Slow gas expansion in saturated natural porous media by gas injection and partitioning with non-aqueous phase liquids

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Slow gas expansion in saturated natural porous media by gas injection and partitioning with non-aqueous phase liquids

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ABSTRACT

The partitioning of volatile non-aqueous phase liquid (NAPL) compounds to a discontinuous gas phase can result in the expansion of that gas phase, and the resulting gas flow can significantly affect the mass transfer from NAPL source zones. This recently reported gas flow generated by the spontaneous expansion of a discontinuous gas phase has not been extensively characterized in the literature. This study measured the expansion rate of a single gas cluster in a 1.1 mm sand above a pool of trans-1,2-dichloroethene (tDCE) in small-scale flow cell experiments. To characterize the gas flow, gas injection experiments in three sizes of sand were conducted at very slow injection rates typical of gas flow rates produced by gas expansion due to NAPL partitioning. Gas cluster spontaneous expansion rates above a tDCE pool were found to be 0.34 ± 0.02 and 0.29 ± 0.01 mL/day in duplicate experiments, which is sufficiently slow to result in discontinuous gas flow in porous media with a grain size diameter greater than 0.02 mm. Measured capillary pressures during gas injection showed patterns consistent with discontinuous gas flow, and identified multiple fragmentation events and expansion by coalescence with trapped clusters. The combination of pressure data and light transmission images were used to identify fragmentation and obtain direct measurements of the critical cluster length (i.e. the length at which withdrawal of the gas phase from a pore space occurs) in quasi-two-dimensional porous media for the first time. The measured critical cluster lengths were 1.4–3.6, 3.2–6.0 and 2.8–6.5 cm in 1.1, 0.7 and 0.5 mm sands, respectively. These values agreed well with estimates of the critical cluster length made using previously reported equations, and parameters derived from the medium’s capillary pressure-saturation relationship.

1. Introduction

Recent studies have shown that gas flow following the spontaneous expansion of a discontinuous gas phase can significantly affect the mass transfer from non-aqueous phase liquid (NAPL) pools [1]. These pools are typically responsible for the persistence of NAPL source zones [2] and the continued contamination of the surrounding groundwater at NAPL-contaminated sites over periods of decades to centuries. This recently reported mechanism of spontaneous gas expansion results in significant vertical gas flow away from the NAPL pool [3], potentially increasing the mass transfer rate and changing the spatial distribution of dissolved NAPL. This could affect efforts to locate NAPL source zones using aqueous concentration data, as well as the prediction of risks and lifetimes associated with NAPL source zones. Spontaneous gas expansion has been observed in the presence of a variety of NAPLs, including tetrachloroethene (PCE), trichloroethene (TCE), 1,1,1-trichloroethane (1,1,1-TCA), and trans-1,2-dichloroethene (tDCE), which have vapor pressures between 2.5 × 10^3 and 4.2 × 10^4 Pa [1,3,4]. Because spontaneous gas expansion is a function of the hydrostatic pressure, capillary pressure, and the concentrations of other dissolved gases in the groundwater, in addition to the vapor pressure of the NAPL, it is more likely to be active at NAPL-contaminated sites with higher volatility NAPL in shallow source zones and coarse media [3]. However, where additional dissolved gases can be generated in the vicinity of NAPL, such as by microbial activity, the additional partial pressure could result in expansion in deeper, finer systems.

This mechanism has not been characterized extensively in the literature. In particular, little is known concerning the nature of the resulting gas flow. Roy and Smith [1] observed repeated fragmentation and mobilization of an expanding discontinuous gas...
phase above pools of PCE, TCE and a mixture of benzene and PCE in 1- and 3-mm glass bead packs. In addition to repeated fragmentation and mobilization, Mumford et al. [3] observed extensive trapping and coalescence of a mobilized gas phase above a pool of 1,1,1-TCA in a 1.1-mm uniform sand. The gas-phase data presented in these previous studies are limited to qualitative observations of pore-scale processes, and measurements of the maximum vertical extent of the gas phase. No quantitative information is presented in these studies, or elsewhere in the literature, concerning the rate of generated gas flow or the transient distribution of the resulting disconnected gas clusters produced via this mechanism in porous media. Measurements of gas flow rate and distribution are important first steps toward better understanding the total mass transfer away from the pool and the dissolution of the volatized NAPL into the groundwater above the pool, respectively.

The current literature concerning gas flow in porous media does not adequately address this mechanism, which is expected to produce very low gas flow rates. This expectation is based on experiments conducted under diffusion-limited conditions, in the absence of porous media, where single gas bubbles were observed to expand at rates of $2 \times 10^{-3}$ and $2 \times 10^{-4}$ mL/day in the presence of tDCE and PCE, respectively [4]. Although these rates were not measured in porous media, they suggest that gas flow generated by spontaneous expansion will be substantially slower than the injection rates used in other studies of gas flow in porous media, including 20–3000 mL/min [5], 10–5000 mL/min [6], 3–186 mL/min [7], and 240–5200 mL/min [8]. Gas was injected as a point source during these studies, using either porous stones (1–2 cm diameter) [5,8], or small-diameter injection points (2–5 mm diameter) [6,7]. Very few studies have reported results for the slow injection of gas in water-saturated porous media [6]. Glass et al. [9] injected CO$_2$ at 1.2 mL/min into uniform sand saturated with water. In an analogous study of unstable, non-wetting fluid injection, Frette et al. [10] injected a sucrose-water solution at 0.03 mL/min into a 18.3 $\times$ 18.3 $\times$ 28.3 cm$^3$ container packed with 2-mm long $\times$ 2-mm diameter plexiglass cylinders, saturated with dibutylphthalate. Their study used the sucrose-water solution as the injected, non-wetting fluid, and dibutyl-phthalate as the wetting fluid in place of gas and water, respectively. Our study investigated gas flow for injection rates of 0.001 and 0.01 mL/min, injected through a 2-mm diameter tube, which is capable of producing discontinuous flow [6] in media finer than 1–2 mm. A grain size of 1–2 mm is typically considered to be the transition point for continuous to discontinuous gas flow reported in the air sparging literature [5].

