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CONTACTS

Roy Long

Technology Manager—
Ultra-Deepwater, Strategic
Center for Natural Gas & Oil
281-494-2520
roy.long@netl.doe.gov

Albert Yost

Technology Manager—
Exploration & Production,
Strategic Center for
Natural Gas & Oil
304-285-4479
albert.yost@netl.doe.gov

Development of Novel Methods for CO₂ Flood Monitoring

A DOE-NETL funded research project by Sky Research, Inc. and Pacific Northwest National Laboratory (PNNL), is developing, and will field validate, novel non-invasive methods to monitor and quantify CO₂ Enhanced Oil Recovery (EOR) flood performance.

The objective of CO₂-EOR - just as for all other EOR methods - is to produce oil which is unrecoverable with primary and secondary methods. Such oil includes that which is bypassed due to reservoir heterogeneity and poor waterflood sweep efficiency; oil that is physically unconnected to a wellbore; and oil that is trapped by viscous, capillary and interfacial tension forces as residual oil. The metric for EOR methods is how well they do in producing remaining oil-in-place compared to standard water flooding, and the incremental costs.

Within the US, two main EOR methods are used: thermal EOR (in which different methods are used to heat the oil, and thus make it less viscous)

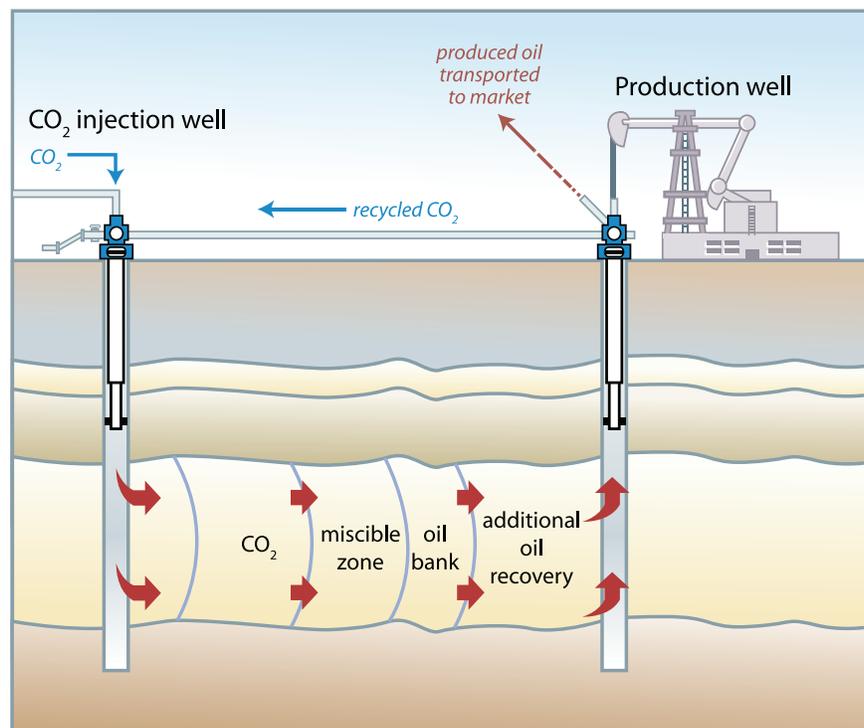


Figure 1. Schematic showing CO₂-EOR. Note that part of the CO₂ that is injected is produced and reinjected. Also note that for optimization reasons CO₂ flood are typically alternated with waterfloods. From IPCC Special Report on Carbon dioxide Capture and Storage, 2005 (IPCC, 2005).

NATIONAL ENERGY TECHNOLOGY LABORATORY

1450 Queen Avenue SW
Albany, OR 97321
541-967-5892

2175 University Avenue South
Suite 201
Fairbanks, AK 99709
907-452-2559

3610 Collins Ferry Road
P.O. Box 880
Morgantown, WV 26507-0880
304-285-4764

626 Cochran Mill Road
P.O. Box 10940
Pittsburgh, PA 15236-0940
412-386-4687

13131 Dairy Ashford, Suite 225
Sugar Land, TX 77478
281-494-2516

Visit the NETL website at:
www.netl.doe.gov

Customer Service:
1-800-553-7681

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Commentary



First used in Scurry County, Texas, CO₂ injection in enhanced oil recovery operations (CO₂ EOR) has been successfully employed throughout the Permian Basin in West Texas and eastern New Mexico. It is now in use, or to be used, to a limited extent in Alabama, Kansas, Mississippi, Wyoming, Oklahoma, Colorado, Utah, Montana, Alaska, and Pennsylvania (U.S. Department of Energy, Enhanced Oil Recovery/CO₂ Injection, Dec. 2011, <http://fossil.energy.gov/programs/oilgas/eor/>). In addition to enhancing oil production,

CO₂ EOR has the benefit of sequestering CO₂ in oil producing formations and is seen as a critical component of future greenhouse gas management programs. This facet of CO₂ EOR produces valuable synergies with the carbon capture, utilization and storage research program within the Department of Energy's Office of Fossil Energy (FE).

Until recently, most of the CO₂ used for EOR has come from naturally-occurring sources – underground reservoirs. But new technologies are being developed to capture CO₂ from industrial processes such as power generation, natural gas processing, and the production of fertilizer, ethanol, and hydrogen in locations where naturally-occurring sources are not available. One demonstration at the Dakota Gasification Company's plant in Beulah, North Dakota is producing CO₂ and delivering it by a 204-mile pipeline to the Weyburn oil field in Saskatchewan, Canada. Encana, the field's operator, is injecting the CO₂ to extend the field's productive life, hoping to add another 25 years and as much as 130 million barrels of oil that might otherwise have been abandoned. As more anthropogenic CO₂ becomes available, it is expected to fuel significant expansion of CO₂ EOR operations.

CO₂ EOR technology is evolving rapidly to a "next generation" phase, partly in anticipation of the arrival of significant amounts of anthropogenic CO₂. The Department's Office of Fossil Energy (FE) through the National Energy Technology Laboratory is actively engaged in supporting the development of next generation technologies. Our R&D program is moving into new areas, researching novel techniques that could significantly improve the technical and economic performance, and expand the applicability of CO₂ injection to a broader group of reservoirs including those in basins much closer to the major sources of man-made CO₂. Next generation CO₂-EOR has the potential to produce as much as 60 billion barrels of economically recoverable oil, using new techniques including injection of much larger volumes of CO₂, innovative flood design to deliver CO₂ to un-swept areas of a reservoir, extending the miscibility pressure, and improving mobility control of the injected CO₂.

In September 2010 DOE competitively selected seven next generation CO₂ EOR research projects. One project is investigating the potential for oil production by CO₂ injection into the residual oil zone: "Next Generation" CO₂-EOR Technologies To Optimize The Residual Oil Zone CO₂ Flood At The Goldsmith Landreth Unit, Ector County, Texas (U. Texas

“*Opportunities to beneficially use captured carbon are, in a sense, “boundless”—especially for the incremental recovery of domestic crude oil.*”

– Permian Basin). Four projects are developing techniques for mobility control of the injected CO₂. Novel foams and gels have the potential to prevent the highly-mobile CO₂ from channeling through high-permeability areas of a reservoir, leaving un-swept, unproductive areas of the reservoir. These projects are:

- Improved Mobility Control in CO₂ Enhanced Oil Recovery using SPI Gels (Impact Technologies, LLC)
- Engineered Nanoparticle-Stabilized CO₂ Foams to Improve Volumetric Sweep of CO₂ EOR Processes (U. Texas - Austin)
- Novel CO₂ Foam Concepts and Injection Schemes for Improving CO₂ Sweep Efficiency in Sandstone and Carbonate Hydrocarbon Formations (U. Texas - Austin)
- Nanoparticle-Stabilized CO₂ Foam for CO₂-EOR Application (New Mexico Institute of Mining and Technology)

Two projects are developing simulation and modeling tools for CO₂ EOR:

- Real Time Semi-Autonomous Geophysical Data Acquisition and Processing System to Monitor Flood Performance (Sky Research, Inc.),
- CO₂-EOR and Sequestration Planning Software (NITEC LLC).

