# Development of Nanoparticle-Stabilized Foams To Improve Performance of Water-less Hydraulic Fracturing

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# Executive summary

The overall objective of this project is to develop a new method of stabilizing foams for frac fluids, namely, the addition of surface-treated nanoparticles to the liquid phase. The research will use fluids already employed in hydraulic fracturing ($CO_2$, $N_2$, water and LPG) and commercially available nanoparticles. This report describes our recent progress in developing (1) $CO_2$-in-water (C/W) foams stabilized by silica nanoparticles and surfactant; and (2) air/water foams stabilized by nanoparticles, surfactant and a thickener, guar gum. To design low-water-content foams to serve as fracturing fluids, we first summarize known examples of $CO_2$-in-water (C/W) foams stabilized with nanoparticles (NPs). We then present the results of using surface-modified, commercially available silica nanoparticles with three carboxybetaine surfactants for generation of high viscosity $CO_2$-in-water (C/W) foams in a beadpack. By using the mixture of nanoparticles and surfactant, much higher viscosity C/W foams were produced than with either nanoparticle of surfactant alone, exhibiting remarkable synergy. Additionally, these foams produced high viscosities that were insensitive to changes in aqueous phase salinity from DI water to 3 % NaCl. The high viscosity from synergy between the nanoparticles and surfactant, shown over a wide range in salinity, is of great interest for potential field applications. Air-in-water (A/W) foams were also generated utilizing the synergy between NPs and surfactants to enhance foam stability. Generation of highly stable A/W foams with guar gum thickened aqueous phase were readily formed and shown to be more stable than foams formed without the guar gum. These findings will better guide us in designing foams that use water minimally.

## Introduction

In developing next-generation fracturing fluids that use no water or use it minimally, the following key advantages of stabilizing foam with nanoparticles will be utilized:

1. Robust stability of foam even at a fairly high internal volume fraction. This attribute is important as the foam bubbles need to be stable even when subjected to the very turbulent flow conditions during the fracture generation process.
2. Beyond the critical internal volume fraction, however, unlike the surfactant-stabilized foams, a catastrophic phase inversion occurs. When the flow-back operation begins after the completion of the fracture generation phase, the pressure inside the fracture decreases significantly, resulting in the expansion of the foam bubbles and subsequent de-stabilization of foam by phase inversion. Such de-stabilization of foam will ensure good hydrocarbon productivity from the fracture.
3. In developing the water-less, $N_2$-in-hydrocarbon foams, use of surfactant to stabilize such foams is believed to be difficult because both $N_2$ and hydrocarbon phases are “hydrophobic”. On the other hand, the nanoparticles with proper surface wettability could stabilize such water-less foams; accordingly, the initial research focus will be to optimize the nanoparticle wettability employing appropriate surfactants.

As described in our project objectives, the following two approaches will be pursued in our effort to develop the nanoparticle-based, next-generation fracturing fluids:

I. Development of a $CO_2$-in-Water Foam with Very High $CO_2$ Volume Fraction as Fracturing Fluids

Generating stable $CO_2$-in-water foams using only bare (un-coated) silica nanoparticles as a stabilizer, that maintain not only robust stability but also high effective viscosity, is generally difficult. We recently found that (Worthen et al., 2013), if a very small concentration of a zwitterionic betaine surfactant is added, very stable foams with high effective viscosity can be generated with silica nanoparticles. The main mechanism for this remarkable synergy is believed to be for the surfactant making the surface of the silica nanoparticles more lipophilic leading to the better hydrophilic-lipophilic-balance, thereby improving the foam stability significantly. Another potential benefit of adding surfactant is the possibility of changing the surface wettability of proppant grains, so that the foam bubbles may stick to the proppants. Such attachment may improve not only the transport of proppants but also reduce the gravity settling of proppants.

We are also looking into the possible addition of polymer with view to reduce the amount of water used to generate foam drastically. There is a potential that the long-chain polymer molecules may serve as a bridge between the nanoparticles adsorbed at the neighboring bubbles' interfaces, so that even if the water film between the $CO_2$/water interfaces is drained drastically, the water film does not collapse, thereby maintaining the stability of foam with minimal volume fraction of water.

## II. Development of a Water-less Hydrocarbon-based Foam as Fracturing Fluids

Because the hydrocarbon that constitutes the foam's external phase will be of low carbon numbers (such as butane and propane from natural gas liquids), the immiscibility between $N_2$ and hydrocarbon phases are critically important. Therefore, the pressure and temperature conditions during the fracturing phase and the flow-back phase, that cover as broad range of hydraulic fracturing operations as possible, need to be established. In this progress report, we first look into the question briefly, as described below.

