THE EFFECT OF CO\textsubscript{2} SEQUESTRATION ON OIL WELL CEMENTS

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Abstract

Experiments were conducted to examine the effects of CO\textsubscript{2} sequestration conditions on cements used to construct and abandon oil and gas wells. The results showed that significant damage, complete loss of the calcium hydroxide phase, can take place over a time span as short as seven days.

Introduction

Depleted oil- and gas-bearing formations represent likely locations for the disposal of CO\textsubscript{2}. Oil- and gas-bearing formations have proved capable of trapping fluids over geologic times. Due to the removal of hydrocarbons from these formations via wells, a potential avenue for leakage has been created. Cements are used in the construction (primary cement) and abandonment (plug cement) of oil and gas wells. Because wells represent a potential leakage pathway, it is important to study the effects of sequestration on the integrity of materials used to make them. In order to study these effects, experiments have been conducted using two different formulations of well cement (one containing the common additive bentonite [1]) and an acidic brine at 23°C, the approximate ground surface temperature, and 50°C, the approximate temperature of a potential sequestration site 1 km below ground surface [2].

Materials and Methods

Samples were made from Class H HSR well cement (LaFarge), deionized water, and unreacted bentonite (Haliburton Energy Services) using two mixes. One mix consisted of only cement and water (neat paste) and had a water-to-cement ratio of 0.38 [3, 4]. The other design used 6% bentonite (mass of bentonite per mass of solids) and had a water-to-solids ratio of 0.70 [5]. The cements were mixed according to API specifications [6]. After mixing, the cement was injected into cylindrical plastic molds and placed in a 0.5-molal NaCl solution (brine) bath at room temperature. After one day the samples were moved to brine baths with nitrogen atmospheres at 23° and 50°C for curing. The cement rods were removed from the molds within three days. The samples were between 7.3 and 7.7 mm in diameter and between 140 and 260 mm long.

Experiments were only run after the cement was mature (28 days or older). The experimental conditions consisted of two influent pHs, 2.4 and 3.7, and two temperatures, 23° and 50°C, considered likely for potential sequestration formations [7]. The leaching fluid for the experiments was made by bubbling CO\textsubscript{2} through the brine, which set the pH of the solution near 3.7. Hydrochloric acid was added to the carbonated brine to lower the pH from 3.7 to 2.4. The continuously stirred reactors used in the experiment had a volume of 1,800 cm\textsuperscript{3} and held a single sample. The flow rates averaged 8.2 cm\textsuperscript{3} min\textsuperscript{-1} for the 23°C experiments and 8.3 cm\textsuperscript{3} min\textsuperscript{-1} for the 50°C experiments. The experiments ranged in length from 1,855 min (1.3 days) to 10,425 min (7.2 days). The influent and effluent pH was monitored using a Thermo Orion 230A pH meter. The pH of the reactors was assumed to be at pseudo-steady-state after five reactor volumes of brine had passed through the reactor. The reaction rates for the cement were calculated based on the pH using Equation 1 [8], assuming that Equation 2 was the governing reaction.

\[
\text{Rate} = \frac{\nu(c_{\text{steady}} - c_0)}{SA} \quad \text{Equation 1}
\]

where \(\nu\) = flow rate (cm\textsuperscript{3} min\textsuperscript{-1}), \(c_{\text{steady}}\) = steady-state concentration of H\textsuperscript{+} (mol cm\textsuperscript{-3}), \(c_0\) = initial concentration H\textsuperscript{+} (mol cm\textsuperscript{-3}), and SA = surface area of the sample (mm\textsuperscript{2}) based on sample dimensions.

\[
\text{Ca(OH)}_2 + 2\text{H}^+ \rightarrow \text{Ca}^{2+} + 2\text{H}_2\text{O} \quad \text{Equation 2}
\]

The thickness of the reacted layers and cores was obtained through direct measurement. The porosity was measured by drying at 105°C and correcting for NaCl remaining in the sample. It was assumed that the NaCl concentration in the sample pore water was the same as that of the brine. The mass loss rate was calculated by

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dividing the difference of the sample mass at the start and end of the experiment by the length of the experiment and then dividing by the surface area of the sample.

