Laboratory Studies of Groundwater Degassing in Replicas of Natural Fractured Rock for Linear Flow Geometry

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February 1998
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Executive Summary

Laboratory experiments to simulate two-phase (gas and water) flow in fractured rock evolving from groundwater degassing were conducted in transparent replicas of natural rock fractures. These experiments extend the work by Geller et al. (1995) and Jarsjö and Geller (1996) that tests the hypothesis that groundwater degassing caused observed flow reductions in the Stripa Simulated Drift Experiment (SDE) (Long et al., 1995). Understanding degassing effects over a range of gas contents is needed due to the uncertainty in the gas contents of the water at the SDE. The main objectives of this study were to:

1. measure the effect of groundwater degassing on liquid flow rates for lower gas contents than the values used in Geller et al. (1995) for linear flow geometry in the same fracture replicas of Geller et al. (1995)
2. provide a data set to develop a predictive model of two-phase flow in fractures for conditions of groundwater degassing
3. improve the certainty of experimental gas contents (this effort included modifications to the experimental system used by Geller et al. (1995) and separate gas-water equilibration tests)

In the degassing experiments, constant inlet and outlet pressure boundary conditions are maintained in order to simulate the boundary conditions of the SDE. Distilled, de-aired water and CO₂ gas are equilibrated at a “bubble pressure” calculated to produce the gas contents of interest. The fracture inlet pressure is held at a value greater than the bubble pressure of the gas. The fracture outlet pressure is initially above the bubble pressure of the gas, and then reduced incrementally, in a manner analogous to the groundwater degassing borehole tests at the Hard Rock Laboratory in Åspö, Sweden (Geller and Jarsjö, 1995).

Two experiments were conducted in a replica of a fracture from Dixie Valley at 3 and 6% gas contents, as measured from the volume of evolved gas at the final fracture outlet pressure. One experiment was conducted in a replica of a fracture from Stripa at 6% gas contents. In all three experiments, the gas contents measured from the volume of gas outflow were several percent higher than the values predicted from the CO₂ equilibration bubble pressure, and a gas phase appeared in the tubing upstream of the fracture replica when the fracture outlet pressure was above the CO₂ equilibration pressure, indicating that the dissolved gas had a higher bubble pressure than designed for.

Calculations and the results of the separate gas-water equilibration tests provide explanations for these observations. The larger gas content was due to the presence of excess gas phase CO₂ in the tank before the tank was pressurized for flow. The higher bubble pressure was due to the partitioning of nitrogen gas into the influent water. The nitrogen gas was used to maintain influent water pressure and drive flow through the fracture; it was in direct contact with the water, and at a higher pressure than the CO₂ equilibration pressure. In the separate gas-water equilibration tests, the nitrogen was isolated from the influent water by means of a bladder, and gas did not evolve at pressures above the CO₂ equilibration pressure.
Because the actual gas contents of the water in the degassing experiments were calculated from the gas collected in the effluent of the experiment, the certainty in the correlation between the measured flow reductions and gas contents is greater than in the previous experiments by Geller et al. (1995) and Jarsjö and Geller (1996), where gas contents were derived from the CO₂ equilibration pressure. Based upon the current work's comparison between gas contents derived from the CO₂ equilibration pressure and evolved gas measured in the effluent, one may assume that the actual gas contents in those experiments were several percent higher than reported.

The nature of preferential flow paths were shown to play an important role in the effects of degassing on liquid flow rates. Preferential flow paths through the two fractures were identified from images of the invasion of dyed water into the liquid saturated fracture and exhibited distinctly different characteristics. In the Dixie Valley replica, flow was well-distributed across most of the entire fracture plane, taking three major flow paths directly across the fracture from inlet to outlet. In the Stripa fracture, one flow path extended across the bottom of the fracture, and a second flow path swirled around an impermeable central region. From images of gas-liquid phase distributions in the replicas during degassing, in the Dixie Valley replica, two flow paths initially filled with gas, with little effect on liquid flow rates; the significant decline in flow rate occurred with gas blockage in the middle of the three flow paths. In the Stripa fracture, liquid flow rates decreased with the first presence of gas in the fracture, and continued to decrease as the gas filled more of the flow paths.

Degassing in the Dixie Valley replica resulted in a transmissivity decrease of 27% and 83% of the single liquid phase values for 3% and 6% measured gas contents, respectively, suggesting a relationship between gas contents and liquid flow rate reduction. In the Stripa fracture, the final transmissivity decreased by 77% from single liquid phase conditions for 6% gas contents. These results extend the range of experiments by Geller et al. (1995). They measured flow reductions of approximately 70 to 80% for gas contents ranging from 12 to 24% in the Dixie Valley fracture, however no significant relationship between gas content and flow reduction was observed in this range. In the Stripa fracture, they measured approximately 90% reduction in liquid flow rate for gas contents ranging from 7% to 13%. Together, the current and previous results suggest that for gas contents up to 6% in the Dixie Valley sample, liquid flow reduction is a function of gas contents. In the Stripa sample, liquid flow reduction may be sensitive to gas contents over a larger range, due to the differences in the aperture distributions of the two samples.

Current and previous laboratory experiments show that the magnitude of flow reduction due to groundwater degassing is near the range observed at the Stripa SDE, and suggest a relationship between gas contents and the magnitude of liquid flow reduction. A model is needed to extrapolate these results to the field scale and to test the sensitivity of degassing effects on boundary conditions and gas contents. Modeling efforts to date have greatly under-predicted the magnitude of flow reduction observed at the Stripa SDE (C. Doughty in Geller et al., 1995) over the same range of gas contents. The hypothesized cause of this discrepancy is that the re-solution of evolved gas as pressures increase due to flow
blockage is mass-transfer limited, and as a consequence, gas-saturations cannot be predicted by the current model, which uses Henry’s Law. The laboratory experiments were designed to test this hypothesis by providing a data set with well-defined boundary conditions, where degassing occurred within the fracture replica, that could be compared to modeling results. This objective was not met in the current study due to degassing upstream of the fracture replica, however a system for improved reliability in controlling gas contents was developed and demonstrated, which supports the interpretation of current and previous results and can be used in subsequent experiments to test this hypothesis.
1.0 Introduction

Laboratory experiments to simulate two-phase (gas and water) flow in fractured rock evolving from groundwater degassing were conducted in transparent replicas of natural rock fractures. The main objectives of this study were to:

1. measure the effect of groundwater degassing on liquid flow rates for lower gas contents than the values used in Geller et al. (1995) for linear flow geometry in the same fracture replicas of Geller et al. (1995)
2. provide a data set to develop a predictive model of two-phase flow in fractures for conditions of groundwater degassing
3. improve the certainty of experimental gas contents (this effort included modifications to the experimental system used by Geller et al. (1995) and separate gas-water equilibration tests)

Constant inlet and outlet pressure boundary conditions were maintained in order to simulate the boundary conditions of the Stripa Simulated Drift Experiment (SDE) (Olsson, 1992). The experimental set-up was modified to address several outstanding issues with regards to previous work.