These 2010 projects joined six ongoing R&D activities in CO₂ EOR previously funded by the Office of Fossil Energy.

Future CO₂ EOR technology development will address five opportunities for improving the performance of current, state-of-art CO₂ EOR, specifically:

- Increasing the volume of CO₂ injected,
- Capturing more of the remaining mobile and immobile oil,
- Improving sweep efficiency and mobility control (reservoir conformance),
- Improving the technology for reservoir surveillance, and
- Lowering the threshold minimum miscibility pressure (MMP).

The research and development in CO₂ EOR underway within NETL's Strategic Center for Natural Gas and Oil (SCNGO) discussed above, and that to be undertaken in the future, will occur in concert with synergistic efforts to reduce CO₂ emissions in Carbon Capture, Utilization and Storage program.

Through NETL, a technology portfolio of safe, cost-effective, commercial-scale CO₂ capture and storage technologies is being developed that will be available for commercial deployment beginning in 2020. The Department's primary capture and storage research and development (R&D) objectives are: (1) lowering the cost and energy penalty associated with CO₂ capture from large stationary sources by more than 50 percent, resulting in less than \$25/Tonne CO₂ captured; and (2) improving the understanding of factors affecting CO₂ storage permanence, capacity, and safety in geologic formations and terrestrial ecosystems. Once these objectives are met, new and existing power plants and fuel processing facilities around the world have the potential to be retrofitted with CO₂ capture technologies.

Opportunities to beneficially use captured carbon are, in a sense, "boundless" – especially for the incremental recovery of domestic crude oil. The Department's commitment to advancing CO₂ EOR technology, while mitigating greenhouse gas emissions, is real and demonstrable. I invite each of you to visit NETL's website for information and to stay apprised of further developments.

We hope you enjoy this issue of E&P Focus and as always, we welcome your comments.



John R. Duda
Director, NETL Strategic Center for Natural Gas and Oil

and gas injection, in which CO₂ is the dominant gas used. CO₂-EOR is often used as part of a Water Alternating Gas (WAG) production approach.

Depending on reservoir conditions (pressure, temperature and oil composition) CO₂ EOR floods can be either miscible - in which the injected CO₂ and the hydrocarbons form a single phase fluid with favorable flow properties, or immiscible in which the gas sweeps the oil but does not mix with it to form a single phase fluid. The majority of CO₂ EOR floods are miscible.

Significant volumes of conventional oil remain in known US oil reservoirs which could be produced economically by CO₂ EOR. Based on data from NETL and industry, an estimated 1,673 fields and reservoirs, collectively accounting for 146 billion barrels of original oil in place, are candidates for CO₂ flooding. CO₂ flooding has been underway for several decades, initially in the Permian basin of West Texas and New Mexico, but currently being pursued at multiple sites across the US. CO₂ EOR currently provides for about 280,000 barrels of oil per day, equal to 6 % of US crude oil production.

While the large majority (roughly 80 %) of the CO₂ for CO₂ EOR has come from natural CO₂ fields an increasing percentage of CO₂ comes from anthropogenic sources (coal gasification, gas processing and fertilizer plants). It is expected that limits on natural sources of CO₂, increased demand for CO₂ for EOR as well as a decrease in cost of anthropogenic CO₂ will result in a substantial change in the amount of anthropogenic CO₂ which will be used in EOR. While a substantial percentage of CO₂ which is being injected in reservoirs is currently being produced with the hydrocarbons and reinjected in the subsurface (and CO₂ remaining in the reservoir at the end of the EOR phase could, at least partially, be produced) the potential of using CO₂-EOR as part of a Carbon Capture, Utilization and Sequestration strategy has been broadly recognized both by the Department of Energy, industry and academia.

Cost of CO₂ EOR

CO₂ EOR requires a substantial upfront investment in infrastructure for producing, compressing, transporting and injecting CO₂. It also requires a substantial investment in CO₂. In general, somewhere between 4-8 thousand cubic feet of CO₂ (0.22-0.44 metric tons of CO₂) will need to be injected per barrel of oil produced. While some of this CO₂ is recycled from production wells, a substantial amount will need to be purchased (especially in the initial years of EOR). While exact costs will vary substantially per site (and are rarely published explicitly), an approximate cost of \$20/metric ton CO₂ at the wellhead for fresh, naturally sourced CO₂ and a cost about \$4/metric ton for recycled CO₂, seem to represent industry costs. Overall injection of CO₂ will thus add substantially (\$5-\$15/barrel) to the cost per barrel of oil recovered.

While CO₂ EOR is, thus, not free, the current price of oil and the large number of candidate sites, as well as all the combination of economic benefits, national security benefits and potential for sequestration all contribute to a substantial enthusiasm for scaling up the application and use of CO₂ EOR. However, it is recognized that this will require the development of several novel EOR technologies.

Next Generation CO₂ EOR Technologies

One of the recognized challenges by the Department of Energy and industry is the need for a suite of next generation EOR technologies

which can substantially increase (by an order of magnitude or more) the number of fields at which EOR would be deployed as well as the amount of injected CO₂ and the percentage of anthropogenic CO₂. Details on the kind of technologies and associated objectives can be found in the NETL publication Improving Domestic Energy Security and Lowering CO₂ Emissions with “Next Generation” CO₂-Enhanced Oil Recovery (CO₂-EOR) (DOE/NETL-2011/1504) available from the NETL website. The technology being developed by Sky Research and PNNL is part of the suite of such next generation technologies. Specifically, the objective of the Sky and PNNL developed technology is to provide a novel and enhanced monitoring capability for CO₂ EOR floods.

CO₂ EOR Flood Characterization

Information on CO₂ EOR behavior is currently primarily obtained by the interpretation of injection and production data coupled with sparse in-well measurements and forward reservoir modeling. While this provides macroscopic insights into flood behavior it only allows for rudimentary flood optimization due to the lack of volumetric spatiotemporal information on flood behavior. Such knowledge would ideally include both displacement and phase changes as well as geochemical reactions associated with the flood. Access to this information would allow industry to refine and optimize injection strategies, and would result in increased oil production and/or reduced operating costs. This in turn would allow CO₂ EOR to be applied to sites where currently it may not be economical to apply, resulting in increased domestic oil production.

Project Approach: Development of Time-Lapse Geophysics for CO₂ EOR flood monitoring

Geophysical methods are a standard tool for obtaining information on volumetric distributions of subsurface physical properties of rocks and fluids. If one collects geophysical datasets with the same parameters at the same position over time, changes in the geophysical data between surveys can be interpreted in terms of dynamic subsurface processes. This approach is known as time lapse or 4-D geophysics, and it has been widely demonstrated to provide actionable information on processes of interest. Within the oil industry, the predominant time lapse geophysical method used is time lapse seismic. However, one of the major changes in physical properties which occur in WAG is a change in electrical conductivity of the reservoir. This electrical conductivity will increase when brine is injected, and decrease when CO₂ is injected. Measurements of electrical properties from measurements done during WAG show that such changes can be of one order of magnitude or more. This motivates the research of the Sky/PNNL project: develop a semi autonomous geophysical data acquisition system to provide near real time information to stakeholders on flood behavior (Figure 2)

In this system, a combination of surface and borehole time lapse time domain electromagnetic and electrical resistivity measurements will be inverted to obtain a spatial and temporal distribution of changes in reservoir electrical properties. By combining these changes with a reservoir model through a coupled inversion this can provide actionable information to field operators on flood behavior. This information could be used to tune and optimize the flood.

Project Progress

This project started in February 2011 and is currently in its second year.

