

SPE-213453-MS

Novel Carbon Dioxide (CO₂) Foamed Fracturing Fluid, an Innovative Technology to Minimize Carbon Footprint

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Copyright 2023, Society of Petroleum Engineers DOI [10.2118/213453-MS](https://doi.org/10.2118/213453-MS)

This paper was prepared for presentation at the Middle East Oil, Gas and Geosciences Show held in Manama, Bahrain, 19 – 21 February 2023. The official proceedings were published online on 7 March 2023.

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Abstract

Decarbonization is one of the greatest challenges that our nation is facing now and can be achieved by lowering the carbon footprint. This is believed to address the climate change (Miralles-Quirós et al.) and this task necessitates the development of technologies for energy production and storage, carbon capture and utilization in a very wider scale (UN FCCC, 2015). The present study is an attempt to utilize carbon dioxide in oilfield operation that does not require any equipment or infra structure other than what already present in a fracturing field location.

Hydraulic and acid fracturing treatments based on foamed fluid reduce the overall amount of liquid pumped, provide better fluid-loss control and diversion, and aid in post-treatment flowback. Foam fracturing causes less damage to formation, fracture face and proppant pack, improving the productivity of oil and gas well. Among nitrogen and carbon dioxide (CO₂) gases used to create foams, use of CO₂ is preferred over nitrogen, though it is operationally complex. Positive impact of low carbon is widely accepted and can be achieved either by producing less carbon dioxide, carbon capture and sequestration, or by its reuse. This paper will describe a novel and highly stable foam fracturing fluid based on a new Spiral Gel (S-Gel 38) polymer-foamer system that is developed to reuse the produced carbon dioxide and thus to lower carbon footprint.

Introduction

Earth's crust has about 0.02% of carbon mainly as fossil fuels, and the atmosphere contains about 0.03% of carbon as carbon dioxide. In the pre-industrial time, the level of CO₂ in the atmosphere was about 280 ppm and now it is about 380 ppm, and this increase may impact the balance of the nature. Industrialization, deforestation, population, burning of fossil fuel and biomass are some of the man-made reasons for the increased carbon footprint in the atmosphere (Fig. 1) and if it goes to the 1200 ppm toxic level, it can seriously impact the balance of nature (Hossain, 2022). As complete decarbonization is a difficult task to achieve, it may take many decades or even centuries to come even close to "net zero".

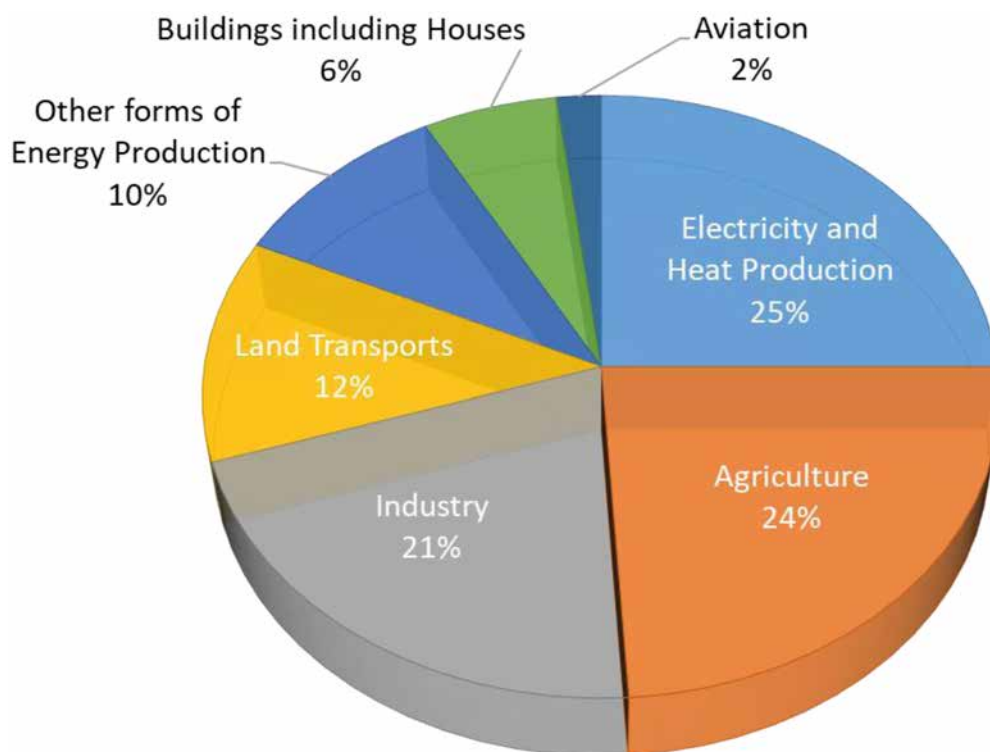


Figure 1—Man-made Carbon Dioxide Sources

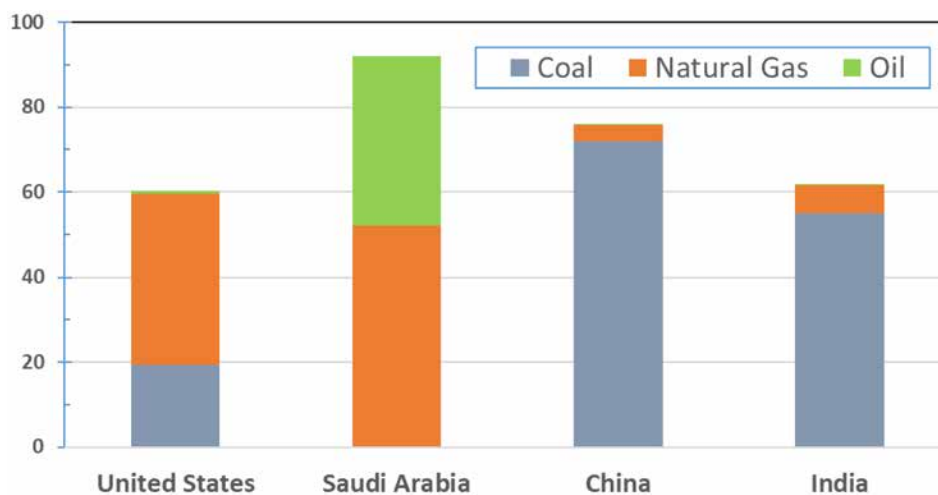


Figure 2—Percentage of Fossil Fuel Used for Electricity Generation

All energy sources including fossil fuels produce CO₂ directly or indirectly, and as responsible organizations, most oil and gas producers are challenged to release less carbon to the atmosphere. The technology that we developed and presented in this publication is a simple extension of current fracturing methodology using a new chemistry that provides enhanced suspension properties and acid frac performance at a lower cost.

Statistical analysis of America's fracturing activity in the last ten years shows that fracturing has roughly tripled in number. Other countries such as China, South Africa, Saudi Arabia and UK have started benefiting from the home-grown energy through shale development. Natural gas has 80% methane and has much higher global warming potential than carbon dioxide. In many cases, it is logistically and economically challenging to transport the produced natural gas and is the main reason for its flaring to CO₂ and release to atmosphere. However, the governments in these countries fear the excessive production of natural gas

and carbon dioxide and are planning to regulate these activities. A "fracking" ban can eliminate about 20 million jobs in the next 5 years and a huge loss of about \$2 to \$3 trillion in tax for these governments. Fracking also helps to lower oil prices and is a very important project which needs to be continued for meeting energy demand.

There is a misconception that electricity is fully clean with no carbon footprint. 60 to 90% of the electricity in major countries are produced from fossil fuels, and it will take lots of research and time to come up with a clean energy that can lead to complete decarbonization to minimize the effects on climate. Until then, we can reuse CO₂ to reduce carbon footprint, and the "hanging foam" technology presented in this paper is one innovative and affordable answer.

Fracturing of oil and gas wells started in the mid 1940's and in the past 80 years, over 2.2 million wells were fracture-stimulated globally. Fracturing has revolutionized the oil and gas industry and is the most effective way of extracting oil and gas out of low permeability reservoirs including shales. Fossil fuels on burning produce CO₂ and its increased concentration in the atmosphere is believed to impact earth's climate adversely. The oil industry is always curious about how to minimize the CO₂ release to the atmosphere and has developed CO₂ capturing and sequestration methodology, but not widely implemented due to extensive infrastructure and expertise requirements.

