

Gas-water-rock interactions in Frio Formation following CO₂ injection: Implications for the storage of greenhouse gases in sedimentary basins

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ABSTRACT

To investigate the potential for the geologic storage of CO₂ in saline sedimentary aquifers, 1600 t of CO₂ were injected at 1500 m depth into a 24-m-thick sandstone section of the Frio Formation, a regional brine and oil reservoir in the U.S. Gulf Coast. Fluid samples obtained from the injection and observation wells before CO₂ injection showed a Na-Ca-Cl-type brine with 93,000 mg/L total dissolved solids (TDS) at near saturation with CH₄ at reservoir conditions. Following CO₂ breakthrough, samples showed sharp drops in pH (6.5–5.7), pronounced increases in alkalinity (100–3000 mg/L as HCO₃) and Fe (30–1100 mg/L), and significant shifts in the isotopic compositions of H₂O, dissolved inorganic carbon (DIC), and CH₄. Geochemical modeling indicates that brine pH would have dropped lower but for the buffering by dissolution of carbonate and iron oxyhydroxides. This rapid dissolution of carbonate and other minerals could ultimately create pathways in the rock seals or well cements for CO₂ and brine leakage. Dissolution of minerals, especially iron oxyhydroxides, could mobilize toxic trace metals and, where residual oil or suitable organics are present, the injected CO₂ could also mobilize toxic organic compounds. Environmental impacts could be major if large brine volumes with mobilized toxic metals and organics migrated into potable groundwater. The δ¹⁸O values for brine and CO₂ samples indicate that supercritical CO₂ comprises ~50% of pore-fluid volume ~6 mo after the end of injection. Postinjection sampling, coupled with geochemical modeling, indicates that the brine gradually will return to its preinjection composition.

Keywords: CO₂ storage, global warming, basinal formation water, chemical composition of fluid, Frio Formation.

INTRODUCTION

Global warming and the resulting climate change are arguably the most important environmental challenges facing the world today (White et al., 2003). There is a broad scientific consensus that global warming results primarily from increased concentrations of atmospheric greenhouse gases, especially CO₂ emitted largely from the burning of fossil fuels (Broecker, 2006). Increased anthropogenic emissions have raised the atmospheric concentration of CO₂ from ~280 ppmv during pre-industrial times to ~380 ppmv today, and, if unabated, is projected to increase to 1100 ppmv by 2100 (White et al., 2003). Carbon storage, in addition to energy conservation and increased use of lower carbon fuels, is now considered necessary to stabilize atmospheric CO₂ levels and global temperatures at values that would not severely impact the global economy (e.g., White et al., 2003). Sedimentary basins in general, and depleted petroleum fields and deep saline aquifers in

particular, are being investigated as possible repositories for large amounts of excess anthropogenic CO₂. Because of economic benefits and over 30 yr of commercial application, injection into depleted fields for enhanced oil recovery (EOR) is expected to be the earliest method of CO₂ disposal. However, deep saline aquifers will likely become preferred geologic storage sites, because of their estimated huge potential capacity, 350–1000 Gt of CO₂ worldwide, and advantageous locations close to major CO₂ sources (Holloway, 2001).

Target reservoirs are likely to have temperatures and pressures higher than 31 °C and 74 bar, the critical values for CO₂, and injected CO₂ will thus initially form a supercritical fluid (White et al., 2003). The injected CO₂ will rapidly dissolve in formation water that contacts it (solution trapping), but mineral trapping, which would depend on the availability of reactive Ca-, Mg-, and Fe-bearing minerals, could be slower, yet more permanent (Hitcho, 1996). In addition to storage capacity

and proximity to CO₂ sources, key questions include the extent of CO₂ leakage related to the storage integrity, and the physical and chemical processes that are initiated by the injected CO₂ (Hepple and Benson, 2005).