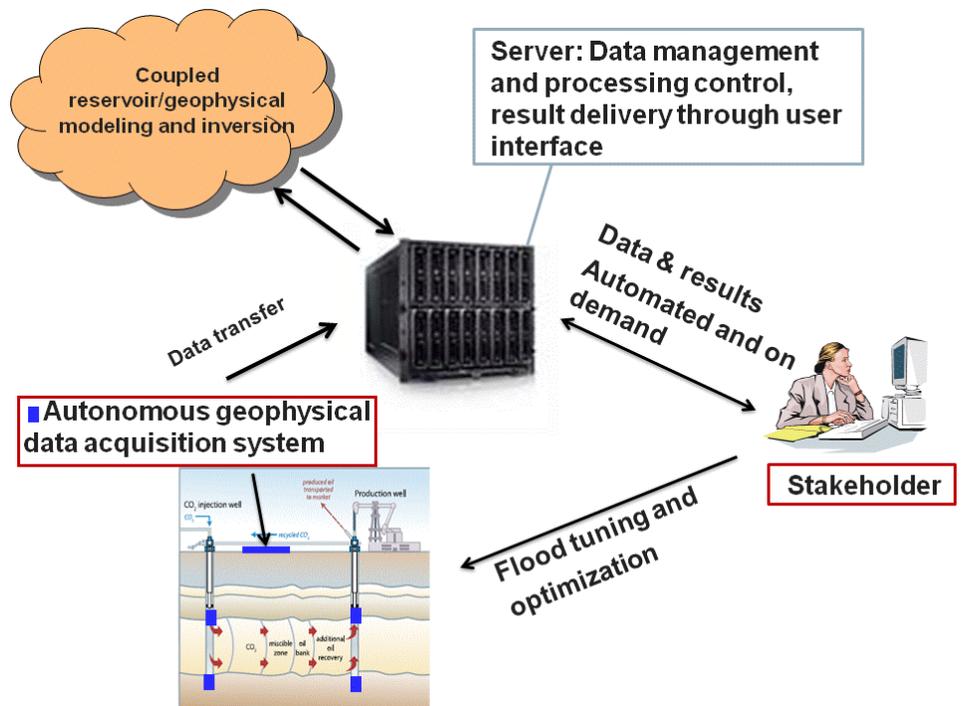


Figure 2. System being developed by Sky Research and PNNL

In the first year a coupling between reservoir modeling of CO₂ EOR and electromagnetic forward modeling of the expected associated signatures, as well as literature studies, validated the overall concept. Also, an industry partner was found with which the project team is working towards a field demonstration in year three of the project. Currently (in year 2) the coupled inversion framework is being developed, and the data acquisition hardware is being completed. This will lead to a system field demonstration which aims to demonstrate and validate this concept, and develop a new tool which can be used by the industry to obtain information on CO₂ EOR floods.

For additional information about this project, contact Roelof Versteeg at Sky Research (roelof.versteeg@skyresearch.com or 603-643-5162), Alain Bonneville at PNNL (alain.bonneville@pnnl.gov or 509-371-7263) or Chandra Nautiyal at NETL (chandra.nautiyal@netl.doe.gov or 281-494-2488).

An Innovative Approach to Creating Stable CO₂ Foam: Nanoparticles

A persistent challenge for operators of CO₂ enhanced oil recovery projects is the poor sweep efficiency that can result from the difference in mobility between the reservoir oil and water and the displacing carbon dioxide gas injectant. One approach that has been put forward for addressing this problem is to increase the viscosity of the CO₂ by adding surfactants to create CO₂ foam. However, maintaining the stability of CO₂ foams can be problematic at downhole conditions. NETL has teamed with the New Mexico Institute of Mining and Technology's Petroleum Recovery Research Center in Socorro, NM to develop and evaluate, through coreflood tests at reservoir conditions, a nanoparticle-stabilized CO₂ foam system that can improve CO₂ sweep efficiency and minimize nanoparticle retention in the reservoir.

Background

Research results have demonstrated that surfactant-induced CO₂ foam is an effective method for mobility control in CO₂ foam flooding. NETL recently published a literature review titled "Mobility and Conformance Control for Carbon Dioxide Enhanced Oil Recovery (CO₂-EOR) via Thickeners, Foams, and Gels – A Detailed Literature Review of 40 Years of Research (DOE/NETL-2012/1540) that highlights the progress of research in this area, among others.

However, surfactant-stabilized CO₂ foams have some potential weaknesses. Because the foam is by nature ultimately unstable, its long-term stability during a field application is difficult to maintain. This is especially true when the foam contacts the resident oil. Even though some high-cost, specialty surfactants are available, under high-temperature reservoir conditions, surfactants generally tend to degrade before they fulfill their long-term function. In addition, surfactant loss in a reservoir due to adsorption onto the rock matrix results in large chemical consumption and reduces the economic viability of CO₂ foam flooding.

New nano-science technologies may provide an alternative for the next generation of stable CO₂ foam. It is known that small solid particles can adsorb at fluid/fluid interfaces to stabilize droplets in emulsions and bubbles in foams. These solid-stabilized dispersions may remain stable for years. The high adhesion energy for the particles enables adsorption and is essentially irreversible; thus solid nanoparticles strongly and preferentially adsorb to either the water or gas phase at the water/CO₂ interface and create a protective barrier around each dispersed bubble of gas (if the nanoparticle is hydrophilic) or drop of water (if the nanoparticle is hydrophobic) to produce highly stable and durable foam. Nanoparticles are solids that can withstand harsh environments and high temperatures. If they can be successfully demonstrated to stabilize CO₂ foams, they could drastically reduce the costs of improving mobility in a CO₂ EOR operation.

Research Accomplishments to Date

The research team has generated stable CO₂ foams at reservoir conditions for a nanoparticle concentration in the 4,000 to 6,000 ppm range. Nanosilica powder, with an average particle diameter of 100-150 nm, was used as the stabilization agent (Figure 1). The effects of different factors such as particle concentration, brine salinity, pressure, and temperature on CO₂ foam generation have been investigated. Adding a small amount (30-50 ppm) of surfactant to a nanoparticle solution significantly improved CO₂

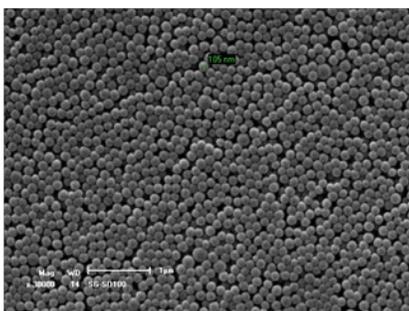


Figure 1. This image is of nanosilica particles with a diameter of 105 nanometers (nm). A nanometer is 1/1000 of a micrometer, which is 1/1000 of a millimeter. For reference, a human hair is about 60 micrometers in diameter. The median diameter of the nanosilica particles used in the CO₂ foam generation experiments were about 100-150 nm, or about 1/500 the diameter of a human hair.

foam generation and foam stability.

For the first time, CO₂ foam was generated as a mixture of supercritical CO₂ and nanosilica and was flowed through sandstone and limestone cores. The apparent viscosity of the mixture with dispersed nanoparticles was 1.5 to 6.1 times higher than that without nanoparticles.

Current Status

The research team is continuing to investigate CO₂ foam generation at dynamic conditions with nanosilica particle-stabilized CO₂ foam. Foam texture is being identified visually via a sapphire observation cell (Figure 2). Particle concentration, phase ratio between CO₂ and nanoparticle solution, and flow rate effects on CO₂ foam generation and foam mobility in the porous media are being investigated. Oil-free coreflooding experiments to investigate nanoparticle transportation in sandstone, limestone, and dolomite are also being performed, and particle retention in the core samples is being estimated. Further research will investigate the impact of nanoparticles as foam stabilizers on residual oil recovery under reservoir conditions.

For additional information on this project, contact Sinisha (Jay) Jikich at NETL (sinisha.jikich@netl.doe.gov or 304-285-4320) or Ning Liu at New Mexico Tech (ningliu@prrc.nmt.edu or 575-835-5739).