The purpose of this study is to characterize the gas flow in natural porous media resulting from the spontaneous expansion of a discontinuous gas phase at the surface of a NAPL pool. Two sets of bench-scale experiments were conducted in natural sand to (1) quantify the expansion rate of a discontinuous gas phase at the surface of a NAPL pool, and (2) measure the transient gas pressures and critical cluster lengths produced by the very slow injection of gas in three different sands. This study is the first to quantify the rate of spontaneous gas expansion above a NAPL pool in porous media, and represents the first data for the injection of gas at these very slow flow rates. In addition, this study provides the first direct measurement of discontinuous gas-cluster lengths in a porous medium with a thickness greater than one grain diameter, made possible by using a combination of imaging techniques and pressure measurements, in contrast to previous studies that measured gas-cluster lengths [11,12] in monolayer packings of glass beads. The results of this study contribute to the refinement of the conceptual model for the spontaneous expansion of a gas phase in the presence of NAPL [1], and provide key quantitative data that will facilitate the incorporation of this mechanism into future numerical models.

2. Background

2.1. Expansion of multi-component discontinuous gas phases

The partitioning of multiple dissolved gases to a discontinuous gas phase is well described by Cirpka and Kitanidis [13] and has been used for numerous applications including the dissolution [14,15] and expansion [1,4,16] of discontinuous gas phases. Cirpka and Kitanidis [13] show that the dissolution or expansion of a multi-component gas phase results from the constraint

$$P_g = P_w + P_c = \sum \frac{P_i}{y_i}$$  \hspace{1cm} (1)

where $P_g$ is the gas pressure, $P_w$ is the bulk liquid pressure, $P_c$ is the capillary pressure, and $P_i$ is the partial pressure of compound $i$ in the gas phase. The capillary pressure is described by the Laplace equation of capillarity

$$P_c = \sigma \left( \frac{1}{r_1} + \frac{1}{r_2} \right)$$  \hspace{1cm} (2)

where $\sigma$ is the gas–liquid interfacial tension, and $r_1$ and $r_2$ are the principal radii of curvature of the gas–liquid interface. The partial pressure is described by Henry’s law, assuming local thermodynamic equilibrium at the gas–liquid interface

$$P_i^l = K_{H,i} C_i$$  \hspace{1cm} (3)

where $K_{H,i}$ is the Henry’s law coefficient for compound $i$, and $C_i$ is the local aqueous phase concentration of compound $i$. The constraint given by Eq. (1) can result in local aqueous concentrations different from those in the bulk solution, which drives mass transfer between the bulk solution and the discontinuous gas phase. The resulting changes in the pressure and volume of the gas phase over time under isothermal conditions follows from the ideal gas law

$$\frac{dn_i}{dt} = \frac{1}{R} \frac{d(P_g V_g)}{dt}$$  \hspace{1cm} (4)

where $n_i$ is the total number of moles in the gas phase, $t$ is time, $R$ is the gas constant, $T$ is the temperature, and $V_g$ is the volume of the gas phase. For mass transfer into a discontinuous gas phase (i.e. $dn_i/dt > 0$) in porous media, the changes to pressure and volume occur in a series of pore-filling (approximately constant pressure) and pressurization (approximately constant volume) steps [17].

2.2. Gas flow in water-saturated porous media

Two different flow patterns have been observed for the upwards flow of gas in otherwise water-saturated porous media: continuous (also called channel or coherent) flow and discontinuous (also called bubbly, slug, or incoherent) flow [5–7]. Continuous flow is characterized by a collection of continuous channels which transport gas along a gas-phase pressure gradient. Discontinuous flow is characterized by the presence of multiple, discrete gas clusters, which may be either trapped or mobile, depending on the magnitude of local capillary and buoyancy forces. The difference between these two gas-phase distributions has a controlling effect on the mass transfer between the gas and aqueous phases [5]. For spontaneous gas expansion in particular, the occurrence of discontinuous gas flow allows the expansion of some gas clusters and the dissolution of others, as the mass transfer is controlled by the local aqueous concentrations at each individual gas–liquid interface [3].

The threshold between continuous and discontinuous flow has been based solely on the consideration of the Bond number [5,8]

$$Bo = \frac{\Delta \rho g r_g^2}{\sigma}$$  \hspace{1cm} (5)
where $Bo$ is the Bond number, $\Delta \rho$ is the density difference between the resident and invading fluids, $g$ is the acceleration due to gravity, and $r_p$ is a characteristic pore radius. In a review of the literature, Selker et al. [8] found that continuous flow dominated for $Bo < 0.03$. Based on the ratio of pore necks to pore bodies used by Brooks et al. [5], this is consistent with the grain size threshold of approximately 1–2 mm for the injection of air in water-saturated porous media referred to in the air sparging literature.