In this report, we discuss geochemical results from a unique multilaboratory field-scale experiment that investigated the potential for geologic storage of CO₂ in saline aquifers. Approximately 1600 t of CO₂ were injected during October 2004 into a 24-m-thick sandstone, the “C” zone, of the Oligocene Frio Formation—a regional petroleum and brine reservoir in the U.S. Gulf Coast (Hovorka et al., 2006). We obtained downhole and well-head samples of formation water and gas from the “C” zone of both the injection and observation wells, and the overlying “B” zone of the observation well, using a variety of sampling tools and methodologies. Samples were obtained before CO₂ injection for baseline geochemical characterization, during the CO₂ injection to track its breakthrough, and after injection to investigate changes in fluid composition and leakage into the overlying B zone.

REGIONAL SETTING AND EXPERIMENTAL METHODS

The Frio site is located on the flank of a salt dome within South Liberty oil field, near Dayton, Texas, a region of the Gulf Coast where industrial sources of CO₂ are abundant. Most of the wells in this field were drilled in the 1950s, with production from the Eocene Yegua Formation at depths of ~2900 m. An inactive oil well, the Sun-Gulf-Humble Fee Tract 1, well #4, was recompleted and perforated in the Frio “C” sandstone at 1528–1534 m for use as an observation borehole. About 30 m downdip, a new CO₂ injection well was drilled and perforated, also in Frio “C” at 1541–1546 m. The Frio Formation has a dip of 16° to the south, and is composed of several reworked fluvial sandstone and siltstone beds that are separated by transgressive marine shale. The Frio “C” injection zone is a

TABLE 1. COMPOSITION OF GAS OBTAINED FROM FRIO C AND B SANDSTONES

Gas	C* (vol%)	C† (vol%)	B‡ (vol%)
He	0.0077	0	0.014
H ₂	0.040	0.19	0.30
Ar	0.041	0	0.063
CO ₂	0.31	96.8	0.22
N ₂	3.87	0.037	2.46
CH ₄	93.7	2.94	96.8
C ₂ H ₆ ⁺	1.95	0.0052	0.11

Note: note the low CO₂ content in background gas from both wells.

*From the injection well before CO₂ injection.

†From the observation well after CO₂ breakthrough.

‡From the observation well 6 mo later.

subarkosic fine-grained, moderately sorted quartz and feldspar sandstone, with minor amounts of illite or smectite and calcite. The zone has high mean porosity of 32% and permeability of 2–3 darcy. Situated immediately above the “C” sandstone, the “B” sandstone has an ~4-m-thick reworked fluvial sandstone bed at the top, but has more shale and siltstone beds, including a ~7-m-thick transgressive marine shale bed at the bottom. However, the main barrier to CO₂ leakage to surface is expected to be the overlying regional thick marine shale beds of the Miocene-Oligocene Anahuac Formation (Hovorka et al., 2006).

Approximately 1600 t of CO₂ were injected at a rate of ~3 kg/s during 4–14 October 2004, with interruptions for instrument repairs and scheduled formation tests. Pre- and post-injection samples were obtained from both wells at the wellhead using gas lift by either N₂ or the injected CO₂, and downhole using evacuated Kuster samplers or the Schlumberger Modular Formation Dynamics Tester syringe-like tool. During the CO₂ injection, intensive fluid sampling was conducted, with gas samples obtained from the top of the observation well and from the CO₂ line before the injection well, and water samples from the novel downhole U-tube system developed for this field experiment (Freifeld et al., 2005). More than 40 water samples were collected from the start of injection until about noon, 7 October, when water became a minor component of fluid, but gas sampling continued until the end of injection. Acquiring frequent samples was necessary to track the arrival of CO₂, to investigate changes in the fluid compositions caused by CO₂ injection, and for geochemical modeling to investigate gas-water-rock interactions.

The drilling fluids used during well recompletion were tagged with Rhodamine WT to allow for identification of the pristine Frio brine. Several perfluorocarbon and noble-gas tracers were injected along with the CO₂, and large numbers of samples were analyzed on-site using a quadrupole mass spectrometer to track the arrival time of CO₂, provide an es-

