Technologies for Tomorrow's E&P Paradigms

CO2 EOR Technology

Oil

Water

CO2 Miscible Zone

NETL

December 2004

CO₂ EOR: TIME IS RIGHT FOR GROWTH

Economics, technology advances, environmental benefits align for 'perfect storm' of opportunity

Carbon dioxide enhanced oil recovery has come into its own.

CO_2 EOR is more than just the fastest-growing EOR process in the U.S.; it is the only such process to have shown growth since EOR's heyday in the 1980s.

While production volumes and the number of projects for thermal, chemical, and other EOR processes in the U.S. have fallen off sharply since the mid-1980s, the number of CO_2 projects has remained steady or increased slightly and CO_2 production volumes have jumped sevenfold (see chart). The CO_2 share of U.S. crude oil production was estimated at almost 206,000 b/d in 2004, according to Oil & Gas Journal's biennial EOR Survey, published April 12, 2004. That's about 4% of the national total.

DOE research role

Research funded by the Department of Energy has played an important role in the commercialization and growth of CO_2 flooding in the U.S. As early as the 1970s, DOE-funded projects were assessing the basic fluid properties of CO_2 regarding pressure, temperature, and oil composition. A special focus was given to developing Minimum Miscibility Pressure correlations, which helped underpin the oil industry's ability to prioritize these properties in order to implement commercial CO_2 projects successfully.

During 1993-2003, DOE funded nearly half of the $100 million spent on Class Program CO_2 EOR field demonstration projects in six states, with a targeted incremental recovery of 23 million barrels of oil.

DOE continues to fund research critical to CO_2 EOR at a time when the big research centers at the major oil companies have all but disappeared. At present, the agency is funding the only U.S. public research on improving reservoir sweep by modifying CO_2 viscosity. Most CO_2 floods entail injection of a large slug of

CO_2, followed by injection of water—which drives the CO_2—to maximize sweep efficiency.

Modifying CO_2 viscosity is critical because differences in CO_2 viscosity and density relative to the crude oil in place can set the stage for premature breakthrough of the gas. Such breakthrough results from a combination of gravity override and the CO_2 channeling through more-permeable zones. The end result: Less oil ultimately recovered.

CO_2 injection well, with a pumpjack in the background, part of a CO_2 flood pilot project operated by Advanced Reservoir Technologies Inc. under subcontract from Occidental USA Inc. in Oxy's West Welch Unit in the Permian Basin of West Texas

The response to this challenge entailed alternating injection of water and gas (WAG), which improved sweep efficiency. However, this posed another problem: While sweep improves with WAG, displacement efficiency may decline because the water can shield the oil from the solvent-like nature of the gas. So DOE has funded much research on alternative ways to bolster CO_2 sweep efficiency—with foams, chemical gels, and direct thickening agents.

While almost all CO_2 flooding targets light oil reservoirs deeper than 3,000 feet, some DOE-funded research has ascertained that its solvent effect also reduces oil viscosity in reservoirs with heavier crudes. Coupled with the increased oil saturation identified with CO_2-induced

swelling, this points to the suitability of CO_2 flooding for a range of reservoirs not typically amenable to miscible displacement processes.

CO_2 potential, costs

CO_2 flooding is the most common form of gas-related EOR, in large part because the gas is readily available at low cost.

Roughly half of the world's CO_2 floods are in the Permian basin of Texas and New Mexico, not far from some of the biggest natural sources of CO_2 in the U.S. Some industry estimates put incremental recovery from CO_2-floodable reservoirs in the Permian basin alone at 500 million to 1 billion barrels.

According to a recent DOE/NETL analysis, CO_2 EOR oil production in the U.S. could double by 2010 and quadruple by 2020 with CO_2 incentives.

As interest in CO_2 flooding has grown in the past two decades, its costs have fallen sharply. Kinder Morgan CO_2 Co. L.P. estimates that CO_2 prices have dropped by 40% and that overall operating costs have plunged to less than half the $1 million per flood pattern seen in the 1980s. Kinder Morgan estimates total operating expenses exclusive of CO_2 costs at $2-3/bbl. In addition, once a flood is under way, the produced CO_2 can be captured and recycled. All of this adds up to a project that can yield a healthy profit even when oil prices are as low as $18/bbl, according to Kinder Morgan.

Environmental benefits

CO_2 EOR's attractiveness can be bolstered still further with the synergies that can come from utilizing an industrial source of CO_2. While more expensive than using natural CO_2 in an EOR project, this approach has the added benefit of capturing and sequestering CO_2 emissions.

DOE is funding research related to this concept, a field demonstration project involving a CO_2 misci-

ble flood in central Kansas that utilizes a CO_2 stream from a nearby ethanol plant. There are no miscible floods in Kansas because of the distance from natural CO_2 sources. Early results are promising, and if this approach is applicable to other fields in Kansas, the ultimate incremental oil production resulting from CO_2 floods in that state could reach 600 million barrels.
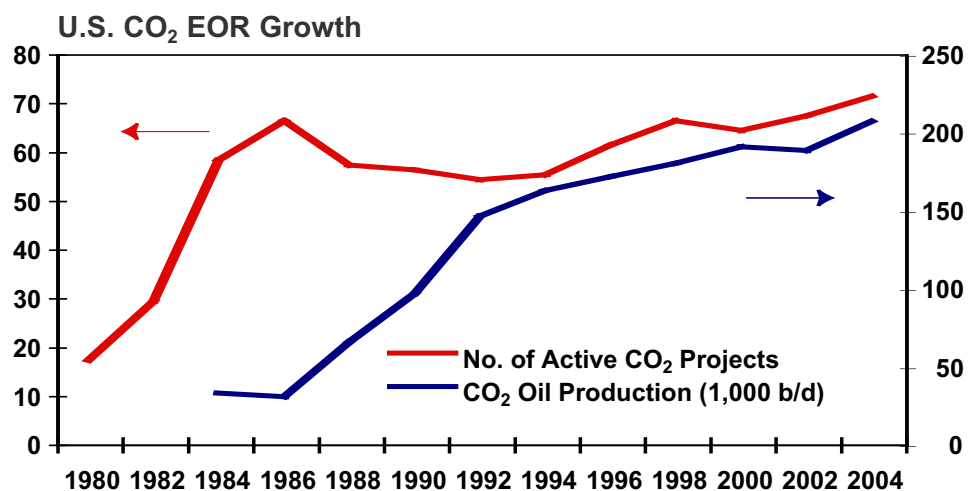
As pressure builds to reduce CO_2 emissions amid concerns over postulated climate change, future CO_2 sequestration efforts are likely to be met with incentives such as fiscal relief or emissions trading credits. That could help level the playing field between natural and industrial sources of CO_2. Broadening use of industrial CO_2, in turn, could expand the applicability of CO_2 EOR to other areas of the U.S. while "closing the carbon cycle."

Supply issues

Many analysts believe a new, higher range for oil prices could persist indefinitely—perhaps permanently.

Meanwhile, DOE's Energy Information Administration (EIA) forecasts steadily rising demand for oil and continued declining crude oil production in the U.S. The nation's dependence on imported oil, as a result, could soar to 70% by 2025, EIA projects.

It follows, then, that DOE deems research into CO_2 EOR, a technology with such a strong potential for widespread commercial application, to be a crucial part of its fossil energy mission in the new millennium.