Results

The influent pH varied between 2.4 and 2.5 (nominally 2.4) for the low pH experiments and 3.7 and 3.8 (nominally 3.7) for the higher pH experiments. The effluent pH (Table 1) of all the systems stabilized within two or three reactor volumes (400 to 600 min) and remained steady for the duration of the experiment with the exception of the E7 series of experiments. In E721R1 and E750R1, which were run with 6% bentonite samples and an influent pH of 2.5, the pH leveled off near 2.8 and then dropped to about 2.5 at around 4,800 min (23 reactor volumes) and stabilized for the duration of the experiment. The reaction rates were on the order of $10^{-7}$ mol-Ca$^{2+}$ mm$^{-2}$ min$^{-1}$ for the low-pH neat paste experiments and $10^{-10}$ mol-Ca$^{2+}$ mm$^{-2}$ min$^{-1}$ for the higher-pH experiments. The reaction rates for the 6% bentonite samples (Table 1) were on the same order as those of the neat paste samples. Two reaction rates were calculated for the E723R1 and E750R1 samples, one for early time and one for late time, because the pH stabilized near 2.8 between 0 and 4,800 min and then dropped to around 2.5 for the remainder of the experiment. Upon post-reaction examination the samples exhibited a two-layer structure; however, E750R2 showed a three-layer structure, and E123R1, E650R2, E723R1, and E750R1 showed a single reacted layer. The layer thicknesses for each reacted sample are given in Table 1. Figure 1 shows a cross section of reacted sample, E623R1, that exhibits the two-layered structure. The average porosity of each sample increased during the experiment. The initial porosities for the samples were 0.38 and 0.44 for the neat paste samples at 23°C and 50°C, respectively, and 0.56 and 0.59 for the 6% bentonite samples at 23°C and 50°C. The reacted porosity increased between 10 and 45% for the neat paste samples and 10 and 33% for the bentonite-containing samples. The reacted porosities are shown in Table 1.

The mass of the samples decreased during the exposure to sequestration-like conditions. The mass loss rate (Table 1) ranged from $2.10 \times 10^{-8}$ to $8.91 \times 10^{-7}$ g mm$^{-2}$ min$^{-1}$ for the neat paste samples and from $3.57 \times 10^{-8}$ to $1.22 \times 10^{-7}$ g mm$^{-2}$ min$^{-1}$ for the bentonite-containing samples. Figure 2 shows plots of outer-layer depth, reaction rate, and mass loss rate versus time for the neat paste and 6% bentonite experiments.

