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The U-Tube: A Novel System for Acquiring Borehole Fluid Samples from a Deep Geologic CO_2 Sequestration Experiment

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Abstract

A novel system has been deployed to obtain geochemical samples of water and gas, at *in situ* pressure, during a geologic CO_2 sequestration experiment conducted in the Frio brine aquifer in Liberty County, Texas. Project goals required high-frequency recovery of representative and uncontaminated aliquots of a rapidly changing two-phase (supercritical CO_2-brine) fluid from 1.5 km depth. The data sets collected, using both the liquid and gas portions of the downhole samples, provide insights into the coupled hydro-geochemical issues affecting CO_2 sequestration in brine-filled formations. While the basic premise underlying the U-Tube sampler is not new, the system is unique because careful consideration was given to the processing of the recovered two-phase fluids. In particular, strain gauges mounted beneath the high-pressure surface sample cylinders measured the ratio of recovered brine to supercritical CO_2. A quadrupole mass spectrometer provided real-time gas analysis for perfluorocarbon and noble gas tracers that were injected along with the CO_2. The U-Tube successfully acquired frequent samples, facilitating accurate delineation of the arrival of the CO_2 plume, and on-site analysis revealed rapid changes in geochemical conditions.

Introduction

The Frio Brine Pilot is a field experiment to evaluate the potential of brine aquifers to serve as a geologic repository for sequestered CO_2 [Hovorka, 2005]. The Frio experiment is part of the U.S. Department of Energy's broad program to explore feasibility and operational issues related to geologic sequestration of CO_2 in a brine-filled reservoir to mitigate the impacts of increasing CO_2 emissions on global climate. Many complex physical and chemical processes arise from the injection of CO_2 into a brine-filled reservoir. The CO_2 has greater mobility and lower density than the brine, resulting in a faster-moving, distinct gaseous phase with potentially significant gravity drive. Chemically, the CO_2 is soluble in the brine, resulting in a lowered brine pH and a diverse range of chemical interactions, particularly with minerals containing alkaline cations trapping CO_2 as carbonates. (The reader is referred to Pruess et al. [2003], Gunter et al. [1993] and Bachu et al. [1994] for a discussion on some of these physical and chemical processes.) One of the prime objectives of the Frio Brine Pilot experiment is to observe

the changes in the formation fluid caused by the introduced CO_2. Acquiring frequent samples is necessary to both define the arrival time and track geochemical changes occurring at the front of the CO_2 plume. This testing can yield insight into the transport processes controlling CO_2 movement and lead to better understanding of the underlying mechanisms controlling geologic CO_2 sequestration.

Obtaining a representative downhole fluid sample from great depths has never been a simple endeavor. During sampling, changes in pressure and temperature produce changes in fluid chemistry [Kharaka and Hanor, 2004]. Traditional sampling in boreholes has been performed either by a submersible pump or by lowering a sampling device within the wellbore [Lerner and Teutsch, 1995]. In two-phase systems, submersible pumps fail to operate and gas separators are needed, drastically changing the composition of the downhole fluid. Sampling devices lowered into the wellbore, such as the flow-through downhole Kuster sampler (Kuster Company, Long Beach, California), require wirelines and need to be run in and out of the borehole for each sample acquired. Because the sample obtained by the sampler is of limited volume, if the wellbore is not purged prior to deploying the sampler, the representativeness of the collected fluid would be in question. There are other methods used for producing fluids from deep boreholes, such as conventional gas lift systems, but these alter the chemical and physical composition of the recovered fluids and are not usually considered acceptable for geochemical sampling.

The U-tube sampling system [Figure 1] developed for the Frio Brine Pilot experiment utilizes a compressed gas to move the fluid to be sampled through a small diameter tube that goes down to the zone of interest and returns to the surface, forming a "U." A short stinger with a check valve runs through a pneumatic packer used to isolate the perforated section of the wellbore and terminates at an inlet filter sitting in formation fluid. This system is fundamentally the same as the porous cup sampler developed for vadoze zone sampling by Wood [1973]. Others have since used this technique for shallow groundwater [Einfeld and Koglin, 2000]. To acquire a sample, the U-tube, as shown in Figure 1, is first purged with compressed nitrogen. The tube is then vented, allowing formation fluid to enter the U through the check valve while purge gas vents. Finally, compressed gas is applied to the drive leg tube, and fluid is collected from the sample leg of the U-tube. While the operation of the sampler is conceptually straightforward, the actual processing of the sample stream for the case of two-phase formation fluids (i.e., both a brine and supercritical CO_2 phase) requires care to maintain controlled conditions during sampling.

This paper is primarily concerned with describing the U-tube sampling process. The ability of the system to process the multiphase brine/CO_2 fluid is demonstrated through the presentation of data collected during CO_2 injection. A simple radial model is used to estimate the CO_2 formation saturation using the measured CO_2 and tracer transport times, suggesting the fundamental behavior of CO_2 to bypass the lower-mobility brine. While the Frio Brine Pilot experiment was limited in size and duration, the data collected are similar to the data required for long-term monitoring and verification of geologic CO_2 sequestration.

Frio Field Site and Experimental Conditions

The Frio Brine Pilot experiment was conducted in a 24 m thick mineralogically complex Oligocene reworked fluvial sandstone located within the Frio formation. The Sun-Gulf-Humble Fee Tract 1 in Liberty County, Texas, Well #4, a nonproducing oil well, was recompleted and perforated between 1,528.3 m to 1,534.4 m to serve as an observation borehole. With an apparent dip of 20 degrees, a new CO_2 injection well was drilled 30 m down-dip, and perforated 12 m deeper, between 1,540.8 m and 1,546.3 m. The perforations were all within the upper 6.1 m of the 24 m thick sand, which logs indicate is isolated by a thin regionally continuous silty-shale layer. Location of the Frio site relative to the upper Texas coast is shown in Figure 2. The testing plan called for the injection of CO_2 at a rate of 3 kg/sec while monitoring downhole pressures, temperatures, fluid composition, and chemical changes at the observation borehole. Geophysical logging using electrical, seismic, and saturation logging tools was carried out both to perform baseline characterization and to understand changes that occur because of the CO_2 injection.

The Frio Brine Pilot experiment posed a series of challenges that seemed to eliminate all of the commonly used methods for downhole sampling. The Frio brines are high total dissolved solids (TDS) (10% by weight) and near saturation with methane; thus, they are easily altered by degassing or oxidation caused by contact with air. The competing sampling requirements—causing minimal disturbance to the flow field while ensuring that the sample represented formation fluid—meant that a delicate balance between purge quantity, sample frequency, and sample size needed to be maintained. The sample fluid was to be kept at pressure, so that there would be no gas loss and the sample would be isolated from external contaminants, particularly oxygen, which would lead to rapid changes in sample chemistry. One of the sampling goals was to determine the arrival time of the CO_2 front and capture the geochemical changes as the plume passed by the observation borehole. This would require a method that could operate both frequently and reliably during a 24-hour-a-day, continuous operation.

