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Physical and chemical alterations in engineered cementitious composite under geologic CO₂ storage conditions



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ARTICLEINFO ABSTRACT Keywords: Geological carbon sequestration is a promising option to slow global warming but leakage of stored CO₂ through fractured wellbore cement can compromise storage security. Novel cementing materials that can withstand chemical attack, prevent fracturing, and potentially self-heal when damaged will improve long-term storage security of sequestered CO₂. Here, a novel engineered cementitious composite (ECC) was exposed to water in equilibrium with CO₂ at 10 MPa under static batch and flow-through conditions at 50 °C. The extent of alteration after 44 days of reaction under static conditions was determined using optical microscopy and backscatter electron spectroscopy. A single carbonated from was observed in the altered zone in contrast to previous studies on previous studies on previous studies on previous studies on previous studies.

after 44 days of reaction under static conditions was determined using optical microscopy and backscatter electron spectroscopy. A single carbonated front was observed in the altered zone in contrast to previous studies on Portland cement in which multiple zones were identified. The rate of alteration was diffusion-controlled with a 50-year projected depth of alteration of 72 mm. A general increase in microhardness of the altered and unaltered zones suggests that the mechanical integrity of the composite will not be compromised following exposure to CO_2 -rich water. While microcracks developed at the rim of the core after greater durations of exposure, the crack widths were generally less than 60 μ m and prior studies have demonstrated self-healing of ECC microcracks of this size. Permeability decrease was observed in saw-cut samples under flow-through conditions and was attributed to a combination of dissolution-driven fracture closure and calcite precipitation.

1. Introduction

Wellbore cement sheaths have been identified as potential leakage pathways for CO₂ from reservoirs utilized for geologic carbon sequestration (GCS) (Bachu and Celia, 2009), and such leakage risks continue to be a major challenge for the long-term success of GCS as a carbon mitigation strategy. According to the U.S Department of Energy, GCS operations must achieve a storage efficiency of 99% to be an effective technology for mitigating the increase in atmospheric concentration of CO₂ (Chow et al., 2003; Deel, 2007). Portland cement, which is the base material for wellbore cementing, consists of tricalcium silicate (3CaO·SiO₂), dicalcium silicate (2CaO·SiO), tricalcium aluminate (3CaO·Al₂O₃), and calcium alumino ferrite (4CaO·Al₂O₃·Fe₂O₃) (Li et al., 2015; Michaux et al., 1990). While the proportion of the various constituents of Portland cement may vary, fully hydrated cement consists of approximately 70% calcium-silicate hydrates (C - S-H), which is the primary binder in hardened cement, and 20% portlandite (Ca (OH)₂), respectively. Numerous studies have been carried out to understand the interaction of hydrated Portland cement with CO2 under GCS conditions. These studies have found that distinct reaction zones develop along the exterior of reacted cement specimens following prolonged contact with CO2-acidified water at typical reservoir temperature and pressure conditions (Bruckdorfer, 1986; Duguid and Scherer, 2010; Fernández Bertos et al., 2004; Kutchko et al., 2008, 2007; Li et al., 2015). The outer zone in direct contact with CO₂-acidified water is altered extensively and is highly porous, with an abundance of amorphous silica relative to that of the unaltered cement (Kutchko et al., 2009, 2007). Next to this outer degraded zone is a region where calcium carbonate precipitates, resulting in reduced porosity and permeability, and an increase in compressive strength compared to the unaltered cement. The reduction in porosity and permeability due to the precipitation of calcium carbonate inhibits the diffusion of CO₂ further into the cement specimens (Bruckdorfer, 1986; Fernández Bertos et al., 2004; Neves Junior et al., 2013). The third zone is characterized by increased porosity and depletion of calcium (Kutchko et al., 2007). The governing chemical reactions and CO₂ transport limitations in these altered zones are presented in Kutchko et al. (2007) and Li et al. (2015). Such alteration of Portland cement has been found to lead to significant deterioration of the mechanical properties of the material (Kutchko et al., 2007; Li et al., 2015; Mason et al., 2013) including reaction-induced fractures that may serve as leakage pathways for sequestered CO₂.

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Although poor-quality well completion and abandonment techniques in legacy oil and gas wells make prevention of CO_2 leakage along wellbores challenging (Carroll et al., 2016; Watson and Bachu, 2009), ensuring the long-term integrity of injection wells drilled for GCS is also a crucial step toward achieving GCS storage security. Prior wellbore integrity studies have helped to develop predictive tools for assessing long-term wellbore integrity that reduce the uncertainties for leakage risk related to the mechanisms governing the alteration of conventional wellbore cementing materials under GCS conditions (Brunet et al., 2016; Carroll et al., 2016; Huerta et al., 2016; Walsh et al., 2013), but there is still a need for innovative solutions to prevent wellbore CO_2 leakage.

Several studies have reported the incorporation of additives such as fibers, micro ribbons, and elastomers into cement slurry to improve the mechanical properties of wellbore cement and promote self-healing of fractured cement sheaths under various reservoir conditions during fossil fuel and geothermal energy extraction (Carter et al., 1968; Cavanagh et al., 2007; Dean and Torres, 2002; Morris et al., 2003; Reddy et al., 2010; Yao and Hua, 2007). Morris et al. (2003), Dean and Torres (2002), and Carter et al. (1968) reported the use of synthetic fibers to enhance the toughness of hardened cement and prevent brittle failure during downhole perforation. Reddy et al. (2010) developed a self-healing cement adopting low viscosity elastomers that promote self-healing independent of contact with reservoir fluid. Engelke et al. (2017) reported the use of a slurry that incorporates CO₂-swellable particles to promote self-healing in wells exposed to CO2-rich environments, while Barlet-Gouédard et al. (2006) reported the testing of a CO₂ resistant cement for application under GCS conditions. Although several of these cement compositions have been successfully adopted to promote self-healing or improve the tensile properties of the cement in the hardened state, these materials may not exhibit strain hardening under tension that is needed to prevent the formation of brittle fractures during GCS where stresses from temperature swings, cvclic CO₂ injection, and volume expansion from secondary carbonation of the cementitious material are expected to occur downhole. Given that GCS wells need to serve as long-lasting barriers for stored CO₂, novel engineered wellbore cementing materials that can withstand such stresses in the downhole region, self-heal when fractures occur, and weather chemical attack from CO2-acidified solutions without compromising their long-term mechanical integrity need to be developed.

Engineered cementitious composites (ECC) are a novel ultra-ductile fiber-based cementitious material also referred to as bendable concrete (Herbert and Li, 2013; Kawabata et al., 2012; Li, 2009, 2003) with unique tensile properties. Fig.1 shows the tensile stress vs. strain curves and material failure mechanisms for conventional cement and ECC, respectively, under tensile and flexural stress. In contrast to conventional wellbore cements that exhibit brittle failure under tensile and flexural stress (Fig.1a), ECC behaves like a ductile material and has a tensile strain capacity of 2-5%, which is about 200-500 times larger than that of conventional Portland cement and fiber reinforced concrete. Under tensile stress, ECC undergoes a stain hardening stage (Fig.1b) during which several microcracks, with crack width below 60 µm, are formed (Kan et al., 2010; Li, 2009). Such tight crack width has been shown to promote effective self-healing (Herbert and Li, 2013; Kan et al., 2010; Li, 2009). The most studied ECC contains polyvinyl alcohol (PVA) fibers that impart reinforcement to the cementitious material and promote the self-healing of cracks by serving as nucleation sites for healing products such as calcium carbonate (Li and Yang, 2007).

