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Author

Wan, Jiamin

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Report on Developing a US-China Joint Project on CO₂-Based Fracturing Techniques

Jiamin Wan

Energy Geosciences Division

Lawrence Berkeley National Laboratory

Berkeley, CA 94720

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Preface

The U.S.–China Clean Energy Research Centers (CERC) are joint initiatives to accelerate research, development, and deployment of clean energy technologies in the U.S. and China. Advanced energy solutions can tap diverse energy sources, improve efficiency, and accelerate the transition to a low-carbon future. With these objectives in mind, CERC facilitates collaborative research and development, engaging scientists and engineers from world-class universities, top research institutions, and industry leaders.

One of the more recently established CERCs is the U.S./China Clean Energy Research Center for Water Energy Technologies (CERC-WET), led by the University of California together with Lawrence Berkeley National Laboratory for the U.S. side, and led by the Research Institute of Petroleum Exploration and Development (RIPED) on the Chinese side. The overall objective of CERC-WET is to build a foundation of knowledge, technologies, human capabilities, and relationships that position the U.S. and China to continue to thrive in a future with constrained energy and water resources.

One of the top water-energy priorities of research on the Chinese side is waterless fracturing using CO₂, which was not in the initial CERC-WET workscope on the U.S. side. Thus, while the Chinese CERC-WET team has a strong interest to establish joint R&D activities on using CO₂ as the alternative to replace water in hydraulic fracturing, the U.S. CERC-WET has had difficulty supporting a research team because the 2016-2020 funding had already been allocated to individual projects focusing on other objectives. Because non-water fracturing is a timely and high-impact topic for the U.S. as well and it aligns well with the overall CERC objective, the CERC director reached out to DOE/FE for seed funding support. The LBNL received such seed funding April 2016-March 2017) to initiate the first step towards designing and developing a productive long-term research collaboration with the Chinese team. The 2016 tasks specified by the DOE/FE are listed below, focusing on analyses of the state-of-the-technology, knowledge sharing with RIPED, and identifying a framework for collaboration.

- Task 1: Conducting analyses of the current state-of-the-art and the application of non-water fluids in oil and gas fracture stimulation, and determining the characteristics of geologic formations amenable to the use of each fluid.
- Task 2: Conducting analyses of CO₂-based stimulation techniques and mechanisms, and identifying the key future research questions for large-scale CO₂ usage in hydraulic fracturing.
- Task 3: Visit RIPED for exploratory discussions, relationship-building, and knowledge sharing regarding current state-of-the-art using non-water stimulation techniques.
- Task 4: Provide input to RIPED on designing and developing a long-term R&D collaboration to advance the most promising CO₂-based hydraulic fracturing techniques.

This report covers Tasks 2-4 described above. Task 1 findings are described in a separate LBNL report (Moridis, 2017).

Abstract

There are several types of hydraulic fracturing methods that have been investigated in the past decades that use little or no water. The criteria for selecting an optimal hydraulic fracturing fluids are many, and no single fluid can meet all the desired characteristics. Developing a set of technologies by using different fracturing fluids can better meet individual geologic, economic, and environmental needs. CO₂ as an alternative of water for hydraulic fracturing has its unique place among all other fracturing fluids, and can meet both economic and environmental objectives under certain circumstances. There are three main categories of CO₂-based fracturing fluids, simple liquid CO₂ (LCO₂), directly thickened LCO₂, and CO₂-foams/emulsions. Although LCO₂ has many advantages, critical disadvantages arise due to its high operating pressure, low viscosity, poor proppant-carrying capacity, and generation of shallower fracture networks. To date, techniques for direct thickening of LCO₂ to overcome these limitations have proven ineffective. To increase the apparent viscosity of CO₂, we propose to further develop CO₂-foam (and emulsion) fracturing techniques. While CO₂-foams have long been used in EOR, the required properties for hydraulic fracturing are different, and relatively few peer-reviewed publications and field test reports are available regarding their applications in fracturing, and the surfactants and additives used are often proprietary. This report describes a brief state-of-the-art analysis of CO₂-based hydraulic fracturing methods and then discusses a joint plan for a long-term R&D collaboration to advance the most promising CO₂-based hydraulic fracturing techniques as part of the U.S.-China Clean Energy Research Center, Water Energy Technology (CERC-WET). The objective of this U.S.-China joint research project is to design and laboratory test a CO₂-foam fracturing fluid system, and then conduct pilot field-tests on them in China's Jilin Oilfield. This joint research project will benefit both U.S. and China for advancing their shared goal of developing better technologies for CO₂-based fracturing. The Chinese CERC-WET has two teams joining the project, one from RIPED, responsible for aboveground infrastructure design and construction. Another team from the Jilin Oilfield will be responsible for the field test design and conducting the test. The U.S. CERC-WET team at LBNL will be responsible for providing the CO₂-foam formulations and their rheology parameters to be tested in the field (a challenging task and a key to success); participating in the equipment design and field test design; assisting in analyzing field data; and reporting to U.S. DOE and CERC-WET.