Flow back studies of hydraulic frac treatments have shown that more than sixty percentage of the polymer and water used are not recovered and can lead to formation damage and thus hinder production (Willberg *et al.*, 1997) especially in water sensitive reservoirs. In the past 25 years, several studies have performed to minimize or eliminate polymers in a fracturing treatment (Samuel *et al.*, 1997 & 1999) and the use of foam to carry proppant is a well accepted way of using less fluids for a hydraulic frac treatment. Oil industry has used both nitrogen and carbon dioxide together with gelling agents (polymer and surfactants) to create stable foams (Foshee & Hurst, 1965). Foams have shown better clean up efficiency than other fracturing fluids, leaving minimal damage to fracture conductivity due to water or polymer.

Until recently foam fluids typically used nitrogen as the internal phase for shallower wells and carbon dioxide for deeper wells, where CO₂ foams gave better fluid recovery than conventional gels or N₂ foams (Horton & Morgan, 1963; Hurst, 1972). There are several advantages of using foamed fracturing fluid: reduction of the amount of gelled fluids pumped into formation and improvement of fracturing fluids recovery after the stimulation treatment. Energized fracturing treatments might consume up to 80% less water compared to conventional ones. Gas released from the liquid phase after fracturing boosts flow-back and clean up in depleted reservoirs.

Though CO₂ foam has many advantages, it is not widely used because of its incompatibility with the conventional fracturing fluids used in the industry. Since the aqueous solution of carbon dioxide is acidic, the gelation reaction between the polymer and the crosslinking agent does not happen due to its high pH requirements. Viscoelastic surfactants (VES) and biopolymers are generally used to improve the stability of the CO₂ foamed fracturing fluid systems. Nevertheless, there are also disadvantages utilizing foamed fracturing fluids. Minor deviations in water or gas mixing rates can lead to the poor foam quality during fracturing, which means high sensitivity of fluid. It is required to have high quality chemistry.

Key point to mention regarding CO₂ is its solubility in water to produce carbonic acid and decrease in pH which cause most of gelled fracturing fluids unstable and loss of its viscosity drastically. Borate crosslinked guar systems and Zirconium crosslinked CMHPG systems are sensitive to pH and CO₂ in water systems will destabilize its crosslinking and stability of fluid especially at high temperatures (Nurlybayev *et al.*, 2023). A Diutan-based biopolymer system (Bower, 2016) is developed for linear gel system (Robb & Pauls, 2005) and for CO₂ foam applications up to 300 degF (Lin *et al.*, 2007; Pena *et al.*, 2009). To attain foam stability at these temperatures, additional surfactants, and stabilizers such as tetraethylenepentamine (TEPA) are required. Because of the specific polymer requirement, sourcing and pricing constraints, the use of this system for CO₂ foam fracturing is very limited (Das & Rahim, 2014).

Diutan gum is a polysaccharide polymer having repeating units of D-glucose, D-gluconaric acid, and 6-deoxy L-mannose (Navarrete *et al.*, 2000). Diutan gum is produced by biopolymer fermentation techniques and the specific characteristics and properties of Diutan gum may vary depending on the techniques by which it is manufactured, and thus the reproducibility from batch to batch may change dramatically (Cano-Barrita & León-Martínez, 2016). Diutan gum has a tetrasaccharide repeating unit in the polymer backbone as depicted in Fig. 3.

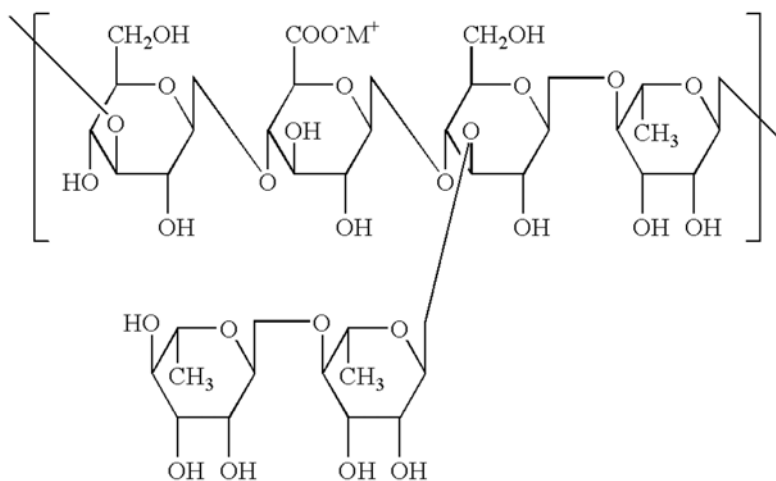


Figure 3—Structure of Diutan Biopolymer

The non-damaging nature of Viscoelastic Surfactant (VES) made it a popular fracturing fluid system in the 1990's (Samuel *et al.*, 1997, 1999 & 2000). As it is a surfactant-based system with very high low shear viscosity, it can be foamed very well and is proven to be a good fluid for foam fracturing (Hull *et al.*, 2015), acidizing (Safwat *et al.*, 2002, Al-Mutawa *et al.*, 2003 & 2005) and acid fracturing (Nasr-El-Din, *et al.* 2003). Several groups have studied the foam generated by CO₂ with VES fracturing fluid system (Chen *et al.*, 2005; Hall *et al.*, 2005; Bustos *et al.*, 2007; Arias *et al.*, 2008; Gomaa *et al.*, 2011). The gelation of VES in water is due to the interaction of surfactant with brine resulting in the formation of crosslinkable worm-like micelle structures as shown in Fig 4. (Samuel *et al.*, 1999 and Cetin & Nasr-El-Din, 2017). These worm-like micelle structure can be disrupted and can form non-crosslinkable spherical micelles with no viscosity in the presence of hydrocarbons (Samuel *et al.*, 1997). Most of the VES fluids are incompatible with CO₂ which is not because of the change in pH when CO₂ is dissolved in water. It is shown that this incompatibility is due to the solvency of supercritical CO₂ as shown in the phase diagram (Fig. 5) that disrupts the micellar structure essential for fluid viscosity. Newly formulated VES systems compatible with CO₂ are available, but not widely used as it is costly, its poor solids suspension and sensitivity to water contamination.