1.1 Flow reduction for linear flow geometry at low gas contents. At the SDE, groundwater degassing is hypothesized to have caused a 90% reduction in water flow to the drift compared to values predicted from borehole tests (Long et al., 1995). Understanding degassing effects over a range of gas contents is needed due to the uncertainty in the gas contents of the water at the Stripa SDE. Gas was observed in the tubing from SDE boreholes when the borehole pressure was lowered from 700 to 170 kPa (Olsson, 1992). Assuming the gas is nitrogen at 10°C, gas contents could be anywhere between 5 and 15%, according to Henry's Law. Gas content values measured at the Stripa mine were 2% to 4%; 95% of the gas was nitrogen (Olsson, 1992). However the measured range is questionable in the light of the observation of gas in the SDE boreholes and the difficulty in obtaining good samples for gas analysis. The minimal effect of degassing in a borehole test by Geller and Jarsjö (1995) was attributed, in part, to the low gas contents of the water (3%-4%), and to the high near-borehole hydraulic gradients due to the radial flow geometry. The presence of these two factors made this test inconclusive as to the potential for groundwater degassing to measurably affect liquid flow. Geller et al. (1995) measured significant flow reductions due to degassing for linear flow geometry in replicas cast from a fracture sample from Stripa, and a fracture from Dixie Valley at gas contents ranging from 7% to 24%. Jarsjö and Geller (1996) found a threshold gas content below which effects on flow from degassing were minimal in radial (converging) flow geometry in fracture replicas cast from Stripa and Äspö samples for gas contents ranging from 1% to 15%. In the present study, experiments are conducted in the fracture replicas used by Geller et al. (1995) for gas contents of 6% and less.

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1 Gas contents is expressed as the percent volume of gas per volume of water corrected to standard temperature and pressure that evolves when the liquid pressure is lowered.
1.2 Modifications for improving the certainty in experimental gas contents. In the laboratory experiments, the gas content of the water is determined from the pressure at which CO$_2$ gas is equilibrated with water. This equilibration pressure is referred to as the "bubble pressure", or the pressure below which a gas phase will evolve. In previous laboratory experiments, gas appeared in the fracture replica when pressures were above the bubble pressure, suggesting errors in the assumption of the gas content values. In the present study, experimental modifications were incrementally made to improve the reliability of the gas content achieved. All tubing of relatively gas permeable nylon was changed to relatively impermeable Teflon PFA. A gas trap was installed downstream of the fracture to measure evolved gas contents during the experiment, and compare with the estimated bubble pressure. In the last of three experiments, nitrogen was introduced into a teadlar bladder installed in the influent tank to limit gas exchange when the tank was pressurized with nitrogen gas to drive flow through the fracture. In a separate series of gas-water equilibration experiments, the influent tank pH was monitored an indicator of dissolved CO$_2$ concentration.

1.3 Endcaps to eliminate capillary barrier effects at fracture inlet and outlet. In previous experiments, the fracture endcaps had open slots to distribute and collect flow through the fracture replica. This geometry can create a capillary barrier and large pressure drops at the inlet and outlet under two-phase flow conditions. The current experiments were assembled with an endcap designed by Persoff et al. (1994) to separate gas and liquid phases at the inlet and outlet, thereby eliminating the capillary barrier and to ensure that observed flow reductions are due to gas trapping in the fracture and not due to end effects.
2.0 Experimental Procedures

2.1 Degassing in fracture replica

The laboratory experiments demonstrate the development of two-phase flow conditions due to gas exsolution in horizontal transparent fracture replicas, for linear flow geometry. The replica is saturated with water having a known gas content, then the outlet pressure is reduced below the bubble pressure of the dissolved gas. The steady-state flow rate occurring for constant pressure boundary conditions under two-phase flow conditions is compared to that occurring for single liquid-phase flow. To simulate the boundary conditions relevant to the Stripa SDE, and to provide well-defined boundary conditions for model testing, the fracture replica inlet and outlet pressures should be above and below the bubble pressure, respectively. With the small fracture samples used here, this requires the use of fractures having relatively low transmissivities, so that reasonable flow rates produce a pressure drop that is large relative to the bubble pressure, allowing gas exsolution to occur within the fracture replica.

The transparent replicas allow the direct observation of the gas and liquid phase distributions during the experiment, a technique used by Nicholl et al. (1994) and Persoff and Pruess (1995). The experiment was mounted over a light table, and observations were photographed. Because water matches the refractive index of the epoxy more closely than does gas, water-occupied spaces transmit light better and appear brighter, and gas-saturated areas are darker. The replicas are clear epoxy resin (Eccobond 27, Emerson and Cuming, Canton, MA) casts of both sides of a natural, rough-walled rock fracture, fabricated according to the methods described in Gentier (1986) and Persoff and Pruess (1995). The contact angle of water on the smooth epoxy surface is 70° measured through the water by the captive drop method as described in Adamson (1982).

Figure 2.1 shows the layout of the apparatus. Distilled water and gas were equilibrated in the influent vessel by injecting gas through a frit in the bottom of the reservoir at the desired pressure for a minimum of 24 hours. Carbon dioxide (CO₂) was used as the dissolved gas because its relatively high solubility in water (ca. 55 times greater than nitrogen gas) permitted the use of low pressures to achieve gas contents of interest.

To drive flow through the fracture, nitrogen (N₂) gas pressure was applied through a Mariotte tube, at a pressure higher than the CO₂ equilibration pressure. The influent vessel was mounted horizontally, 1 m above the plane of the fracture replica, to minimize the pressure gradient in the tank. In the last of three experiments, a deflated tedlar gas sampling bag (Alltech Associates Inc., Deerfield, IL) was attached to the end of the Mariotte tube which inflated when N₂ pressure was applied to drive flow, to eliminate gas exchange with the influent water.

Constant effluent pressure was maintained with an overflow tube in the outlet vessel, or an overflow tube to a beaker on an electronic balance. Effluent pressure was controlled by the elevation of the outlet or by application of N₂ gas to the outlet vessel to achieve higher pressures. The tubing material was Teflon PFA, which has a very low gas permeability.
All gas pressures were controlled with pneumatic pressure regulators that operate from 107 to 400 kPa (Fairchild Industrial Products Co., Winston-Salem, NC, model 65A). Liquid phase differential pressure across the fracture, and absolute pressures of the fracture outlet and inlet tank were continuously monitored with pressure transducers (Validyne DP15 and AP10, Northridge, CA) and acquired to a PC. Flow rates were measured either by the change in water level of the outlet vessel or by the mass collected over measured time intervals.