Recent research, however, shows that the consideration of the Bond number alone is insufficient for the characterization of gas flow. Geistlinger et al. [6] and Stöhr and Khalili [7] report similar expressions for a critical flow rate, at which the friction forces resulting from the flow of gas in a channel stabilize the flow

$$Q_{\text{crit}} = \frac{\pi \Delta \rho g r_c^2}{\mu_g}$$

where $Q_{\text{crit}}$ is the critical gas flow rate above which gas flow is stable and continuous, $r_c$ is the gas channel radius, and $\mu_g$ is the gas dynamic viscosity. A value of $Q_{\text{crit}}$ capable of stabilizing the gas flow is only attainable in media where capillary forces dominate over gravity forces at the scale of a single pore [7]. Eq. (6) shows that discontinuous flow is not limited to media of greater than 1–2 mm in diameter; it will occur in much finer media when the gas flow rate is sufficiently small.

### 2.3. Fragmentation and mobilization

The flow of discontinuous gas clusters in porous media is controlled by both capillary and buoyancy forces, as described by studies that model gas flow using modified invasion percolation (MIP) in a gradient with fragmentation and mobilization [18–20]. For an immobile discontinuous gas phase (Fig. 1a) to expand, whether due to the injection of additional gas or the partitioning of additional volatile compounds, the gas pressure in the cluster must overcome the sum of the hydrostatic and entry pressures in one of the adjacent pore throats

$$P_g \geq P_w + P_e$$

where $P_e$ is the throat entry pressure. The entry pressure can be expressed as

$$P_e = \frac{2\sigma}{r_t}$$

where $r_t$ is an effective pore throat radius, which implicitly includes contact angle considerations. Thus, the capillary pressure increases with the gas pressure until the throat entry pressure is reached. Once this local gas-phase entry pressure is achieved the gas phase expands into the adjacent pore body (Fig. 1b) and the capillary pressure drops. This capillary pressure may be greater or less than the capillary pressure in the previous pore body, depending on the geometry of the new gas–liquid interface. This alternating sequence of pressurization and pore-entry [17] results in a dynamic fluctuating gas pressure. As expansion continues it is biased towards growth in the upwards vertical direction (Fig. 1c) since the hydrostatic pressure decreases with height making the entry into pore throats above the cluster generally more favorable [21]. Therefore, although the gas pressure fluctuates, due to local pressurization and pore-entry events, the mean pressure decreases with increasing cluster height, due to the decrease in hydrostatic pressure as the cluster expands upward.

As the length of the cluster extends vertically, the local curvature of the gas–liquid interface adjusts to maintain a uniform gas pressure throughout the cluster despite a decrease in hydrostatic pressure with height. This results in greater radii of curvature (lower capillary pressure) towards the bottom of the cluster and lesser radii of curvature (high capillary pressure) towards the top. Once the length of the cluster reaches a critical value, the capillary pressure towards the bottom of the cluster drops to a value where the re-invasion of water into previously gas-occupied pore space is possible. This pressure is referred to as the withdrawal threshold [12,20] and is analogous to the terminal pressure ($P_t$) used to describe the formation of NAPL residual, which has been previously defined on the macroscopic scale using capillary pressure-saturation curves [22]. This re-invasion results in either the mobilization (Fig. 1d) or the fragmentation (Fig. 1e) of the cluster, depending on the location of the pore where re-invasion occurs. Following fragmentation, the lower gas cluster is at a lower capillary pressure than what is required for the entry into any of its adjacent pore throats. Therefore, pressurization of the entire cluster must occur again before repeated growth of that cluster is possible.

Expressions for estimating the critical cluster length have been reported based on a balance of pressure at the upper and lower tips of the cluster, and consideration of the hydrostatic pressure drop [6,9]

$$h_{\text{crit}} = \frac{P_{\text{top}} - P_{\text{bottom}}}{\Delta \rho g}$$

where $h_{\text{crit}}$ is the critical cluster length, $P_{\text{top}}$ is the capillary pressure at the top of the cluster and $P_{\text{bottom}}$ is the capillary pressure at the bottom.
of the cluster, when fragmentation occurs. When it is reasonable to assume that \( P_{\text{top}} > P_{\text{bottom}} \), the critical length will be proportional to \( B_0^{-1} \cdot r_p \) [21]. Geistlinger et al. [6] estimated the critical length to be on the order of the grain size for the injection of air into water-saturated uniform glass beads greater than 3 mm in diameter, and Glass et al. [9] estimated the critical length to be 4.2 cm for the injection of \( \text{CO}_2 \) into water-saturated uniform sand with a median grain size of 1.1 mm. Glass et al. [9] reported that their estimated value was consistent with their experiments, as multiple fragmentation events were observed over a distance of approximately 20 cm, and Geistlinger et al. [6] reported that their estimated value was consistent with previously reported observations of discontinuous gas flow in media with grain sizes greater than 3 mm. This suggests that Eq. (9) can provide appropriate estimates of the critical cluster length. However, a direct comparison of experimental and predicted critical cluster lengths was not possible because the critical cluster lengths were not measured during the experiments.

