Carbon-Dioxide-Enhanced Oil Production from the Citronelle Oil Field in the Rodessa Formation, South Alabama

Quarterly Progress Report

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Executive Summary

Objective

The team of Alabama Agricultural and Mechanical University, Denbury Resources, Inc., Geological Survey of Alabama, Southern Company, University of Alabama, University of Alabama at Birmingham, and University of North Carolina at Charlotte are engaged in a Cooperative Agreement with the NETL Strategic Center for Natural Gas and Oil, to evaluate the potential for carbon-dioxide-enhanced oil recovery to increase oil yield and extend the productive life of the Citronelle Oil Field in Mobile County, Alabama. To accomplish this objective, our analysis of the field and its response to CO_2 flooding has the following components: (1) Stratigraphy, sedimentology, and petrology, (2) Reservoir fluid properties and miscibility behavior, (3) Reservoir simulation and visualization, (4) CO_2 injection and oil production monitoring, (5) Environmental monitoring, (6) Seismic monitoring, and (7) Technology transfer.

The Citronelle Field, discovered in 1955, is operated by Denbury Onshore, LLC, a subsidiary of Denbury Resources, Inc., of Plano, TX. OOIP is estimated to have been 378.6 million bbl (Fowler et al., 1998), of which 172 million bbl, or 45%, have been produced to date. Secondary recovery by water flooding has been underway since 1961. Present production is approximately 600,000 bbl/year, or 7% of the peak of 8.2 million bbl produced in 1963. The field is approaching the ultimate recovery possible using conventional secondary recovery techniques.

According to the criteria enumerated by Kovscek (2002), the Citronelle Field is a good candidate for both CO_2-EOR and CO_2 sequestration. From the reservoir engineering prospective, the site is mature and water-flooded, with existing infrastructure, including deep wells, and from the geological prospective, the field consists of fluvial-deltaic sandstone reservoirs in a simple structural dome and, because of the presence of a regionally extensive anhydrite seal, four-way structural closure, and lack of faulting, is naturally stable with respect to CO_2 storage. However, the geology of Citronelle Field is quite different from that of the carbonate strata of the Permian Basin in Texas and New Mexico and the Williston Basin in North Dakota and Montana, well-known sites of commercially successful CO_2-EOR projects. The present project is designed to evaluate the potential of CO_2-EOR for tertiary recovery from highly heterogeneous sandstone reservoirs of the type found at Citronelle, and the capacity of oil reservoirs and adjacent saline formations at Citronelle for sequestration of carbon dioxide.

Impact

The Citronelle Field is Alabama's largest oil producer, and a significant contributor to the economy of the State and employment in the region. Estimates of the EOR potential at Citronelle range from 26 to 64 million bbl. Assuming a conservative 10% of OOIP to be economically recoverable (38 million bbl) using CO_2-EOR and a production rate increased to 1.2 million bbl/year (twice present production), the life of the field would be extended by 30 years.

The capacity of Citronelle Dome for CO_2 storage is estimated to be 530 to 2100 million short tons (Esposito et al., 2008), sufficient to sequester the CO_2 produced from coal-fired generation at nearby Alabama Power Plant Barry (12 million tons/year) for at least 40 years. Plant Barry is the host site for a major demonstration of carbon capture and sequestration technology, including pipeline transport and geologic storage of CO_2 in a saline formation in Citronelle Dome (Esposito et al., 2011b; Koperna et al., 2012). Plant Barry is anticipated, by Southern Company, Alabama Power Company, and Denbury Resources, to be a source of CO_2 for EOR in the Citronelle Field, if the present project indicates that CO_2-EOR will be profitable and provides the desired guidance for management of the reservoir under CO_2 flooding.

Accomplishments

Phase I. An inverted five-spot well pattern and two target sands were chosen for testing. A detailed study of the geology of the sands established their permeability and connectivity. Reservoir simulations showed that 7500 tons of CO_2 were sufficient to demonstrate CO_2-EOR and produce significant incremental oil. Background conditions of CO_2 in air, CO_2 flux from soil, and the species distribution and growth rate of vegetation were established, for comparison with conditions during and after CO_2 injection. A rolling ball viscometer was designed, assembled, and calibrated, for measurement of CO_2-oil miscibility behavior.

Highlights of the work done in preparation for the first injection of CO_2 were: (1) the stratigraphy, sedimentology, and petrology of the Rodessa Formation in the vicinity of the test site were analyzed and documented at an unprecedented level of detail; (2) realistic and informative reservoir simulations were performed; (3) the minimum miscibility pressure and absence of precipitation from oil in the presence of CO_2 were established; (4) a geomechanical stability analysis showed that only small deformations from overburden pressure and no rupture of the target formation were likely; (5) the baseline environmental and ecological conditions surrounding the site were documented; (6) seismic surveys to the depth of the target formation were recorded during the baseline water flood; (7) a favorable economic analysis was conducted that identified the optimum CO_2 slug size for water-alternating-gas oil recovery under specified CO_2 cost and oil price constraints; and (8) the wells in the inverted five-spot were prepared for testing and the equipment and infrastructure for CO_2 storage, pumping, and injection were put in place.

Phase II. The first CO_2 injection, of 8036 tons, began in December 2009 and was completed on September 25, 2010. Oil production at B-19-8 Tank Battery, which receives oil from producers B-19-7, B-19-8, and B-19-9, had experienced an average decline of 20 bbl/day/year during the period from March to December 2009. Beginning in January 2010, coinciding with the start of continuous CO_2 injection, the decline in production was reversed, and, from January to September 2010, when the first CO_2 injection was complete, oil production increased at the average rate of 18 bbl/day/year. However, four problems having significant bearing on the design of a commercial CO_2 flood at Citronelle occurred: (1) excessive produced gas, primarily CO_2, appeared at Well B-19-11, in the southwest corner of the inverted five-spot, (2) on returning to water injection following the CO_2 injection, the injection rate, which had been an average of 160 bbl water/day before injection of CO_2, decreased to approximately 60 bbl water/day, (3) excessive wear of the down-hole power oil pumps occurred, due to erosion by particulate matter mobilized by the CO_2, and (4) oil production at B-19-8 Tank Battery decreased from its peak of 59 bbl/day in September 2010, at the end of the CO_2 injection, to only 21 bbl/day in March 2011. Change of materials and increase in the length of stroke in the power oil pumps restored the frequency of pump pulls to normal and oil production at B-19-8 Tank Battery recovered some of its loss, averaging 39 bbl/day from June 2011 to December 2013.

Documentation of the presence or absence of environmental consequences of CO_2 flooding also has high priority. Measurements of soil gas composition versus depth, CO_2 flux from soil, soil temperature, soil moisture, and soil elements (carbon, nitrogen, and phosphorus), were made before, during, and following CO_2 injection, at 15 locations surrounding the injector, three producers, and a plugged and abandoned well within the test pattern. Measurements of CO_2 in ambient air were recorded at least once each quarter from September 2007 to June 2012, at 104 points on a grid across Citronelle. The CO_2 measurements are consistent with the seasonal variations and long-term trends of the local NASA satellite-based Atmospheric Infrared Sounder data and worldwide average atmospheric CO_2 levels. There has been no significant short or long-term effect of storage, handling, and injection of CO_2 on the levels of CO_2 in ambient air at Citronelle. The growth of trees and plants and their species distribution are being monitored in test plots near the injector, producers, and tank batteries. Of the eight vegetation test plots established at the wells and tank batteries, a significant and consistent increase in the rate of growth of vegetation was observed only in the plot near the injector, Well B-19-10 #2, though this observation is at odds with the measurements of CO_2 in ambient air and measurements of CO_2 fluxes from soil near the well.

Advancement of diagnostic techniques for monitoring interaction between the CO_2 plume and geologic formation is another priority. Shear-wave velocities were measured using the Refraction Microtremor (ReMi) technique to depths of 12,500 feet using wireless geophones placed along two straight paths spanning 30,100 and 25,600 feet, to the south and southwest, respectively, of the injection well. Shear-wave velocities recorded before and during CO_2 injection suggested a 10% increase in stress associated with CO_2 injection, in layers above the injection zone. The record of normalized well-head pressure at the injector is consistent with the normalized equivalent stresses from the seismic sensor array at the depth of the target sands during CO_2 injection.

Phase III. An array of standard and advanced measurement techniques has been brought to bear on the measurement and monitoring of production, the reservoir, and the environment:

Oil production - monitored by conventional methods at the tank batteries.

Produced water - monitored by conventional methods at the tank batteries.

Water injection rate - turbine flow meter at the injector.

CO_2 in produced gas - Draeger tube.

Proof of injected CO_2 in produced gas - carbon-13 isotope ratio.

Seismic monitoring - refraction microtremor technique.

Geology - spontaneous potential, resistivity, and neutron well logs.

Petrology - microscopic analysis of thin sections.

Minimum miscibility pressure - rolling ball viscometer.

CO_2 in ambient air - portable gas analyzer.

Seepage of CO_2 from soil - sampling and analysis of CO_2 from a chamber on the ground.

Soil chemistry - collection of samples and analysis in the laboratory.

Vegetation - counts of species in test plots and measurement of stems and trunks.

The key questions to be answered during Phase III were: (1) What property of the formation (e.g. fracture or high permeability zone) is responsible for the early CO_2 breakthrough and excessive gas production at Well B-19-11, to the Southwest of the injector? (2) What are the causes of the marked loss in injectivity observed on switching from CO_2 injection back to water, and can it be reversed? (3) Are significant environmental and ecological effects present after a longer period of time? (4) Did the reservoir simulations capture important features of the performance of the pilot test and can their accuracy and predictive power be improved by fine-grid, large-scale simulations? and (5) Is continuous CO_2 injection or WAG the better strategy for commercial EOR at Citronelle?

To address the critically important Items 1 and 2, a 15-day-long pressure-transient test on the injection well, consisting of two cycles of shut-in and water injection, was conducted from November 28 to December 12, 2011. The data, analyzed by Eric Carlson, showed that there is a hydraulic fracture adjacent to the injector having a total length of 600 to 1000 ft, in a zone having a permeability of only 0.4 mdarcy. The estimates of fracture length and permeability are approximate, but the results strongly suggest the presence of a large, high-conductivity fracture in a very low permeability zone. The pressure-transient test does not provide any information about the direction of the fracture, but the most likely direction is that of maximum horizontal compressive stress in the Southeastern U.S., typically N70E to N80E. Two of the wells at which early breakthrough of CO_2 was detected lie on the line at N69E relative to the injector. The fracture evidently provided a preferential pathway for CO_2 and compromised its sweep efficiency.

An injection profile test run on the injector in January 2012 established that 35% of the flow is to Sand 14-1 and 65% is to Sand 16-2, so neither injection zone is completely blocked. Treatment of injected water with surfactant, from July 25 to November 7, 2012, restored approximately one-third of the loss in injectivity to water following CO_2 injection. The conclusion from the surfactant treatment is that while capillary blocking of water injection is significant, it was not the only effect responsible for the loss in injectivity experienced on returning to water injection following the CO_2 slug.

Flakes of the internal plastic coating (IPC) of the tubing were found in the injector during repair of a tubing leak that occurred during injection of the surfactant. Problems with IPC were experienced by Denbury Resources throughout its oilfield operations. The cause of the problem was determined to be a lapse in quality control on the part of the supplier. The coated tubing was replaced with bare steel tubing, and the well was flowed back to flush out the flakes of coating. Plugging of perforations by fragments of the IPC is considered the most likely cause of the well's low injectivity to water following the CO_2 injection.

Treatment of the injector with hydrocarbon solvent and dispersant had only a small effect on its injectivity to water. Paraffins and asphaltenes left behind when supercritical CO_2 mobilized lighter components are not thought to have made a significant contribution to the loss in injectivity to water following the CO_2 injection.

The combined effects of the change to uncoated tubing, treatment with solvent, and flow-back to clear the IPC fragments was a small increase in water injection rate, from a range of 77 to 87 bbl/day to the range from 79 to 94 bbl water/day. Flow-back appears to have had the most lasting effect, supporting the suggestion that flaking of the IPC is the likely cause of poor injectivity to water following the CO_2 injection.

Work in the field was complemented by ongoing study of the stratigraphy, sedimentology, and petrology of Citronelle Dome at the Geological Survey of Alabama. Petrographic analysis of the Donovan Sand has shown that framework composition ranges from subarkose to arkose. Major cements in the sandstone are calcite, dolomite, and anhydrite. Calcite and anhydrite formed shortly after burial, whereas dolomite is deep burial cement. All reservoir sandstone samples show extensive evidence for feldspar dissolution, including vacuolized feldspar grains and grain-size voids that were probably once occupied by feldspar. In all, about 40% of the porosity in the Donovan sand is dissolution porosity, and the remainder is interparticle porosity. Feldspar dissolution pre-dates hydrocarbon migration and is interpreted to be a product primarily of diagenesis in the vadose zone. Whereas feldspar was dissolved from some sandstone, illuvial clay, derived in part from this dissolution, apparently accumulated in the pore system of non-reservoir sandstone. Observations in core indicate that the vast majority of the Donovan Sand was deposited as a redbed sequence and that reducing colors are largely the product of the invasion of reducing brine, most of which was oil-bearing.

A key component of the effort to interpret and understand the behavior of CO_2 during and following the Phase II injection was the development of nSpyres, the open-source, in-house reservoir simulator under development by Eric Carlson at the University of Alabama. With recently implemented enhancements and improvements, large-scale, fine-grid simulations of 50 years of waterflooding at the test site were accomplished using a regular grid of 8.2 million cells, each measuring 52.8 x 52.8 x 1 ft. Geostatistical methods have been applied to generate permeability distributions leading to high flow capacity zones, consistent with the early breakthrough of CO_2 observed in the field. Enhanced local directional permeability will be introduced to mimic hydraulic fractures around the wells. The primary reservoir engineering objectives of the simulations are:

A full-field analog model of Citronelle.

Detailed simulations illustrating the effects of changing characteristics.

Comparison of simulation results to overall Citronelle production history - history guidance but without any intent to history match.

Simple but realistic models for fractures.

Identify strategies that might increase production from Citronelle, or confirm that the current production strategy is economically sound.

Technology Transfer

Staff members at the Geological Survey of Alabama have developed a core workshop focused on the sedimentology, diagenesis, and reservoir characteristics of the Donovan Sand in the Citronelle Field. The Donovan Sand was laid down in a complex mosaic of depositional environments and was subsequently affected by several dramatically different episodes of diagenesis, beginning with repeated development of oxidized soils, formed when parts of the Donovan landscape were exposed while the unit was still being deposited. The core workshop focuses on the geologic history of the Donovan and its depositional, diagenetic, and reservoir complexity, as an illustration of how sedimentology can control critical characteristics of this type of hydrocarbon reservoir. The workshop will be used to educate interested groups about the Citronelle Field. Also, it will serve as an example of a sedimentologically and diagenetically complex but structurally simple siliciclastic reservoir. A preliminary version of the workshop was presented publicly in June 2013. Further work was done during the quarter under review, to improve the workshop for future presentations.

During the quarter under review, Shen-En Chen and his coworkers at the University of North Carolina at Charlotte completed two manuscripts for publication. The first, entitled, "Evaluation of Lumped-mass Model for Studying Wave Propagation in a Depleted Oil Field," by Yangguang Liu, Shen-En Chen, and Vincent Ogunro, demonstrates the ability of a lumped mass model to interpret measurements using the surface wave monitoring technique developed by Dr. Chen and his coworkers for detection of changes in subsurface wave propagation associated with CO_2 injection. The second paper, entitled, "CO_2 Injection Monitoring at Citronelle Oil Field using Passive Seismic Monitoring," by Yangguang Liu, Shen-En Chen, and Peng Wang, describes the application of the passive microseismic monitoring technique to detect changes in the subsurface static stress distribution during CO_2 injection for enhanced oil recovery.

Fourteen peer-reviewed papers describing work directly related to the project have been published, including comprehensive reviews of the geology of Citronelle Dome and its prospects for CO_2-enhanced oil recovery and capacity for CO_2 storage (Esposito et al., 2008, 2010). Results of work under the project have been presented by members of the project team at sixteen national and international conferences and at twelve regional and local meetings.

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1. Introduction

1.1. Background

The team of Alabama Agricultural and Mechanical University, Denbury Resources, Inc., Geological Survey of Alabama, Southern Company, University of Alabama, University of Alabama at Birmingham, and University of North Carolina at Charlotte are engaged in a Cooperative Agreement with the NETL Strategic Center for Natural Gas and Oil, to evaluate the potential for carbon-dioxide-enhanced oil recovery to increase oil yield and extend the productive life of the Citronelle Oil Field in Mobile County, Alabama. The Citronelle Unit, largest oil producer in the State of Alabama, is operated by Denbury Onshore, LLC, a subsidiary of Denbury Resources, Inc., of Plano, TX.

The geology and history of the Citronelle Oil Field, discovered in 1955, have been described by Eaves (1976), Fowler et al. (1998), and Kuuskraa, Lynch, and Fokin (2004). Oil is produced from the Donovan Sands in the Rodessa Formation (Lower Cretaceous). An estimate of the original oil in place (OOIP) is 378.6 million bbl (Fowler et al., 1998). Production peaked in 1963 at 8,220,364 bbl/year (Alabama State Oil and Gas Board, 2012). Present production is approximately 50,000 bbl/month, or about 7% of the peak. Most of the field has undergone water flooding since 1961 (Eaves, 1976; Fowler et al., 1998). Cumulative production, as of March 2011, was 171,669,283 bbl, or 45% of OOIP. These figures indicate that the Citronelle is a mature oil field with present cumulative production not far from ultimate production using conventional recovery practices.

Kuuskraa et al., (2004) estimated the oil recoverable from Citronelle Field using CO_2-EOR to be 64 million bbl, or 17% of the original oil in place. Denbury Resources' estimate of the Field's EOR potential is 26 million bbl. Assuming 10% of OOIP to be economically recoverable (38 million bbl) using CO_2-EOR and a production rate increased to 1.2 million bbl/year (twice present production), the life of the field would be extended by 30 years.

The geology of the heterogeneous siliciclastic rocks in Citronelle Field is different from most fields where CO_2-EOR has been applied commercially, such as in carbonate strata of the Permian Basin in Texas and New Mexico and in the Williston Basin in North Dakota and Montana. The present project is designed to evaluate the potential of CO_2-EOR for tertiary recovery from Alabama's uniquely structured petroleum resources. Holtz, Núñez López, and Breton (2005) estimated the miscible CO_2-EOR potential of all Alabama oil fields to be 98 million bbl.

A component of the present investigation is an assessment of the capacity of the oil reservoir and adjacent saline formations for sequestration of carbon dioxide, in parallel with CO_2-EOR, or when tertiary oil recovery operations are complete. According to the criteria enumerated by Kovscek (2002), the field is an ideal site for both CO_2-EOR and CO_2 sequestration. From the reservoir engineering prospective, the site is mature and water-flooded, with existing infrastructure, including deep wells, and from the geological prospective, the field consists of fluvial-deltaic sandstone reservoirs in a simple structural dome and, because of the presence of the regionally extensive Ferry Lake Anhydrite seal, four-way structural closure, and lack of faulting, is naturally stable with respect to CO_2 storage (Jack C. Pashin, Geological Survey of Alabama, personal communication, 2006).

1.2. Scope of Work

The technical work to be done under the project is divided into three phases:

Phase I (January 1, 2007 to August 31, 2008). Selection of an inverted five-spot pattern of injection and production wells for testing. Detailed analysis of the geology of the Rodessa Formation at Citronelle, petrographic analysis of drill cores, and characterization of reservoir fluids. Conduct water flood in the chosen test area to bring the formation to conditions representative of the field and provide baseline production data. Analysis of test and production data and associated environmental measurements, and determination of whether seismic instruments are able to detect changes in the formation on pressurization with water.

Phase II (September 1, 2008 to December 31, 2010). The first CO_2 injection and enhanced oil recovery test begun in the selected test area. Analysis of the test data and associated environmental measurements, and determination of whether seismic instruments are able to detect changes in the formation and the presence and migration of CO_2 in the reservoir. Studies include the effect of nitrogen on oil-CO_2 interactions, a stability analysis of the formation, and refined reservoir simulations and visualizations. Analysis of the test data and associated environmental measurements, with testing and verification of simulation versus field results.

Phase III (January 1, 2011 to January 31, 2014). A second CO_2 injectivity and enhanced oil recovery test was planned, but has been dropped for lack of funding. Migration of CO_2 and stability of the formation will continue to be monitored at the first field test site. An analysis of all of the test data and associated environmental measurements will be done, the reservoir management plan will be refined, a comprehensive assessment will be performed, and the results disseminated through the final report to DOE, publications in technical journals, and presentations at workshops and conferences.

The complete Statement of Project Objectives is attached as Appendix A.

2. Progress of the Work

2.1. Communication and Technology Transfer

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2.1.1. Collaboratory Web Site

The collaboratory web site for members of the research group, at <http://www.citronelleoil.us/>, is maintained by Eric Carlson. All reference material related to the project can be found there, including field data, Eric's reservoir simulations, our reports, reports of other investigations related to the present project, and presentations by members of the group at project review meetings.

2.1.2. Publications, Presentations, and Workshops

Shen-En Chen and his coworkers at the University of North Carolina at Charlotte have prepared two manuscripts for publication. The first, entitled, "Evaluation of Lumped-mass Model for Studying Wave Propagation in a Depleted Oil Field," by Yangguang Liu, Shen-En Chen, and Vincent Ogunro, demonstrates the ability of a lumped mass model to interpret measurements using the surface wave monitoring technique developed by Dr. Chen and his coworkers for detection of changes in subsurface wave propagation associated with CO_2 injection. The second paper, entitled, "CO_2 Injection Monitoring at Citronelle Oil Field using Passive Seismic Monitoring," by Yangguang Liu, Shen-En Chen, and Peng Wang, describes the application of a passive microseismic monitoring technique to detect changes in the subsurface static stress distribution during CO_2 injection for enhanced oil recovery.

Konstantinos Theodorou presented and successfully defended his doctoral dissertation in Interdisciplinary Engineering, entitled "Carbon Dioxide Enhanced Oil Recovery from the Citronelle Oil Field and Carbon Sequestration in the Donovan Sand, Southwest Alabama," on July 10, 2013 (Theodorou, 2013). Konstantinos's dissertation contains estimates of the CO_2 storage capacity of saline formations and depleted petroleum reservoirs in the Citronelle Dome, estimates of CO_2-enhanced oil recovery potential from the Upper and Lower Donovan Sands, and calculations of the distribution of CO_2 among supercritical, solution, and mineral phases during and following CO_2 injection into the Middle Donovan saline formation separating the two hydrocarbon-bearing zones at Citronelle. Konstantinos's work is presented in Sections 2.9 and 2.10.1 of the present report.

The most recent presentation of work under the project was given by Loutrina Staley, of Alabama A&M University. Ms. Staley presented a poster with coauthors Ermson Nyakatawa and Latasha Lyte, entitled, "Potential for Carbon Storage in the Citronelle Oil Field: A Geological Sink in South Alabama," at the 4th North American Carbon Program All-Investigators Meeting in Albuquerque, NM, February 4-7, 2013. The abstract of the paper follows <http://www.nacarbon.org/cgi-bin/meeting_2013/mtg2013_ab_search.pl?action=3&ab_id=73>:

> Anthropogenic greenhouse effect is the enhancement of Earth's natural greenhouse effect by the addition of greenhouse gases from the burning of fossil fuels. This rising atmospheric concentration of gases, mainly carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O) and water vapor results in global warming which can have a seriously negative impact on the environment. Carbon sequestration in terrestrial sinks such as forest soil ecosystems presents an opportunity to mitigate global warming. The state of Alabama is endowed with a wealth of potential geological CO_2 sinks which presents an opportunity to sequester C in underground geological formations using CO_2 enhanced oil recovery (EOR). The objectives of this study are to measure and document soil CO_2 fluxes in a forest soil around oil wells in the Citronelle Oil Field in South Alabama before and after CO_2 injection for EOR and relate them to soil chemical and hydrological properties. Soil gas samples were collected using static PVC chambers and analyzed for CO_2 concentration using a Varian GC equipped with an FID coupled to a methanizer. The carbon dioxide fluxes were highest in the warmer months which had a mean of 0.95 mg CO_2 m^{-2} min^{-1} and lowest in the cooler months which had a mean of -0.06 mg CO_2 m^{-2} min^{-1}. Our study shows that soil CO_2 fluxes were generally influenced by soil temperatures and moisture content during gas sampling periods, with variation from well to well.

The most recent publication describing work related to the project is a paper by Xiongwen Chen, entitled, "Distribution patterns of invasive alien species in Alabama, USA," published in *Management of Biological Invasions*, **2012**, *3*(1), 25-36 <http://www.reabic.net/journals/mbi/2012/1/MBI_2012_1_Chen.pdf>, an open access, peer-reviewed, online journal.

A bibliography of the presentations, workshops, publications, and reports describing work supported by, or connected with, the present project may be found in Appendix B. Work under the project has been described in 28 presentations at technical meetings, 14 peer-reviewed publications in journals, 4 theses and dissertations, and 33 reports. The intent is to keep the reservoir engineering and carbon storage communities well informed about the progress of the work, its implications for successful CO_2-EOR and storage in geologic formations of the type found in Citronelle Dome, and the benefits to be gained from thorough analysis and pilot testing in the design of a commercial CO_2 flood.

2.1.3. Citronelle Field Data

A bibliography of publications containing data and information on the Citronelle Oil Field and Southwestern Alabama geology is attached as Appendix C to this report. The bibliography is revised as additional publications are found and as new studies of the Field and region are published, including those resulting from work under the present project. The reports containing engineering data on the Field are also available to members of the research team on the web site maintained by Eric Carlson at <http://www.citronelleoil.us/>.

2.1.4. Meetings of the Research Group

The Principal Investigator, Peter Walsh, is in frequent contact with each of the other members of the research team regarding the progress of laboratory and field measurements, modeling and simulation work, and interpretation of results. Frequent communication among the members of the group, by e-mail and telephone, has been the most effective means for exchanging information and distributing results throughout the research group.

2.1.5. Visits to Citronelle Oil Field

Visits to the oil field have been made periodically, throughout the project, to gather the following data and samples:

- Measurement of the composition of ambient air across the Oil Field and City of Citronelle, and monitoring of specimens in test plots established to observe the species distribution and growth of vegetation near the injector, producers, and tank batteries by Kathleen Roberts and Xiongwen Chen of Alabama A&M University.
- Measurement of soil properties, soil gas composition, and CO_2 fluxes from soil near the injector and producers, by Ermson Nyakatawa, Loutrina Staley, and Rogers Atugonza from Alabama A&M University.
- Seismic surveys using wireless geophones at 48 well sites to the south and southwest of the injector by Shen-En Chen and Peng Wang of the University of North Carolina at Charlotte.
- Collection of produced gas samples by Michael Sullivan of Denbury Onshore and Peter Walsh of the University of Alabama at Birmingham.

The most recent visit was by Loutrina Staley and Rogers Atugonza, working with Ermson Nyakatawa at Alabama A&M University, who visited the Citronelle Field on October 25, 2012, for soil sampling and measurements of soil conditions, including CO_2 fluxes, at their instrumented test sites around the injector and producers. Work by Ermson Nyakatawa and his research group is described in Section 2.7.1 of this report.

2.2. Geology and Petrology

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Geological Survey of Alabama

2.2.1. Core Workshop

Staff members at the Geological Survey of Alabama (GSA) have developed a core workshop focused on the sedimentology, diagenesis, and reservoir characteristics of the Donovan Sand in the Citronelle Field. The Donovan Sand was laid down in a complex mosaic of depositional environments and was subsequently affected by several dramatically different episodes of diagenesis, beginning with repeated development of oxidized soils, formed when parts of the Donovan landscape were exposed while the unit was still being deposited. The core workshop focuses on the geologic history of the Donovan and its depositional, diagenetic, and reservoir complexity, as an illustration of how sedimentology can control critical characteristics of this type of hydrocarbon reservoir. The workshop will be used to educate interested groups about the Citronelle Field. Also, it will serve as an example of a sedimentologically and diagenetically complex but structurally simple siliciclastic reservoir. A preliminary version of the workshop was presented publicly in June 2013. Further work was done during the quarter under review, to improve the workshop for future presentations.

2.2.2. Stratigraphic Columns

During the last quarter of 2012, staff at GSA began to prepare the final drawings of the stratigraphic columns with graphic color logs, as described in the report of work during the previous quarter. A standard format for graphic presentation was developed for the twelve stratigraphic columns described from the core data examined from the Citronelle Oilfield. An example of one of the drawings for the well borehole P-2993 (Well A-26-8 #2), is included as Figure 2.2.1. Each technical drawing is a composite illustration that integrates:

- The detailed stratigraphy of the slabbed core including sedimentary structures and the nature of contacts;
- the lithologic logs from chip samples that were collected separately from the slabbed core; and
- the color that was quantitatively described using a Munsell color chart - at the visual color change boundary for each core, independent of lithologic unit.

About one-half of the twelve drawings were completed during the last quarter of 2012. As shown in Figure 2.2.1, the lithologic data from both the chip and slabbed core logs were combined. No lithologic contact information could be inferred from the chip data, displayed as open-ended borders. The border outlining the right side of the stratigraphic column represents the grain-size textural data.

Petrographic analysis of the Donovan Sand has shown that framework composition ranges from subarkose to arkose. Major cements in the sandstone are calcite, dolomite, and anhydrite.

*Jack Pashin is now a member of the faculty in the Boone Pickens School of Geology at Oklahoma State University in Stillwater, OK.

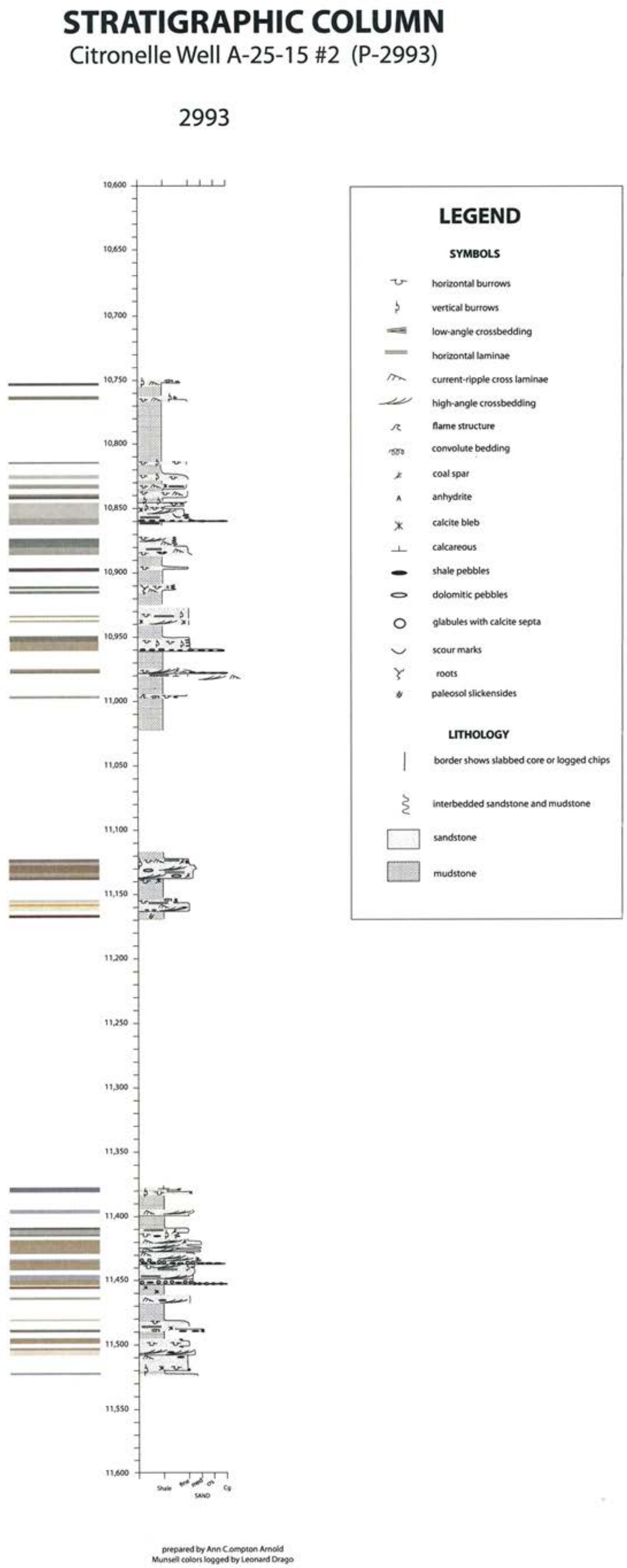


Figure 2.2.1. Stratigraphic column, Well A-25-15 #2.
Prepared by Ann Compton Arnold. Munsell colors logged by Leonard Drago.

Calcite and anhydrite formed shortly after burial, whereas dolomite is deep burial cement. All reservoir sandstone samples show extensive evidence for feldspar dissolution, including vacuolized feldspar grains and grain-size voids that were probably once occupied by feldspar. In all, about 40% of the porosity in the Donovan sand is dissolution porosity, and the remainder is interparticle porosity. Feldspar dissolution pre-dates hydrocarbon migration and is interpreted to be a product primarily of diagenesis in the vadose zone. Whereas feldspar was dissolved from some sandstone, illuvial clay, derived in part from this dissolution, apparently accumulated in the pore system of non-reservoir sandstone. Observations in core indicate that the vast majority of the Donovan Sand was deposited as a redbed sequence and that reducing colors are largely the product of the invasion of reducing brine, most of which was oil-bearing.

2.2.3. Samples

Thin Section Archive. During the quarter under review, GSA staff evaluated the GSA thin-section archive, with particular attention to the hundreds of thin sections from the Citronelle Field collected during the present project. The effort was focused on modernizing and standardizing the records of the archive into a resource more accessible to potential users.

Porosity and Permeability. The slabbed core from Wells P-3232 (the injection well, B-19-10 #2) and P-3336 (C-11-15 #2), was drilled at 97 selected sample depths, for porosity and permeability testing. The 1-inch diameter plugs were drilled perpendicular to the core, for horizontal in-situ permeability data. A total of 62 plugs were drilled from Well P-3232 and 35 plugs from P-3336. The core samples were submitted to the laboratory for analysis in December 2012.

2.2.4. CO_2 Breakthrough

Early breakthrough of CO_2 to wells B-19-11 and B-20-5 indicates major extension of the CO_2 plume toward the east-northeast and the west-southwest, as shown in Figure 2.2.2. Accordingly, breakthrough occurred in wells outside the original inverted five-spot pattern employed in this study. All production wells in the area have been hydraulically fractured, whereas the injection well has not, to our knowledge, been hydraulically fractured. Observations from cores indicate that natural fractures in the Donovan Sand are extremely rare, and so induced fractures are the only known fractures that could affect the CO_2 flood. The maximum horizontal compressive stress in the subsurface of Alabama is typically between an azimuth of 70 to 80^o, and plume extension may have been close to this direction. One explanation of the early breakthrough is that the plume extended along induced fractures and was captured by wells favorably located along the maximum horizontal stress. Whether a fracture was induced in the injection well during water or gas injection is unclear, although the lack of natural fractures in the reservoir may indicate that the reservoir is under significant stress and can be fractured easily when pore pressure is increased. Regardless of the precise causes, unexpected plume extension has strong implications for the applicability of CO_2-enhanced recovery in Citronelle Field and should be considered when selecting injection and production wells for enhanced recovery operations.

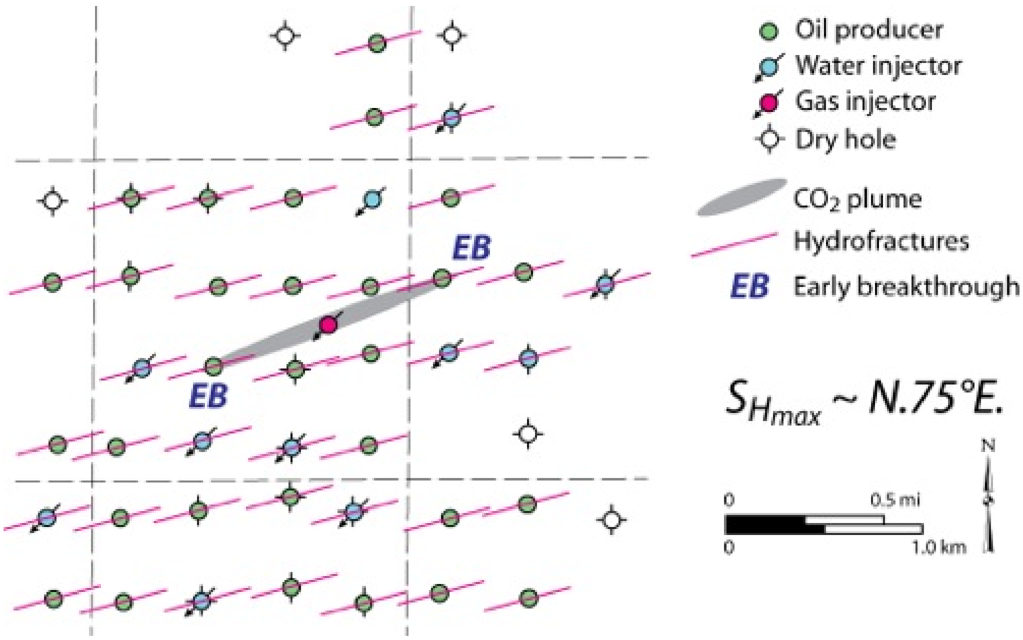


Figure 2.2.2. Wells in the vicinity of the CO_2 injection pilot test (the injector, Well B-19-10 #2 is indicated by the red-filled circle near the center), showing the likely orientation of hydraulic fractures in the direction of maximum horizontal compressive stress, ~ North 75^o East, the preferential migration of the CO_2 plume in the direction of the fractures, and the location of wells where early breakthrough of CO_2 was observed.

2.3. Reservoir Fluid Properties and Phase Behavior

César A. Turmero† and Peter E. Clark*†
Oklahoma State University* and University of Alabama†

Peter Clark is now in the Department of Chemical Engineering at Oklahoma State University in Stillwater, where he holds the Sampson and Ward Chair in Petroleum Engineering. He retains his laboratory and an appointment as Adjunct Professor at the University of Alabama.

Peter and his colleagues at OSU have found an improved model for flow in porous media. The simulation in Figure 2.3.1 is the result from a preliminary model showing oil (red) being displaced by carbon dioxide (blue). The horizontal slot on the right represents a small fracture in the rock. The pores were originally completely saturated with oil, and the carbon dioxide is flowing from left to right. Notice the oil stranded in small pores and the bypassing caused by the fracture. The model has great potential as a tool for instruction and research.

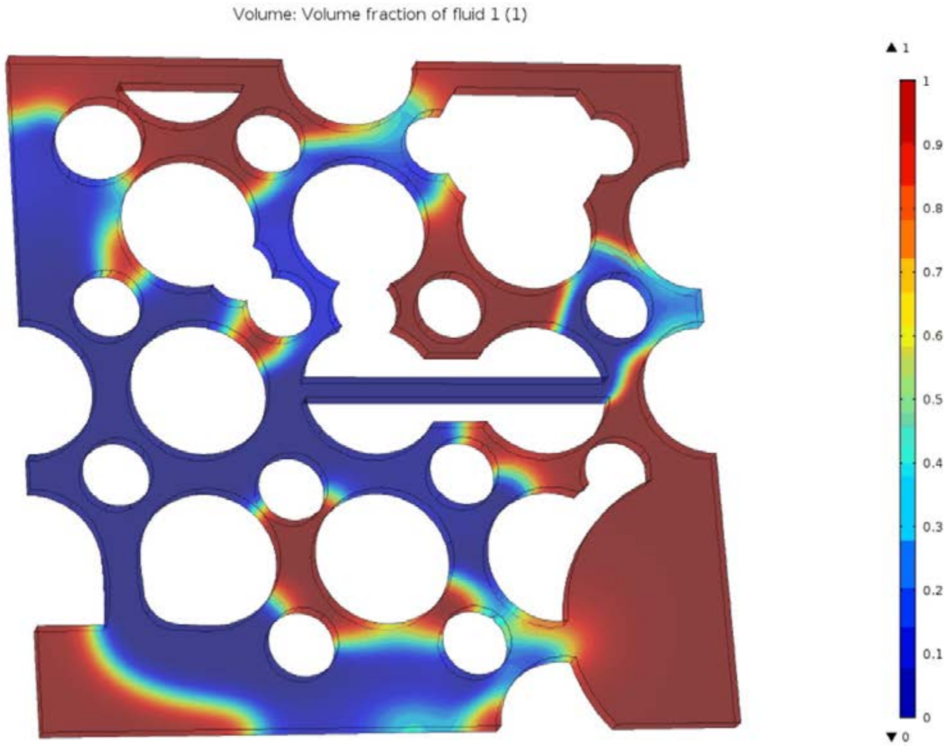


Figure 2.3.1. Simulation of oil (red) being displaced by carbon dioxide (blue). The carbon dioxide flow is from left to right. The horizontal slot on the right represents a small fracture. The color scale indicates oil saturation.

In the laboratory at the University of Alabama, a high-pressure, high-temperature system has been developed to study the interactions of CO_2 in oil by visual observation of the development of miscibility between CO_2 and the reservoir oil. The major component of this system is a high-pressure PVT cell, shown in Figure 2.3.2. A floating-piston accumulator is connected to the system to introduce pressurized CO_2 into the cell. The system temperature is controlled by a natural convection oven. The experimental runs will be performed under reservoir conditions. The gas behavior and pressure changes inside the system are monitored and recorded using a data acquisition system.

The system has undergone preliminary testing using water and CO_2 up to 900 psig. A modification to the pressurization system was then made to increase the pressure limit to 3,500 psig. The visualization cell is rated to 5,000 psig.

The first tests were done using gaseous carbon dioxide at 500 psig. A series of runs was made to measure the solubility of CO_2 in water and the preliminary results compared favorably with a computer model of carbon dioxide-water solubility behavior. Once the system is fully tested, the researchers will undertake the investigation of carbon dioxide-oil systems.

The gaseous CO_2/liquid CO_2 interface and the liquid CO_2/water interface can be seen clearly in Figure 2.3.2. A pH-sensitive dye will be added to improve the contrast between the two liquids at the interface. The research group will be exploring methods for accurately measuring the volume expansion that accompanies carbon dioxide dissolution into oil or water phases.

