

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 CO₂ flooding has the following components: (1) Stratigraphy, sedimentology, and petrology, (2) Reservoir fluid properties and miscibility behavior, (3) Reservoir simulation and visualization, (4) CO₂ 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 CO₂-EOR and CO₂ sequestration. From the reservoir engineering perspective, the site is mature and water-flooded, with existing infrastructure, including deep wells, and from the geological perspective, 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 CO₂ 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 CO₂-EOR projects. The present project is designed to evaluate the potential of CO₂-EOR for tertiary recovery from highly heterogeneous sandstone reservoirs of the type found at Citronelle, and the capacity of those oil reservoirs and adjacent saline formations 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 40 to 64 million bbl. Assuming a conservative 10% of OOIP to be economically recoverable (38 million bbl) using CO₂-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 CO₂ storage is estimated to be 530 to 2100 million short tons (Esposito et al., 2008), sufficient to sequester the CO₂ 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 CO₂ in a saline formation in Citronelle Dome (Esposito et al., 2011b). Plant Barry is anticipated, by Southern Company, Alabama Power Company, and Denbury Resources, to be a source of CO₂ for EOR in the Citronelle Field, if the present project indicates that CO₂-EOR will be profitable and provides the desired guidance for management of the reservoir under CO₂ 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 CO₂ were sufficient to demonstrate CO₂-EOR and produce significant incremental oil. Background conditions of CO₂ in air, CO₂ flux from soil, and the species distribution and growth rate of vegetation were established, for comparison with conditions during and after CO₂ injection. A rolling ball viscometer was designed and built, for measurement of CO₂-oil miscibility behavior.

Highlights of the work done in preparation for the first injection of CO₂ 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 CO₂ 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 CO₂ slug size for water-alternating-gas oil recovery under specified CO₂ cost and oil price constraints; and (8) the wells in the inverted five-spot were prepared for testing and the equipment and infrastructure for CO₂ storage, pumping, and injection were put in place.

Phase II. The first CO₂ 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 CO₂ injection, the decline in production was reversed, and, from January to September 2010, when the first CO₂ 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 CO₂ flood at Citronelle occurred: (1) excessive produced gas, primarily CO₂, appeared at Well B-19-11, in the southwest corner of the inverted five-spot, (2) on returning to water injection following the CO₂ injection, the injection rate, which had been 170 bbl water/day before injection of CO₂, 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 CO₂, and (4) oil production at B-19-8 Tank Battery decreased from its peak of 59 bbl/day in September 2010 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 recovered some of its loss, increasing to 44 bbl/day in March 2012. Having solved the problem with the pumps, the next problem being addressed is the low injectivity to water following CO₂. Restoration of the initially-observed enhanced recovery has the highest priority during the remainder of the project.

Documentation of the presence or absence of environmental consequences of CO₂ flooding also has high priority. Measurements of soil gas composition versus depth, CO₂ flux from soil, soil

temperature, soil moisture, and soil elements (carbon, nitrogen, and phosphorus), have been made since August 2008, before, during, and following CO₂ injection, at 15 locations surrounding the injector, three producers, and a plugged and abandoned well within the test pattern. Monthly measurements of CO₂ in ambient air have been recorded at 104 points on a grid across Citronelle since September 2007. The CO₂ 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 CO₂ levels. There has been no significant short or long-term effect of storage, handling, and injection of CO₂ on the levels of CO₂ 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 CO₂ in ambient air and measurements of CO₂ fluxes from soil near the well. Monitoring of CO₂ in air, CO₂ fluxes from soil, and growth of vegetation will continue to the end of the project.

Advancement of diagnostic techniques for monitoring interaction between the CO₂ plume and geologic formation is another priority. Shear-wave velocities are being 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 CO₂ injection suggested a 10% increase in stress associated with CO₂ 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 CO₂ injection. This encouraging result suggests that the ReMi technique may be useful for monitoring formation pressure.

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.

CO₂ in produced gas - Draeger tube.

Proof of injected CO₂ 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.

CO₂ in ambient air - portable gas analyzer.

Seepage of CO₂ from soil - sampling and analysis of CO₂ 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 remaining to be answered are: (1) What is the cause of the marked loss in injectivity observed on switching from CO₂ injection back to water, and can it be reversed? (2) Are significant environmental and ecological effects present after a longer period of time? (3) 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 (4) Is continuous CO₂ injection or WAG the better strategy for commercial EOR at Citronelle?

To address the critically important Item 1, the loss of injectivity to water following the CO₂ flood, 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 millidarcy. 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 tight 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 N60E to N80E. Two of the wells at which early breakthrough of CO₂ was detected lie on the line at N69E relative to the injector. The fracture evidently provided a preferential pathway for CO₂ 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.

The plan for diagnosis of the loss in injectivity and restoration of enhanced oil recovery is as follows:

- Examine possible approaches to re-establishing previous injection rates, for example: (1) injection of surfactant to reduce capillary pressure, if CO₂ is blocking the water flow, (2) treatment with acid to remove clay fines or precipitated carbonate, and (3) injection of a small slug of CO₂ (less than the full 7500 tons planned for the second CO₂ injection) to determine whether its injectivity remains at the level observed during the first CO₂ injection (average of 31 tons/day).
- After restoring injectivity, conduct a step rate test to determine the fracture opening stress, with a view to implementing a "smart" well in which the injection pressure is adjusted to minimize bypassing of water and CO₂ through the fracture.
- Proceed with a management plan with which to maximize oil recovery from the pilot test, considering such options as: (1) continue water injection as originally planned, until the optimum oil yield from the WAG cycle is realized, then proceed to the second of the two originally-planned CO₂ injections, or (2) proceed immediately to the second of the two originally-planned CO₂ injections. In either case, continue CO₂ injection as long as possible with the available funding, to provide the maximum amount of data for testing and validation of reservoir simulations.

Substantial value would be added by continuing Phase III until the damage to the target formations following CO₂ injection is understood, the proper treatments to restore injectivity have been applied, enhanced oil recovery has been restored, and a second CO₂ injection has demonstrated the anticipated EOR potential of Citronelle Field.

Technology Transfer

Thirteen 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 CO₂-enhanced oil recovery and capacity for CO₂ storage (Esposito et al., 2008, 2010). Results of work under the project have been presented by members of the project team at fourteen national and international conferences and at eleven regional and local meetings.

Contents

Disclaimer	ii
Acknowledgment	iii
Executive Summary	iv
List of Tables	x
List of Figures	xi
1. Introduction	1
1.1. Background	1
1.2. Scope of Work	2
2. Progress of the Work	3
2.1. Communication and Technology Transfer	3
2.1.1. Project and Collaboratory Web Sites	3
2.1.2. Publications, Presentations, and Workshops	3
2.1.3. Citronelle Field Data	4
2.1.4. Meetings of the Research Group	5
2.1.5. Visits to Citronelle Oil Field	5
2.2. Geology and Petrology	5
2.3. Reservoir Fluid Properties and Phase Behavior	7
2.4. Petroleum Reservoir Simulation	8
2.4.1. Simulation of CO ₂ -EOR Pilot Test	8
2.4.2. Calculation and Display of CO ₂ , Oil, and Water Saturations	11
2.4.3. Effect of Reservoir Permeability on Oil Recovery	16
2.4.4. Development of Reservoir Simulator and Large-Scale, Fine-Grid Simulation	18
2.5. CO ₂ Liquefaction, Transportation, and Storage	19
2.6. Site Preparation, Water Flood, and CO ₂ Injection	19
2.6.1. Site Preparation and Water Flood	19
2.6.2. CO ₂ Injection	20
2.6.3. Response to CO ₂ Injection	23
2.7. Surface Monitoring	30
2.7.1. Soil Properties and CO ₂ Fluxes from Forest Soils at the Test Site	30
2.7.2. Vegetation and Ambient Air Monitoring	35
2.8. Seismic Measurements	40
2.9. Visualization of the Migration of CO ₂ , Oil, and Water	45
2.10. Reservoir Management	46

Contents (continued)

3. Milestone Status	48
3.1. Status Summary	48
3.2. Phase I Milestones	49
3.3. Phase II Milestones	49
3.4. Phase III Milestones	51
4. Summary and Conclusions	55
Acronyms and Abbreviations	62
References	63
Appendix A: Statement of Project Objectives	A1
A.1. Objectives	A1
A.2. Scope of Work	A1
A.3. Tasks to be Performed	A1
A.4. Deliverables	A10
A.5. Briefings/Technical Presentations	A11
Appendix B: Technology Transfer	B1
B.1. Presentations and Workshops	B1
B.2. Publications	B3
B.3. Theses and Dissertations	B4
B.4. Reports	B5
Appendix C: Bibliography of Publications on the Citronelle Oil Field and Southwest Alabama Geology	C1

List of Tables

2.4.1.	Summary of calculated incremental oil recovery (above the water flood baseline) from the production wells in the simulation area during the CO ₂ -EOR pilot test.	11
2.6.1.	Analyses of Samples of Produced Gas and Injected CO ₂ Collected on August 4, 2010.	27
2.6.2.	CO ₂ Content of Produced Gas from Wells in and near the Test Pattern, April 12, 2011.	28
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.	33
2.7.2.	Regression Models Relating Soil CO ₂ Fluxes to Soil Temperature and Soil Moisture during Gas Sampling at Wells in the Test Pattern at Citronelle.	34
2.7.3.	Locations and Descriptions of the 10 m x 10 m Vegetation Plots.	39
2.8.1.	Wireless Sensor Testing Locations.	41
2.8.2.	Summary of Linear Equations and R-Squared Values for the Ten Tests.	42
3.3.1.	Critical Path Milestones, Research Phase II (Budget Period 2), September 1, 2008 to December 31, 2010.	50
3.4.1.	Critical Path Milestones, Research Phase III (Budget Period 3), January 1, 2011, to August 31, 2012.	51
3.4.2.	Locations and Descriptions of the 10 m x 10 m Vegetation Plots.	53

List of Figures

2.2.1.	Preliminary draft stratigraphic column, SECU D-9-8 No. 2, Citronelle Field, Southeastern Unit.	6
2.3.1.	The gaseous CO ₂ /liquid CO ₂ interface and the liquid CO ₂ /water interface.	8
2.4.1.	Comparison of simulated CO ₂ -EOR pilot test oil production rates to the rates under injection of water only.	10
2.4.2.	Comparison of simulated CO ₂ -EOR pilot test cumulative and incremental oil recovery to cumulative and incremental oil recovery under injection of water only.	10
2.4.3.	Screen shots from the animations of CO ₂ , oil, and water flows in Sands 14-1 and 16-2, at four stages before and during injection of two slugs of 7500 tons of CO ₂ , each, separated by water.	12
2.4.4.	Calculated rate of oil production versus time, over a 10-year period, from Sands 14-1 and 16-2 in the pilot test simulation area.	17
2.4.5.	Effects of permeability changes on cumulative oil production during 10-year CO ₂ -EOR from Sands 14-1 and 16-2 in the pilot test simulation area.	17
2.4.6.	Dependence of cumulative incremental oil recovery from the test pattern on permeability, during 10 years of CO ₂ -EOR from Sands 14-1 and 16-2.	17
2.6.1.	Aerial photograph of the Citronelle oil field in the vicinity of the test well pattern.	20
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.).	22
2.6.3.	Response to CO ₂ injection at Tank Battery B-19-8.	24
2.6.4.	Response to CO ₂ injection at Tank Battery B-19-11.	25
2.6.5.	Analysis of the pressure-transient test data by Eric Carlson shows the presence of a hydraulic fracture having a length determined from the dependence of the pressure decay on the square root of time.	29
2.7.1.	Soil gas sampling system.	30
2.7.2.	Arrangement of three 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.	31

List of Figures (continued)

2.7.3.	Measurements of soil surface CO ₂ fluxes around the five wells in the CO ₂ -EOR test pattern in the Citronelle Oil Field, August 2008 to August 2010, before and during CO ₂ injection.	33
2.7.4.	Average atmospheric CO ₂ volume fraction at ground elevation across the City of Citronelle and Citronelle Oil Field from September 2007 to March 2012.	35
2.7.5.	Area-averaged time series (AIRX3C2M.005) in the region 88-89° West and 31-32° North, including the City of Citronelle and the Citronelle Oil Field.	36
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 March 2010, March 2011, and March 2012.	37
2.7.7.	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.	38
2.8.1.	The seismic testing lines, superimposed on the aerial photo of Citronelle Field from Denbury Onshore.	40
2.8.2.	Bi-linear model of the shear wave velocity profile for Line 1, for the three stages of the injection process: before, during, and after CO ₂ injection.	43
2.8.3.	Bi-linear model of the shear wave velocity profile for Line 2, for the three stages of the injection process: before, during, and after CO ₂ injection.	44
2.8.4.	Porous concrete sample formed in Shen-En Chen's laboratory at UNCC, for simulation of rock formations saturated with oil, water, and CO ₂ having different strengths and stiffness.	45
2.9.1.	Corey Shum, in the Enabling Technology Laboratory VisCube, testing an interactive immersive 3-D visualization of the pressure distribution surrounding a CO ₂ injector, calculated by Konstantinos Theodorou using MASTER 3.0.	46
3.4.1.	Average atmospheric CO ₂ volume fraction at ground elevation across the City of Citronelle and Citronelle Oil Field from September 2007 to March 2012.	52
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.	53

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, 2011). 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 CO₂-EOR to be 64 million bbl, or 17% of the original oil in place. Denbury Resources' estimate of the Field's EOR potential is 40 million bbl. Assuming 10% of OOIP to be economically recoverable (38 million bbl) using CO₂-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 CO₂-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 CO₂-EOR for tertiary recovery from Alabama's uniquely structured petroleum resources. Holtz, Núñez López, and Breton (2005) estimated the miscible CO₂-EOR potential of all Alabama oil fields to be 98 million bbl.

A parallel investigation is assessing the capacity of the oil reservoir and adjacent saline formations for sequestration of carbon dioxide, when tertiary oil recovery operations are complete. According to the criteria enumerated by Kovscek (2002), the field is an ideal site for both CO₂-EOR and CO₂ 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 CO₂ 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 CO₂ injectivity 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 CO₂ in the reservoir. Studies include the effect of nitrogen on oil-CO₂ 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 August 31, 2012). A second CO₂ injectivity and enhanced oil recovery test was planned, but is now on hold pending availability of funding. Migration of CO₂ 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. Project and Collaboratory Web Sites

The project web site at <<http://me-wiki.eng.uab.edu/citronelle/>>, maintained by David Brown, is periodically updated to revise the project partners' pages and introduce research results provided by members of the group. The site provides general information on the project for public education to raise awareness of the technologies and benefits of CO₂-enhanced oil recovery.

The collaboratory web site for members of the research group, at <<http://www.citronelloil.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

A paper by Kathleen A. Roberts and Xiongwen Chen, entitled, "Considerations for Ecological Monitoring of CO₂-mediated Enhanced Oil Recovery," appears in the current issue of the *International Journal of Ecological Economics and Statistics* (Vol. 27, No. 4, 2012) and is available on-line at <<http://www.ceserp.com/cp-jour/index.php?journal=ijees&page=article&op=view&path%5B%5D=1374>>. The abstract of the paper follows:

"The simultaneous need for inexpensive, reliable fuel and the reduction of greenhouse gases has led to the exploration of natural geological reservoirs as a means of storing CO₂. CO₂ storage is still in the early stages of development, however, the recovery of previously unavailable crude using CO₂ injection may provide information on how to facilitate and monitor CO₂ storage. Ecological monitoring is necessary to determine if there are adverse ecological consequences to CO₂-mediated enhanced oil recovery (CO₂-EOR). This paper presents the general processes of EOR activities and provides an overview of available monitoring techniques, strategies and mechanism analyses that may be used in establishing monitoring regimes of varying temporal and spatial scales. Our considerations may help to determine reservoir integrity and refine future monitoring strategies for safe geological CO₂ storage."

Yangguang Liu, Research Assistant in Shen-En Chen's research group at the University of North Carolina at Charlotte, completed his Master's Thesis, entitled, "DoReMi – A Passive Geophysical Technique and Development of Bilinear Model for CO₂ Injection," and successfully defended it on January 30, 2012. Yangguang Liu's thesis presents the theory of the DoReMi passive geophysical monitoring technique and reports the group's observations of changes in shear-wave velocity before, during, and after the pilot CO₂ injection in the inverted five-spot test pattern at Citronelle.

Latasha Lyte, Research Assistant in Ermson Nyakatawa's research group at Alabama A&M University, has published her Master's Thesis, entitled, "Carbon Dioxide Fluxes in a Forest Soil in the Citronelle Oil Field in South Alabama." Latasha received her M.S. degree from the Department of Natural Resources and Environmental Sciences at AAMU and is now a Soil Scientist with the Forest Service in the U.S. Department of Agriculture.

Shen-En Chen is attending the 3rd Annual World Congress of Well Stimulation and EOR, in Xi'an, China, April 25-28, 2012, to present a paper with co-author Peng Wang, entitled, "CO₂ Injection Monitoring Using an Innovative Surface Monitoring Technique." The paper describes the DoReMi passive seismic monitoring technique that Shen-En and his research group have developed and their observations from its application at Citronelle.

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 25 presentations at technical meetings, 13 peer-reviewed publications in journals, 3 theses and dissertations, and 28 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 CO₂-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 CO₂ 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.citronelloil.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 the results. Of greatest concern, at present, is the low water injection rate being experienced at the test site. Frequent communication among the members of the group, by e-mail and telephone, has been the most effective means for exchanging information and the results of tests conducted to analyze and resolve this problem.

2.1.5. Visits to Citronelle Oil Field

Regular visits to the oil field are made 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 CO₂ fluxes from soil near the injector and producers, by Ermson Nyakatawa and his students 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, Yangguang Liu, 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.

Kathleen Roberts, working with Xiongwen Chen at Alabama A&M University, visited Citronelle on March 26-27 for measurements of CO₂ and other minor and trace species in ambient air across the Oil Field and City of Citronelle. The measurements of CO₂ in air are presented in Section 2.7.2 of this report.

2.2. Geology and Petrology

Ann C. Arnold, David C. Kopaska-Merkel, and Jack C. Pashin
Geological Survey of Alabama

During the quarter under review, staff at the Geological Survey of Alabama described core from the Lower Cretaceous Donovan Sand and completed a draft version of the detailed stratigraphic column, shown in Figure 2.2.1. The described core (SECU D-9-8 No. 2) was recovered by Denbury Resources from a monitoring well that was drilled as part of the SECARB Phase III Anthropogenic Test. This core provides one of the few continuous records of Donovan sandstone bodies and the intervening shale units and has contributed immeasurably to our understanding of Donovan sedimentology. The wellbore from which the core was recovered is located in the southeast region of the Citronelle Field, Mobile County. Approximately 214 feet of

core was described, from depths of 10,946 to 11,160 feet. An additional 58 feet of core was described from a deeper core spanning depths from 11,548 to 11,606 feet.

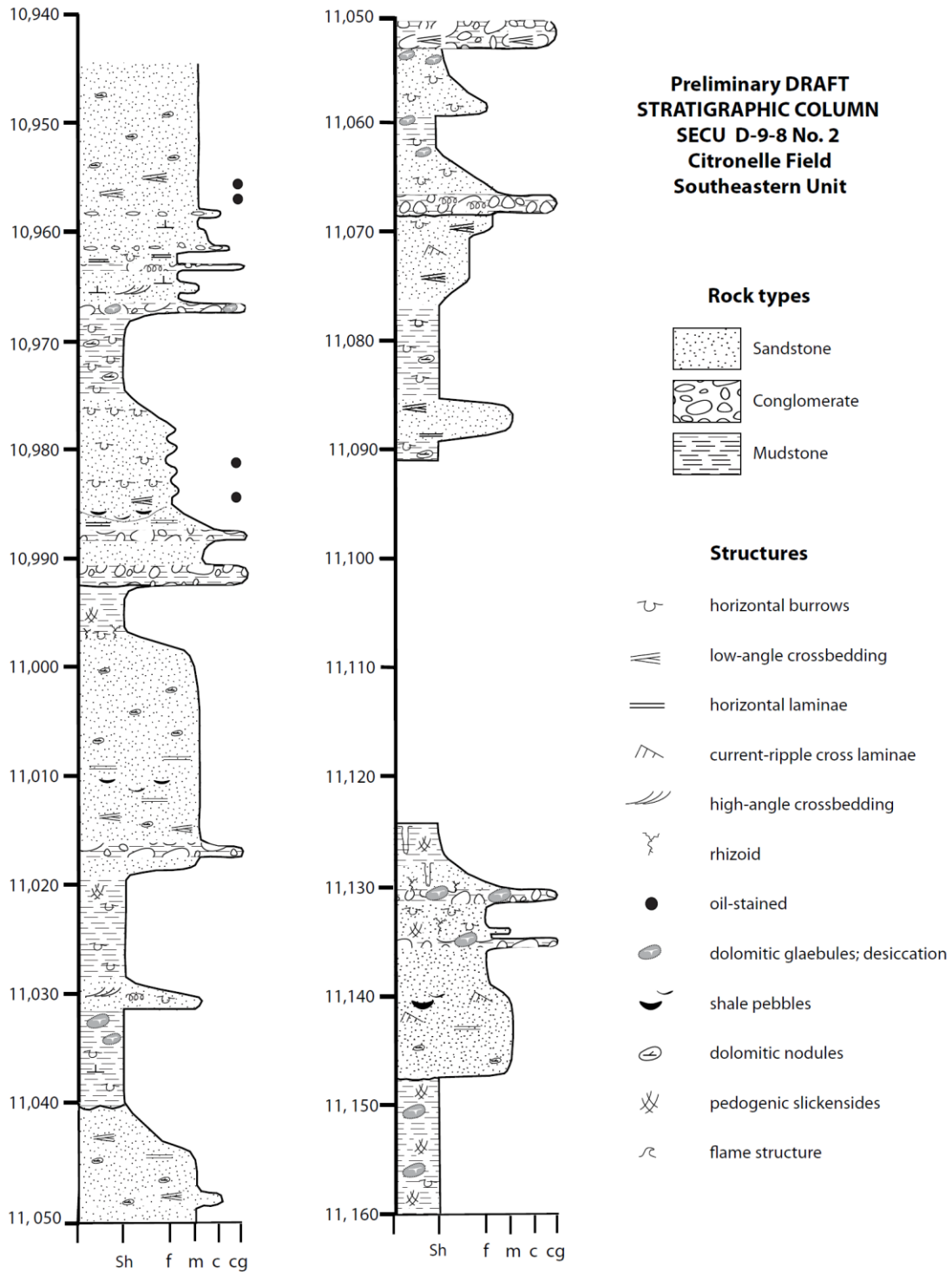


Figure 2.2.1. Preliminary draft stratigraphic column, SECU D-9-8 No. 2, Citronelle Field, Southeastern Unit.

