Hydrocarbon Mobilization Mechanisms Using CO₂ in an Unconventional Oil Play


aEnergy & Environmental Research Center, 15 North 23rd Street, Stop 9018, Grand Forks, North Dakota 58202-9018, United States
bMelzer Consulting, 415 West Wall, Suite 1106, Midland, Texas 79701, United States

Abstract

Enhanced oil recovery (EOR) processes using CO₂ in tight unconventional plays like the Bakken formation are expected to be very different from the processes which control EOR in conventional permeable reservoirs. During CO₂ EOR in conventional reservoirs, CO₂ flows through the permeable rock, while in the Bakken, CO₂ flow will be dominated by fracture flow, and not significantly through the rock matrix. Fracture-dominated CO₂ flow could essentially eliminate the "flushing" mechanisms responsible for increased recovery in conventional reservoirs. As a result, other mechanisms must be optimized in reservoirs such as the Bakken.

To investigate this concept, rock samples from the middle Bakken (low permeability), lower Bakken (very low permeability), and a conventional reservoir (high permeability) were exposed to CO₂ at Bakken conditions of 110°C and 5000 psi (230 °F, 34.5 MPa) to determine the effects of CO₂ exposure time on hydrocarbon production. Varying geometries of each rock ranging from small (mm) "chips" to 1 cm-diameter rods were exposed for up to one week, and mobilized hydrocarbons were collected for analysis. Nearly complete (>95%) hydrocarbon recovery occurs in hours with the more permeable middle Bakken and conventional reservoir rocks, while several days of exposure is required to achieve high recoveries from the lower and upper Bakken shales (1-cm diameter rods). Hydrocarbon recovery rates are greatly enhanced by higher rock surface areas, which supports the proposed conceptual model that CO₂ EOR is dominated by fracture flow, followed by permeation into the Bakken rock with subsequent mobilization of the oil based on lowered viscosity, swelling and solubilization of oil hydrocarbons. These results also demonstrate that the micropores in even the very tight Bakken shales are accessible to CO₂, and indicate that the shales may have substantial CO₂ storage capacity.

© 2013 The Authors. Published by Elsevier Limited.
© 2014 Energy & Environmental Research Center, University of North Dakota. Published by Elsevier Limited. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/3.0/).
Peer-review under responsibility of the Organizing Committee of GHGT-12

* Corresponding author. Tel.: +1-701-777-5256; fax: +1-701-777-5181.
E-mail address: shawthorne@undeerc.org
Introduction

Recently there has been a dramatic increase in exploration and development of oil and gas resources in tight, shale-dominated formations in North America. An example is the rapid and expanding development of the Bakken Formation in the Williston Basin of the United States and Canada. Despite the enormous original oil-in-place (OOIP) resources that have been identified in the low-porosity Bakken petroleum system, oil recovery is only ca. 3 to 6% of the oil in place \[1,2\]. These low recovery factors are largely due to gaps in knowledge of the physical and geochemical properties of these tight unconventional reservoirs. Since recent estimates of the OOIP in the Bakken range from 160 to 900 billion barrels \[2-4\], even a small incremental increase in recoveries could yield many billions of barrels of additional produced oil. In addition, there are large organic rich members of these formations which contain substantial oil that is not currently considered to be amenable to production.

Efforts to increase oil recovery in these unconventional formations could include carbon dioxide (CO\(_2\)) enhanced oil recovery (EOR) with associated storage of large quantities of CO\(_2\). The processes and mechanisms which enhance oil production and trap CO\(_2\) in conventional oil reservoirs are expected to be very different than those in tight unconventional reservoirs \[5\]. In conventional reservoirs, CO\(_2\) flows through the permeable rock, and oil is mobilized by a combination of oil swelling, reduced viscosity, hydrocarbon stripping, and CO\(_2\) flushing, especially when above the minimum miscibility pressure. But even in tight conventional reservoirs, the long term nature of the production speaks to mechanisms beyond conventional miscible displacement processes. In tight unconventional oil reservoirs, CO\(_2\) flow will be dominated by fracture flow, and not significantly through the rock matrix. Therefore, the "flushing" mechanisms responsible for increased recovery in conventional permeable reservoirs are unlikely to be significant in tight unconventional plays. As such, other mechanisms must be optimized in these unconventional oil reservoirs.

