The role of host rock properties in determining potential CO₂ migration pathways

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Abstract

This work examines CO₂-brine-cement-rock interactions and the associated permeability changes to understand the role of host rocks in determining CO₂ migration pathways into groundwater aquifers under conditions relevant to geological carbon sequestration. Composite sandstone-cement and limestone-cement cores were used for an eight-day flow-through experiment. X-ray Micro-CT imaging revealed that CO₂-brine-cement interaction predominated at the sandstone-cement interface, leading to a permeability increase by a factor of three. In the limestone-cement core, however, the CO₂-rich flow diverted itself primarily into the higher permeability limestone, creating wormholes and a dominant flow path inside the limestone, resulting in a permeability increase by a factor of twenty four. Mass balance measurement indicates that the limestone-cement core lost about three times more of its original mass compared to the sandstone-cement core. These observations suggest differing CO₂ migration pathways into underground drinking water resources through preferential pathways in host rocks.

Keywords: Carbon sequestration; carbonate dissolution; host rock; wellbore cement; X-ray tomography.

1. Introduction

Geological carbon sequestration (GCS) has been considered as a viable option for carbon mitigation (Bachu, 2008; Benson and Cole, 2008; Lal, 2008; Stevens *et al.*, 2001). A major concern about GCS is the possibility of CO₂ leakage into the atmosphere and into underground drinking water resources through conductive pathways. Observations at natural analog sites in New Mexico and Arizona have documented the upward intrusion of injected CO₂ and brackish brine into shallow drinking water aquifers through fault zones (Keating *et al.*, 2014; Keating *et al.*, 2013). Experimental and modeling studies, including both multi-phase flow and reactive transport simulation and reduced order models, have shown that CO₂ enrichment can reduce pH, increase total dissolved solids, and mobilize metals (Apps *et al.*, 2010; Atchley *et al.*, 2013; Carroll *et al.*, 2009; Carroll *et al.*, 2014; Dai *et al.*, 2014; Frye *et al.*, 2012; Lawter *et al.*, 2015; Little and Jackson, 2010; Siirila *et al.*, 2012; Wunsch *et al.*, 2014).

Large volumes of CO₂ injection at an industrial scale can result in CO₂-enriched zones with elevated pressure during and after injection, potentially extending kilometers from the injection site (Birkholzer *et al.*, 2014; Birkholzer *et al.*, 2009). In order to protect underground drinking water from crossover migration and contamination from CO₂-enriched zones, the United States Environmental Protection Agency (USEPA) created the Class VI Rule, a federal technical criteria for injection well permitting process which requires a base-line subsurface geochemical survey within a specified Area of Review (AoR, <http://water.epa.gov/type/groundwater/uic/wellssequestration.cfm>). An AoR includes the vicinity of injection wells, where cement and host rocks are often in close contact and the risks to water quality must be assessed. Fractures or faults in this area could add vulnerability to underground drinking water deposits (Birkholzer *et al.*, 2014).

Cement is commonly used to seal the annular space between the casing and the formation rock to prevent fluid loss and keep the casing in place. Cement is also used to plug and isolate the well during well abandonment (Nelson, 1990). As a result, cement is often in direct contact with host rocks in the AoR. Under CO₂-rich conditions during geological carbon sequestration, cement-CO₂-brine interactions can potentially affect the wellbore integrity and increase the possibility of CO₂ upward migration. Injected CO₂ can leak through defects within wellbore cement, poorly bonded interfaces between cement and host rocks, or incomplete plugs or channels (Gasda *et al.*, 2004; Nordbotten *et al.*, 2005; Nordbotten *et al.*, 2009; Zhang and Bachu, 2011). The properties of host rocks can potentially play an important role in determining CO₂ upward migration. In particular, sedimentary rocks that are suitable for geological carbon sequestration are often distributed with spatially heterogeneous properties, including permeability and reactivity (Koltermann and Gorelick, 1996). Understanding and evaluating potential permeability alterations during cement-rock-CO₂ interactions is essential to assess risks associated with GCS.