When exposed to CO_2 and water under atmospheric conditions, ECC microcracks undergo autogenous self-healing which is a desirable property in wellbore cement where the integrity of the cement matrix is crucial (Herbert and Li, 2013; Yang et al., 2009a, b). These beneficial properties (strain-hardening, autogenously controlled tight crack width, and self-healing ability) make ECC a prime candidate for consideration as a leak-proof wellbore cementing material. Additionally,

because ECC is a cement based composite, with similar preparation procedures as conventional wellbore cement, it could serve as a substitute cementing material that requires minimal modification to current cementing machinery making it a potentially attractive alternative to operators. It is therefore important to understand the nature of the alterations in ECC following chemical attack under GCS conditions to assess its suitability as a substitute wellbore cementing material over conventional Portland cement.

This study was undertaken to evaluate the alteration of ECC chemical and mechanical properties after contact with CO₂-acidified water under GCS reservoir conditions. A combination of static batch and flowthrough experiments were carried out to investigate the alteration in ECC under diffusive and advective mass transport conditions, respectively. The changes in the microstructure of the composite were characterized to predict long-term integrity of ECC. Although the rheological properties, such as plastic viscosity and yield stress, of the conventional ECC used in this study are not yet optimized for wellbore cementing operations, the objective of this research is to gain an initial understanding of the unique interactions between ECC and CO₂-rich fluids under GCS conditions and to evaluate the impact of such interactions on its microstructural and micromechanical properties.

2. Materials and methods

2.1. ECC raw materials and design considerations

The ECC used in this study is the standard M45 mix with proportions optimized for multiple microcracking during strain hardening up to strain capacity of 5% (Li, 2009), while maintaining a crack width of 60 µm or less. The mix proportions of the materials by weight of the binder are presented in Table 1. The cement used is Type I Portland cement, similar to Class A wellbore cement, intended for cementing from surface to 6000 ft in environments where special properties are not required. Class F fly ash, the most common pozzolanic admixture in oil well cement slurries (Nelson et al., 1990), was added to the mix to enhance its flowability, improve the tensile strain capacity, and reduce the crack width during the strain hardening stage. Fly ash improves the ductility of ECC because of its ability to enhance the interfacial friction bond between the fiber and the matrix through densification of the fiber/matrix interface (Li et al., 2015; Yang et al., 2009a; Yang et al., 2007). In the absence of fly ash, conventional cement with microfiber admixture may not exhibit the desired tight crack width and strain hardening behaviors under tension. The silica sand is finely graded with an average particle size of 110 µm, which is similar to silica sand added to cement slurries designed for downhole environments where low permeability and high compressive strength are required (Le Saoût et al., 2006; Nelson et al., 1990). Although finely graded sand is added to ensure volume stability in the design of standard M45 mix used in this study, the mix composition of ECC can be re-engineered, excluding sand, without compromising its inherent strain hardening capacity. REC15 polyvinyl alcohol (PVA) fibers (Kuraray, Japan) with average diameter of $39\,\mu m$ and length of $12\,mm$ were added to the mix at 2%volume of slurry. The fibers were surface-coated with a proprietary hydrophobic oiling agent (1.2% by weight) to reduce the fiber/matrix interfacial bonding. To improve the workability of the mixture in the fresh state, a polycarboxylate superplasticizer (SP) was added. Further design considerations for standard M45 ECC are presented in Li (2009).

2.2. Sample preparation

The fresh slurry was cast in 2-inch cubic molds, de-molded after 24 h, and cured in plastic bags at 23 ± 3 °C for 28 days. Several 1-inch and 0.5-inch diameter cylindrical cores were subsequently made from the ECC cubes using a water-cooled core drill similar to the approach used in previous wellbore cement studies (Barlet-Gouédard et al., 2009, 2007, 2006; Rimmelé et al., 2008). The cores were then wrapped in



Fig. 1. Tensile stress vs. strain curves for (a) conventional cement and (b) ECC. Inserts in the figure show the failure mechanisms for both conventional cement and ECC under tension and flexural stress, respectively. For conventional cement and ECC, "1" represents the first crack point under the stress strain curves which corresponds to the failure point for conventional cement. "2" is the strain hardening stage during which multiple micro cracks are generated in ECC. Point "3" represents crack localization and "4" is the failure point.

Table 1

Design proportions by weight for standard ECC-M45.

	Cement	Fly ash	Sand	SP	Water	Fiber (vol. %)
Proportion by weight of cement	1	1.2	0.8	0.012	0.56	0.02

paper towels to expel the surficial water prior to the start of the experiment. A 0.5-inch core was sliced into two half-cylinder sections using a precision saw with a diamond blade (Isomet) and the surface of one half-cylinder was roughened using 60-grit sandpaper to serve as a fluid-flow pathway for the flow-through studies.

2.3. Experimental procedure

2.3.1. Static batch study

Six 1-inch ECC cores were oriented lengthwise in a 600-mL stainless steel batch reactor (Parr Instrument) and stacked in a grid as shown in Fig. 2. The cores were separated using thin boat-shaped teflon strips to maximize direct exposure of the samples to the CO₂-saturated water. 490 mL of deionized (DI) water with a resistivity greater than 18.2 MΩcm was added to the reactor at the beginning of the experiment, resulting in a solid to water ratio of approximately 1:6. The solid to water ratio was constrained by the volume of the reactor and the need to ensure that the cores were fully submerged during the experiment. Given the relatively small volume of water, it is likely that the build up of Ca²⁺ in the reactor may have slowed the rate of calcium leaching over time (Matteo et al., 2018; Matteo and Scherer, 2012). A syringe pump (500D, Teledyne Isco) was used to maintain a constant headspace CO_2 pressure (P_{CO2}) of 10 MPa and a temperature of 50 ± 1 °C was maintained via a heating jacket and a temperature regulator (Briskheat). This temperature and pressure condition was chosen in accordance with typical GCS conditions and an approximate storage depth of 1 km (Bachu, 2000; Barlet-Gouédard et al., 2006; McGrail et al., 2006; Schaef and McGrail, 2009). Samples were removed from the batch reactor after 2, 9, 16, 23, 30, and 44 days of exposure to the CO_2 -saturated water. For each sample retrieval, the temperature in the vessel was decreased to 35 °C after which the CO_2 pressure in the headspace was slowly reduced to atmospheric conditions over 90 min, and 82 mL of water was removed from the batch reactor to maintain a constant solid to water ratio in the reactor. Subsequently, the pressure and temperature conditions in the reactor were restored as detailed above. Each retrieved sample was dried in an oven at 50 °C for 24 h followed by a second round of drying during which the temperature



Fig. 2. Experimental setup for the static-batch study. Cores were separated using boat-shaped teflon strips to maximize direct exposure of the samples to the CO_2 -saturated water.



Fig. 3. Experimental setup of the flow-through study. Purple, green, and blue flow lines represent the CO2, acidified water, and confining fluid streams, respectively.

was elevated to 80 °C to expel the water from the cement pores.

Although GCS reservoirs will typically be highly saline, DI water was used in this work to simplify the parameter space for studying fundamental interactions of ECC with CO2 and water under GCS temperature and pressure conditions. This approach, which has also been adopted in previous wellbore integrity studies such as those by Rimmelé et al. (2008) and Huerta et al. (2016), is reasonable as the major impact of salinity on the reaction process is limited to its effect on the extent of CO₂ solubility, the pH of the initial system, and the activity of the aqueous species (Duan and Sun, 2003; Spycher and Pruess, 2005). In a study carried out by Barlet-Gouédard et al. (2009) on Portland cement, the alteration pattern characterized by a series of carbonation and dissolution fronts was similar for the test performed with pure water and that with 4 M NaCl brines. However, the extent of alteration observed in the system with pure water was 10 times greater than in the system with saline water due to faster reaction kinetics at lower pH (Barlet-Gouédard et al., 2009). By carrying out this study using DI water, we have evaluated the composite under the most extreme initial reactive environment at the given experimental pressure and temperature conditions.

