Abstract

Carbon sequestration in abandoned petroleum fields may be a short-term solution to reducing anthropogenic emissions of CO₂. If sequestration is adopted on a large scale, it will be important to understand how CO₂ may leak out of sequestration formations. Possible avenues for leakage are abandoned wells. The results of a set of cement degradation experiments were used to get a rough estimate of the rate of degradation of the cement that is used to construct and abandon wells when it is exposed to carbonic acid. The rates that were calculated give an estimate of the time to degrade 25 mm of cement under static conditions at pH and temperature conditions that one might expect in a sequestration formation. The results of the estimate indicate that it will take tens to hundreds of thousands of years to degrade 25 mm of cement.

Keywords: Cement; Carbonation; CO₂; Sequestration; Degradation; Leakage; Well; Brine

1. Introduction

Carbon sequestration in abandoned petroleum fields may be a short-term solution to reducing anthropogenic emissions of CO₂. If sequestration is adopted on a large scale, it will be important to understand how CO₂ may leak out of sequestration formations. Possible avenues for leakage are abandoned wells. Watson and Bachu [1] have statistically assessed the leakage potential for wells using a population of 316,500 abandoned wells in Alberta, Canada. The researchers looked at surface casing vent flows and gas migration from the well. They found that 4.6% of the wells had some sort of leakage. Further analysis showed that the major factors related to leakage were the geographic area of the well, the deviation of the well, the type of well (abandoned open hole or abandoned cased hole), the abandonment method, oil price and regulatory environment, and uncemented casing/hole annulus. Of the leaks that occurred 81% of them were above the top of the cement which indicates that the cement is a factor in preventing leaks and providing zonal isolation.

Deep wells are typically a series of nested pipes called casings that are cement into place. When wells are abandoned plugs of cement are placed at places within the well. Figure 1 shows an example of an abandoned well. It is important to note that plug location and abandonment procedures have varied greatly in the past. Within an abandoned petroleum well, there are multiple pathways that CO₂ may use to escape. These include leakage through the cement that makes up the primary and/or plug cement in the well, leakage along the interface between the primary cement and the geologic formation, leakage along the interface between the well cement and the well casing, and leakage through the casing into the wellbore. Figure 2 shows schematic representations of these pathways.

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When the carbonic acid created by the dissolution of CO₂ into the formation brine reaches an abandoned well it will, most likely, first encounter the interface between the geologic formation and the well cement. To examine the effect of carbonic acid on cement at this interface a series of experiments was conducted at 20° and 50°C. The experiments looked at the effect of carbonic acid on the cement-formation interface using composite samples constructed from Berea sandstone and Class H neat paste.

When CO₂ comes in contact with brine, some of the CO₂ dissolves into the brine and becomes carbonic acid, H₂CO₃, (Equation 1, Table 1). In Equation 1, H₂CO₃* is the sum of H₂CO₃ and dissolved CO₂. Then carbonic acid attack will cause the cement to carbonate and then cause the carbonate to dissolve, leaving a more porous silica gel where the calcium hydroxide and calcium silica hydrate (C-S-H) had been (Equations 2 through 7, Table 1). In Equations 3 and 5 (Table 1), SiO₂OH₄ is an amorphous silica gel, and C₃₄-S₂-H₈ is calcium-silicate-hydrate (C-S-H), which is the binding phase in cement paste.
Carbonation does not occur at the same time for each of the cement phases; in particular, calcium hydroxide reacts before C-S-H. The pH of the cement pore solution is around 13; above pH 10.5, carbonate ($CO_3^{2-}$) is the dominant carbonate species, so the calcium carbonate ($CaCO_3$) will be stable. This will actually cause the cement to become less permeable by blocking some of the connected pores as the calcium carbonate precipitates [2]. However, as the calcium hydroxide and alkali phases are depleted, the pH of the pore solution will fall, and carbonate will no longer be the dominant species; instead, bicarbonate ($HCO_3^-$) predominates (Equation 6) [3]. This process eventually causes the calcium in the major cement phases to be dissolved out of the cement, so that only a porous silica gel will remain.