1. Analyses of Various CO₂-based Stimulation Techniques

1.1. Generally Advantageous Aspects of CO₂-based Fracturing

CO₂ has been recognized as a promising alternative fluid for replacing water in fracturing for decades (Sinal and Lancaster, 1987), with benefits of both liquid and supercritical CO₂ as fracturing fluids summarized in a number of reviews (Gupta, 2009a; Gupta and Bobier, 1998; Liu et al., 2014; Middleton et al., 2015; Rogala et al., 2013; Wang et al., 2012). The following are favorable attributes.

- (1) *Not adding water.* Water's immiscibility with gas and oil interferes with the return flow from reservoir matrix pores to the stimulated fractures and wells (**Figure 1**). The detrimental impact of water is often not simply limited to immiscible phase reduction of permeability, but often extends to alteration of reservoir rock pores to finer pore-size distributions because of clay hydration and swelling. The significance of this impact is evident from the fact that injected water largely remains in close proximity to stimulated fractures, with typically only about 30% recovered at the well head as flowback (Clark et al., 2013). Given the large volumes of water used in fracturing, averaging $\sim 10^6$ gallons/well (Gallegos et al., 2015), a valuable resource is largely lost to the formation. Moreover, the recovered flowback water requires costly treatment.
- (2) *Miscibility* of CO₂ with natural gas and its pressure-dependent miscibility with oil enhances their mobilization by *lower viscosity and lower interfacial tension with oil*. These properties facilitate access into microfractures and pores, as well as flowback.
- (3) *Energized fracturing fluid.* The compressibility of scCO₂ during fracturing is expected to generate more complex and finer fractures (Li et al., 2016; Qajar et al., 2016).
- (4) *CO₂ sorption and CH₄ desorption from shale surfaces.* Strong adsorption of CO₂ relative to CH₄ drives desorption of the latter, thereby enhancing gas production (Wang et al., 2012).
- (5) *Carbon capture, utilization, storage.* Storage of CO₂ in depleted shale gas reservoirs would provide another set of subsurface formations useful for keeping this greenhouse gas out of the atmosphere (Khosrokhavar et al., 2014).

Figure 1. Conceptual drawing comparing regions along hydraulic fractures generated (a.) with water, and (b.) with supercritical CO₂. In water-based fracturing, water from newly formed fractures imbibes into the shale matrix to block return flow of gas. With CO₂ as a stimulation fluid, no blockage of gas return flow occurs.

1.2. General Limitations of CO₂-based Fracturing

Despite having advantages over water-based hydraulic fracturing technologies, the different CO₂-based reservoir stimulation approaches to be discussed in following sections share several basic challenges; in particular, low viscosity of CO₂ (Enick et al., 2012), pipe friction, infrastructure requirements, and availability of CO₂ (Liu et al., 2014).

- (1) *Viscosity and friction.* In contrast to the advantages noted above, low viscosities of CO₂, about 10% of water, severely limits proppant carrying capacity. The limitations imposed by the viscosity of CO₂ have motivated research on thickening and foaming in order to more effectively transport proppants. Moreover, the high injection rates needed during fracturing and proppant delivery are constrained by friction losses along the delivery system. Unlike water-based fracturing fluids that have relatively cost-effective friction reducers (polyacrylamide), economical friction reducers suitable for CO₂ injection have yet to be developed.
- (2) *Infrastructure requirements.* Requiring transportation and onsite storage at elevated pressures (~ 2 MPa) and low temperature (~ -30 °C), and high pressure blending equipment add expense.
- (3) *CO₂ availability* is currently a limiting factor in many locations (**Figure 2**). Proximity to natural CO₂ reservoirs and sources of concentrated anthropogenic CO₂ are limited, and require compression and transport. Indeed, EOR is the major consumer of CO₂ from these sources, that currently amount to only 4 to 7 gigatonnes (Godec et al., 2013).

Additional limitations of CO₂ have been raised. For example, a modeling comparison of natural gas production resulting from CO₂ enhanced gas recovery (CO₂-EGR, coupled to geologic CO₂ sequestration) versus hydraulic re-fracturing concluded that the latter approach performed better

(Eshkalak et al., 2014). However, a more meaningful comparison would have also included a simulation of re-fracturing with CO₂, because modeled production will generally be more significantly increased with introduction of new fractures.