2.3.2. Flow-through study

To investigate the alteration of ECC under advective-flow conditions such as may occur due to the generation of cracks during CO₂ injection, a flow-through experiment was conducted using a tri-axial coreflooding cell (Core Laboratories; Fig. 3). DI water was saturated with CO_2 in a 600-mL stainless steel batch reactor at a P_{CO2} of 10 MPa and a temperature of 50 °C. The CO2-acidified solution was then injected through the fractured core at a constant rate of 1 mL/h. Discrete effluent samples aggregated over 2-hour periods were collected at various intervals for 192 h. A backpressure regulator was installed downstream of the core and set at a pressure of approximately 10.4 MPa to prevent degassing of the CO2 during flow. The differential pressure in the system was monitored over the duration of the experiment using pressure transducers installed in the upstream and downstream sections of the reactor flow line. Changes in the pressure gradient were used to infer permeability evolution along the fracture according to the cubic law for flow of an incompressible fluid between two parallel smooth plates (Zimmerman and Bodvarsson, 1996).

2.3.3. Characterization of aqueous chemistry and reaction products

Post-reaction aqueous samples from the batch reactor and effluent samples from the flow-through experiment were obtained and pH was estimated based on charge balance calculations. Cation analysis (Ca, Mg, Fe, Si, Na, K, and Al) was carried out via inductively coupled plasma mass spectrometry (ICPMS; 7900 Agilent Technologies, CA) on samples acidified with HNO₃ to a pH < 2, while anion analysis was done using ion chromatography (Agilent Technologies, CA). CO₂ solubility under each experimental condition was calculated using the thermodynamic model presented by Duan and Sun (2003) and equilibrium constants were adjusted to account for the system temperature (50 °C) and pressure (10 MPa) conditions using SUPCRT92 with the DPRONS92 database (Johnson et al., 1992). The activity coefficients of the aqueous species were estimated using the Davies equation, and the pH of the solution at each sampling point was calculated based on the measured cations and anions concentrations within the constraint of electroneutrality. Secondary mineral phases in the reacted samples were characterized using Raman spectroscopy (Renishaw inVia microscope) with a 532-nm laser, and the mineral species were identified using the RRUFF database (Armbruster and Danisi, 2015; Lafuente et al., 2015).

2.3.4. X-ray computed tomography (XCT)

The extent of mineral precipitation in the pores and along the PVA fibers following CO₂-ECC reactions was determined by comparing preand post-reaction XCT scans (XTH225, Nikon Metrology, Inc.) of the cores from the batch experiment. The scans used a beam energy of 140 KV and current of 115 μ A. 3141 projections were taken at steps of 0.11° with a 4-frame integration per projection. The data was reconstructed using CT Pro (XT5.1.3, NikonMetrology, Inc.), and ImageJ (National Institutes of Health, Bethesda, Maryland) was used for image analysis.

2.3.5. Scanning electron microscopy (SEM) and optical microscopy

150 μ m petrographic thin sections were made from each reacted sample and a scanning electron microscope (JEOL 7800-FLV) equipped with a backscatter electron (BSE) detector was used to obtain grayscale images of the reacted samples. Changes in the grayscale intensities and textures of the different alteration zones in the BSE images were used to infer the extent of alteration of ECC following reaction with CO₂-acidified water. Energy dispersive spectroscopy (EDS) elemental maps were collected to evaluate changes in the elemental composition of the altered ECC material. Optical images of the petrographic thin sections were also obtained using an optical microscope (Scienscope) and a Sobel edge-detection filter (Kanopoulos et al., 1988) was used to determine the penetration depth of the reaction front.

2.3.6. Microhardness

Vickers microhardness (HV) analysis was carried out on the reacted and unreacted ECC samples to infer the change in the mechanical strength of ECC following CO_2 reaction. The samples were dry-polished using a series of finer sandpaper grit sizes, with a final polish using 4000-grit sandpaper. To capture the evolution of microhardness from the altered zone to the unaltered region, the polished sample surfaces were divided into multiple sections from the edge to the center of the core as shown in Fig. 4a. The first two millimeters in the altered zone were divided into four 0.5-mm sections while the last eleven



Fig. 4. (a). Optical image of the thin section of an unreacted sample. Colored boxes represent the pre-defined sections for micro hardness analysis. Sections 1 to 4 are 0.5 mm wide while sections 5, 6, and 7 are 1 mm, 2 mm, and 8 mm wide respectively. (b). Model and mathematical correlation for calculating HV of a carbonated sample. Indent 2 is on a more carbonated region than indent 1. Hence, it has a higher HV.

millimeters were divided into 1-mm, 2-mm, and 8-mm sections, respectively. This was done to obtain higher resolution measurements in the altered region. Seven representative indents were made on the surface of the polished cementitious material in each zone with a Vickers microhardness probe (LECO LM2) using a 500-g load and a dwell time of 15 s (Kutchko et al., 2007; Zhang et al., 2013). Given the heterogeneity of the ECC samples and the presence of the large sand grains in the material, indents were made only on the cementitious material and the areal extents of the indents were converted to HV values using the expression:

$$HV = \frac{1854.4F}{d^2}$$

where d (μ m) represents the average length of the diagonal impressions of the indenter and F (g) is the load applied (Dieter and Bacon, 1986) (Fig. 4b). The average of the seven hardness values was then used to infer the overall hardness in each zone.

3. Results and discussion

3.1. Physical characteristics and extent of alteration

In the static batch study, the pH of the CO₂-saturated water remained acidic (4.5 to 4.8) throughout the course of the experiment (see Supporting Information S1 and Fig. S1 for aqueous chemistry and pH evolution). Following the reaction of the cores with the CO₂-rich water, a distinct orange coloration developed on the exterior of all the samples. This is consistent with prior studies that exposed cement to CO₂acidified fluids (Carey, 2013; Duguid and Scherer, 2010; Kutchko et al., 2008, 2007; Li et al., 2015). Optical images of petrographic thin sections of the cores revealed an increase in the depth of the orange altered zone with the duration of exposure (Fig. 5a). Previous attempts to characterize the chemical composition of this orange-colored alteration zone suggest the presence of non-crystalline Fe(III) hydroxides (Carey, 2013; Li et al., 2015). In this study, EDS maps of the altered zone indicated no variation in the relative abundance of Fe along this zone as a function of distance from the edge of the core. While the exact mineral reaction products within this altered region are not known, similar orange coloration has also been observed in cement following hydrochloric acid attack (Huerta et al., 2009) and can be used to infer the



Fig. 5. (a). Optical images of thin sections of reacted cores showing the progression of the altered front after 2, 9, 16, 23, 40, and 44 days of reaction with CO_2 acidified solution at 50 °C and 10 MPa of CO_2 . The blue coloration of the sample is from blue epoxy with which the samples have been impregnated. **(b)**. Optical images of cross sections of the ECC cores stained with phenolphthalein pH indicator to reveal the extent of carbonation of the cores. The pink region of each core is the unaltered zone, while the colorless region is the carbonated zone.

extent of penetration of acidic fluids following the interaction of ECC with $\rm CO_2$ -acidified solution.