The core contains more terrestrial redbed facies than other cores previously described in the Citronelle Field. The detailed lithologic description indicates the energy of deposition and type of environment during sediment deposition. 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 this core. Diagenetic features were also documented in the core description and 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. Photographs were taken of the complete core in boxes, to not damage the delicate paleosols.

Color was determined using the Munsell Soil Color Chart. Colors are useful in this core to indicate reduction or oxidation conditions of the fluid migrating through the rock. In general, reddish colors show oxidizing conditions, typical of subaerial exposure, whereas gray to greenish gray indicate reducing conditions, associated with hydrocarbon fluid rather than water. GSA staff are currently completing a color graph to include on the stratigraphic column.

Core collected from adjacent well borings in the Citronelle Oilfield of the Rodessa Formation, Donovan Sand Member will be described in detail, to further map the basin depositional environment. The purpose of more detailed stratigraphy is to possibly identify species consistent with biofacies, using sedimentary structures and the intensity and type of feeding and dwelling burrows for the class of organisms.

Petrologic work also continued during the quarter. Twenty-seven thin sections were described and documented, including recording and annotating 281 photomicrographs. Information provided by study of these thin sections was added to graphic core descriptions, modifying and refining the results of the initial core descriptions. An additional 1,050 photomicrographs, taken during previous quarters but not fully documented, were annotated and described.

2.3. Reservoir Fluid Properties and Phase Behavior

César A. Turmero and Peter E. Clark, University of Alabama

A high-pressure, high-temperature system has been developed to study the interactions of CO₂ in oil by visual observation of the development of miscibility between CO₂ and the reservoir oil. The major component of this system is a high-pressure PVT cell, shown in Figure 2.3.1. A floating-piston accumulator is connected to the system to introduce pressurized CO₂ into the PVT 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.

During the quarter under review, the system underwent preliminary testing using water and CO₂ 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 CO₂ in water and the preliminary results compared favorably with a computer model of carbon dioxide-water solubility behavior. Once the system is fully tested, we will begin the investigation of carbon dioxide-oil systems.

The gaseous CO₂/liquid CO₂ interface and the liquid CO₂/water interface can be seen clearly in Figure 2.3.1. A pH-sensitive dye has been ordered to improve the contrast between the two liquids at the interface. During the coming quarter, we will be exploring methods for accurately measuring the volume expansion that accompanies carbon dioxide dissolution into oil or water phases.

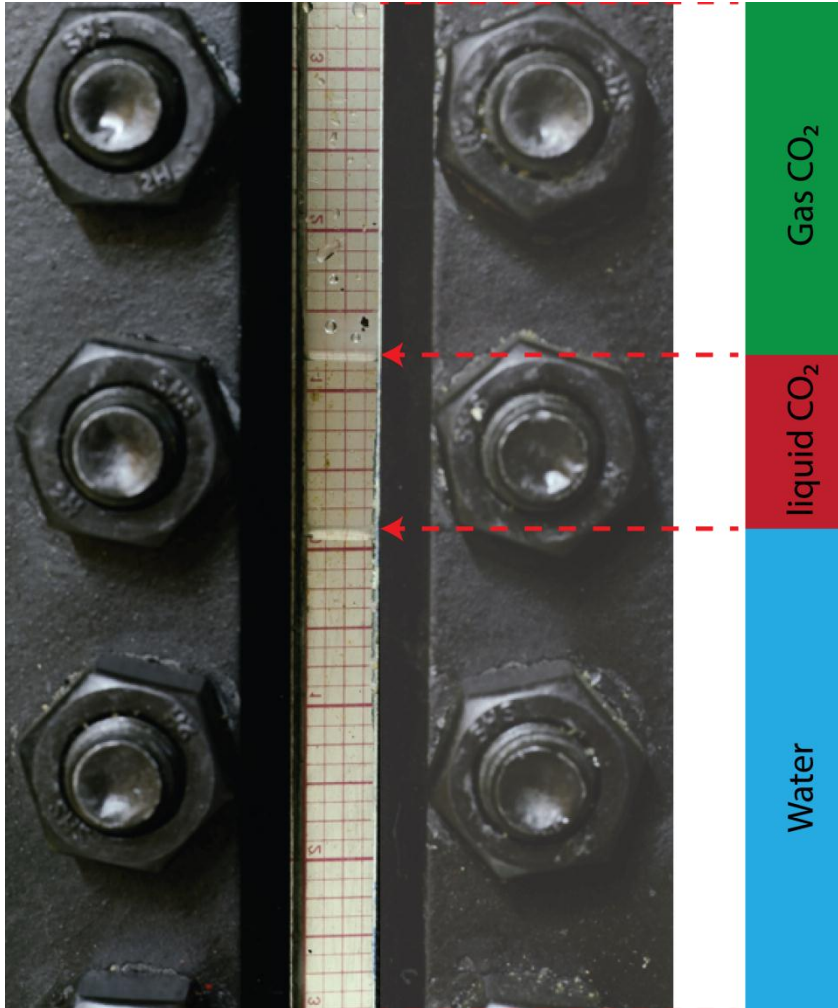


Figure 2.3.1. The gaseous CO₂/liquid CO₂ interface (upper arrow) and the liquid CO₂/water interface (lower arrow).

2.4. Petroleum Reservoir Simulation

2.4.1. Simulation of CO₂-EOR Pilot Test

Konstantinos Theodorou, University of Alabama at Birmingham

This section, with Table 2.4.1 and Figures 2.4.1 and 2.4.2, appeared in our previous Quarterly Progress Report (January 30, 2012, pp. 9-11). The section is repeated here to provide the background for new material in Section 2.4.3.

Field observations during and after the CO₂-EOR pilot test provide valuable information regarding the effectiveness of the CO₂ injection and its ability to mobilize a significant volume of oil. The primary metric for effectiveness of CO₂-EOR is the daily oil production rate, which can be

measured and compared to past production records. However, oil production rates during CO₂ or water injection can be influenced directly by sweep efficiency (vertical and horizontal), gravity override, fingering, and variations in water and oil saturations. Obtaining field information regarding these parameters is a difficult task and often one has to rely on simulations.

A simulation was performed using MASTER 3.0 (Ammer and Brummert, 1991; Ammer, Brummert, and Sams, 1991; Zeng, Grigg, and Chang, 2005) for the time period of the CO₂-EOR pilot test. The objective was to calculate oil production rates for the duration of the pilot test and CO₂, oil, and water saturations at the end of each of the three phases in the pilot test. The simulation results for the oil production rates are presented here.

During the simulation, the CO₂ injector, Well B-19-10 #2, was rate-controlled and emulated the actual CO₂ injection schedule experienced in the field. The schedule of CO₂ delivery and injection was recorded daily. All the other wells in the simulation area were pressure-controlled, with output values for water injection and production rates based on mobility.

Figure 2.4.1 shows the calculated daily oil production rate during the CO₂-EOR pilot test, compared to the rate for the same time period if water flooding had continued. Day 10196 marks the beginning of the first CO₂ injection, which ends on Day 10458. Water injection begins on Day 10459 and ends on Day 10708. The second CO₂ injection begins on Day 10709 and ends on Day 10897.

In the first phase of CO₂ injection the oil production rate increases only marginally (by approximately 5 STB/day) in response to the injection of CO₂. The mobilization of oil takes place in the region of the injected CO₂ but its migration is hindered by the higher water pressure ahead of the CO₂ front. However, the injection of water during the interim phase of the CO₂-EOR pilot test results in a significant increase (by approximately 40 STB/day) in oil production and completes a single WAG cycle. The calculated production record in Figure 2.4.1 has encouraging similarities to the production history observed in the field, shown in Figure 2.6.3. The simulated oil production rates continue to increase throughout the second phase of CO₂ injection, as shown in Figure 2.4.1, demonstrating the effectiveness of the WAG scheme.

The calculated record of cumulative oil recovery by the WAG is compared with recovery by water flooding only in Figure 2.4.2. The incremental cumulative volume of oil recovered and the percent increase above the base line (water flooding only) are summarized in Table 2.4.1.

The CO₂ volume injected, during the simulation of the CO₂-EOR pilot test, totaled 15,000 tons. The injected CO₂ volume represents only 0.04245 of the estimated hydrocarbon pore volume. Although restricted to Sands 14-1 and 16-2, the simulated response of the reservoir to the relatively small ratio of CO₂ volume to hydrocarbon pore volume is encouraging.

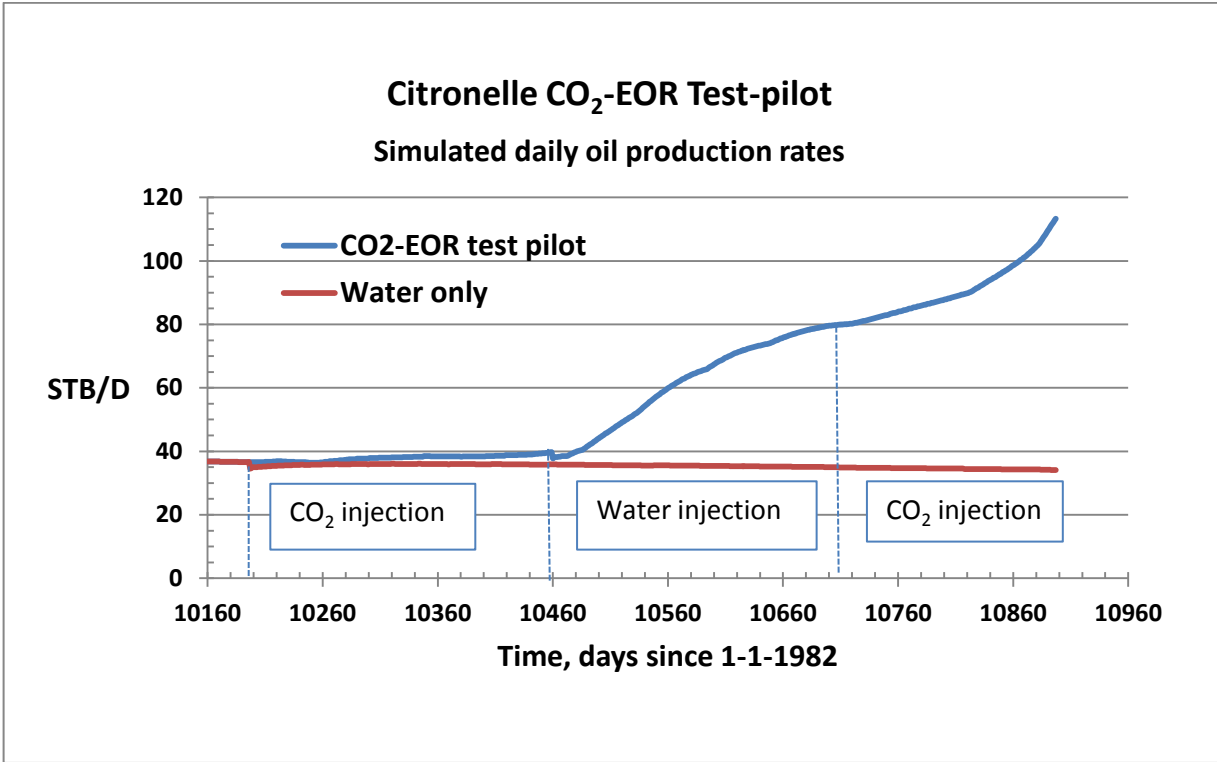


Figure 2.4.1. Comparison of simulated CO₂-EOR pilot test oil production rates to the rates under injection of water only.

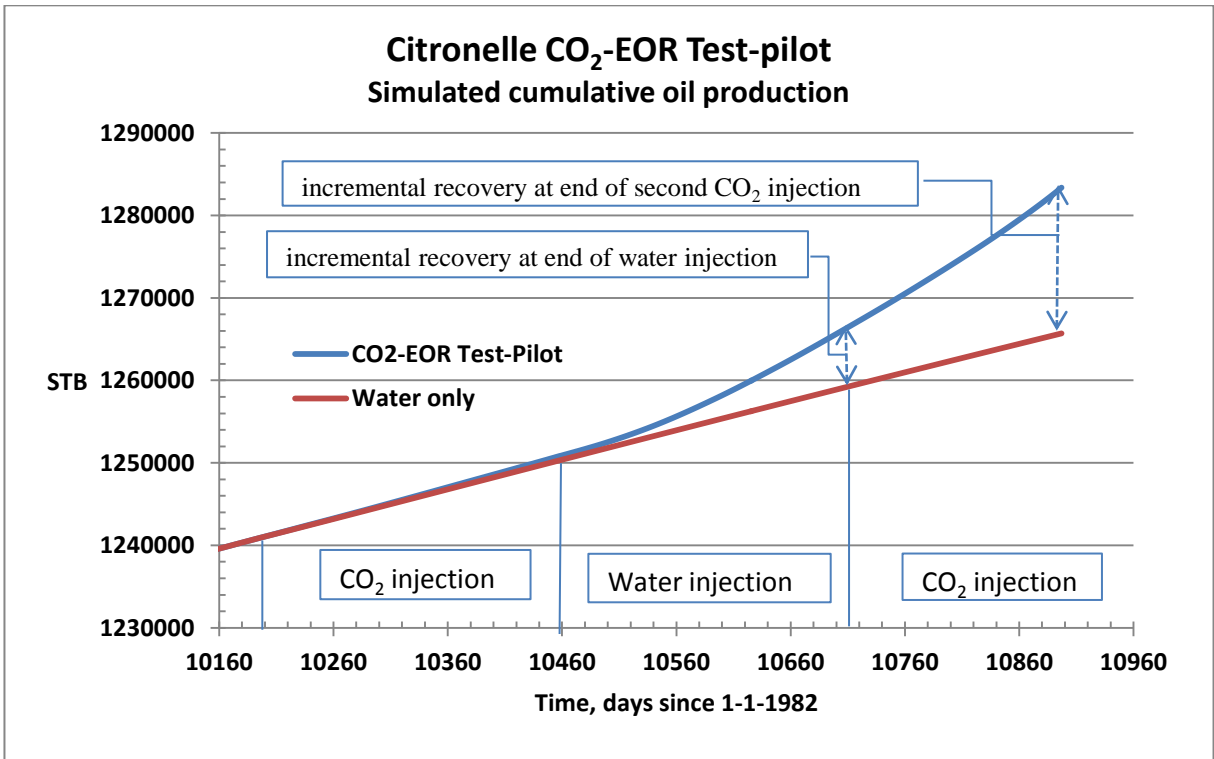


Figure 2.4.2. Comparison of simulated CO₂-EOR pilot test cumulative and incremental oil recovery to cumulative and incremental oil recovery under injection of water only.

Table 2.4.1. Summary of calculated incremental oil recovery (above the water flood baseline) from the production wells in the simulation area during the CO₂-EOR pilot test.

CO ₂ -EOR pilot test phase	Volume of incremental oil, STB	% increase
End of first CO ₂ injection	522	0.04175
End of interim water injection	7,151	0.568
End of second CO ₂ injection	17,679	1.40

2.4.2. Calculation and Display of CO₂, Oil, and Water Saturations

Corey Shum and Konstantinos Theodorou, University of Alabama at Birmingham

The complexity of the interaction between CO₂, oil, and water in a geologic formation makes animation of the evolution of fluid saturations during CO₂ and water flooding an especially useful tool for understanding enhanced oil recovery and its dependence on reservoir conditions and injection parameters. With the reservoir simulation results obtained by Konstantinos Theodorou using MASTER 3.0, described above, Corey Shum, in the UAB Enabling Technology Laboratory, programmed animations showing the evolution of fluid saturations in the 14-1 and 16-2 Sands during two CO₂ injections of 7500 tons each. Screen shots from the visualization are shown in Figures 2.4.3a-d.

The raw output from the reservoir simulation was parsed with a custom application to extract the oil, water, and CO₂ 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.

As shown in Figure 2.4.3a, 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 CO₂, 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 in the upper-left of the image. As the simulation progresses, the day and the injection activity are displayed in the lower-right corner of the image.

CO₂, oil, and water saturations in Sands 14-1 and 16-2 are shown before any CO₂ was injected (Figure 2.4.3a), at the end of the first CO₂ injection (Figure 2.4.3b), at the end of the water injection (Figure 2.4.3c), and at the end of the second CO₂ injection (Figure 2.4.3d). The progress of CO₂ 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.

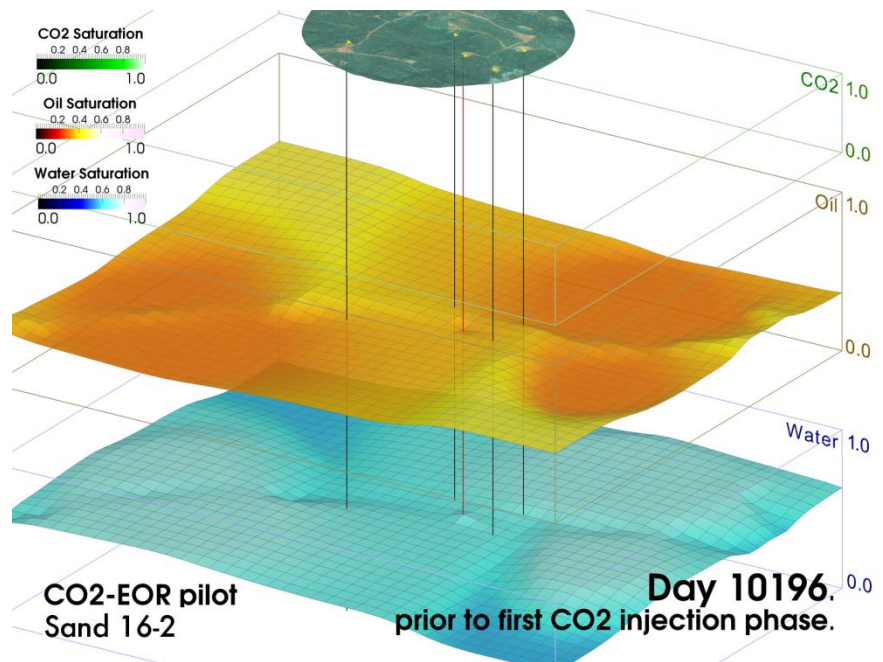
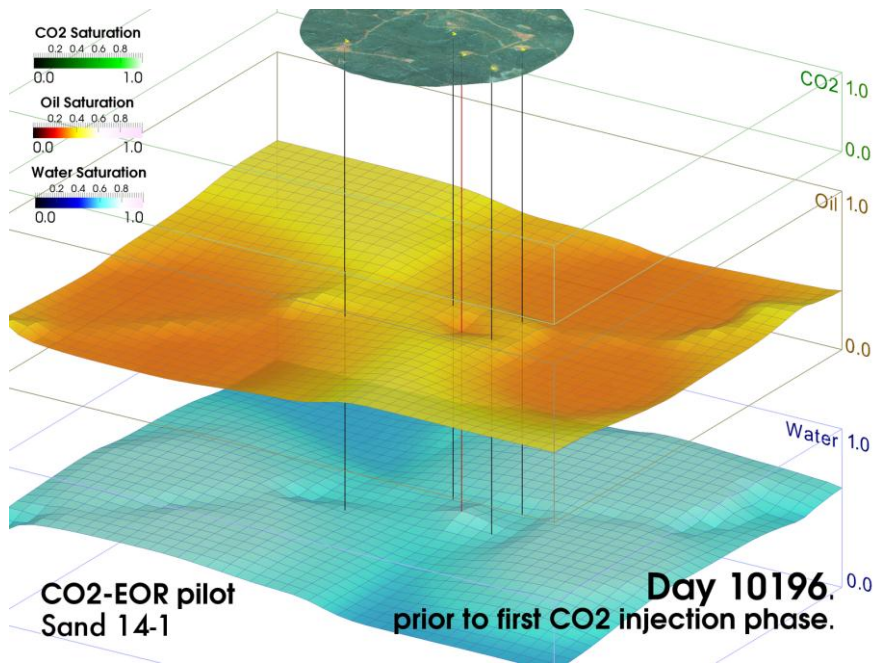


Figure 2.4.3a. Screen shots of the animations of oil and water flows in Sands 14-1 (top) and 16-2 (bottom), before CO₂ injection. The animation was programmed by Corey Shum, based on the simulation by Konstantinos Theodorou described in a previous Quarterly Progress Report (October 30, 2010, Section 2.11). An aerial 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 CO₂ and water injection.

