

# Monitoring Geological CO<sub>2</sub> Sequestration using Perfluorocarbon Gas Tracers and Isotopes



Phelps, T.J., McCallum, S.D., Cole, D.R., Kharaka, Y.K., and Hovorka, S.D.

<sup>1</sup>Oak Ridge National Laboratory, Oak Ridge, TN, 37831-6036, U.S.A.; <sup>2</sup>U.S. Geological Survey, Menlo Park, CA 94205, U.S.A.; <sup>3</sup>Bureau of Economic Geology, University of Texas, Austin, TX 78713, U.S.A.  
\*Corresponding author: Tommy J. Phelps, phelpstj@ornl.gov, 865-574-7290

## ABSTRACT

The Frio Brine Field Test, Phase I, demonstrated the relatively straight forward method of CO<sub>2</sub> injection and its rapid transport to the monitoring well. Our field monitoring methodologies, especially measurements of conservative perfluorocarbon gas tracers (PFTs), pH, alkalinity, gas compositions and stable isotopes proved to be sensitive for tracking the injected CO<sub>2</sub>. Multiple PFT tracer suites were introduced via an injection well at three separate times during the Frio Test. The use of PFT suites provided data for identification of multiple breakthroughs at a monitoring well 30 meters up-dip. Travel times for each injection varied between 50.3 and 51.7 hours. The travel time data have application for validation of subsurface flow models used to support this field test.

The tracking of brine-rock-CO<sub>2</sub> interactions was later confirmed by laboratory determinations, including dissolved Fe, Mn, and Ca, and isotopes, especially  $\delta^{18}\text{O}$  values of brine and CO<sub>2</sub>,  $\delta^{13}\text{C}$  values of DIC and CO<sub>2</sub>, and  $^{87}\text{Sr}/^{86}\text{Sr}$  in the brines. The  $\delta^{18}\text{O}$  values for brine and CO<sub>2</sub> proved a valuable tool for calculating the brine/CO<sub>2</sub> ratios which demonstrated that supercritical CO<sub>2</sub> comprises ~50% of fluid in Frio sandstone ~6 months after cessation of injection. Chemical data coupled with geochemical modeling indicate rapid dissolution of minerals, especially calcite and iron oxyhydroxides caused by low pH of the brine in contact with the injected supercritical CO<sub>2</sub>. Rapid mineral dissolution could have important environmental implications with regard to creating pathways in the rock and well cements that could facilitate leakage of CO<sub>2</sub> and brine.

## INTRODUCTION

In an effort to characterize geologic sequestration to store anthropogenic CO<sub>2</sub> the Frio Test was conducted in October of 2004 in Dayton, Texas (Hovorka and Knox, 2002). Multiple organizations were involved with the geochemical and geophysical analysis of the injected CO<sub>2</sub> plume (Freifeld et al., 2005 and Kharaka et al., 2006a, 2006b). This study focuses on the perfluorocarbon tracer (PFT) and data collected after the injection was completed and the isotope data collected pre and post injection.

Approximately 1600 tons of CO<sub>2</sub> was introduced into the C-sand of the Frio formation. The C-sand was isolated from the overlying B-sand by ~4m of low permeability shale layers (Galloway et al., 1982 and Galloway and Cheng, 1985) (Figure 1). Approximately 30m up-dip from the injection well was a monitoring well. After completion of the CO<sub>2</sub> injection, the injection well was sealed to allow only fluids from the C-sand to enter the well casing. The monitoring well was sealed to allow only fluids from the B-sand to enter the well casing. Sealing the injection and monitoring wells in this manner allowed fluid sampling that would target either the C-sand (injection well) or the B-sand (monitoring well).

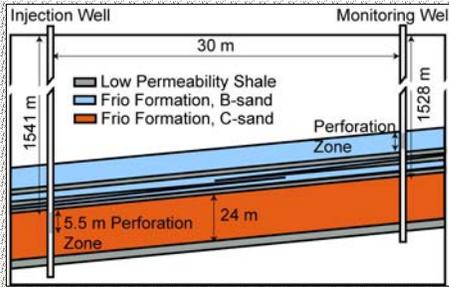


Figure 1: Cross section of the Frio formation showing injection and monitoring wells, the C-sand, B-sand, shale layers, and perforation zones. The schematic is not to scale.

## METHODS

Carbon isotope compositions (relative to PDB) were measured in CO<sub>2</sub> and CH<sub>4</sub> gas samples, and dissolved inorganic carbon (precipitated as SrCO<sub>3</sub>). Oxygen (via CO<sub>2</sub>-equilibration method) and hydrogen (via the zinc reduction method) isotopes were measured in select brine samples. Hydrogen isotopes were also measured in the CH<sub>4</sub>. Gas analyses were determined by conventional gas chromatography.