Conceptual mechanisms that may occur when CO\(_2\) interacts with these tight formations include: (1) CO\(_2\) flows through the fractures, (2) unfractured rock is exposed to CO\(_2\) at fracture surfaces, (3) CO\(_2\) permeates the rock driven by pressure, carrying some hydrocarbon inward; however, the oil is also swelling, which forces oil out of the pores, (4) oil migrates to the bulk CO\(_2\) in the fractures via swelling and reduced viscosity, (5) as the CO\(_2\) pressure gradient gets smaller, oil production is driven by concentration gradient diffusion from pores into the bulk CO\(_2\) in the fractures, and (6) some fraction of the injected CO\(_2\) is trapped in the irreducible fluids that remain in the reservoir after the production phase. The purpose of the present study is to perform laboratory exposures to investigate these proposed CO\(_2\) exposure processes in tight unconventional systems.

Samples

To investigate these concepts, rock samples from the Bakken Middle Member (low permeability, oil-saturated siltstone), Bakken Upper and Lower Shale Members (very low permeability oil-saturated shale), and a conventional reservoir (high permeability oil-saturated sandstone) were obtained. The conventional reservoir rock has ca. 25% porosity, and ca. 1000 millidarcies permeability. The middle Bakken rock has ca. 4.5-8.1% porosity and ca. 0.002 to 0.04 millidarcies permeability \[4\]. Measured values for the upper and lower shales are not known, but permeability of the shales is substantially lower than that of the middle Bakken rock. The upper, middle, and lower Bakken samples all came from the same well in Dunn County, North Dakota. Different rock sample sizes including 1-cm diameter X 3-4 cm long round rods, and rock crushed to pass through a 3-mm screen were prepared.
Figure 1: Schematic of rock exposure apparatus used to determine the rate of oil recovery from Bakken reservoir rock and shales.

**Experimental Methods**

Rock samples were exposed to CO$_2$ at typical Bakken conditions of 110°C and 5000 psi (230°F, 34.5 MPa) in an ISCO model SFX-210 supercritical extraction unit equipped with an ISCO 260D pump to supply CO$_2$ as shown in Figure 1. At certain intervals (typically hourly for the first 8 hours of exposure, then daily after that), the mobilized hydrocarbons were collected by flushing the sample cell with ca. 2-void volumes of CO$_2$, through a 1-mL/min flow restrictor into ca. 15 mL of methylene chloride. It is important to note that, as shown in Figure 1, the CO$_2$ is not forced to flow through the rock sample, but is allowed to flow around the rock sample so that the proposed fracture flow mechanism could be investigated.

Extracted hydrocarbons (C$_7$ to C$_{36}$) were analyzed using high-resolution GC with flame ionization detection (GC/FID) after the addition of hexadecylbenzene as a quantitative internal standard. Quantitative calibration was achieved with a weighed solution of a Bakken crude oil.

**Results and Discussion**

GC/FID analyses of the hydrocarbons recovered from 1-cm diameter X 3 to 4-cm long reservoir rocks are shown in Figures 2-4. Note that, even though the CO$_2$ was not forced through the rock samples, (but rather was...
allowed to flow around the rock samples to mimic the proposed flow through fractures expected to dominate in tight unconventional formations), hydrocarbon recovery from the conventional (permeable) reservoir rock was quite rapid, with the majority of oil recovered in less than an hour of CO₂ exposure. Although much less permeable than the conventional reservoir rock, the middle Bakken sample showed nearly all of the oil recovered in three hours (Figure 3). Although hydrocarbon recovery was much slower for the upper and lower Bakken shales, the majority of oil was recovered with long (96 hour) exposure times, even though these shales are very impermeable.