Physical research on cement carbonation has been conducted in the laboratory under conditions similar to the in situ conditions of the cement in an abandoned well by Duguid et al. [2, 4], Barlet- Gouédard [5], Kutchko [6], Andac and Glasser [7], Onan [8] Bruckdorfer [9]. All of the researchers noted that the CO2-cement systems created multiple reaction fronts within the cement.

Duguid et al. [2, 4] conducted experiments on well cements on Class H well cement ($w/c = 0.38$) at atmospheric pressure and at room temperature and $50^\circ$C with the pH adjusted to be consistent with a pressure of 10 MPa. One set of experiments looked at the affect of flowing carbonic acid on cement pastes at influent pH 2.4 and 3.7 (effluent pH around 3 and 5 respectively). The experiments flowed carbonic acid over 8-mm-diameter rods of cement and showed that severe degradation (total removal of calcium hydroxide and calcium-silica-hydrate) occurred over 31 days in some samples. The degradation produced a ring-shaped pattern with different cement and reaction phases reacting at different rates from the edge of the cement into the center of the sample [4]. Analysis of the of the rings that formed using X-ray diffraction showed an outer brown layer at room temperature, or brown and orange layers at $50^\circ$C, depleted of calcium hydroxide and calcium-silica-hydrate, a white layer where calcium carbonate was precipitating, a gray layer where calcium hydroxide was depleted, and a core of unreacted cement. The authors note that the formation of the white, calcium carbonate-rich layer has a protective effect and slowed that rate of reaction of the cement but because the layer itself is susceptible to degradation it did not stop the degradation.

[Table 1]

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Chemical equations governing the formation of carbonic acid, cement carbonation, and calcium carbonate dissolution.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$CO_2$ dissociation</td>
<td>$CO_2 + H_2O \leftrightarrow H_2CO_3^{+} \leftrightarrow H^+ + HCO_3^- \leftrightarrow 2H^+ + CO_3^{2-}$</td>
</tr>
<tr>
<td>1</td>
<td>Cement Carbonation</td>
</tr>
<tr>
<td>2</td>
<td>$Ca(OH)_2(s) + 2H^+ + CO_3^{2-} \rightarrow CaCO_3(s) + 2H_2O$</td>
</tr>
<tr>
<td>3</td>
<td>$Ca(OH)_2(s) + 2H^+ + CO_3^{2-} \rightarrow CaCO_3(s) + 2H_2O$</td>
</tr>
<tr>
<td>4</td>
<td>$Ca(OH)_2(s) + H^+ + HCO_3^- \rightarrow CaCO_3(s) + 2H_2O$</td>
</tr>
<tr>
<td>5</td>
<td>Calcium carbonate dissolution</td>
</tr>
<tr>
<td>6</td>
<td>$CO_2 + H_2O + CaCO_3(s) \leftrightarrow Ca^{2+} + 2HCO_3^-$</td>
</tr>
<tr>
<td>7</td>
<td>$2H^+ + CaCO_3(s) \leftrightarrow CO_2 + Ca^{2+} + H_2O$</td>
</tr>
</tbody>
</table>

The results of Kutchko et al. [6] showed that a series of rings formed in the cement as it degraded. The outermost ring showed a depletion of calcium from cement grains, the middle ring showed an increase in calcium in the layer, and the core showed no depletion of calcium from cement grains. Microindentation of the rings to examine their structural properties revealed that there was around a large increase in the Vickers hardness of the calcium-rich ring compared with that of the core (127.5 HV/10g compared to 64 HV/100g) and around a large reduction in the Vickers hardness of the calcium depleted zone compared with that of the core (25 HV/100g compared to 64 HV/100g). Kutchko et al. found that the degradation front reached about 440 microns into the sample after 90 days.

Andac and Glasser [7] found that the cement had a total leached depth of 600 to 800 microns by the end of the experiment at 3 months and the degraded region contained five individual degraded layers. Layer one (closest to the outer edge) was 200-300 microns deep and was low in calcium. Layer two (moving toward the center of the sample) was a cracked zone. The third layer, which was between 100 and 200 microns deep, was also low in calcium. The fourth layer, around 80 microns thick, was also...
lower in calcium than the unleached cement, but it was richer in calcium than the outer leached layers. The last layer constituted a transition between layer four and the unleached portion of the sample.

