***Reactive transport of CO₂-saturated water in a cement fracture:
Application to wellbore leakage during geologic CO₂ storage***

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Reactive transport of CO₂-saturated water in a cement fracture: Application to wellbore leakage during geologic CO₂ storage

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Graphical abstract

Abstract

Time dependence of fluid flux up a leaky well has significant implications for the feasibility of geologic CO₂ storage. We present laboratory experiments that study various boundary conditions, fluid fluxes, and residence times to understand the range of behavior in fractured cement cores. Carbonic acid progressively reacts with cement by dissolving phases which neutralize the acid and liberate calcium ions. This dissolution does not increase the aperture of the fracture, due to the formation of an amorphous silicate residue. Where aqueous calcium concentration and pH are sufficiently high calcium carbonates become insoluble and precipitate in the open fracture. When the driving force for fluid flux is a constant pressure differential precipitation leads to a progressive reduction in fluid flux and the development of self-limiting behavior. With sufficient residence time precipitation leads to sealing of the leaky well.

Keywords:

Cement, wellbore integrity, reactive transport, leakage, fracture

1. Introduction

1.1. CO₂ storage and wellbore leakage risk

Geologic CO₂ storage has the potential to significantly reduce CO₂ emissions (Metz et al., 2005). However, a key responsibility for operators is to predict where the CO₂ will move once injected and to

assess the risks associated with the injection of vast volumes of CO₂. One particular risk is for CO₂ to migrate from the intended storage volume and leak into an overlying formation or back to the atmosphere (Zhang and Bachu, 2011). In regions where storage is ideal the most direct pathway for migration is along leaky wells (Nicot, 2009). Thus, characterizing the time-dependent fluid flux along a fractured wellbore and what phenomena might alter the leak path conductivity over time is vital for risk assessment.

1.2. Wellbore leakage studies

Despite the importance of understanding leaking wells, much remains poorly understood. Field-scale studies of wellbore cement exposed to CO₂-rich fluids for years show significant reaction, but the few available studies show little evidence for sustained CO₂ leakage (Carey et al., 2007; Crow et al., 2010; Watson and Bachu, 2009). These observations should not be construed to indicate that wells do not leak. In fact the buildup of pressure in the annular space between casing strings, called sustained casing pressure, is surprisingly common (Bourgoyne Jr. et al., 1999; Watson and Bachu, 2009). The pressure buildup rate can even be used to estimate the conductivity a leaky well (Tao et al., 2011). A well can fail for numerous reasons during all parts of the life of a well. Failure can also occur in various locations in the well construction. For example failure can occur along the cement-earth interface, within a cemented annulus as tensile fractures, or by debonding of cement from the cement-casing interface (Ravi et al., 2002). Typically leaks that remain or develop post completion are difficult to detect and are associated with failure somewhere within the wellbore system or along casing-cement-earth interfaces. We study the case of a single leak path with a cement-to-cement interface that typically occurs due to tensile failure of the cement sheath. This leak path can be considered to be a natural closed fracture. This type of fracture has a flow field that is significantly affected by locally varying aperture size (Lee et al., 2003; Watanabe et al., 2008) which has a direct control on solute residence

time (Boutt et al., 2006), mixing (Emmanuel and Berkowitz, 2005), and chemical reactions (Dijk and Berkowitz, 1998; Singurindy and Berkowitz, 2005).

1.3. Carbonic attack on cement

Locally, reaction between the fluid and cement occurs via the mechanisms proposed by Kutchko et al. (2008, 2007) and modified by Mason et al. (2013). The process can be summarized as the following. Carbonic acid in the fluid initially lowers pH at the cement-water interface and later diffusion also lowers pH in the cement's pore water. The cement phases, principally portlandite and calcium silicate hydrate (C-S-H), become soluble and release calcium and hydroxide ions that buffer the water's acidity. As the fluid pH rises, calcium carbonate minerals become insoluble, which begin to precipitate. Further exposure to infiltrating acidic fluid leads to dissolution of calcium carbonate minerals. The final product of this attack is an amorphous zeolite (Mason et al., 2013). While these studies develop a mechanistic understanding, the reaction was either diffusion dominated or the residence time was so short that the coupling effects of dissolution/precipitation and advection were not captured. Our current work looks at the coupling of fluid advection along the fracture with the reaction mechanisms described above.

1.4. Dynamic experiments

In earlier work (Huerta et al., 2013) we injected dilute hydrochloric acid solution (HCl) at a range of pH into cement fractures and observed acid attack mechanisms that were similar to the work summarized in section 1.3. Huerta et al. (2013) documented evidence of secondary phase (e.g. calcite) precipitation on the fracture surface, mostly bounding the reacted pathway. The experiments were performed at constant flow rate and an increase in pressure differential often occurred as the experiment progressed. We proposed that secondary calcite precipitation caused a restriction in the flow to develop, which provides evidence for sealing of the fracture. Other studies (Abdoulghafour et al., 2013; Luquot et al., 2013; Mason et al., 2013; Walsh et al., 2014a, 2014b) have also observed a decrease

in the hydraulic aperture but use smaller cores which results in a short residence time. Mason et al. (2013) attributed sealing to changes in mechanical properties due to chemical leaching of cement and noted no mineral precipitate on their fracture surface, perhaps due to shorter residence time of fluid in the fracture, larger fracture aperture, and smoother surfaces on the interface (Walsh et al., 2014a, 2014b). Abdoulghafour et al. (2013) attributes permeability decrease to swelling of the remaining silicate material. While the previous studies provide significant insights to the mechanisms involved, there are challenges to capturing the role that residence time and local heterogeneity play. In order to capture the phenomenon of precipitation induced blocking it is imperative to have sufficient aqueous concentrations of calcium and carbonate (at a high enough pH) for precipitation to occur. Capturing this phenomenon within the relatively short length of a typical laboratory setup is challenging and requires careful experiment design. Favorable laboratory conditions would include slow flow, long flow path, narrow flow path, rough fracture surface, and maximum concentration of CO₂ in the fluid. In the field, where the flow path will be much longer than we can simulate in the laboratory, the other factors would likely not be as critical.

