

High Pressure Flow-Through System for Simulating Gas and Fluid Flow through Geologic Materials

¹McCallum S.D., ²Cole D., ¹Fisher L.S., ¹Palumbo A.V., ²Blencoe J., ¹Moline G.R., ¹Parker J.C.,
¹Riesterberg D.E., ¹Phelps T.J.

¹Environmental Sciences Division, Oak Ridge National Laboratory, TN 37831-6036

²Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6110

Abstract:

One of the more promising and readily available techniques for storage of CO₂ is geologic sequestration in deep porous subsurface formations. Previously produced oil and gas reservoirs provide geologic traps in which CO₂ can be stored. However, the injected CO₂ should be monitored to assess losses and to verify the overall effectiveness of sequestration. One possible technique for evaluating fluid flow in the subsurface is the monitoring of natural and conservative tracers in the injected CO₂. In order to evaluate the behavior of selected tracers in geologic material, a high pressure flow-through system (HPFS) was developed. The test cell of the flow-through system can be filled with geologic substrate representative of the injection site, saturated with brine and/or hydrocarbons, and is operational at temperatures up to 100°C and pressures up to 31 MPa. Simulation of subsurface conditions allows for a more accurate assessment of how tracers will interact with geologic material, fluids (i.e., brine and hydrocarbons), and CO₂. Data generated using the high pressure flow-through column can be used to validate flow models and increase the accuracy of predictive codes. Preliminary tests on packed sand columns have shown detection of the tracer perfluorodimethylcyclohexane (PDCH) in amounts as low as 0.1 pg per 250 µl of analyte.

Introduction:

Of the various methods proposed for sequestration of CO₂, subsurface sinks are among the most favored (Lackner, 2003) and offer a means for large scale sequestration (Holloway, 2001). Subsurface sinks include depleted oil/gas reservoirs, saline aquifers, and coal bearing formations (Bachu et al., 1994; Tanaka et al. 1995; Stevens et al. 1998; Van Der Meer 2002). The CO₂ storage capacity is ~920 Gt in depleted oil/gas reservoirs, 400 – 10,000 Gt in deep saline aquifers, and in excess of 15 Gt in unminable coal seams (IEA Greenhouse Gas R&D Programme, 2001). Subsurface injection of CO₂ offers an environmentally low impact method for reducing atmospheric CO₂ concentrations.

Various processes could affect the fate of injected CO₂. Hydrodynamic and geochemical processes include advection, dispersion, diffusion, dissolution, partitioning into hydrocarbons, sorption onto mineral phases, biogeochemical reactions, and loss of injected CO₂. Tracking of the CO₂ plume to monitor transport and storage can be accomplished using natural and added conservative tracers. Natural tracers could include carbon stable isotope analyses, while added tracers could include use of non-reactive noble gases or perfluorocarbons.

Reactions between CO₂ and a selected tracer suite, as well as the evaluation of geochemical and hydrodynamic processes, can be assessed using a High Pressure Flow-Through System (HPFS) (Figure 1) constructed at Oak Ridge National Laboratory (ORNL). The data generated in these experiments could contribute to the accuracy of predictive codes for geophysical models concerned with CO₂ plume modeling.

The primary objectives of the HPFS are to: i) understand the subsurface behavior of the selected tracers and the CO₂, which will help validate predictive codes and models, ii) determine the physical, geochemical, and transport related interactions of tracers and CO₂ with reservoir materials, iii) test the accuracy of using periodically introduced tracers to predict breakthrough behavior, and iv) make the HPFS available for laboratory scale assessments of geologic sequestration of carbon.

HPFS design:

The HPFS is capable of operating at a maximum working pressure of 31 MPa and maximum temperature of 100°C. The maximum pressure (31 MPa) constrains the simulation of subsurface depths to less than 3.2 km, based on calculations of hydrostatic pressure assuming a fluid density of 0.001 kg cm⁻³. Depending on the thermal gradient (15°C/km to 30°C/km), the system temperature constraint of 100°C limits the HPFS to simulation of depths ranging from 3 – 6 km. The HPFS can operate with CO₂ as a gas, liquid, or supercritical fluid, and is also capable of accommodating experiments requiring the use of brines and/or hydrocarbons. Because brines and/or hydrocarbons may be used in the system, it was constructed of corrosion resistant steel alloys. At all brine injection points and brine flow paths the corrosion resistant alloy Monel-400 was used (www.specialmetals.com). The test cell was constructed using a 6.1 m length of 9.5 mm (3/8 inch) 2507 Super-Duplex alloy, a corrosion resistant alloy with a

small volume expansion when heated (www.super-duplex.com). The remaining tubing and valves are corrosion resistant 316 stainless steel.

