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Polyelectrolyte Complex Stabilized CO₂ Foam Systems for Hydraulic Fracturing Application

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Abstract

Hydraulic fracturing of oil and gas wells is a water intensive process. Limited availability, cost and increasing government regulations restraining the use and disposal of fresh water have led to the need for alternative fracturing fluids. Using CO₂ foam as a fracturing fluid can drastically reduce the need for water in hydraulic fracturing. We address the addition of polyelectrolyte complex nanoparticles (PECNP) to surfactant solutions to improve foam stability, durability and rheological properties at high foam qualities. Polyelectrolyte pH and polyanion/polycation ratios were varied to minimize particle size and maximize absolute zeta potential of the resulting nanoparticles. Rheological tests were conducted on foam systems of varying surfactant/PECNP ratios and different foam quality to understand the effect of shear on viscosity under simulated reservoir conditions of 40°C and 1300 psi. The same foam systems were tested for stability and durability in a view cell at reservoir conditions. Supercritical CO₂ foam generated by surfactant alone resulted in short lived, low viscosity foam because of surfactant drainage from foam lamellae. However, addition of PECNP strengthens the foam film by swelling the film due to increased osmotic pressure and electrostatic forces. Electrostatic interactions reduce dynamic movement of surfactant micelles, thereby stabilizing the foam lamellae, which imparts high durability and viscosity to supercritical CO₂ foams. From the rheology test results, it was concluded that increasing foam quality and the presence of PECNP resulted in improved viscosity. Also, foam systems with PECNP showed promising results compared with foam generated using surfactant alone in the view cell durability test. The addition of optimized polyelectrolyte nanoparticles to the surfactant can improve viscosity and durability of supercritical CO₂ foam during hydraulic fracturing, which can lead to large reductions in water requirements.

Introduction and Literature Review

Hydraulic fracturing is a stimulation technique to increase rock permeability through creation of fractures to increase in-place hydrocarbon flow (Kohshour et al., 2016). It is estimated that more than 100,000 wells will be drilled and 1 to 2 million fracturing stages could be stimulated in the next eight to ten years (Ahmed and Meehan, 2016). Based on the prediction of Environmental Protection Agency, 70 to 140 billion gallons of water are needed annually for hydraulic fracturing in the US (EPA, 2011).

Fracturing fluid is an essential component of hydraulic fracturing, it must have high enough viscosity to suspend and transport proppant into the fracture to make sure that the fracture stays open after removing injection pressure, and provide sufficient hydraulic pressure to overcome the tensile strength of the rock for the successful propagation of fracture into the formation (Economides and Nolte, 2000). It is also required to flow back to the surface after the fracturing job for effective fracture clean-up (Samuel et al., 1999). Therefore, productivity of the stimulated well is affected by the choice of fracturing fluid (Armstrong et al., 1996). Using more viscous fracturing fluids such as cross-linked gels might reduce the productivity of the well due to the damage it causes to the fracture conductivity (Barati and Liang, 2014; Barati et al., 2009). To minimize damage, less viscous fluids such as slickwater are used commonly in shale gas hydraulic fracturing, but, 30 to 90% of injected water can remain in the formation, which causes capillary pressure shifts and formation damage, resulting in less water recovery and negative impact on production (Penny et al., 2006; Barati et al., 2009; Economides and Nolte, 2000; Makhanov et al., 2012; Sharma and Agrawal, 2013; "Injected Water", 2017).

Using foam as a fracturing fluid addresses the shortcomings of slickwater and cross-linked polymers. It improves clean-up efficiency, lowers fluid loss due to its two-phase nature, has low hydrostatic head and low pressure drop due to friction, minimizes formation damage, has higher sand-carrying capability compared to slick-water, and drastically reduces water usage (Blauer and Kohlhaas, 1974; Cawiezel and Niles, 1987). CO₂ foam has been used and tested to give acceptable results as far back as the 1980s in South Texas (Frieauf et al., 2009). Recent studies indicate that fracturing using CO₂ foam can achieve economically significant hydrocarbon recovery and improve well performance by 1.6 to 2.1 times compared to non-foam based fracturing fluids like gelled or water-based fluids. (Burke and Nevison, 2011; Yost, 1994; Frieauf et al., 2009; Frieauf and Sharma, 2009; Linde, 2013)

Foam is a colloidal dispersion with liquid as the continuous phase and gas as the discontinuous phase. At a given temperature and pressure, "foam quality" is defined as the volumetric gas content; that is, the ratio of gas volume to foam volume (Grundmann and Lord, 1983). For hydraulic fracturing, foam quality ratios of above 70 % are typically preferred (Kohshour et al., 2016).