**Hydraulic fracturing conditions.** In view of the importance of the phase behavior between $N_2$ and hydrocarbon phases, a plot of pressure and temperature for a typical hydraulic fracturing operation in a shale reservoir was generated and is given in Figure 1. Even though the pressure and temperature conditions in U.S. shale fields vary widely, this plot is a reasonable representation of the conditions at shale plays such as the Marcellus or Barnett (Fontaine, Johnson et al. 2008, Cipolla, Lolon et al. 2010, Jacot, Bazan et al. 2010, Thompson, M'Angha et al. 2011, Manchanda, Roussel et al. 2012, Elamin, Fathi et al. 2013), and is presented in the style of Friehauf (Friehauf 2009). It is envisioned that foam is injected at the wellhead (ambient T, liquid $CO_2$ conditions) down the wellbore where pressure builds due to the hydrostatic column. While flowing down the wellbore, the $CO_2$ state changes from liquid to supercritical due to the increase in temperature. At the perforations and during fracturing, the pressure is ~1500 psi higher than that at reservoir conditions to allow fracture propagation, and the temperature of the foam rises towards the reservoir temperature. After fracturing is completed, the pressure decreases due to leakoff into the reservoir, and the temperature nearly equilibrates with the reservoir. During production, the reservoir pressure is further decreased (not shown) to allow the production of hydrocarbon from the reservoir. The fracturing process is expected to last roughly 4-8 hours.

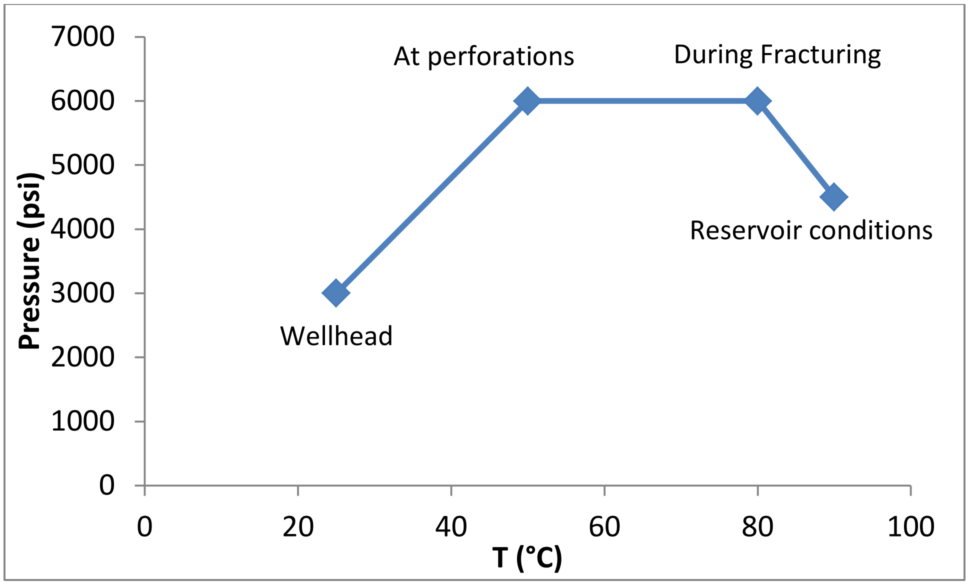


**Figure 1.** Typical pressure/temperature path for a hydraulic fracturing operation. The wellhead-to-during fracturing portion of the path defines the region where foam stability is needed. Between during-fracturing and reservoir-conditions we seek foam destabilization.

We hypothesize that the above pressure and temperature conditions are typical of those during the stages of the fracturing operation, and can be used for our initial design purpose:

(1) To formulate high viscosity foams to carry proppant down the well and into fractures, and
(2) To destabilize foam to have low viscosity after the fracturing, and the flow-back operation starts.

## $CO_2$-in-water (C/W) foam generation with silica nanoparticles

Table 1 summarizes state-of-the-art examples of C/W foams and emulsions stabilized with particles. Given are the particles used, the experimental conditions, and the shear viscosity result of various foams in a bulk state (i.e. not in porous media). A more general survey that includes results from earlier research will be assembled for future reference.

**Table 1.** Summary of viscous C/W foams or emulsions stabilized with particles.

| **Source** | **Particle (Surfactant)** | **Conditions (T, P, salinity, quality)** | **Shear viscosity (shear rate)** |
|---|---|---|---|
| (AlOtaibi, Kokal et al. 2013) | 2 % Aerosil 974 surface-modified silica (no surf.) | 93C, 1800 psi, DI water, Q = 0.50 | 2.35 cP (1200 $s^{-1}$) |
| (AlOtaibi, Kokal et al. 2013) | 2 % Aerosil 972 surface-modified silica (no surf.) | 93C, 1800 psi, DI water, Q = 0.50 | 2.5 cP (1200 $s^{-1}$) |
| (Worthen, Bagaria et al. 2013) | 1% 50 % SiOH silica particles (no surf.) | 50C, 2800 psi, DI water, Q = 0.75 | 7.25 cP (1200 $s^{-1}$) |
| DOE contract DE- | 1 % EOR-5XS surface- | 50C, 2800 psi, Synthetic | 10.5 cP (1200 $s^{-1}$) |

| | | | |
|---|---|---|---|
| DE0005917, Y3Q1 report (Bryant, Johnston, Worthen et al.) | modified silica (no surf.) | seawater, Q = 0.75 | Note: ~2 cP in DI water |
| DOE contract DE-DE0005917, Y3Q1 report (Bryant, Johnston, Worthen et al.) | 1 % EOR-5XS surface-modified silica (no surf.) | 50C, 2800 psi, Synthetic seawater, Q = 0.75 | 15.3 cP (1200 $s^{-1}$)<br>Note: ~2 cP in DI water |
| (Worthen, Bagaria et al. 2013) | 3% Short-chain PEG-coated silica (no surf.) | 50C, 3000 psi, DI water, Q = 0.90 | 15.7 cP (580 $s^{-1}$) |
| (Worthen, Bryant et al. 2013) | 1 % bare colloidal silica (0.5 % CAPB) | 50C, 2800 psi, 1 % NaCl, Q = 0.75 | 40 cP (580 $s^{-1}$)<br>Note: NPs or surfactant alone ~1 cP |
| DOE contract DE-DE0005917, Y2Q2 report (Bryant, Johnston, Worthen et al.) | 3% Short-chain PEG-coated silica (no surf.) | 50C, 2800 psi, API brine, Q = 0.75 | 59 cP (580 $s^{-1}$) |

