Increased Oil Production With

Something Old, Something New

Stephen Rassenfoss, JPT Emerging Technology Editor



nhanced oil recovery (EOR) has become fertile ground for emerging—and re-emerging—technologies.

Emerging from laboratories are materials based on nanotechnology that could change what is possible with aging reservoirs. Researchers are working on making carbon dioxide foams built to last, time-release coatings to deliver gels deep into reservoirs, and tracers for real-time waterflood tracking.

Re-emerging are chemical EOR methods that have been around for 30 years but whose development was stunted by a long stretch of low oil prices. Higher prices are now inspiring a second look at EOR methods, taking advantage of advances in chemistry and computing to create cost-effective ways to rework underperforming old fields.

"It didn't happen when the technology stopped developing in the 1980s," said Jeff Harwell, a professor at the University of Oklahoma, who has been a catalyst for this reemerging technology. "My perception is we are just to the point in the industry where oil prices have risen to the level where it is economic."

Continued oil prices near USD 100/bbl makes EOR an attractive possibility—the estimated cost to produce plus the profit margin needed to justify the risk is about USD 60/bbl, Harwell said—but, for the many independents that own older fields, the cost of reducing salinity levels in their fields in order to use the available chemicals has been prohibitive—ly high.

Harwell said he and others he knew in EOR realized that, while the economics once again favored it, work was needed to make EOR a realistic option for small and mid-sized operators whose budgets and appetite for risk are both limited. They worked with chemical companies to develop improved surfactants that worked without having to make costly modifications to fields, improved techniques for analyzing and planning EOR projects to increase the chance of success, and started a company to demonstrate what they could do.

He is not alone. Harwell pointed out that others, such as Gary Pope, a professor at The University of Texas at Austin, whom he describes as the EOR guru, is working with a chemical company to create improved surfactants. Big EOR service providers, such as Tiorco and Surtek, are also working on new things.

It is a tough sell, but one with big potential. In Oklahoma, only 14 billion bbl of the 82 billion bbl in the ground have been produced, he said. Many fields date back to the early days of oil exploration when the focus was on pumping oil as fast as possible. "It was really before petroleum engineering was a discipline," Harwell said. Production was limited by early overproduction and poorly done waterflooding experiments, adding to the petroleum engineering expertise required to rework these fields.

"A lot of mature waterfloods are badly in need of optimization. I really think we can recover as much oil as has been produced," Harwell said.

In Oklahoma, he puts that at more than 10 billion bbl, which compares to the 7 billion bbl in estimated oil reserves in the Eagle Ford and Bakken shale oil plays, according to a

2011 study by Intek, commissioned by the US Department of Energy (DOE).

But the numbers that matter most will be the production levels as more EOR projects are completed.

"We need to prove it in the field," he said. "Once chemical flooding starts to develop a successful track record, the sky's the limit. Until then, it will be the risk takers who blaze the trail."

Next-Generation Carbon Dioxide

A study commissioned by the US DOE's National Energy Technology Laboratory (NETL) predicted that improved EOR using next-generation CO_2 technology could increase the amount of recoverable US oil reserves by 68 billion bbl, or about 4 million B/D of oil output.

Based on grants by NETL, next generation means using more carbon dioxide. That will require producing more of it because the number of ongoing projects is limited by the supply of the gas. The supply keeps the price of CO_2 relatively high, which limits the amount injected and the parts of the US where it is used.

Another line of research is finding ways to make carbon dioxide thicker so that it can improve the ability of the waterflood to evenly sweep a reservoir and produce more oil.

A third area of research, carbon dioxide sequestration, shows how the US government and the industry perceive the benefits differently.

Federal officials want to take carbon dioxide, which is said to affect global warming, out of smokestack emissions and bury it forever in the ground. The industry needs more ${\rm CO}_2$, which industrial facilities produce a lot of, to increase the amount of oil it can get out of the ground.

One of the hard parts of the next generation plans is finding ways to capture what comes out of a smokestack cheaply enough to cover the cost of building a pipeline network to deliver it. Another is changing the nature of CO_2 to realize its potential to mobilize oil and get it out of the reservoir.

" CO_2 or any gas is a lot more mobile. It snakes through the reservoir," increasing the chance of premature breakthrough, said Mehran Sohrabi, a professor at Heriot-Watt University. In a core flood test simulating reservoir conditions at the university in Edinburgh, Scotland, the CO_2 foam cleared out twice as much heavy crude oil in porous rock as did a mixture of water and straight CO_2 .