The stability of microscopic and mesoscopic thin liquid films between gas bubbles strongly governs the stability of foams (Kristen and Klitzing, 2010). Numerous studies of nanoparticle stabilized CO₂ foam show that it is longer lasting compared to surfactant generated CO₂ foam due to higher adhesion energy of the nanoparticle at the fluid interface resulting in slower drainage (Yu et al., 2012a; Nguyen et al., 2014; Yu et al., 2012b). Also, research on foams containing polyelectrolyte and surfactant has shown that polyelectrolytes stabilize the foam due to electrostatic and entropic interactions (Klitzing et al., 1997). Polyelectrolytes are polymers with electrolytes in their repeating group, and adding them to the surfactant solutions stabilizes the foam film by decreasing the surface elasticity (Kristen et al., 2010). Further, it has been found that adsorption of surfactants on proppants is reduced by adding polyelectrolytes to the surfactant solutions (He et al., 2015).

The main objective of this research was to improve the stability of the surfactant generated supercritical CO₂ foam using polyelectrolyte complex nanoparticles (PECNP). In this work, optimized pH of polyethylenimine and optimized mass ratio of polyethylenimine to dextran sulfate were determined based on minimizing particle size and maximizing absolute zeta potential test of prepared PECNP. Then, the effects of varying foam quality and addition of PECNP to surfactant on rheological properties were studied. View cell tests were conducted to observe the stability and durability of CO₂ foam.

Materials

Polyethylenimine

The Polyethylenimine (PEI) used in this work is a branched polycation composed of the amine group and two carbon aliphatic CH_2CH_2 spacer as the repeating groups. It contains primary, secondary and tertiary amino groups in the approximate ratio of 1:2:1 (Figure 1). The PEI is a liquid with a density of 1.03 g/ml at 25°C.

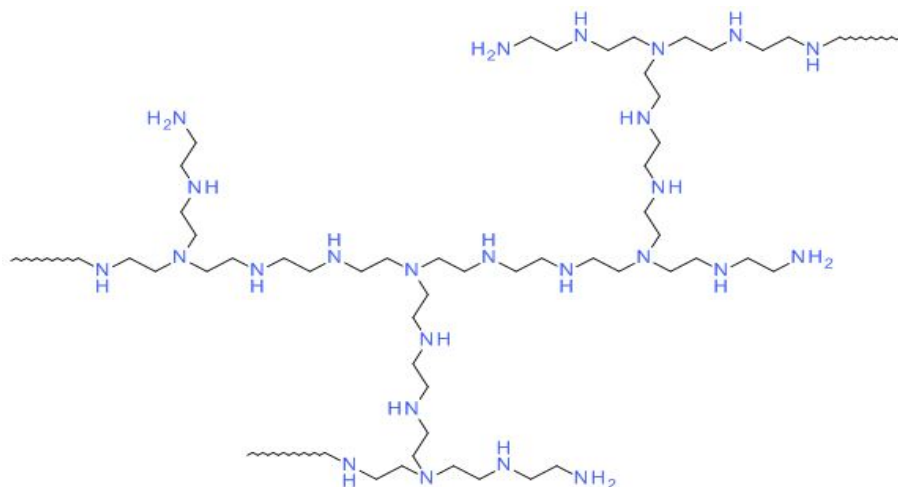
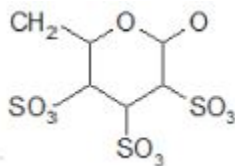


Figure 1. Chemical structure of branched PEI

Dextran Sulphate

Dextran Sulphate (DS) is a polyanion with an average molecular weight of $500,000 \text{ g}\cdot\text{mol}^{-1}$. Figure 2 below shows the chemical structure of DS.



Surfactant

The surfactant used was an aqueous solution of a proprietary surfactant designated HDP 0761-12-2AM. We will refer to it as “2AM” in this paper. The main composition of 2AM is 3-chloro- 1,-2-propanediol, sodium chloride and water. It has a density of 1.0688 g/ml at 25°C.

Brine

2 wt% sodium chloride (NaCl) was prepared using deionized water.