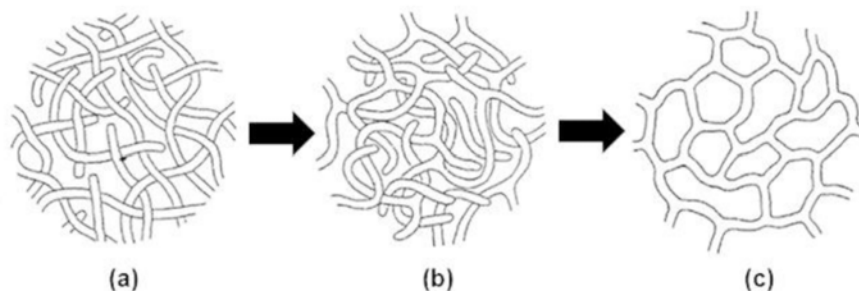


Figure 4—Different forms of Crosslinked Worm-like Micelles

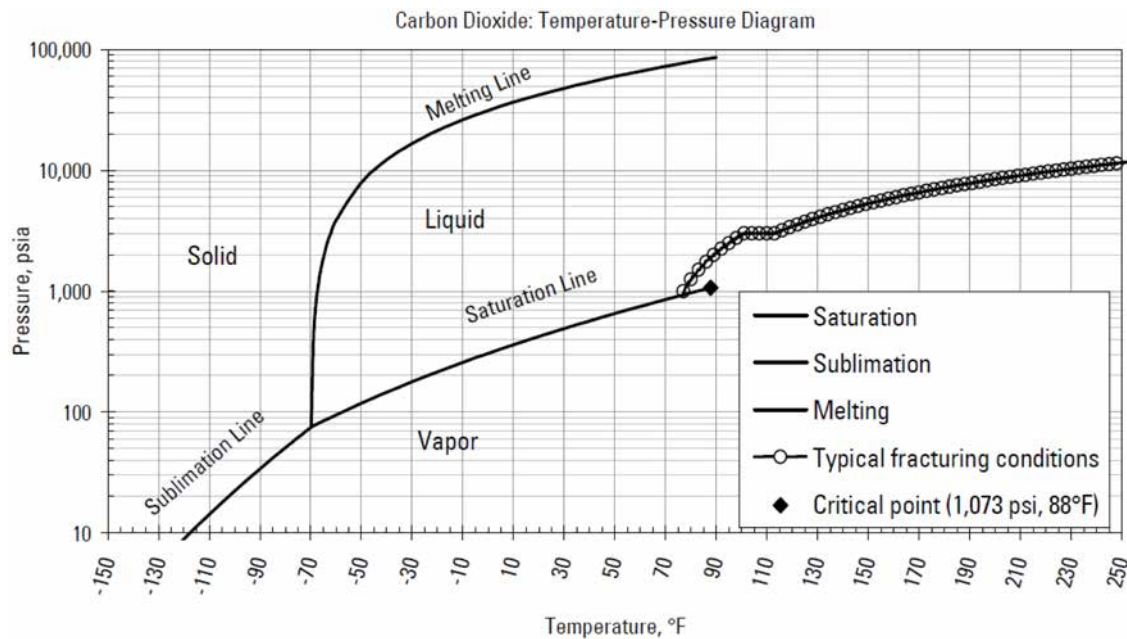


Figure 5—CO₂ Phase Diagram

Though VES and biopolymer CO₂ foam systems can be used for fracturing, they have lower viscosity even at high additive concentrations and are expensive for applications at high temperatures. To eliminate these limitations, we have developed a new CO₂ foamed fracturing fluid using a revolutionary Spiral Gel (S-Gel 38) polymer systems.

The unique S-Gel Polymer chemistry present in this paper allows the use of CO₂ for foaming a highly stable "hanging foam" with excellent solid suspension capacity. Unlike other CO₂ foam systems available in the industry, it was observed that this system provides stable foam rheology up to 300 degF. The retained permeability on cores shows significant cleanup (>70%) even in the absence of a breaker. In the laboratory, more than 70% quality foam that is stable for more than 4 hours was produced and was shown to have excellent proppant suspension capacity based on settling studies. The system performance is also found to be unaffected by pH variations, and its use in hydraulic and acid fracturing. This application can be expanded to sand control, frac packing, hydraulic fracturing of conventional and unconventional reservoirs and many other treatments.

This CO₂ foam fracturing technology allows the reuse of CO₂ more manageably with the existing equipment and design methodologies at a much lower cost when compared to other methods in the industry. This knowledge is easily expandable to global use and will show the industry responsibility to the world towards climate change.

Novel System

The newly developed "hanging foam" (Fig. 6) is made from a cationic micropolymer S-Gel 38 which has a spiral molecular configuration. Similar to other oilfield gellants, this product is also available as powder, emulsion or as a slurry in diesel or mineral oil. It is found that this CO₂ foam system has higher viscosity, require lower loading of the gelling agent and is more cost-effective than the conventional VES and biopolymer-based CO₂ fracturing fluid systems and does not require any crosslinking. Due to the structural configuration of the molecule, it has a unique ball bearing effect, and the fluid system has a much lower surface tension.



Figure 6—The New "Hanging Foam"

Experimental Procedures & Results

Base Fluid Preparation

Take the required quantity of water in a Waring blender and adjust the blender speed to create a vortex. Add the required quantity of additives such as clay stabilizer, biocide etc. to the mixing cup. Add 5, 10 or 15 gpt of the S-Gel Polymer 38 to the mixture and continue mixing for 10 minutes. This base fluid can be used for base-fluid rheology measurements or to create the CO₂ foam. Before measuring the HT rheology of the base-fluid, add the foamer and breaker to the base-fluid with a slow stirring speed to avoid foaming of the fluid in air. When using encapsulated breaker, the mixing speed must be kept very slow to eliminate the breaking of the encapsulation, and the premature release of the live breaker into the solution.

HT-HP Rheology of the Base-Fluid

The 15 gpt S-Gel polymer base-fluid mixed with the foamer is transferred to a Chandler Rheometer cup and run the rheology measurements at 275 degF at 100 s⁻¹ shear rate using the API protocol (Fig. 7).

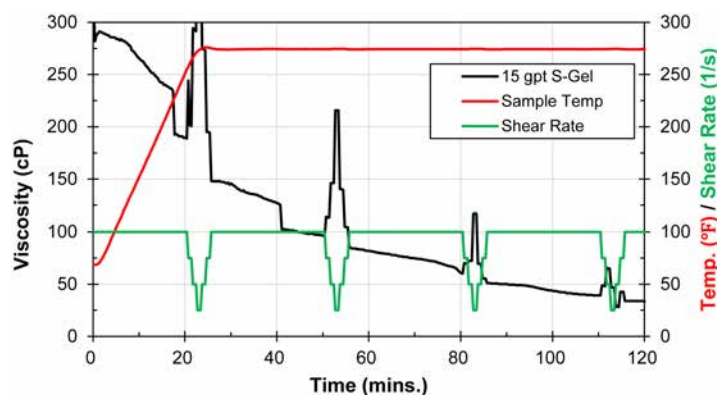


Figure 7—Viscosity of UnFoamed base Fluid (15 gpt S-Gel Polymer and 5 gpt Foamer)

The HP-HT Rheology is also performed with lower polymer loading (10 gpt) at 275 degF. The effect of breaker on the viscosity reduction as a measure of the cleanup potential is also examined (Fig. 8).

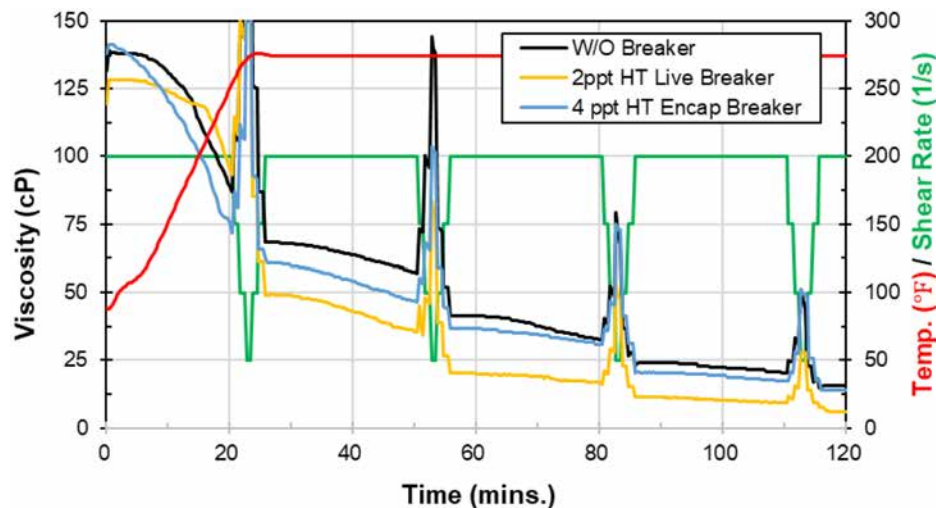


Figure 8—Viscosity of UnFoamed base Fluid (10 gpt Polymer) at 275 degF with HT Breakers

Because of the wellbore and fracture cooling, the rheology is examined on the Chandler HP-HT Rheometer with and without live LT breakers and its encapsulated versions (Fig. 9). Rheology data at both high and low temperatures indicate that the fluid has sufficient viscosity to use in acid fracturing applications as a fluid even without foaming.