Figure 2. U.S. CO₂-EOR activity.

Table 1. Significant Volumes of Anthropogenic CO₂ Are Already Being Injected for EOR^a

location of oil fields	location of CO ₂ sources	CO ₂ supply [million cubic feet per day (MMcfd)]	
		geologic	anthropogenic
Texas, New Mexico, Oklahoma, and Utah	geologic (CO and NM), gas processing, and fertilizer plant (TX)	1600	101
Colorado and Wyoming	gas processing (Wyoming)		300
Mississippi	geologic (Mississippi)	850	
Michigan	gas processing (Michigan)		10
Oklahoma	fertilizer plant (Oklahoma)		35
Saskatchewan	coal gasification (North Dakota)		150
total (MMcfd)		2450	596
total (million tonnes per year)		47	12

^aSource: ARI (2012). ^bMMcfd of CO₂ can be converted to million metric tons per year by first multiplying by 365 (days per year) and then dividing by 18.9×10^3 (Mcf/tonne).

in: Godec et al., Energy Fuels, 2013, 27, 1183-4189.

Figure 2. Map and table of U.S. CO₂ sources (Godec et al., 2013).

1.3. Developments in CO₂-based Fracturing

1.3.1. Liquid CO₂-sand Fracturing

The earliest CO₂-based fracturing process injects only sand and carbon dioxide into reservoirs. A closed system blender augers sand out of its pre-loaded closed system pressure vessel. The process developed by Canadian FracMaster in the 1980's had widespread commercial success in Canada, with more than 1200 jobs performed on tight unconventional gas formations (Arnold, 1998; Rogala et al., 2013; Sinal and Lancaster, 1987). Introduced to the U.S. marketplace by American FracMaster in the 1980's, and further applied the 1990's through Universal Well Service (Meadville, PA), DOE-sponsored field tests with Devonian Shale operators demonstrated commercial feasibility (Yost, 1993; Yost et al., 1994). The technology held promise particularly for stimulating water-sensitive shale reservoirs in that the CO₂ is pumped in

liquid and supercritical fluid phases to hydraulically create fractures, and then vaporizes at reservoir conditions, leaving liquid-free sand packed hydraulic fractures (**Figure 3**). The process consists of a proppant (sand) mixed and transported with liquid CO₂ down the wellbore, warming and pressurizing further to the supercritical state within the reservoir, with entrained proppants limiting fracture closure. The technology held promise for stimulating liquid-sensitive reservoirs (like many shales) in that the CO₂ is pumped as a liquid to hydraulically create fractures, and then vaporizes at reservoir conditions, leaving water-free sand packed hydraulic fractures. Because there are no other additives used in this type of fracturing, there are no residual flowback constituents from the fracturing process that must be handled at the surface during flowback (other than CO₂ in the gas stream, which could be separated for reuse). The process is non-damaging to the reservoir compared to water- and gel-based fracturing fluids; exhibits reduced relative permeability damage associated with capillary fluid retention in low pressure formations, and is non-damaging to water sensitive clays that can plug pore throats and reduce permeability. Production results from DOE's field experiments in the Devonian Shale in Kentucky indicated CO₂-sand fracturing increased production rates five-fold compared to a nitrogen foam fractured well. The process has been used most successfully where formation damage near the wellbore needs to be overcome with small to moderate scale fracture lengths. Although the process resulted in superior performance compared to water based hydraulic fracturing, the application has been limited due to CO₂ availability, and an apparent reluctance of the oilfield service community to replace existing nitrogen equipment with new CO₂ infrastructure. Implementation of the process is likely to expand as affordable supplies of CO₂ are developed. For controlling costs, mixtures of N₂ with CO₂ have been used, although this economization comes with decreased densities and viscosities (Gupta, 2009b).

More recent accounts of CO₂-based stimulation efforts in unconventional reservoirs by Praxair (DryFrac) and by General Electric have appeared in press releases and web news (MacRae, 2015; Topf, 2014), but no technical reports or journal publications related to these newer activities have been found.

Figure 3. Phase diagram of CO₂, showing steps in CO₂ fracturing cycle (after Gupta and Bobier, 1998). The typical range of depth-dependent pressure-temperature combinations are indicated in the blue band.