Creating a CO_2 foam able to do that in the ground has been an industry goal for a decade. Doing so would require changing the nature of something that is inherently unstable. "Like a beer foam, it will collapse," said Chun Huh, a research professor at The University of Texas at Austin.

While carbon dioxide foams can easily be made from surfactants, which are the chemicals used to make soap bubbles, tests of that approach in the 1980s ended with more misses than hits. That technology was largely dormant until recently, when a new surfactant developed by Dow Chemical and the University of Texas was tested in the Sacroc field in west Texas. Looking ahead, researchers at The University of Texas and New Mexico Tech are trying to create low-cost, durable CO_2 foams using commercially available silica $[\mathrm{SiO}_2]$ nanoparticles. They

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Heavy oil in rock sample.

Oil remaining after waterfloooding.

One hour of CO₂ foam injection.

In a test at Heriot-Watt University, CO_2 foam removed 90% of the heavy oil in a micro-model, which allowed observation of what goes on inside a rock.

are specially treated to ensure they adhere to the surface of each ${\rm CO_2}$ bubble, acting like chainmail, preventing bubbles from collapsing, which is called coalescence.

They have created foams able to survive long periods at the pressures found in reservoirs. Huh said they are "making slow but steady progress" on creating fortified foams able to survive in harsh reservoir conditions. A graduate student on his team, Andrew Worthen, has generated a durable foam at 50°C with a high salinity brine [8% sodium chloride and 2% calcium chloride], Huh said.

The goal is to create foams able to stand up to high-temperature, high-salinity reservoirs, where alternative chemicals used for EOR cannot be used, and then leave the carbon dioxide behind.

This technology is young—the first paper on nanoreinforced CO_2 foams for oil recovery was published in 2010 by a University of Texas team—and nowhere near ready for a field test, which will be closely watched.

"When I do a presentation at a conference, people from the industry want to know if you have done some field testing," said Ning Liu, a research scientist at New Mexico Tech, which, along with The University of Texas, is developing and testing nanotech foams with NETL support. The answer is, "not yet."

Sinisha "Jay" Jikich, a project manager at NETL who manages next-generation CO_2 research work—which he defines as early-stage work that would not be able to draw investor support—said he is pushing the universities to conduct foam field tests when their contracts conclude in 2014. He said an international oil company has expressed an interest in participating.

Past efforts at making foams found that contact with crude is destructive. Liu of New Mexico State said nano-reinforced CO_2 foams should stand up better to oil than CO_2 foams made using surfactants, but neither lab has tested that yet.

A review of the previous generation of CO_2 foam testing, which ended in 1990, offered multiple reasons why CO_2 foams did not work that were not related to the staying power of the foam. The challenge this time around will be to deliver better results than those achieved with current methods, such as alternating injections of water and CO_2 [water alternating gas [WAG]].

 ${\rm ``CO_2}$ foams would have to compete with WAG for mobility control," said Robert Enick, a professor at the University

ty of Pittsburgh who was the lead author on the NETL survey of past work. "Until there are a few field tests showing that this can be reliably done, I don't think $\rm CO_2$ foams will be widely implemented."

Seeking a Delayed Reaction

The increased financial rewards for improved oil recoveries has also increased the interest in ways to get more out of the current technology by delivering chemicals farther into reservoirs.

University of Kansas Professor Jenn-Tai Liang explains the purpose of this work by saying, "You can only recover oil that you can get into contact with."

The problem has to do with the ways gels are created in the ground. The ingredients are injected into a reservoir, where they combine to form a gel. This normally occurs within a few hours of injection, placing the gel in the reservoir relatively close to the well where it is not likely to move much.

Liang has created a chemical carrier that can delay gel formation by days or weeks. "It is like a targeted cancer treatment. To protect the healthy organs in a human body, you need to be able to delay its release until you have reached the target cancerous cells," Liang said.

The formulation—chemically, it is a polyelectrolyte complex (PEC)—can be varied to time the reaction. More than 5 years of work, supported by ConocoPhillips, has gone into adapting the PEC chemistry to oilfield conditions. Liang said it is ready for field trials and several companies have expressed an interest in doing so.