Fluid samples were collected from both the C and B-sands at 6 months post injection (4 samples) and 15 months post injection (10 samples). Gas samples were collected either at the surface (well head) or at depth (Kuster sampler). Samples were stored in 100-300 mL pressure cylinders. The cylinders were transported to the laboratory for perfluorocarbon and isotopic analysis. The perfluorocarbon analysis consisted of sub-sampling the pressure cylinders in 100uL aliquots and then analyzing each aliquot using a gas chromatograph equipped with an electron capture detector (GC-ECD).

## RESULTS AND DISCUSSION OF ISOTOPIC ANALYSIS

- Fluid samples obtained from the injection and monitoring wells before CO<sub>2</sub> injection show a Na-Ca-Cl type brine with 93,000 mg/L TDS at near saturation with CH<sub>4</sub> at reservoir conditions (Table 1).
- Following CO<sub>2</sub> breakthrough, samples showed:
  - Sharp drops in pH (6.5-5.7) (Figure 2).
  - Pronounced increases in alkalinity (100-3,000 mg/L as HCO<sub>3</sub><sup>-</sup>) and Fe (30-1,100 mg/L) (Figure 2 and 3).
  - Significant shifts in the isotopic compositions of DIC, H<sub>2</sub>O, and CH<sub>4</sub> (Figure 4, 5, and 6).
- Geochemical modeling indicates that brine pH would have dropped lower, if not 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 CO<sub>2</sub> and brine leakage.
- Dissolution of minerals, especially iron oxyhydroxides, could mobilize trace metals and organic compounds (Figure 3).
- Shifts in the  $\delta^{18}\text{O}$  values for brine and CO<sub>2</sub> samples indicate that supercritical CO<sub>2</sub> comprised ~50% of pore-fluid volume ~6 months after the end of injection (Kharaka et al., 2006a, 2006b) (Figure 6).

Table 1: Chemical composition of Frio gases. Note that prior to CO<sub>2</sub> injection the Frio brine is at saturation with CH<sub>4</sub>. Even after breakthrough of CO<sub>2</sub> in the brine, the gas is still CH<sub>4</sub> rich. Migration of CO<sub>2</sub> into the Frio B-sand was not obvious with these data.

	Injection well before CO <sub>2</sub> injection	Monitoring well before CO <sub>2</sub> injection	Monitoring well after CO <sub>2</sub> injection	Monitoring well "B" sand
H <sub>2</sub>	0.027	0.028	0	0.024
N <sub>2</sub>	0.040	1.38	0.191	0.285
Ar	0.0418	0.0207	0	0.0609
CO <sub>2</sub>	0.0719	0	0	0.748
CH <sub>4</sub>	0.39	0.046	0.83	0.294
H <sub>2</sub> O	415	210	0.027	0.17
CO	3	0	0	<0.001
HCN	0.04	0.04	0.234	0.04
C <sub>2</sub> H <sub>6</sub>	0.016	0.181	0.0002	0.003
C <sub>3</sub> H <sub>8</sub>	0.038	0.001	0.0002	0.0002
C <sub>4</sub> H <sub>10</sub>	1.78	0.007	0	<0.0005

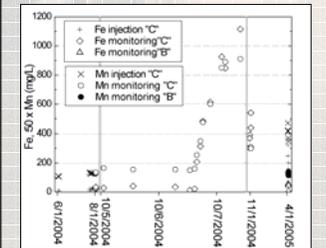


Figure 3: Concentrations of Fe (X, O, Δ) and Mn (X, O, ●) in Frio brines from June, 2004 to April, 2005. Sharp increases in metal content during October 6, 2004, at the time of CO<sub>2</sub> breakthrough.

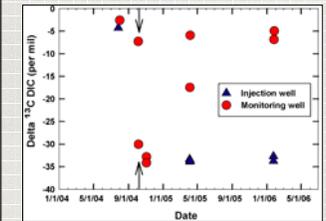


Figure 5: Carbon isotope compositions of dissolved inorganic carbon (DIC) plotted against sample date for brines from the injection and monitoring wells. The arrow denotes the date of CO<sub>2</sub> breakthrough, 10/6/04. At Frio brine temperatures the DIC should be roughly 4-5 per mil enriched in <sup>13</sup>C relative to the injection gas (see Figure 4). Samples collected after 1/1/05 where taken from the B-sand, which contains CO<sub>2</sub> that is similar to the naturally occurring C-sand CO<sub>2</sub>, and is why the DIC reflects initial values. The DIC from the injection well continues to be influenced by the isotopically light injection CO<sub>2</sub>.

