CO_2 EOR: Nanotechnology for Mobility Control Studied

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Most domestic conventional oil resources have been produced using primary and secondary recovery techniques, with an average recovery factor estimated at 35%. Additional recovery is possible by using innovative enhanced oil recovery (EOR) techniques. One of these, carbon dioxide (CO_2) miscible flooding, is the fastest growing EOR technique in the United States because of the many reservoirs amenable to the process. Current production is almost 310,000 B/D (EOR Survey, *Oil and Gas Journal,* April 2012), representing approximately 5% of total US oil output.

A revised national resource assessment for CO_2 EOR conducted by the National Energy Technology Laboratory (NETL) of the United States Department of Energy (DOE) in 2011 indicated that "next generation" CO_2 EOR can provide 137 billion bbl of additional, technically recoverable domestic oil, with about half (67 billion bbl) economically recoverable at an oil price of USD 85 per bbl. CO_2 EOR has the benefit of sequestering CO_2 in oil producing formations and is seen as a critical component of future greenhouse gas management programs. This facet of CO_2 EOR produces valuable synergies with the carbon capture, utilization, and storage research program with the DOE's Office of Fossil Energy.

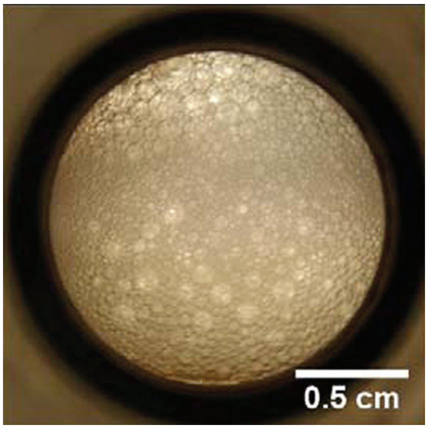

Fig. 1—Quality of the foam generated with 6-nm nanoparticle dispersion.

The CO_2 EOR process is limited by technology, cost, and the geographic availability of CO_2. Technology improvements are needed to increase the displacement efficiency of the process. Not only would advances in displacement efficiency increase oil recovery, it would also lead to the sequestration of additional CO_2 volumes.

Background

The Office of Fossil Energy has historically supported a large number of laboratory and field tests in an effort to improve oil recovery processes. A majority of the projects were related to advanced reservoir characterization, mobility control, and conformance of CO_2 flooding. In September 2010, the NETL awarded a number of new research projects to further development of the next generation of CO_2 EOR, encouraging applicants to pursue small field or pilot testing. Two of the awarded research projects are related to mobility control in CO_2 flooding using nanoparticle technologies.

The University of Texas at Austin (UT) is evaluating inexpensive alternative nanoparticles (microscopic particles with at least one dimension less than 100 nm) to provide the large volumes needed for foam stabilization in field-scale CO_2 floods. The study entails using low-cost, commercially available "bare" nanoparticles (e.g., silica, fly ash, and iron oxide) and applying a polyethylene glycol (PEG) or other in-house coating to produce low-cost alternatives to develop CO_2 foam.

A research initiative by the New Mexico Institute of Mining and Technology (New Mexico Tech) is conducting a complementary research on the use of nanoparticles to increase CO_2 flood sweep efficiency. The effects of particle retention on core permeability and porosity will be investigated using long-term core flooding experiments and nanoparticle-stabilized CO_2 foams. Additionally, surfactant molecule effects on the stability and performance of nanoparticle-based CO_2 foams will be examined and evaluated for field application.

Other CO_2 EOR research projects supported by NETL focus on

- Development of mobility control agents using surfactants injected with CO_2, rather than water, for CO_2 EOR in heterogeneous carbonate and sandstone reservoirs.
- Field testing gels for conformance control.
- Development of advanced computer simulation and visualization capabilities.
- Designing and testing an electromagnetic monitoring system to track the CO_2 flood front.
- A field case study of an existing CO_2 flood targeting the residual oil zone.