U.S. CO_2 EOR Growth

No. of Active CO_2 Projects
CO_2 Oil Production (1,000 b/d)

Source: Oil & Gas Journal

Strategic Center for Natural Gas and Oil

P R O J E C T
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U.S. DEPARTMENT OF ENERGY
OFFICE OF FOSSIL ENERGY
NATIONAL ENERGY TECHNOLOGY LABORATORY
STRATEGIC CENTER FOR NATIONAL GAS AND OIL

TIME-LAPSE SEISMIC MODELING AND INVERSION OF CO_2 SATURATION FOR SEQUESTRATION AND ENHANCED OIL RECOVERY

PARTNERS

4th Wave Imaging Corp.
Aliso Viejo, CA

MAIN SITE

Aliso Viejo, CA

Background/Problem

Time-lapse seismic monitoring during CO_2 injection is still in its infancy. Seismic monitoring requires knowledge of the rock and fluid properties of the oil reservoir to track changes in CO_2 saturation and pressure over time. In addition, the behavior of supercritical CO_2 is complex, and its interaction with brine and oil in porous rock systems is not well understood. Modeling CO_2 behavior often can lead to numerical instabilities that create large artifacts in modeled time-lapse seismic data and in maps of CO_2 saturation and pressure changes.
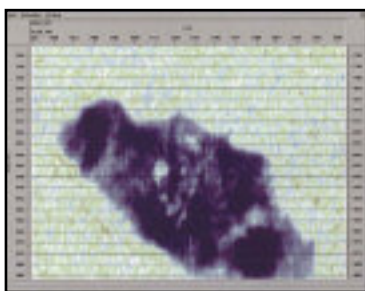
Project Description

The goal of this project is to improve current methods of rock physics and time-lapse seismic reflection modeling for CO_2 sequestration and miscible CO_2 floods in oil and gas reservoirs, and to develop new strategies to invert such data to estimate changes in pressure, oil saturation, water saturation, and CO_2 saturation over time.

Time-lapse CO_2 seismic data set showing a clear amplitude anomaly caused by increasing CO_2 saturation at this level.

The project consists of three phases. In Phase I new ways to calculate fluid properties of oil-water-CO_2 mixtures under varying reservoir conditions are being investigated. A thorough literature search has revealed two major approaches for accomplishing this: using either an equation-of-state (EOS) formulation or molecular dynamics simulations. These two approaches are being compared for robustness and accuracy. A preliminary EOS formulation has been developed that is capable of calculating bulk fluid properties from multiple liquid and gas phases for supercritical CO_2 mixtures.

In Phase II this EOS is being used to perform 1-D time-lapse seismic modeling by calculating changes in well-log velocities and densities under varying CO_2 saturations and pressures. In addition, progress has been made in building a 3-D seismic modeling tool that can be used to predict time-lapse seismic anomalies in 3-D field data.

In Phase III, a method is being developed to invert time-lapse seismic anomalies to yield maps of CO_2 saturation and pressure changes over time. The first step of this method—which generates seismic attributes as a function of CO_2 saturation and pressure changes, including changes in both miscible and free CO_2 levels—has been completed.

NETL

...Accurate modeling methods enable high-resolution CO_2 flood front imaging

Accomplishments

In this project calculations were enhanced to determine rock and fluid properties of CO_2-oil-water mixtures in porous rock systems in order to better predict how CO_2 affects time-lapse seismic data. New tools were developed that use these data to 1) model the time-lapse seismic response of a reservoir during CO_2 injection, and 2) invert time-lapse seismic anomalies to yield estimates of CO_2 saturation and pressure changes.

Among other accomplishments, the project participants:

- Investigated new ways to compute fluid properties of oil-water-CO_2 mixtures using both EOS methods and molecular dynamics modeling.

- Developed a 1-D seismic modeling program that uses time-lapse changes in well-log velocities and densities to predict changes in seismic data during CO_2 injection.

- Wrote an algorithm to accomplish the first step of the inversion procedure, namely, the generation of time-lapse seismic attribute changes as a function of changes in CO_2 saturation and pressure.

- Completed a preliminary evaluation of time-lapse seismic anomalies in different vintages of a 3-D data set from Sleipner gas field in the Norwegian North Sea.

Benefits

Miscible CO_2 flooding has become an increasingly important enhanced oil recovery (EOR) technique in the U.S. for recovering residual or bypassed oil. For example, roughly half the CO_2 floods in the world are located in the Permian Basin, producing more than 20% of the area's total oil production.

By developing an accurate approach for tracking CO_2 fronts during EOR operations, this project is expected to help improve recovery rates, optimize well patterns, locate bypassed oil, and minimize the cost of injected CO_2. Project results also will benefit the public by improving current methods for monitoring reservoir leaks and verifying the location and quantity of sequestered CO_2 in order to minimize its impact on the environment. CO_2 sequestration in oilfields is getting more attention because of concerns over the gas's role in purported climate change.

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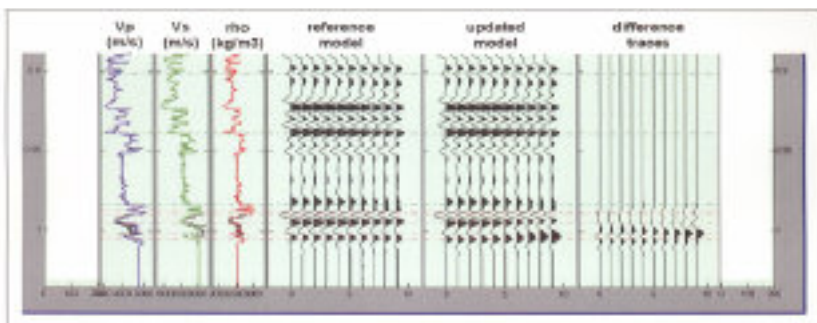purna.halder@netl.doe.gov

TOTAL ESTIMATED COST
$0.8 million

COST SHARING

DOE	$0.6 million
Non-DOE	$0.2 million

WEBSITE

www.netl.doe.gov

Example of time-lapse seismic modeling of well-log velocities and densities during CO_2 injection.

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NATIONAL ENERGY TECHNOLOGY LABORATORY
STRATEGIC CENTER FOR NATIONAL GAS AND OIL

PARTNERS

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Bakersfield, CA

Stanford University
Stanford, CA

Core Laboratories
Bakersfield, CA

**Lawrence Livermore
National Laboratory**
Livermore, CA

**Lawrence Berkeley National
Laboratory**
Berkeley, CA

MAIN SITES

**Buena Vista Hills field
Lost Hills field**
Kern County, CA

*CO$_2$ gauging facilities at Lost
Hills field.*

ADVANCED RESERVOIR CHARACTERIZATION IN THE ANTELOPE SHALE TO ESTABLISH THE VIABILITY OF CO$_2$ ENHANCED OIL RECOVERY IN CALIFORNIA'S MONTEREY FORMATION SILICEOUS SHALES

Background/Problem

Buena Vista Hills and Lost Hills oil fields in Kern County, CA, have large volumes of remaining oil in bypassed zones after over 40 years of primary and secondary production. The Monterey Formation siliceous shales at both fields, the Antelope and Brown shales at Buena Vista Hills, and the Belridge Diatomite at Lost Hills pose unique problems for enhanced oil recovery. The Buena Vista Hills reservoir produced 9 million barrels of oil from 1952 to 1995, but this represented only 6.5% of the estimated 130 MMB of the original-oil-in-place. By 1995 production was in decline, and several wells were in danger of abandonment. At Lost Hills field the small pore size, high porosity, and low permeability have led to low primary recovery (3-4% OOIP), and after 10 years of waterflooding production the field is in decline.

Project Description/Accomplishments

Project participants conducted extensive reservoir characterization to evaluate the potential for CO$_2$ flooding of the two fields' reservoirs. Phase I focused on reservoir characterization of the Antelope and Brown shales; results indicated that very low oil saturation at Buena Vista Hills field did not make it a viable candidate for CO$_2$ recovery. Phase II was conducted at Lost Hills field. The application of state-of-the-art reservoir characterization and reservoir management techniques attempted to establish the viability of CO$_2$ enhanced oil recovery.