Onan [8] and Bruckdorfer [9] looked at the effects of supercritical CO$_2$ on the compressive strength of well cement. Onan conducted experiments on 5.08-cm cubes of Class H cement at 19.3 MPa (with a CO$_2$ atmosphere) and 41°C for 6 weeks. The results showed that the compressive strength remained similar for both the control and test specimens. However, the air permeability was higher in the reacted sample, $4.15 \times 10^{-14}$ m$^2$, than in the control sample, $9.90 \times 10^{-17}$ m$^2$. The overall depth of the carbonation reaction for all the experiments ranged between 0.32 and 0.64 cm. Bruckdorfer’s [9] samples were cubes that were 5.08 cm on a side, cylinders that were 2.54 cm OD by 5.05 cm long, and cylinders that were 7.0 mm OD by 12.7 mm long. The samples were cured for 3 days at 20.68 MPa and 79.4°C or 51°C. The carbonation experiments were conducted at the same pressure and temperature as Onan’s work. The experiments were static with respect to water, but the reactors were recharged with CO$_2$ every few days for 4 to 6 weeks. The cements examined were Classes A, C, and H well cements. All three types of cement showed no decrease of compressive strength after 31 days in the larger samples (cubes and cylinders). The smaller samples provided a larger volume of reacted cement per volume of the sample and showed an 80% strength loss. Similar results were also found for the small cylinders tested at a lower temperature. Bruckdorfer found that Portland cements lose compressive strength and structural stability in wet CO$_2$-rich environments. He also found that a high cement-to-water ratio (or low water-to-cement ratio) helps improve CO$_2$ resistance.

This paper will briefly describe the methods and materials used to conduct the experiments and the results of the experiments. These methods and materials are fully described in Duguid et al. [2]. It will then discuss how the results can be used to calculate rough estimates of the time required to completely degrade a depth of cement equivalent to the thickness of the cement sheath (The distance between the casing and formation, about 25 mm). Finally it will discuss the implications of the results.

2. Methods and Materials

The experiments were run at 20° and 50°C, corresponding roughly to the temperature of the earth at the surface and 1 km below the ground surface. The experiment were run under conditions that would be similar to those of a sandstone host formation. The leaching solution for the experiments was a CO$_2$-saturated 0.5 M NaCl solution saturated with SiO$_2$ (the leaching solutions is referred to as brine throughout this paper).

The cement used in the experiments was LaFarge Class H High Sulfate Resistant cement with a water/cement ratio (W/C) of 0.38. The deionized water used to mix the cement paste. The W/C ratio is the same as the one used by Onan [8] and Bruckdorfer [9] in their carbonation experiments. All of the cement used was mixed according to API 10B [10].

The samples were composite samples made from Class H well cement and Berea sandstone. The composite design of the samples made it possible to study the effects of CO$_2$ sequestration on the cement at the cement-rock interface. Based on the results of modeling using EQ3/6 [11], pH 3, 4, and 5 were chosen for the sandstone-cement experiments. HCl had to be added to lower the pH below 3.7 and NaOH had to be added to raise the pH. pH 3.7 was the value of pH achieved at atmospheric pressure using CO$_2$.

Three sets of samples were made for each temperature, one set for each pH tested. The samples were produced by filling sandstone cylinders with class H neat paste, allowing the cement to cure, and then slicing the filled cylinders into discs. The stone cylinders were 55 mm in diameter by ~10 cm tall. Each of the cylinders had a 25-mm axial hole, drilled through it off center from the long axis (Figure 3) where the cement was placed. The hole was placed such that the minimum depth of stone between the outside of the cylinder and the hole was 3.0 mm. The hole in the stone cylinders was drilled using a coring tool, so each cylinder had a corresponding core that was also used in the experiments to look for any changes that occurred in the stone as a result of exposure to carbonic acid. The samples were cured for about 7 months in brine with an N2 headspace to allow them to hydrate. Cement is normally about 70% hydrated after 28 days [12].

![Figure 3 Sectioned schematic of a stone cement sample prior to slicing.](image)

After the cement in the stone cylinders was cured, the cylinders were sliced into discs that were ~8 mm thick. The faces of the discs were sealed by clamping PTFE gasket material over them using 316 stainless steel discs to hold the PTFE in place.
Because the faces of each sample were sealed, the exposure to carbonated brine was only by diffusion in the radial direction, which would be the same exposure condition that a well may encounter in the earth assuming there is no vertical leakage pathway at the interface.