Once the fracture outlet pressure was decreased to near atmospheric pressure, evolved gas was collected downstream of the fracture in a trap, constructed of an inverted 100 mL glass graduated cylinder with a stopper in the bottom that contained the inlet and outlet ports. The fracture replica was photographed during the course of the experiment with a 1024x1024 pixel by 12 bit gray-scale digital camera (SpectraSource Instruments, MCD1200, Westlake Village, CA).

The fracture replicas used in the experiments were cast from a faulted rock fracture from Dixie Valley, a geothermal area in Nevada, and from a natural granite fracture from the Stripa mine in Sweden (as in Geller et al., 1995). The fracture replicas were 7.6 cm x 7.6 cm in area and compressed between two 10 cm-thick Lucite blocks to a stress of approximately 130 kPa. The endcaps were from a design by Persoff et al. (1994) to eliminate capillary barrier effects at the fracture boundaries by separating the gas and liquid phases, and are shown schematically in Figure 2.2. The open grooves and plenum transmit and collect the gas phase, while the ceramic that contacts the fracture edge transmits the liquid phase. The ceramic has an air entry pressure of 300 kPa, which is well above the gas phase pressures in the experiment and is therefore expected to remain liquid-saturated. The pressure taps for fracture differential and outlet absolute pressure measurement contact the fracture edge through the ceramic endcaps. Filter paper was placed between the ceramic and the fracture inlet, with slits at the gas grooves, to ensure liquid phase continuity between the ceramic teeth and the fracture. In the tubing immediately upstream and downstream of the fracture, there was a tee for a gas line to connect to the gas plenum.

Transmissivity Measurement. Initially the transmissivity \( T \) of each fracture replica is measured for fully water-saturated conditions using distilled, de-aired water. The term \( T \) is evaluated from Darcy's Law:

\[
Q = \frac{T}{\rho_L} \frac{\Delta P}{g} W
\]

where \( Q \) is the flow rate, \( \rho_L \) is the liquid density, \( g \) is the acceleration of gravity, \( \Delta P \) is the differential pressure across the fracture, \( L \) is the length of the fracture edge from inlet to outlet, and \( W \) is the width of the fracture edge at the inlet. \( T \) is determined from the linear regression of flow rate vs. differential pressure.

The effective hydraulic aperture, \( b \), is computed as follows:
where $\mu_l$ is the liquid viscosity.

**Dye injection.** After hydraulic conductivity was measured for water-saturated conditions, the fracture replica was saturated with dyed, de-aired water. Dyed water (10% Liquitint Patent Blue, Milliken Chemical, Inman, SC), was injected into the water-saturated fracture and photographed to reveal the dominant liquid flow paths. The dye concentration was set to establish the best resolution of the expected aperture values (described in following paragraph).

**Aperture distribution.** The aperture distribution was derived from the light intensity map of the image of the fracture saturated with dyed water, normalized by the image of the fracture saturated with clear water. The attenuation of light is a function of the distance the light travels, and is correlated to the width of open space of the fracture by calibration to the intensity of light transmitted through known apertures filled with the same liquids. The range of calibrated apertures was 7.6 to 1570 microns for the Dixie Valley replica, and 20 to 500 microns for the Stripa replica. Apertures outside the calibrated range are extrapolated from the measured light intensity vs. aperture curves.

**Gas-water equilibration.** The influent tank is 89 cm long by 6.3 cm diameter. For gas-water equilibration, the tank is mounted vertically, CO$_2$ gas is delivered to the bottom of the tank and tank pressure is measured from a tube at the bottom of the tank. The initial water level in the tank is a few mm below the top. A needle valve is attached to a vent at the top of the tank and is adjusted to achieve the desired tank pressure during gas-water equilibration.

For the low values of $P_{CO_2}$ and the vertical orientation of the tank, the hydrostatic pressure head and the relative elevation of the pressure transducer to the tank must be accounted for in estimating the actual gas content from the tank pressure. The relative elevations are shown in Figure 2.3. The tank pressure measured at the transducer elevation, $z_3$, is $P_{z_3}$. The difference in pressure before and during the application of CO$_2$ gas is $\Delta P_{z_3}$. The average $P_{CO_2}$ is calculated at the midpoint of the tank, or:

$$P_{CO_2} = \Delta P_{z_3} + \rho_l g(z_1 - z_2)/2 + P_{atm}$$

(2.1.3)

where $z_1$ and $z_2$ are the elevations of the tank top and bottom, respectively, and $P_{atm}$ is atmospheric pressure.
The percent of gas evolving at a given pressure $P_o$ is calculated from Henry’s Law:

$$\%_v = \frac{P_{CO_2} - P_o}{H_{CO_2}} \left( \frac{\bar{V}_{CO_2}}{\bar{V}_{H_2O}} \right) \times 100$$

(2.1.4)

where $H_{CO_2}$ is Henry’s Law Constant, and $\bar{V}_{CO_2}$ and $\bar{V}_{H_2O}$ are the molar volumes of CO$_2$ and water, respectively.

After gas-water equilibration, the vent valve is closed and the tank is mounted horizontally, 1 m above the plane of the fracture replica, to minimize the pressure gradients in the tank that would cause gradients in $P_{CO_2}$. Nitrogen pressure is applied to maintain the tank pressure above the bubble pressure of CO$_2$ and to drive the flow of water through the fracture.

2.2 Gas-water equilibration experiments

After the degassing experiments and remaining uncertainties in gas contents described in Section 3.1, gas-water equilibration experiments were performed. The experiments were similar to the degassing experiments, except that the fracture was replaced by a needle valve, across which pressure went from above to below the bubble pressure. A gas trap was installed downgradient of the needle valve. De-aired distilled water and CO$_2$ gas were equilibrated as for the degassing experiments, then the tank was mounted horizontally, and water was allowed to flow through the system by applying nitrogen gas pressure to the influent tank (with the tedlar bladder described in section 2.1). The flow rate was controlled by the needle valve, and the pressure at the gas trap was controlled by the elevation of the effluent line. A pH electrode was installed in the influent tank, as an indicator of the dissolved CO$_2$ concentration during gas-water equilibration. The electrode was a submersible, self-cleaning, double junction pH electrode connected to a benchtop standard pH meter (Cole-Parmer Instrument Co., Chicago, Ill.) . The pressure at the gas trap and the tank pressure and temperature were logged; pH, gas volume and mass of water collected were recorded intermittently. The assembly is shown in Figure 2.5.