The objectives of this study are to determine if similar dissolution/precipitation reaction mechanisms that were observed in the analog experiments are observed when CO₂-saturated water is injected into fractured cement cores. Additionally, we wish to study how dissolution/precipitation reactions affect fracture permeability. Finally, we study the role that increased residence time and constant pressure differential driving force have on time-dependent changes in leak path conductivity.

2. Materials and methods

2.1. Experimental apparatus

All experiments were performed with core flow units built by Coretest Systems, Inc. (Model CFS-839Z). The units were designed to perform flow experiments at elevated pore pressure, confining pressure, temperature, a range of flow rates, and flow modes. The CO₂-saturated water was mixed and injected using 2 L stainless steel accumulators. The cement sample was held in a bi-axial core holder. Water was used as the confining fluid and elevated to confining pressure by a pressure intensifying booster pump. Quixiz QX pumps were used to drive fluid from the accumulators. Quartzdyne digital pressure transducers were used to monitor all system pressures. Back pressure was maintained by a two stage system. The first was a digital back pressure regulator built by Coretest Systems, Inc. to dynamically control downstream pressure. To limit instability due to Joule-Thompson cooling of any CO₂ coming out of solution, a second heated backpressure regulator was used to step down pressure from an intermediate value to atmospheric pressure.

The sample was placed in the core holder, the confining system filled with water, and confining pressure was applied. Prior to reactive fluid injection, distilled water was injected into the fracture to achieve the required experimental pore (or fracture) pressure, measure a baseline flow rate to pressure differential relationship, and estimate the initial hydraulic aperture. Dead volume, defined as the tubing volume between the accumulator and fracture core face, was estimated at 6.87 mL and the time required to travel through this volume was accounted for in experiments.

2.2. Fluid conditions and mixing method

The goal of our work was to study the simplest chemical system and maximize the amount of CO₂ dissolved. Thus we used distilled water with no added salinity and conducted experiments at ambient temperature (Table 1). These conditions maximize the concentration of dissolved CO₂ in the water. Using distilled water also allowed us to study the fundamental processes independent of perturbations imposed by variable brine composition that occurs in nature.

CO₂ was mixed with distilled water by first filling one accumulator with a volume of water (typically 1.5 L). A second accumulator was chilled to 5 °C and the calculated volume of liquid CO₂ was metered in. The chilled accumulator was brought up to ambient temperature and experiment pressure. Next the water was pushed into the accumulator containing liquid CO₂. The system was allowed to equilibrate and the volume change was monitored while applying constant pressure to identify when CO₂ had stopped dissolving. Mixing was typically completed by 24 hours. CO₂ saturation was estimated using the equation of state of Duan and Sun (2003). An excess of the amount of CO₂ was mixed in order to ensure saturation.

2.3. Cement sample preparation

The fractured cores of API class H neat cement (Lafarge, Montgomery, TX) were prepared according to the API Recommended Practice 10B (API, 1997) with more details in Huerta et al. (2013). Class H neat cement was mixed with deionized water using a water-to-cement ratio of 0.38. Samples were cured at ambient pressure and 50 °C for three days in cylindrical molds. After three days the samples were removed from the molds and submerged in deionized water to continue curing at ambient pressure and 50 °C for 28 days. After curing, we created natural fractures via the Brazilian method in order to obtain irregular, rough walled fractures similar to fractures in a wellbore. This technique generates a single tensile fracture by applying stress down the length of the core. The equipment used was either a loading frame with two flat platens or a core splitter with one flat platen and a dull blade. The blade concentrated the load along a single line and improved the success rate of creating fractured samples. The re-assembled core, when slightly offset, provided a so-called closed natural fracture that was propped open by randomly distributed touching asperities. To prevent flow outside of the fracture caulk (DAP KWI-K SEAL) was used to seal the sides of the sample.

Some limitations of our approach are that each sample is unique and the local fracture aperture heterogeneity cannot be accounted for *a priori*. The fractures tend to deviate from the applied stress lines, typically along local heterogeneity, and are not located at the center of the core. This is especially true as the length of the core is increased. As a result, individual fractured cores are less than 10 cm in length.

For the constant flow rate experiments, a single fractured core and a set flow rate was used for each experiment. To achieve experiments with larger residence time, we stacked individual cores end-to-end to extend the total sample length. To ensure a continuous flow path between cores, the fracture plane of each core was rotated 90° to the proceeding core. While the junction between points represents a significant flow restriction, the experiments still show behavior similar to the single core experiments. This approach also simulates the significant junctures, splitting, and flow path narrowing that are expected as fractures propagate along a well.

2.4. Analytical equipment

To analyze changes on the fracture surface, a Philips/FEI XL3 scanning electron microscope (SEM) was used. Analysis was performed in environmental SEM mode on uncoated and unpolished samples. Secondary electron (SE) images, back scattered electron (BSE) images, and energy dispersive X-ray spectroscopy (EDS) maps were collected. Specific experimental conditions are noted on the respective image.

To identify secondary precipitated phases on the fracture surface, a Rigaku DMax micro-diffractometer (μ XRD) with an UltraX18 Cu rotating anode X-ray source and Rapid II 180° curved imaging plate detector was used on select samples. The X-rays were collimated to a 100 μ m spot size and scans were collected at 50 keV, 300 mA for 5 to 10 minutes. The data was integrated using the 2DP software,

and phase identification was performed using Rigaku PDXL software equipped with the ICDD-PD4 database.

Effluent samples were collected at ambient conditions at varying intervals and durations for the constant rate experiments to observe the evolution of the chemical reactions occurring in the fracture. Samples were microwave digested before analysis to dissolve any secondary precipitation. A Perkin Elmer model Optima 3000 XL coupled plasma atomic emission spectrometer was used to measure cation concentration.

2.5. Experimental method

2.5.1. Constant flow rate short core experiments

The purpose of the constant flow rate experiments with CO₂-saturated water was to emulate the conditions of previous work (Huerta et al., 2013) with more representative fluid and chemical interactions. Specifically we compared chemical reactions involving the dissolution of cement phases and precipitation of secondary phases in the present study to the previous work where a HCl solution was the reactive fluid. We measured the changes in pressure differential, effluent fluid cation concentration, and analyzed the altered fracture surface to observe changes in chemistry, texture, and mineralogy.