1.3.2. Approaches to Enhancing Proppant Carrying Capacity of CO₂-based Fluids

Overview

The low viscosities of liquid and supercritical CO₂ over all pressures and temperatures found in reservoirs prevent effective transport of proppants deep into stimulated fractures. To counter this limitation, two general strategies have been pursued; thickening CO₂ and foaming CO₂. Many attempts have been made to directly thicken the CO₂ phase through addition of two types of thickeners: polymer thickeners and small molecule thickeners. Polymer thickeners tend to be composed of ultra-high molecular weight polymers, as these are optimal for increasing viscosity. Small molecule thickeners are ones that can bond and create structures. The majority of literature on thickened CO₂ applications is related to enhanced oil recovery, EOR (Olsen and Enick, 2011), and rather than hydraulic fracturing. Similarly, the literature on foams is much more extensive for EOR applications than for hydraulic fracturing. Summaries of thickened CO₂ and CO₂ foams provided below briefly reference efforts in EOR, and identify efforts targeted for hydraulic fracturing with CO₂.

Polymer Thickeners

Many attempts have been made to find a polymer that would thicken CO₂ effectively and at the right temperature and pressure, but most have failed. The polymers that did dissolve at optimal conditions were unpractical for application due to number of factors (Enick et al., 2012). In one study by Heller et al., the best polymers found increased viscosity by a multiple of 1.3, while what was needed was 20x or 30x (Heller et al., 1985). Enick et al. developed the first successful polymers to increase the viscosity of liquid CO₂ using fluoroacrylate-styrene copolymers (Enick et al., 2001). To date, these may be the only effective polymer thickeners (Lee et al., 2016), are

very expensive, and only increased viscosity by about a factor of 5. It should be noted that a CO₂ thickener “TNJ” used in CO₂ fracturing has been reported to increase viscosities by up to 490x when added at a concentration of 2% (Song et al., 2014). However, that account did not disclose the chemical structure and cost of TNJ, nor were any details provided on the viscosity measurement method.

Small Molecule Thickeners

The use of small molecules to thicken CO₂ via formation of macromolecular structures has been explored (Enick et al., 2012). The molecules should have a hydrophobic segment to promote dissolution in the CO₂ and a hydrophilic segment to allow it to form structures with the adjacent molecules. Unfortunately, developing this type of thickener has been even less successful than polymer thickeners. Several compounds have been tested, hydroxyaluminum disoaps (the same type of molecule used in napalm) (Eastoe et al., 2003; Enick, 1991), semi-fluorinated alkanes (Iezzi et al., 1989), small organic compounds and gels (Gullapalli et al., 1995; Lancaster et al., 1987), and co-polymers (Llave et al., 1990). However, while some of these can dissolve and thicken CO₂ to a small degree, no field tests have been conducted because the compounds are too expensive and are required to be in great concentrations (2-10% by weight) (Enick et al., 2012).

Worm-like Micelles (WLM)

A third method of increasing the viscosity of liquid CO₂ is through the use of surfactants to create rod-like or worm-like micelles within the CO₂ phase. These micelles are worm-shaped rods of surfactants that interlace with each other and increase the viscosity of the fluid. To create these structures, additives include cosurfactants, slightly polar co-solutes such as medium chain alcohols and amines. These have been reported with a variety of surfactant types including, cationic–anionic and, ionic–non-ionic, and mixed non-ionic systems. Salts and fluorosurfactants also promote reversible WLM growth (Trickett and Eastoe, 2008; Trickett et al., 2010). However, even at additions up to 10% fluorinated surfactants in CO₂, only a 90% increase in viscosity was achieved (Trickett et al., 2010).

1.3.3. CO₂-Foam Fracturing

By stabilizing large volume fractions of CO₂ in water with surfactants in foams and emulsions, the advantageous aspects of CO₂ can be retained while diminishing or even overcoming the problem of viscosity. Foams containing a large volume percentage (or foam quality) of CO₂ (75-95%), surfactant-stabilized in substantially less water have been used commercially for mobility control in EOR for decades (Enick et al., 2012; Heller, 1994), but foam applications in fracturing have been much less common. Nevertheless, efforts to develop viscoelastic surfactant stabilized foams for fracturing reservoirs also go back decades (Almond and Harris, 1984; Blauer and Durborow, 1976). In 2012, Chesapeake Energy tested carbon dioxide foam fracturing as an alternative to water in Utica Shale in Ohio (Downing, 2012). More recently CO₂ foam fracturing utilizing 9,226 m³ of CO₂ was reported to yield 1,768 BOE/D (barrels of oil equivalent /day) from the Middle Montney (Downing, 2016).