Methods and Procedures

Sample Preparation

Polyethylenimine Solution

A 1 wt% PEI solution was prepared using 2 wt% NaCl brine, stirred at 600 rpm for 60 minutes. For the Zeta potential measurement, PEI solution of pH 8, 8.5, 9, 9.5 were prepared by addition of 12N HCl solution. As pH of 8.5 gave the most optimized particles (presented in the Results and Discussion section), all the other tests were performed using PEI solution of pH 8.5. It took 2.88 g of 12N Hydrochloric acid (HCl) to lower the pH of 350g of 1wt% PEI solution from 11.19 (initial pH) to 8.5.

Dextran Sulphate Solution

The DS solution was prepared using 2 wt% NaCl brine. The solution was stirred at 600 rpm for 60 minutes and the final concentration of the DS in the solution was 1 wt%.

Surfactant Solution

The surfactant (2AM) solution was prepared using 2 wt% NaCl brine. The solution was stirred at 600 rpm for 20 minutes and the final concentration of the 2AM in the solution was 1 wt%.

Polyelectrolyte Complex Nanoparticles (PECNP)

Initially four different mass ratios of 1:1:0.1, 2:1:0.1, 3:1:0.1 and 4:1:0.1 for solutions of PEI: DS: 2 wt% NaCl and four different pH values of 8, 8.5, 9 and 9.5 for 1wt% PEI were prepared. Based on the particle size and Zeta potential test (presented in the Results and Discussion section), 3:1:0.1 ratio of PEI: DS: 2wt% NaCl with pH of 8.5 for 1wt% PEI showed the most optimum properties. Therefore, for all the other tests PECNP was prepared in the ratio of 3:1:0.1 of PEI (1wt%, pH 8.5): DS (1wt %): 2% NaCl and was stirred at 600 rpm for 20 minutes.

Surfactant-PECNP Solution

The surfactant solution was prepared in brine and was mixed with PECNP solution in 7 different ratios from 3:7 to 9:1 of 2AM: PECNP. Based on the particle size and zeta potential measurements (see Results and Discussion), 6:4, 7:3, 8:2, and 9:1 were determined to be the best ratios for 2AM: PECNP. Surfactant solution of 1.67 wt%, 1.43 wt%, 1.25 wt% and 1.11 wt% were prepared and mixed with PECNP solution at 600 rpm for 20 minutes to prepare solutions of 2AM: PECNP ratio of 6:4, 7:3, 8:2, and 9:1 respectively. The final concentration of surfactant in the 2AM: PECNP solutions was kept constant at 1 wt%.

Zeta Potential and DLS Particle Size Measurements

In order to select the optimized ratio of PEI: DS: brine, 2AM: PECNP as well as the most favorable pH for 1 wt% PEI, zeta potential and mean particle size were measured for different samples using Brookhaven ZetaPALS instrument (Brookhaven Instruments Corporation, New York, USA).

The electro kinetic motion of the particles away from the charged inner surface within the electrical double layer is measured by the Zeta potential or electro kinetic potential. The magnitude of Zeta potential directly affects the degree of colloidal stability; an increase in absolute Zeta potential increases electrostatic repulsion and this results in more stable nano particles. The interaction energy between the charged particles is determined by the potential distribution, which in turn is responsible for the stability of particles towards coagulation and affects many aspects of the flow behavior of the colloidal suspension. (Hunter, 1988; Moayedi et al., 2011).

Rheology Measurements

The viscosity of the surfactant generated CO₂ foam and surfactant-PECNP CO₂ foam at four different foam qualities (volumetric gas content) of 70%, 80%, 90% and 95% was measured using an Anton Paar Rheometer.

Figure 3 shows the schematic diagram of the experimental setup used for the rheology measurements. The experiment is conducted at 1300 psi and 40°C. Supercritical CO₂ and aqueous phase (surfactant or PECNP-surfactant) were pumped from two Isco pumps through a 7- μ m inline mixer to generate foam. Flow rates of ISCO pump A (CO₂) and B (aqueous phase) were set based on the desired foam quality at which the experiments were to be performed and for all four foam qualities the total flow rate of pump A and B combined was always 6 ml/min. For example, to generate 90% foam quality, pump A was operated at a flow rate of 5.4 ml/min and pump B at a flow rate to 0.6 ml/min, which resulted in a total flow rate of 6ml/min. The temperature of CO₂ in pump A was maintained at 40 °C using a heated water jacket connected to a recirculating water bath, and the flow lines were wrapped in heating tape and temperature was controlled electrically.