Extensive studies have been carried out to examine CO₂-induced cement alteration within wellbore cement plugs under diffusion-controlled (Brunet *et al.*, 2013; Kutchko *et al.*, 2009; Kutchko *et al.*, 2008; Matteo and Scherer, 2012; Zhang *et al.*, 2013) and dynamic flow conditions (Huerta *et al.*, 2011; Huerta *et al.*, 2013). Studies have focused on cement alteration and associated conductive property change when subjected to different cementing and bonding conditions. In some cases, cement cores with fractures or voids exhibited reduced fracture permeability due to calcite precipitation along the surfaces of fractures in a CO₂-rich environment (Huerta *et al.*, 2011; Huerta *et al.*, 2013; Liteanu and Spiers, 2011; Walsh *et al.*, 2012; Wigand *et al.*, 2009). In contrast, other cases showed that the presence of bonding defects or fractures led to further cement degradation that promoted favorable conditions for CO₂ leakage (Bachu and Bennion, 2009; Cao *et al.*, 2013; Yalcinkaya *et al.*, 2011). Such discrepancy in

experimental observations, that is, fracture closure and opening, has been attributed to a strong feedback between flow conditions and the initial cement conditions—in particular, initial fracture aperture (Cao *et al.*, 2015).

The cement-rock interface has also been studied as a potentially important CO₂ leakage preferential pathway. Duguid *et al.* (2011) was among the first to create a composite rock-cement core by filling sandstone/limestone cylinders with class H neat paste to study the CO₂-brine effect on cement at the rock-cement interface in a batch reactor under ambient conditions for 12 months. Visible signs of cement degradation were observed with core permeability increased by an order of magnitude. Cao *et al.* (2013) performed coreflood experiments on composite sandstone-cement samples with pre-existing voids or cracks to investigate the deterioration of a defective wellbore cement plug in the presence of CO₂-charged brine. Newell and Carey (2012) studied the transport of CO₂-brine through the cement-rock interface using half-cylinders of wellbore cement and siltstone, which showed that the self-limiting flow along wellbore defects can be attributed to the precipitation of reaction products along the flow path. Mason *et al.* (2013) analyzed chemical and mechanical alterations of the cement phase by injecting CO₂-brine through a core consisting of half cement–half caprock separated by a plane of constant aperture. Their work suggested that geochemical and mechanical property alteration in both cement and caprock contributed to permeability evolution. Using core-flood experiments and geochemical modeling, Walsh *et al.* (2014a, b) found that the carbonated-brine-induced reaction zones at the cement/caprock interfaces led to deformation and fracture closure, resulting in a decrease in hydraulic apertures.

Although speculated to be important in assessing CO₂ migration into groundwater resources, the interaction between CO₂ and host rock has received much less attention. Smith *et al.* (2013b) flooded

CO₂-rich brine through low-permeability carbonate cores from the Weyburn–Midale CO₂-enhanced oil recovery and storage site. Aqueous geochemistry data and CT-images revealed the formation of fast flow pathways due to the heterogeneity of core sample properties. Their companion modeling work (Hao *et al.*, 2013) highlighted the importance of heterogeneity on wormhole formation and the permeability evolution. In general, however, CO₂ interactions with the surrounding host rock in the vicinity of injection wells remains largely underexplored and poorly understood.

The objective of this work is to understand the role of host rock in determining the potential CO₂ migration pathways into groundwater aquifers in the vicinity of injection wells *under* conditions relevant to geological carbon sequestration. In particular, sandstone and limestone have been suggested as potential host rocks for geological carbon sequestration due to their ubiquitous occurrence in sedimentary rocks and geologic formations (Haldar and Tišljär, 2014; Knauss *et al.*, 2005; Selley, 2005; Stow, 2005) and therefore were selected as host rocks in this work. CO₂-flooding experiments were carried out in two sets of composite cores: sandstone-cement and limestone-cement. Permeability evolution was monitored during the course of experiments and X-ray Micro-Computed Tomography (MCT) imaging was used to visualize cement/rock alterations.