3. Materials and methods

3.1. Flow cell

Both the NAPL pool and gas injection experiments were conducted using a small-scale (100 mm \( \times \) 80 mm \( \times \) 8 mm) glass flow cell (Fig. 2). The flow cell was constructed of rectangular glass tubing, heated at the bottom to create a sealed base and then cut to length. 10-mm diameter glass tubing was installed on either side of the flow cell to serve as influent and effluent ports. The top of the flow cell was sealed by the compression of a rubber gasket along the top surface. Construction of the flow cell in this manner eliminated any seals near the bottom of the flow cell that could be incompatible with NAPL and allowed visualization of the entire domain.

3.2. Porous media

One of three size fractions of natural sand (Accusand, Unimin Corporation) were used in all experiments: 12/20, 20/30, and 30/40, referred to here as 1.1, 0.7, and 0.5 mm sand, with selected properties listed in Table 1. Bond numbers and critical flow rates were calculated using Eq. (5) and Eq. (6), respectively, for the displacement of water by air. These sands have been used extensively in bench-scale experiments of two-phase and three-phase flow processes due to the high degree of batch-to-batch reproducibility available from the manufacturer [23] and their ability to transmit sufficient light to allow visualization of flow processes in transparent, two-dimensional models [8,9,24–27].
All sands were used as received from the manufacturer with no further processing except a thorough rinsing with distilled water to remove any fines that may have accumulated during shipping. Microscopic and macroscopic air entrapment in the sand were minimized by placing the sand in water under vacuum prior to packing, and continuously pouring the wet sand into the water-filled flow cell. The continuous pouring, together with the tapping of the flow cell walls with a small rubber mallet following the pour, achieved a reasonably homogeneous pack. The porosity of the sand pack in each experiment (Table 2 and Table 3) was determined based on the known volume of the flow cell and the mass of sand used in the packing.

### 3.3. Gas expansion above a NAPL pool

To measure the expansion of a discontinuous gas phase above the surface of a NAPL pool in experiments #1 and #2, the flow cell was packed as shown in Fig. 2a. The center of the cell was packed with 1.1 mm sand, the bottom corners were packed with finer glass beads (0.6–0.8 mm diameter, Potters Industries) to contain the NAPL pool, and the influent and effluent walls were packed with 4 mm glass beads (Propper Manufacturing Co. Inc.) to distribute the flow along the height of the flow cell.

Midway through the packing procedure 0.6 mL of trans-1,2-dichloroethene (tDCE, AfA Aesar, 98%) dyed with 100 mg/L of Sudan 4 (Acros Organics) was emplaced at the bottom of the cell to create a pool with a length of 4.3 cm. The tDCE was emplaced using a gastight syringe and a stainless steel needle, inserted into the packing from the top and subsequently withdrawn. tDCE was selected for this experiment due to its relatively high vapor pressure of \(4.2 \times 10^4\) Pa at 25 °C [28], which was expected to result in relatively rapid expansion of the gas phase [4]. Following emplacement of the NAPL pool, a 4 μL bubble of laboratory air was emplaced 4 mm above the pool surface near the center of the front wall of the flow cell using the same technique as for the NAPL emplacement. Both the tDCE and the air were emplaced midway through the packing to allow easier insertion and withdrawal of the injection needle, and limit the creation of a preferential gas flow path due to rearrangement of the sand grains during needle withdrawal. By emplacing the tDCE and air midway through the packing, this potential preferential pathway was limited to a height of 2 cm above the pool surface.

Distilled water saturated with laboratory air was pumped through the flow cell using a peristaltic pump (Cole-Parmer, model No. 7550-50). The effluent exited the flow cell through a port located near the bottom of the cell, and was discharged through tubing at a fixed elevation located 1.5 cm below the top of the flow cell. The influent contained 200 mg/L of sodium azide to act as a biocide [29–31]. The flow rate was measured periodically by weighing the effluent (Table 2), which was collected in a flask covered to minimize evaporative losses.

To quantify the expansion of the gas phase the packed flow cell was placed on a laboratory balance (Mettler Toledo, model No. PG5002-SDR) throughout the experiment to measure the water mass lost from the flow cell due to displacement by the expanding gas. The water-mass loss was corrected for mass lost due to NAPL dissolution using a dissolution rate calculated from periodic sampling of the effluent and subsequent analysis of dissolved tDCE in experiment #2. The effluent from experiment #1 was not sampled, but the tDCE pools in each experiment were visually observed to dissolve at similar rates. Analysis of dissolved tDCE was conducted by gas chromatography–mass spectroscopy (Agilent 6890 GC, Agilent 5973 MS mass selective detector, Restek Rtx-502.2 60 m, 0.32 mm ID, 1.8 μm film thickness column) equipped with a headspace autosampler (Agilent 7694E). The temperature program for the GC oven was 40 °C hold for 6 min, ramp at 10 °C/min to 120 °C, and ramp at 25 °C/min to 220 °C. The total effluent mass of 0.72 ± 0.03 g, determined by integration of the breakthrough curve, was not significantly different from the injected mass of 0.76 ± 0.03 g, which indicates a satisfactory mass balance. Based on the breakthrough data, tDCE was lost at a linear rate of \(6.4 \times 10^{-5} \pm 2 \times 10^{-5}\) g/day, with no distinction between mass lost directly from the pool to the aqueous phase and mass lost from the pool to the aqueous phase through the gas phase. Assuming that all of the dissolved tDCE was replaced by water, the dissolution of the pool resulted in a change in mass of the flow cell of 1.25 \(\times 10^{-2} \pm 4 \times 10^{-4}\) g/day, which was used to correct the mass data. This rate represents 4% of the total mass change due to dissolution of the pool, and the displacement of water by the expanding gas phase.