Further analysis was carried out to estimate the depth of CO_2 penetration based on variations in the pH of the carbonated zone while the unaltered zone is identified by the pink coloration that occurs at pH values above 9 (Verbeck, 1958). The depth of alteration for each sample was estimated from the average of 20 measurements from the edge of



Fig. 6. Combined plot of the alteration depth vs. SQRT time using Sobel edge detection, phenolphthalein pH indicator. Equations Ys and Yp describe CO_2 diffusion and depth of alteration in ECC as a function of time using the Sobel edge detection filter and phenolphthalein pH indicator, respectively. Error bars represent the standard deviation of 20 measurements of the altered depth from the rim of the core to the leading edge of the alteration zone. The goodness of the linear fit of the alteration depth vs. square root (SQRT) of time indicates that CO_2 transport in ECC is a diffusion controlled process.

the core to the leading edge of the alteration zone determined via optical image analysis of sample thin sections through application of a Sobel edge detection filter (see Supporting Information Fig. S2) and pH variation using phenolphthalein solution. The rate of alteration was determined using a form of Fick's second law that correlates the depth of alteration under a constant concentration boundary with the square root of time (Kutchko et al., 2009, 2008; Neville, 2011):

$L = \propto t^{0.5}$

where L is the depth of the altered zone in mm, α is the diffusion coefficient in $mm/t^{0.5}$, and t is the duration of exposure in days. The plots of L versus square root of exposure time using both Soble edge detection and pH indicator exhibited linear correlations ($R^2 = 0.98$ and 0.97) with diffusion coefficients of 0.53 and $0.52 \text{ mm/day}^{0.5}$, respectively (Fig. 6). Thus, the rate of alteration of ECC due to penetration of CO2-acidified water is demonstrated to be a diffusion-controlled process, which is consistent with prior GCS wellbore cement integrity studies (Barlet-Gouédard et al., 2006; Kutchko et al., 2009, 2008). Based on these correlations and assuming that the alteration mechanism will progress similarly over periods greater than the duration of the experiment, the depth of alteration of intact ECC after 50 years of reaction with CO_2-acidified water at 50 $^\circ C$ and 10 MPa P_{CO2} is predicted to be approximately 72 mm. In a similar study carried out by Kutchko et al., (2009) on samples with a pozzolan to cement ratio of 35:65, a total altered depth of approximately 224 mm was predicted after 50 years of exposure to CO₂-acidified water under similar temperature and pressure conditions of 50 $^\circ$ C and 15 MPa. Although the higher P_{CO2} used in the Kutchko et al. (2009) study will decrease the system pH below that of the current study, it is unlikely that such enhanced acidity will lead to a threefold increase in the depth of alteration over the same period. Furthermore, since the pozzolanic composition of the material used by Kutchko et al. (2009) is lower than that used in this study (fly ash:cement ratio of 55:45), and since higher proportions of pozzolan have been shown to lead to faster rates of CO₂ penetration in cementitious materials (Kutchko et al., 2009; Lye et al., 2015; Zhang and Li, 2013), it is concluded that the ability of standard M45 ECC to limit the penetration of CO2-acidified water through uncracked cementitious material under a constant P_{CO2} boundary condition is greater than that of a typical 35:65 pozzolan:cement mix used for wellbore cementation.

3.2. Extent of mineral carbonation

BSE images (Fig. 7) of the petrographic thin sections provide further insight into the textural and microstructural changes in the reacted zone of the ECC. The pore spaces and the PVA fibers appear as the



Fig. 7. BSE image of unreacted ECC sample and reacted samples after 2, 9, and 44 days of reaction respectively. The white arrow represents the direction of the altered front from the constant concentration boundary. Pore filling and texture refinement of the parent material were observed at the edge of the core due to carbonation of the composite.

lowest grayscale intensity (black) while the sand grains and C-S-H appear as dark-gray materials distributed within the matrix. The sand grains are identifiable by their distinct grain boundaries, while the unhydrated cement phase appears as the brightest intensity (Stutzman, 2001). BSE images of the unreacted sample reveal an abundance of the unhydrated cement prior to carbonation. Following exposure to the CO₂-rich water, the abundance of the unhydrated phase in the altered zone decreased and the grainy texture in the unreacted material was converted to a smooth, more-homogeneous consistency due to the conversion of the calcium-rich cementitious materials into calcium carbonate (Kutchko et al., 2009, 2007). The presence of calcium carbonate within the pores was confirmed by Raman analysis as the spectra of the precipitates corresponded to the vibrational modes of CO_3^{2-} in calcite (see Supporting Information Fig. S3). In contrast to previous studies on neat Portland cement in which three distinct altered zones have been found following the reaction of cement with CO2acidified water, only one distinct alteration zone was observed in the reacted ECC and is characterized by pores filled with secondary mineral precipitates. The absence of multiple distinct reaction zones has been reported in previous studies on fly ash-amended cement following carbonation under static batch conditions (Zhang et al., 2014) (Kutchko et al., 2009) and in sidewall cores retrieved from a well penetrating a natural CO₂ production reservoir (Crow et al., 2010). This can be attributed to lower portlandite content and pH of the matrix, in comparison to ordinary Portland cement, because of increased pozzolanic reactions in the presence of fly ash (Lye et al., 2015). Such low portlandite content will lead to lower dissolution of the matrix and mobility of OH- and Ca²⁺ species, promoting in place carbonation. In this study, the depth of the pore-filled region increased as the duration of CO₂ reaction increased and was comparable to the depth of the orange zone observed in the optical image.

3.3. The role of PVA fibers for mineral carbonation

BSE images and EDS maps of the area around the fiber of the unreacted sample (Fig. 8a) reveal the presence of Ca, O, C, and Si-rich materials consistent with hydrated cement. Higher magnification of this region identifies a gap between the ECC matrix and the fibers in the unreacted ECC sample (Fig. 8a insert, see Supporting Information Fig. S4). This gap is referred to as the fiber/matrix interfacial transition zone (ITZ) (Sakulich and Li, 2011) and is vital for maintaining the strain hardening property exhibited by ECC under tensile loading (Redon et al., 2001). It is promoted by the oil coating applied on the PVA fibers, which reduces the hydrophilicity of the fibers and consequently the chemical bond between the fibers and the ECC matrix. Thus, instead of rupturing under tensile load, the fibers pull out as the ITZ acts as a slipping plane, promoting ECC ductility and maintenance of tight crack



Fig. 8. (a) BSE and EDS maps of the region around a fiber in an unreacted sample. EDS analysis of the area marked "1" in purple showed that the material is rich in C, Ca, Si, O, which are the primary elemental constituents of hydrated cement. The area marked "2" represents a polyvinyl alcohol (PVA) fiber. Area marked with the red star indicates the fiber/matrix interfacial transition zone (ITZ) prior to carbonation (**b**) BSE and EDS maps of the region around a fiber in a reacted sample. The area marked "3" is rich in Ca, C, and O in comparable proportion to calcite. PVA fiber is marked as "4".

width (Kan et al., 2010; Sahmaran et al., 2007; Tosun-Felekoğlu et al., 2014).

Fig. 8b shows a similar fiber after 4 weeks of contact with CO_2 acidified water where is it clear that a secondary precipitate appears to fill the gap between the fiber and the ECC matrix. EDS mapping of the region shows that the secondary material is calcium-rich, and its EDS point analysis showed a molecular weight percent ratio which is comparable to the composition of calcium carbonate (CaCO₃; Ca:C:O weight percent of 40:12:47).

