Mineral Trapping of CO_2 with Oriskany Brine

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INTRODUCTION

The main greenhouse gas from combustion of fossil fuel is carbon dioxide (CO_2), the major contributor to global warming [1]. While many studies to capture and sequester CO_2 are currently being conducted, geological sequestration is an immediately available and technologically feasible option [2]. Carbon dioxide may be sequestered in various geological formations, such as depleted oil and gas reservoirs, uneconomic coal beds for coal bed methane recovery, and deep saline aquifers [1]. Among many geologic CO_2 sequestration options, injection into saline aquifer formations is one of the most promising one. This option is attractive, because there are regionally extensive aquifers capable of accepting large volumes of CO_2 from power plants without the need for long transport pipelines. Upon injection of CO_2 into saline aquifers, CO_2 may be stored by hydrodynamic and/or mineral trapping. The most critical concern of hydrodynamic trapping is the potential for CO_2 leakage through imperfect confinement. In mineral trapping, CO_2 is converted into carbonate minerals by a series of reactions with aqueous ions found in the saline aquifer. Various carbonates such as calcite, magnesite, dolomite, and siderite can be formed in the brine aquifer. These carbonate minerals can be stored in saline aquifer formations for millions of years [1-4]. However, conversion of CO_2 to stable carbonate minerals is expected to be slow. Researchers from Alberta Research Council in Canada [3] calculated times for precipitation of the various carbonates to be on the order of hundreds of years. These results suggest that mineral trapping may contribute significantly to CO_2 sequestration within saline aquifers but only in the long term.

Sass et al., [5] studied CO_2 and brine reactions with mineral rocks for 7 days at a pressure of 5.44 MPa and 110 °C. They found increased levels of Ca, Mg, and carbonate in solution, due to the dissolution of dolomite. Lebro'n and Suarez [6] reported the precipitation rate of calcite increased as the partial pressure of CO_2 increased (0.035 to 10 kPa). Their interpretation suggested that by increasing the partial pressure of CO_2, the solution pH decreases and the ionic strength increases. These conditions strongly influence nucleation of new calcite crystals. However, no extensive laboratory studies directed at the sequestration of CO_2 in brine aquifers have been conducted. In the present investigation, brine from the Oriskany Sandstone aquifer of the Appalachian Basin is examined to assess its ability to sequester CO_2 in the near term *via* the mineral trapping pathway upon reaction with CO_2.

A simulation program, PHREEQC [7], was used to model carbonation of Oriskany brine. PHREEQC is designed to perform a variety of low-temperature aqueous geochemical calculations. PHREEQC simulates chemical reactions and transport processes in natural as well as polluted waters. It is based on equilibrium chemistry of aqueous solutions interacting with minerals, gases, solid solutions, exchangers, and sorption surfaces. PHREEQC can be used as a speciation program to calculate saturation indices, distribution of aqueous species, and moles of solid precipitate. For an equilibrium calculation, each component in the system is distributed among the aqueous phase, pure phases, solid solutions, gas phase, exchange sites, and surface sites to attain system equilibrium. Furthermore, it is possible to simulate precipitation of solid solutions from supersaturated conditions with no pre-existing solid and to dissolve solid solutions completely.

This study attempts to evaluate the ability of Oriskany brine alone to serve as a mineral trapping medium. It is prudent to investigate the variables that effect mineral carbonates formation in brines in the absence of complicating factors introduced by the presence of formation rocks. Specifically, the effects of pH, CO_2 pressure, and temperature on the reaction between CO_2 and brine to form carbonate minerals were studied. The optimum reaction conditions that favor the formation of mineral carbonates were investigated with autoclave experiments and geochemical modeling.

EXPERIMENTAL

To examine the process of mineral trapping under controlled temperature and pressure conditions in an autoclave

reactor, brine samples were collected from the Oriskany Sandstone aquifer in Indiana County, PA. Samples were collected directly from the well after purging at a formation depth of 2,800 meters. No effort was made to prevent oxygen from contacting the brine. The brine was tested as received without further filtration.