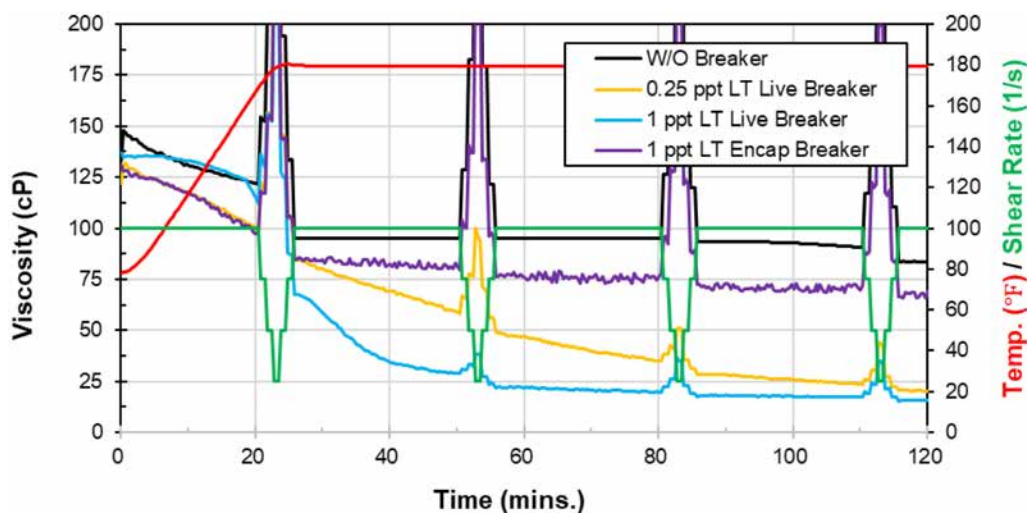


Figure 9—Viscosity of UnFoamed base Fluid (10 gpt S-Gel Polymer) at 180 degF with LT Breakers

CO₂ Foamed Fracturing Fluid Preparation (at Atmospheric Pressure): Take 100 mL of the base fluid prepared and place it in a Waring blender mixing cup. While stirring at low speed, charge the fluid with CO₂ for at least 10 mins. Using pH meter measure the pH, until the pH does not change within 3 mins. Add the required quantity of a special foamer (5 gpt is recommended) into the mixing cup and increase stirring speed above 8,000 rpm and stir for an additional minute to get the CO₂ foamed fracturing fluid.

Foam Quality and Half-Life

Measure 100 mL of the base-fluid prepared and convert that into a CO₂ foam as described earlier. Immediately transfer all the foam into a 500 mL graduated cylinder. Because of its viscoelastic and sticky nature, it is not easy to transfer all the foam to the 500 mL graduated cylinder. However, for accurate determination of foam quality and half-life, this step is very important. Record the total volume (V) of the

foam in ml (total volume is based on the reading on the top of the foam). Foam quality can be determined by using the below equation:

$$\text{Foam Quality} = \frac{V - 100}{V} \times 100\% \quad (1)$$

It is found that the quality of form is more than 70% when different loading of S-Gel is used, and the data is tabulated in Table 1.

Table 1—Foam Quality and Half-Life of CO₂ Foamed S-Gel Fracturing Fluid at Room Temperature

Description	Base S-Gel Loading (gpt)			Unit
	15	10	5	
S-Gel Polymer 38	15	10	5	gpt
Foaming agent	5	5	5	gpt
Foam Quality	>70	>70	>70	%
Half-Life	>180	>180	>180	min.

To determine the half-life of the foam at any desired temperature, place the foam taken in the 500 mL graduated cylinder to a bath set at that temperature. When using 100 mL of the base fluid, the time required for 50 mL of the base fluid to break out of the foam is recorded as the half-life (Table 1).

Rheology of CO₂ Foam at Low Temperature: Low temperature rheology of the foam at the standard atmospheric temperature and pressure (STP) is determined on a Fann 35 rheometer. The CO₂ foam is prepared as described earlier and transferred into a beaker/ graduated cylinder. The quality of foam is determined every time before continuing with the rheology measurement. The beaker containing the foam is pre-heated in a water bath at the temperature at which the rheology is measured. The foam quality after heating is also determined as there is expansion in the volume of foam at the temperature and 1 atmospheric pressure.

Once the foam is heated to the desired temperature, mix the foam using a spatula and transfer a portion of the foam to a Fann 35 cup, and determine the rheology at the temperature. Since the fluid is viscoelastic, record the steady dial reading at the various shear rates and calculate the viscosity. Experiments were repeated at different temperature using various S-Gel concentrations, and the data is shown in Figure 10.

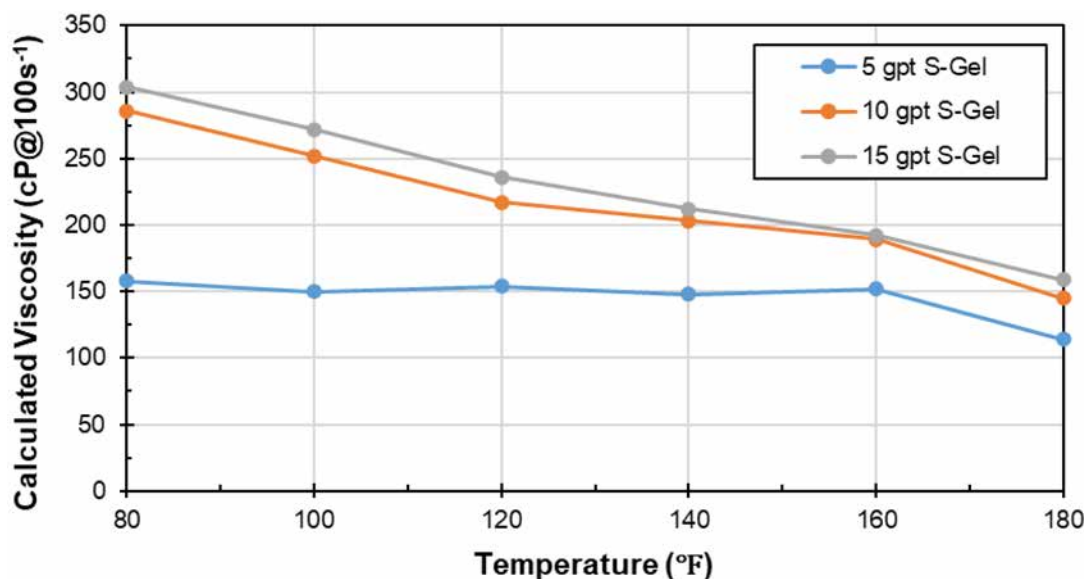


Figure 10—S-Gel CO₂ Foam Viscosity of at Various Temperatures at Different Gel Concentrations

Rheology of CO₂ Foam at HT and HP: To determine the HP-HT rheology of the CO₂ foam from S-Gel, a HAKKE MARS III rheometer was used (Fig. 11 & 12).



Figure 11—HAKKE MARS III rheometer and Key Components



Figure 12—Sample Cup and Rotor for HAKKE MARS III rheometer

The main measuring unit is a closed chamber including an internal bob, and an external bob supporting the internal bob through a bearing. The internal bob is driven by electromagnetic coupling. The bob transmits the torque it receives to the torque sensor through electromagnetic coupling to make it rotational in an angle, which is correlated to the shear stress on the bob.

To measure the HP-HT Rheology of the S-Gel CO₂ foam system, the linear S-Gel fluid (Aqueous phase) is prepared as described earlier. Take the desired volume of linear gel and add to the sample cup of the HAKKE MARS III rheometer. The Rheometer is then connected to a CO₂ Booster pump and use this pump to deliver CO₂ into the sample cup and close the valve when the pressure exceeds 7.4MPa. At this time, set the shear rate to 500s⁻¹, and continue shearing at room temperature for 5 minutes to fully mix the CO₂ and the linear S-Gel. When the foam quality reached 70%, the temperature is set to 275°F and lower the shear

rate to 100s^{-1} and run the rheometer. Continue to run until the temperature reaches 275°F . Collect rheology data during this time and for another 2 hrs at the temperature (275 degF) and is plotted in Fig. 13.