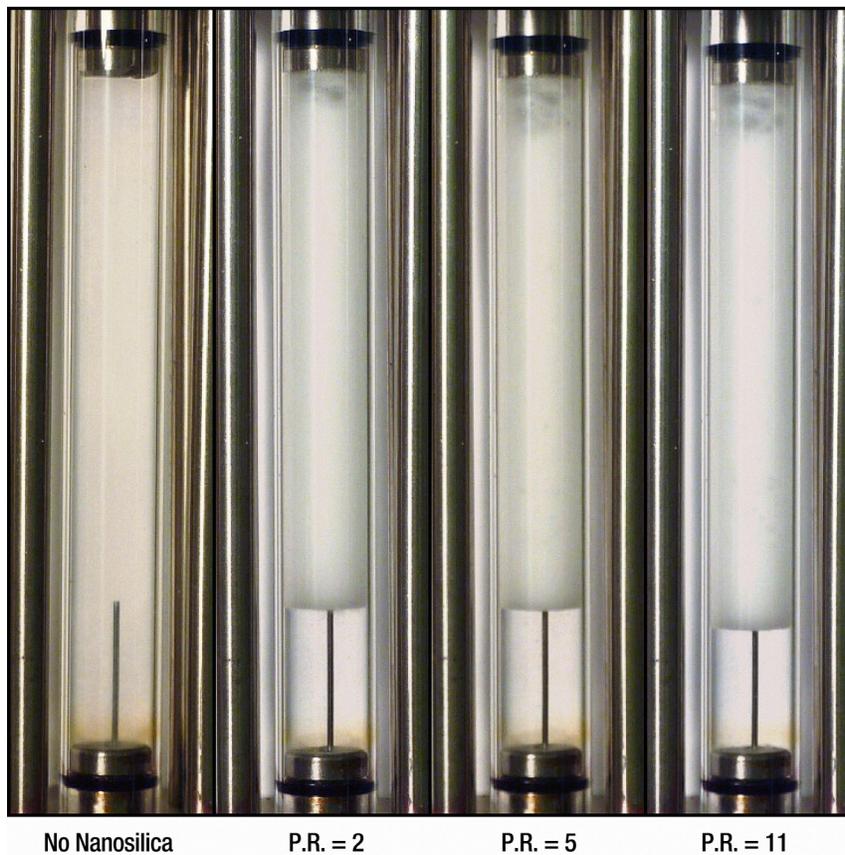


Figure 2. Images of CO₂ foam generation in a sapphire cell with varied phase ratios. The volumetric phase ratio is the volume of supercritical CO₂ to the volume of nanosilica dispersion, sometimes called CO₂ fraction or CO₂ quality. It can be seen that the CO₂ foams are generated successfully over a wide range of phase ratios. The CO₂ foam depicted here was micron-scaled and displays a very uniform morphology

Improving Mobility Control in CO₂ Enhanced Recovery Using SPI Gels

A project being undertaken by The Letton-Hall Group, Impact Technologies LLC and Clean Tech Innovations LLC (CTI), with funding from the National Energy Technology Laboratory (NETL), will demonstrate the ease of use and potential of carbon dioxide (CO₂) injection/ production profile modifications using Silica Polymer Initiator (SPI)-CO₂ gel systems. The objective is to advance SPI-CO₂ Enhanced Oil Recovery (EOR) gel technology by performing multiple small- scale, field injectivity tests using both 'Huff & Puff' and conventional pattern flood applications. A secondary objective of the project is to improve the SPI-CO₂ gel integrity by testing a Super Absorbent Polymer (SAP) instead of the polyacrylamide (PAM) currently being used.

Issues associated with using CO₂ for EOR are its low density and viscosity compared to the crude oil and brine in the reservoir. The injected CO₂ has substantially higher mobility relative to the crude oil and brine, which promotes "fingering" and early breakthrough of the CO₂ to the production wells. High conformance or sweep efficiency (i.e., good contact with all the crude oil in the reservoir) is particularly critical in costlier CO₂ floods where the end result of poor sweep efficiency is less oil recovered with substantially higher costs resulting from multiple handling (production, compression, and reinjection) of the CO₂.



Figure 1. SPI gel with internal initiator



Figure 2. SPI gel with CO₂ initiator.

Research has gone into developing gels for the primary CO₂ phase, but none are low cost and commercial. A unique, state-of-the-art SPI gel system may offer a promising solution to the conformance problem with CO₂ floods. Of particular importance to this and other CO₂ injection

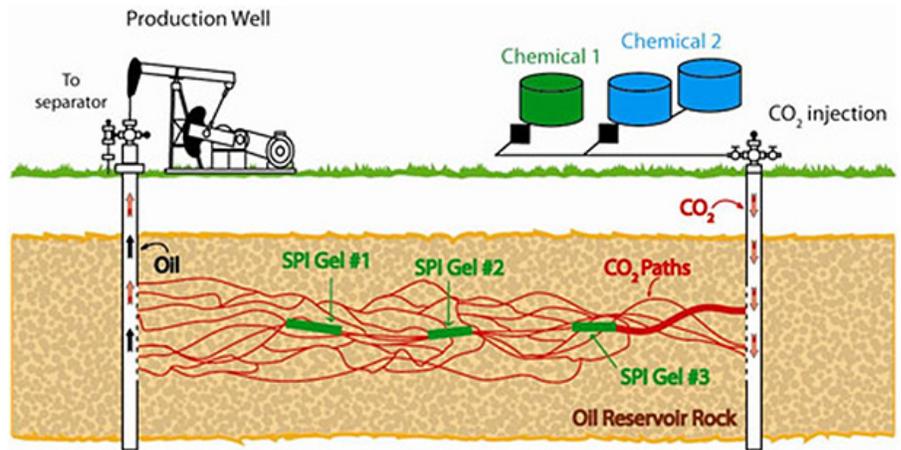


Figure 3. CO₂ flows through aqueous SPI in the reservoir to form carbonic acid which initiates the gelation process.

projects is the use of an external initiator such as CO₂. In SPI-CO₂ gels, the CO₂ becomes the external initiator of the SPI fluid following its placement in the reservoir (Figure 1 and 2).

An SPI mix slug will be incorporated in the water cycle of a Water Alternating Gas (WAG) injection and the CO₂ slug that follows will “finger” through and permeate the more viscous aqueous SPI mixture in the flow path, generating carbonic acid, which will immediately initiate the gelation process. This newly set SPI gel diverts the CO₂ that follows and causes it to finger and dissolve into fresh SPI mix, leading to SPI gel formation at additional locales. The process continues until the CO₂ is fully blocked or all the SPI mix is consumed (Figure 3).

The SPI gel can improve sweep efficiency to a greater degree than conventional systems because it sets up in the high permeability paths that had been travelled previously by the CO₂ and is unique in that it is silicate based and will remain a low viscosity fluid until gel initiation is triggered by CO₂. This is a clear improvement over current technology where the gel gradually sets up as a function of time, regardless of location. In addition, the final product in commercial quantities is expected to be less expensive than competing polymer gels or other systems.

U.S. CO₂ EOR production has grown by four percent/year over the last 20 years to today’s level of 280,000 barrels of oil per day. The use of SPI gels is anticipated to further improve those levels by one percent/year within a few years of a successful demonstration and up to three percent/year in future years. SPI could add over 300 million barrels of otherwise bypassed reserves over 10 years.

Accomplishments

The team has been in contact with major CO₂ flood operators to ascertain their needs and to inquire about performing tests in their fields. Several industry contacts have indicated that SPI gels have a place in the CO₂ market if the gels perform as expected during the project’s field test. Legal agreements are being pursued with two companies and one company has provided the project team with field data, fluids, and core segments for use and analysis. One major CO₂ flood operator wants to get to the field right away, while other operating companies have expressed interest.

The CTI lab performed over 600 gel forming bench tests, half at room temperature (74°F) and half at 140°F. Approximately 40 additives have

been evaluated to date at various concentrations and combinations with additional additives. Three formulations look very promising as candidates for further sand pack testing.