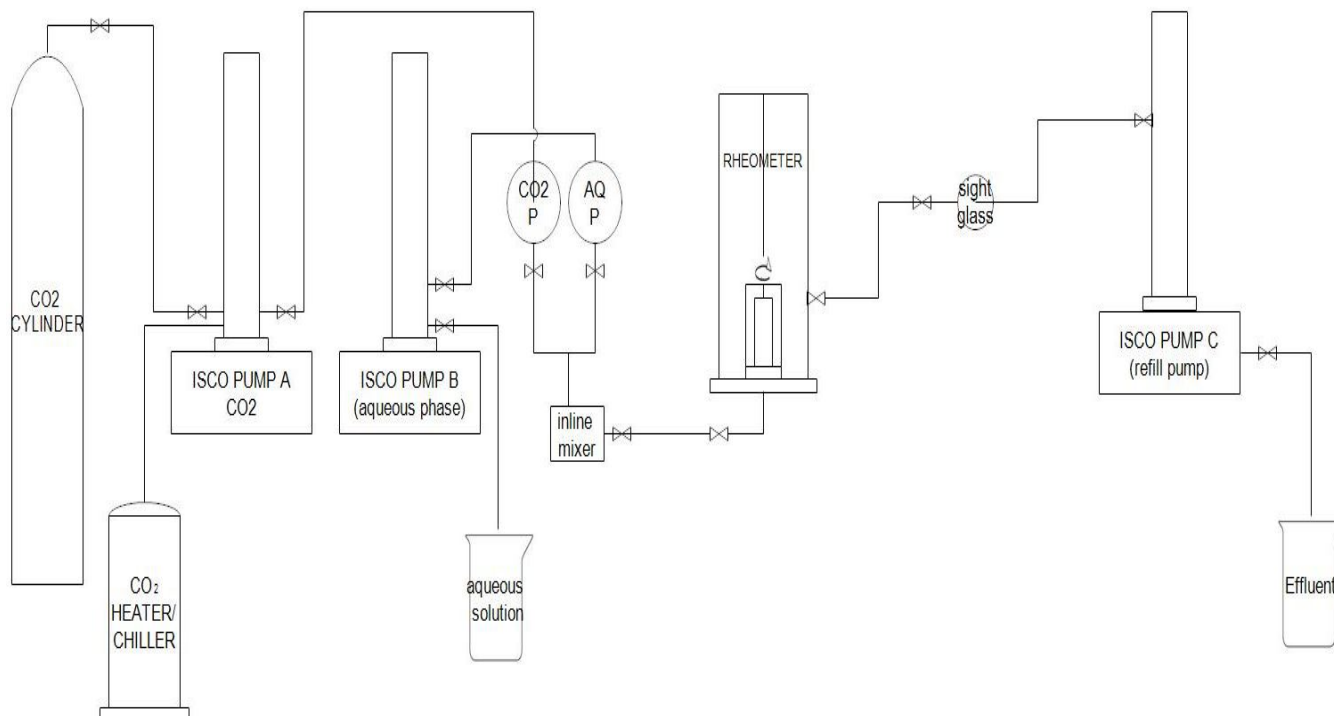


Figure 3. Schematic diagram of the Rheometer Setup

CO₂ foam generated after the inline mixer was injected into the bottom of the annulus between two coaxial cylinders in the measuring cup, which was also maintained at 40 °C. The geometry is double gap and the cylinder that rotates was in the annulus between two stationary cylinders with the torque values of up to 300 mN.m, using a magnetic coupling provided drive to rotate the cylinder. After exiting the top of the measuring cup, the foam passed through a glass view cell to check the quality of the foam at the beginning of the test. Next, foam reached the receiving ISCO pump, which was refilled at the same rate at which the foam was being injected, thereby maintaining the pressure in the system.

The viscosity was measured against time in the dynamic test. In this test, the foam was generated continuously at the desired foam quality and sheared at 2000 s⁻¹ for 45 minutes, with the viscosity being recorded at 30 s⁻¹ intervals (i.e. 90 measurements). After the dynamic test, foam generation (i.e. all the three pumps) was stopped and valves on both sides of the rheometer were used to isolate it at constant pressure to perform static test. The foam in the measuring cup was sheared again at 2000 s⁻¹ for 45 minutes with 90 measuring points and viscosity vs time was measured. Finally, a ramp test was performed, foam was sheared from 2000 s⁻¹ to 100 s⁻¹ (ramp down) and then sheared from 100 s⁻¹ to 2000 s⁻¹ (ramp up) for a total time of 30 minutes with 60 measuring points for each test.