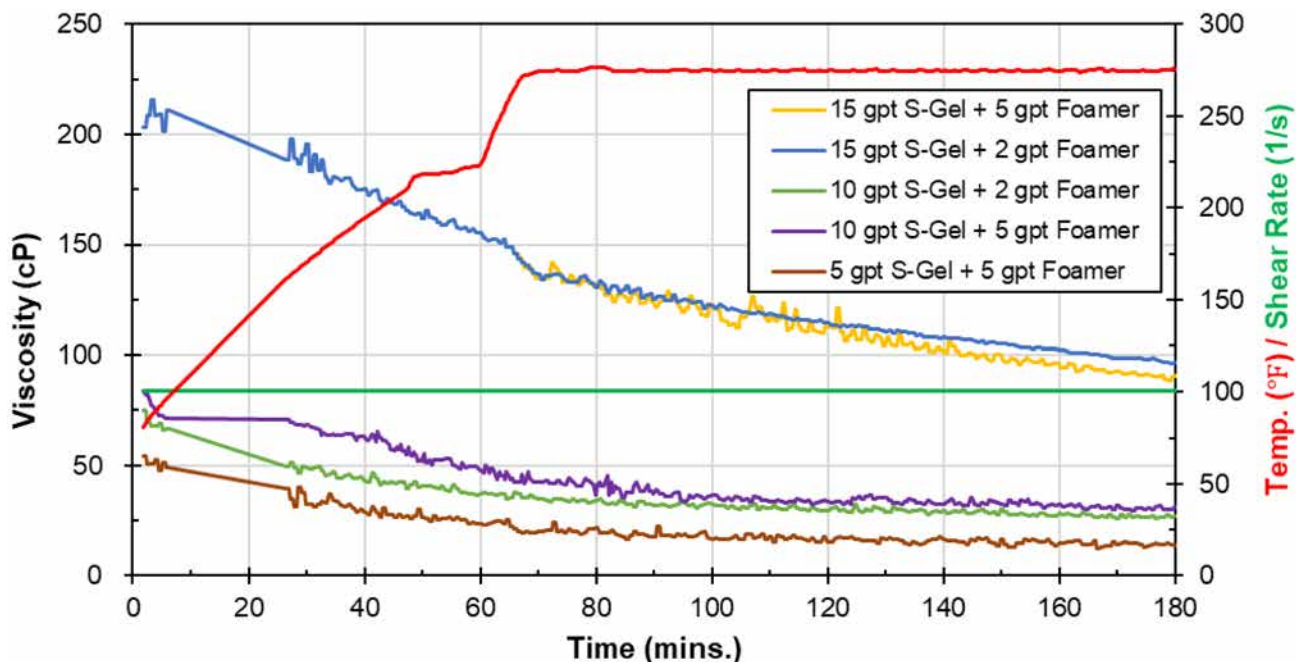


Figure 13—S-Gel CO₂ Foam HT-HP Rheology with Various Polymer Loads

Experiments are repeated with different concentrations of the S-Gel polymer at 2 and 5 gpt foamer concentration. When using 15 gpt of the S-Gel, the foam maintains the viscosity of above 100 cP for the duration of the pump time. When using lower concentrations of the foamer, the viscosity started at about 50 to 70 cP at 275 degF and declined to about 35 cP (for 10 gpt S-Gel) and 20 cP (for 5 gpt S-Gel) when exposed for 2 more hrs at 275 degF . By changing the foamer concentration, there is no significant change in the viscosity profile (Fig. 13). For hydraulic fracturing where it needs significant proppant carrying capability, 15 gpt of the S-Gel polymer may be required. However, for applications in acid fracturing and other applications, where low viscosity is required, 5 or 10 gpt of the S-Gel is sufficient.

Proppant Settling

For applications in hydraulic fracturing, examination of proppant suspension capability of the S-Gel CO₂ foam is performed. To the required amount of water in a Waring blender add clay stabilizer and biocide and adjust blender speed to create a vortex. To this add 10 gpt of the S-Gel polymer and mix for 10 mins. Charge this fluid with CO₂ for at least 10 mins. Add the foaming agent to the mixing cup and increase stirring speed above 5000 rpm and stir for another minute to create the CO₂ foam. While stirring at low speed add the required quantity of proppant (eg. 4 ppg of 40-70 Ceramic proppant) into the mixing cup, continue stirring for 2 minutes until all the proppant is uniformly dispersed (Fig. 14). Immediately transfer the slurried foam to a 500 mL graduated cylinder fitted with a lid and record the total foam volume. Close the cylinder and secure the lid with wire. Place the graduated cylinder into a water bath preheated to the set temperature and start timing. Observe and record the proppant volume settled every 5 minutes intervals for 30 minutes. Continue recording every 10 minutes intervals for another 30 minutes.



Figure 14—Proppant Suspension of the S-Gel CO₂ Foam in a Waring Blender

It is observed that there is no proppant settling in the CO₂ foam made using 10 gpt of the S-Gel polymer at 180 degF (Fig. 15). Thus, the sand setting experiment is repeated with lower concentration (5 gpt) of the polymer and found no settling of the proppant in the first 1 hr. at 180 degF.



Figure 15—Sand Settling study of 10 gpt S-Gel CO₂ Foam at 180°F using 4 ppa of 40/70 Mesh Ceramic Proppant

Fluid Leakoff under Static Conditions

Fluidloss studies were performed using unfoamed S-Gel fracturing fluid (base fluid). The leakoff was performed using a #170-55 Ceramic Filter Disc (2.5" × 0.25"). Before the study, the disc is saturated with the base fluid or synthetic formation fluid (2wt.% KCl Solution). In case of unknown formation fluid, the core shall be saturated with a non-sensitive brine solution that doesn't react with the matrix mineralogy. Place the spacer and a pre-saturated ceramic disk at the bottom of the cup of the fluid loss cell. Making sure the bottom valve is closed, introduce the base fluid into the cell to assure all the dead volume is filled and assemble the porous medium. Assemble the top and close the upper valves. Place the cell into a heat

jacket and connect the back-pressure receiver if the test temperature is above the boiling point of the fluid. Connect the pressure line to the top valve.

Start the experiment with applying a constant pressure to the cell, typically 6895 kPa (1000 psi) above the intended backpressure, by opening the top valve. Allow the fluid to reach test temperature. Optionally, a shut-in time may be applied. Once the test temperature (or completion shut-in time) is reached, open the bottom valve, and collect the filtrate into a graduated cylinder and record the collected volume as a function of time. Typically, time intervals of 1 min, 2 min, 4 min, 9 min, 16 min, 25 min and 36 min are used. The volume may be collected in a container, making sure the evaporation is minimized (the volume may be calculated from fluid mass by collecting the fluid in a tared container). This data is used for calculating the spurt loss, the fluid-loss coefficient or the completion fluid's filtrate viscosity.

A graph is constructed by plotting the filtrate volume versus time in minutes using rectilinear coordinates. A plot of the data is linear if the fluid loss is viscosity controlled. If the fluid loss is wall-building, the plot will be non-linear with respect to time, and it will follow the square root of time.

Viscosity-controlled Leakoff Coefficient

If the leakoff plot is linear through the origin, the filtrate viscosity, μ (cP), at test temperature, is calculated according to Equation (2):

$$\mu = \frac{kA\Delta P}{QL} \quad (2)$$

Where:

K — the permeability to liquid, D;

A — The cross-sectional area of porous medium surface exposed to liquid, cm²;

ΔP — The differential pressure across the filtration medium, atm;

Q — The flow rate, cm³/s;

L — The length of filtration medium, cm.

Using the calculated filtrate viscosity, the fluid-loss control coefficient, C_V (ft/min^{1/2}), due to fluid viscosity, can be determined using the general Equation (3):

$$C_V = 0.0469 \sqrt{\frac{k\phi\Delta P}{\mu}} \quad (3)$$

Where:

k is the permeability to liquid, D;

ϕ is the effective porosity of the filtration medium, dimensionless fraction;

ΔP is the differential pressure across the filtration medium, psi;

μ is the viscosity of the filtrate at test temperature, cP.

Wall-building Coefficient: When the plot of filtrate volume versus time is non-linear, then plot the filtrate volume, expressed in milliliters, against the square root of time. Using the last three data points collected (typically 16 min, 25 min, 36 min), project a straight line back to the ordinate axis to obtain a zero-time intercept visually and to calculate the slope of the line. Alternatively, one may use the least square error to calculate the intercept and slope. The slope, m , for the three data points, is calculated as given in Equation (4):

$$m = \frac{3 \sum_{i=1}^3 t_i v_i - \sum_{i=1}^3 t_i \sum_{i=1}^3 t_i}{3 \sum_{i=1}^3 t_i^2 - \left(\sum_{i=1}^3 t_i \right)^2} \quad (4)$$

Where:

t_i is the square root of time;

v_i is the filtrate volume eluted at time t_i ;

i is the number of the data point, 1 to 3.

The intercept, b , is calculated as follows:

$$b = \bar{v} - m\bar{t}_i \quad (5)$$

Where:

\bar{t}_i is the average of the square root of time readings;

\bar{v} is the average of the volume eluted readings.

Using these two values, calculate the wall-building leakoff coefficient, C_w (ft/min^{1/2}), as given in Equations (6) and spurt loss, S_L (gal/ft²), as given in Equations (7):

$$C_w = 0.0164 \frac{m}{A} \quad (6)$$

$$S_L = 0.246 \frac{b}{A} \quad (7)$$

Where:

m is the slope of the fluid-loss curve, (cm³/min^{1/2});

A is the cross sectional area of the filter medium, cm²;

b is the value of filtrate volume at $t_i = 0$ from the fluid-loss curve, cm³.