We theorized before the test that at some point during the CO_2 injection, the wellbore fluids in the observation borehole would transition from single-phase brine to a supercritical CO_2/brine mixture that would lift itself, owing to the low density of the fluid. While it would have been possible to allow the well to produce itself at this point, the relatively large diameter of the production tubing would have resulted in either (1) perturbing the flow field through rapid production or (2) poor temporal resolution and large fractionation of brine and CO_2 phases if production in the tubing was throttled back. The U-tube optimized transport of mixed-phase fluids to the surface at a high velocity, providing samples with minimal phase separation and good temporal resolution.

The U-Tube Sampling System

To meet the requirements of sampling at the Frio field site, we designed the U-tube sampling system in parallel with the observation well completion. A pneumatic packer was used to isolate the perforated interval. From a geochemical sampling standpoint, it

would have been best to put the bottom of the packer just above the top perforation, minimizing the volume below the packer. However, to accommodate some of the planned logging operations, the packer was set 14.3 m above the top perforation. The inlet port to the U-tube, a 60 cm long piece of 40-micron sintered stainless steel (Mott Corporation, Farmington CT), was located 30 cm below the bottom of the packer. The volume of the cased interval between the bottom of the packer and the top of the perforations was 177.1 l, with the 6.1 m perforated interval having an additional 75.4 l volume.

The decision to move the packer above the zone of interest to facilitate geophysical logging had implications for the composition of the sampled fluid. The supercritical CO_2, being buoyant, would preferentially displace brine and accumulate beneath the bottom of the packer. This behavior is beneficial for identifying the earliest time of arrival for the gaseous components. However, it may not reflect the true composition of the formation fluid. We can assume that the composition of the collected fluid, in a single-phase system, reflects a permeability-weighted average of the fluid immediately outside of the borehole perforations, but the situation in a multiphase system is more complicated. Because the mobility of the supercritical CO_2 is much greater than the native brine, the CO_2 will preferentially enter the wellbore, to the possible exclusion of any brine within the formation.

The inner diameter of the U-tube tubing is the most important design factor in determining the behavior of the sampler and the ability to obtain fresh formation fluid. As the tubing diameter increases, the sample size gets larger, but the amount of compressed gas required to drive the sample also increases. To prevent degassing and phase segregation in the sample tubing, the U-tube is back-pressured to bottom-hole conditions at the top of the sample tube. The pressure required to drive the sample to the surface at formation pressure requires that the bottom of the U-tube be maintained at twice the formation pressure during sampling. Since the Frio observation well bottomhole pressure is approximately 146.3 bar, the resulting pressure at the bottom of the closed U-tube is 292.6 bar. Since the hydrostatic pressure in the U-tube (because of the 1,513.9 m column of nitrogen) adds approximately 43.6 bar to the downhole pressure, the surface compressor must therefore be capable of delivering nitrogen at 249.0 bar to retrieve a sample at formation pressure.

A 9.5 mm O.D. × 1.2 mm wall-thickness stainless steel tube was used for the drive and sample legs of the U-tube. With this geometry and an installed depth of 1,513.9 m, the total volume of the U-tube was 117.7 l. Since the hydrostatic fluid level at the Frio is approximately 100 m below ground surface, the sampling tubes filled with 102.1 l during the U-tube venting process. Four 200-bar-rated stainless steel sample-collection pressure vessels, each with a volume of 13 l, were used to accumulate fluid.

Lifting the water from the sampling interval to the ground surface via the U-tube, and purging the sampling equipment of residual water between samples, was an eight-step process. A description of the eight operating steps is provided below, along with the major components of the automated U-tube sampling equipment, including the flow manifolds, data-acquisition system, and control software.

Custom-built flow manifolds, a data acquisition system, and software were combined to form an integrated hardware and software system to lift the water and to automatically control the sample processes. The flow manifolds consisted of various combinations of manual, pressure release, check and/or pneumatic-actuated valves, filters, pressure regulators, tanks, pumps, compressors, pressure gauges and transducers, and piping (Figure 3). These hardware components stored, conveyed, and controlled the movement of fluids from the sample interval in the well to the surface, where the water and gases were sampled and analyzed.

The individual flow manifolds, shown in Figure 3, comprise the U-tube sampler and were used to control specific processes that will be described shortly, along with the eight sample processes. The data acquisition system consisted of sensors (pressure transducers and strain gauges), programmable data logging devices that had both input (logging) and output (control) capabilities, and a personal computer. These hardware components measured, recorded, and stored test data, provided a feedback mechanism for the software to control processes, and provided the computer platform on which the control software operated. Custom-software was written using LabVIEW graphical programming language (National Instruments, Austin, TX) to log and archive the data, control the hardware, and automate the sampling processes.

A 12,000 l capacity liquid nitrogen (LN) dewar was brought on-site and used as the source of high-purity nitrogen gas, to lift the water in the U-tube and to purge residual water from the system after sampling. LN was drawn from the dewar through a passive, short-tube vertical evaporator—where it boiled, producing nitrogen gas. The nitrogen gas was then compressed from the inlet pressure of 1.1 bar to 272 bar using a five-stage 30 horsepower compressor and stored in four 14,000 l (at standard pressure) capacity high-pressure gas cylinders. The LN dewar, compressor, and high-pressure gas cylinders are referred to as the high-pressure gas supply manifold (Figure 3).

Filling of the high-pressure gas cylinders was accomplished by continuously measuring pressures in the high-pressure gas supply manifold, using a 0–680 bar pressure transducer (gauge P1, Figure 3), whose output signal was recorded by the data-acquisition system. Feedback from the pressure transducer was monitored by the control software, which started and stopped the compressor by switching a control relay in the compressor's power supply. The software compared the measured pressures against lower and upper pressure-set points, defined by the user, to determine when to start and stop the compressor, respectively. A poppet valve on the compressor served as a safety back-up in case of a problem with the control system.

The first step in the sampling process, referred to as the U-tube fill cycle, consisted of filling the U-tube with water from the test interval. This was accomplished by venting the upstream and downstream limbs of the U-tube to the atmosphere through the vent manifold (Figure 3). Venting the U-tube caused the check valve, located in the well at the bottom of the U-tube assembly, to open. Water then flowed from the packed-off section of the well (i.e., sample interval) through the downhole check valve, into both limbs of

the U-tube. Water entered and rose in the upstream and downstream limbs of the U-tube, as long as the fluid pressure in the tube on the downstream side of the check valve was below the upstream pressure. In this case, the upstream pressure is equal to the bottom-hole pressure in the well. The maximum water level rise in the tube is achieved by venting the U-tube to the atmosphere. Water will then seek a maximum level equal to the hydraulic head in the reservoir. For the Frio Brine Pilot, the U-tube was allowed to fill with water for approximately 15 minutes, at which point, closing the vent manifold ended the cycle.