2. Methodology

2.1 Sample preparation and flow-through experiment

In order to represent cement and formation rock bonding conditions in laboratory samples, several composite cement-host rock core samples were created. They were prepared by injecting cement slurry into bored rock cores. Berea sandstone and Oolitic limestone were provided by Cleveland Quarries with a 1.27 cm diameter bore drilled in the center of each core which has a dimension of 10.16 cm in diameter and 30.48 cm in length. The porosity of the Berea sandstone core was 20% and the permeability was 100 mD as provided by the providers (Cleveland Quarries) and confirmed by flow-through and mercury porosimetry experiments performed on the same batch of Berea sandstone core. Limestone porosity and permeability was around 8.5% and 1.5 mD, respectively. They were roughly estimated from the initial porosity and permeability measurements on the composite limestone-cement core assuming homogeneity and ideal geometry of the core sample. Their phase compositions (Table 1) were determined by XRD (X-ray diffraction) analysis. The cementing procedure used is similar to that documented in Cao *et al.* (2013) with some improvement. Figure 1A is a scheme of the curing experimental setup. Briefly, the samples were vacuum-saturated with 1% (by weight) NaCl brine in a curing vessel. Cement slurry was prepared by mixing Portland type H neat cement (Lafarge, Pittsburgh) with distilled water via a mud mixer using a water-to-cement ratio of 0.38 according to the API Recommended Practice 10B. Immediately following mixing, the cement slurry was poured into a Temco fluid accumulator with a Teflon floating piston at the bottom to isolate the injected fluid from the cement slurry and ensure a piston-like displacement. Water was pumped from the bottom of the accumulator at 1.38 MPa by a Quizix[®] pump. Cement slurry was displaced out from the top of the accumulator and flowed into the center of the rock sample. A back-pressure pump was programmed to

receive displaced brine from the core at a constant back pressure of 0.138 MPa. The confining pressure around the core was maintained at a pressure 1.38 MPa higher than the injection pressure. This pressure difference ensured good bonding between the injected cement slurry and host rock. The injection process continued until a pre-calculated cement volume (equal to the volume of the center bore and passing-through tubing) was injected into place. Finally, the nitrogen pressure was elevated to 8.96 MPa and the curing vessel wrapped by heating tapes was kept at 50°C for 72 hours to complete the curing process. The sandstone-cement and limestone-cement samples were prepared using the same procedure.

After curing, the composite cement-rock samples were trimmed into cores of 3.81 cm in diameter and 7.6 cm in length with a 1.27 cm diameter cement column in the center (see Figure 1B and 1C). The effective porosity of the sandstone-cement core and limestone-cement core was measured to be 15.4% and 13.9%, respectively. According to literature, an unreacted cement column with water-to-cement ratio of 0.38 has a total porosity of 31% and an effective permeability of 4~8 μD (Um *et al.*, 2011). These core plugs were then dried overnight in an oven before the core flooding experiments. Both cores were vacuum saturated by distilled water at a pH of 6.7 for 24 hours. Although this might lead to some cement dissolution, we expect that the extent of dissolution is much smaller than that during acidic, CO_2 -rich flooding. The weight of the dry core (composite core) after the core flooding experiment was also measured using the same method, which gave the total mass change of each core before and after the experiment.

Table 1: Phase compositions of host rocks

Sandstone Phases (%)		Limestone Phases (%)	
Silica (SiO_2)	93.13%	Calcite (CaCO_3)	99.6%
Alumina (Al_2O_3)	3.86%	Quartz (SiO_2)	0.4%

Ferric Oxide (Fe_2O_3)	0.11%
Ferrous Oxide (FeO)	0.54%
Magnesium Oxide (MgO)	0.25%
Calcium Oxide (CaO)	0.10%

Figure 1: (A) Schematic of experimental setup for sample curing; (B) picture of the cross-section of cured sandstone-cement core plug (core plug diameter is 3.81 cm and sample length is 7.59 cm); (C) picture of the cross-section of cured limestone-cement core plug (core plug diameter is 3.81 cm and sample length is 8.37 cm).

The flow-through apparatus was fully described in Cao *et al.* (2015). A CO_2 -rich brine solution was prepared with distilled water with 1% wt NaCl and by bubbling CO_2 into the brine at 0.069 MPa for approximately six hours to reach CO_2 -brine equilibrium prior to core flooding. The solution reached an average pH value of 3.8. During the experiment, CO_2 was continuously bubbled at that pressure to maintain a stable pH condition. The pH of the CO_2 -saturated brine was measured twice a day to ensure stable CO_2 solubility using a digital Origin pH meter. A Temco back-pressure regulator was used for effluent sample collection. A back pressure of 4.14 MPa was maintained throughout the experiment