Brine carbonation experiments were carried out in a ½ liter autoclave (Hastelloy C-276) manufactured by Progressive Equipment Corp. A schematic representation of the laboratory apparatus is shown in Figure 1. Experiments were conducted in the batch-mode [8]. In a representative experiment, the reactor was charged with 180 ml of brine. The reactor was purged/evacuated with carbon dioxide three times. Finally, a predetermined amount of CO_2 was charged into the reactor to achieve the desired testing pressure. The brine-CO_2 mixture was agitated at 400 or 800 rpm during both heating to the desired temperature and testing to prevent the settling of precipitate. At the completion of each test, the slurry was cooled to room temperature. The remaining CO_2 was vented, and the slurry was removed from the reactor and filtered to separate the solids from the aqueous solution. A digital pH meter (Sentron-1001 pH) was used to determine the pH of the brine before and after reaction. The pH meter was calibrated with buffer solutions before each measurement. The brine was either used as received, or the pH was adjusted before reaction by adding KOH. The effects of pH (3.6 to 11), CO_2 pressure (0.34 to 7.63 MPa), and temperature (50 to 170°C) on brine carbonation were investigated.

The brines and brine carbonation products were prepared for analysis by filtration through a 0.45 m membrane (Millipore - type HA) aided by reduced pressure provided by a water aspirator. The collected solids were rinsed with deionized water on the membrane and dried in a nitrogen-purged oven at 110°C. The filtered solutions were acidified (pH < 2.0) by adding trace metal grade nitric acid. Due to the high concentration of alkali and alkaline earth metals in solutions, 200-fold dilutions were prepared using distilled, deionized water. Metal concentrations were then determined using inductively coupled plasma - atomic emission spectroscopy (ICP-AES) on a Perkin Elmer Optima 3000 ICP spectrometer. The determinations were performed using an online internal standard to correct for variations during sample introduction. The reproducibility of the analytical results for cations by ICP is approximately +/- 3%. A low-flow gem cone nebulizer was employed so that solids loading could be accommodated, and a glass cyclonic spray chamber was employed to minimize contamination between analyses.

RESULTS AND DISCUSSIONS

The autoclave experiments and simulations were conducted to study the reaction of CO_2 with brine samples as a function of pH at constant temperature (155°C) and CO_2 pressure (6.87 MPa) (Figure 2). In the autoclave experiments the initial pH was adjusted from 3.6 to 11.0 by adding KOH. After reaction, the pH of the solution was measured and found to be lower than the starting pH (Figure1a – solid circles). A similar trend between the pH before reaction and the pH after reaction with CO_2 is observed in the simulation results (Figure 2a – dashed line). The pH of the brine decreases following reaction with CO_2 because CO_2 dissolves in solution to form carbonic acid, H_2CO_3. In addition, CO_2 is not present after reaction because the reactor was depressurized. Ca and other metals are removed from solution by precipitation, causing the remaining solution become more acidic. The mineral dolomite was not allowed to precipitate in the simulation even though the saturation index for it was positive. The kinetics for dolomite precipitation are relatively slow and it is likely that this mineral may not precipitate out of solution [9]. In addition, XRD analysis of the solid precipitate from the autoclave reactions did not detect dolomite.

As the initial pH of the raw aqueous brine was increased from 3.6 to 11, the concentration of the aqueous ion Ca in the reacted brine decreased by 25 %. The total grams of precipitate increased from 0.08 to 7.5 g/L (Figure 2b – solid circles). The simulation results indicate a similar trend as pH increases, the total grams of solid precipitate increases from 0.1 grams at pH 2.7 to 30.5 grams at pH 11 (Figure 2b – dashed line). However, the total grams of precipitate predicted by the model deviates significantly from experimental observations in that the model predicts almost four times as much solid precipitate than is observed experimentally. This may be due to the fact the simulation is predicting total grams of precipitate under equilibrium conditions, while the total grams solid precipitate from the autoclave experiments is measured after six hours of reaction followed by degasing CO_2 and cooling down to room temperature. Although the results obtained experimentally and by simulation differ on the amount of solid precipitate formed as pH is increased, both results follow the same general trend in that the total mass of solid precipitate increases as the pH increases (Figure 2b). Only 0.09 g of Ca per gram of precipitate was observed at the initial brine pH of 7.2. Significantly more Ca precipitate was observed after the initial brine pH was increased to 9 and higher. The concentration of solid Ca precipitate increased by one order of magnitude