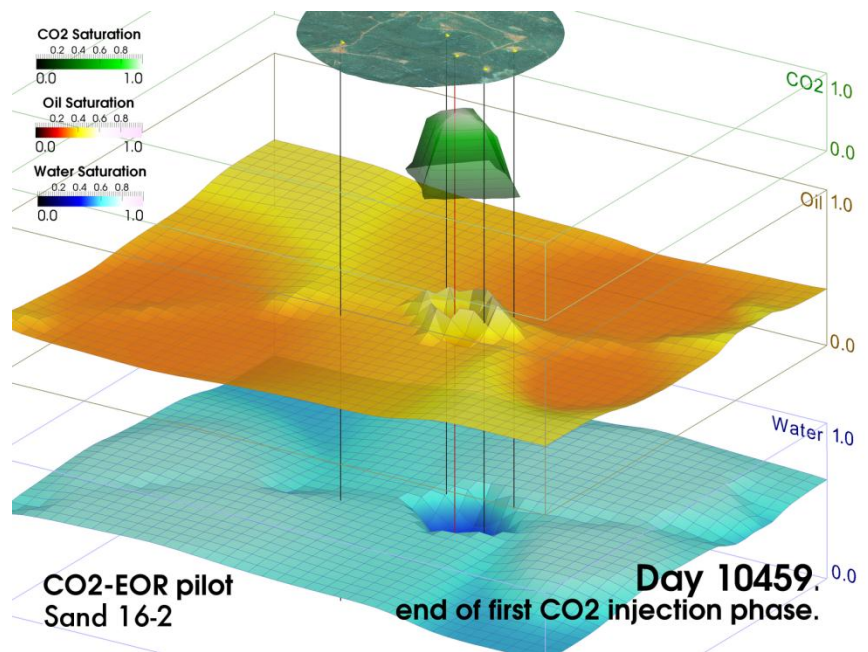
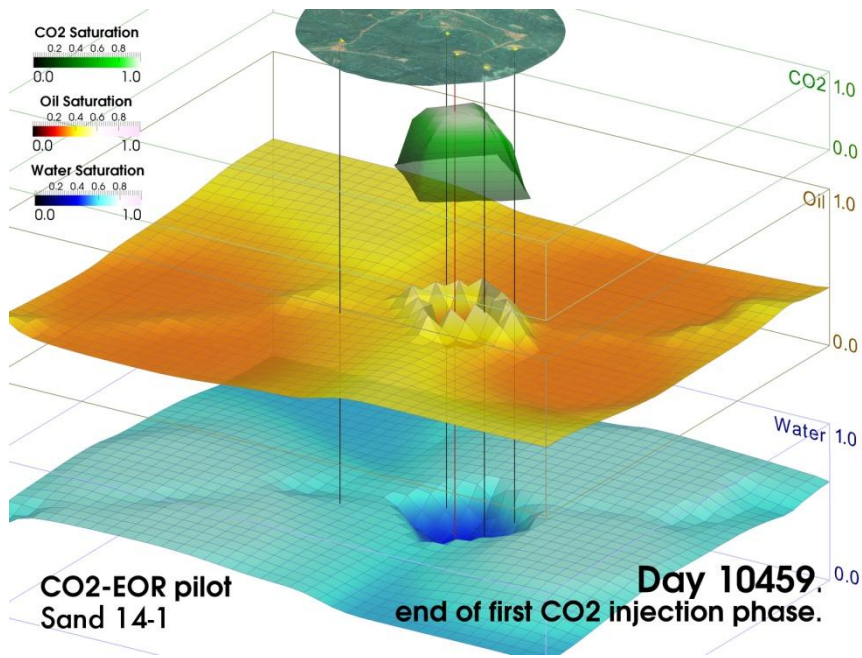


Figure 2.4.3b. Screen shots of the animations of CO₂ (shown in green), oil, and water flows in Sands 14-1 (top) and 16-2 (bottom), at the end of the first injection of 7500 tons of CO₂, after 263 days of CO₂ injection. Elevated oil saturations associated with the oil banks are clearly visible, but the banks have not yet reached all three of the producers closest to the injector.

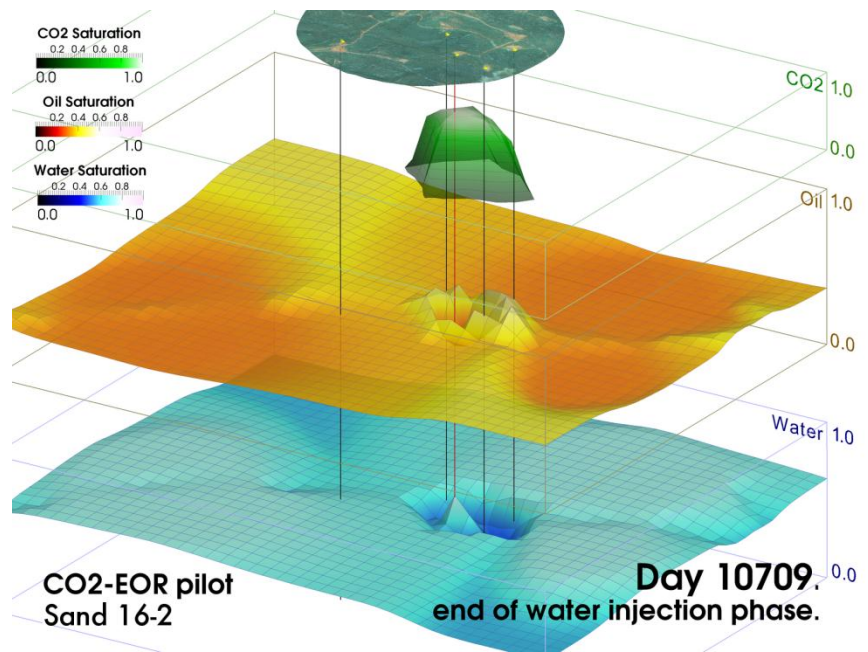
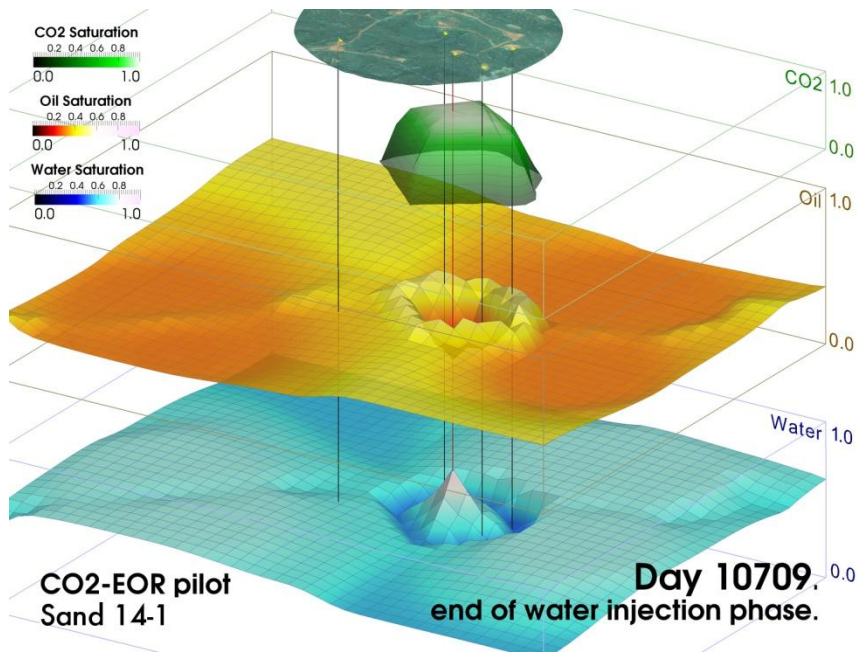


Figure 2.4.3c. Screen shots of the animations of CO₂, water, and oil flows in Sands 14-1 (top) and 16-2 (bottom), at the end of the water injection period following the first injection of 7500 tons of CO₂, 513 days after the beginning of the first CO₂ injection.

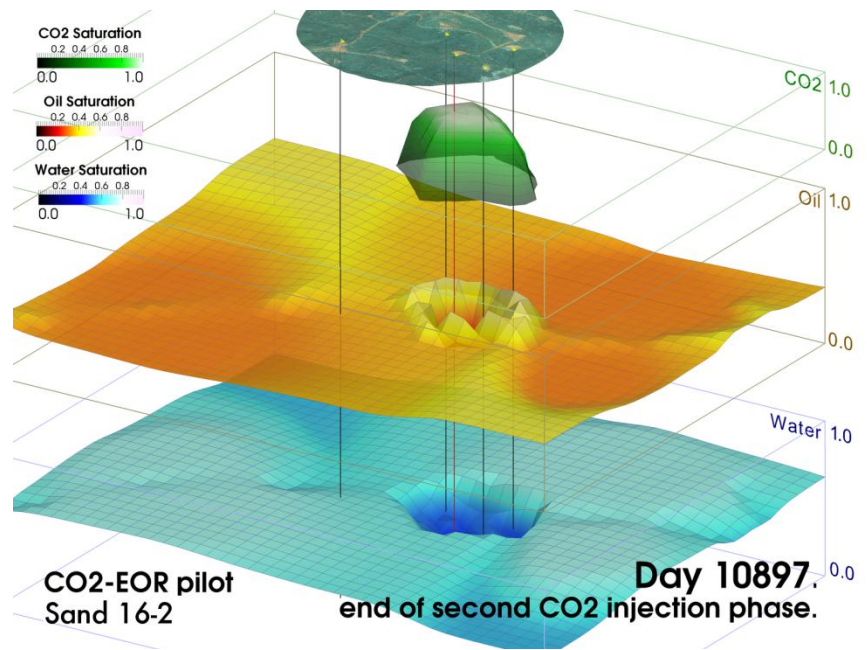
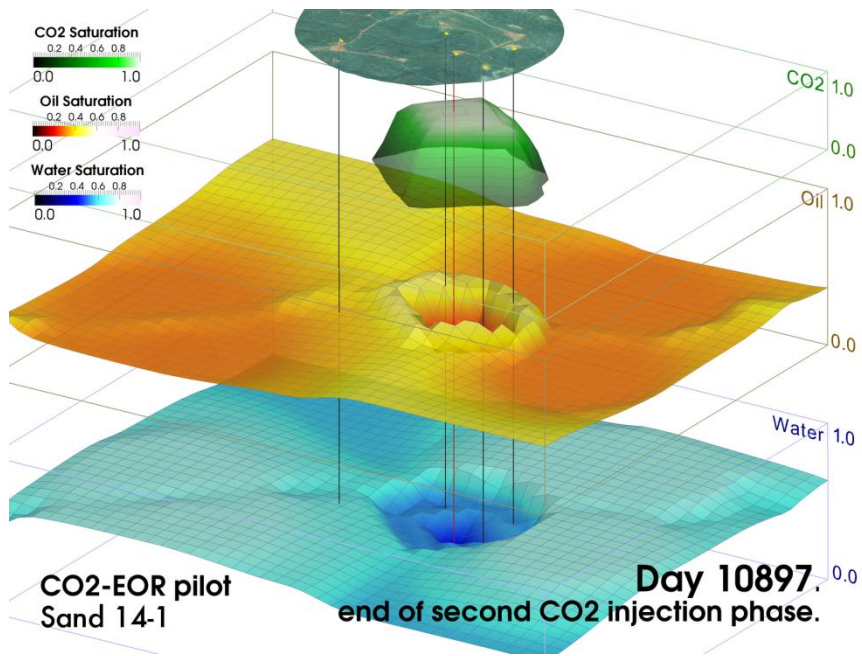


Figure 2.4.3d. Screen shots of the animations of CO₂, water, and oil flows in Sands 14-1 (top) and 16-2 (bottom), at the end of the second injection of 7500 tons of CO₂, 701 days after the beginning of the first CO₂ injection.

2.4.3. Effect of Reservoir Permeability on Oil Recovery

Konstantinos Theodorou, University of Alabama at Birmingham

Results of CO₂-EOR simulations using MASTER 3.0 are presented in Sections 2.4.1 and 2.4.2, above, and in previous Quarterly Progress Reports (e.g. January 30, 2011, pp. 40-42). Among the simulations considered were several 10-year-long WAG injection schemes, from which to observe oil production response and identify optimal oil recovery schemes. The 10-year WAG schemes began immediately after the CO₂-EOR pilot test.

The simulations were conducted using the CO₂-EOR pilot test grid area and the Upper Donovan Sands, 14-1 and 16-2. The average permeability for Sands 14-1 and 16-2 was set at 10 mdarcy, as reported by Fowler et al. (1998). The range of permeability of Donovan sands is 0.02 to 13 mdarcy (Esposito et al., 2010). A new set of calculations was performed to examine the response of the oil recovery simulation to permeability changes.

The optimal oil production scheme, 12 months of CO₂ injection followed by 6 months of water injection, identified in earlier simulations, was repeated using permeability values of 2, 3.8, and 12.5 mdarcy. The low value of 2 mdarcy and the high value of 12.5 mdarcy, were the limits of performance of the simulator using pressure-controlled wells, where the injection rate is calculated based on total fluid mobility within the grid block containing the well. To simulate performance outside this range of permeabilities would have required changing the grid size, already set near the maximum allowed by MASTER 3.0. Another option would have been to reduce the pressure at the injection well, which would not be consistent with the observed injection pressures. The value of 3.8 mdarcy is the geometric mean of the range from 2 to 12.5 mdarcy.

Results of the simulations are presented in Figures 2.4.4 and 2.4.5. As shown in Figure 2.4.4, reduction in permeability decreases the rate of oil production during the waterflood-only period but increases the rate of oil production during WAG recovery. Smaller permeability values decrease mobility, allowing longer contact time between oil and CO₂, increasing the volume of CO₂ mobilized. It is also possible that smaller permeability values reduce fingering and gravity override.

As shown in Figure 2.4.5, incremental cumulative oil recovery decreases with increasing permeability during the WAG period, suggesting that within the current range of permeabilities, the trend of decreasing oil recovery with increasing permeability is correct. Incremental oil recovery is measured since the beginning of the CO₂-EOR pilot test on December 1, 2009. As shown in Figure 2.4.6, the reduction in incremental cumulative oil recovery is a logarithmic function of permeability.

Further investigation would be necessary to identify whether or not the trend is similar over a greater range of permeability, or if changes in grid size would reveal a different reservoir response. A finer grid near the injection and production wells would be more appropriate if the simulator allowed for greater grid size at points far removed from the wells. Changing pressures at the injection and production wells is not possible because the pressures would not then correspond to the observations in the field.

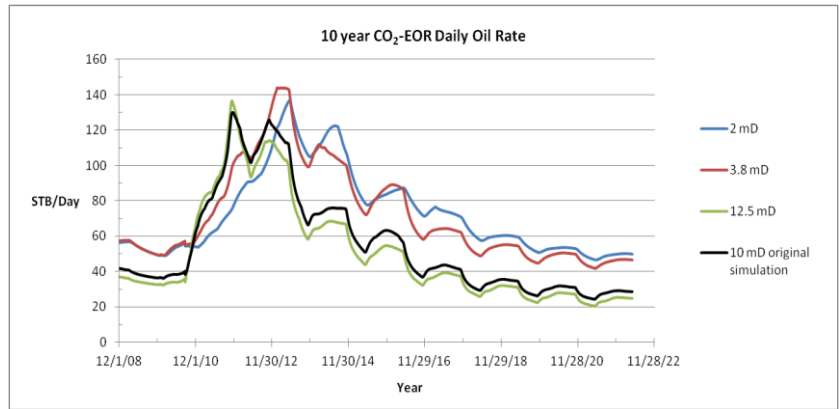
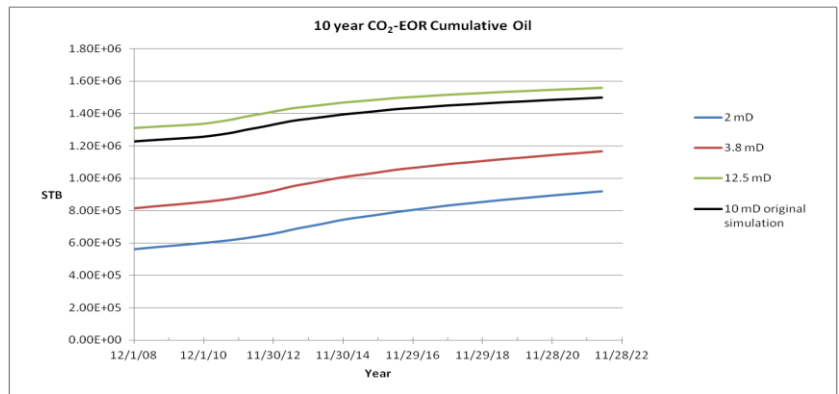


Figure 2.4.4. Calculated rate of oil production versus time, over a 10-year period, from Sands 14-1 and 16-2 in the pilot test simulation area. The WAG scheme employed is 12 months of CO₂ followed by 6 months of water. The CO₂-EOR pilot test began on December 1, 2009. WAG recovery begins on December 7, 2011, immediately following the pilot test.



Figures 2.4.5. Effects of permeability changes on cumulative oil production during 10-year CO₂-EOR from Sands 14-1 and 16-2 in the pilot test simulation area. Same WAG scheme and time periods as in Figure 2.4.4.

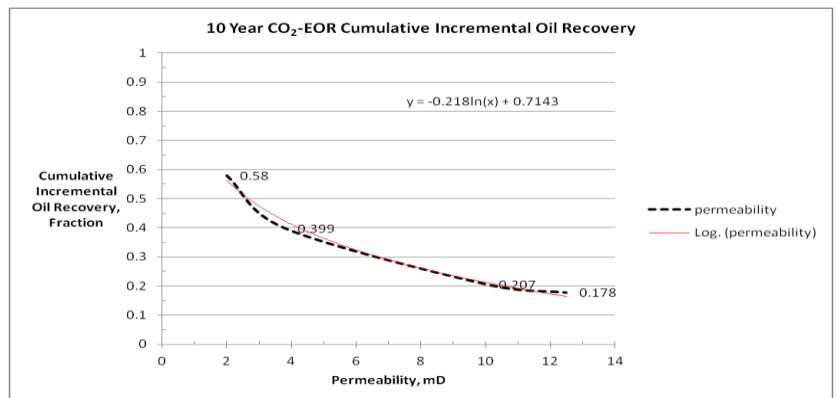


Figure 2.4.6. Dependence of cumulative incremental oil recovery from the test pattern on permeability, during 10 years of CO₂-EOR from Sands 14-1 and 16-2. Incremental recovery is measured over the 10-year period following the start of continuous CO₂ injection for the CO₂-EOR pilot test on December 1, 2009. The solid red curve is a logarithmic function (equation inset) fit to the simulation results.

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

Eric S. Carlson, University of Alabama

During the past quarter, the reservoir engineering team has focused on two issues. The first of these concerns trying to figure out how to deal with the extended well fractures, diagnosed from the well test during the previous quarter, in the simulations. The second issue related to setting up an environment for large-scale parallelization.

Throughout this project, the primary motivation for simulation development came from our desire to properly predict responses to CO₂ injection in a highly heterogeneous system on fine grids. The outcome of this is nSpyres, which is currently set up to efficiently solve complex hydrocarbon/water/CO₂ problems. On a single workstation, we can set up highly heterogeneous problems with 10's of millions of cells and get results in a day. One thing that it doesn't do, yet, is handle discrete natural or induced fractures. Since these fractures can dominate production responses to injection, this is a critical shortcoming.

We have investigated a number of options during the past quarter, and the most promising one is similar to that put forth by Lee, Jensen, and Lough (2000). Historically, fractures have been handled in coarse grids by using extreme anisotropy and/or non-neighbor connections. The Lee-Jensen-Lough approach treats each discrete fracture like a well spanning multiple cells with a net flow of zero and no storage. This approach makes it easy to solve for pressure distributions, and we nearly have things set for saturations and mole fractions. During the next quarter, we will make runs with enhanced anisotropy, but by mid-summer hope to have the discrete fracture models ready to go.

In order to run problems with more than 30 million cells (a full field simulation at Citronelle will require 400 to 600 million cells), it will be necessary to perform simulations on a cluster. Most independent oil companies do not have the expertise or resources to set up dedicated clusters. A much more likely circumstance is that the companies will have multiple dedicated workstations, which can be set up as a cluster of workstations. We have successfully set up a cluster of workstations, but the process was vastly more challenging than it should have been. Most of the documentation on the web is outdated or has critical missing information. After much trial and error and cross-referencing from many sites, we pieced together the correct sequence of steps that has allowed us to split a single simulation run over several computers. We will post all of these instructions on the nSpyres web site later in the summer.