Recent developments in foam research include ultradry foams and nanoparticle-stabilized foams for EOR. While conventional foams still contain significant fractions of water by volume (one tenth to one quarter) that can contribute to formation damage, ultra-dry foams containing less 5% water. Ultradry foams have been under laboratory development (Da et al., 2016; Johnston et al., 2016; Xue et al., 2016b) for EOR, but information on field tests was not located.

Nanoparticle-stabilized foams have also been developed for EOR. Silica nanoparticles (5 nm diameter) treated with polyethylene glycol and added at up to 0.5% have stabilized CO₂/water foams with qualities up to 89% and up to 18-fold increase in viscosity (Espinosa et al., 2010). Highly variable and foam quality-dependent increases in effective viscosities of scCO₂-water foams were reported for experiments with 6 nm surface modified silica nanoparticles with a mixture of betaine surfactants pumped through high permeability (1.2 and 23 Darcy) glass bead packs (Prigiobbe et al., 2016). They observed up to about 30x enhancements in effective viscosities when nanoparticles were increased to 3% concentration.

Ultradry nanoparticle-surfactant-polymer foams are currently being developed specifically for hydraulic fracturing. Prodanovic and Johnston have made supercritical CO₂-water dry foams stabilized with silica nanoparticles, lauramidopropylbetaine, and partially hydrolyzed polyacrylamide in laboratory (Prodanovic and Johnston, 2016; Xue et al., 2016a). They obtained effective viscosities of ~100 cP at 90% foam quality (50 °C, 20 MPa, 2% KCl). Given the complexity of fracturing with these complex fluids, simulations may provide insights that are difficult to gain through experiments because of variability in foam generation and in the low permeability porous media being fractured. The modeling study of Qajar et al. predicted that high quality (90 to 95%) dry foams generate fractures with smaller half widths and half-lengths relative to 70% quality foams (Qajar et al., 2016). They also modeled larger leak-off with the higher foam quality, although this is expected, especially given the reservoir permeability and porosity assumed in the model (1 md and 0.1, respectively).

We (Wan et al., 2017) have recently discovered a promising natural biogenic surfactant (NBS) contained in the Earth's subsurface sediments that is inexpensive and abundant. We developed a method to extract the NBS that does not generate toxic wastes. Using this NBS we successfully generated CO₂ (N₂) foams containing CO₂ up to ~80 v% with viscosities up to 40 cP (3 orders of magnitudes higher than that of pure supercritical CO₂ at the same pressure and temperature. The viscosity of these CO₂/N₂ foams are expected can entrain different types of proppants to different depths. An image of generated scCO₂-foam is shown in **Figure 4**. This new surfactant is effective, economical and environmentally benign. We will further study this surfactant and develop its applications in CO₂-foam fracturing.

Figure 4. A natural biogenic surfactant (NBS) suitable for generating CO₂-foams. (a) Abundant raw material containing NBS. (b) High pressure and temperature foam generator and rheology parameter measurements. (c) Highly viscous supercritical NBS-CO₂-foam with no addition of synthetic chemicals. (Wan et al, manuscript in preparation)

1.4. Fracturing Dynamics of CO₂

The thermomechanical properties of CO₂ result in significantly different fracturing behavior relative to more viscous and less compressible water. Middleton et al. propose that use of CO₂ enhances generation of more complex and extensive fractures because of thermal shock from Joule-Thompson cooling through fluid expansion at the propagating fracture tip (Middleton et al., 2015). Some experimental support for the generation of more complex fractures with CO₂ relative to water-based fracturing is available (Li et al., 2016; Ribeiro et al., 2017), and modeling of CO₂ fracturing reflects such differences (Qajar et al., 2016).

1.5. CO₂ Costs, Availability

A 2011 report on CCS estimated CO₂ costs ranging from \$15 to \$19/ton (Parsons-Brinkerhoff and Institute, 2011). A more recent report provided a mid-range forecast for the price of CO₂ at \$20/ton, and a levelized price of \$41/ton over the years 2020 through 2050 (Lucknow et al., 2015). The 2011 global demand for CO₂ was 8x10⁷ tons/year, with use in CO₂-EOR within North American accounting for most of this, at about 5x10⁷ tons/year.

2. Knowledge Sharing with China RIPED

The LBNL and RIPED teams have met twice, once in August 2016 and more recently in March 2017. During these meetings the teams engaged in knowledge sharing and discussions on a variety of related technical issues on non-water fracture stimulation technologies. The following is a summary of what we have learned: the motivation of RIPED's CO₂-based fracturing research and development, their successes and problems, and their strong desire to move forward the R&D together with the LBNL team under the CERC-WET.