The pH was measured without temperature compensation, so the meter values ($pH_m$) were corrected for the actual tank temperature by the following relationship derived from the Nernst equation, where $T$ is the tank temperature in degrees Kelvin:

$$pH(T) = pH_m \frac{T}{298.15}$$

(2.2.1)
The relationship between the partial pressure of CO$_2$ ($P_{CO_2}$) and pH is derived in the appendix, which may be combined with Eq. (2.1.4) to relate pH to the volume of gas evolving:

\[
\% \text{v/v} = \left( \frac{10^{-2pH} K_{a,1} H_{CO_2}}{P_o} \right) \left( \frac{\bar{V}_{CO_2}}{\bar{V}_{H_2O}} \right) \times 100 \quad (A.9)
\]

Eq. (A.9) is plotted in Figure 2.4 for the following values at 20°C: $K_{a,1} = 10^{-6.38}$, $H_{CO_2} = 1.44 \times 10^5$ kPa/mole-fraction; $\bar{V}_{H_2O} = 0.018036$ L/mole; $\bar{V}_{CO_2} = 24.05$ L/mole (ideal gas assumption) and $P_o = 101.4$ kPa (atmospheric pressure). The calculation shows that for the range of gas contents of interest, pH varies by only 0.03 units. The slopes of the plots indicate that for the precision of most pH measurements of 0.01 units, the detectable change in gas contents is 4.6% and in partial pressure of CO$_2$ is 5 kPa.
3.0 Experimental results

3.1 Degassing in Fracture Replicas

3.1.1 Water-saturated Transmissivity

In all experiments, the water-saturated transmissivity of the replica decreased with time, until steady values were reached. Similar behavior was noted by Jarsjö and Geller (1996). These values and the calculated hydraulic apertures are summarized in Table 3.1. Because steady values are ultimately attained, the decrease in transmissivity is most likely due to a combination of creep of the epoxy under load and swelling of the epoxy as it absorbs water, and not due to biological growth, in which case a steady value would not necessarily be reached. The water-saturated transmissivities over time are shown in Figure 3.1. In DV97-1, the replica was water-saturated for three months before the degassing experiment, and periodic monitoring of the transmissivity indicated that after two months, there was no further decrease in transmissivity (Fig. 3.1 (a)). In DV97-2 and ST97-1, experiments began two weeks after initially saturating with water, at which point most of the transmissivity decrease was presumed to have occurred. However, the resaturation of DV97-2 following the degassing experiment showed a further decrease in water-saturated transmissivity, where $\frac{dQ}{d\Delta P}$ decreased from 2.90 mL/hr/kPa before degassing to 1.70 mL/hr/kPa after resaturation. ST97-1 was not resaturated after the degassing experiment.

<table>
<thead>
<tr>
<th>Exp’t</th>
<th>$T$ (m$^2$)</th>
<th>$\frac{dQ}{d\Delta P}$ (mL/hr/kPa)</th>
<th>Hydraulic Aperture ($\mu$m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DV97-1</td>
<td>5.8e-9</td>
<td>2.13</td>
<td>19.1</td>
</tr>
<tr>
<td>DV97-2</td>
<td>7.9e-9</td>
<td>2.90</td>
<td>21.2</td>
</tr>
<tr>
<td>ST97</td>
<td>3.6e-9</td>
<td>1.30</td>
<td>16.2</td>
</tr>
</tbody>
</table>

DV97 is the Dixie Valley fracture; this fracture was reassembled between DV97-1 and DV97-2.
ST97 is the Stripa fracture.
3.1.2 Aperture Distributions and Dyed Water Injection

**DV97-1.** The aperture distribution for DV97-1 is shown in Fig. 3.2. The aperture distribution shows bands of relatively larger apertures on top and bottom (green), with central large-aperture lakes (black) bounded by smaller apertures. Asperity contacts appear mostly in the central band of the fracture, indicated in red. The low values of the apertures (10 microns or less with the exception of the lakes) are outside the calibrated range and are inconsistent with the hydraulic aperture of 19.1 microns. This may have been the result of the light table controller malfunctioning; it was replaced after this experiment. Therefore the aperture distribution must be viewed in terms of relative and not absolute values.

Dye injection to reveal preferential flow paths was mistakenly done into the opposite end of the fracture as the degassing experiment, so the reader is referred to the dye injection for DV97-2 (next section) for the discussion of preferential flow paths in the Dixie Valley fracture.

**DV97-2.** Fig. 3.3 shows the aperture distribution for DV97-2. The replica was reassembled following the experiment with DV97-1. The general distribution is similar to DV97-1, except that the aperture values are larger and on average are consistent with the hydraulic aperture measurement of 21.2 microns.

The injection of dyed water (Fig. 3.4) shows that the preferential flow paths occur in mostly horizontal bands across the fracture, consistent with the aperture distribution. Dye was visible in the top part of the fracture first, then the middle and bottom, swirling along the bottom, with bands of the fracture apparently impermeable to the flowing water.

**ST97.** The aperture distribution in Fig. 3.5 shows that the open apertures form an annular region around the tighter center of the fracture. The orientation of this fracture is rotated 90° counter-clockwise from the orientation in the experiments reported in Geller et al. (1995). The injection of dyed water (Fig. 3.6) shows that the bottom of the fracture is the most accessible, then liquid flows along the inlet side, around the top of the fracture and finally fills the outlet side of the fracture.
3.1.3 Fracture Replica Degassing Experiments

The experiment boundary conditions and results are summarized in Table 3.2. Each experiment is discussed in detail in the subsequent sections, followed by an overall summary and discussion of gas contents.

3.1.3.1 DV97-1

The results of the first degassing experiment, DV97-1, are summarized in Fig. 3.7. Gas bubbles were observed in the inlet tubing immediately after the injection of CO$_2$-saturated water to the fracture began, at which point the influent tank pressure was raised from 103 to 115.9 kPa where it was maintained throughout the experiment. As the tank was mounted 1 m above the fracture, the total pressure at the fracture inlet was 125.9 kPa. Gas bubbles still appeared in the inlet tubing. Fig. 3.7 (a) shows the fracture outlet pressure (P$_o$) during the course of the experiment. P$_o$ was maintained above the bubble pressure of 103.7 kPa for about 2.5 days while the fracture was saturated with CO$_2$-equilibrated water, and then lowered in two stages, above and below the bubble pressure. Gas was observed in the fracture bottom at about 1.25 days.

The measured liquid flow rates (Q) and the accumulated gas volume collected (V$_g$) are plotted in Fig. 3.7 (b). A gas phase appeared in the effluent line after the outlet pressure was lowered from 125.3 to 111.7 kPa at about 2.4 days. The measurement of accumulated gas volume began at 2.59 days, so gas leaving the fracture prior to this time was not collected. From 2.66 to 3.35 days, flow rates decreased from 36 to 22 mL/hr while P$_o$ was an average 113 kPa. After the outlet pressure was dropped to 103 kPa at 3.48 days, the flow rate decreased considerably over the first hour, then remained fairly steady afterwards. The change in the slope of V$_g$ with time reflects changes in the rate of gas production. After 3.8 days, the rate of gas production dropped considerably, probably due to stripping of CO$_2$ in the influent tank by the nitrogen used to drive flow (the nitrogen was not contained in a tedlar bladder in this experiment).