2.5. CO₂ 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 is provided by Denbury Onshore from its wells in the natural CO₂ reservoir at Jackson, MS. During the Phase II CO₂ injection, Airgas Carbonic received the CO₂ from Denbury Onshore, liquefied it, and transported it to Citronelle.

A refurbished 50-ton liquid CO₂ tank was purchased from TOMCO₂ 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 CO₂ is stored at approximately 0 °F and 300 psig in the refrigerated tank. The first shipment of CO₂ was delivered to the test site by Airgas Carbonic on March 2, 2009.

CO₂ is delivered to the test site in tank trucks, each carrying ~19 tons of CO₂. 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 got 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 CO₂ Injection

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

2.6.1. Site Preparation and Water Flood

The injection well in the first 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 CO₂ 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 CO₂,

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).

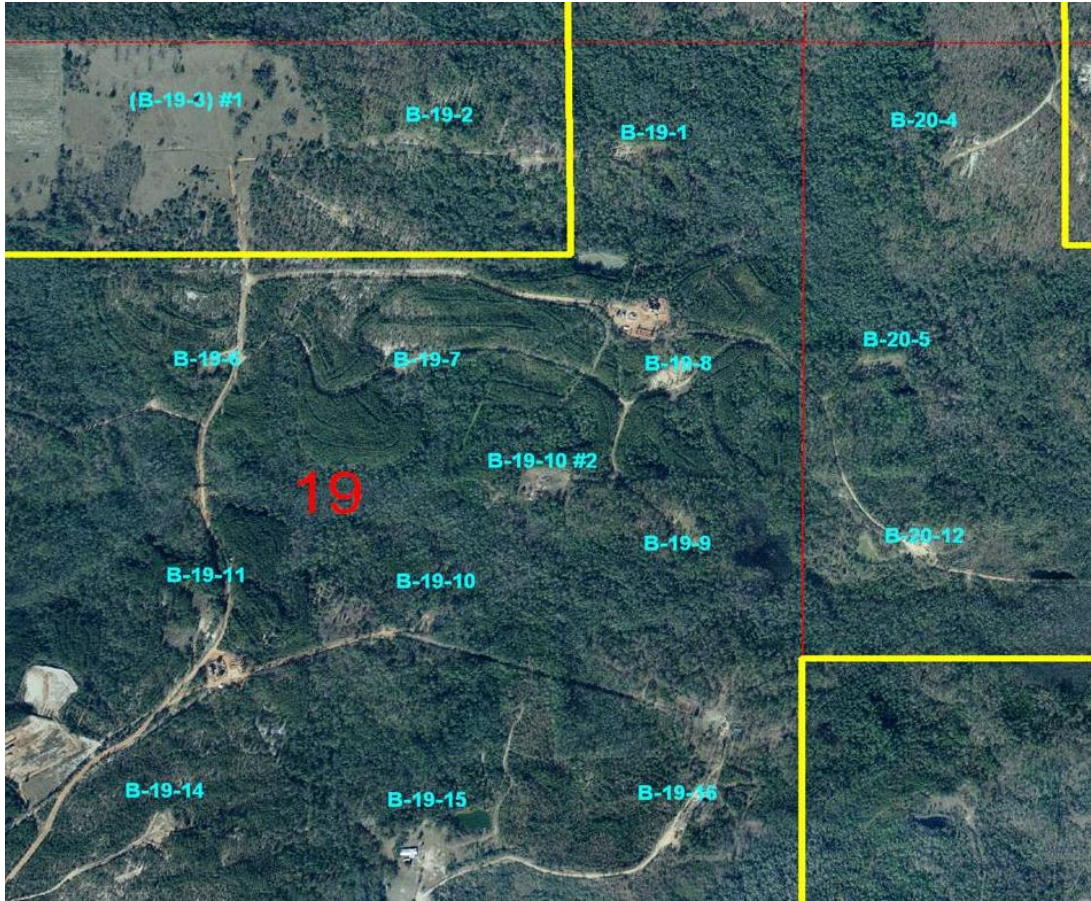


Figure 2.6.1. Aerial photograph of the Citronelle oil field in the vicinity of the test well pattern. The test pattern consists of injector B-19-10 #2 and producers B-19-7, B-19-8, B-19-9, and B-19-11. The top edge of the photograph faces North. Tank Battery B-19-8 is visible just to the Northwest of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

2.6.2. CO₂ Injection

After the first delivery of CO₂ on March 2, 2009, a number of problems were encountered during attempts to begin CO₂ injection. In spite of several rounds of improvements to the pumping system during this early period, steady, continuous CO₂ 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 CO₂. On returning to his office following the meeting, the Principal Investigator contacted Reliant Gases, who had conducted the successful pilot injection of CO₂, 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 CO₂.

Denbury Resources then retained Steve Wegener, a senior engineer from Jacobs Linder Engineering (Metairie, 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 CO₂ 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 CO₂ 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 CO₂ to compress, which created a temperature spiral until eventually the CO₂ 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 CO₂ injection at the test site on December 22, 2009. The injection rate settled at 46.5 tons CO₂/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 CO₂/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 CO₂ were typically injected each day; equal to slightly more than half of the desired minimum rate (35 tons/day). Then, on December 29th, a tubing leak was detected, requiring a complete shut-down for repair. CO₂ 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 CO₂ resumed on January 27. The average rate of CO₂ injection, including down time for maintenance, then stabilized at 31 tons/day. The history of CO₂ 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 CO₂ 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 CO₂ 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 CO₂, 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.

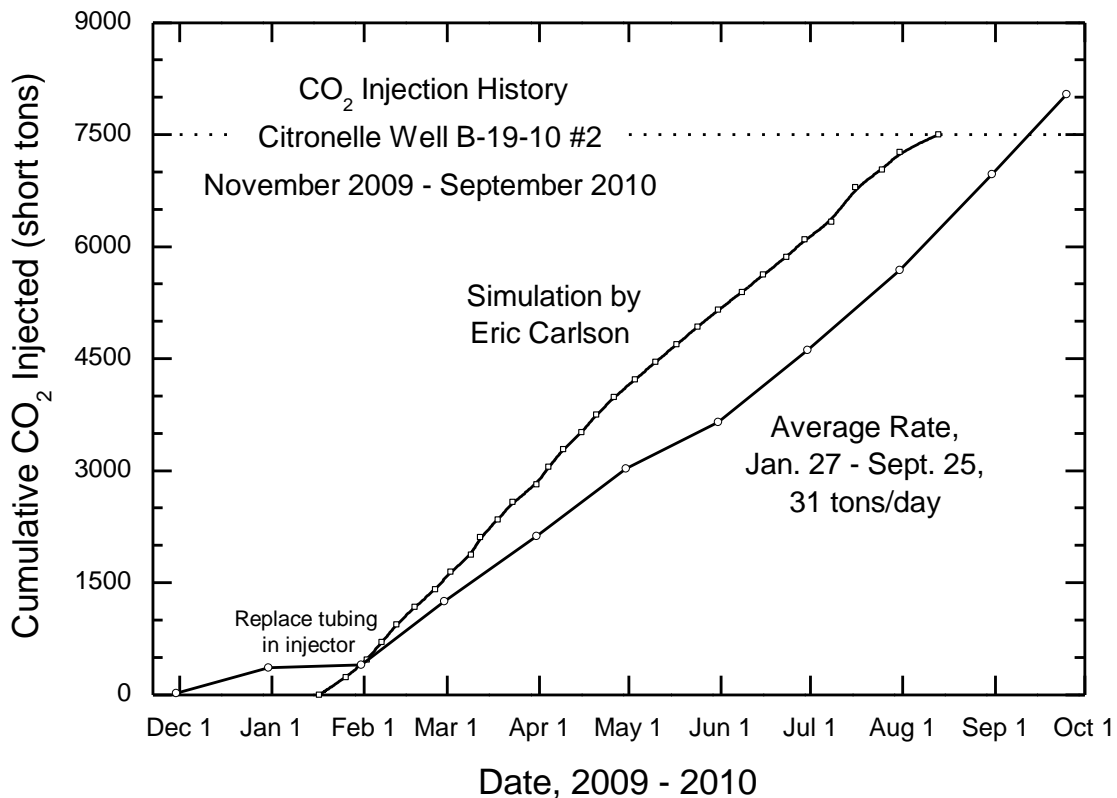


Figure 2.6.2. Record of the CO₂ injection during Phase II and comparison with the reservoir simulation by Eric Carlson using SENSOR (Coats Engineering, Inc.). The average injection rate from January 27 to the end of the injection, including down time for maintenance, was 31 tons/day. The total amount of CO₂ injected was 8036 tons.

2.6.3. Response to CO₂ 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 CO₂ injection, to March 2012, 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 CO₂ injection, the decline in production was reversed, and, from January to September 2010, when the first CO₂ 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 to only 36% of the rate at the September 2010 peak in March 2011 and to less than half of the rate just before the start of CO₂ 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 particles mobilized by CO₂ contaminating the power oil. The frequency of pump pulls had begun to increase in August 2010, just before the end of the CO₂ 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 has been a corresponding increase in oil production over the past 12 months, to 44 bbl oil/day in March 2012. The present rate 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 CO₂ injection in December 2009, but it is significantly higher than the decline curve established during the 10 months of water flood, from March to December 2009, prior to CO₂ injection, as shown in Figure 2.6.3a.

Integration of the difference between the actual oil production shown in Figure 2.6.3a and the production anticipated by the decline curve, over the period from January 2010 to March 2012 gives an (unofficial) estimate of incremental oil production at this tank battery arising from the CO₂ injection of 9722 bbl. While less than the approximately 20,000 bbl of incremental recovery predicted to date by Eric Carlson's reservoir simulations using SENSOR (Coats Engineering, Inc.) (the water flood has continued for a longer period than originally planned), the shortfall is less than might have been expected, considering that the production figure is for only three of the four producers and the problems with the pumps.

The response to CO₂ 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 of water flood. Then, coinciding with the breakthrough of CO₂ 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 CO₂ injection and return to water injection in September 2010.

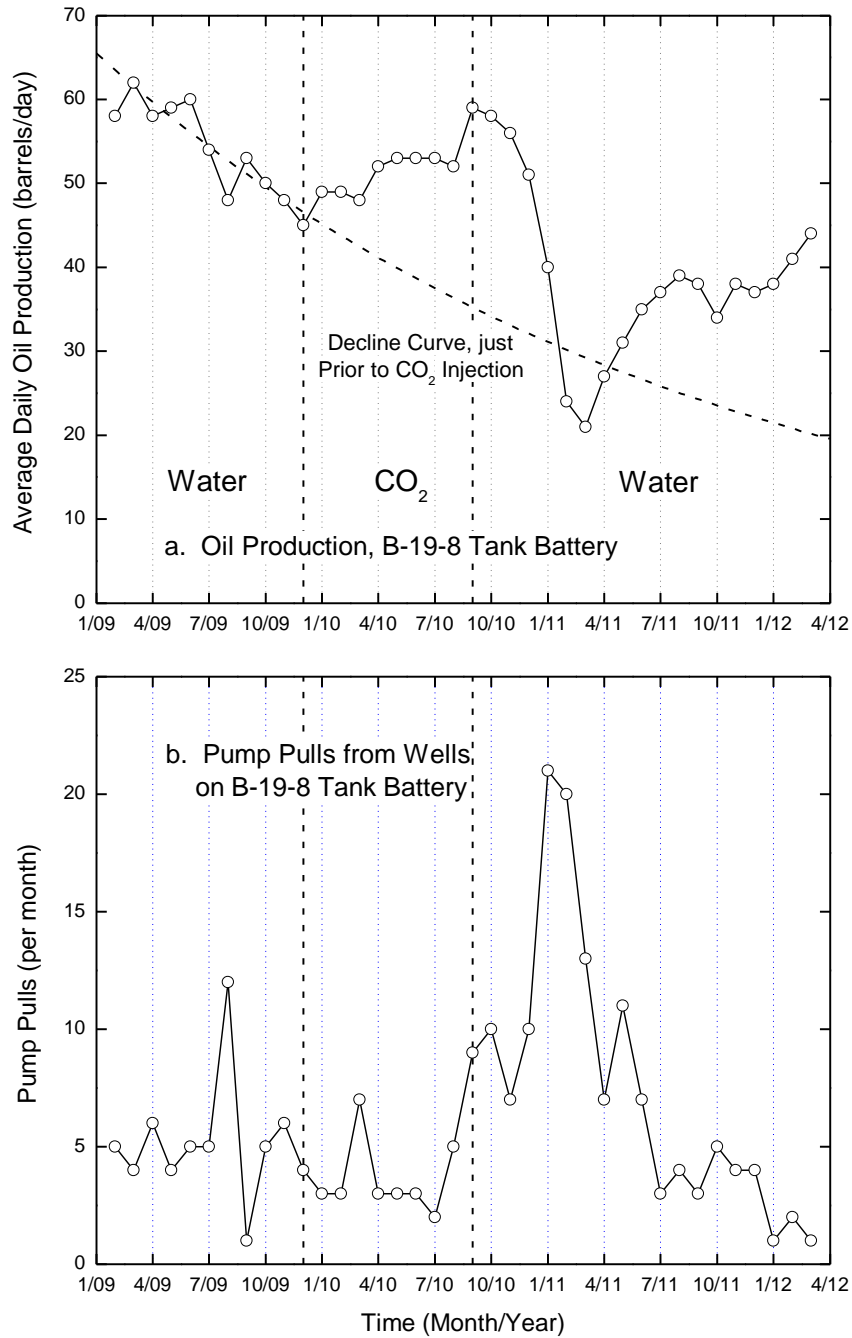


Figure 2.6.3. Response to CO₂ injection at Tank Battery B-19-8. a. Oil production at B-19-8 Tank Battery, which receives fluids from Wells B-19-7, B-19-8, and B-19-9, from February 2009 to March 2012. b. Number of times per month that power oil pumps in wells on B-19-8 Tank Battery had to be pulled for maintenance or replacement, from February 2009 to March 2012.

Integration of the difference between the decline curve and production data shown in Figure 2.6.4a, from January 2010 to March 2012, gives an (unofficial) incremental deficit of

9872 bbl. Combining the deficit with the incremental production at B-19-8 Tank Battery gives an overall loss, to March 2012, of $9722 - 9872 = -150$ bbl. Our goal in Phase III is to erase this deficit and realize a significant net incremental gain in oil production.

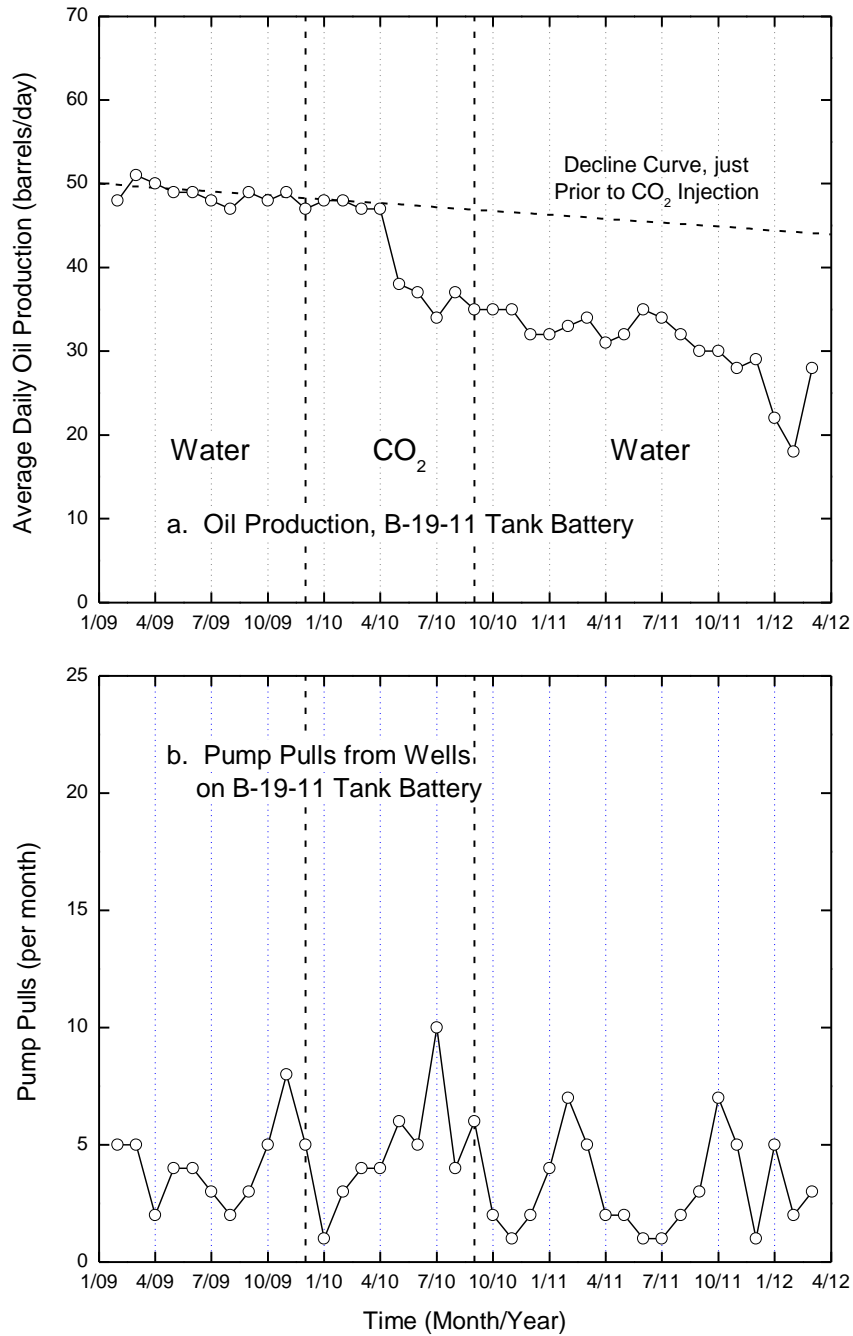


Figure 2.6.4. Response to CO₂ injection at Tank Battery B-19-11. a. Oil production at B-19-11 Tank Battery, which receives fluids from Well B-19-11, from February 2009 to March 2012. b. Number of times per month that power oil pumps in wells on B-19-11 Tank Battery had to be pulled for maintenance or replacement, from February 2009 to March 2012.

A second reason for the decline in oil production, beginning at the end of the CO₂ injection and return to water injection in September 2010, is that the water injection rate, which had been 170 bbl water/day before CO₂ injection, decreased to approximately 60 bbl water/day and remained, except for occasional spikes, at this low level. A test campaign is now underway 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. 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.

On May 25, 2010, only five months after continuous CO₂ 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 CO₂. 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 CO₂ ($\delta^{13}\text{CO}_2$) in the sample of produced gas with the isotope ratio in the injected CO₂, showed that the CO₂ in produced gas at B-19-11 was breakthrough from CO₂ injection at B-19-10 #2. Rapid breakthrough of CO₂ 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.

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 CO₂, from the storage tank, are compared in Table 2.6.1. The gas from one well, B-19-7, has approximately the same CO₂ content as gas from all of the wells before CO₂ injection began, and its low value (large negative number) for $\delta^{13}\text{CO}_2$ is characteristic of solution gas. The CO₂ and $\delta^{13}\text{CO}_2$ analyses for the other wells show that the order of CO₂ 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 CO₂ using Draeger Tubes. The record of CO₂ in produced gas in April 2011 is summarized in Table 2.6.2. The injector and the wells at which CO₂ is present at high concentration in produced gas are aligned along the general direction of the maximum horizontal compressive stress in the Southeastern U.S. (typically N60E to N80E). Breakthrough at Well A-25-10, far to the southwest of the injector, is very surprising and provides evidence for distant travel of CO₂ across depositional trends.

Testing to determine the cause of low injectivity to water, following the CO₂ 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 2.6.5, 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 N60E to N80E. Two of the wells at which early breakthrough of CO₂ 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 CO₂ injection into Well B-19-10 #2, and (2) The fracture provided a preferential pathway for CO₂, compromising the sweep efficiency of CO₂ in the first field test.

Understanding of these observations has been given high priority in the work to be done during the remainder of the project. They have significant bearing on the design and management of a commercial CO₂ flood at Citronelle. During the coming quarter, surfactant will be added to the injected water, to determine if the blockage to water injection is due to capillary effects. If surfactant injection has little effect, the injector will be treated with acid to remove clay fines that may have been mobilized, or carbonate that may have been precipitated by carbon dioxide in the near-wellbore region. If injectivity can be restored, a step rate test will be run to determine the fracture opening stress, with a view to implementing a "smart" well in which the injection pressure can be adjusted to minimize bypassing of water and CO₂ through the fracture.

Table 2.6.1.
Analyses of Samples of Produced Gas and Injected CO₂ Collected on August 4, 2010.

