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## **Novel CO<sub>2</sub> Foamed Fracturing Fluid for Acid Fracturing: From Lab to Field Deployment**

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### **Abstract**

Carbon dioxide (CO<sub>2</sub>) foamed acid fracturing is gaining importance in maximizing flowback recovery. Under reservoir conditions, CO<sub>2</sub> is absorbed by water and transformed into carbonic acid. This paper presents a systematic approach to deploying in the field a novel CO<sub>2</sub> foamed fracturing fluid during acid fracturing.

For CO<sub>2</sub> foamed acid fracturing treatment, it is crucial to design pad stages using foamed fracturing fluids. The thermal stability of foam at high temperature is one of the main challenges. In this work, a CO<sub>2</sub> foaming acrylamide based terpolymer fracturing fluid was developed for temperatures up to 350°F. A circulating flow loop foam rheometer was used to measure the rheological behavior of foamed fluid. For successful field deployment, CO<sub>2</sub> foamed fracturing fluid was evaluated in the following sequence: chemical management, quality control, pre-job lab testing, compatibility testing, field mixing, on-site QA/QC, friction analysis and execution of main treatment.

In this study, a linear gel having 25 cp viscosity at 511 l/s share rate was prepared using a 35 ppt polymer loading. The foaming conditions were measured on site using a blender test. Static foam stability, which describes the change in foam height or liquid drainage with time known as foam half-life. Using the blender test, around 66.6% foam quality was achieved, which gave a 40-minute foam half-life. The compatibility of foamed frac fluid was also measured by mixing different ratios with acid blends and other diversion fluids. The rheological properties of CO<sub>2</sub> foamed linear gel were studied at 75% foam quality and two different temperatures. It gave 64 cp at 100 l/s at 300°F and slightly decreased to 54 cp at 350°F, measured at 2000 psi. The field performance of CO<sub>2</sub> foamed fracturing fluids was evaluated for two wells, one single stage vertical wells and another six staged horizontal well. Each stage utilized approximately 200 tons of CO<sub>2</sub>. The stability of CO<sub>2</sub> foam depends upon the optimum hydrophilic-lipophilic balance (HLB) of surfactants, and it was achieved was achieved by optimizing various formulations using suitable surfactants with fracturing fluid as an external fluid.

## Introduction

CO<sub>2</sub> in its supercritical state behaves like a gas and has liquid-like densities. This makes CO<sub>2</sub> the most preferred gas over other gases to utilize for hydraulic fracturing. Secondly, a huge amount of fresh water is being used for hydraulic fracturing, which can be mostly replaced by CO<sub>2</sub>. Not all pumped stimulation fluids are recovered following hydraulic fracturing; some water and CO<sub>2</sub> may absorb in rock under reservoir conditions, and some may react to form carbonic acid, thereby assisting in carbon capture (Aldhafeeri et al. 2023 SPE-214779-MS, Palencia et al. 2023 URTEC-2023-3969779-MS). In a technical publication in the 1960's was demonstrated that CO<sub>2</sub> can be used as acidizing agents to remove water or emulsion blocks and recover stimulating fluids (Neill et al., 1964). Implementation of foamed acid can be traced back to the 1970s to control leak-off and improve acid retardation during acid fracturing (Holcomb, 1977; Scherubel and Crowe, 1978; and Briscoe, 1979). Numerous studies from the 1980's contributed to our understanding of rheology, reaction kinetics, leak-off, etched fracture conductivity, and field deployment for foamed acid systems made of N<sub>2</sub> and CO<sub>2</sub>. (Ford, 1981; Ford and Roberts, 1985; Reidenbach et al., 1986; Anderson and Fredrickson, 1989).

In acid fracturing, acid is injected into a hydraulically created fracture. The acid flows unevenly along the fracture, leaks off into the formation, and gets reacted with by the formation. After dissipating hydraulic pressure, the fracture closes, and conductivity is maintained by an etching process where relatively undissolved regions act as pillars that leave more dissolved regions as open channels. The uneven etching along the fracture walls yields lasting conductivity after closure (Deng et al., 2012). For acid stimulation treatments to be successful, acid reactivity, fluid loss, and conductivity generation needs to be addressed during designing (Gdanski, 2005). Acid reactivity is influenced by the content and temperature of carbonate minerals, governs how quickly carbonate rocks dissolve. In acid fracturing, synthetic polymer gelled acids are employed to regulate reactivity and mass transfer. During acid fracturing treatment, it is challenging to maintain net pressure required fracture propagation as result of excessive fluid leak-off. It results in limited volume of stimulated reservoir. Viscosifying acid with polymers, surfactants, foams, and emulsions can reduce fluid loss. Gaining good conductivity generation requires reactivity management and fluid loss. Conductivity creation during acid fracturing is improved by sufficient and uneven carbonate removal (Karadkar et al. 2018 SPE-192392-MS).