using nitrogen. A confining pressure of 6.34 MPa was maintained throughout the experiment. The CO₂-rich brine was continuously injected through the core plug using a Quizix[®] pump at a constant flow rate of 0.5 cm³/min for a total of eight days. Pressure drop across the core was measured using an Omega differential pressure transducer and a data acquisition system. During the experiment, a constant temperature (25°C) was maintained using heating tapes and a temperature controller. According to the CO₂ solubility model by (Duan and Sun, 2003), this temperature and pressure condition leads to the same CO₂ solubility of 1.053 mol/L in brine as those at 8.96 MPa and 50°C, which represents the condition at a depth of approximately 1,000 m with a standard in-situ reservoir pressure gradient of 9.79 Pa/m and a temperature gradient of 58.30 °C/m (Fridleifsson, 2008; Oldenburg and Rinaldi, 2011).

2.2 Aqueous effluent and rock sample analysis

Effluent samples from the core flooding experiment were typically collected under ambient condition twice a day, except for more frequent sampling during the first 24 hours of the experiment. Effluent pH was measured immediately after sampling using a digital pH meter. Total inorganic carbon (TIC) was measured using Shimadzu TOC-VCPH by acidifying the solution followed by quantifying the amount of carbon dioxide. Due to the sudden pressure drop when effluents came out of the core, CO₂ escaped from the solution. So the measured pH and TIC do not accurately reflect the in-situ inorganic carbon concentrations. Aqueous samples were preserved and analyzed at the end of experiment. Concentrations of cations (Ca, Si, Mg, Na, K, Sr) were measured using the Perkin-Elmer Optima 5300 UV inductively coupled plasma atomic emission spectrometry (ICP-AES).

After each experiment, 3D images of the core specimens were obtained using a GE phoenix X-ray MCT scanner. This three-dimensional nondestructive imaging technique can visualize possible spatial

microstructure alterations and preferential alteration along the cement-rock interfaces and host rock. Image segmentation and visualization was performed using the imaging process software AVIZO 7.1. The voxel resolution for the sandstone-cement sample images was 44.0 μm and 43.8 μm for the limestone-cement sample.

Energy Dispersive X-ray Spectroscopy (SEM/EDS) was conducted to identify mineralogical alterations in the vicinity of the cement-rock interface. It can provide rapid qualitative and quantitative analysis of elemental composition within a sampling depth of 1-2 μm on the sample surface. In conducting the EDS analysis, the reacted core sample was sawed perpendicularly to the transverse cross-sectional plane along the main axis into two halves using a blade diamond saw. Three 1 mm x 1 mm observation windows were selected at the interface of cement and host rock with different proximity to the CO₂-brine injection point. In each analysis window, two spots were chosen to generate the spot spectrum maps—one in the cement zone and the other in the sandstone zone.

3. Results and Discussion

3.1 Visual evidence of core sample alterations

Figure 2 presents two-dimensional, longitudinal and transverse cross-sections of the sandstone-cement core from X-ray MCT imaging after exposure to CO₂-brine flow. Alteration occurred at the interface of the sandstone and cement zone, in particular within the cement zone. This is because sandstone is primarily composed of silica quartz, which reacts at rates that are orders of magnitude lower than cement. Due to the more than 4 orders of magnitude in permeability contrast between the sandstone (100 mD, reported by the provider) and cement zone (4-8 μ D, *Um et al.*, 2011), CO₂-brine primarily flowed through the more permeable sandstone zone. As a result, the acidic brine degraded the cement at the interface of sandstone and cement zone. The cement zone near the inlet experienced more severe degradation, which is consistent with previous observations (*Cao et al.*, 2013). This is because the core inlet face was in direct contact with fresh CO₂-equilibrated brine under constant flow conditions. A thin layer of cement was eroded and washed away after eight days of continuous exposure. With the dissolution of hydrated cement phases in acidic brine, hydrogen ions were consumed and pH increased. In addition, Ca(II) ions were produced and transported to the downstream, resulting in decreasing brine acidity and increasing concentrations of reaction products along the flow direction (*Cao et al.*, 2013). This could potentially lead to lower reaction rates in the downstream regions. As a result, no obvious alteration was observed in the middle-to-outlet section, as revealed by the MCT images (Figure 2C). At the outlet of the core, some cement degradation was observed (Figure 2D), primarily due to the accumulation of CO₂-saturated brine near the flow distributor connecting to the core sample. According to the measurement of the weight change of the dry core before and after the experiment (section 2.1), the sandstone-cement core lost about 1.4% of its original mass and its porosity increased

1.3% in average. As manifested in the CT images (Figure 2), sandstone was essentially intact after the flow-through experiment. Therefore, this porosity and mass change are believed to be mostly due to cement dissolution at the vicinity of the inlet, primarily portlandite because portlandite dissolves much faster than C-S-H.