### Table 1
Porous media properties.

<table>
<thead>
<tr>
<th>Size fraction 12/20</th>
<th>0.7 mm sand</th>
<th>0.5 mm sand</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air-entry pressure (cm of H2O)</td>
<td>5.42</td>
<td>8.66</td>
</tr>
<tr>
<td>Uniformity coefficient</td>
<td>1.231</td>
<td>1.19</td>
</tr>
<tr>
<td>Median grain size (mm)</td>
<td>1.105</td>
<td>0.713</td>
</tr>
</tbody>
</table>

### Table 2
Conditions and observations for gas expansion above a NAPL pool.

<table>
<thead>
<tr>
<th>Experiment no.</th>
<th>Packing</th>
<th>Porosity</th>
<th>Aqueous flow rate (ml/min)</th>
<th>Average gas expansion rate (ml/day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 1.1 mm sand</td>
<td>0.335</td>
<td>0.130</td>
<td>0.34 ± 0.02</td>
<td></td>
</tr>
<tr>
<td>2 1.1 mm sand</td>
<td>0.334</td>
<td>0.125</td>
<td>0.29 ± 0.01</td>
<td></td>
</tr>
</tbody>
</table>
3.4. Gas injection

To align the flow of a slowly injected gas phase in experiments #3–#17, the flow cell was packed as shown in Fig. 2b. The flow cell was packed with 1.1, 0.7, or 0.5 mm sand. A 2-mm ID glass tube was inserted into a port and connected to a gastight syringe (Hamilton, 2.5 mL, model No. 1002) on a syringe pump (KD Scientific, model No. 230). The syringe pump was used to inject 1000 μL of laboratory air at rates of 1 μL/min or 10 μL/min (Table 3), which are well below the calculated Qcrit values. A relatively large-diameter injection tube was used to avoid the creation of an artificial fragmentation point, as would be created by using a tube with a diameter significantly less than that of the surrounding pore spaces, and promote fragmentation within the sand pack.

The second port was connected to a 9.7-cm diameter water reservoir. As a result of this wide diameter, the displacement of water by the injected air resulted in an increase in water level of only 0.1 mm by the end of the injection, effectively maintaining a constant water pressure on the flow cell throughout the experiment. The water reservoir was open to the atmosphere via a small hole in a Parafilm® cover. The water in the reservoir and the flow cell was saturated with laboratory air prior to beginning the experiment to minimize any changes in volume due to dissolution of the gas phase.

The pressure of the injected gas phase was measured using a differential pressure sensor (Honeywell, model No. DC005NDC4) attached to the tubing from the syringe and the water reservoir. The differential pressure was measured once per 0.5 s and was recorded using a datalogger (Campbell Scientific, model No. CR23X).

3.5. Visualization

Digital images of experiments #2–#17 were collected using a CCD camera (Canon A640) connected to a personal computer equipped with software from the camera manufacturer. Images were collected at a resolution of (0.05 mm)²/pixel. The flow cell was located between the camera and a light source, which consisted of light from three 50 W halogen bulbs (Liteline Corporation, model No. CF-130-B) reflected off a white background. This allowed visualization of the depth-averaged gas saturation by light transmission [25,32,33].

The digital images for experiments #3–#17 were processed by aligning the images to correct for shifts between the camera and the flow cell, converting the collected RGB image to a grayscale intensity image, and then subtracting the background image by calculating the difference in optical density [3] using [34]

$$\Delta OD = OD_t - OD_0 = \log \left( \frac{I_{ref(t)}}{I_{ref(0)}} \right)$$

where ΔOD is the difference in optical density, OD is the optical density, I is the transmitted light intensity and \(I_{ref}\) is the average transmitted light intensity over the reference region. The subscripts 0 and t refer to images collected initially and at time t, respectively. The intensity of the reference region was used to correct for temporal changes in lighting, and the reference region consisted of a 2.4 cm × 1 cm section of the sand that was unaffected by the injected gas phase. Following background subtraction, noise was reduced by processing using a median filter on a 3 × 3 pixel² (0.14 × 0.14 mm²) area. Alignment of the images and measurement of critical cluster lengths were conducted using ImageJ (http://rsb.info.nih.gov/ij/), and all other processing was done using MatLab (Release 13, MathWorks, Inc.).

4. Results and discussion

4.1. Gas expansion above a NAPL pool

During experiments #1 and #2, repeated expansion, fragmentation, and mobilization of the gas phase was observed. The discontinuous gas phase expanded across the surface of the NAPL pool, was vertically mobilized, and accumulated at the top boundary of the flow cell and in the coarse bead packs along the influent and effluent walls. Mobilized gas entered the coarse bead packs by migrating along the top boundary of the cell and by penetrating the right-hand coarse bead pack near the NAPL injection point. Fig. 3 shows the approximate distribution of the gas phase at three times for experiment #2, which were similar to those observed in experiment #1. The general behavior of the gas phase is consistent with previous experiments conducted in the 1.1 mm sand [3].

