



Plains CO₂ Reduction (PCOR) Partnership
Energy & Environmental Research Center (EERC)

INVESTIGATION OF CRUDE OIL COMPOSITIONAL CHANGES DURING CO₂ EOR

**Plains CO₂ Reduction (PCOR) Partnership Phase III
Task 9 – Milestone M55**

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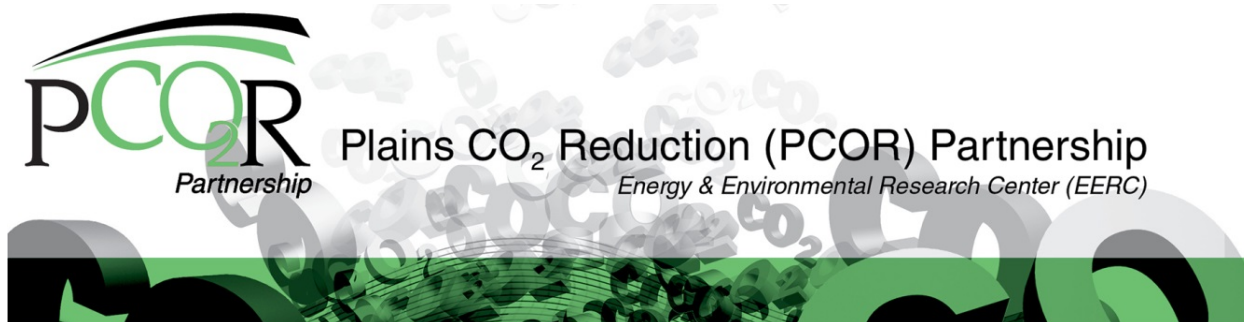
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INVESTIGATION OF CRUDE OIL COMPOSITIONAL CHANGES DURING CO₂ EOR

BACKGROUND

The Plains CO₂ Reduction Partnership (PCOR) Partnership, led by the Energy & Environmental Research Center (EERC), is working with Denbury Resources Inc. (Denbury) to study incidental carbon dioxide (CO₂) storage associated with a commercial enhanced oil recovery (EOR) project at the Bell Creek oil field located in southeastern Montana, which is operated by Denbury Onshore LLC. Denbury is managing all injection, production, and recycle activities as part of its commercial CO₂ EOR operation. The EERC, through the PCOR Partnership, is studying the behavior of reservoir fluids and injected CO₂ to demonstrate safe and effective CO₂ storage associated with a commercial EOR project. The PCOR Partnership is developing practices and technologies that will allow future commercial-scale CO₂ storage projects to make informed decisions regarding site selection, injection programs, operations, and monitoring strategies that improve storage efficiency and effective storage capacity in clastic geologic formations.

The present task is to investigate the effect on the molecular weight distribution of produced oil during CO₂ EOR and associated CO₂ storage and, by extension, the composition of crude oil hydrocarbons left in the reservoir. Two experimental approaches have been (and will be) utilized, including 1) the temporal collection and analysis of the produced crude oil before and after CO₂ injection and appearance at the production wells and 2) laboratory-based sampling and analysis of the hydrocarbon composition found in the CO₂-dominated “miscible” phase when Bell Creek crude oil is exposed to CO₂ at reservoir temperature and pressures.

INVESTIGATION OF CRUDE OIL COMPOSITIONAL CHANGES DURING CO₂ EOR

Produced Crude Oil Collection and Analysis

A total of 90 produced crude oil samples have been collected beginning in 2013 from six wells in development Phase 1, three wells in development Phase 3, and five wells in development Phase 4, as shown in Table 1 and Figure 1. Initial analyses of the molecular weight distributions in the earlier samples of produced crude oil have indicated that program goals will be better met the longer the sample collections can occur. Therefore, we presently plan to continue the produced crude oil collection activities until the beginning of 2018. At that time, all of the crude oil samples will be analyzed as a single batch to minimize the analytical variability so that subtle changes in crude oil molecular weight distributions before and after CO₂ enhanced oil production can best be monitored. We anticipate a total of 110–130 crude oil samples will be analyzed and final reporting

Table 1. Oil Sampling and Analyses

Date Sampled	Production Stream by Development Phase, Well													
	Phase 1						Phase 3			Phase 4				
	56-14R	32-02	05-06	05-04	33-12	04-04	28-02	21-10	21-14	34-09	34-07	34-03	35-03	35-13
Nov 2013					X									
Jan 2014	X	X	X											
Mar 2014	X	X		X										
May 2014	X	X	X											
Jun 2014	X	X	X											
Jul 2014	X	X	X											
Sep 2014	X	X	X											
Oct 2014	X	X												
Nov/Dec 2014	X	X												
Jan 2015		X	X											
Jun 2015	X	X	X											
Nov 2015	X		X											
Apr/May 2016	X	X	X			X	X	X	X					
Jun/Jul 2016	X		X			X	X	X	X					
Aug/Sep 2016	X	X				X	X	X	X	X				
Oct 2016			X											
Nov/Dec 2016	X	X	X			X	X	X	X	X	X	X		
Feb 2017	X	X				X	X	X	X	X	X	X		
May 2017	X	X	X			X	X	X	X	X	X	X		
July 2017	X					X	X	X	X	X	X	X	X	X