2.5.2. Constant pressure differential composite core experiments

Based on the results from the constant flow rate experiments and in an attempt to more realistically model down-hole conditions we used longer cores with a constant pressure differential driving force. Extended core length allowed longer residence times and also increased the ability to detect small changes in conductivity due to precipitation on the fracture surface. With a constant pressure

differential driving force we were able to capture self-limiting behavior as a decrease in fluid flux. This allowed us to test the hypothesis that these systems seal given sufficient residence time.

3. Results

Table 1 contains summary parameters for all experiments. Length in the constant pressure differential experiments refers to total length of the composite core. Flow rate is the initial stable rate recorded by the software. Pressure differential is taken as the difference between upstream and downstream pressure transducer readings. Temperature and confining pressure were measured by the core flow equipment software. CO₂ saturation was estimated as described in section 2.2. using the upstream pressure, temperature, and pure water assumption (Duan and Sun, 2003). Hydraulic aperture was estimated using the cubic equation for flow between two parallel plates (Bear, 1972):

$$Q = \frac{B^3 W}{12} \frac{\Delta P}{\mu L} \quad (1)$$

where Q is the flow rate, B is the hydraulic aperture, W is the sample width, ΔP is the pressure differential, μ is the fluid dynamic viscosity, and L is the sample length.

Permeability is a unit of measure more suitable for flow through porous media. However because it is used as convention in models that estimate wellbore leakage (Nordbotten et al., 2005; Tao et al., 2011), we also present our results in those units. Permeability (k) can be related to aperture by equating Darcy's equation to the cubic equation:

$$kA = \frac{WB^3}{12} \quad (2)$$

The choice of an appropriate average fracture area (A) is not trivial and leads to drastically different values depending on the assumed area. For example, to understand how an experiment with a fractured sample behaves relative to a sample with normal pore structure the use of the core's cross sectional area is appropriate. This would yield an **equivalent sample permeability** given by:

$$k = \frac{B^3}{3\pi W} \quad (3)$$

To estimate the **equivalent fracture permeability** the area would instead be given by the estimated hydraulic aperture and the fracture width, and the equation would be:

$$k = \frac{B^2}{12} \quad (4)$$

Thus different definitions for A lead to orders of magnitude different estimates of k , so care should be exercised when comparing aperture and equivalent permeability. In this work we use equivalent sample permeability.

Moles of CO_2 injected (n_{CO_2}) as a function of time (t) are calculated during each experiment (Eqn. 5). This value represents the amount of CO_2 that has been injected into the core as a dissolved component of the water and not as free phase CO_2 . The effect of dead volume upstream of the core (6.87 mL) was accounted for in the experiments. Plotting experimental results as a function of n_{CO_2} normalizes for flow rate and experimental conditions (temperature and upstream pressure), which control amount of dissolved CO_2 (wt.% $_{\text{CO}_2}$) that contacts the core. Also included in the calculation is the density of the fluid (ρ_f) and the molecular weight of CO_2 (MW_{CO_2}). The equation is:

$$n_{CO_2} = \frac{tQ\rho_{wt.\%CO_2}}{MW_{CO_2}} \quad (5)$$

Fluid flux is calculated by dividing the flow rate by the cross-sectional area of the fracture, and residence time is calculated by dividing the sample length by the fluid flux. Because these fractures are not open, smooth-walled channels the fluid flux and residence times are most likely overestimates of the true values but provide insight to the scale of transport occurring within the fracture.

Table 1 - Summary of experiment parameters

Constant flow rate experiments				
Sample name	NA7-11	NA9-3	QB4-3	QB6
Length × Width, cm	6.25 × 2.54	5.37 × 2.54	7.24 × 2.54	6.17 × 2.54
Flow rate, mL/min	1	0.5	0.25	3
Pressure differential, psi	0.9	0.35	0.2	5.7
Temperature, °C	21	22	21	21
Confining pressure, psi	1,519	1,653	1,528	1,540
CO₂-saturation, wt. %	6.38	6.25	6.34	6.33
Hydraulic aperture, μm	43	44	47	33
Sample permeability, mD	317	351	415	148
Residence time, s	4	7	21	1
Total time, min	477	2,827	3,034	474
Constant pressure differential experiments				
Sample name	JA1	JA5	JA8	JA9
Length × Width, cm	23.4 × 2.54	24.03 × 2.54	21.9 × 2.54	24.38 × 2.54
Flow rate, mL/min	0.011	0.13	0.011	0.006
Pressure differential, psi	2.0	7.4	21.3	55.1
Temperature, °C	21	22.5	23.5	22
Confining pressure, psi	1,986	1,896	2,457	2,385
CO₂-saturation, wt. %	6.57	6.42	6.39	6.52
Hydraulic aperture, μm	12	17	5	3
Sample permeability, mD	6	19	0.5	0.12

Residence time, s	360	48	153	193
Total volume injected to seal, mL	6.51	-	1.172	3.5

3.1. Constant rate short core experiments

3.1.1. Flow rate and pressure differential history

Flow rate was selected over a range of values to observe changes in pressure differential due to dissolution of cement phases and precipitation of secondary phases which were observed in previous work (Huerta et al., 2013). For the current constant rate experiment we observed that the pressure differential remains essentially constant, especially compared to results using the HCl analog fluid (Huerta et al., 2013). Although there was no pronounced trend in the pressure differential, analysis of effluent fluid samples and inspection of the post experiment fracture surfaces show that there was significant reaction on the fracture surface.

3.1.2. Effluent history

Figure 1 shows effluent concentrations of the key cations plotted versus amount of dissolved CO₂ injected. Several cations (calcium, iron, and silicon) that make up a significant portion of cement are used to describe the experiment evolution. Because of dead volume the first effluent sample contains a mixture of pre-experiment fluid and effluent from injection of the CO₂-saturated water.

Figure 1 – Effluent concentrations for four constant rate experiments. The solid horizontal lines represent the sampling interval.

Calcium is the most abundant cation in all effluent samples and its effluent history has two distinct types of behavior. In QB4-3 and NA7-11 there is an early concentration spike followed by a general flattening effluent concentration as the experiment progresses. In QB6 and NA9-3 there is a low

sustained effluent concentration history. While the slowest (QB4-3) and fastest (QB6) flow rates have a large and small effluent concentration respectively, there is no direct correlation between flow rate and effluent calcium behavior.

