Bond numbers ranged from 5.38×10^{-8} to 1.6×10^{-8} and 3.91×10^{-6} to 5.07×10^{-5} , respectively. In the experiments with higher Bond number (coarse and medium sands), it is reasonable to assume that there was a stable gas phase invasion front. In the cases with lower Bond numbers (fine sands) it is possible that the gas phase front was unstable.

The hydrostatic pressure at the injection port (hereafter, referred to as the injection pressure, P_{inj}) in the long column was 39.2 kPa. The injection pressure in the short column was variable and ranged from 17.1 to 25.9 kPa. The amount of dissolved CO₂ in the injected CO₂-saturated water was specified by the saturation pressure, P_{sat} , which ranged from 10 to 50 kPa. Saturation sensors were placed at several locations throughout the column (see Fig. 1) and measurements were recorded every minute to observe the evolution of CO₂ gas within the column. The saturation sensors provide measurements for a 3x1x5.5 cm³ averaging volume and were placed in the sand sufficiently far away from any heterogeneous interface to ensure the saturation measurements were representative of the sand in which it was packed (Sakaki et al., 2011).

Table 1: Experimental sand properties (Sakaki et al., 2013)

	Coarse	Medium	Fine
Accusand #	12/20	30/40	50/70
Mean Particle Diameter (mm)	1.04	0.52	0.27
Permeability (m ²)	3.8×10^{-10}	1.1×10^{-10}	3.0×10^{-11}
Porosity	0.32	0.33	0.34
Air Entry Pressure (kPa)	0.8	1.6	3.4
Uniformity Coefficient	1.23	1.21	1.20

2.2. FEHM Model & Simulations

The experiments described in Sect. 2.1 were modeled using FEHM (Finite Element Heat and Mass Transfer), a porous media multi-phase flow simulator with the ability to solve fully coupled heat, mass, and stress balance equations (Zyvoloski et al., 2011). The code is based on a control volume finite element (CVFE) discretization approach with the flexibility to use unstructured grids, and a Newton-Raphson iteration scheme is used in which the discretized balance equations are solved using pre-conditioned Krylov space solvers with generalized minimal residual (GMRES) or biconjugate gradient stabilized (BCGSTAB) acceleration. FEHM

Figure 1: Illustration of the experimental systems and sand configurations within the columns. The circles within the column represent the locations of the saturation sensors. Adapted from Plampin et al. (2014a,b)

has been used extensively for several applications including those addressing CO₂ sequestration (e.g., Class et al., 2009) and CO₂-Brine leakage in shallow aquifers (e.g., Keating et al., 2012, 2013).

In the context of this work, two mobile phases (water and CO₂ gas) are considered with water and CO₂ as components. The conservation of mass for water is expressed as

$$\frac{\partial}{\partial t} \phi [\rho_{\text{CO}_2} S_{\text{CO}_2} Y_w + \rho_w S_w X_w] + \nabla \cdot [Y_w \rho_{\text{CO}_2} \mathbf{v}_{\text{CO}_2} + X_w \rho_w \mathbf{v}_w] + \nabla \cdot [\mathbf{D}_{\text{CO}_2} \rho_w \nabla X_{\text{CO}_2}] + q_w = 0 \quad (1)$$

where ϕ is the porosity, S is the saturation, ρ is the density, X is the fraction of total mass of a given component within the water phase, Y is the fraction of total mass of a given component within the CO₂ gas phase, $\mathbf{v}$ is the velocity, $\mathbf{D}_{\text{CO}_2}$ is the CO₂ diffusivity, q_w is a water source or sink, and the subscripts CO₂ and w represent the CO₂ gas and water phases, respectively. In this work we do not consider water in the CO₂ phase so Eq. (1) can be simplified since $Y_w = 0$. The CO₂ diffusivity is defined as $\mathbf{D}_{\text{CO}_2} = \tau \phi D_{\text{CO}_2}^0 S_w \mathbf{I}$, where τ is the tortuosity and $D_{\text{CO}_2}^0$ is the CO₂ diffusion coefficient. The conservation of mass for CO₂ is