The reservoir characterization phase at Buena Vista Hills field produced several firsts. The first coreflood analysis of siliceous shales compiled data from 160 wells into a database. The first high-resolution crosswell reflection images were made of any oil field in the San Joaquin Valley. The project also demonstrated the first successful application of the TomoSeis seismic data acquisition system in siliceous shales. In addition, the study at Buena Vista Hills was the first detailed reservoir characterization of the Brown and Antelope siliceous shales in the San Joaquin Valley. ChevronTexaco undertook numerous technology transfer workshops, presentations, and publications, making information about of the siliceous shales available to the public for the first time.

Study of Lost Hills field during Phase II provided the opportunity to conduct and publish a detailed reservoir characterization of the Belridge diatomite. The Belridge Diatomite has unusual composition and characteristics. It has high oil saturation (50%) and high porosity (45-70%), but low permeability (< 1 millidarcy). CO$_2$ flood production forecasts generated by ChevronTexaco's proprietary reservoir simulation software suggested that CO$_2$ injectivity is two to three times greater than that of water or steam.

...Analysis of potential for CO_2 flooding of siliceous shales

The project evaluated the economic uncertainties for CO_2 flooding of the Belridge Diatomite. Part of the project involved identification and demonstration of several systems to monitor CO_2 flood movement within the reservoir and to image the CO_2 migration. Implementation of the CO_2 flood at Lost Hills field resulted in installing a four-pattern, 2.5 acre pilot; upgrading facilities; reworking several injection wells and drilling two new injection wells; constructing CO_2 facilities and lines; and setting up a CO_2 monitoring system. CO_2 injection began in August 2000. The study evaluated how injection of a very low-viscosity gas differed from injection of water into the diatomite in terms of fracture azimuth, injectivity, and areal and vertical sweep.

Over 2½ years a total of 375,113 Mcf of CO_2 was injected into the diatomite. An initial oil response was observed in one well as a result of CO_2 injection. However, sanding problems eventually caused that well to be shut in and the CO_2 injection pilot to be terminated. Remedial work on the wells to correct subsidence-related casing damage and exhaustive analysis suggested that CO_2 injection played a major role in the sanding problems in the Belridge Diatomite.

Monitoring demonstrated that CO_2 flowed through natural fractures, faults, and induced hydraulic fractures, and that neither injection rates nor corrosion were issues for the project. CO_2 injection profiles were able to display lateral and vertical flow.

Benefits/Impacts

Reservoir characterization of the Antelope and Brown shales at Buena Vista Hills field and the Belridge Diatomite at Lost Hills field added extensively to the knowledge of these formations and understanding of how siliceous shales react to CO_2 flooding. Because the siliceous shales are widespread in the San Joaquin Valley and hold millions of barrels of remaining OOIP, publication of the reservoir characterization will assist future gas flooding in these reservoirs. The lessons learned in the demonstration show that CO_2 is capable of increasing oil recovery from diatomite, and that CO_2 is very good at finding the "path of least resistance" and bypassing matrix oil.

Historic wooden pumps and derricks remain in the Buena Vista Hills area north of Taft, Calif.

Although the CO_2 flood was not an economic and technical success, the pilot monitoring and surveillance program at Lost Hills field was a huge success. Technologies for monitoring and imaging CO_2 floods conducted by Lawrence Livermore and Lawrence Berkeley national laboratories were demonstrated and proved highly effective.

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TOTAL ESTIMATED COST
$10.0 million

COST SHARING

DOE	$5.0 million
Non-DOE	$5.0 million

WEBSITE

www.netl.doe.gov

PROJECT facts

PARTNERS

ElectroMagnetic Instruments, Inc.
Richmond, CA

Lawrence Livermore National Laboratory
Livermore, CA

Geo-BILT
Richmond, CA

ChevronTexaco Corp.
San Francisco, CA

Schlumberger Ltd.
Houston, TX

MAIN SITES

EMI Test Site
Richmond, CA

Lost Hills field
Kern County, CA

Kern River field
Kern County, CA

Vacuum field
Lea County, NM

Crosswell receiver being prepared to lower in wellbore.

OIL RESERVOIR CHARACTERIZATION AND CO_2 INJECTION MONITORING IN THE PERMIAN BASIN WITH CROSSWELL ELECTROMAGNETIC IMAGING

Background/Problem

Crosswell electromagnetic imaging technology, based on earlier radar imaging technology, will help interpret the reservoir rock and fluid flow through the reservoir between wells. The necessary resolution to accurately map fluid properties has been missing from conventional seismic analysis.

Crosswell EM imaging is designed to give accurate measurement of oil saturations in the areas between wells. Previous logging techniques could only generate oil saturation data close to the wellbore. Crosswell EM logging can provide the operator with an actual image of fluid migration and show where specific areas of undeveloped reservoir remain.

Project Description/Accomplishments

The Crosswell Electromagnetic Imaging Tool was developed at Lawrence Livermore National Laboratory (LLNL) from 1991 to 2000. ElectroMagnetic Instruments, Inc. (EMI) was created by former LLNL scientists to further the research and commercialization of the Crosswell Electromagnetic Imaging down-hole logging tool. EMI developed a five-well pattern test site in Richmond, CA, to continue testing and construction of the tool prior to commercial field tests.

Crosswell electromagnetic logging involves the use of a string of receivers in one well and a transmitter lowered into a neighboring wellbore and moved up and down. The development of sensitive receivers, advanced transmitters, and fiber optics was an essential part of the implementation of crosswell logging, and these advances have been incorporated into the development of the EM extended-logging tool. The DOE project has refined transmitter and geophone receiver design and deployed the EM tool in uncased, fiberglass-cased, and steel-cased wellbores.

EM logging depends on interpretation of three-components: compressional, vertical shear, and horizontal shear waves between transmitter and receiver. Using a multiple array of receivers and moving the transmitter up and down the neighboring well allows imaging of a roughly elliptical region between the wells. Several transmitter-receiver combinations are used per survey to gather data. Currently, EM logging of a 1,000 ft section of an uncased wellbore can be accomplished in 12 hours. The logging tool can be used in uncased and fiberglass-cased wells with no difficulty, and has been successfully demonstrated when one well of a pair is steel-cased. Steel casing significantly slows transmission time and interferes with the signals.

...Improved interwell logging applicable to CO_2 flooding

Field Demonstration Results

The first field applications of crosswell EM logging were conducted in 1997-98. A crosswell survey was conducted at Kern River oil field in California in 1998 to map the residual oil saturation and determine which factors controlled steam and oil flow in the heavy oil reservoir. Identification of the steam path allowed redesign of the steamflood to produce unswept areas. Crosswell imaging applied at Lost Hills field in California in 1997-98 imaged the waterflood performance of the Belridge Diatomite. Chevron USA Inc. used two fiberglass-cased wells to observe the results of water injection in this fractured reservoir. Imaging resistivity changes over time demonstrated that crosswell data could be used to map migration of the waterflood front, providing an excellent means for understanding reservoir dynamics and optimizing the oil recovery process of the waterflood.

The Geo-BILT tool, a modified prototype EM imaging tool designed and tested by EMI, successfully demonstrated that multicomponent logging was applicable in several different geological environments. Geo-BILT has the advantage that it is capable of single-well extended logging. The tool uses a transmitter situated 3 meters above the receivers on a line and provides a 3-D image of the wellbore area up to a radius of 50 to 250 meters. Single-well logging will significantly reduce logging cost while providing critical reservoir data.

