PARAMETRIC INVESTIGATION OF CARBON SEQUESTRATION USING BRINE

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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 US production is over 20 billion gallons.[1] The existence of large volumes of brine at the surface provides a potential feedstock for the conversion of CO_2 into geologically stable mineral carbonates, such as calcium carbonate and magnesium carbonate. Under the appropriate conditions, CO_2 dissolves in brine to initiate a series of reactions that ultimately leads to the bonding of carbonate anions to various metal cations inherent in brine to precipitate carbonates.

In addition to ex-situ processing to efficiently drive the reaction, much emphasis has been placed on the injection of CO_2 into subsurface saline formations. US deep saline aquifers are estimated to provide storage for approximately 130 giga-tons carbon equivalent, which is approximately 80 times the US's total carbon emissions in 2001.[2,3] Following the injection of anthropogenic CO_2 below a typical depth of 800 meters, the storage mechanism is initially hydrodynamic as the CO_2 is stored as a dense supercritical fluid. On a separate timescale, and following the dissolution of CO_2 in brine, chemical interactions with the brine may form mineral carbonates.[4]

The rate of the mineral trapping process is slow and serves as the major disadvantage of this technology.[5] It was suggested by Soong et al.[5] that pH has a significant effect on both conversion rates and on the specific species that are precipitated. The conversion to 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 objective of this study is to further investigate the effects of temperature, pressure, and most importantly pH on the formation of mineral carbonates during the reaction of CO_2 with various natural gas well brines. 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 a brine's ability to maintain an elevated pH over time.

Experimental

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 a 1158 m well in Guernsey, Ohio and a 1030 m well in Youngstown, Ohio, respectively.

ICP-AES Analysis. The brine samples underwent analysis by inductively coupled plasma – atomic emission spectroscopy (ICP-AES) screening with no acid pretreatment to determine the elemental metal concentrations in the liquid phase. Additionally, ICP-AES screening following acid treatment with HNO_3 was conducted to determine the total metal concentration in solution.

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 to a value low enough so that iron hydroxide did not precipitate. Iron hydroxide has a much lower solubility product ($K_{sp} = 4.87 \times 10^{-17}$) than the hydroxyl forms of the other metals. OH-2 had the highest iron composition, and accordingly a pH of approximately 7 would promote precipitation. Using a 0.24 M KOH solution, the pH of each brine sample was adjusted to approximately 6.3. Over a five-day period, the pH was measured using a digital pH meter to obtain a relationship between brine pH and time.

Autoclave CO_2/Brine Reactions. A 250 ml Parr high pressure/high temperature reactor (model series 4576, T316 stainless steel) will be used to conduct reactions between CO_2 and brine. A liquid sampling valve will allow for brine extraction throughout the course of the reaction. Various experiments of 12 hours in duration will be conducted at temperatures and pressures between 20 to 200 °C and 200 to 1200 psi, respectively. Initial brine pH will range from the inherent pH to 11. The CO_2/brine mixture will be constantly stirred to promote interaction and to prevent the settling of precipitates. Samples extracted from the autoclave during reaction will be analyzed using ICP-AES, and the pH will be measured. Additional experiments will be conducted in which no liquid sampling will occur. These studies will yield precipitates that will be characterized using X-ray diffraction (XRD).

Results and Discussion

Brine Characterization. Table 1 presents the ICP-AES analysis results conducted with and without acid pretreatment, and also includes the pH measurements of the natural untreated brine. For the four brine samples studied, the pH values are around 2.3, except for OH-2, which is less acidic with a pH value of 4.2. Both data sets reveal the major compositional differences between the brine samples. Importantly, PA-1 is representative of a relatively calcium-rich brine, while OH-1 represents a 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.

Table 1. Metal Concentrations (ppm) as Analyzed by ICP-AES and pH of the Brine Samples

	PA-1	PA-2	OH-1	OH-2
pH	2.3	2.4	4.2	2.3
No Acid Pretreatment				
Ba	1021	696	<5	<5
Ca	33515	21460	19570	19350
Fe	224	121	9	476
K	2520	1490	2225	1180
Mg	1975	1215	3440	2055
Na	60680	41040	69660	48500
Sr	11170	8380	2000	1800
Acid Pretreatment with HNO_3				
Ba	1270	789	5.66	7.3
Ca	42900	23600	22500	21600
Fe	295	223	15.9	635
K	3270	1770	2560	1380
Mg	2650	1440	4070	2380
Na	74400	44900	78900	53900
Sr	13800	8910	2330	2020

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.

pH Stability Measurements. Figure 1 illustrates the results of the pH stability measurements conducted on the four brine samples. OH-1 behaved uniquely in the pH stability study as it was the only brine that remained near the adjusted pH value over the five-day period. The pH of OH-1 remained especially constant over the entire course of the study. In contrast, PA-1, PA-2, and OH-2 experienced a rapid decline in pH during the first 12 hours, after which the decline seemed to level off. 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). Further studies are being conducted to understand the relationship between brine composition and observed pH stability.