Silicon has a low concentration in the effluent samples. The low effluent concentration, despite its relatively high abundance in cement, is evidence that silica remains generally insoluble. In all experiments effluent silicon concentration has a distinct spike followed by an asymptotic decay. When plotted versus total CO₂ injected all curves are nearly identical, with a minor trend showing that faster flow rate yields lower effluent concentration.

Total effluent iron concentrations are low compared to the calcium and silicon effluent concentrations. In most experiments effluent iron concentration increases with time. The one exception, QB6, has detectable iron in only one effluent sample. There is no correlation with flow rate, as the fastest (QB6) and slowest (QB4-3) show the lowest effluent concentration. At intermediate rates (NA9-3 and NA7-11) effluent concentrations rise at a similar rate.

Aluminum is below detection limits in the effluent samples and is further evidence that certain key elements remain immobilized during the experiments.

Based on effluent calcium concentration it is clear that no simple relationship exists between fluid flux and effluent concentration profile and thus complex coupled transport and reaction processes are occurring within the cement fracture.

3.1.3. Fracture surface, SEM, and μ XRD analysis

Figure 2 shows photographs of one reacted fracture surface for each sample. Shown to the right of each image is an illustration identifying the caulk (white), unreacted cement (grey), and reacted flow path (black). In all images flow is from top to bottom. Key regions of interest are also labeled and

269 discussed in this section. In all experiments a distinct reacted pathway forms. In most experiments the
270 pathway is broad and covers most of the available flow area, though there are lateral flow restrictions in
271 all samples. At the boundary between the reacted channel and unreacted cement there is either a sharp
272 zone of white precipitate or a broader boundary that is medium grey in color.

Figure 2 – Images of one half of the fracture surface for the constant flow rate experiments. For each sample, the left side is an image of the surface while the right side shows our interpretation of the distribution of caulk (white), unreacted cement (grey), or reacted cement (black).

Sample NA7-11 was selected for further analysis by SEM and EDS to characterize textures and changes in relative element concentration in the zones identified in Figure 2. Figure 3 shows BSE images taken at location A, which is an example of a sharp transition between the reacted channel (above blue

line) and unreacted cement (below blue line). The reacted channel has a visually distinct cracked texture, while the transition and unreacted zone contains micron scale euhedral grains. Figure 4 shows BSE images taken at location B, which show the transition between reacted and unreacted cement. An enlarged BSE image (Figure 4 – red box) shows most of the material in the reacted channel is very fine grained and lacks distinct crystal shape. Figure 5 contains BSE images near the outlet (location C) and is an example of the more gradational texture associated with a broad boundary. Much larger euhedral crystals are immediately next to reacted cement. Location D is also near the outlet and Figure 6 shows BSE images progressively zoomed in to show the distinct crystal shapes in a complex relationship with the reacted channel. Zoomed in images show the crystals actually contain imperfections to the bulk crystal habit that seem to be along cleavage planes (Figure 6 – red arrows). Figure 7 shows BSE, SE, and EDS element maps for location E. In the reacted channel (left side of images and maps) calcium is depleted, which leaves silicon relatively enriched. Iron and aluminum also remain in the reacted channel which helps to explain their relatively low concentration in the effluent samples.

Figure 8 shows μ XRD analysis of a large area of secondary precipitate on the fracture surface of sample QB4-3, this location is highlighted by the red arrow in Figure 2. The identified precipitated phases are calcite, portlandite, and trace vaterite.

Location A

Figure 3 – NA7-11 (left) BSE image showing a sharp transition between reacted (above blue line) and unreacted zones (below blue line). (right) A zoomed in BSE image shows distinct euhedral crystals present in the unreacted zone.

Location B

Figure 4 – NA7-11 (left) BSE image of the transition between reacted and unreacted cement. (right) A zoomed in image right at the transition between zones shows fine grained materials.

Location C

Figure 5 – NA7-11 (left) BSE image near the outlet showing reacted cement surrounding a core of large euhedral crystals that we infer to be calcite. (right) A zoomed in BSE image shows the crystals typically display a rhombohedral shape.

Location D

Figure 6 – NA7-11 BSE images that progressively zoom in to show the dissolution of the large euhedral crystals that we infer to be calcite.

Location E

Figure 7 – NA7-11 (top left) BSE Image showing distinct textural differences between reacted and unreacted zones. (top right) SE image showing the surface morphology. (middle left) Calcium EDS map showing that calcium is most abundant in the unreacted zone. (middle right) Silicon EDS map showing that silicon concentration does not decrease in the reacted zone. (bottom left) Aluminum EDS map and (bottom right) iron EDS map also show that they remain in the reacted zone.

Figure 8 – QB4-3 (top) Image of zone analyzed with μ XRD. (bottom) The resulting XRD pattern is shown in red, with the crystalline phases identified as calcite (blue), portlandite (green), and vaterite (purple).

3.2. Constant pressure differential composite core experiments

3.2.1. Flow rate and pressure differential history

Figure 9 shows flow rate and pressure differential history for each of the four constant pressure differential composite core experiments. Flow rate and pressure differential was recorded every 30 seconds and was smoothed using a 5-point average to dampen noise.

Sample JA1 (Figure 9 – top left) was the first constant pressure differential experiment on a composite core. Flow rate for the first few hours was steady at 0.011 mL/min. This flow rate corresponds to an initial residence time of 390 seconds. After 3 hours the flow rate began to decrease. The flow rate continued to decrease until just before 10 hours when the flow rate became negligible. In

an attempt to reestablish flow through the core, the upstream pressure was increased at 11 hours so that the pressure differential across the core was 10 psi. After no significant flow was established, the upstream pressure was increased at 13.4 hours (and 4.7 mL of fluid injected) until the pressure differential was 50 psi. A flow rate below 0.005 mL/min did periodically occur but the sample permeability remained very small. These conditions were held for 50 hours with less than 6 mL of additional fluid injected. At the end of the experiment, the pressure differential was increased to 200 psi for a short time with no development of significant flow.