The second, third, and fourth steps, referred to as the sampler purge, bleed-down and evacuation cycles, respectively, were performed in parallel with the U-tube fill cycle to save time. The second step consisted of purging the gas-sample manifold, sample vessels, and liquid-sample manifold (Figure 3) with nitrogen gas to remove any residual fluid from these components prior to sampling. This process helped minimize cross-contamination from previous samples and took about 6 minutes to complete. Gas from the high-pressure supply manifold was allowed to flow through the N_2-purge manifold (Figure 3), sweeping residual water from the sample manifolds and vessels, out through the drain manifold and into a large tank. Once the purge cycle was completed, the nitrogen gas was turned off at the start of the third step, and the gas pressure in the various manifolds was allowed to bleed down through the drain manifold to the atmosphere. All manifolds were shut in at the completion of the bleed-down cycle, which lasted approximately 4 minutes.

The fourth step, or evacuation cycle, involved using a vacuum pump to remove residual nitrogen gas from the sample manifolds and vessels before collecting the next sample. Any residual nitrogen would serve to dilute the gases collected during sampling and therefore reduce the sensitivity of the measurements. The vacuum manifold (Figure 3) was opened, and a rotary-vane vacuum pump was turned on to evacuate the gas from the sampling manifolds and vessels. A maximum vacuum of 660 mm Hg could be obtained with this pump. The manifold was closed and the pump was turned off at the end of the evacuation cycle, which took approximately 2 to 2.5 minutes to complete.

The fifth step involved charging the U-tube drive leg with nitrogen gas to produce water under high pressure from the sample interval. Sample recovery was initiated by pressurizing the drive leg of the U-tube, using the nitrogen gas (at 272 bar) stored in the high-pressure gas supply manifold. Pressurizing the fluid in the U-tube caused the downhole check valve to close, preventing water (and nitrogen) from flowing back into the sample interval. It also created the driving force to push the water in the U-tube "uphill" to the surface, via the sample leg of the tube. At the same time that the drive leg of the tube was charged with gas, water (and any residual gas located at the top of the water column) flowed up the sample leg of the U-tube to the surface, where it discharged through the high-pressure vent (Figure 3). A backpressure regulator, located before the high-pressure vent and set at 136 bar, maintained the sample fluid within the U-tube near the downhole reservoir pressure.

It was important to maintain the samples at reservoir conditions, both to prevent dissolved gases from coming out of solution and to minimize changes in brine chemistry during the sampling process. It was common practice during Step 5 to "dump" the first 10 minutes of sample (about 20 to 25 l) out the vent, because it was felt that this water was less representative of formation conditions than the fluid located near the bottom of the U-tube. This is because brine initially enters the U-tube under reservoir conditions and then depressurizes as it moves up the tube during the U-tube fill cycle (Step 1). Therefore, the initial 20 to 25 l of water came from the top of the water column in the downstream limb of the U-tube, where depressurization is greatest and changes in dissolved gas and water chemistry would be most pronounced. At the end of the dump cycle (i.e., Step 5), we collected grab samples for aqueous geochemistry and offsite PFT analysis.

After dumping the prescribed amount of water, the high-pressure vent was closed and the sixth step, or sampling cycle, began. Water flowing up the U-tube during the dump cycle was immediately diverted from the high-pressure vent to the liquid-sample manifold, consisting of four sample vessels (Figure 3). It typically took 10 to 12 minutes to lift 52 l of water to the surface and to fill the four sample vessels to capacity at approximately 150 bar. The combined weight of the vessel, water, and gas were continuously measured throughout the sampling cycle, using electronic strain gauges located at the base of each sample vessel. These measurements were recorded by the data acquisition system and saved to an output file.

Pressure measurements from a 0–680 bar pressure transducer, located at the top of the sample vessels in the gas-sample manifold (gauge P3, Figure 3), were used as the criteria for ending the sampling cycle. The output from the transducer was recorded by the data acquisition system and used as input to the control software. The control software automatically stopped the sampling cycle when the measured pressures in the manifold exceeded the bottom-hole formation pressure (i.e., > 150 bar). The sample manifold closed automatically at the end of the cycle, where the sample remained until analyzed.

The seventh and eighth steps in the sampling process were performed concurrently and are referred to here as the analysis and U-tube purge cycles, respectively. The analysis cycle consisted of opening the analysis manifold, allowing water and dissolved gas to flow from the top of the sample vessels into a gas separator kept at atmospheric pressure. Free gas in the sample, and exsolved gases coming out of solution, were pumped from the top of the gas separator through a quadrapole mass spectrometer (Pfeiffer Vacuum Technology Inc., Nashua, NH) analyzer and a Gem 2000 Landfill Gas analyzer (CES-Landtec, Coltron, CA). Both instruments were used to analyze gas compositions, with the Gem 2000 device intended to provide immediate estimates of the methane, oxygen, and CO_2 compositions. The analysis cycle was the only sampling step that was not fully automated, since the quantity of exsolved gas was expected to be highly variable throughout the test. The analyst was required to manually open the analysis manifold to prevent the accidental loss of sample during the analysis process—a critical step, deemed important enough to warrant the undivided attention of the analyst to prevent the accidental loss of data. A 500 cc five-layer aluminized sampling bag (Calibrated

Instruments, Hawthorne, NY) was filled, so that if replicates of analysis on the mass spectrometer were needed, they could be performed at a later time.

The eighth and final step in the sampling process was to purge the remaining water from the U-tube prior to repeating the entire sampling process (Steps 1–8) again. This process was performed in parallel with the gas analyses. Immediately following the closure of the sample manifold (Step 6), water traveling up the U-tube was diverted back to the vent manifold and out the atmospheric vent to the drain. Periodically, the purged fluid was diverted to collection tanks. In several instances the 20 to 25 l of fluid were filtered through 0.1 micron filters, and the filters were analyzed for any CO_2 induced changes in microbial biomass. Nitrogen gas was swept through the U-tube for approximately 15 minutes to remove residual water. Both the vent manifold and high-pressure gas supply manifolds were closed at the end of the U-tube purge cycle.

The sampling processes described above required approximately 50 minutes to collect one sample from a depth of 1.5 km. To minimize errors produced by manually operating the sampling system for the anticipated two weeks of around-the-clock sampling, the U-tube sampling system was automated. A software program was developed that allowed the user to manually open and close key valves that controlled the flow of water or nitrogen through the various manifolds. Air-actuated valves fitted with electric solenoids were used because they could be easily controlled by the software and control hardware. (Automated valves are designated with an "A" and manual valves with an "M" preceding the valve number in Figure 3.) The equipment was operated in the manual mode to determine the appropriate combination of valves that needed to be opened and closed to accomplish each of the eight sampling steps described above. The duration of each sampling step or cycle was also determined during manual operation. Once the manual valve-control program was completed, a second program was written to automatically open and close key combinations of valves, corresponding to the eight sampling steps. Timing was also built into the automated program, allowing the user to control the duration of each process to fine-tune the system as sampling progressed. As noted earlier, pressure was also measured and used to control the duration of the sampling cycle (Step 6).

