

CO₂ Reaction with Hydrated Class H Well Cement under Geologic Sequestration Conditions: Effects of Flyash Admixtures

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The rate and mechanism of reaction of pozzolan-amended Class H cement exposed to both supercritical CO₂ and CO₂-saturated brine were determined under geologic sequestration conditions to assess the potential impact of cement degradation in existing wells on CO₂ storage integrity. The pozzolan additive chosen, Type F flyash, is the most common additive used in cements for well sealing in oil-gas field operations. The 35:65 and 65:35 (v/v) pozzolan–cement blends were exposed to supercritical CO₂ and CO₂-saturated brine and underwent cement carbonation. Extrapolation of the carbonation rate for the 35:65 case suggests a penetration depth of 170–180 mm for both the CO₂-saturated brine and supercritical CO₂ after 30 years. Despite alteration in both pozzolan systems, the reacted cement remained relatively impermeable to fluid flow after exposure to brine solution saturated with CO₂, with values well below the American Petroleum Institute recommended maximum well cement permeability of 200 μD. Analyses of 50:50 pozzolan–cement cores from a production well in a sandstone reservoir exhibited carbonation and low permeability to brine solution saturated with CO₂, which are consistent with our laboratory findings.

Introduction

Geologic sequestration of CO₂ requires long-term storage and low leakage rates to be effective (1). Active and abandoned wells in storage formations are possible leakage points, so data are needed on the durability of cements in wells penetrating candidate formations for geologic sequestration of CO₂ to determine risks they pose to long-term CO₂ storage integrity. Wells are typically constructed with steel casing

lined externally (annulus between pipe and rock) with cement to prevent vertical fluid migration and to provide mechanical support. Also, abandoned wells are sealed with cement. Previous work focused on understanding the alteration of Class H neat cement upon exposure to CO₂-saturated brine (2) and on determining the rate of reactive penetration in cement exposed to supercritical CO₂ and to CO₂-saturated brine (3). Due to the common use of additives in cement (typically to control the fluid properties, the cure rate, or the cost), it is also important to evaluate the reaction of cement–additive blends upon exposure to CO₂ under typical conditions of a deep saline aquifer (15 MPa, 50 °C).

Pozzolans are one of the most common types of cement extenders used in cement mixes for well sealing in oil-gas fields (4). Pozzolan is added to reduce the density of the slurry (5) and reduce the amount of cement needed, thereby reducing the cost. Type F flyash, the most common pozzolan used in well cement, consists mainly of siliceous spherical particles and is a byproduct of coal combustion (5).

Pozzolan additives such as flyash combine with Ca(OH)_{2(s)} to form secondary calcium silicate hydrate (C–S–H), thereby slowly increasing the density of C–S–H in the paste. Cements containing flyash ultimately show improved durability to acid attack if allowed to cure long enough (6–9). Carbonation of cement blends is reported to improve structural performance in that it reduces porosity and permeability and increases the strength of the cement (6). The pozzolanic reactions also decrease the amount of Ca(OH)_{2(s)} in the hardened cement, a material that generally maintains the pH of the cement porewater between 12 and 13 (6). The reactivity of Type F flyash during cement hydration is slow, and extended curing is needed to achieve the same hydration state of hydrated neat cement (7).

The objective of the study was to evaluate cement–pozzolan blend integrity upon exposure to supercritical CO₂ and to CO₂–brine under sequestration conditions. Specifically, we determined how the extent of cement alteration and penetration rate are affected by pozzolan additives commonly used in cement preparation compared to those of neat cement by measuring pozzolan–cement permeability before and after exposure to CO₂-saturated brine solution for two systems with pozzolan to cement volume ratios of 65:35 and 35:65. These represent the maximum and minimum ratios that are typically used, respectively. The implications of cement–additive blend alteration reactions for geologic sequestration of CO₂ are discussed.

Experimental Procedures

Cement Curing and Exposure to CO₂. Two pozzolan (flyash) systems were studied: 35:65 and 65:35 (by volume) pozzolan–cement blend Class H cement. The pozzolan used in this study, Pozmix A (Halliburton, TX), is commonly used in oil field applications (see Supporting Information Figure S1). The pozzolan–cement systems were mixed according to American Petroleum Institute (API) Recommended Practice (RP) 10B (section 17.4) (10). The slurry densities for the pozzolan–cement systems were chosen to represent an average slurry density used for the mixes in the field. A slurry density of 14.5 lbm/gal (1.74 g/cm³) was used for the 35:65 pozzolan–cement mix (water/solids ratio of 0.51) and 13.7 lbm/gal (1.64 g/cm³) for the 65:35 pozzolan–cement mix (water/solids ratio of 0.56). The slurry density of Class H neat cement with a standard water content of 0.38 is 16.45 lbm/gal (1.97 g/cm³) (5). All cement–pozzolan blends also included 2% by volume bentonite, which is commonly added

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to improve slurry properties and to prevent formation of free water (5).