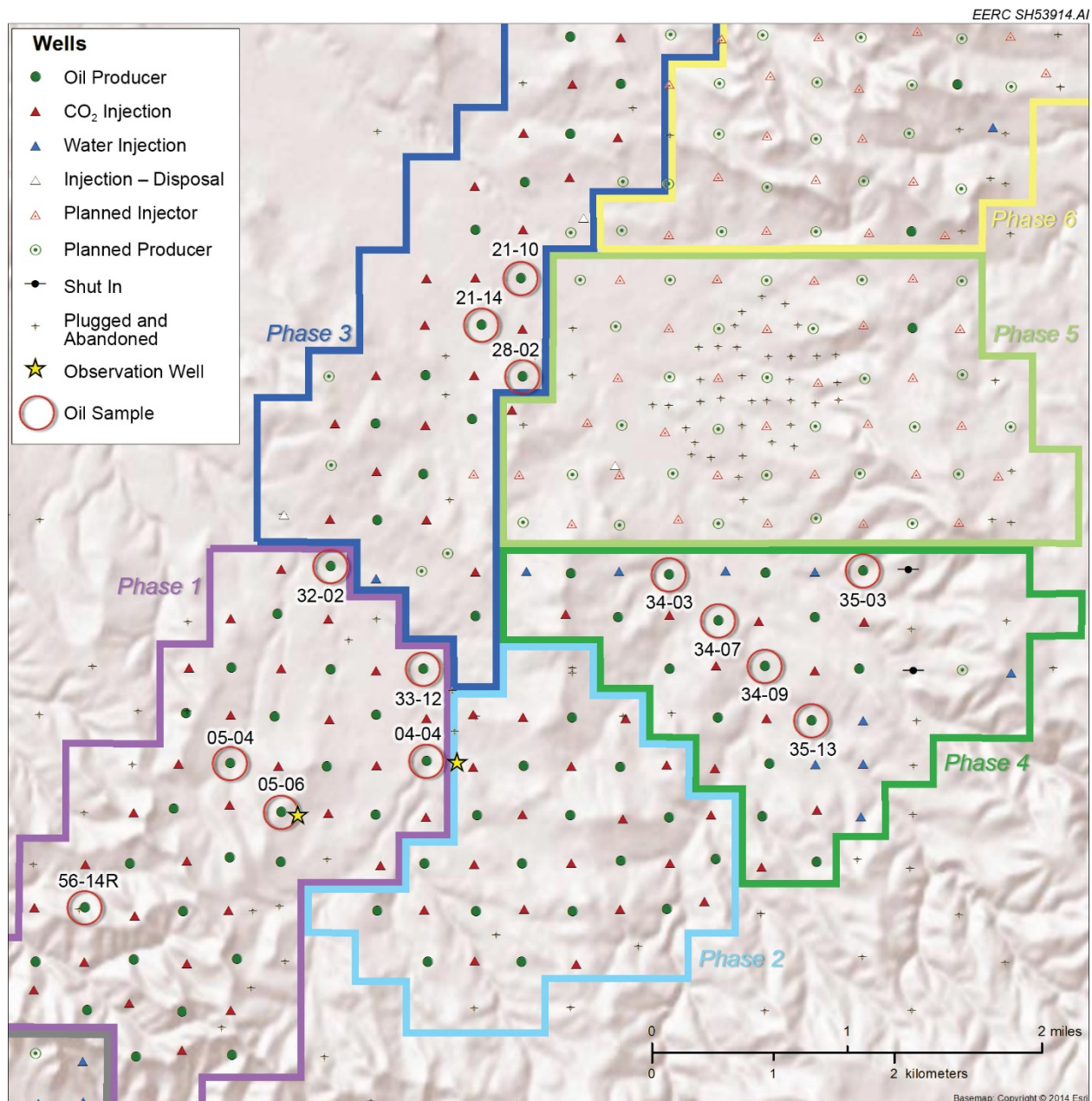


Figure 1. Produced crude oil sample well locations.

via a technical paper or journal article completed by March 2018. The results will be correlated with field activities (e.g., the appearance of CO₂ in production wells).

Hydrocarbon Composition in the CO₂-Dominated “Miscible” Phase

When CO₂ is equilibrated with crude oil, the upper CO₂-dominated phase is deemed the “miscible” phase, assuming that the pressure is above the minimum miscibility pressure (MMP) of the crude oil at the relevant reservoir temperature. For Bell Creek, the experimentally

determined MMP values have been 1400–1450 psi at the 42°C reservoir temperature. In order to allow quantitative sampling of the CO₂-dominated miscible phase, a high-pressure view cell was modified to allow small sample volumes of the CO₂-mobilized crude oil to be collected without disturbing either the cell pressure or temperature. These samples then flow through a small heated restrictor orifice and are directly purged into methylene chloride to collect the crude oil hydrocarbons that were present in the miscible phase, as well as to vent the CO₂. This allows direct analysis using capillary gas chromatography coupled with flame ionization detection of both the total concentration of crude oil mobilized into the CO₂-dominated miscible phase as well as the molecular weight distribution of the mobilized crude oil hydrocarbons.

CONCLUSION

The results of these investigations clearly demonstrate that both the quantity of CO₂-mobilized crude oil and its molecular weight distribution are heavily dependent on the CO₂ pressure, regardless of if the CO₂ pressure is below, at, or significantly above MMP; that is, the total mass of crude oil mobilized by CO₂ increases greatly with higher pressures (whether below, at, or above MMP). In addition, the ability to mobilize higher molecular weight crude oil hydrocarbons also increases with higher CO₂ pressures. These results are presently being prepared for review and publication.