Figure 2: (A) 2D longitudinal cross-section of sandstone-cement core with flow direction from left to right; 2D transverse cross-section of sandstone-cement core at different locations: (B) 0.68 mm from the inlet; (C) 38.72 mm from the inlet; (D) 75.33 mm from the inlet.

Figure 3A shows 2D X-ray MCT images of the limestone-cement core before the experiment. Figures 3B-3D show the images along the longitudinal and transverse planes after the experiment that are significantly different from the sandstone-cement samples. Figure 3B shows the formation of the preferential flow paths inside the limestone matrix along the flow direction after the experiment. Figure 3C shows the channels at the inlet of the core, confirming severe deterioration of the host rock close to the CO₂-rich brine source. The three-dimensional view of the flow channels in Figure 3D indicates that reactions mainly took place in the host limestone, which was very different from the sandstone-cement

core. When CO₂-rich brine flowed through the more permeable rock, limestone dissolved and dissolution pathways gradually propagated along the flow direction. With continuous injection, these channels became the primary flow conduits. Ultimately, the core sample was measured to lose 3.4% of its original mass at the end of the experiment. Carbonate dissolution in acidic environments has been observed in many studies (Carroll *et al.*, 2013; Elkhoury *et al.*, 2013; Gharbi *et al.*, 2013; Kharaka *et al.*, 2006; Salehikhoo and Li, 2015; Smith *et al.*, 2013a; Smith *et al.*, 2013b). These highly conductive and spatially non-uniform flow channels are often referred to as wormholes (Fredd and Fogler, 1998). Wormholes are typically formed when there are coupled flow and dissolution processes in heterogeneous porous rock (Smith *et al.*, 2013b).

The differences in degradation patterns observed in the sandstone-cement and limestone-cement cores indicate the strong influence of host rock type on the severity of cement degradation. Both limestone and cement are highly reactive under acidic conditions. Because limestone has much higher permeability (1.5 md as estimated from initial measurement) than that of cement (4~8 μ D, Um *et al.*, 2011), the CO₂-rich brine propagated into the more permeable limestone and developed highly conductive channels.

Figure 3: (A) 2D cross-sections of limestone-cement core before flooding experiment; (B) 2D longitudinal cross-section of limestone-cement core after reacting with CO₂-brine (flow direction is from left to right); (C) 2D transverse cross-section of sandstone-cement core, 0.079 mm from core inlet; (D) 3D spatial view of wormholes (shown in blue) developed after the experiment.

3.2 Mineralogical Alterations

Based on the X-ray MCT image analysis, the cement matrix was found to be intact in the limestone-cement core. No alteration of cement phases was observed from the SEM microanalysis. Therefore, only analysis for the sandstone-cement core is discussed here. Before the flow-through experiment, we picked several spots on the inlet and outlet faces of the sandstone core to measure the initial Ca/Si ratio using SEM and elemental analyses, assuming the homogeneity of the core before reacting with CO₂-brine. From the SEM image, we identified the interface of cement and sandstone zone.

After the core flooding experiment, the sandstone-cement core was dried in the oven at 30°C for 24 hours. Then the core was sawed into two halves and was dried again for another 24 hours before the SEM analysis for the cut surface. Figure 4A shows the red dotted observation windows for SEM analysis. Figure 4B shows the representative EDS image along with the corresponding spot spectrum maps obtained from the post-experiment sandstone-cement core half. Elemental analysis focused on Ca and Si composition, given their characteristic abundance in cement and sandstone. Average Ca/Si element weight percentage ratio from all measurements was used to represent the initial value before the experiment assuming a homogeneous sample. The Ca/Si ratios of the post-experiment sample were measured from the observation windows (Table 2). Ca/Si ratios at the same location were not able to be compared before and after the experiment because the cut surface of the core sample was unattainable for SEM analysis before the core flood experiment.