Automated control of the U-tube sampler worked flawlessly until the CO_2 began to enter the observation well in large quantities. As the quantity of CO_2 increased, Joule-Thomson cooling of the CO_2 as it expanded through valving caused the brine to freeze in the vent manifold, thus blocking the outlet. The sampler had to be shutdown and allowed to thaw before sampling resumed in the manual operating mode. The CO_2 eventually completely displaced the brine in the well, changing the composition of the U-tube samples from a mixture of brine and gas to all CO_2 gas. Freezing problems became less severe when the system became self-lifting, meaning that the pressure of the CO_2 gas was sufficient to push or lift it from the test interval via the U-tube to the surface. Thus, nitrogen gas was no longer needed to lift the sample.

Changes were made to the sampling process and a new automated program was written to optimize CO_2 gas production when the well became self-lifting. Only the bleed-down

(Step 3), sampling (Step 6), and analysis (Step 7) cycles were retained; the remaining sample processes were no longer needed. The new sampling process essentially consisted of repeatedly filling and emptying the sample vessels of wellbore fluid, predominantly CO_2. The automation program was modified so that the sampling (i.e., fill) cycle ended, and the bleed-down cycle began, when the gas pressure in the sample vessel exceeded 48 bar. Likewise, the bleed-down cycle ended, and the fill cycle began, when the pressure dropped below 7 bar. Lowering the pressure of the gas from 150 bar downhole (where it is in the supercritical state) to 48 bar in the sample vessels helped prevent freezing at the outlet, allowing much smoother operation of the system. Eliminating the sampler (Step 2) and U-tube (Step 8) purge steps using nitrogen gas, coupled with the pressure-controlled cycling noted above, meant that the sample vessels were always filled with fluid from the well. The sampling process took approximately 11 minutes and served to continuously "pump" the well. Gas composition was continuously monitored by feeding gas into the mass spectrometer in parallel with the fill and bleed-down cycles.

As a final note, the data acquisition system recorded fluid pressures in the high-pressure supply, downstream U-tube, and sampling manifolds (gauges P1 through P3, Figure 3) and the sample weights. These measurements were saved to an output file for further evaluation. This procedure produced a continuous record of U-tube sampling conditions. The status of each automated valve (i.e., open or closed) was also monitored by the automated program and saved to a separate output file, to document system-operating conditions.

Results

The Frio Brine Pilot experiment resulted in the injection of approximately 1,600 tons of food-grade CO_2 over a period of 10 days. CO_2 injection started on 4 October, 2004 at 11:34, at a rate of approximately 3 kg/s. Figure 4 shows changes in the bottomhole pressure for the Frio injection well and observation well, along with the CO_2 injection rate. The two pressure declines that occurred on 5 October at 22:30 and on October 6 at 14:30 were pauses in CO_2 injection caused by problems in an injection booster pump. The two longer pauses in injection that occurred on 7 October at 11:43 until 8 October at 18:14 and 12 October at 18:03 until 13 October at 17:56 were performed to observe pressure transients and perform geophysical logging. Injection was halted on 14 October at 14:13, and the final pressure fall off was monitored until 29 October, 12:30.

The U-tube collected 41 brine or brine/supercritical CO_2 samples between the start of the initial injection and 7 October, at 11:24. Short duration pressure transients in the observation zone corresponding to the U-tube sample times are shown in Figure 5. After the CO_2 arrival, the pressure transients became greater in duration and amplitude as a result of the increased fluid compressibility from two-phase conditions. As noted previously, increasing concentrations of CO_2 made sampling problematic, because Joule-Thomson expansion would cool valves and the brine would freeze. The U-tube sampling protocol was subsequently modified to accommodate the self-lifting borehole fluid as described in the U-tube Design and Operation section. The U-tube was operated in self-lifting mode until 11 October, at 15:13, when the automated analysis equipment on the

surface was shut down and demobilized. During this later period of gas sampling, the mass spectrometer analyzed 327 samples. The U-tube was subsequently closed at the surface and available for periodic monitoring. Post-injection test geophysical logging operations required the eventual removal of all downhole equipment.

The mass spectrometer analysis of the gas evolved from the pressurized samples is shown in Figure 6. The first sample confirming the arrival of the CO_2 was collected 50.9 hours after the start of injection, on 6 October at 14:28. While previous samples contain less than 1% CO_2, this sample contains 3.6% CO_2. The CO_2 concentration steadily increased throughout the next day of sampling as CO_2 replaces CH_4 as the primary gaseous constituent in the sample stream. The oxygen and argon content in the early samples suggests contamination of the formation fluid caused by the introduction of surface water during the wellbore completion. Despite the well being produced using nitrogen lift in an attempt to remove this fluid, the continuing presence of oxygen and argon serves as a geochemical tracer, indicating the persistence of non-native fluid in the formation.

Figure 7 shows the density of the fluid collected in the high-pressure cylinders. The weight measurement was recorded when the sample cylinders reached the formation pressure of 146.3 bars. Note that supercritical CO_2 at 33°C and 146.3 bars has a density of 830 kg/m^3, which closely matches the values measured for four of the last five samples acquired. This agrees with the gas composition analysis, which indicated that the sample was almost entirely composed of CO_2.

Three chemical parameters—electrical conductance, pH, and alkalinity—measured at the site immediately after sample collection from the observation well using the U-tube are shown in Figure 8. Results revealed that the electrical conductance was constant throughout the experiment at ~120 mS/cm (at T = 21–23 °C), but there were major changes in the composition of recovered brine as the CO_2 reached the observation well, including a sharp drop in pH (from 6.7 to 5.7) and sharp increases in alkalinity (from 100 to 3,000 mg/L as bicarbonate), as shown in Figure 9, and (not shown in Fig. 9) dissolved Fe (from 30 to 1,100 mg/L). The chemical data measured at the site at the start of the CO_2 injection were so close to the values obtained for brine samples collected using a downhole Kuster sampler from both the injection and the observation wells before CO_2 injection—that we decided it was redundant to deploy the Kuster sampler downhole at the same time that the U-tube was operating.

Water collected using the U-tube, the Kuster sampler, and other tools were subjected to detailed chemical analysis in the laboratory, using the methodologies described in Kharaka and Hanor (2004). Results showed that the unmodified Frio brine was a Na-Ca-Cl type water, with a salinity of 93,000 mg/l TDS, and with low Br/Cl ratios (indicating dissolution of halite from the nearby salt dome). The unmodified brine is close to saturation with methane, comprising ~95% of total dissolved gas at subsurface conditions (63°C and 143 bar). Results of geochemical modeling indicated that brine pH would have dropped lower than the measured value of 5.7, but for the fact that carbonate and iron oxyhydroxide minerals in the Frio were dissolving rapidly, causing the major increases in alkalinity and dissolved Fe (Kharaka et al., 2005).