The base SPI polyacrylamide polymer was changed to a much easier to hydrolyze ultra-high molecular weight polymer. This has benefits of easier mixing in the field and better isolation of the SPI mix within high permeability zones, a key interest of the industry.

A full CO₂ capable sand pack system was developed at the CTI laboratory in Bartlesville, Oklahoma. Operational improvements to the modified sand pack system have been completed allowing the use of supercritical CO₂ at 1500 psi. These improvements include:

- Safe handling and discharging of carbon dioxide,
- Accurate means to meter and deliver supercritical carbon dioxide to core apparatus for sand pack testing, and
- Accurate means to meter and account for all gas and liquid mass exiting the system, and other improvements to aid in closing a mass balance (a 2% mass balance closure is anticipated).

Impact Technologies is continuing to communicate with chemical providers and CO₂ operators on a frequent basis with the goal of securing multiple CO₂ flood operators for field testing of the SPI gel. By early 2012, Impact Technologies plans to begin ordering the required chemicals necessary to complete testing and begin treatments in selected fields.

Test plans for field activity will be developed and will include: preparation of the well and site for the field injectivity test (i.e. roads to the well site must be accessible); access to electricity to the site must be made available, unless generation is anticipated and desired; finalization of legal documents (liability releases, safety training, data releases) before moving onto the site; obtaining injection well and offset well data (oil rates, water rates, CO₂ rates, pressures, profile surveys, tracer surveys) to establish a pre-test base line; ordering and delivery of pumps, rate/ pressure recording and metering equipment to the field site.

For additional information on this project contact William Fincham at NETL (william.fincham@netl.doe.gov or 304-285-4268) or Kenneth Oglesby at Impact Technologies (kdo2@impact2u.com or 918-627-8035)

Assessing Near Miscible CO₂ Applications to Improve Oil Recovery (IOR) in Arbuckle Reservoirs

Since the 1910's, several billion barrels of oil have been produced from the Central Kansas Uplift (CKU), primarily from carbonate reservoirs within the Arbuckle and Lansing-Kansas City groups. The majority of Arbuckle reservoirs in central Kansas were drilled prior to 1955 and constitute a series of giant and near giant oil fields. Improved oil recovery through CO₂ flooding has the potential to increase recovery from this mature reservoir. However, due to the lack of coring, modern well logging, and well testing in the past, Arbuckle reservoirs have not been well characterized. Current understanding of the Arbuckle is based on a conceptual model with limited petrophysical, drill stem test and pressure build up data. The uncertain reservoir properties make IOR challenging in Arbuckle reservoirs as the nature of flow is affected by reservoir properties and heterogeneity.

In order to ultimately predict IOR in a future CO₂ flood, an evaluation plan was designed to obtain data that pertain to the pressure, residual oil saturation, reservoir properties and the nature of the flow from well to well. The evaluation methods include single well transient pressure tests, multiple well interference tests, single well tracer tests, and inter-well tracer tests (Figure 1).

All tests are designed to determine the nature of the flow paths and average properties in the reservoir, to assess the effect of geology on process performance, to calibrate a reservoir simulation model, and to identify operational issues and concerns for future IOR applications.

The Arbuckle reservoir characterization project, with funding from NETL, is being conducted by the Tertiary Oil Recovery Project (TORP) at the University of Kansas at a selected oil field producing from the Arbuckle formation. The participating consortium members include University of Kansas Center for Research, Inc., TORP, University of Kansas, Kansas Geological Survey and Carmen Schmitt, Inc., a small independent producer.

A field-based research project will be conducted at the Ogallah unit (Figure 2) located at Trego County in Kansas to evaluate:

- **Pressure distribution in the field using single well pressure build up tests.** The well testing study will determine the potential operational pressure and flow capacity, wellbore conditions and other pertinent information in selected wells for which this information does not exist. The entire well test data set developed from this program will be collected and analyzed.
- **Permeability-thickness between wells using well-to-well interference tests.** These tests will determine whether or not there is communication between the test wells and surrounding wells and the capacity of flow between wells. Pulse testing will be used in this study. Before the start of pulse testing, all the test wells are shut-in until the pressures stabilize. The active well is then allowed to produce at a constant rate and the pressure response in the observation well(s) is observed and recorded. The pressure data responding to the production of the active well depend on the properties of rock and fluid and can be analyzed by commercial well test software to determine permeability-thickness property between wells. Completion of this task allows for the determination of flow capacity and

Engineering Characterization

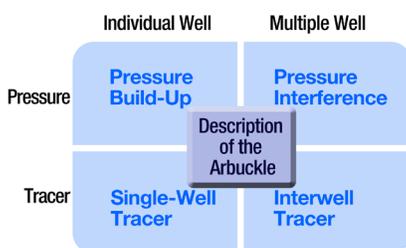


Figure 1. A multi-faceted testing program will be used to describe the flow characteristics of the Arbuckle reservoir in Kansas.

Ogallah Unit Average Shut in pressure ~ 1226 psi (Near Miscible)

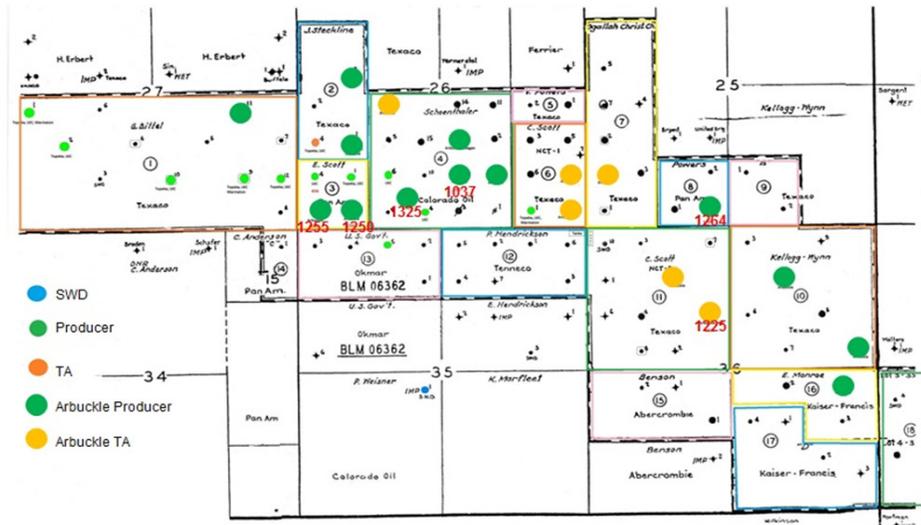


Figure 2. The Arbuckle formation in Ogallah unit at Trego County, Kansas, has produced since the 1950s but still has significant reserves that are recoverable by near-miscible CO₂ flooding.

communication between wells which is valuable and complimentary to the well-to-well tracer tests to characterize the flow path between wells.

- Reservoir properties and continuity between wells using well-to-well tracer technology.** Inter-well tracer tests will be performed to gather information on flood patterns within the reservoir such that the uncertainty about flow paths and reservoir continuity may be reduced. The tracer program will be designed to: 1) select the type of tracer, 2) calculate the tracer volume, 3) select the well to be injected and wells to be monitored, 4) determine the sampling frequency, and 5) specify sampling and detection techniques. The field execution plan will be coordinated with field personnel to implement the tracer injection and sample collection from producers. Finally, the tracer in the samples will be analyzed and documented to: 1) qualitatively derive the information about reservoir continuity and barriers and, 2) model tracer transport for validation as necessary. Completion of this task will allow completion of the characterization of potential sites for future CO₂ injection at near-miscible conditions.
- Residual oil saturation in the reservoir for CO₂ application using single well tracer technology.** Single well tracer tests will be used for measuring residual oil saturation. The test will be designed such that a reacting partitioning (primary) tracer is injected and produced through the same well following a shut-in period of time. During the shut-in, the primary tracer undergoes hydrolysis to generate a non-partitioning secondary tracer. Once the producer brings back the fluid after the occurrence of hydrolysis, the secondary tracer will arrive at the wellbore earlier than the primary tracer in a volume less than the injected volume. Based on the chromatographic theory, the separation of primary and secondary tracers can be quantitatively related to the residual oil saturation. Special interpretation techniques and design procedures will be considered to cope with tracer response characteristics arising from the double porosity structure of carbonate if it exists. This task will be subcontracted to Chemical Tracers, Inc. for the test. Completion of this task allows for determination of the residual oil saturation in the reservoir prior to CO₂ injection. The data

will be used for economic analysis in the pattern design.

