Experimental multi-phase H_2O-CO_2 brine interactions at elevated temperature and pressure: Implications for CO_2 sequestration in deep-saline aquifers

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Introduction

The burning of fossil fuel and other anthropogenic activities have caused a continuous and dramatic 30% increase of atmospheric carbon dioxide (CO_2) over the past 150 years[1]. CO_2 sequestration is increasingly being viewed as a tool for managing these anthropogenic CO_2 emissions to the atmosphere. The disposal of this excess CO_2 into deep-saline aquifers is one of several potential storage repositories, but the details of the geochemical reactions between supercritical CO_2 and potential host fluids and formation rocks are largely unknown.

The initial reaction between liquid CO_2 and the aquifer fluid is the dissolution of CO_2 (eqn. 1) and is fundamentally important because it is the aqueous, not the supercritical form of CO_2 that is reactive toward the formation rocks.

$$CO_2 + H_2O \leftrightarrow H_2CO_3 \quad (1)$$

The aqueous solubility of CO_2 is temperature, pressure, and ionic-strength dependent. At 25°C, the solubility of CO_2 in an aquifer fluid with total dissolved solids of ~22% is approximately threefold less than in pure water[2]. The dissociation of carbonic acid into reactive hydrogen ion and bicarbonate (eqn. *2*) potentially initiates a complex series of reactions with aquifer fluids and formation rocks to fix CO_2 in mineral phases.

$$H_2CO_3 \leftrightarrow H^+ + HCO_3^- \quad (2)$$

The dissociation of carbonic acid is also temperature dependent. There is a maximum in the log K of reaction 2 at about 50°C beyond which log K decreases continuously with increasing temperature such that a weak acid becomes increasingly weak at elevated temperature. Reactions involving supercritical CO_2 and carbonic acid with aquifer fluids and formation rocks are many and varied, depending on the matrix of the fluid and the composition of the rock. In general, thermodynamics favor the dissolution of carbonate phases in limestones and dissolution of silicates and precipitation of carbonates in arkosic sandstones.

Reactions in limestone (ionic trapping). Reactions of CO_2 saturated aquifer fluids with limestone are characterized by dissolution of calcite due to the increased acidity produced by the dissociation of carbonic acid (eqn. 3)

$$CaCO_3 + CO_2 + H_2O \rightarrow Ca^{+2} + 2HCO_3^- \quad (3)$$

for a net increase of an additional mole of CO_2 stored as bicarbonate relative to the simple solubility of CO_2. Calcite has a retrograde solubility, becoming less soluble and less efficient at trapping CO_2 at elevated temperature. Similar reactions can be written for the dissolution of dolomite and siderite.

Reactions in arkosic sandstones (mineral trapping). Reactions of CO_2 saturated aquifer fluids with arkosic sandstones are characterized by dissolution of silicates due to the increased acidity produced by the dissociation of carbonic acid and precipitation of carbonates. An example of the mineral trapping of CO_2 is the dissolution of the anorthitic component of palgioclase (eqn. 4)

$$2H^+ + CaAl_2Si_2O_8 + H_2O \rightarrow Ca^{+2} + Al_2Si_2O_5(OH)_4 \quad (4)$$

and the subsequent precipitation of calcite (eqn. 5)

$$Ca^{+2} + HCO_3^- \rightarrow CaCO_3 + H^+ \quad (5)$$

for a net reaction shown in equation 6.

$$CaAl_2Si_2O_8 + H_2CO_3 + H_2O \rightarrow CaCO_3 + Al_2Si_2O_5(OH)_4 \quad (6)$$

The log K of this reaction decreases with increasing temperature, resulting in competing effects of favorable thermodynamics versus kinetic limitations.

We present here the results of CO_2-saturated brine-rock experiments carried out to evaluate the effects of multiphase H_2O-CO_2 fluids on mineral equilibria and the potential for CO_2 sequestration in mineral phases within deep-saline aquifers

Methods

Experimental. Experiments were carried out in a combination of titanium-lined fixed-volume and flexible-gold reactions cells secured to high-temperature-pressure autoclaves and rotating furnaces. Temperature was maintained by a proportional controller (Love™) and measured with a type K thermocouple calibrated to a platinum RTD. Pressure was measured with dead-weight calibrated gauges and transducers. Experiments were carried out at 22° and 120°C and at 300 bars.