For sample JA5 (Figure 9 – top right) the residence time was 48 seconds, which was less than the previous experiment. A pressure differential of 7.4 psi was used, which corresponded to an initial flow rate of 0.13 mL/min. Because the residence time was short, the important behavior occurred within the first 3 hours. In this experiment, the flow rate began to decrease at 0.64 hours and 4.9 mL injected (solid green line). This decrease was sooner than the time (dashed green line at 0.89 hours) to inject the estimated dead volume and in the middle of the time where flow rate was decreasing. After minimizing, the flow rate became stable at 0.03 mL/min. The downstream tubing began to plug from precipitation after 32 hours (not plotted) but did not affect results as the precipitation front had broken through well before that time. The sample was removed after 72.3 hours.

Sample JA8 (Figure 9 – bottom left) had a low sample permeability (0.5 mD) so to get an initial flow rate of 0.011 mL/min we used a pressure differential of 21.3 psi. For 0.3 hours the flow rate was noisy but stable and then began to decrease. By 4.1 hours flow rate had decreased to around 0.003 mL/min. At this point the confining pressure fluid began to leak into the fracture fluid system, ending the experiment.

Sample JA9 (Figure 9 – bottom right) had a very low sample permeability of 0.12 mD so a larger pressure differential of 55.1 psi was required to get an initial flow rate of 0.006 mL/min, which was just

within the equipment's lower limit. The corresponding residence time was 186 seconds. The initial flow rate lasted for 6.5 hours. After this time the flow rate decreases to essentially no flow condition until 42 hours, when the pressure differential was raised to 64 psi. Consequently, there was a small increase in flow rate but it was well below the initial value.

Figure 9 – Pressure differential (blue line) and flow rate (black line) plotted versus time for the four constant pressure differential experiments. The red line on JA1 (22.37 hr, 10 mmol) and on JA9 (42.18 hr, 5.2 mmol) are the limits of the curves plotted on Figure 11. On the JA5 plot, the green solid line corresponds to the time when precipitate begins to seal the sample based on flow rate decrease and the green dashed line corresponds to the estimated time required to flush the dead volume.

3.2.2. Fracture surface analysis

Figure 10 shows the reacted surfaces for the constant pressure differential experiments. In this figure both halves of the cement core are shown and flow is from left to right.

JA1 has a distinct reacted channel at the inlet similar the reaction patterns observed in the constant flow rate experiments. A distinct secondary white mineral precipitate is highlighted in the blue box (Figure 10) and appears to be located within a previously developed reacted channel. Precipitation within a reacted channel does not occur on other samples and could have occurred because the upstream pressure was raised several times, which resulted in short surges of new acid into the fracture. Secondary precipitate also occurs in the second core but it is distributed across the entire surface. The yellow dashed line (Figure 10) indicates a sharp boundary beyond which no precipitate is visible. Thereafter the fracture surface has a texture that is indicative of minor reaction with the distilled water that was injected into the core before the experiment began.

Similar to the constant flow rate experiments, each core section in JA5 has a distinct reacted channel. The formation of reaction patterns similar to those observed in single cores occurs across the entire composite core. Similar reaction patterns suggest that the narrow cross-over sections do not impart significantly different behavior to the overall sample. There is significant narrowing of the reacted channel toward the outlet. However, evidence that a reaction occurred along the sample's entire length corroborates the flow rate data, which indicated a breakthrough of the precipitation front before the system could completely seal.

In sample JA8, the observed reaction pattern is more complicated. The reacted zone propagated into most of the second core and minor secondary mineral precipitation is indicated by white material near the inlet of the first core (Figure 10 – red arrow) and across the surface of the third core (Figure 10 – red box).

Sample JA9 is overall lighter in color because the cores dried before photographs were taken. Minor reaction occurred across the first core. In the second core, a distinct band of precipitation crosses the

386 core and is highlighted by the magenta box (Figure 10). Beyond this band there is no evidence for
 387 reactive fluid injection and only evidence for the pre-experiment distilled water moving in the fracture.

Figure 10 – Both fracture halves for the four constant pressure differential experiments. Flow is from left to right. Colored boxes, lines, and arrows indicate locations of interest discussed in Section 3.2.2.

4. Discussion

4.1. Discussion of experimental results

4.1.1. Constant flow rate experiments

The processes of combined leaching and precipitation that are observed in the constant flow rate experiments with CO₂-saturated water, reported here, are similar to those identified in our previous work with an analog system using HCl (Huerta et al., 2013) and compatible with our understanding of the diffusion-dominated system (Kutchko et al., 2007; Mason et al., 2013). In the experiments reported here a distinct reacted channel develops on the fracture surface that is broader than in the HCl experiments. The reacted channel is calcium depleted and relatively enriched in silicon. This relationship matches observations from the reacted surface of the analog experiments (Huerta et al., 2013), what occurs in diffusion experiment (Kutchko et al., 2008, 2007), and observations in short core experiments (Mason et al., 2013). The absence of aluminum in the effluent and growing iron concentration with time in all experiments support the conceptual model of Mason et al. (2013) and Huerta et al. (2013) in which the iron-rich calcium-aluminate phases in the amorphous zone are dissolved, freeing the iron but trapping the aluminum in an amorphous zeolite. The relatively insoluble silicon-rich solid phases remain behind in the reacted zone and further reaction into the cement becomes diffusion limited (Kutchko et al., 2008). When plotted versus total CO₂ injected the effluent silicon concentration for the four experiments is very close, especially when compared to the calcium and iron plots (Figure 1).

The effluent silicon histories do show a trend where slower flow rate allows for more reaction time between the fluid and solid silicon-rich phases. The result of longer reaction time is that silicon is increased in the fluid phase. The early spike in effluent silicon concentration might be related to silicon-rich solid particles (e.g. unhydrated clinker or C-S-H) that are left behind on the fracture surface after fracturing and advected out of the core at the beginning of the experiments. And while no particles

were visible in the effluent samples, this mechanism might explain both the early spike in effluent silicon and why the reacted surfaces are visibly smoother (Figure 2). The presence of the remaining silicon as solid phases and their nearly insoluble nature explains why no significant decrease in the pressure differential due to increasing aperture is observed.