Crosswell electromagnetic imaging was used to monitor CO_2 injection performance in New Mexico's Vacuum field, operated by ChevronTexaco. This 3-year DOE project involved development of crosswell EM dual-steel casing logging tools, software development, data processing, and imaging of low-induction frequencies. The results were used to develop resistivity models showing the distribution, size, and depth of the low-resistivity zones, which could be correlated to interwell CO_2 migration.

Benefits/Impacts

Crosswell EM imaging has been demonstrated successfully for use in monitoring steamfloods, waterfloods, and CO_2 floods. Crosswell EM imaging was proved to be 10 times more effective than the previous logging techniques used at Vacuum field to monitor CO_2 flooding. Information obtained from EM surveys will allow field operators to optimize production and produce more oil in a cost-effective manner. The progress of imaging through fiberglass and steel casing will increase significantly the application of the technique in regions where uncased wells cannot be used. The newest advances in single-wellbore imaging holds great potential for use in offshore drilling, where the expense of idling wells for logging procedures will be reduced by cutting the number of wells necessary to complete the EM survey.

Following successful demonstrations of the tool's effectiveness, specifically single-borehole imaging, imaging through steel casing, and CO_2 monitoring, EMI was purchased by Schlumberger Ltd., a major oilfield service company. Schlumberger is backing the continued development and implementation of the Crosswell EM tool with a capital investment of $15 million, indicating their confidence that crosswell EM logging tools have a secure place in the future of the petroleum industry.

DEMONSTRATION OF MICROHOLES FOR OIL EXPLORATION, PRODUCTION, AND EMPLACEMENT OF SUBSURFACE SEISMIC INSTRUMENTATION

PARTNERS

Los Alamos National Laboratory
Los Alamos, NM

Rocky Mountain Oilfield Testing Center
Casper, WY

Lawrence Berkeley National Laboratory
Berkeley, CA

University of Wyoming
Laramie, WY

MAIN SITE

Naval Petroleum Reserve No. 3
Casper, WY

Foreground:LBNL microgeophone array sonde in the deployment cable. Background: contract vibroseis unit.

Background/Problem

The use of production and injection wells for seismic data acquisition has a number of disadvantages. Deploying seismic sensors and other logging-type tools interrupts field operations, resulting in loss of money through temporarily stopped production and idle time for expensive equipment and personnel. Often, production and injection wells are not positioned in the most advantageous locations for obtaining reservoir data. Conventional wells dedicated to seismic monitoring are expensive to drill.

Microholes (wellbores less than 3½-inch diameter) have the advantage of being relatively inexpensive to drill, and locations and completion designs can be selected for optimal acquisition of seismic data.

In previous DOE-funded projects, Los Alamos National Laboratory has demonstrated that coiled-tubing microdrilling of wells as small as 1¾-inch in diameter and as deep as 800 ft can be achieved. The Los Alamos team also successfully field-tested geophysical micro-instrumentation in microholes cased with 1¼-inch tubing.

Project Description

The overall goal of this project is to demonstrate the technical and economic feasibility of a highly mobile, self-contained, microhole drilling system as an enabling technology for commercially viable seismic-data acquisition. Succeeding in these objectives will result in reduced access (well) cost and improved quality of data. Air-filled microholes completed with PVC (or other nonmetallic casing) are expected to provide the lowest noise environment possible for retrievable seismic instrumentation.

Microhole technologies will be used to monitor a separately DOE-funded carbon-sequestration project. The CO_2 Geological Storage R&D Project is being conducted at the Naval Petroleum Reserve No. 3 in central Wyoming by the Rocky Mountain Oilfield Testing Center. Up to four instrumented microwells will be drilled to monitor the injection, sequestration, and long-term storage of CO_2 in a depleted Tensleep formation oil reservoir.

…Small-diameter instrumented wells expected to enable CO$_2$ sequestration monitoring

A second goal of the project is to evaluate new commercial drilling and completion equipment. The Los Alamos microdrilling equipment serves as a platform to evaluate commercial technology that is, or may be, appropriate for microdrilling and completion services. By testing and evaluating as many commercial products as possible during field operations in the drilling of micro-instrumentation holes, the project will provide real, full-field conditions for assessing these products.

Accomplishments

The acoustic performance of the geologic formations in the CO$_2$ injection area has been modeled and was used to select four well locations for CO$_2$ flood monitoring. Seismic arrays were selected, and the equipment needed to assemble and deploy the arrays was procured.

The first micro-instrumentation CO$_2$-monitoring hole was drilled and completed in October 2004. The 808-ft well was completed with PVC casing set below 587 ft, where intermediate steel casing was cemented to isolate the Shannon formation. The second micro-instrumentation hole was drilled to 407 ft and similarly completed. A multi-offset, vertical seismic profile survey was conducted successfully in one of the 800 ft microholes. The high-resolution seismic data are being processed. Completion of the second monitoring well and drilling and completion of two additional microwells will begin in the spring of 2005. CO$_2$ injection is presently scheduled to begin in 2006.

Benefits

Micro-instrumentation holes can cost from one tenth to one fourth that of conventional holes. Successful demonstration of a nonmetallic casing such as PVC line pipe will reduce noise and improve the performance of a micro-instrumentation hole dedicated to reservoir-monitoring service.

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TOTAL ESTIMATED COST

$1.3 million

COST SHARING

DOE	$1.3 million
Non-DOE	$0

WEBSITE

www.netl.doe.gov

Microdrilling site at the Naval Petroleum Reserve No. 3. The Los Alamos drilling mud cleaning system and coiled tubing drilling rig are shown, from left to right.

Strategic Center for Natural Gas and Oil

PROJECT
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U.S. DEPARTMENT OF ENERGY
OFFICE OF FOSSIL ENERGY
NATIONAL ENERGY TECHNOLOGY LABORATORY
STRATEGIC CENTER FOR NATIONAL GAS AND OIL

IMPLEMENTING A NOVEL CYCLIC CO_2 FLOOD IN PALEOZOIC REEFS

PARTNERS

Michigan Technological University
Houghton, MI

MAIN SITE

Dover field
Otsego County, MI

Background/Problem

The Michigan Basin contains over 700 reef fields that have produced over 300 million barrels of oil and 2 trillion cubic feet of gas. Most of the wells in these fields are now shut-in or plugged and abandoned, even though the primary recoveries were only 25-40%. These reefs are valuable resources and obvious targets for enhanced recovery. Few enhanced recovery projects have been implemented, even though many of them may produce hydrocarbons nearly equal in volume to the original primary recovery—in some cases an additional 250,000 - 500,000 barrels of oil per reef.

Two CO_2 projects in the Michigan pinnacle reefs have reported additional production due of 160,000 and 430,000 barrels. Those volumes represent 14% and 33% of the primary recovery in just 5 years. One of the projects, at Dover field in Otsego County, is close to the demonstration well proposed for this project. Data released to the State of Michigan indicate that the CO_2 nearly restored the production to initial conditions. However, the details of the operations have not been made public, and this has been a serious impediment to widespread adoption of this technology.

Project Description

The primary goals of this project are to 1) show that significant quantities of bypassed hydrocarbons can be recovered from pinnacle reefs using a novel CO_2 cycling technology by conducting a field demonstration, 2) identify abandoned or shut-in reefs that are suitable candidates for similar recovery efforts, and 3) communicate the project results and data to small, independent producers via an aggressive technology transfer program.