(Figure 2c). The XRD analyses of the solid precipitate from the autoclave reactions identified $CaCO_3$ (major) and Fe_2O_3 (minor) to be the main components of the solid samples at pH values greater than 9. Thus, the grams of $CaCO_3$ per total grams of precipitate (g Ca/g ppt) increases as the pH value is raised from 9 to 11 (Figure 2c).

Next, a series of autoclave experiments and simulations were conducted to study the reaction of CO_2 with brine samples as a function of pressure at constant pH (pH = 11.0) and temperature (155 ^oC) (Figure 3). The CO_2 pressure was varied from 0.34 to 7.64 MPa. The pH after reaction, concentration of the aqueous components, total grams of precipitate, and grams of Ca per total grams of precipitate *versus* pressure did not change significantly as pressure was increased (Figure 3a-c). Based upon these results, pressure does not seem to play a large role in the formation of carbonate minerals as long as a minimum CO_2 pressure is maintained in the reactor. Therefore, high CO_2 pressures are not required for the precipitation of carbonate minerals from Oriskany brine.

Finally, a series of autoclave experiments and simulations were conducted to study the reaction of CO_2 with brine samples as a function of temperature at constant pH (pH = 11.0) and CO_2 (0.34 MPa) pressure (Figure 4a-c). The temperature was varied from 50 to 170 ^oC. The pH after reaction, concentration of the aqueous components, total grams of precipitate, and grams of Ca per total grams of precipitate *versus* temperature changed very little for the autoclave experiments (Figure4a-c). However, the simulation results predict a general increase in total grams of precipitate and grams of Ca per total grams of precipitate *versus* temperature. The simulation predicts total grams of precipitate under equilibrium conditions, while the total grams solid precipitate from the autoclave experiments is measured after six hours of reaction followed by CO_2 degassing and cooling from reaction temperature to ambient condition. From these results, the experimental data suggests that temperatures above 50^oC do not play a large role in the formation of carbonate minerals.

Mineral trapping may occur *via* simplified reactions (1-5) shown below. CO_2 gas dissolves into solution (1) and reacts with water to form carbonic acid (2). Then, equilibrium is established between the dissolved CO_2 and H2CO3, carbonic acid (2), which then dissociates into bicarbonate (3) and carbonate ions (4). Thus, pH of an aqueous solution decreases with the addition of CO_2 [6,10]. As carbon dioxide dissolves in brine, an equilibrium is established involving the carbonate ion, CO_3^{2-}. Then carbonate anion interacts with cations in brine. Ions such as Ca, Mg, and Fe react with carbonate ions to form minerals such as calcite, dolomite, siderite, and magnesite (5a-5d), respectively.

1) $CO_2\ (gas) \quad CO_2\ (aq)$

2) $CO_2\ (aq) + H_2O \quad H_2CO_3$

3) $H_2CO_3 \quad H^+ + HCO_3^-$

4) $HCO_3^- \quad H^+ + CO_3^{2-}$

5a) $Ca^{++} + CO_3^{2-}$ <--> $CaCO_3$ (calcite)

5b) $Ca^{++} + Mg^{++} + CO_3^{2-}$ <--> $CaMg(CO_3)_2$ (dolomite)

5c) $Fe^{++} + CO_3^{2-}$ <--> $FeCO_3$ (siderite)

5d) $Mg^{++} + CO_3^{2-}$ <--> $MgCO_3$ (magnesite)

The pH of the brine affects the reaction rate and species precipitated. In a closed system dissolved carbon dioxide, CO_2(aq) and H_2CO_3 (carbonic acid) dominate at low pH, HCO_3^- (bicarbonate) dominates at mid pH, and CO_3^{2-} (carbonate) concentration increases at high pH. The solubility of carbonate also increases as the pH decreases. Thus, aqueous-phase equilibrium with CO_2(g) promotes carbonate precipitation under basic conditions, while acidic conditions favor carbonate dissolution. Therefore, to favor the precipitation of mineral carbonates, the pH must be basic. As demonstrated here, brine pH affects whether carbonate minerals will precipitate from solution (Figure 2c).