The amended cement samples were cast in the form of cylinders (12 mm diameter \times 130 mm). The casts were submerged in a 1 wt % NaCl brine solution and allowed to cure at 50 °C and 15 MPa in the absence of CO₂ to simulate well cement in contact with a deep saline aquifer at a depth of approximately 1300 m on the basis of a typical hydrostatic and thermal gradient (2). After a 28 day curing period, the hardened cement samples were partially submerged in a 1% NaCl solution (without drying) and the vessel was pressurized with CO₂. The temperature and pressure were kept constant at 50 °C and 15 MPa. In the high-pressure vessels, the headspace mimics cement exposure to humidified supercritical CO₂ whereas the submerged (aqueous) phase simulates exposure to the CO₂ dissolved in brine (2, 3). The volume ratio of brine to sample was approximately 7:1, which was assumed to be large enough to prevent saturation of the solution with respect to the cement. The CO₂ exposure experiments were carried out under static conditions as this best simulates downhole conditions at a well some distance from the injector, where flow velocity is minimal (11). Note that these experiments were designed to address existing wells in a formation, rather than the injection well itself. Following the CO₂ exposure tests, the cement samples were removed from the vessels, cut into \sim 1 cm slices, and polished for electron and optical microscopy analysis and microhardness testing as described in Kutchko et al. (2).

Chemical and Structural Analysis. A scanning electron microscope equipped with a backscattered electron (BSE) image detector and energy-dispersive spectrometer was used to determine the chemical and textural changes in the hardened cement blends due to continuous exposure to CO₂ under sequestration conditions. Analysis included measuring the depth of alteration as well as evaluating the changes in structure and elemental composition. The depth of the altered zones within each cement sample was measured using a Keyence VHX-600 digital optical microscope. Powder X-ray diffraction (XRD) was used to identify crystallized phases.

Mechanical Strength. Vickers microhardness testing was used to assess the mechanical strength of the hardened pozzolan–cement samples. A minimum of six representative measurements in each altered zone were reported as averages in Vickers hardness values (HV) for a 100 g load. The hardness values of the altered portions of the cement were compared to that of unexposed cement samples. Hardness measurements were performed to examine the loss (or gain) of mechanical strength and structural integrity in the altered cement.

Permeability. Measurements of permeability were conducted on the pozzolan–cement samples before and after exposure to sequestration conditions. To allow permeability measurements, larger diameter cement cylinders (50.8 mm diameter by 40 mm) were formed with the 35:65 and 65:35 pozzolan–cement systems and cured in the same manner described above. After the curing period, the hardened pozzolan–cement samples were completely submerged in a 1% NaCl solution and the vessel was pressurized to 15 MPa with CO₂. Thus, only the CO₂-saturated brine condition was tested. Permeability tests were conducted by Geotechnics (Pittsburgh, PA) using ASTM standard test method D 5084-03 (12). Acceptance criteria specified for the ASTM test are that the ratio of outflow to inflow water volume is between 0.75 and 1.25 and four or more consecutive hydraulic conductivity readings fall within \pm 50% of the mean value for those readings. If the measurements met the ASTM criteria, then the average of the last four measurement values was used.

Computer Tomography Imaging. X-ray computer tomography (X-CT) imaging was used to examine density changes in the reacted 50.8 mm diameter cement cores for

the CO₂-saturated brine case. The reacted cement cores were scanned as a sequence of thin (2 mm) 2-D slices collected along the axial direction of the cylindrical cement cores. This nondestructive method allows for a compilation of high-resolution 2-D images into a 3-D spatial scan of the entire cement core. High-resolution images and CT numbers are generated for each scan. Each pixel generated from the cement matrix represents a specific CT number derived from the X-ray attenuation coefficient. Higher CT numbers indicate denser material (13). The CT numbers were converted to relative density magnitudes and displayed using graphic software.

Results

Pozzolan–Cement Blend of 35:65 Ratio. Assessment of the effects of exposure to the pozzolan–cement blends were determined on the basis of the results of 5, 7, 9, 14, and 31 day exposure to dissolved CO₂-saturated brine and supercritical CO₂.