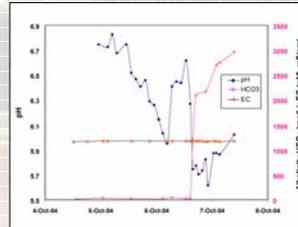


Figure 2: Electrical conductance (EC), pH, and alkalinity of Frio brines from the monitoring well determined on site during CO<sub>2</sub> injection. Note the sharp drop in pH and increase in alkalinity with the breakthrough of the CO<sub>2</sub> on 10/6/04.

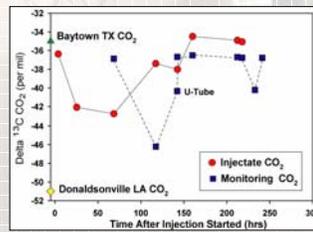


Figure 4: Two different sources of CO<sub>2</sub> were used in the Frio injection. This plot demonstrates that the resulting carbon isotope signal measured in CO<sub>2</sub> gas sampled from the monitoring well can mimic the "mixed" signal from the two sources if no other exchange process is involved.  $\delta^{13}\text{C}$  compositions as of January 2006 have now leveled off at about -38 per mil (data not shown).

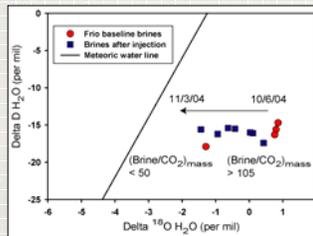


Figure 6: Oxygen isotope shifts in the brine and CO<sub>2</sub> reflect exchange toward an equilibrium partitioning ( $K_{\text{CO}_2:2\text{H}_2\text{O}} = \delta^{18}\text{O}_{\text{CO}_2} / \delta^{18}\text{O}_{\text{brine}}$ ), which at Frio brine temperatures of roughly 67°C, is approximately 33 per mil. As the volume of CO<sub>2</sub> increases during injection its mass of oxygen begins to dominate the total in the system so the magnitude of the shift becomes increasingly greater for the brine. Hence the brine/CO<sub>2</sub> mass ratio drops.

- <sup>18</sup>O/<sup>16</sup>O shifts in brine due to interaction with CO<sub>2</sub>
- Use mass balance to estimate mass ratios of brine/CO<sub>2</sub>
- Need to know isotopic shifts in both brine and CO<sub>2</sub>
- $X_{\text{CO}_2} = \frac{\delta^{18}\text{O}_{\text{CO}_2} - \delta^{18}\text{O}_{\text{brine}}}{\delta^{18}\text{O}_{\text{CO}_2} - \delta^{18}\text{O}_{\text{brine}} + 33}$
- Requires no assumption about attainment of equilibrium
- Values range from >105 @ 10/6/04 to <50 @ 11/3/04

## RESULTS AND DISCUSSION OF PERFLUOROCARBON ANALYSIS

- Multiple PFT injections exhibited similar retention times compared to the isotope data (Table 2).
- PFTs were identified in both the Frio C and B-sands at 6 and 15 months post-injection (Figure 7a-c).
- The presence of PFTs in the C-sand implied that residual CO<sub>2</sub> remained in the formation long after the CO<sub>2</sub> plume migrated up-dip.
- The observed ratio of individual PFTs changed compared to injection ratios. The ratio change was likely due to differential sorption (Dietz, 1986; Dugstad et al., 1992, 1993; Sullivan et al., 1998), partitioning (Whitley et al., 1999; Dugstad et al., 1992, 1993), and diffusivity (Wilke and Lee, 1955; Hyduck and Laudie, 1974) of each PFT.
- PFTs in the B-sand implied migration through the formation or more likely through the well bore.
  - The dominant PFTs seen in the B-sand were PMCH and PTCH.
  - It is likely that the leading edge of the CO<sub>2</sub> plume mobilized in-situ particulates in the C-sand (Figure 3), which clogged pathways to the B-sand so that PFTs injected later were not observed in the B-sand.

Table 2: Summary of PFT injections.