Foamed Hydrochloric acid (HCl) systems have shown improvements in stimulating fluid for managing fluid loss and controlling reactivity and producing conductivity. Ford and Roberts (1985) observed that mass transfer or diffusion regulated the amount of HCl spent during foaming with N<sub>2</sub>. Foaming acid eliminates the requirement for polymers to control fluid loss (Ford, 1981). Anderson and Fredrickson (1989) found that foaming acid significantly increased fracture conductivities when comparing nonfoamed and foamed acid etched fracture conductivities for different acids and test conditions. Foaming increases the corrosive impact and aids in removing fines from the fracture face. The published research demonstrating the enhanced application of foamed acid for acid fracturing was compiled by Karadkar et al. (2018).

Foam is characterized by mainly three parameters: quality, texture, and rheology (Hutchins and Miller, 2003). Foam quality, % ( $\Gamma$ ) at a given temperature and pressure, is determined using the following equation:

$$\Gamma = \frac{100V_g}{V_g + V_l} \dots\dots\dots(1)$$

where  $V_g$  is gas volume and  $V_l$  is liquid volume.

In this paper, a new CO<sub>2</sub> foamed fracturing fluid based on an acrylamide-based terpolymer was developed for high-temperature acid fracturing applications. The thermal stability of foam at high temperature is one of the main challenges. This was addressed by optimizing base fluid viscosity and optimizing amphoteric surfactants. For successful field deployment, a novel CO<sub>2</sub> foamed fracturing fluid was evaluated in the following sequence: chemical management, pre-job lab testing, field mixing scenarios, on-site QAQC, pumping main frac treatment, and post stimulation well performance.

## Experimental Methods

### Materials

The linear gel was prepared using 35 lb/1000 gal acrylamide-based terpolymer in mixing water obtained from a water well. The low pH buffer was used to adjust pH 5. The foaming agent used was amphoteric surfactants. The 1 gal/1000 gal live breaker was also used to break the polymer after the treatment. Liquid CO<sub>2</sub> was used from a cylinder having 99.5% purity. A booster pump was used to set the required test pressure to maintain CO<sub>2</sub> at supercritical state.

### Static foam analysis using column test

The CO<sub>2</sub> foam was generated in the liquid column by purging CO<sub>2</sub> at a rate of 0.5 liter per minute through 5-micron porous media. In a 0.5 liter graduated cylinder, 100 ml of fracturing fluid system was taken to generate 80% foam quality at the start of each experiment at room temperature and atmospheric conditions. The decay in foam height was noted with respect to time to determine foam half-life. Figure 1 shows CO<sub>2</sub> foam generated in liquid column to measure foam half-life. The foaming agent concentration was optimized using a column test before performing tests under high pressure, high temperature (HPHT) conditions.



Figure 1. CO<sub>2</sub> foam generation in liquid column.

### Compatibility tests

To study the compatibility of fracturing fluid with other fluids used in acid fracturing treatment, a 50:50 mixture was prepared and then studied for static foam analysis using blender test. To perform the blender test, a 100 ml acid blend was sheared at 5000 RMP for 30 sec and allowed to produce foam by air entrainment. These tests were carried out for a field-based on-site foam quality verification. Treated water, a 28% hydrochloric acid blend, and viscoelastic acid prepared using 15% hydrochloric acid were used in the compatibility study.

## Foam rheology testing

The viscosity of CO<sub>2</sub> foam was measured using a circulating-loop foam rheometer. It is made from a 10-foot-long, helically-coiled tube with an inner diameter of 0.25 inches. To evaluate foam stability, a 75% foam quality was maintained and adjusted. A schematic of the circulating-loop foam rheometer is shown in Figure 2. To assess foam stability, a 300 1/s shear rate was applied while retaining the foam quality, then it was lowered to 100 1/s. The viscosity of the foam was calculated using the ratio of shear stress to shear rate. The fluid is pumped at a constant rate across the coiled loop, where the rate is used to calculate the shear rate and the differential pressure across the coil is used to calculate the shear stress. A required quality of foam inside the flow loop was generated by replacing the liquid with CO<sub>2</sub>. CO<sub>2</sub> is inserted inside the flow loop in the foam generator while maintaining constant system pressure.