A very thin (<100 μ m) dense ring of calcium carbonate was observed in the interior of the cement samples exposed for 5, 7, and 9 days to CO₂-saturated brine and supercritical CO₂ (Figure 1). The depth of penetration of this ring increased with exposure time. The cement paste outside that ring was carbonated, as evident by the appearance of CaCO_{3(s)} within the pore structure of the cement paste. X-ray diffraction indicated that calcite was the dominant crystalline phase in the cement paste with minor amounts of vaterite and aragonite (see Supporting Information Figures S2 and S3). The formation of CaCO_{3(s)} in the cement matrix is known to decrease cement permeability to water and to increase its compressive strength (11). The carbonated region compared to unexposed cement appeared less porous when using backscattered electron analysis. The carbonated cement paste shows a more uniform microstructure containing primarily CaCO_{3(s)} and decalcified cement grains (Figure 2).

The cement inside the carbonated ring structure contained chloride as observed by SEM–energy-dispersive spectroscopy (EDS). Minor amounts of chloride-bearing cement phases such as chlorocalcium sulfoaluminate, ettringite, Friedels salt, and Cl-rich unhydrated cement grains were observed. All chloride and chloride-bearing cement phases were absent from the carbonated region of the cement. Evidence of cement phases was provided by SEM–EDS and XRD (see Figures S2 and S3 in the Supporting Information for X-ray diffraction patterns). The absence of chloride and calcium sulfoaluminates is not surprising as neither are typically present in carbonated cement. Chloride is liberated by the carbonation process, while sulfates such as ettringite are not stable at the lower pH (7) (see the X-ray maps in Supporting Information Figure S4 showing a decrease in chloride and sulfur in the carbonated region). Within 14 days of exposure, the hardened cement paste was completely carbonated throughout (no ring observed) (Supporting Information Figure S6).

Vickers microhardness testing showed a significant increase in hardness of the thin calcium carbonate ring (81 HV/100 g) as compared with the unexposed cement (33 HV/100 g). In the region inside the thin ring, the cement was softer (26 HV/100 g), whereas, outside the ring in the fully carbonated region, the cement was slightly harder (39 HV/100 g) than the unexposed cement (see Supporting Information Figure S7). The increased hardness is due to the precipitation of calcium carbonate in the pores of the cement paste (Figure 1).

The permeabilities of unexposed and exposed 50.8 mm diameter cylindrical pozzolan–cement samples were measured. The permeability of an unexposed 35:65 pozzolan–cement sample was $1.1 \pm 0.5 \mu$ D. The average permeability results of two replicate 35:65 cement–pozzolan samples

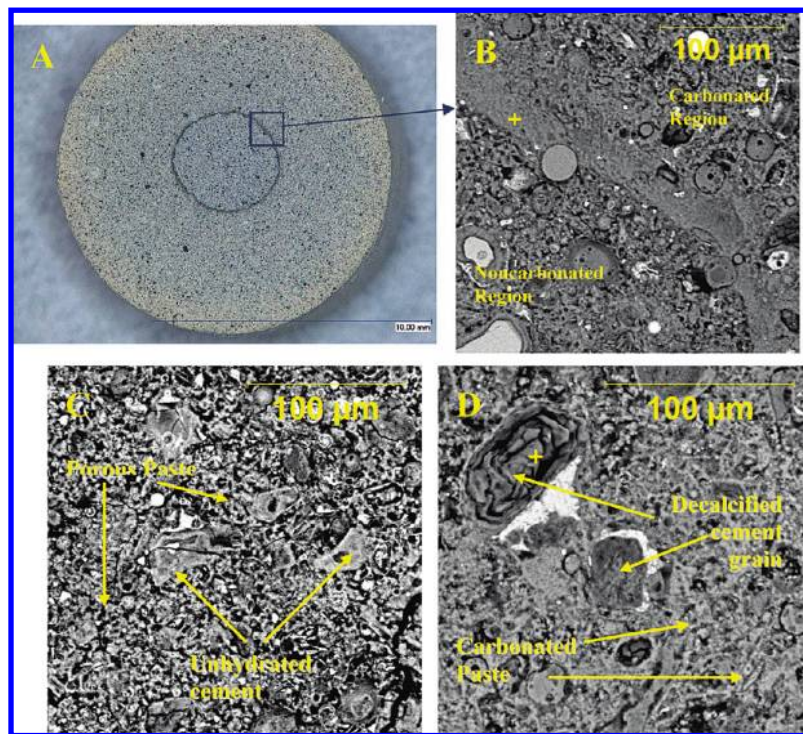


FIGURE 1. (A) Optical and (B) scanning electron microscopy (SEM) images of a Class H 35:65 pozzolan–cement sample (12 mm diameter) exposed to CO₂-saturated brine at 50 °C and 15 MPa for 9 days showing the ring structure. SEM images of (C) unexposed 35:65 cement and (D) 35:65 cement exposed to CO₂-saturated brine at 50 °C and 15 MPa for 9 days showing CaCO_{3(s)} precipitated in the pores of the cement matrix. This is observed as a more uniform microstructure (containing primarily CaCO_{3(s)} and decalcified cement grains).