2.1. Why China is Interested in Using CO₂ as the Alternative Fracturing Fluids?

China has vast tight gas/oil reservoirs, estimated to equal about 20 billion m³ (personal communication with Qinghai Yang). Most of these reservoirs are located in China's arid regions (**Figure 5**). These regions of China are also severely short of water resources. Freshwater resources amount to about 2.8×10^{12} m³, 6% of the global total. The water resource per capita is only 1/4 of the world average. On average, 1 to 4 million gallons of water per well is needed for water-based hydraulic fracturing. Because of this disparity between water scarcity and high water demands in water-based hydraulic fracturing, China needs to develop alternative non-water fracturing technologies.

China is still in the era of heavily depending on coal burning power plants. Large quantities of the power plant generated CO₂ have been captured in recent years. The industrial utilization of captured greenhouse gases has a large economic incentive in China. In addition, natural CO₂ reservoirs are abundant near many of the oil/gas fields. In China, CO₂ is relatively low cost and available.

Figure 5. Most of China's tight gas/oil reservoirs are located in water-scarce geographic regions, shown in red on map (a). The water map (b) shows water-scarce regions in pink and yellow.

2.2. Summary of RIPED's Past Field Tests

China has a fairly long history of experimenting with CO₂-based fracturing of reservoirs. In 1997, Jinlin Oilfield purchased some CO₂ foam fracturing equipment from the US. In 2005, a pure liquid CO₂ (no sand added) fracturing field test was conducted in the Changqing Oilfield. In 2006, the airtight mixer device were developed in a Chuanqing engineering institution for conducting LCO₂/sand fracturing. In 2015, Jilin, Changqing, and Yanchang Oilfields used LCO₂/sand as the fracturing fluid, and all these tests were reported to be successful (Liu et al., 2014)(Wang et al., 2016). Examples of data and more detailed information from the Jilin Oilfield are presented below.

The Jilin Oilfield complex is located in northeastern China, in the western plain of Jilin province, neighboring Daqing Oilfields in the Songliao Basin. It is one of China's eight largest onshore oil/gas assets and is made up of oil and gas fields: Fuyu, Honggang, Mutou, Xinbei, Xinli, Yingtai, and Gan'an. The largest among these is the Fuyu Oilfield.

The 2015 LCO₂/sand fracturing tests were conducted in Fuyu reservoir in H87 and R53 tight oil blocks. The core samples from H87 tight oil block were characterized, and results indicate that the rock is cemented by carbonate (9%) and pyrite. Clay minerals comprise 4.6% of the rock; 80% of the clay is illite and the rest is mixed layer illite-montmorillonite. Porosities of the H87 block range from 0.04 to 0.13. Permeability ranges from 0.02 mD to 6.0 mD, with an average permeability of 0.63 mD (Wang, 2016).

A total of 3 wells in H87 and one in R53 were fractured using LCO₂/sand. The three in H87 were for re-fracturing old oil wells, and one in R53 was for testing a new gas well. The specific fracturing parameters are show in Table 1. Among these, well R53-P9-3 was injected with an average sand volume of 20.5 m³ per stage, liquid volume 696 m³ per stage.

The 3 re-fractured wells achieved better stimulation effects. After the LCO₂/sand fracturing, oil production more than doubled compared with rates prior to refracturing (Table 2). All three wells are currently in steady production. However, well R53-P9-3 (the new gas well) was unsuccessful. Additional information from that well could not be obtained at this time.

Table 1. Liquid-CO₂/sand fracturing parameters (Wang et al., 2016)

Well	Fracturing section m	Preferation thick m	Displacement m ³ /min	Sand volume m ³	Average sand ratio %	Liquid CO ₂ volume m ³	Fracturing pressure MPa	Pump stopping pressure MPa	Remark
H87-22-4	2345.0-2292.4	15.6	2.4-3.3	/	/	573.2	40-61	18.2	Oil tube fracturing
H87-19-17	2295.0-2274.4	9.6	2.4-3.8	8.4	5.8	601	38-63	Sand plugging	
H87-11-4	2299.4-2214.6	12.8	4.5-7.6	11	4.3	657	22.4-33	16.8	Casing pipe fracturing
R53-P9-3	2268.8-2281.2	9.4	4.0-7.9	20.5	6.2	696	28-17.5	16	

Table 2. Comparison of oil and water production before and after refracturing (Wang et al., 2016)

Well	Fracturing Section m	Perforation thick m	Liquid CO ₂ volume m ³	Daily oil production t/d	Daily liquid production t/d	Calibration oil before fracturing t/d	Calibration liquid before fracturing t/d
H87-22-4	2345.0— 2292.4	15.6	573.2	2.87	5.56	0.67	2.46
H87-19-17	2295.0- 2274.4	9.6	601	1.23	3.20	0.46	1.28
H87-11-4	2299.4- 2214.6	12.8	657	2.91	5.18	0.92	3.01

The following discusses some advantages of CO₂ fracturing based on the Chinese experiments.