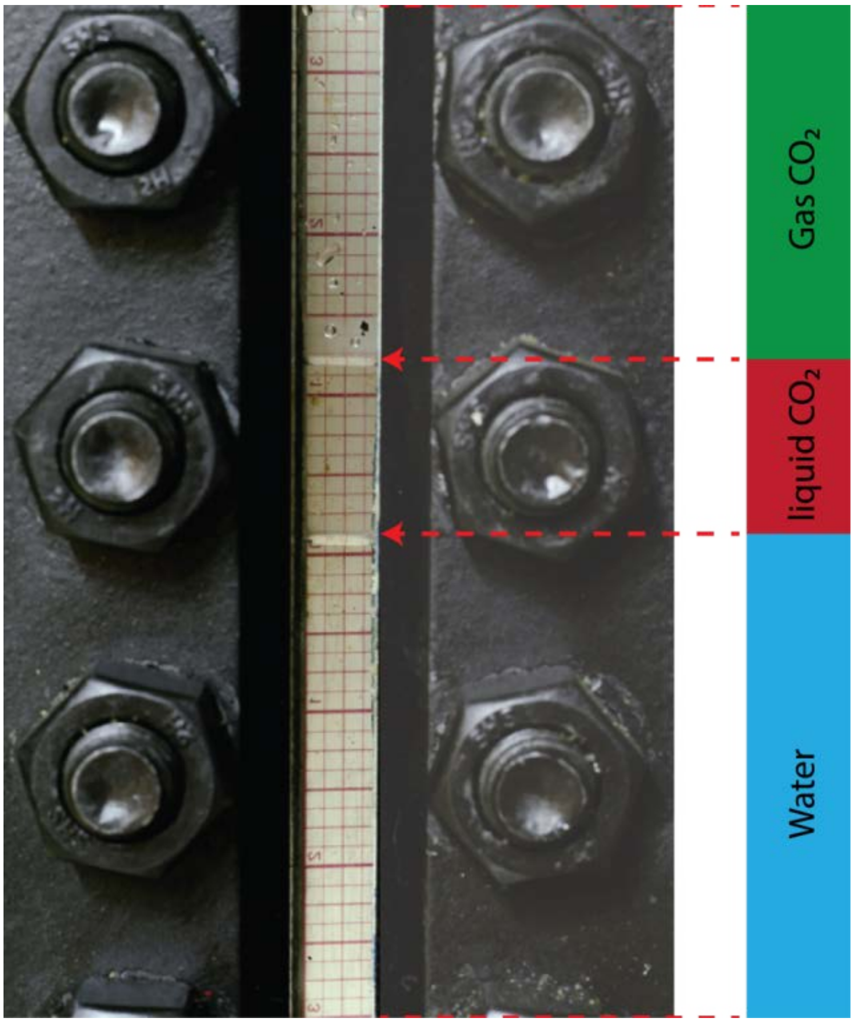


Figure 2.3.2. High-pressure, high-temperature cell for study of CO_2-oil phase behavior. The gaseous CO_2/liquid CO_2 and the liquid CO_2/water phase boundaries are visible (upper and lower arrows, respectively).

2.4. Petroleum Reservoir Simulation

Eric S. Carlson, University of Alabama

2.4.1. Development of Reservoir Simulator and Large-Scale, Fine-Grid Simulation

During the quarter under review, Eric Carlson has been working to set up a Beowulf cluster. The objective is to develop the technology that can be used for some post-project assessments. The system is being set up as a low-cost cluster that would be in the budgets of even a small independent oil company, and set up in such a way that the computers can be used as individual workstations and drafted, when needed, for larger tasks. The following steps have been completed:

Eleven of twelve 6-core Xeon nodes are up, and waiting for a replacement on a DOA motherboard to get the 12th one set up. With all 12, the hardware will be able to run 600-million-cell simulation jobs, enough to do a detailed simulation of the entire Citronelle field.

The Infiniband networking hardware and software are all installed, creating extremely fast (up to 3.5 GigaBYTES per second) and low latency (small signal delays).

The Message Passing Interface (MPI) is set up to quickly launch parallel jobs on the cluster.

All visualization software and all support programs are successfully set up.

All computers have common access to high-speed network drives

MPI has been successfully applied to Dr. Carlson's simulation framework.

Calculation types that can be substantially parallelized and those that can't have been identified.

The following tasks remain to be completed in the near term:

Port the parallel version of the algebraic multigrid solver, AGMG, so that it works under Python.

Parallelize the scalar codes for solving the SPE 10 simulation benchmark. The best scalar time now is 95 seconds (in July 2012 the next best time was 28 minutes). The target is to get the solution down to 25 seconds on a single workstation.

A detailed (parallel) simulation of 50-year waterflood performance in the 2 mile by 2 mile region around the test pattern at Citronelle. This will differ from previous simulation work as it will use substantially more complicated porosity and permeability distributions.

The ultimate objectives are:

A full-field analog model of Citronelle.

Detailed simulations illustrating the effects of changing characteristics.

Comparison of simulation results to overall Citronelle production history - history guidance but without any intent to history match.

Simple but realistic models for fractures.

Identify strategies that might increase production from Citronelle, or confirm that the current production strategy is economically sound.

We have created a prototype program for automatic installation of SciPylot and all of the associated Python programming dependencies. The program does nothing more than download an archive, extracts the archive files to any local directory, and creates a desktop shortcut for starting SciPylot. Users have several options for package installation, but so far all of these work only under Windows. We have used the program on 15 different systems having a variety of versions and system security settings, and all of the installations have succeeded. That said, the installation program requires a specific runtime library that is not guaranteed to be present on arbitrary systems. In these cases, users have the option to either install the runtime library or to download and unpack the archive manually. As mentioned in previous reports, the primary barrier to using SciPylot has been installation. The new installation system not only overcomes those problems, but also sets up a Python framework that is completely consistent with the needs of SciPylot. Furthermore, by using this system we can preinstall a number of modules that can be very difficult to make work under Windows, and thus users can have a highly functional sequential version of nSpyres, our open source reservoir simulation system. All of this can be done without requiring administrative authorization for a given system – everything is set up so that anyone with access to a Windows machine can run our programs.

Although SciPylot itself is platform independent, setting up the underlying framework depends strongly on the operating system. Although it is possible to use SciPylot under OS X, the only reasonable way to install the framework is to use a commercial system from Enthought, Inc. Even with the Python framework, it is nearly impossible to build all of the libraries required for nSpyres. Under Linux, things can be done more easily and it is possible to build a system-optimized Python installation capable of running not only SciPylot, but highly optimized versions of nSpyres. It is currently the only way to run parallel versions of nSpyres, and during the next quarter we will develop instructions for accomplishing this.

In order to appreciate the results of our injection pilot study in the context of the entire field, we have begun studying the entire reservoir. At this point, we have focused primarily on studying summaries of core reports (although no actual core reports) and setting up a well database. Right now, we have common names, locations, elevations, and subsea top of the formation keyed to permit numbers. With this information, we hope to be able to quickly estimate production zones in various sands throughout the field, through custom programs that will allow us to quickly digitize maps and a few cross sections from geologic studies in the 1960's. All of this information will be used in an attempt to build a full field three-dimensional analog model for the Citronelle Field.

We developed a methodology to allow us to automatically estimate porosity and permeability at each cell of a simulation grid, if we have porosity as a function of depth at various locations in the formation. The method uses multidimensional interpolation, and it's set up specifically to honor the well data. All of the grid data can be geostatistically perturbed, but at this point we are more concerned with assessing the potential for continuity. Figure 2.4.1 shows isosurfaces generated from the output of a generic nine-well system. The image sequence starts with identification of bounding volumes of all possible pay zones and works its way through various bounding zones of progressively better quality. In this case, it is possible to identify high porosity/permeability zones that have extended volumes and others that are clearly local around particular wells. At this point, we must use the generic example because we do not yet have even hypothetical distributions for porosity or permeability at wells, including in our pilot area.

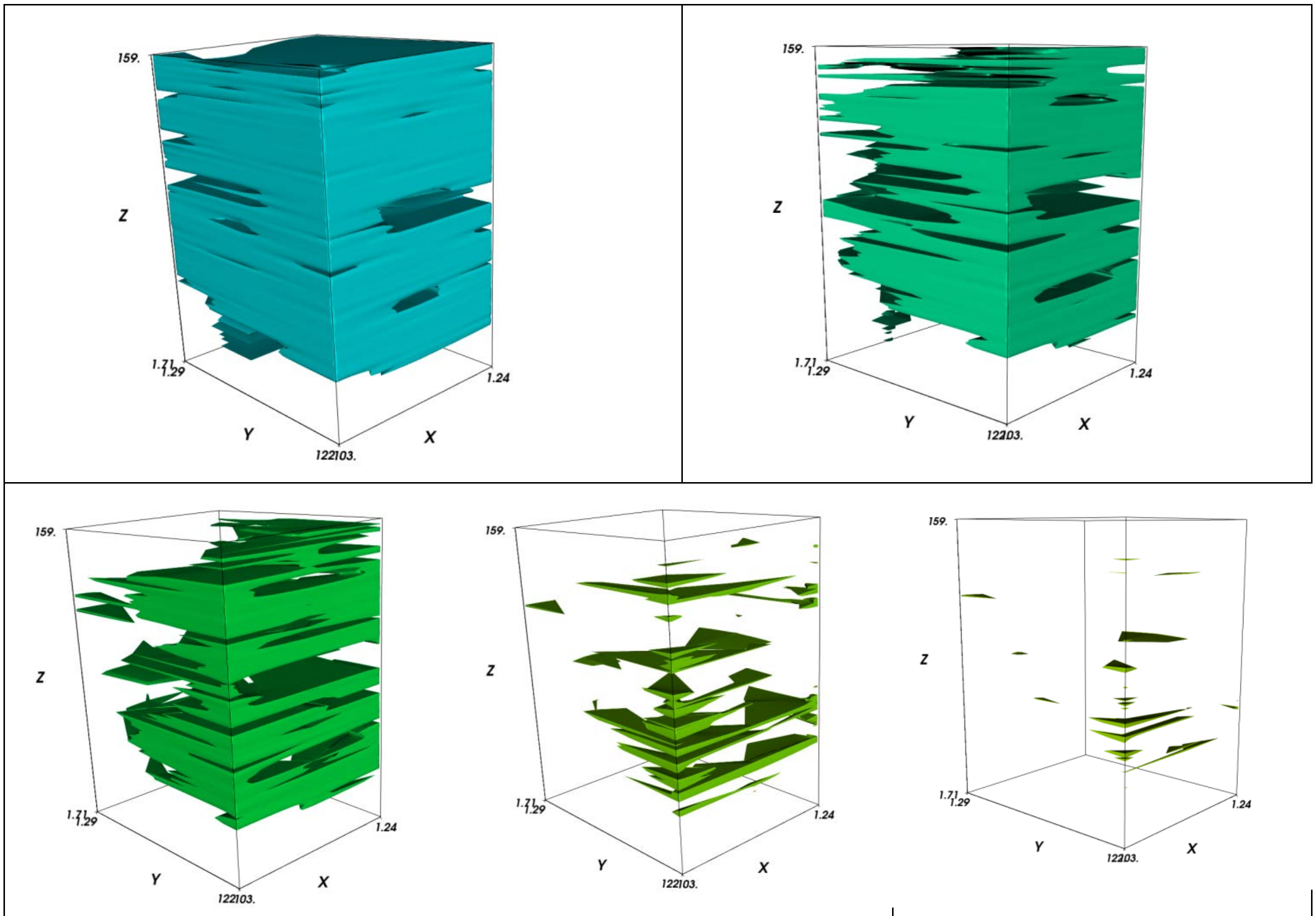


Figure 2.4.1. Bounding isosurfaces of various minimum qualities, generated from the interpolation methodology. Sample calculation performed for 9 wells.

Figures: Upper left, porosity > 0.06
Upper right, porosity > 0.08
Lower left, porosity > 0.10
Lower middle, porosity > 0.12
Lower right, porosity > 0.13

2.4.2. Examination of Production Behavior

While rock property distributions, considered in Section 2.4.1, above, are a critical component of the work that will enable us to explore the significance of the pilot test results for the field as a whole, examination of production behavior provides an approach to the problem from a different perspective. For this purpose, we have begun to dig up and analyze production data throughout the field. Figure 2.4.2 shows the full field production for Citronelle throughout its life, and Figure 2.4.3 gives a close-up view of the oil production and decline curve fit over the past 27 years. The equation

$$\text{Monthly oil production} = 164{,}000 \exp[0.046\,(t - 30)]$$

gives a very reasonable fit for the oil rates on average for the past 27 years, where t is the time in years since the beginning of production. Using this fit, Citronelle could produce 11 million more barrels of oil over the next 50 years, compared with 166 million barrels already produced. The additional recovery of 11 million barrels is a small fraction of the (very conservatively) estimated 200 million barrels remaining in place.

The full-field data show an average of about 75 bbl of fluid per day per well, which is not horribly out of line with the rate related to the 7-md results for the test runs made with nSpyres last summer, as shown in Figure 2.4.4. Although the total fluid rate is not bad, the simulated water fractions shown in Figure 2.4.5 are way off, 30% calculated versus 85% actual. Since in a homogenous reservoir volumetric recovery depends so much on total pore volumes of injected fluid, the water cut variation between the three different formation permeability cases presented in Figure 2.4.5 only reflects the difference caused by injection rate. Since the low-perm calculated rates are comparable to those observed in the field, we have strong evidence of channeling due to permeability variation (and not just from crazy variation of reservoir geometry).

Thus far, the most consistent explanation for injection response and well test results is the presence of some fracturing - most likely induced hydraulic fractures. Simulation of fluid flow with these types of discrete fractures is extremely challenging. As a first pass, the use of fine grids provides an option of using highly anisotropic permeability with grids oriented approximately in the fracture direction. A better method is to explicitly account for a fracture, and we hope to use constraints and methodologies similar to those currently used for well modeling. We will begin to make simulator modifications once it is clear that these are necessary for confirming pilot behaviors.

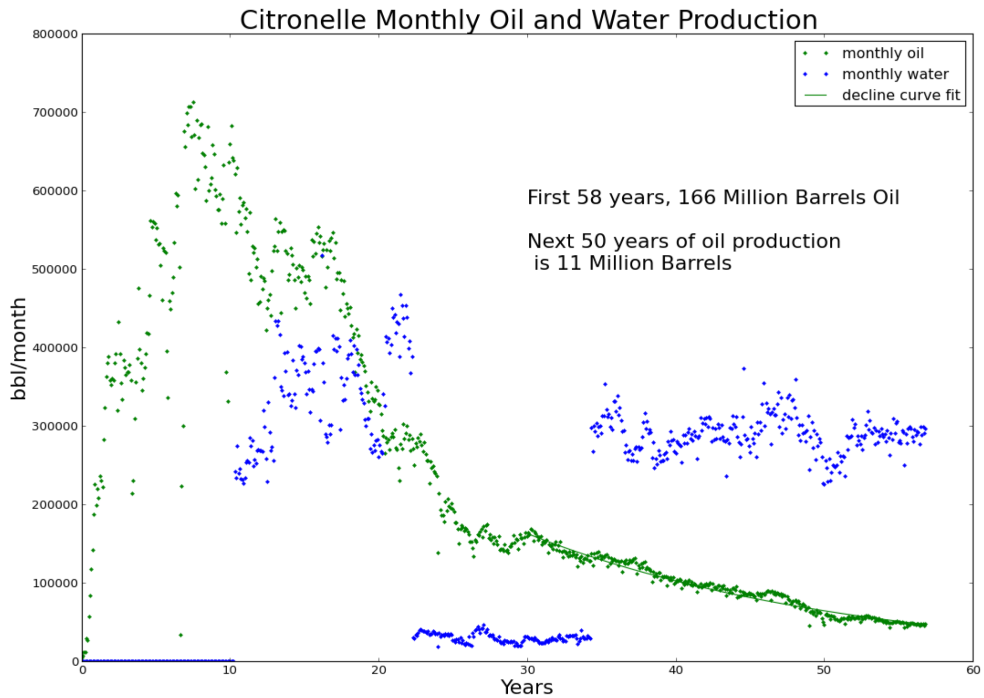


Figure 2.4.2. Total production from Citronelle Oil Field throughout its lifetime.

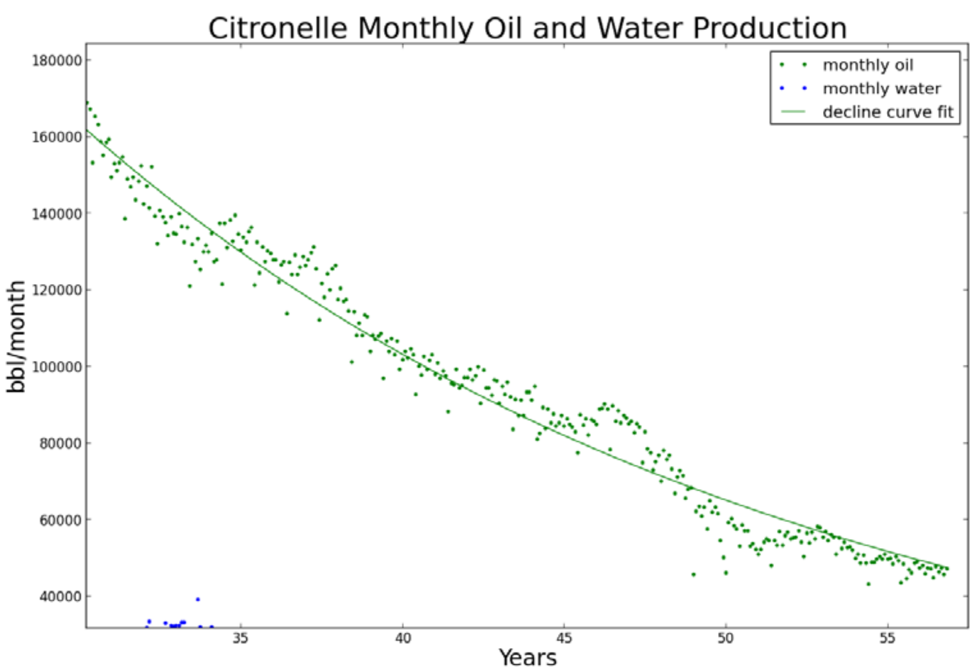


Figure 2.4.3. Decline fit for monthly oil production at Citronelle for the past 27 years: Monthly oil = 163,430 exp[0.0459603636 (t - 30)], with t in years since start of production from the field.

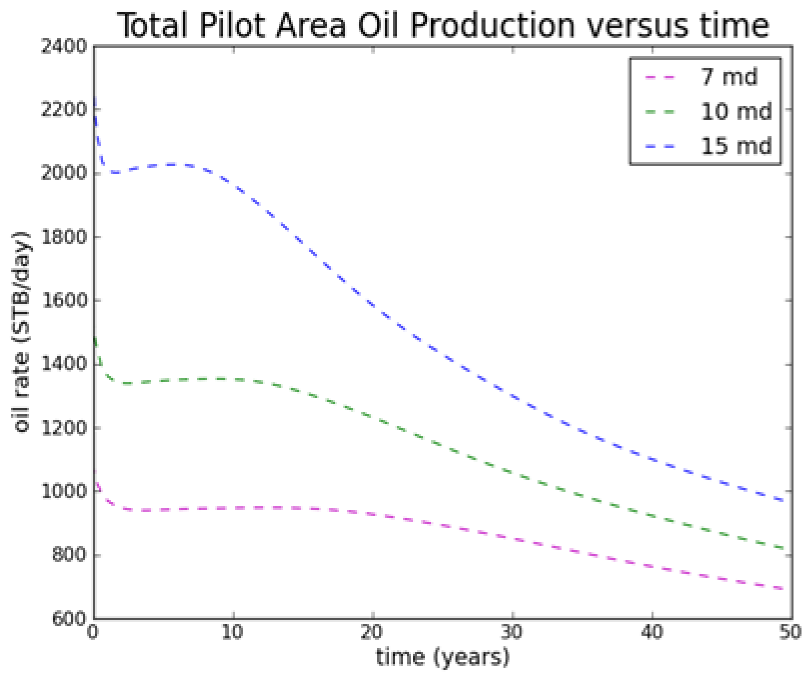


Figure 2.4.4. Fine-grid simulation results for 50-year oil production rates from the pilot region. These simulations used nSpyres and assumed uniform permeability distributions but highly irregular geometry.

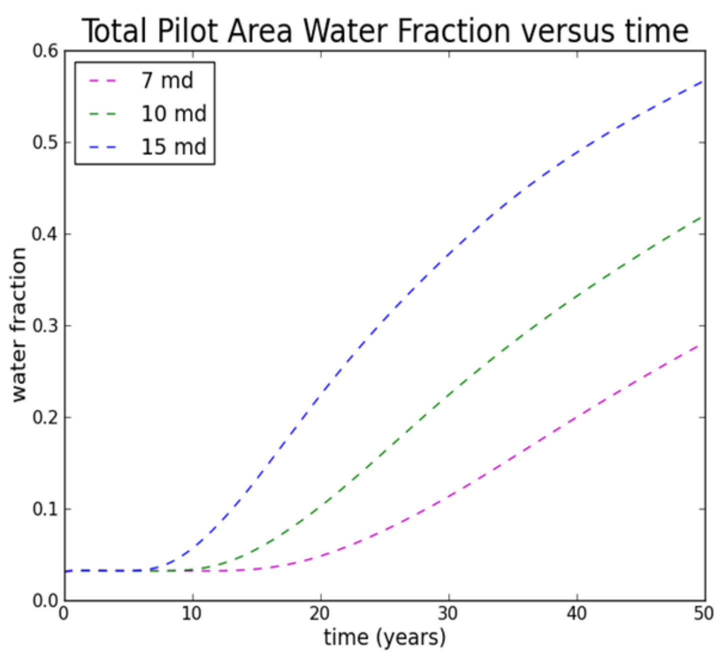


Figure 2.4.5. Fine-grid simulation results for 50-year produced water fraction from the pilot region. These simulations used nSpyres and assumed uniform permeability distributions but highly irregular geometry.

2.5. CO_2 Liquefaction, Transportation, and Storage

Michael Sullivan, Franklin Everett, Steven Brewer, Tommy Henderson, and Tommy Miller, Denbury Onshore, LLC
Peter M. Walsh, University of Alabama at Birmingham

Carbon dioxide for the project was provided by Denbury Onshore from its wells in the natural CO_2 reservoir at Jackson, MS. During the Phase II CO_2 injection, Airgas Carbonic received the CO_2 from Denbury Onshore, liquefied it, and transported it to Citronelle.

A refurbished 50-ton liquid CO_2 tank was purchased from TOMCO$_2$ Equipment Co. (Loganville, GA), moved to the test site in December 2008, and set on a reinforced concrete pad prepared by Denbury Onshore at the B-19-8 Tank Battery. The liquid CO_2 is stored at approximately 0 ^oF and 300 psig in the refrigerated tank. The first shipment of CO_2 was delivered to the test site by Airgas Carbonic on March 2, 2009.

CO_2 was delivered to the test site in tank trucks, each carrying ~19 tons of CO_2. At the average injection rate of 31 tons per day, the 50-ton tank provided 1.6 days of storage capacity and delivery of 1.6 truckloads, on average, were required each day. To keep up, two loads were delivered every other day and, when the level in the storage tank was low, on successive days. Toward the end of the Phase II test, injection rates increased to more than 40 tons per day, so two truckloads were required nearly every day, and three truckloads on some days.

2.6. Site Preparation, Water Flood, and CO_2 Injection

Gary N. Dittmar, Tommy Chatfield, Thomas Boelens, Steve Walker, Pete Guerra, Rick Jolly, and William C. Williams, Denbury Resources, Inc.
Michael Sullivan, Tommy Miller, Franklin Everett, Tommy Henderson, Bartley Lambeth, Steven Brewer, and Danny Beasley, Denbury Onshore, LLC

2.6.1. Site Preparation and Water Flood

The injection well for the test was B-19-10 #2 (Permit No. 3232). The producers being monitored most closely are B-19-7 (Permit No. 1215), B-19-8 (Permit No. 1235), B-19-9 (Permit No. 1205), and B-19-11 (Permit No. 1209). What was originally intended to be a more symmetric inverted five-spot well pattern became distorted by substitution of Well B-19-11 for the plugged and abandoned Well B-19-10 (Permit No. 1206), which, in spite of a heroic attempt at workover by Denbury Onshore, could not be returned to production. An aerial photograph of the oil field in the vicinity of the test pattern, with the wells identified by number, is shown in Figure 2.6.1.

Water injection into Well B-19-10 #2, to establish the baseline for oil production, began on March 25, 2008, and stabilized at a steady injection rate of 170 bbl/day of water, with Wells B-19-7 and B-19-9 each producing 4 to 5 bbl/day of oil and Wells B-19-8 and B-19-11 each producing 8 to 9 bbl/day of oil.

The 50-ton liquid CO_2 storage tank, charge pump, and triplex plunger positive displacement pump are located at the B-19-8 Tank Battery. Produced fluids from Wells B-19-7, B-19-8, and B-19-9 are collected at B-19-8 Tank Battery, and fluids from Well B-19-11 go to B-19-11 Tank Battery. Both tank batteries are equipped with gas-liquid cylindrical cyclone separators, to separate produced oil and water from gas. Oil and water are collected, but the gas, which is primarily CO_2, because of the unusually low gas yield from Citronelle oil, is vented. The flow meters installed to measure power oil and produced fluid flow rates going to and from the production wells were found not to have sufficient resolution to distinguish the power oil and produced fluid flow rates (4-9 bbl/day of produced oil versus 450-500 bbl/day of power oil per well).

2.6.2. CO_2 Injection

After the first delivery of CO_2 on March 2, 2009, a number of problems were encountered during attempts to begin CO_2 injection. In spite of several rounds of improvements to the pumping system during this early period, steady, continuous CO_2 injection could not be maintained for more than a short time. At the end of the project review meeting at the Geological Survey of Alabama on August 12, 2009, Project Manager Chandra Nautiyal and Olayinka Ogunsola, from DOE Headquarters, recommended that advice be sought from organizations having experience in handling and injecting liquid CO_2. On returning to his office following the meeting, the Principal Investigator contacted Reliant Gases, who had conducted the successful pilot injection of CO_2, supported by U.S. DOE through the Southeast Regional Carbon Sequestration Partnership, into a saline formation at Mississippi Power Company's Plant Daniel, near Pascagoula, MS. In spite of his being on vacation, Vance Vanderburg at Reliant kindly offered to look at the diagram of the pumping system to see if he could identify potential problems. Vance's conclusion, from inspection of the diagram, was that the system was properly configured. In his opinion, the most likely source of problems was the positive displacement pump, which, in his experience, can be quite temperamental when pumping liquid CO_2.

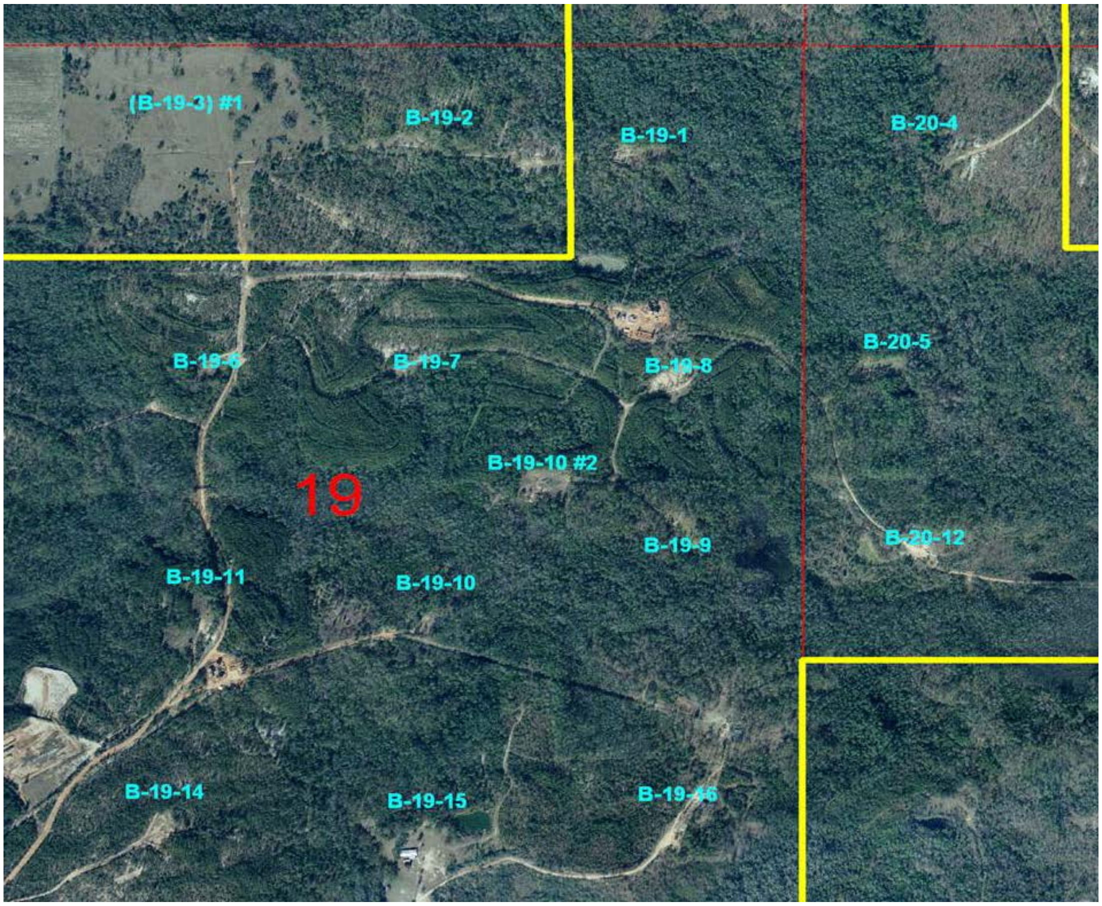


Figure 2.6.1. Aerial photograph of the Citronelle oil field in the vicinity of the test well pattern. The top edge of the photograph faces North. The test pattern consists of injector B-19-10 #2 and producers B-19-7, B-19-8, B-19-9, and B-19-11. Tank Battery B-19-8 is visible just to the Northwest of Well B-19-8. Tank Battery B-19-11 is to the South of Well B-19-11, between the roads.

Denbury Resources then retained Steve Wegener, a senior engineer from Jacobs Linder Engineering (Metarie, LA) to study the system and make recommendations. A meeting of Steve Wegener with all those concerned with the performance of the injection system was held at Denbury Onshore's offices and at the test site in Citronelle on October 15, 2009. A follow-up meeting of the Denbury group with Steve Wegener was held in Citronelle on November 18, 2009, to witness a test of the CO_2 pumping system. That test was not successful, but based on the information and analysis that Steve Wegener provided, and observations during the test, Pete Guerra of Denbury designed a retrofit of the triplex positive displacement pump, which resulted in the following report by Pete to the research team on November 25th:

> We were successful pumping CO_2 into the well at Citronelle today. We pumped against 1800 psig for 20 minutes at 150 bbl/day. We also pumped against the choke to 3000 psi at 160 bbl/day. The solution was to fill the dead volume inside the pump cylinders with custom-made Teflon inserts. The dead space was around the plunger and between the inlet and outlet valves. The dead space was allowing the CO_2 to compress, which created a temperature spiral until eventually the CO_2 vaporized between the valves and would stop

pumping around 1500 psig. The pump efficiency increased (the flow rate increased) as the discharge pressure increased, so I'm confident that we have the vapor-lock issue solved.

The next steps are as follows.

1. Re-sheave the pump maximum speed – to get our rate up.
2. Add a flow switch with shutdown on low flow – to protect against vapor lock.
3. Run the pump to low level in the tank to determine whether or not we'll need to lower the charge pump to achieve sufficient net positive suction head.

The Denbury group in the field at Citronelle replaced the sheave and implemented the low-flow shut-down system needed to protect the triplex pump and began around-the-clock CO_2 injection at the test site on December 22, 2009. The injection rate settled at 46.5 tons CO_2/day, the exact center of the range of 35 to 58 tons/day anticipated from the reservoir simulations by Eric Carlson and Dino Theodorou and Denbury's experience in carbonate reservoirs.

However, after a short period of trouble-free operation at the injection rate of 46.5 tons CO_2/day, problems with the triplex pump surfaced again, as damage to the Teflon sleeves, described in Pete Guerra's message above, that had been installed to minimize dead volume in the pump. In spite of these problems, Michael Sullivan and Franklin Everett, leading the work in the field, were able to continue injection, with constant attention and maintenance to the pump, for about 11 hours per day. Twenty tons of CO_2 were typically injected each day; equal to slightly more than half of the anticipated minimum rate (35 tons/day). Then, on December 29th, a tubing leak was detected, requiring a complete shut-down for repair. CO_2 in the ground at that point stood at 380 tons. A workover rig was brought in to replace the tubing as quickly as possible.

Replacement of the tubing in the injector was completed on January 25, 2010, and pumping and injection of CO_2 resumed on January 27. The average rate of CO_2 injection, including down time for maintenance, then stabilized at 31 tons/day. The history of CO_2 injection, beginning on December 1, 2009, is shown in Figure 2.6.2. At the average rate of 31 tons/day, injection of the 7500 tons allocated for injection in Phase II was expected to be complete in September 2010. To allow some additional time for trouble shooting, observation of response, and analysis of data, an 8-month no-cost extension of Phase II, from April 30 to December 31, 2010, was requested by UAB and approved by NETL.

Continuous injection of CO_2 was maintained at the average rate of 31 tons/day from January 27 to the end of the Phase II injection. The original injection target of 7500 tons CO_2 was reached on September 12, but because the contract with Airgas Carbonic, the provider of the liquefaction and transportation services, provided for an extra 5 to 10% of CO_2, to allow for possible losses during processing and trucking, the injection was continued to 8036 tons, which was reached on September 25th, concluding the Phase II injection. The record of the injection is shown in Figure 2.6.2, compared with the reservoir simulation performed by Eric Carlson using SENSOR (Coats Engineering, Inc.). The average injection rate of 31 tons/day is in good agreement with the average rate of 35 tons/day anticipated by the simulation. As mentioned in Section 2.5 and shown in Figure 2.6.2, the injection rate gradually increased toward the end of the test, reaching over 40 tons/day on some days, during the final weeks.

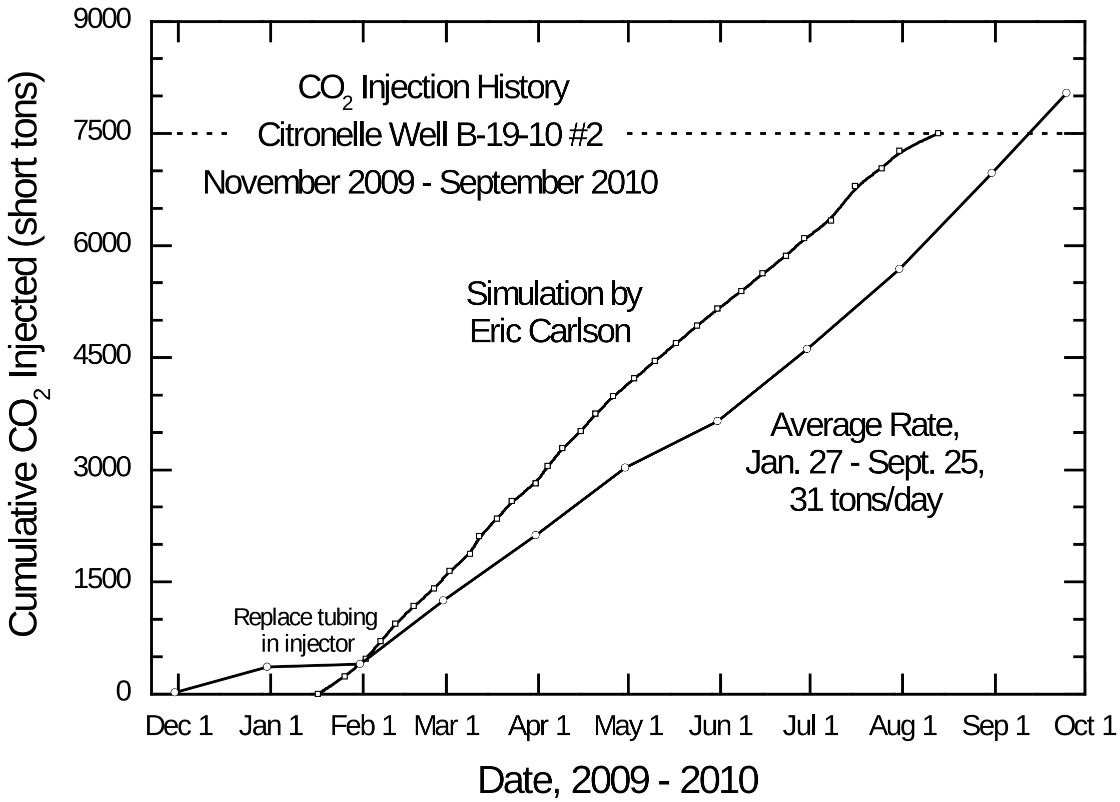


Figure 2.6.2. Record of the CO_2 injection during Phase II and comparison with the reservoir simulation by Eric Carlson using SENSOR (Coats Engineering, Inc.). The average injection rate from January 27 to the end of the injection on September 25, including down time for maintenance, was 31 tons/day. The total amount of CO_2 injected was 8036 tons.

2.6.3. Response to CO_2 Injection

Oil produced from three wells in the test pattern (B-19-7, B-19-8, and B-19-9) is gathered, along with production from five other wells to the north and east, at Tank Battery B-19-8. Produced oil from well B-19-11 in the test pattern goes to Tank Battery B-19-11, along with production from three other wells to the west and south.

The record of oil production at B-19-8 Tank Battery during the period from February 2009, long before the start of CO_2 injection, to December 2013, is shown in Figure 2.6.3a. From March to December 2009 the tank battery had been experiencing an average decline of 20 bbl/day/year. A decline curve based on production during that period is shown in the figure. Beginning in January 2010, coinciding with the start of continuous CO_2 injection, the decline in production was reversed, and, from January to September 2010, when the first CO_2 injection was complete, oil production increased at the average rate of 18 bbl/day/year.

However, in October 2010, following the return to water injection, oil production began to decline. The decline accelerated in subsequent months, dropping, by March 2011, to only 36% of the rate at the September 2010 peak and to less than half of the rate just before the start of CO_2 injection. One reason for the decline is apparent in Figure 2.6.3b, which shows the frequency with which the power oil pumps in wells whose fluids are gathered at B-19-8 Tank Battery had to be pulled because of excessive wear due to contamination of the power oil with particles mobilized by CO_2. The frequency of pump pulls had begun to increase in August 2010, just before the end of the CO_2 injection, and increased by approximately a factor of ten from July 2010 to January and February 2011, when oil production approached its lowest point. As they were pulled, the pumps were replaced by new ones having longer stroke and parts made from harder material, so the frequency of pump maintenance began to decline in February 2011 and there was a corresponding increase in oil production over the next 12 months, to 44 bbl oil/day in March 2012. The recent average rate of 39-40 bbl/day is lower than the peak rate of 59 bbl oil/day recorded in September 2010 and slightly less than the rate of 45 bbl oil/day just before the start of CO_2 injection in December 2009, but it is significantly higher than the decline curve established during the 10 months from March to December 2009, prior to CO_2 injection, as shown in Figure 2.6.3a.

The response to CO_2 injection at B-19-11 Tank Battery, shown in Figure 2.6.4a, was quite different from that observed at B-19-8 Tank Battery. In contrast to the immediate increase in oil production observed at B-19-8 Tank Battery, production at B-19-11 Tank Battery continued for four months on the trajectory that it had been following for the previous 10 months. Then, coinciding with breakthrough of CO_2 at Well B-19-11, discussed below, production at the battery abruptly declined, by approximately the typical production from Well B-19-11 (8 to 9 bbl/day), then continued a steady decline, with no significant response to the termination of CO_2 injection and return to water injection in September 2010. Following injection of surfactant, from July to November 2012, discussed below, oil production at B-19-11 Tank Battery began to recover, but in July 2013 it began to decline again, and it remains below the decline curve established before CO_2 injection.

The production data for Tank Batteries B-19-8 and B-19-11 are shown again in Figures 2.6.5a and b, respectively, with the time scales shifted to emphasize the response to CO_2 injection. Integration of the difference between the actual oil production and the decline curve gives the cumulative incremental oil production assignable to EOR. The cumulative incremental production at Tank battery B-19-8 and the cumulative incremental deficit at Tank Battery B-19-11 are shown in Figure 2.6.5c. Their sum gives the net cumulative incremental oil for the project. The estimate of incremental oil production at Tank Battery B-19-8, to December 31, 2013 is 25,411 bbl (unofficial) and the estimate of the incremental deficit in oil production at Tank Battery B-19-11 is -20,981 bbl (unofficial), giving a net positive cumulative incremental production of 4430 bbl.

A second reason for the decline in oil production, beginning at the end of the CO_2 injection and return to water injection in September 2010, is that the water injection rate, which had been 170 bbl water/day before CO_2 injection, decreased to approximately 60 bbl water/day and remained, except for occasional spikes, at this low level. A test campaign was conducted to determine the cause of the apparent blockage and the means to correct it. The first step was a pressure-transient injection and fall-off test, conducted in November and December 2011, which produced some surprising results, described below.