View Cell Test

In order to determine the stability and durability of the CO₂ foam, view cell experiments were performed. The experimental setup (Figure 4) was designed to withstand high temperature and pressure, and was constructed inside a large oven. A sapphire view cell was used to observe the decay of foam, time-lapse images of the foam decay were acquired without opening the oven by using a GoPro camera and LED light source, were later analyzed to plot foam column height versus time.

A temperature-controlled ISCO pump was filled with CO₂ at lower temperature (6 °C) and by increasing the temperature to 40 °C, the pressure reached 1300 psi, establishing supercritical conditions for CO₂. Meanwhile, the left accumulator was filled by the aqueous phase (surfactant solution or surfactant-PECNP). Aqueous phase and supercritical CO₂ was allowed to flow through a 7- μ m inline mixer to generate foam. System pressure was maintained during foam generation by means of a back-pressure

regulator. The sapphire view cell was filled by the generated foam and valve 13 and 14R in Figure 4 was closed to isolate the view cell. Foam column height versus time was plotted.

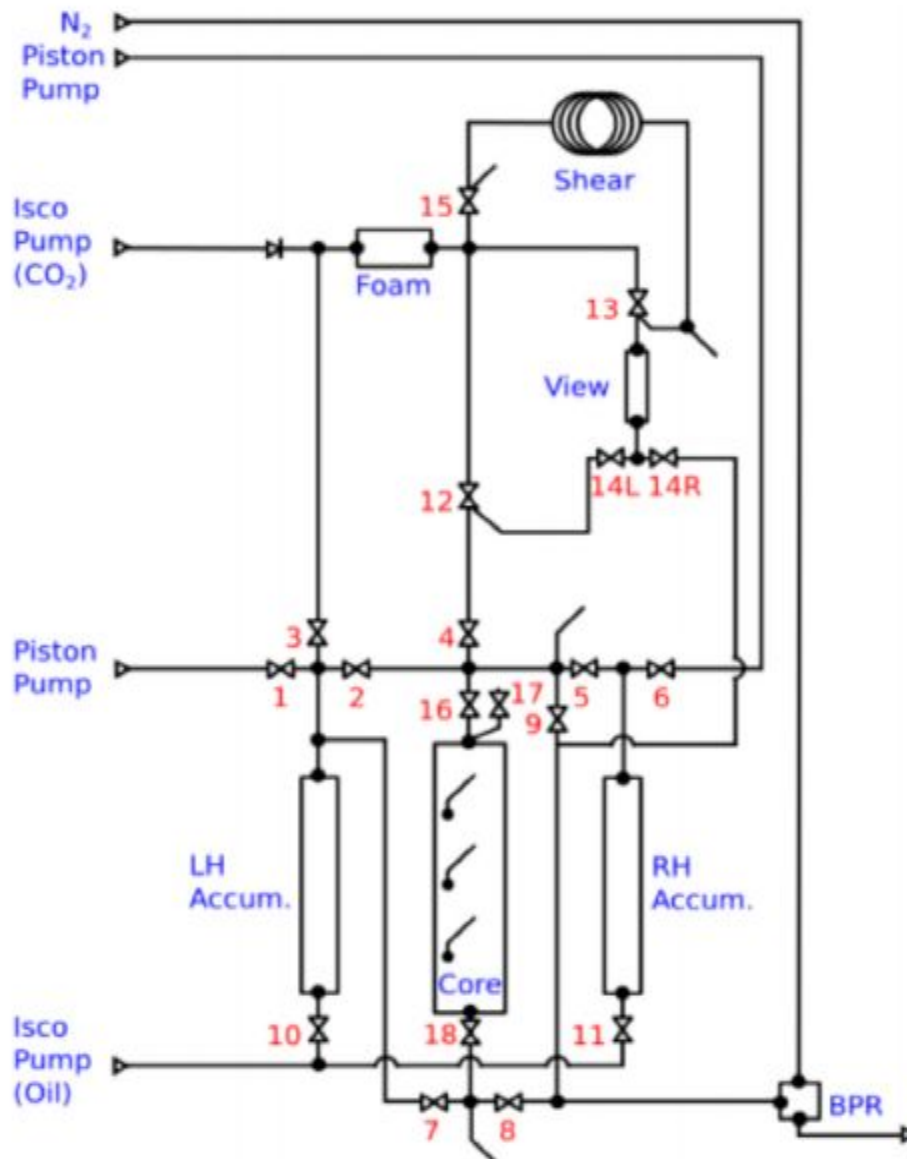


Figure 4. Schematic diagram of high pressure high temperature view cell setup (Nazari et al., 2017) (with permission from energies)