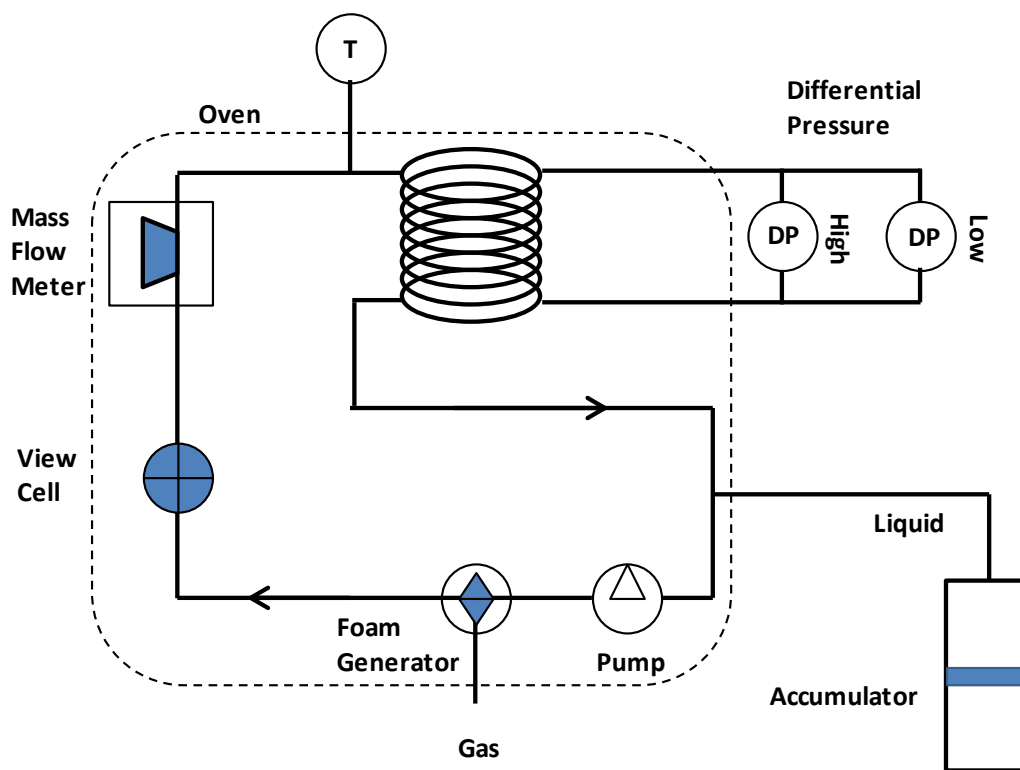


Figure 2. Schematic of circulating-loop foam rheometer.

## Results and Discussion

### Lab Developments

Polymer based fracture fluids are utilized as PAD fluid during acid fracturing treatment in order to provide fluid diversion, control leak-off, and generate the fracturing geometry. The most often utilized polymer in hydraulic fracturing are guar gum and its derivatives. Guar polymer-based fracturing fluids for high-temperature wells need to be made with a higher polymer loading and a high pH that leaves insoluble residue and promotes the formation of divalent ion scales. This study produced a novel acrylamide-based terpolymer fracturing fluid that is compatible with CO<sub>2</sub> and low pH environments. The linear gel-based fracturing fluid system consists of a foaming agent (amphoteric surfactant), a buffering agent to adjust pH of 5, and a polymer having 35 lb/1000 gal loading.

### Foam half-life

The ability of a surfactant to make foam, or its foamability, is measured by static foam stability, which measures the change in foam height over time after foam formation (Belhaj et al. 2014). When doing static foam stability tests to assess foaming agent performance, foam half-life is frequently mentioned as a technique. To evaluate the fluid system's quality and confirm its ability to produce foam, these tests can be carried out by purging CO<sub>2</sub> from the liquid column through porous media. It is allowed to grow in foam height depending on the required foam quality and decay under static conditions, and the decrease in foam height is measured with respect to time. In this study, 80% foam quality CO<sub>2</sub> foam was generated by purging CO<sub>2</sub> in a 100 ml frac fluid system to generate 500 ml of total foam volume. Figure 3 shows the percentage for decay in foam height with respect to time for frac fluid system prepared using different concentrations of foaming agent. The linear gel based on an acrylamide copolymer without a foaming agent showed foaming characteristics, which we improved by adding a foaming agent. As expected, the gel without foaming agent showed faster decay in foam. By adding only 0.2% (vol.) of foaming agent, the foam half-life was increased to 224 seconds from 64 seconds. Additionally, the use of a foaming ingredient improved the foam half-life. The foam half-life decreased slightly when 1.0% weight (vol.) of foaming agent was used, although this was taken into consideration for HPHT testing, because foam degrades thermally.