Temperature and pressure measurements are acquired using type T thermocouples and piezoelectric transducers (0 – 41 MPa) respectively. Temperature and pressure data are monitored and recorded using LabView equipment. The pore volume of the test cell is measured using helium porosimetry. Porosimetry measurements would be performed before experiments or after any changes to the test cell, such as the addition of a fluid (i.e., brine and/or hydrocarbon). Upstream flow and pressure are controlled by a High Performance Liquid Chromatography (HPLC) pump, which is capable of metered flow rates ranging from 0.1 – 10.0 mL min⁻¹. A back pressure regulator (BPR) located at the downstream end of the HPFS protects the gas chromatograph (GC) from high pressures in the system.

Samples used in the HPFS are composed of CO₂ and/or N₂ and selected conservative tracers. Tracer types include stable isotopes, noble gases, non-reactive salts, and perfluorocarbons (PFTs). Samples introduced to the test cell are first allowed to homogenize in one of several gas homogenization reservoirs (GHR) with volumes of 95, 150, or 300 mL. After homogenization the sample enters (by way of valving) the test cell, where partitioning and sorption are likely to occur. Once the sample exits the test cell it passes through a static sample loop that can be sealed and isotopically analyzed offline. The sample then passes through a Valco sample valve, which injects a 250 µl slug of the sample into a GC equipped with an electron capture detector (ECD). Figure 2 presents a generalized schematic of the experimental experiment.

Tracers:

Chemically inert perfluorocarbon tracers (PFTs) with different molecular weights, solubilities, and clay and hydrocarbon sorption characteristics (Dugstad et al., 1992) were chosen as conservative tracers. The differences in molecular weights of the PFTs allows for GC separation, with heavier PFTs eluting later than lighter ones (Figure 3). Attributes of PFTs include stability at temperatures up to 500°C, low detection limits at femtoliter levels, non-toxicity, and lack of interactions, which allows simultaneous use of multiple PFTs (Phelps and Fredrickson, 2002). Air and water diffusivities of select PFTs have been calculated using methods of Tucker and Nelken (1982) (Figure 4). Calculation of the diffusivities of the tracers SF₆, perfluorodimethylcyclobutane (PDCB), perfluoromethylcyclopentane

(PMCP), perfluoromethylcyclohexane (PMCH), perfluorodimethylcyclohexane (PDCH), and perfluorotrimethylcyclohexane (PTCH) show an inverse correlation with molecular weight. The greater the tracers molecular weight the lower the diffusivity. Therefore, highest to lowest diffusivity is in the order of SF₆, PDCB, PMCP, PMCH, PDCH, and PTCH (Figure 4). The PFT suite is introduced in paired stepwise injections to differentiate mass transfer and specific transport processes. This technique aids in determining how closely the flow path of the PFTs replicate the flow path of the CO₂.

Results:

Experiments were performed using the PFT perfluorodimethylcyclohexane (PDCH) with a carrier gas (N₂) to assess the resolution of detection and separation of isomers of the PDCH after it passed through the HPFS. A mass of 2 µg of PDCH for a 10 mL injection volume was introduced to the HPFS using a gas tight syringe heated to 70°C while the system was under vacuum. The PDCH tracer was directed by way of valving to a 300 mL GHR where it was allowed to homogenize for greater than 15 hours with the carrier gas (N₂). The experimental parameters after homogenization were a pressure of 4.8 MPa, a temperature of 19°C, and a flow rate of 3 mL min⁻¹. The PDCH in the N₂ carrier gas was then introduced to the test cell, which was filled with Ottawa sand (clean quartz sand). Upon exiting the HPFS the PDCH was detected by the GC (Figure 5), and the amount was determined to be 0.1 pg per 250 µl analyte based on the standard curve (Figure 6). The resulting concentration of 0.1 pg/250 µl approached the instrument detection limit, being approximately 10 fold above the baseline. Instrument detection limit was determined to be a concentration of 1×10^{-14} g/mL or a mass of $\sim 5 \times 10^{-15}$ g.

