Carbon sequestration using brine of adjusted pH to form mineral carbonates

Matthew L. Druckenmiller*, M. Mercedes Maroto-Valer

The Energy Institute and the Department of Energy and Geo-Environmental Engineering,
The Pennsylvania State University, University Park, PA 16802, United States

Abstract

The permanent mineral storage of carbon using brine is a critical component of geologic carbon sequestration in saline aquifers. It is suggested that pH has a significant effect on the precipitation of mineral carbonates. The design of an ex situ process to efficiently drive this otherwise geologic reaction requires an understanding of the evolution of brine pH from the initial step of pH adjustment, through to the final stages of the conversion. The effects of temperature, pressure, and pH on the formation of carbonates, such as calcite, during the reaction of CO₂ with natural gas well brine were investigated. A high pressure/high temperature reactor equipped with a liquid sampling valve allows for the monitoring of brine pH and composition throughout 6-h reactions at temperatures of 75 and 150°C and pressures of 600 and 1500 psi. Results show that temperature has a greater control on changes in pH than pressure. However, initial brine pH is the main factor controlling the formation of carbonates. ICP-AES analysis of brine samples to identify changes in brine composition during reaction suggests that a much longer reaction time is needed to approach steady state and to establish a clear correlation between variations in solution chemistry and the precipitation of carbonates. XRD has confirmed the precipitation of calcite in experiments with an adjusted initial pH to approximately 9.

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* Corresponding author. 401 Academic Activities Bldg, University Park, PA 16802. Tel.: +1 814 862 8422; fax: +1 814 863 8892.
E-mail address: mxd272@psu.edu (M.L. Druckenmiller).

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1. Introduction

In the shadow of mass fossil fuel consumption and the looming threat of global climate change, carbon sequestration using brine has emerged as a promising technology in carbon management. Brine is a saline-based solution that is produced as a waste product during the extraction of oil and natural gas. In Pennsylvania, annual brine production is estimated at 59 million gallons, while total U.S. production is over 20 billion gallons [1]. The existence of large volumes of brine at the surface provides a potential feedstock for the above-ground conversion of CO₂ into geologically stable mineral carbonates, such as calcite (calcium carbonate) and magnesite (magnesium carbonate). Under the appropriate conditions, CO₂ dissolves in brine to initiate a series of reactions that ultimately lead to the bonding of carbonate ions to various metal anions inherent in brine to precipitate carbonates.

In addition to above-ground processing to efficiently drive the reaction, much emphasis has been placed on the injection of CO₂ into subsurface saline formations. U.S. deep saline aquifers are estimated to provide storage for approximately 130 gigatons carbon equivalent, which is approximately eighty times the U.S.’s total carbon emissions in 2001 [2,3]. Following the injection of anthropogenic CO₂ below a typical depth of 800 m, the storage mechanism is initially hydrodynamic as the CO₂ is immobilized as a dense supercritical fluid. On a separate timescale, and following the dissolution of CO₂ in brine, chemical interactions with the brine may form mineral carbonates [4].

CO₂ reacts with brine’s metal cations to form carbonate precipitates via the following reaction sequence, in which selected likely precipitates are shown [5,6]:

\[
\text{CO}_2(g) \leftrightarrow \text{CO}_2(aq) \quad (1)
\]

\[
\text{CO}_2(aq) + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{CO}_3 \quad (2a)
\]

\[
\text{H}_2\text{CO}_3 \leftrightarrow \text{H}^+ + \text{HCO}_3^- \quad (2b)
\]

\[
\text{CO}_2(aq) + \text{OH}^- \leftrightarrow \text{HCO}_3^- \quad (3)
\]

\[
\text{HCO}_3^- \leftrightarrow \text{H}^+ + \text{CO}_3^{2-} \quad (4)
\]

\[
\text{Ca}^{2+} + \text{CO}_3^{2-} \leftrightarrow \text{CaCO}_3 \downarrow \quad (5a)
\]

\[
\text{Mg}^{2+} + \text{CO}_3^{2-} \leftrightarrow \text{MgCO}_3 \downarrow \quad (5b)
\]

\[
\text{Ca}^{2+} + \text{Mg}^{2+} + 2\text{CO}_3^{2-} \leftrightarrow \text{CaMg(CO}_3)_2 \downarrow \quad (5c)
\]

The dissolution of CO₂ in water (reaction 1) is dependent on temperature, pressure, and brine salinity. Reactions 2a and 2b represent the formation of carbonic acid, which reduces the pH of the system, and the dissociation of carbonic acid to form bicarbonate, respectively. The bicarbonate ion may then dissociate (reaction 4) to form
the carbonate ion. The metals then react with the carbonate ion to form the carbonate minerals in reactions 5a, 5b, and 5c, which are calcite, magnesite, and dolomite, respectively.