expressed as

$$\frac{\partial}{\partial t} \phi [\rho_{\text{CO}_2} S_{\text{CO}_2} Y_{\text{CO}_2} + \rho_w S_w X_{\text{CO}_2}] + \nabla \cdot [Y_{\text{CO}_2} \rho_{\text{CO}_2} \mathbf{v}_{\text{CO}_2} + X_{\text{CO}_2} \rho_w \mathbf{v}_w] + q_{\text{CO}_2} = 0 \quad (2)$$

where q_{CO_2} is a CO_2 source or sink. The following constraints also apply

$$S_{\text{CO}_2} + S_w = 1 \quad (3)$$

$$X_{\text{CO}_2} + X_w = 1 \quad (4)$$

$$Y_{\text{CO}_2} + Y_w = 1 \quad (5)$$

To complete the governing equations it is assumed that Darcy's law applies for the momentum of each phase

$$\mathbf{v}_i = \frac{k k_i}{\mu_i} (\nabla P_i - \rho_i g) \quad (6)$$

where k is the intrinsic permeability, k_i is the relative permeability, μ is the viscosity, P is the pressure, g is gravity, and the subscript $i = \text{CO}_2, w$. The phase pressures are related by $P_c = P_{\text{CO}_2} - P_w$, where P_c is the capillary pressure with the functional form given by van Genuchten (1980).

In FEHM, the density of water is dynamically calculated according to spatially and temporally varying pressure, temperature, salt concentration (Hass, 1976), and dissolved CO_2 concentration (Garcia, 2001). The solubility of CO_2 is calculated using the formulation of Duan et al. (2008), which takes into account variations in pressure, temperature, and salt concentration. We note that salt concentration is not applicable in this work since the experiments were conducted with DI water. The development of CO_2 gas phase is estimated through a variable-switching approach. At each time step, the dissolved CO_2 mass fraction (X_{CO_2}) is compared with the solubility limit or equilibrium CO_2 mass fraction ($X_{\text{CO}_2}^{eq}$) at the corresponding pressure and temperature. Below the solubility limit the independent variables include P , T , and X_{CO_2} . Above the solubility limit ($X_{\text{CO}_2} > X_{\text{CO}_2}^{eq}$) a small amount (ϵ) of free phase CO_2 gas saturation S_{CO_2} is introduced and the independent variables are switched from P , T , and X_{CO_2} to P , T , and S_{CO_2} . Similar variable-switching approaches have been used for simulating phase change processes (e.g., Forsyth and Sammon, 1984).

Each simulation starts from hydrostatic conditions (gravity equilibrium) and then CO_2 -saturated water, with a specified saturation pressure, is injected into the bottom of the simulation domain at a flow rate of $4 \text{ cm}^3 \text{ min}^{-1}$. The outlet boundary is specified to be atmospheric pressure. We used the Corey (1954) and Brooks and Corey (1964) relative permeability relationships for water and CO_2 gas, respectively, and the van Genuchten (1980) relationship for capillary pressure. Parameters for these relationships were history matched to the steady-state saturation profiles using PEST. Initial parameter values were taken from existing air-water multi-phase flow data (Sakaki et al., 2013; Plampin et al., 2014a, and reference therein). Further details regarding the PEST analysis are provided in Section 3.

2.3. CO₂ Evolution: Critical Pressure

Our goal in this section is to derive a simple equation that predicts the critical pressure at which CO₂ evolution occurs in the column, which we denote as P_{cr} . In other words, P_{cr} corresponds to the depth, z_{cr} below which the water saturation, S_w , is equal to 1, and above which continuum-scale multi-phase flow occurs. Since our goal is to develop an equation that predicts where multi-phase flow will occur in the column, the following theoretical developments only consider single-phase flow theory (i.e., Darcy's law). In addition, we assume isothermal conditions since the temperature is relatively constant in the experiments, and more importantly in most shallow aquifers. Figure 2 illustrates the experimental configuration and an arbitrary location, z_{cr} , above which multi-phase flow occurs. Plampin et al. (2014a, Sec. 3.1 & Fig. 4), defined the critical pressure as