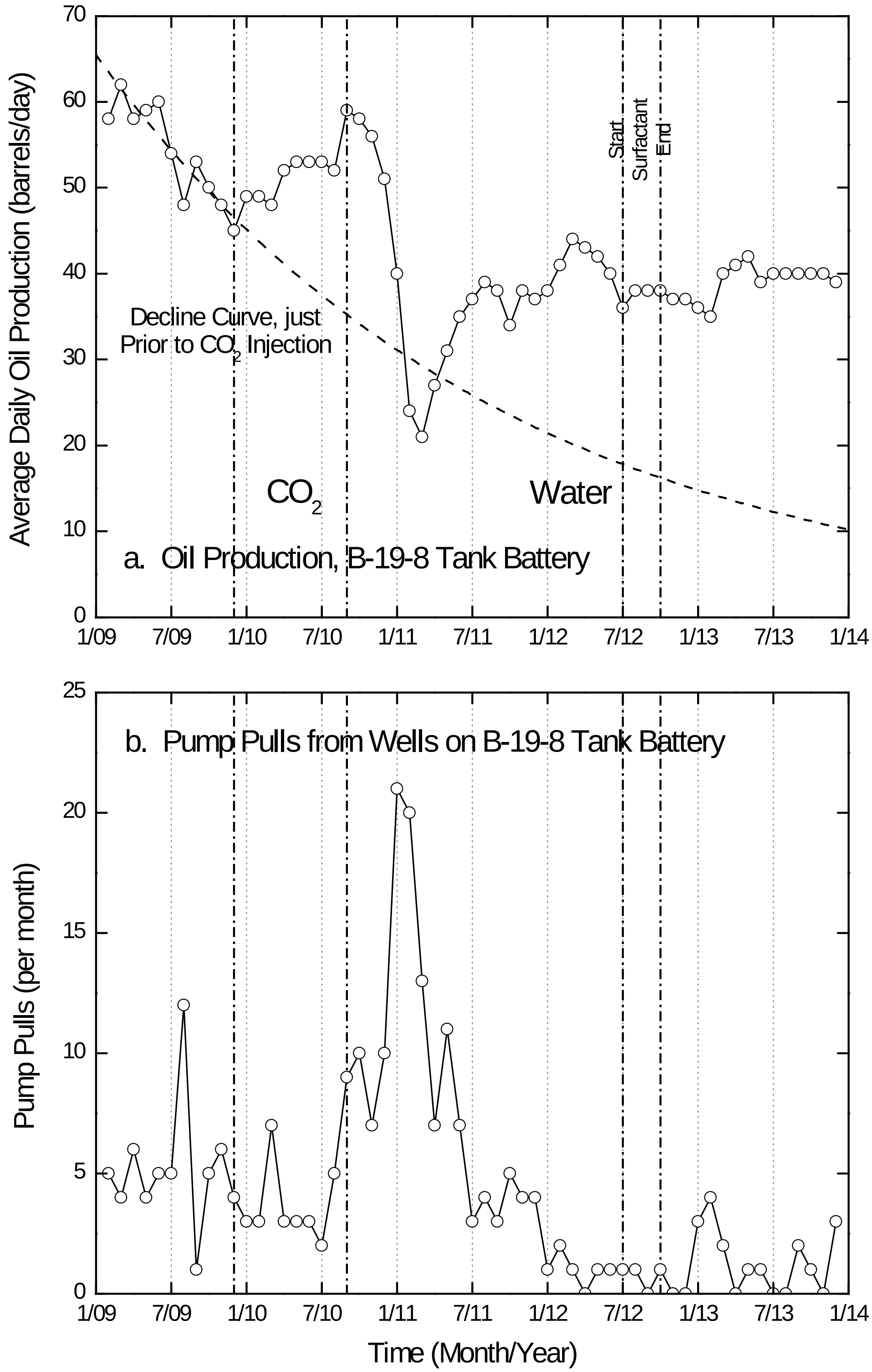


Figure 2.6.3. Response to CO_2 injection at Tank Battery B-19-8. a. Oil production at B-19-8 Tank Battery, which receives fluids from Wells B-19-7, B-19-8, and B-19-9, from February 2009 to December 2013. b. Number of times per month that power oil pumps in wells on B-19-8 Tank Battery had to be pulled for maintenance or replacement, from February 2009 to December 2013.

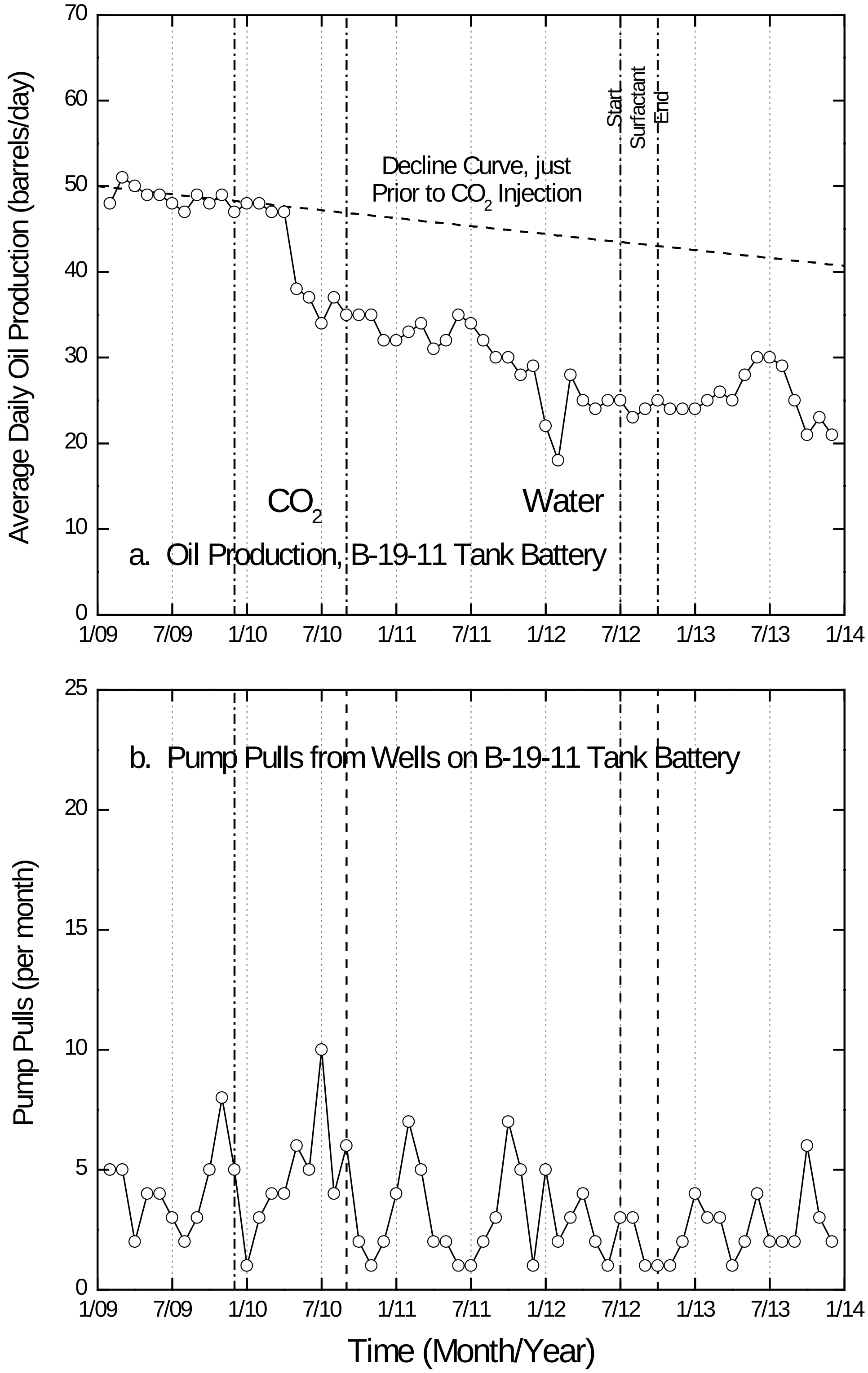


Figure 2.6.4. Response to CO_2 injection at Tank Battery B-19-11. a. Oil production at B-19-11 Tank Battery, which receives fluids from Well B-19-11, from February 2009 to December 2013. b. Number of times per month that power oil pumps in wells on B-19-11 Tank Battery had to be pulled for maintenance or replacement, from February 2009 to December 2013.

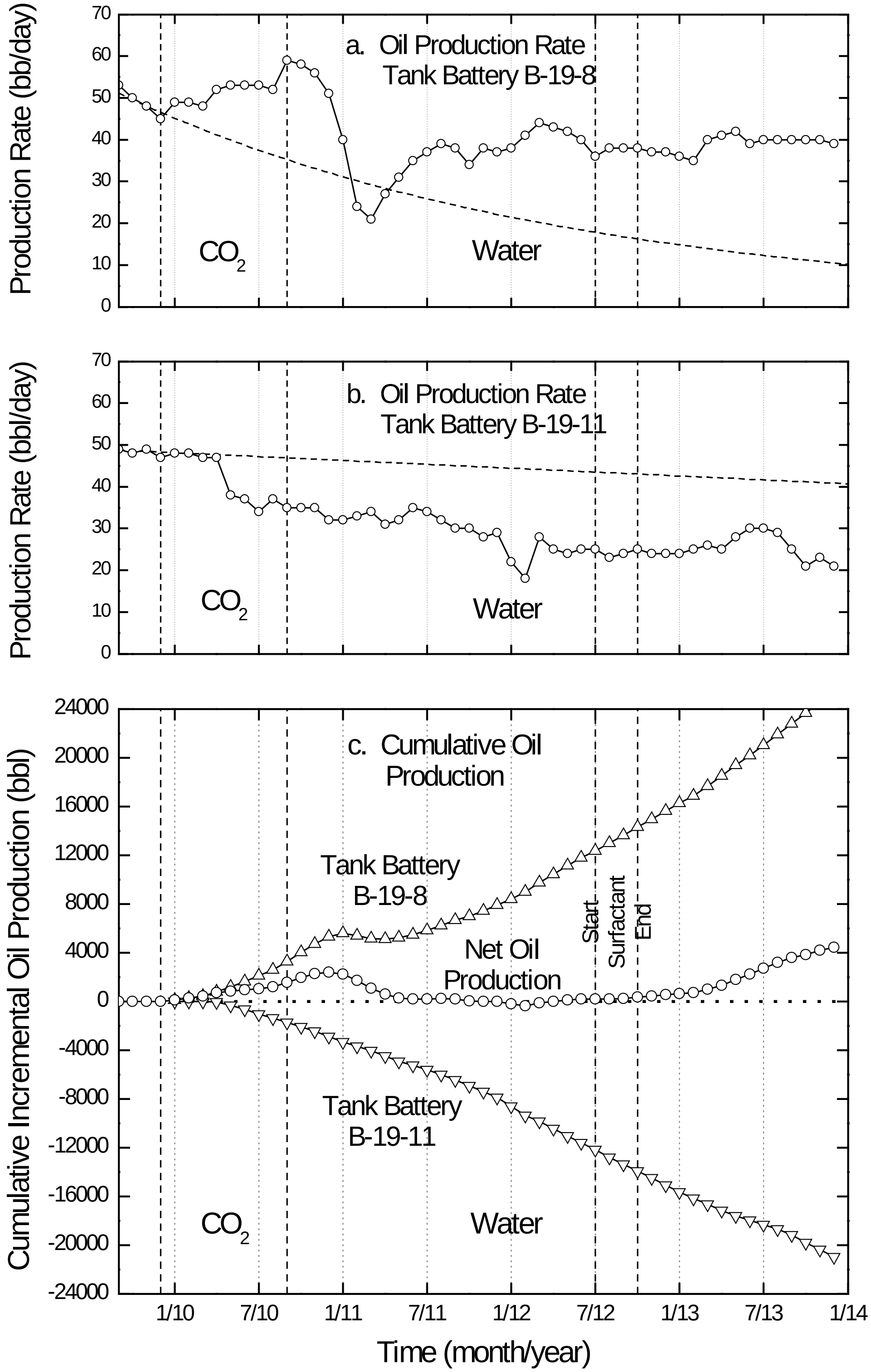


Figure 2.6.5. Oil production rates and cumulative incremental oil to the end of December 2013. a. Oil production at Tank Battery B-19-8 (same as Figure 2.6.3a). b. Oil production at Tank Battery B-19-11 (same as Figure 2.6.4a). c. Cumulative incremental oil production from Tank Battery B-19-8 (Δ symbols); cumulative incremental loss in production at Tank Battery B-19-11 (∇ symbols); and the combined net cumulative production for the two batteries (O symbols). Recent net production continues to be positive.

On May 25, 2010, five months after continuous CO_2 injection began, high pressure was detected in the vertical oil/water separator at B-19-11 Tank Battery, where produced fluids from Well B-19-11 are collected. Well B-19-11 is the producer in the southwest corner of the test pattern, farthest from the injector. Tommy Miller and Michael Sullivan tested the gas in the head space of the power oil tank using a Draeger tube and detected a high level of CO_2. Produced gas samples, for detailed analysis, were collected by Peter Walsh on the same day. Close agreement of the delta carbon-13 isotope ratio in CO_2 ($\delta^{13}CO_2$) in the sample of produced gas with the isotope ratio in the injected CO_2, showed that the CO_2 in produced gas at B-19-11 was breakthrough from CO_2 injection at B-19-10 #2. Rapid breakthrough of CO_2 was a great surprise, because no evidence of natural fractures had ever been seen in all of the work with drill core from Citronelle sands by Jack Pashin and his coworkers at the Geological Survey of Alabama. The records also indicate that Well B-19-10 #2 had never been intentionally hydraulically fractured.

Another set of produced gas samples was collected on August 4, 2010. The composition of produced gas from all four producers in the test pattern and the analysis of the injected CO_2, from the storage tank, are compared in Table 2.6.1. The gas from one well, B-19-7, has approximately the same CO_2 content as gas from all of the wells before CO_2 injection began, and its low value (large negative number) for $\delta^{13}CO_2$ is characteristic of solution gas. The CO_2 and $\delta^{13}CO_2$ analyses for the other wells show that the order of CO_2 breakthrough at the producers was B-19-11, B-19-9, then B-19-8.

Produced gas from wells both inside and outside the test pattern was then monitored for increased CO_2 using Draeger Tubes. The record of CO_2 in produced gas in April 2011 is summarized in Table 2.6.2. Breakthrough at Well A-25-10, far to the southwest of the injector, is very surprising and provides evidence for distant travel of CO_2 across depositional trends.

Testing to determine the cause of low injectivity to water, following the CO_2 injection, began with a pressure-transient injection and fall-off test, from November 28 to December 12, 2011. The results from that test were analyzed by Eric Carlson. His conclusion, supported by his data analysis shown in Figure 2.6.6, is that there is a substantial hydraulic fracture originating at the injector, having a total length of 600 to 1000 ft. The pressure-transient test does not provide any information about the direction of the fracture, but the most likely direction is that of maximum horizontal compressive stress in the Southeastern U.S., typically N70E to N80E.* Two of the wells at which early breakthrough of CO_2 was detected lie on the line at N69E relative to the injector. The other two wells at which early breakthrough was detected lie on the line at N44E relative to the injector. The following are likely conclusions: (1) A hydraulic fracture along the direction of maximum horizontal compressive stress was opened by water or CO_2 injection into Well B-19-10 #2, and (2) The fracture provided a preferential pathway for CO_2, compromising the sweep efficiency of CO_2 in the pilot test.

*Please see the additional discussion of early CO_2 breakthrough and fracturing by the Geological Survey of Alabama, in Section 2.2.4 and Figure 2.2.2.

Table 2.6.1.
Analyses of Samples of Produced Gas and Injected CO_2 Collected on August 4, 2010.

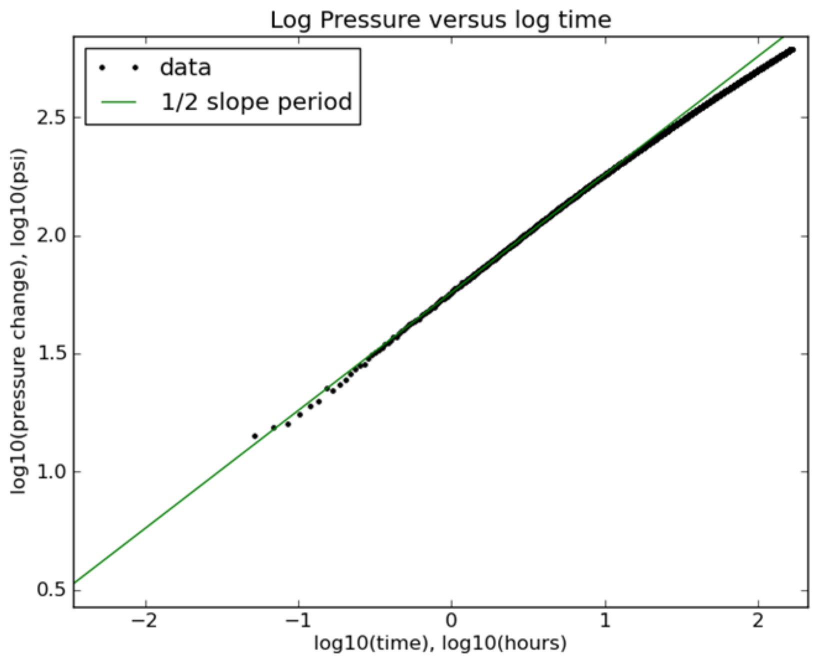
Well Name	B-19-11	B-19-11	B-19-7	B-19-8	B-19-9	CO2 Tank
Gas Composition						
C1	0.66	0.67	20.57	29.02	36.17	0.02
C2	0.45	0.44	5.50	5.58	6.26	0.01
C2H4	0.00	0.00	0.00	0.00	0.00	0.00
C3	1.13	1.05	8.27	7.59	7.14	0.06
iC4	0.67	0.62	3.18	2.85	2.46	0.03
nC4	1.24	1.14	5.53	5.07	4.11	0.09
iC5	0.41	0.38	1.12	1.06	0.80	0.03
nC5	0.87	0.80	1.99	1.93	1.40	0.06
C6+	1.21	1.07	1.98	1.46	1.12	0.08
H2S	0.00	0.00	0.00	0.00	0.00	0.00
He	0.00	0.00	0.05	0.12	0.12	0.00
H2	0.01	0.02	0.03	0.08	0.09	0.00
Ar	0.00	0.00	0.43	0.25	0.06	0.00
O2	0.01	0.02	0.83	0.42	0.02	0.03
N2	0.14	0.19	47.49	30.96	11.60	0.14
CO	0.02	0.02	0.00	0.00	0.00	0.00
CO2	93.18	93.58	3.03	13.61	28.65	99.45
Units	%	%	%	%	%	%
Gas Isotope						
*δ13CO2	-2.8	-2.8	-19.9	-8.2	-6.8	-2.9

* $\delta^{13}CO_2 = [(^{13}C/^{12}C)_{sample}/(^{13}C/^{12}C)_{reference} - 1] \times 1000$

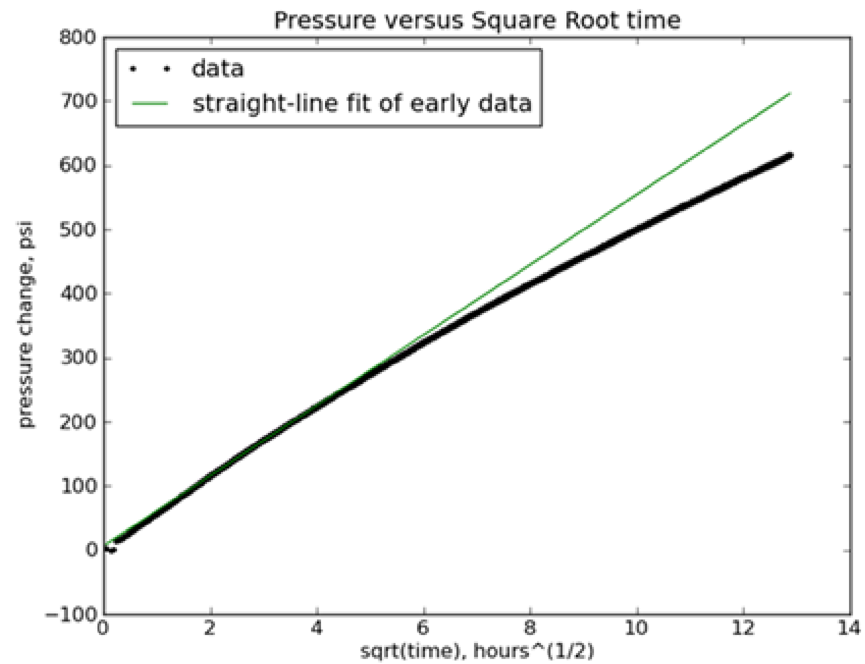
Table 2.6.2.
CO_2 Content of Produced Gas from Wells
in and near the Test Pattern, April 12, 2011.

Well	CO_2, volume %[a]
A-25-8	~ 0
A-25-10	15
B-19-7	~ 0
B-19-8	25
B-19-9	~ 0
B-19-11	57
B-20-4	~ 0
B-20-5	10
B-30-4	~ 0

a. ~ 0 indicates a level of CO_2 not significantly greater than the 3 vol% typical of Citronelle solution gas.



a. Slope of ½ on the log-log plot of pressure vs. time during shut-in is evidence for the presence of a fracture.



b. Slope of the plot of pressure vs. time$^{1/2}$ during shut-in indicates a fracture length of 600 to 1000 ft.

Figure 2.6.6. Analysis of the pressure-transient test data by Eric Carlson shows the presence of a hydraulic fracture (figure at left) having a length determined from the dependence of the pressure decay on the square root of time (figure at right).

2.6.4. Loss of Injectivity to Water Following CO_2 Injection

Well B-19-10 #2, the injector in the inverted five-spot well pattern for the CO_2-EOR pilot test, experienced a marked decrease in injectivity on returning to water injection in September 2010, following injection of the 8036-ton slug of CO_2. The problem can be seen in the injection data for Well B-19-10 #2 during the pilot test, shown in Figure 2.6.7. The earliest measurements of the water injection rate began in May 2008, shortly after conversion of Well B-19-10 #2 from producer to injector. The average injection rate during the long period of steady water injection from July 2008 to March 2009, toward the left in Figure 2.6.7, was 160 ± 18 bbl/day (mean and standard deviation). Following that observation of baseline performance, the well was shut in for approximately 9 months, for trials and trouble-shooting of the CO_2 pumping and injection system. The 8036 tons of CO_2 were injected from December 2009 to September 2010.

The CO_2 injection was completed on September 25, 2010, and water injection began the next day. On September 26, 259 bbl of water were injected, followed by 293 bbl on September 27. However, on September 28, the injection rate dropped to just 40 bbl/day, and has remained at low levels ever since, averaging 67 ± 21 bbl/day from September 28, 2010, to July 24, 2013, as shown in the record on the right in Figure 2.6.7.

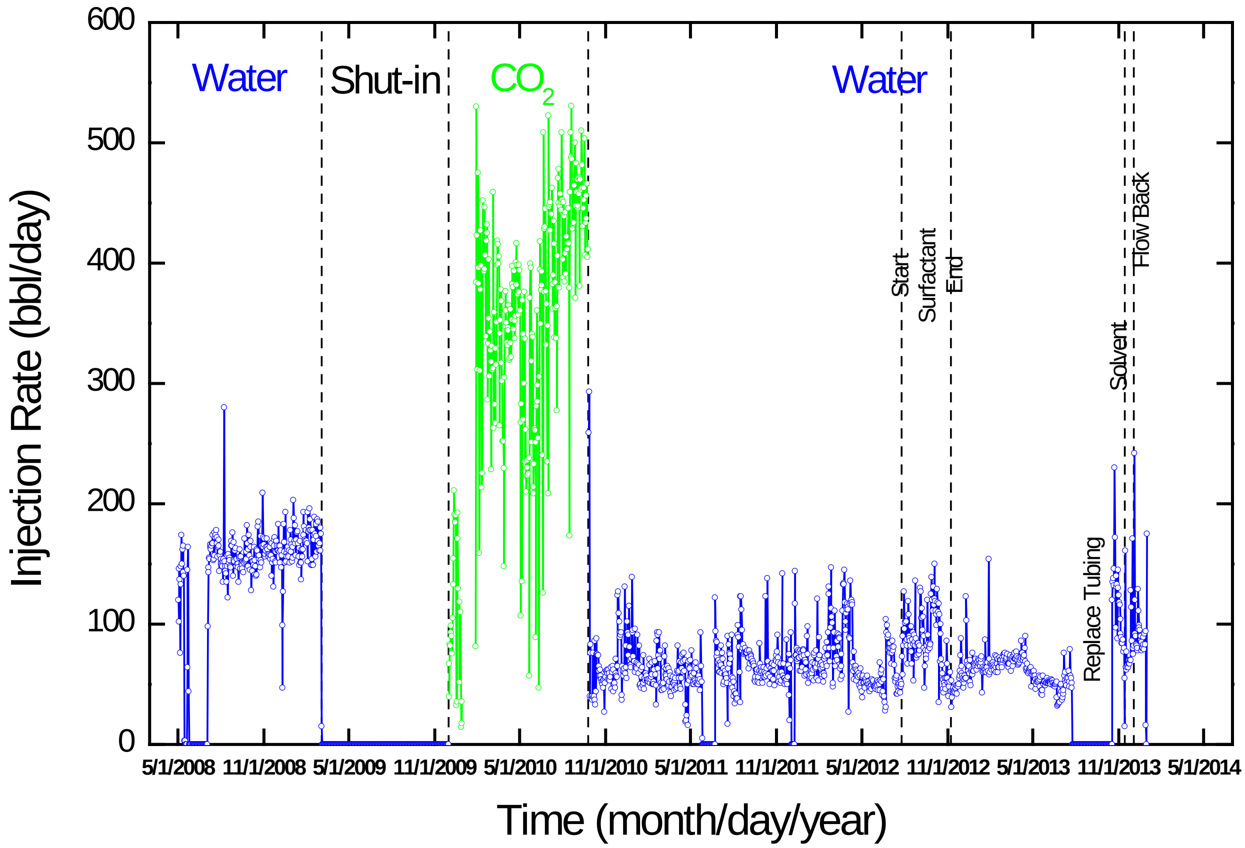


Figure 2.6.7. History of the rates of water and CO_2 injection into Well B-19-10 #2, by volume, from May 2, 2008, to December 31, 2013. The feature of greatest interest is the low injectivity to water following the CO_2 slug.

Several explanations for such a large and rapid loss in injectivity to water were suggested:

Capillary blocking of water flow by supercritical CO_2 trapped in pores.

Plugging of pore throats by particles mobilized by the action of acidified brine on minerals.

Dissolution of minerals followed by precipitation of solids when conditions such as pressure and pH change as the fluids move outward from the well bore.

Precipitation of paraffins or asphaltenes left near the well bore by the extraction and outward migration of lighter hydrocarbons with the CO_2.

Further tests were conducted to identify possible causes of the low injectivity to water.

2.6.5 Surfactant Treatment

Denbury Onshore's chemicals supplier, Baker Hughes, was contracted to treat the water at the injector with surfactant, to evaluate the importance of capillary blocking. The injection rate data are shown on expanded scales in Figure 2.6.8, along with wellhead pressure measurements. The average injection rate during the period beginning at the left in Figure 2.6.8, up to the start of surfactant injection, from October 15, 2011 to July 24, 2012 was 67 bbl water/day.

Injection of Baker Hughes Surfactant WCW87 began on July 25, 2012 at the initial rate of 4 gallons/day. As is standard practice, the high initial rate was reduced one week later, on August 1, to 2 quarts/day. The water injection rate responded almost immediately, increasing from 50 bbl water/day on July 23-25 to 80-120 bbl water/day from August 8 to 14. The injection rate continued to increase, reaching 100 to 150 bbl water/day from September 26 to October 12, with an average of 120 bbl water/day.

In mid-October, the Denbury group in Citronelle began an effort to increase the pressure and water injection rates on other wells. The higher pressure resulted in some line leaks, requiring that those lines be shut in and that a pump be shut down to prevent blowing out other lines. The pressure at the injector during this period, beginning on October 15, 2012, was first unstable, then settled down at a value 100 psi lower than before. Surfactant treatment was stopped shortly thereafter, on November 7, 2012. The reduction in pressure provides an explanation for the low injection rates observed from October 23 to November 7. Interestingly, after stopping the surfactant treatment on November 7, the water injection rate began a consistent upward trend, which continued even after a further reduction in pressure from 3800 to 3750 psig on December 12, 2012. That upward trend reversed, however, during April, May, and June 2013.

The water injection rate during surfactant injection, when the pressure was constant at 3900 psig, from July 30 to October 14, 2012, averaged 95 bbl water/day. During the period following CO_2 injection but before the surfactant treatment, from September 26, 2010 to July 24, 2012, on the days when the pressure was 3900 psig, the average water injection rate was 63 bbl water/day. The surfactant treatment was therefore associated with a 50% increase in injection rate. Though certainly significant, the increase accompanying surfactant injection did not come close to restoring the injection rate to the average level of 160 bbl water/day before CO_2 injection, when the average pressure was only 3600 psig.

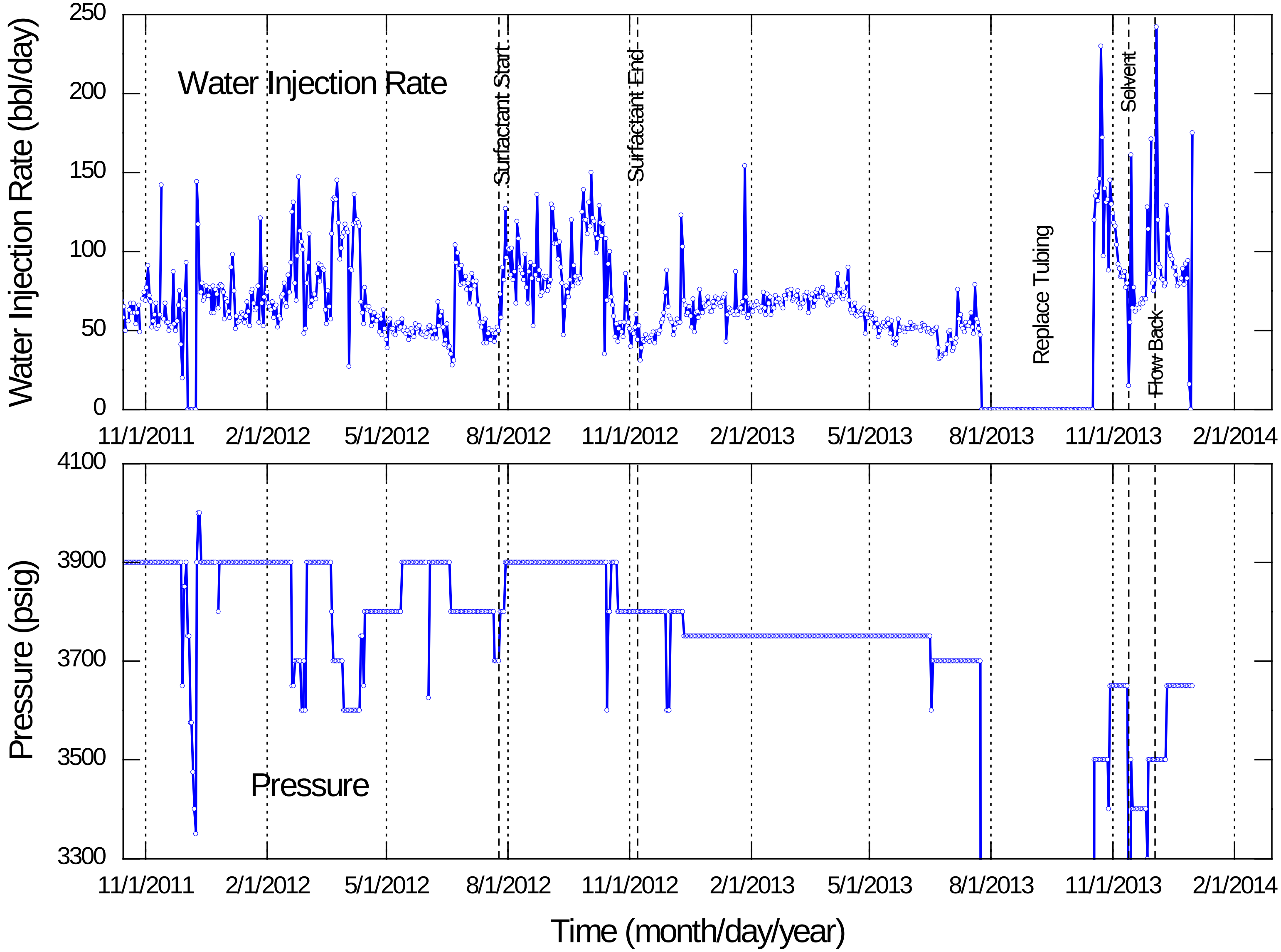


Figure 2.6.8. Rates (top) and pressures (bottom) of water injection into Well B-19-10 #2 in the inverted five-spot test pattern at Citronelle, from October 15, 2011, to December 31, 2013. Surfactant treatment began on July 25, 2012 and ended on November 7, 2012. The well was shut in for repair of a tubing leak on July 25, 2013.

The period during which injected water was treated with surfactant is indicated on the records of oil production at Tank Batteries B-19-8 and B-19-11 in Figures 2.6.3, 2.6.4, and 2.6.5. We note that, with the start of surfactant treatment in July 2012, the decline in production experienced at Tank Battery B-19-8 from March to July 2012 was halted, with oil production remaining at 35-42 bbl oil/day from August 2012 through June 2013. Oil production at Tank Battery B-19-11 began a gradual increase in January 2013, perhaps in response to the decrease in water injection pressure from 3800 to 3750 psig on December 12, 2012, allowing partial closure of the fracture. The conclusion from the surfactant treatment is that while capillary blocking of water injection is significant, it is not the only effect responsible for the loss in injectivity experienced on returning to water injection following the CO_2 slug.

The next test to be performed, originally scheduled for July 2013, was treatment of the injector with a hydrocarbon solvent and an asphaltene dispersant. Near the beginning of treatment of Well B-19-10 #2 with solvent in July, a leak developed in the tubing, interrupting the test on July 24, 2013. While pulling the tubing it was found that the internal plastic coating (IPC) of the tubing was flaking off. Problems with IPC were experienced by Denbury Resources throughout its oilfield operations. The cause of the problem was determined to be a lapse in quality control on the part of the supplier. Plugging of perforations by the chips of coating is therefore another possible explanation for the low injectivity to water. The coated tubing was replaced with regular bare steel tubing and the well was brought back on line with water injection on October 11, 2013. The cumulative effects of the change in tubing, flow-back to remove IPC chips, and treatment with solvent have restored the water injection rate to the range from 79 to 94 bbl water/day. Flow-back appears to have had the most lasting effect, suggesting that flaking of the IPC is the likely cause of poor injectivity to water following the CO_2 injection.

2.6.6. Injection Profile Tests

Injection profile tests were run to determine the distribution of water and CO_2 between the two injection targets, Sands 14-1 and 16-2. The tests were conducted before, during, and following the CO_2 injection, with the results shown in Table 2.6.3. Comparison of water flow rates, in bbl/day, in the two columns on the far right in the table, shows that it was a reduction of the flow into Sand 14-1 that was primarily responsible for the loss in injectivity following the CO_2 injection.

David Kopaska-Merkel, at the Geological Survey of Alabama, made the following observations regarding the 14-1 and 16-2 Sands:

> "The 14-1 Sand is much thinner than the 16-2 Sand and much finer grained. The one thin section from the 14-1 Sand is very fine. Thin sections from the 16-2 Sand indicate that it grades upward from conglomerate to silty very fine sand. The 14-1 Sand appears to contain less carbonate cement than the 16-2 Sand, so I don't think this could be a significant part of the problem. Because it is much finer grained, it wouldn't take much to clog the pores; I suspect this is what is going on. The thicker 16-2 unit is normally graded and parts of it aren't very permeable. However, it contains plenty of rock that is coarser and more permeable than any of the 14-1 Sand. It contains a fair amount of carbonate cement, but obviously this has not been remobilized in any deleterious fashion, because this is not the unit that is experiencing problems. Mineralogically there is not much difference between the two sand units, beyond the difference in carbonate cement abundance."

Table 2.6.3.
Distribution of Fluid Flow from Injection Well B-19-10 #2 into Sands 14-1 and 16-2,
Determined from Injection Profile Tests before, during, and following CO_2 Injection.

Date	Fluid	Condition	Fraction of Flow (%)		Total flow	Flow Rate (bbl/day)	
			Sand 14-1	Sand 16-2	(bbl/day)	Sand 14-1	Sand 16-2
Sept. 22, 2008	Water	Baseline	82	18	249[a]	131[a]	29[a]
June 10, 2010	CO_2	EOR	60	40	170[b]	102[b]	68[b]
January 19, 2012	Water	WAG	35	65	69	24	45
May 16, 2013	Water	Following surfactant treatment and reduced injection pressure	44	56	68	30	38

Notes:

a. The water injection rate of 249 bbl/day during the baseline injection is highly unusual. The average rate during the period of steady injection beginning on July 4, 2008, following the conversion of Well B-19-10 #2 from producer to injector, and ending with shut-in of the well for trials of CO_2 injection on March 3, 2009, was 160 ± 18 bbl/day (mean and standard deviation). The flow rates entered in the last two columns were calculated using the latter value for the total flow.

b. The conditions of temperature and pressure at which these barrels of CO_2 are defined are not specified in the injection profile test report.

2.7. Surface Monitoring

2.7.1. Soil Properties and CO_2 Fluxes from Forest Soils at the Test Site

Ermson Z. Nyakatawa and Loutrina T. Staley
Alabama Agricultural and Mechanical University

Instrumentation. Ermson Nyakatawa and his students at AAMU set up soil probes and sampling chambers with which to measure soil gas composition versus depth, CO_2 flux from soil, soil temperature, and soil moisture at three locations surrounding the injection well, three of the four producers, and the plugged and abandoned well within the test pattern. The suite of instrumentation is shown in Figure 2.7.1 and the arrangement of the 15 complete sampling stations around the injector, producers, and plugged and abandoned well is shown in Figure 2.7.2.

The instruments were installed during a visit to the field by Ermson and three of his students on June 11-12, 2008. The first set of soil samples, one at each sampling station to be taken annually, were also collected during that visit. Complete sets of baseline measurements and soil gas samples were gathered by Ermson and students Latasha Lyte, Christina Igono, and Rogers Atugonza during subsequent visits to the test site, on August 7, September 22, October 10, and October 30, 2008, on March 11 and November 12, 2009, and, during CO_2 injection, on August 11, 2010. Examples of the suite of soil properties which the investigators are using to define soil conditions were presented in a previous Quarterly Progress Report (January 30, 2009, pp. 26-27). The properties include moisture content, temperature, pH, electrical conductivity, nitrogen, phosphorus, carbon, and CO_2 flux.

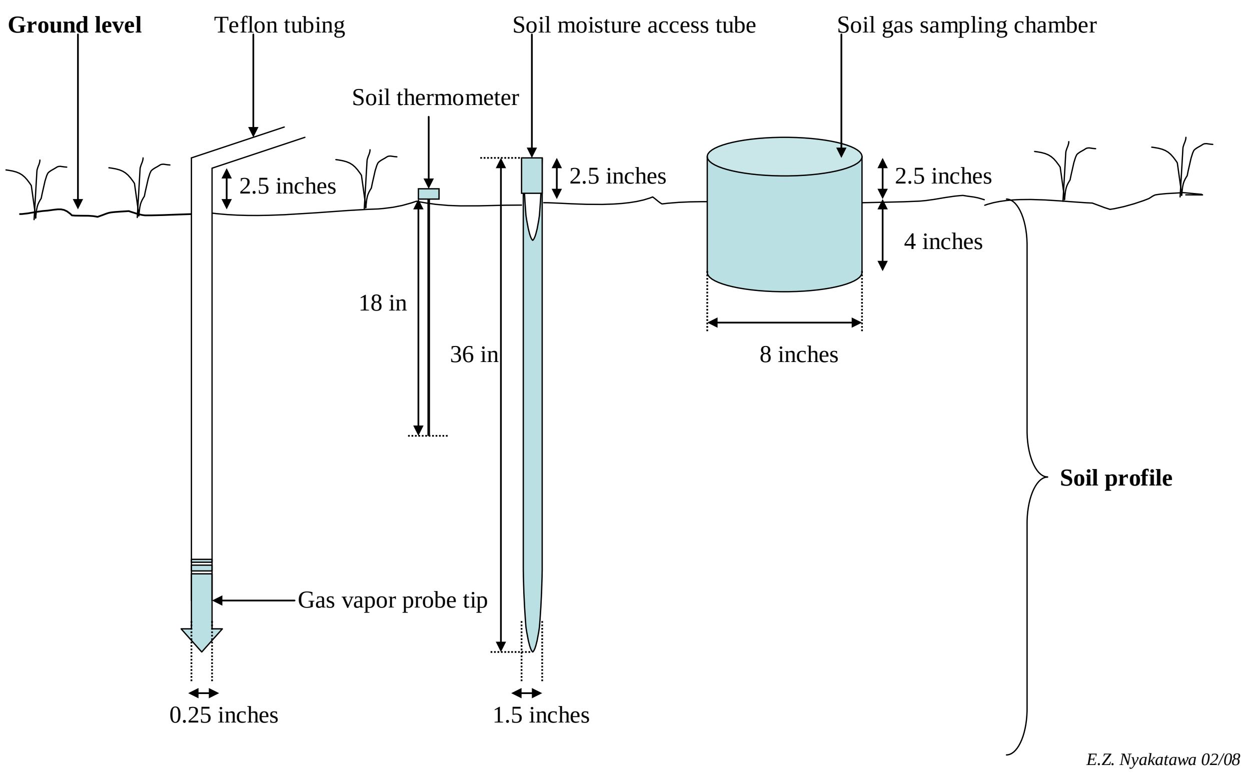


Figure 2.7.1. Soil gas sampling system (Ermson Nyakatawa, Alabama A&M University).

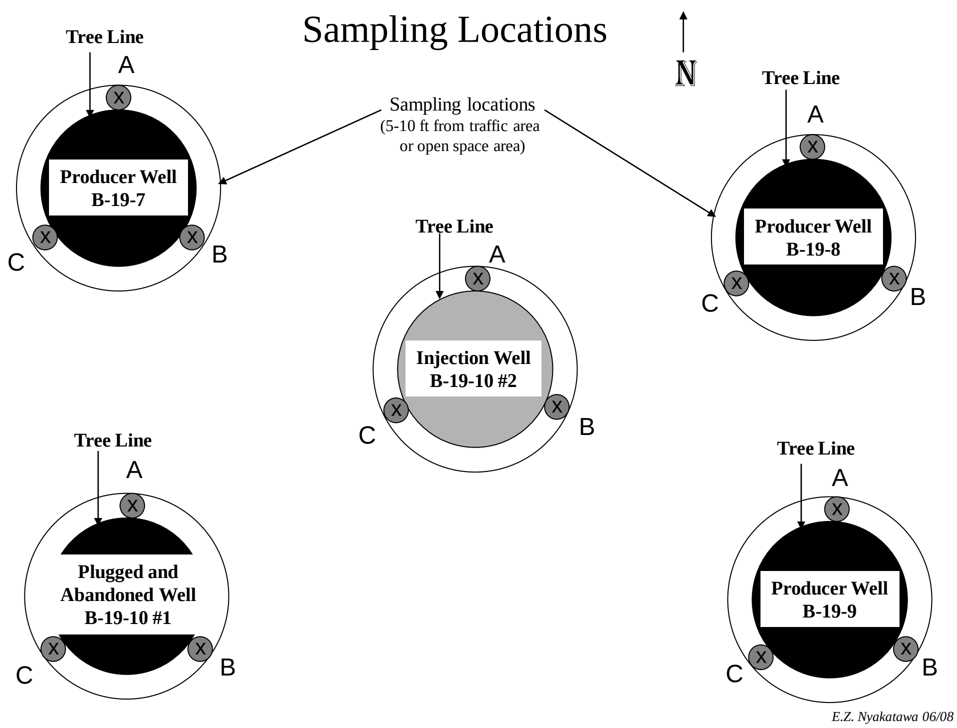


Figure 2.7.2. Arrangement of soil gas sampling stations at the CO_2 injection well, three production wells, and the plugged and abandoned well in the pilot test well pattern. There are three sampling stations at each well (Ermson Nyakatawa, Alabama A&M University).

The work at Citronelle by Ermson Nyakatawa's research group was presented and discussed by Latasha Lyte in her Master's Thesis, entitled, "Carbon Dioxide Fluxes in a Forest Soil in the Citronelle Oil Field in South Alabama" (Lyte, 2011). A summary of the observations and conclusions from the soil measurements to mid-2011 is presented below.