The reactors at pH 3 and 5 held 5.3 L of solution at the beginning of the experiment. The reactors had an initial sample-volume-to-reactor-fluid-volume ratio of 0.04. In addition to the cement-stone samples, each of these reactors contained a stone core that was taken when the hole was drilled in the stone. The pH 4 reactor held 5.6 L of solution at the beginning of the experiment and had a sample-volume-to-reactor-fluid-volume ratio of 0.04. The brine in these experiments was never refreshed but gas was bubbled through the reactor fluid throughout the experiment to stir it and ensure that the reactor fluid was CO₂-saturated. Samples were removed from the reactor vessels at the beginning of the experiment, 0 months, and at 1, 2, 3, 6, and 12 months after the start of the experiment.

The depth of reaction was measured at five locations around the perimeter of the cement-rock interface using a Nikon SMZ-U optical microscope and Nikon DS-SM digital camera. The locations were at the thinnest point in the rock, which will be referred to as the 0-degree position; the rest of the locations were spaced out every 45 degrees until 180 degrees was reached. The 180-degree position corresponded to the widest section of rock in the sample. The shortest distances from the cement to the rock at these points were 3.0 mm at the 0-degree position, 4.9 mm at the 45-degree position, 10.0 mm at the 90-degree position, 17.8 mm at the 135-degree position, and 26.9 mm at the 180-degree position. The face used for measurement on each of the samples used for optical microscopy was polished using 220-grit polishing prior to measurement.

3. Results

The average temperature was 19.9 ± 0.8°C for the 20°C experiments and 50.2 ± 1.5°C for the 50°C experiments. The degradation pattern showed a single visible reaction zone formed and progressed over time. The color of the reaction zone changed over the course of the experiments. At the 0-degree position after one month it was a cream color. By the second month the zone had changed to a light orange. And by the end of the experiment the reacted zone was a bright orange at the interface, becoming lighter in color toward the center of the cement. Figure 4 shows the reacted zone at the thin side of the stone for the samples reacted at pH 3 and 20°C. The color and progress of the reaction zone in this set of samples is representative for the samples that were reacted at the other pHs and temperatures.

At each pH the advance of the visible degradation front showed a change in rate after 2 to 3 months. Because the samples were exposed under diffusion conditions and diffusion is proportional to the square root of time the measurements at all positions are plotted versus the square root of time in Figure 5. The depth of the degradation front versus the square root of time for the 20°C experiments is shown in Figures 6 A, B, and C.

![Figure 4](image_url) Photos of sandstone-cement samples reacted over a year at pH 3 and 20°C.

The cement in the 50°C experiments invaded the stone to a depth of 0.8-1.0 mm during either the casting or curing of the samples. The depths described for the 50°C samples are measured from the outer edge of the invaded zone and not from the cement-sandstone interface. Also, the sandstone in the pH 4 and 5 experiments reacted and turned orange during the course of the experiments making it impossible to distinguish the reacted cement zone from the discolored sandstone. Therefore only the results from the pH 3-50°C sandstone-cement experiment are reported in this section. For more information on the cement invasion and the pH 4 and 5-50°C sandstone-cement experiments, the reader is directed to Duguid et al. [2]. The slope of the straight line fitted to the first part of the pH 3-50°C data was 2.33 x 10⁻⁵ mm/month₁/² (R² = 0.876) and the slope for the straight line fitted to the second part of the data was 4.29 x 10⁻⁶ mm/month₁/² (R² = 0.265). The plot of the pH3-50°C data is shown in...
Figure 6 D. The maximum depths of the visible reaction zone for each of the conditions described was 0.310 mm, 0.307 mm, 0.270 mm, and 0.577 mm for the pH 3, pH 4, pH 5-20°C and pH 3-50°C experiments, respectively.

Figure 5 Reaction depth data versus the square root of time divided by the distance to the shortest distance, r, to the outside of the sample for all measurement points (0 to 180-degrees) for the pH 3, pH 4, pH 5-20°C and pH 3-50°C experiments.