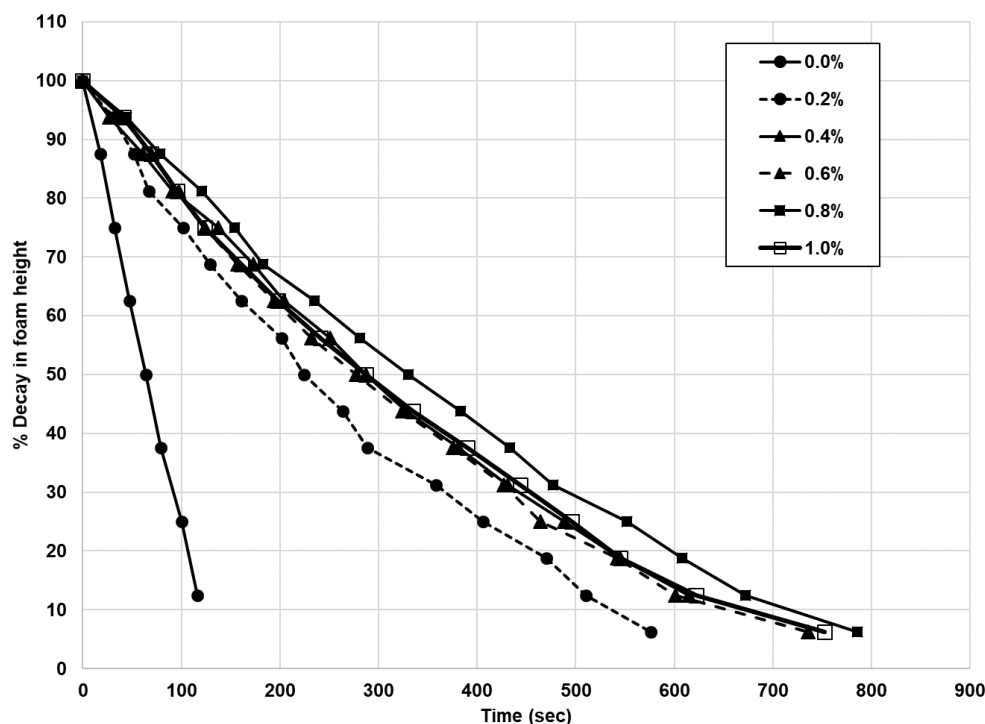


Figure 3. CO<sub>2</sub> foam half-life measurement increasing foaming agent concentration % (vol.) using column test at atmospheric conditions.

### CO<sub>2</sub> Foam Rheology

Fluid leak-off, which affects fracture width and extension, is influenced by the rheological characteristics of the fracturing fluids. Foam rheology is a time-dependent viscosity measurement governed by the external phase of the two-phase fluids system. A flowing foam will attain an equilibrium texture, which depends on the shear rate, temperature, pressure, and viscosity of the external phase. Foam rheological measurement gives structural stability of foam to optimize surfactant/stabilizer concentrations. The thermal stability of foam at high temperatures is one of the main challenges. The gas-liquid interface of foam tends to collapse

with temperature. The stability of CO<sub>2</sub> foam depends upon the optimum hydrophilic-lipophilic balance (HLB) of surfactants. After screening several surfactants, the amphoteric surfactant with the best performance was chosen for this investigation. The viscosity of foam was calculated using the Power-law model. Figure 4 illustrates the CO<sub>2</sub>-foamed viscosity composed of 35 lb/1000 gal of a linear gel made of acrylamide and 1% (vol/vol) foaming agent. Using CO<sub>2</sub>, shearing fluid at 300 1/s, 2000 pressure, and 300°F resulted in a 75% foam quality. The shear rate was reduced to 100 1/s after foam stabilization and remained there for the duration of the test. The viscosity of non-foamed fracturing fluid was stabilized to 4 cp at a 300 1/s shear rate and 300°F, which was exponentially increased to 60 cp after foaming with CO<sub>2</sub>. After dropping the shear rate to 100 1/s, the viscosity was picked up to 75 cp and stabilized to 64 cp. When the temperature was raised to 350°F, the viscosity of the foam that was produced dropped to 55 cp from a stabilized 64 cp at 100 1/s.