Figure 2: Illustration of the experimental system containing an interface at which free phase CO₂ gas forms.

$$P_{\text{cr}}^* = P_{\text{sat}}. \quad (7)$$

This definition follows from Henry's law and accounts for the hydrostatic pressure within the column. However, there is an additional pressure drop in the column due to single phase flow. To account for this additional pressure drop, we propose the following definition

$$P_{\text{cr}} = P_{\text{sat}} - \Delta P_{\text{flow}} \quad (8)$$

where ΔP_{flow} is the pressure drop in the column due to fluid flow. Here, we subtract ΔP_{flow} since flow is upward in the column. We also assume ΔP_{flow} is caused by single phase flow only since, in the relevant cases (i.e., $P_{\text{cr}} < P_{\text{inj}}$), this pressure drop will form prior to the existence of any free phase CO₂ gas. In the cases, where $P_{\text{cr}} \geq P_{\text{inj}}$, CO₂ free phase gas will form over the entire column and Eq. (8) does not apply. In

homogeneous porous media, it follows from Darcy's law that ΔP_{flow} is expressed as

$$\Delta P_{\text{flow}} = \Delta P - \rho g(L - z_{\text{cr}}) = -\frac{\mu q(L - z_p)}{k}, \quad (9)$$

where $\Delta P = P_{\text{inj}} - P_0$ is the total pressure drop, k is the permeability, μ is the viscosity of water, q is the injection rate of CO₂-saturated water (note q is negative since flow is upward in the column), ρ is the density of water, and z_p is the location of the top of the porous medium. Substituting, Eq. (9) into Eq. (8) results in

$$P_{\text{cr}} = P_{\text{sat}} + \frac{\mu q(L - z_p)}{k}. \quad (10)$$

Equation (10) can easily be extended to layered heterogeneous systems in which the direction of flow is perpendicular to the layer interface by considering the vertically (harmonic) averaged effective permeability, k_{eff} , defined as $k_{\text{eff}} = \frac{\sum_i b_i}{\sum_i b_i/k_i}$ where k_i and b_i are the permeability and thickness, respectively, of each sand layer in the column. Thus, for layered heterogeneous systems the critical pressure is

$$P_{\text{cr}} = P_{\text{sat}} + \frac{\mu q(L - z_p)}{k_{\text{eff}}}. \quad (11)$$

Thus, the newly proposed definition for P_{cr} (Eq. 11) accounts for the pressure drop due to flow and heterogeneity. We note here that for heterogeneous shallow aquifer systems the geometric average is likely a better choice for k_{eff} (Warren and Price, 1961) and is straight forward to incorporate into Eq. (11). In Sec. 3 we compare Eq. (7) and (11) to the experimental and simulated saturation data to validate applicability of these expressions.

3. Results

3.1. PEST Analysis

The model parameters that are most important for these experiments are the residual wetting phase saturation, S_{wr} , the critical gas saturation, S_{gc} , the pore-size distribution parameter, λ , in the Brooks-Corey relative permeability equation, and the two parameters, α (the inverse of the entry pressure) and n (the pore-size distribution), in the van Genuchten capillary pressure – saturation relationship. Conventionally, these parameters are measured from drainage or imbibition experiments within a given homogeneous porous medium for a specific fluid pair. However, recent studies have suggested that these parameters are process-dependent (e.g., Zuo and Benson, 2014). In lieu of experimentally measured parameters for water and CO₂ gas resulting from exsolution experiments, we have chosen to estimate parameters for the homogeneous experiments using PEST. Thus, the above model parameters were optimized to the experimentally measured steady-state saturation profiles. The parameters for our PEST analysis were initialized with experimentally

measured air-water parameters within the same sands (Sakaki et al., 2013; Plampin et al., 2014a, and references therein). This is a reasonable starting point, and we note that Enouy et al. (2011) assumed that existing air-water parameters were appropriate for their exsolution modeling study. PEST analysis of the homogeneous coarse and fine sand experiments allows us to compare model outputs using optimized parameters to those using the air-water drainage experiment parameters. We then used the parameters from the homogeneous simulations in our heterogeneous simulations.