In this project, CO_2 will be injected into the top of the reef, and the hydrocarbons will be collected from a horizontal drain well drilled at the base of the reef. The CO_2 will be obtained from nearby natural gas wells producing from the Antrim formation, compressed and dehydrated, then piped one mile to the demonstration well. There it will be injected to bring the reef back to nearly virgin pressure and the re-mobilized hydrocarbons will tend to migrate to the bottom of the reservoir as the gas cap expands. This CO_2 is currently vented to the atmosphere as a waste product.
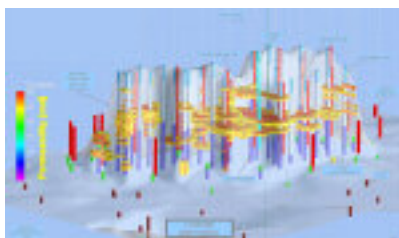
Visualization of a Belle River Mills reef showing core permeability voxels.

…*Visualization of reservoir parameters expected to increase hydrocarbon recovery in mature pinnacle reefs*

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TOTAL ESTIMATED COST
   $2.2 million

COST SHARING
   DOE $1.1 million
   Non- DOE $1.1 million

WEBSITES

   www.netl.doe.gov

Nearby well logs that penetrate the reef will be analyzed using a new approach that has been developed at Michigan Technological University. This approach has been termed Log Curve Amplitude Slicing (LCAS) and uses suites of well logs to map the horizon of interest at 1-ft intervals, essentially utilizing the full information content of the log. The technique is similar to mapping formation tops from log picks or driller's reports except that the attribute is mapped at much more closely spaced intervals. All available geologic and engineering data, cores and core analyses, reservoir pressures, and production history data will be collected. These data, along with the wireline log data derived from the LCAS process, will be integrated to build an interactive database and geologic model.

Seventeen reefs and 130 wells have been identified in the vicinity of the proposed demonstration well. This region will be evaluated for enhanced recovery potential as part of this project.

Accomplishments

A production response of more than 80 barrels of oil per day has resulted from the initial stage of repressurization of a depleted Niagaran pinnacle reef using Antrim waste CO_2. Detailed reservoir modeling of Niagaran reefs using well log tomography is producing a new reservoir characterization tool that can be used for the visualization of permeability and porosity distribution in oil and gas reservoirs.

Benefits

If successful, the project will demonstrate a simple operation that can be widely implemented at a relatively low cost. The demonstration well in Otsego County is expected to produce an additional 400,000 to 600,000 barrels of oil—nearly equal to the original production. Estimated costs to acquire, compress, and inject the CO_2 and recover the oil are about $3 million per well. The breakeven point would be about 75,000 barrels, assuming $40/barrel oil. Assuming that 100 of the 700 discovered reefs could be candidates for CO_2 injection, and assuming an average recovery of 400,000 barrels, the potential basin-wide recovery approaches 40 million barrels.

Since the CO_2 to be injected will come from nearby Antrim production, an additional benefit will be to sequester this CO_2 rather than vent it to the atmosphere.
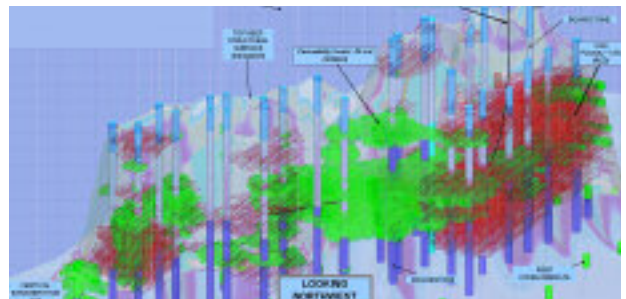
Visualization of a Belle River Mills reef showing permeability voxels >25md (green) and >13md (red).

Strategic Center for Natural Gas and Oil

PROJECT
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NATIONAL ENERGY TECHNOLOGY LABORATORY
STRATEGIC CENTER FOR NATIONAL GAS AND OIL

IMPROVING CO_2 EFFICIENCY FOR RECOVERING OIL IN HETEROGENEOUS RESERVOIRS

PARTNERS

New Mexico Petroleum
Recovery Research Center
(PRRC)
New Mexico Institute of
Mining and Technology
Socorro, NM

MAIN SITE

New Mexico Petroleum
Recovery Research Center
(PRRC)
New Mexico Institute of
Mining and Technology
Socorro, NM

SEM results of limestone core cross sections identify precipitation (lighter zones) that results in decreased permeability and thus injectivity reduction.
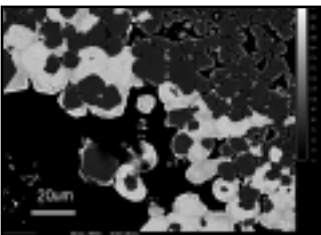
Background/Problem

Despite favorable characteristics of CO_2 for enhanced oil recovery, CO_2 floods frequently experience poor sweep efficiency caused by gas fingering and gravity override, augmented by reservoir heterogeneity as well as low productivity resulting from lower-than-expected injectivity. Poor sweep efficiency results from a high mobility ratio caused by the low viscosity of high-density CO_2 compared to that of water or oil. The effectiveness of water injection alternating with gas (WAG), a common process used for mobility control during CO_2 floods, is reduced by gravity segregation between water and CO_2 and amplified by permeability differences. Foaming agents introduced in the aqueous phase control mobility. However, costs incurred by the loss of expensive chemicals to adsorption on reservoir rock often exclude this potentially beneficial option for many well operators.

Results of previous work on DOE-funded CO_2 research projects at PRRC have resulted in 40 publications on specific topics, including injectivity, phase behavior and multiphase flow, pressure effects, mobility control and foam properties, selective mobility reduction, foam mechanisms, mixed surfactants and sacrificial agents, gravity drainage, imbibition, interfacial tension, field foam modeling and history matching, numerical methods, and CO_2 reservoir injection studies.

Project Description/Accomplishments

The current project focuses on determining the mechanisms of adsorption and desorption of surfactants in a reservoir, the effects of reservoir conditions on surfactant solution/CO_2 foamability, and causes of injectivity changes in CO_2 injection systems. The objectives are to increase effectiveness and viability of CO_2 mobility control using foaming systems, to minimize injectivity losses, and to model these mechanisms. This will include an improved understanding of foaming agents and injectivity. Most of the study will be laboratory-related, with supporting modeling and field liaison projects.

Project participants are developing systems with lower concentrations of good foaming agents that will reduce cost. These systems are derived using a sacrificial agent or a co-surfactant that shows synergistic improvements when mixed with the good foaming agents.

...Research into improved CO$_2$ mobility control

Enhanced recovery WAG processes frequently reduce injectivity, and the addition of mobility control agents inherently compounds this problem. Normally, improved mobility ratios will reduce injectivity. Improved injectivity also will result from the lower chemical concentrations and from some of the synergistic improvements using the co-surfactant systems. The high flow rates at near-wellbore conditions have been considered as a cause of decreased injectivity. Injectivity reduction can be due to decreased permeability within the reservoir triggered by precipitation of carbonates as a result of pressure drop causing a supersaturated solution to form. CO$_2$ mobility control using foam can reduce injectivity problems, if properly understood and applied.
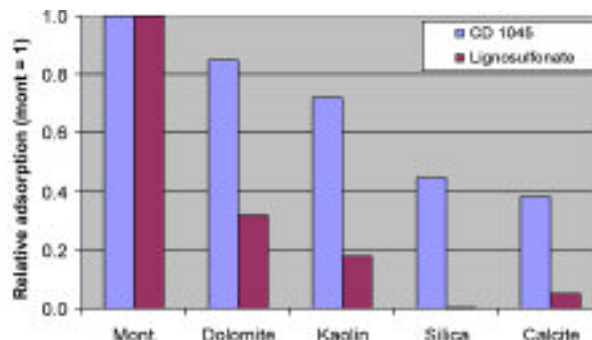
In addition research is continuing to determine the surfactant sorption properties of five pure minerals common in reservoir rock (montmorillonite, dolomite, kaolin, silica and calcite).