Mineral trapping is also controlled by CO_2 pressure and temperature but by a lesser extent when compared to pH. Temperature and pressure also play an important role in determining the solubility of CO_2 in solution [11]. However, experimental results suggest that temperature does not play a major role in brine carbonation above 50^oC (Figure 4). The CO_2 pressure affects the CO_2-brine reaction, but is very dependent upon pH. Dreybodt et al. [12] conducted a study of the precipitation kinetics of calcite in the system $CaCO_3$-H_2O-CO_2. They concluded that the rate limiting step is equation 3, the formation of HCO_3^- (bicarbonate). If the same rate limiting

step applied to CO_2-brine system, then the pH of the system controls the outcomes of the reactions. Basic environments at high pH condition, pH= 11, provide an abundant supply of OH^-(aq), that leads to the formation of HCO^-_3 and CO_3^{2-} and finally the formation of $CaCO_3$. The formation of calcite is expected to slow, once the OH^- (aq) is consumed. The pH also determines the amount of CO_2 can be dissolved in brine. Therefore, pH has more impact on the carbonation reaction than temperature and pressure. The overall equilibrium equation for calcite formation can be described by equations 6 and 7:

6) $$Ca^{2+} + CO_2(g) + H_2O \qquad CaCO_3(s) + 2H^+$$

7) $$K = \frac{[H^+]^2}{[Ca^{2+}]P_{CO2}}$$

According to equation 7, the calcite formation is dependent upon the square of hydrogen ion concentration, CO_2 pressure, and Ca ion concentration. As shown in Figure 3, when the CO_2 pressure increases, the amount of calcite precipitate remains the same. As the CO_2 pressure is increased, the pH decreases because carbonic acid is formed. As CO_2 pressure continues to increase, the pH drops from 11 to 4.5. At low pH values, calcite no longer precipitates from solution. As discussed earlier, calcite precipitation is favored at high pH, while calcite dissolution is favored at low pH. Thus, the amount of Ca precipitate is limited by the pH, not the CO_2 pressure, as long as a minimum CO_2 pressure is maintained in the reactor. In order to increase the amount of $CaCO_3$ precipitation with increasing CO_2 pressure, the pH will need to be buffered at values higher than 9.0.

The application of PHREEQC to model carbon sequestration is limited because PHREEQC was designed to model natural waters at ambient temperatures. Two of the most important concerns for modeling a CO_2/brine system with PHREEQC are the high ionic strength of the brine and the CO_2 pressure. PHREEQC uses ion-association and Debye-Huckel expressions to account for the non-ideality of aqueous solutions. This type of aqueous model is adequate at low ionic strength but may break down at higher ionic strengths found in brine, (ionic strength > 0.26). Others have attempted to extend the range of applicability of the PHREEQC model to higher ionic strength systems through the use of an ionic –strength term in the Debye-Huckel expressions [13]. These terms have been fit for the major ions using chloride mean-salt activity-coefficient data. Thus, in sodium chloride dominated systems such as brines, the model may be reliable at higher ionic strengths. For high ionic strength waters, it is recommended to incorporate the Pitzer equations, which combined the Debye-Huckel equation with additional terms to account for high ionic strength [14]. For the brine samples modeled in this study the ionic strength calculated with Na and Cl ions is 5.