exposed for 31 days to CO₂-saturated brine were 13.5 ± 1.9 and $26.3 \pm 4.2 \mu\text{D}$ (Supporting Information Table S2).

CT imaging of the exposed 50.8 mm cement core showed a well-defined alteration zone on the outer rim of the sample. The CT density data indicated that the altered zone is denser than the unreacted region of the cement core (see Figure 3). This is consistent with the SEM–EDS observations showing CaCO_{3(s)} precipitation and a lower porosity in the carbonated/ altered region (see Figure 2). CT imaging also revealed microcracks in the 50.8 mm reacted cement cores (Figure 2). Microcracks were only observed in the 35:65 pozzolan–cement samples, not in the 65:35 pozzolan–cement samples discussed below.

The density increased and the porosity decreased in the altered region, but the average permeability increased. This is inconsistent with expectations because increased porosity typically results in increased permeability. This discrepancy suggests that the flow may be channeling somewhere through the inner zone (which had a decrease in microhardness), between the boundary of the altered and inner regions, or through microcracks in the altered ring. The cracks appeared subsequent to the exposure experiments, after being removed from a pressurized environment. Regardless of where the flow is occurring, the average permeability values indicate that the pozzolan-amended cement remained relatively impermeable with a permeability well below the API recommended maximum well cement permeability of 200 μD .

Pozzolan–Cement Blend of 65:35 Ratio. Assessment of the effects of exposure of the 65:35 pozzolan–cement blend samples to CO₂-saturated brine and supercritical CO₂ were determined on the basis of the results of a 2, 8, 9, and 31 day exposure time. The cement exposed to the supercritical CO₂ was completely reacted within 2 days. The cement exposed for 2 days to CO₂-saturated brine featured a very thin dense ring of calcium carbonate at a depth of approximately 5 mm. Within 8 days of exposure, both supercritical CO₂- and CO₂-brine-exposed phases of cement were completely

reacted. According to SEM–EDS, the cement exposed to CO₂-saturated brine appeared to have more silica in the cement matrix than the unexposed cement (see Figure 3). However, Vickers microhardness testing showed an increase in hardness in the CO₂-saturated brine-exposed cement (25 HV/100 g) as compared with the unexposed cement (15 HV/100 g). CT scans of the 50.8 mm 65:35 pozzolan–cement core showed a continuous change in alteration and density as compared with the 35:65 pozzolan–cement, which had a sharp boundary dividing zone (Figure 3). According to the density data obtained from the CT scan, the reacted cement material was less dense near the edge of the sample than in the interior of the cement core.

The average permeability of an unreacted sample was $1.1 \pm 0.3 \mu\text{D}$. The sample met the ASTM criterion for being within $\pm 50\%$ of the average, but the inflow to outflow ratio was not in compliance with the ASTM criterion, perhaps because the cement was consuming intrusive water for hydration. Although this sample had the same cure time as the 35:65 blend, the hydration rate was slower due to the added pozzolan content. The reacted sample met both ASTM requirements and had a mean permeability of $20.8 \pm 3.1 \mu\text{D}$, which is comparable to the 35:65 case (Supporting Information Table S2). The reacted sample showed a higher permeability than the unreacted sample but was still well below the API recommended maximum value of 200 μD . There were no cracks apparent in any of the 65:35 samples.

Penetration Rates. The 35:65 pozzolan–cement exposed to both the supercritical CO₂ and CO₂-saturated brine showed a uniform progression of carbonation. A version of Fick's second law of diffusion is typically used to estimate the depth of ordinary carbonation in cement (7):

$$l = \alpha t^{1/2} \quad (1)$$

where l = depth of carbonation (mm), t = time of exposure (days), and α is a constant related to the effective rate of