Influence of Soil Conditions on CO_2 Flux. Natural soil CO_2 fluxes are an indication of microbiological activity in the soil, responsible for mineralization of organic matter. Microbial activity occurs in soil surface layers where organic material, such as leaf litter, accumulates and provides a source of energy for soil microbes. The temperature and moisture content of soil are the most important physical factors affecting decomposition, and can have direct impact on soil CO_2 fluxes. Microbial activity and mineralization generally increase with temperature, the activity doubling with each 10 ^oC rise in temperature over the range from 5 to 35 ^oC. Also, decomposition rates usually increase with water potential over the range from about -5 to about -0.05 MPa. However, the effects of moisture on gas fluxes are confounded with those of temperature and other soil biological and physical properties. For example, soil CO_2 can be low due to reduced oxygen diffusion into soil under high soil moisture conditions.

Soil physical and chemical conditions are being monitored to determine their effect on CO_2 fluxes, and to determine if these differences could account for the variation in gas fluxes from well to well. The distributions of ammonium nitrogen and phosphorus in soil versus depth at the sampling locations surrounding the wells, under baseline conditions (prior to CO_2 injection), were presented and discussed in earlier Quarterly Progress Reports (October 30, 2009, pp. 29-30 and January 30, 2010, p. 26).

CO_2 Flux from Forest Soils at Oil Wells in the Test Pattern. The baseline soil CO_2 fluxes around representative wells in the Citronelle Oil Field study area were established before injection of CO_2 for enhanced oil recovery. The importance of the baseline measurements is that forest soil is a source of CO_2 from natural processes such as microbial and root respiration. Therefore, it was important to account for the background CO_2 fluxes prior to injection of CO_2 in order to be able to discriminate natural CO_2 from CO_2 leakage, should it occur. The wells selected for baseline surface CO_2 flux monitoring were producers B-19-7, B-19-8, and B-19-9, plugged and abandoned B-19-10 #1, and injector B-19-10 #2.

CO_2 flux data from soil gas samples collected before, during, and after CO_2 injection are presented in Figure 2.7.3, showing the CO_2 fluxes at different times during the study. Compared to the soil CO_2 fluxes observed in August 2008, before CO_2 injection, the fluxes in August 2010, during CO_2 injection, were lower than expected at Well B-19-7 (2.28 mg CO_2 m^{-2} min^{-1} vs. 0.12 mg CO_2 m^{-2} min^{-1}), at Well B-19-10 #1 (1.29 mg CO_2 m^{-2} min^{-1} vs. -0.05 mg CO_2 m^{-2} min^{-1}), and at Well B-19-10 #2 (0.53 mg CO_2 m^{-2} min^{-1} vs. -0.09 mg CO_2 m^{-2} min^{-1}) as shown in Table 2.7.1. At Well B-19-8, soil CO_2 fluxes during CO_2 injection, in August 2010, were slightly higher than those in August 2008, before CO_2 injection (0.40 mg CO_2 m^{-2} min^{-1} vs. -0.21 mg CO_2 m^{-2} min^{-1}).

Regression analysis for a model relating CO_2 fluxes from soil to environmental soil conditions. The Statistical Analysis System (SAS) Version 9.1.3 software (SAS Institute Inc., Cary, NC) was used to determine the best-fit regression models relating soil CO_2 fluxes to the environmental variables, soil temperature and soil moisture, measured during gas sampling. The statistical criteria used to establish the best model were the Adjusted Coefficient of Determination (adjusted R^2), Mallow's C_p Statistic, and the Mean Square Error. Since the objective was to find the best model and not necessarily to include all the variables in the model, any variable (at linear, quadratic, or higher order) that did not explain significant variation (based on adjusted R^2) was dropped from the model. The best regression models relating soil CO_2 fluxes to soil temperature (T) and soil moisture (M) during gas sampling at each well are given in Table 2.7.2.

The regression models having the highest adjusted R^2 were obtained at Well B-19-7 (R^2 = 0.71) and Well B-19-10 #2 (R^2 = 0.70). This indicates that the environmental variables of soil temperature and moisture measured during gas sampling, as they appear in the model, accounted for at least 70% of the variation in observed soil CO_2 fluxes at these two wells. The regression model with the lowest adjusted R^2 was the one fit to the measurements at Well B-19-8, where soil temperature and soil moisture accounted for only 11% of the variation in observed soil CO_2 fluxes.

Attempts to include properties such as soil chemical composition in the model are complicated by the fact that chemical properties were determined from soil samples, which are collected less frequently than the gas samples, moisture measurements, and temperature measurements. The approach is therefore to find possible associations between these variables and soil CO_2 flux data using correlation analyses, as opposed to establishing their possible roles as predictor variables. Chemical properties such as C and N in the soil profile may play a significant role in explaining some of the remaining variation.

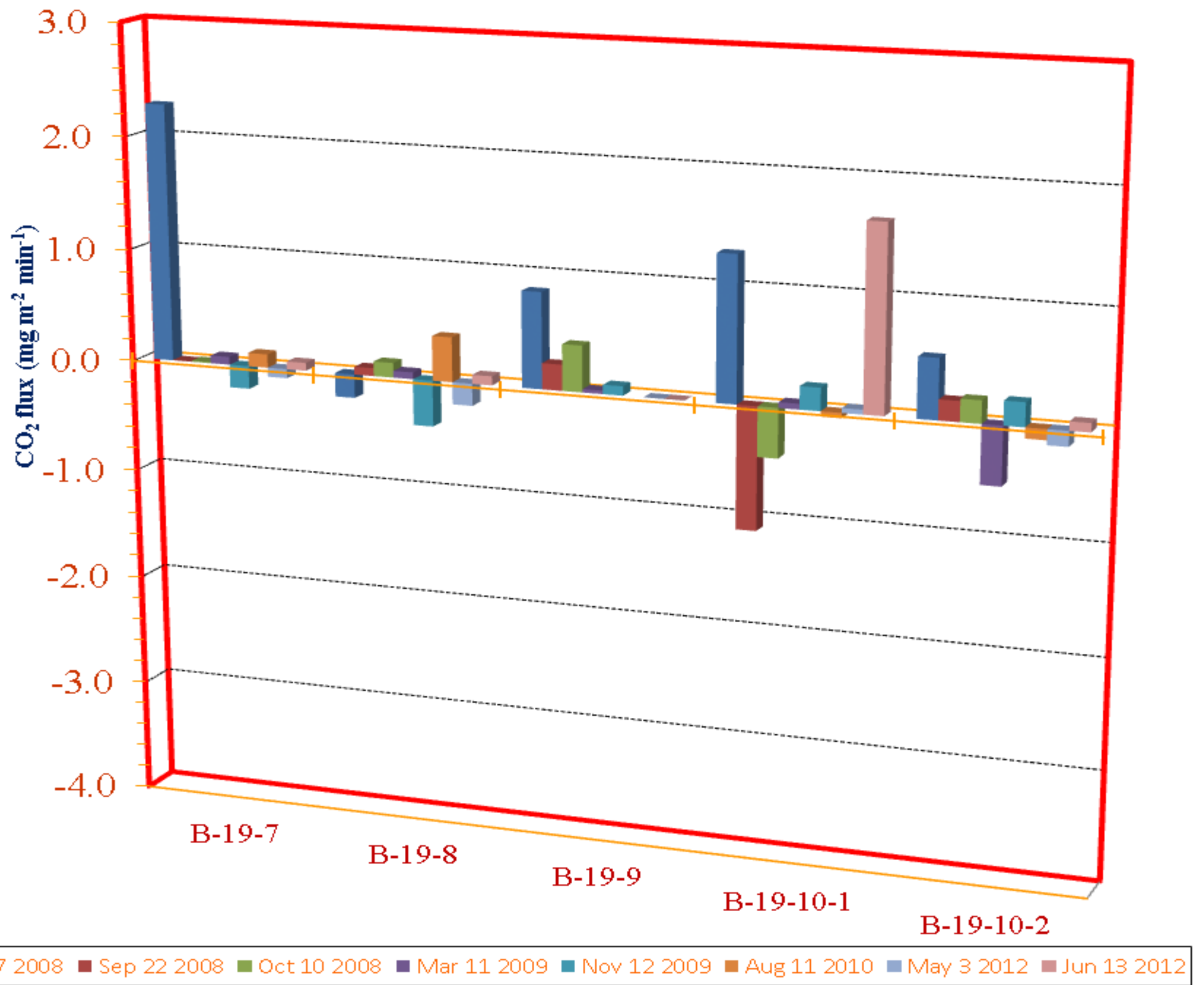


Figure 2.7.3. Measurements of soil surface CO_2 fluxes near five wells in the CO_2-EOR test pattern in the Citronelle Oil Field, August 2008 to June 2012, before, during, and after CO_2 injection.

Table 2.7.1.
Measurements of soil surface CO_2 fluxes near five wells in the CO_2-EOR test pattern in the Citronelle Oil Field, August 2008 and August 2010, before and during CO_2 injection, respectively.

	B-19-7	B-19-8	B-19-9	B-19-10 #1	B-19-10 #2
Sampling date	------------------------- Soil CO_2 flux (mg CO_2 m^{-2} min^{-1}) -------------------------				
08/07/ 2008	2.28	-0.21	0.85	1.29	0.53
08/11/2010	0.12	0.40	-----	-0.05	-0.09

Table 2.7.2.
Regression Models Relating Soil CO_2 Fluxes to Soil temperature (T) and Soil moisture (M) during Gas Sampling at Wells in the Test Pattern at Citronelle.

Well	Regression Model
B-19-7	$CO_2 = 4.3 + 9.0\,T - 0.1\,T^2 + 53.8\,M - 345\,M^2 + 565.3\,M^3$ ($R^2 = 0.71$)
B-19-8	$CO_2 = 15.8 - 2.6\,T + 0.1\,T^2 + 23.0\,M - 143.9\,M^2 + 218.5\,M^3$ ($R^2 = 0.11$)
B-19-9	$CO_2 = 0.9 + 0.01\,T - 10.4\,M + 20.1\,M^2$ ($\mathrm{R}^2 = 0.35$)
B-19-10 #1	$CO_2 = 52.6 - 6.4\,T + 0.3\,T^2 - 222.2\,M + 2039.0\,M^2 - 5488.9\,M^3$ ($R^2 = 0.37$)
B-19-10 #2	$CO_2 = 78.2 + 12.0\,T - 0.6\,T^2 - 16.7\,M + 43.0\,M^2 - 25.5\,M^3$ ($R^2 = 0.70$)

Recent Measurements of Soil CO_2 Flux. The measurements of CO_2 flux from soil continue, with the objective to monitor post-injection CO_2 emissions from soil around the injection and production wells used in the CO_2-enhanced oil recovery pilot test. Recent measurements of soil CO_2 fluxes, on May 3 and June 13, 2012, are included in Figure 2.7.3, for comparison with the earlier measurements before, during, and after CO_2 injection and at different times of the year, from 2008 to 2012. Baseline soil surface CO_2 fluxes around the oil wells were higher in June, with values of 1.64 mg CO_2 m^{-2} min^{-1} at Well B-19-10 #1, 0.08 mg CO_2 m^{-2} min^{-1} at Wells B-19-8 and B-19-10 #2, and 0.07 mg CO_2 m^{-2} min^{-1} at Well B-19-7. In May the fluxes were 0.042 mg CO_2 m^{-2} min^{-1} at Well B-19-10 #1, -0.196 mg CO_2 m^{-2} min^{-1} at Well B-19-8, -0.136 mg CO_2 m^{-2} min^{-1} at Well B-19-10 #2, and -0.081mg CO_2 m^{-2} min^{-1} at Well B-19-7.

As highlighted in the summary of previous work, above, soil surface CO_2 fluxes around the oil wells have typically been significantly lower in the months from September through May. We also see that the soil CO_2 fluxes in May 2012, which averaged -0.09 mg CO_2 m^{-2} min^{-1} were significantly lower than those in June 2012, which averaged 0.47 mg CO_2 m^{-2} min^{-1}. These observations are consistent with those reported earlier, that there are no indications that post-injection soil CO_2 fluxes around the oil wells follow a different pattern compared to pre-injection (baseline) soil CO_2 fluxes. We therefore conclude that the fluctuations or differences in the observed soil CO_2 fluxes are simply due to the natural variability associated with soil gas fluxes, which can be attributed to natural processes such as soil biochemical activity and to variation in soil physical properties such as temperature and moisture content.

Loutrina Staley presented a poster with coauthors Ermson Nyakatawa and Latasha Lyte, entitled, "Potential for Carbon Storage in the Citronelle Oil Field: A Geological Sink in South Alabama," at the 4th North American Carbon Program All-Investigators Meeting in Albuquerque, NM, February 4-7, 2013. The abstract of the paper is reprinted in Section 2.1.2 of this report and may be found on line at <http://www.nacarbon.org/cgi-bin/meeting_2013/mtg2013_ab_search.pl?action=3&ab_id=73>.

2.7.2. Vegetation and Ambient Air Monitoring

Xiongwen Chen and Kathleen A. Roberts
Alabama Agricultural and Mechanical University

Measurements of CO_2 and other Species in Ambient Air. Xiongwen Chen and Kathleen Roberts measured CO_2, O_2, CH_4, SO_2, H_2S, and aerosol in ambient air at least once every quarter from September 2007 to June 2012 at 104 sampling locations in the Oil Field and City of Citronelle. The measurements for a given month or quarter were made at all of the sampling points over two consecutive days; one day in the City of Citronelle and the other in the Oil Field. The large number of sampling points enabled the investigators to construct contour plots showing the distribution of species concentrations across the region.

The last measurements of CO_2 in ambient air at the 104 measurement locations were made on June 28-29, 2012. The average of the measurements is shown in Figure 2.7.4, along with the earlier observations. The average CO_2 in ambient air at Citronelle on June 28-29 was 378 ± 17 ppmv, lower than the regional value expected from the NASA satellite-based Atmospheric Infrared Sounder <http://airs.jpl.nasa.gov/> during June, based on the recent trend shown in Figure 2.7.5. The data shown in Figure 2.7.5 are the area-averaged time series for the CO_2 volume fraction in the region 88-89^o West and 31-32^o North, including the City of Citronelle and the Citronelle Oil Field. The measurements are integrated over the column of atmosphere from Earth's surface to the NASA satellite in low Earth orbit. Similarities in the seasonal changes in CO_2 are visible in the NASA measurements and the measurements at ground level, in Figure 2.7.4. The recent (2012) world-wide annual average volume fraction of CO_2 is 392.55 ± 0.10 ppmv (Ed Dlugokencky and Pieter Tans, NOAA/ESRL <www.esrl.noaa.gov/gmd/ccgg/trends/>), increasing at the rate of approximately 2 ppmv/year.

Contour plots, in Figure 2.7.6, show the spatial distribution of CO_2 across the region in June 2008 (Figure 2.7.6a), June 2009 (Figure 2.7.6b), June 2010 (Figure 2.7.6c), May 2011 (Figure 2.7.6d), and June 2012 (Figure 2.7.6e). No correlation with the location or timing of the CO_2 injection can be discerned from the CO_2 contours. The spatial distributions of average CO_2 volume fractions before and after breakthrough of CO_2 at Well B-19-11 in May 2010, and the change in CO_2 volume fraction after breakthrough, are shown in Figure 2.7.7.

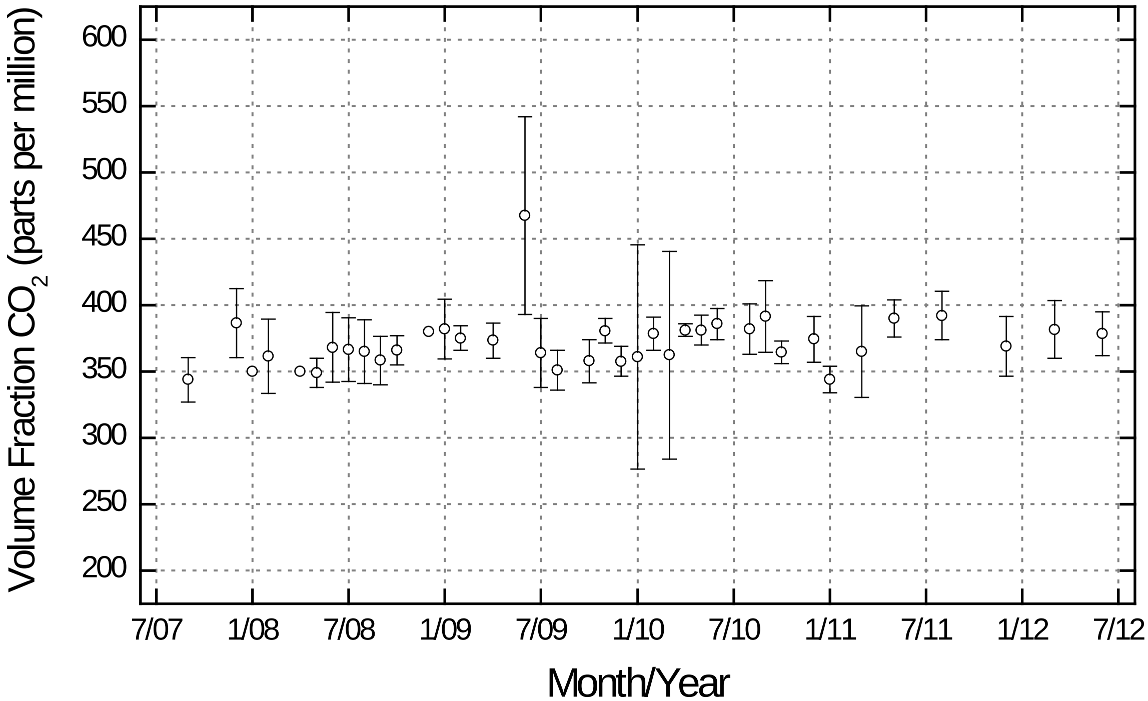


Figure 2.7.4. Average atmospheric CO_2 volume fraction (parts per million) at ground elevation across the City of Citronelle and Citronelle Oil Field from September 2007 to June 2012.

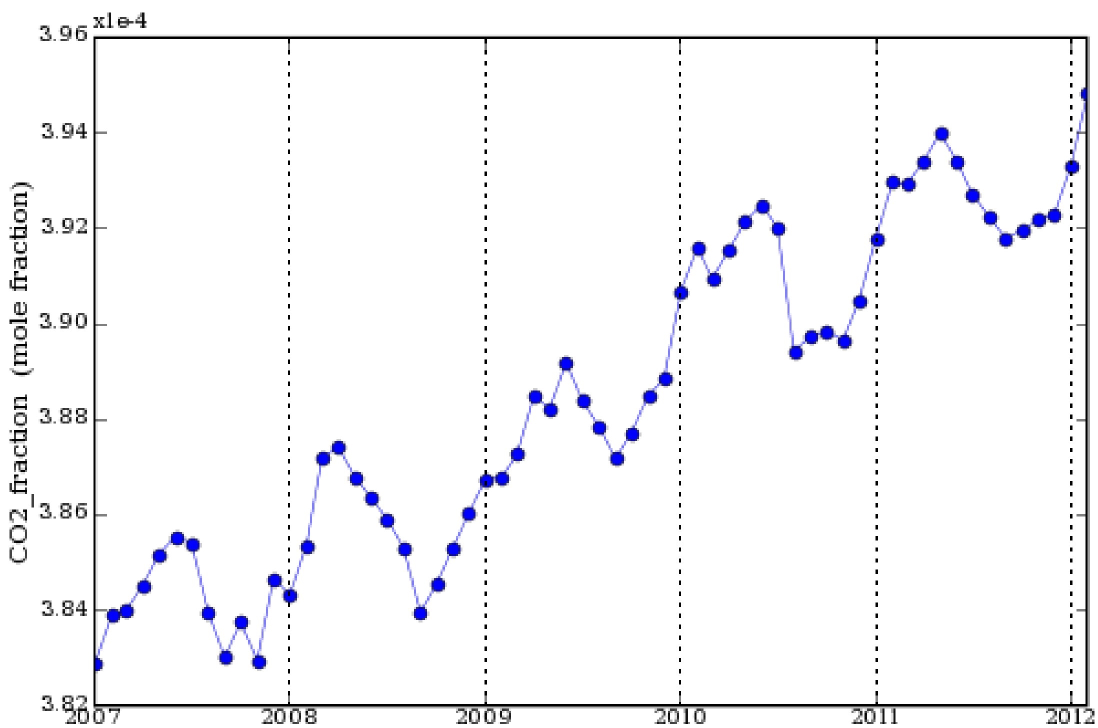


Figure 2.7.5. Area-averaged time series (AIRX3C2M.005) in the region 88-89^o West and 31-32^o North, including the City of Citronelle and the Citronelle Oil Field. Data from the NASA Atmospheric Infrared Sounder <http://airs.jpl.nasa.gov/>. Multiply the mole fraction values on the y-axis by 100 to convert to mole or volume parts per million.

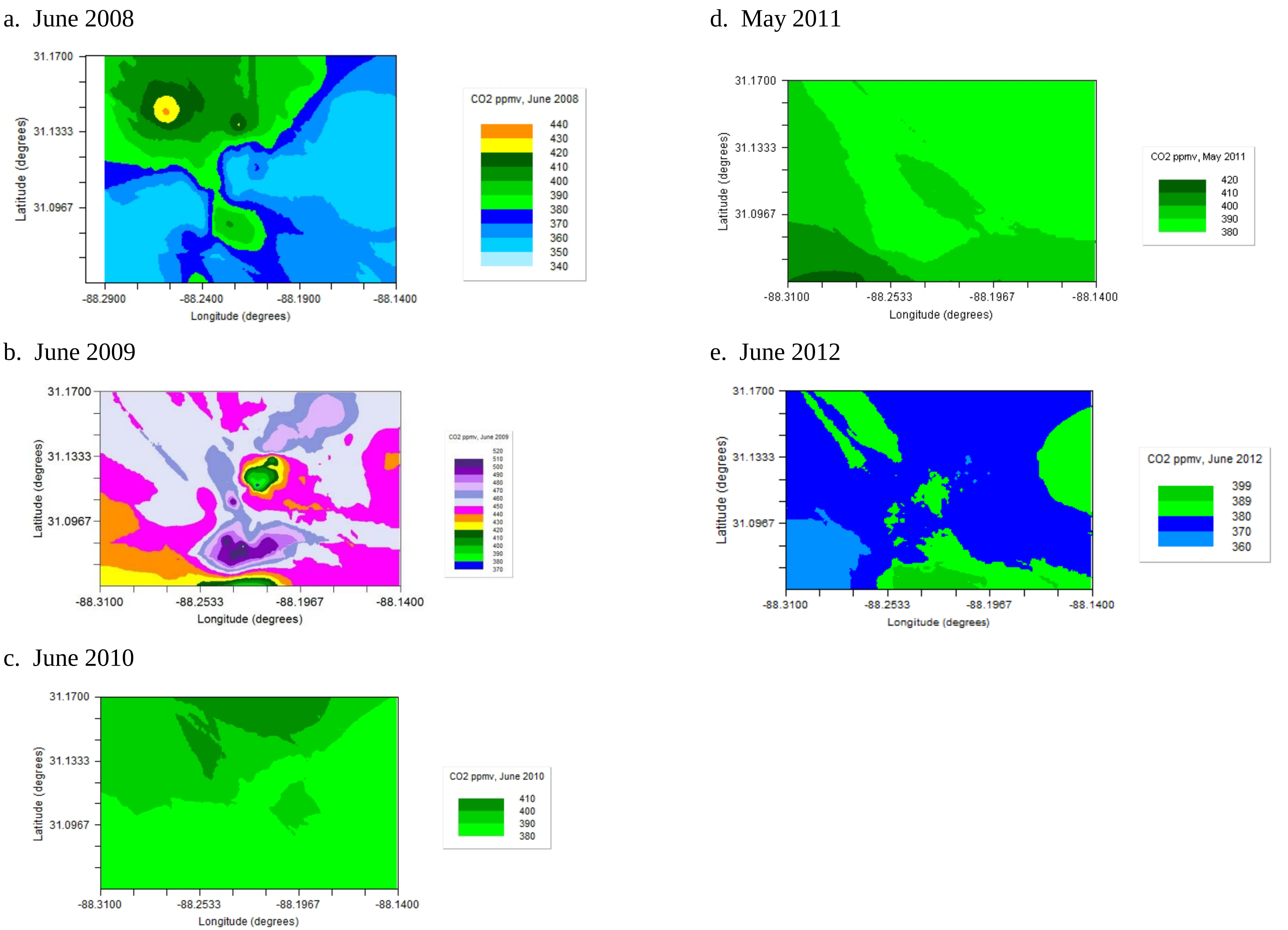


Figure 2.7.6. Contour plots showing the spatial distribution of the CO_2 volume fraction across the City of Citronelle and Citronelle Oil Field in June 2008, June 2009, June 2010, May 2011, and June 2012.

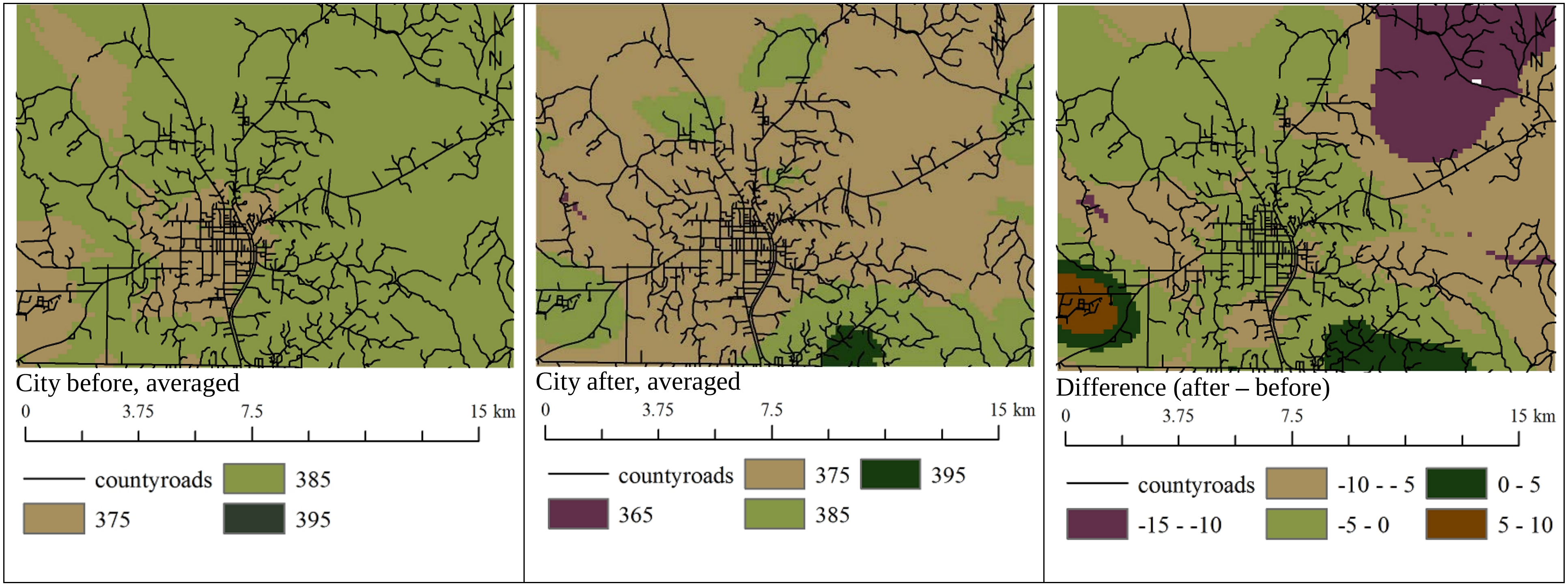


Figure 2.7.7. Spatial distributions of the average CO_2 volume fraction before (figure at left) and after (figure at center) breakthrough of CO_2 at Well B-19-11 in May 2010, and the change in CO_2 volume fraction after breakthrough (figure at right). The globally-averaged marine surface annual mean CO_2 increased from 380.93 ± 0.10 ppmv in 2006 to 390.48 ± 0.10 ppmv in 2011 (Ed Dlugokencky and Pieter Tans, NOAA/ESRL <www.esrl.noaa.gov/gmd/ccgg/trends/>). In the legends of the two figures to the left, "375" indicates CO_2 volume fractions in the range from 370 to 380 ppmv, "385" indicates CO_2 volume fractions in the range from 380 to 390 ppmv, and "395" indicates CO_2 volume fractions in the range from 390 to 400 ppmv.

Growth of Vegetation. Xiongwen Chen and Kathleen Roberts of AAMU also established 10 m x 10 m test plots near the injector, producers, and tank batteries, in which to monitor plant species distribution and growth. Field inventories of the vegetation plots were conducted in 2008, 2009, 2010, and 2011. Due to harvesting of timber in a few of the plots by land owners, some of the original plots are no longer available. The growth of woody plants in the remaining plots during the three time intervals, 2008-2009, 2009-2010, and 2010-2011 is shown in Figure 2.7.8. A key to the locations and functions of the plots is provided in Table 2.7.3. Four new vegetation plots near a golf course (GC1, GC2, GC3, and GC4) were added as controls in 2009 after the original control plots were destroyed by a change in land use at the wildlife management area where they were located. The most recent measurements were made on September 6-8, 2011.

Comparison of the 2008-2009 growth rates with those in 2009-2010 shows that the plant growth rate increased from the first period to the second in two plots and decreased in five of them. Comparison of the 2009-2010 growth rates with those in 2010-2011 shows that the plant growth rate increased from the second period to the third in three plots and decreased in five of them. The overall trend is one of decreasing growth rates, rather than the increase in rates that might be expected under the influence of elevated levels of CO_2.

One plot, VP1, on the far left in Figure 2.7.8, does exhibit a significant and consistent increase in the rate of growth of vegetation during the four-year period. As shown in Table 2.7.3, Plot VP1 is located near the injector, Well B-19-10 #2. This is an interesting observation, in view of the fact that elevated levels of CO_2 in ambient air were not consistently detected there, nor were elevated CO_2 fluxes from soil near that well reported by Ermson Nyakatawa and Latasha Lyte (Section 2.7.1). We leave open the possibility that vegetation near Well B-19-10 #2 may have been influenced by CO_2 from the pilot test, and will continue to monitor CO_2 in ambient air and the growth of vegetation at this location and at all of the other observation points. With the exception of vegetation near Well B-19-10 #2, the differences in growth rate from place-to-place and year-to-year are more likely explained by patterns of rainfall, temperature, and solar insolation than by CO_2 plumes associated with the CO_2 storage tank, injection equipment, wells, or tank batteries.

Xiongwen Chen and Kathleen Roberts are also examining an alternative method for assessment of the growth of vegetation, from changes in the normalized difference vegetation index (NDVI) for each land use category (e.g. deciduous forest, evergreen forest, mixed forest, grassland, pasture, woody wetlands, and emergent herbaceous vegetation), extracted from satellite images of the injection area, oil field, and surrounding area, available from USGS <http://glovis.usgs.gov/>. Kathleen Roberts presented a paper describing this work, with coauthor Xiongwen Chen, at the 97th Annual Meeting of the Ecological Society of America in Portland, OR, August 5-10, entitled, "Direct and indirect assessment of vegetation located near CO_2-mediated enhanced oil recovery (CO_2-EOR) activities." The paper includes analysis of data from two sources: (1) direct measurement of the growth rates of woody plants in test plots established near the inverted five-spot well pattern and control plots in the golf course to the west of the City of Citronelle, and (2) indirect measurement, from changes in the normalized difference vegetation index (NDVI) for each land use category, extracted from the satellite images available from USGS. The abstract of the paper follows <http://eco.confex.com/eco/2012/webprogram/Paper38361.html>:

> This study examined the potential of vegetation monitoring to determine if there are local ecological effects of CO_2 mediated Enhanced Oil Recovery (CO_2-EOR). Injection of CO_2 into geological reservoirs containing crude reduces the viscosity and

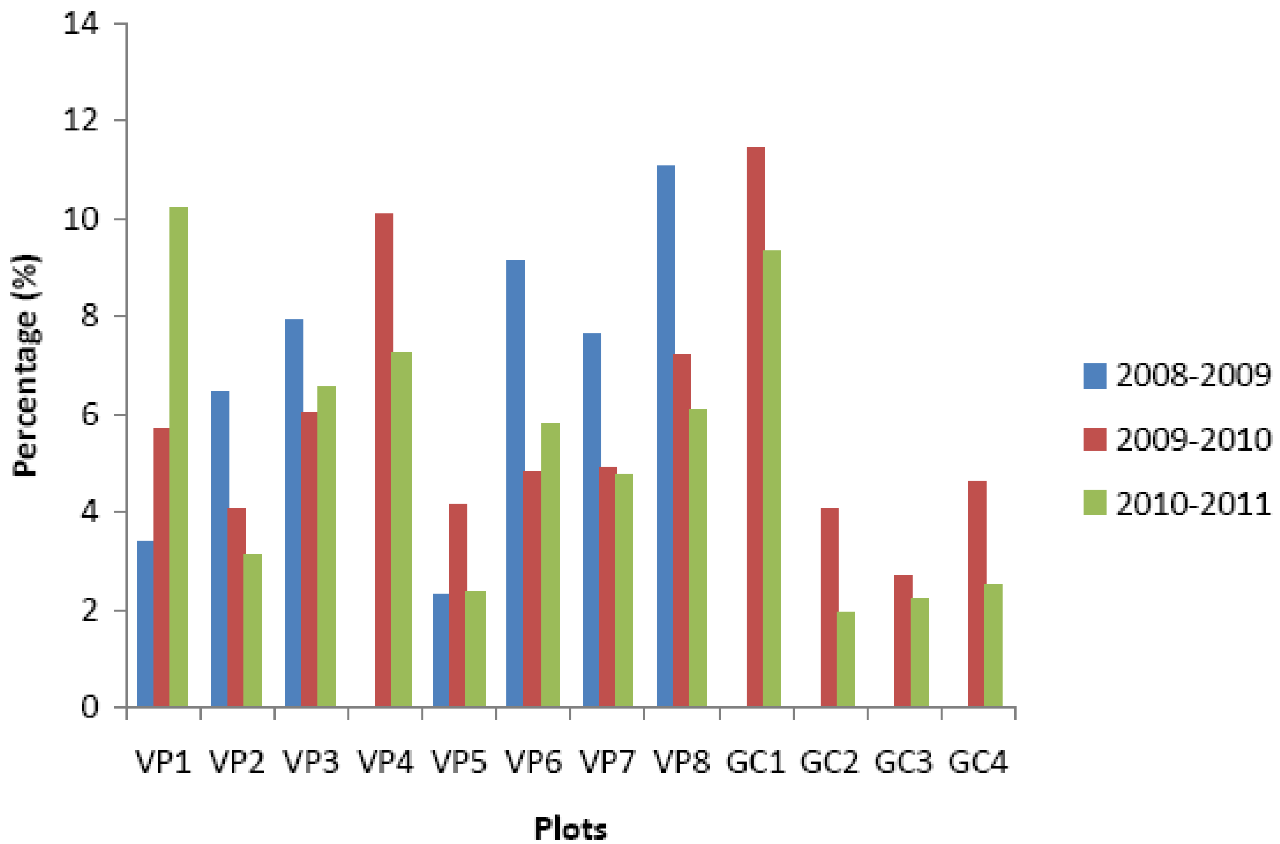


Figure 2.7.8. Comparison of growth, as the fractional (%) increase in basal area, in vegetation plots across Citronelle during the three periods, 2008-2009, 2009-2010, and 2010-2011. The locations of the plots are specified in Table 2.7.3.

Table 2.7.3. Locations and Descriptions of the 10 m x 10 m Vegetation Plots.

Vegetation Plot	Location	Description
VP1	Well B-19-10 #2	Injection well
VP2	Well B-19-7	Production well
VP3	Well B-19-8	Production well
VP4	Well B-19-9	Production well
VP5	Well B-19-10 #1	Plugged and abandoned well
VP6	B-19-8 Tank Battery	Tank battery
VP7	Well B-19-11	Production well
VP8	B-19-11 Tank Battery	Tank battery
GC1	Citronelle Golf Course	Control
GC2	Citronelle Golf Course	Control
GC3	Citronelle Golf Course	Control
GC4	Citronelle Golf Course	Control

allows for the movement and recovery of crude that was previously cost prohibitive using other methods. CO_2 injection into geological reservoirs may also serve as a means to reduce atmospheric CO_2 through geological sequestration. However, monitoring and verification is essential to ensure that geological sequestration is effective and without negative effects to the surrounding environment. Monitoring of vegetation was accomplished using small scale, direct measurement, as well larger scale indirect measurements to determine whether CO_2-EOR activities impact surrounding vegetation. The direct, small scale component was accomplished by examining the basal area increase in plots located adjacent to oil field structures as well as control plots outside of the oilfield, before and after CO_2 breakthrough. Indirect larger scale measurements were used to look for stress in vegetation adjacent to the injection area as well as the larger oilfield area and areas just beyond. Normalized Difference Vegetation Index (NDVI) values for hardwoods, evergreen and mixed forest were determined by Land Use Land Cover (LULC) 2006 classification.

Results of a before after control impact paired (BACIP) analysis of the basal area of plots indicate that there is no statistical significance between control and impact areas between all basal area, hardwoods, conifers and size for all plots after reported breakthrough. Some plots experienced high increase in percent growth. Two plots with a greater increase were subjected in part to logging activity and the growth may be attributed to an increase in available sunlight. This does not suggest influence of CO_2 on growth; however, it does suggest that additional observation and study are needed to separate influences of logging activity and potential CO_2 influence. Small differences in NDVI values are observed in both deciduous and mixed forest but these differences appear to be similar with respect to season. There were no differences observed in NDVI of evergreen forests. Overall, detrimental impacts on vegetation surrounding an EOR-CO_2 project were not observed at the scales of observation used in this study.

A paper by Xiongwen Chen, entitled, "Distribution patterns of invasive alien species in Alabama, USA," was published in *Management of Biological Invasions*, **2012**, *3*(1), 25-36 <http://www.reabic.net/journals/mbi/2012/1/MBI_2012_1_Chen.pdf>, an open access, peer-reviewed, online journal.

2.8. Seismic Measurements

2.8.1. Geophysical Testing at Citronelle

Shen-En Chen, Yangguang Liu, and Peng Wang
University of North Carolina at Charlotte

Geophysical testing, using the passive Refraction Microtremor (ReMi) technique, is being conducted to compare the seismic properties of the oil field before, during, and after CO_2 injection. The measurements are made at well sites along lines running from North to South and from Northeast to Southwest, to the South and Southwest of the injection well, as shown in Figure 2.8.1. The sensors are placed at 24 locations on each line, at the sites of the wells listed in Table 2.8.1. Line 1 covers a 30,100-ft span with 1,309 ft typical sensor spacing, while Line 2 covers a 25,600-ft span with 1,113 ft typical sensor spacing. The injection well is located near the intersection of the two lines, in the northeast corner of the Field.

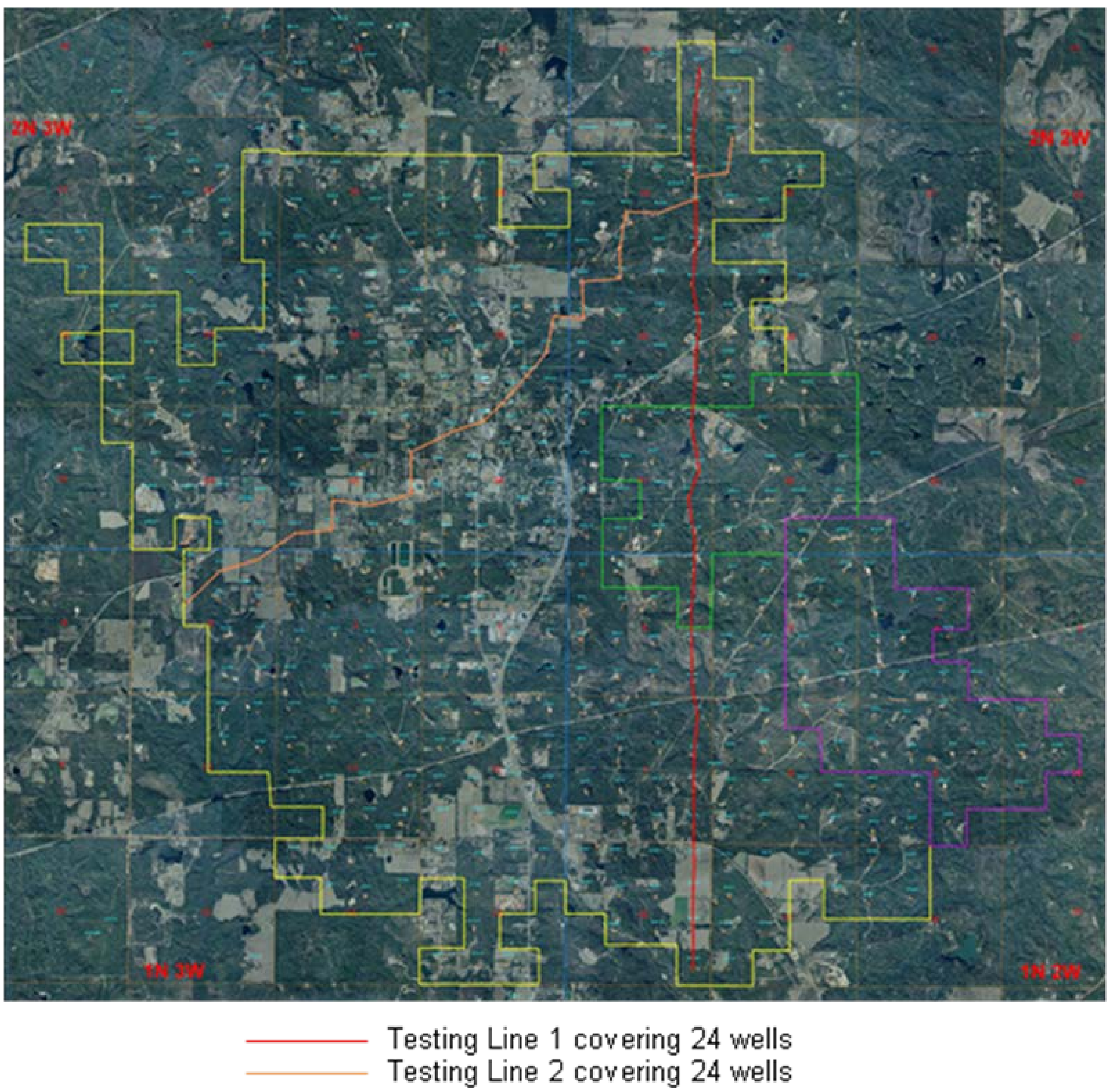


Figure 2.8.1. The seismic testing lines, superimposed on the aerial photo of Citronelle Field from Denbury Onshore.