Fig. 9a presents XCT scans of a section of the core before and after carbonation. In the pre-reaction scan, fibers (solid-gray) can be seen streaking through a vug and are not covered with any material. Following six weeks of reaction, there is clear evidence of mineral precipitates on the PVA fibers shown in the XCT data. This suggests that in addition to improving the mechanical performance of the cementitious material under tensile loading conditions, the fibers incorporated in ECC can serve as nucleation sites for secondary mineral carbonates, thereby promoting secondary carbonation and filling of macropores within the ECC (Fig. 9b). Such filling of ECC porosity will aid in reducing the permeability of the cementitious material to CO₂ and lead to improved wellbore seal integrity. Furthermore, carbonation improves the compressive strength of the cementitious material in the long-term (Bruckdorfer, 1986; Kutchko et al., 2007). In contrast to the section where fibers extend into a vug and serve as nucleation sites for carbonate precipitates, BSE images show that carbonation occurred within the matrix for sections of the fiber embedded in the matrix. Although



Fig. 9. (a) XCT scans showing mineral carbonation in a vug with fibers acting as nucleation sites for secondary mineral precipitation. Microcracks generated in the sample are indicated by the red arrows and were measured to be < $60 \,\mu m$ in width. (b) XCT scans showing the pre and post-reaction (after 6 weeks) condition of the pores. Multiple pores have been filled with secondary calcite precipitates. Ovals surrounding the pre and post reaction sections of the core are color-coded similarly to aid interpretation.

carbonation occurred along the ITZ, the ITZ did not appear to be fully clogged by the new material as some gaps were clearly visible between the precipitates and the fiber, potentially allowing for maintenance of the positive strain hardening property of ECC following carbonation.

3.4. Effect of carbonation on the mechanical strength of ECC

Fig. 10 shows a plot of Vickers's michrohardness values (HV) for unreacted and reacted ECC samples up to 6 weeks of high P_{CO2} exposure, with error bars corresponding to the standard deviation of seven data points. For this discussion, the rim region represents the section of the core with the light orange color, i.e. 0 to 1 mm and 0 to 1.5 mm from the exposed surface for samples reacted for 2 to 16 days and 23 to 44 days, respectively, while the carbonated region represents the section of the core with the brown coloration, i.e. 1 to 2 mm and 1.5 to 3 mm for samples reacted for 2 to 16 days and 23 to 44 days, respectively. For the unreacted ECC samples, the HV was consistent in all regions tested with a mean of 35.7 \pm 2.2 HV/500 g. The mapping of the HV for ECC along the altered front following exposure to CO₂acidified water showed a general increase in HV in comparison to the HV of unaltered ECC, and the HVs within and outside the colored zone for all reacted cores were generally higher than the HV for unreacted ECC. For samples exposed for 2 days to 16 days, the highest HV was recorded between 0.5 to 2 mm from the edge of the core while for the samples reacted for 23 days to 44 days, the highest HVs were measured between 1.5 to 3 mm from the edge.

The region with the highest hardness value corresponds to the zone with the thick brown color and is potentially the most carbonated region. The highest HV was not observed right at the edge of the core due to the higher porosity along the outer edge of the core compared to that of the inner carbonated region. The increase in HV near the rim of the core is supported by observations from post-reaction BSE images which show extensive pore filling in the entire altered zone in comparison to materials in the unaltered zone (Fig. 11). This general increase in hardness suggests that the carbonation of ECC may lead to an increase in its compressive strength (Bruckdorfer, 1986; Kutchko et al., 2007).



Previous studies by Zhang et al. (2013) and Kutchko et al. (2009) on Pozzolan-amended Portland cement have also reported a general increase in HVs following reaction with CO_2 -acidified solutions, with the increase in HV attributed to precipitation of calcite in the pores. However, continuous pore refinement of the ECC matrix due to the pozzolanic activity of the fly ash under high-temperature and pressure conditions may have contributed to the increase in hardness observed in the interior of the core (Kutchko et al., 2007). The fact that some probed regions on the altered core had HVs comparable to the unreacted material can be explained by the heterogeneity of the material, the varying degree of pozzolanic activity, and the presence of isolated regions for which penetration of reactive fluid was hindered (Cao et al., 2015).

To evaluate the accuracy of the 50-year estimate of the extent of alteration derived using the edge detection approach, the limit of the carbonated zone was determined based on the point of transition from elevated hardness to original hardness of the unaltered material. The distance from the edge of the core to this transition point when plotted as a function of the square root of time exhibits a linear trend $(R^2 = 0.94)$ with a diffusion coefficient of $0.48 \text{ mm/day}^{0.5}$ (see Supporting Information Fig. S5). Assuming that the rate of change in the penetration depth of the carbonation front measured by changes in HV is also a diffusion-controlled process, the extent of alteration after 50 years of contact between ECC and CO2-acidified water under GCS conditions is estimated to be 64 mm. This difference in estimation of the long-term CO₂ penetration depth in comparison to that predicted by the Sobel edge detection and phenolphthalein approaches (Section 3.1) may be due to the fact that the HV estimate is based on a single data point while the Sobel edge detection and phenolphthalein estimates are based on the mean of 20 measurements taken from the rim of the core to the alteration front. However, the HV estimate is not significantly different as it falls within the margin of statistical error of the Sobel estimate.

Fig. 10. Vickers microhardness (HV) for reacted and unreacted ECC samples exposed to CO_2 -acidified water for 2, 9, 16, 23, 30, and 44 days. Error bars represent the standard deviation of the HV for seven indents made in each region, as illustrated in the figure insert. The insert on the top right corner highlights the zones defined in Section 3.4.

3.5. Development of microcracks in carbonated ECC

In contrast to previous studies on Portland cement in which fracturing and spalling have been observed following reaction with CO2acidified solutions (Barlet-Gouédard et al., 2006; Brandl et al., 2011; Li et al., 2015), physical examination of the ECC samples following reaction under static batch conditions showed no fracturing. However, optical images of the thin sections of the reacted samples revealed the development of microcracks at the rim of the core after 9 days of reaction (Fig. 5a). The extent and occurrence of these microcracks increased with greater time of exposure to the CO₂-acidified water. While thermal stresses can lead to the generation of cracks in cement, the fact that the cracks did not show up until later times when carbonation of the core was more extensive and were limited to the rim of the core (Fig. 5a) where carbonation occurred, suggests that they were initiated by stresses from secondary mineral carbonation in the pores as the reaction progressed. Precipitation of calcium carbonate leads to the generation of stresses because calcium carbonate has a higher molar volume than the parent hydrated cement phases (Fabbri et al., 2009; Pham and Prince, 2014; Thiery et al., 2005). In this study, the crack apertures observed from BSE and XCT images were generally less than 60 µm after 6 weeks of reaction, which is comparable to the microcrack width observed in ECC undergoing strain hardening (Kan et al., 2010; Li, 2009). The self-controlled microcrack width ensures improved longterm secure storage of CO2 relative to typical wellbore cements that undergo brittle fracturing, as several studies have shown that with tighter cracks the potential for self-healing is enhanced (Carroll et al., 2016; Huerta et al., 2016; Luquot et al., 2013).

3.6. Permeability evolution in flow-through study

Post reaction BSE image and EDS maps of the mid-section of the core showed erosion of the ECC into the matrix adjacent to the fracture (Fig. 11). This is likely due to the low pH conditions of the influent



Fig. 11. BSE image and EDS maps of the altered region in the flow-through experiment. The white arrow indicates the direction of the reaction front perpendicular to the fracture surface.