Enhanced Digital Exploration

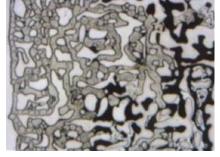
Advanced chemistry is not going to change the fact that "it is hard to fix things in a reservoir," Harwell said. Enhanced oil recovery will continue to depend on an understanding of the reservoir, which may indicate that increased recoveries will require directional drilling.

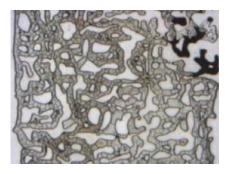
A large leap in available computing power is a positive in that regard. In the early days of chemical EOR, personal computer owners were happy if the machine could run a word processing program.

"The software is just night and day compared to what it was, as is the computing power," Harwell said. "We can sit around the table with a laptop and explore different scenarios."

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Two hours of CO₂ foam.

Five hours of CO₂ foam.

24 hours of CO₂ foam.

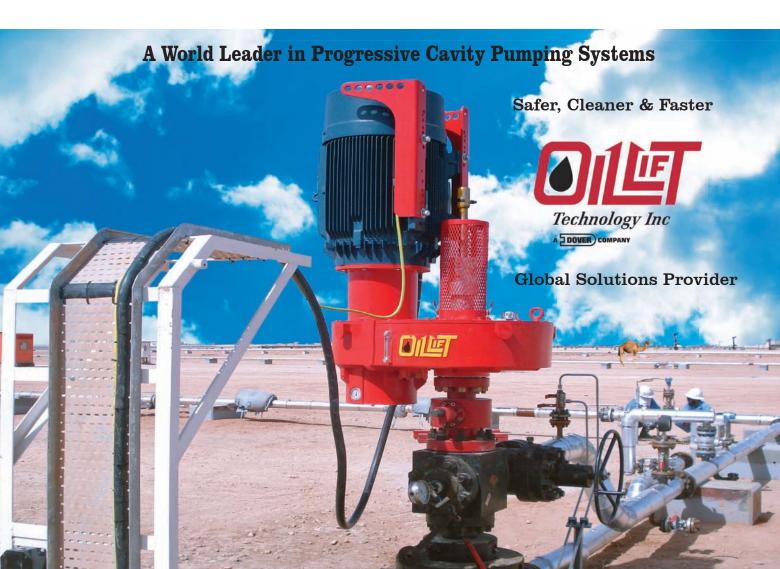
Labs testing next-generation materials are also engaged in improving the simulations of how these molecules will behave in the ground.

"We noticed a lot of conventionally available simulators are unable to reproduce what we have seen in the lab," said Sohrabi, director of the Centre for Enhanced Oil Recovery and CO_2 Solutions at Heriot-Watt. The university is now working on a simulation based on the work with CO_2 foam and heavy oil.

On the molecular scale, Baker Hughes nanotechnology experts are working on applying computational physics pro-

grams originally developed for materials research in US government laboratories to predict what sort of molecular structures would be able to do things, such as reduce the interfacial tension binding an oil molecule to a rock.

"I believe this problem of recovering more oil comes down to the surface chemistry at a very microscopic level," said Guarav Agrawal, director of Enterprise R&D for Baker Hughes. The company has used the approach to improve the way it makes artificial diamonds for drill bits. "By doing some computer games, we can eliminate some options," Agrawal said. **JPT**







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EOR Made Simpler

asol Olefins and Surfactants has returned to selling chemicals for enhanced oil recovery (EOR) after a hiatus dating back to the early 1980s. Since then it has focused on making surfactants for detergents, shampoos, plastics, and paints, as well as supplying chemicals others used to make EOR chemicals. There was far more demand for surfactants capable of cleaning grease off fry pans than ones to free oil from reservoir rock.

Things began to change for the former Conoco unit 5 years ago with a US-funded research project to develop sur-



Bruce Roberts, who helped start Chemical Flooding Technologies after retiring as a senior scientist for an oil company, works on a pump used to transfer fluids for a test to see if the company's approach can deliver increased oil production in an oil Oklahoma field.

factants to clean up the ground around leaking tanks at gasoline stations. That was followed by a project to create costeffective surfactants for oil fields with high salinity levels.