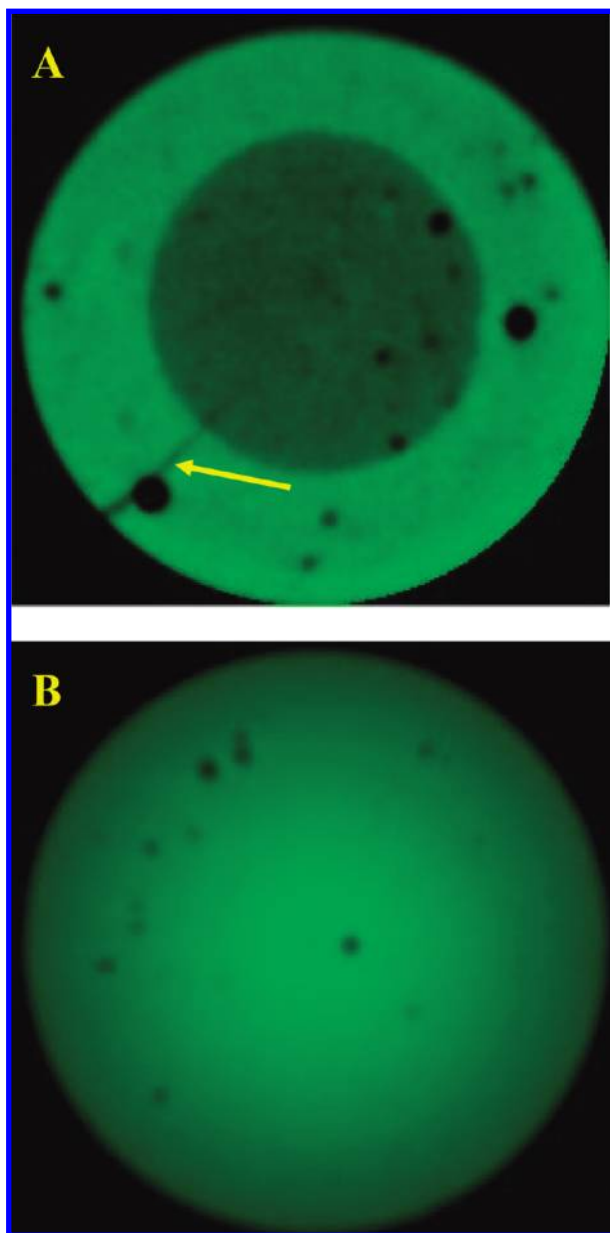


FIGURE 2. CT images of 2 in. pozzolan–cement cores exposed to CO₂-saturated brine at 50 °C and 15 MPa. (A) Pozzolan blend of 35:65 ratio exposed for 31 days. The arrow points to a microcrack in the lower left side of the core. The density data indicate that the altered region is denser than the inner region of the core. This is due to carbonation (precipitation of CaCO_{3(s)}). (B) Pozzolan blend of 65:35 ratio exposed for 60 days. The density data indicate that the altered region is less dense than the inner region likely due to the process of carbonation followed by decalcification.

diffusion of ionic species through the cement matrix (mm d^{-0.5}). The penetration depths of both supercritical CO₂ and CO₂-saturated brine exposure exhibited a linear relationship with respect to the square root of time (Figure 4), indicating a diffusion-limited process.

The relationship of penetration depth versus $t^{1/2}$ shown in Figure 4 was extrapolated to estimate CO₂ penetration into the cement matrix for times longer than those studied. To take into account the uncertainty in the data, a series of Monte Carlo simulations (14) was run to determine the range of extrapolated penetration depths for the 35:65 pozzolan–cement samples. Randomly generated values were selected for each data point within a normal distribution of measured

values to create 1000 sets of synthetic data. The resulting synthetic data sets were then individually fitted with eq 1, and the resulting parametrized equation was used to estimate the penetration depth at 90 and 365 days of exposure, as well as 30 and 50 years (Figure 4).

Since the 65:35 pozzolan–cement exposed to supercritical CO₂ was fully reacted within 2 days, and the CO₂-saturated brine-exposed portion of the same material had a penetration depth of 5 mm within 2 days, it was not possible to accurately determine an alteration rate for that system. Application of eq 1 to the data for the 2 day brine-exposed portion provides an estimate and yields a rate constant α of 4.9 mm d^{-0.5}, a factor of 2.9 greater than that determined for 35:65 pozzolan–cement.

Discussion

The 65:35 pozzolan–blend had a much faster rate of penetration than the 35:65 blend. This may be a result of the lower slurry density and higher water to cement ratio (which ultimately relates to the permeability of the set cement). According to the SEM–EDS and density data obtained from the CT scans, the 35:65 pozzolan–cement sample was carbonated, which led to a denser and harder material. Microcracks appeared in the samples only after they were removed from the high pressure. This is likely because of the heterogeneity in hardness (with sharp interfaces) and the change in the stress field associated with depressurizing. It was not possible with the current experimental setup to measure permeability without first removing the sample from the pressure vessels, so the permeabilities are likely dominated by the fractures.