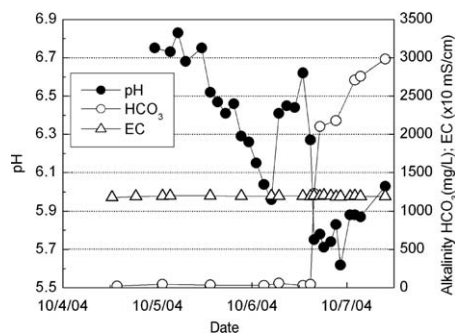


Figure 1. Electrical conductance (EC), pH, and alkalinity of Frio brine samples from “C” sandstone of observation well determined on-site during CO₂ injection on 4–7 October 2004. Note sharp drop of pH and alkalinity increase with breakthrough of CO₂ on 6 October.

timate of the residual brine saturation, and quantify tracer breakthrough curves (Freifeld et al., 2005). Water and gas samples collected were subjected to on-site and laboratory detailed chemical and isotopic analyses by methodologies described in Kharaka and Hanor (2004).

RESULTS AND DISCUSSION

Chemical analyses of water samples obtained from both wells prior to CO₂ injection show that the Frio brine is a Na-Ca-Cl-type water, with a relatively constant salinity of 93,000 ± 3000 mg/L total dissolved solids (TDS). The brine also has relatively high concentrations of Mg and Ba, but low values of SO₄, HCO₃, dissolved organic carbon (DOC), and organic acid anions. The high salinity and the low Br/Cl ratios (~0.0013) relative to seawater indicate that the brine composition is strongly influenced by dissolution of halite from the nearby salt dome (Kharaka and Hanor, 2004). Careful measurements of the volumes of water and evolved gas obtained with downhole samplers show that the pristine Frio brine has 40–45 mM dissolved CH₄, which is close to saturation at reservoir conditions (65 °C and 150 bar). Gas analysis shows that CH₄ makes up 95 ± 3% of total gas, but CO₂ gas is low at ~0.3%; N₂, C-2, and higher hydrocarbon gases compose the bulk of the remaining gas (Table 1).

The observed Frio brine and dissolved gas compositions are within the range of results obtained from petroleum-well data and extensive field testing conducted during the oil crisis of the 1970s to assess the dissolved CH₄ and other geopressed geothermal resources in the northern Gulf of Mexico basin (e.g., Kharaka and Hanor, 2004). Results show that pore waters to depths >6 km have salinities from ~10,000 to >300,000 mg/L TDS, where the higher-salinity brines are generally associated with salt domes or bittern water. The

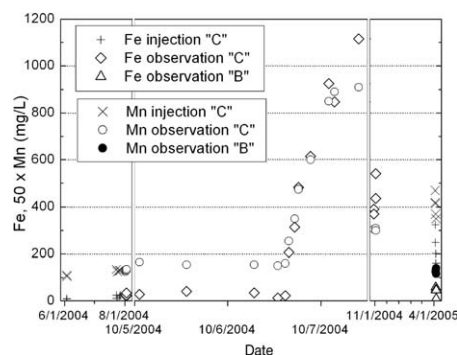


Figure 2. Concentrations of Fe and Mn in Frio brine from June 2004 to April 2005. Note sharp increases in metal content during 6 October 2004 at time of CO₂ breakthrough.

data show that formation waters are generally saturated with CH₄, and gas content is a strong function of reservoir temperature, pressure, and water composition. The dissolved CO₂ in basinal waters is commonly low and far below its saturation (0.8 M in Frio brine) at reservoir conditions, but several authors have noted increases with in situ temperature, from CO₂ fugacities of 0.1 bar at 50 °C to 100 bar at 175 °C (Kharaka and Hanor, 2004).

During the CO₂ injection, on-site measurements (Fig. 1) show only a small increase in electrical conductance (EC) from a preinjection value of ~120 mS/cm (at 22 °C); whereas major chemical changes were observed as the CO₂ reached the observation well, including a sharp drop in pH (from 6.5 to 5.7) and pronounced increases in alkalinity (from 100 to 3000 mg/L as bicarbonate). Additionally, laboratory determinations showed major increases in dissolved Fe (from 30 to 1100 mg/L) and Mn (Fig. 2), and marked increases in the concentration of Ca. The most dramatic changes in chemistry occurred at CO₂ breakthrough, 52 h after the start of injection (Fig. 1), as shown also by on-site analyses of gas samples, which show CO₂ concentrations increasing from 0.3% to 3.6% of total gas (Freifeld et al., 2005). The time to CO₂ breakthrough compares well with the 2.5–6 d range predicted by transport modeling using TOUGH2 (Hovorka et al., 2006). The CO₂ content of gas measured on-site and in the laboratory then quickly increased, reaching values of up to 97% of total gas, with CH₄ comprising the bulk of the remaining 3% (Table 1).