Nanoparticle-Stabilized Foams

Extensive research on the use of surfactant-stabilized CO_2 foams has been conducted over the years. The formation of CO_2-in-water foams lowers the CO_2 mobility, resulting in improved sweep efficiency. However, there are problems associated with surfactant-based foams. They require continuous regeneration;

the surfactant is adsorbed on the rock, leading to increased material costs; and the surfactant is prone to degradation in harsh reservoir conditions.

The solution pursued in the selected projects is to continue to use foam—as it is effective in increasing CO_2 sweep efficiency—but to stabilize it by a different mechanism. Nanoparticles are of great interest for forming emulsions and foams because of their robust chemical stability (even in harsh reservoir conditions) and extremely strong and selective adsorption at targeted fluid-to-fluid interfaces. Their surface coating can be tailored to favor CO_2/water foam without forming oil/water emulsions.

Moreover, the mechanism of generating nanoparticle-stabilized foam by coinjecting CO_2 and nanoparticle dispersion requires a threshold shear rate. In the field, high shear rates are associated with preferential flow through high permeability zones. These properties raise the possibility of creating "self-guiding" fluids that selectively reduce CO_2 mobility by generating foam only in regions where CO_2 is flowing rapidly, such as fractures and gravity override regions that contain little oil. The same foam breaks in the presence of resident oil to enable high recovery by contact with the now mobile CO_2.

UT researchers successfully generated CO_2-in-water foams in a column packed with 180 μm glass beads, using fumed silica as the stabilizer (Espinosa et al. 2010; Worthen et al. 2012). The idea of generating CO_2-in-brine foams in situ by coinjecting or alternately injecting an aqueous dispersion of nanosilica into a porous medium followed by the injection of CO_2 was intended to provide an alternative to surfactant-based CO_2 foams for mobility and/or conformance control.

When foam was generated, it had two to 18 times more resistance to flow than the same fluids without nanoparticles. Nanoparticle foam was generated at temperatures up to 95°C. The researchers also observed the creation of foam within fractures, which is even more advantageous in carbonates. Foam generation occurred only above a threshold shear rate. The threshold shear rate was independent of the CO_2/water ratio, thereby indicating that shear rate is of the first-order influence.

The team at UT demonstrated that low-cost, natural nanoparticles such as nanoclays, fumed silica, or inexpensive iron oxide nanoparticles, can be coated to provide foam-stabilizing performance similar to that of surfactants—with the economics comparable to or better than that of surfactants. The team also observed the remarkable capability of a component of fly ash to stabilize oil/water emulsions and CO_2/water foams (NETL 2011a).

After constructing the apparatus to test nanoparticle foams at reservoir conditions, the researchers examined various coated and uncoated nanoparticles. Foam was generated by coinjecting liquid CO_2 at ambient temperature and reservoir pressure (1800 psia) and an aqueous solution of nanoparticles. In the following example, uncoated and coated commercially supplied nanoparticles in the range of 6 nm to 20 nm were tested. **Fig. 1** shows a photograph of the foam generated with 6-nm nanoparticle dispersion, seen through a view cell window that is 1.5 cm in diameter. (Other denser and smaller-grain foams display only a homogeneous gray picture and are not shown.)

The 6-nm nanoparticle dispersion of 0.5 wt%, coated with short chain PEG molecules, was injected at 1 cm^3/min along with 5 cm^3/min CO_2 at 25°C and 1450 psia through a bead pack with 180 μm beads.

UT has developed a capability to test for foam generation during flow in rough-walled fractures at reservoir conditions. A novel procedure for fracturing cores was developed by placing plastic shrink wrap around the core, warming it to induce shrinking, and placing it in a conventional load frame.

Loading the core resulted in failure under tension along the length of the core, resulting in irregular fracture geometry similar to naturally occurring fractures. The shrink wrap proved effective in confining the path of the fracture. Foam was generated in the fractures by coinjecting CO_2 and a dispersion of 5-nm PEG-coated nanoparticles at constant flow rate at ambient temperature and a pressure of 1800 psia. The apparent viscosity of the generated foam ranged from 1.1 cp to 2.7 cp, depending on the phase ratio used.