The accumulation of gas in the flow cell over time is shown in Fig. 4 for each of the duplicate experiments. The initial 4 μL air bubble expanded to 4.2 mL of gas after 13.1 days in experiment #1, and 4.5 mL of gas after 13.7 days in experiment #2. Treating the entire volume of the sand pack as a representative elementary volume, this represents a change in the macroscopic gas-phase saturation of 3 orders of magnitude, from 3 × 10⁻³ to 3 × 10⁻¹. The
The transient distribution of the injected gas phase is illustrated in Fig. 5 for experiments #8, #12, and #16, conducted in the 1.1, 0.7, and 0.5 mm sand, respectively. Fig. 5 shows that the expansion of the injected gas is dominated by growth in the vertical direction, as expected for systems where gravitational forces play a significant role [21]. Growth was seen to occur as a series of short duration macroscopic events, referred to as “bursts” [18], separated by longer periods of no movement. These bursts were attributed to both the alternating pore-scale mechanisms of pressurization and pore-filling associated with the growth of a non-wetting fluid cluster [17] and the fragmentation and mobilization associated with the growth of a non-wetting fluid cluster subjected to a gravity field [18].

Evidence of burst growth is given in Fig. 6, which shows two pairs of successive images from experiment #8 as the difference in optical density from the background image. The time between each image in a pair is 30 s. Fig. 6 also shows the difference between each of the images in a pair. The two burst events shown in Fig. 6 are the result of fragmentation and migration of the discontinuous gas cluster. Upon reaching the critical cluster length, the drop in the gas-phase pressure resulted in a corresponding drop in the local capillary pressure near the gas injection point. This resulted in the reinvasion of pores with water, fragmentation of the cluster, and the significant mobilization of gas from lower parts of the cluster to new pore spaces near the top of the cluster. The discontinuous nature of the gas clusters is highlighted by the results in Fig. 6f, which show the mobilization of gas from the right-hand side of the gas distribution but not from the left-hand side.

4.3. Gas Injection: pressure measurements

Transient pressure measurements for experiments #8, #12, and #16 are shown in Fig. 7, conducted in the 1.1, 0.7, and 0.5 mm sand, respectively. These results are representative of the general patterns observed in all other gas injection experiments. Fig. 7 shows three phases in the evolution of the capillary pressure: (1) initial pressurization, (2) drainage, and (3) pressure fluctuation, which have also been reported for air injection into glass beads [6]. During the initial pressurization phase the capillary pressure rises as gas is injected into the pore space immediately adjacent to the injection tube. Since the gas phase is continuous throughout the injection syringe, injection tube, and pressure sensor tubing, this pressurization requires a greater gas volume than what is expected for the pressurization of a gas cluster in a single pore. The total gas injection and pressure measurement system had a volume of 9 mL, which affected the volume required to pressurize the gas phase during the initial pressurization and the pressure fluctuation phases. The initial pressurization phase ends when the first pore space adjacent to the injection tube is invaded and the gas cluster begins to expand within the porous medium. Entry pressures at the end of the initial pressurization stage were measured to be 7 ± 1, 11 ± 2, and 19 ± 5 cm in the 1.1, 0.7, and 0.5 mm sand, respectively. As expected, this entry pressure increased with decreasing grain size, and did not vary substantially between experiments at the same grain size due to the uniformity of these sands. However, it is not equal to the value of the air-entry pressure reported for the sands (Table 1) since not all pore spaces are available for entry. Therefore, the displacement values observed here represent the lowest local capillary pressure of the available adjacent pore spaces.

During the drainage phase the capillary pressure generally decreased with additional gas injection due to vertical growth of the gas cluster, which resulted in decreased hydrostatic pressure at the upper gas–liquid interface and lower gas pressures. The short-term periods of increasing capillary pressure during this phase are caused by the invasion of pores with greater local capillary pressure during gas expansion. The drainage phase ends when the gas cluster reaches the critical cluster length for the first time, and fragmentation occurs.

During the pressure fluctuation phase the capillary pressure undergoes cycles of increasing and decreasing pressure due to the repeated fragmentation of the gas cluster attached to the
injection tube, which indicates discontinuous gas flow [6]. These cycles are bounded by maximum and minimum pressures (Table 3), which represent the pore-scale entry \( P_e \) and terminal \( P_t \) pressures, respectively, at the fragmentation point. As discussed for the initial pressurization phase, the entry pressures are not necessarily equal to the air-entry pressures reported for these sands due to the limited pore spaces sampled by the gas phase. However, as expected, they follow the same trend as the reported air-entry pressures and increase with decreasing grain size. The ratio \( P_t/P_e \) had an average value of 0.60 and was not significantly different between the different sands. This is consistent with values of \( P_t/P_e \) between 0.44 and 0.71 reported by Gerhard and Kueper [22] based on their analysis of data from capillary pressure-saturation curves in several multi-fluid porous media systems in the literature and their own NAPL infiltration experiments.