Results and Discussion

Zeta Potential and Particle Size Measurements

Zeta potential measurements were used as the initial screening test to determine the most optimum system of PECNP, surfactant: PECNP ratio and pH of 1 wt% PEI. Next, these systems were used to perform rheology measurements and view cell test. Table 1 and Table 2 show the particle size, polydispersity and zeta potential measurements for different ratios of PEI: DS: 2% NaCl with/without 2AM: PECNP. Polydispersity is a measure of heterogeneity or degree of “non-uniformity” of a distribution of the sizes of particles in the colloidal dispersion.

It can be observed from Table 1 that PEI: DS: 2% NaCl ratio of 3:1:0.1 gave the highest zeta potential value at a pH of 8.5. This ratio of PECNP was used to prepare seven different ratios of surfactant-PECNP.

Among the seven different ratios of surfactant-PECNP, 9:1, 8:2, 7:3 and 6:4 were the top four systems based on the zeta potential values, which are shown in Table 2. The most desirable systems in Table 1 and Table 2 are highlighted, and these were selected for rheological investigation.

Table 1. Particle size and zeta potential values for different ratios of PEI: DS: 2% NaCl (PECNP)

PECNP	pH	Effective Diameter (nm)	Polydispersity	Zeta Potential (mV)
3:1:0.1	8	223.99 ± 2.21	0.178 ± 0.078	22.63 ± 1.32
3:1:0.1	8.5	177.38 ± 1.09	0.268 ± 0.014	24.37 ± 1.22
3:1:0.1	9	157.28 ± 2.31	0.232 ± 0.005	13.84 ± 1.86
3:1:0.1	9.5	180.63 ± 1.06	0.142 ± 0.012	11.29 ± 2.34
4:1:0.1	8	164.59 ± 0.29	0.243 ± 0.006	11.39 ± 0.65
4:1:0.1	8.5	162.38 ± 0.75	0.263 ± 0.011	16.24 ± 2.48
4:1:0.1	9	164.84 ± 1.55	0.542 ± 0.110	14.09 ± 2.99
4:1:0.1	9.5	177.2 ± 1.02	0.180 ± 0.003	10.97 ± 1.15

Table 2. Particle size and zeta potential values for different ratios of surfactant: PECNP

2AM: PECNP	Effective Diameter (nm)	Polydispersity	Zeta Potential (mV)
9:1	214.15 ± 3.78	0.207 ± 0.010	24.42 ± 2.32
8:2	173.56 ± 1.01	0.246 ± 0.015	19.45 ± 1.54
7:3	185.82 ± 1.72	0.198 ± 0.003	19.90 ± 1.13
6:4	186.58 ± 0.66	0.203 ± 0.010	19.81 ± 1.28
5:5	180.76 ± 0.22	0.205 ± 0.005	14.44 ± 4.04
4:6	189.63 ± 1.81	0.212 ± 0.008	14.17 ± 0.18
3:7	188.18 ± 1.72	0.220 ± 0.012	14.28 ± 1.74

Rheology Measurements

In order to suspend and transport proppant to the fracture CO₂ foam must have reasonable viscosity. The main purpose to perform the rheological measurements was to find whether addition of PECNP improves the viscosity and whether foam quality increases the viscosity.

Dynamic Viscosity Test

In this test CO₂ foam was continuously generated and sheared at 2000 s⁻¹. The generated foam was subjected to tangential force due to continuous generation of foam and normal force due to rotation of middle cylinder in the rheometer.