Despite using natural fractures that impart local aperture variability and thus flow variability, the reaction patterns (e.g. channelization) and effluent history are very consistent. Effluent calcium concentration is always the dominant cation, silicon is a minor component, and both iron and aluminum are trace. Lateral flow restrictions and unreacted 'islands' on the fracture surface show that both heterogeneous flow and non-uniform reactions are occurring across the sample width (Wenning et al., 2013). These heterogeneities provide low velocity regions where local residence time is increased, which allows for favorable precipitation conditions. Unreacted cement, protected by a layer of secondary precipitate might form geomechanical supports that will resist closure due to stress which seemed not to occur in the short residence time experiments (Mason et al., 2013).

The constant flow rate experiments do not exhibit the significant increase in pressure differential that was observed in the HCl experiments, which was correlated to secondary mineral precipitation. The dissolution reaction is comparable in both HCl and CO₂ experiments, where higher acid concentration and residence time enhance reaction on the surface. For example, QB4-3 has the longest residence time, the most reacted texture, and the largest calcium concentration in the effluent. In contrast QB6 has the shortest residence time, less visible reaction on the fracture surface, and low effluent calcium concentration.

A significant difference between the HCl and CO₂ experiments is how the reaction affects channel development and secondary calcite precipitation. NA7-11 and NA9-3 had similar residence times (4 and 7 seconds respectively) but almost three times as much CO₂ was injected into NA9-3 which has a much

broader reaction pathway. In NA7-11, SEM analysis indicates that the secondary precipitation bounding the reacted channel is dissolving and the reacted channel is growing laterally and is less stable than in the HCl experiments. Significant channeling of the flow (NA7-11), the formation of narrow reacted channel zones (NA9-3 and QB6), and precipitation of secondary minerals (QB4-3) are apparently insufficient to cause an increase in the pressure differential during these experiments with dissolved CO₂. Overall mineral precipitation is less dominant than it was in the analog experiments and is often only well-developed next to where the caulk was located in the fracture (zones of minimal velocity and high local residence time).

In the HCl system (which was equilibrated with atmospheric CO₂), once the acid is consumed the pH rises and affects mineral solubility to promote precipitation. Because of the buffering nature of the CO₂-saturated water system, there is more capacity for reaction for carbonic acid than with an HCl solution of similar pH. For example in a HCl system with a pH of 3 the acid concentration is 0.001 M but in a CO₂-saturated water system the CO₂ concentration can be several orders of magnitude larger (1.42 M assuming a 6.3 wt.%CO₂). To capture the coupling between fluid flow and reaction, the CO₂ system therefore requires an increase in residence time by extending core length as we have done in the composite cores discussed next.

4.1.2. Constant pressure differential experiments

The constant pressure differential experiments clearly show self-limiting behavior which is caused by the coupling between mineral precipitation and fluid flux. Figure 11 plots key experimental times for the three experiments that did not show breakthrough of the low-pH fluid. As CO₂ is injected the sample permeability remains constant for some time before decreasing until the flow is shut off (in all but JA8 which failed at after 4 hours and 2 mmol of CO₂ was injected). In fact, after effectively sealing the fracture, two samples (JA1 and JA9) were able to withstand significantly higher pressure differentials

461 across the sample without reestablishing significant fluid flow (Figure 9). To seal, precipitation need not
462 occur as a thick uniform band (as in JA9) but needs to only seal a sufficient portion of the fracture to
463 prevent flow (JA1 and JA8). Given sufficient time and diffusion across the precipitate zone a more
464 uniform band might develop, as in the diffusion dominated experiments (Kutchko et al., 2007 and 2008)
465 or what was observed in the field (Carey et al., 2007; Crow et al., 2010).

466 Although the residence time in sample JA5 was too short to fully seal the fracture before the
467 precipitation zone was advected out of the sample, the reduction in flow rate provides evidence for self-
468 limiting behavior. This experiment's residence time was more than double the slowest constant rate CO₂
469 experiment, which did not exhibit a pressure differential spike. In sample JA5, the post-breakthrough
470 permeability is lower than the initial permeability and the reacted zone is narrow in the last section of
471 core (Figure 10), which is evidence that lateral restriction in flow occurred.

Figure 11 – Permeability evolution for the constant pressure differential composite core experiments. Permeability is normalized to initial sample permeability and plotted versus total dissolved CO_2 injected into the core.

4.2. Coupled reaction and flow mechanisms

This section presents a summary of the inferred reaction and transport processes occurring in the fractured cores during the flow of CO_2 -saturated water. Figure 12 shows a schematic of the process.

Figure 12 – Conceptual model of the self-sealing process. ($t = 1$) As carbonic acid is injected into the fracture it diffuses into cement (black arrows), dissolving cement phases and forming a reaction zone (orange) that is comprised of an amorphous silica phase preceded by a thin carbonated zone (green). Within the fracture there is a front that separates the initial fluid and the injected fluid (black dashed line). As fluid is injected this front is advected down the core. Behind this front, is a front where the pH has risen sufficiently to begin calcite precipitation in the open fracture (green dashed line). ($t = 2$) Continuous injection of acid causes the diffusion limited reaction to propagate into the cement. Within the fracture, sufficient calcite has precipitated to begin to slow fluid flux. However, because fluid is still moving across the precipitated calcite a dissolution front (red dashed line) develops as the precipitation front moves along the fracture. ($t = 3$) Precipitation causes sufficient reduction in fluid flux that the system becomes self-sealing.

Time $t = 1$ shows the early system behavior. The injected fluid displaces the initial fluid in the fracture that was in equilibrium with the cement (black dashed line). The injected fluid contains dissolved CO_2 , which has speciated to form carbonic acid. The principle reaction is between the injected fluid and the cement. Where the carbonic acid concentration is high, the reaction of CO_2 -saturated water with cement releases calcium and hydroxide ions from portlandite dissolution and C-S-H alteration (with other phases to form the amorphous zeolite) and consumes carbonic acid (orange zone). Preceding this reacted zone (i.e. further into the cement) is a calcite precipitation zone, that previous work as shown can act to retard acid diffusion into the cement (green zone) (Kutchko et al., 2008). However, as the alteration front penetrates deeper into the cement, the process quickly becomes diffusion limited as the ions must diffuse through the remaining amorphous zeolite and the low porosity

calcium carbonate zone to react with cement and diffuse back out into the fracture channel. Thus the cement's ability to raise pH diminishes with time. This behavior is similar to reactions observed in diffusion controlled cement dissolution experiments (Kutchko et al., 2008). In lateral zones where flow slows down, local residence time is increased and allows more carbonic acid to react with cement phases, resulting in a pH increase that promotes the precipitation of calcite and other calcium carbonates (green dashed line). The precipitation of calcium carbonates next to the regions of high flow leads to a strong flow localization.