Injection #	Injection time (hours after CO2 start and date)	Injection Duration (hours)	Peak Arrival Time (hours and date)	PFT Travel Time (hours) (GC)	PFT Travel Time (hours) (MS)
#1 PMCH/PTCH	2 (13:26, 10/4/04)	4	54 (17:34, 10/6/04)	50	49
#2 PECH	19 (7:00, 10/05/04)	12	n/a	n/a	n/a
#3 PMCP/PDCH	103 (18:19, 10/8/04)	0.6	157 (00:34, 10/11/04)	52	49
#4 PMCH/PTCH	120 (11:37, 10/9/04)	0.5	173 (16:34, 10/11/04)	51	53
#5 oPDCH	163 (7:00, 10/11/04)	12	n/a	n/a	n/a
#6 PDCB	222 (18:00, 10/11/04)	6	n/a	n/a	n/a

Modified from McCallum et al., 2005

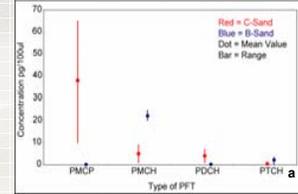


Figure 7a-c: The plots show the mean value (dot) and the range of values (bar) for each PFT in the Frio C-sand (red) and B-sand (blue).

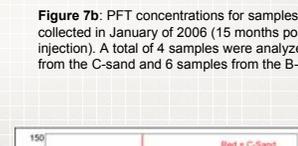


Figure 7b: PFT concentrations for samples collected in January of 2006 (15 months post-injection). A total of 4 samples were analyzed from the C-sand and 6 samples from the B-sand.

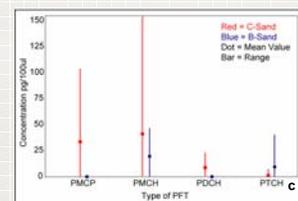


Figure 7c: Combined plot of PFT concentrations for samples collected in April of 2005 and January of 2006. A total of 6 samples were analyzed from the C-sand and 8 samples from the B-sand.

## SUMMARY

- Alkalinity and pH determinations are an excellent and rapid field indicator for tracking injected CO<sub>2</sub>, while the PFTs and stable isotopes trace the plume movements.
- Low pH values resulting from CO<sub>2</sub> injection could have important implications regarding mobilizing metals and mineral dissolution leading to migration and/or plugging for brine and gas.
- The carbon isotope signal of the dissolved inorganic carbon (DIC) exhibits a very rapid change soon after injection begins.
- Oxygen isotope shifts in the brine and CO<sub>2</sub> can be used to estimate the mass proportions of brine and CO<sub>2</sub> in the system.
- In post-injection samples PFTs were identified in the Frio C-sand and overlying B-sand.
  - PFTs in the C-sand imply residual saturation of CO<sub>2</sub> in the brine persisting
  - PFTs in the B-sand imply that PFTs migrated from the C-sand through the formation or through the well bore

## REFERENCES

Beckwith, R. L., and Hovorka, S. D., 2002. Sequestration and application of carbon dioxide in the Frio sandstone reservoir. *Proc. Natl. Acad. Sci. USA*, 99(11), 7033-7038.

Cheng, S. H., and Galloway, G. D., 1982. Geochemistry and geophysics of the Frio sandstone reservoir. *Proc. Natl. Acad. Sci. USA*, 79(11), 6315-6320.

Dietz, R. J., 1986. *CO<sub>2</sub> Storage in the Frio Sandstone Reservoir*. Ph.D. Thesis, University of Texas at Austin.

Dugstad, S. E., Whitley, J. R., and Hovorka, S. D., 1992. Geochemistry and geophysics of the Frio sandstone reservoir. *Proc. Natl. Acad. Sci. USA*, 89(11), 5315-5320.

Dugstad, S. E., Whitley, J. R., and Hovorka, S. D., 1993. Geochemistry and geophysics of the Frio sandstone reservoir. *Proc. Natl. Acad. Sci. USA*, 90(11), 5315-5320.

Hovorka, S. D., Phelps, T. J., and Kharaka, Y. K., 2005. Geochemistry and geophysics of the Frio sandstone reservoir. *Proc. Natl. Acad. Sci. USA*, 102(11), 12315-12320.

Hovorka, S. D., Phelps, T. J., and Kharaka, Y. K., 2006a. Geochemistry and geophysics of the Frio sandstone reservoir. *Proc. Natl. Acad. Sci. USA*, 103(11), 12315-12320.

Hovorka, S. D., Phelps, T. J., and Kharaka, Y. K., 2006b. Geochemistry and geophysics of the Frio sandstone reservoir. *Proc. Natl. Acad. Sci. USA*, 103(11), 12315-12320.

Hyduck, R. L., and Lee, C. Y., 1955. Estimation of diffusion coefficients for gases and vapors. *Ind. Eng. Chem. Anal. Ed.*, 27(1), 125-127.

ACKNOWLEDGMENTS: We gratefully acknowledge support from the Department of Energy, Office of Fossil Energy, National Energy Technology Laboratory (Program manager: Dr. Karen Cohen). ORNL is managed by UT-Battelle, LLC, for the U.S. Department of Energy under contract DE-AC05-00OR2272Z.