The pH determines which steps dominate the reaction sequence, and accordingly the proportions of the carbonic species [5]. At a low pH (~4), the production of $\text{H}_2\text{CO}_3$ dominates, at a mid pH (~6) $\text{HCO}_3^-$ production dominates, and at a high pH (~9) $\text{CO}_3^{2-}$ dominates [6]. Therefore, at a basic pH the precipitation of carbonate minerals is favored because of the availability of carbonate ions. Conversely, the dissolution of carbonates increases as the solution becomes increasingly more acidic.

The rate of the mineral trapping process is slow and serves as the major disadvantage of this technology [6]. In the low to mid pH range, the rate limiting step of this reaction is the hydration of CO$_2$ to form carbonic acid in reaction 2a, which has a forward reaction rate constant of $6.2 \times 10^{-2}$ s$^{-1}$ at 25 °C [7]. However, in the high pH range the rate limiting step is the first dissociation of carbonic acid to form bicarbonate [6].

The parameters that affect the efficiency of the carbonate forming process for both above and underground sequestration operations are brine composition, temperature, pressure, and pH. These parameters must be further understood since they determine both the economic viability of the technology as well as help to identify locations that favor sequestration.

Soong et al. [6] suggest that pH has a significant effect on both conversion rates and on the specific species that are precipitated. The formation of carbonates can thus be promoted by increasing brine pH through the addition of a strong base. Their research qualitatively identifies the effects of various parameters on carbonate precipitation. However, pH evolution throughout the reaction is not documented.

The purpose of this study was to characterize the natural geologic processes that form mineral carbonates using a laboratory scale unit over a short reaction period of 6 h by controlling the brine pH, temperature and pressure. The ultimate formation of carbonates is observable through the characterization of precipitates and changes in brine solution composition. Additionally, the evolution of brine pH following a pH adjustment yet prior to reaction with CO$_2$ is studied. This analysis will help determine a relationship between brine composition and brine’s ability to maintain an elevated pH over time.

The range of experimental conditions described herein is applicable to the various methods of CO$_2$ sequestration in brines that are currently being explored. Lower temperature and pressure with a pH adjustment will favor above-ground sequestration within large scale reactors, which may be retrofitted to react with CO$_2$-rich flue gas from a power plant. This method may be favorable due to the cost savings associated with lower temperature and pressure and also because large quantities of brine are currently stored in above-ground storage tanks following its separation from oil or gas. Higher temperatures and pressures without pH adjustment will favor sequestration that is to take place underground within brine filled aquifers. Pressures and temperatures above the critical pressure and temperature of CO$_2$ (1070 psi and 31.1 °C, respectively) are desired due to the advantages of injecting supercritical CO$_2$. Supercritical fluids are efficiently injected because they have the solubility of a liquid and the dynamic viscosity of a gas [4].
2. Experimental method

Four brine samples were obtained from various natural gas wells: PA-1 and PA-2 from nearby 2800 m wells in Indiana County, Pennsylvania, and OH-1 and OH-2 from an 1158 m well in Guernsey, Ohio and a 1030 m well in Youngstown, Ohio, respectively. This section describes the analysis of the brine samples using inductively coupled plasma-atomic emission spectroscopy (ICP-AES), the pH stability studies conducted on the brines, and the high pressure/high temperature reactor experiments used to explore brine–CO₂ interactions. In addition, the methods used to analyze the extracted brines and the precipitated solids from the reactor experiments are described, in which ICP-AES and X-ray diffraction (XRD) were employed, respectively.

2.1. ICP-AES analysis of unreacted brine

The brine samples underwent characterization analysis by ICP-AES using a Leeman Labs PS3000UV ICP spectrophotometer. ICP-AES screening with no acid pretreatment was conducted to determine the elemental metal concentrations in the liquid phase. The brine samples were analyzed for the following metals: Al, Ba, Ca, Fe, K, Mg, Mn, Na, P, Si, and Sr.