Tracers were injected into the CO_2 injection stream at three different times (Table 1). The purpose of the tracer injections was twofold: first, arrival timed are indicative of the formation CO_2 saturation, and second, differences in the travel times of tracers with different brine/CO_2 partitioning coefficients provide an estimate of the residual brine saturation. The first tracer injection consisted of a five-hour-long injection pulse of perfluorocarbon tracers (PFT), consisting of 1.55 kg perfluoromethylcyclohexane (PMCH) and 1.55 kg perfluorotrimethylcyclohexane (PTCH), on 4 October at 13:26, two hours after the initial CO_2 injection. A second tracer injection, consisting of 150 grams perfluoromethylcyclobutane (PMCB) and 150 grams perfluorodimethylcyclohexane (PDCH), was injected on 8 October at 18:19. The last tracers, injected beginning October 9 at 11:37, consisted of a suite of 83.80 gram krypton, an undetermined (caused by pumping problems) quantity of sulfur hexafluoride (< 200 gram), 150 gram PMCH, and 150 gram PTCH tracer. Figure 9 shows the initial PFT breakthrough plotted along with the CO_2 concentration as a percent of gas recovered in the sample, and Figure 10 shows the tracer gas breakthrough for the second PFT injection and third suite of tracers as determined by quadrupole mass spectrometer analysis.

Discussion

The deployment of the U-Tube was considered in comparison to other more common methods of sampling. Because we could find no previous deployment of a U-tube system at the depths we would be operating, no knowledge base on the potential pitfalls of this method was available to guide us. To reduce the impact of potential U-Tube failure on the overall Frio Brine Pilot, two alternative methods of sampling the observation borehole were kept available: (1) downhole sampling with a flow-through sampler and (2) gas-lift production of the observation well. To enable gas lift, a simple port was installed outside of the production tubing for use if the U-tube were to fail. Neither backup method was considered ideal. The gas-lift system would result in substantial changes in fluid composition and would impact the flow field, and the Kuster sampler could have difficulty in obtaining fresh formation fluid if it were not combined with gas lift to ensure sampling fresh fluid. In the end, the reliable performance of the U-tube obviated the need to employ either of the back-up systems.

The fact that the only moving part in the downhole installation was a check ball made the sampling system extremely reliable. The large surface area of the sintered metal filter and small pore size protected the check valve from particulates that could cause the ball from seating properly. Furthermore, cyclical testing of the check valve in both the check and flow directions at operational pressures was performed prior to installation, to minimize potential mechanical failures.

In contrast to the reliable performance of the downhole system, the surface installation required oversight and maintenance. The inlet pressure of the nitrogen compressor needed to be maintained within a narrow band to prevent either starving the compressor or creating an overpressure condition. Tuning the LN-storage tank, vaporizer, and pressure regulators, to maintain stable operating conditions with minimal user oversight,

was necessary during the first two days of operation. The compressor created some difficulties because of the vibration it transmitted throughout the sampling system. In retrospect, vibration-isolating components would have reduced valve maintenance issues. Finally, the high concentration of supercritical CO_2 required heat be applied to critical venting valves to prevent them from icing. Heat was applied using halogen lamps and heat guns; however, as the amount of supercritical CO_2 rose to almost 100% of the sampled fluid, adding enough heat to keep fluids moving slowed the sampling operation.

A compilation of the travel times for the CO_2 and gaseous tracers is shown in Table 1. The table includes the initial arrival time and peak arrival time, calculated based on the estimated time of entry into the U-tube sampler, and not when the sample was collected at the surface. To obtain the travel time for the CO_2 plume, the time at the start of injection is subtracted from the initial arrival. The travel time for the tracers has been calculated as the mean injection time subtracted from the peak arrival time.

A simple radial flow model can be used to estimate CO_2 saturation using the tracer travel time. If we neglect buoyancy and assume the CO_2 flow field can be represented by a uniform radial disk with a formation thickness of 6.1 m and a porosity of 0.35, we can estimate the CO_2 saturation as:

$$S_{CO_2} = \frac{Qt}{\pi r^2 l \phi_f}$$

where Q is the volumetric injection rate, t is the mean arrival time, r is the distance from injection borehole to observation borehole, l is the formation thickness, and ϕ_f is the formation porosity. CO_2 saturation in the formation when the CO_2 front initially reached the observation well was 15.6%, based on the initial PFT tracer arrival. The formation saturation increased to 16.3% and 17.1% for the second and third tracer tests, respectively.

This simple analysis is not meant as a substitute for more detailed modeling efforts currently underway, but rather it represents a first-order estimate for CO_2 saturation. It is indicative of the higher-mobility, supercritical CO_2 bypassing the brine. A more detailed analysis using a multiphase radial flow model (e.g., Bachu et al., 2004), is required to better understand the complexity of the CO_2 plume. The results with Bachu et al.'s model indicate that the effects of buoyancy cannot be neglected in a high-permeability formation such as the Frio. Accurate relative permeability and capillary pressure-saturation parameters are critical to understanding the CO_2/brine interaction, since these will affect the plume characteristics.

Conclusion

The demands of the Frio Brine Pilot experiment for multiphase geochemical samples, specifically the need for (at most) minimal disturbance of the flow field, placed very stringent requirements on the sampling system. The U-tube was able to provide frequent high-quality 52 l samples from the 1.5 km deep observation borehole at formation

pressure. The sampling and tracer test data collection could not have been accomplished through more commonly deployed systems such as submersible pumps or downhole samplers. The samples obtained during the Frio Brine Pilot experiment are anticipated to provide a wealth of information, information that will shed important light on the geochemical and physical processes affecting sequestration of CO_2 in deep brine filled formations.

The U-tube sampling system could see use in other applications requiring representative geochemical samples. Monitoring and verification programs for both CO_2 sequestration and geologic storage of radioactive wastes are anticipated to span many decades. The U-tube is an attractive solution for long term sampling requirements, because of its simplicity and high reliability. Since the U-tube system provides high quality samples under two phase conditions, it is a potentially valuable tool for fluid sampling needed for understanding the state of geothermal systems. In geothermal systems, corrosive downhole conditions and high temperatures make a U-tube constructed of corrosion resistant alloys an attractive alternative to specialized downhole samplers. The deployment of sampling systems, utilizing either multiple sample points within a single boring or multiple points throughout a dispersed well field, is practical because of the low cost of the U-tube downhole equipment.

Acknowledgments

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Table 1. Tracer Injection Times and Arrival Times for the Frio Brine Pilot Experiment.