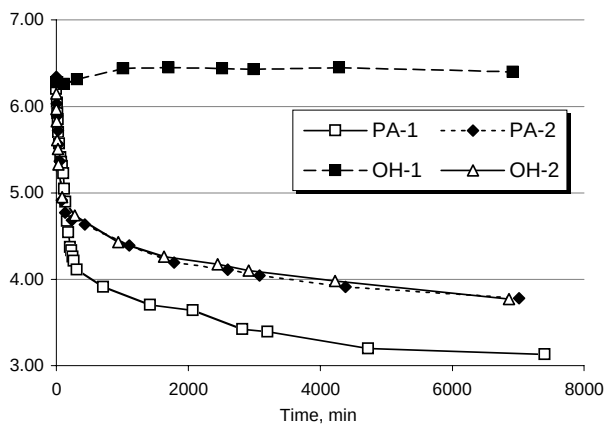

Figure 1. pH measurements of brine samples that underwent a pH adjustment to approximately 6.3 using KOH.

CO_2/Brine Reactions. CO_2 reacts with brine's metal cations to form carbonate precipitates via the following reaction sequence, in which selected likely precipitates are shown:[5,6]

$$CO_2(g) \Leftrightarrow CO_2(aq) \quad (1)$$
$$CO_2(aq) + H_2O \Leftrightarrow H_2CO_3 \quad (2a)$$
$$H_2CO_3 \Leftrightarrow H^+ + HCO_3^- \quad (2b)$$
$$CO_2\,(aq) + OH^- \Leftrightarrow HCO_3^- \quad (3)$$
$$HCO_3^- \Leftrightarrow H^+ + CO_3^{2-} \quad (4)$$
$$Ca^{2+} + CO_3^{2-} \Leftrightarrow Ca\,CO_3\downarrow \quad (5a)$$
$$Mg^{2+} + CO_3^{2-} \Leftrightarrow Mg\,CO_3\downarrow \quad (5b)$$
$$Ca^{2+} + Mg^{2+} + 2CO_3^{2-} \Leftrightarrow CaMg(CO_3)_2\downarrow \quad (5c)$$

The dissolution of CO_2 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, which is necessary to form the carbonate minerals in reactions 5a through 5b. The pH determines which steps dominate the reaction sequence, and accordingly the proportions of the carbonic species.[6] At a low pH (~4), the production of H_2CO_3 dominates, at a mid pH (~6) HCO_3^- production dominates, and at a high pH (~9) CO_3^{2-} dominates.[5] Therefore, at a basic pH the precipitation of carbonate minerals is favored because of the availability of carbonate ions. Oppositely, the dissolution of carbonates increases as the solution becomes increasingly more acidic. The rate limiting step of the overall conversion to carbonates has been identified as the hydration of CO_2 in reaction 2a, which has a forward reaction rate constant of $6.2 \times 10^{-2}\ s^{-1}$ at 25 °C and zero ionic strength.[7]

Conclusions

The abundance of brine both at the surface due to the production of oil and natural gas and in subsurface saline aquifers provides the capacity to sequester a significant amount of anthropogenic CO_2. Subsurface saline aquifers may sequester CO_2 in various forms. However, any ex-situ sequestration process will rely on an efficient conversion to mineral carbonates. An investigation into the parameters, most importantly pH, that affect this conversion rate is warranted. The evolution of brine pH following a pH adjustment and during reaction with CO_2 at various temperatures and pressures is highly variable.

Preliminary results reveal large differences in the metal concentrations of brines from various depths and locations. These compositional differences are related to brine's ability to maintain an elevated pH after treatment with a strong base to address the natural acidity of brine. The CO_2/brine reactor system described herein will allow for the achievement of a relationship between pH and the formation of specific mineral carbonates throughout the duration of an experiment.

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