Table 2: Ca/Si element weight percentage ratios at different locations before and after the experiment

Location of sampling window	Sandstone zone Ca/Si		Cement zone Ca/Si	
	Before experiment	After experiment	Before experiment	After experiment
Inlet	0.46($\pm$ 0.03)	3.75($\pm$ 0.05)	9.43($\pm$ 0.03)	0.11($\pm$ 0.05)
Middle		3.88($\pm$ 0.05)		0.76($\pm$ 0.05)
Outlet		3.35($\pm$ 0.05)		0.17($\pm$ 0.05)

Cement is rich in Ca while the sandstone is rich in Si. The two major components of the class H cement portlandite ($\text{Ca}(\text{OH})_2$) and C-S-H can both dissolve and leach Ca, although portlandite dissolves much faster than C-S-H (Brunet *et al.*, 2013). Cement- CO_2 -brine interactions are typically characterized by several reactions as shown below:

Various studies have observed that calcite precipitation occurred following the cement dissolution and Ca(II) release, often considered as the cause of clogging (Brunet *et al.*, 2013; Cao *et al.*, 2015; Kutchko *et al.*, 2007; Newell and Carey, 2012) As expected, before the experiment the Ca/Si ratio in the cement zone (9.43) was more than an order of magnitude higher than that in the sandstone (0.46). After the experiment, Ca/Si ratios indicated significant decrease in the cement zone with Ca/Si ratios between 0.11 to 0.76. These values indicate essentially no presence of Ca-containing phases, which implies the close to complete dissolution of portlandite and C-S-H and the dominance of the leftover silica gel in

these locations within 500 μm from the cement-sandstone interface, as has been similarly observed in literature (Brunet *et al.*, 2013; Kutchko *et al.*, 2008; Mason *et al.*, 2013). In contrast, the Ca/Si ratios increased significantly to values between 3.35 to 3.88 in the sandstone zone at the sandstone-cement interface. This change indicates more of the dissolution of the Ca-rich solid phase instead of sandstone dissolution, because sandstone dissolution rates are orders of magnitude lower than cement dissolutions. The increase in Ca/Si ratio implies that Ca(II) leached from the cement zone and migrated into adjacent more porous sandstone through diffusion and dispersion processes. Interestingly, in both sandstone and cement zones, the Ca/Si ratio of the middle section is the highest (0.76 in the cement zone and 3.88 in the sandstone). This suggests the likelihood of slight calcite precipitation in the middle section of the core, although undetectable by CT and SEM imaging. As discussed in literature, calcite precipitates are commonly observed as a result of Ca(II) release. The precipitation location depends on specific conditions depending on the concentration and pH increase along the flow path. It often progresses as a moving front as a result of CO₂-cement-brine interactions (Brunet *et al.*, 2013). In this case, calcite potentially precipitated however not sufficiently to clog any gap between the sandstone zone and cement zone. Lower Ca/Si ratio from the outlet section compared to the middle section is primarily due to the dissolution of the cement phase as a result of the accumulation of CO₂-saturated brine around the flow distributor connecting to the core sample outlet.

Figure 4: (A) Illustration of Scanning Electron Microscope (SEM) sampling windows: inlet, middle, outlet. Note that the size of the red dotted window is for better illustration and does not reflect the actual size of the observation window in the analysis; (B) Left: EDS image of a 1 mm x 1 mm window on the cut surface of reacted sandstone-cement core. Right: Spot spectrums maps for white circles picked up in sandstone zone and cement zone respectively.

3.3 Permeability and effluent composition evolution during reactive flow

Differential pressure across the composite core sample was measured over time during the experiment and permeability of the cores was calculated via Darcy's law. Given constant flow during the experiment, this is essentially the same as the ratio calculated by dividing the pressure drop data at

the later times over the pressure drop at the initial time so it quantifies the magnitude of alteration during the experiment. The corresponding evolution of normalized core permeability (permeability at later times over its initial permeability) was obtained for both sandstone-cement and limestone-cement cores (Figure 5A). The permeability of both core samples increased due to increased pore connectivity either through the cement dissolution or the dissolution of limestone matrix. The permeability evolution shows that the major alteration occurred at the early stage followed by a stabilized stage at later times. The transition between the two stages occurred at approximately 20–30 hours for the sandstone-cement core, and approximately at 70 hours for the limestone-cement core. At the end of the experiments, the permeability of the sandstone-cement core increased by about three times (from approximately 10 md to 33 md), while that of the limestone-cement core increased by about 24 times of its initial value (from approximately 1 md to 24 md), the magnitude of which was about eight times higher than that of the sandstone-stone core. This is in line with the observations from the X-ray MCT images that limited cement alteration occurred at the cement-rock interface while highly conductive flow wormholes developed in the limestone matrix.