CO₂ effect on energy storage. Liquid CO₂ has more compressibility. It achieves greater energy storage prior to onset of fracturing relative water. LCO₂ was injected into well H87-22-4 up to a volume of 573 m³ during fracturing, which increased reservoir pressure from 22.11 MPa to 24.39 MPa. Slickwater was used for well H87-11-1 for the volume of 1508 m³, which increases reservoir pressure from 22.05 MPa to 25.26 MPa. The reservoir pressure increase achieved using LCO₂ was 1.9 times of that obtained with slickwater per unit liquid volume (Table 3).

Table 3. Comparison of the energy storage effects between CO₂ and slickwater (Wang et al., 2016)

Well	Technique	Fracturing displacement (m ³ /min)	Fracturing liquid volume (m ³)	Initial reservoir pressure (MPa)	Measurement of the reservoir pressure (MPa)	Increase of reservoir pressure per unit liquid volume (MPa/1000m ³)
H87-22-4	Preposition CO ₂ energy storage	2.4-3.3	573	22.11	24.39	3.94
H87-11-1	Slick water volume fracturing	12-8	1507.9	22.05	25.26	2.13

CO₂ effect on oil expansion and viscosity reduction. Under the reservoir pressure and temperature conditions, with CO₂ dissolving in oil, the oil volume expands and the oil viscosity simultaneously reduces. The oil volume expansion and oil viscosity reductions are shown in Table 4. The reduction of viscosity improves the mobility ratio and thereby increases the oil phase recovery.

Table 4. Oil viscosity variation after CO₂ saturated in Jinlin oil field (Wang et al., 2016)

Origin of oil sample	Reservoir pressure/MPa	Reservoir temperature /°C	CO ₂ solubility /mol%	Oil volume expansion multiples	Oil viscosity reduction /%
H87-2	21.20	101.6	48.30	1.23	56.70
Qianan	18.50	76.0	45.90	1.27	58.40
Hei59	24.20	98.9	63.96	1.47	63.20
Hei79	23.11	97.3	63.58	1.41	59.62

Oil miscibility measurements. The capillary method was used to measure the minimum CO₂-oil miscible pressure in the Fuyu Reservoir, H87 block. A CO₂-oil minimum miscible pressure of 27.45 MPa was obtained. The bottom hole pressure during CO₂ fracturing was stable at 41 MPa, 128 hrs after the fracturing injection, greater than the oil minimum miscible pressure 27.45 MPa (**Figure 6**). After CO₂ fracturing, increased heavier oil recovery was observed while lighter compositions decreased, indicating that CO₂ mobilized the trapped oil. The water/oil ratio dropped from 21.4% before fracturing to 12.2%. CO₂ concentration increased in the gas phase from 4.5% to 63%. After mixing, the injected CO₂ mobilized the trapped heavy oil and enhanced oil production.

Figure 6. Recorded Well H87-22-4 pressures during and after fracturing, showing that the bottom hole pressure was greater than the CO₂-oil miscible pressure. (Wang et al., 2016)

2.3. Conclusions

Four field tests using LCO₂/sand (a CO₂ thickener, fluorinated acrylate styrene was added) were conducted at the Jilin Oilfield in 2015, with three wells for re-fracturing and one well for new fracturing. These tests demonstrated the following:

- *The LCO₂/sand fracturing worked well for re-fracturing.* Oil production significantly increased for all 3 re-fracturing wells. The average oil production increased 2 to 3 times compared to that before re-fracturing. However, the new well fracturing did not work. We will obtain more information in the next step.
- *Increased heavy oil composition was observed in the recovered oil, indicating CO₂-oil mixing and oil mobilization.* The bottom-hole pressure is above the measured minimum miscible CO₂-oil pressure.
- *Direct thickening of LCO₂ using fluorinated acrylate styrene (practically the only polymer that has reasonable solubility in LCO₂) did not work.* It increased LCO₂ viscosity to about 5 cP at room temperature. However when temperature increased to about 40°C, viscosity dropped to 0.1 cP, equivalent to the original viscosity of LCO₂. Direct thickening of LCO₂ is not an approach that should be continued.
- *High pump rates are required* to deliver the mixture down to the bottomhole and while minimizing sand separation. This sets higher requirements on fracturing pumps while also incurring unacceptable friction.
- *High fluid loss* also due to the low viscosity of LCO₂ was observed.
- *Poor proppant carrying capacity* of LCO₂ is the key disadvantage of LCO₂/sand fracturing.