Fig. 12. Permeability evolution of a saw-cut half-inch ECC core under flowthrough conditions, determined using the cubic law for flow of an incompressible fluid between two parallel smooth plates. Permeability along the fracture pathway decreased from approximately 930 mD to 100 mD after 192 h.

during the flow-through experiment (pH = 3.1; Supporting Information Fig. S6), leading to greater dissolution along the fluid flow path. This contrasts with the observations of minimal ECC dissolution in the batch experiment and shows that CO2-acidified waters may have a negative effect on the integrity of the cementing material if fracture pathways exist within the composite or along cement/casing or cement/caprock interfaces. This observation is consistent with prior work from Luquot et al. (2013) and Deremble et al. (2011) who saw extensive dissolution of the cement matrix adjacent to the fracture during the flow of CO₂rich water. XCT scans revealed that the pores adjacent to the eroded section of the fractured ECC core filled extensively with secondary mineral carbonates. Over the course of 120 h, the permeability of the fracture decreased from approximately 930 mD to 100 mD (Fig. 12). Permeability reductions can result from dissolution-driven processes such as particle mobilization leading to clogging of the fracture aperture (Ellis et al., 2013) and dissolution of critical asperities leading to closure of the fracture (Brunet et al., 2016; Tsang and Witherspoon,

1981), or through precipitation-driven processes whereby secondary minerals clog the fracture pathway (Cao et al., 2015; Luquot et al., 2013). Post reaction SEM analysis of the fracture pathway revealed no evidence of mineral carbonation in the upstream section of the core, but did confirm the presence of rhombohedral calcium carbonate crystals along the downstream section of the core (Fig. 13). Such localized downstream precipitation has been reported in previous studies by Cao et al. (2015) and Huerta et al. (2011), and is attributed to the increase in pH and concentration of calcium ions in the downstream section of the core, conditions which can promote precipitation of secondary carbonate minerals (e.g., CaCO₃). In this study, the pH of the injected fluid development of preferential flow channels along increased from 3.1 (influent) to over 4 (effluent) during the experiment. XCT analysis also showed the development of preferential flow channels along the fracture pathway, which may be due to reaction front instabilities or non-uniform aperture distribution of the initial fracture. An orange coloration similar to that observed in the batch study maps the flow path along the fracture (Fig. 13).

4. Conclusion

Although it is unlikely that diffusion of CO_2 through well-placed cement will lead to CO_2 leakage from reservoirs during GCS operations (Carroll et al., 2016; Crow et al., 2010), spalling and brittle fracturing of wellbore cement following carbonation or cyclic stresses may compromise the long-term safety and security of CO_2 storage (Barlet-Gouédard et al., 2006; Li et al., 2015). In this work, a novel fiber-reinforced cementitious material engineered for superior tensile ductility and intrinsically tight crack width in comparison to conventional Portland cement was tested under typical GCS temperature and pressure conditions to investigate its performance as an effective barrier for CO_2 leakage. Optical microscopy, XCT, and BSE analyses all showed that the depth of carbonation was limited to the rim of the core with a 50-year estimated altered depth of 72 mm. This suggests that diffusion of CO_2 into the ECC matrix is unlikely to lead to CO_2 leakage from the



Fig. 13. Image of half sections of saw-cut 0.5-inch core following the flow-through experiment (left). The orange coloration delineates the region of preferential flow in the second half of the core (left). Precipitate identified to be calcite was found in the downstream section of the core (right). EDS maps show that the precipitate in the downstream section of the core is rich in Ca and C.

reservoir. Microhardness results also showed that carbonation reactions did not diminish the mechanical integrity of ECC. The absence of spalling as well as limited occurrence and width of microcracks, which were generally less than $60 \,\mu$ m, showed that carbonation did not induce extensive damage to the core because of the engineered properties of ECC. This suggests that the use of ECC as a wellbore cementing material may serve to limit crack width, which could help promote self-healing in damaged wellbore cement. ECC was also shown to withstand prolonged contact with aggressive CO₂-acidified fluids while maintaining its mechanical integrity under GCS conditions. However, further studies are needed to understand the more detailed effect of carbonation on the tensile strength and crack healing potential in ECC used for GCS wellbore sealing applications.

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Appendix A. Supplementary data

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References

- Armbruster, T., Danisi, R.M., 2015. Highlights in Mineralogical Crystallography. De Gruyter, Berlin, Boston. https://doi.org/10.1515/9783110417104.
- Bachu, S., 2000. Sequestration of CO2 in geological media: criteria and approach for site selection in response to climate change. Energy Convers. Manage. 41, 953–970. https://doi.org/10.1016/S0196-8904(99)00149-1.
- Bachu, S., Celia, M.A., 2009. Assessing the potential for CO2 leakage, particularly through wells, from geological storage sites. Geophysical Monograph Series. American Geophysical Union, Washington, D. C, pp. 203–216.
- Barlet-Gouédard, V., Rimmelé, G., Goffe, B., Porcherie, O., 2006. Mitigation strategies for the risk of CO2 migration through wellbores. Presented at the Presented at the IADC/ SPE Drilling Conference 17. https://doi.org/10.2118/98924-MS.
- Barlet-Gouédard, V., Rimmelé, G., Goffé, B., Porcherie, O., 2007. Well technologies for CO2 geological storage: CO2-Resistant cement. Oil Gas Sci. Technol. - Rev. IFP 62, 325–334. https://doi.org/10.2516/ogst:2007027.
- Barlet-Gouédard, V., Rimmelé, G., Porcherie, O., Quisel, N., Desroches, J., 2009. A solution against well cement degradation under CO2 geological storage environment. Int. J. Greenh. Gas Control 3, 206–216. https://doi.org/10.1016/j.ijggc.2008.07.005.
 Brandl, A., Cutler, J., Seholm, A., Sansil, M., Braun, G., Incorporated, B.H., 2011.

Cementing Solutions for Corrosive Well Environments. pp. 12.

- Bruckdorfer, R.A., 1986. Carbon Dioxide Corrosion in Oilwell Cements. Presented at the SPE Rocky Mountain Regional Meeting. Society of Petroleum Engineershttps://doi. org/10.2118/15176-MS.
- Brunet, J.-p.L., Li, L., Karpyn, Z.T., Huerta, N.J., 2016. Fracture opening or self-sealing: critical residence time as a unifying parameter for cement–CO2–brine interactions. Int J Greenh Gas Control 47, 25–37. https://doi.org/10.1016/j.ijggc.2016.01.024.
- Cao, P., Karpyn, Z.T., Li, L., 2015. Self-healing of cement fractures under dynamic flow of CO2-rich brine. Water Resour. Res. 51, 4684–4701. https://doi.org/10.1002/ 2014WR016162.
- Carey, J.W., 2013. Geochemistry of wellbore integrity in CO2 sequestration: portland Cement-Steel-Brine-CO2 interactions. Rev Miner. 77, 505–539. https://doi.org/10. 2138/rmg.2013.77.15.
- Carroll, S., Carey, J.W., Dzombak, D., Huerta, N.J., Li, L., Richard, T., Um, W., Walsh, S.D.C., Zhang, L., 2016. Review: role of chemistry, mechanics, and transport on well integrity in CO2 storage environments. Int J Greenh Gas Control 49, 149–160. https://doi.org/10.1016/j.ijggc.2016.01.010.

Carter, L.G., Slagle, K.A., Smith, D.K., 1968. Stress capabilities improved by resilient cement. Presented at the Drilling and Production Practice.

Cavanagh, P.H., Johnson, C.R., Le Roy-Delage, S., DeBruijn, G.G., Cooper, I., Guillot, D.J., Bulte, H., Dargaud, B., 2007. Self-healing cement - novel technology to achieve leak-Free Wells. Presented at the SPE/IADC Drilling Conference. https://doi.org/10.2118/ 105781-MS.