Table 2: Optimized FEHM parameters for the coarse sand simulations. The sensitivity for each parameter is provided in parentheses.

Parameter	Experimental	PEST				
	Values	$P_{\text{sat}} = 50 \text{ kPa}$	$P_{\text{sat}} = 40 \text{ kPa}$	$P_{\text{sat}} = 30 \text{ kPa}$	$P_{\text{sat}} = 20 \text{ kPa}$	$P_{\text{sat}} = 10 \text{ kPa}$
S_{wr}	0.25*	0.15 (7×10^{-4})	0.35 (0.0)	0.35 (0.001)	0.15 (0.0)	0.25 (0.0)
S_{gc}	0.25*	0.32 (0.20)	0.29 (0.19)	0.31 (0.25)	0.28 (0.26)	0.28 (0.45)
λ	4.28	3.50 (0.002)	12.7 (0.001)	17.0 (0.001)	5.22 (8×10^{-4})	1.00 (0.003)
α (1/m)	12.3	15.0 (4×10^{-4})	14.5 (5×10^{-4})	2.22 (0.002)	15.0 (8×10^{-4})	15.0 (8×10^{-4})
n	9.21	9.17 (1×10^{-4})	9.21 (0.0)	6.76 (8×10^{-4})	3.82 (0.0)	7.81 (0.0)

* Experimental values were not available for this parameter, this is an initial guess.

Table 3: Optimized FEHM parameters for the fine sand simulations. The sensitivity for each parameter is provided in parentheses.

Parameter	Experimental	PEST				
	Values	$P_{\text{sat}} = 50 \text{ kPa}$	$P_{\text{sat}} = 40 \text{ kPa}$	$P_{\text{sat}} = 30 \text{ kPa}$	$P_{\text{sat}} = 20 \text{ kPa}$	$P_{\text{sat}} = 10 \text{ kPa}$
S_{wr}	0.25*	0.35 (0.004)	0.29 (0.003)	0.35 (0.003)	0.35 (0.0)	0.25 (0.002)
S_{gc}	0.25*	0.24 (0.15)	0.29 (0.19)	0.25 (0.22)	0.26 (0.29)	0.30 (0.67)
λ	4.09	2.11 (0.003)	1.00 (0.004)	1.36 (0.004)	2.00 (0.005)	4.10 (0.005)
α (1/m)	2.89	3.89 (0.002)	5.83 (0.002)	3.80 (0.003)	15.8 (0.001)	2.92 (0.003)
n	10.2	8.21 (4×10^{-4})	25.0 (3×10^{-4})	6.84 (8×10^{-4})	17.0 (0.0)	10.2 (0.0)

* Experimental values were not available for this parameter, this is an initial guess.

The results from the PEST optimization simulations are presented in Table 2 and 3. The initial values for the PEST simulations are provided in the column labeled “Experimental Values”. The sensitivity value for each parameter (shown in parentheses) measures the composite changes in model outputs that are incurred by a fractional change in the value of the parameter. Thus, a sensitivity value of 0.0 means that changes in the parameter value had no affect on the model outputs, whereas larger values indicate that changes in the parameter value had more influence on the model outputs. The small sensitivity values for all parameters, except S_{gc} , indicate that the model results were insensitive to these parameter values, which explains the variability. In both the coarse and fine sands S_{gc} was the only sensitive parameter in the optimization procedure. The mean value and corresponding standard deviation for the critical gas saturation for the

homogeneous coarse and fine sands are $0.30 (\pm 0.02)$ and $0.27 (\pm 0.03)$, respectively. This indicates that S_{gc} was relatively constant within each sand. Based on these observations, the parameters for the heterogeneous sands were set to the Experimental Values in Table 2 and 3, while S_{gc} was set to 0.30 and 0.27 for the coarse and fine sands, respectively.