Component	Mass Injected	Injection Time (Rel. time hr.)	Injection Duration (hr)	Arrival Time (Rel. time hr.)	Peak Time (Rel. time hr.)	Travel time[†] (hr.)
CO_2	3 kg/s[*]	4 Oct 11:34 (0.00+0.0/-2.0)	N/A	6 Oct 14:28 50.90+0.0/-2.0	N/A	50.9+0.0/-2.0
PMCH, PTCH	3.1 kg	4 Oct 13:26 (1.87)	3.9	6 Oct 14:28 50.90+0.0/-2.0	6 Oct 15:20 (51.8±0.9)	48.0±0.9
PMCP, PDCH	0.3 kg	8 Oct 18:19 (102.75)	1.0	10 Oct 15:32 (147.97±0.5)	10 Oct 22:52 (155.3±0.5)	50.22±0.5
PMCH, PTCH	0.3 kg	9 Oct 11:37 (120.05)	1.0	11 Oct 11:42 (168.13±0.5)	11 Oct 18:36 (175.03±0.5)	52.67±0.5
SF_6	< 200g[‡]	9 Oct 11:37 (120.05)	0.58	11 Oct 10:26 (166.87±0.5)	11 Oct 18:22 (174.80±0.5)	52.63±0.5
Kr	83.8 g	9 Oct 12:39 (121.08)	0.13	11 Oct 10:37 (167.05±0.5)	11 Oct 20:01 (176.45±0.5)	53.47±0.5

[*] The CO_2 injection was continuous so the mass injected is given as a rate. All other tracers were injected over a short time period.
[†] CO_2 travel time measured from first injection to first arrival, all other travel times measured as mean injection time subtracted from peak arrival time. Travel time for 8 October and 9 October injection have 110 minutes subtracted to account for travel time up the U-tube.
[‡] Problems with the injection pump prevented an accurate determination of the quantity of SF_6 injected.
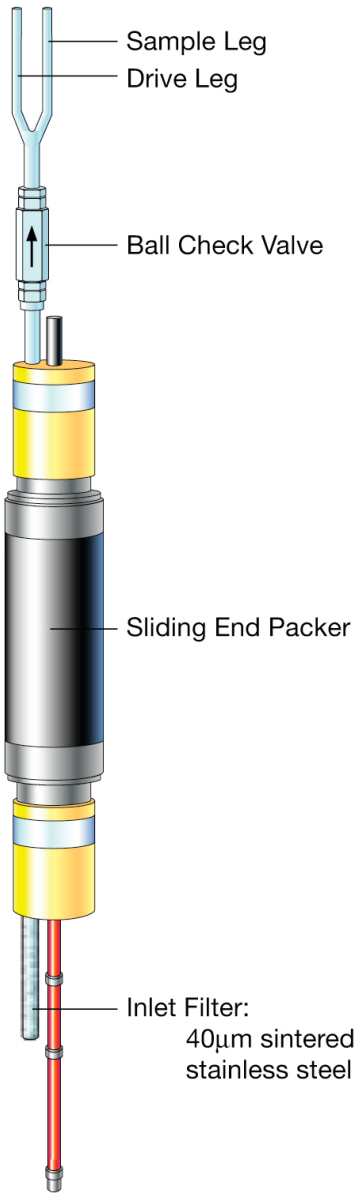
Figure 1. Details of the U-Tube sampling system downhole assembly.