A few general trends are clear from the information in Table 1:

1. Only silica NPs have been used to stabilize viscous C/W foams.
2. Dichlorodimethyl silane modified particles (50 % SiOH, Aerosil 972, and Aerosil 974) in DI water tend to stabilize foams of low viscosity (<10 cP)
3. Particles modified with short chain PEG or the proprietary modifiers (EOR-5XS, and EOR-12) form high viscosity (>10 cP) foams without added surfactant when used at high salinity
4. With added surfactant, even bare colloidal silica NPs can form high viscosity foams (even though the NPs or surfactant alone did not form viscous foams)

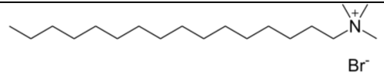
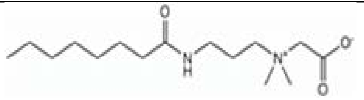
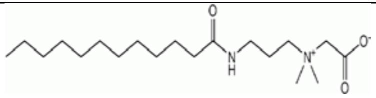
In view of the significant synergy obtained by the combined use of silica nanoparticles and zwitterionic betaine surfactants, our initial study on the generation of high-quality $CO_2$-in-water foams is to screen the effectiveness of different betaine surfactants. Guar gum, which is commonly employed as a viscosifier for fracturing fluids, is also employed as a potential additive to increase the foam quality significantly, as briefly described above.

**Materials.** Bare colloidal silica nanoparticles (SNOWTEX-30, Lot No. 230828, Nissan Chemical America Corporation) and surface-modified colloidal silica nanoparticles (EOR-5XS, Lot No. LB130204, Nissan

Chemical America Corporation) were received as a 20 % w/v aqueous dispersion. The surface-modified nanoparticles have a proprietary, covalent surface modification as provided by the manufacturer.

Cetyltrimethylammonium bromide (CTAB, solid powder) and guar gum (solid powder) were purchased from Sigma-Aldrich. Caprylamidopropyl betaine (CAPB) (Mackam OAB, batch UP1K17X18, 30 % w/v), octyl betaine (OB) (Mackam BW-139, Lot UP0G02X07, 38 % w/v), and lauramidopropyl betaine (LAPB) (Mackam DAB-ULS, Lot UP1J13X04, 35 % w/v) were gifts from Rhodia and were used as received.

**Table 2.** CTAB, CAPB, OB, and LAPB surfactant structures.

| Surfactant | Structure |
|---|---|
| CTAB |  |
| CAPB |  |
| OB |  |
| LAPB |  |

**Methods.** The foams in Table 1 (those studied by our group) were generated in an apparatus similar to that shown in Figure 2, where an aqueous phase (containing the NPs and/or surfactant) is mixed with a $CO_2$ phase, then passed through a foam generator. The foam then passes through a capillary tube viscometer and the apparent foam viscosity ($\mu_{app}$) is calculated from the measured pressure drop ($\Delta P$) with the Hagen–Poiseuille equation:

$$\mu_{app} = \frac{\pi \cdot \Delta P \cdot R^4}{8 \cdot q \cdot L} \tag{1}$$

where $R$ is the capillary tube inner radius, q is the volumetric flow rate, and L is the length between the $\Delta P$ cells. The system temperature and pressure are maintained with a water bath and back pressure regulator, respectively.