In the 65:35 cement, a different phenomenon was observed. In this case, the carbonation “front” had penetrated through the sample completely. The continuous change in density shown in Figure 2 is likely due to leaching that takes place subsequent to carbonation. The absence of a defined front indicates that this process is reaction rate limited rather than diffusion limited. This will likely cause the permeability to increase over longer time scales.

Comparison to Neat Cement. It was previously shown that alteration of Class H cement from exposure to CO₂–brine occurs by a different mechanism than for supercritical CO₂ (3). In contrast to the results for Class H neat cement, there were no obvious differences observed between the CO₂-saturated brine- and supercritical CO₂-exposed portions of the 35:65 pozzolan–cement blend samples upon their removal from the vessels.

Several other differences were also observed in the pozzolan–cement samples exposed to supercritical CO₂ and CO₂-saturated brine compared to previous results with CO₂ exposure of class H neat cement (2, 3). First, the pozzolan–cements reacted with CO₂-saturated brine and with supercritical CO₂ by the same mechanism whereby CaCO_{3(s)} formed in place, i.e., ordinary carbonation (15). Class H neat cement exposed to supercritical CO₂ reacted similarly to the pozzolan–cement. Exposure to CO₂-saturated brine, however, displayed a different reaction mechanism with localized CaCO_{3(s)} dissolution and calcium leaching from the cement matrix to form a degraded zone comprised mostly of decalcified, amorphous SiO_{2(s)}. The leaching of calcium is a more gradual process in the pozzolan blends which does not proceed to completion in any of the experiments studied here.

Vickers microhardness measurements showed that the unexposed Class H neat cement was harder (64 HV/100 g) compared with both of the unexposed pozzolan–cements. This may be a result of comparing “same age” cement samples where the hydration rates are significantly different. Strength tests performed on pozzolan–cement blends the same age

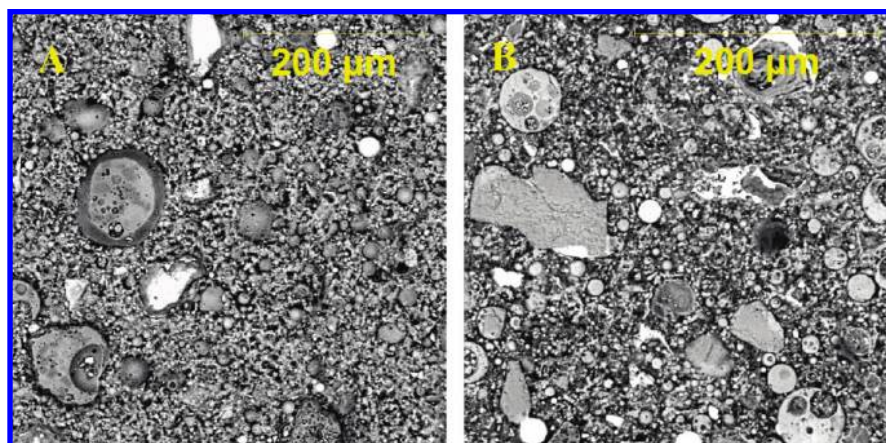


FIGURE 3. (A) Unexposed 65:35 and (B) 65:35 cement exposed for 9 days to CO₂-saturated brine at 50 °C and 15 MPa showing an increase in silica gel as observed by the increase in small dark regions in the cement matrix.

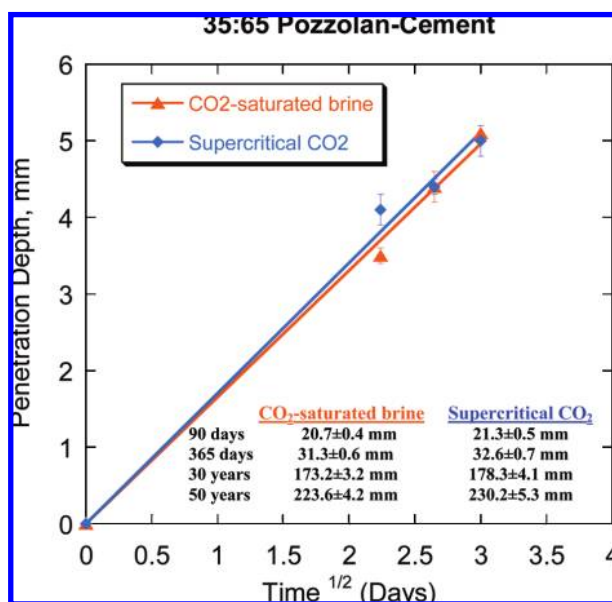


FIGURE 4. Progression of the penetration depth for Class H 35:65 cement cured at 50 °C and 15 MPa. The penetration depths due to supercritical CO₂ and CO₂-saturated-brine exposure exhibited a linear relationship with respect to the square root of time. Extrapolated penetration depths are inset.