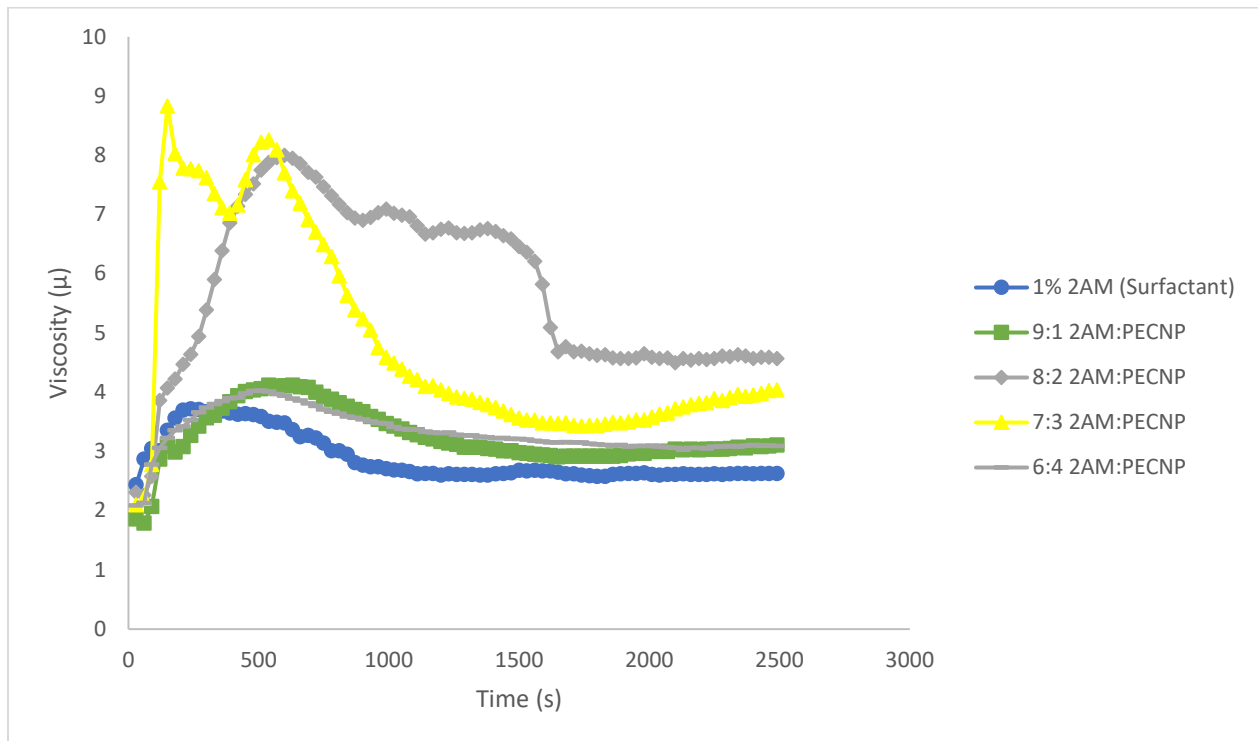


Figure 5. Viscosity vs time for different surfactant-PECNP systems at 70% foam quality with supercritical CO₂ as the discontinuous phase