Additionally, the National Energy Technology Laboratory (NETL) supplied preliminary ICP results in which the brines were treated with HNO₃ prior to screening to ensure that all metals were dissolved [8]. Acid pretreatment provides results that show the total metal concentration in solution. When compared to the ICP-AES screening results with no acid pretreatment, it allows one to determine what percentage of the metals are present as solids and not dissolved in the liquid phase.

2.2. pH stability study

The stability of adjustments of brine pH was studied at room temperature and pressure using the four brine samples. Based on the various brine compositions, it was preliminarily determined to raise the pH from the initial pH values, which range from 2.3 to 4.2, to an upper pH limit below the point at which iron hydroxide precipitates. Iron hydroxide has a much lower solubility product ($K_{sp}=4.87\times10^{-17}$) than the hydroxyl forms of the other abundant cationic species. OH-2 had the highest iron composition, and accordingly a pH of 6.8 would promote precipitation. Accordingly, a pH value of approximately 6.3 was selected for the pH stability study, thus providing an upper limit well below 6.8.

Using a 0.24 M KOH solution, the pH of 100 ml brine samples was adjusted to approximately 6.3. The pH was measured to obtain a relationship between brine pH and time. During the first few hours following the addition of KOH, pH measurements were taken approximately every 5 to 10 min. After the initial few hours, pH was measured approximately every 12 h over a 12-day period. This experiment was conducted in triplicate to verify observations. The pH of the OH-1 brine that was the most stable in terms of the first pH adjustment to 6.3 was then adjusted to 8.8 and monitored over an additional 6-day period.
2.3. High pressure/high temperature reactions between CO₂ and brine

A 180 ml Parr high pressure/high temperature reactor (model series 4576, T316 stainless steel, custom 1.5 in. internal diameter) was used to conduct reactions between CO₂ and brine. Fig. 1 shows a schematic of the reactor system. A total of sixteen experiments of 6 h in duration were conducted using the OH-1 brine at temperatures of 75 and 150 °C and pressures of 600 and 1500 psi. Initial brine pH at the start of the experiments ranged from the brine’s natural pH of 4.2 to 9.0. The CO₂/brine mixture was constantly stirred at 400 rpms to promote interaction and to prevent the settling of precipitates. Initial experiments were conducted in which no liquid sampling occurred. However, later experiments utilized a liquid sampling valve for the extraction of brine samples throughout the course of the reactions.

Brine samples of 75 ml were used for the experiments in which no sampling took place, and 95 ml was used for the experiments in which samples were extracted. Although a specific volume of CO₂ was charged to the reactor, given the rates of carbonate formation, it can be assumed that the system operated as an open system with a constant supply of CO₂.

Prior to placing the brine in the reactor, the pH of the brine sample was adjusted using KOH in the same manner as previously described in the pH stability study. Following closing of the bomb cylinder, the body of the reactor was placed in the heater assembly and the thermocouple, stirrer drive system, and water coolant supply were put in place. The gas supply hook-up both for N₂ and CO₂ was attached at valve 3 (see Fig. 1). The system was then purged four times with CO₂ at 600 psi. After the final purge, the heating of the system began. Once the appropriate temperature was reached, the system was pressurized. For the experiments conducted at 600 psi, total pressure was supplied by CO₂.

Fig. 1. Schematic of the high pressure/high temperature reactor. Valves labeled 1 through 8 refer to the specific valves mentioned in the method used for experiment setup in Section 2.3.
In the cases performed at higher pressures (1500 psi), 600 psi of CO$_2$ was initially charged, with the remaining pressure requirement supplied by N$_2$. Coleman grade CO$_2$ of 99.99% purity and grade 5.0 UHP N$_2$ of 99.999% purity were used.

In the initial experiments in which no sampling occurred, the pressure was monitored and recorded approximately every hour. During the latter experiments in which sampling occurred, six samples of approximately 10 ml were extracted during the course of the run. The pH of the extracted samples was immediately measured to minimize cooling and degassing. The samples were then placed under refrigeration prior to analysis.

At the end of each experiment, the bomb cylinder was depressurized and removed from the heater assembly. Cooling of the bomb cylinder was accelerated by placing it in a cold tap-water bath at a level just below the split ring enclosure of the cylinder. Following cooling, the bomb cylinder was opened and the brine and precipitates were removed. The pH of the solution was immediately measured.