The variations in the measured pH proved the most sensitive parameter for tracking the arrival of CO₂ at the observation well (Fig. 1). The initial drop in pH from 6.7 to 6.5 resulted from changes in sampling location and protocol. The gradual decrease thereafter, to pH 5.9, likely resulted from mixing of formation water with brine that had increasing amounts of dissolved injected CO₂. Because the solu-

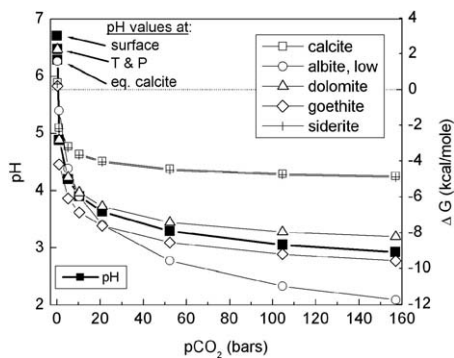
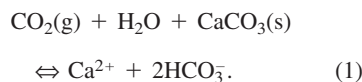


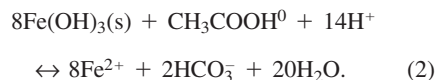
Figure 3. Computed pH values and saturation states of selected minerals in pristine Frio brine as a function of CO₂ partial pressure at subsurface conditions. Note sharp initial drop of pH from average computed (at temperature, pressure, and calcite saturation) subsurface value of 6.4.

bility of CO₂ in Frio brine was high (0.8 M at reservoir conditions; Spycher and Pruess, 2005), dissolved CO₂ was expected to reach the observation well before the supercritical phase. The significant pH rise from 5.9 to 6.5 on 6 October (Fig. 1) likely resulted from a 4 h pause in CO₂ injection due to problems in an injection pump, when pristine formation water reoccupied the observation well. The sharp drop in pH and increases in alkalinity, dissolved iron, measured CO₂ (Freifeld et al., 2005), and other constituents in the sample collected at 15:45 on 6 October, marked the time of breakthrough of the supercritical CO₂ plume.

Results of geochemical modeling, using updated SOLMINEQ (Kharaka et al., 1988), indicate that Frio brine in contact with supercritical CO₂ would have a pH of ~3 at subsurface conditions, and this low pH would cause the brine to become highly undersaturated with respect to carbonate, aluminosilicate, and most other minerals present in the Frio Formation (Fig. 3). Because mineral dissolution rates are generally higher by orders of magnitude at such low pH values, the observed increases in concentrations of HCO₃⁻ and Ca likely result from the rapid dissolution of calcite by:

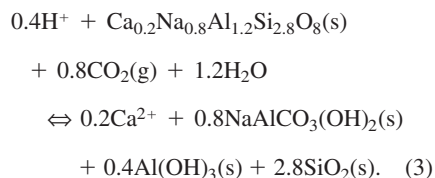


The large increases observed in concentrations of Fe and equivalent bicarbonate alkalinity could result from dissolution of siderite, but no siderite was observed in the retrieved core. Hence, these increases likely are caused by dissolution of the observed iron oxyhydroxides, depicted in redox reaction 2, where acetic acid is the reductant:



A similar reaction may be written for Mn, which also increased from 3 to 18 mg/L. There were also increases in the concentration of other metals, including Zn, Pb, and Mo, which are generally associated (sorbed and co-precipitated) with iron oxyhydroxides.