Time $t = 2$ shows the advancement of the precipitation front (dashed green line), the dissolution front (dashed red line), and the zone of precipitation (green material between green and red lines) along the fracture. Precipitation of calcite in the open fracture space is caused by a rise in pH relative to the infiltrating fluid, the presence of liberated calcium, and injected carbonate ions. However, once precipitated the calcite becomes immobile and fresh fluid can pass over the solid, which will allow subsequent dissolution and transport of ions down the fracture. Evidence for this behavior is best seen in the magenta box of sample JA9 (Figure 10), where the carbonate is bound in a discrete zone and followed by the reacted zone. In the constant flow rate experiments, sufficient precipitation can close a portion of the fracture, which leads to a spike in the pressure differential. However if the fluid advection is too fast the front of calcium and carbonate ions will exit the core before pH is sufficiently high to initiate precipitation. Further calcium release (and pH neutralization) would come by much slower processes, e.g. via diffusion through the reacted channel or through mixing of fluids with lateral slow flow regions. Thus there is a critical length scale or residence time relative to the reaction rate that must be achieved to begin the process of precipitation leading to a pressure differential spike. Even if a critical length is satisfied under constant flow rate conditions (and assuming pore pressure does not exceed confining pressure) there will come a point where the precipitation zone is advected out of the system. Hence the need to study the condition that is actually present in the subsurface, that of a pressure

differential driving force. Time $t = 3$ shows the scenario where calcite precipitation in the fracture has begun to significantly restrict fluid flow. Diffusive penetration into the sample has slowed down and the size of the precipitation zone in the fracture has increased. Once plugging begins the flow rate constantly decreases with time and thus CO₂ leakage slows.

The time required to seal the core depends on several parameters that will be unique to the well and field. The specific geometry of the fracture will control the time it takes to seal the leak. The reactivity of the system will also control the time required to liberate ions to sufficient saturation that allows the precipitation of calcite. If the well cement is made from a formulation that has a low portlandite or C-S-H concentration and is high in more insoluble material (silica grains or fly ash for example) it could take longer to seal the system. Older wellbores would have cement with less clinker phases (as complete cement hydration can take many years) and could be subject to some carbonation from natural carbonic acid in the subsurface. A specific formation's brine chemistry and concentration will significantly affect not only CO₂ saturation (Duan and Sun, 2003; Duan et al., 2006) but also possibly affect mineral species solubility and reaction kinetics (Lopez et al., 2009; Zuddas and Mucci, 1998). Less aqueous CO₂ would reduce total reaction capacity but also reduce the CO₂'s pH buffering capacity and the amount of reaction needed to allow precipitation. Elevated temperature would increase reaction rates and lower CO₂ saturation, which might accelerate sealing. Thus the behavior observed in this study needs to be further studied under a variety of conditions to more fully understand how leak paths might evolve in the subsurface.

5. Conclusions

This work serves to expand upon current understanding of wellbore leakage of CO₂-saturated liquids. When the flow of CO₂-saturated water occurs in fractured cement cores, carbonic acid attacks cement by progressively dissolving calcium phases. However, residual amorphous silicate is left behind

so that the fracture aperture does not significantly increase and no positive feedback due to dissolution is observed. Experiments with a sufficiently long residence time (as observed in the composite core experiments) capture precipitation processes that lead to self-sealing of the core. Constant pressure differential allows the direct observation of reduced flow rate due to reduction in fracture conductivity and increased residence time. A reduction in fracture conductivity, for constant pressure differential, is correlated to precipitation of calcite across the fracture surface. These experimental results provide strong evidence that reactive transport of dissolved CO₂ along fractures in well bore cement does not provide a significant leakage hazard.