Reactants. A natural near-surface brine (PVB) and a synthetic aquifer brine (PVA), both from Paradox Valley, CO, were reacted with limestone from the Leadville Limestone, CO (38% calcite), and arkosic and banded sandstones from Mount Tom, MA and Coconio, AZ, respectively in the presence and absence of liquid CO_2. Both sandstones contained quartz, plagioclase, (oligoclase), K-spar and kaolinite. Brine compositions are given in **table 1**.

Table 1. Composition of Paradox Valley Brines

Species (mg/L)	Surface (PVB)	Aquifer (PVA)
Na	77,000	70,000
K	3,630	2,100
Ca	1,187	10,900
Mg	1,278	1,220
Cl	127,100	132,000
SO_4	5,100	454
TDS	215,000	218,000

Analytical. Periodically, aqueous samples were withdrawn from each experiment and analyzed for total carbon by coulometric titration (UIC Coulometrics™), dissolved cations by inductively coupled plasma (ICP), and dissolved anions by ion chromatograph, except chloride which was determined by coulometric titration (Labconco™). The mineralogy of the solids was determined by x-ray diffraction (XRD) and chemistry by total dissolution and ICP (Xral Cooporation)

Results and Discussion

Limestone PVB Reactions. At 25°C, the reaction of CO_2 saturated PVB is characterized by dissolution of calcite and a pressure dependent enhanced solubility of CO_2 shown in **figure 1**.

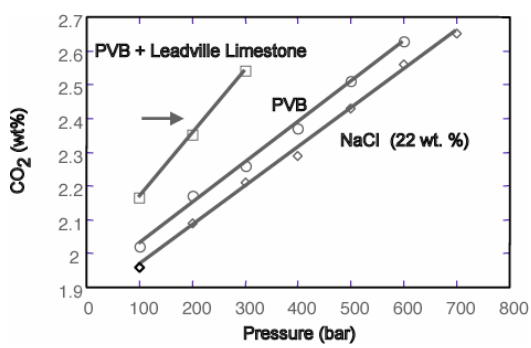

Figure 1. The solubility of CO_2 in PVB in the presence and absence of limestone and in equivalent ionic strength NaCl.

The solubility is enhanced 8.8% at 25°C and 5.7% at 120°C and 300 bars. Also, there is a temperature dependent offset in the solubility of CO_2 between the natural brine and NaCl due to the presence of divalent cations in the brine[2]. At 120°C, the reaction of PVB with limestone is independent of CO_2 concentration except for the dissolution of some calcite early in the experiment containing CO_2. Both experiments are dominated by the precipitation of anhydrite and dolomitization of the limestone shown as a time series plot in **figure 2**. Based on mass balance calculation for Mg, Ca, and SO_4, 25% of the original calcite dissolved or was dolomitized. Net molar volume changes result in a formation porosity increase of 5%.

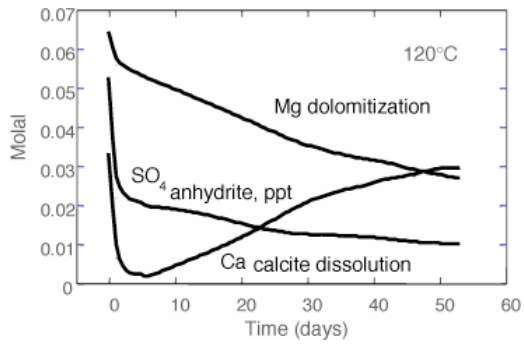

Figure 2. Compositional changes in PVB when reacted with limestone both in the presence and absence of liquid CO_2.

Limestone PVA Reactions. The reaction of limestone with PVA is characterized by calcite dissolution and desiccation of the brine shown in **figure 3**. Dolomite dissolves during heating and it or magnesite precipitate at the experimental conditions of 120°C. These reactions result in a net porosity increase of 2.6%.