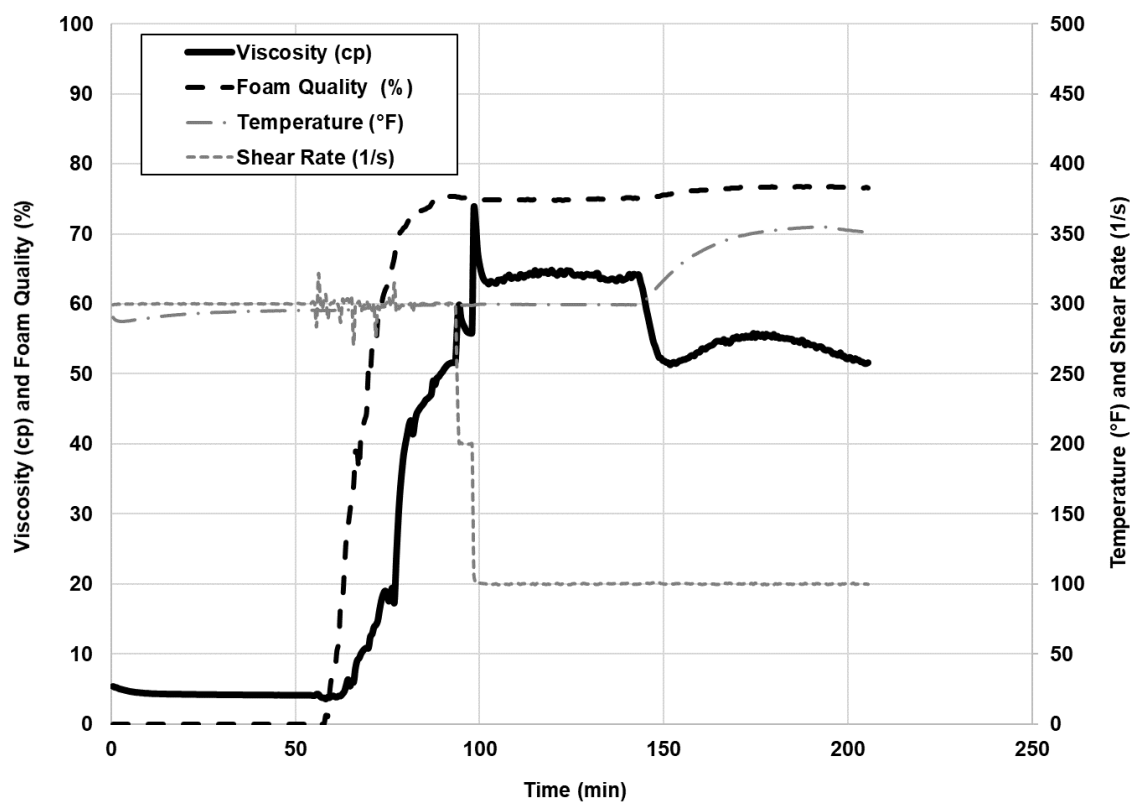


Figure 4. CO<sub>2</sub> foamed viscosity of fac fluid was measured at 300 and 350°F.

### Compatibility studies

During acid fracturing treatment, different fluid systems, such as acid, diverter, treated water, and linear/crosslinked gel are pumped. It is crucial to analyze the compatibility of foamed fluid with other stimulation fluids. Figure 5 shows the compatibility study of foamed fluid system with treated water, a 28% hydrochloric acid blend, and viscoelastic surfactant based acid diverter prepared using 15% hydrochloric acid. All fluids were mixed in a 50:50 ratio to study fluid compatibility. All fluids showed homogeneous mixtures after foam decay and did not show any incompatibility issues.

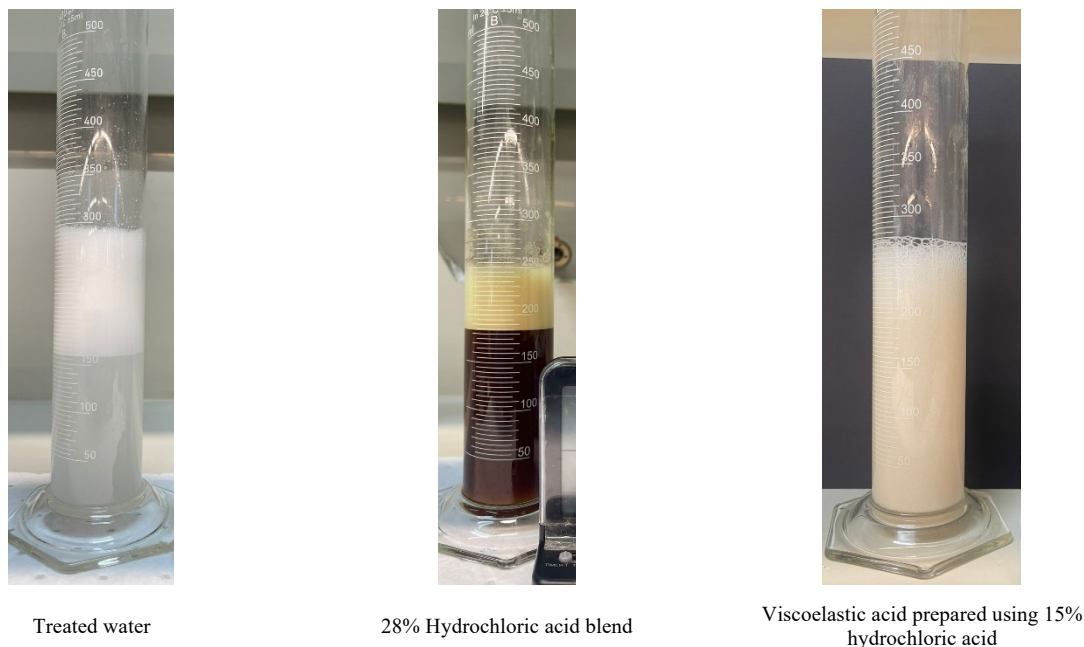


Figure 5. Compatibility of frac fluid with stimulation fluids after mixing 50:50 ratio followed by blender test.