The transition from the minimum to maximum capillary pressures is due to pressurization of the gas cluster, and appears as a constant, positive-slope pressure increase at the beginning of each fluctuation cycle in Fig. 7. The slope of this line is an artifact of the experimental set-up caused by the volume of the injection syringe and pressure sensor tubing, as discussed for the initial pressurization phase. In the absence of equipment and instrumentation, this volume required for pressurization would be significantly less. The effect of the injection syringe and pressure sensor tubing volume...
was verified in a separate experiment where the volume of the measurement system was changed, and a corresponding change in the pressurization slope was observed (data not shown).

The transition from maximum to minimum capillary pressure is due to expansion of the gas cluster, which occurs in a manner unlike during the initial drainage phase due to the presence of trapped gas clusters along the pathway of expansion. These trapped clusters form portions of a disconnected “pipeline” [18] that provides access to gas-occupied pore spaces at greater elevations. Where larger trapped clusters are located close together, minimal volume is required to reconnect a cluster of critical length, and the decrease in capillary pressure followed by fragmentation is very rapid. This is the case for most of the cycles in experiments #12 and #16. In the remaining cycles, and the cycles observed in experiment #8, the trapped clusters are smaller and more separated, resulting in several coalescence events prior to the achievement of the critical cluster length. These coalescence events result in rapid changes in the capillary pressure with no fragmentation, and produce the secondary fluctuations prevalent in the data from experiment #8.

The pattern of fluctuating pressure in each experiment is very consistent between cycles. The consistent maximum and minimum pressures indicate that fragmentation is occurring in the same pore space and returning to a lower capillary pressure dictated by the critical cluster length following fragmentation. The consistent pattern of secondary fluctuation during the decrease from maximum to minimum pressure indicates that the same pathway is being followed during expansion. Changes in this pattern of secondary fluctuation represent a change in the expansion pathway. The differences observed in experiment #16 following the injection of 0.7 and 0.9 mL of gas were due to a difference in the distribution of trapped clusters caused by fragmentation and mobilization events at greater elevations. This resulted in secondary fluctuations in capillary pressure prior to achieving the critical cluster length in two of the eight cycles. The change in the secondary fluctuation observed in experiment #8 after 0.33 mL of gas injected was due to branching of the injected gas cluster, which produced an additional drainage event between 0.33 and 0.46 mL injected. Branching here refers to the selection of different flow paths by mobilized gas clusters between subsequent mobilization events. Branching of the clusters was observed in 7 of the 12 experiments conducted in the 1.1 and 0.7 mm sands, despite the very slow flow rates and nearly inviscid non-wetting phase. This type of branching in natural porous media under the conditions used...
experiments #8 and #12, and at a narrow concentration boundary layers above NAPL pools [38,39]. An expanding gas cluster will reach greater heights at a much faster rate if trapped gas is available for pipeline growth. Due to the narrow concentration boundary layers above NAPL pools [38,39] and a NAPL pool will be under conditions that favor dissolution due to hydrostatic and capillary pressures. Most of the trapped gas above a NAPL pool will be under conditions appropriate for branch dissolution due to hydrostatic and capillary pressures. However, the sensitivity is expected to be greater in less uniform media, and additional investigation is warranted.

4.4. Gas injection: critical cluster length

Direct measurement of the critical cluster length requires a clear indication of when fragmentation of a gas cluster occurs. Visually identifying closely spaced, but separated clusters in a quasi-two-dimensional porous medium using light transmission is not possible due to the point-wise errors associated with the light transmission technique [25], and the additional blurring of the image associated with sharp transitions between phases and gas clusters that do not occupy the entire width of the pack [9]. This prevents the accurate differentiation between two clusters separated by a few pores and two sub-clusters connected by a single gas-filled pore. To overcome this limitation, the time of fragmentation was identified using the transient pressure measurements, rather than the image data. At the end of a drainage phase (Fig. 7) the minimum pressure is achieved and the gas cluster undergoes fragmentation for the first time. Until that fragmentation occurs, the gas exists as a single, connected phase that extends from the injection point to the top of the cluster. The height of this connected cluster is equal to the critical cluster length. Therefore, the image collected immediately prior to fragmentation at the end of the drainage phase can be used to measure the critical cluster length. An example is shown in Fig. 6, where the fragmentation that occurred between 249 and 254 µL was the fragmentation at the end of the drainage phase (Fig. 7), and the length of the cluster in Fig. 6a is equal to the critical cluster length.

Measurements of the critical cluster length are listed in Table 3 for each of the gas injection experiments. Critical cluster lengths range from 1.4–3.6, 3.2–6.0, and 2.8–6.5 cm in the 1.1, 0.7, and 0.5 mm sands, respectively. For comparison, theoretical values of the critical cluster lengths were calculated using (9), where \( P_{top}^{c} \) and \( P_{bottom}^{c} \) were estimated according to the method proposed by Glass et al. [9]. \( P_{bottom}^{c} \) was taken to be the capillary pressure at an effective non-wetting saturation of 0.3, calculated here using the Brooks-Corey capillary pressure-saturation relationship and parameters reported for main drainage [23], and \( P_{top}^{c} \) was taken to be \( 1/2P_{top}^{c} \). Estimates of the critical cluster length from each of the three sands were fit to a power-law relationship, which is shown as the solid line in Fig. 8. A value of \( S_{enw} = 0.3 \) was selected by Glass et al. [9] based on the approximate percolation threshold in an uncorrelated cubic lattice. However, they found that their estimates were not sensitive to the choice of \( S_{enw} \), which was also found here. To illustrate the sensitivity of the theoretical critical cluster length estimates to the choice of \( S_{enw} \), power-law relationships were also fit to estimates based on \( S_{enw} = 0.2 \) and \( S_{enw} = 0.4 \) (Fig. 8), and only minor differences exist. This is expected for these sands, which have little variation in pore sizes, and show little change in capillary pressure with saturation at intermediate saturations. However, the sensitivity is expected to be greater in less uniform media, and additional investigation is warranted.