Effluent ions (Ca, Si, Mg, Na, K, Sr) were measured for both sandstone-cement and limestone-cement core flooding experiments. Their concentrations are listed in Table S1 and S2 in the support information. Figure 5B shows the effluent concentration of calcium, one of the abundant cations that are closely related to cement dissolution and calcite dissolution and precipitation. For both experiments, the very earliest concentrations were the highest primarily due to fast release of calcium from the cement phase when the cores were soaked in brine before the experiments started. After the initial pulse, the concentrations were high in the early stage, indicating high reaction rates. The transition between early and later stages occurred at around 20 hours for the sandstone-cement experiment. For the limestone-

cement core, the transition occurred between 70 and 100 hours. The transition times were very similar to that of the permeability increase, suggesting connections between geochemical reactions and conductive property evolution.

Figure 5: (A) Evolution of normalized permeability (later pressure drop data normalized by the initial pressure drop data under constant flow conditions) during the core flooding experiments; (B) measured effluent Ca(II) concentration from sandstone-cement core flooding experiment (black star) and limestone-cement core flooding experiment (grey triangle).

For the sandstone-cement core, although the acidic brine mostly flowed through the sandstone, the reactions mostly occurred at the sandstone-cement interface close to the inlet due to the non-reactive nature of the sandstone, as has been observed in Figure 2. The alteration was largely due to the fast dissolution of portlandite that released Ca(II) , which could potentially react with injected carbonate acid to form calcite. The calcite-rich zone then served as a barrier for further CO_2 -cement interactions (Brunet *et al.*, 2013). These reactions have been observed to occur quickly early on and then slow down

under both diffusion-controlled (Kutchko *et al.*, 2008) and flow conditions (Cao *et al.*, 2013; Huerta *et al.*, 2013). As such, the released Ca(II) concentrations were high early on until around 20 hours, after which Ca(II) concentration stabilized at lower concentrations, indicating slow rates at later stages. Correspondingly, the permeability increase also slowed down after about 20 hours.

Figure 6: Measured effluent concentrations of silica (A), TIC (B) and pH (C) from sandstone-cement core flooding experiment (black star) and limestone-cement core flooding experiment (grey triangle).

Figure 7: Calcium (A) and silica (B) dissolution rates from sandstone-cement core flooding experiment (black star) and limestone-cement core flooding experiment (grey triangle).

For the limestone-cement core, the flow was similarly diverted to the limestone as in the sandstone case. Due to the much higher reactivity of limestone than sandstone, calcite dissolution occurred rapidly in the limestone, as indicated by the prolonged period and high Ca(II) concentration until about 70 hours, after which Ca(II) concentration decreased to a similar level as those in the sandstone-cement core. Between 70 and 80 hours, Ca(II) concentration decreased sharply and was accompanied by the large variation in permeability, which indicated the “breakthrough” of the preferential flow path.

Figure 6 shows the effluent evolution of some other species, including Si, the dissolution product of quartz in sandstone and C-S-H in cement, as well as total inorganic carbon (TIC) and pH values. As expected, Si effluent concentration was higher coming from the sandstone-cement sample due to the abundant presence of quartz. The low Si concentration in the limestone-cement sample supports the low

sandstone and C-S-H dissolution rates and the relatively minor alterations observed in Figure 2. Both TIC and pH were measured at ambient temperature and therefore do not reflect the in situ values in the brine solution within the core. However, these data do allow the observation of the trend of the change during the experiment. For example, the effluent evolution of these two species exhibited an obvious “jump” down similar to Ca(II) at about 70 hours, possibly when the breakthrough of a connected flow path took place.