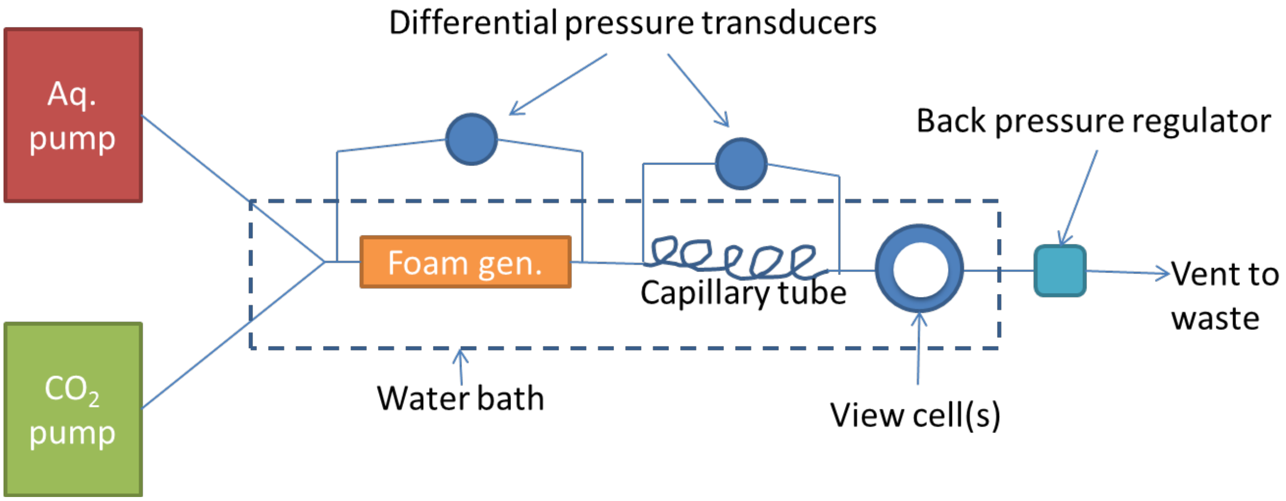


**Figure 2.** Generalized foam generation and characterization apparatus like the equipment used in the examples given in Table 1.

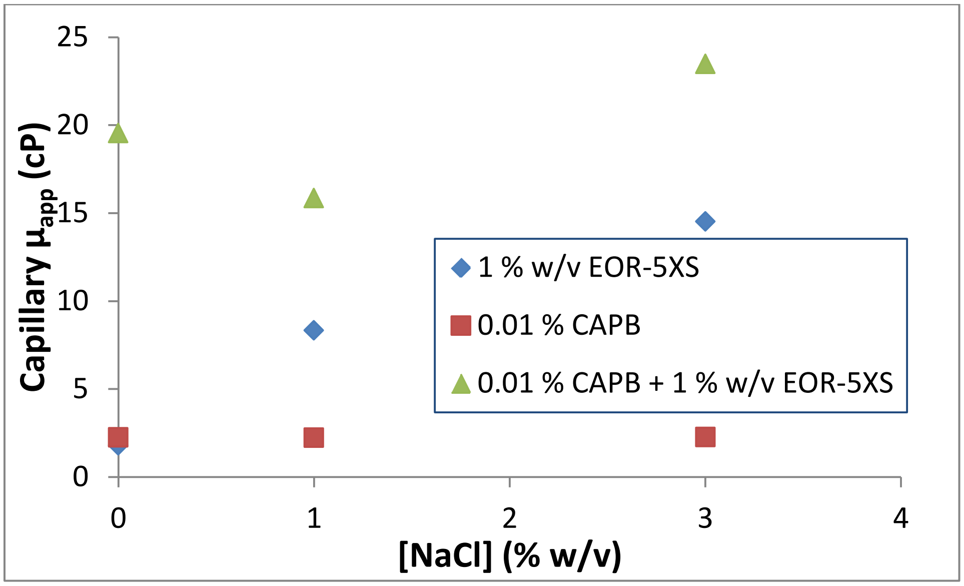
In the present study and all examples in Table 1 except those by AlOtaibi et al., the foam generator was a 4 mm ID x 113 mm long beadpack filled with 180 µm glass beads (Figure 1).

The air-in-water (A/W) foams were generated with an Ultra-Turrex T25 homogenizer with a N8G 8 mm dispersing head operating at 13500 rpm for 2 min at pH 7. SNOWTEX-30 bare silica nanoparticles at 1 wt. % and CTAB cationic surfactants of three different concentrations, 0.0036 wt. %, 0.036 wt. %, 0.36 wt. %, respectively, were used to generate stable A/W foams. Similarly, A/W foams with aqueous thickeners of 30 bbl/Mgal (0.36 wt. %) guar gum were generated following the same procedure.