Results of chemical analyses of samples collected ~20 d and 6 mo after CO₂ injection demonstrate decreases in the concentrations of Fe, Mn (Fig. 2), HCO₃⁻, and Ca, and increases in pH. Geochemical modeling indicates that the brine pH increases from dissolution of carbonate and iron oxyhydroxide minerals discussed above, as well as from dissolution of oligoclase and other aluminosilicate minerals present in the Frio Formation. Aluminosilicate mineral dissolution generally is not congruent, but likely follows an incongruent reaction (3), where dawsonite, gibbsite, and amorphous silica are precipitated, and/or where kaolinite and amorphous silica are precipitated (White et al., 2003):



As the pH increases from mineral interactions and the mixing of CO₂-saturated and pristine brines, modeling indicates that mineral saturations reverse the trend shown in Figure 3, resulting in precipitation of carbonate and other minerals. The overall result is the brine gradually evolving toward its pre-injection composition, but additional fluid sampling is planned to further investigate gas-water-rock interactions in this system.

Dissolved Organics

Brine samples obtained before and during CO₂ injection were analyzed for dissolved organic carbon (DOC) and only a limited number of dissolved organic species, since there is no petroleum production from the Frio Formation at this site. The DOC values measured were expectedly low (1–5 mg/L) in the pristine Frio brine from both the “B” and “C” sandstones. The DOC values obtained from the “C” sandstone during the CO₂ injection increased moderately to 5–6 mg/L; the values, however, increased unexpectedly by a factor of 100 in samples collected 20 d after injection stopped. The concentrations of C₁–C₅ organic acid anions, and benzene, toluene, ethylbenzene, and xylene (BTEX) in all the samples were low (<1 mg/L), but with for-

mate, acetate, oxalate, and toluene exhibiting higher values in the enriched DOC samples.

As a result of the very high DOC values obtained, a more detailed sampling protocol was used that included aliquots for oil and grease and detailed gas chromatography–mass spectrometry (GC-MS) analysis for volatile organic compounds (VOCs) and semi-VOCs. Results show all oil and grease values were below detection limit, and for samples from the “C” zone of the injection well, we obtained low levels of VOCs (up to 30 ppb phenol) and semi-VOCs (30 ppb naphthalene), and only elevated DOC values (4.5–7.5 mg/L) were comparable to those obtained from zone “C” of the observation well during CO₂ injection.

It is difficult to rule out contamination as the source for the very high DOC values, but they likely represent a ‘slug’ of organic matter mobilized by the injected CO₂, as generally happens during EOR operations (Shiraki and Dunn, 2000). If this conclusion is supported by future studies, then mobilization of organics, including BTEX and other toxic organics from non-oil-bearing saline aquifers, could have major implications for the environmental aspects of CO₂ storage and containment. The concern here is warranted as high concentrations of toxic DOCs, including benzene, toluene (up to 60 mg/L for BTEX), phenols (20 mg/L), and polyaromatic hydrocarbons (up to 10 mg/L for PAHs), have been reported in oil-field waters (e.g., Kharaka and Hanor, 2004).

Isotopic Composition of Water and Gases

We observed significant shifts in the isotopic compositions of H₂O and dissolved inorganic carbon (DIC) following CO₂ injection, but only subtle changes in the δD and δ¹³C values of CH₄. The δ¹³C values of DIC became profoundly lighter, shifting from –3‰ to –33‰, reflecting the fact that the injected CO₂ is the dominant C source and is depleted, with δ¹³C = –34‰ to –44‰, depending on the mixing proportions of the two gas sources. The δ¹⁸O values of brine became isotopically lighter with time, shifting from 0.80‰ to –11.1‰, and there was a corresponding increase in the δ¹⁸O values of CO₂, from 9‰ to 43‰. Because water and CO₂ rapidly exchange oxygen isotopes, even at low temperature, it is possible to use their δ¹⁸O values in mass balance equations to estimate the brine to CO₂ mass and volume ratios in the reservoir. The equation for a closed system and no isotopic exchange with minerals is given (Clark and Fritz, 1997) by:

$$\frac{X_{\text{brine}}}{X_{\text{CO}_2}} = \frac{\delta^{18}\text{O}_{\text{CO}_2}^f - \delta^{18}\text{O}_{\text{CO}_2}^i}{\delta^{18}\text{O}_{\text{H}_2\text{O}}^i - \delta^{18}\text{O}_{\text{H}_2\text{O}}^f} \quad (4)$$