### Field Execution

The novel CO<sub>2</sub> foamed acrylamide-based terpolymer fracturing fluid was successfully field-deployed in two different wells. The well candidate selected for first field deployment was a single-stage vertical well, while the other well was completed with six stages horizontally. Figure 5 shows the typical site layout for the CO<sub>2</sub> foamed acid frac operation. All fluid systems, such as treated water, a 28% HCl acid blend, a diverter system, and fracturing fluids, were premixed. Linear gel was prepared by adding the desired amount of polymer using a liquid additive (LA) pump. The pH of the linear gel was adjusted to 5 using a low pH buffer. The mixture was circulated for 15 minutes by using a centrifugal pump to hydrate the gel. The viscosity of linear gel was measured using Fann 35 and reported to be 25 cp at a 511 1/s shear rate and 70°F. Depending on pumping schedule, different fluids were drained by centrifugal pump from respective tanks and discharge to suction side of high-pressure manifold. The foaming agent was added on-the-fly using a liquid additive (LA) pump. The discharges from a series of pumps were connected to a high-pressure manifold supplying the well head. The liquid CO<sub>2</sub> was transported to the location using transport and loaded into CO<sub>2</sub> tanks before the job. By sucking CO<sub>2</sub> from storage tanks, sending it through high pressure positive displacement pumps, and then sending it through a high pressure manifold to the well head. The liquid CO<sub>2</sub> and stimulation fluids were mixed at the wellhead as shown in Figure 6.

On-site quality control tests were conducted to make sure stimulation fluids possessed the required quality. The strength of the HCl acid and iron content in the acid were measured before preparing a 28% HCl acid blend. The linear gel was prepared with 35 lb/1000 gal polymer loading, and the viscosity of gel was measured to 25 cp at 511 1/s at room temperature. The foamability of the foaming agent was also measured using a blender test.

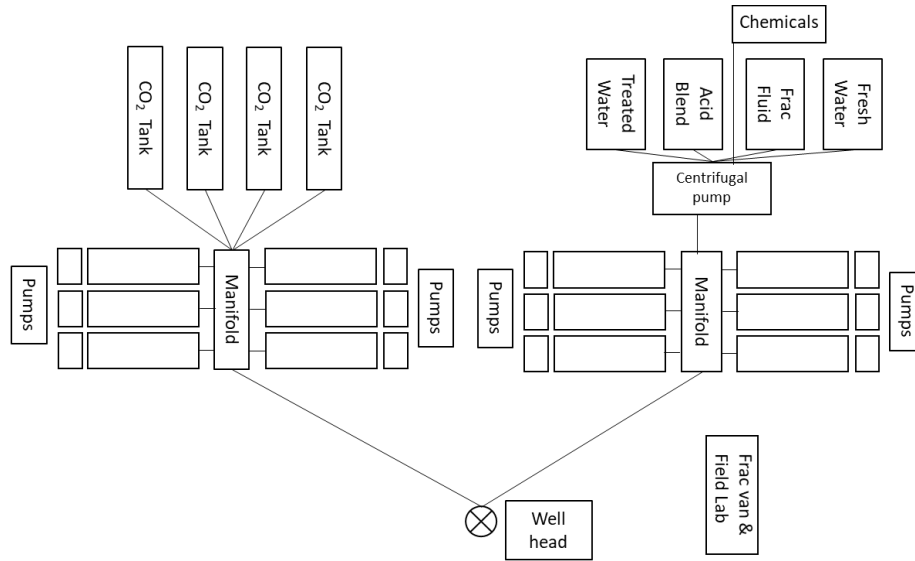


Figure 6. Typical acid frac operation site layout.

To create etching patterns in heterogeneous carbonate reservoirs, the acid-fracturing pumping schedule utilizes multiple fluid systems. Usually, the first step in the treatment process involves pumping treated water to the rock to cool down, condition it, and make it water wet. 28% HCl is pumped in after the treated water to establish injection and prepare it for the main treatment. Frac fluids, which also assist in the creation of fracturing geometry, are pumped as pad fluids to initiate and propagate the fracture, followed by acid mixtures to produce a viscous fingering effect. The Pad/acid/diverter cycles are repeated to generate irregular etched patterns over the fracture face. Fluids move to a low-permeability zone via a diverter step. Table 1 shows pumping schedule employed to one of the stages during field deployment of newly developed fracturing fluid system.

Table 1. Pumping schedule of CO<sub>2</sub> foamed acid fracturing treatment.