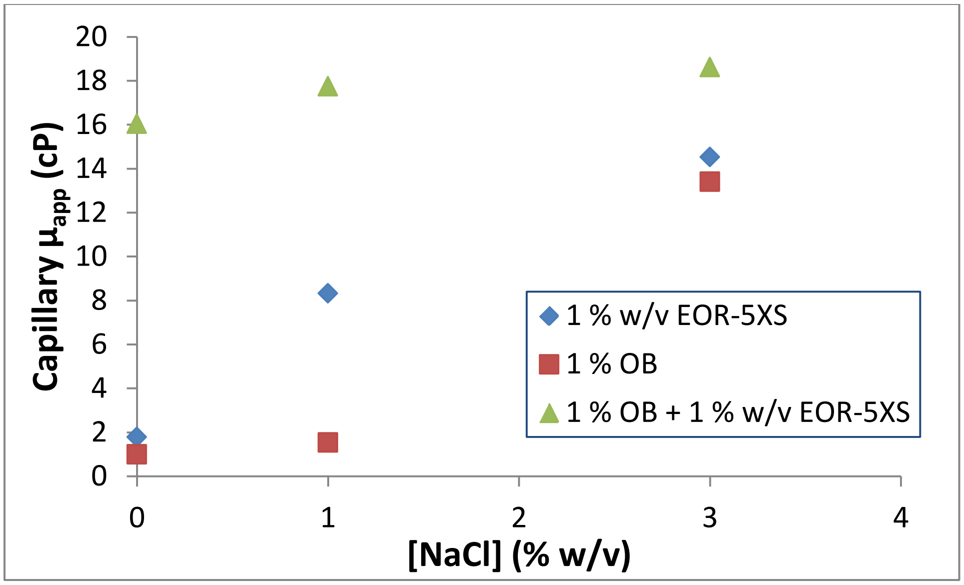
## Results and discussion

### *High viscosity C/W foams generated by mixtures of surface-modified silica nanoparticles and betaine surfactants.*

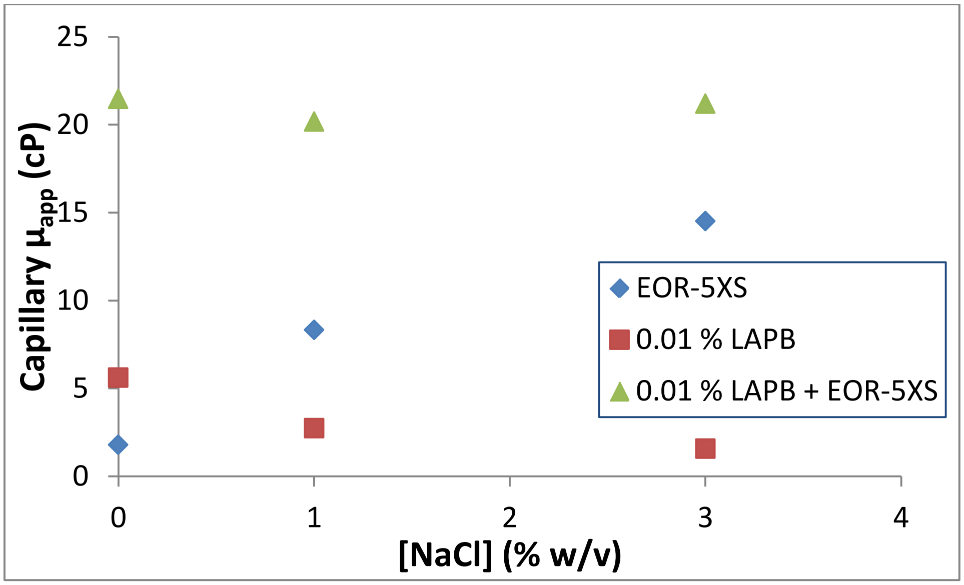
The apparent viscosity of foams produced with surface-modified EOR-5XS nanoparticles and three betaine surfactants are given in Figure 3. In Figure 3a, data for 1 % w/v EOR-5XS alone, 0.01 % CAPB alone, and a mixture of the nanoparticles with surfactant are presented. The apparent viscosity measured with the nanoparticles without surfactant was very low (1.8 cP) in DI water (0 % w/v NaCl) and no foam was visually observed. In 1 % w/v NaCl brine, the viscosity increased to 8 cP and weak foam was visually observed. In 3 % w/v NaCl brine, high viscosity foam (15 cP) was produced and fine, opaque white foam was present in the view cell, again without any added surfactant. In contrast, with 0.01 % w/v CAPB only, no foam was observed at each salinity and the highest viscosity measured was 2.3 cP. Interestingly, when the surfactant and nanoparticle were combined, significant synergy was observed where the viscosities of the foams were much higher than expected from a combination of the values from each species alone. At all salinities tested, the opaque white foams had viscosities that were insensitive to salinity (16-23 cP), despite the viscosity of the nanoparticles alone being sensitive to salinity and the surfactant not producing foam at any condition tested. In Figure 3b, parallel results are shown but with 1 % w/v OB as the surfactant. Here, the OB surfactant alone produced foams that increased in viscosity from 1 cP in DI water to 1.5 cP in 1 % w/v NaCl to 13 cP in 3 % NaCl. However, the foams produced by the mixture of nanoparticles and OB surfactant were again insensitive to the salinity and remained at 16-19 cP. In Figure 3c, a similar phenomenon is observed with LAPB where there was a significant synergy with respect to the foam apparent viscosity when nanoparticles and surfactant were combined in DI water, and the mixture again produced foams that were insensitive to salinity.



(a)



(b)



(c)

**Figure 3.** $CO_2$-in-water foam apparent viscosities measured in a capillary tube at 2800 psia, 50 °C with a of 1 % w/v EOR-5XS alone, surfactant alone, and nanoparticles mixed with (a) 0.01 % CAPB; (b) 1 % w/v OB; or (c) 0.01 % LAPB as a function of aqueous phase salinity. The shear rate in the capillary tube was held constant at 1200 $s^{-1}$.

### *Highly stable A/W foams generated by mixtures of bare colloidal silica nanoparticles and cationic surfactant with and without added guar.*