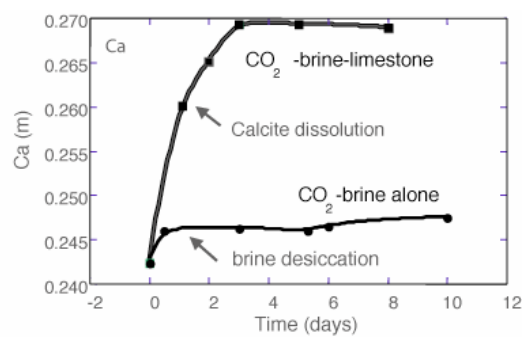

Figure 3. Compositional change in dissolved Ca during reaction of CO_2 saturated brine in the presence and absence of limestone at 120°C.

Sandstone PVA Reactions. Reactions of arkosic and iron-rich banded sandstones with PVA are characterized by large changes in elemental abundances, enhanced CO_2 solubility, and significant desiccation of the brines. Prior to injection of liquid CO_2, changes occurred in dissolved Ca, Mg, K, and Na during equilibration with minerals in the solid phase. After injection of liquid CO_2, total dissolved solids (TDS), including Cl, increased markedly due to transfer of H_2O from the brine to liquid CO_2 as shown in **figure 4**. The solubility of liquid H_2O in liquid CO_2 is temperature and pressure dependent[3] and has implications for solutions already near saturation with mineral phases. Experiments by Kazuba et al[4] have shown a 25% increase in dissolved Cl when CO_2 was injected into a saline brine at 200°C and 200 bars. Highly saline aquifers near saturation with NaCl would precipitate halite under these conditions.

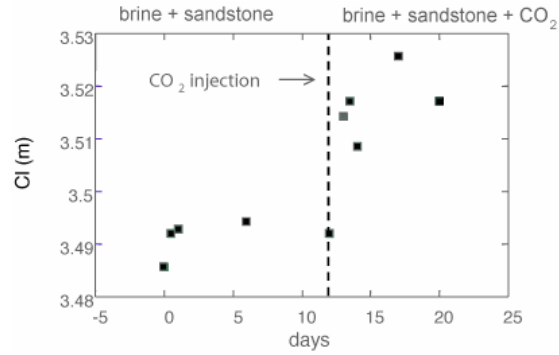

Figure 4. Concentration of dissolved Cl before and after injection of liquid CO_2 when PVA brine is reacted with arkosic sandstone.

Dissolved elemental concentrations did not all increase proportionally with dissolved Cl (7%), and ranged up to 12% for dissolved Mg immediately after injection of CO_2 into the brine, indicative of a variety of fluid-rock interactions. The decrease of dissolved Ca with time when PVA reacts with arkose is shown in **figure 5**, suggesting fixation of CO_2 as calcite. Significant metals were released to solution, in particular from the banded sandstone, leading to the possibility of siderite precipitation.

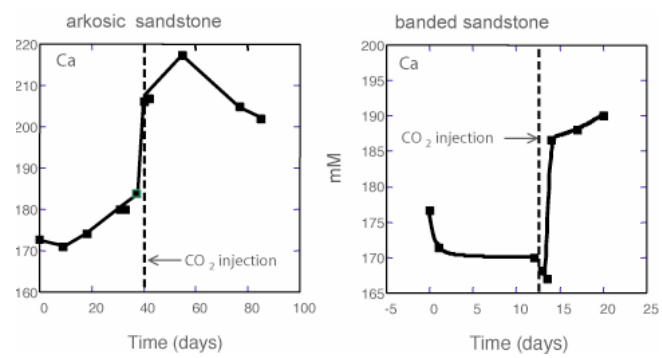

Figure 5. Time series plot of dissolved Ca when PVA is reacted with arkosic and banded sandstones at 120°C and 300 bars.

Conclusions

Experimental results are generally consistent with theoretical thermodynamic calculations. CO_2-saturated brine-limestone reactions are characterized by compositional and mineralogical changes in the aquifer fluid and rock that are dependent on initial brine composition, especially dissolved sulfate, as are the changes in formation porosity. The solubility of CO_2 is enhanced in brines in the presence of both limestone and sandstone relative to brines alone.

Reactions between CO_2 saturated brines and arkosic sandstones are characterized by desiccation of the brine and changes in the chemical composition of the brine suggesting fixation of CO_2 in mineral phases. These reactions are occurring on a measurable but kinetically slow time scale at 120°C.

References

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