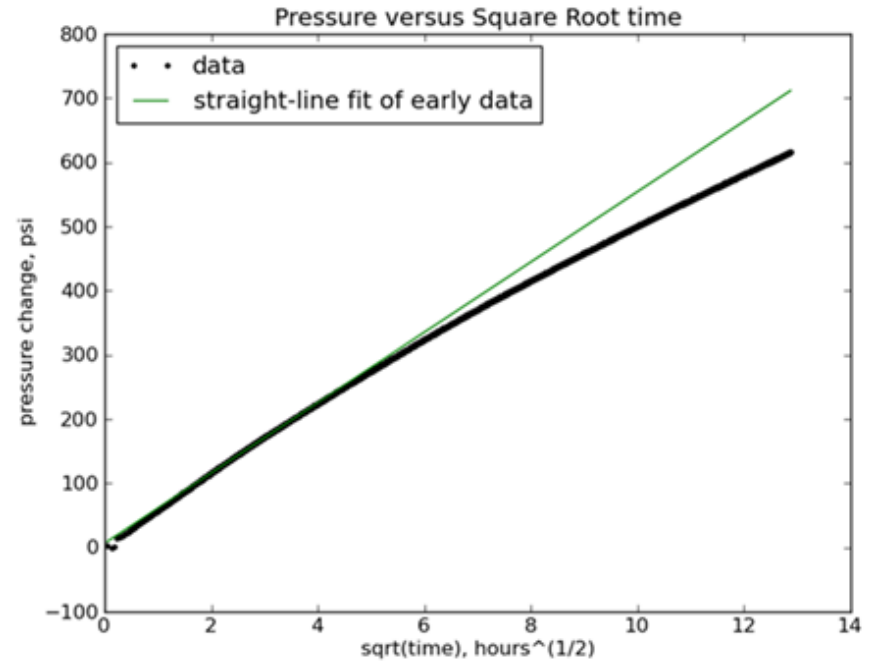
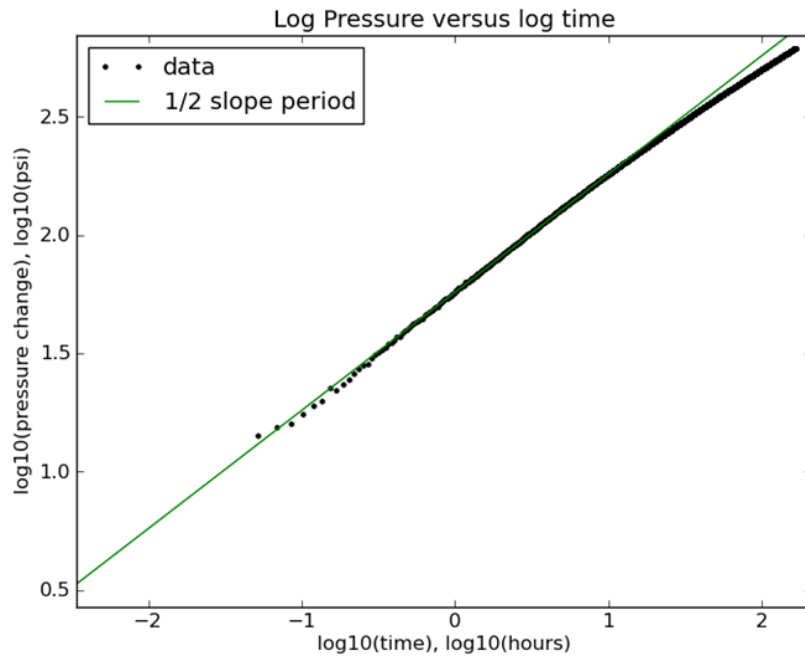
Well Name	B-19-11	B-19-11	B-19-7	B-19-8	B-19-9	CO ₂ Tank
Gas Composition						
C1	0.66	0.67	20.57	29.02	36.17	0.02
C2	0.45	0.44	5.50	5.58	6.26	0.01
C2H4	0.00	0.00	0.00	0.00	0.00	0.00
C3	1.13	1.05	8.27	7.59	7.14	0.06
iC4	0.67	0.62	3.18	2.85	2.46	0.03
nC4	1.24	1.14	5.53	5.07	4.11	0.09
iC5	0.41	0.38	1.12	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

$$* \delta^{13}\text{CO}_2 = [({}^{13}\text{C}/{}^{12}\text{C})_{\text{sample}}/({}^{13}\text{C}/{}^{12}\text{C})_{\text{reference}} - 1] \times 1000$$

Table 2.6.2.
CO₂ 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 CO₂ not significantly greater than the 3 vol% typical of Citronelle solution gas.



- a. Slope of $\frac{1}{2}$ 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. $\text{time}^{1/2}$ during shut-in indicates a fracture length of 600 to 1000 ft.

Figure 2.6.5. 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).

2.7. Surface Monitoring

2.7.1. Soil Properties and CO₂ Fluxes from Forest Soils at the Test Site

Ermson Z. Nyakatawa and Latasha J. Lyte
Alabama Agricultural and Mechanical University

Work by Ermson Nyakatawa and his group has been on hold, first pending authorization and funding to proceed with Phase III, then by his search for a research assistant to replace Latasha Lyte, who received her M.S. Degree and graduated in Summer 2011. This section has been carried over, without change, from previous Quarterly Progress Reports (April 30, July 30, and October 30, 2011, and January 30, 2012). Ermson has recently hired a new graduate research assistant to continue the laboratory and field work begun by Latasha Lyte. The new research assistant is Karen Nanton, who is working on her Ph.D. in forestry ecosystems. Ermson and his team plan to visit Citronelle again on May 2, for collection of a new set of soil and gas samples at their test sites near the injector and producers.

Instrumentation. Dr. Nyakatawa and his students at AAMU installed soil probes and sampling chambers with which to measure soil gas composition versus depth, CO₂ 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.

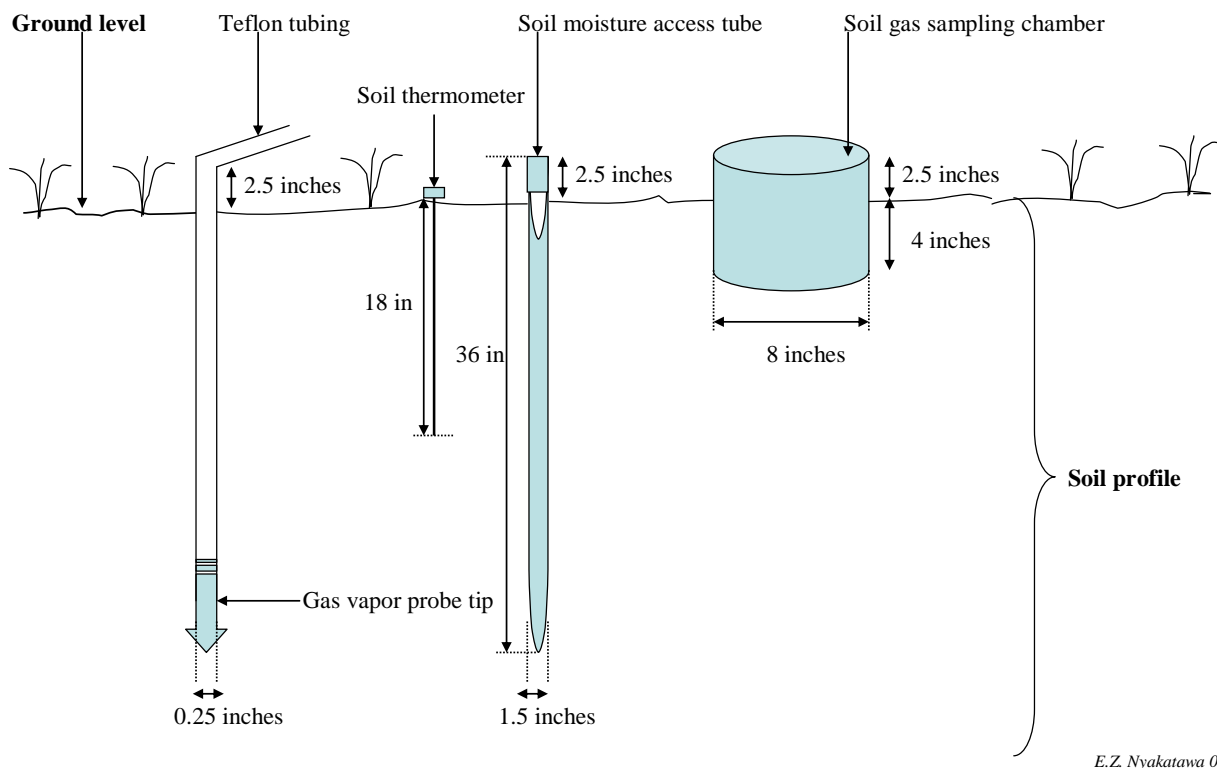


Figure 2.7.1. Soil gas sampling system (Ermson Nyakatawa, Alabama A&M University).

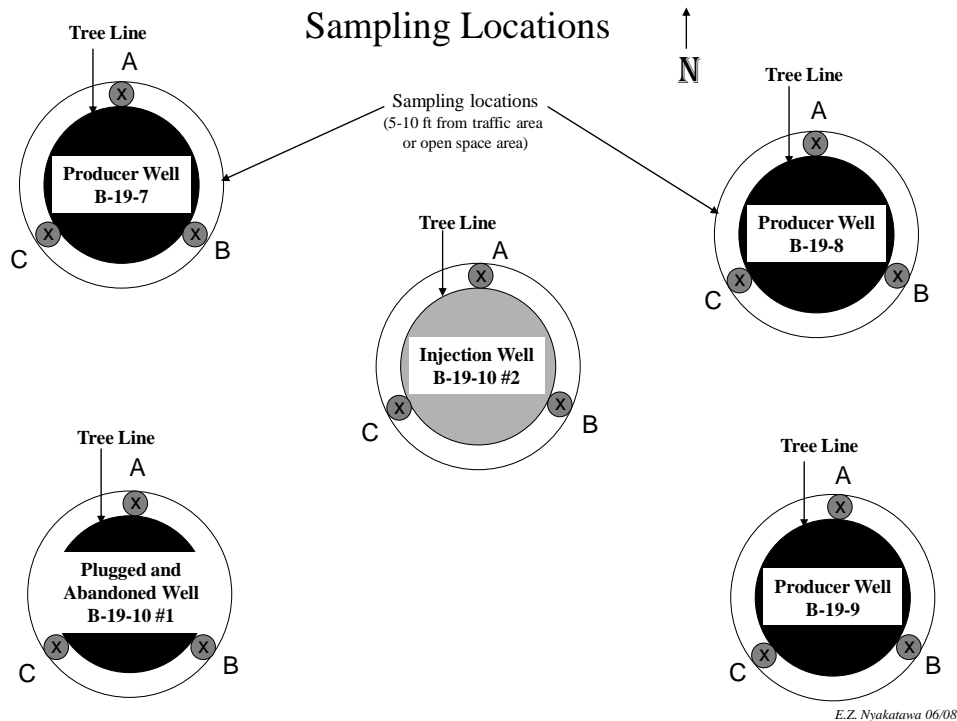


Figure 2.7.2. Arrangement of soil gas sampling stations at the CO₂ injection well, three production wells, and the plugged and abandoned well in the pilot test well pattern. There are three sampling stations at each well (Ermson Nyakatava, Alabama A&M University).

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 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 CO₂ flux.

Latasha Lyte's Master's Thesis, entitled, "Carbon Dioxide Fluxes in a Forest Soil in the Citronelle Oil Field in South Alabama," was published during the quarter under review. Summaries of Latasha's work have been presented in previous Quarterly Progress Reports (April 30, 2011, pp. 19-21 and July 30, 2011, pp. 20-22) and are reproduced below.

Influence of Soil Conditions on CO₂ Flux. Natural soil CO₂ 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 CO₂ fluxes. Microbial activity and mineralization generally increase with temperature, the activity doubling with each 10 °C rise in temperature over the range from 5 to 35 °C. 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 CO₂ 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 CO₂ 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 CO₂ injection), were presented and discussed in earlier Quarterly Progress Reports (October 30, 2009, pp. 29-30; January 30, 2010, p. 26).

CO₂ Flux from Forest Soils at Oil Wells in the Test Pattern. The baseline soil CO₂ fluxes around representative wells in the Citronelle Oil Field study area were established before injection of CO₂ for enhanced oil recovery. The importance of the baseline measurements is that forest soil is a source of CO₂ from natural processes such as microbial and root respiration. Therefore, it was important to account for the background CO₂ fluxes prior to injection of CO₂ in order to be able to discriminate natural CO₂ from CO₂ leakage, should it occur. The wells selected for baseline surface CO₂ 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.

CO₂ flux data from soil gas samples collected both before and during CO₂ injection are presented in Figure 2.7.3, showing the CO₂ fluxes at different times during the study. Compared to the soil CO₂ fluxes observed in August 2008, before CO₂ injection, the fluxes in August 2010, during CO₂ injection, were lower than expected at Well B-19-7 (2.28 mg CO₂ m⁻² min⁻¹ vs. 0.12 mg CO₂ m⁻² min⁻¹), at Well B-19-10 #1 (1.29 mg CO₂ m⁻² min⁻¹ vs. -0.05 mg CO₂ m⁻² min⁻¹), and at Well B-19-10 #2 (0.53 mg CO₂ m⁻² min⁻¹ vs. -0.09 mg CO₂ m⁻² min⁻¹) as shown in Table 2.7.1. At Well B-19-8, post injection soil CO₂ fluxes in August 2010 were slightly higher than those in August 2008 (0.40 mg CO₂ m⁻² min⁻¹ vs. -0.21 mg CO₂ m⁻² min⁻¹).

Regression analysis for a model relating CO₂ 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 CO₂ 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), Mallows' 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 CO₂ fluxes to soil temperature (T) and soil moisture (M) during gas sampling at each well are given in Table 2.7.2.

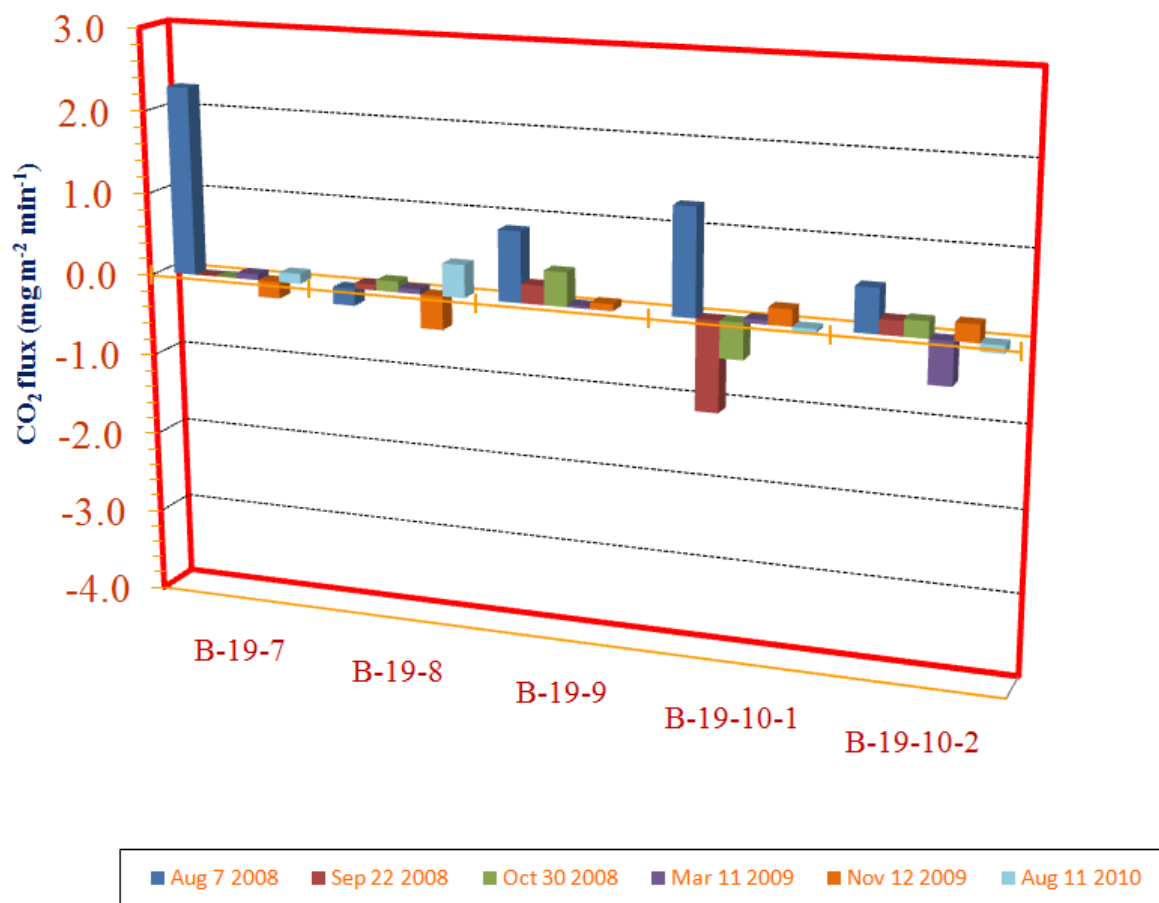


Figure 2.7.3. Measurements of soil surface CO₂ fluxes near five wells in the CO₂-EOR test pattern in the Citronelle Oil Field, August 2008 to August 2010, before and during CO₂ injection.

Table 2.7.1.

Measurements of soil surface CO₂ fluxes near five wells in the CO₂-EOR test pattern in the Citronelle Oil Field, August 2008 and August 2010, before and during CO₂ 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 CO₂ 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	$CO_2 = 0.9 + 0.01 T - 10.4 M + 20.1 M^2$ ($R^2 = 0.35$)
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	$CO_2 = 78.2 + 12.0 T - 0.6 T^2 - 16.7 M + 43.0 M^2 - 25.5 M^3$ ($R^2 = 0.70$)

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 CO₂ 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 CO₂ 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 CO₂ 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 also play a significant role in explaining some of the remaining variation.

2.7.2. Vegetation and Ambient Air Monitoring

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

Xiongwen Chen and Kathleen Roberts have been measuring CO₂, O₂, CH₄, SO₂, H₂S, and aerosol in ambient air at least once every quarter since September 2007 at 104 sampling locations in the Oil Field and City of Citronelle. The measurements for a given month are 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 enables the investigators to construct contour plots showing the distribution of species concentrations across the region. During the quarter under review, Kathleen Roberts and Xiongwen Chen continued the collection and analysis of these data.

The average CO₂ volume fraction in ambient air at the 104 measurement locations, on March 26-27, 2012, is shown in Figure 2.7.4, along with the earlier measurements. The average CO₂ volume fraction in ambient air at Citronelle on March 26-27 was 381 ± 22 ppmv, lower than the regional value expected from the NASA satellite-based Atmospheric Infrared Sounder <<http://airs.jpl.nasa.gov/>> during March, 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 CO₂ volume fraction in the region 88-89° West and 31-32° 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 CO₂ are visible in the NASA measurements and the measurements at ground level, in Figure 2.7.4. The recent (2011) worldwide annual average volume fraction of CO₂ is 390.45 ± 0.10 ppmv (Thomas Conway and Pieter Tans, NOAA/ESRL, www.esrl.noaa.gov/gmd/ccgg/trends/), increasing at the rate of approximately 2 ppmv/year.

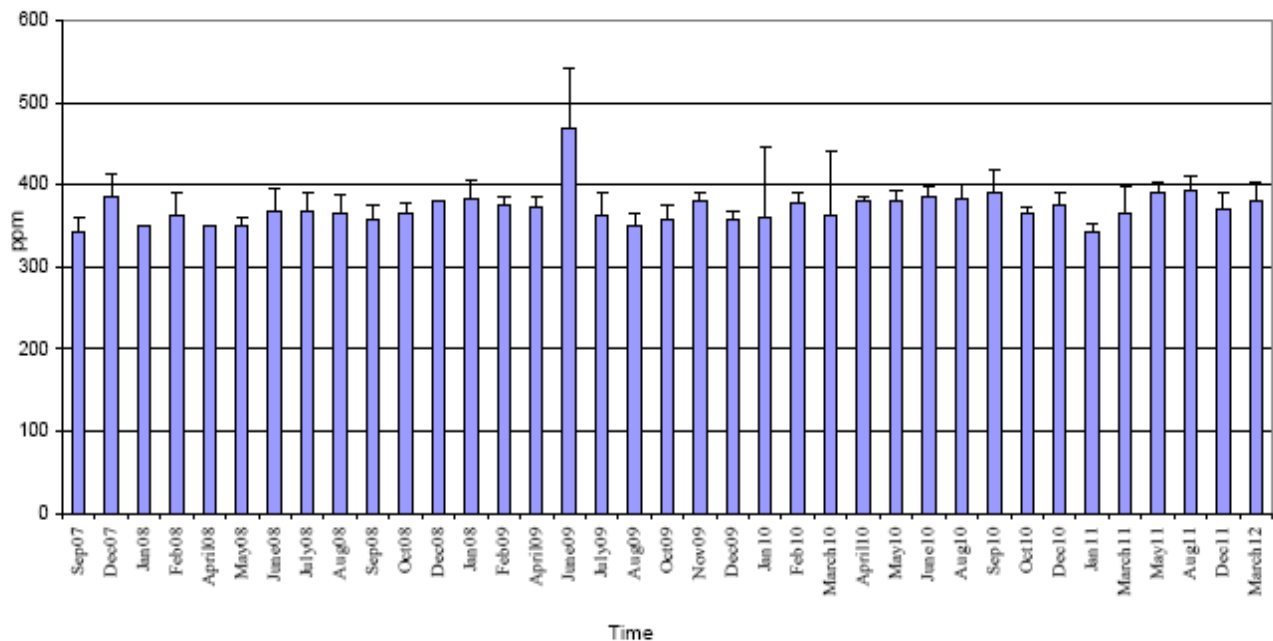


Figure 2.7.4. Average atmospheric CO₂ volume fraction (parts per million) at ground elevation across the City of Citronelle and Citronelle Oil Field from September 2007 to March 2012.