The brine was then gravity-filtered to remove solids. 10 ml of filtrate was collected and immediately refrigerated. The filter paper was rinsed using deionized water to retrieve solids. The solids were then dried in an oven at 90°C for approximately 24 h. Following drying, the solids were ground into a fine powder in preparation for characterization.

2.4. ICP-AES of liquid products

In order to verify the precipitation of specific carbonates, the liquid products were analyzed using ICP-AES. A quantitative analysis of the brine samples reveals how the elemental composition of brine changes during reaction with CO$_2$. Prior to analysis, all samples were gravity-filtered and stored in a refrigerator at 5°C. ICP-AES without acid pretreatment was used to analyze the 10 ml liquid samples collected at the end of each experiment and those extracted during experiments.

2.5. XRD of solid products

Solids recovered from the reactor experiments were analyzed using a Scintag model X-ray diffractometer. XRD analysis was conducted over an angle range of 20° to 60°. The scanning rate was continuous at 1.2°/min. The radiation wavelength was 1.5406 Å. A qualitative analysis of the solids allows the compositional changes in brine to be attributed to the precipitation of specific minerals.

3. Results and discussion

3.1. ICP-AES analysis of unreacted brine

Table 1 presents the ICP-AES screening results conducted with and without acid pretreatment, and also includes the pH, TSS, and TDS measurements of the natural untreated brine. For the four brine samples studied, the pH values are around 2.3, except for OH-1, which is less acidic with a pH value of 4.2. OH-1 perhaps has a higher pH than the other samples due to the fact that it has the lowest amount of suspended solids. Due to
reasons discussed in Section 3.2, a low TSS value indicates that a small amount of iron oxide precipitated and thus the pH did not severely drop. Brines PA-1 and OH-1 clearly have the largest amounts of TDS at 399,000 and 332,000 g/l, respectively. Due to the high measured concentrations of Na ions present within the brines, it is assumed that the abundance of TDS is due to large amounts of NaCl dissolved in solution. Both data sets in Table 1 reveal the major compositional differences between the brine samples. Importantly, PA-1 is representative of relatively calcium-rich brine, while OH-1 represents magnesium-rich brine. OH-1 also has a significantly lower iron concentration than the other three samples. Finally, the Pennsylvania samples show much higher concentrations of barium and strontium in comparison with the Ohio samples. In general, the differences between the two data sets reveal that 75 to 95% of the metals are in the liquid phase. An exception exists for iron in PA-2 and OH-1, in which approximately 55% is in the liquid phase.

These results clearly show the variability in brine composition that can be obtained even in the case of nearby wells, such as for PA-1 and PA-2, which are located only 5 miles apart. The chemical weathering of halite, carbonates, and feldspars (silicates) is responsible for the presence of dissolved metals in brine. The differences between various brine samples can be attributed both to differences in local geology and the depth from which brine is extracted. For example, [Sr] in brine usually increases with depth due to the increased dissolution of Sr-bearing carbonates, such as strontianite [(Sr, Ca)CO₃] [9]. Accordingly, the difference in depth between the Pennsylvania brines (2800 m) and the Ohio brines (1130 and 1158 m) may be related to the observed variance in [Sr].
3.2. pH stability study

Fig. 2 illustrates the results of the pH stability measurements conducted on the four brine samples. Results obtained from the OH-1 brine revealed the solution pH to be relatively constant over the 12-day period. In contrast, PA-1, PA-2, and OH-2 experienced a rapid decline in pH during the first 12 h, after which the decline seemed to level off. These results were well replicated with two additional duplicate experiments. This observed difference in stability of brine pH at an adjusted elevated value may be attributed to the major difference in iron composition in the liquid phase between OH-1 and the other samples. OH-1 has a significantly lower iron concentration than the other three brine samples (9 ppm for OH-1 vs. 224, 121 and 476 ppm for PA-1, PA-2 and OH-2, respectively). The oxidative precipitation of iron oxide, which is the transition of the soluble divalent ferric ion Fe$^{2+}$ to the oxidized insoluble trivalent form Fe(III) oxide, is responsible for reducing the pH [10].