Baseline data, prior to CO_2 injection, were collected during visits to the test site in October 2008, January 2009, and May 2009. An analysis of those data was presented in an earlier Quarterly Progress Report (October 30, 2009). Measurements coinciding with the start of significant CO_2 injection were made on December 9-10, 2009; then during steady CO_2 injection on March 11-12, 2010, and September 8-9, 2010. Measurements after returning to water injection were made on November 17-18, 2010, March 16-17, 2011, and May 17-18, 2011.

Table 2.8.1. Wireless Sensor Testing Locations.

Line 1	Well #	Line 2	Well #
1	B-18-9	1	B-20-4
2	B-18-16	2	B-20-5
3	B-19-1	3	B-19-8
4	B-19-8	4	B-19-9
5	B-19-9	5	B-19-10 #1
6	B-19-16	6	B-19-11
7	B-29-4	7	B-19-14
8	B-30-8	8	B-30-3
9	B-30-9	9	B-30-4
10	B-30-16	10	B-30-5
11	B-31-1	11	A-25-8
12	B-31-8 #1	12	A-25-9
13	B-31-9	13	A-25-15 #1
14	B-31-16	14	A-36-3
15	D-6-1 #1	15	A-36-4
16	D-6-8	16	A-35-8
17	D-6-9	17	A-35-9
18	D-6-16	18	A-35-10#2
19	D-7-1	19	A-35-11
20	D-7-8	20	A-35-14
21	D-7-9	21	A-35-13
22	D-7-16	22	C-2-4
23	D-18-1	23	C-3-1
24	D-18-8	24	C-3-7

The micro-seismic data from the 24 measurement locations in each of the two sensor lines are placed in seven groups: Channel 1 to Channel 18 as Group 1, Channel 2 to Channel 19 as Group 2, Channel 3 to Channel 20 as Group 3, Channel 4 to Channel 21 as Group 4, Channel 5 to

Channel 22 as Group 5, Channel 6 to Channel 23 as Group 6, and Channel 7 to Channel 24 as Group 7. A two-dimensional shear-wave velocity profile for each sensor line is then constructed by combining the profiles obtained from the seven groups of data. The shear-wave velocity versus depth data from the seven groups for each line of sensors are then averaged to obtain the shear-wave velocity profile versus depth for that line. Analyses of the tests conducted on May 17-18, 2011, were presented in a previous Quarterly Progress Report (July 30, 2011, pp. 29-31).

An analysis of all the passive seismic measurements to date was presented by Yangguang Liu, Research Assistant in Shen-En Chen's research group at the University of North Carolina at Charlotte, in his Master's Thesis, entitled, "DoReMi – A Passive Geophysical Technique and Development of Bilinear Model for CO_2 Injection" (Liu, 2012). The thesis presents the theory of the DoReMi passive geophysical monitoring technique and reports the Group's observations of changes in shear-wave velocity during the pilot CO_2 injection in the inverted five-spot test pattern at Citronelle. One of the key contributions of Yangguang Liu's work is the use of a bi-linear model to describe the geo-static pressure distribution, before, during, and after injection of CO_2, summarized in Table 2.8.2.

Table 2.8.2. Summary of Linear Equations and R-Squared Values for the Ten Tests.

Test No.	Injection	Line1-Top	Line1-Bottom	Line2-Top	Line2-Bottom
1	Water	y = 0.8423x –1321 R^2 = 0.9173	y = 2.9947x–17318 R^2 = 0.7101	y = 0.9956x–1393 R^2 = 0.9298	y = 2.559x–10718 R^2 = 0.8299
2	Water	y = 0.8619x –770 R^2 = 0.9271	y = 3.3249x–18337 R^2 = 0.774	y = 1.0562x–1765 R^2 = 0.8579	y = 3.505x–19217 R^2 = 0.7555
3	Water	y = 0.919x –1373.9 R^2 = 0.8942	y = 2.1086x–7979 R^2 = 0.7702	y = 0.9327x–1398 R^2 = 0.9066	y = 3.426x–18414 R^2 = 0.7028
4	CO_2	y = 0.6336x –888.5 R^2 = 0.9183	y = 2.8679x–15287 R^2 = 0.8069	y = 0.7069x–1196 R^2 = 0.8829	y = 1.8893x–6689 R^2 = 0.8064
5	CO_2	y = 0.8235x –1131 R^2 = 0.9452	y = 2.3749x–10666 R^2 = 0.8275	y = 0.7606x–833 R^2 = 0.8636	y = 1.415x–2426 R^2 = 0.8325
6	CO_2	y = 0.979x – 1515 R^2 = 0.9252	y = 1.8158x–7328 R^2 = 0.7833	y = 1.0254x–1705 R^2 = 0.91	y = 1.7348x–6294 R^2 = 0.8242
7	CO_2	y = 0.9384x –1377 R^2 = 0.9326	y = 1.9345x –8701 R^2 = 0.8231	y = 1.0957x–1939 R^2 = 0.8367	y = 1.1354x–1171 R^2 = 0.8136
8	Water	y = 0.9696x – 1492 R^2 = 0.9393	y = 1.9233x–8220 R^2 = 0.8239	y = 0.9515x–1369 R^2 = 0.9091	y= 1.6881x–6134 R^2 = 0.8259
9	Water	y = 0.9755x - 1395 R^2 = 0.9339	y = 1.5094x-5065.2 R^2 = 0.7751	y= 0.9975x-1494 R^2 = 0.9052	y= 1.4032x-3910 R^2 = 0.7941
10	Water	y = 0.9656x - 1348 R^2 = 0.9402	y= 1.5672x–5653 R^2 = 0.7913	y= 0.9936x - 1468 R^2 = 0.9243	y= 1.4889x-4864 R^2 = 0.7837

The composite bilinear curves constructed using the average values from each of the three stages of CO_2 injection (before, during, and after injection), and for each of the two sensor lines, indicated that two distinct behaviors can be observed, as shown in Figures 2.8.2 (Sensor Line 1) and 2.8.3 (Sensor Line 2). The gap between the two sets of lines is identified as the Wilcox Group (calcareous clay, > 4000 ft) and Selma Group (chalk, ~ 5000 ft).

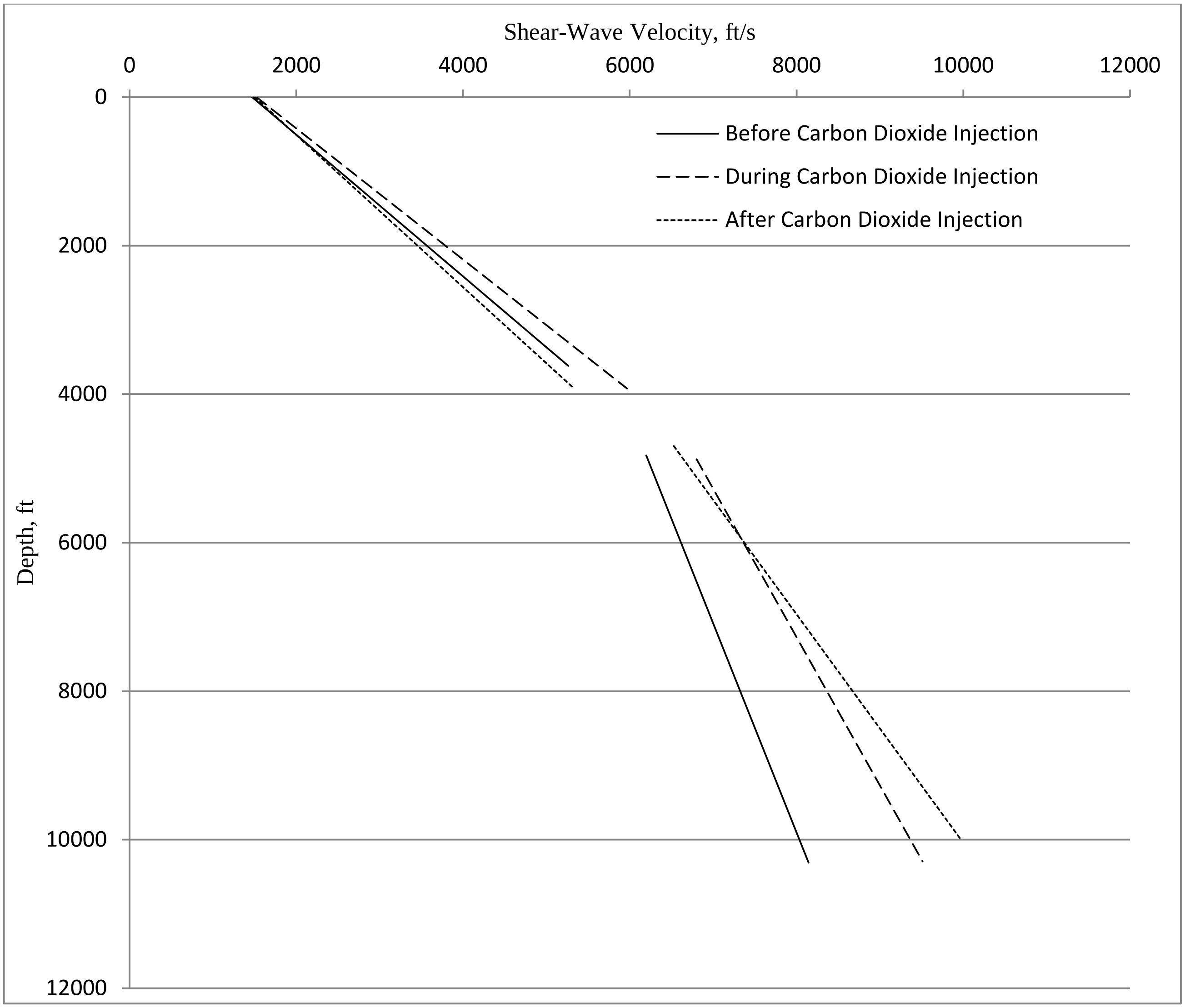


Figure 2.8.2. Bi-linear model of the shear wave velocity profile for Sensor Line 1, for the three stages of the injection process: before, during, and after CO_2 injection.

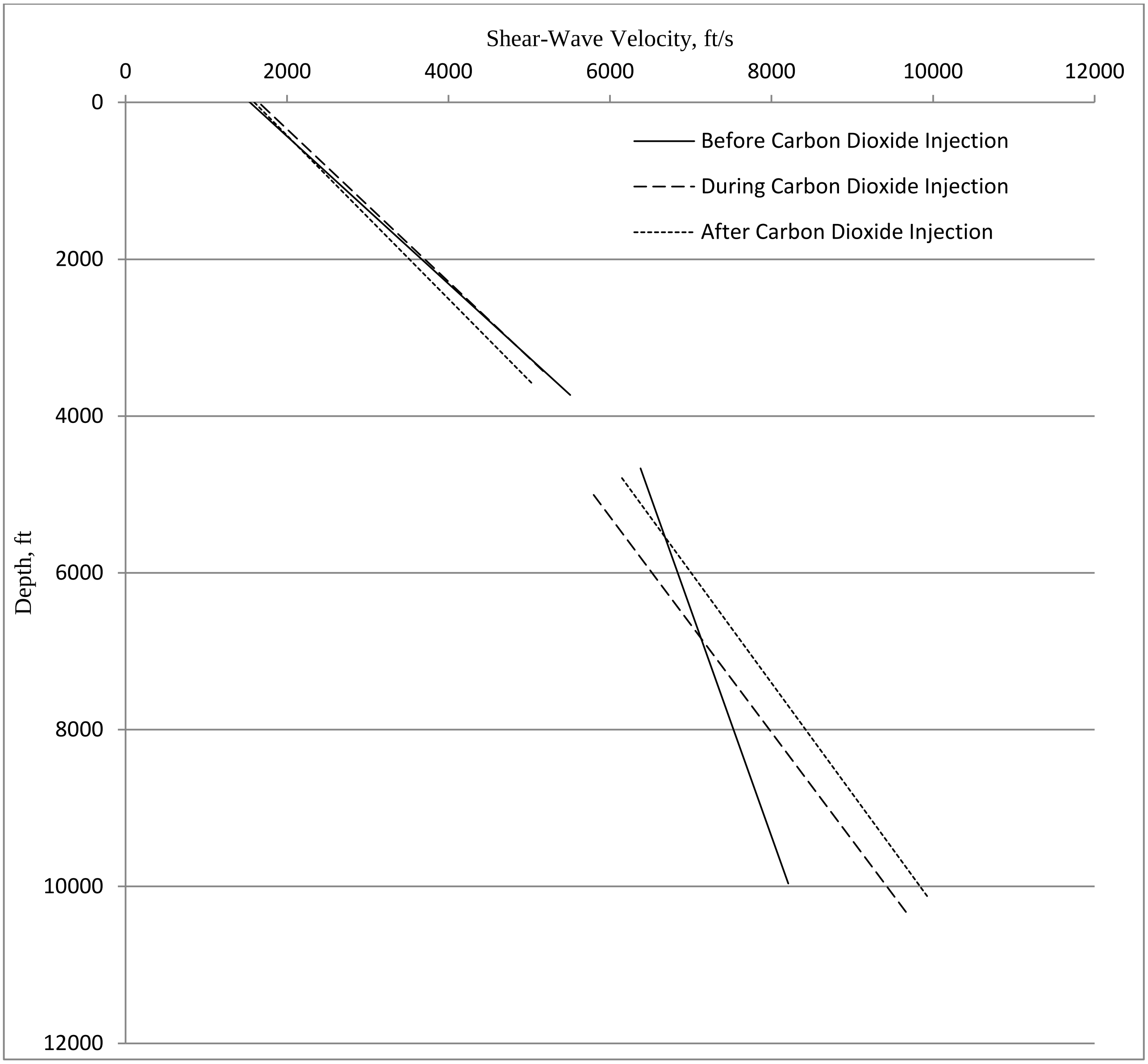


Figure 2.8.3 Bi-linear model of the shear wave velocity profile for Sensor Line 2, for the three stages of the injection process: before, during, and after CO_2 injection.

During the quarter under review, Shen-En Chen and his coworkers at the University of North Carolina at Charlotte completed two manuscripts for publication. The first, entitled, "Evaluation of Lumped-mass Model for Studying Wave Propagation in a Depleted Oil Field," by Yangguang Liu, Shen-En Chen, and Vincent Ogunro, demonstrates the ability of a lumped mass model to interpret measurements using the surface wave monitoring technique developed by Dr. Chen and his coworkers for detection of changes in subsurface wave propagation associated with CO_2 injection. The second paper, entitled, "CO_2 Injection Monitoring at Citronelle Oil Field using Passive Seismic Monitoring," by Yangguang Liu, Shen-En Chen, and Peng Wang, describes the application of the passive microseismic monitoring technique to detect changes in the subsurface static stress distribution during CO_2 injection for enhanced oil recovery.

2.8.2. Simulation of CO_2 Flow through Porous Media

Shen-En Chen, Peng Wang, Benjamin Smith, and Bradford Garrigues, Jr.
University of North Carolina at Charlotte

To understand the effects of porosity and saturation on stress waves, a laboratory experiment was designed to simulate high-porosity rocks saturated with mixed crude oil, water, and CO_2, to determine the effects of the fluid saturations on stiffness and shear-wave velocity. A type of specimen has been developed for the purpose, called a Simulated Carbon Ash Retention Cylinder (SCARC), to simulate rapid CO_2 flow through high-porosity rock. The SCARC specimen is designed to investigate the Biot correlation between wave speed and the change in density of fluid in the pore space, during CO_2 flow. Three experiments were conducted. The first experiment utilized a cylindrical structure of high-porosity material and Fiber Bragg Grating (FBG) sensors to measure the external hoop strain during material expansion. The second experiment involved testing the strength of the high-porosity material. The third experiment focused on CO_2 adsorption within the material.

Experiment 1: Simulated Carbon Ash Retention Cylinder. The "Physical Problem" is the mechanical monitoring of cylindrical specimens filled with variable mixtures and permeated with CO_2. The SCARC model is created through a simple cement casting process to form a cylinder having a hollow center. The casting process necessitates the use of simple materials: two polyvinyl chloride (PVC) tubes having different diameters, to create the inner and outer surfaces of the cylinder; a base plate, to prevent the cement from leaking out from the cylindrical boundaries and to form the base; and a release agent, to prevent the PVC mold from adhering to the final product. A photograph of a cylinder after its initial construction is shown in Figure 2.8.4. The average dimensions of the SCARC are: outer diameter, 15.5 cm; inner diameter, 9 cm; and height, 30 cm.

Figure 2.8.4. Experimental design for fiber optic monitoring of a SCARC specimen.

The FBG sensors are attached to the cylinders and the planar (hoop) strains are evaluated at three locations; the top, middle, and bottom of the specimen. Each location has a distributed sensing fiber with eight FBG regions, equally spaced around the circumference. The fibers continuously monitor the wavelength of the distributed sensors, which is typically in the vicinity of 1,500 nm. The spacing of the sensors provides the wavelength differentials that are transformed into hoop strain values using the following equation,

$$Strain = 0.845 \cdot (f_1 - f_0) \cdot 1000 \quad (1)$$

where f_0 is the initial wavelength and f_1 is the measured wavelength. It is recognized that under perfect construction, testing, and instrumental conditions the sensors should register identical hoop strain values. It is expected that differences in the strain values, among distributed sensors on the same fiber, will provide evidence of local mechanical behavior caused by differences in geometry, load propagation, or material nonuniformity.

Following the formation of the hollow cylindrical specimens and the application of the FBG sensors, mixtures having variable constituent percentages are introduced into the mold. The components of the mixture are fly ash, cement, water, and aluminum powder. The aluminum powder is used to generate large void spaces in the dried specimen. The aluminum reacts with water and slowly expands the mixture, creating large void spaces.

To date, one cylinder test, designated Cylinder #5, has been completed. Cylinder #5 had 24 fully functional FBG sensors in three rings of eight sensors each, set up to record the hoop strain values. The sensor locations around the circumference of the cylinder at the top, middle, and bottom sections are shown in Figure 2.8.5. The SCARC mold was filled with a blend of fly ash, cement, water, and powdered aluminum, at an ash-to-cement ratio of 50% by weight. The interaction of the mixture and its cylindrical containment was studied for 100 hours. The strain behavior for the top, middle, and bottom rings of Cylinder #5 is shown in Figures 2.8.6, 2.8.7, and 2.8.8. Using the FBG sensor measurements, cracking of the concrete cylinder can be traced and the straining of the cylinder in both tension (positive microstrain) and compression (negative microstrain) can be determined.

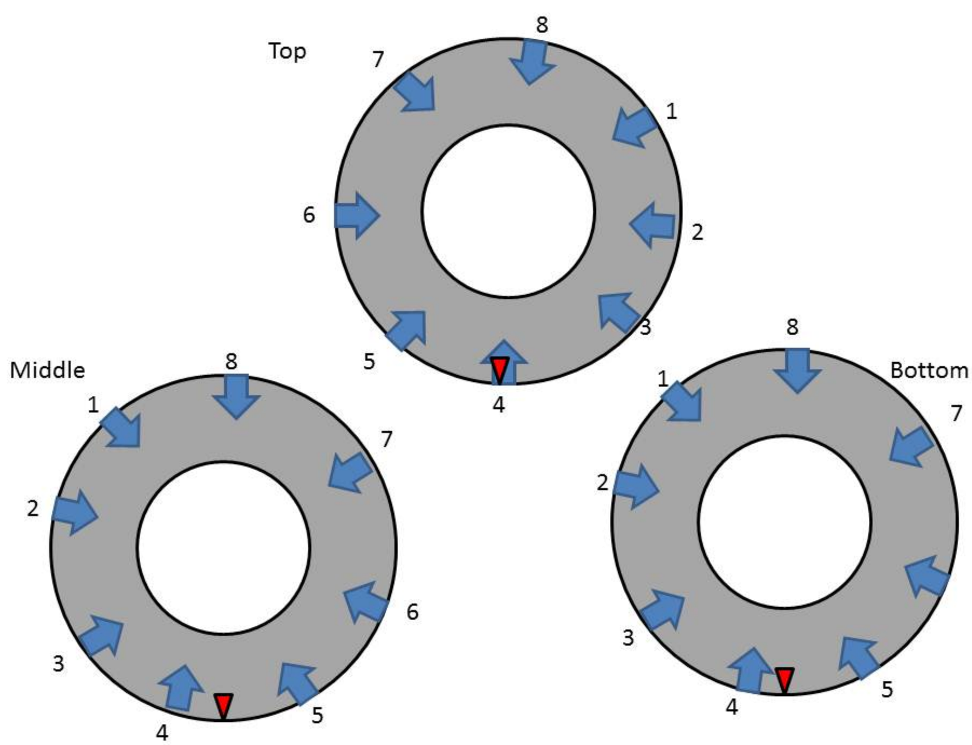


Figure 2.8.5. Cylinder #5 sensor locations.

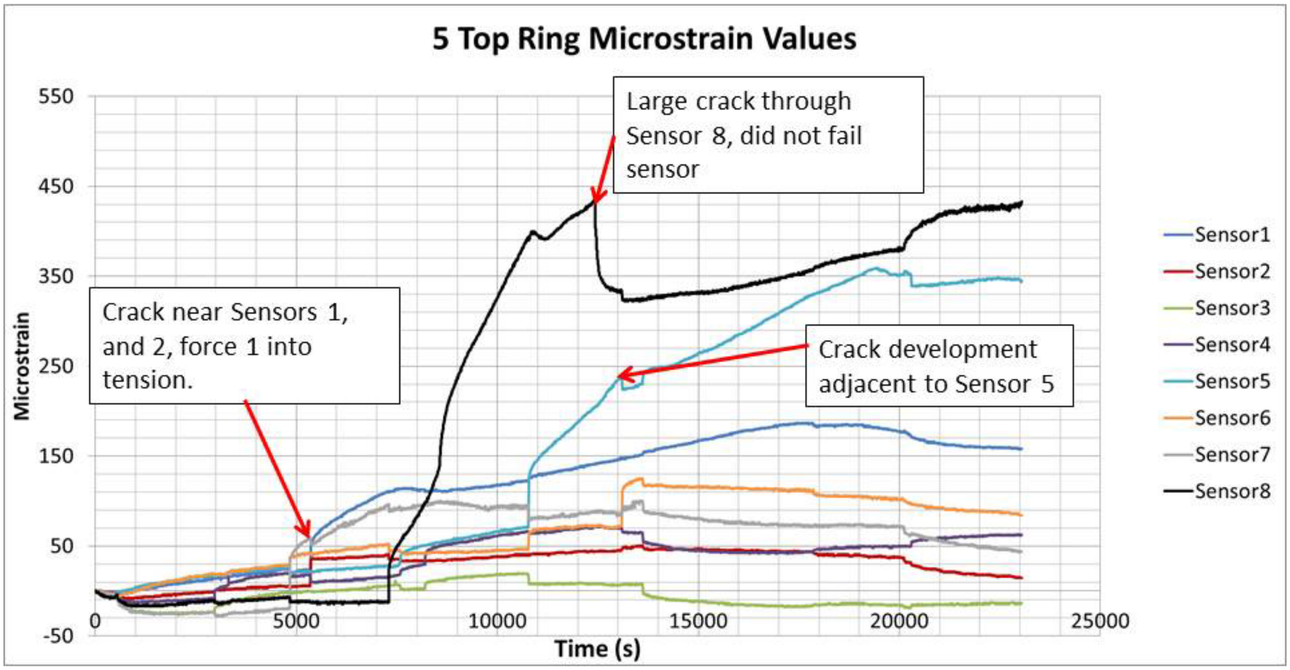


Figure 2.8.6. Cylinder #5 Top Ring FBG sensor responses in microstrain vs. time.

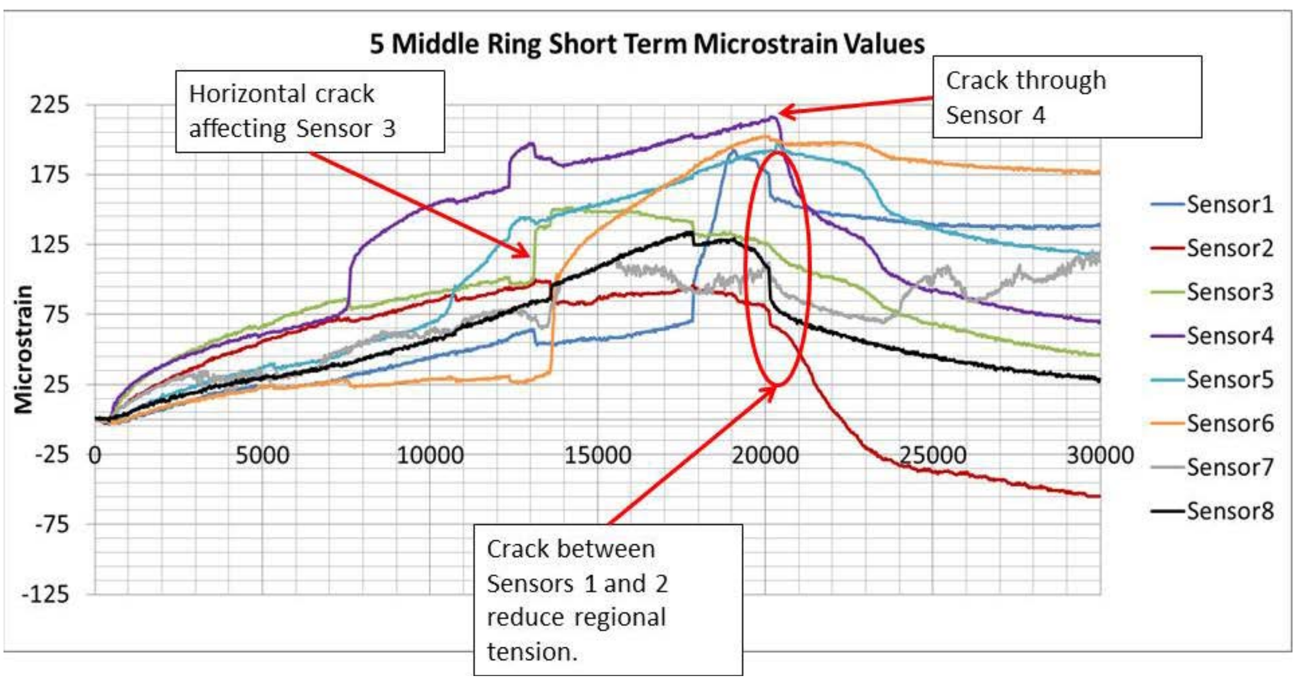


Figure 2.8.7. Cylinder #5 Middle Ring FBG sensor responses in microstrain vs. time.

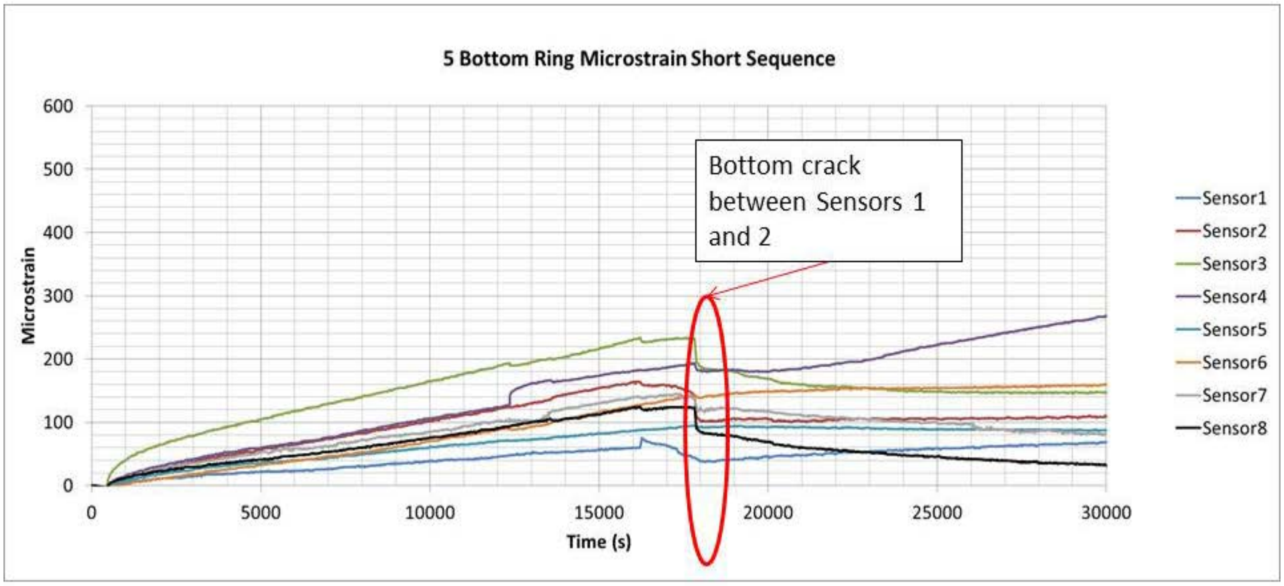


Figure 2.8.8. Cylinder #5 Bottom Ring FBG sensor responses in microstrain vs. time.

Experiment 2: Mixture Experiments. Several mixture proportions by weight, formed inside the hollow cylindrical mold have been studied. For strength testing, 70.7 x 70.7 x 70.7 mm cubic specimens have been cast following ASTM C-109, "Standard Test Methods for Compressive Strength of Hydraulic Cement Mortars." Standard load tests were conducted using a mechanical threshold stress machine. Load test results for the cubic specimens having different mixture compositions are shown in Figure 2.8.9. The results indicate that void formation significantly reduces the strength of the solid. Based on the load test results, a mixture composition is selected for the cylindrical specimen.

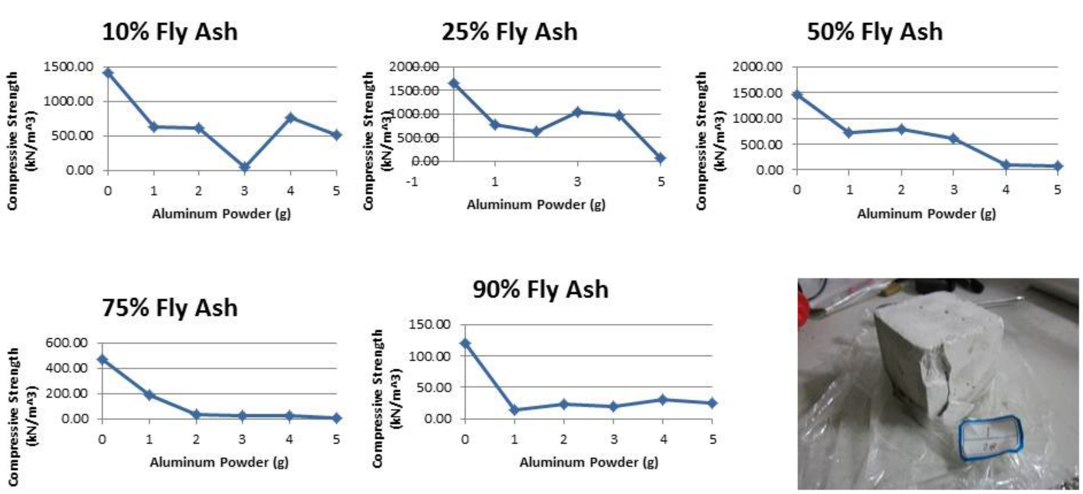


Figure 2.8.9. Strengths of cubic specimens having different compositions.

Experiment 3: CO_2 Adsorption Experiments. The objectives of the adsorption experiment are to:

1. Study the CO_2 adsorption ratios in different types of mixture compositions.
2. Study the relationship between material porosity and degree of physical adsorption.

The experimental set-up includes the reaction cell (Figure 2.8.10a), reference cell (Figure 2.8.10b), high precision pressure sensor (Figure 2.8.10c), and data logger (Figure 2.8.10d). A diagram of the experimental set-up is shown in Figure 2.8.11.

a. b. c. d.

Figure 2.8.10. Instrumentation for the adsorption measurements.
a. Reaction cell.
b. Reference cell.
c. High-precision pressure sensor.
d. Data logger.

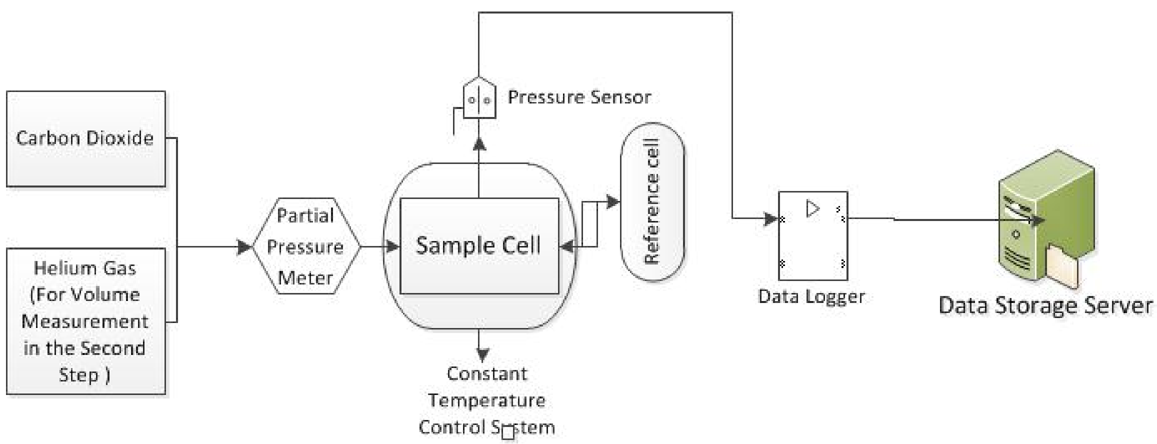


Figure 2.8.11. Diagram of the adsorption experiment.

The different mixture proportions, by weight, placed inside the evacuated sample cell are specified in Table 2.8.3. Seven tests have been completed to date. To increase the void space, different amounts of aluminum power were added to the specimens, creating a significant fraction of void space. The sample compositions, observed pressure drop, and amounts of CO_2 adsorbed are given in Table 2.8.3. The preliminary measurements of adsorption, over 1½ hours, are shown in Figure 2.8.12. The adsorption of CO_2 is measured by the pressure drop and is reported in pressure. The mass of CO_2 adsorbed is computed using the ideal gas law. The experimental results indicate that the adsorption test is able to distinguish physical and chemical adsorption. Further analysis will be done to understand the reaction phenomena.

Table 2.8.3. Sample Composition, Pressure Drop, and Mass of CO_2 Adsorbed.

Sample Composition	Free Gas Volume (mL)	Pressure Drop (MPa)	Mass CO_2 (g)
50%Ash+50%Cement+0gAl	554.1-192.367	0.102	0.63
100%Ash+0%Cement+0gAl	551.1-132.454	0.136	0.81
100%Ash+0%Cement+5gAl	554.1-188.02	0.142	0.89
0%Ash+100%Cement+0gAl	551.1-176.345	0.425	2.73
50%Ash+50%Cement+2gAl	551.1-156.373	0.433	2.94
50%Ash+50%Cement+5gAl	554.1-161.04	0.447	3.01
0%Ash+100%Cement+5gAl	554.1-153.043	0.5	3.46

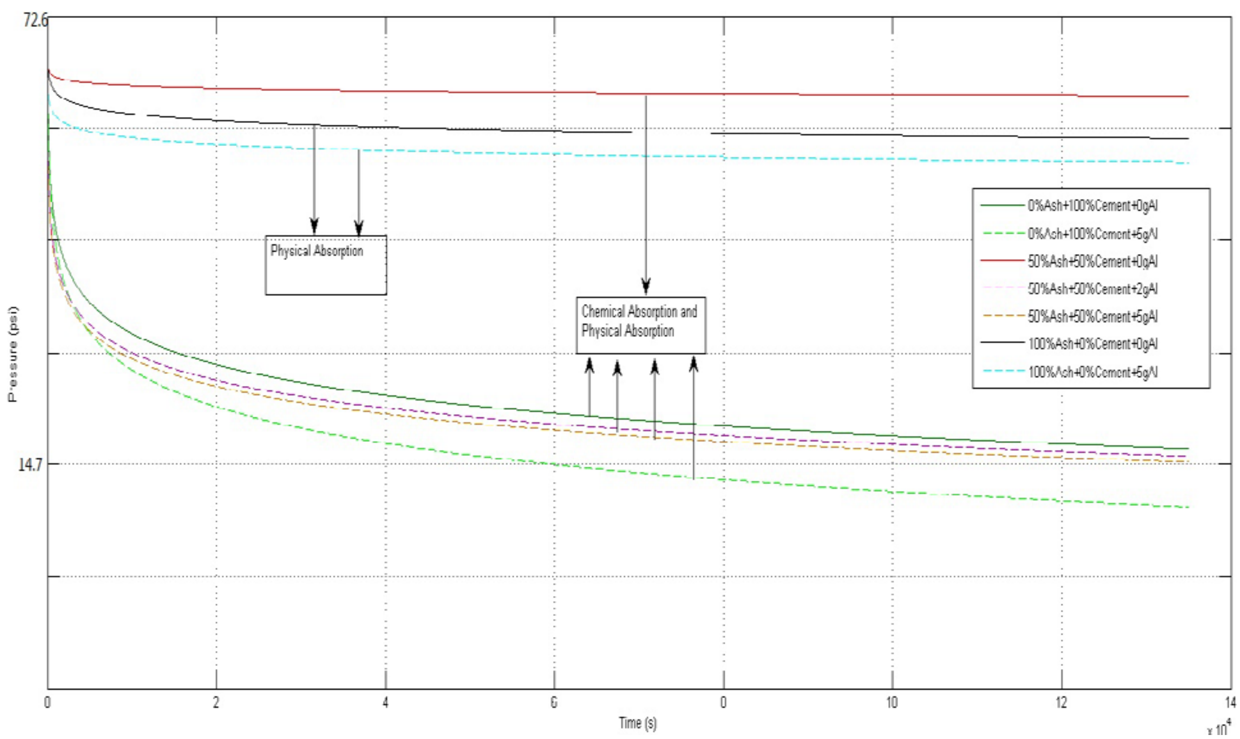


Figure 2.8.12. Observation of pressure drop due to adsorption of CO_2 by the seven samples during 1½ hours.

2.8.3. Simulation of Oil and CO_2 Flow through Porous Media

Shen-En Chen, Peng Wang, and Benjamin Smith
University of North Carolina at Charlotte

During the quarter under review, we assembled two new sensors into our experimental setup and spent most of our effort on debugging the sorption test instrumentation. One test with a specimen of simulated rock (the hardened cement, representing high density soft rock) with an oil sample from the Citronelle Field was completed. Figure 2.8.13 shows the rock sample with a cored depression in the middle, serving as a reservoir for oil. Figure 2.8.14 shows the reservoir filled with oil. The sample was then placed under CO_2 saturation. Figure 2.8.15 shows that the oil was being completely forced into the specimen. Figure 2.8.16 shows the CO_2 pressure (in microvolts) versus time, indicating that a significant amount of CO_2 was being absorbed into the specimen. The next step will be to determine approaches to allowing oil passage through the sample.

Figure 2.8.13. Specimen with cored reservoir.

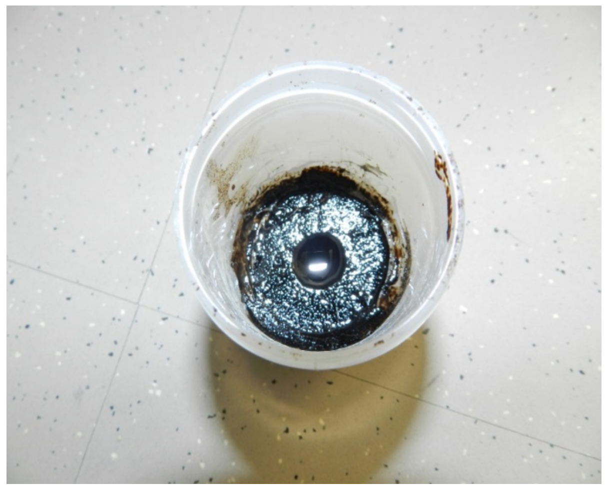


Figure 2.8.14. Reservoir filled with oil.

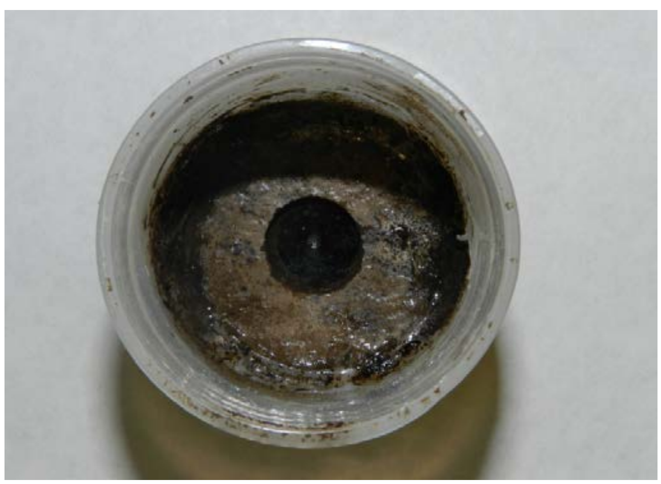


Figure 2.8.15. Oil forced into the rock by CO_2.

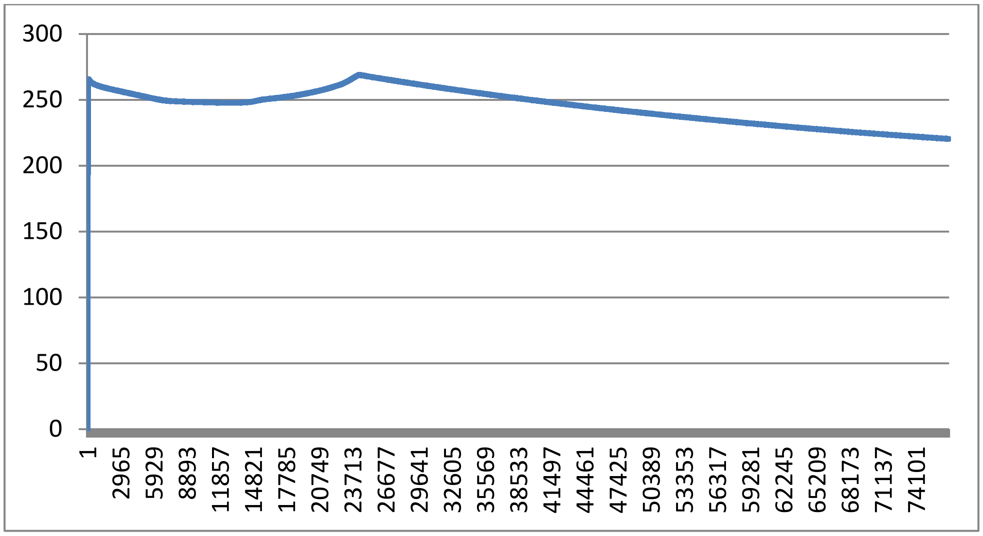


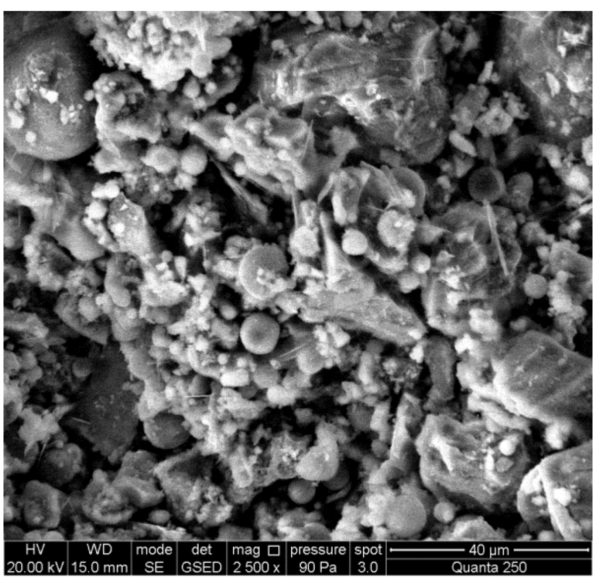
Figure 2.8.16. CO_2 pressure (in microvolts) versus time in seconds for the first oil/rock sample.