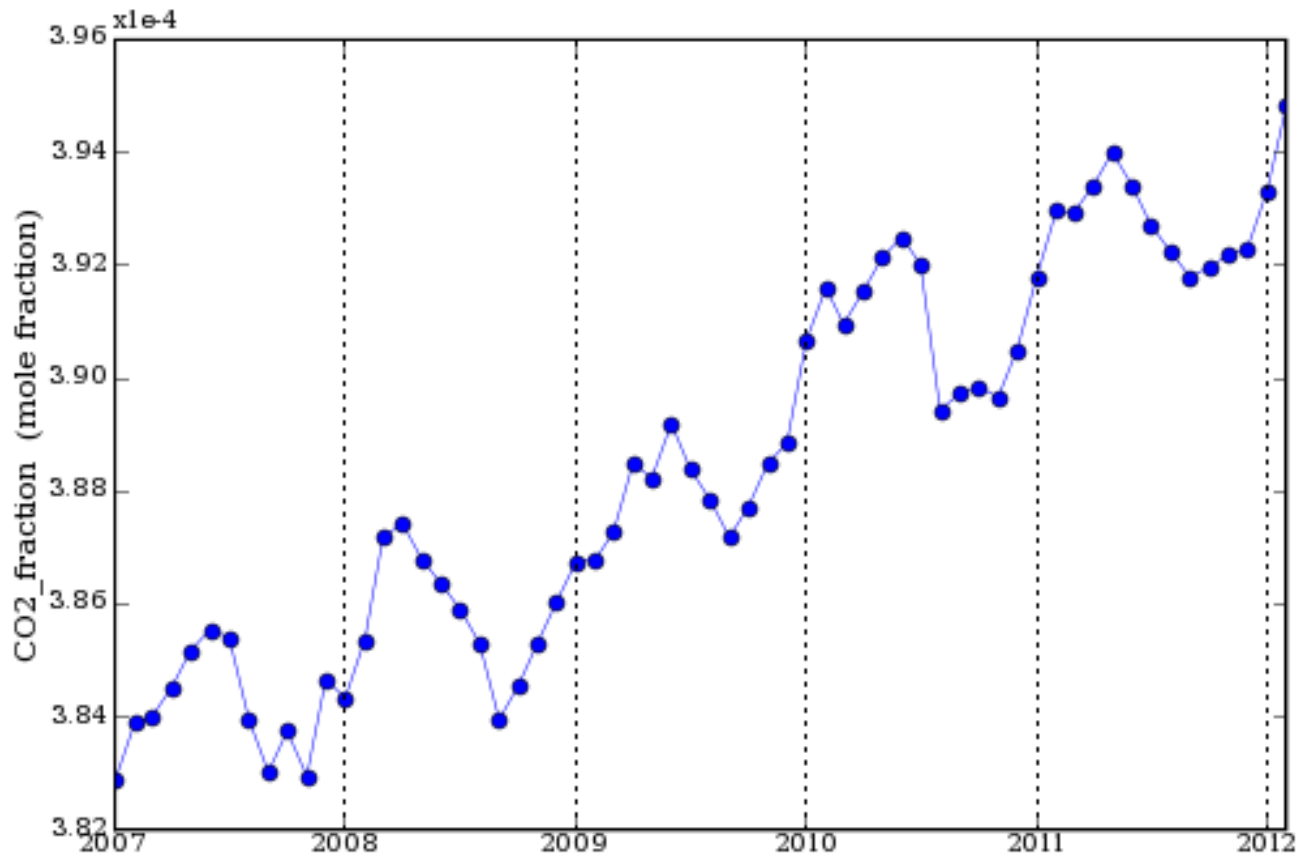
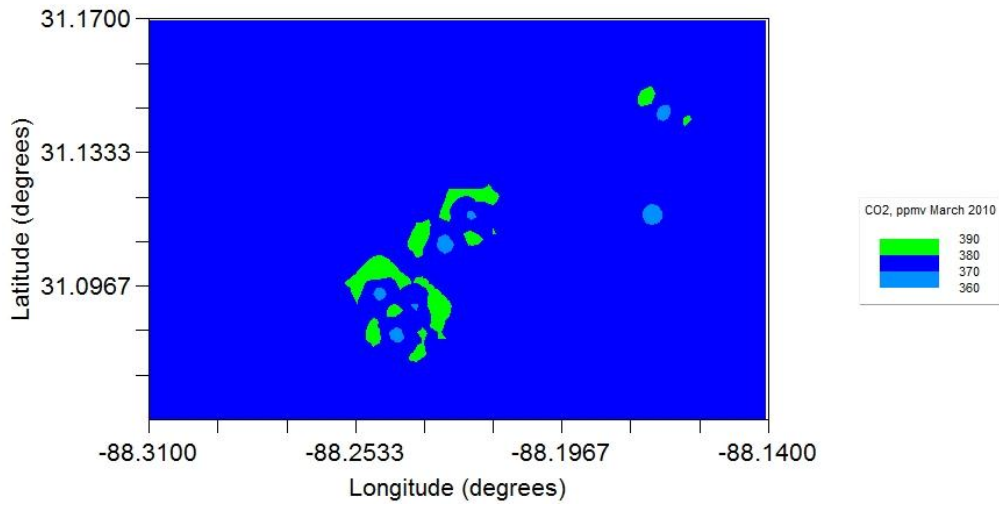


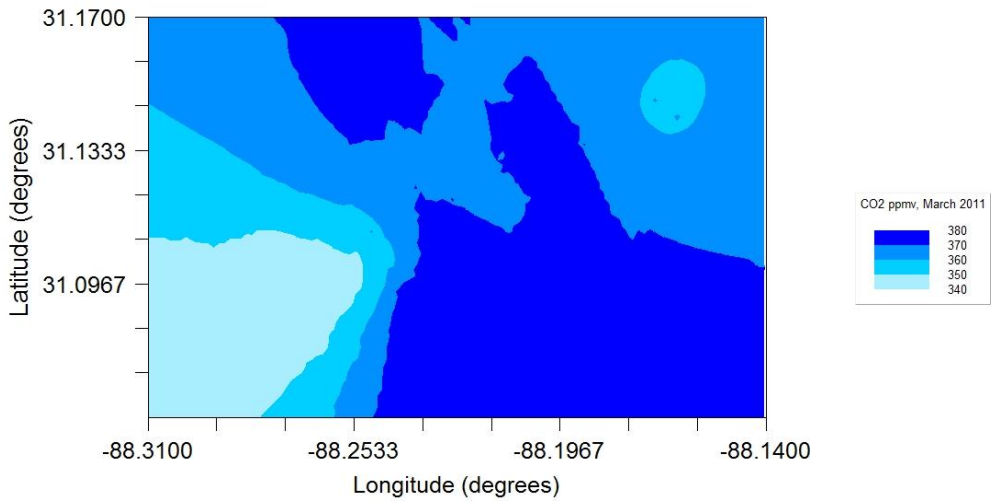
Figure 2.7.5. Area-averaged time series (AIRX3C2M.005) in the region 88-89° West and 31-32° North, including the City of Citronelle and the Citronelle Oil Field. Data from the NASA Atmospheric Infrared Sounder <<http://airs.jpl.nasa.gov/>>. Multiply the mole fraction values on the y-axis by 100 to convert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

Contour plots, in Figure 2.7.6, show the spatial distribution of CO₂ across the region in March 2010 (Figure 2.7.6a), March 2011 (Figure 2.7.6b), and March 2012 (Figure 2.7.6c). No correlation with the location or timing of the CO₂ injection can be discerned from the CO₂ contours.

a. March 2010



b. March 2011



c. March 2012

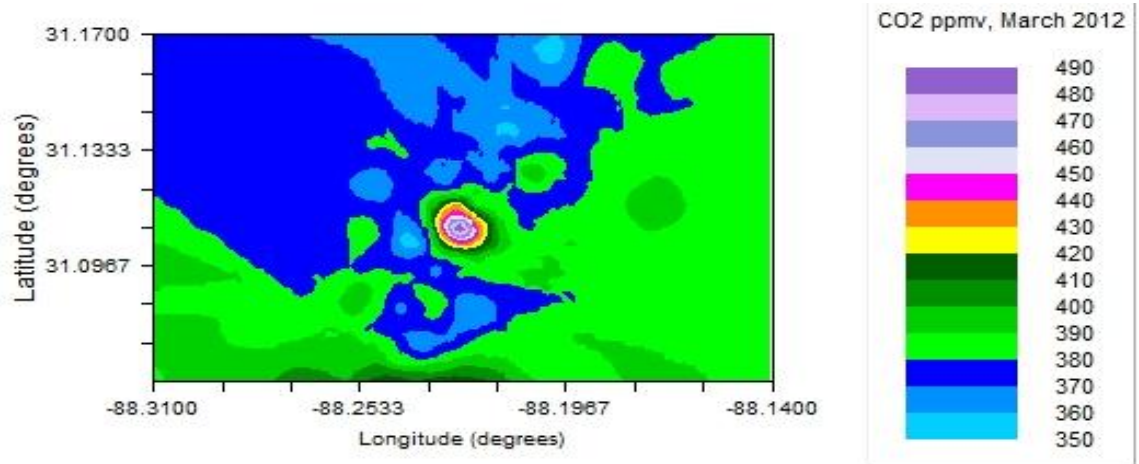


Figure 2.7.6. Contour plots showing the spatial distribution of the CO₂ volume fraction across the City of Citronelle and Citronelle Oil Field in March 2010, March 2011, and March 2012.

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 the original plots by land owners, some of the original plots are no longer available. The growth of trees in the remaining plots during the three time intervals, 2008-2009, 2009-2010, and 2010-2011 are shown in Figure 2.7.7. 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 CO₂.

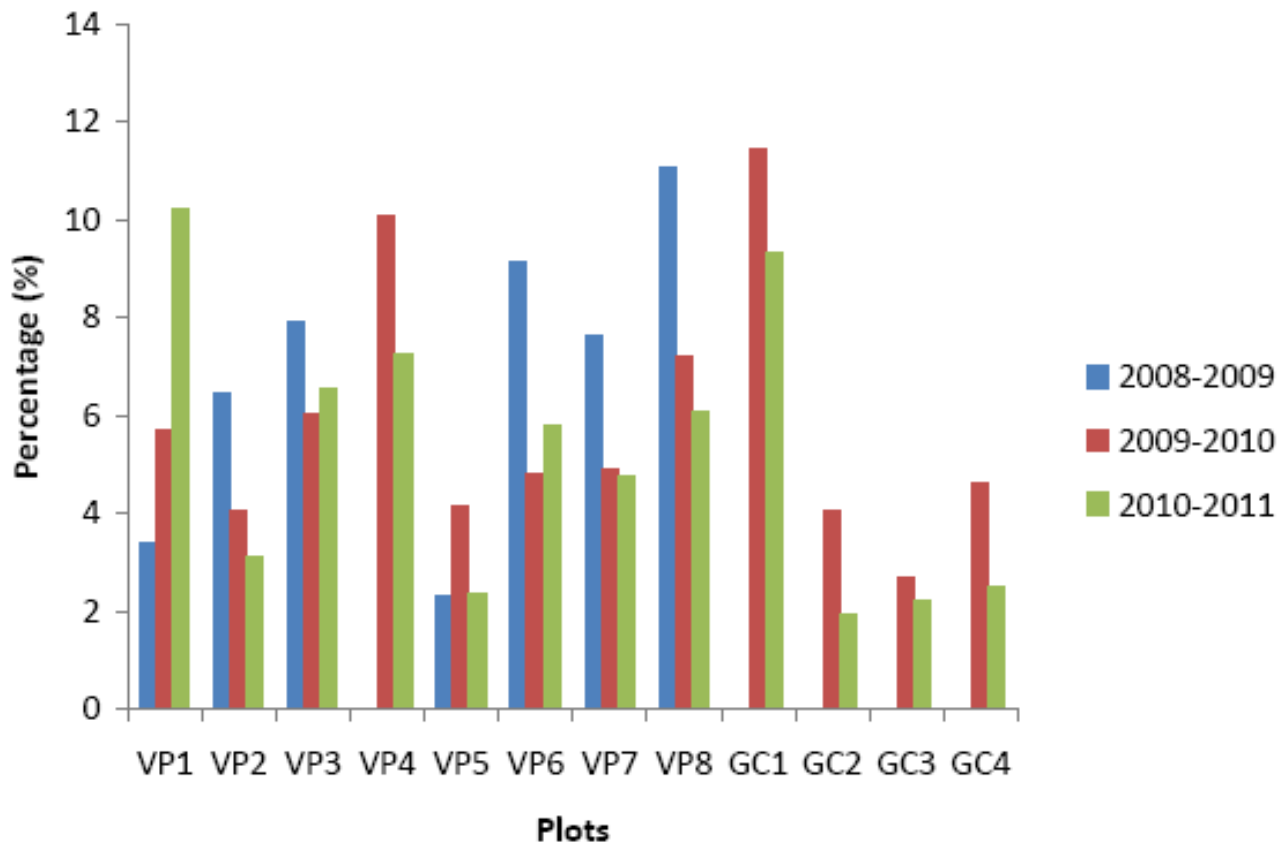


Figure 2.7.7. Comparison of growth, as the fractional (%) increase in basal area, in vegetation plots across Citronelle during the three periods, 2008-2009, 2009-2010, and 2010-2011. The plots are identified in Table 2.7.3.

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

One plot, VP1, on the far left in Figure 2.7.7, 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 CO₂ in ambient air were not consistently detected there, nor were elevated CO₂ fluxes from soil near that well reported by Ermson Nyakatawa and Latasha Lyte (Section 2.7.1, pp. 42-46). We leave open the possibility that vegetation near Well B-19-10 #2 may have been influenced by CO₂ from the pilot test, and will continue to monitor CO₂ in ambient air and the growth of vegetation at this location and at all of the other observation points. 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 CO₂ plumes associated with the CO₂ storage tank, injection equipment, wells, or tank batteries.

There has been no significant short or long-term effect of storage, handling, and injection of CO₂ on the levels of CO₂ 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 CO₂ in ambient air and measurements of CO₂ fluxes from soil near the well. Monitoring of CO₂ in air, CO₂ fluxes from soil, and growth of vegetation will continue to the end of the project.

A paper by Kathleen A. Roberts and Xiongwen Chen, entitled, "Considerations for Ecological Monitoring of CO₂-mediated Enhanced Oil Recovery," has been published in the *International Journal of Ecological Economics and Statistics* (Vol. 27, No. 4, 2012).

2.8. Seismic Measurements

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

Geophysical testing is being done using the passive Refraction Microtremor (ReMi) technique, to compare the seismic properties of the oil field before, during, and after CO₂ 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.

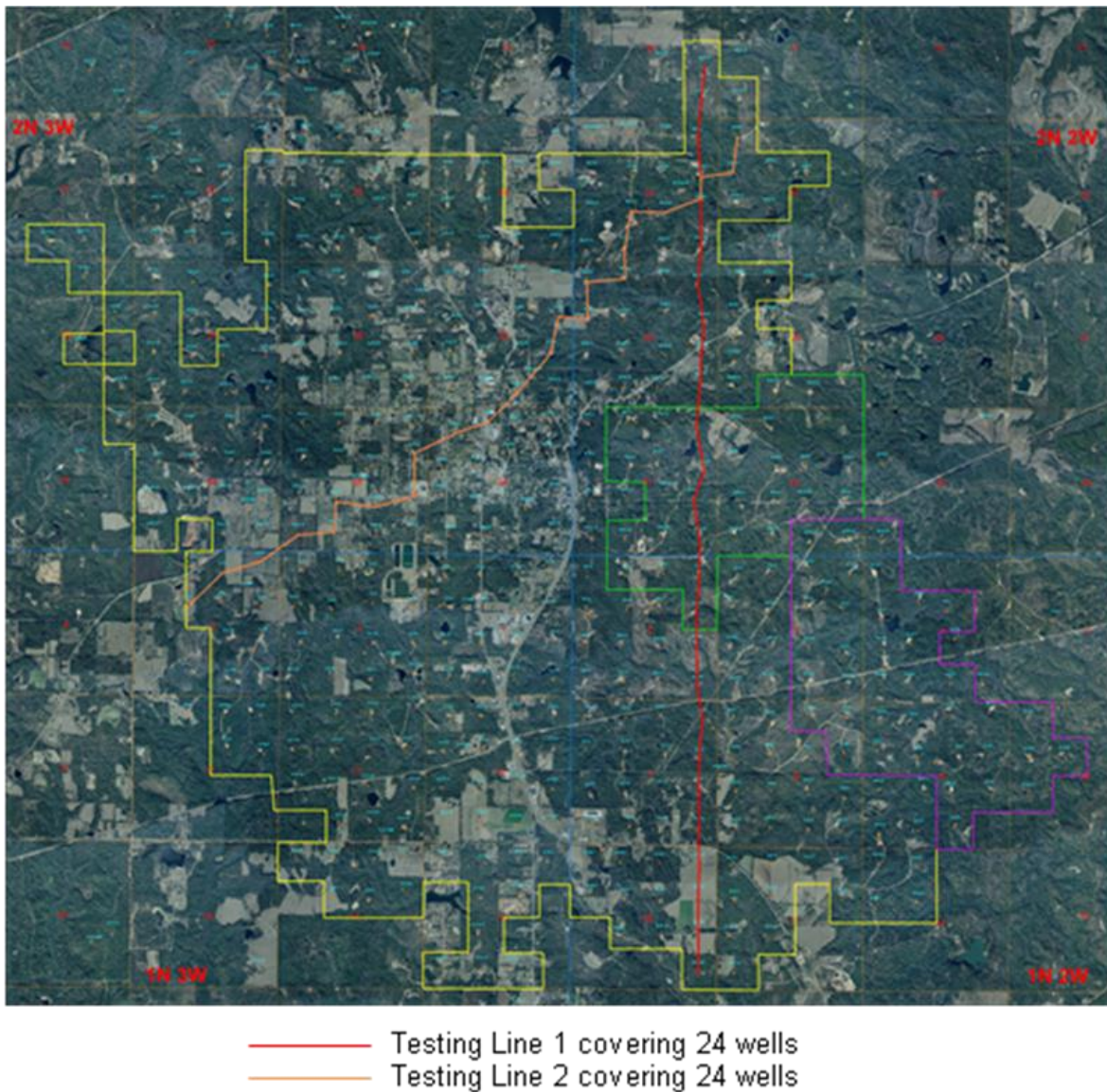


Figure 2.8.1. The seismic testing lines, superimposed on the aerial photo of Citronelle Field from Denbury Onshore.

Baseline data, prior to CO₂ 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 CO₂ injection were made on December 9-10, 2009; then during steady CO₂ 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).

During the quarter under review, Yangguang Liu, Research Assistant in Shen-En Chen's research group at the University of North Carolina at Charlotte, completed and successfully defended his Master's Thesis. His thesis presents the theory of the DoReMi passive geophysical monitoring technique and reports the Group's observations of changes in shear-wave velocity before, during, and after the pilot CO₂ injection in the inverted five-spot test pattern at Citronelle. One of the key contributions of his work is the use of a bi-linear model to describe the geo-static pressure distribution, before, during, and after injection of CO₂, 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 CO₂ injection (before, during, and after injection), and for each of the two sensor lines, clearly indicated that two distinct behaviors can be observed, as shown in Figures 2.8.2 (Line 1) and 2.8.3 (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).