Benefits/Impacts

CO$_2$ mobility control will result in more-efficient CO$_2$ flooding in heterogeneous reservoirs and will include the following benefits:

1. Extending the life of the petroleum reservoir (thus maintaining or increasing industry employment), increasing oil recovery, and expanding the range of reservoirs amenable to CO$_2$ flooding.

2. Reducing of chemical cost by optimizing oil saturation tolerance of foam, decreasing primary foaming agent adsorption, and decreasing required primary foaming agent concentration.

3. Delaying production of CO$_2$ and increasing retention of CO$_2$ in the reservoir (sequestration).

4. Improving injectivity of CO$_2$ and water and decreasing mobility of CO$_2$ during the alternate injection of brine and CO$_2$.

5. Bolstering CO$_2$ flooding predictions.

CO$_2$ flooding potential has been demonstrated in the US, particularly in the Permian Basin of west Texas and southeast New Mexico. Much of the research on CO$_2$ flooding methods can be applied to other gas flooding processes, such as hydrocarbon injection projects. Today over 300,000 b/d of oil is being produced by gas injection in the U.S., and that volume scarcely hints at the potential of a remaining untapped oil resource pegged at 351 billion barrels.

Relative adsorption density of two surfactants onto five minerals.

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TOTAL ESTIMATED COST
$1.5 million

COST SHARING

DOE $1.0 million
Non-DOE $0.5 million

WEBSITE

www.netl.doe.gov

Strategic Center for Natural Gas and Oil

FIELD DEMONSTRATION OF CARBON DIOXIDE MISCIBLE FLOODING IN THE LANSING-KANSAS CITY FORMATION, CENTRAL KANSAS

PARTNERS

University of Kansas
  Kansas Geological Survey
  Tertiary Oil Recovery Project
Lawrence, KS

Murfin Drilling Company and working interest partners
Wichita, KS

U.S. Energy Partners, LLC
Russell, KS

EPCO Carbon Dioxide Products, Inc.
Monroe, LA

MAIN SITE
  Hall-Gurney Field
  Russell County, KS

Carter Colliver #1 CO_2 injection well is shown in the background and the Colliver #13 producing well in the foreground, both part of the first CO_2 flood in Kansas.

Background/Problem

This CO_2 miscible flood demonstration project represents the first use of CO_2 for enhanced oil recovery (EOR) in Kansas. The goal is to demonstrate the technical feasibility of the process in a major Kansas reservoir. The Hall-Gurney field, the largest Lansing-Kansas City formation oil field in Kansas, is one of several CO_2 flood candidate fields in central Kansas. There have been no miscible CO_2 floods in Kansas primarily due to the distance to the sources for CO_2.

This electricity co-generation, ethanol fuel production, and CO_2 EOR project is a unique scalable model for linked energy systems. Waste heat from a 15-megawatt, gas-fired turbine municipal electrical generator provides heat input for a 25 million gallon per year ethanol plant. CO_2, is obtained as a byproduct from ethanol production and will be utilized by the CO_2 miscible flood project in Hall-Gurney field. The full CO_2 stream from the ethanol plant could supply a small oil field capable of producing 5 million barrels of oil and sequestering 1.5 million tons of CO_2 over a 20 year period. An additional byproduct of ethanol production will be cattle feed. Meanwhile, U.S. ethanol demand is projected to double this decade.

Project Description/Accomplishments

Initial studies of the Lansing-Kansas City carbonate reservoir have determined the technical and economic feasibility of using CO_2 miscible flooding to recover residual and bypassed oil in central Kansas. The demonstration will mark the first time that CO_2 from an ethanol plant has been used for EOR. If proven to be technically and economically feasible, the project offers potential to add significant value to waste CO_2 through EOR. Currently the CO_2 is being vented. Part of the CO_2 stream (10-20%) will be used for the nearby EOR demonstration at Hall-Gurney field.

CO_2 flooding began in Kansas in December 2003. The CO_2 is trucked 7 miles from the ethanol plant in Russell, KS, and injected into the depleted Lansing-Kansas City reservoir.

If the technology is proven technologically and economically feasible the estimated incremental oil production in the state of Kansas is 100-600 million barrels over 20 years.

...Enhanced oil recovery provides CO_2 sequestration

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TOTAL ESTIMATED COST
$5.4 million

COST SHARING
DOE $1.9 million
Non-DOE $3.5 million

WEBSITE
www.netl.doe.gov
www.kgs.ku.edu/CO2/index.html

The pilot covers half of a traditional 5-spot pattern on 10 acres with one central injector, three producers, and two water injection containment wells; 270 million cubic feet of CO_2 will be injected over a four year period. The injected CO_2 will be pressured to above 1,250 psi (minimum miscible pressure for the formation) prior to injection into the Lansing-Kansas City formation. Modeling of the CO_2 flood anticipates 26,000 bbl of incremental oil from the 10-acre pilot, and if successful the technology will be expanded to a larger part of the Hall-Gurney field.

CO_2 breakthrough and the first incremental oil production began in May 2004. Cumulative incremental output was 550 bbl for the pilot as of September 1, 2004, averaging 2.5 b/d for the two producers; the third well had not yet responded.

Benefits/Impacts

CO_2 flooding demonstrated in this project may prevent up to 6,000 mature oil fields in Kansas from being abandoned. The potential target for CO_2 flooding in Kansas may total over 250-500 million barrels of incremental oil, equivalent to 5-10 years of additional Kansas production. The project's original objective, to demonstrate to Kansas independents the feasibility of CO_2 flooding and to find a viable supply of CO_2, is being met by joint industry ventures. This will benefit agriculture, ethanol production, and electrical generation in addition to independent oil producers. At the same time the public will gain the environmental benefit of less CO_2 in the atmosphere.

The electrical co-generation, ethanol production, and EOR project is unique in that it brings together three distinctly separate industries in a way that improves the economics of each while also providing a mechanism for value-added geologic sequestration of CO_2. If the full CO_2 stream from the ethanol plant is utilized for EOR for a 10-year period, the benefits from the three industry linkages would total $88 million.

Currently, the CO_2 project uses only 10% of the CO_2 produced from the ethanol plant. The Hall-Gurney field could use the full CO_2 output of five similar-sized ethanol plants at full-field CO_2 EOR development.

Hall-Gurney field and nearby ethanol plant, Russell, Kansas.

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STRATEGIC CENTER FOR NATIONAL GAS AND OIL

PARTNERS

University of Kansas
Center for Research
Lawrence, KS

MAIN SITE

Hall-Gurney Field
Russell County, KS

IVI Minivib2 outfitted with DGPS receiver, tracking system, and Atlas high-output rotary valve.

4-D HIGH-RESOLUTION SEISMIC REFLECTION MONITORING OF MISCIBLE CO₂ INJECTION INTO A CARBONATE RESERVOIR

Background/Problem

Time-lapse 3-D (or 4-D) seismic reflection surveying has been proven an effective tool during the last decade to evaluate the effectiveness of conventional EOR programs. Consistency and repeatability of 3-D surveys has been the most frequently identified problem associated with time-lapse monitoring of reservoir production. Seismic monitoring has been considered viable only for the most prolific fields, possessing the greatest potential for significant returns from identification of stranded reserves. Most U.S. Midcontinent reservoirs would not be considered candidates for 4-D monitoring using historical criteria.