Discussion:

The HPFS is effective at detecting trace amounts of PFTs and has the potential to evaluate physical and geochemical controls of long term sequestration of CO₂. The HPFS can accommodate experiments requiring various gases (e.g., CO₂, N₂, and He), liquids (i.e., brine and/or hydrocarbon), and tracers (i.e., stable isotopes, noble gases, non-reactive salts, and PFTs). This system is also versatile enough to be used for alternate subsurface experiments requiring high pressure and high temperature. As part of the Geologic Sequestration project, in which numerous national labs participate, one of the objectives is to make the expertise and ORNL HPFS facilities available for other CO₂ sequestration

projects. This includes the use of additional subsurface materials for hydrodynamic and geochemical process analysis.

Future research:

Plans for future research include utilizing PFTs in stepwise concentrations and addition of helium porosimetry for the determination of substrate porosity, as well as a series of experiments examining the effects of brines and/or hydrocarbons on CO₂ transport. These experiments will be performed using a variety of experimental pressures and temperatures with representative formation material.

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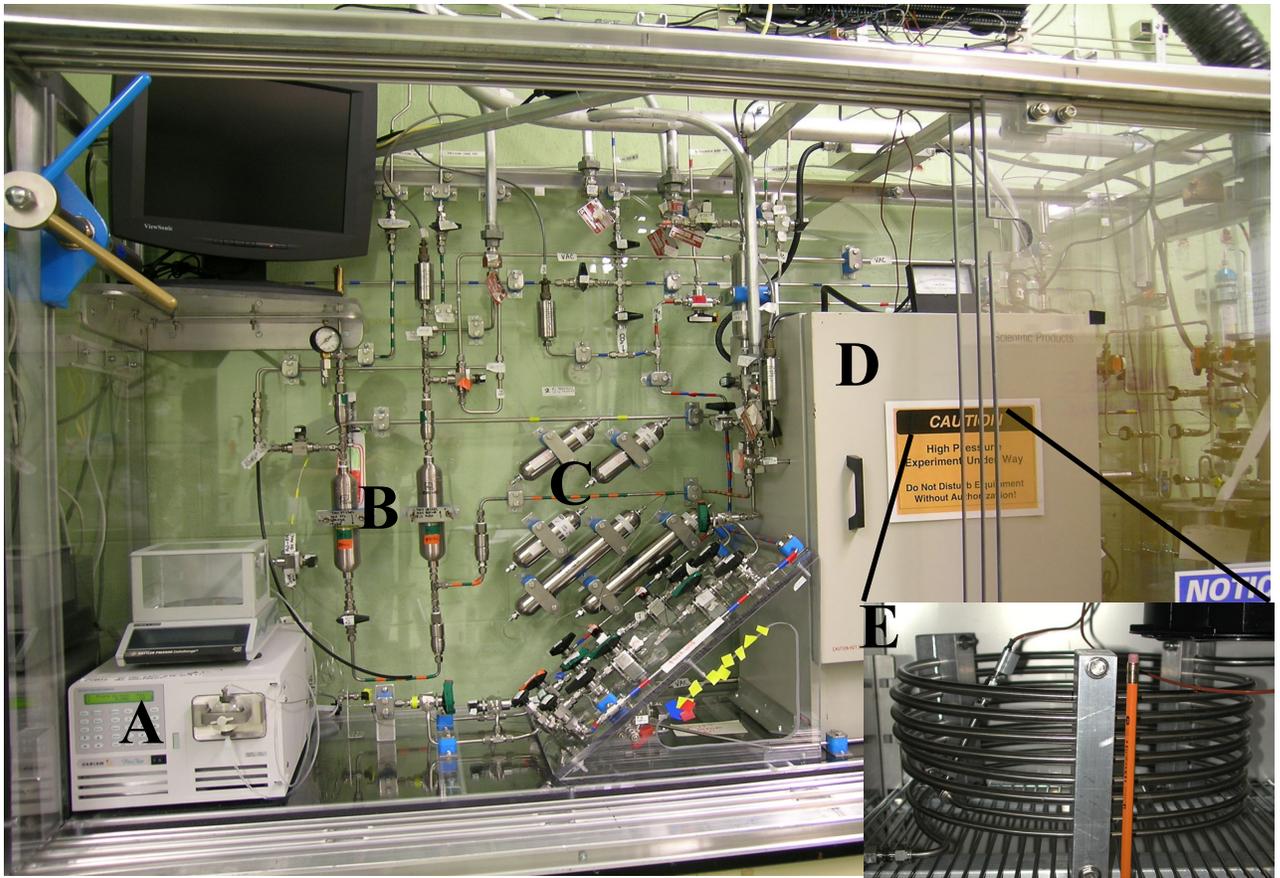


Figure 1. Picture displays the primary components of the HPFS. A) HPLC pump, B) Brine reservoirs, C) Gas homogenization reservoirs, D) Isotemp oven, E) Test cell (located inside isotemp oven). Gas chromatograph is off the photo to the right not shown.