- **Flooding pattern design for future CO₂ injection with the simulation study conducted at TORP, University of Kansas.** A verified and updated reservoir model with all the data collected from the proposed field tests will be used to design the flooding pattern. The pattern design will consider the operational issues and economic concerns for the CO₂ injection applications. Simulation will be conducted to evaluate the flooding pattern for optimization of CO₂ injection at near-miscible pressure. Completion of this task allows for development of an appropriate plan for field testing of CO₂ displacement processes at near-miscible conditions.

With improved reservoir characterization as a result of this proposed approach, a first near miscible CO₂ application based upon a better description of the reservoir system will be field tested to prove the technology utilizing existing, easily accessed sources of CO₂ (Figure 3).

Successful completion of the Arbuckle reservoir characterization, and the subsequent demonstration project, will lead to additional oil recovery from Arbuckle reservoirs in Kansas. The potential benefits could be significant with an increase in the resource base for CO₂ flooding and an expanded opportunity for small producers to apply CO₂ flooding.

For additional information on this project, contact Charlotte Schroeder at RPSEA (schroeder@rpsea.org or 281-313-9555) or Jun-Syung Tsau (tsau@ku.edu or 785-864-2913).

CO₂ Resources and Oil Fields in Kansas



Kansas Geological Survey

Figure 3. Proximity to sources of anthropogenic CO₂ will enhance near-miscible CO₂ flooding in the Arbuckle formation in Trego County, Kansas.

CO₂ EOR in Residual Oil Zones Showing Expansive Potential

Interest in the potential of residual oil zones (ROZ) has risen exponentially over the past decade. First noted in the Permian Basin of West Texas and Eastern New Mexico, ROZs there consist of previously untapped oil reserves found below the oil/water contact in mature (very often water flooded) San Andres formation oil fields. Original oil-in-place reserves for the Permian Basin have historically been estimated at about 100 billion barrels of oil. ROZs have the potential to increase those reserve estimates to 135 billion barrels. Oil saturation in ROZs range from 20-40%, averaging 32%, similar to the oil saturation in mature waterflooded reservoirs (Figure 1).

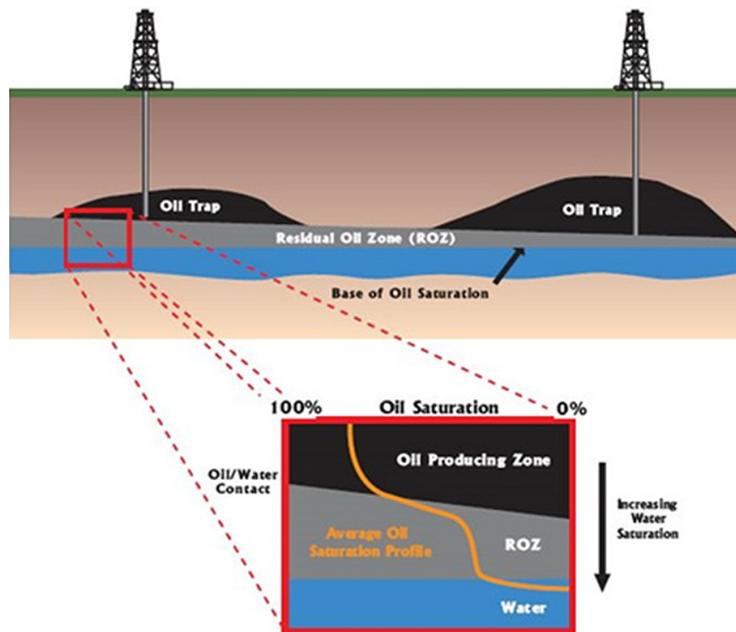


Figure 1. Illustration of a residual oil zone with average oil saturation profile.

At this point, the leading hypotheses for their origin are: 1) early geological entrapment with subsequent flushing caused by uplift, or 2) transition zones formed primarily by capillary forces within the pore system and basin-wide tilt. The north and east side of the Delaware Basin and west side of the Central Basin Platform provide evidence of ROZs in several stratigraphic horizons (the San Andres, Grayburg, Glorieta and Clearfork intervals).

A key to the production potential of those ROZ reserves is CO₂ EOR. The Permian Basin has a long history of CO₂ EOR, which currently produces over 200,000 bopd in the region. Recent development of nine CO₂ projects in Permian Basin ROZs accounts for 10,000 bopd and production is rising. More recently, ROZ potential has been assessed in other mature production areas in the US, with encouraging results.

NETL has funded research in CO₂ EOR applications in ROZs since 2009. Two important studies address the characterization of ROZs and the optimization of technical and economic performance of these resources. The first was designed to describe and gather the data needed to determine the distribution of ROZs in a portion of the Permian Basin, and to develop a methodology template for determining the presence and distribution of ROZs in other areas of the Permian Basin. The University of Texas Permian Basin, Chevron Corporation, Yates Petroleum, and Legado

Resources participated in the project.

The project collected data such as well logs, field specific oil-water contact data, groundwater samples and core data from specific horizons and defined a flow path (or fairway) that might have flushed oil from geological entrapment. Zonal properties were established, flow channels approximated, and input and choke point (exit) conditions bounded. A regional hydrological model was constructed of the hydrodynamic fairway that helped develop a consistency with the observed data points of sulfur deposits, water salinity observations, and tilted oil/water contacts in reservoirs within the flow path. The data acquired and the model developed will provide features of the ROZs that can be tested with new wells and cores. A final report will document the spectrum of data suggesting origins and distribution of the residual oil zones in the Permian Basin, and a methodology for determining the presence and distribution of ROZs in other fairways within the Permian Basin area and other regions of the country will be outlined.

The overall nature and extent of the maximum oil entrapments in the carbonate rocks rimming the north rims of the Delaware and Midland Basins is being investigated. The same is being done for the west and east sides of the Central Basin Platform (CBP). Particular attention is also being placed on the south side of the CBP as an exit path. The zonal properties are being established, the flow channels or fairways approximated, and input and choke point (exit) conditions bounded. With this flow path hypothesis, a regional hydrologic model is under construction. The data gathered will support an examination of charge and discharge points in an attempt to develop a consistency with the observed data points within the flow path. The scope of the relic entrapment indicators include residual oil presence and saturations, water salinities and acidity, sour nature of the oil and gas, and oil-water-contact (OWC) tilts.

The research team is also investigating basin-wide sulfur deposits. This should prove to be a critical data set. Elemental sulfur deposits form where hydrocarbon-bearing fluids exit a water-drive system through fractured sulfur-bearing (anhydrite, gypsum) strata. The moving fluids contact the sulfur-bearing seals whereby the displaced hydrocarbons are consumed by sulfate-reducing bacteria. The fact that continual hydrocarbon nourishment is present due to the flushed hydrocarbons and that the sulfates are extensive, leads to large sulfur deposits. In the Permian Basin, locations of the sulfur deposits are indicators of hydrodynamic flow paths and, more specifically, suggest fairways of water movement and exit pathways.

The data acquired and model developed will provide features of the ROZs that can be tested with new wells and cores. The results of this study could be extended to a demonstration project wherein the developed understanding can be tested through new wells and/or pilot flooding.

The second ROZ project funded by NETL seeks to optimize the technical and economical performance of a ROZ CO₂ flood and transfer the knowledge to other operators. The objectives are to (1) characterize the main pay zone (MPZ) and ROZ within the ROZ pilot area; (2) conduct laboratory analyses and reservoir simulation to evaluate the performance of the ROZ pilot flood; and (3) provide recommendations for an optimum field wide expansion of the CO₂ flood in the ROZ and MPZ at the Goldsmith Field. The project is being conducted by The University of Texas of the Permian Basin with Legado Resources, Melzer Consulting and Advanced Research International.