2.8.4. Evidence for Carbonation

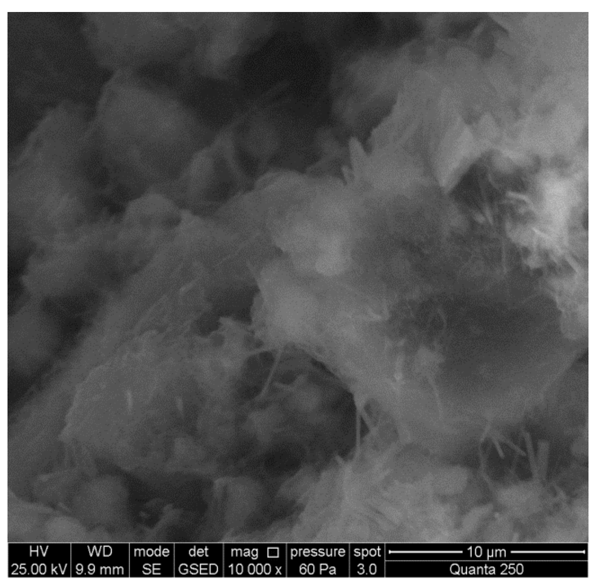
Shen-En Chen, Peng Wang, and Benjamin Smith
University of North Carolina at Charlotte

During the previous quarter, October through December 2012, we sought evidence for carbonation in the laboratory experiments. Carbonation has been identified in previous studies of CO_2 injection in oil fields. The effect is potential blockage of flow paths and reduced EOR. SEM (Scanning Electronic Microscope) and EDS (Energy Dispersive X-ray Spectroscopy) measurements were performed on the samples, providing evidence for carbonation, as shown in the figures below.

Scanning Electron Microscopy

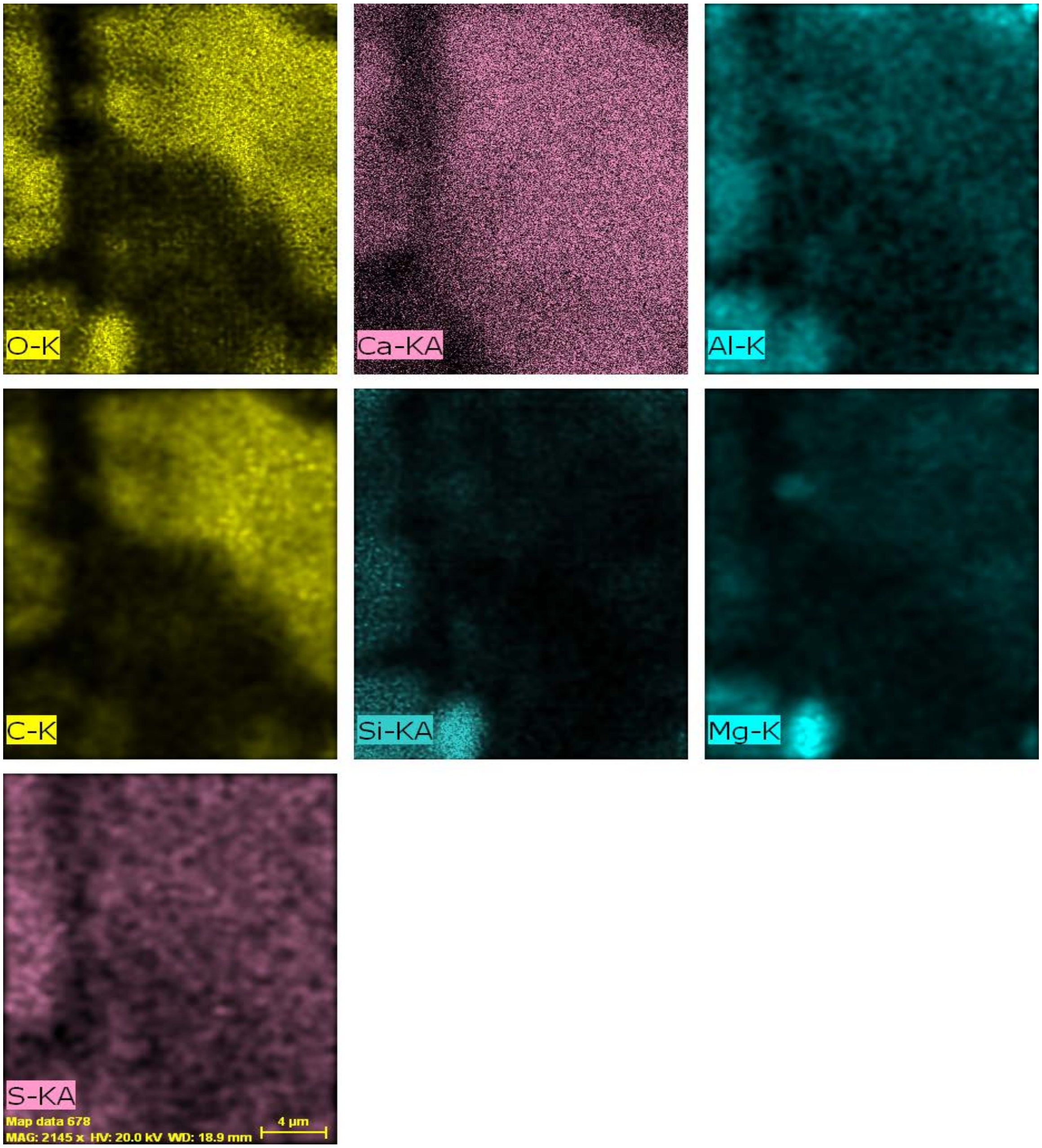


Non-Carbonated Specimen
(90% Cement + 10% Ash)



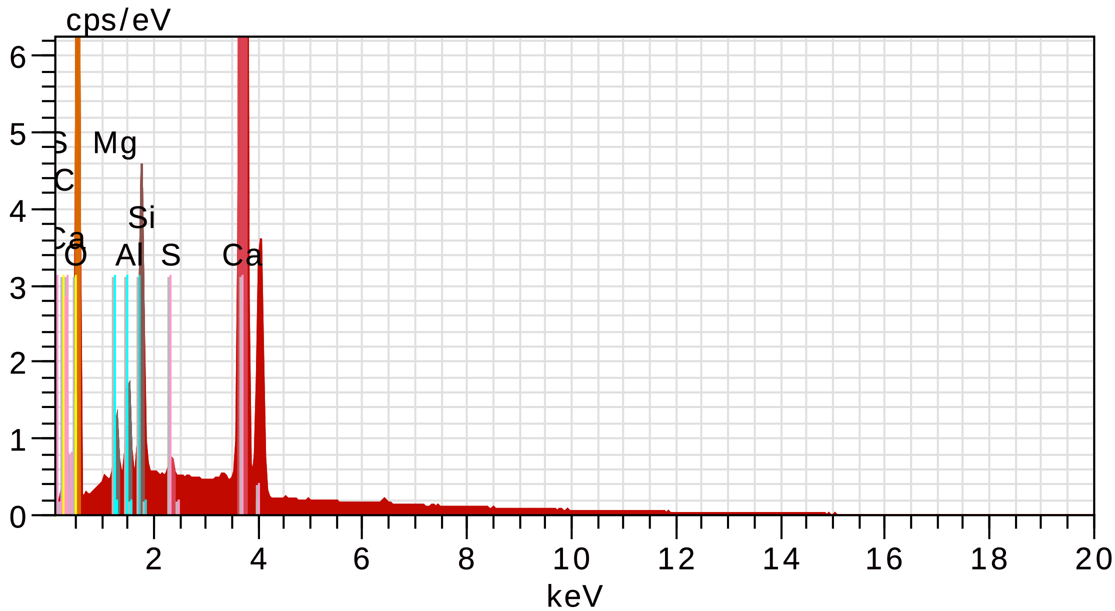
Carbonated Specimen
(90% Cement + 10% Ash)

Figure 2.8.17. SEM images compare the structures of carbonated and non-carbonated specimens.



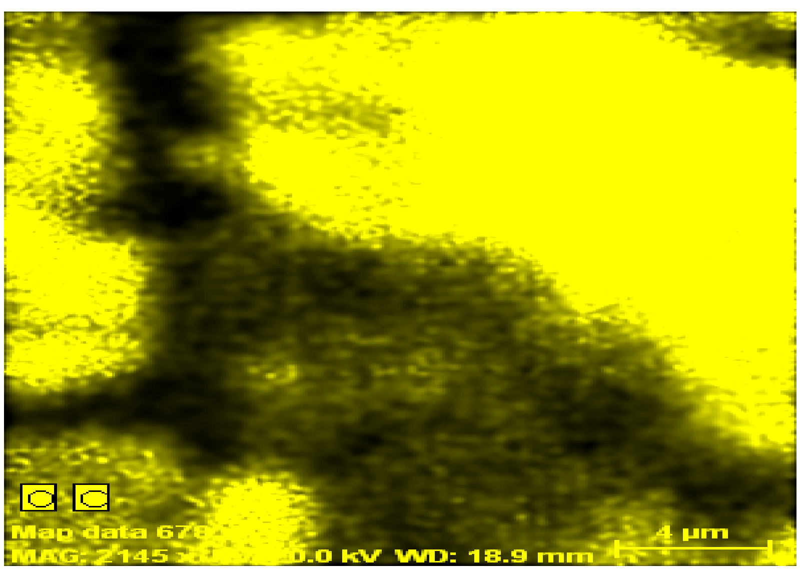
O-K, Ca-KA, Al-K, C-K, Si-KA, Mg-K, S-KA
Date: 12/19/2012 11:45:40 AM
Image size: 300 x 394
Mag: 2144.77211796247x

Figure 2.8.18. The similarity of the oxygen (top row, left) and carbon (middle row, left) element maps provides evidence for the presence of carbonates.



Date: 12/19/2012 11:35:22 AM, HV: 20.0 kV

Figure 2.8.19. The energy spectrum showing strong carbon and oxygen peaks, again suggesting the presence of carbonates.



Map data 678, Date: 12/19/2012 11:35:23 AM
Image size: 300 x 394, Mag: 2144.77211796247x, HV: 20.0 kV

Figure 2.8.20. EDS image of the porous sample with yellow coloring indicating carbon content, interpreted as carbonated material.

2.8.5. Simulation of Wave Propagation

Shen-En Chen, Yangguang Liu, Peng Wang, and Benjamin Smith
University of North Carolina at Charlotte

During the previous quarter the UNCC Group began numerical simulations of wave propagation using Multiple-Degrees of Freedom (MDF) lumped mass models. The modeling is done using Matlab. The oil field is divided into four layers and the entire oil field is modeled as 57 different layers. The vibration source is assumed to be random waves having multiple frequency components, with a forcing amplitude of 675 lb force. The results indicate that waves having frequencies up to 4 Hz can travel to ground surface (Node 1). Figure 2.8.21 shows the wave propagation (from Node 1 to Node 57) and Figure 2.8.22 shows the wave motions in the frequency domain. Due to attenuation by rock, the waves arriving at the surface have a magnitude of ~9 x 10^{-4} ft. The model will be used to quantify the wave effects through the geo-media.

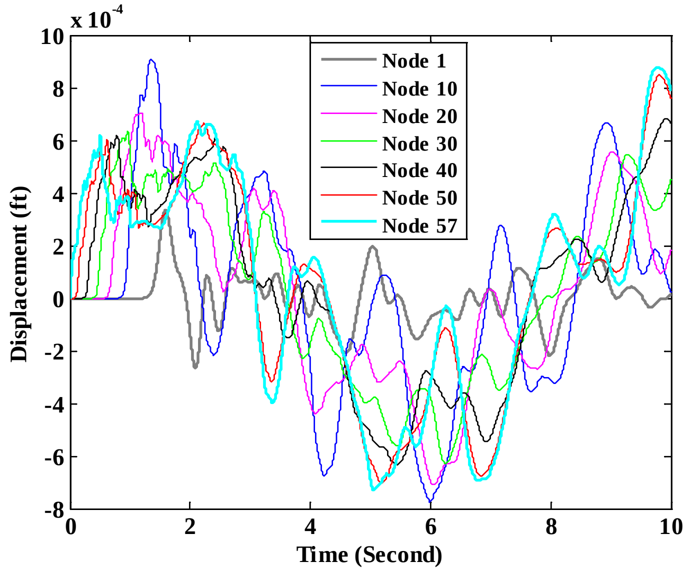


Figure 2.8.21. Displacements of selected nodes versus time.

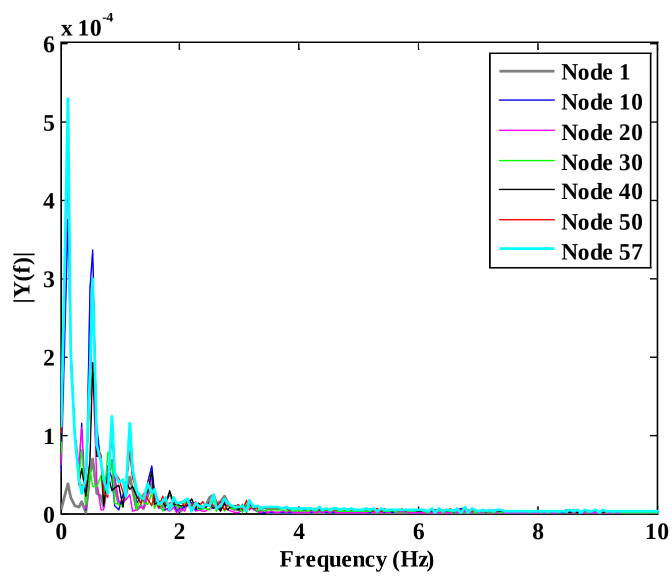


Figure 2.8.22. Displacements of selected nodes in the frequency domain.

2.9. Visualization of the Migration of CO_2, Oil, and Water

P. Corey Shum, University of Alabama at Birmingham
Konstantinos Theodorou, Jefferson State Community College

The complexity of the interaction between CO_2, oil, and water in a geologic formation makes animation of the evolution of fluid saturations during CO_2 and water flooding an especially useful tool for understanding enhanced oil recovery and its dependence on reservoir conditions and injection parameters. Using reservoir simulation results obtained by Konstantinos Theodorou (2013) using MASTER 3.0 (Ammer and Brummert, 1991; Ammer, Brummert, and Sams, 1991; Zeng, Grigg, and Chang, 2005), Corey Shum, in the UAB Enabling Technology Laboratory, programmed animations showing the evolution of fluid saturations in Sands 14-1 and 16-2 of the Citronelle Oil Field during two CO_2 injections of 7500 tons each, separated by a period of water injection. The raw output from the reservoir simulation was parsed with a custom application to extract the oil, water, and CO_2 saturation results for each point in space and time. This data was then exported to a standard 3-D data visualization format, VTK. ParaView and custom tools were then used to create animations of the time-dependent data.

The latest versions of the animations may be downloaded and run from the following URL's:

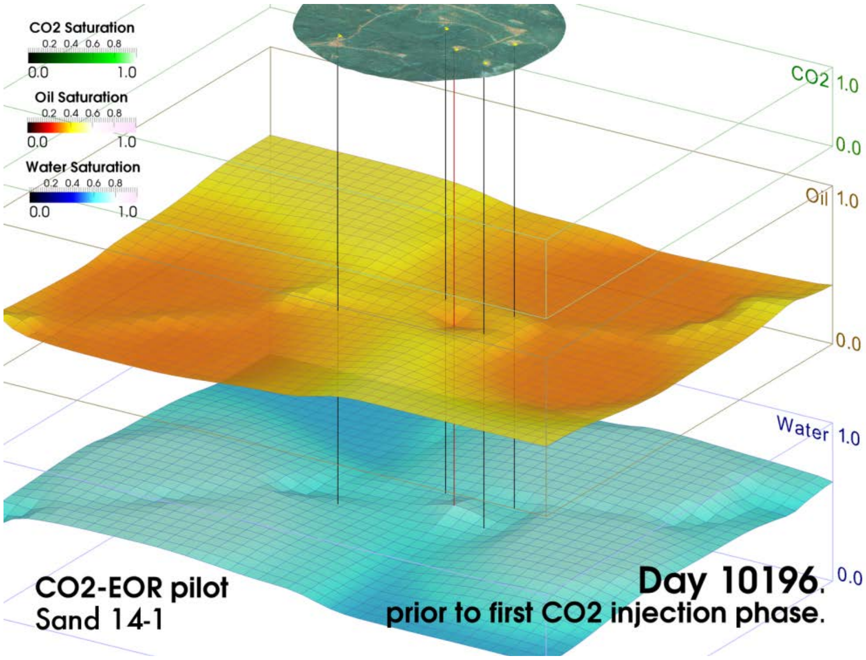
Simulation of CO_2-EOR in Sand 14-1: https://dl.dropbox.com/s/9br413mpbsyd8ek/oil14.mp4?dl=1

Simulation of CO_2-EOR in Sand 16-2: https://dl.dropbox.com/s/77oprxjx9gxafxa/oil16.mp4?dl=1

Should any difficulty in locating or running the videos be encountered, please send a message to Peter Walsh at <pwalsh@uab.edu>.

Screen shots from the animations are shown in Figures 2.9.1 to 2.9.4. As shown in Figure 2.9.1, the inverted five-spot test pattern in the Citronelle Oil Field is represented at the top with a cutout of satellite photographic imagery. Lines from the well locations are extruded down the image, to identify corresponding locations in the CO_2, oil, and water saturation graphs. The levels of saturation are represented both by the height of each location on each graph within its segment and also by its color, according to the color legend at the upper left in the image. As the simulation progresses, the day and the injection activity are displayed in the lower-right corner of the image. The days are counted from the beginning, in 1982, of the Alabama State Oil and Gas Board record of production from the Citronelle Field (Alabama State Oil and Gas Board, 2012).

CO_2, oil, and water saturations in Sands 14-1 and 16-2 are shown before any CO_2 was injected in Figure 2.9.1, at the end of the first CO_2 injection in Figure 2.9.2, at the end of the water injection in Figure 2.9.3, and at the end of the second CO_2 injection in Figure 2.9.4. The progress of CO_2 sweep, the development and migration of the oil bank, and the residual oil and water saturations left behind are all clearly visible. Watching the animation provides a new perspective and appreciation of the complex interactions among the fluids and phases.



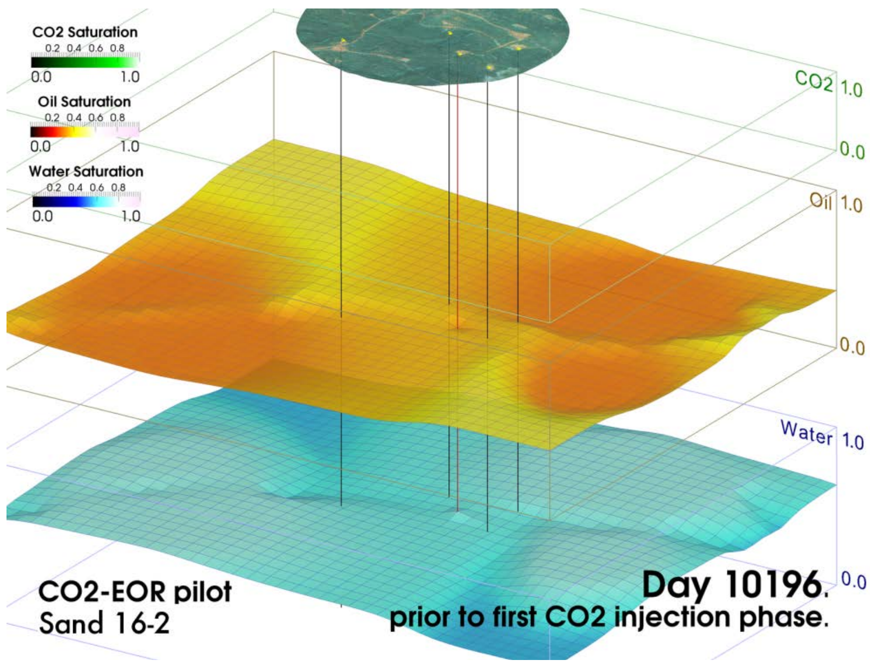


Figure 2.9.1. Screen shots of the animations of oil and water flows in Sands 14-1 (top) and 16-2 (bottom), before CO_2 injection. The animation was programmed by Corey Shum, based on simulations by Konstantinos Theodorou (2013) using MASTER 3.0 (Ammer and Brummert, 1991; Ammer, Brummert, and Sams, 1991; Zeng, Grigg, and Chang, 2005). An aereal view of the test well pattern is shown at the top of each figure, with the oil (yellow/orange), and water (blue) saturations on scales from 0 to 1, below. The vertical lines represent the injector (red) and producers (black). The saturations are also indicated by variations in intensity of the color. Low saturations are shown by more intense color, and vice versa, so that regions of high saturation do not obscure regions of lower saturation behind them, when peaks appear in the plots due to CO_2 and water injection.

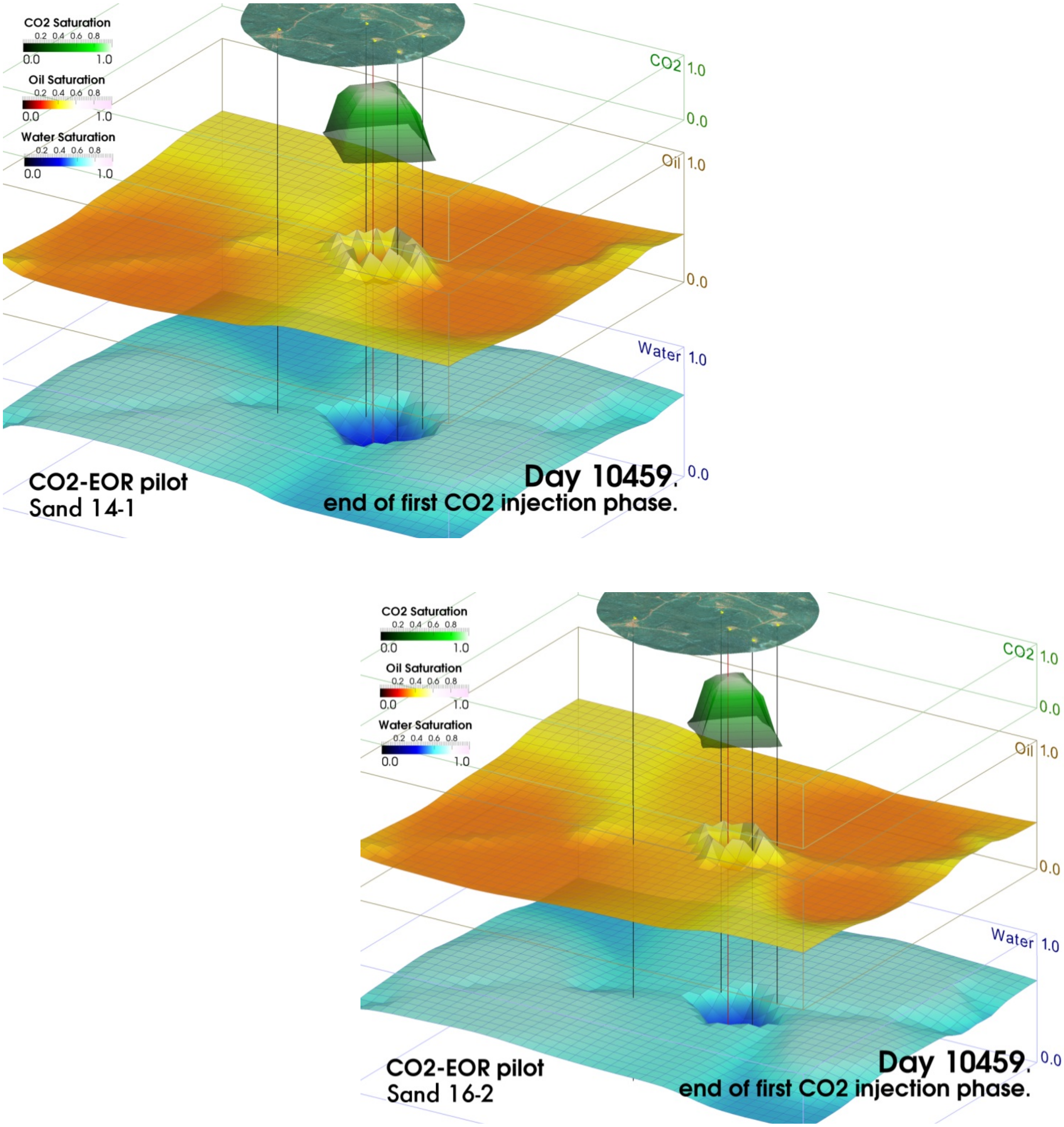
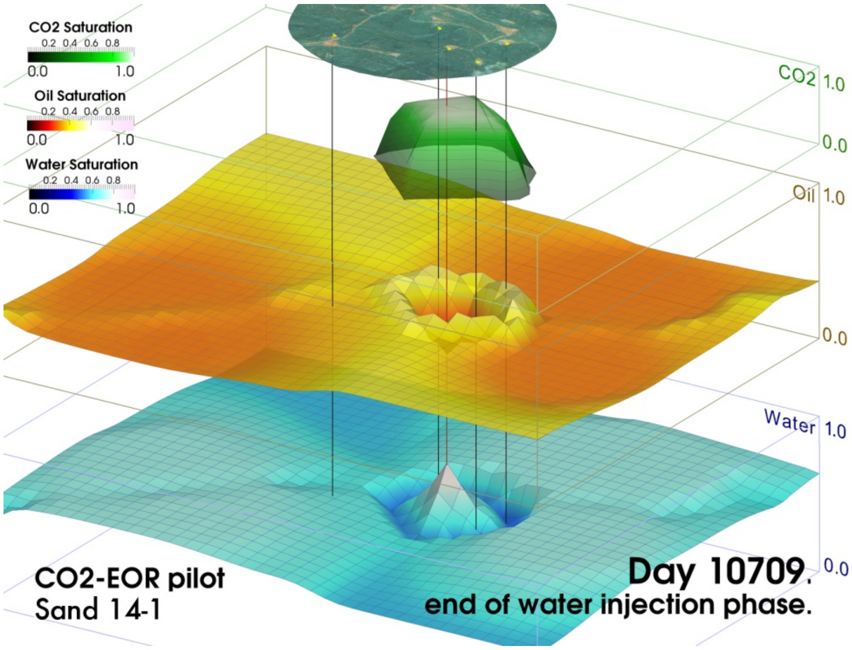


Figure 2.9.2. Screen shots of the animations of CO_2 (shown in green), oil, and water flows in Sands 14-1 (top) and 16-2 (bottom), at the end of the first injection of 7500 tons of CO_2, after 263 days of CO_2 injection. Elevated oil saturations associated with the oil banks are clearly visible, but the banks have not yet reached all three of the producers closest to the injector. The CO_2 flow into Sand 14-1 is greater than into Sand 16-2, resulting in further progress of the oil bank away from the injector.



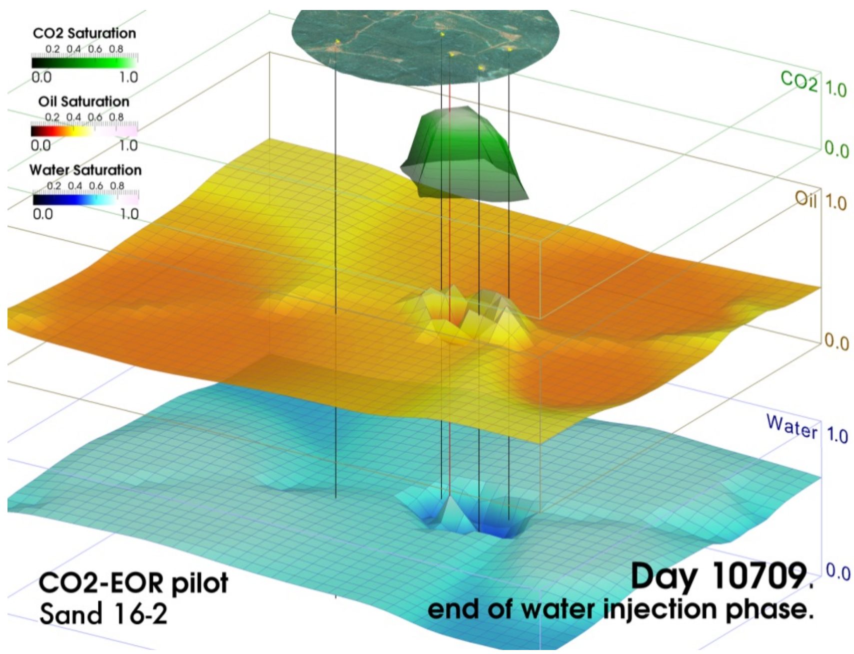


Figure 2.9.3. Screen shots of the animations of CO_2, water, and oil flows in Sands 14-1 (top) and 16-2 (bottom), at the end of the water injection period following the first injection of 7500 tons of CO_2, 513 days after the beginning of the first CO_2 injection. Water injection produces a peak in water saturation at the injector, but CO_2 saturation remains at a high level near the injector, even at the end of the water injection phase. The distance of the oil bank from the injector is greater in Sand 14-1 than in Sand 16-2, continuing the trend established during CO_2 injection, because the water flow, as well as the CO_2 flow, into Sand 14-1 is larger than into Sand 16-2.

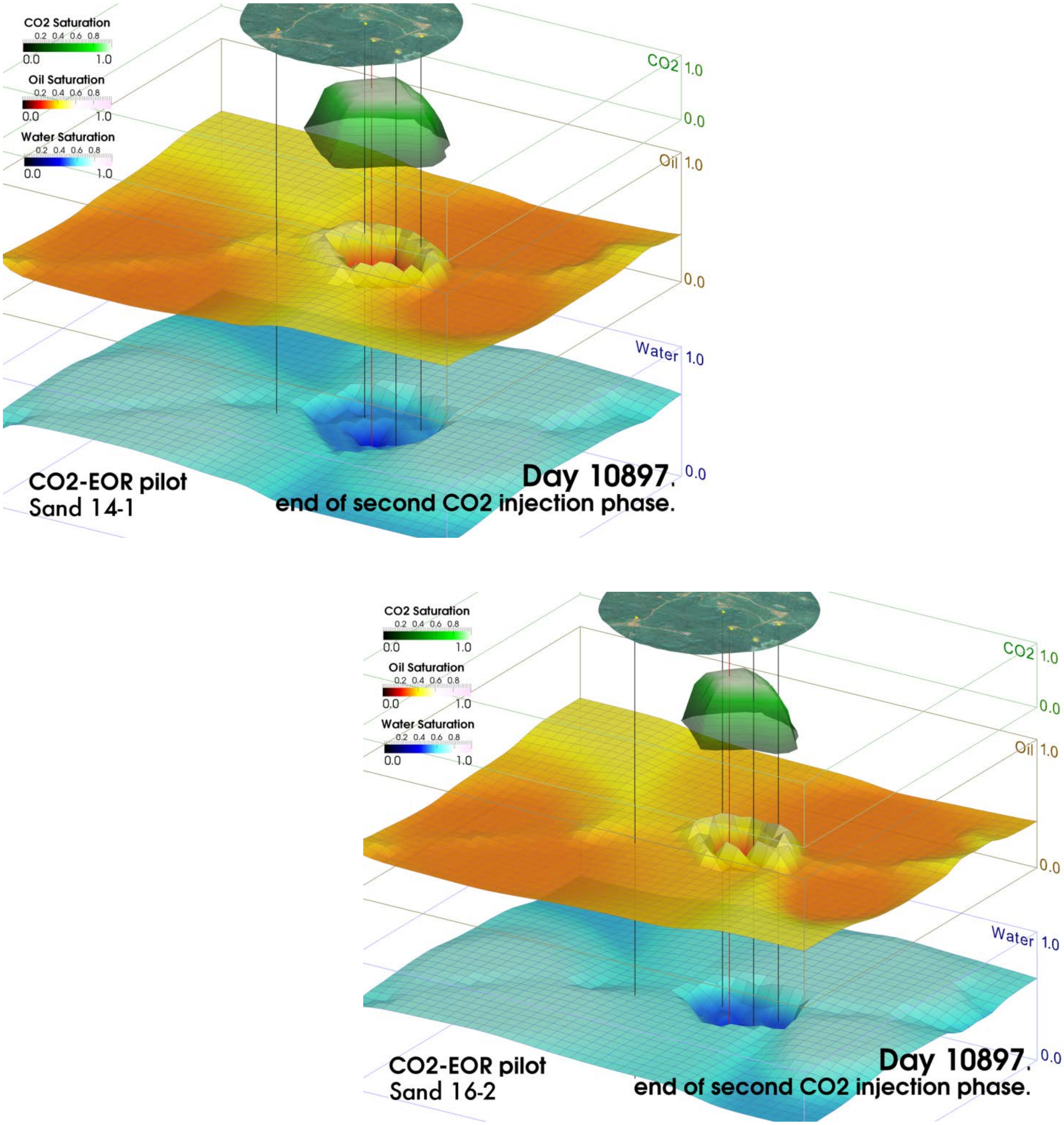


Figure 2.9.4. Screen shots of the animations of CO_2, water, and oil flows in Sands 14-1 (top) and 16-2 (bottom), at the end of the second injection of 7500 tons of CO_2, 701 days after the beginning of the first CO_2 injection. The oil bank has now reached three of the four production wells in both sands.

2.10. Reservoir Management

2.10.1. Performance of Water Alternating Gas Recovery

Konstantinos Theodorou, Jefferson State Community College

A series of simulations was conducted using MASTER 3.0 (Ammer and Brummert, 1991; Ammer, Brummert, and Sams, 1991; Zeng, Grigg, and Chang, 2005) to examine the post-pilot-test performance of the oil field when CO_2 is injected under various WAG schemes for enhanced oil recovery (Theodorou, 2013). The simulations utilized the 40 by 32-block grid with the same wells in the extended pattern as in previous simulations. As before, the fraction of CO_2 into Sand 14-1 was 57% while the fraction into Sand 16-2 was 43%. The injected water was divided into 82% into Sand 14-1 and 18% into Sand 16-2. The porosity and permeability of the sands were 13.61% and 10 mdarcy, respectively.

The CO_2-EOR pilot test was simulated according to the actual CO_2 injection rates recorded during the first CO_2 injection. All the WAG schemes examined followed immediately after the pilot test injection period. The 10-year WAG was simulated assuming a constant CO_2 injection rate of 28.1 t/day (31 short tons/day) into Well B-19-10 #2. The input parameters were as given in Table 2.10.1.

Results for the oil production rates are shown in Figure 2.10.1 for symmetric WAG schemes, in which the water injection interval has the same duration as the CO_2 injection interval. Figure 2.10.2 shows the results for asymmetric WAG schemes, in which the water injection interval was held constant at 6 months while the CO_2 injection interval was varied from a short period of 2 months to a long period of 24 months. Incremental oil recoveries for the various WAG schemes and the total and net amounts of CO_2 injected are summarized in Table 2.10.2.

Table 2.10.1. Model Parameters used in the CO_2-EOR Pilot Test and WAG Recovery Simulations.

Parameter	Value	Source
Average oil reservoir pressure	31.0 MPa (4500 psi)	Field pressure log, 1992
Reservoir oil saturation	0.55 dimensionless	Unit Manager’s Report, 1999
Reservoir water saturation	0.45 dimensionless	Unit Manager’s Report, 1999
CO_2-oil miscibility pressure	19.3 MPa (2800 psi)	Gilchrist, 1981
Average porosity	0.1361 dimensionless	Fowler et al., 1998
Average permeability	10 mdarcy	Fowler et al., 1998

Figure 2.10.1 indicates that symmetric WAG schemes perform better than continuous CO_2 injection, particularly after 5 to 6 years of oil recovery. Figure 2.10.2 indicates that, for asymmetric WAG schemes, oil recovery increases as the length of the CO_2 injection interval increases. However, this pattern reaches a point of maximum return and begins to decline when the CO_2 injection interval reaches 24 months.

Table 2.10.2 indicates that the optimal symmetric WAG schedule is 3 months CO_2 followed by 3 months of water. Compared with the symmetric WAG schedules, continuous CO_2 injection yields the best production rates in the short term, but it declines more rapidly and lags all the WAG schemes after about 5 to 6 years.

Continuous CO_2 injection underperforms all the asymmetric WAG schedules except 2 months of CO_2 followed by 6 months of water. The best performing WAG cycle, 12 months of CO_2 injection followed by 6 months of water injection, results in incremental oil recovery of 128,735 STB over 10 years, a 10% increase in recovery compared with continuous CO_2 injection. However, the low water injection rate experienced in the Field following CO_2 injection, discussed in Sections 2.6.3 and 2.6.4, casts the effectiveness of WAG recovery at Citronelle into doubt.

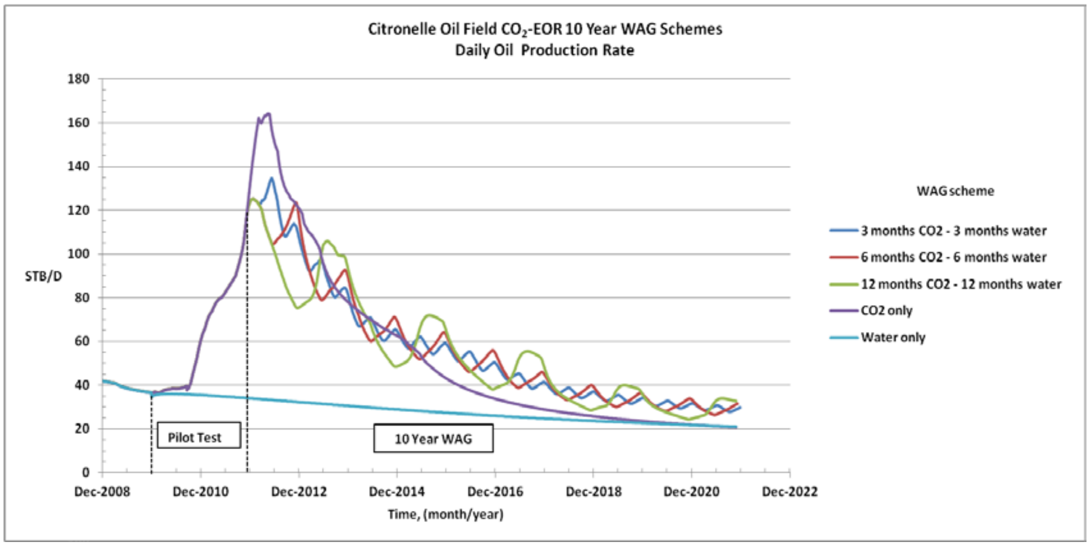


Figure 2.10.1. Simulated oil production rates for symmetric WAG schemes. Water-only and CO_2-only schemes are also included.

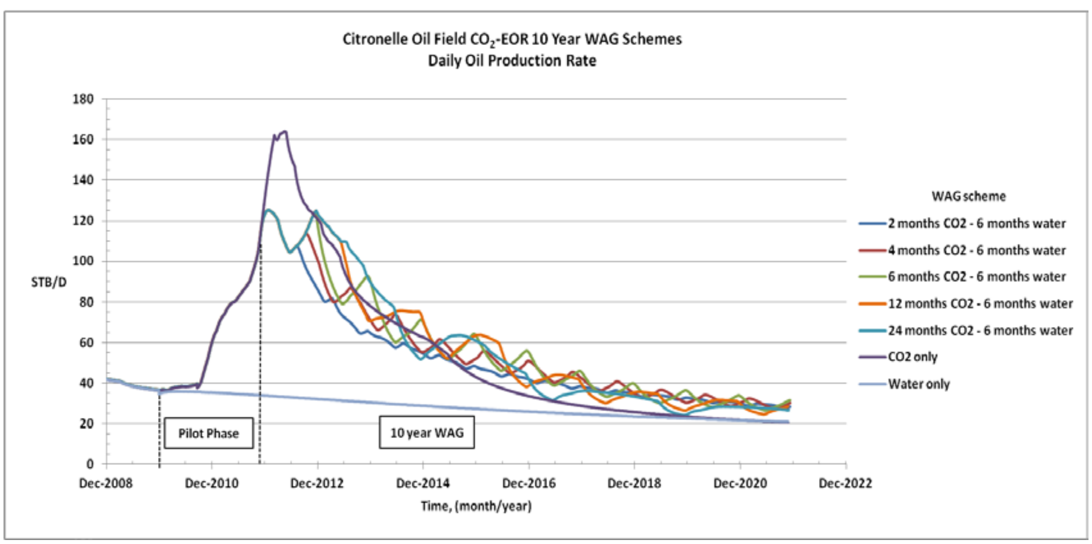


Figure 2.10.2. Simulated oil production rates for asymmetric WAG schemes. The water injection interval is held constant at 6 months while the CO_2 injection interval is progressively increased. Water-only and CO_2-only schemes are also included.

Table 2.10.2.
Oil Production and CO_2 Utilization for WAG Scenarios Using
Symmetric Schemes (GROUP 1) and Asymmetric Schemes (GROUP 2).

---- WAG Schedule ----	------------------------- Results -------------------------				
		GROUP 1	**Symmetric (water interval = CO_2 interval)**		
WAG injection schedule (total time is 10 years)	**EOR oil, STB**	**EOR incremental oil, STB**	**CO_2 injected, 1000 scf**	**CO_2 recovered, 1000 scf**	**Net CO_2 in place, 1000 scf**
3 months CO_2 - 3 months water	249,806	127,675	1,466,125	909,727	556,398
6 months CO_2 - 6 months water	248,394	126,263	1,466,125	900,141	565,984
12 months CO_2 - 12 months water	244,668	122,537	1,466,125	887,508	578,617
		GROUP 2	**Asymmetric (water interval ≠ CO_2 interval)**		
WAG injection schedule (total time is 10 years)	**EOR oil, STB**	**EOR incremental oil, STB**	**CO_2 injected, 1000 scf**	**CO_2 recovered, 1000 scf**	**Net CO_2 in place, 1000 scf**
2 months CO_2 - 6 months water	228,837	106,706	858,250	426,804	431,446
4 months CO_2 - 6 months water	243,275	121,144	1,223,015	701,774	521,241
6 months CO_2 - 6 months water	248,394	126,263	1,466,125	900,141	565,984
12 months CO_2 – 6 months water	250,866	128,735	1,830,826	1,253,621	577,205
24 months CO_2 – 6 months water	249,133	127,002	2,195,565	1,578,381	815,506
Only CO_2	238,607	116,476	2,681,905	2,114,059	567,846
Only water	122,131	0	0	0	0

2.10.2. Problems Experienced During and Following CO_2 Injection

The team is observing the response of the inverted five-spot well pattern to the injection of 8036 tons of carbon dioxide, followed by water, and conducting tests to determine the causes of unexpected consequences of the CO_2 injection that will have significant bearing on the design of a commercial CO_2 flood in the Citronelle Field.