All gas components in PHREEQC are assumed to behave according to the ideal gas law. The fugacity (activity) of a gas component is assumed to be equal to its partial pressure. For CO_2 pressures (3 MPa and greater) and temperatures (155 ^oC) used in this study, CO_2 does not behave as an ideal gas. At 25 °C and 5 MPa, for example, CO_2 deviates from the ideal gas law by a factor of 0.72.

Another limitation of PHREEQC and most geochemical models in general is a lack of internal consistency in the data in the databases. Typically log K's and enthalpies of reaction have been taken from various literature sources. No systematic attempt has been made to determine the aqueous model that was used to develop the individual log K's or whether the aqueous models defined by the current database files are consistent with the original experimental data. For this study, the Lawrence Livermore National Laboratory database (llnl.dat) was chosen over the default database for PHREEQC (phreeqc.dat), because the llnl.dat is more complete in that it contains more mineral species and includes expressions for calculation of equilibrium conditions at temperatures between 0-300 °C.

The reactions between CO_2 and the brine can be modeled as either an open or closed system. In a closed system, a fixed number of moles of CO_2 are allowed to react with the brine. In an open system, a head pressure of CO_2 above the brine sample is defined. An infinite supply of CO_2 is then available during the reaction in order to maintain user-defined head pressure. The experimental apparatus in this study is a closed reactor, because the CO_2 is charged into the reactor to a desired head pressure and the supply of CO_2 is then shut off. However, the CO_2 pressures used for the autoclave experiments are in excess, in

other words, the amount of CO_2 charged to the reactor is large when compared to the amount of CO_2 consumed during reaction (CO_2 consumed is < 35%). Thus, the autoclave reactor essentially behaves like an open system. The reactions investigated with PHREEQC assume CO_2 is reacting with the brine in an open system unless stated otherwise.

In summary, the current model is not able to predict the exact experimental observations. However, the model is capable of demonstrating the general trends, such as the effects of pH and the CO_2 pressure on the mineral trapping process.

CONCLUSIONS

The reactions between CO_2 and brine samples collected from the Oriskany formation in Indiana County, PA were investigated experimentally using a ½ liter autoclave under various conditions and theoretically using the geochemical code PHREEQC. The experimental results indicate that the amount of calcite precipitate depends primarily on the pH of the brine. The CO_2 pressure and temperature have lesser impact on the formation of carbonates. Furthermore, the simulation model used in this investigation is able to predict the trends on the effects of pH and CO_2 pressure in the carbonation reaction.

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Figure 1. Schematic diagram of the experimental apparatus.

Figure 2. Comparison of experimental and predicted results for brine carbonation as a function of pH under reaction conditions at 6.87 MPa CO_2 and 155 ^oC. a. pH after reaction versus pH before reaction. b. Total grams of precipitate per liter of solution versus pH before reaction. c. Grams of precipitated Ca^{2+} per total grams of precipitate versus pH before reaction.

Figure 3. Comparison of experimental and predicted results for brine carbonation as a function of CO_2 pressure at pH 11 and 155 ^oC. a. pH after reaction versus CO_2 pressure. b. Total grams of precipitate per liter of solution versus CO_2 pressure. c. Grams of precipitated Ca^{2+} per total grams of precipitate versus CO_2 pressure.

Figure 4. Comparison of experimental and predicted results for brine carbonation as a function of temperature at 0.343 MPa CO_2 (autoclave experiments), 6.52 MPa CO_2 (PHREEQC model) and pH 11. a. pH after reaction versus temperature. b. Total grams of precipitate per liter of solution versus temperature. c. Grams of precipitated Ca^{2+} per total grams of precipitate versus temperature.