- Chow, J.C., Watson, J.G., Herzog, A., Benson, S.M., Hidy, G.M., Gunter, W.D., Penkala, S.J., White, C.M., 2003. Separation and capture of CO 2 from large stationary sources and sequestration in geological formations. J. Air Waste Manag. Assoc. 53, 1172–1182. https://doi.org/10.1080/10473289.2003.10466274.
- 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, The Ninth International Conference on Greenhouse Gas Control Technologies 4, 186–197. https://doi.org/10.1016/j.ijggc.2009.10.010.
- Dean, G.D., Torres, R.S., 2002. Novel cement system for improved zonal isolation in steam injection Wells. Presented at the SPE International Thermal Operations and Heavy Oil Symposium and International Horizontal Well Technology Conference. https://doi. org/10.2118/78995-MS.
- Deel, D., 2007. Carbon Sequestration Technology Roadmap and Program Plan 2007. pp. 48.
- Deremble, L., Loizzo, M., Huet, B., Lecampion, B., Quesada, D., 2011. Stability of a leakage pathway in a cemented annulus. Energy Procedia, 10th International Conference on Greenhouse Gas Control Technologies 4, 5283–5290. https://doi.org/ 10.1016/j.egypro.2011.02.508.

Dieter, G.E., Bacon, D.J., 1986. Mechanical Metallurgy. McGraw-hill, New York.

- 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. https://doi.org/10.1016/S0009-2541(02)00263-2.
- Duguid, A., Scherer, G.W., 2010. Degradation of oilwell cement due to exposure to carbonated brine. Int. J. Greenh. Gas Control 4, 546–560. https://doi.org/10.1016/j. ijggc.2009.11.001.
- Ellis, B.R., Fitts, J.P., Bromhal, G.S., McIntyre, D.L., Tappero, R., Peters, C.A., 2013. Dissolution-Driven Permeability Reduction of a Fractured Carbonate Caprock. Environ. Eng. Sci. 30, 187–193. https://doi.org/10.1089/ees.2012.0337.
- Engelke, B., Miranda, D.R.C., Daou, F., Petersen, D., Aponte, S.A., Oliveira, F., Ocando, L.M.S., Conceição, A.C.F., Guillot, D., 2017. CO₂ self-healing and resistant cement technology from laboratory to the Field. Presented at the SPE/IADC Drilling Conference and Exhibition. https://doi.org/10.2118/184641-MS.
- Fabbri, A., Corvisier, J., Schubnel, A., Brunet, F., Goffé, B., Rimmele, G., Barlet-Gouédard, V., 2009. Effect of carbonation on the hydro-mechanical properties of Portland cements. Cem 39, 1156–1163. https://doi.org/10.1016/j.cemconres.2009.07.028.
- Fernández Bertos, M., Simons, S.J.R., Hills, C.D., Carey, P.J., 2004. A review of accelerated carbonation technology in the treatment of cement-based materials and sequestration of CO2. J. Hazard. Mater. 112, 193–205. https://doi.org/10.1016/j. jhazmat.2004.04.019.
- Herbert, E.N., Li, V.C., 2013. Self-Healing of Microcracks in Engineered Cementitious Composites (ECC) Under a. Nat. Environ. Mater. 6, 2831–2845. https://doi.org/10. 3390/ma6072831.
- Huerta, N.J., Bryant, S.L., Strazisar, B.R., Kutchko, B.G., Conrad, L.C., 2009. The influence of confining stress and chemical alteration on conductive pathways within wellbore cement. Energy Procedia 1, 3571–3578.
- Huerta, N.J., Bryant, S.L., Strazisar, B.R., Hesse, M., 2011. Dynamic alteration along a fractured cement/cement interface: implications for long term leakage risk along a well with an annulus defect. Energy Procedia 4, 5398–5405. https://doi.org/10. 1016/j.egypro.2011.02.524.
- Huerta, N.J., Hesse, M.A., Bryant, S.L., Strazisar, B.R., Lopano, C., 2016. Reactive transport of CO2-saturated water in a cement fracture: application to wellbore leakage during geologic CO2 storage. Int. J. Greenh. Gas Control 44, 276–289. https://doi.org/10.1016/j.ijggc.2015.02.006.
- Johnson, J.W., Oelkers, E.H., Helgeson, H.C., 1992. SUPCRT92: A software package for calculating the standard molal thermodynamic properties of minerals, gases, aqueous species, and reactions from 1 to 5000 bar and 0 to 1000 C. Comput. Geosci. 18, 899–947.
- Kan, Shi, H.-s., Sakulich, A.R., Li, V.C., 2010. Self-healing characterization of engineered cementitious composite materials. ACI Mater. 107, 617–624.
- Kanopoulos, N., Vasanthavada, N., Baker, R.L., 1988. Design of an image edge detection filter using the Sobel operator. IEEE J. SolidState Circuits 23, 358–367. https://doi. org/10.1109/4.996.
- Kawabata, Y., Kato, E., Iwanami, M., 2012. Enhanced Long-term Resistance of Concrete With Marine Sessile Organisms to Chloride Ion Penetration [WWW Document]. URL.
- 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. https://doi.org/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 42, 6237–6242. https://doi.org/10.1021/es800049r.
- Kutchko, B.G., Strazisar, B.R., Huerta, N., Lowry, G.V., Dzombak, D.A., Thaulow, N., 2009. CO2 reaction with hydrated class H well cement under geologic sequestration conditions: Effects of flyash admixtures. Environ. Sci. 43, 3947–3952. https://doi. org/10.1021/es803007e.
- Lafuente, B., Downs, R.T., Yang, H., Stone, N., 2015. 1. the power of databases: the RRUFF project. Highlights in Mineralogical Crystallography. De Gruyter, Berlin, Boston. https://doi.org/10.1515/9783110417104-003.
- Le Saoût, G., Lécolier, E., Rivereau, A., Zanni, H., 2006. Chemical structure of cement aged at normal and elevated temperatures and pressures, Part II: Low permeability class G oilwell cement. Cem. Concr. Res. 36, 428–433. https://doi.org/10.1016/j. cemconres.2005.11.005.
- Li, V.C., 2003. On engineered cementitious composites (ECC). J. Adv. 1, 215-230.
- Li, V.C., 2009. Engineered cementitious composites (ECC) material, structural and durability performance. Concrete Construction Engineering Handbook. CRC Press, Boca Raton.

- Li, V.C., Yang, E.-H., 2007. Self healing in concrete materials. Self Healing Materials, Springer Series in Materials Science. Springer, Dordrecht, pp. 161–193. https://doi. org/10.1007/978-1-4020-6250-6_8.
- Li, Q., Lim, Y.M., Flores, K.M., Kranjc, K., Jun, Y.-S., 2015. Chemical reactions of Portland cement with aqueous CO2 and their impacts on cement's mechanical properties under geologic CO2 sequestration conditions. Environ. Sci. Technol. 49, 6335–6343. https://doi.org/10.1021/es5063488.
- 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. https://doi.org/10.1016/j.ijggc.2013.04.002.
- Lye, C.-Q., Dhir, R.K., Ghataora, G.S., 2015. Carbonation resistance of fly ash concrete. Mag. Concr. Res. 67, 1150–1178. https://doi.org/10.1680/macr.15.00204.
- Mason, H.E., Frane, D., Walsh, Stuart D.C., Dai, Zurong, Charnvanichborikarn, Supakit, Carroll, Susan A., 2013. Chemical and Mechanical Properties of Wellbore Cement Altered by CO2-Rich Brine Using a Multianalytical Approach 2013. pp. 1745–1752. https://doi.org/10.1021/es3039906.
- Matteo, E.N., Scherer, G.W., 2012. Experimental study of the diffusion-controlled acid degradation of Class H Portland cement. Int. J. Greenh. Gas Control 7, 181–191. https://doi.org/10.1016/j.ijggc.2011.07.012.
- Matteo, E.N., Huet, B., Jové-Colón, C.F., Scherer, G.W., 2018. Experimental and modeling study of calcium carbonate precipitation and its effects on the degradation of oil well cement during carbonated brine exposure. Cem. Concr. Res. 113, 1–12. https://doi. org/10.1016/j.cemconres.2018.03.016.
- McGrail, B.P., Schaef, H.T., Ho, A.M., Chien, Y.-j., Dooley, J.J., Davidson, C.L., 2006. Potential for carbon dioxide sequestration in flood basalts. J. Geophys. Res. 111. https://doi.org/10.1029/2005JB004169.
- Michaux, M., Nelson, E.B., Vidick, B., 1990. 2 chemistry and characterization of Portland cement. In: Nelson, E.B. (Ed.), Developments in Petroleum Science, Well Cementing. Elsevier, pp. 2–21. https://doi.org/10.1016/S0376-7361(09)70300-0.
- Morris, W., Criado, M.A., Robles, J., Bianchi, G., 2003. Design of high toughness cement for effective long lasting well isolations. Presented at the SPE Latin American and Caribbean Petroleum Engineering Conference. https://doi.org/10.2118/81001-MS.
- Nelson, E.B., Baret, J.-F., Michaux, M., 1990. 3 cement additives and mechanisms of action. In: Nelson, E.B. (Ed.), Developments in PeTroleum Science, Well Cementing. Elsevier, pp. 3–31. https://doi.org/10.1016/S0376-7361(09)70301-2.
- Neves Junior, A., Toledo Filho, R.D., Fairbairn, E. de, M.R., Dweck, J., 2013. CO2 sequestration by high initial strength Portland cement pastes. J. Therm. Anal. Calorim. 113, 1577–1584. https://doi.org/10.1007/s10973-013-3117-0.