Figure 3 shows the steady-state water saturation obtained from the FEHM simulations for all three homogeneous sands. For the coarse and fine sands the PEST parameters for each P_{sat} value in Table 2 and 3 were used in the simulations, whereas in the medium sand the parameters were $S_{wr} = 0.25$, $S_{gc} = 0.25$, $\lambda = 8.71$, $\alpha = 6.13 \text{ m}^{-1}$, and $n = 17.81$, taken from (Sakaki et al., 2013; Plampin et al., 2014a, and references therein), for all P_{sat} . The three sets of simulations clearly show that the depth at which CO_2 gas evolution occurs decreases as the permeability decreases and supports the theoretical developments in Sect. 2.3.

Figure 3: FEHM simulations of the homogeneous sand configurations. For the coarse and fine sands the PEST parameters were used in the simulations.

3.2. Long Column Sands

As a first step in validating FEHM we compare the experimentally measured and simulated outflow rates of water and CO_2 gas. This comparison is shown in Figure 4 for a subset of the experiments modeled. In all cases, the water outflow rate increases to a value that exceeds the injection flow rate, which indicates the development of gas saturation within the column. Increases in the gas outflow rate coincide with the decreases in the water outflow rate. This is expected since more gas is leaving the system and water must fill the vacated pore space, leading to a decrease in the water outflow rate. The noise in the experimental data, especially at late times, is due to temperature fluctuations in laboratory. It was observed that as the temperature measured at the top of the column increased the gas meter recorded an increase in gas flow rate, and vice versa. In Figure 4A, CO_2 gas exsolution occurs over the entire column (See Fig. 3) and begins immediately upon injection of CO_2 -saturated water since $P_{cr} > P_{inj}$. Thus, transient water outflow

214 is observed almost immediately in this experiment. In the other cases there is a delay in the transient water
 215 outflow, as expected $P_{cr} < P_{inj}$. Overall, the FEHM simulations adequately capture the water and CO₂ gas
 216 outflow, with the largest discrepancy occurring in the layered coarse-fine sand where the simulated transient
 217 water outflow begins 3-4 hours prior to that observed in the experiment. This indicates that the equilibrium
 218 mass transfer assumption within FEHM is justified. It is noted here, that Enouy et al. (2011) used a
 219 rate-limited mass transfer expression containing an *ad hoc* nucleation gas saturation parameter designed to
 220 prevent unrealistically small mass transfer rates during the initial stages of gas phase formation. They found
 221 that this parameter had to be set to 0.03 in order for their model to accurately describe the dynamics of gas
 222 accumulation in their column experiments.

Figure 4: Comparison of water and CO₂ gas outflow rates for the experiments and FEHM simulations. (A) Coarse sand, $P_{sat} = 50$ kPa. (B) Coarse-fine sand, $P_{sat} = 20$ kPa. (C) Layered coarse-medium sand, $P_{sat} = 40$ kPa. (D) Layered coarse-fine sand, $P_{sat} = 30$ kPa

223 To further validate FEHM and test the applicability of Eq. (7) and (11) we now compare them with the
 224 steady-state saturation profiles observed in the experiments. The steady-state saturation profiles provide a
 225 metric that is consistent with the long-term fate and transport of CO₂ gas in natural aquifer settings, which
 226 is important for risk analysis regarding regulatory and management decisions. For the homogeneous coarse