The results of leakoff volume (mL) against time is plotted (Figure 16) and showed a linear relationship indicating a viscosity controlled leakoff when using S-Gel as a fluid. The leakoff of foamed fluid is expected to follow a similar behavior, but not confirmed in the laboratory.

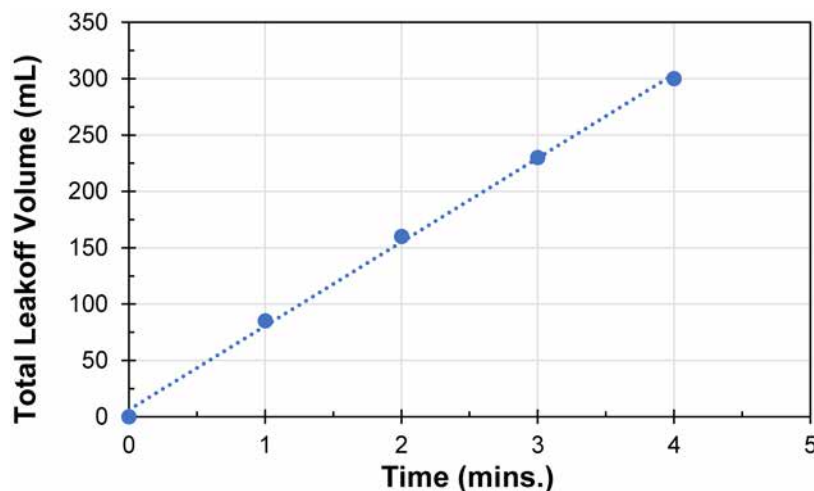


Figure 16—Fluidloss plot when using unfoamed 10 gpt S-Gel Fluid System

Regained Permeability

The formation damaging tendency of this fluid is determined by evaluating the regained permeability of a Berea Sandstone core from the Kocurek Industries (USA) using frac fluid treated with low temperature breaker to break the S-Gel completely. To the prepared unfoamed S-Gel fracturing fluid in a glass bottle, 2 ppt of live ammonium persulfate breaker is added and leave that in a water bath preheated to 190 degF until the gel is completely broken to water-like viscosity (normally it will take 2 to 3 hrs). Cool the fluid to room temperature and filter it with a Whatman filter paper. Collect the filtrate of broken fracturing fluid into a 1000 mL of beaker. Repeat the process to get at least 1000 mL of broken fracturing fluid before starting the core study.

Accurately weigh 5.0% KCl and dissolve that in distilled water taken in a beaker. The mix is heated or stirred carefully until all the solids are completely dissolved. The prepared standard brine is filtered with a glass filter funnel ($\phi 100G4\#$) and degassed with a vacuum pump for 1 hour.

Before the regained permeability measurements, dry the core at 221 degF for at least an hour, cool it to room temperature and get the weight. Use standard 5% KCl brine to vacuum saturate the core and weigh the core accurately. Install the core plug on the equipment, and set the temperature to 275°F. When the temperature reaches the set temperature, displace the standard brine in the forward direction (consistent with the flow direction of the reservoir fluid) until the flow rate and pressure difference are stable. Keep the flow rate at 1 mL/min and stabilization time not less than 60 minutes. Record the pressure difference and flow rate and calculate the core permeability K_1 .

The broken fracturing fluid is then loaded into an intermediate container and pressurized with a pressure source to make the fluid enter the core from the other end of the core (opposite to the flow direction of the reservoir fluid). When the filtrate starts to flow out, record the time and the cumulative volume outflow of the filtrate. When the cumulative outflow reaches 4-5 times of the pore volume, close the valves at both ends of the gripper to keep the fracturing fluid in the core for 2 hrs at temperature.

Following the steps listed above, displace the standard brine water in the production direction (consistent with the flow direction of the reservoir fluid) again until the flow rate and pressure difference are stable for more than 60 minutes, record the pressure difference and flow rate, calculate the core permeability K_2 after the treatment with the broken frac fluid.

Core permeability calculation:

$$K = \frac{Q\mu L}{\Delta p A} \times 10^{-1} \quad (8)$$

Where:

K is core permeability, μm^2

Q is flow rate, cm^3/s

μ is viscosity of standard brine at experimental temperature, $\text{mPa}\cdot\text{s}$

L is length of core plug, cm

Δp is pressure difference, MPa

A is cross-sectional area of core plug, cm^2

Regained Permeability Rate Calculation:

$$\eta_d = \frac{K_2}{K_1} \times 100\% \quad (9)$$

Where:

η_d is Regained permeability rate, %

K_1 is core permeability before damage, μm^2

K_2 is core permeability after damage, μm^2

It is found that when 15 gpt of broken nonformed S-Gel is used for the regained permeability study at 275 degF on a 32 mD Berea core, the regained permeability was 65.9% (Fig 17). While under the same conditions, a 5 gpt of the same fluid on an 80 mD core resulted in about 97.1% regained permeability (Fig. 18). A summary of the tests and results are summarized in the Table 2.

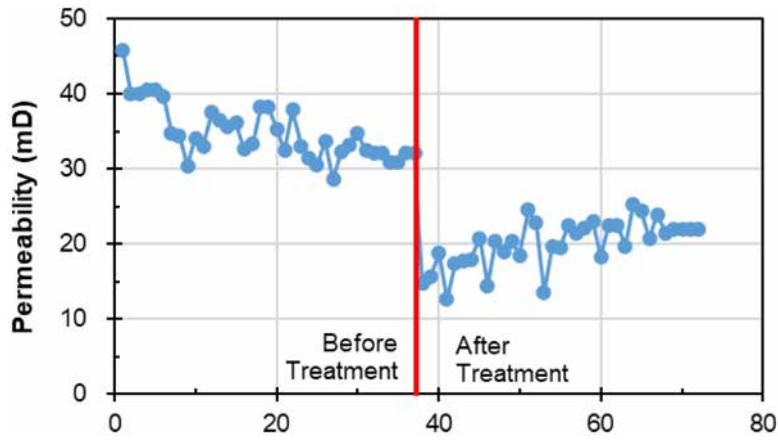


Figure 17—Regained Permeability of 15 gpt S-Gel on a 32 mD Berea Sandstone Core

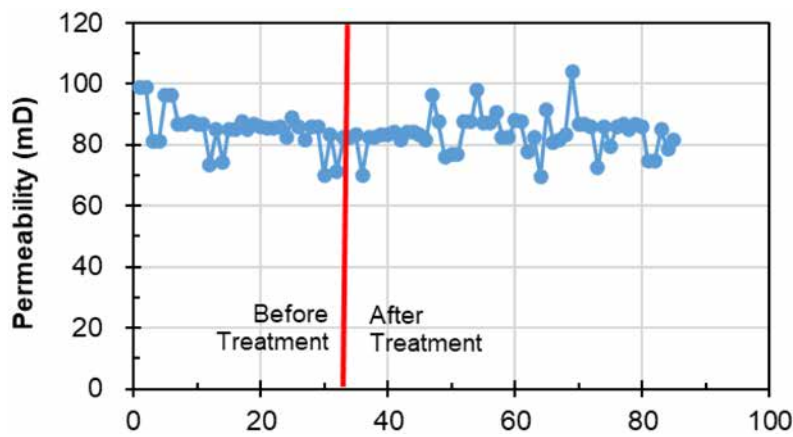


Figure 18—Regained Permeability of 5 gpt S-Gel on an 80 mD Berea Sandstone Core

Table 2—Regained Permeability Test Results of Broken Fracturing Fluid on Berea Sandstone

Regained Permeability Study	1	2
Brine	5% KCl	5% KCl
Basic Information		
Diameter of Core, cm	2.55	2.55
Length of Core, cm	5.14	5.07
Pore Volume, mL	4.74	4.99
Viscosity of Brine, mPa s	0.3	0.3
Sandstone Core Plug	Berea	Berea
Test Conditions		
Test Temperature	275°F	275°F
Confining Pressure, MPa	6	6
Back Pressure, MPa	0.4	0.4
Test Result before Treatment		
Flow Rate, mL/s	0.017	0.0162
Differential Pressure, MPa	0.006	0.015
Permeability before damage, mD	85.55	32.1
Test Result after Treatment		

Regained Permeability Study	1	2
Flow Rate, mL/s	0.0165	0.0163
Differential Pressure, MPa	0.006	0.023
Permeability after damage, mD	83.03	21.15
Retained Permeability Rate, %	97.10%	65.90%

Surface Tension

Because of the spiral configuration of the S-Gel, it has a unique ball bearing property to reduce the surface tension of the fluid system without the addition of any additional surfactants. The recommended surface tension for treatment fluids for the oilfield should be less than 32 dynes/cm. The broken S-Gel polymer without any additional surfactants has a surface tension of about 28.0 dynes/cm, which is way below the general requirement.

