

# UNDERSTANDING CARBONATE FORMATION DURING CARBON DIOXIDE SEQUESTRATION IN SALINE BRINE FORMATIONS



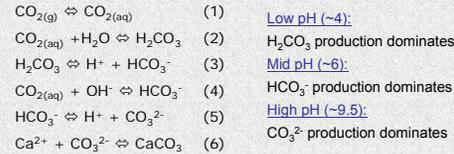
M. Mercedes Maroto-Valer and Matthew L. Druckenmiller

The Energy Institute and The Department of Energy & Geo-Environmental Engineering, The Pennsylvania State University

## Introduction

- With the proximity of US electricity generators to deep saline formations of large estimated capacity, geologic sequestration is a capable method to reduce the US's CO<sub>2</sub> emissions, which in 2001 were 1.57 GtC; 24% of the total global carbon releases from CO<sub>2</sub>.<sup>1</sup> The total US available storage in deep saline aquifers is estimated to be 130 GtC carbon (~ 83 times the US emissions of carbon in 2001).<sup>2</sup>
- Additionally, the existence of large volumes of easily accessible subsurface brine at the surface provides a potential high capacity route for the conversion of CO<sub>2</sub> into geologically stable mineral carbonates, such as calcium carbonate and magnesium carbonate. (Refer to the chemical reactions at right.)
- Subsurface saline aquifers may sequester CO<sub>2</sub> in various forms. However, any ex-situ sequestration process will rely on an efficient conversion to mineral carbonates. The rate of the mineral trapping process is slow and serves as the major disadvantage of this technology. It has been suggested that pH has a significant effect on both conversion rates and on the specific species that are precipitated.<sup>3</sup>
- An investigation into the parameters, most importantly pH, that affect this conversion rate is warranted since the evolution of brine pH following a pH adjustment and during reaction with CO<sub>2</sub> at various temperatures and pressures is highly variable.

## Chemistry

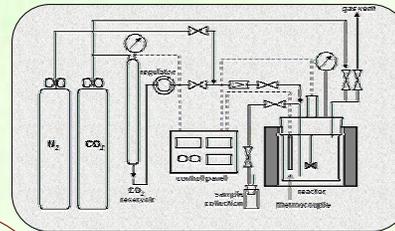


*A basic solution favors the precipitation of carbonates, while an acidic solution favors the dissolution of carbonates. The rate limiting step at a low to mid pH is the hydration of CO<sub>2</sub> to form carbonic acid, and at a high pH it is the formation of HCO<sub>3</sub><sup>-</sup> via reaction 3.*<sup>3,4</sup>

## Method

- Four brine samples were obtained from natural gas wells in the Eastern U.S. Oriskany Sandstone Formation, two from Pennsylvania (PA-1 and PA-2) and two from Ohio (OH-1 and OH-2).
- Brine samples underwent characterization analysis by inductively coupled plasma – atomic emission spectroscopy (ICP-AES) to determine the total concentration ions (Ca<sup>2+</sup>, Mg<sup>2+</sup>, etc.) necessary for carbonate formation.
- Brine pH was adjusted using KOH to address the natural acidity. The stability of the adjustments of pH were studied at room temperature and pressure.
- A 180 ml Parr high pressure/high temperature CSTR reactor was used to conduct reactions between CO<sub>2</sub> and brine. A liquid sampling valve allowed for brine extraction throughout the course of the reactions. Various experiments were conducted at temperatures and pressures between 75 to 150 °C and 600 to 1500 psi, respectively. Initial brine pH ranged from the natural pH to 9.
- The evolution of pH during the CO<sub>2</sub>/brine reactions was monitored. The formation of carbonates was observed by the characterization of precipitates using x-ray diffraction (XRD) and measured changes in brine solution composition using ICP-AES.

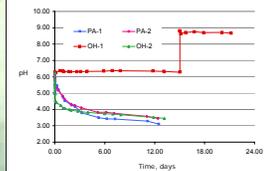
## Reactor Schematic



## Results

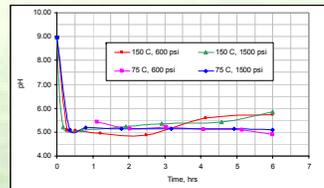
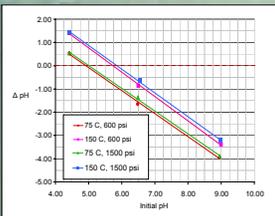
**Figure 1. pH stability**

The pH of the four brines was adjusted to approximately 6.5, and monitored over 12 days. OH-1 behaved uniquely as it was the only brine that remained near the adjusted pH value. This observed difference in stability may be attributed to the difference in [Fe<sup>2+</sup>]. OH-1 has a significantly lower iron concentration than the other three brine samples (25 ppm for OH-1 vs. 260, 117 and 559 ppm for PA-1, PA-2 and OH-2, respectively). OH-1 was then adjusted to a pH of 8.8, and pH stability was once again observed. For this reason OH-1 was used as the experimental brine in the high temperature/high pressure CO<sub>2</sub>/brine reactions.

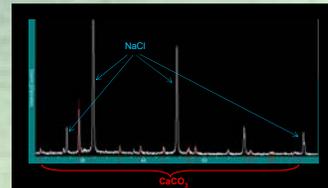


**Figure 2. pH drop during CO<sub>2</sub>/brine reactions**

12-6 hour experiments were conducted in the CSTR. The low temperature runs group together and the high temperature runs group together. Secondly, the runs at the higher temperatures clearly all have a higher final pH value. Higher pressure results in a higher final pH, however, temperature has a greater control on a higher final pH than pressure.



**Figure 3. pH evolution during CO<sub>2</sub>/brine reactions**  
An initial drop in pH takes place due to the formation of carbonic acid. After 30 minutes, the pH of the low temperature runs remains constant, while the pH of the high temperature runs steadily increases throughout the duration of the experiment.



**Figure 4. XRD Analysis**  
Calcite (CaCO<sub>3</sub>) precipitate formation is verified, amongst NaCl crystals, which are unavoidable when removing precipitates since the brines are rich in NaCl. [This specific pattern is from a 6 hour experiment with OH-1 at 150 °C, P<sub>CO2</sub> = 600 psi, P<sub>total</sub> = 1500 psi, and an initial pH of 6.97.]

## Conclusions

- The large estimated storage capacity for CO<sub>2</sub> in deep brine formations and the existence of substantial volumes of produced brine at the surface warrants an investigation into the kinetics of the carbonate forming reactions.
- Certain brines are more stable following an adjustment to an elevated pH using KOH. Initial experiments suggest that a low iron content is the cause.
- In terms of the high pressure/high temperature CO<sub>2</sub>/brine reactions, temperature has a greater influence on a high final pH value as opposed to pressure. At high temperatures (~150°C), the pH of brine increases, following the initial drop, toward a pH value that promotes the precipitation of carbonate minerals. A much longer analysis time is needed to determine the extent of this increase.
- XRD has verified that calcite formation is achievable on a time scale of 6 hours given the experimental conditions described herein.
- Present work using ICP-AES to correlate changes in brine composition (Ca<sup>2+</sup>, Mg<sup>2+</sup>, Fe<sup>2+</sup>) with pH changes and the precipitation of carbonates has yet to prove conclusive.

## References

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