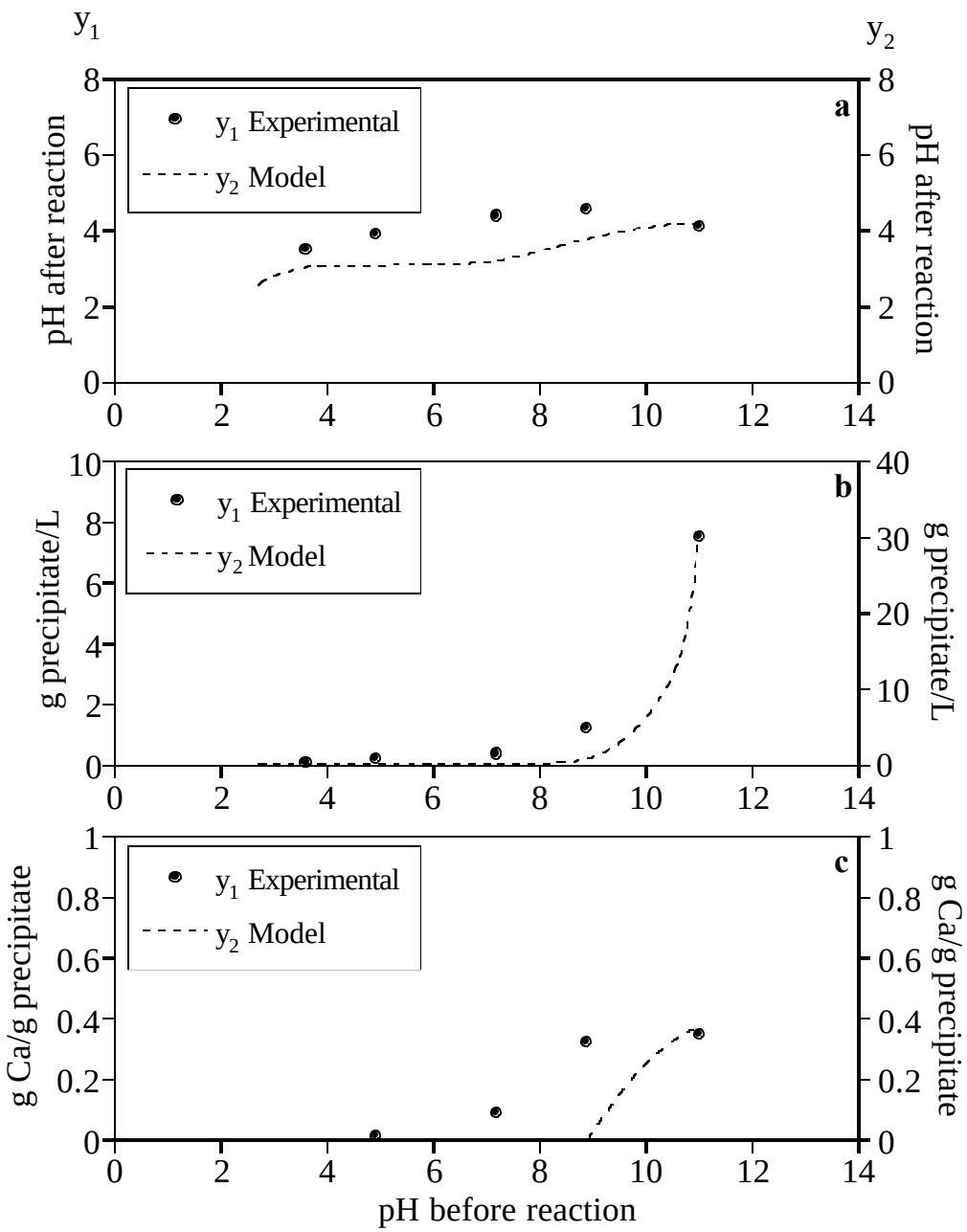
y1
y2
a
y1 Experimental
y2 Model
pH after reaction
pH after reaction
b
y1 Experimental
y2 Model
g precipitate/L
g precipitate/L
c
y1 Experimental
y2 Model
g Ca/g precipitate
g Ca/g precipitate
pH before reaction