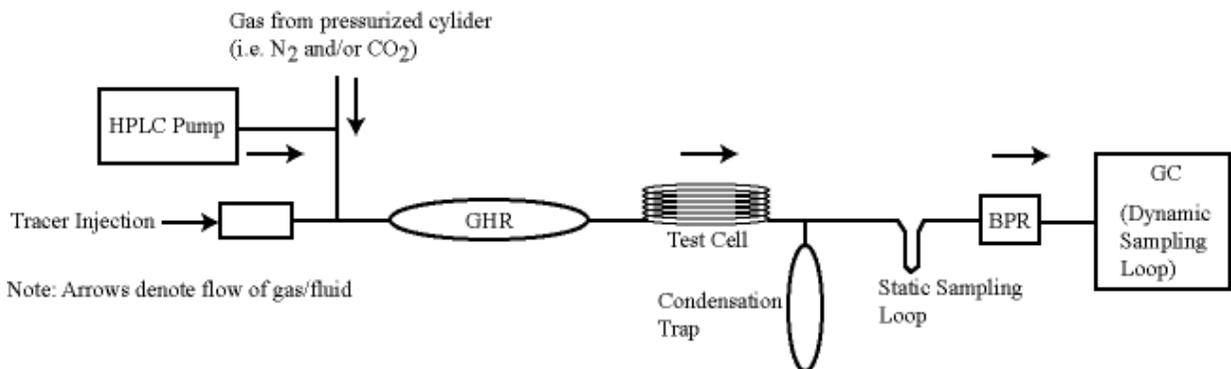


Figure 2. Schematic of generic experimental method. Pefluorocarbon tracers (PFTs) are injected and introduced to the GHR alongside of carrier gas(es) (i.e. CO_2 and/or N_2). The HPLC pump supplies the upstream pressure and controls the flow rate. The carrier gas(es) and PFTs are then introduced into the test cell where partitioning and sorption are likely to occur. The concentrations and travel times are then measured by the in-line GC connected to the downstream section of the HPFS.

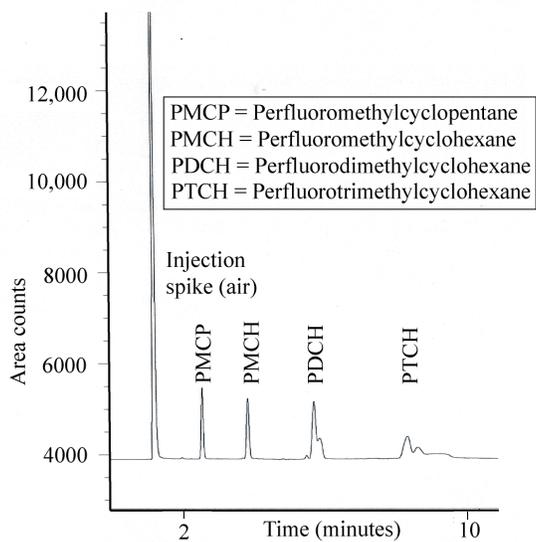


Figure 3. Gas chromatograph displaying the differing elution times of the 4 PFTs

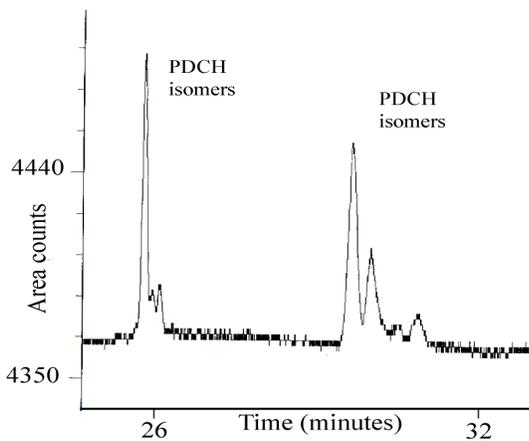


Figure 5. GC Response for PDCH determined from preliminary PFT injections on flow-through system sampled from gas sample valve.