The unexpected consequences of the CO_2 injection, the tests being conducted to understand them, and steps implemented or proposed to mitigate them are described below.

1. ***Early and excessive CO_2 breakthrough at a well to the southwest of the injector.***

   Explanation: presence of a fracture or high permeability streak between the injector and producer.
   Test performed: a pressure fall-off test provided evidence for a fracture, probably along the direction of maximum horizontal compressive stress in the southeastern U.S., approximately northeast to southwest.
   Proposed Solution: when a fracture is present, adjust injection pressure to prevent its opening; when a high permeability streak is present, implement mobility control.

2. ***Low injectivity to water following CO_2 injection.***

   Explanation: (1) capillary blocking by gas, (2) heavy hydrocarbons precipitated after extraction of light ends by CO_2, (3) plugging of perforations by chips of internal plastic coating from the tubing.
   Tests performed: injection profile showed that both of the target formations are accepting water. Surfactant injection showed that capillary blocking is significant, but not the only explanation for low injectivity. Treatment with hydrocarbon solvent and asphaltene dispersant had little effect. Flow-back restored some injectivity, suggesting that flaking of IPC was the principal cause of the loss in injectivity.
   Solution: (1) replacement of coated tubing with bare steel tubing and flow-back to flush out IPC chips, (2) treatment of water with additives, or continuous CO_2 injection rather than WAG.

3. ***Rapid deterioration of down-hole power oil pumps on returning to water injection following CO_2.***

   Explanation: erosive particles and scale, mobilized by CO_2, accumulating in the power oil.
   Solution: replacement of the pumps by ones having longer stroke and built from erosion-resistant alloys.

Following the solution of the erosion-corrosion problem in the power-oil pumps, in November 2011, work was focused on understanding the loss of oil production at Well B-19-11 and the loss in injectivity to water experienced following the injection of CO_2. Both of these effects have significant bearing on the design of a commercial CO_2 flood at Citronelle.

Early Breakthrough of CO_2. Though 25,400 bbl of incremental oil assignable to EOR are estimated to have been recovered from three of the wells in the inverted five-spot, this good performance has been offset by the loss of production from the fourth well in the test pattern, where excessive gas was produced.

A pressure-transient test in the injector, conducted in November and December 2011 provided strong evidence for the presence of a 600 to 1000-foot-long vertical fracture intersecting the injection well. The presence of a fracture was completely unexpected, because the injection well had never been intentionally hydraulically fractured and the hydrocarbon-bearing sands at Citronelle are free of natural fractures. Although the direction of such a fracture cannot be determined from the results of the pressure-transient test, a fracture in the direction of maximum horizontal compressive stress in the Southeastern U.S. would explain the early excessive breakthrough of CO_2 and loss of oil production from the producer to the southwest of the injector (Well B-19-11, Figure 2.2.2). Elevated levels of CO_2 have also appeared, earlier than expected, in produced gas from other wells to the northeast and southwest of the CO_2 injector, consistent with a fracture in the approximate direction of maximum horizontal compressive stress.

Low Injectivity to Water, Following CO_2. The water injection rate before CO_2 injection was approximately 160 to 170 bbl water/day. After returning to water when the CO_2 injection was complete, the rate dropped to only 50 to 70 bbl water/day. This has almost certainly had negative impact on production from the three wells accounting for the 25,400 bbl of incremental oil.

Four processes were thought to be the most likely contributors to loss in injectivity: (1) capillary blocking by CO_2 gas trapped in pores, (2) plugging by heavy hydrocarbons, (3) plugging by fine clay particles mobilized by the CO_2, (4) precipitation of solids by reaction of CO_2, minerals, and brine solutes, and (5) plugging of perforations by flakes of coating from the tubing. The latter problem is fixed by proper quality control of the IPC. The ability to mitigate formation damage due to interaction of CO_2, minerals, and brine, if it occurred, will be a critical component of the decision whether or not to conduct WAG recovery at Citronelle.

To examine the importance of capillary blocking, injected water was treated with surfactant from July 25 to November 7, 2012. The conclusion from the surfactant treatment is that while capillary blocking of water injection is significant, it is not the only effect responsible for the loss in injectivity experienced on returning to water injection following the CO_2 slug. Treatment of the injected water with hydrocarbon solvent and dispersant was done to determine whether precipitated hydrocarbons may have been responsible for the portion of the loss in injectivity, approximately 67%, not explained by capillary blocking.

Treatment with heavy hydrocarbon solvent and asphaltene dispersant began in July 2013, but was interrupted by a tubing leak. Flakes of internal plastic coating were discovered while pulling the tubing. The tubing was replaced by bare steel tubing and when the injector was brought back on line the water injection rate was initially quite high, ranging from 88 to 230 bbl/day, but then declined, over a period of just a few days, to 77 to 87 bbl/day.

The combined effects of the change in tubing, treatment with hydrocarbon solvent, and flow-back to remove IPC chips increased the water injection rate slightly, to the range from 79 to 94 bbl/day. Flow-back appears to have had the most lasting effect, suggesting that flaking of the IPC is the likely cause of the low injectivity to water following the CO_2 injection.

The possibility of formation damage on switching from CO_2 to water, as during WAG recovery, would limit the options available for reservoir management. Extension of Denbury's CO_2 pipeline from its easternmost point, at Eucutta, MS, to Citronelle, will be a large and costly undertaking. An attractive alternative is to use CO_2 captured from coal combustion products at

Alabama Power Company's Plant Barry, only 12 miles from Citronelle. It is with this scenario in mind that a large-scale demonstration of CO_2 capture, pipeline transport, and underground injection for storage in the Citronelle Southeast Unit is underway at Plant Barry, led by the Southeast Regional Carbon Sequestration Partnership (SECARB) and primary sponsors, U.S. DOE, National Energy Technology Laboratory, and Southern States Energy Board, with industrial partners, Advanced Resources International, Alabama Power Co., Denbury Resources, Electric Power Research Institute, Geological Survey of Alabama, Southern Company, and Southern Natural Gas. WAG recovery would be an attractive option if CO_2 were supplied from Plant Barry, because it would provide a means to adjust for planned and unplanned outages at the Plant, stretch the CO_2 supply for EOR, and because WAG can increase oil recovery, compared with continuous CO_2 injection, as shown by the simulations performed by Konstantinos Theodorou using MASTER 3.0, under the present project (Theodorou, 2013).

3. Milestone Status

3.1. Status Summary

The project is divided into three research phases, corresponding to the three budget periods. The emphasis in Phase I (Budget Period 1: January 1, 2007 to August 31, 2008) was on selection of a test site, detailed study of its geology, determination of oil-CO_2 minimum miscibility pressure, reservoir simulation of CO_2-EOR, and establishment of background conditions at the site. The focus in Phase II (Budget Period 2: September 1, 2008 to December 31, 2010) was on the first CO_2 injection, of 8036 tons, and the associated measurements and monitoring. A no-cost extension of Phase II from its original end date of April 30, 2010, to December 31, 2010, was approved, to complete the first CO_2 injection. Work in Phase III (Budget Period 3: January 1, 2011 to January 31, 2014) includes documentation of the response to the first CO_2 injection and presence or absence of environmental effects, large-scale fine grid reservoir simulations and visualization, oil-water-CO_2 phase behavior, development of a reservoir management plan, seismic monitoring, and a comprehensive evaluation of the findings from all components of the project. A request for no-cost extension of the project to January 31, 2014, was approved by NETL, to provide time to perform the proposed tests and complete the analysis of the response to CO_2 injection.

The stratigraphy, sedimentology, and petrology of the Rodessa Formation in the vicinity of the test site have been analyzed and documented at an unprecedented level of detail; realistic and informative reservoir simulations have been performed; the environmental and ecological conditions surrounding the site have been documented, before, during, and following CO_2 injection; seismic signals from the target formation have been recorded under the baseline water flood condition, during CO_2 injection, and during CO_2 migration from the injection zone; the minimum miscibility pressure and absence of precipitation from oil in the presence of CO_2 were established; and a favorable economic analysis was conducted that identifies the optimum CO_2 slug size for water-alternating-gas oil recovery under specified CO_2 cost and oil price constraints.

The first injection, of 8036 tons of CO_2, began on a continuous basis in January 2010 and was completed in September 2010. Incremental oil appeared in January 2010 and continued through September 2010, reversing a long period of declining production. However, several problems associated with the CO_2 injection appeared, including excessive gas production at Well B-19-11, to the southwest of the injector, a low water injection rate on returning to water injection at the conclusion of the CO_2 injection, and problems with the down-hole power oil pumps, due to erosion by particulate and scale mobilized by carbon dioxide.

Incorporation of better materials in the power oil pumps and replacement of the pumps with ones having longer stroke brought the frequency of pump pulls back to normal.

A pressure-transient test in November and December 2011 made the unexpected discovery of a hydraulic fracture originating at the injector and having a total length of 600 to 1000 ft. The fracture, probably in the direction of maximum horizontal compressive stress in the Southeastern

U.S., would explain the early breakthrough of CO_2 at wells to the northeast and southwest of the injector and likely provided a preferential pathway for CO_2, undermining the sweep efficiency of CO_2 in the pilot test.

An injection profile test was conducted in January 2012 to determine if either of the target sands was primarily responsible for the low water injection rate. The test established that 35% of the water flow was to Sand 14-1 and 65% was to Sand 16-2, so neither injection zone was completely blocked, but comparison with the results of an injection profile run before CO_2 injection showed that loss of flow into the upper Sand 14-1 was primarily responsible for the low injectivity to water.

Injected water was treated with surfactant from July 25 to November 7, 2012, to determine whether capillary blocking was responsible for the loss in injectivity to water following the injection of CO_2. The water injection rate responded to the surfactant, recovering approximately one-third of the loss resulting from the CO_2 injection. Though significant, the improvement accompanying surfactant injection did not come close to restoring the injection rate to the average level before CO_2 injection. The discovery of flakes of internal plastic coating during repair of a leak in the injector tubing suggested an alternative explanation for low injectivity. The tubing was replaced with bare steel tubing and the well was flowed back to flush out the IPC flakes. Treatment of the injector with hydrocarbon solvent and dispersant was also done to remove any heavy components that may have been left behind when CO_2 mobilized lighter fractions. The combined effects of these measures was a modest increase in water injection rate, but the injectivity could not be restored to levels approaching those observed before the CO_2 injection.

The completion of Milestones in Phases I and II and the status of Milestones in Phase III are described in the following Sections, 3.2, 3.3, and 3.4, respectively.

3.2. Phase I Milestones

There were four Milestones scheduled during Research Phase I (Budget Period 1). They were completed as follows:

Oil-CO_2 MMP determined: Measured as 2340 ± 250 psig using the rolling ball viscometer designed and built especially for this project.

Permit to conduct Field Test No. 1: Infill well B-19-10 #2 was re-permitted as a gas injector.

Economic and market analysis: Determined the optimum CO_2 slug size during WAG recovery as a function of oil price and discount factor.

Justification for proceeding to Phase II: Submitted and approved.

3.3. Phase II Milestones

The critical path milestones scheduled during research Phase II are specified in Table 3.3.1. The conclusions, findings, and accomplishments from completion of the Milestones are described below.

Geomechanical stability analysis (Phase II Milestone): Geomechanical stability analyses were performed using a 1-dimensional effective stress model, a 3-dimensional finite element model, and the geophysical testing results. Both models indicate only small deformations as a result of overburden pressure on the Donovan Sands (0.56 to 0.75 ft for the Upper Donovan and 0.28 to 0.39 ft for the Lower Donovan) and a strain rate of 0.14 to 0.19%, below the expected rupture limit of 0.3% for quasi-brittle materials.

Shear-wave velocities were measured using the Refraction Microtremor (ReMi) technique to depths of 12,500 feet using wireless geophones placed along two straight paths spanning 30,100 and 25,600 feet, to the south and southwest, respectively, of the injection well. Shear-wave velocities recorded before and during CO_2 injection suggest a 10% increase in stress associated with CO_2 injection, in layers above the injection zone. Detection of changes associated with CO_2 injection at the depth of the Donovan Sands by Refraction Microtremor measurements is unprecedented and would represent a significant advance in the application of the ReMi technique.

Table 3.3.1.
Critical Path Milestones, Research Phase II (Budget Period 2),
September 1, 2008 to December 31, 2010.

Phase II Task	Critical Path Milestone Description	Completion Date
Task 23	Geomechanical stability analysis completed.	July 1, 2009
Task 30	Documentation, through measurements of atmospheric CO_2, of the presence or absence of environmental effects of CO_2 injection.	Sept. 2, 2010
Task 32	Justification for proceeding to Phase III submitted.	Oct. 14, 2010
Task 17	Phase II CO_2 injection, 7500 tons, completed.	Sept. 15, 2010

Documentation of environmental effects (Phase II Milestone): Measurements of soil gas composition versus depth, CO_2 flux from soil, soil temperature, soil moisture, and soil elements (carbon, nitrogen, and phosphorus) were made from August 2008 to August 2010, before and during CO_2 injection, at 15 locations surrounding the injector, three producers, and a plugged and abandoned well within the test pattern. The growth of trees and plants and their species distribution were monitored in test plots near the injector, producers, and tank batteries. Monthly measurements of CO_2 in ambient air were recorded at 104 points on a grid across Citronelle, from September 2007 to June 2012. No elevated levels of CO_2 above the normal variation, no unusual CO_2 flux from soil, and no significant changes in the growth or distribution of vegetation were associated with the injection of CO_2 during Phase II, but please see the discussion of the growth of vegetation under Phase III, below.

Justification for proceeding to Phase III (Phase II Milestone): The justification and application for continuation of the project into Phase III and Budget Period 3 were submitted to the Project Manager on October 14, 2010.

Phase II CO_2 injection complete (Phase II Milestone): The first injection of 8036 tons of CO_2 was completed on September 25, 2010. After initial problems pumping liquid CO_2, all of which were resolved by the persistent efforts of Denbury's team of engineers and technicians, continuous carbon dioxide injection into the inverted five-spot chosen for testing began at the end of January 2010 and continued to the end without significant interruption at an average rate of 31 tons/day, in good agreement with the rate of 35 tons/day anticipated by reservoir simulations using SENSOR (Coats Engineering, Inc.).

3.4. Phase III Milestones

The critical path Milestones to be met during Phase III are specified in Table 3.4.1. The milestones include four key components of the project: (1) documentation and analysis of the response of the reservoir to CO_2 injection, (2) documentation of the presence or absence of environmental effects, (3) reservoir simulation and visualization, and (4) the capacity of the formation for CO_2 storage.

Table 3.4.1.
Critical Path Milestones, Research Phase III (Budget Period 3),
January 1, 2011, to January 31, 2014.

Phase III Task	Critical Path Milestone Description	Completion Date
Task 44	Evaluation of Rodessa Formation CO_2 storage capacity.	May 31, 2011
Task 33	Field Test No. 2 completed.[a]	Nov. 30, 2011
Tasks 41 & 42	Documentation, through measurements of atmospheric CO_2 and growth of vegetation, of the presence or absence of environmental effects of CO_2 injection.	Mar. 31, 2012
Task 36	Presentation of results as dynamic simulations.	Aug. 31, 2012
New Task[b]	Surfactant injection to test for capillary blocking by gas.	Nov. 30, 2012

a. In the absence of a second CO_2 injection, the title of this task is understood to read: "Monitoring of response to the Phase II CO_2 injection," with a completion date of January 31, 2014.
b. The new task was dictated by the need to diagnose low water injectivity following CO_2 injection. The Milestone was added following approval of a no-cost extension from August 31, 2012 to February 28, 2013, to satisfy the requirement that there be at least two Milestones in each year of the project.

Evaluation of Rodessa Formation CO_2 storage capacity (Phase III Milestone): The capacity of Citronelle dome for sequestration of CO_2 has been examined in detail. The total capacity of Citronelle Dome, including both saline formations and the oil reservoirs, according to the conservative estimation procedure of the DOE Carbon Sequestration Regional Partnerships (2006) is between 60 and 240 x 10^9 kg (66 to 265 million short tons). A more detailed analysis by Esposito et al. (2008), including factors accounting for formation heterogeneity and residual oil and water saturation, estimated that the total CO_2 storage capacity is between 480 and 1900 x 10^9 kg (530 to 2100 million short tons). A calculation based upon the work of Pruess et al. (2001) and Xu et al. (2001), suggests that up to 315 x 10^9 kg (350 million short tons) of the stored CO_2 could be mineralized by conversion to solid carbonates over geologic time.

Documentation, through measurements of atmospheric CO_2 and growth of vegetation, of the presence or absence of environmental effects of CO_2 injection (Phase III Milestone): Xiongwen Chen and Kathleen Roberts of Alabama A&M University measured CO_2 in ambient air at least once each quarter, from September 2007 to June 2012, at 104 sampling locations in the Citronelle Oil Field and City of Citronelle. The measurements were made at all of the sampling points over two consecutive days; one day in the City of Citronelle and the other in the Oil Field. The average and standard deviation of each set of measurements are shown versus time in Figure 3.4.1.

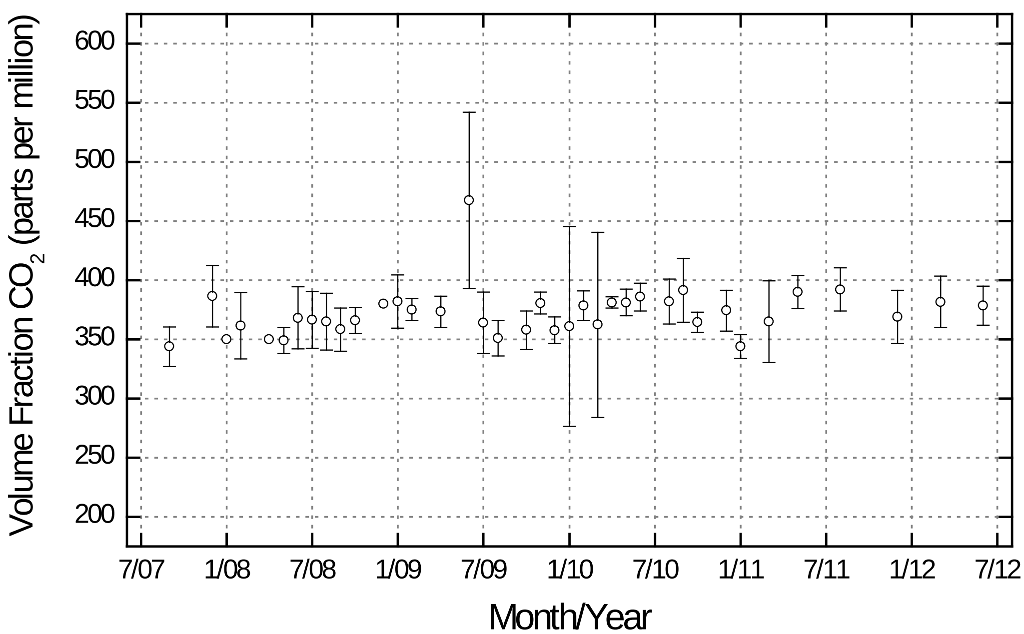


Figure 3.4.1. Average atmospheric CO_2 volume fraction (parts per million) at ground elevation across the City of Citronelle and Citronelle Oil Field from September 2007 to June 2012.

Only one anomalous reading appears in the entire set of CO_2 measurements, in June 2009, after filling the CO_2 storage tank in March 2009 and during unsuccessful attempts to inject CO_2, but before continuous CO_2 injection began in December 2009. The rest of the CO_2 measurements are consistent with the seasonal variations and long-term trends of the local NASA satellite-based Atmospheric Infrared Sounder data (http://airs.jpl.nasa.gov/) and worldwide average atmospheric CO_2 levels, and with the worldwide rate of increase in atmospheric CO_2 of approximately 2 ppmv/year. The worldwide annual average volume fraction of CO_2 in ambient air during the year 2012 was 392.55 ± 0.10 ppmv (Ed Dlugokencky and Pieter Tans, NOAA/ESRL <www.esrl.noaa.gov/gmd/ccgg/trends/>).

Xiongwen Chen and Kathleen Roberts of AAMU also established 10 m x 10 m test plots near the injector, producers, and tank batteries, in which to monitor growth of vegetation. Inventories of the vegetation plots were conducted in 2008, 2009, 2010, and 2011. Due to harvesting of timber by land owners, a few of the original plots were lost. The growth rates of trees and shrubs in the remaining plots during the three time intervals, 2008-2009, 2009-2010, and 2010-2011 are shown in Figure 3.4.2. A key to the locations and functions of the plots is provided in Table 3.4.2. Four new vegetation plots near a golf course (GC1, GC2, GC3, and GC4) were added as controls in 2009 after the original control plots were destroyed by a change in land use at the wildlife management area where they were located. The most recent measurements were made on September 6-8, 2011.

Comparison of the 2008-2009 growth rates with those in 2009-2010 shows that the plant growth rate increased from the first period to the second in two plots and decreased in five of them. Comparison of the 2009-2010 growth rates with those in 2010-2011 shows that the plant growth rate increased from the second period to the third in three plots and decreased in five of them. The overall trend is one of decreasing growth rates, rather than the increase in rates that might be expected under the influence of elevated levels of CO_2.

One plot, VP1, on the far left in Figure 3.4.2, does exhibit a significant and consistent increase in the rate of growth of vegetation during the four-year period. As shown in Table 3.4.2, Plot VP1 is located near the injector, Well B-19-10 #2. This is an interesting observation, in view of the fact that elevated levels of CO_2 in ambient air were not consistently detected there, nor were elevated CO_2 fluxes from soil near that well reported by Ermson Nyakatawa and Latasha Lyte of AAMU (Section 2.7.1). We leave open the possibility that vegetation near Well B-19-10 #2 may have been influenced by CO_2 from the pilot test, and will continue to monitor CO_2 in ambient air and the growth of vegetation at this location and at all of the other observation points. With the exception of vegetation near Well B-19-10 #2, the differences in growth rate from place-to-place and year-to-year are more likely explained by patterns of rainfall, temperature, and solar insolation than by CO_2 plumes associated with the CO_2 storage tank, injection equipment, wells, or tank batteries.

There has been no significant short or long-term effect of storage, handling, and injection of CO_2 on the levels of CO_2 in ambient air at Citronelle. Of the eight vegetation test plots established at the wells and tank batteries at the test site, a significant and consistent increase in the rate of growth of vegetation was observed only in the plot near the injector, Well B-19-10 #2, though this observation is at odds with the measurements of CO_2 in ambient air and measurements of CO_2 fluxes from soil near the well.

Presentation of results as dynamic simulations (Phase III Milestone): The complexity of the interaction between CO_2, oil, and water in a geologic formation makes animation of the evolution of fluid saturations during CO_2 and water flooding an especially useful tool for understanding enhanced oil recovery and its dependence on reservoir conditions and injection parameters. Using reservoir simulation results obtained by Konstantinos Theodorou (2013) using MASTER 3.0 (Ammer and Brummert, 1991; Ammer, Brummert, and Sams, 1991; Zeng, Grigg, and Chang, 2005), Corey Shum, in the UAB Enabling Technology Laboratory, programmed animations showing the evolution of fluid saturations in Sands 14-1 and 16-2 of the Citronelle Oil Field during two CO_2 injections of 7500 tons each, separated by a period of water injection. The raw output from the reservoir simulation was parsed with a custom application to extract the oil, water, and CO_2 saturation results for each point in space and time. The data were then exported to a standard 3-D data visualization format, VTK. ParaView and custom tools were used to create animations of the time-dependent data.

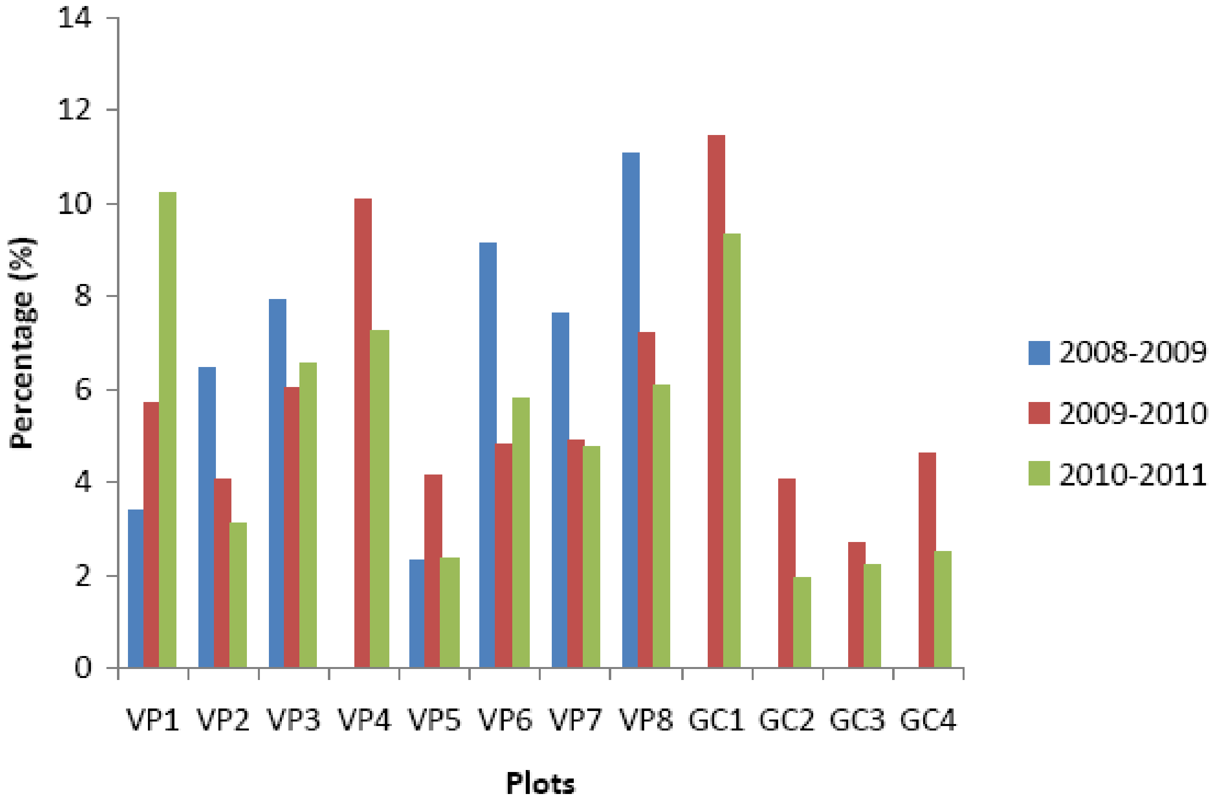


Figure 3.4.2. Comparison of growth, as the fractional (%) increase in basal area, in vegetation plots across Citronelle during the three periods, 2008-2009, 2009-2010, and 2010-2011. The plots are identified in Table 3.4.2.

Table 3.4.2. Locations and Descriptions of the 10 m x 10 m Vegetation Plots.

Vegetation Plot	Location	Description
VP1	Well B-19-10 #2	Injection well
VP2	Well B-19-7	Production well
VP3	Well B-19-8	Production well
VP4	Well B-19-9	Production well
VP5	Well B-19-10 #1	Plugged and abandoned well
VP6	B-19-8 Tank Battery	Tank battery
VP7	Well B-19-11	Production well
VP8	B-19-11 Tank Battery	Tank battery
GC1	Citronelle Golf Course	Control
GC2	Citronelle Golf Course	Control
GC3	Citronelle Golf Course	Control
GC4	Citronelle Golf Course	Control

The latest versions of the animations may be downloaded and run from the following URL's:

Simulation of CO_2-EOR in Sand 14-1: https://dl.dropbox.com/s/9br413mpbsyd8ek/oil14.mp4?dl=1

Simulation of CO_2-EOR in Sand 16-2: https://dl.dropbox.com/s/77oprxjx9gxafxa/oil16.mp4?dl=1

Should any difficulty in locating or running the videos be encountered, please send a message to Peter Walsh at <pwalsh@uab.edu>.

Screen shots from the animations are shown in Figures 2.9.1 to 2.9.4 in the present report. CO_2, oil, and water saturations in Sands 14-1 and 16-2 are shown before any CO_2 was injected in Figure 2.9.1, at the end of the first CO_2 injection in Figure 2.9.2, at the end of the water injection in Figure 2.9.3, and at the end of the second CO_2 injection in Figure 2.9.4. The progress of CO_2 sweep, the development and migration of the oil bank, and the residual oil and water saturations left behind are all clearly visible. Watching the animation provides a new perspective and appreciation of the complex interactions among the fluids and phases.

Surfactant injection to test for capillary blocking by gas (Phase III Milestone): Injected water was treated with surfactant from July 25 to November 7, 2012. The water injection rate during surfactant injection, and during the period from July 30 to October 14, 2012, when the pressure was constant at 3900 psig, averaged 95 bbl water/day. During the period following CO_2 injection but before the surfactant treatment, from September 26, 2010, to July 24, 2012, on the days when the pressure was 3900 psig, the average water injection rate was 63 bbl water/day. The surfactant treatment was therefore associated with a 50% increase in injection rate. Though certainly significant, the increase accompanying surfactant injection did not come close to restoring the injection rate to the average level of 160 bbl water/day before CO_2 injection, when the average pressure was only 3600 psig. The conclusion from the surfactant treatment is that while capillary blocking of water injection is significant, it is not the only effect responsible for the loss in injectivity experienced on returning to water injection following the CO_2 slug.

4. Summary and Conclusions

The most significant accomplishments and conclusions from each of the principal research efforts in which the team has been engaged since the beginning of the project (February 6, 2007 through March 31, 2013) are summarized below.

Communication and Technology Transfer. The wiki-based collaborative web site has proven to be an effective means for rapid dissemination of technical information through the research group. The site contains links to difficult-to-find reports of previous engineering work in the Citronelle Oil Field, reports generated under the present project, presentations at project review meetings, a wealth of data from the field, and results of the simulations of CO_2-EOR using the SENSOR reservoir simulation software package.

Fourteen peer-reviewed papers describing work directly related to the project have been published, including comprehensive reviews of the geology of Citronelle Dome and its prospects for CO_2-enhanced oil recovery and capacity for CO_2 storage (Esposito et al., 2008, 2010). Results of work under the project have been presented by members of the project team at sixteen national and international conferences and at twelve regional and local meetings. A publicly accessible web site makes the results available to specialists in the fields of enhanced resource recovery and carbon storage and to interested students, educators, and the general public. The project was the subject of the lead article in the Fall 2009 issue of *E&P Focus*.

Geology and Petrology. Detailed study of the petrology, sedimentology, and stratigraphy of Citronelle Dome at the Geological Survey of Alabama has shown that depositional environments in the Rodessa Formation differ significantly from the model developed in early published work that guided past development and production from the Citronelle Field. The Donovan Sands have historically been correlated with the Rodessa Formation, but the research at GSA indicates that the Donovan is associated with a larger interval that is equivalent to the carbonate-rich strata of the Pine Island, James, and Rodessa formations and spans about 5 million years of geologic time. The Citronelle Field occurs in the transition zone between the marine carbonate sedimentation that predominated in the ancient Gulf of Mexico and the terrestrial siliciclastic sedimentation that predominated on the Gulf coastal plain.

The Donovan constitutes a series of about 50 stacked, aggradational sandstone units that fine upward into red and gray shale. Some thin limestone beds are present in the section. The sandstone units are generally thinner than 30 feet and contain sedimentary structures and fossils that indicate sedimentation in estuarine and beach-barrier environments, and the shale units contain a variety of depositional features that indicate sedimentation in lagoons and tidal flats, punctuated by episodes of exposure, weathering, and soil formation. Each sandstone-shale interval is interpreted as a depositional sequence of about 100,000 years, so each interval is considered a product of 5th-order sea-level variation. Vertical trends of sandstone thickness define two 3rd-order sequence sets, and thinning upward of the sandstone bodies in each set suggests retrogradation of the coastal plain in response to overall relative rises of sea level. Successive stacking of aggradational sandstone bodies in each sequence set and the alteration of those bodies by subaerial, subaqueous, and burial processes gave rise to complex patterns of reservoir heterogeneity. This heterogeneity must be given thorough consideration when developing a strategy for implementation of CO_2-enhanced oil recovery technology in the Citronelle Field.

All of the available cores from the Citronelle Field have been described by the staff at the Geological Survey of Alabama, including the Southeast Citronelle Unit D-9-8 #2 core from the Lower Cretaceous Donovan Sand recovered by Denbury Resources from a monitoring well drilled in the southeast region of the Citronelle Field for the SECARB Phase III Anthropogenic Test. That core provides one of the few available continuous records of Donovan sandstone bodies and intervening shale units. It contains more terrestrial redbed facies than other cores previously described in the Citronelle Field. Most strata in the core appear to represent sandy, bedload-dominated fluvial or estuarine facies and strongly oxidized vertic paleosols. Only one marine interval is preserved in the core. Diagenetic features include reduction structures that record viscous fingering between oil-bearing fluids and the original reservoir fluids. These structures demonstrate that most of the Donovan sand was deposited as redbeds and that most gray sandstone and mudstone units are the products of secondary reduction that occurred as oil migrated into the reservoir.

Most reservoir sandstone units have been correlated with the geophysical well logs, in spite of the difficulties presented by the low resolution of the logs and inaccuracy in depth determination during coring, especially where multiple reservoir sandstone units are closely spaced. A detailed stratigraphic cross section is being prepared, documenting the complex facies heterogeneity in the Citronelle Field and identifying patterns in the distribution of continental, estuarine, and barrier-shoreline facies in the Donovan Sand.

Petrographic analysis of the Donovan Sand has shown that the framework composition ranges from subarkose to arkose. Major cements in the sandstone are calcite, dolomite, and anhydrite. Calcite and anhydrite formed shortly after burial, whereas dolomite is deep burial cement. All reservoir sandstone samples show extensive evidence for feldspar dissolution, including vacuolized feldspar grains and grain-size voids that were probably once occupied by feldspar. Approximately 40% of the porosity in the Donovan Sand is dissolution porosity, and the remainder is interparticle porosity. Feldspar dissolution pre-dates hydrocarbon migration and is interpreted to be a product primarily of diagenesis in the vadose zone. Whereas felspar was dissolved from some sandstone, illuvial clay, derived in part from this dissolution, apparently accumulated in the pore system of non-reservoir sandstone. Observations in core indicate that the vast majority of the Donovan Sand was deposited as a redbed sequence and that reducing colors are largely the product of the invasion of reducing brine, most of which was oil-bearing.

Early breakthrough of CO_2 to Wells B-19-11 and B-20-5 indicates major extension of the injected CO_2 plume toward the east-northeast and the west-southwest. All of the production wells in the area were hydraulically fractured, but the injection well was not. Observations from cores indicate that natural fractures in the Donovan Sand are extremely rare, so induced fractures are expected to be the only fractures that could affect the CO_2 flood. One explanation of the early breakthrough is that the plume extended along induced fractures and was captured by wells favorably located along the maximum horizontal compressive stress. The maximum horizontal compressive stress in the subsurface of Alabama is typically between an azimuth of 70 and 80^o, consistent with the locations, relative to the injector, of production wells where early breakthrough occurred. Whether a fracture was induced in the injection well during water or gas injection is unclear, although the lack of natural fractures in the reservoir may indicate that the reservoir is under significant stress and can be fractured easily when pore pressure is increased. Unexpected plume extension has strong implications for the applicability of CO_2-enhanced recovery in Citronelle Field and should be considered when selecting injection and production wells for enhanced recovery operations.

Reservoir Fluid Properties and Phase Behavior. A rolling ball viscometer with which to measure properties of oil-CO_2 mixtures at reservoir temperature and pressure was designed, assembled, tested, and calibrated. The instrument was used to establish that the minimum miscibility pressure for Citronelle oil is 2340 ± 250 psig, well below the upper limit of 2800 psi reported by Gilchrist (1981). A miscible CO_2 flood is therefore virtually assured in the Upper Donovan Sands at Citronelle, at depths near 11,000 feet. The rolling ball viscometer is also an excellent tool with which to evaluate two important influences on miscibility: (1) the effects of impurities such as N_2 naturally present in a formation, or remaining in CO_2 after incomplete separation from gaseous combustion products, and (2) the extension of oil-CO_2 miscibility through addition of other gas constituents, such as light hydrocarbons, a component of the advanced CO_2-EOR technology proposed by Kuuskraa and Koperna (2006) and Kuuskraa et al. (2011).

A high-pressure, high-temperature system has been developed to study the interactions of CO_2 with oil, under reservoir conditions, by visual observation of the development of miscibility between CO_2 and the oil. The gas behavior and pressure changes inside the system are monitored and recorded using a data acquisition system. The system has undergone preliminary testing using water and CO_2 up to 900 psig. A modification to the pressurization system has been made to increase the pressure limit to 3,500 psig. Measurements of the solubility of CO_2 in water compared favorably with a computer model of carbon dioxide-water solubility behavior.

Petroleum Reservoir Simulation. With recently implemented enhancements and improvements, fine-scale simulations of 50 years of waterflooding at the pilot test site were accomplished using nSpyres, the open-source, in-house reservoir simulator under development by Eric Carlson at the University of Alabama. The simulation used a regular grid of 8.2 million cells, each measuring 52.8 x 52.8 x 1 ft. The purpose of these simulations is to evaluate water migration and saturation trends prior to CO_2 injection. The reservoir was divided into two regions: a "pay" zone having high porosity and permeability, and a "not-pay" zone having very low porosity and permeability. Vertical permeability in the pay zone is one-tenth of its horizontal permeability. Cumulative oil production increased with increasing permeability in the pay zone and the water cut increased with time as the waterflood progressed, as expected, but the water rate was lower than observed. In the next phase of the simulation study, geostatistical methods will be applied to generate permeability distributions leading to high flow capacity zones, consistent with the early breakthrough of CO_2 observed in the field. Enhanced local directional permeability will be introduced to mimic hydraulic fractures around the wells. The primary reservoir engineering objectives are:

1. To investigate plausible alternatives to the extensive well hydro-fracture model shown in Figure 2.2.2 to explain well test results and early CO_2 breakthrough.
2. To explore the significance of the pilot-test results for the field as a whole.

3. To develop new technologies/methodologies that will let us accurately simulate the effects of discrete fractures.

Eric Carlson estimates that 11 million bbl of oil would be recovered over the next 50 years, by continuing conventional secondary recovery at Citronelle, only a small fraction of the (very conservatively) estimated 200 million bbl remaining in place.

A parametric study of WAG recovery, using the MASTER 3.0 reservoir simulator, showed that a properly designed WAG recovers more oil than continuous CO_2 injection. The optimum cycle, under conditions expected to be representative of the Citronelle Field, and over a 10-year project, is 12 months of CO_2 injection followed by 6 months of water injection. Using the simulation results, three-dimensional animations were programmed showing the evolution of fluid saturations in Donovan Sands 14-1 and 16-2 during two CO_2 injections of 7500 tons each, separated by water injection. The animations nicely capture the mobilization of oil by CO_2, development of the oil bank, the role of water in driving the bank, and the residual oil left unrecovered. A study of the sensitivity of oil recovery to reservoir permeability showed that oil recovery increased with decreasing permeability, due to the associated decrease in mobility and increase in CO_2-oil contact time. Notice the contrast between this response and that during the simulation of waterflooding described in the previous paragraph.

CO_2 Liquefaction, Transportation, and Storage. A 50-ton, refrigerated, liquid CO_2 storage tank was purchased from the TOMCO_2 Equipment Co. (Loganville, GA), moved to Citronelle, and installed on a pad at the test site in December 2008. Airgas Carbonic was chosen from among three bidders to provide liquefaction and transportation services. The first shipment of 40 tons of CO_2 was delivered by Airgas to Citronelle on March 2, 2009. Scheduling of deliveries to maintain CO_2 supply was not a problem until near the end of the Phase II test, when injection rates increased to ~40 tons/day, sometimes requiring delivery of three tanker truckloads of liquid CO_2 per day.

Well Preparation, Water Flood, and CO_2 Injection. Water flood, to establish baseline production, began in March 2008. Oil production from each of the four producers, under water flood, ranged from 4 to 9 bbl/day. An interference test established that there is communication between the injector and at least one nearby producer. No obvious short circuits or evidence for significant layering were detected. The low effective permeability of the sands suggested the presence of low permeability baffles and relative permeability effects on total mobility. An injection profile run in the injector showed that Sand 14-1 was taking water at a higher rate than Sand 16-2 (82 and 18% of the flow, respectively). A second tracer test, during CO_2 injection, showed that 57% of the CO_2 was flowing to Sand 14-1 and 43% to Sand 16-2. The injector, four producers, CO_2 storage tank, charge pump, triplex pump, piping, flow meters, and gas/liquid separators were in place, connected, and prepared for CO_2 injection in July 2009. During the period from July to November 2009, the principal barrier to CO_2 injection was poor performance of the triplex positive displacement pump. Modifications to the pump enabled the Denbury Onshore group in Citronelle to begin continuous CO_2 injection on January 27, 2010, and maintain an average injection rate of 31 tons/day to the end of the injection on September 25, 2010.

Response to CO_2 Injection. Breakthrough of CO_2 was detected at Well B-19-11, the well farthest from the injector, in May 2010, and at two other wells (B-19-8 and B-19-9) in August 2010. The carbon-13 to carbon-12 isotope ratio in CO_2 was used to positively establish the presence of injected CO_2 in produced gas. A survey of the CO_2 content of produced gas from wells within and outside the test pattern on April 12, 2011, detected CO_2 levels above that in native Citronelle gas (> 3 vol%) at Wells B-19-11 (57 vol%) and B-19-8 (25 vol%) in the inverted five-spot test pattern, at Well B-20-5 (10 vol%) to the northeast of the injector, and at Well A-25-10 (15 vol%) far to the southwest of the test pattern.