Only recently has the potential of seismically monitoring the injection of miscible CO_2 into thin carbonate reservoirs been studied. Field tests of this technique to date have used conventional approaches with minimal regard to the economics of routine application or to the spatial and temporal sampling necessary for application to the size of most reservoirs found in the Midcontinent. Changes in reservoir characteristics between baseline and monitoring surveys have assumed linearity and have not been incorporated into improved production schemes. This project follows on the DOE Class Revisit being conducted at Hall-Gurney field to evaluate the feasibility of CO_2 flooding in central Kansas.

Project Description/Accomplishments

High-resolution seismic monitoring of this CO_2 flood has to date included five 3-D seismic surveys shot using the same single-patch, modified brick design. A single high-frequency vibrator has occupied each of the more than 800 shotpoints in this approximately 2.3 km² patch within 0.5 m of ideal using a differential global positioning (DGPS) tracking system. Identical equipment, parameters, and procedures were used for each survey. Processing has been completed using an iterative approach, where processing enhancements identified for each survey were used to improve and modify processing parameters of previous surveys.

Selected 4-D seismic attribute maps that have undergone weak-anomaly enhancement through color balancing have successfully monitored the movement of the injected miscible CO_2 front and illuminated bypassed hydrocarbon areas.

…Seismic data a potential tool for routine CO_2 sequestration

The role 4-D seismic can play in the evolution of reservoir modeling and accelerating model development is being evaluated. One- and two-layer models adequately predicted primary production. Subsequent waterflooding required the introduction of more layers and lateral heterogeneity to the models. 3-D seismic revealed lateral heterogeneities that also were indicated by well interference testing but not fully quantified. 4-D seismic revealed that the movement of injected CO_2 was constrained both in response to the observed heterogeneities and the interaction of pressures generated by water-containment injectors.

CO_2 injection well with DGPS receiver and part of the distributed seismograph.

High-resolution seismic images acquired before and during this CO_2 flood have highlighted changes consistent with expected CO_2 movement, based on production data, fluid-injection volumetrics, and reservoir simulations. Instantaneous frequency of earth volumes (which include the production zone) is an excellent, quick, relatively low-resolution indicator of changes that appear consistent with changes in CO_2 saturation. Amplitude attributes have proven most sensitive to and effective in mapping changes in reservoir properties.

With injection of CO_2 continuous now for almost a year, preparations are underway for acquiring the first 2-C, 2-D shear wave monitoring survey in early December 2004. Sensitivity of several seismic attributes to changes in fluid characteristics from movement of CO_2 across this field is being evaluated. Amplitude appears to have the greatest potential to track CO_2. No attributes studied so far require inversion and therefore avoid problems of instability and non-uniqueness.

Benefits/Impacts

Successful 4-D monitoring of this multi-year EOR project will reveal critical components and considerations necessary for routine incorporation of 3-D high-resolution seismic monitoring with CO_2 EOR programs in thin, relatively shallow, mature carbonate reservoirs. Changes in production schemes made possible by incorporating nearly real-time monitoring data into CO_2 injection EOR programs could dramatically improve the efficiency and economics of that technology in many Midcontinent fields. Refinements to 3-D high-resolution reflection-imaging approaches resulting from this study could make seismic data a tool for providing assurances essential for routine sequestration of CO_2 in depleted oil/gas reservoirs or brine aquifers.

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TOTAL ESTIMATED COST
$2.9 million

COST SHARING

DOE	$2.3 million
Non-DOE	$0.6 million

WEBSITE
www.netl.doe.gov

INEXPENSIVE CO_2 THICKENING AGENTS FOR IMPROVING MOBILITY CONTROL OF CO_2 FLOODS

PARTNERS

University of Pittsburgh
Pittsburgh, PA

MAIN SITE

University of Pittsburgh
Pittsburgh, PA

Background/Problem

About 1.5 billion standard cubic feet per day of CO_2 is injected in U.S. oil reservoirs each day, producing more than 200,000 barrels oil per day. Despite the maturity of this technology, its performance still has much room for improvement. For example, about 8,000 standard cubic feet of CO_2 is required for each barrel of oil recovered, which translates into the injection of 3.5 barrels of dense CO_2 at reservoir conditions for each barrel of oil produced. Further, large slugs of water must be injected alternately with slugs of CO_2 (water-alternating-gas, or WAG) in order to make the CO_2 flow more uniformly through the reservoir rather than "fingering" from the injection well to the production well and bypassing large regions of oil-bearing rock. Sweep efficiency problems are directly associated with the low viscosity of CO_2 compared with that of the oil to be displaced.

The University of Pittsburgh research group, under previous funding from the DOE, designed, synthesized, and evaluated the first CO_2 thickener, poly(fluoroacrylate-styrene) or polyFAST, in the laboratory. PolyFAST remains the only CO_2 thickener that has ever been reported. Although this result proved that a thickening agent could be designed for CO_2, it was not a practical thickener for field application. Specifically, it was expensive, biologically and environmentally persistent, and not available in large quantity. All of these negative attributes were directly the result of the polymer having a high content of fluorine.

Project Description/Accomplishments

The goal of this project was to identify an inexpensive polymer capable of dissolving in carbon dioxide and increasing its viscosity, thereby enabling improved mobility control of CO_2 floods.

This project evaluated numerous polymers that contained *no fluorine* for this CO_2 thickening application. Rather than performing a trial-and-error study of what dissolves in CO_2, specific chemical groups that were known to have a strong and favorable interaction with CO_2 were selected.

The design of a thickener consists of two steps. First, a high-molecular-weight "base polymer" that is extremely soluble in CO_2 must be designed. Second, the base polymer must be modified to become a thickener by adding a small amount of "CO_2-phobic" groups that cause the dissolved thickener molecules to interact with one another. This type of interaction forms large, viscosity-increasing macro-molecules to form in the CO_2.
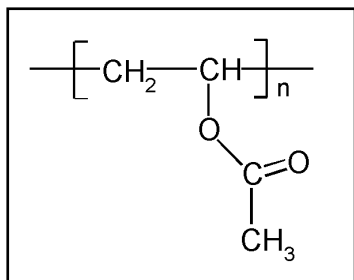
As of 2004, the most CO_2-soluble high-molecular-weight polymer composed solely of C, H, O is poly(vinyl acetate), PVAc.

…Eliminating need for WAG injection

Unfortunately, this modification will always make the thickener less soluble in CO_2 than the base polymer. Therefore, the base polymer must be soluble in CO_2 at pressures less than the minimum miscibility pressure (MMP), or the pressure at which the CO_2 flood is conducted.

This project focused on the first step- making the most CO_2 soluble polymer possible. Oxygen-rich hydrocarbons (chemical groups composed of carbon, hydrogen, and oxygen) were determined to be the most promising "CO_2-philic" groups. Ether, carbonyl, and acetate groups were determined to be particularly promising components for making a polymer that dissolves in CO_2.

Several low-molecular-weight polymers (a.k.a. oligomers) of comparable CO_2 solubility were identified, including sugar acetates, polypropylene oxide, poly-methyl acrylate, and polyvinyl acetate. The CO_2-solubility of high-molecular-weight versions of these polymers varied dramatically.

Poly(vinyl acetate), PVAc, was clearly the most CO_2-soluble, inexpensive, high-molecular-weight, commodity polymer identified. For example, 5 wt% PVAc with a molecular weight of 600,000 could dissolve in CO_2. Unfortunately, the pressure required to dissolve PVAc was much greater than the range of MMP values of CO_2 floods.

About 25 novel polymers were designed. Each was a candidate for being a CO_2-soluble base polymer. However, none were more CO_2 soluble than PVAc. After identifying PVAc, computing tools needed to design inexpensive polymers that are even more soluble in CO_2 were developed.

During the final stages of this project, computational tools were used to design CO_2-soluble polymers. These tools allowed a qualitative explanation of why certain polymers were (or were not) CO_2 soluble. At the end of the project the design of a new polymer—poly(3-acetoxy oxetane) or PAO—that should be more CO_2-soluble than PVAc was identified.