Table 1  Neat paste and 6% bentonite reaction experiment data

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Composition</th>
<th>Average effluent pH</th>
<th>Time (min)</th>
<th>Reaction rate (mol-Ca$^{2+}$ mm$^{-2}$ min$^{-1}$)</th>
<th>Sample diameter (mm)</th>
<th>Layer 1 thickness (mm)</th>
<th>Layer 2 thickness (mm)</th>
<th>Reacted porosity</th>
<th>Mass loss rate (g mm$^{-2}$ min$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>E123R1</td>
<td>Neat</td>
<td>4.62</td>
<td>3,950</td>
<td>9.69 x $10^{-11}$</td>
<td>7.45</td>
<td>0.005</td>
<td>NV</td>
<td>0.50</td>
<td>3.82 x $10^{-8}$</td>
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<tr>
<td>E623R2</td>
<td>Neat</td>
<td>4.37</td>
<td>7,725</td>
<td>1.09 x $10^{-10}$</td>
<td>7.49</td>
<td>0.185</td>
<td>2.08</td>
<td>0.54</td>
<td>3.49 x $10^{-8}$</td>
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<tr>
<td>E423R1</td>
<td>Neat</td>
<td>2.68</td>
<td>2,875</td>
<td>1.37 x $10^{-9}$</td>
<td>7.67</td>
<td>0.090</td>
<td>1.26</td>
<td>0.51</td>
<td>6.39 x $10^{-8}$</td>
</tr>
<tr>
<td>E623R1</td>
<td>Neat</td>
<td>2.70</td>
<td>7,725</td>
<td>1.04 x $10^{-9}$</td>
<td>7.29</td>
<td>0.360</td>
<td>1.08</td>
<td>0.56</td>
<td>3.83 x $10^{-8}$</td>
</tr>
<tr>
<td>E250R1</td>
<td>Neat</td>
<td>2.84</td>
<td>2,920</td>
<td>1.70 x $10^{-9}$</td>
<td>7.67</td>
<td>0.300</td>
<td>1.11</td>
<td>0.49</td>
<td>8.91 x $10^{-8}$</td>
</tr>
<tr>
<td>E150R1</td>
<td>Neat</td>
<td>5.03</td>
<td>3,950</td>
<td>1.28 x $10^{-10}$</td>
<td>7.63</td>
<td>0.273</td>
<td>1.15</td>
<td>0.55</td>
<td>8.59 x $10^{-8}$</td>
</tr>
<tr>
<td>E650R2</td>
<td>Neat</td>
<td>4.78</td>
<td>7,725</td>
<td>1.32 x $10^{-10}$</td>
<td>7.46</td>
<td>0.284</td>
<td>NV</td>
<td>0.55</td>
<td>2.10 x $10^{-8}$</td>
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<tr>
<td>E523R1</td>
<td>6%</td>
<td>4.43</td>
<td>2,010</td>
<td>1.90 x $10^{-10}$</td>
<td>7.68</td>
<td>0.175</td>
<td>1.56</td>
<td>0.65</td>
<td>1.16 x $10^{-7}$</td>
</tr>
<tr>
<td>E723R2</td>
<td>6%</td>
<td>4.32</td>
<td>10,425</td>
<td>1.56 x $10^{-10}$</td>
<td>7.72</td>
<td>0.430</td>
<td>NV</td>
<td>0.69</td>
<td>3.57 x $10^{-8}$</td>
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<tr>
<td>E323R2</td>
<td>6%</td>
<td>2.70</td>
<td>1,855</td>
<td>1.80 x $10^{-9}$</td>
<td>7.68</td>
<td>0.230</td>
<td>0.78</td>
<td>0.66</td>
<td>1.07 x $10^{-7}$</td>
</tr>
<tr>
<td>E723R1</td>
<td>6%</td>
<td>2.86</td>
<td>10,425</td>
<td>1.67 x $10^{-9}$</td>
<td>7.65</td>
<td>0.754</td>
<td>NV</td>
<td>0.72</td>
<td>4.03 x $10^{-8}$</td>
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<tr>
<td>E723R1 late time</td>
<td>2.55</td>
<td>--</td>
<td>2.36 x $10^{-10}$</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>E350R1</td>
<td>6%</td>
<td>2.83</td>
<td>3,015</td>
<td>2.32 x $10^{-9}$</td>
<td>7.56</td>
<td>0.258</td>
<td>1.13</td>
<td>0.66</td>
<td>9.72 x $10^{-8}$</td>
</tr>
<tr>
<td>E750R1</td>
<td>6%</td>
<td>2.78</td>
<td>10,425</td>
<td>1.99 x $10^{-9}$</td>
<td>7.18</td>
<td>1.161</td>
<td>NV</td>
<td>0.75</td>
<td>7.52 x $10^{-8}$</td>
</tr>
<tr>
<td>E750R1 late time</td>
<td>2.58</td>
<td>--</td>
<td>4.85 x $10^{-10}$</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>E550R1</td>
<td>6%</td>
<td>4.76</td>
<td>2,010</td>
<td>1.71 x $10^{-10}$</td>
<td>7.44</td>
<td>0.230</td>
<td>3.49</td>
<td>0.62</td>
<td>1.22 x $10^{-7}$</td>
</tr>
<tr>
<td>E750R2</td>
<td>6%</td>
<td>4.67</td>
<td>10,425</td>
<td>1.77 x $10^{-10}$</td>
<td>7.38</td>
<td>0.579</td>
<td>0.18**</td>
<td>0.70</td>
<td>5.39 x $10^{-8}$</td>
</tr>
</tbody>
</table>

* No inner layer was visible.  ** Combined thickness of layer 2 (0.01 mm) and layer 3 (0.17 mm).
$ Late time is after 4,860 min.  Note:  Experiment temperature is in the sample ID; E123R1 was run at 23°C.
Figure 1 Reacted cement core showing the outer reaction layer, middle reaction layer, and central core.