The pH of OH-1 was then adjusted to 8.8 and stability was once again observed over an additional 6-day period. Further work is being conducted to understand the relationship between brine composition and observed pH stability. A current study using a buffer solution of 1.0 M NaCl and 0.6 M NaHCO$_3$ to adjust the brine pH as opposed to KOH will allow for a greater understanding as to whether the low iron content of the OH-1 brine is the cause of its stability. The use of this buffer solution will also allow for a comparison with KOH in terms of successfully treating natural brines to elevated pH values.

3.3. High pressure/high temperature reactions between CO$_2$ and brine

Table 2 summarizes sixteen experiments of 6 h that were conducted in the reactor. The OH-1 brine was used for these experiments based on its performance in the pH stability study. In this work, the sampled and final pH values reported are not quantitatively

![Fig. 2. pH stability of brine samples following a pH adjustment to approximately 6.3 for all samples, and an additional adjustment to 8.8 for OH-1.](image-url)
representative of the in situ pH, but are rather useful in making qualitative comparisons between experiments. When the samples used for pH measurements are withdrawn from the high temperature and pressure conditions of the reactor, CO2 degassing immediately takes place and thus has an effect on the measured pH values. As degassing progresses the pH will increase. Although the amount of time between sample extraction and measurement was minimized, the unconstrained degassing must be considered. Current research is addressing this issue with a modeling program for geochemical aqueous speciation-solubility calculations that can be used to back-calculate what the in situ pH was at specified reactor pressure and temperature conditions.

For the first twelve experiments, no sampling occurred and only final products were analyzed. Fig. 3 presents pH changes that took place during the reactions as a function of initial pH. Results show that the low temperature runs and the high temperature runs separately group together. The experiments conducted at higher temperature clearly reflect a higher final pH value. Experiments conducted at higher pressure also resulted in a higher final pH. In this work, temperature has a greater control on a higher final pH value than does pressure. The variation in pH over the course of the reaction as function of initial pH reveals a linear relationship for constant temperature and pressure. Fig. 3 also shows at which initial pH values one can expect an overall increase in pH over the course of the reaction. For example, if operating at 75 °C and 1500 psi, one can expect the pH to increase if the initial pH is 5.0 or below. If one assumes that pH is the main control on the ultimate precipitation of calcite, it can be concluded from these results that temperature has a greater effect on calcite precipitation than pressure. If higher temperatures produce a higher final pH then it is logical to conclude that during the course of the reaction the

Table 2
Experiments conducted to react CO2 with brine in the high pressure/high temperature reactor

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Pressure (psi)\textsuperscript{a}</th>
<th>Temperature (°C)</th>
<th>Initial pH\textsuperscript{b}</th>
<th>Final pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>600</td>
<td>75</td>
<td>4.78</td>
<td>4.97</td>
</tr>
<tr>
<td>2</td>
<td>600</td>
<td>150</td>
<td>4.78</td>
<td>5.83</td>
</tr>
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<td>3</td>
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<td>5.64</td>
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<td>600</td>
<td>75</td>
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<td>600</td>
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<tr>
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<td>1500</td>
<td>150</td>
<td>4.78</td>
<td>5.85</td>
</tr>
<tr>
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<td>1500</td>
<td>75</td>
<td>6.49</td>
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</tr>
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<td>10</td>
<td>1500</td>
<td>150</td>
<td>6.55</td>
<td>5.92</td>
</tr>
<tr>
<td>11</td>
<td>1500</td>
<td>75</td>
<td>8.95</td>
<td>5.05</td>
</tr>
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<td>75</td>
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<td>4.91</td>
</tr>
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</tr>
<tr>
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<td>1500</td>
<td>75</td>
<td>8.95</td>
<td>5.09</td>
</tr>
<tr>
<td>16</td>
<td>1500</td>
<td>150</td>
<td>8.95</td>
<td>5.86</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Pressures of 1500 psi represent a CO2 partial pressure of 600 psi and the remaining pressure supplied by N2. \textsuperscript{b} pH measurements were taken of the brine following refrigeration at 10 °C.
system spends more time at a pH value that is conducive to calcite precipitation. This conclusion is consistent with the results of a study by Soong et al. [11], in which similar experiments were conducted using an autoclave to react natural brines with CO₂ under high pressure and high temperature conditions.