Figure 2. Location of the Frio Field Site in relation to the state of Texas and the nearby cities of Dayton and Houston.
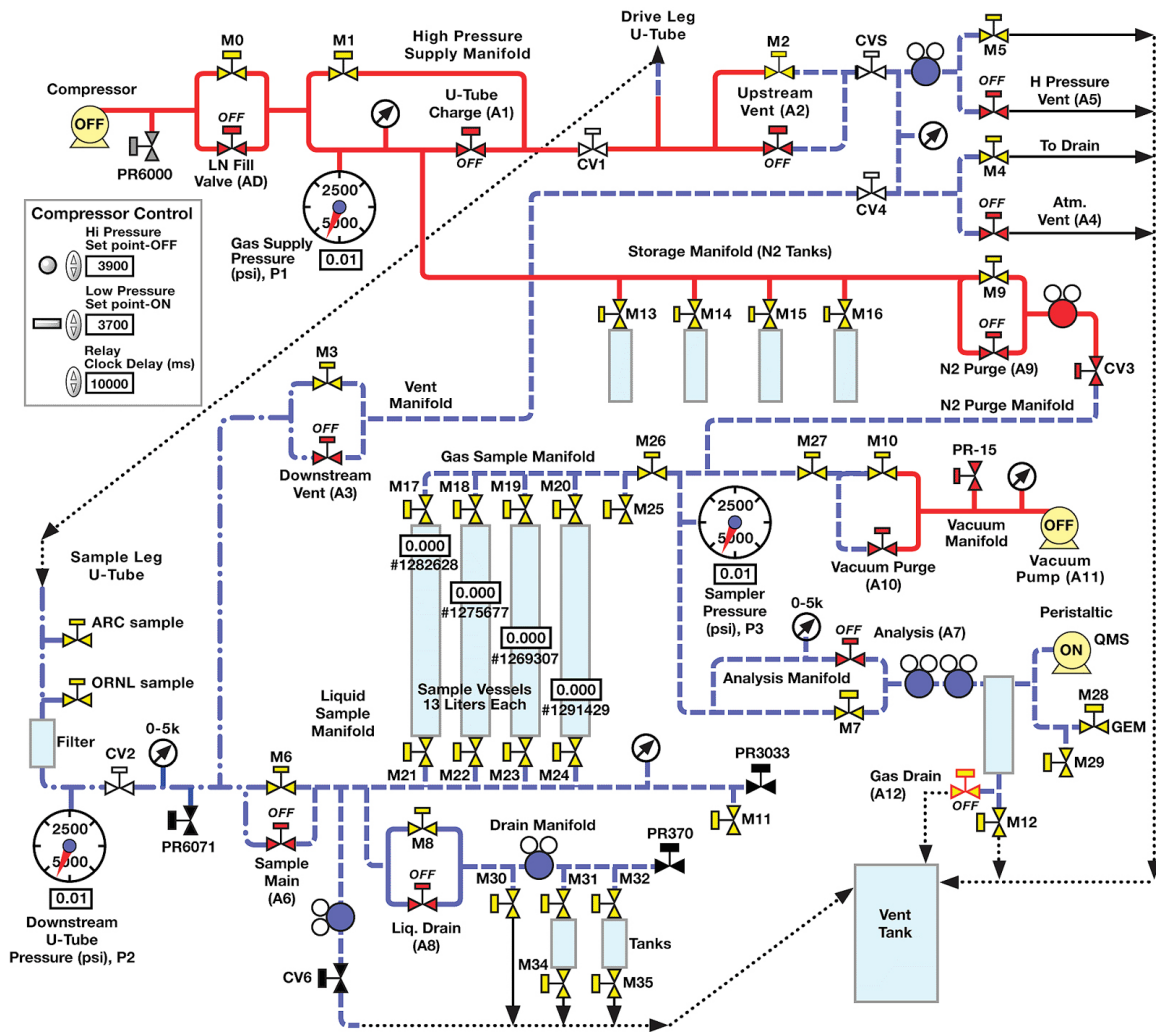
Figure 3. Schematic for the U-tube sampling system. This is the same diagram visible on the computer control system, allowing the user to control all of the automated valves, labeled as "A." The automated program sequences through the operation of the valves, using pressure set points and time delays to control the sampling operation.
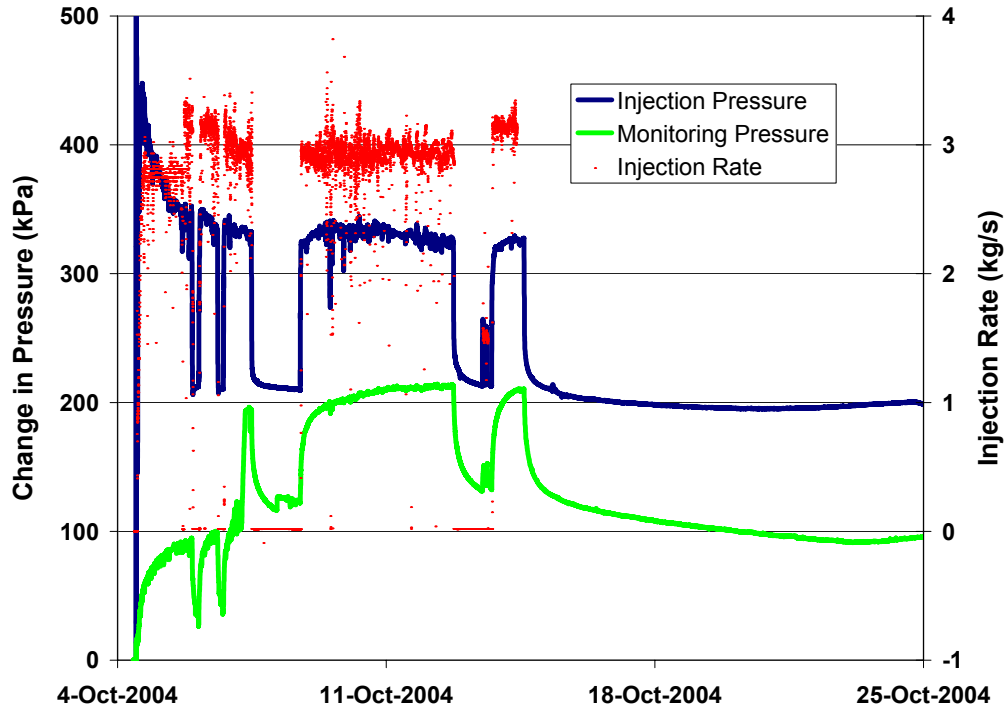
Figure 4. Changes in bottomhole pressures and injection flowrate measured during the Frio CO$_2$ sequestration experiment. The sharp mid-injection pressure declines correspond to pauses in the injection.
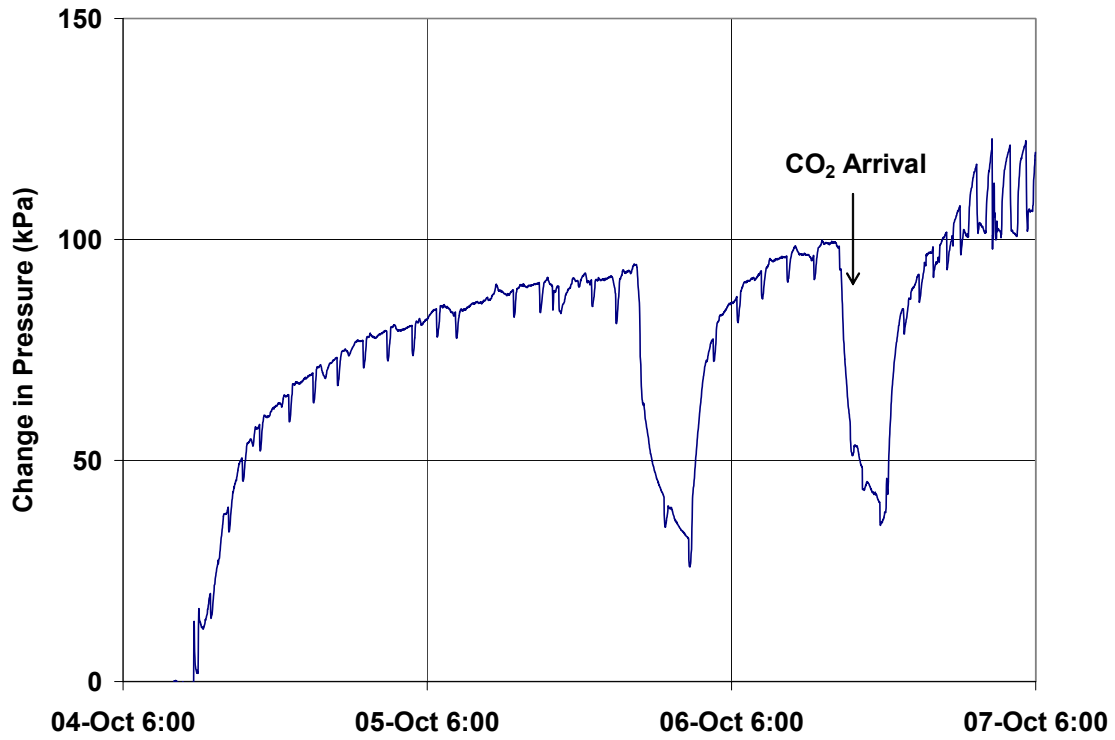
Figure 5. Short transitory pressure fluctuations associated with U-Tube sampling events are apparent in the observation borehole bottomhole pressure. After CO₂ arrival the pressure transients became longer in duration and greater in amplitude.
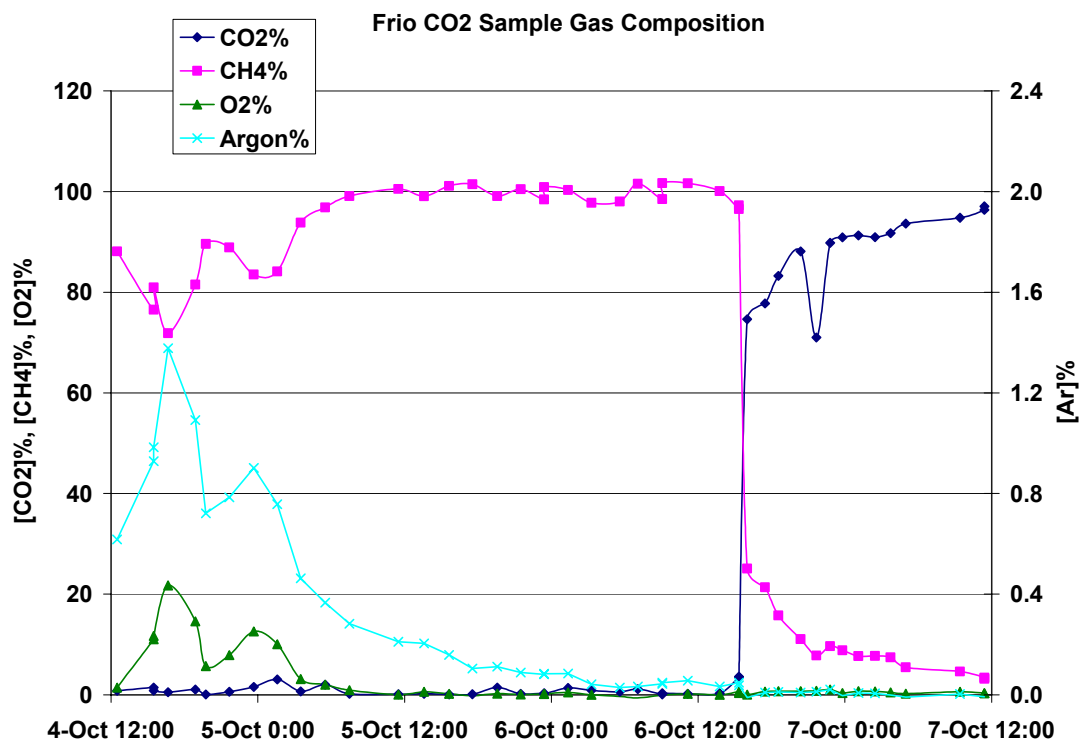
Figure 6. Analysis of gas composition in U-tube samples measured using a quadrupole mass spectrometer. The gas composition changes drastically after the CO_2 arrived in the observation well, with methane being displaced as the predominant component. The oxygen and argon reveal contamination of the formation that occurred during the sampling string installation.