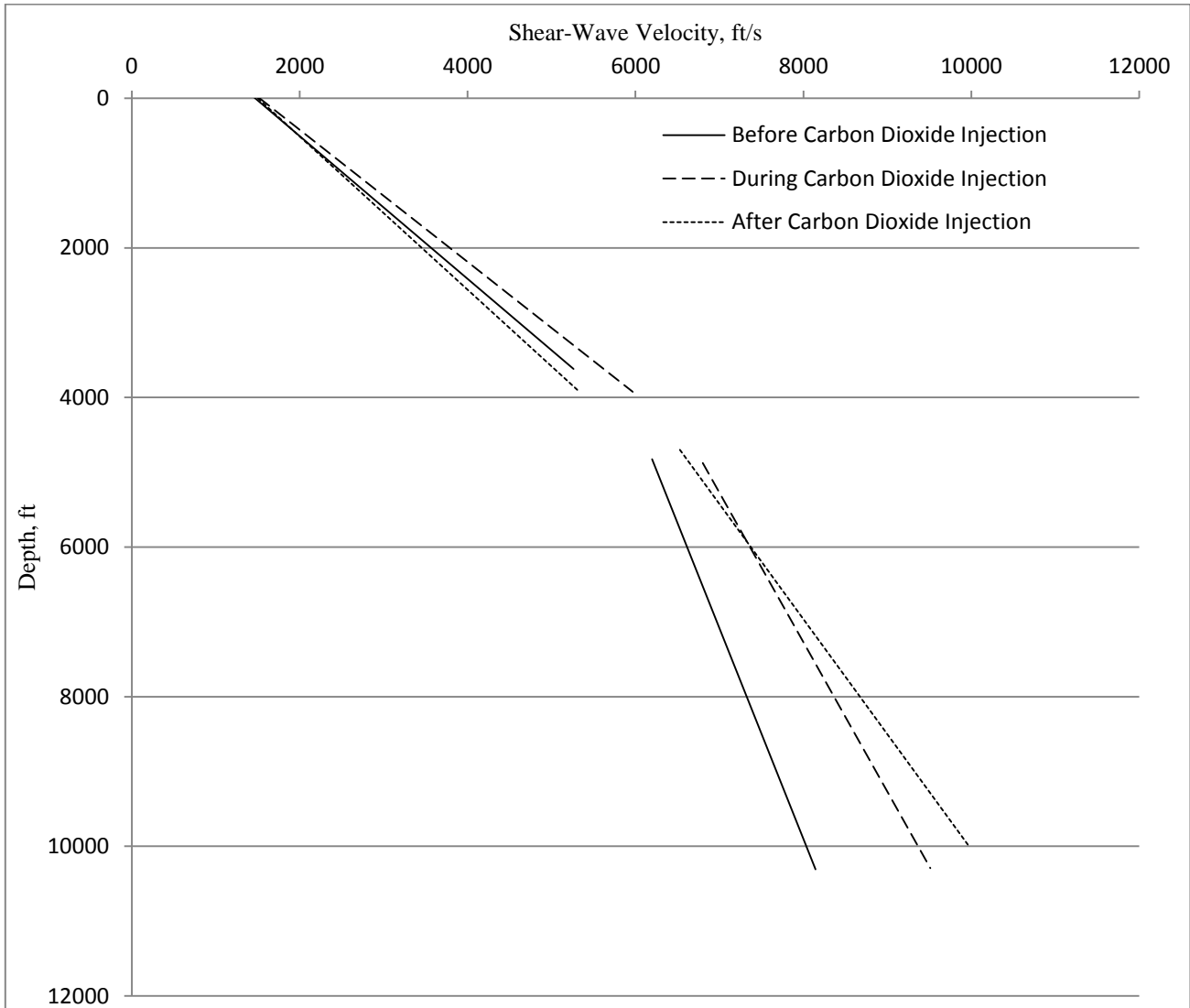


Figure 2.8.2. Bi-linear model of the shear wave velocity profile for Line 1, for the three stages of the injection process: before, during, and after CO₂ injection.

To understand the effects of porosity and saturation on stress waves, a laboratory experiment has been designed to simulate, using concrete, high porosity rocks saturated with mixed crude oil, water, and CO₂, to determine the effects of the fluid saturations on stiffness and shear-wave velocity. Just before the cement sets, the liquid mixture is bubbled through and becomes trapped in the hardened concrete. Three simulated rock samples having different porosities and stiffness have been constructed. A photograph of the surface of one of the samples is shown in Figure 2.8.4.

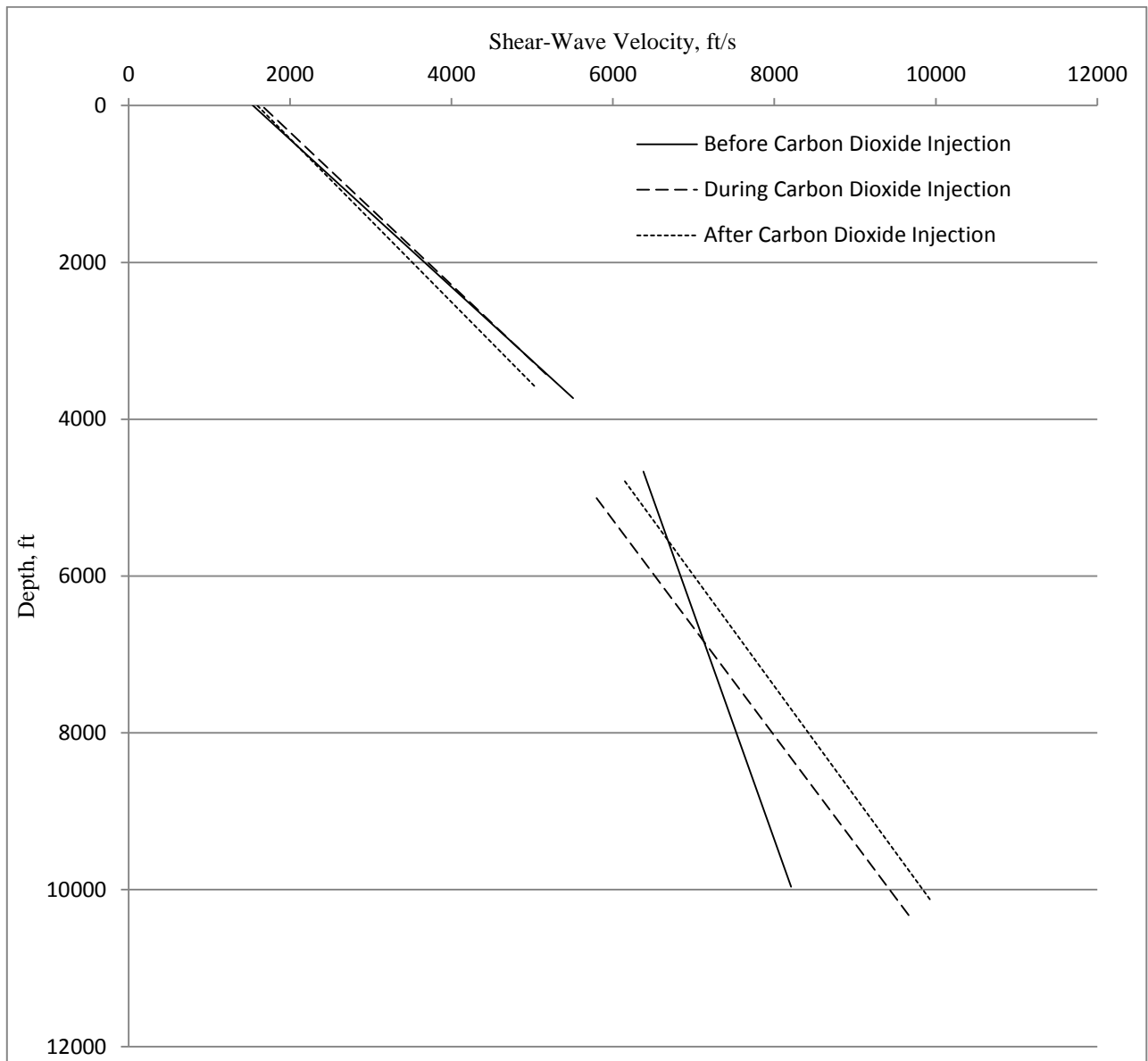


Figure 2.8.3 Bi-linear model of the shear wave velocity profile for Line 2, for the three stages of the injection process: before, during, and after CO₂ injection.

Shen-En Chen is attending the 3rd Annual World Congress of Well Stimulation and EOR in Xi'an, China, April 25-28, 2012, to present a paper with co-author Peng Wang, entitled, "CO₂ Injection Monitoring Using an Innovative Surface Monitoring Technique." The paper describes the DoReMi passive seismic monitoring technique that Shen-En and his research group have developed and their observations from its application at Citronelle.



Figure 2.8.4. Porous concrete sample formed in Shen-En Chen's laboratory at UNCC, for simulation of rock formations saturated with oil, water, and CO₂ having different strengths and stiffness.

2.9. Visualization of the Migration of CO₂, Oil, and Water

P. Corey Shum and Konstantinos Theodorou

University of Alabama at Birmingham

The complexity of the interaction between CO₂, oil, and water in a geologic formation makes animation of the evolution of fluid saturations during CO₂ and water flooding an especially useful tool for understanding enhanced oil recovery and its dependence on reservoir conditions and injection parameters. The UAB high performance computing facility includes advanced visualization display systems with which faculty, students, and programmers transform the output from simulations into animated visualizations for display on flat screens or in 3-dimensional immersive environments. The most advanced of the display systems is a four-walled VisCube immersive 3-D virtual reality system. It features three large rear-projection walls and a front-projected floor. The VisCube can be configured as a turn-key immersive virtual reality system, complete with a tracking system and graphics workstation. The turn-key virtual reality option adds the newest in PC graphics workstation hardware, a six degrees of freedom tracked input device, and head tracking. The result is a system that outperforms much more costly traditional virtual reality hardware.

For transfer of geologic storage technology to fellow specialists, education and training of students, and outreach to the public, display on a standard flat screen is often most effective. Screen shots from the animation of MASTER 3.0 simulations of CO₂-EOR, at various stages of WAG recovery, are shown in Figures 2.4.3a-d in the present report. Feedback from viewers of those visualizations indicated that many had difficulty understanding the meaning of elevation in the context of the fluid saturations. While the width and depth, in the images, represent spatial coordinates surrounding the injection well, elevation represents saturation, not a spatial elevation. Techniques for representing the results in a more natural way are being examined, including: (1) the use of glyphs to indicate relative pressure, (2) the use of hue to indicate concentration, and (3) the inclusion of satellite imagery to indicate the context.

A photograph of Corey Shum, working in the VisCube on an interactive immersive 3-D visualization of the pressure distribution surrounding a CO₂ injector is shown in Figure 2.9.1.

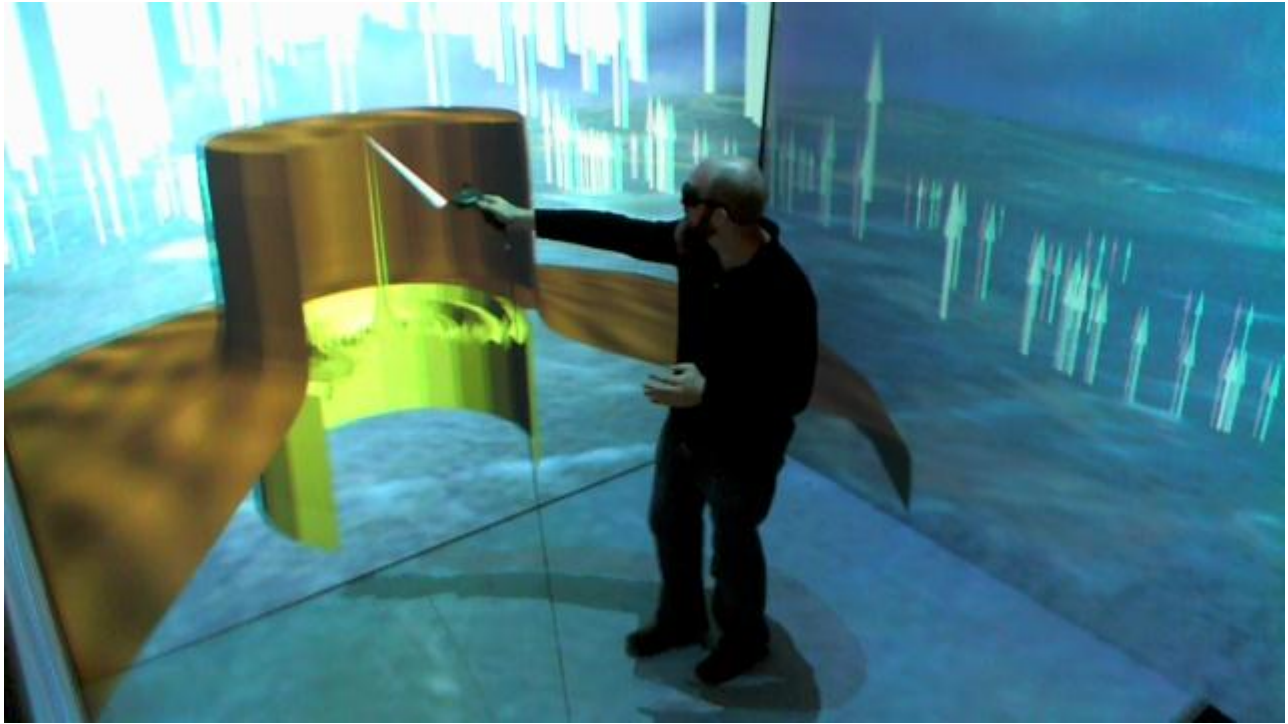


Figure 2.9.1. Corey Shum, in the Enabling Technology Laboratory VisCube, testing an interactive immersive 3-D visualization of the pressure distribution surrounding a CO₂ injector, calculated by Konstantinos Theodorou using MASTER 3.0.

2.10. Reservoir Management

Three unexpected problems were experienced during and following the injection of the first slug of CO₂ for enhanced oil recovery at Citronelle:

1. Erosion of the power oil pumps by particulate and scale mobilized by the CO₂.
2. Detection, by pressure-transient test, of a 600 to 1000-ft-long hydraulic fracture originating at the injector.
3. Low injectivity to water following the CO₂ injection.

The pump erosion problem was solved by switching to power oil pumps having longer stroke and fabricated using harder materials. The frequency of pump pulls from wells on the tank battery most affected has returned to normal levels and oil production at the battery has recovered, from a low of 21 bbl/day in March 2011, to 44 bbl/day in March 2012.

A test campaign, to determine the causes of poor sweep efficiency and low injectivity to water began in November 2011. Its purpose was to begin a careful study of the low water injection rates experienced on returning to water injection following the injection of CO₂, identify a strategy for correcting the problem, and develop recommendations for reservoir management that will avoid such problems during a commercial CO₂ flood.

A pressure-transient test in the injector, in November and December 2011, revealed a fracture, thought to be responsible for poor sweep efficiency and early breakthrough of CO₂, even at

wells far removed from the injector. The unexpected discovery of the fracture is the most important accomplishment of recent work under the project. It completely alters the approaches to reservoir simulation and reservoir management.

Our proposal is to manage fractures by adjustment of injection pressures. This will first be examined by conducting a step-rate test to determine the pressure at which the fracture discovered at Well B-19-10 #2 opens. If funding for a second CO₂ injection is available, we propose to monitor the CO₂ flow rate and down-hole pressure continuously during the injection, controlling the pressure to prevent opening of the fracture. Active control of the fracture would, we anticipate, improve sweep efficiency and increase oil recovery.

The third problem is the low injectivity to water. Not having the ability to inject water after CO₂ limits 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 CO₂ 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 CO₂ capture, pipeline transport, and underground injection for storage in the Citronelle Southeast Unit is underway at Plant Barry, led by the DOE Southeast Regional Carbon Sequestration Partnership, Southern Company, Denbury Resources, and Advanced Resources International (Esposito et al., 2011b). WAG would be an attractive option if CO₂ were supplied from Plant Barry, because it would provide a means to adjust for planned and unplanned outages at the Plant and stretch a limited CO₂ supply, and because WAG can increase oil recovery, as shown by simulations using MASTER 3.0 by Konstantinos Theodorou, under the present project.

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 flow is to Sand 14-1 and 65% is to Sand 16-2, so neither injection zone is completely blocked. Three other tests are planned to determine the cause of low injectivity:

1. Injection of surfactant to reduce capillary pressure if CO₂ is blocking the water flow.
2. Treatment with acid to remove clay fines or precipitated carbonate.
3. Injection of a small slug of CO₂ (less than the full 7500 tons planned for the second CO₂ injection) to determine whether its injectivity remains at the level observed during the first CO₂ injection (average of 31 tons/day).

After restoring injectivity, either to water or CO₂, we propose to proceed with a management plan with which to maximize oil recovery from the pilot test, considering such options as: (1) continue water injection as originally planned, until the optimum oil yield from the WAG cycle is realized, then proceed to the second of the two originally-planned CO₂ injections, or (2) proceed immediately to the second of the two originally-planned CO₂ injections. In either case, continue CO₂ injection as long as possible with the available funding, to provide the maximum amount of data for testing and validation of reservoir simulations.

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-CO₂ minimum miscibility pressure, reservoir simulation of CO₂-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 CO₂ 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 CO₂ injection. Work in Phase III (Budget Period 3: January 1, 2011 to August 31, 2012) includes documentation of the response to the first CO₂ injection and presence or absence of environmental effects, large-scale fine grid reservoir simulations and visualization, oil-water-CO₂ phase behavior, development of a reservoir management plan, seismic monitoring, a comprehensive evaluation of the findings from all components of the project, and a second injection of 7500 tons of CO₂, if funding permits.

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 CO₂ injection; seismic signals from the target formation have been recorded under the baseline water flood condition, during CO₂ injection, and during CO₂ migration from the injection zone; the minimum miscibility pressure and absence of precipitation from oil in the presence of CO₂ were established; and a favorable economic analysis was conducted that identifies the optimum CO₂ slug size for water-alternating-gas oil recovery under specified CO₂ cost and oil price constraints.

The first injection, of 8036 tons of CO₂, began on a continuous basis in January 2010 and was completed on September 25, 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 CO₂ injection then surfaced, 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 CO₂ injection, and problems with the down-hole power oil pumps, due to erosion by particulate and scale mobilized by carbon dioxide. As a result, oil production suffered a marked decline from October 2010 to March 2011, to less than half of the rate just before the start of CO₂ injection. 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. Oil production then recovered some of its loss, reaching 44 bbl/day in March 2012, a rate slightly less than that just before the start of continuous CO₂ injection. These results have significant implications for the design of a commercial CO₂ flood at Citronelle.

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 compressive stress in the Southeastern U.S., would explain the early breakthrough of CO₂ at wells to the northeast and southwest of the injector and likely provided a preferential pathway for CO₂, undermining the sweep efficiency of CO₂ in the first field 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 flow is to Sand 14-1 and 65% is to Sand 16-2, so neither injection zone is completely blocked. The next steps will be treatment of the injector with surfactant, followed by acid, to determine if either of these remedial measures is effective in restoring injectivity and incremental oil recovery.

All of the Deliverables of Phases I and II have been completed and all of the Milestones scheduled in Phases I and II have been met, as described in the sections that follow. The first Milestone of Phase III, a report on the CO₂ storage capacity of the Rodessa Formation, has been submitted to the Project Manager in draft form. The final version of the report will be completed when the best values have been established for the critical heights of CO₂ columns that can be stored in each of the candidate reservoirs in the Rodessa Formation.

3.2. Phase I Milestones

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

Oil-CO₂ 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 CO₂ 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 CO₂ injection suggest a 10% increase in stress associated with CO₂ injection, in layers above the injection zone. Detection of changes associated with CO₂ 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, CO₂ 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 CO₂ 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 CO₂ in ambient air were recorded at 104 points on a grid across Citronelle, beginning in September 2007. No elevated levels of CO₂ above the normal variation, no unusual CO₂ flux from soil, and no significant changes in the growth or distribution of vegetation were associated with the injection of CO₂ 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 of the research and Budget Period 3 were submitted to the Project Manager on October 14, 2010.

Phase II CO₂ injection complete (Phase II Milestone): The first injection of 8036 tons of CO₂ was completed on September 25, 2010. After initial problems pumping liquid CO₂, all of which were resolved by the persistent efforts of Denbury's team of engineers and technicians, 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) the second CO₂-EOR pilot test, (2) documentation of the presence or absence of environmental effects, (3) reservoir simulation and visualization, and (4) the capacity of the formation for CO₂ storage following tertiary oil recovery.

Table 3.4.1.
Critical Path Milestones, Research Phase III (Budget Period 3),
January 1, 2011, to August 31, 2012.

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

a. In the absence of a second CO₂ injection, the title of this task is understood to read: "Monitoring of response to the Phase II CO₂ injection," with a completion date of August 31, 2012."

Evaluation of Rodessa Formation CO₂ storage capacity (Phase III Milestone): The capacity of Citronelle dome for sequestration of CO₂ 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 10⁹ 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 CO₂ storage capacity is between 480 and 1900 x 10⁹ kg (530 to 2100 million short tons). An estimate based upon the work of Pruess et al. (2001) and Xu et al. (2001), suggests that up to 315 x 10⁹ kg (350 million short tons) of the stored CO₂ could be mineralized by conversion to solid carbonates over geologic time.

A preliminary version of the report presenting these results has been prepared. Measurements of CO₂-brine surface tension (Bachu and Bennion, 2009), of which we were previously unaware, have recently come to our attention. These new data may change our values calculated for the critical heights of CO₂ columns that can be stored in each of the candidate reservoirs in the Rodessa Formation. We will continue this work until we are satisfied that we have the best possible estimates of the formation's carbon sequestration capacity.

Documentation, through measurements of atmospheric CO₂ and growth of vegetation, of the presence or absence of environmental effects of CO₂ injection (Phase III Milestone): Xiongwen Chen and Kathleen Roberts of Alabama A&M University have measured CO₂ in ambient air at least once each quarter since September 2007 at 104 sampling locations in the Citronelle Oil Field and City of Citronelle. The measurements are 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.