For experiments 13 through 16, sampling occurred throughout the duration of the experiments. Fig. 4 shows the evolution of the pH during runs conducted with an initial pH of approximately 9. An initial drop in pH takes place due to the formation of carbonic acid, which likely happens entirely during the CO₂ purging process of the reactor prior to heating. This drop in pH as a result of pressurization corresponds to what was observed in comparable experiments conducted at 200 °C and 2900 psi by Kaszuba et al. [12], in which the pH dropped from 5.2 to 3.4 as indicated by ex situ measurements of extracted brine.
samples. Fig. 4 also shows that after approximately 30 min the pH of the low temperature runs remains constant, while the pH of the high temperature runs increases throughout the duration of the experiment. It is unclear as to how high the pH of the high temperature runs would continue to rise given a reaction time greater than 6 h. Current work is addressing this question by extending the reaction time to 18 h. This will hopefully either confirm an increase in pH or dismiss the observed trend as a fluctuation in the system.

3.4. ICP-AES of liquid products

Fig. 5 shows the results of the ICP-AES data for the Ca, Mg, Fe, and Na concentrations of the final liquid products of experiments 1 through 12. Ca, Mg, and Fe are shown because they are the metals most likely to form carbonate precipitates, such as calcite (CaCO₃), magnesite (MgCO₃), dolomite [CaMg(CO₃)₂], and siderite (FeCO₃). Na is shown because it is the most abundant metal. The controls are the corresponding elemental concentrations in the unreacted OH-1 brine as measured at the same time as the reacted samples.

The experiments that yielded precipitates that were successfully characterized as calcite by XRD (see Section 3.5) are runs 5, 6, 11, and 12, as highlighted in Fig. 5. The concentration of Ca decreases in all experiments with the exception of experiment 3. It should be noted that this anomaly is perhaps due to the fact that experiment 3 had the lowest final pH, as shown in Table 2. The dissolution of calcite is promoted at a low pH [11]. Therefore, it is expected that the Ca concentration in solution will be highest in the samples with the lowest final pH. Additionally, the experiments that yielded precipitates characterized as calcite did show the greatest decrease in Ca ranging from 6 to 11%, except for experiment 8, in which Ca decreased by 12%. The presence of the lowest concentration of Ca in experiment 8, which had an initial pH of 4.78, prevents a definitive linkage between the formation of calcite and a low final concentration of Ca.

Moreover, the lowest concentrations of Ca, amongst the runs that did yield calcite, were present in the runs conducted at 75 °C, which decreased by 9% in run 5 and 11% in run 11. The experiments conducted at 150 °C (experiments 6 and 12) both showed a decrease of 6%. This result did not support the previous claim that higher temperatures promote the greatest precipitation of carbonates. A longer reaction time under the same conditions, which is planned for current and future work, could potentially address whether this is observed as a result of a true influence of temperature or rather due to the uncertainty of experimental measurements.

The concentration of magnesium in Fig. 5 appears to remain relatively constant for the experiments, except for experiment 3, which was also the experiment that revealed a significant increase in Ca. The Na concentration was somewhat stable for the experimental runs. However, each dropped by 5 to 12% from the Na concentration of the control. Although the Fe concentration appears rather random, it is clear that Fe increases in the experiments conducted at 600 psi (runs 1 through 6) and decreases in the experiments at 1500 psi (runs 7 through 11). This suggests that the higher pressures are perhaps either promoting the precipitation of iron oxides or Fe-bearing carbonates, such as siderite.

Fig. 6 graphically shows the concentration of Ca and pH versus time for experiments 13 through 16, which had 10 ml samples extracted throughout the 6-h long reactions. These
Fig. 5. Ca, Mg, Fe, and Na concentrations as analyzed by ICP-AES of the final liquid products from experiments 1 through 12. The Fe concentration for experiment 12 is not available. The control represents an unreacted brine sample.
Fig. 6. Ca concentration and pH versus time for experiments 13 through 16. pH uncertainties are smaller than the size of the symbols.
experiments each had an initial pH adjusted to approximately 9 (see Table 2), which was determined based on the XRD results from experiments 1 though 12 that showed calcite precipitation only for the runs at an initial pH near 9 (see Section 3.5) The precipitation of calcite in experiments 13 through 16 was confirmed as well. The results in Fig. 6 do not illustrate any clear relationship between Ca concentration and pH. A decrease in the concentration of Ca is expected since calcite is formed and will hence remove Ca ions from solution and immobilize them in a solid mineral. However, the Ca concentration only appears to decrease for experiments 13 and 14, which were both conducted at 600 psi and 75 and 150 °C, respectively. Experiment 15 shows an overall increase in Ca. The Ca concentration reported in experiment 16 experiences a slight initial drop and then increases back to a value approximately the same as the starting concentration. The fact that a decrease in Ca is not observed in experiments 15 and 16 is likely because the system has not yet reached steady state. In this scenario a decrease in Ca due to the precipitation of calcite may be smaller than fluctuations in the Ca concentration; therefore, prohibiting measurements of the decrease in Ca due to the formation of calcite. This conclusion is supported by previous work of Kaszuba et al. [12]. In their system brine was reacted with silicate minerals at elevated temperatures and pressures and permitted to reach equilibrium. Next, CO2 was injected and chemical and pH changes of the brine were monitored over a time period of months. Kaszuba et al. found that their similar experimental setup, which operated at a pH of approximately 5 and at 200 °C and 2900 psi, took 1330 h to reach steady state.