TABLE 2. CALCULATED BRINE/CO₂ VOLUME RATIOS IN THE FRIO FORMATION FOLLOWING CO₂ INJECTION BASED ON THE δ¹⁸O VALUES FOR BRINE AND CO₂

Date	δ ¹⁸ O shift brine	δ ¹⁸ O shift CO ₂	Brine/CO ₂ volume ratio*
10-5-04	0	0	∞
10-6-04	0.37	32	43
10-6-04	0.69	32	23
10-6-04	0.77	32	21
10-6-04	1.22	32	13
10-7-04	2.24	32	7.1
11-3-04	1.43	32	11
11-3-04	1.74	32	9.1
4-4-05	11.2	22	0.97
5-4-05	11.7	22	0.93
6-4-05	11.9	22	0.92

*To convert from mole oxygen basis (equation 4 in text) to brine/CO₂ volume ratio at reservoir conditions, we multiplied by 0.495, using a density (gm/cm³) of CO₂ = 0.60 and brine = 1.0.

where the superscripts i and f are the initial and final δ values for brine and CO₂, respectively, and X is the atomic oxygen in the subscripted component.

Results from the observation well (Table 2) show that, initially, the system is brine dominated, with CO₂ comprising ~10% of the fluid at reservoir conditions from one day after the CO₂ breakthrough on 7 October 2004 through 3 November 2004. However, samples collected from the injection well on 4–6 April 2005 yield a value of ~50% for the volume of CO₂ at reservoir conditions. The initial brine-dominated system could indicate that the injected CO₂ acts like a piston pushing the pore water out with minimal mixing and isotopic exchange. Contact and isotopic equilibration with a larger volume of injected CO₂ is indicated from data of April 2005. These results are comparable to residual CO₂-saturation values obtained with the reservoir saturation (RST) and other geophysical tools (Hovorka et al., 2006), indicating the usefulness of this isotopic approach.

CO₂ STORAGE IN SEDIMENTARY BASINS

Deep saline aquifers and depleted petroleum fields in sedimentary basins provide advantageous locations close to major CO₂ sources and huge potential capacity for the storage of large amounts of this greenhouse gas (Holloway, 2001). The Frio brine field test demonstrated the relatively straightforward method of CO₂ injection and its rapid transport to the observation well. Our field geochemical methodologies, especially measurements of pH, alkalinity, and gas compositions (Freifeld et al., 2005) proved highly effective

for tracking the injected CO₂. The tracking of CO₂ was later confirmed by laboratory determinations of dissolved Fe, Mn, and Ca, and isotopes, especially δ¹⁸O values of brine and CO₂, and δ¹³C values of DIC and CO₂. The δ¹⁸O values for brine and CO₂ proved a valuable tool for calculating the brine/CO₂ ratio in the Frio sandstone; results from the observation well show that, initially, the system is brine dominated, but ratios from the injection well demonstrate that supercritical CO₂ comprises ~50% of the fluid volume in Frio sandstone 6 months later.

The chemical data coupled with geochemical modeling indicate rapid dissolution of minerals, especially calcite and iron oxyhydroxides caused by low pH values of the brine in contact with the injected supercritical CO₂. Such rapid mineral dissolution could have important environmental implications with regard to creating pathways in the rock seals and well cements that could facilitate leakage of CO₂ and brine. Maintaining reservoir integrity that prevents the ultimate escape of CO₂ back to the atmosphere by limiting its leakage to extremely low levels is essential to the success of injection operations (Hepple and Benson, 2005). Preventing brine leakage into overlying drinking water supplies is also important, because dissolution of iron oxyhydroxides would mobilize Fe, Mn, and other toxic components, in addition to the chemicals present in the pristine brine. Mobilization of organics, including BTEX, phenols, and other toxic compounds, from this non-oil-bearing saline aquifer would further compound the environmental severity of CO₂ and brine leakage.

Data on brine and gas (Table 1) compositions of samples from the “B” sandstone of the Frio Formation ~6 mo after the end of the injection test indicate no significant CO₂ leakage from the underlying “C” sandstone. This important result, together with additional changes in brine and gas compositions of fluids in the C sandstone, is being investigated further with additional brine and gas samples from this well-characterized site.

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