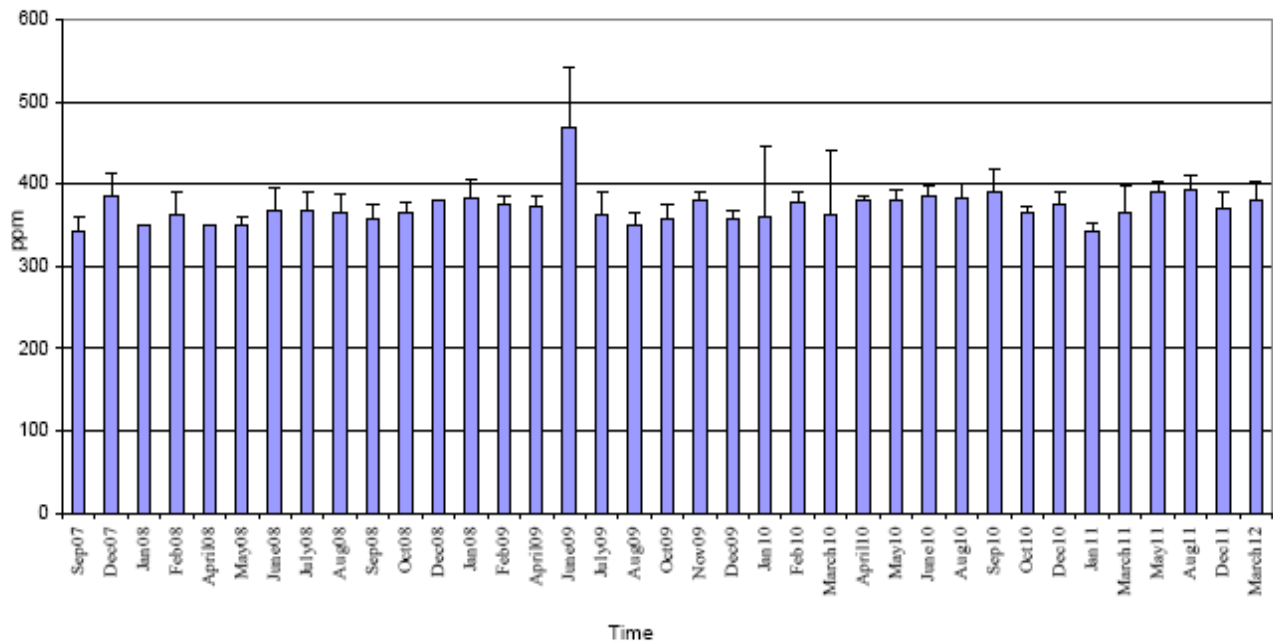


Figure 3.4.1. Average atmospheric CO₂ volume fraction (parts per million) at ground elevation across the City of Citronelle and Citronelle Oil Field from September 2007 to March 2012.

Only one anomalous reading appears in the entire set of CO₂ measurements, in June 2009, after filling the CO₂ storage tank in March 2009 and during unsuccessful attempts to inject CO₂, but before continuous CO₂ injection began in December 2009. The rest of the CO₂ 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 CO₂ levels, and with the worldwide rate of increase in atmospheric CO₂ of approximately 2 ppmv/year. The worldwide annual average volume fraction of CO₂ in ambient air during the year 2011 was 390.45 ± 0.10 ppmv (Thomas Conway 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. 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.

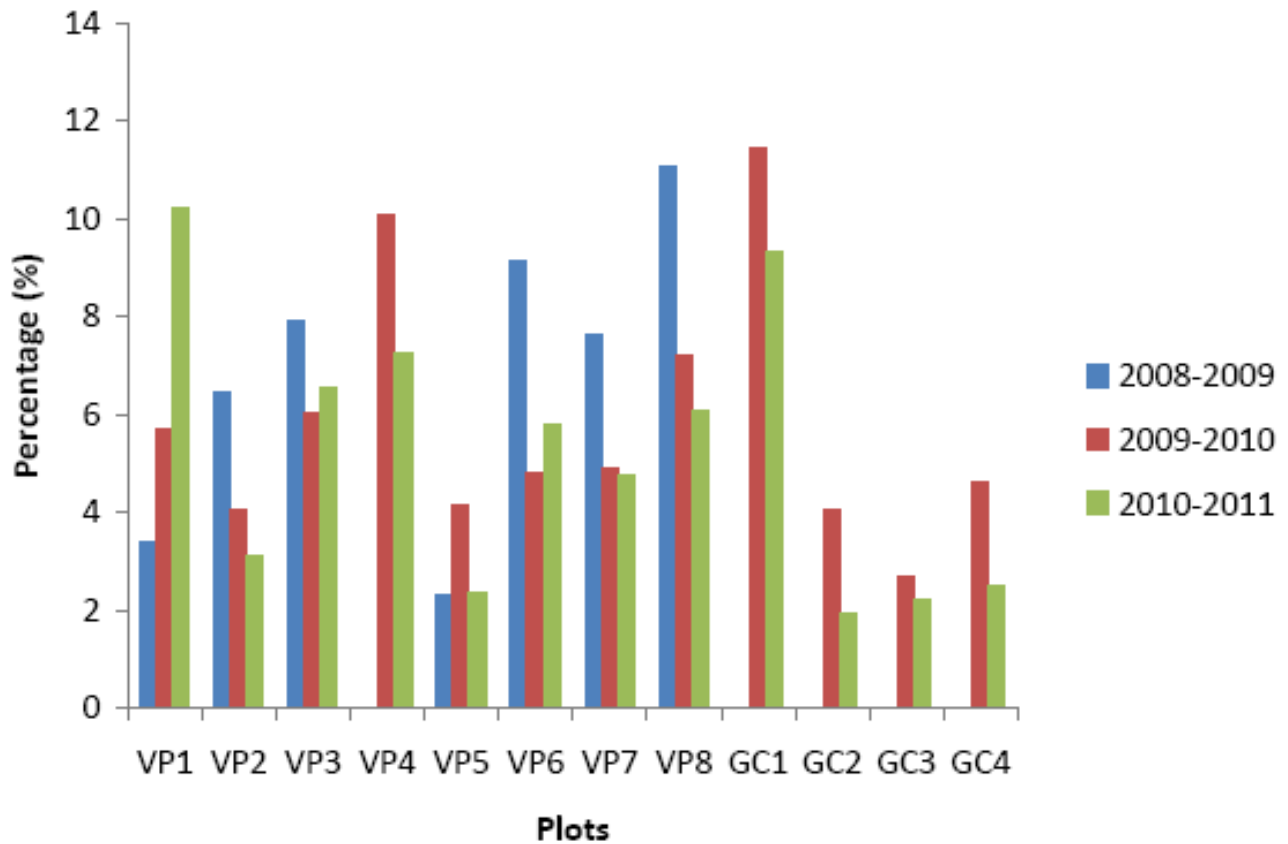


Figure 3.4.2. Comparison of growth, as the fractional (%) increase in basal area, in vegetation plots across Citronelle during the three periods, 2008-2009, 2009-2010, and 2010-2011. The plots are identified in Table 3.4.2.

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

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 CO₂.

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 CO₂ in ambient air were not consistently detected there, nor were elevated CO₂ fluxes from soil near that well reported by Ermson Nyakatawa and Latasha Lyte, also of AAMU (Section 2.7.1, pp. 42-46). We leave open the possibility that vegetation near Well B-19-10 #2 may have been influenced by CO₂ from the pilot test, and will continue to monitor CO₂ in ambient air and the growth of vegetation at this location and at all of the other observation points. 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 CO₂ plumes associated with the CO₂ storage tank, injection equipment, wells, or tank batteries.

Conclusion: There has been no significant short or long-term effect of storage, handling, and injection of CO₂ on the levels of CO₂ 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 CO₂ in ambient air and measurements of CO₂ fluxes from soil near the well. Monitoring of CO₂ in air, CO₂ fluxes from soil, and growth of vegetation will continue to the end of the project.

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, 2012) 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 CO₂-EOR using the SENSOR reservoir simulation software package.

Thirteen 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 CO₂-enhanced oil recovery and capacity for CO₂ storage (Esposito et al., 2008, 2010). Results of work under the project have been presented by members of the project team at fourteen national and international conferences and at eleven 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 CO₂-enhanced oil recovery technology in the Citronelle Field.

During the quarter under review, staff at the Geological Survey of Alabama described a new core from the Lower Cretaceous Donovan Sand recovered by Denbury Resources from a monitoring well drilled in the southeast region of the Citronelle Field as part of the SECARB Phase III Anthropogenic Test. The new 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.

Reservoir Fluid Properties and Phase Behavior. A rolling ball viscometer with which to measure properties of oil-CO₂ 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 CO₂ 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 N₂ naturally present in a formation, or remaining in CO₂ after incomplete separation from gaseous combustion products, and (2) the extension of oil-CO₂ miscibility through addition of other gas constituents, such as light hydrocarbons, a component of the advanced CO₂-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 CO₂ with oil, under reservoir conditions, by visual observation of the development of miscibility between CO₂ and the oil. The gas behavior and pressure changes inside the system are monitored and recorded using a data acquisition system. During the quarter under review, the system underwent preliminary testing using water and CO₂ 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 CO₂ in water compared favorably with a computer model of carbon dioxide-water solubility behavior.

Petroleum Reservoir Simulation. A parametric study of WAG recovery, using the MASTER 3.0 reservoir simulator, showed that a properly designed WAG recovers more oil than continuous CO₂ 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 CO₂ injections of 7500 tons each, followed by water. The animations nicely capture the mobilization of oil by CO₂, development of the oil bank, the role of water in driving the bank, and the residual oil left unrecovered. During the quarter under review, a study was made of the sensitivity of oil recovery to the assumed reservoir permeability. Oil recovery increased with

decreasing permeability, due to the associated decrease in mobility and increase in CO₂-oil contact time.

CO₂ Liquefaction, Transportation, and Storage. A 50-ton, refrigerated, liquid CO₂ storage tank was purchased from the TOMCO₂ 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 CO₂ was delivered by Airgas to Citronelle on March 2, 2009. Scheduling of deliveries to maintain CO₂ 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 CO₂ per day.

Well Preparation, Water Flood, and CO₂ 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 is taking water at a higher rate than Sand 16-2 (82 and 18% of the flow, respectively). A second tracer test, during CO₂ injection, showed that 57% of the CO₂ was flowing to Sand 14-1 and 43% to Sand 16-2. The injector, four producers, CO₂ storage tank, charge pump, triplex pump, piping, flow meters, and gas/liquid separators were in place, connected, and prepared for CO₂ injection in July 2009. During the period from July to November 2009, the principal barrier to CO₂ injection was poor performance of the triplex positive displacement pump. Modifications to the pump enabled the Denbury Onshore group in Citronelle to begin continuous CO₂ 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 CO₂ Injection. Breakthrough of CO₂ 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 CO₂ was used to positively establish the presence of injected CO₂ in produced gas. A survey of the CO₂ content of produced gas from wells in and outside the test pattern on April 12, 2011, detected CO₂ 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 CO₂ injection then surfaced, including excessive gas production at the well where CO₂ first appeared (Well B-19-11), a low water injection rate on returning to water injection at the conclusion of the CO₂ 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 CO₂ injection. Improvements to the power oil pumps restored the frequency of pump pulls to normal and oil production at B-19-8 Tank Battery has recovered some of its loss over the past 12 months, returning to 44 bbl/day in March 2012.

Integration of the difference between the actual oil production and the production anticipated by the decline curve established during water flood, just prior to CO₂ injection, over the period from January 2010 to March 2012 gives an (unofficial) estimate of incremental oil production at B-19-8 Tank Battery of 9722 bbl. While less than the approximately 20,000 bbl of incremental recovery predicted to date by Eric Carlson's reservoir simulations using SENSOR (Coats Engineering, Inc.), the shortfall is less than might have been 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 CO₂ 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 of water flood. Then, coinciding with the breakthrough of CO₂ 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 CO₂ 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 March 2012, gives an (unofficial) incremental deficit of 9872 bbl. Combining the deficit with the incremental production at B-19-8 Tank Battery gives an overall loss, to March 2012, of $9722 - 9872 = -150$ bbl. Our goal in Phase III is to erase this deficit and realize a significant net incremental gain in oil production.

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 CO₂ 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 six sets of soil gas samples were collected from August 2008 to August 2010. Carbon dioxide fluxes from soil range from approximately -1 to +2 mg/(m²·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 CO₂ injection, showed no evidence of CO₂ seepage.

CO₂ in ambient air has been measured at least once each quarter since September 2007 at 104 sampling locations in the Citronelle Oil Field and City of Citronelle. Only one anomalous reading appears in the entire set of CO₂ measurements, in June 2009, after filling the CO₂ storage tank in March 2009 and during unsuccessful attempts to inject CO₂, but before continuous CO₂ injection began in December 2009. The rest of the CO₂ 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 CO₂ 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 CO₂.

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 CO₂ in ambient air were not consistently detected there, nor were elevated CO₂ fluxes from soil observed near that well. Vegetation near Well B-19-10 #2 may have been influenced by CO₂ from the pilot test. Monitoring of CO₂ in air, CO₂ fluxes from soil, and growth of vegetation will continue at all of the sampling locations to the conclusion of the project. 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 CO₂ plumes associated with the CO₂ 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 CO₂ 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 4500 ft. While the slope in the upper region, above ~4500 ft, has remained within relatively narrow limits during CO₂ and subsequent water injection, the slope in the lower region, below ~4500 ft, which was initially much steeper, has been steadily declining and approaching the slope in the upper region, evidently a result of pressurization by CO₂ 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 CO₂ injection. This encouraging result suggests that the geophysical testing technique may be useful for monitoring formation pressure.

Reservoir Management and Economics. Three unexpected problems were experienced during and following the injection of the first slug of CO₂ for enhanced oil recovery at Citronelle:

1. Erosion of the power oil pumps by particulate and scale mobilized by the CO₂.
2. Detection, by pressure-transient test, of a 600 to 1000-ft-long hydraulic fracture originating at the injector.
3. Low injectivity to water following the CO₂ injection.

The pump erosion problem was solved by switching to power oil pumps having longer stroke and fabricated using harder materials. The frequency of pump pulls from wells on the tank battery most affected (B-19-8) have returned to normal levels and oil production at the battery has recovered over the past 12 months, from a low of 21 bbl/day in March 2011, to 44 bbl/day in March 2012.

A pressure-transient test on the injection well in November and December 2011 revealed a fracture thought to be responsible for early breakthrough of CO₂ at wells far removed from the injector and poor sweep efficiency. The completely unexpected discovery of the fracture is the most important accomplishment of recent work under the project. It completely alters the approaches to reservoir simulation and reservoir management.

Our proposal is to manage fractures by adjustment of injection pressures in a "smart" well. This will first be examined by conducting a step-rate test to determine the pressure at which the fracture opens. If funding for a second CO₂ injection is available, we propose to monitor the CO₂ flow rate and down-hole pressure continuously during the injection, controlling the pressure to prevent opening of the fracture. Active control of the fracture would, we anticipate, improve sweep efficiency and increase oil recovery.

The third problem is the low injectivity to water. Not having the ability to inject water after CO₂ limits 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 CO₂ 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 CO₂ capture, pipeline transport, and underground injection for storage in the Citronelle Southeast Unit is underway at Plant Barry, led by the DOE Southeast Regional Carbon Sequestration Partnership, Southern Company, Denbury Resources, and Advanced Resources International (Esposito et al., 2011b). WAG would be an attractive option if CO₂ were supplied from Plant Barry, because it would provide a means to adjust for planned and unplanned outages at the Plant and stretch a limited CO₂ supply, and because WAG can increase oil recovery, as shown by the simulations using MASTER 3.0.

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 flow is to Sand 14-1 and 65% is to Sand 16-2, so neither injection zone is completely blocked. Three other tests are planned to determine the cause of low injectivity to water:

1. Injection of surfactant to reduce capillary pressure if CO₂ is blocking the water flow.
2. Treatment with acid to remove clay fines or precipitated carbonate.
3. Injection of a small slug of CO₂ (less than the full 7500 tons planned for the second CO₂ injection) to determine whether its injectivity remains at the level observed during the first CO₂ injection (average of 31 tons/day).

After restoring injectivity, either to water or CO₂, we propose to proceed with a management plan with which to maximize oil recovery from the pilot test, considering such options as: (1) continue water injection as originally planned, until the optimum oil yield from the WAG cycle is realized, then proceed to the second of the two originally-planned CO₂ injections, or (2) proceed immediately to the second of the two originally-planned CO₂ injections. In either case, continue

CO₂ injection as long as possible with the available funding, to provide the maximum amount of data for testing and validation of reservoir simulations.

Reservoir simulations using SENSOR showed that cumulative oil production increases with increasing amount of CO₂ injected, regardless of the assumed permeability distribution. However, in all cases considered, there was an optimum CO₂ slug size, from the point of view of the profitability of a CO₂-EOR project. The optimum size of CO₂ slug increases with increasing oil price. The discount factor has little impact on the optimum size of CO₂ 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 CO₂ storage under different WAG schedules. WAG is preferred if CO₂ supply at Citronelle is limited. According to the model examined, all except one of the WAG scenarios (2 months CO₂ - 6 months water) outperformed incremental oil production from CO₂-only injection. The best performing sequence, with respect to oil recovery, was 12 months of CO₂ injection followed by 6 months of water injection. The net amount of CO₂ stored under this schedule can be increased by 40%, by lengthening the period of CO₂ injection 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 CO₂-EOR to be 64 million bbl, or 17% of the original oil in place. Denbury Resources' estimate of the Field's EOR potential is 40 million bbl. Assuming 10% of OOIP to be economically recoverable (38 million bbl) using CO₂-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 CO₂ storage is estimated to be 530 to 2100 million short tons (Esposito et al., 2008), sufficient to sequester the CO₂ 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 CO₂ in a saline formation in Citronelle Dome (Esposito et al., 2011b).

Acronyms and Abbreviations

AAMU	Alabama Agricultural and Mechanical University, Normal, AL
ANSYS	ANSYS, Inc., Canonsburg, PA
DOE	U.S. Department of Energy, National Energy Technology Laboratory, Pittsburgh, PA
DoReMi	derivative of refraction microtremor
DRI	Denbury Resources, Inc., Plano, TX, and Citronelle, AL
EOR	enhanced oil recovery
GSA	Geological Survey of Alabama, Tuscaloosa, AL
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
OOIP	original oil in place
SAS	Statistical Analysis System (SAS Institute Inc., Cary, NC)
SECARB	Southeast Regional Carbon Sequestration Partnership
SENSOR	System for Efficient Numerical Simulation of Oil Recovery (Coats Engineering, Inc., 2009)
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 (CO₂-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-CO₂ minimum miscibility pressure, simulation of CO₂-EOR, and establishment of background conditions at the test site. The focus in Phase II is on the first CO₂ injection and associated measurements and monitoring. The focus in Phase III will be on the second CO₂ 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)

Task 1.0 - Establish Collaboratory Environment

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 CO₂ 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-CO₂ 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 CO₂, and measure the viscosity of the oil at reservoir temperature as a function of CO₂ 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 CO₂-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 CO₂ Fluxes and Ecology

The Recipient shall establish baseline CO₂ 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 CO₂ injection strategy to optimize oil recovery and revenue.

Task 12.0 - Economic and Market Analysis

The Recipient shall verify that production using CO₂-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 CO₂ 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 CO₂ and provide for onsite storage of CO₂, installation of CO₂-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 CO₂ 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 CO₂.

Task 18.0 - Site Characterization by Geophysical Testing

The Recipient shall perform seismic measurements before, and two months after the start of CO₂ injection, to observe the effects of CO₂ 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 CO₂ in shallow boreholes and measure concentration profiles in soil near the surface to determine whether CO₂ 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-CO₂ Interaction

The Recipient shall determine the sensitivity of the minimum miscibility pressure to the nitrogen content of CO₂, 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 CO₂-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 CO₂ 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 CO₂ 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 CO₂.

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 CO₂ injection at the site of Field Test No. 2, if different wells are selected.

Task 30.0 - CO₂ Fluxes and Ecology

The Recipient shall continue monthly monitoring for CO₂ 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 CO₂ 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 - August 31, 2012)

Task 31.0 - Preparation for Field Test No. 2

The Recipient shall prepare the wells and site for the second CO₂ injection, including provision for onsite storage of CO₂, installation of CO₂-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 CO₂ 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 CO₂-EOR simulation and monitor the production wells in the test pattern for produced oil, water, and gas, including CO₂.

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 CO₂ 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 CO₂ 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 CO₂, oil, and water as functions of reservoir properties and time, the oil yield by CO₂-EOR, and the capacity of the formation for CO₂ 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 CO₂ 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 CO₂ 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 CO₂ from sources in the region. This will include a topical report on the capability of the Rodessa Formation for storage of CO₂. Dissemination of results via the final report to DOE, presentations, and publications.

Task 45.0 - Follow Up

The Recipient shall continue to monitor production, seepage, ecological effects, and progress of negotiations for transition of the Citronelle Oil Field to a CO₂ 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 CO₂ 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 CO₂ 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, "CO₂-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 CO₂-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, "CO₂-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, "CO₂-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 CO₂ 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 CO₂-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 CO₂-EOR and Sequestration," Paper No. 0920, International Coalbed and Shale Gas Symposium, University of Alabama, Tuscaloosa, AL, May 18-22, 2009.

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