Figure 7 compares the release rates of Ca and Si calculated by multiplying the constant flow rates $0.5 \text{ cm}^3/\text{min}$ by effluent concentrations. In the sandstone-cement sample, the Ca release rates reflect the combined rates of cement dissolution as Ca sources and potential calcite precipitation as Ca sinks. In the limestone-cement core, the Ca release rates primarily reflect the calcite dissolution in limestone, as cement was mostly intact. The Ca rates in the limestone-cement are about three times higher than those from sandstone-cement in average, which is consistent with the measured 3.4% and 1.4% mass loss in the limestone-cement and sandstone-cement, respectively. In addition, Ca rates show much more variation over time, supporting the breakthrough dynamics in the limestone-cement sample. In particular, calcite dissolution became slower after the breakthrough of the preferential flow path at about 70 hours. This is consistent with literature observation where mineral overall reaction rates are typically lower in more connected porous media because of the formation of preferential flow path and the smaller extent of mass transfer between the high permeability and low permeability zones (Salehikhoo and Li, 2015; Wang and Li, 2015). The Si release rates were about two orders of magnitude lower than Ca, which is expected due to the much lower reactivity of sandstone and Si-containing cement phase (C-S-H).

The development of the flow path suggests the important role of spatial variation in conductive properties in the limestone. Although not rigorously measured, the generated flow path likely had higher

initial permeability than the rest of the sample and therefore conducted most of the flow through the core. If the permeability of the limestone is more evenly distributed, the preferential flow path may not form or likely will take much longer time to form a full path from one end of the sample to the other. This reaction-induced formation of preferential flow path and the development of unstable dissolution fronts have been observed in dolostones by Hao *et al* (2013) and Smith *et al* (2013a, b). They found that the fast pathway development led to an increase in bulk permeability values by several orders of magnitude, which is in agreement with our observation from the limestone-cement core experiment. As discussed in literature, more permeable reactive zones tend to drive more water-rock interactions in heterogeneous porous media (Bao *et al.*, 2014; Li *et al.*, 2014). Since limestone is typically more permeable than cement, this leads to favorable conditions for the potential development of CO₂ migration pathways through the limestone surrounding cemented wells. However, in hastily completed injection wells, or old wells which may not have been sealed properly, the higher permeability in the cement zone will likely lead to reactive flow through the cement zone and therefore enhanced (Cao *et al.*, 2013) or decreased conductive property evolution depending on specific flow and cement fracture/void conditions (Cao *et al.*, 2015).

4. Conclusions

This work presents comparative experimental observations of sandstone-cement and limestone-cement cores subject to CO₂-rich flow via visual inspection, permeability measurements and analysis of mineral dissolution products. Results from this work demonstrate the dominant influence of host rock type on the permeability increase and on CO₂ migration pathways in the vicinity of the cemented zone under CO₂-rich environments.

Experimental observations demonstrate the preferential flow of CO₂-rich brine through the higher permeability sandstone surrounding an intact cement core plug, leading to modest alteration of the cement phase at the cement-sandstone interface. On the other hand, in the limestone-cement core, the cement remained largely intact while the limestone reacted to a much larger extent, generating preferential pathways (wormholes) responsible for the permeability increase by a factor of twenty four. Wormhole formation in carbonate rocks and associated permeability increase has been well-recognized in many other studies (Fredd and Fogler, 1998; Golfier *et al.*, 2006; Hinch and Bhatt, 1990; Kalia and Balakotaiah, 2007; Szymczak and Ladd, 2011). In this case, although the reactive limestone prevented cement degradation and CO₂ leakage through wellbore, the opening of the flow path in limestone suggests the potential of CO₂ migration into drinking water aquifers through the development of preferential flow path. In particular, in the region where CO₂ injection leads to high pressure, CO₂ can find its way through initially high permeability zones in carbonate rocks. This is particularly true for highly heterogeneous carbonate host rocks where permeability values can vary by orders of magnitude (Balsamo *et al.*, 2012; Fitz-Diaz *et al.*, 2011; Obrador *et al.*, 2004; Sharma *et al.*, 2013). This suggests that detailed characterization of host rock permeability distribution, especially identification of high

permeability zones in carbonate host rocks, are important in meeting the Class VI rules for carbon injection.

This work suggests that preferential leakage pathways can develop within more permeable, reactive host rocks in acidic environments, which highlights the importance of further studies of host rock-CO₂ interactions. It will have important and interesting implications for the risk assessment of geological carbon sequestration.

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