Sr. No.	Stage	Fluid System	Bottomhole Calculations				Surface Calculations			
			Slurry Volume	Injection Rate	Foam Quality	Liquid Stage Volume	Liquid Rate	CO <sub>2</sub> Rate	CO <sub>2</sub> Stage Volume	CO <sub>2</sub> Stage Volume
			gal	bpm	%	gal	bpm	bpm	bbl	ton
1	Injection	Treated Water	1898	4.49	0.0	1898	4.49	0.0	0.0	0.0
2	Spearhead	28% HCl	2456	3.2	0.0	2456	2.9	0.0	0.0	0.0
3	Pad	Frac Fluid	8390	10.25	56.4	3996	4.88	4.9	104.6	16.9
4	Acid	28% HCl blend	14128	19.94	65.4	4891	6.9	11.9	219.9	35.7
5	Diverter	Viscoelastic Fluid	6707	23.09	64.5	2378	8.18	13.6	103.1	16.7
6	Pad	Frac Fluid	9548	30.79	58.9	4017	12.95	16.2	131.7	21.3
7	Acid	28% HCl blend	12188	33.29	60.3	4834	13.2	18.3	175.1	28.4
8	Diverter	Viscoelastic Fluid	6545	33.28	60.3	2598	13.21	18.3	94.0	15.2
9	Pad	Frac Fluid	10088	33.28	60.3	4004	13.21	18.3	144.9	23.5
10	Acid	28% HCl blend	13400	36.67	61.4	5169	14.14	20.5	196.0	31.8
11	Flush	Treated Water	7411	32.68	44.8	4092	18.04	13.3	79.0	12.8
12	OverFlush	Treated Water	11014	35.19	0.0	11014	35.19	0.0	0.0	0.0



The main treatment plot for the CO<sub>2</sub> foamed acid fracturing treatment for the pumping schedule stated in Table 1 is shown in Figure 7. The X-axis numbers indicate the stage at which a sub-stage is beginning. A total of 203 tons of CO<sub>2</sub> and 286 barrels of 35 lb/1000 gal of fracturing fluid were pumped during the treatment. The range of 60–65% has been shown to be the highest CO<sub>2</sub> foam quality during the treatment. The treatment was pumped at a maximum total flow rate of 35.4 bpm, with an average rate of 13.8 bpm of CO<sub>2</sub> and 9.7 bpm of liquid. With the use of newly developed frac fluid systems, all planned stages were pumped without any operational problems.

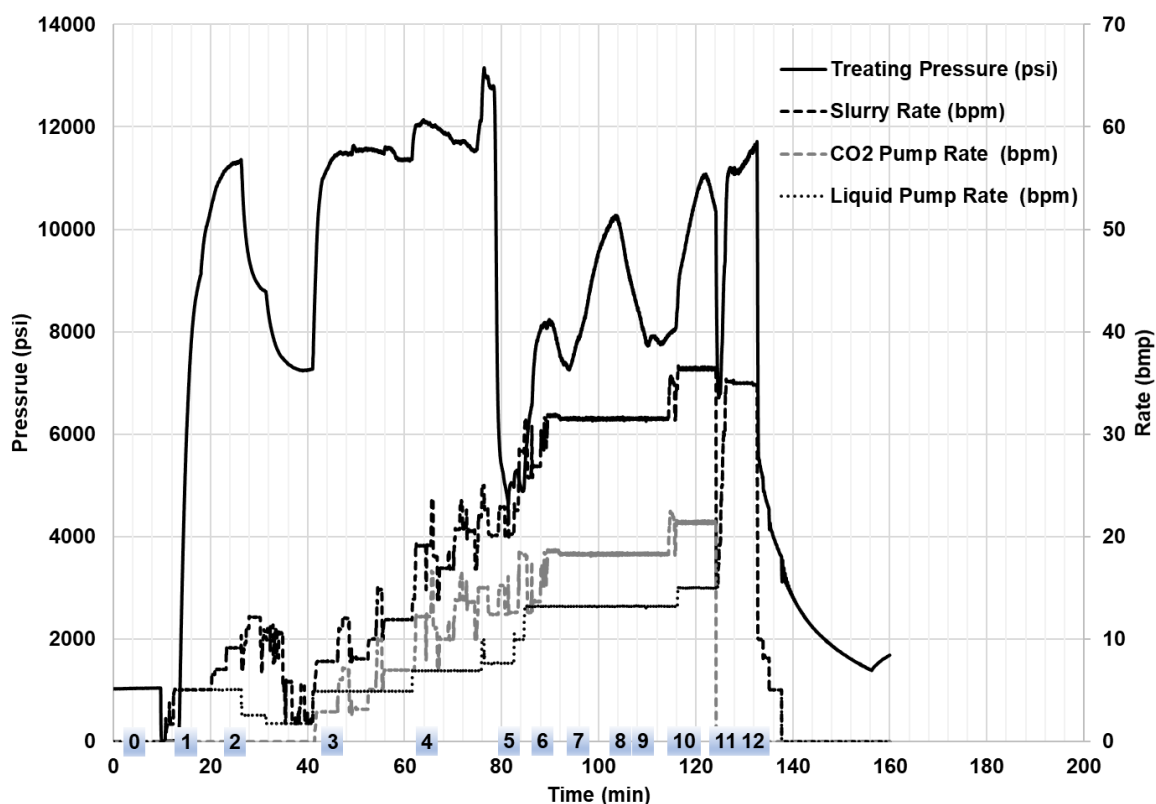


Figure 7. Main treatment plot of CO<sub>2</sub> foamed acid fracturing treatment.