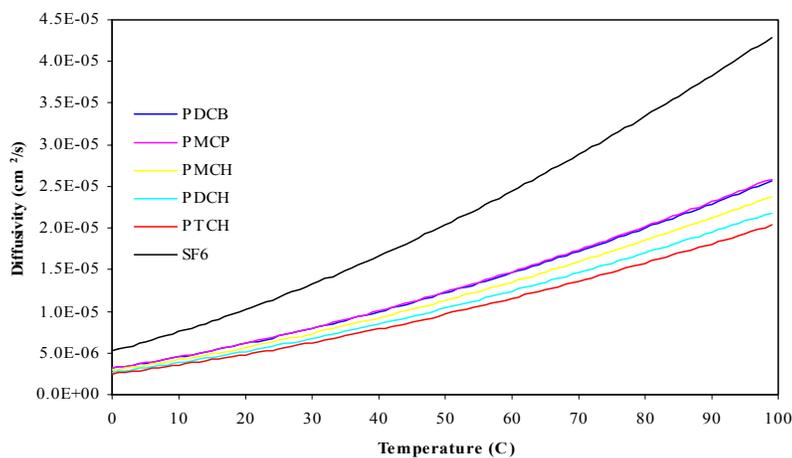


Figure 4. Diffusivity of various tracers in water (modeled from Tucker and Nelken, 1982). From lowest to greatest the molecular weight of the tracers is SF6, PDCB, PMCP, PMCH, PDCH, and PTCH.

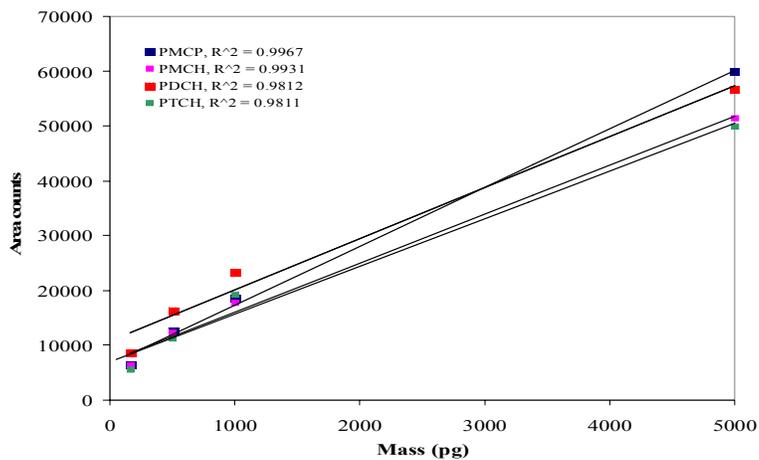


Figure 6. Standard curve generated using 4 tracers at a 50 μ l analyte volume.

References cited:

Bachu, S., Gunter, W.D., and E.H. Perkins. 1994. Aquifer Disposal of CO₂ : Hydrodynamic and Mineral Trapping. *Energy Convers. Mgt.* 35:269-279.

Dugstad O., Bjornstad T., and Hundere I.A., 1992. Construction of a slim-tube equipment for gas tracer evaluation at simulated reservoir conditions. *Applied Radiation and Isotopes* 43, 527-535 (1992).

Holloway S., 2001. Storage of fossil fuel-derived carbon dioxide beneath the surface of the earth. *Annual Review of Energy and the Environment* 26, 145.

IEA Greenhouse Gas R&D Programme, Putting carbon back into the ground, ISBN 1 898373 28 0 (2001).

Lackner K.S., 2003. A guide to CO₂ sequestration. *Science* 300, 1677-1678.

Phelps T.J. and Fredrickson J.K., 2002. Drilling, Coring, and Sampling the Subsurface Environment. *In* Manual of Environmental Microbiology. C.J. Hurst (Ed.). ASM Press, Washington, D.C.

Stevens, S.H., Kuuskraa, V.A., Spector, D., and P. Riemer. 1998. CO₂ Sequestration in Deep Coal Seams: Pilot Results and Worldwide Potential. GHGT Conference Proceedings, 30 August-2 September, Interlaken, Switzerland.

Tanaka, S., Koide, H., and A. Sasagawa. 1995. Possibility of Underground CO₂ Sequestration in Japan. *Energy Conservs. Mgmt.* 36:527-530.

Van der Meer, L.G.H. 2002. CO₂ Storage in the Subsurface. GHGT Conference Proceedings, Abstract A1-0, 1-4 October, Kyoto, Japan.

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<http://www.super-duplex.com>