4. Discussion

The slopes calculated from the plots of the data described in the previous section were used to make rough estimates of the amount of time it will take for 25 mm of cement to be degraded under the conditions of the experiments. The slopes were used to calculate the estimate by using the square root of time relationship seen in the results of the experiment, distance equals the rate multiplied by the square root of time.

The design of the experiment and the samples forces the degradation to be controlled by diffusion through the pores of the stone. The data for the depth of the degradation front in the samples showed a change in rate somewhere between two and three months for all of experiments. This change in slope may be due to the precipitation of calcium carbonate in the larger cement pores (Equations 2 through 5, Table 1) and a switch from the degradation of calcium hydroxide to the degradation of calcium carbonate (Equations 6 and 7, Table 1). An X-ray map of calcium of the pH 3-20°C sample at 6 months shows calcium deposits at the leading edge of the visible (orange) reaction front (Figure 7). The calcium deposits or grains do not have corresponding features in the X-ray maps for iron and silica, which indicates that they are not unhydrated cement phases. Furthermore because of the long (6 months) exposure to carbonic acid, the calcium grains are not likely to be calcium hydroxide, which should be the first calcium phase in the cement to be destroyed.

Assuming that once the reactions controlling the ingress of the visible reaction front haves switched from the degradation of calcium hydroxide and C-S-H to the degradation of calcium carbonate and that degradation of calcium carbonate is the final degradation regime [4]; Then an extrapolation can be conducted using the rates calculated with the data after the break in slope. This ignores the time for the first few months of exposure, but that time is small compared to the amount of time to degrade 25 mm of cement, so it can be ignored with little effect on the total time. Using the slopes after the break in slope for the experiments (Figure 5) the time to react 25 mm of Class H well cement will be 33,400 years for the pH 3-20°C experiment, 724,300 years for pH 5-20°C, and 29,300 years for pH 3-50°C. The time at pH 4-20°C could not be calculated due to the negative slope after the break.
Figure 6 Reaction depth data versus the square root of time for the 0-degree measurement point for the pH 3, pH 4, pH 5-20°C and pH 3-50°C experiments.

Figure 7 X-ray maps of the pH 3 room temperature sample at 6 months showing white grains outlined by the rectangular boxes in the calcium map (left) and showing no corresponding grains in the iron map (center) and the silicon map (right).

It is possible to re-interpret the break in slopes for the pH 4-20°C experiment (Figure 8). Using the data after the break in slope the time to degrade 25 mm of cement at pH 4-20°C is 11,264 years. It seems unlikely that the pH 4-20°C condition would have a more severe degradation rate than the more severe pH 3-20°C condition.

Figure 8 Potential alternate interpretations of the data for the pH 4-20°C.
The rates calculated in this paper probably represent conservative (fast) estimates for the rates of degradation for well cements. Analysis of samples by the Carbon Capture Project [13] and from SACROC field [14] have shown that well cement exposed to a CO₂ environment for around 30 years did not show the complete degradation often seen in laboratory experiments at the thin side of the samples which indicates that in, at least, some cases cement under actual field condition will be slower to degrade than even the slowest rate calculated here.

The rates calculated for the experiments describe attack on the cement in a sandstone system that may be similar to a storage formation. Assuming that the caprock is at least a few orders of magnitude less permeable and that the cement does not have a severe crack network or extensive annular pathway than one would expect diffusion through the caprock to be much smaller and the rates of degradation in the caprock to be correspondingly smaller. However one cannot rule out the possibility of attack in a cap due to the existence of high porosity zones, fractures or annuli at the interface allowing exposure to carbonic acid. In modeling of the SACROC samples conducted by Carey and Lichtner [15], they had to assume diffusion rates for a shale that are more typical of sandstone to fit observations of the samples which indicates that even in through or adjacent to the caprock there was a pathway for CO₂ transport that allowed the cement to carbonate.

5. Conclusions

It is clear from the experimental work described by here and by others that well cements are subject to degradation due to exposure to carbonic acid. The rate of degradation in the field will depend on the quality of the cement and the quality of the cementing job within a well. For a well that has good zonal isolation and no pathways for flow the mechanism for attack will likely be diffusion and the rate of degradation will be between 30,000 and 700,000 years to degrade 25 mm of neat paste in a sandstone reservoir, and possibly longer to destroy the cement passing through the cap rock.

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References