Since the majority of oil can be recovered from the Bakken samples (although very slowly for the upper and lower shales), these results demonstrate that the pores are interconnected (even in the shales), and therefore, CO₂ can access these pores. Therefore, the oil recovery results indicate that there is potential to use the upper and lower Bakken shales as well as the middle Bakken reservoir rock for CO₂ storage in conjunction with EOR.

The contact times required to achieve high oil recoveries are quite long even with these small samples (especially for the upper and lower shales). However, since even a small incremental increase in recovery would be hugely beneficial, the CO₂ exposure times required to achieve 40% recoveries were determined. As shown in Table 1, 40% recovery was achieved in only a few minutes from the conventional reservoir rock. This time was increased to 55 minutes for the middle Bakken, while approximately one full day was required to achieve the 40% recovery goal for the upper and lower shales (Table 1).

Based on the proposed mechanism described above, increasing the rock surface area exposed to the CO₂ should greatly increase the oil recovery rate. This was tested by crushing fresh shale samples to pass a 3-mm sieve, and repeating the 96-hour CO₂ exposures. As shown in Table 1, the times to recover 40% of the oil from the upper and lower Bakken shales were reduced to only ca. 1/2 hour (Table 1), and more than 80% recovery was obtained in 2-4 hours for both the upper and lower shales. These results demonstrate that the exposed surface area of the rock, as well as the CO₂ contact time, are the two major factors controlling hydrocarbon recoveries and, by analogy, CO₂ storage.

![Conventional Reservoir Rock, 1-cm rod](image)

Figure 2: Hydrocarbon recovery from a conventional (permeable) reservoir rock with CO₂ at 5000 psi and 110°C.
Table 1: CO₂ Exposure Time (5000 psi, 110°C) to Achieve 40% Hydrocarbon Recovery from a Conventional Reservoir Rock, Middle Bakken Reservoir Rock, and Upper and Lower Bakken Shale

<table>
<thead>
<tr>
<th>Rock Sample</th>
<th>Time to 40% Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conventional reservoir rock, 1-cm round rod</td>
<td>&lt; 10 minutes</td>
</tr>
<tr>
<td>Middle Bakken, 1-cm round rod</td>
<td>55 minutes</td>
</tr>
<tr>
<td>Upper Bakken, 1-cm round rod</td>
<td>22 hours</td>
</tr>
<tr>
<td>Lower Bakken, 1-cm round rod</td>
<td>25 hours</td>
</tr>
<tr>
<td>Upper Bakken, &lt; 3 mm</td>
<td>25 minutes</td>
</tr>
<tr>
<td>Lower Bakken, &lt; 3 mm</td>
<td>40 minutes</td>
</tr>
</tbody>
</table>

Figure 3: Hydrocarbon recovery from Middle Bakken reservoir rock using CO₂ at 5000 psi and 110°C.
Figure 4: Hydrocarbon recovery from lower Bakken shale with CO₂ at 5000 psi and 110°C.

Conclusions

1. Hydrocarbon recoveries were unexpectedly high with the CO₂ exposure. However, the exposure time required for near quantitative oil recovery is long, especially for the upper and lower Bakken shales.

2. The rate of hydrocarbon recovery is greatly enhanced by exposed rock surface area. These results indicate that a better understanding of CO₂ transport through rock microfractures is critical to exploiting CO₂ EOR and storage in tight unconventional formations.

3. Experimental results support the proposed EOR processes for tight unconventional reservoirs where the CO₂ flows primarily through fractures around rock surfaces, but not easily through the rock as occurs in conventional permeable formations.

4. Given the observation that oil can be largely removed from even the upper and lower Bakken shales, it seems reasonable to conclude that the microporous structure in the shale is accessible to CO₂ for storage.

Acknowledgments

The authors thank Basak Kurtoglu (Marathon Oil) and the North Dakota Geological Survey for providing the samples used in these investigations. Financial support from the U.S. Department of Energy, National Energy Technology Laboratories (NETL) and the North Dakota Oil and Gas Research Council are also gratefully acknowledged.
References