A/W foam test tube experiments at room temperature and ambient pressure were employed as screening tests to select formulation candidates for high quality high viscosity nitrogen/water foams for hydraulic fracture fluids. Foamability (initial volume of foam generated) and foam stability (decay of foam volume vs. time) were measured to compare different formulations. The images of as-generated foams, after 30min, and after 3 days are shown in Figure 4. The foamability and foam stability based on measuring the height of the foam and the height of residual water were shown in Figure 5. Clearly, CTAB is a good foamer and generated large volume of A/W foam. However, the foam stabilized by CTAB is subject to quick drainage and coalescence, as indicated by the quick decrease of foam height, and completely disappears after 3 days. Silica NPs alone did not generate foam due to the highly hydrophilic nature of bare colloidal silica. Silica NPs and CTAB mixtures show decreased foamability (decreased initial foam height) as compared to using CTAB alone, likely due to strong electrostatic attraction between negatively charge silica and cationic CTAB. Likely, a large fraction of CTAB surfactants were adsorbed onto silica NP and thus become unavailable to adsorb at the air-water interface to aid foam generation. However, the stability of the A/W foam was greatly extended with NPs present, possibly due to the large disjoining pressure of the water lamella stabilized with surfactant-modified silica NPs. Interestingly, even with the guar-thickened aqueous solution (viscosity data at 100°F given in Figure 6), A/W foams were generated following the same procedures. Enhanced foamability is observed when guar was included in the aqueous phase as compared to silica NP and CTAB mixtures with 0.0036 and 0.036 % CTAB. The creaming velocity of the air bubbles is greatly reduced due to the highly viscous nature of the aqueous phase, resulting in foams with higher stability.

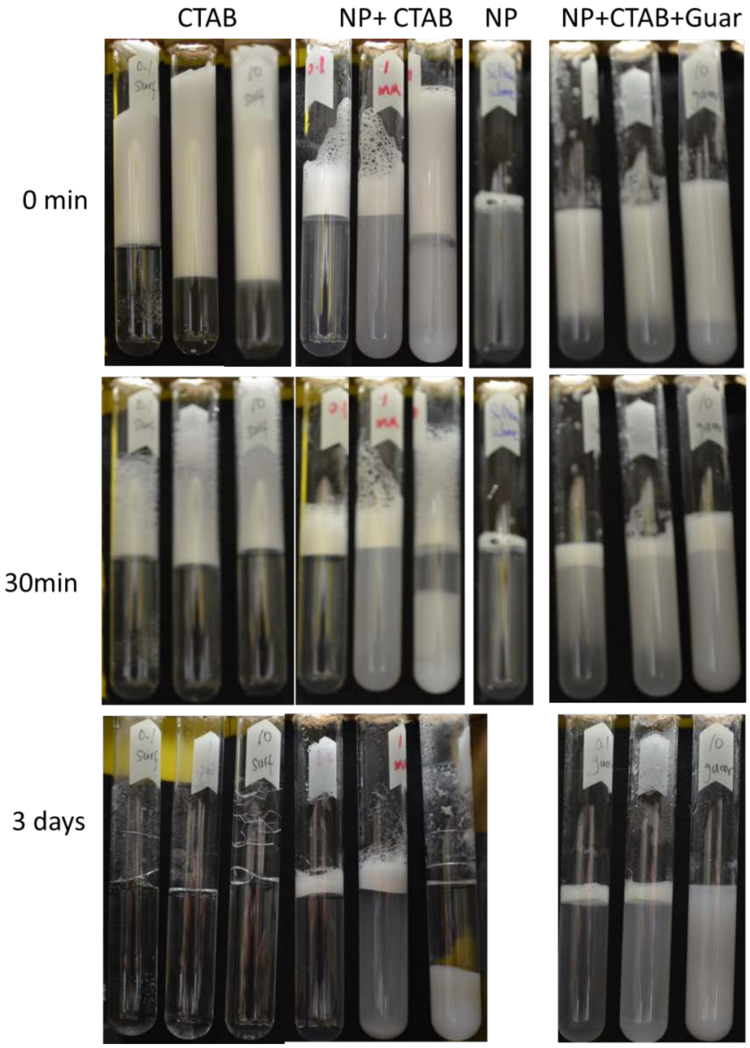
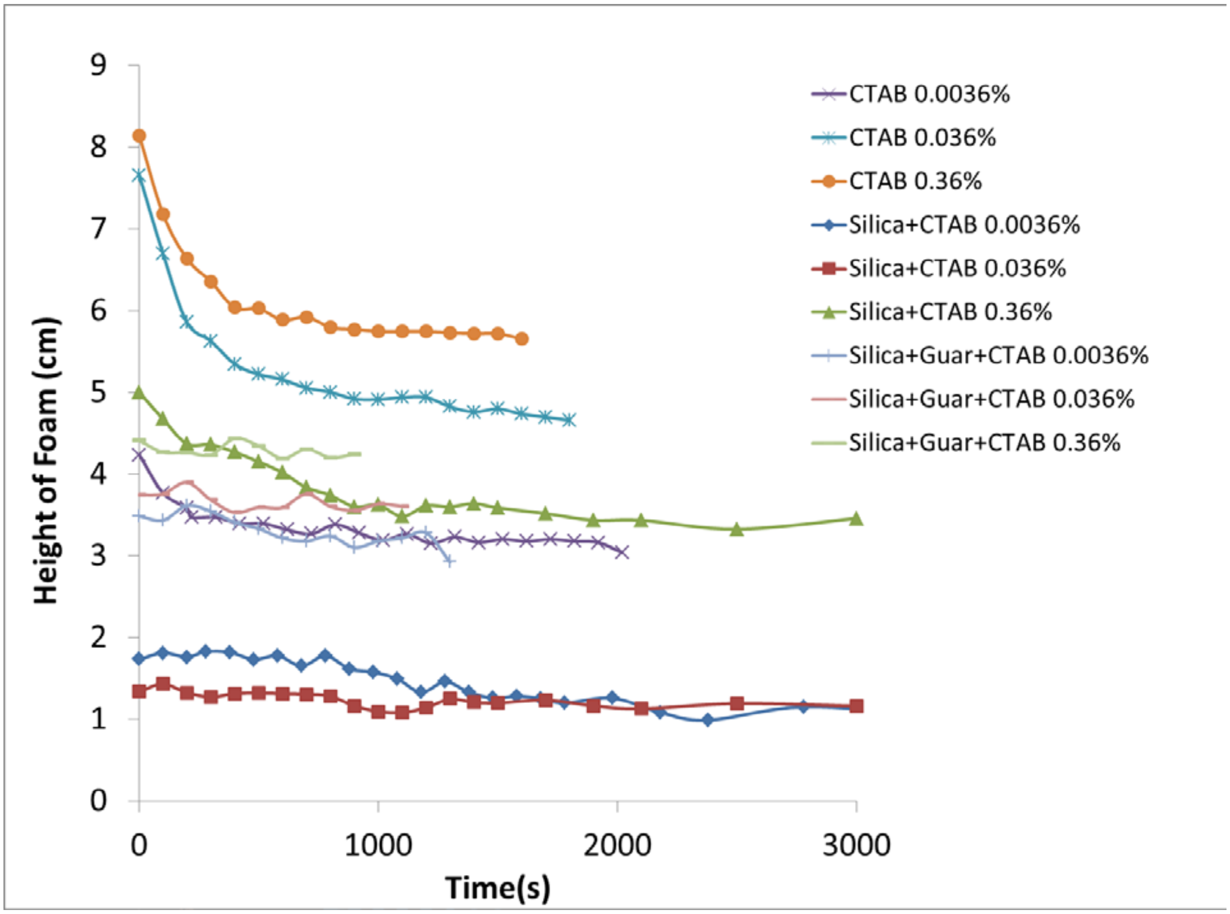