Figure 7. Fluid density measured in the U-tube samplers using strain gauges mounted below each high-pressure sampling cylinder.

Figure 8. Electrical conductance, pH, and alkalinity of water samples collected with U-tube. Note the essentially constant conductance of ~120 mS/cm, but the major drop in pH and increase of alkalinity as the CO_2 reached the observation well.
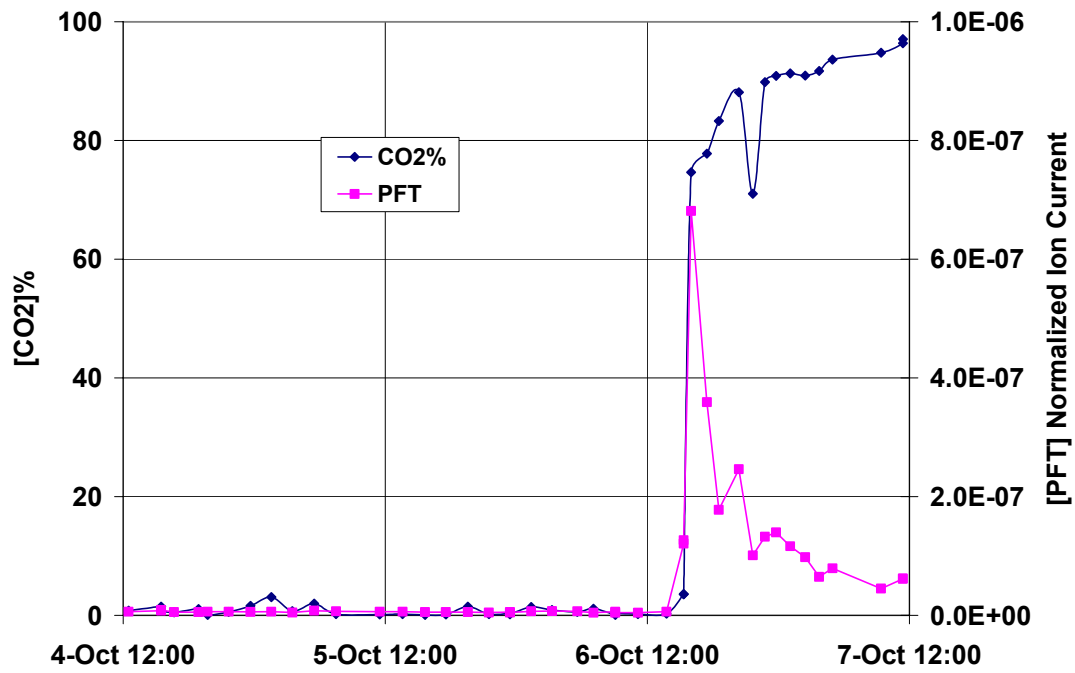
Figure 9. The initial breakthrough of the CO₂ plume and the PFT tracer breakthrough. CO₂ is measured as a percent of total gas recovered and the PFT tracer concentration is mass spectrometer ion current normalized to total mass current.
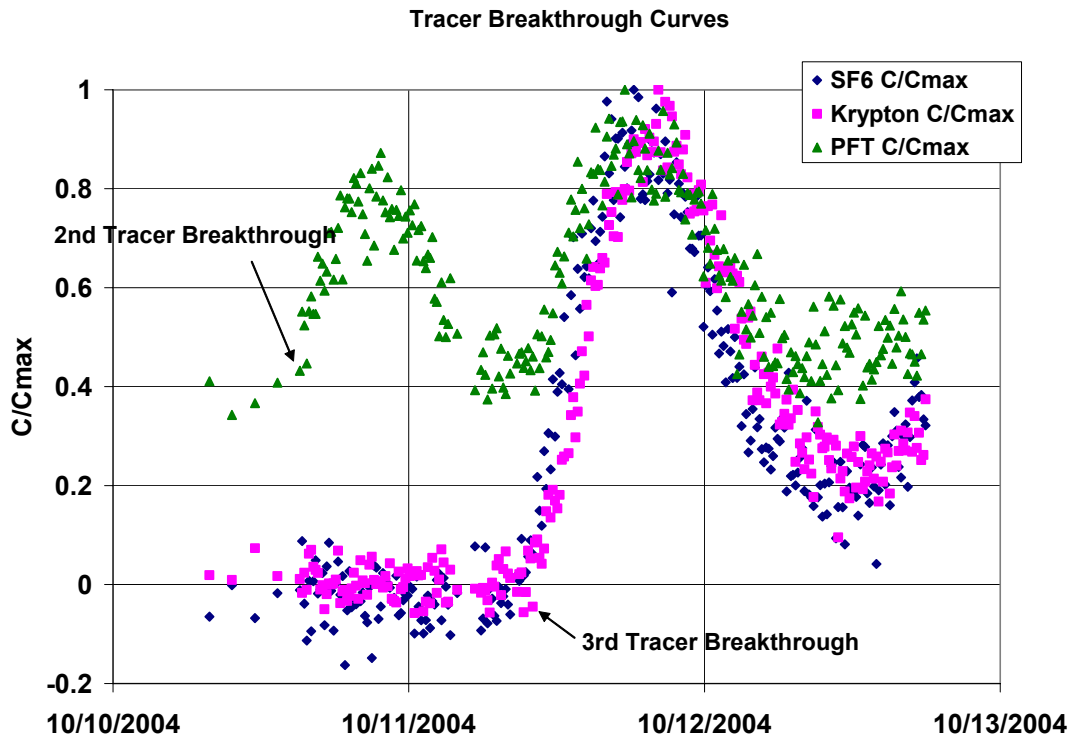
Figure 10. Tracer breakthrough curves for the second and third tracer injections. Note that PFT starting concentration is non-zero because of prior use of PFT tracers.