227 and fine sands we compare two FEHM simulations, namely those obtained using the experimental parameters
 228 and those obtained using the PEST parameters (See Table 2 and 3). Figure 5 shows the comparison for the
 229 homogeneous coarse sand. First we note that the two FEHM simulations are very similar and they both
 230 show good agreement with the experimental steady-state saturation profiles for all cases. More importantly,
 231 the simulations capture the transition from single- to multi-phase flow of water and CO₂ gas. The critical
 232 pressures calculated from Eq. (7) and (11) are almost identical due to relatively large permeability for the
 233 coarse sand, resulting in a negligible pressure drop due to flow. Both equations adequately predict the
 234 location at which CO₂ evolution occurs in all of the experiments. The comparison for the homogeneous fine
 235 sand is shown in Figure 6. Once again, the two simulations are very similar; they both show good agreement
 236 with the experimental steady-state saturation profiles and capture the transition from single- to multi-phase
 237 flow. The permeability of the fine sand is smaller than that of the coarse sand leading to an appreciable
 238 pressure drop due to flow, and thus differences in the critical pressures obtained from Eq. (7) and (11).
 239 Clearly, Eq. (11) is more consistent with the experiments and simulations than Eq. (7) for the fine sand.

Figure 5: Comparison between the experiments, FEHM simulations, and the critical pressure expressions for the coarse homogeneous sand.

240 We now turn our attention to the heterogeneous sand configurations. First we consider the long column
 241 coarse-fine sand configuration in which the fine sand lies above the coarse sand (See Fig 1). With this

Figure 6: Comparison between the experiments, FEHM simulations, and the critical pressure expressions for the fine homogeneous sand.

configuration (finer sand over coarser sand) it is expected that if CO_2 gas evolution occurs in the coarse sand then CO_2 gas will accumulate underneath the fine sand since gas will not enter the fine sand until the capillary entry pressure is exceeded. Figure 7 shows the comparison between the coarse-fine sand experiments, the simulations and the predicted critical pressures (Eq. (7) and (11)). In all cases the simulations capture the steady-state saturation profiles. The simulation for $P_{\text{sat}} = 50$ kPa shows CO_2 gas evolution over the entire column as expected (since $P_{\text{cr}} > P_{\text{inj}}$), which is consistent with the experiments. For $P_{\text{sat}} = 40$ kPa, the simulation shows CO_2 gas evolution occurring at a depth of approximately 3.8 m, which is consistent with the prediction from Eq. 11. In both cases, the simulations indicate significant gas accumulation just below the interface separating the two sands, which is not observed in the experiments. However, one must keep in mind that the closest saturation sensor is 12.5 cm away from the interface and will not capture additional gas accumulation if it is occurring close to the interface between the two sands. In the simulations it is possible to control the amount of gas accumulation by adjusting the parameters in the capillary pressure–saturation relationship (i.e., α and n). We have not shown this here since we do not have any data regarding accumulation in experiments. We address this in more detail in Sec. 3.3. For $P_{\text{sat}} = 20$ kPa, we see that the simulation and Eq. 11 accurately capture the depth at which CO_2 gas evolution occurs and the transition

from single- to multi-phase flow. In addition, there is a noticeable pressure drop due to flow in the fine sand for this heterogeneous sand configuration and Eq. 11 is more consistent with the observed CO₂ gas evolution than Eq. 7.

Figure 7: Comparison between the experiments, FEHM simulations, and the critical pressure expressions for the coarse-fine heterogeneous sand configuration. The dotted line shows the location of the coarse-fine sand interfaces.

We now consider the layered coarse-fine experiments and note that experiments were only conducted for saturation pressures of 40 and 30 kPa. A comparison between the experiments, simulations, and predicted critical pressures is shown in Figure 8, indicating that the simulations sufficiently capture the observed steady-state saturation profiles. For $P_{\text{sat}} = 40$ kPa, CO₂ evolution is observed at all saturation sensors and the simulations show the transition from single- to multi-phase flow occurring at a depth of approximately 3.9 m, which is expected based on the results from the homogeneous coarse and fine sand simulations. Moreover, the simulations are consistent with the depth associated with the critical pressure predicted by Eq. 11. For $P_{\text{sat}} = 30$ kPa, the simulations and Eq. 11 provide depth estimates of CO₂ evolution that are slightly lower than that observed in the experiment, but sufficiently similar to still be useful in most applications. Once again, the simulations show large saturation spikes beneath the fine sand layers which is discussed in detail in Sec. 3.3. On average, the steady-state gas saturation in the coarse sand increased by only 4% in this heterogeneous sand configuration when compared to homogeneous coarse sand, making it difficult to conclude with certainty that heterogeneity lead to additional accumulation of gas within the column.