A) Depth of outer layer versus time for neat paste samples

B) Reaction rate versus time for neat paste samples

C) Mass loss rate versus time for neat paste samples

D) Depth of outer layer versus time for 6% bentonite samples

E) Reaction rate versus time for 6% bentonite samples

F) Mass loss rate versus time for 6% bentonite samples

Figure 2 Plots showing neat paste samples (A, B, and C) and 6% bentonite samples (D, E, and F).
Discussion

The change in effluent pH of experiments E723R1 and E750R1 indicates a loss of the sample’s ability to buffer the system. Phenolphthalein tests on the reacted samples (E723R1 and E750R1) showed no color change, indicating that the change in pH may have been due to a complete loss of calcium hydroxide in the cement.

The plots of the reaction rates versus time for the influent pH 2.4 experiments show a drop between long and short experiments for both the neat paste and 6% bentonite samples. The drop in rate also implies a drop in the buffering capacity of the cement, possibly a drop in the amount of calcium hydroxide in the sample. This is particularly evident in E723R1 and E750R1, where two pseudo-steady-state pHs were reached and two rates can be calculated. The phenolphthalein test shows more depletion (less intense color) between short and long experiments. In the pH 3.7 experiments the plots of reaction rate versus time show little variation from short to long experiments, which indicates the attack is slower in the higher-pH systems and the cement will be able to buffer the system longer. The reaction rates in Table 1 represent a lower limit. If, instead of Equation 2, Equation 3, a bicarbonation reaction, were assumed [9], the reaction rate would be twice as fast as the results presented in Table 1. Further analysis of the effluent composition will be conducted to determine the dominant reaction mechanism.

\[
\text{Ca(OH)}_2 + \text{H}^+ + \text{CO}_2 \rightarrow \text{Ca}^{2+} + \text{HCO}_3^- + \text{H}_2\text{O} \quad \text{Equation 3}
\]

The outer reacted layer, layer 1, increased with every pH and temperature combination over time. Further experiments are needed to determine if depth of layer 1 is controlled by diffusion. The multilayer structure seen in the reacted samples is similar to multilayered cement degradation seen by Andac and Glasser [10]. Further analysis using microscopic techniques will be conducted to determine the layer composition. When the phenolphthalein indicator is used, layer 1 is always completely depleted of calcium hydroxide (no color change). Layer 2 is somewhat depleted (some color change), and the core is sometimes somewhat depleted, with the exception of E723R1 and E750R1, which were totally depleted of calcium hydroxide. The porosity always increased with experiment length. The increase was always smallest for pH 3.7 at 23°C, the least harsh condition, and largest for pH 2.4 at 50°C, the most harsh condition. The mass loss rate slowed down between short and long experiments for all temperatures and pHs. This is another possible sign that the more reactive phases are reacted away quickly.

Conclusion

It is likely the subsurface conditions that may exist in a CO\(_2\) sequestration site will damage the cement that makes up the primary and plug cement in an abandoned well. The samples reacted at the temperature closest to that of a sequestration site, 50°C, at either pH 2.4 or 3.7, exhibited more damage than those reacted at 23°C. Under all experimental conditions the bentonite-containing cement had the highest reaction rates, between 1.56 x 10\(^{-9}\) and 2.32 x 10\(^{-9}\) mol-Ca\(^{2+}\) mm\(^{-2}\) min\(^{-1}\); the deepest attack, 0.75 to 1.2 mm (layer 1) over 10,425 minutes (7.2 days); and the most depletion of calcium hydroxide, with total depletion in the E723R1 and E750R1. These results imply even a short exposure to carbonated brines could damage the sealing properties of the cement in an abandoned well.

References