Behind both projects was Jeff Harwell, a professor from the University of Oklahoma. Back then, he was thinking oil prices were finally high enough to justify EOR. The idea started turning into action when Bruce Roberts, who had recently retired as a senior scientist at Kerr McGee, said to him, "Have you seen what's happening with oil prices? We need to get back into chemical EOR. It is going to work this time."

They decided to pursue that thought, with Roberts preparing the economic analysis needed to win a grant from the US DOE's National Energy Technology Laboratory (NETL) to develop improved surfactants and EOR methods for small operators. That led to work with Sasol and three other chemical makers—Huntsman, Dow, and Pilot Chemical.

Starting With Surfactants

Developing surfactants capable of mobilizing oil that years of waterflooding had not was an essential first step. Affordable new versions of the chemicals used to reduce the surface tension bonding oil to rock and mobilize the crude so it can be pushed out by the waterflood were needed. And they had to work in reservoirs with high salinity levels.

That last detail was the hard part. Surfactant makers were asked to create a molecule able to work in reservoirs with salinity levels in excess of 20% of the brine weight. At the time, Harwell said the commonly assumed limit was 5%, so saltier reservoirs required fresh waterflooding for those surfactants to work. "You start looking at multiple pipelines and water-treatment facilities, and you never make it past the capital investment," he said.

It was up to the chemical companies to create molecules able to tolerate that level of salinity in formations with temperatures of around 50°C .

A lot of surfactants were eliminated immediately because they cannot tolerate high levels of salt. The list was narrowed further because many surfactants require agitation. Water injected into oil fields to maintain production moves a foot or less per day. That is not enough agitation to activate the sort of surfactants used in laundry detergent to lift dirt off cloth and then emulsify it in the wash water, said Victoria Stolarski, market development manager for the Americas at Sasol Olefins & Surfactants.

In addition to being effective in sluggish, highly saline waterfloods, the surfactants developed by Sasol and others had to be cost competitive. Sasol created an alcohol propoxy

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Peter Lohateeraparp, who planned the field test in August for Chemical Flooding Technologies, consults a laptop on top of tank containing chemical tracers used to measure the amount of oil displaced by the chemical EOR test.

sulfate surfactant brand named Alfoterra, that can be used in concentrations of 0.1 to 0.5% of the volume of injected water, or about 10% of what was required for older options, according to Sasol.

Covering the Risk

The next step is to demonstrate that the chemicals and methods developed by Harwell and his team work. That led to the start of an EOR consulting company—Chemical Flooding Technologies [CFT]—along with Mid-Con Energy Partners, which is majority owner.

"We will do a 5-acre pilot starting in the design phase and do the whole thing for less than USD 1 million," he said. An important part of that is developing a reliable, affordable system to test if chemical EOR is a good option.

Multiple surfactant suppliers were needed because CFT's approach uses a blend of them. Work by another original team member, Ben Shiau, an assistant professor of petroleum engineering at the University of Oklahoma, found that multiple surfactants are best able to deal with variations in the reservoir rock.

CFT, which has a handful of jobs lined up, has tested three pilot wells in a field in Oklahoma where it is now conducting a field test. Harwell likens these first few jobs to the early wells drilled leading up to the shale boom. The future will depend on whether they can generate enough positive case studies to

convince the many small operators that own wells in states like Oklahoma, where 90% of the wells produce less than 10 B/D.

The estimated incremental cost of adding a barrel of production using chemical EOR is USD 10–15 per bbl, Harrell said. Adding the costs of producing a barrel of oil in an older field brings the total estimated cost per barrel to around USD 40. On top of all that, the profit margin needs to be high enough to justify the risk, pushing the estimated minimum oil price to justify chemical EOR up to around USD 60 per bbl, he said.

The next goal for CFT is to demonstrate that its system for testing reservoirs and planning EOR jobs can reduce the risk and popularize what is now just a pilot project. One limit is the expertise required to analyze reservoirs and design jobs tailored to the conditions, which can determine the success of a project.

During the EOR downtime, advances in the hardware and software available for petroleum geology have made the computing power needed for EOR project planning both cheap and portable. Harwell is working on an easier way to create reservoir simulations based on pilot test data with funding from the Research Partnership to Secure Energy for America.

But, he and Roberts are part of a small group of experienced experts in the field that was largely dormant after the oil price collapse in the early 1980s. "I am 60 years old, and I earned one of the last PhDs in this area," Harwell said. "There is a big gap in graduate students in this area." **JPT**

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