The saturation profiles for the layered coarse-medium sand experiments are shown in Figure 9 along with the simulations and predicted critical pressures. In all cases the simulations show good correspondence with the observed saturation data. For $P_{\text{sat}} = 20$ and 10 kPa, the simulations capture the transition from single- to multi-phase flow sufficiently well. The critical pressures calculated from Eq. (7) and (11) are very similar and correspond well with the experiments and simulations. The similarities between the critical pressures indicates that the pressure drop due to flow is negligible and can likely be ignored in systems with relatively

Figure 8: Comparison between the experiments, FEHM simulations, and the critical pressure expressions for the layered coarse-fine heterogeneous sand configuration. The dotted line shows the location of the coarse-fine sand interface.

high permeability values.

3.3. Short Column Heterogeneous Sand Configurations

The short column experiments were designed to test whether or not CO₂ gas accumulation occurs at heterogeneous interfaces and if it can be quantified with the saturation sensors. Thus, sensors were placed 5 cm above and below the interface separating the two sands (See Fig. 1). It is noted that the sensors placed at these locations measure saturation for a region spanning 3.5 to 6.5 cm away from the interface separating the sands. With these experiments we can better parameterize the simulations to control the saturation spikes observed in Section 3.2 for which no experimental data was available. Here, we conducted PEST simulation to determine optimal values for the capillary pressure – saturation relationship (i.e., α and n), all other parameter values are the same as those used in the long column simulations. The optimized PEST parameters are listed in Table 4.

Table 4: Optimized FEHM parameters for the short column coarse-fine sand configuration.

Parameter	Initial Value		$P_{inj} = 17.1$ kPa		$P_{inj} = 22.9$ kPa		$P_{inj} = 25.9$ kPa	
	Coarse	Fine	Coarse	Fine	Coarse	Fine	Coarse	Fine
α (1/m)	12.3	2.89	9.63	3.41	22.3	5.62	13.7	6.60
n	9.21	10.2	2.10	10.1	1.82	10.3	1.77	10.1

Experimental results for the short column coarse-fine sand configuration are presented in Figure 10 and show that CO₂ gas accumulates underneath the fine sand layer for $P_{inj} = 17.1$ kPa and $P_{inj} = 22.9$ kPa, but not for $P_{inj} = 25.9$ kPa. It is not entirely clear why additional CO₂ gas accumulation is not observed in the $P_{inj} = 25.9$ kPa experiment, however efforts to better understand this phenomenon are underway (see Plampin et al., 2014b). Overall, the FEHM simulations capture the experimental steady-state saturation

Figure 9: Comparison between the experiments, FEHM simulations, and the critical pressure expressions for the layered coarse-medium heterogeneous sand configuration.

profiles for all three experiments, including the additional CO₂ gas accumulation underneath the fine sand for the $P_{inj} = 17.1$ kPa and $P_{inj} = 22.9$ kPa experiments. In these two simulations the maximum gas saturation is approximately 60% at the interface separating the two sands and the accumulation zones (where gas saturation is greater than S_{gc} in the coarse sand) extend 0.1 to 0.15 m below the interface. Although there is not enough data to fully characterize the accumulation zone, these results suggest the accumulation zone is relatively localized and would be difficult to capture in natural (larger) aquifer systems. The critical pressures calculated from Eq. (7) and (11) are also plotted for the $P_{inj} = 22.9$ kPa experiment and adequately predict the location where CO₂ gas evolution is observed in the experiments and simulations.

Comparing these simulations with the long column heterogeneous simulations (Fig. 7 and 8) we see that the maximum gas saturation in the long column simulations is likely over-predicting the amount of CO₂ accumulation by approximately 10%. This suggests that the α and n values for the coarse sand in the long column experiments are likely not the best values for heterogeneous systems. However, the long column simulations consistently show localized accumulation zones extending 0.1 to 0.15 m below the sand interfaces, which is consistent with the short column simulations. Further characterization of the accumulation zone is required, however these results could be useful in guiding modeling efforts in shallow aquifer systems by

providing an average height of the accumulation zone.