Evolved gas as a percent of liquid by volume is shown in Fig. 3.7 (c). Each point is calculated over the time increment from the previous point. At the point of highest gas production, the values ranged from 0.5 to 4.8%, illustrating the episodic nature of gas flow rates.

In Fig. 3.7 (d), flow rates are plotted as a function of P$_o$. Flow rates are linear with P$_o$ until the lowest pressure was achieved, even though gas was present in the fracture at the higher pressures. This supports the concept of a threshold gas content below which degassing does not cause a reduction in flow rates. The box symbols indicate the data selected for determining the linear trend for water-saturated transmissivity. The correlation coefficient ($R^2$) of the linear portion of the curve is 0.9884.

Images of the gas in the fracture at different times during the experiment are shown in Figs. 3.8 and 3.9. Flow is from right to left in each image. In Fig. 3.8, the images are normalized by the image taken at 2.40 days just before P$_o$ was lowered to 111.7 kPa.
this time, there was a little gas in the bottom of the fracture, and dyed water was still visible in the larger apertures in the central portion of the fracture. The darker shades in the images in Fig. 3.8 indicate gas that has appeared since the time of the normalizing image; the lighter shade indicates either resaturation of areas that were previously occupied by gas, or where dyed water has been displaced by clear water.

In the bottom of Fig. 3.8 (a), taken just after the effluent pressure was lowered to 111.7 kPa, the presence of both darker and lighter shades indicates that the phase occupancy of the bottom strip of the fracture is changing. In the middle of the fracture, the lighter shades indicate the displacement of dyed water by clear water. In the upper right hand corner of the image, gas is beginning to enter the fracture.

In Fig. 3.8 (b), gas has entered the upper right hand side of the fracture, filling a continuous strip on the very top edge, gas saturation has increased along the bottom edge, and appears in the large apertures on the outlet side of the fracture. There is no obvious gas path from the right hand side to the outlet side in the mid-section, so it is possible that gas from the adjacent endcap plenum was pushed into the larger apertures along the downstream fracture edge. Between Fig. 3.8(a) and (b), flow rates have not changed, and the change in gas saturation within the fracture does not appear to affect the flow rate. In Fig. 3.8 (c), just before lowering \( P_o \) to below the bubble pressure, gas saturation has increased across the top and along the outlet edge, but there is still no gas in the center of the fracture. The darker halo in Figs. 3.8 (b) and (c) is from a dyed water spill that seeped between the outside of the replica and the Lucite confining plates that evaporated and darkened with time.

The images in Fig. 3.9 are normalized by the image in Fig. 3.8 (c). They are taken after \( P_o \) was lowered to below the bubble pressure. New gas appears in the center of the fracture; its appearance correlates with the flow reduction seen in Fig. 3.7 (b). The white and dark areas in the locations where gas appeared in Fig. 3.8 (c) indicate oscillation of phase occupancy, characteristic of two-phase flow.

### 3.1.3.2 DV97-2

The results of the second degassing experiment, DV97-2, are summarized in Table 3.2 and Fig. 3.10. The influent tank pressure was constant at 116.5 kPa. The 1 m height of the tank above the fracture provided a fracture inlet pressure of 126.5 kPa. Fig. 3.10 (a) shows the fracture outlet pressure \( (P_o) \) during the course of the experiment. \( P_o \) was maintained above the bubble pressure of 106.0 kPa for about 2.5 days while the fracture was saturated with \( \text{CO}_2 \)-equilibrated water. Gas was observed in the tubing between the influent tank and the fracture soon after injection began, and the first occurrence of gas in the fracture bottom was observed at about 1.3 days, after \( P_o \) was lowered to 111.7 kPa.

The measured flow rates \( (Q) \) and the accumulated gas volume collected \( (V_g) \) are plotted in Fig. 3.10 (b). Flow rates decreased after \( P_o \) was lowered to 111.7 kPa. The flow rate after the outlet pressure was dropped to 103.3 kPa decreases over more than one day, then remains fairly steady for the last day of the experiment, with oscillations characteristic of
two-phase flow conditions. The measurement of accumulated gas began at 1.47 days, when the outlet pressure was lowered from 125.3 to 117.3 kPa. Gas volumes increased immediately after lowering the outlet pressure further. The rate of gas production dropped off about 15 hours after the first pressure lowering, and similarly after dropping pressure below the bubble pressure, as was observed in DV97-1.

Evolved gas as a percent of liquid by volume is shown in Fig. 3.10 (c). Each point is calculated over the time increment from the previous point. At the point of highest gas production, a peak of 43% occurred as the sudden drop in effluent pressure displaced gas that had accumulated in the endcap plenums.

In Fig. 3.10 (d), flow rates are linear with $P_o$ until the intermediate pressures of 113.4 kPa, and then significantly deviate from the linear trend after lowering the outlet pressure to below the bubble pressure. The box symbols indicate the data selected for determining the linear trend. The variation of $P_o$ at each elevation of the outlet is due to two-phase flow effects. The correlation coefficient ($R^2$) of the linear trend is 0.879.

The images of gas evolution during the experiment are shown in Fig. 3.11. Fig. 3.11 (a) shows the location of gas (dark areas) just before lowering the effluent pressure from 125.3 to 111.7 kPa, with some gas at the top and bottom of the fracture. After lowering $P_o$ to 113.4 kPa, gas filled a large portion of the lower fracture (Fig. 3.11 (b)), at which time flow rates dropped from the linear trend shown in Fig. 3.10 (d). Gas saturation did not change significantly until the time $P_o$ was further lowered to 103.3 kPa (Fig. 3.11 (c)). Over the next 3.5 hours, gas began to fill the middle portion of the fracture, and flow rates declined from 41 to 30 mL/hr (Figs. 3.11 (d) - (f)). Over the next 2.5 days, flow rates declined further to 12 mL/hr, but the images reveal no obvious differences in the gas phase distribution. This is shown by taking difference images between Fig 3.11 (f) and subsequent images at 3.67 days (Fig 3.12 (a)), 4.35 days (Fig 3.12 (b)) and 4.96 days (Fig. 3.12 (c)) where the flow rates were 20, 11 and 12 mL/hr, respectively. In these images, the white areas indicate resaturation by water, and the darker areas indicate resaturation by gas. In Fig. 3.12 (a), there appears to be a net increase in gas saturation in the lower and middle portions of the fracture, albeit small relative to previous changes in gas saturation. It may be that the decrease in flow rates from 20 to 12 mL/hr is due to a combination of gas accumulation in the endcaps, and decrease in the fracture transmissivity due to swelling of the epoxy.
3.1.3.3 ST97-1

Figure 3.13 summarizes the results of the degassing experiment in the Stripa fracture. The influent tank pressure was maintained at 116.8 kPa with nitrogen delivered to a tedlar bladder in the tank throughout the experiment. As in the previous experiments, the tank was mounted horizontally 1 meter above the plane of the fracture replica. Fig. 3.13 (a) shows the fracture outlet pressure ($P_o$) during the course of the experiment. $P_o$ was maintained above the bubble pressure of 106 kPa for about 2.5 days while the fracture was saturated with CO$_2$-equilibrated water. Gas was observed in the tubing between the influent tank and the fracture soon after injection began, and the first occurrence of gas in the fracture bottom was observed at about 1.4 days.