**Figure 4.** Air-in-water foams generated with (from left to right) CTAB of 0.0036 %, 0.036 %, 0.36 %, silica NPs of 1% & CTAB mixtures, silica NPs, silica NPs & CTAB & 30bbl/Mgal Guar at (from top to bottom) 0s, 30min and 3 days.


9
8
7
6
5
4
3
2
1
0
Height of Foam (cm)
0
1000
2000
3000
Time(s)
CTAB 0.0036%
CTAB 0.036%
CTAB 0.36%
Silica+CTAB 0.0036%
Silica+CTAB 0.036%
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Silica+Guar+CTAB 0.0036%
Silica+Guar+CTAB 0.036%
Silica+Guar+CTAB 0.36%

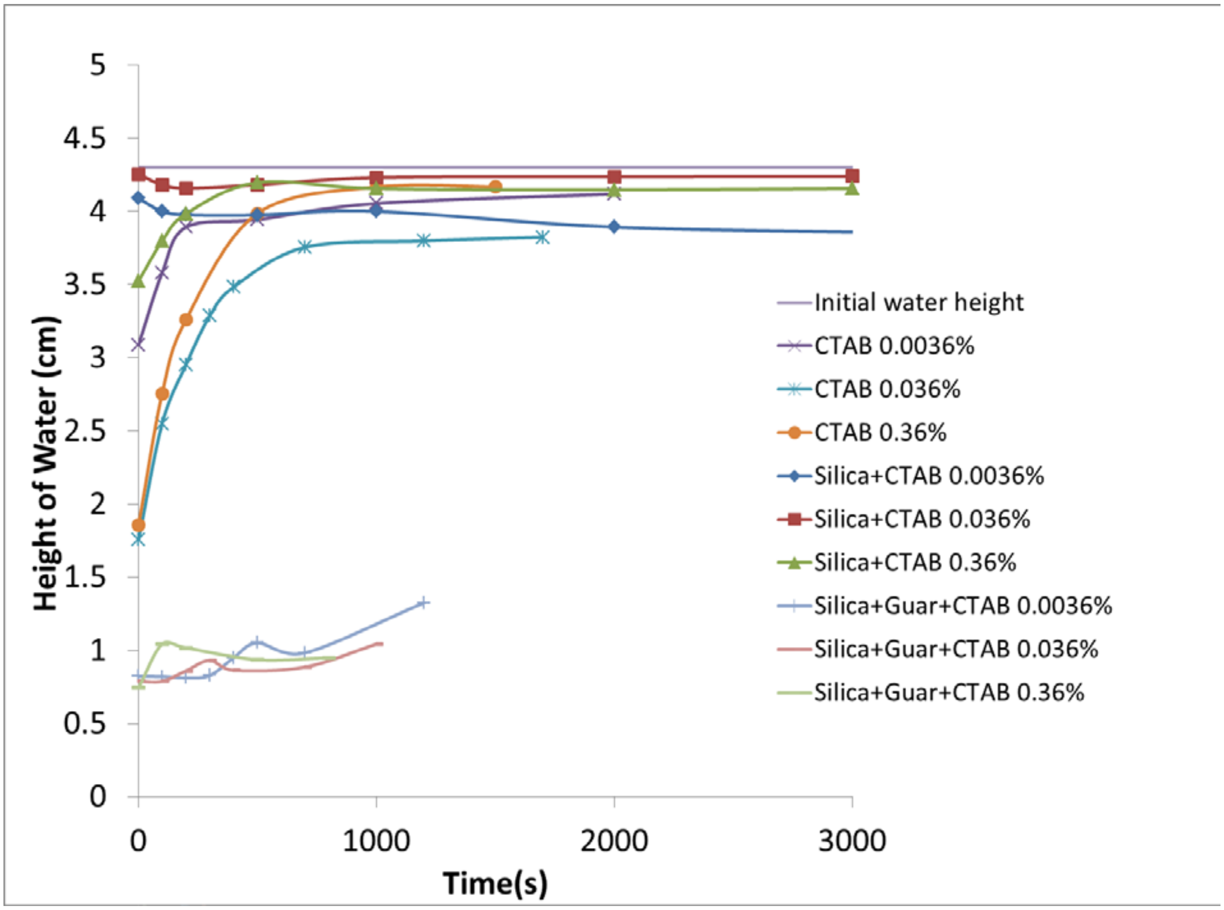

**Figure 5.** (top) Foam height vs. time of different aqueous phase formulations. Silica NP is at 1% and guar is at 0.36% (30 bbl/Mgal) for all formulations. (bottom) Drainage water height vs. time of different aqueous