3.5. XRD of solid products

XRD analysis of the first twelve experiments was performed to qualitatively characterize the precipitates. Very small amounts of precipitates were formed over a 6-h period; therefore, any effort to quantify produced solids proved difficult. XRD analysis
revealed calcite was formed in experiments with the highest initial pH value corresponding to 9, specifically experiments 5, 6, 11 and 12 as shown in Table 2. Powder XRD patterns of the solid precipitate obtained in experiment 11 are illustrated in Fig. 7. The peaks of calcite (CaCO$_3$); the most tightly-packed polymorph of calcium carbonate, and halite (NaCl) are clearly visible. Halite is present because the brines are both rich in Na and Cl. The precipitates were rinsed with water following filtration. However, extensive washing to thoroughly remove the halite was not conducted because it was found desirable to leave residual halite crystals in order to yield sufficient amounts of solid samples for XRD analysis.

4. Conclusions

The large estimated storage capacity for CO$_2$ in deep brine formations and the existence of substantial volumes of produced brine at the surface warrants an investigation into the parameters of the carbonate forming reactions. This work has shown that certain brines are more stable following an adjustment to an elevated pH using KOH. Preliminary experiments suggest low iron content within the OH-1 brine is the probable cause. Future work to compare the use of either KOH or a buffer solution of 1.0 M NaCl and 0.6 M NaHCO$_3$ to treat various brines will help to address this issue and to further understand brine pH stability.

In terms of the high pressure/high temperature CO$_2$/brine reactions, temperature has a greater influence on a high final pH value as opposed to pressure. Therefore, it is likely that temperature has a greater influence on calcite precipitation than pressure. At a high temperature of 150 °C and an initial pH of 9, the pH of brine increases, following the initial drop due to the formation of carbonic acid, toward a pH value that promotes the precipitation of carbonates. A much longer analysis time is needed to determine the extent of this increase. Present work using ICP-AES to correlate changes in brine composition (Ca, Mg, and Fe) with pH changes and the precipitation of carbonates has yet to prove conclusive using a reaction time of 6 h. A much longer analysis time on the order of weeks or months is potentially needed to reach steady state. XRD has verified that calcite formation is achievable on a time scale of 6 h given an initial pH of 9, and temperatures and pressures between 75 to 150 °C and 600 to 1500 psi, respectively.

The findings of this study have primary implications for an above-ground carbon sequestration operation using brine. Brine pH, which has been identified as having the greatest control on the precipitation of calcite, as opposed to temperature or pressure, is capable of adjustment when stored at the surface. However, brine composition plays a role in its ability to maintain an elevated pH following adjustment, yet prior to reaction with CO$_2$. Feasibility for an industrial scale operation is currently limited by the extent that pH needs to be elevated to promote the rapid formation of carbonates.

Future work will address longer CO$_2$/brine reaction times on the order of days. This expansion will help to further identify in situ trends of brine composition and pH. Current work is also aimed at analyzing brine samples extracted during the course of the reactions in terms of not only Ca but of other major carbonate forming elements as well, such as magnesium and iron. Additionally, the characterization of solid products will be improved.
by accompanying XRD analysis with SEM/EDS (Scanning Electron Microscopy/Energy Dispersive Spectroscopy) data. SEM provides a magnified image of a solid surface, while EDS identifies and quantifies the elemental composition of an area on that surface. A better understanding of the chemical composition and microstructure of the precipitates formed during the CO2/brine reactions will result.

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