Benefits/Impacts

An inexpensive, environmentally benign, safe CO_2 thickener composed of carbon, hydrogen, and oxygen (sulfur and nitrogen are also acceptable) added to CO_2 as it is being injected will increase oil recovery with CO_2 injection. The thickener prevents early breakthrough of CO_2, reduces the amount of CO_2 required to recover a barrel of oil, increases the rate of oil production and ultimately increases the amount of oil that could be recovered from the formation. Use of effective thickeners would eliminate the additional cost of conducting a water-alternating-gas (WAG) process.

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TOTAL ESTIMATED COST
$1.2 million

COST SHARING

DOE	$1.0 million
Non-DOE	$0.2 million

WEBSITE

www.netl.doe.gov

P R O J E C T
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NATIONAL ENERGY TECHNOLOGY LABORATORY
STRATEGIC CENTER FOR NATIONAL GAS AND OIL

SYNTHESIS AND EVALUATION OF CO$_2$ THICKENERS

PARTNERS

University of Pittsburgh
Pittsburgh, PA

MAIN SITE

University of Pittsburgh
Pittsburgh, PA

Background/Problem

The University of Pittsburgh research group, under previous funding from DOE, designed, synthesized, and evaluated the first CO$_2$ thickener, poly(fluoroacrylate-styrene) or polyFAST, in the laboratory. PolyFAST remains the only CO$_2$ thickener that has ever been reported.
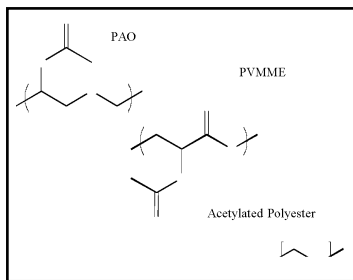
Although this project proved that a thickening agent could be designed for CO$_2$, it was not a practical thickener for field application. Specifically, PolyFAST was expensive, biologically and environmentally persistent, and not available in large volumes. All of these negative attributes were directly the result of the polymer having a high content of fluorine.

A second project, also funded by DOE, researched inexpensive polymers that could dissolve in carbon dioxide and increase its viscosity, thereby improving mobility control of CO$_2$ floods. The project evaluated numerous polymers that contained no fluorine for this CO$_2$ thickening application. Specific chemical groups that were known to have a strong and favorable interaction with CO$_2$ were selected for study. The research identified the most CO$_2$-soluble, high-molecular-weight, commodity polymer that has yet been reported: poly(vinyl acetate), or PVAc. Unfortunately, the pressure required to dissolve PVAc in CO$_2$ was much greater than the range of the pressures used in most CO$_2$ floods.

Initial candidates for CO$_2$ soluble compounds designed by molecular modeling.

Project Description

In this project, molecular modeling will be used to design polymers that are more CO$_2$-soluble than PVAc. If successful, these "base polymers" will then be modified to become direct CO$_2$ viscosifiers, or thickeners.

The objectives of this project are to design and synthesize novel polymers composed solely of carbon, hydrogen, and oxygen that are more CO$_2$-soluble than PVAc. Specifically, the polymer should be able to dissolve in CO$_2$ at pressures less than the minimum miscibility pressure (MMP). In addition to qualitative guidelines that developed for designing CO$_2$-soluble compounds, were molecular modeling tools will be used to design CO$_2$-soluble polymers. Although these calculations cannot predict the precise solubility of the polymer in CO$_2$, they do provide quantitative comparisons of how strongly the polymer interacts with CO$_2$.

NETL

...Design based on molecular modeling

Design of a thickener consists of two steps. First, a high-molecular-weight "base polymer" that is extremely soluble in CO_2 must be designed. Second, the base polymer must be modified to become a thickener by adding a small amount of "CO_2-phobic" groups that cause the dissolved thickener molecules to interact with one another. This type of interaction forms large, viscosity-increasing macro-molecules to form in the CO_2. Unfortunately, this modification always makes the thickener less soluble in CO_2 than the base polymer; therefore the base polymer must be soluble in CO_2 at pressures less than the MMP at which the CO_2 flood is conducted.

This project will initially focus on the first step in making the most CO_2-soluble polymer possible. PVAc was the most CO_2-soluble, inexpensive, high-molecular-weight, commodity polymer identified in prior studies. Therefore PVAc will be the initial standard for assessing new polymers. The ultimate goal, however, is to identify an oxygenated hydrocarbon polymer that is soluble in CO_2 at the MMP of typical reservoirs. Only if such a polymer is identified will the second step of the thickener design—the introduction of viscosity-enhancing groups to the polymer—be initiated.

Based on initial results, the first new polymers to be synthesized and evaluated include:

- Poly(3-acetoxy oxetane), PAO
- Poly(vinyl methoxy methyl ether), PVMME
- Acetylated Polyester

Benefits/Impacts

An inexpensive, environmentally benign, direct CO_2 viscosifier will be developed to increase mobility control in CO_2 floods. The thickener prevents early break-through of CO_2, reduces the amount of CO_2 required to recover a barrel of oil, increases the rate of oil production, and ultimately increases the amount of oil that could be recovered from the formation. Use of effective thickeners would eliminate the additional cost of conducting a water-alternating-gas (WAG) process.

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TOTAL ESTIMATED COST
$1.6 million

COST SHARING
DOE $0.7 million
Non-DOE $0.9 million

WEBSITE
www.netl.doe.gov

Strategic Center for Natural Gas and Oil

NETL FUNDED CO$_2$ EOR PROJECTS

Performer	Project #	Title
4th Wave Imaging Corp	DE-FC26-03NT15417	Time-Lapse Seismic Modeling and Inversion of CO$_2$ Saturation for Sequestration and Enhanced Oil Recovery
Advanced Resources International	DE-FC26-04NT15514	Demonstration of a Novel, Integrated Multi-Scale Procedure for High-Resolution 3-D Reservoir Characterization & Improved CO$_2$-EOR/Sequestration Management, SACROC Unit/Breakout
Chevron USA Inc.	DE-FC22-95BC14938	Advanced Reservoir Characterization in the Antelope Shale to Establish the Viability of CO$_2$ Enhanced Oil Recovery in California's Monterey Formation Siliceous Shales — Class III
Electromagnetic Instruments Inc	DE-FC26-00BC15307	Oil Reservoir Characterization and CO$_2$ Injection Monitoring in the Permian Basin with Crosswell Electromagnetic Imaging
Los Alamos National Laboratory	FEW03FE06-4	Technology Development and Demonstration of Microhole Oil Production at the Rocky Mountain Oilfield Test Center
Michigan Technological University	DE-FC26-02NT15441	Implementing a Novel Cyclic CO$_2$ Flood in Paleozoic Reefs
Petroleum Recovery Research New Mexico Tech	DE-FC26-01BC15364	Improving CO$_2$ Efficiency for Recovering Oil in Center-Heterogeneous Reservoirs
University of Kansas	DE-FC26-00BC15124	Field Demonstration of CO$_2$ Miscible Flooding in the Lansing-Kansas City Formation, Central Kansas
University of Kansas Center for Research	DE-FC26-03NT15414	4-D High-Resolution Seismic Reflection Monitoring of Miscible CO$_2$ Injected into a Carbonate Reservoir
University of Pittsburgh	DE-FC26-01BC15315	Inexpensive CO$_2$-Thickening Agents for Improved Mobility Control of CO$_2$ Floods
University of Pittsburgh	DE-FC26-04NT15533	Synthesis and Evaluation of Inexpensive CO$_2$ Thickeners Designed by Molecular Modeling/Breakout