3. A Framework for Collaboration Toward a China-funded Field Test

The following is a draft proposal for U.S.-China joint research on the subject of CO₂-based hydraulic fracturing as an additional joint project in the current CERC-WET initiative. The assumption is that the project will be initiated with the start of July 2017 and will continue for the remainder of CERC-WET, about three years.

3.1. Background

Tight/shale gas/oil have become a main development subject for both China and the U.S. Hydraulic fracturing has been commonly used to stimulate these reservoirs, which leads to consumption of large quantities of groundwater, costly wastewater treatment, and environmental harm. Waterless CO₂ fracturing is regarded as an alternative technology, which provides multiple benefits including conservation of groundwater, reducing pollution, sequestration of greenhouse gases, and enhancing gas/oil productivity (by eliminating water leak-off caused formation damage, and enhancing gas/oil release). However, as liquid CO₂ suffers from its low viscosity and high friction, many problems arise in liquid CO₂ fracturing operations, such as high operating pressure, and poor proppant-carrying capacity. To overcome these problems that are

mainly caused by the low viscosity of liquid CO₂, here we propose to use CO₂-foams for the first field test.

3.2. Objectives

The objective of this joint research project is to eventually (aiming for Year 3) conduct a fracturing field test in China's Jilin Oilfield, using a CO₂-foam fracturing fluid system designed and laboratory tested by LBNL. This joint research project will benefit both U.S. and China for advancing the shared goal of developing better technologies for CO₂-based fracturing.

3.3. Approaches

For the U.S. DOE, an attractive aspect of this joint R&D project is the Chinese offer to sponsor the field test, including constructing the aboveground facility, and providing all the necessary supplies. The Chinese CERC-WET team has recently formally staffed from the Jilin Oilfield to be responsible for the field test design and for conducting the test. Another team from RIPED is responsible for aboveground infrastructure. The collaboration team-leads and responsibilities are briefly described.

US: Jiamin Wan, LBNL: Responsible for fracturing fluid system design, laboratory testing and optimizing; participating in the equipment design, field test design, and assisting analyzing field data; reporting to US DOE and CERC-WET.

China: Qinghai Yang, RIPED (China-CERC-WET Topic 2 lead): Responsible for aboveground equipment design and construction, developing the method for post-fracturing management system, and also participating the fluid system design, laboratory testing, and optimizing; Reporting to CERC-WET.

China: Jianguo Xu, Jilin Oilfield (Chief engineer and vice chair of Jilin Oilfield): Responsible for integrating the fluid system design and equipment design into the field experiment design; conducting the field experiment, analyzing the data. Xu will closely work with Wan and Yang through the entire process.

3.4. Tasks (U.S. Side)

1. Upgrade the laboratory equipment for foam generator and foam rheology studies to meet the new demands on elevated pressure, temperature, mixing under extreme conditions, and the anticipated large number of tests.
2. Provide the CO₂-foam formulations and their rheology parameters that will be tested in the field. This is the most challenging task, and the key to success. Although there is long history of CO₂-foam EOR, and many surfactants and foam formulas exist in the literature, none has been demonstrated to function at such high P and T, particularly while adequately suspending proppants. The foam fracturing fluids need to meet a set of criteria and the foam stability under such pressure and temperature is a steep challenge. We will conduct this task through the following main steps.

- **Foam formulations: design, test, and optimize**
 - *Controllable* viscosities (up to 100 cP) for different applications under different geological settings
 - Optimal foam qualities (90% to 95% of CO₂ phase)
 - Using environmentally benign, and cost effective surfactants/particulates, proppants, and additives
 - Rheology parameters of these foams
 - Varied temperature and pressure
 - Varied pump rates
 - Mixing with proppant
 - Mixing with oil
3. Quantitatively understand the relationship between fracturing-fluid rheology parameters and fracture initiation, propagation, and proppant placement. Without this understanding, fluid selection and fracturing design will remain empirical. This requires testing the performance of the new CO₂-based fracturing fluids in core-scale hydraulic fracturing lab experiments (regarding proppant transport and packing, fracture formation and connectivity, interactions with the native formation water, resource extraction, etc.).
 3. Participate the aboveground equipment design to prepare the equipment needed, and chemicals needed for the field test.
 4. Participate the field test design
 5. Participating the field test and after fracturing monitoring, and assisting field data analyses
 6. Write reports

There was a nice graph that was shown by the Chinese at the CERC meeting, showing collaboration

4. References

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