Although much of the data accumulated over the 40-year history of CO₂ enhanced oil recovery (CO₂ EOR) research are available, there are no publically available geologic and reservoir characterization data on ROZs nor any comprehensive field studies of CO₂ EOR projects in ROZs. This project will document the application of state-of-the-art geologic and reservoir characterization, laboratory work, and field testing to the ROZ in the Goldsmith Field, Ector County, Texas where Legado Resources has initiated a ROZ CO₂ EOR pilot project as well as an MPZ CO₂ flood in parts of the ROZ pilot area.

This project involves the application and testing of a variety of advanced methods for increasing the recovery of oil from the ROZ of the San Andres Formation, Goldsmith Field. At completion in 2013, it should lead to:

- Optimization of CO₂ flood design using high-resolution reservoir characterization and full-scale compositional reservoir modeling plus laboratory and bench-scale core studies of the San Andres ROZ. The optimized CO₂ flood design will lead to higher oil recovery efficiencies and improved economics for developing the ROZ.
- Incorporation of real-time data acquisition and diagnostic tools to monitor CO₂ flood performance (using conformance surveys and chemical tracers to establish CO₂ flow paths and sweep efficiency). The real-time data will be linked with a full-scale reservoir simulator to control and modify the CO₂ flood on a continuing basis with the purpose of achieving improved reservoir conformance, and with it, more optimum use of injected CO₂ for oil recovery.
- Analyses of the flow unit properties, depositional facies, mineralogy, diagenetic dolomitization, and reservoir fluids will form a more complete understanding of the impact of late stage diagenesis and flushing on the ROZ, and how it affects CO₂ sweep efficiency. This first-of-its-kind detailed geologic and engineering reservoir characterization will provide a standard for future ROZ CO₂ flood data acquisition and design. It will also provide industry with a geologic/engineering based reservoir characterization and field testing process that will increase the potential for future successful CO₂ floods in the ROZ.

The larger benefits of this project are that it will build a publicly available scientific base of information on the nature of ROZs and provide optimized CO₂ flooding designs for this highly promising oil resource. This information is not currently available, and access to the information would greatly accelerate the timely and efficient recovery of oil from the residual oil zones of the Permian Basin and other ROZ-rich basins in the U.S.

Findings to Date

Reservoir core description has led to the identification and documentation of differences between the depositional facies and diagenetic overprint in the MPZ, ROZ, and interval below the ROZ, suggesting that the ROZ has undergone a different diagenetic history than the MPZ. Additionally, diagenetic "markers" seen in core from ROZs in other fields including the presence of native sulfur in voids near the base of ROZ, a transition from partially dolomitized limestone below the base of the ROZ to partial to pervasive dolomitization above the base of the ROZ, and a sequence of unaltered anhydrite replaced to leached skeletal grains in the ROZ is seen. These changes are believed to be associated with "Mother Nature's Waterflood" of the ROZ.

Oil and water samples from the pilot CO₂ flood have been collected and

are being analyzed. Additional samples will be taken to help establish a base line for the fluids in a ROZ CO₂ flood. The team continues to monitor the progress of the CO₂ flood in the Goldsmith Field. There has been a continued, significant increase in the production from the expanding pilot. The reservoir engineering data from Legado Resources has been transferred to the research team, and the engineering reservoir characterization is in progress.

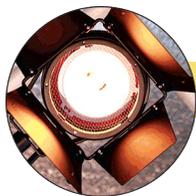
Current Activity

The project team continues core description of the ROZ. The cores from the GLSAU #190 and GLSAU #204R wells are being studied for similarities and differences in the depositional facies and diagenetic overprint among the MPZ, ROZ, and Water Zone beneath the ROZ. Detailed core description for the #190 is near completion and description of the #204R is underway. Legado Resources indicated that additional older (1960's vintage) cores have been located and would soon be made available.

The project team is investigating the use of a downhole sensor technique that is capable of diagnosing the presence of a variety of molecular components in the near wellbore fluids. The sensors are currently proprietary but are very small and can be conveyed on tubing strings in producing wells. With the goal of identifying MPZ vs. ROZ oil and water production, the technique may prove of extreme value. Innovative methods will have to be employed to transmit the data streams to the surface.

Legado Resources has made available to the project two separate wells perforated in only the ROZ interval. They recently put both wells on production test. Samples were gathered using some applications of conventional technologies (well site test separators, both pressurized and flash samplers) on the ROZ wells isolated from the MPZ.

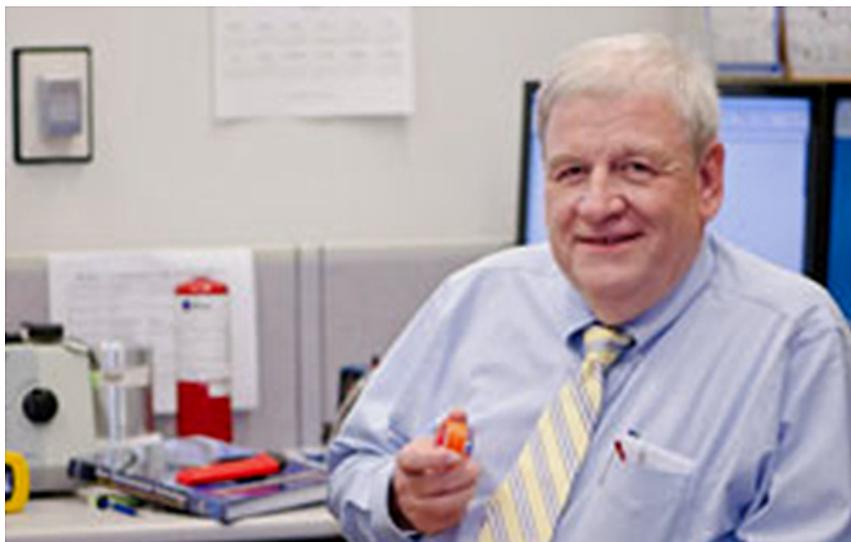
For additional information on either of these projects, contact Robert Trentham (trenthamr@utpb.edu or 432-552-2432) or Chandra Nautiyal (chandra.nautiyal@netl.doe.gov or 281-494-2549).



Spotlight

Remote Gas Well Monitoring Technology Applied to the Marcellus Shale

A technology to remotely monitor conditions at energy-rich Marcellus Shale gas wells to help ensure compliance with environmental requirements has been developed through a research partnership funded by the U.S. Department of Energy (DOE).



NETL-RUA researcher Dr. Michael McCawley has developed a technology to remotely monitor the environment around energy-rich Marcellus Shale gas wells. Photo courtesy of West Virginia University.

The technology – which involves three wireless monitoring modules to measure volatile organic compounds, dust, light and sound – is currently being tested at a Marcellus Shale drilling site in Washington County, Pa. It was developed by Dr. Michael McCawley, a research associate professor in West Virginia University's (WVU) Department of Community Medicine, as part of the NETL's Regional University Alliance for Energy Technology Innovation (NETL-RUA). NETL is the research laboratory for DOE's Office of Fossil Energy.

Shale gas is natural gas trapped inside formations of shale, fine-grained sedimentary rocks that can be rich sources of petroleum and natural gas. Shale gas production, which has increased twelve-fold over the past decade according to the U.S. Energy Information Administration, is contributing to a rejuvenation of domestic natural gas supply. The Marcellus formation is a large shale deposit (estimated to be a third of the nation's recoverable resource) located in the subsurface beneath much of Ohio, West Virginia, Pennsylvania and New York, and smaller areas of Maryland, Kentucky, Tennessee and Virginia.

The project is significant because it streamlines a process to remotely monitor shale gas well drilling sites in areas where the terrain typically hinders monitoring and the lack of nearby power and phone lines makes traditional monitoring difficult. Having remote monitoring available becomes even more significant considering that West Virginia,

for example, has more than 1,400 Marcellus Shale gas wells and permits have been issued for 1,200 more.