as neat cement will typically be lower due to the slow rate of pozzolanic reaction (6). The slow rate of pozzolanic reaction is also manifested in the slow change in the permeability of pozzolan–cement mix times. Only after 160 day curing can the pozzolan–cement permeability be reduced by more than 1 order of magnitude (6). Both pozzolan–cement systems showed some increase in hardness upon CO₂ exposure with

the formation of CaCO_{3(s)}, with the 65:35 pozzolan–cement system showing the most significant increase (Table 1).

Comparison to Field Observations. In the field, the cement microstructure and permeability can be affected by a variety of processes. Cement cure conditions, CO₂ exposure properties, and additives are just a few influencing parameters. Although it is not possible to replicate field conditions exactly, experiments can give us insight and narrow the uncertainties. Our laboratory results were compared to a published report describing analysis of a pozzolan–cement sample recovered from the annulus of a 30 year old production well exposed to a natural CO₂ production reservoir (16). The well from which the samples were recovered was located within a sandstone reservoir containing 96% CO₂ fluid. Ten wellbore cement samples were collected along the well using a sidewall coring tool between 3874 ft (1181 m) and 4775 ft (1455 m) below ground surface. The estimated reservoir temperature and pressure for the samples were 60 °C and 20.7 MPa. The cement used to line the well was a Class G 50:50 pozzolan–cement blend (by volume) with an estimated slurry density of 14.2 lbm/gal (16). Class G well cement differs from Class H cement examined in our laboratory studies only in fineness of the cement powder (5). Bentonite (2%) was used in the tail slurry to prevent free water development.

Crow et al. (16) observed that the pozzolan–cement wellbore samples from the field were carbonated in varying degrees, depending on the core location along the depth of the well. Analyses suggest that carbonation of cement occurred as CO₂ migrated along the cement/formation interface and diffused into the cement, perhaps at defects within the cement. Carbonation was observed by mineralogical changes in the cement extending to the replacement of primary cement phases with calcium carbonate phases, primarily calcite (16). Crow et al. (16) found that carbonation

TABLE 1. Vickers Microhardness Measurements of Class H 35:65 and 65:35 Pozzolan–Cement Cured and Then Exposed to CO₂ at Conditions of 50 °C and 15 MPa Compared with Class H Neat Cement Cured and Then Exposed to CO₂ at Conditions of 50 °C and 30 MPa^a

sample section	Vickers microhardness testing: load 100 gf ^b		
	35:65 cement	65:35 cement	neat cement
unexposed cement	33 ± 9	15 ± 6	64 ± 7
exposed: CaCO ₃ ring	83 ± 17	too small to measure	128 ± 28
exposed: decalcified zone	none	none	25 ± 7
exposed: carbonated region	41 ± 7	25 ± 6	none

^a All samples were exposed for 9 days before measurements were taken. ^b All units of measurements are given in HV/100 g.

increased the permeability of the wellbore cement from ~ 1 to $\sim 30 \mu\text{D}$ and concluded that the wellbore was providing an effective barrier system for long-term CO_2 storage on the order of decades. In comparison, both of our unexposed pozzolan–cement laboratory samples (35:65 and 65:35 pozzolan–cement blends) had a permeability of $\sim 1 \mu\text{D}$ (see Table S2 in the Supporting Information). After exposure to CO_2 -saturated brine in the laboratory, the permeability of the 65:35 pozzolan–cement was increased to $20.8 \mu\text{D}$, meaning the laboratory experiments were comparable in magnitude of change to the field results. Well cement cores consisting of a 50:50 pozzolan–cement system recovered after 30 years of CO_2 exposure exhibited carbonation yet maintained low enough permeability to prevent major CO_2 migration.

Implications. The incorporation of pozzolan additive in wellbore cement changed both the rate and mechanism of CO_2 alteration significantly compared to those of neat Class H cement. In all cases tested the observed penetration rate was notably higher in the pozzolan-amended cement in comparison with the neat Class H cement. However, the alteration of the cement's chemical properties was not reflected as significantly in changes in the physical properties and in leaching of calcium in the pozzolanic blend.