Figure 10: Comparison between the experiments, FEHM simulations, and the critical pressure expressions for the short column coarse-fine heterogeneous sand configuration.

4. Discussion & Conclusions

In this work, we conducted FEHM simulations of intermediate-scale CO₂ leakage experiments in homogeneous and heterogeneous sand configurations conducted by Plampin et al. (2014a,b). The experiments were designed to investigate the combined processes of CO₂ gas exsolution, free phase migration and accumulation. The long-term affect of these processes within shallow aquifers constitutes a leakage scenario that must be understood to ensure CO₂ sequestration operations do not negatively affect shallow groundwater resources. The main objective was to assess how well the numerical simulator, FEHM, captures the experimental observations, as well as provide a simple expression that predicts the height in the column above which multi-phase flow occurs.

PEST analysis was conducted for the long column homogeneous sand configurations in order to determine suitable simulation parameters for the heterogeneous long column experiments. The comparison between the two different FEHM simulations in Fig. 5 and 6 clearly indicates that the optimized PEST parameters provided little or no value to overall model output in the homogeneous sands as suggested by the sensitivity values and the relatively constant values of S_{gc} discussed in Section 3.1. This finding is potentially very helpful in the the context of exsolution in shallow aquifer systems since it suggests that model parameters obtained from air-water drainage experiments may sufficiently represent CO₂ evolution processes. It was demonstrated that FEHM, and the equilibrium mass transfer assumption, faithfully captured the water and gas out flow rates observed in the experiments. Moreover, FEHM captured the experimental steady-state saturation profiles and the transition from single- to multi-phase flow in all cases. The heterogeneous long column simulations produced saturation spikes at the interfaces separating the sands. These spikes were not observed in the experiments since the saturation sensors were too far away from these interfaces. The

short column experiments were designed to measure CO₂ gas accumulation near the sand interfaces. FEHM was able to capture the observed gas accumulation near the sand interfaces by adjusting the van Genuchten parameters for the capillary pressure-saturation relationship in the coarse sand (where gas accumulation was observed). These simulations indicate that the capillary pressure-saturation parameters are sensitive parameters in heterogeneous systems. Moreover, the simulations provide guidelines for the height of the gas accumulation zone expected to occur when a fine layer lies above a coarse layer in shallow aquifer systems. Overall, the simulations provide confidence that FEHM faithfully represents the underlying physical processes despite the fact that it does not explicitly account for exsolution at the pore-scale.

Our simple analytic expression for the critical pressure above which CO₂ evolution occurs (Eq. (11)) was shown to reliably predict the location at which transition from single- to multi-phase flow occurred in the experiments. Eq. (11) is an extension of previous theoretical developments (Eq. (7)) in which Henry's law and the hydrostatic pressure (Plampin et al., 2014a) was taken into account. Here we considered Darcy's law and took into account the pressure drop due to single phase flow in heterogeneous porous media. Several of the results shown in Section 3 show good correspondence between Eq. (11) and (7) and substantial differences are only observed in cases that contain the fine sand. The cause of this is easily explained by permeability, which has to be sufficiently small to produce a significant pressure drop due to flow. In this study, the permeability of the fine sand was 3.0×10^{-11} m², which is higher than many permeability values for shallow aquifers (e.g., Oldenburg et al., 2010; Spangler et al., 2010; Humez et al., 2011; Keating et al., 2012; Peter et al., 2012; Keating et al., 2013). Thus, in natural systems, it is expected that the pressure drop due to flow is significant and Eq. (11) is more appropriate than Eq. (7). We note that Eq. (11) has its limitations since it strictly applies to 1-dimensional flow systems. In shallow aquifer systems there exists horizontal background flow that will most likely affect CO₂ evolution. We are currently working on extending the findings of this work to 2-dimensional systems.

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