The measured flow rates ($Q$) and the accumulated gas volume collected ($V_g$) are plotted in Fig. 3.13 (b). The flow rate after the outlet pressure was dropped to 110 kPa generally decreases, with oscillations characteristic of two-phase flow conditions. Gas production began at this time, and did not drop off as in the previous two experiments. Once the outlet pressure was lowered to 101.6 kPa, the flow rates dropped significantly over the next 7 hours. The smaller decrease in flow rates over the next three days may be in part due to problems with controlling the inlet tank pressure. The rate of gas production was greater at the lower outlet pressure compared to the first lowering of the outlet pressure.

Evolved gas as a percent of liquid by volume is shown in Fig. 3.13 (c). Each point is calculated over the time increment from the previous point. Evolved gas contents are fairly constant at 0.25% for $P_o = 110$ kPa. Once the pressure is dropped further at 6.4 days, there is a sudden increase in evolved gas content, after which the values appear to fluctuate about a mean of approximately 6%.

In Fig. 3.13 (d), there is a linear trend of flow rates with $P_o$, however there is significant scatter in the values of $Q$ over all outlet pressures. The box symbols indicate the data selected for determining the linear trend. There is increased deviation from the trend at the lower values of $P_o$.

The images of gas evolution during the experiment are shown in Fig. 3.14 through 3.16. Fig. 3.14 (a) shows the location of gas (dark areas) just before and after lowering the effluent pressure from 120.2 to 110 kPa, where gas enters the bottom portion of the fracture. Figure 3.15 shows the evolution of gas phase occupancy for effluent pressures of 110 kPa. These images note the decline in flow rates as gas fills more of the apertures. The same behavior is shown in Fig 3.16 for effluent pressure below the bubble pressure ($P_o = 101.6$ kPa), where gas occupies all the preferential liquid flow paths shown in Fig. 3.6.

3.1.3.4 Summary of degassing experiments

Table 3.2 summarizes the results of the degassing experiments. The value of $\frac{dQ}{d\Delta P}$ from the single liquid phase measurement is compared with transmissivity derived from
the linear trend of the $Q$ vs. $P_o$ plots for the degassing experiments. These two measures are close for DV97-1, where the fracture was water saturated for a long period of time before the degassing experiment. In DV97-2 and ST97, the linear trend gave a lower transmissivity than measured with the fully liquid-saturated test about one week preceding the test. In ST97, the plot for $Q$ vs. $P_o$ for ST97 showed two-phase flow effects even at the higher values of $P_o$, and consequently a linear fit did not represent single liquid phase transmissivity. For consistency, flow reduction due to degassing is expressed as $Q_f/Q_i$, or the ratio of the final measured liquid flow rate at the lowest value of $P_o$ to $Q$ at the same $P_o$ as determined from Table 3.1.

The magnitude of flow reduction is greater at higher gas contents. At the higher evolved gas contents, flow reduction in DV97-2 was somewhat greater than in ST97. The final column in Table 3.2 shows the calculated value of $P_{CO_2}$ from the measured evolved gas, assuming the gas is 100% $CO_2$, and the final $P_o$, using Eq. (2.1.4). These values are less than the values of $P_o$ at which a gas phase was first observed.

Two sources of gas in addition to the $CO_2$ introduced during gas-water equilibration may cause the evolution of a gas phase at higher pressures. First is the nitrogen used to pressurize the influent tank to drive water through the fracture. Second is the remaining headspace in the influent tank after gas-water equilibration, which is presumably filled with $CO_2$ and may be dissolved into the water when the influent tank pressure is increased. It had been assumed that due to the relatively low solubility of nitrogen in water, and the minimal interfacial contact area between the nitrogen and water, that the dissolution of nitrogen into the water would be insignificant. However, the persistent appearance of gas at pressures above the $CO_2$ equilibration pressure brings this assumption into question.

If the influent tank water equilibrates with nitrogen gas, then the bubble pressure of the water is equal to the influent tank pressure, which would explain why gas appears in the tubing just downstream of the influent tank. However, the volumetric gas content for nitrogen gas is lower than for $CO_2$ because of nitrogen’s lower solubility in water. The Henry’s Law constant for nitrogen in distilled water at 20°C is 8.15E6 kPa/(mole-fraction). Assuming that the presence of dissolved $CO_2$ does not affect the solubility of nitrogen in water, the additional volumetric content of the water due to $N_2$ from Eq. (2.1.4) is about 0.2% v/v. The additional gas contents due to the dissolution of $CO_2$ in the headspace of the influent tank is a more significant source of gas volume. The additional gas content is 1.1% v/v per cm of headspace. The initial headspace was not measured, but values between one to two cm can account for the discrepancy of calculated and measured evolved gas contents shown in Table 3.2.
Table 3.2 Summary of degassing experiments

<table>
<thead>
<tr>
<th>Exp’t</th>
<th>(P_{\text{CO}_2})</th>
<th>(P_o) final</th>
<th>(\frac{dQ}{d\Delta P}) (mL/hr/kPa)</th>
<th>Qf/Qi from Table 3.1</th>
<th>calc.(^3) Eq. 2.1.4</th>
<th>meas.(^4) (STP) evolved gas @ (P_o) (%v/v)</th>
<th>(P_{\text{CO}_2}) calculated from measured evolved gas(^5) (kPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DV97-1</td>
<td>103.7</td>
<td>101.6</td>
<td>2.13</td>
<td>2.28</td>
<td>0.73</td>
<td>1.85</td>
<td>3.4 to 0.48</td>
</tr>
<tr>
<td>DV97-2</td>
<td>106.0</td>
<td>103.3</td>
<td>2.90</td>
<td>1.97</td>
<td>0.17</td>
<td>2.5</td>
<td>6.3 to 0.26</td>
</tr>
<tr>
<td>ST97</td>
<td>106.0</td>
<td>101.6</td>
<td>1.30</td>
<td>0.631</td>
<td>0.23</td>
<td>4.1</td>
<td>6</td>
</tr>
</tbody>
</table>

DV97 is the Dixie Valley fracture; this fracture was reassembled between DV97-1 and DV97-2.