The pozzolan–cement systems underwent carbonation where $\text{CaCO}_{3(s)}$ was distributed in the pores throughout the reacted portion rather than the complete decalcification observed in neat cement. In the cases we studied, the process increased the strength of the cement and enabled it to maintain low permeability, well below the API recommended $200 \mu\text{D}$ for a good seal. There was evidence of fracturing of the cement in the case where the hardness heterogeneity was significant. This occurred only after the stress state of the solid was significantly changed by removing it from the pressure vessel. It is possible that similar changes in the stress state could occur in the field case, which may also lead to fracturing, but it is difficult to draw any definitive conclusions with respect to the fracturing of cement. The results obtained here provide parameters for abandoned well cement alteration rates that will be useful for risk assessment and the evaluation of potential geologic sequestration sites penetrated by wells sealed with amended cements.

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Supporting Information Available

Figures showing a BSE image, X-ray diffraction patterns, SEM X-ray maps, optical images, Vickers microhardness measurements, and histograms of pixel intensities, tables giving the cement slurry recipe and permeability measurements, and text describing the permeability tests. This material is available free of charge via the Internet at <http://pubs.acs.org>.

Literature Cited

- (1) U.S. Department of Energy. *Carbon Sequestration Technology Roadmap and Program Plan*; U.S. DOE: Washington, DC, 2007.
- (2) Kutchko, B. G.; Strazisar, B. R.; Dzombak, D. A.; Lowry, G. V.; Thaulow, N. Degradation of well cement by CO_2 under geologic sequestration conditions. *Environ. Sci. Technol.* **2007**, *41* (12), 4787–4792.
- (3) Kutchko, B. G.; Strazisar, B. R.; Lowry, G. V.; Dzombak, D. A.; Thaulow, N. Rate of CO_2 attack on hydrated Class H well cement under geologic sequestration conditions. *Environ. Sci. Technol.* **2008**, *42* (16), 6237–6242.
- (4) American Petroleum Institute. *Worldwide Cementing Practices*; API: Dallas, TX, 1991.
- (5) Nelson, E. B. *Well Cementing*; Schlumberger Educational Services: Sugar Land, TX, 1990.
- (6) Hewlett, P. C. *Lea's Chemistry on Cement and Concrete*; Arnold: London, 1998.
- (7) Neville, A. M. *Properties of Concrete*, 4th ed.; John Wiley and Sons: New York, 2004.
- (8) Sideris, K. K.; Savva, A. E.; Papayianni, J. Sulfate resistance and carbonation of plain and blended cements. *Cem. Concr. Res.* **2006**, *28*, 47–56.
- (9) Roy, D. M.; Arjunan, P.; Silsbee, M. R. Effect of silica fume, Mata kaolin, and low-calcium fly ash on chemical resistance of concrete. *Cem. Concr. Res.* **2001**, *31*, 1809–1813.
- (10) American Petroleum Institute. *API Recommended Practice 10B: Recommended Practice for Testing Well Cements*; API: Washington, DC, 1997.
- (11) Bertos, M. F.; Simons, S. J. R.; Hills, C. D.; Carey, P. J. A review of accelerated carbonation technology in the treatment of cement-based materials and sequestration of CO_2 . *J. Hazard. Mater.* **2004**, *B112*, 193–205.
- (12) ASTM International. *ASTM Standards Related to Environmental Site Characterization*; ASTM: Conshohocken, PA, 2006.
- (13) Wong, R. C. K.; Chau, K. T. Estimation of air void and aggregate spatial distributions in concrete under uniaxial compression using computer tomography scanning. *Cem. Concr. Res.* **2005**, *35*, 1566–1576.
- (14) R Development Core Team. *R: A Language and Environment for Statistical Computing*; R Foundation for Statistical Computing: Vienna, Austria, 2006.
- (15) Thaulow, N.; Lee, R. J.; Wagner, K.; Sahu, S. Effect of calcium hydroxide on the form, extent, and significance of carbonation. In *Calcium Hydroxide in Concrete*; Skalny, J., Gebauer, J., Odler, I. Eds.; The American Ceramic Society: Westerville, OH, 2001.
- (16) Crow, W.; Williams, D. B.; Carey, B.; Celia, M.; Gasda, S. CO_2 capture project field study of a wellbore from a natural CO_2 reservoir for the Carbon Capture and Sequestration Conference. *7th Annual Conference on Carbon Capture and Sequestration*, Pittsburgh, PA; Exchange Monitor: Washington, DC, 2008.

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