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References

- Abdoulghafour, H., Luquot, L., Gouze, P., 2013. Characterization of the Mechanisms Controlling the Permeability Changes of Fractured Cements Flowed Through by CO₂-Rich Brine. *Environ. Sci. Technol.* 47, 10332–10338. doi:10.1021/es401317c
- API, 1997. Recommended Practice for Testing Well Cements 10B.
- Bear, J., 1972. Dynamics of Fluids in Porous Media. American Elsevier Publishing Company, Inc., New York.
- Bourgoyne Jr., A.T., Stuart L. Scott, Wojciech Manowski, 1999. A review of sustained casing pressure occurring on the OCS (MMS Report No. 008DE). Minerals Management Service.
- Boutt, D.F., Grasselli, G., Fredrich, J.T., Cook, B.K., Williams, J.R., 2006. Trapping zones: The effect of fracture roughness on the directional anisotropy of fluid flow and colloid transport in a single fracture. *Geophys. Res. Lett.* 33, 1–6. doi:10.1029/2006GL027275
- Carey, J.W., Wigand, M., Chipera, S.J., WoldeGabriel, G., Pawar, R., Lichtner, P.C., Wehner, S.C., Raines, M.A., Guthrie Jr., G.D., 2007. Analysis and performance of oil well cement with 30 years of CO₂ exposure from the SACROC Unit, West Texas, USA. *Int. J. Greenh. Gas Control* 1, 75–85. doi:10.1016/S1750-5836(06)00004-1
- Crow, W., Carey, J.W., Gasda, S., Brian Williams, D., Celia, M., 2010. Wellbore integrity analysis of a natural CO₂ producer. *Int. J. Greenh. Gas Control* 4, 186–197. doi:10.1016/j.ijggc.2009.10.010
- Dijk, P., Berkowitz, B., 1998. Precipitation and dissolution of reactive solutes in fractures. *Water Resour. Res.* 34, 457–470. doi:10.1029/97WR03238
- Duan, Z., Sun, R., 2003. An improved model calculating CO₂ solubility in pure water and aqueous NaCl solutions from 273 to 533 K and from 0 to 2000 bar. *Chem. Geol.* 193, 257–271. doi:10.1016/S0009-2541(02)00263-2
- Duan, Z., Sun, R., Zhu, C., Chou, I.-M., 2006. An improved model for the calculation of CO₂ solubility in aqueous solutions containing Na⁺, K⁺, Ca²⁺, Mg²⁺, Cl⁻, and SO₄²⁻. *Mar. Chem.* 98, 131–139. doi:10.1016/j.marchem.2005.09.001
- Emmanuel, S., Berkowitz, B., 2005. Mixing-induced precipitation and porosity evolution in porous media. *Adv. Water Resour.* 28, 337–344. doi:10.1016/j.advwatres.2004.11.010
- Huerta, N.J., Hesse, M.A., Bryant, S.L., Strazisar, B.R., Lopano, C.L., 2013. Experimental Evidence for Self-Limiting Reactive Flow through a Fractured Cement Core: Implications for Time-Dependent Wellbore Leakage. *Environ. Sci. Technol.* 47, 269–275. doi:10.1021/es3013003
- Kutchko, B.G., Strazisar, B.R., Dzombak, D.A., Lowry, G.V., Thaulow, N., 2007. Degradation of Well Cement by CO₂ under Geologic Sequestration Conditions. *Environ. Sci. Technol.* 41, 4787–4792. doi:10.1021/es062828c
- Kutchko, B.G., Strazisar, B.R., Lowry, G.V., Dzombak, D.A., Thaulow, N., 2008. Rate of CO₂ Attack on Hydrated Class H Well Cement under Geologic Sequestration Conditions. *Environ. Sci. Technol.* 42, 6237–6242. doi:10.1021/es800049r
- Lee, J., Kang, J.M., Choe, J., 2003. Experimental analysis on the effects of variable apertures on tracer transport. *Water Resour. Res.* 39, 1–11. doi:10.1029/2001WR001246
- Lopez, O., Zuddas, P., Faivre, D., 2009. The influence of temperature and seawater composition on calcite crystal growth mechanisms and kinetics: Implications for Mg incorporation in calcite lattice. *Geochim. Cosmochim. Acta* 73, 337–347. doi:10.1016/j.gca.2008.10.022
- Luquot, L., Abdoulghafour, H., Gouze, P., 2013. Hydro-dynamically controlled alteration of fractured Portland cements flowed by CO₂-rich brine. *Int. J. Greenh. Gas Control* 16, 167–179. doi:10.1016/j.ijggc.2013.04.002

- Mason, H.E., Du Frane, W.L., Walsh, S.D.C., Dai, Z., Charnvanichborikarn, S., Carroll, S.A., 2013. Chemical and Mechanical Properties of Wellbore Cement Altered by CO₂-Rich Brine Using a Multianalytical Approach. *Environ. Sci. Technol.* 47, 1745–1752. doi:10.1021/es3039906
- Metz, B., Davidson, O., de Coninck, H., Loos, M., Meyer, L. (Eds.), 2005. IPCC Special Report on Carbon Dioxide Capture and Storage.
- Nicot, J.-P., 2009. A survey of oil and gas wells in the Texas Gulf Coast, USA, and implications for geological sequestration of CO₂. *Environ. Geol.* 57, 1625–1638. doi:10.1007/s00254-008-1444-4
- Nordbotten, J.M., Celia, M.A., Bachu, S., Dahle, H.K., 2005. Semianalytical Solution for CO₂ Leakage through an Abandoned Well. *Environ. Sci. Technol.* 39, 602–611. doi:10.1021/es035338i
- Ravi, K., Bosma, M., Gastebled, O., 2002. Safe and Economic Gas Wells through Cement Design for Life of the Well. Society of Petroleum Engineers. doi:10.2118/75700-MS
- Singurindy, O., Berkowitz, B., 2005. The role of fractures on coupled dissolution and precipitation patterns in carbonate rocks. *Adv. Water Resour.* 28, 507–521. doi:10.1016/j.advwatres.2005.01.002
- Tao, Q., Checkai, D., Huerta, N., Bryant, S.L., 2011. An improved model to forecast CO₂ leakage rates along a wellbore. *Energy Procedia* 4, 5385–5391. doi:10.1016/j.egypro.2011.02.522
- Walsh, S.D.C., Mason, H.E., Du Frane, W.L., Carroll, S.A., 2014a. Experimental calibration of a numerical model describing the alteration of cement/caprock interfaces by carbonated brine. *Int. J. Greenh. Gas Control* 22, 176–188. doi:10.1016/j.ijggc.2014.01.004
- Walsh, S.D.C., Mason, H.E., Du Frane, W.L., Carroll, S.A., 2014b. Mechanical and hydraulic coupling in cement–caprock interfaces exposed to carbonated brine. *Int. J. Greenh. Gas Control* 25, 109–120. doi:10.1016/j.ijggc.2014.04.001
- Watanabe, N., Hirano, N., Tsuchiya, N., 2008. Determination of aperture structure and fluid flow in a rock fracture by high-resolution numerical modeling on the basis of a flow-through experiment under confining pressure. *Water Resour. Res.* 44, 1–11. doi:10.1029/2006WR005411
- Watson, T., Bachu, S., 2009. Evaluation of the Potential for Gas and CO₂ Leakage Along Wellbores. *SPE Drill. Complet.* 24. doi:10.2118/106817-PA
- Wenning, Q.C., Huerta, N.J., Hesse, M.A., Bryant, S.L., 2013. Reactive Flow Channelization in Fractured Cement-implications for Wellbore Integrity. *Energy Procedia* 37, 5773–5780. doi:10.1016/j.egypro.2013.06.500
- Zhang, M., Bachu, S., 2011. Review of integrity of existing wells in relation to CO₂ geological storage: What do we know? *Int. J. Greenh. Gas Control* 5, 826–840. doi:10.1016/j.ijggc.2010.11.006
- Zuddas, P., Mucci, A., 1998. Kinetics of Calcite Precipitation from Seawater: II. The Influence of the Ionic Strength. *Geochim. Cosmochim. Acta* 62, 757–766. doi:10.1016/S0016-7037(98)00026-X