Figure 2

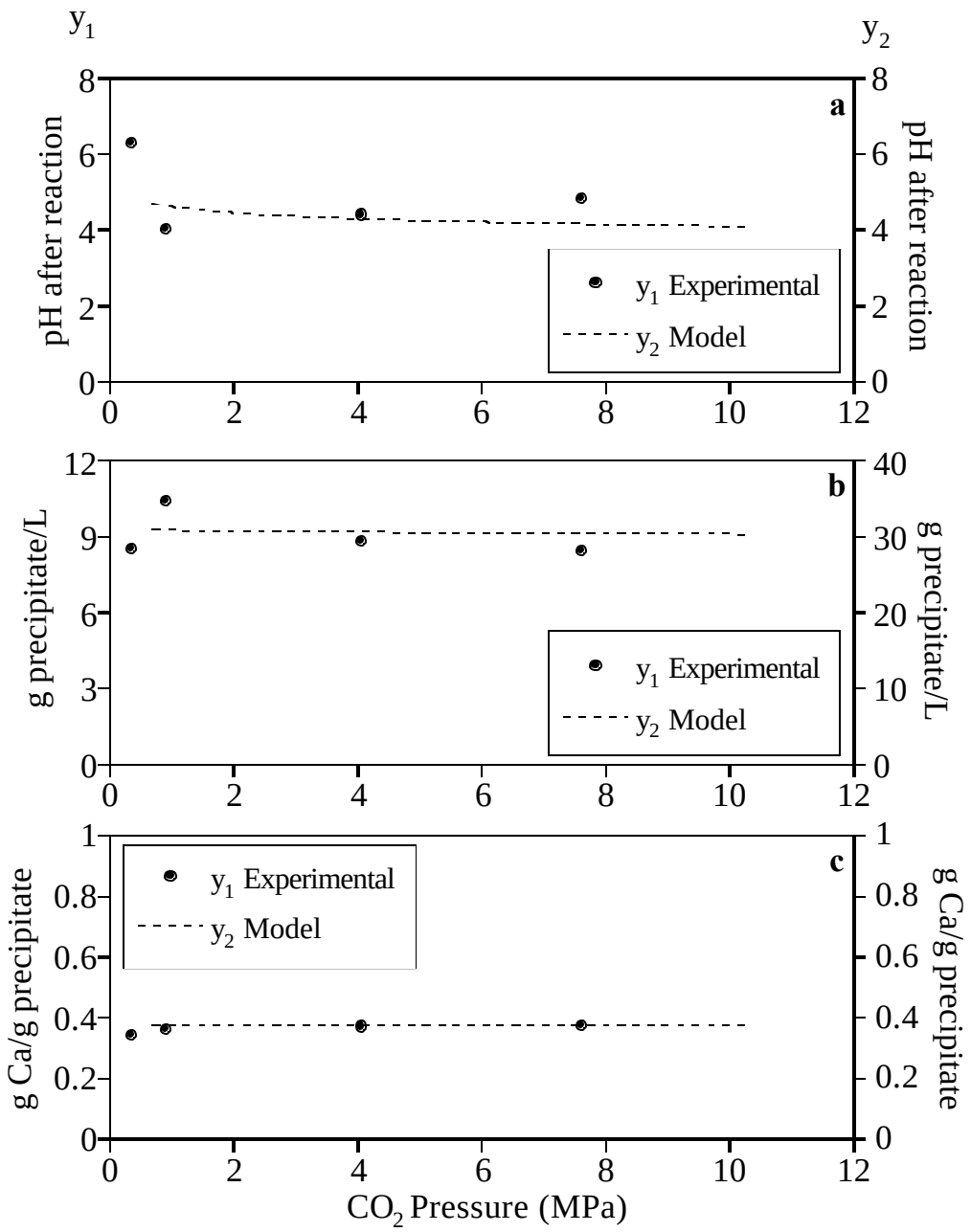
y1
y2
a
pH after reaction
pH after reaction
y1 Experimental
y2 Model
b
g precipitate/L
g precipitate/L
y1 Experimental
y2 Model
c
g Ca/g precipitate
g Ca/g precipitate
y1 Experimental
y2 Model
CO2 Pressure (MPa)