### From Laboratory to Field Trials

Challenges from the field and the results of research and development provided a path to deploy a newly developed thermally stable, CO<sub>2</sub>-compatible fracturing fluid system in the field. The thermal stability of foam at high temperatures is one of the main challenges. The gas-liquid interface of foam tends to collapse with temperature. The stability of CO<sub>2</sub> foam greatly depends upon the optimum hydrophilic-lipophilic balance (HLB) of surfactants and the viscosity of the liquid. Thermally stable acrylamide-based polymer and optimized foaming agent greatly supported CO<sub>2</sub> foamed fracturing fluid to withstand temperatures up to 350°F. Different tasks to implement this new frac fluid from the laboratory to the field are shown in Figure 8. Following research and development, a pilot-scale synthesis of a polymer package was carried out in association with chemical manufacturing companies. Subtasks including bulk chemical manufacturing, MSDS preparation, transportation, import permission paperwork, chemical handling, and storage were included in chemical management duties. The fracturing fluid formulation was optimized during pre-job lab testing after a well candidate was selected based on the water source, BHST, and job design. A semi-batch mixing procedure was used, taking into consideration the equipment that was

on available. QA/QC testing of the water sample, fracturing fluid, and other stimulation systems were carried out after chemicals were transported to the site to ensure everything was going according to plan. There were no operational problems during the pumping of all seven stages in the main frac of two different well candidates. In the end, the well was flowed back for post stimulation well performance.

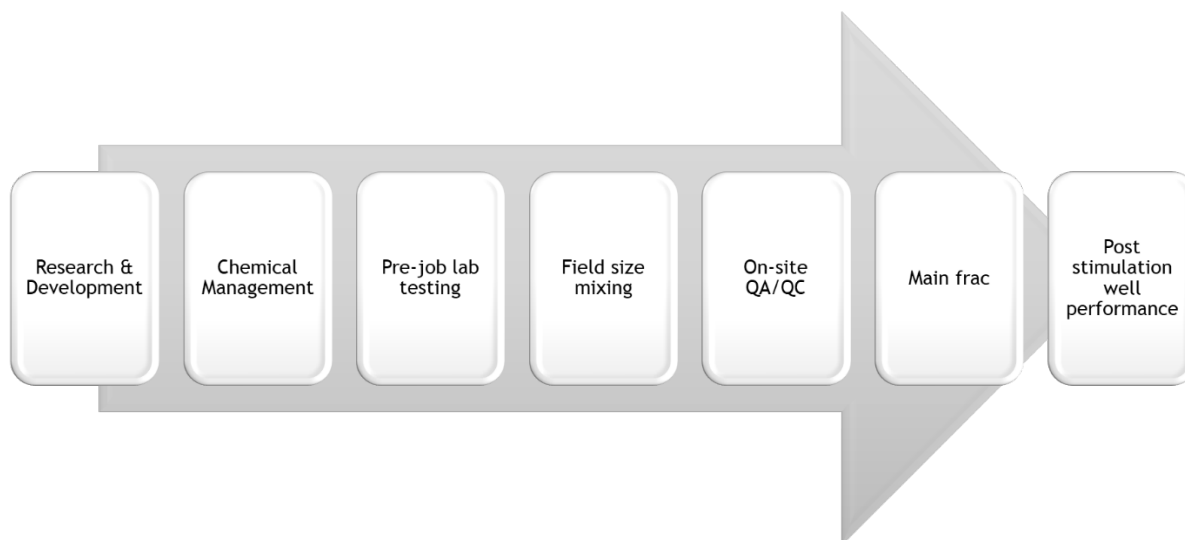


Figure 8. Different tasks involved in deployment of newly developed CO<sub>2</sub> foamed frac fluid system.

## Conclusions

CO<sub>2</sub> foamed acid fracturing using novel acrylamide copolymer based fracturing fluid system offers advantages over guar-based fracturing fluid such as lower polymer utilization and excellent CO<sub>2</sub> foam stability at high temperature. Developing from laboratory research to field implementation, the following conclusions can be drawn:

- An amphoteric surfactant used in this work showed excellent foaming characteristics.
- CO<sub>2</sub> foamed rheological studies showed excellent thermal stability up to 350°F.
- Other stimulation fluids used in acid fracturing did not show any incompatibility issues with the newly developed CO<sub>2</sub> foamed fracturing fluid system.
- Confirmation of fluid consistency in both lab and field conditions was provided by on-site quality control.
- During the main frac, a series of stimulation fluids with new fracturing fluids were pumped as per the pumping schedule.
- All seven stages in two well candidates were stimulated without any operational issues. Typically, 200 tons of CO<sub>2</sub> were used and 500 bbl of fresh water was conserved per stage.

Hydraulic fracturing using CO<sub>2</sub>-foamed fracturing fluids presented in this paper offers means of CO<sub>2</sub> utilization, freshwater conservation, faster and more efficient flowback recovery and improved hydrocarbon recovery due to CO<sub>2</sub> miscibility with reservoir fluids.

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