![Fig. 7. Capillary pressure measured at the gas injection point for experiments #8, #12, and #16. The 1 mL of gas was injected at 10 µL/min for 100 min in experiments #8 and #12, and at 1 µL/min for 1000 min in experiment #16. The end of the drainage phase, and the occurrence of the first fragmentation event, is indicated by the white arrows for each experiment.](image1)

![Fig. 8. Measured critical cluster lengths (symbols) for the 1.1, 0.7, and 0.5 mm sand compared to theoretical estimates (lines) based on Eq. (9), calculated using capillary pressure values at effective non-wetting saturations of 0.2, 0.3, and 0.4.](image2)
Fig. 8 shows that the data agree well with the theoretically predicted values. Variation in the critical cluster length between experiments is expected due to the pore-scale heterogeneity present in even these relatively uniform sands. The low values of 1.4, 3.2, and 2.8 cm observed in experiments #3, #14, and #17, respectively, represent situations where conditions favorable to fragmentation were present in the packing (i.e., larger pore spaces with lower $P_c$ present above smaller pore spaces with greater $P_c$). The results in Fig. 8 provide the first experimental evidence that the critical cluster length may be reasonably estimated using data obtained from capillary pressure-saturation curves. However, additional studies designed to test the relationship in different media, and using different fluids, would be beneficial.

5. Conclusions

In this study the spontaneous expansion rate of discontinuous gas in 1.1 mm sand above a NAPL pool was quantified, and the gas flow was characterized by slowly injecting air into 1.1 mm, 0.7, and 0.5 mm sands at rates similar to the flow produced by the partitioning of volatile NAPL compounds to a discontinuous gas phase. The expansion of a single, initially NAPL-free gas cluster above a 4.3 cm-long tDCE pool in 1.1 mm sand resulted in discontinuous gas flow, with repeated expansion, fragmentation, and mobilization of the gas phase. Average expansion rates of 0.34 ± 0.02 and 0.29 ± 0.01 mL/day were measured in duplicate experiments, which resulted in an expansion from 4 to 4.2–4.5 μL of gas in 13.1–13.7 days. This work shows that the spontaneous expansion of gas due to the partitioning of volatile NAPL can be expected to result in discontinuous gas flow in porous media with a grain size greater than 0.02 mm.

Injections of air into 1.1, 0.7, and 0.5 mm sand at 1 and 10 μL/min resulted in discontinuous gas flow characterized by vertically-dominated gas distribution patterns and growth as short-duration bursts. Measured gas pressures showed the consistent, repeated return of capillary pressure to maximum and minimum values that represent pore-scale entry ($P_e$) and terminal ($P_t$) pressures, respectively, at the fragmentation point. The average value of $P_e/P_t = 0.60$ was consistent with values reported in the literature.

Patterns in the transient pressure data were used to identify fragmentation events, which was not possible using images from light transmission data alone. This allowed the first direct measurement of critical gas cluster lengths in quasi-two-dimensional porous media. Critical cluster lengths were measured to be 1.4–3.6, 3.2–6.0 and 2.8–6.5 cm in the 1.1, 0.7 and 0.5 mm sands, respectively. These values agreed well with estimates of the critical cluster length made using previously reported equations, and parameters derived from the medium's capillary pressure-saturation relationship.

Patterns in the transient pressure data were also used to provide insight into pipeline growth behavior and the onset of branching during expansion of the gas phase. Understanding pipeline growth, where rapid vertical expansion of the gas phase occurs through coalescence with trapped clusters above, is important for understanding the effect of expanding discontinuous gas clusters on NAPL pool dissolution. If pipeline growth can be sustained above a NAPL pool, due to slower dissolution of upper gas clusters compared to the growth of those near the pool surface, then the effect of spontaneous gas expansion on the spatial distribution of dissolved NAPL will be greater. Prediction of this effect will require numerical models capable of reproducing the fragmentation and migration processes that are controlled at the pore-scale, as well as simulating multi-component partitioning to a discontinuous gas phase. While modified invasion percolation (MIP) techniques have been successful in reproducing flow patterns produced by the unstable displacement of a wetting fluid by a non-wetting fluid with fragmentation [18–20], the expansion of the non-wetting fluid is not coupled to mass transfer. Published models for multi-component mass transfer to a discontinuous gas phase [13,15,40] make use of a continuum formulation that cannot simulate the onset of mobilization [13] without the use of empirically-derived expressions [16]. Future research will look at coupling mass transfer to models capable of simulating pore-controlled behavior, similar to the approach employed to study the drying of porous media (e.g., [41,42]).

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References