Although the number of possible monitors that can be networked is virtually unlimited, the remote monitoring system at the Washington County site consists of three wireless monitoring modules. Each module is comprised of a radio transceiver, a 12-volt battery-powered monitoring device, and a battery, all encased in a bright orange box. A 2-foot by 5-foot solar panel maintains the battery charge, even on cloudy days. A base station module, which houses a notebook-sized computer with a cell phone modem, receives data from the monitoring devices and facilitates the remote monitoring, which can be accessed from a desktop computer at WVU.

Prior to the drilling effort in Washington County, WVU had been testing the remote, wireless system for the past year. Its success during testing demonstrates its ability to be a cost-effective, portable, user-friendly, off-the-shelf technology applicable to a variety of monitoring projects. To date, at least one major company has demonstrated an interest in the technology.



Modules consisting of a radio transceiver, a 12-volt battery-powered monitoring device, and a battery, all encased in a bright orange box, measure volatile organic compounds, dust, light, and sound. Photo courtesy of West Virginia University.

NETL has spearheaded efforts to develop technologies associated with shale gas extraction, monitoring, and environmental protection. NETL has historically collaborated with industry to advance horizontal drilling techniques by drilling the first-ever Appalachian Basin directional shale well, as well as introducing techniques such as hydraulic fracturing to eastern shales. Associated with these advances, NETL has addressed environmental concerns by studying air emissions at drilling sites and other environmental issues.

New Models Help Optimize Development of Bakken Shale Resources

Exploration and field development in the largest continuous oil play in the lower 48 states, located in North Dakota and eastern Montana, will be guided by new geo-models developed with funding from NETL.

The three-year project to develop exploration and reservoir models for the Bakken Shale resource play was conducted by the Colorado School of Mines (CSM), through research funded by NETL.

A “play” is a shale formation containing significant accumulations of natural gas or oil. The U.S. Geological Survey estimates the Bakken Shale play contains 3.65 billion barrels of oil and 1.85 trillion cubic feet of natural gas that can be recovered using current technologies. The development of new fields, combined with advances in horizontal drilling and other production technologies, continues to increase these estimates.

Hydrocarbon traps in the Bakken petroleum system appear to be controlled by pinch-outs, where the formation tapers out against a nonporous sealing rock, and high areas in the geologic structure, where hydrocarbons tend to accumulate. Natural fractures and fracture concentrations are key elements for establishing Bakken Shale production “sweet spots,” locations with the best production potential.

CSM determined that previously undetected oil accumulation areas could be outlined by mapping the distribution of shale within the reservoir, the impermeable rocks that form the reservoir’s top and base seals, pinch-out zones, and fracture distribution in areas of subtle structure. With this in mind, CSM integrated information about rock physics, the formation’s rock strata, and seismic, fracture and thermal maturity data—all compiled during the course of the project—into a series of reports that can be used as an exploration model to predict high-potential fairways and traps for the Bakken hydrocarbon system.

CSM also developed a second model, a 3-D reservoir geo-model, that includes detailed subsurface mapping of depositional and fracture trends along with core-calibrated porosity from well logs. The reservoir model was built using data from the Elm Coulee Field, where there is an extensive geological and production database to validate the model. Located in Richland County, Mont., the western portion of the Williston Basin, the Elm Coulee is the largest producing oilfield in the basin. More than 350 horizontal wells have been drilled in the Elm Coulee Field since the initial horizontal well was drilled in 2000. Several major and independent operators work the field.

In Elm Coulee wells, primary oil recovery, in which natural mechanisms drive oil from the reservoir, is only 5–10 percent of the estimated oil-in-place because of the shale reservoir’s low porosity and low permeability. This poor primary recovery makes Elm Coulee an excellent candidate for secondary oil recovery, in which pressure is applied to force the oil from the reservoir. The poor quality of the reservoir essentially eliminates water injection as a secondary recovery method,

but CO₂ flooding could be a preferred enhanced recovery method.

A consortium of 29 companies consisting mainly of independents, and initiated in conjunction with this DOE project, has been using the results of the study to further develop the Bakken. Information in the reports can be used to identify high potential yield areas by mapping critical elements such as fracture distribution, hydrocarbon maturity, and reservoir quality that were obtained during field studies and sub-regional mapping.

DOE Releases Comprehensive Review of CO₂ Enhanced Oil Recovery Mobility Control

A thorough review of 40 years of RD&D related to the past successes and failures of lab- and field-scale efforts to reduce CO₂ mobility using CO₂ thickeners, foams, and gels is now available. Results clearly indicate that mobility and conformance control for CO₂ EOR can be technically and economically attainable. Carbon dioxide (CO₂) has been used commercially to recover oil from geologic formations by enhanced oil recovery (EOR) technologies for over 40 years.

The U.S. Department of Energy Office of Fossil Energy and its predecessor organizations have supported a large number of laboratory and field projects over the past decades in an effort to improve the oil recovery process, including investments to advance reservoir characterization, mobility control, and conformance of CO₂ flooding.

Currently, CO₂ EOR provides about 280,000 barrels of oil per day, just over 5 percent of the total U.S. crude oil production. Recently CO₂ flooding has become so technically and economically attractive that CO₂ supply, rather than CO₂ price, has been the constraining developmental factor. Carbon dioxide EOR is likely to expand in the United States in upcoming years due to “high” crude oil prices, natural CO₂ source availability, and possible large anthropogenic CO₂ sources through carbon capture and storage (CCS) technology advances.

A revised national resource assessment for CO₂ EOR (July 2011) prepared by Advanced Resources International for DOE indicated:

- “Next Generation” CO₂ EOR can provide 137 billion barrels of additional technically recoverable domestic oil, with about half (67 billion barrels) economically recoverable at an oil price of \$85 per barrel.
- This volume of economically recoverable oil is sufficient to support nearly 4 million barrels per day of domestic oil production (1.35 billion barrels per year for 50 years), reducing oil imports by one-third.
- Federal/state treasuries would be a large beneficiary, receiving \$21.20 of the \$85 per barrel oil price in the form of royalties on Federal /state lands plus severance, ad valorem and corporate income taxes. Total revenues to Federal/state treasuries would equal \$1,420 billion.
- The general U.S. economy would be the largest beneficiary, receiving



\$25.80 of the \$85 per barrel of oil price, in the form of wages and material purchases. Total revenues would equal \$1,730 billion.

Nearly 20 billion metric tons of CO₂ would need to be purchased by CO₂ EOR operators to recover the 67 billion barrels of economically recoverable oil. Of this, at least 18 billion metric tons would need to be provided by anthropogenic CO₂ captured from coal-fired power plants and other industrial sources.

“Next Generation” technologies include increasing CO₂ injection volumes by 50% or more, drilling horizontal wells for injection or production, improving mobility ratio and flood conformance, extending the conditions under which miscibility between the oil and CO₂ can be achieved, and applying advanced methods for monitoring flood performance.

Despite its well-established ability to recover oil, the CO₂ EOR process could be improved if the high mobility of CO₂ relative to reservoir oil and water can be effectively and affordably reduced. The CO₂ EOR industry continues to use water-alternating-with-gas (WAG) as the technology of choice to control CO₂ mobility and/or mechanical techniques (e.g., cement, packers, well control, infield drilling, and horizontal wells) to help control the CO₂ flood conformance.

If the “next generation” CO₂ EOR target of 67 billion barrels is to be realized, new solutions are needed that can recover significantly more oil than the 10–20% of the original oil in place associated with current flooding practices. This literature review concentrates on the history and development of CO₂ mobility control and profile modification technologies in the hope that stimulating renewed interest in these chemical techniques will help to catalyze new efforts to overcome the geologic and process limitations such as poor sweep efficiency, unfavorable injectivity profiles, gravity override, high ratios of CO₂ to oil produced, early breakthrough, and viscous fingering.