ST97 is the Stripa fracture.

1. From the \(\text{CO}_2\)-water equilibration pressure.
2. Linear trend is from the \(Q\) vs. \(P_o\) plots for the degassing experiments.
3. Calculations done for values at 20°C: \(H_{\text{CO}_2} = 1.439 \times 10^5\) kPa/(mol-fraction); \(\bar{\nu}_{\text{CO}_2} = 24.05\) L/mol (ideal gas); \(\bar{\nu}_{\text{H}_2\text{O}} = 0.018036\) L/mol.
4. Measured in gas trap; range in values for DV97 indicates initial to final values after effluent pressure lowered to \(P_o\).
5. Assumes that the gas is 100% \(\text{CO}_2\).

### 3.1.4 Gas-water equilibration tests

Three experiments were performed, indicated by their dates, and are summarized in Table 3.3. The second and third experiments were from the same batch of gas-equilibrated water, but with different outlet pressures.

The pH of the de-aired distilled water before introduction into the tank was close to 7, however once it was introduced into the tank, pH values were close to 5.5, indicating that the water had equilibrated with atmospheric \(\text{CO}_2\). It took about three to four hours of gas-water equilibration for the pH to attain its steady value of around 3.9. In the experiment of 091797, the water and gas were equilibrated for four days. In the second and third experiments, the equilibration period was 24 hours.

During all experiments, gas was not observed in the tubing upstream of the needle valve, where pressure was above \(P_{\text{CO}_2}\), contrary to the observations in the fracture replica experiments. Immediately downstream of the needle valve where the pressure dropped to below the bubble pressure, small gas bubbles were observed to grow on the tubing wall, which were periodically scouried by a larger bubble exiting the valve body, and transported to the trap. This illustrates the interplay of the various stages of gas phase formation including heterogeneous nucleation, and bubble growth, detachment, coalescence and transport. Gas was observed downstream of the gas trap, either because pressures were
lower than in the trap, or because of inadequate residence time in the trap for all the gas to evolve, or limited nucleation sites.

The measured evolved gas was determined from the ratio of the slopes of the mass of water in the effluent (giving the mass flow rate of water) and the volume of gas in the trap over time (giving the gas evolution rate). The slopes were determined from linear regression. These plots are shown in Fig. 3.17. Generally, liquid flow rates did decline over time, as seen in the change of slopes, however in the experiment of 091797, the change was especially large due to leaks in the tedlar bladder and tank when pressurized with nitrogen for flow; the leaks made it difficult to maintain a steady pressure in the inlet tank.

Despite the higher pressure gradient in experiment 092497 caused by the lower outlet elevation, the liquid flow rate was lower than for 092397 (5.68 compared to 34.40 mL/hr). This may be due to the higher evolved gas content obstructing flow downstream of the gas trap. At the lower outlet elevation, large portions of the vertical tubing just downstream of the gas trap were filled with gas. This geometry, that creates gravity-driven liquid flow (downward) against buoyancy-driven gas flow (upward), may significantly contribute to liquid flow reduction due to degassing, as the gas appeared to "choke" the flow of water.

Table 3.3 shows that the calculated values for evolved gas were consistently higher than the measured values. This is reasonable, based upon the observations of evolved gas downstream of the trap, and that not all evolved gas may have been collected. However, this is contrary to the results of the degassing experiments in Section 3.1.3, where measured gas contents were greater than the calculated values from the equilibration pressure. The pH did not vary more than a few one hundredths units in a given test, however the trend of pH increase with increasing $P_{CO2}$ is not reasonable. Calculated values for evolved gas from the pH are inconsistent with the all the other measures of evolved gas. While pH may be a good indicator of when gas-liquid equilibration is achieved, it is a poor predictor of gas contents due to the strong effect of temperature variations and the poor sensitivity at the range of gas content values of interest.

<table>
<thead>
<tr>
<th>Table 3.3. Summary of gas content measurements</th>
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<tbody>
<tr>
<td>date</td>
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<tr>
<td>------</td>
</tr>
<tr>
<td></td>
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<td>091797</td>
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Notes: $P_{CO2}$ is calculated from Eq. (2.1.3); $P_o$, Tank Temp. and pH are the average values during the degassing experiment. pH values are temperature corrected, according to Eq. (2.2.1).
4.0 Summary and conclusions

In the laboratory experiments for linear flow geometry in the range of 3% to 6% gas contents, the extent of liquid flow reduction due to groundwater degassing is less at lower gas contents. This is consistent with the experimental results of Jarsjö and Geller (1996) for radial flow geometry. These experiments also showed that the effect of degassing on liquid flow is dependent upon the presence of multiple preferential flow paths, and that there are critical flow paths which have the largest effect on liquid flow rates when blocked by gas. In the Dixie Valley replica, presence of gas in the top and bottom areas had minimal effect on transmissivity, and most of the flow reduction occurred when gas entered the center portion of the fracture. In the Stripa fracture, transmissivities decreased with the first presence of gas in the fracture, and continued to decrease as gas occupied more of the flow path.

Calculations and the results of separate gas-water equilibration tests explain why gas contents measured in the effluent were a few percent larger than predicted from the CO₂-water equilibration pressure, and why gas appeared at pressures above the CO₂-water equilibration pressure. The larger gas content was due to the presence of excess gas phase CO₂ in the tank before the tank was pressurized for flow. The higher bubble pressure was due to the partitioning of nitrogen gas (used to maintain influent water pressure and drive flow through the fracture) into the influent water. Separate gas-water equilibration tests showed that when the nitrogen gas was isolated from the influent water by means of a bladder, gas did not evolve at pressures above the CO₂ equilibration pressure.

Because the actual gas contents of the water in the degassing experiments were calculated from the gas collected in the effluent of the experiment, the certainty in the correlation between the measured flow reductions and gas contents is greater than in the previous experiments by Geller et al. (1995) and Jarsjö and Geller (1996), where gas contents were derived from the CO₂ equilibration pressure. One may assume that the actual gas contents in these experiments were several percent higher than reported, based upon the current work’s comparison between gas contents derived from the CO₂ equilibration pressure and evolved gas measured in the effluent.

Degassing in the Dixie Valley replica resulted in a transmissivity decrease of 27% and 83% of the single liquid phase values for 3% and 6% measured gas contents, respectively, suggesting a relationship between gas contents and liquid flow rate reduction. In the Stripa fracture, the final transmissivity decreased by 77% from single liquid phase conditions for 6% gas contents. These results extend the range of those measured by Geller et al. (1995). They measured flow reductions of approximately 70 to 80% for gas contents ranging from approximately 12 to 24% in the Dixie Valley fracture, however no significant relationship between gas content and flow reduction was observed in this range. In the Stripa fracture, they measured approximately 90% reduction in liquid flow rate for gas contents ranging from 7% to 13%. Together, the current and previous results suggest that for gas contents up to 6% in the Dixie Valley sample, liquid flow reduction is a function of gas contents. In
the Stripa sample, liquid flow reduction may be sensitive to gas contents over a larger range, due to the differences in the aperture distributions of the two samples.