Incremental oil appeared in January 2010 at B-19-8 Tank Battery, where oil from three of the producers in the inverted five-spot is collected, and continued through September 2010, reversing a long period of declining production. However, several problems associated with the CO_2 injection then surfaced, including excessive gas production at the well where CO_2 first appeared (Well B-19-11), a low water injection rate on returning to water injection at the conclusion of the CO_2 injection, and excessive wear of the down-hole power oil pumps due to erosion by particulate and scale mobilized by the carbon dioxide. As a result, oil production at B-19-8 Tank Battery suffered a marked decline from October 2010 to March 2011, to less than half of the rate just before the start of CO_2 injection. Improvements to the power oil pumps restored the frequency of pump pulls to normal and oil production at B-19-8 Tank Battery recovered some of its loss over the next 12 months, returning to 44 bbl/day in March 2012. The recent average rate of 39-40 bbl/day is lower than the peak rate of 59 bbl oil/day recorded in September 2010 and slightly less than the rate of 45 bbl oil/day just before the start of CO_2 injection in December 2009, but it is significantly higher than the decline curve established during the 10 months from March to December 2009, just prior to CO_2 injection.

Integration of the difference between the actual oil production and the production anticipated by the decline curve established before CO_2 injection, over the period from January 2010 to December 2013, gives an (unofficial) estimate of incremental oil production at B-19-8 Tank Battery of 25,411 bbl, consistent with the approximately 20,000 bbl of incremental recovery predicted by Eric Carlson's reservoir simulations using SENSOR (Coats Engineering, Inc.), though it has taken longer to achieve it, as expected, considering that the production figure is for only three of the four producers and the problems with the power oil pumps.

The response to CO_2 injection at B-19-11 Tank Battery, where oil from the fourth producer in the inverted five-spot is collected, was quite different from that observed at B-19-8 Tank Battery. In contrast to the immediate increase in oil production observed at B-19-8 Tank Battery, production at B-19-11 Tank Battery continued for four months on the trajectory that it had been following for the previous 10 months. Then, coinciding with the breakthrough of CO_2 at Well B-19-11, production at the battery abruptly declined, by approximately the typical production from Well B-19-11 (8 to 9 bbl/day), then continued a steady decline, with no significant response to the termination of CO_2 injection and return to water injection in September 2010. Integration of the difference between the decline curve and production data for B-19-11 Tank Battery, from January 2010 to December 2013, gives an (unofficial) incremental deficit of -20,981 bbl. Combining the deficit with the incremental production at B-19-8 Tank Battery gives an overall gain, to December 31, 2013, of 25,411 - 20,981 = 4430 bbl.

Surface Monitoring. A detailed study of soil conditions at the test site is being conducted by members of the AAMU team, including measurements of soil moisture, temperature, pH, electrical conductivity, carbon, nitrogen, phosphorus, and CO_2 fluxes at three locations surrounding four of the five wells in the test pattern and around the plugged and abandoned well within the pattern. Four sets of soil samples and eight sets of soil gas samples were collected from August 2008 to June 2012. Carbon dioxide fluxes from soil range from approximately -1 to +2 mg/(m^2·min), depending on location, and exhibit seasonal changes. The fluxes at all of the measurement sites were positively correlated with soil temperature and the measurements at most sites were negatively correlated with soil moisture, as expected. Soil gas samples collected in August 2010, toward the end of the Phase II CO_2 injection, showed no evidence of CO_2 seepage.

CO_2 in ambient air was measured at least once each quarter, from September 2007 to June 2012, at 104 sampling locations in the Citronelle Oil Field and City of Citronelle. Only one anomalous reading appears in the entire set of CO_2 measurements, in June 2009, after filling the CO_2 storage tank in March 2009 and during unsuccessful attempts to inject CO_2, but before continuous CO_2 injection began in December 2009. The rest of the CO_2 measurements are consistent with the seasonal variations and long-term trends of the local NASA satellite-based Atmospheric Infrared Sounder data and worldwide average atmospheric CO_2 levels.

Ten meter by ten meter square test plots were established near the injector, producers, and tank batteries, in which to monitor growth of vegetation. Inventories of the vegetation plots were conducted in 2008, 2009, 2010, and 2011. Comparison of the growth rates during 2008-2009 with those during 2009-2010 shows that the plant growth rate increased from the first period to the second in two plots and decreased in five of them. Comparison of the growth rates during 2009-2010 with those during 2010-2011 shows that the plant growth rate increased from the second period to the third in three plots and decreased in five of them. The overall trend is one of decreasing growth rates, rather than the increase in rates that might be expected under the influence of elevated levels of CO_2.

One plot did exhibit a significant and consistent increase in the rate of growth of vegetation during the four-year period. That plot is located near the injector, Well B-19-10 #2. This is an interesting observation, in view of the fact that elevated levels of CO_2 in ambient air were not consistently detected there, nor were elevated CO_2 fluxes from soil observed near that well. Nonetheless, vegetation near Well B-19-10 #2 may have been influenced by CO_2 from the pilot test. With the exception of Well B-19-10 #2, the differences in growth rate from place-to-place and year-to-year are more likely explained by patterns of rainfall, temperature, and solar insolation than by CO_2 plumes associated with the CO_2 storage tank, injection equipment, wells, or tank batteries.

Seismic Imaging and Geostability Analysis. Constraints imposed by the nature of land ownership and use at the test site required examination of alternatives to traditional seismic imaging techniques, but the great depth and small thickness of the target sands made this task especially challenging. A passive sensing technique using wireless sensors and Refraction Microtremor (ReMi) technology was developed that is able to construct subsurface seismic profiles at the test site using only ambient noise. Shear-wave velocity profiles were constructed from data recorded during nine field measurement campaigns, before, during, and following CO_2 injection.

Geomechanical stability analyses were performed using a 1-dimensional effective stress model, a 3-dimensional finite element model, and the geophysical testing results. Both models indicate only small deformations as a result of overburden pressure on the Donovan Sands (0.56 to 0.75 ft for the Upper Donovan and 0.28 to 0.39 ft for the Lower Donovan) and a strain rate of 0.14 to 0.19%, below the expected rupture limit of 0.3% for quasi-brittle materials. This work completed the critical path milestone entitled, "Geomechanical Stability Analysis."

An interesting trend appears in the time dependence of the slope of shear-wave velocity versus depth in the region below about 5000 ft. While the slope in the upper region, above ~4000 ft, has remained within relatively narrow limits during CO_2 and subsequent water injection, the slope in the lower region, below ~5000 ft, which was initially much steeper, has been steadily declining and approaching the slope in the upper region, evidently a result of pressurization by CO_2 and water.

The record of normalized well-head pressure at the injector is consistent with the normalized equivalent stresses from the seismic sensor array at the depth of the target Donovan Sands during CO_2 injection. This encouraging result suggests that the geophysical testing technique may be useful for monitoring formation pressure.

A laboratory experiment has been designed and set up at UNCC, with which to measure the effects of solid matrix composition, porosity, and fluid saturations (oil, water, and CO_2) on stiffness and shear-wave velocity. The results of these experiments are intended to assist in the interpretation of the observed variation of shear-wave velocity with depth and the volumes of CO_2 and water injected in the field.

Reservoir Management. Three unexpected problems were experienced during and following the Phase II injection of CO_2 for enhanced oil recovery at Citronelle:

1. Erosion of the power oil pumps by particulate and scale mobilized by the CO_2.
2. Early and excessive breakthrough of CO_2 at producers in the directions east-northeast and west-southwest from the injector.
3. Low injectivity to water following the CO_2 injection.

The pump erosion problem was solved by switching to power oil pumps having longer stoke and fabricated using harder materials. The frequency of pump pulls from wells on the tank battery most affected (B-19-8) has returned to normal levels and oil production at the battery has recovered, from a low of 21 bbl/day in March 2011, to an average of 39 bbl/day from June 2011 to December 2013.

A pressure-transient test on the injection well in November and December 2011 revealed a fracture thought to be responsible for early breakthrough of CO_2 at wells far removed from the injector and a likely contributor to poor sweep efficiency. The completely unexpected discovery of the fracture is one of the most important accomplishments of recent work under the project. Though the direction of the fracture cannot be determined from the results of the pressure-transient test, the locations of the wells where early breakthrough was observed lie in the direction of maximum horizontal compressive stress in the Southeast.

The third problem is the low injectivity to water. Not having the ability to inject water after CO_2 would limit the options available for reservoir management. Constructing a pipeline to Citronelle from Jackson Dome is a large and costly undertaking. An attractive option is to use CO_2 captured from coal combustion products at Alabama Power Company's Plant Barry, 11 miles from Citronelle. It is with this scenario in mind that a large-scale demonstration of CO_2 capture, pipeline transport, and underground injection for storage in the Southeast Citronelle Unit is underway at Plant Barry, led by the Southeast Regional Carbon Sequestration Partnership (SECARB) and primary sponsors, U.S. DOE, National Energy Technology Laboratory, and Southern States Energy

Board, with industrial partners, Advanced Resources International, Alabama Power Co., Denbury Resources, Electric Power Research Institute, Geological Survey of Alabama, Southern Company, and Southern Natural Gas (Esposito et al., 2011b; Koperna et al., 2012). WAG would be an attractive option if CO_2 were supplied from Plant Barry, because it would provide a means to adjust for planned and unplanned outages at the Plant, stretch a limited CO_2 supply for EOR, and because WAG can increase oil recovery, as shown by the simulations using MASTER 3.0 (Theodorou, 2013).

An injection profile test was conducted in January 2012 to determine if either of the target sands was primarily responsible for the low water injection rate. The test established that 35% of the water flow was to Sand 14-1 and 65% was to Sand 16-2, so neither injection zone was completely blocked, but comparison with the results of an injection profile run before CO_2 injection showed that loss of flow into the upper Sand 14-1 was primarily responsible for the low injectivity to water.

Denbury Onshore's chemicals supplier was contracted to add surfactant to the water at the injector, to reduce capillary pressure, should CO_2 be blocking the water flow. Injection of Baker Hughes Surfactant WCW87 began on July 25, 2012 at the rate of 4 gallons/day. The high initial rate was reduced to 2 quarts/day on August 1 and continued to November 7, 2012. The water injection rate during surfactant injection, and during the period from July 30 to October 14, 2012, when the pressure was constant at 3900 psig, averaged 95 bbl water/day. During the period following CO_2 injection but before the surfactant treatment, from September 26, 2010 to July 24, 2012, on the days when the pressure was 3900 psig, the average water injection rate was 63 bbl water/day. The surfactant treatment was therefore associated with a 50% increase in injection rate. The ability of the surfactant to increase injectivity indicates that capillary pressure at the interfaces between water or brine and CO_2 trapped in pores is the likely cause of at least part of the loss in injectivity. However, the increase accompanying surfactant injection did not come close to restoring the injection rate to the average level of 160 bbl water/day before CO_2 injection, when the average pressure was only 3600 psig. The conclusion from the surfactant treatment is that while capillary blocking of water injection is significant, it is not the only effect responsible for the loss in injectivity experienced on returning to water injection following the CO_2 slug.

Flakes of the internal plastic coating (IPC) of the tubing were found in the injector during repair of a tubing leak. Plugging of perforations by fragments of the IPC is considered the most likely cause of the well's low injectivity to water following the CO_2 injection. Problems with IPC were experienced by Denbury Resources throughout its oilfield operations. The cause of the problem was determined to be a lapse in quality control on the part of the tubing supplier.

Treatment of the injector with hydrocarbon solvent and dispersant had only a small effect on its injectivity to water. Paraffins and asphaltenes left behind when supercritical CO_2 mobilized lighter components are not thought to have made a significant contribution to the loss in injectivity to water following the CO_2 injection.

The combined effects of a change to uncoated tubing, treatment with solvent, and flow-back to clear the IPC fragments was a small increase in water injection rate, from a range of 77 to 87 bbl/day to the range from 79 to 94 bbl water/day. Flow-back appears to have had the most lasting effect, supporting the suggestion that flaking of the IPC is the likely cause of poor injectivity to water following the CO_2 injection.

Reservoir simulations using SENSOR showed that cumulative oil production increases with increasing amount of CO_2 injected, regardless of the assumed permeability distribution. However, in all cases considered, there was an optimum CO_2 slug size, from the point of view of the profitability of a CO_2-EOR project. The optimum size of CO_2 slug increases with increasing oil price. The discount factor has little impact on the optimum size of CO_2 slug at high oil prices, but does have some impact at low oil prices.

An investigation of WAG performance was conducted using the MASTER 3.0 reservoir simulator, to compare incremental oil yield and CO_2 storage under different WAG schedules. WAG is preferred if CO_2 supply at Citronelle is limited. According to the model examined, all except one of the WAG scenarios (2 months CO_2 - 6 months water) outperformed incremental oil production from CO_2-only injection. The best performing sequence, with respect to oil recovery, was 12 months of CO_2 injection followed by 6 months of water injection, as mentioned under *Petroleum Reservoir Simulation*, above. The net amount of CO_2 stored can be increased by 40%, by lengthening the period of CO_2 injection from 12 months to 24 months, with only a 1.4% penalty in incremental oil production.

Kuuskraa et al. (2004) estimated the oil recoverable from Citronelle Field using CO_2-EOR to be 64 million bbl, or 17% of the original oil in place. Denbury Resources' estimate of the Field's EOR potential is 26 million bbl. Assuming 10% of OOIP to be economically recoverable (38 million bbl) using CO_2-EOR and a production rate increased to 1.2 million bbl/year (twice present production), the life of the field would be extended by 30 years.

The capacity of Citronelle Dome for CO_2 storage is estimated to be 530 to 2100 million short tons (Esposito et al., 2008), sufficient to sequester the CO_2 produced from coal-fired generation at nearby Alabama Power Plant Barry for 40 years. Plant Barry is the host site for a major demonstration of carbon capture and sequestration technology, including pipeline transport and geologic storage of CO_2 in a saline formation in Citronelle Dome, now in progress (Esposito et al., 2011b; Koperna et al., 2012).

Acronyms and Abbreviations

AAMU	Alabama Agricultural and Mechanical University, Normal, AL
ANSYS	ANSYS, Inc., Canonsburg, PA
DOE	U.S. Department of Energy
DoReMi	derivative of refraction microtremor
DRI	Denbury Resources, Inc., Plano, TX, and Citronelle, AL
EOR	enhanced oil recovery
FBG	fiber Bragg grating
GSA	Geological Survey of Alabama, Tuscaloosa, AL
IMPES	implicit pressure, explicit saturation
LBNL	Lawrence Berkeley National Laboratory, Berkeley, CA
MASTER	Miscible Applied Simulation Techniques for Energy Recovery (Ammer and Brummert, 1991; Ammer, Brummert, and Sams, 1991; Zeng, Grigg, and Chang, 2005)
MMP	minimum miscibility pressure
NDVI	normalized difference vegetation index
NETL	National Energy Technology Laboratory
OOIP	original oil in place
SAS	Statistical Analysis System (SAS Institute Inc., Cary, NC)
SCARC	simulated carbon ash retention cylinder
SECARB	Southeast Regional Carbon Sequestration Partnership
SENSOR	System for Efficient Numerical Simulation of Oil Recovery (Coats Engineering, Inc., 2009)
SEQ	sequential implicit
STB	stock tank barrel
ReMi	refraction microtremor
TOUGH	Transport of Unsaturated Groundwater and Heat (Pruess et al., 1999; Pruess, 2005; Pruess and Spycher, 2006; Xu et al., 2004a, 2004b)
UA	University of Alabama, Tuscaloosa, AL
UAB	University of Alabama at Birmingham, Birmingham, AL
UIC	Underground Injection Control
UNCC	University of North Carolina at Charlotte, Charlotte, NC
WAG	water-alternating-gas method of enhanced oil recovery

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Appendix A: Statement of Project Objectives, October 14, 2010

A.1. Objectives

The objectives of the work are: (1) to assess the oil recovery potential and identify the optimum conditions for a commercial carbon-dioxide-enhanced oil recovery (CO_2-EOR) project in the Citronelle Oil Field, in Mobile County, Alabama, and (2) determine the capacity of the depleted oil reservoir and adjacent saline formations for carbon dioxide storage.

A.2. Scope of Work

The technical work to be done under the project is divided into three phases, each of 20 months duration. The emphasis in Phase I was on selection of a test site, detailed study of its geology, determination of oil-CO_2 minimum miscibility pressure, simulation of CO_2-EOR, and establishment of background conditions at the test site. The focus in Phase II is on the first CO_2 injection and associated measurements and monitoring. The focus in Phase III will be on the second CO_2 injection and a comprehensive evaluation of the results of both tests.

A.3. Tasks to be Performed

Phase I (Budget Period 1: January 1, 2007 - August 31, 2008)

<u>Task 1.0 - Establish Collaboratory Environment</u>

The Recipient shall set up a secure web-based system, to which only the project partners will have access, for on-line discussion, exchange of data, distribution of information, and monitoring of project activity.

Task 2.0 - Establish Publicly Accessible Web Site

The Recipient shall set up a website describing the project.

Task 3.0 - Application for Permit to Conduct Field Test No. 1

The Recipient shall apply for a Class II Underground Injection Control (UIC) permit from the State of Alabama for injection of CO_2 at the site.

Task 4.0 - Analysis of Rock Samples

The Recipient shall measure porosities and permeabilities of 19 plugs from the drill core from the injection well taken at one-foot intervals in the target sands. The Recipient shall perform microscopic analyses to determine the lithology of at least 12 of those plugs.

Task 5.0 - Analysis of Oil and Oil-CO_2 Interaction

The Recipient shall determine the minimum miscibility pressure of a sample of oil from Citronelle, evaluate the propensity for oil components to precipitate in the presence of CO_2, and measure the viscosity of the oil at reservoir temperature as a function of CO_2 pressure.

Task 6.0 - Construct Advanced Geologic Models of Rodessa Reservoirs

The Recipient shall incorporate in the model the results of the analysis and information from the updated site stratigraphy provided by the work under Task 4.0. The Recipient shall quantify and visualize reservoir architecture and heterogeneity using methods, such as architectural element analysis and sequence stratigraphy, and technologies, such as immersive 3D visualization, not employed in earlier work.

Task 7.0 - Reservoir Simulation

The Recipient shall examine the available reservoir simulators and choose the one best suited for simulation of oil production using CO_2-EOR. The Recipient shall perform at least 30 simulations during Phase I of the project to provide analysis that will assist in selection of the test and monitoring wells (Task 8.0), development of the reservoir management plan (Task 11.0), the economic and market analysis (Task 12.0), and visualization of the flows (Task 13.0).

Task 8.0 - Selection of Test and Monitoring Wells

The Recipient shall choose an injection well and four surrounding wells for testing, based upon analysis of drill cores from the Geological Survey of Alabama collection, production records of the Alabama State Oil and Gas Board, and calculations using the reservoir simulator.

Task 9.0 - Geophysical Testing Method Development

The Recipient shall acquire equipment for passive sensing and develop a technique for geophysical testing that is able to detect microseismic signals at the injection well.

Task 10.0 - Baseline Soil CO_2 Fluxes and Ecology

The Recipient shall establish baseline CO_2 concentrations and fluxes from soil, tabulate the sizes and species of vegetation, and quantify the ecology in test plots established near each of the five wells in the test pattern, as found.

Task 11.0 - Reservoir Simulation

The Recipient shall, on the basis of the available data, the 30 reservoir simulations (Task 7.0), and the economic and market analysis (Task 12.0), develop a preliminary CO_2 injection strategy to optimize oil recovery and revenue.

Task 12.0 - Economic and Market Analysis

The Recipient shall verify that production using CO_2-EOR at this site is viable under current and projected economic conditions. Input to the analysis will be obtained from the results of the analysis of miscibility (Task 5.0), geologic modeling (Task 6.0), reservoir simulation (Task 7.0), and development of the reservoir management plan (Task 11.0).

Task 13.0 - Visualization of Geologic Structure and Flows

The Recipient shall prepare graphic displays of the geologic structure in the vicinity of each of the five test wells and the results of the calculations of oil, water, and CO_2 flows using the reservoir simulator.

Task 14.0 - Preparation of Wells for Field Test No. 1

The Recipient shall develop the plan for transport, storage, and injection of CO_2 and provide for onsite storage of CO_2, installation of CO_2-compatible flow lines, the skid for the compressor, replacement of the well head, and workover of the wells, where required.

Task 15.0 - Water Injection

The Recipient shall conduct five months of water injection into the test pattern, to provide background production data, to bring the five-spot to a typical water-flooded condition, and to reach the minimum miscibility pressure.

Task 16.0 - Justification for Proceeding to Phase II

The Recipient shall prepare and submit, by August 31, 2008, a Continuation Application justifying continuation of the work into Phase II, including: (1) a report on the progress toward meeting the objectives of Phase I, including all significant findings, conclusions, and developments, (2) the plan for injecting 7500 tons of CO_2 during Field Test No. 1 and performing the associated geophysical and environmental measurements and reservoir simulations, and (3) updated economic, market, and environmental analyses and reservoir management plan, with reevaluation of the long-term viability of the project.

Phase II (Budget Period 2: September 1, 2008 - December 31, 2010)

Task 17.0 - Field Test No. 1

The Recipient shall inject 7500 tons of carbon dioxide into the test pattern for measurement of transient behavior (pressure decay following an injection pulse) and flow versus pressure. The Recipient shall monitor surrounding wells B-19-7, B-19-8, B-19-9, and B-19-11 twice each month, for produced oil, water, and gas, including CO_2.

Task 18.0 - Site Characterization by Geophysical Testing

The Recipient shall perform seismic measurements before, and two months after the start of CO_2 injection, to observe the effects of CO_2 flooding.

Task 19.0 - Ecological Processes Dynamics

The Recipient shall monitor, once each month, any changes in the surrounding landscape during and following injection of carbon dioxide into the oil reservoir, to observe any evolution of the types, populations, and spatial distributions of vegetation on the site, in the soil, and in the surrounding landscape over the course of the project.

Task 20.0 - Monitor for Seepage

The Recipient shall make monthly measurements of CO_2 in shallow boreholes and measure concentration profiles in soil near the surface to determine whether CO_2 seeps from the formation to the atmosphere.

Task 21.0 - Analysis of Data from Field Test No. 1

The Recipient shall prepare a complete analysis and summary of the test data and associated environmental measurements.

Task 22.0 - Effect of Nitrogen on Oil-CO_2 Interaction

The Recipient shall determine the sensitivity of the minimum miscibility pressure to the nitrogen content of CO_2, at four levels of nitrogen over the range from 0 to 40 vol%, and at reservoir temperature, to establish the degree of separation of flue gas and other process streams required for successful and economic CO_2-EOR and sequestration.

Task 23.0 - Geomechanical Stability Analysis

The Recipient shall conduct a geomechanical stability study, including production-induced stress analysis and reservoir stability analysis through finite element nonlinear static stress analysis (ANSYS) and Distinct Element Analysis (3DEC from Itasca). A stability analysis of the anhydrite dome will be conducted assuming uplift pressure from supercritical CO_2 permeating into the dome via fault or fracture points.

Task 24.0 - Refine the Reservoir Simulation

The Recipient shall, based upon the results of Field Test No. 1, refine the physical submodels and parameters describing the geologic structure and flows in the reservoir, to improve the accuracy of the simulation of supercritical carbon dioxide behavior in oil-bearing porous rock formations.

Task 25.0 - Refine the Visualization of Oil, Water, and CO_2 Flows

The Recipient shall improve the visualization and perform a parametric study of oil yield, examining at least 30 sets of conditions, using the reservoir simulator.

Task 26.0 - Refine the Reservoir Management Plan

The Recipient shall incorporate the results from Field Test No. 1 in an updated reservoir management plan.

Task 27.0 - Selection of Test and Monitoring Wells for Field Test No. 2

The Recipient shall based upon available engineering analysis of the data (the results from Field Test No. 1, analysis of rock samples from the wells (Task 4.0), the geology in the vicinity of the test wells (Task 6.0), reservoir simulations (Tasks 7.0 and 24.0), the environmental measurements (Tasks 10.0, 19.0, and 20.0), geophysical testing (Task 18.0), and the need for data with which to refine the reservoir management plan (Task 26.0)), decide whether to conduct Field Test No. 2 using the same wells, or choose another set of five wells for testing in consultation with DOE.

Task 28.0 - Application for Permit to Conduct Field Test No. 2

The Recipient shall apply, if necessary, for another Class II Underground Injection Control (UIC) permit from the State of Alabama for the second injection of CO_2.

Task 29.0 - Geophysical Testing

The Recipient shall continue semiannual seismic measurements at the site of Field Test No. 1 and perform seismic measurements before, and two months after the start of CO_2 injection at the site of Field Test No. 2, if different wells are selected.

Task 30.0 - CO_2 Fluxes and Ecology

The Recipient shall continue monthly monitoring for CO_2 seepage at the site of Field Test No. 1 and perform monthly baseline measurements at the site of Field Test No. 2, if different.

Task 32.0 - Justification for Proceeding to Phase III

The Recipient shall prepare and submit the Continuation Application justifying continuation of the work into Phase III, including: (1) a report on the progress toward meeting the objectives of Phases I and II, describing all significant findings, conclusions, and developments, (2) the plan for injecting 7500 tons of CO_2 during Field Test No. 2 and performing the associated geophysical and environmental measurements and reservoir simulations, (3) updated economic, market, and environmental analyses and reservoir management plan, with reevaluation of the long-term viability of the project, and (4) a concise description of the additional insight, knowledge, data and findings that are expected from Field Test No. 2

Phase III (Budget Period 3: January 1, 2011 - January 31, 2014)

Task 31.0 - Preparation for Field Test No. 2

The Recipient shall prepare the wells and site for the second CO_2 injection, including provision for onsite storage of CO_2, installation of CO_2-compatible flow lines, the skid for the compressor, replacement of the well head, and workover of wells, where required.

Task 33.0 - Field Test No. 2

The Recipient shall inject 7500 tons of CO_2 into the chosen test pattern under the optimum conditions identified in Field Test No. 1 and confirmed by using reservoir simulation (Task 7.0). The Recipient shall collect detailed surface and downhole data (pressure, flows, seismic, and environmental) for refinement of the CO_2-EOR simulation and monitor the production wells in the test pattern for produced oil, water, and gas, including CO_2.

Task 34.0 - Monitoring by Geophysical Testing

The Recipient shall repeat the geophysical tests conducted in Phases I and II on a semiannual basis at the sites of the earlier injections, to monitor the migration of CO_2 and the stability of the formation, and to identify possible deviations from initial projections.

Task 35.0 - Ecosystem Dynamics

The Recipient shall model the behavior of surrounding ecosystems and landscapes associated with the CO_2 injections, using as input the results from Task 19.0 and supplemental information about streams, bodies of water, and regional processes such as carbon cycling. The Recipient shall simulate, using these data, in combination with the underlying mechanisms of ecological processes, the ecosystem and landscape dynamics in subsequent years. Cellular automata and ecosystem dynamics models will be used in the first stage, then, depending on impacts, more comprehensive spatially explicit models may be employed.

Task 36.0 - Presentation of Results as Dynamic Simulations

The Recipient shall display, using the reservoir simulation, the flows of CO_2, oil, and water as functions of reservoir properties and time, the oil yield by CO_2-EOR, and the capacity of the formation for CO_2 sequestration.

Task 37.0 - Refine the Reservoir Management Plan

The Recipient shall incorporate the results of Phase II in an updated reservoir management plan.

Task 38.0 - Geophysical Testing

The Recipient shall continue semiannual seismic measurements at the site of Field Test No. 1.

Task 39.0 - Soil Fluxes and Ecology

The Recipient shall continue monthly monitoring for seepage at the site of Field Test No. 1.

Task 40.0 - Geophysical Monitoring of the Flood

The Recipient shall perform semiannual seismic measurements to monitor the progress of the CO_2 flood and changes in the formation during Field Test No. 2.

Task 41.0 - Ecological Processes Dynamics

The Recipient shall continue monthly monitoring of the ecology in tests plots at each well, at the sites of Field Test No. 1 and Field Test No. 2.

Task 42.0 - Monitor for Seepage

The Recipient shall make monthly measurements for seepage of CO_2 at the site of Field Test No. 2.

Task 43.0 - Analysis of Data from Field Test No. 2

The Recipient shall prepare a complete analysis and presentation of the test data and associated environmental measurements.

Task 44.0 - Comprehensive Assessment and Dissemination of Results

The Recipient shall prepare and submit to DOE/NETL the Final Scientific/Technical Report, containing a complete analysis of oil recovery, estimates of capacity and integrity of storage, ecological effects, economic and market analysis, and the prospects for separation and sequestration of CO_2 from sources in the region. This will include a topical report on the capability of the Rodessa Formation for storage of CO_2. Dissemination of results via the final report to DOE, presentations, and publications.

<u>Task 45.0 - Follow Up</u>

The Recipient shall continue to monitor production, seepage, ecological effects, and progress of negotiations for transition of the Citronelle Oil Field to a CO_2 sequestration site on completion of production from the Field. The Recipient shall continue to inform industry and DOE/NETL of new developments.

A.4. Deliverables

The recipient shall provide reports in accordance with the Federal Assistance Reporting Checklist and Instructions accompanying the checklist, attached to the Notice of Financial Assistance Award:

- Quarterly Progress and Financial Status Reports will be submitted within 30 days after the end of each quarter, beginning with the quarter ending on March 31, 2007.
- Special Status Reports will be submitted immediately (within 3 working days), to transmit results having major impact on the course of the project.
- Informal Reports to the DOE Contracting Officer's Representative on completion of Critical Path Milestones.
- Topical Report on the Rodessa Formation CO_2 sequestration capability. Other Topical Reports will be submitted, when appropriate, to describe significant new technical advances.
- Final Scientific/Technical Report, including raw data, models, and relevant field data, submitted within 90 days after the end of the project, before March 30, 2012.
- Scientific/technical conference papers and proceedings.

- Patent and Property Certifications will be submitted at the conclusion of the project, i.e. on December 31, 2011. The Final Financial Status Report will be submitted within 90 days after the end of the project, before March 30, 2012.

A.5. Briefings/Technical Presentations

The Recipient shall prepare and present technical papers at the DOE/NETL Annual Conferences on Carbon Capture and Sequestration, organized by NETL and held in Pittsburgh, PA.

The Recipient shall invite representatives from NETL to attend, either in person or by teleconference, meetings of the research team held periodically in Birmingham, Tuscaloosa, or Citronelle, AL, to review the progress of the project and plan future work.

Appendix B: Technology Transfer

B.1. Presentations and Workshops

J. C. Pashin and R. A. Esposito, "Citronelle Dome: A Giant Opportunity for Multi-Zone Carbon Storage and Enhanced Oil Recovery in the Mississippi Interior Salt Basin of Alabama," Presented at the Annual Convention and Exhibition of the American Association of Petroleum Geologists, Long Beach, CA, April 1-4, 2007.

J. C. Pashin, R. A. Esposito, and P. M. Walsh, "Citronelle Dome: A Giant Opportunity for Multi-Zone Carbon Storage and Enhanced Oil Recovery in the Mississippi Interior Salt Basin of Alabama," Poster presentation at the DOE/NETL Sixth Annual Conference on Carbon Capture and Sequestration, Pittsburgh, PA, May 7-10, 2007.

E. S. Carlson, Workshop on visualization for reservoir simulation, Rocky Mountain Mathematics Consortium Summer School, "Flow in Porous Media with Emphasis on Modeling Oil Reservoirs," University of Wyoming, Laramie, WY, June 18-29, 2007.

Wen-Ya Qi, Shen-En Chen, P. M. Walsh, R. A. Esposito, and J. C. Pashin, "Geosensing for CO_2 Sequestration Monitoring in an Oil Field: Possible Global Warming Solution," Presented at the 3rd National Conference on Environmental Science and Technology, North Carolina A&T State University, Greensboro, NC, September 12-14, 2007.

J. C. Pashin and R. A. Esposito, "Citronelle Dome: A Giant Opportunity for Multi-Zone Carbon Storage and Enhanced Oil Recovery in the Mississippi Interior Salt Basin of Alabama," Presented at the 2007 Annual Convention of the Gulf Coast Association of Geological Societies and the Gulf Coast Section of the Society for Sedimentary Geology, Corpus Christi, TX, October 21-23, 2007.

R. A. Esposito, J. C. Pashin, and P. M. Walsh, "Citronelle Dome: A Giant Opportunity for Multi-Zone Carbon Storage and Enhanced Oil Recovery in the Mississippi Interior Salt Basin of Alabama," *Gulf Coast Association of Geological Societies Transactions*, **2007**, *57*, 213-224.

J. C. Pashin, "CO_2-EOR Pilot in Tidal Deposits of the Cretaceous Donovan Sand, Citronelle Field, SW Alabama," Presented at the Annual Convention and Exhibition of the American Association of Petroleum Geologists, San Antonio, TX, April 20-23, 2008.

J. C. Pashin, R. A. Esposito, and P. M. Walsh, "Pilot Design for CO_2-EOR and Sequestration Potential in the Citronelle Oil Field in the Mississippi Interior Salt Basin of Alabama," Presented at the Seventh Annual Conference on Carbon Capture and Sequestration, Pittsburgh, PA, May 5-8, 2008.

J. C. Pashin, "CO_2-Enhanced Oil Recovery Program in Citronelle Field, Southwest Alabama," Presented at the annual State of Alabama - U.S. EPA Region IV Underground Injection Control Meeting, hosted by the Alabama State Oil and Gas Board, Mobile, AL, October 29, 2008.

J. C. Pashin, D. J. Hills, D. C. Kopaska-Merkel, R. A. Esposito, and P. M. Walsh, "CO_2-Enhanced Oil Recovery Program in Citronelle Field, Southwest Alabama," Presentation at the monthly luncheon meeting of the New Orleans Geological Society, New Orleans, LA, November 3, 2008.

D. J. Hills, J. C. Pashin, D. C. Kopaska-Merkel, and R. A. Esposito, "Stratigraphy of the Citronelle Oil Field, AL: Perspectives from Enhanced Oil Recovery and Potential CO_2 Sequestration," Presented at the Fall Meeting of the American Geophysical Union, San Francisco, CA, December 15-19, 2008. Citation for the abstract: *Eos Trans. AGU, 89*(53), Fall Meet. Suppl., Abstract U41C-0020.

D. J. Hills, D. C. Kopaska-Merkel, J. C. Pashin, P. M. Walsh, and R. A. Esposito, "Geologic Characterization Supporting Enhanced Oil Recovery Pilot, Citronelle Oil Field, Southwest Alabama," Paper No. 22-5, Poster presentation by D. J. Hills at the 58th Annual Meeting of Southeastern Section of the Geological Society of America, St. Petersburg, FL, March 12-13, 2009. Geological Society of America, *Abstracts with Programs*, **2009**, *41* (1), 55. http://gsa.confex.com/gsa/2009SE/finalprogram/abstract_154650.htm

J. C. Pashin, D. J. Hills, D. C. Kopaska-Merkel, R. A. Esposito, and P. M. Walsh, "Multizone CO_2-EOR Pilot in Heterogeneous Sandstone, Citronelle Field, Southwest Alabama," Presented at the Eighth Annual Conference on Carbon Capture and Sequestration, Pittsburgh, PA, May 4-7, 2009.

Wenya Qi and Shen-En Chen, "Geophysical Sensing for CO_2-EOR and Sequestration," Paper No. 0920, International Coalbed and Shale Gas Symposium, University of Alabama, Tuscaloosa, AL, May 18-22, 2009.

J. C. Pashin, "Revitalizing Alabama's Largest Oil Field: Paleoenvironments of the Early Cretaceous Donovan Sand, Citronelle Field, Southwest Alabama," Presentation to the Alabama Paleontological Society, Birmingham, AL, July 6, 2009.

L. J. Lyte and E. Z. Nyakatawa, "Carbon Dioxide Fluxes in a Forest Soil in the Citronelle Oil Field of South Alabama," poster presentation at the 2009 Annual Meeting of the American Society of Agronomy, Crop Science Society of America, and Soil Science Society of America, Pittsburgh, PA, November 1-5, 2009.

J. C. Pashin, "Enhanced Oil Recovery and Carbon Sequestration Potential of Estuarine Sandstone Deposits, Donovan Sand (Lower Cretaceous), Citronelle Field, Southwest Alabama," Colloquium in the Department of Geology and Geography, Auburn University, Auburn, AL, November 12, 2009.

J. C. Pashin, "Carbon Sequestration Activities in Alabama," U.S. EPA Region IV State Water Directors Meeting, Lake Guntersville State Park, Guntersville, AL, November 18, 2009.

K. A. Roberts and X. Chen, "Ecological Monitoring and Assessment of EOR at Citronelle, Alabama," Poster presented at the joint Alabama Academy of Science and Alabama A&M

University Science, Technology, Engineering, and Mathematics Day, Huntsville, AL, March 31, 2010.

D. J. Hills, D. C. Kopaska-Merkel, and J. C. Pashin, "Depositional and Diagenetic Factors Influencing CO_2-Enhanced Oil Recovery in Estuarine Sandstone Facies of the Donovan Sand (Lower Cretaceous), Citronelle Field, Southwest Alabama," Poster presented at the American Association of Petroleum Geologists, AAPG Annual Convention and Exhibition, New Orleans, LA, April 11-14, 2010.

Shen-En Chen, Y. Liu, and P. Walsh, "DoREMI for CO_2-EOR and Sequestration," Presented at the 2010 Sino-US Environmental Protection and Energy Summit & Expo, Atlanta, GA, April 24-25, 2010.

P. M. Walsh, K. Theodorou, A. M. Shih, P. C. Shum, G. N. Dittmar, T. Boelens, S. Walker, T. Miller, M. Sullivan, J. C. Pashin, D. J. Hills, D. C. Kopaska-Merkel, R. A. Esposito, E. Z. Nyakatawa, L. J. Lyte, K. A. Roberts, X. Chen, E. S. Carlson, F. Dumkwu, C. A. Turmero, P. E. Clark, S.-E. Chen, Y. Liu, and W. Qi, "Carbon-Dioxide-Enhanced Oil Recovery and Sequestration in Citronelle Dome, Southwest Alabama," Proceedings of the Ninth Annual Conference on Carbon Capture and Sequestration, Pittsburgh, PA, May 10-13, 2010. The slides may be downloaded at <http://me-wiki.eng.uab.edu/citronelle/?cat=3>.

L. Lyte and E. Nyakatawa, "Carbon Dioxide Fluxes and their Relationship to Forest Soil Properties," Poster presented at the joint American Society of Agronomy, Crop Science Society of America, and Soil Science Society of America 2010 International Annual Meetings, Long Beach, CA, October 31 to November 4, 2010.

Shen-En Chen, Yangguang Liu, and Peng Wang, "DoReMi - A Passive Geophysical Monitoring Technique for CO_2 Injection," SPE-149265-PP, Society of Petroleum Engineers Eastern Regional Meeting, Columbus, OH, August 17-19, 2011.

Shen-En Chen and Peng Wang, "CO_2 Injection Monitoring Using an Innovative Surface Monitoring Technique," 3rd Annual World Congress of Well Stimulation and EOR, Xi'an, China, April 25-28, 2012.

E. S. Carlson, A. Islam, F. Dumkwu, and T. Bertalan, "nSpyres, An Open-Source, Python-based Framework for Simulation of Flow though Porous Media," Session on Open Source Software for Porous Media, 4th International Conference on Porous Media and Annual Meeting of the International Society for Porous Media, Purdue University, West Lafayette, IN, May 14-16, 2012.

P. M. Walsh, K. Theodorou, P. C. Shum, E. Z. Nyakatawa, X. Chen, K. A. Roberts, L. J. Lyte, G. N. Dittmar, K. Murphy, S. Walker, T. Boelens, P. Guerra, T. Miller, T. Henderson, M. Sullivan, D. Beasley, S. Brewer, F. Everett, J. C. Pashin, D. J. Hills, D. C. Kopaska-Merkel, R. A. Esposito, K. M. Ellison, E. S. Carlson, P. E. Clark, A. W. Islam, C. A. Turmero, F. Dumkwu, S.-E. Chen, W. Qi, Y. Liu, and P. Wang, "Citronelle Dome, Southwest Alabama: CO_2-Enhanced Oil Recovery Pilot Test and Opportunities for CO_2 Storage," Research Experience in Carbon Sequestration 2012, Birmingham, AL, June 3-13, 2012.

K. A. Roberts and X. Chen, "Direct and indirect assessment of vegetation located near CO_2-mediated enhanced oil recovery (CO_2-EOR) activities," Ecological Society of America, 97th Annual Meeting, Portland, OR, August 5-10, 2012.

L. T. Staley, E. Z. Nyakatawa, and L. J. Lyte, "Potential for Carbon Storage in the Citronelle Oil Field: A Geological Sink in South Alabama," Poster presentation at the 4th North American Carbon Program All-Investigators Meeting, Albuquerque, NM, February 4-7, 2013. Poster No. 176. <http://www.nacarbon.org/cgi-bin/meeting_2013/mtg2013_ab_search.pl?action=3&ab_id=73>

B.2. Publications

X. Chen and Y. Wang, "Emergent Spatial Pattern of Herpetofauna in Alabama, USA," *Acta Herpetologica*, **2007**, *2* (2), 71-89.

X. Chen and K. A. Roberts, "Roadless Areas and Biodiversity: A Case Study in Alabama, USA," *Biodiversity and Conservation*, **2008**, *17*, 2013-2022.

R. A. Esposito, J. C. Pashin, and P. M. Walsh, "Citronelle Dome: A Giant Opportunity for Multi-Zone Carbon Storage and Enhanced Oil Recovery in the Mississippi Interior Salt Basin of Alabama," *Environmental Geosciences*, **2008,** *15* (2), 53-62.

X. Chen, "Topological Properties in the Spatial Distribution of Amphibians in Alabama USA for the use of Large Scale Conservation," *Animal Biodiversity and Conservation*, **2008**, *31.1*, 1-13.

X. Chen and R. Fraser, "Quantifying Impacts of Land Ownership on Regional Forest NDVI Dynamics: A Case Study at Bankhead National Forest of Alabama, USA," *Photogrammetric Engineering & Remote Sensing*, **2009**, *75* (8), 997-1003.

R. A. Esposito, J. C. Pashin, D. J. Hills, and P. M. Walsh, "Geologic Assessment and Injection Design for a Pilot CO_2-Enhanced Oil Recovery and Sequestration Demonstration in a Heterogeneous Oil Reservoir: Citronelle Field, Alabama, USA," *Environmental Earth Sciences 60,* **2010**, 431-444.

X. Chen and S. Burton, "Power Law Relationships in the Branches of Loblolly Pine, Red Maple and Sugar Maple Trees," *Dendrobiology*, **2010**, *63*, 3-9.

X. Chen, W. M. Post, R. J. Norby, and A. T. Classen, "Modeling Soil Respiration and Variations in Source Components using a Multi-Factor Global Climate Change Experiment," *Climatic Change*, **2011**, *107*, 459-480.

X. Chen, "Spatial Geometry of Amphibian Distribution in Alabama, USA," *Wildlife Biology in Practice*, **2010**, *6* (2), 57-68.

X. Chen, "Trends of Forest Inventory Data in Alabama, USA, During the Last Seven Decades," *Forestry*, **2010**, *83* (5) 517-526.
http://forestry.oxfordjournals.org/content/early/2010/10/29/forestry.cpq034.full.pdf+html

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