Additive Compatibility

The compatibility of the new fluid with all other additives present in the various acid frac systems were examined for the S-Gel linear and foamed system as examined for VES systems before its implementation (Al-Ghamdi *et al.*, 2004). This study is the subject matter for another paper that will be published later this year.

Acid Fracturing Field Application

For the stimulation of carbonate reservoirs, it is vital to have high leakoff control system that can create deep wormholes, and it should be the prime property of an acid fracturing system. To tackle such design criteria, retardation of acid fluid system is critical and a combination of different types of gelled acid, mixtures of organic and mineral acid fluids, and emulsified acid systems are used (Nasr-El-Din *et al.*, 2008). An example of an acid frac fluid system design is outlined in Table 3. A typical acid frac treatment chart is shown in Fig. 19.

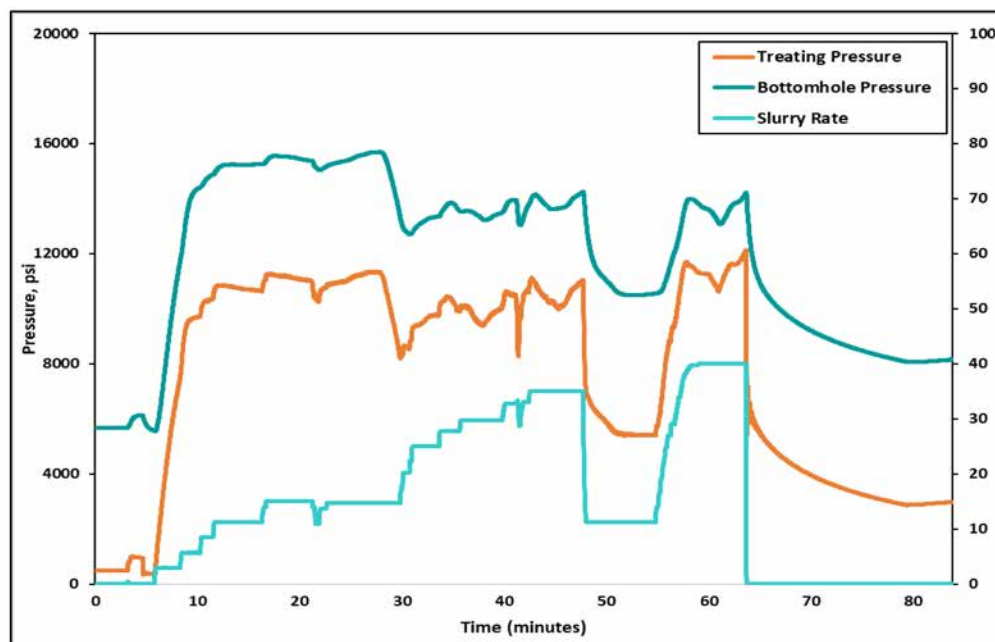


Figure 19—Conventional Acidfrac Treatment Chart

Table 3—A typical Acidfrac Treatment Stages in Saudi Arabia

Stage #	Stage Name	Fluid Type	Pump Rate (BPM)	Fluid Volume (BBL)
1	Establish injection	Treated water	10	4,200
2	Spearhead acid	HCL Acid	10	2,000
3	Pad	Crosslinked fluid	15	3,100
4	Delayed acid	Emulsified acid	15	2,600
5	Straight acid	HCL Acid	20	2,500
6	Diversion #1	Diversion fluid	20	2,600
7	Pad	Crosslinked fluid	25	3,100
8	Delayed acid	Emulsified acid	25	2,700
9	Straight acid	HCL Acid	30	2,500
10	Diversion #2	Diversion fluid	30	2,600
11	Pad	Crosslinked fluid	35	3,100
12	Delayed acid	Emulsified acid	35	2,700
13	Straight acid	HCL Acid	35	2,500
14	75% Over-Flush	Treated water	40	5,625
15	Flush	Treated water	40	7,500
16	Shut-in			
Total Treatment Volume Used				37,625 BBL

Historically one of the first handling of liquified CO₂ and N₂ in stimulation treatments was in the 1960s by Moran & Horton (1963) and Foshee & Hurst (1965) and others. During these periods energized fluids proved their effectiveness in low bottomhole pressure formations, as the high energy spread by the gasses capacitates swift cleanup of stimulation fluids from the reservoir and becomes cost-efficient compared to conventional flow-back methods. However, pumping energized fluid (specifically CO₂) requires additional pumping and support equipment, which means the challenge of not only operational complexity but expensive capitalization. Pumping the foamed fluid systems also requires more area for spotting the fracturing equipment compared to conventional acidfrac equipment layout (Yudhin *et al.*, 2023) in a field location (Fig. 20), and it is worse in the case of offshore operations.

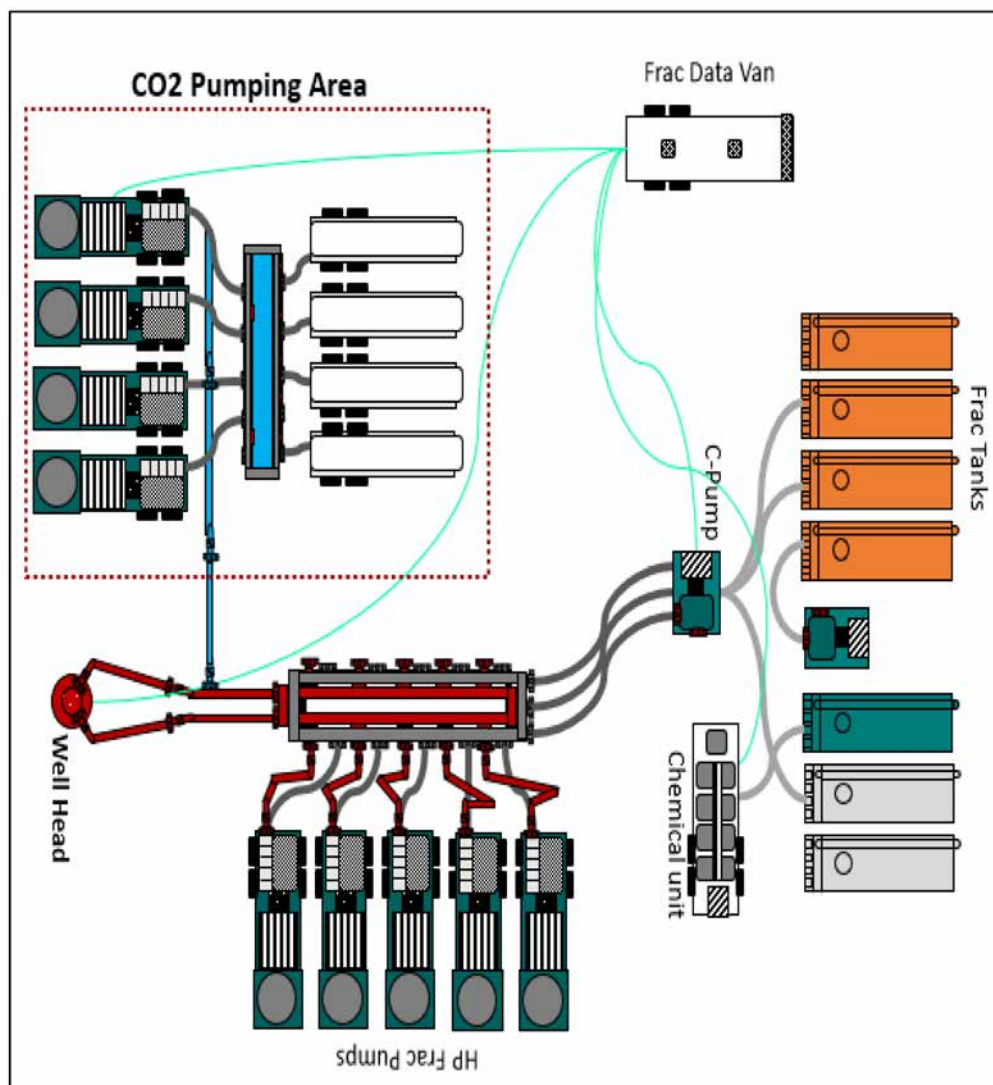


Figure 20—CO₂ Fracturing Equipment Layout

A typical foamed acid fracturing application utilizing Nitrogen uses more or less similar fluid systems as conventional. However, when CO₂ is used the systems needs to be compatible with CO₂, and the S-Gel system described here is compatible typical CO₂ foam acid fracturing job, and the PAD stage will be initially replaced with the S-Gel foam system as shown in Table 4. A typical foamed acid frac treatment chart is presented in Fig. 21. Since this new system is compatible with acid, the Diversion Fluid and VES Acid (Chang *et al.*, 2007) will also be eventually replaced with the S-Gel system containing acid.