Current and previous laboratory experiments show that the magnitude of flow reduction due to groundwater degassing is within the range observed at the Stripa SDE, and that there may be a relationship between gas contents and the magnitude of liquid flow reduction. A model is needed to extrapolate these results to the field scale and to test the sensitivity of degassing effects on boundary conditions and gas contents. Modeling efforts to date have greatly under-predicted the magnitude of flow reduction observed at the Stripa SDE (C. Doughty in Geller et al., 1995). The hypothesized cause of this discrepancy is that the re-solution of evolved gas as pressures increase due to flow blockage is mass-transfer limited, and as a consequence, gas-saturations cannot be predicted by the current model, which uses Henry's Law. The laboratory experiments were designed to test this hypothesis by providing a data set with well-defined boundary conditions, where degassing occurred within the fracture replica, that could be compared to modeling results. This objective was not met in the current study due to degassing upstream of the fracture replica, however a system for improved reliability in controlling gas contents was developed and demonstrated, which supports the interpretation of current and previous results and can be used in subsequent experiments to test this hypothesis.

Acknowledgment

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References


Appendix

The relationship between the partial pressure of CO₂ ($P_{CO₂}$) and pH in distilled water is derived from the following chemical equilibria and charge balance in the solution:

\[ CO₂(g) + H₂O ↔ CO₂(aq) \]  \hspace{1cm} (A.1)

\[ H₂CO₃ ⇔ HCO₃⁻ + H⁺ \]  \hspace{1cm} \[ \frac{[H^+][HCO₃⁻]}{[H₂CO₃]} = K_{a₁} \]  \hspace{1cm} (A.2)

\[ HCO₃⁻ ⇔ CO₃^{2⁻} + H⁺ \]  \hspace{1cm} \[ \frac{[CO₃^{2⁻}][H⁺]}{[HCO₃^-]} = K_{a₂} \]  \hspace{1cm} (A.3)

\[ [H⁺] = [OH⁻] + [HCO₃⁻] + 2[CO₃^{2⁻}] \]  \hspace{1cm} (A.4)

where $[H₂CO₃]$ = $[CO₂](aq)$ + $[H₂CO₃]$ and $K_{a₁}$ and $K_{a₂}$ are dissociation constants for the reactions in Eq.’s (A.2) and (A.3), respectively. The equilibrium expression for (A.1) is equivalent to Henry’s Law:

\[ [H₂CO₃] = \frac{P_{CO₂}}{H_{CO₂} \bar{V}_{H₂O}} \]  \hspace{1cm} (A.5)

Assuming that $[HCO₃⁻] >> 2[CO₃^{2⁻}]$ and $[H⁺] >> [OH⁻]$ for the expected pH value of less than 7, Eq. (A.4) reduces to:

\[ [HCO₃⁻] ≡ [H⁺] \]  \hspace{1cm} (A.6)

Substituting into Eq. (A.6) into Eq. (A.2):

\[ \frac{[H⁺]^2}{[H₂CO₃]} = K_{a₁} \]  \hspace{1cm} (A.7)

Then substituting Eq. (A.5) into Eq. (A.6), rearranging and using the relationship $pH = - \log[H⁺]$ gives:

\[ pH = - \frac{1}{2} \log \left[ \frac{K_{a₁}P_{CO₂}}{H_{CO₂} \bar{V}_{H₂O}} \right] \]  \hspace{1cm} (A.8)

Rearranging Eq. (A.8) and substituting into Eq. (2.1.4) gives a relationship between pH and the volume of gas evolving:

\[ \% \text{ v/v} = \left( \frac{10^{-2pH} H_{CO₂} \bar{V}_{H₂O}}{K_{a₁}} - P_{a} \left( \frac{\bar{V}_{CO₂}}{\bar{V}_{H₂O}} \right) \right) \times \frac{100}{H_{CO₂}} \]  \hspace{1cm} (A.9)
Figure 2.1. Experimental assembly for degassing tests in fracture replicas for linear flow geometry
(a) ceramic geometry (after Persoff and Pruess, 1995)

(b) tubing connections to endcaps

Figure 2.2. Endcap arrangement
Needle valve

\[ z_1 = z_2 + 89 \text{ cm} \]

Influent Tank

hydrostatic pressure at atmospheric pressure \( P_t \)

total tank pressure with application of \( \text{CO}_2 \)

datum (floor)

Figure 2.3. Relative Elevations of Tank and Pressure Transducer during Gas-Water Equilibration
Figure 2.4. Estimated volume of gas evolving as a function of pH at atmospheric pressure from Eq.s (A.8) and (A.9)
Figure 2.5. Experimental assembly for pH monitoring of gas contents
Figure 3.1 Water-saturated transmissivity for the three degassing experiments

(a) DV-97-1, Saturated Transmissivity

(b) DV97-2, Saturated Transmissivity

(c) ST97-1, Saturated Transmissivity
Figure 3.2 Aperture map for DV97-1
Figure 3.3 Aperture map for DV97-2
Fig. 3.4 Dye injection to DV97-2. Flow is from right to left.
Figure 3.5 Aperture map for ST97
Figure 3.7 Degassing in DV97-1 and reduction in transmissivity
3.8 Gas evolution in DV97-1. \( P_0 = 113.4 \text{kPa} \).
Figure 3.9  Gas evolution in DV97-1. Relative to image in 3.8 (c), white areas have filled with water, and dark areas have filled with gas.
Figure 3.10 Degassing in DV97-2 and reduction in transmissivity
Fig. 3.12  Change in gas saturation with respect to Fig. 3.11(f). Po=103.3 kPa.
White indicates change from gas to water; dark grey indicates change from water to gas.
Outlet pressure of fracture ($P_o$) since beginning injection of CO$_2$-sat water

Evolved gas

Liquid Flow Rates ($Q$) and Accumulated Gas Volume ($V_g$)

Liquid Flow Rate ($Q$) vs Outlet Pressure ($P_o$)

Fig. 3.13 Degassing in ST97 and reduction in transmissivity
Fig. 3.14  Gas evolution in ST97. Just before and after lowering from 120.2 to 110.0 kPa
Fig 3.15 Gas evolution in ST97 for Po=110 kPa
Fig 3.16  Gas evolution in ST97. $P_e=101.6\,kPa$

(a) $t=6.56\,d$, $Q=9.3\,mL/hr$
(b) $t=7.35\,d$, $Q=7.1\,mL/hr$
(c) $t=9.36\,d$, $Q=6.3\,mL/hr$
Figure 3.17. Gas-water equilibration experiments