Figure 3

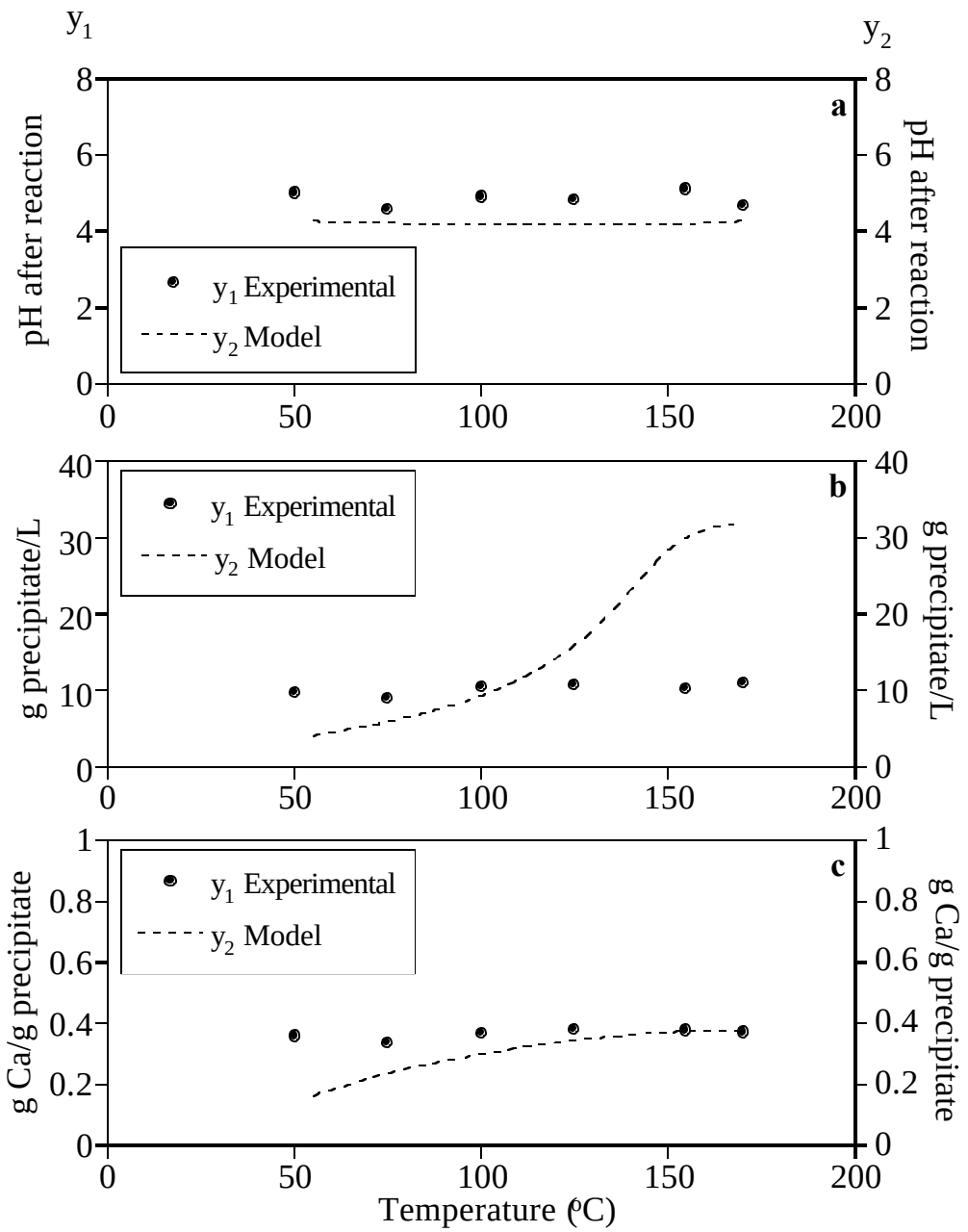
y1
y2
a
pH after reaction
y1 Experimental
y2 Model
b
g precipitate/L
c
g Ca/g precipitate
Temperature (°C)

Figure 4