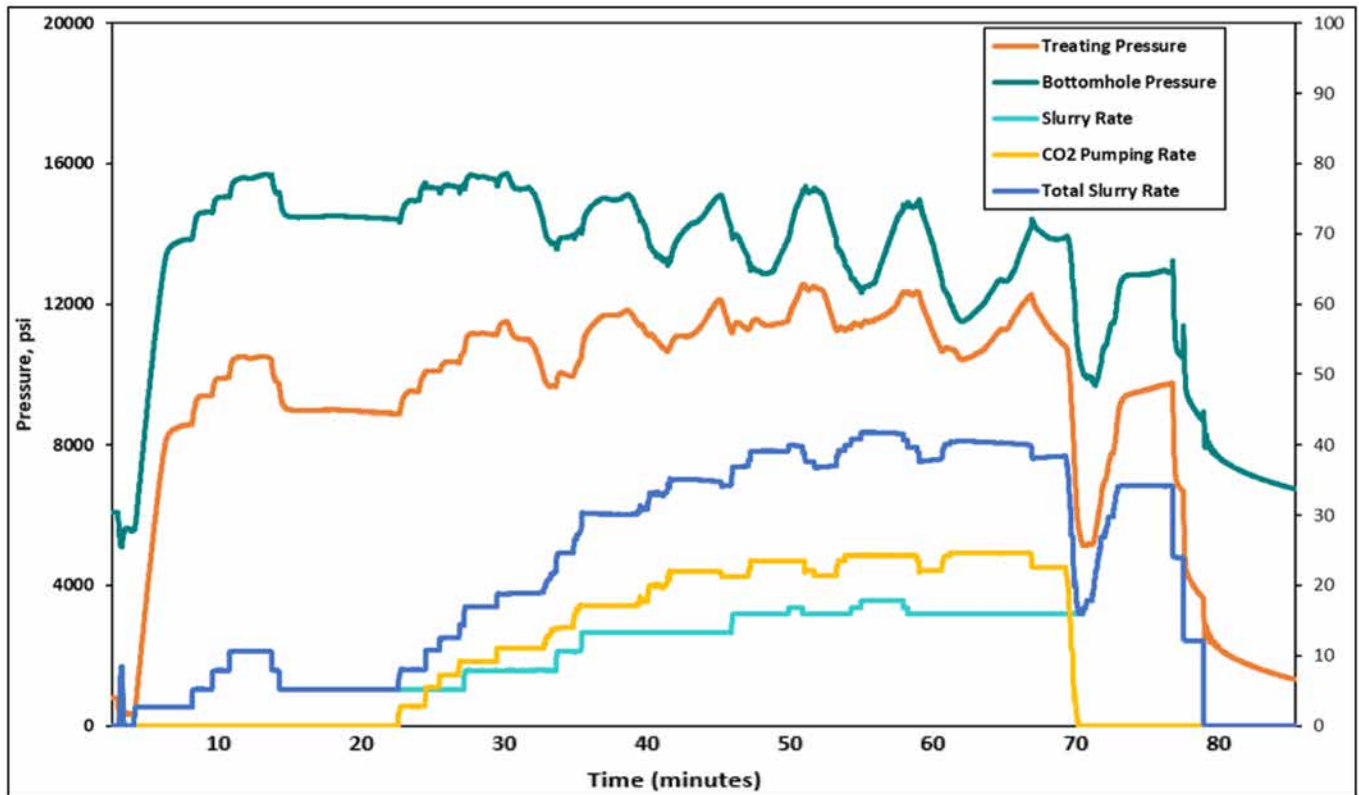


Figure 21—CO₂ Acidfrac Treatment Chart

Table 4—Acid Frac Stages for a CO₂ Foamed Treatment using S-Gel.

Stage #	Stage Name	Fluid Type	Pump Rate (BPM)	Liquid Rate (BPM)	CO ₂ Rate (BPM)	Clean Fluid Volume (Non-CO ₂) Gal	Foam Volume (Gal)	Foam Quality [%]
1	Cool down stage	Treated Water	10	10	0	3150	3150	0
2	Acid-0	HCL Acid	12	12	0	2000	2000	0
3	Acid Displacement	Treated Water	12	12	0	12500	12500	0
4	Pad-1	Foamed S-Gel	17	6.5	10	1314	3550	63
5	Acid-1	HCL Acid	17	6.5	10	1943	5250	63
6	Diversion-1	Diversion fluid	17	6.5	10	1010	2730	63
7	Pad-2	Foamed S-Gel	20	9	10	1688	3750	55
8	Acid-2	HCL Acid	20	9	10	2453	5450	55
9	Diversion-2	VES Acid	25	11	13	1275	2834	55
10	Pad-3	Foamed S-Gel	25	11	13	1823	4050	55
11	Acid-3	HCL Acid	30	13	16	2543	5650	55
12	Overflush - with CO ₂	Treated Water	44	20	24	4050	9000	55
13	Flush - no CO ₂	Treated Water	30	30	0	12000	12000	0
Total Treatment Volume Used						16,049 BBL		

In the above example, it is found that the CO₂ foamed acid fracturing treatment can lower the volume of the main treatment fluids (excluding treated water) from 37,000 bbl to 16,000 bbl, which is a significant reduction in the fluid that is pumped into a well.

Conclusions

1. The paper presented a new and unique Spiral Gel Polymer (S-Gel) for stabilizing CO₂ foam, and this fluid system has proven effective for applications in acid fracturing and hydraulic fracturing.
2. The CO₂ foamed fracturing fluid has a half-life of more than 180 minutes at room temperature, and a foam quality of more than 70%.
3. The viscosity of CO₂ foamed fracturing fluid decreases slightly with temperature, but the viscosity is greater than 100 cP even for 5 gpt system up to 180°F.
4. The viscosity of the new CO₂ foamed fracturing is higher than 70 cP even after shearing at 100s⁻¹ for 2hrs at 275 F when 15 gpt of the polymer is used.
5. Unlike other foams, this CO₂ system can produce a "hanging foam" and can suspend proppant at any concentration that needs to be used in fracturing very effectively.
6. Even 5 gpt S-Gel CO₂ foamed fracturing fluid systems have good solids suspension performance. At 180°F, there was no settling of the proppant for more than 1 hr.
7. The regained permeability of broken base fluid on Berea sandstone core is found to be more than 65 percent when high concentrations of polymer is used at the experimental conditions. At lower concentrations (5 gpt), this polymer will not affect the permeability of the rock and gave close to 100% regained permeability.
8. The fluid loss of base fluid is viscosity controlled. At 180°F, the filtrate viscosity of 10 gpt S-Gel is about 170 cP.
9. Because of the spiral conformation of the S-Gel, it has a unique property to reduce the surface tension of the fluid system without addition of any surfactants.
10. At concentrations that are normally used for fracturing, the clay stabilizers, biocide and other additives used for acid fracturing applications are compatible with the S-Gel linear gel system and the S-Gel CO₂ foam system.
11. Conventional persulfate and bromate breakers can be used to lower the viscosity of this fluid similar to guar-based fluids. Encapsulated breakers can be used to further delay breaking.
12. The treatment fluid volume (excluding treated water) of a CO₂ foam job is roughly half of the conventional acid frac treatment fluid volume. This is a significant reduction in fluid volume that can result in delivering a better well for the operator.

Acknowledgements

The authors want to acknowledge management of TAQA Frac and OPT companies for the permission to publish subject manuscript. We also thank Saudi Aramco Management for supporting this project. Thanks to Dr. Elsamma Samuel and Mr. Alexey Yudhin for proofreading the manuscript.

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