phase formulations. The height of the white foam region at the top of the test tube is measured as foam height. For foams generated with silica NP + CTAB + Guar, the translucent region (low quality foam) in the middle is also included as the foam height. Water height is defined as the height of the aqueous region below the foam region, including the height of sedimented silica NPs (white sediments at the bottom of test tubes).

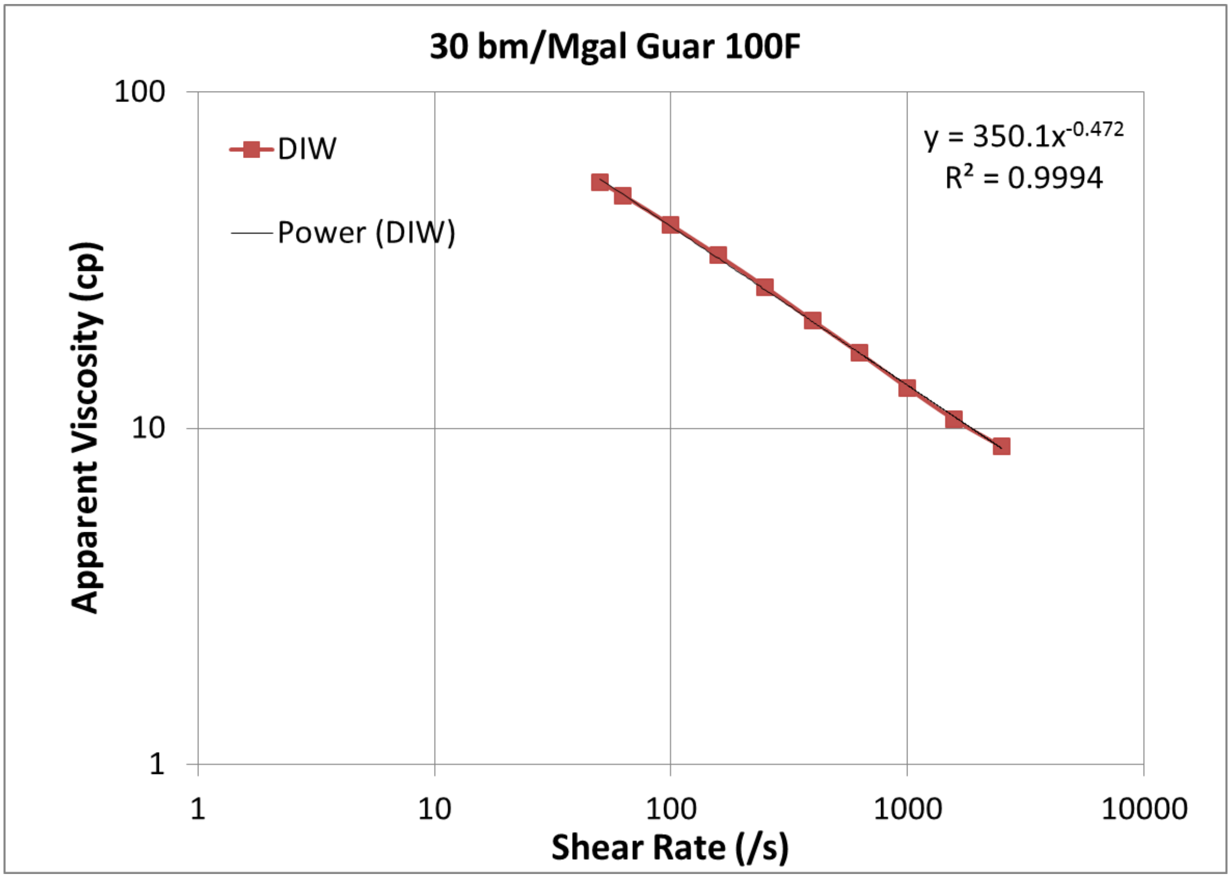

**Figure 6.** Rheogram of 30 bbl/Mgal guar gum aqueous solutions at 100 F. The viscosity of guar solutions agrees with reported data by Khade et al (Khade and Shah 2003). The shear-thinning behavior can be fitted with power law model.

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