Neville, A.M., 2011. Properties of Concrete, 5th ed. Pearson, Harlow, England ; New York.

- Pham, S.T., Prince, W., 2014. The carbonation of calcium-silicate-hydrate C-S-H in cement mortar studied using thermal analysis and gas pycnometer: determination of the quantity of calcium carbonate produced and the increase in molar volume. Adv. Mater. 931, 411–415. https://doi.org/10.4028/www.scientific.net/AMR.931-932. 411.
- Reddy, B.R., Liang, F., Fitzgerald, R., 2010. Self-healing cements that heal without dependence on fluid contact: a laboratory study. SPE Drill. Complet. 25, 309–313. https://doi.org/10.2118/121555-PA.
- Redon, C., Li, V.C., Wu, C., Hoshiro, H., Saito, T., Ogawa, A., 2001. Measuring and modifying interface properties of PVA fibers in ECC matrix. J. Mater. Civ. Eng. 13, 399–406.
- Rimmelé, G., Barlet-Gouédard, V., Porcherie, O., Goffé, B., Brunet, F., 2008. Heterogeneous porosity distribution in Portland cement exposed to CO2-rich fluids. Cem. Concr. Res. 38, 1038–1048. https://doi.org/10.1016/j.cemconres.2008.03.022. Sahmaran, M., Li, M., Li, V.C., 2007. Transport properties of engineered cementitious composites under chloride exposure. ACI Mater. 104, 604–611.
- Sakulich, A.R., Li, V.C., 2011. Nanoscale characterization of engineered cementitious

Schaef, H.T., McGrail, B.P., 2009. Dissolution of Columbia river Basalt under mildly acidic conditions as a function of temperature: experimental results relevant to the geological sequestration of carbon dioxide. Appl. Geochem. 24, 980–987. https://doi org/10.1016/j.apgeochem.2009.02.025.

composites (ECC). Cem 41, 169-175. https://doi.org/10.1016/j.cemconres.2010.11.

Spycher, N., Pruess, K., 2005. CO2-H2O mixtures in the geological sequestration of CO2. II. Partitioning in chloride brines at 12–100°C and up to 600 bar. Geochim. Cosmochim. Acta 69, 3309–3320. https://doi.org/10.1016/j.gca.2005.01.015.

Stutzman, P.E., 2001. Scanning electron microscopy in concrete petrography. Natl. Inst. 2.

- Thiery, M., Dangla, P., Villain, G., Platret, G., 2005. A prediction model for concrete carbonation based on coupled CO2-H2O-ions transfers and chemical reactions. Proc. of 10 Th DBMC. Conference on Durability of Building Materials and Components. pp. 1–8.
- Tosun-Felekoğlu, K., Felekoğlu, B., Ranade, R., Lee, B.Y., Li, V.C., 2014. The role of flaw size and fiber distribution on tensile ductility of PVA-ECC. Compos. Part B Eng. 56, 536–545. https://doi.org/10.1016/j.compositesb.2013.08.089.
- Tsang, Y.W., Witherspoon, P.A., 1981. Hydromechanical behavior of a deformable rock fracture subject to normal stress. J. Geophys. Res. Solid Earth 86, 9287–9298. https://doi.org/10.1029/JB086iB10p09287.
- Verbeck, G., 1958. Carbonation of hydrated Portland cement. In: Committee C-1, Committee C-9 (Eds.), Cement and Concrete. ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA 19428-2959. https://doi.org/10.1520/ STP39460S. pp. 17-17–20.
- Walsh, S.D.C., Frane, W.L.D., Mason, H.E., Carroll, S.A., 2013. Permeability of wellborecement fractures following degradation by carbonated brine. Rock Mech. Rock Eng. 46, 455–464. https://doi.org/10.1007/s00603-012-0336-9.
- Watson, T.L., Bachu, S., 2009. Evaluation of the potential for gas and CO2 leakage along wellbores. SPE Drill 24, 115–126. https://doi.org/10.2118/106817-PA.
- Yang, E.-H., Yang, Y., Li, V.C., 2007. Use of high volumes of fly ash to improve ECC mechanical properties and material greenness. ACI Mater. J. Farmington Hills 104, 620–628.
- Yang, Sahmaran, M., Yang, Y., Li, V.C., 2009a. Rheological control in production of engineered cementitious composites. ACI Mater. J. Farmington Hills 106, 357–366.
- Yang, Y., Lepech, M.D., Yang, E.-h., Li, V.C., 2009b. Autogenous healing of engineered cementitious composites under wet–dry cycles. Cem 39, 382–390. https://doi.org/ 10.1016/j.cemconres.2009.01.013.
- Yao, X., Hua, S., 2007. Design of novel composite agent for improving the toughness of oil-Well cement sheath. Presented at the International Symposium on Oilfield Chemistry. https://doi.org/10.2118/106010-MS.
- Zhang, P., Li, Q.-F., 2013. Combined effect of polypropylene fiber and silica fume on workability and carbonation resistance of concrete composite containing fly ash. Proc. Inst. Mech. Eng. Part J. Mater. Des. Appl. 227, 250–258. https://doi.org/10. 1177/1464420712458198.
- Zhang, L., Dzombak, D.A., Nakles, D.V., Hawthorne, S.B., Miller, D.J., Kutchko, B.G., Lopano, C.L., Strazisar, B.R., 2013. Characterization of pozzolan-amended wellbore cement exposed to CO2 and H2S gas mixtures under geologic carbon storage conditions. Int. J. Greenh. Gas Control 19, 358–368. https://doi.org/10.1016/j.ijggc. 2013.09.004.
- Zhang, L., Dzombak, D.A., Nakles, D.V., Hawthorne, S.B., Miller, D.J., Kutchko, B.G., Lopano, C.L., Strazisar, B.R., 2014. Rate of H2S and CO2 attack on pozzolan-amended Class H well cement under geologic sequestration conditions. Int. J. Greenh. Gas Control 27, 299–308. https://doi.org/10.1016/j.ijggc.2014.02.013.
- Zimmerman, R.W., Bodvarsson, G.S., 1996. Hydraulic conductivity of rock fractures. Transp. Porous Media 23, 1–30. https://doi.org/10.1007/BF00145263.