The team at the Petroleum Recovery Research Center at New Mexico Tech investigated foam generation at dynamic conditions and nanosilica particle-stabilized CO_2 foam transport across porous media (NETL 2011b). Initial research showed that stable CO_2 foam could be generated when the nanoparticle concentration was in the range of 4,000 ppm to 6,000 ppm, using commercial silica nanoparticles. However, it was observed that brine salinity, reservoir pressure, and temperature can affect foam generation by nanoparticles. CO_2 nanofoam was also dependent on phase ratio and flow rate.

Recently, the New Mexico Tech team studied nanosilica particle transport in three core samples: Berea sandstone, Indiana limestone, and dolomite. It was observed that silica nanoparticles could easily pass through the sandstone core without changing the core permeability. Little adsorption was observed as nanosilica particles flooded the limestone core, but the core permeability was not changed. A high particle recovery was obtained with the dolomite core. However, pressure drop across the core was observed to increase continuously, indicating that core plugging occurred and core permeability was changed.

The coreflood performed in a sandstone core with permeability of 57.6 md is illustrated in **Fig. 2.** The figure displays nanoparticle concentration and pressure drop across the core during the coreflood. A slight decrease in pressure drop was observed when the coreflood was switched from nanosilica dispersion to brine. The decrease in pressure drop occurred probably because of the viscosity change, which removed some adsorbed particles from the pore surface. However, there was no evidence of alteration of core permeability or core plugging by the nanosilica particles (Yu et al. 2012).

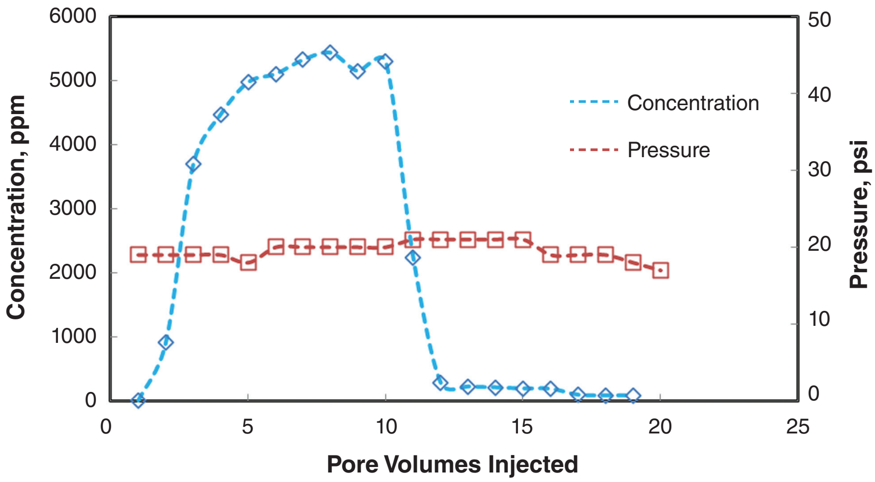

Fig. 2—Effluent concentration and pressure drop change with injected volume in sandstone core.

Summary

Nanoparticle-stabilized foams may provide a novel means of generating improved mobility control agents for CO_2 EOR. Aqueous nanoparticle dispersions may provide an alternative to the use of surfactants, especially in reservoirs with harsh conditions, where surfactant-produced foams may degrade because of adsorption on the reservoir rock and high temperature. Commercial fumed nanosilica can be purchased at very low cost, at less than USD 4/lbm. The costs can be reduced further by use of other nanoparticles (e.g., nanoclays or fly ash). Proof-of-concept tests in real porous media have shown that it is possible to propagate these dispersions through a porous medium without the adsorption or trapping of nanoparticles in pores.

The results are promising at laboratory scale. More tests are needed to show the ability of nanofoam to improve conformance for better volumetric sweep efficiency. Although this technology is still in its early development, some operators have expressed interest in limited field testing.

Acknowledgments

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