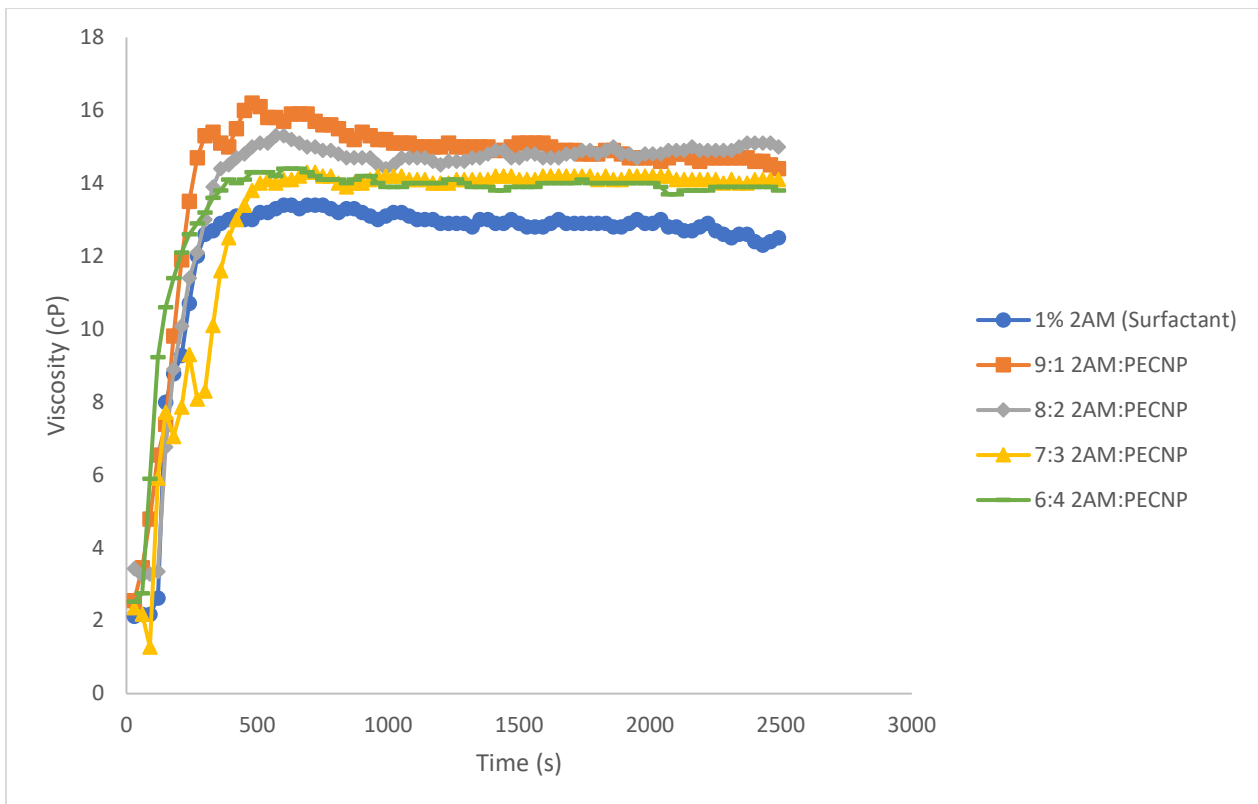


Figure 6. Viscosity vs time for different surfactant-PECNP systems at 80% foam quality with supercritical CO₂ as the discontinuous phase

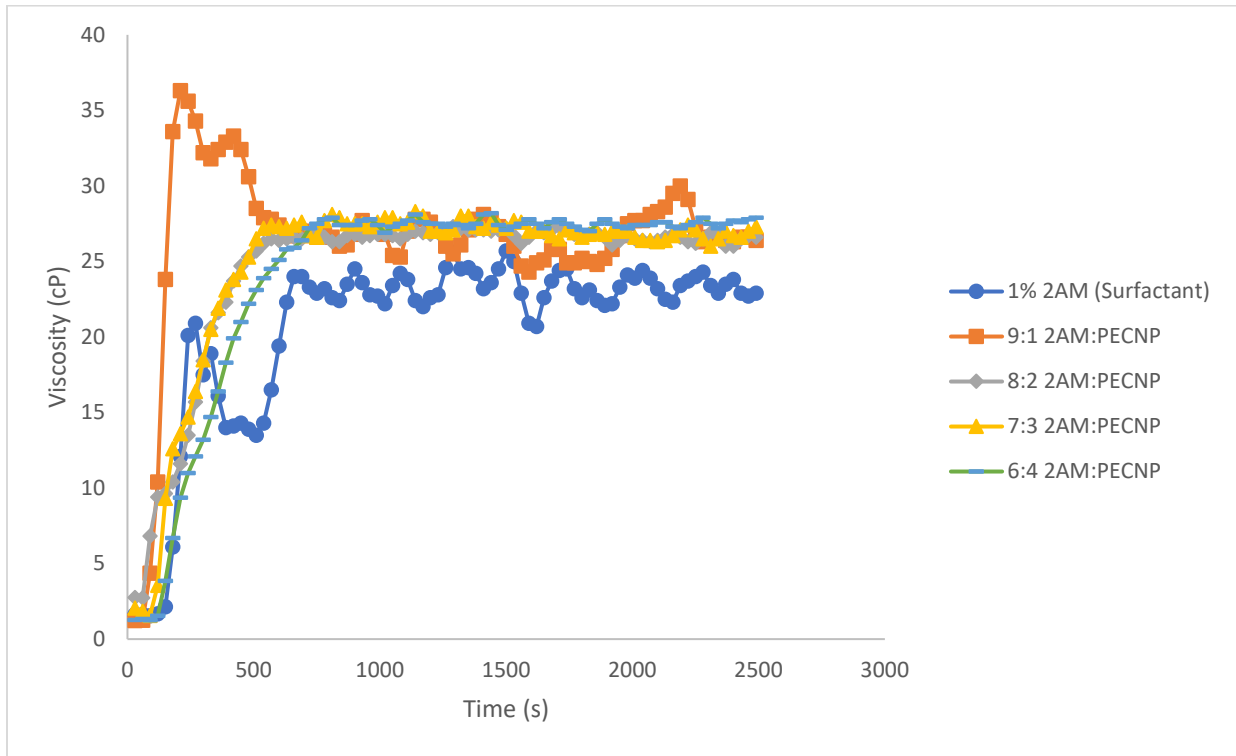


Figure 7. Viscosity vs time for different surfactant-PECNP systems at 90% foam quality with supercritical CO₂ as the discontinuous phase

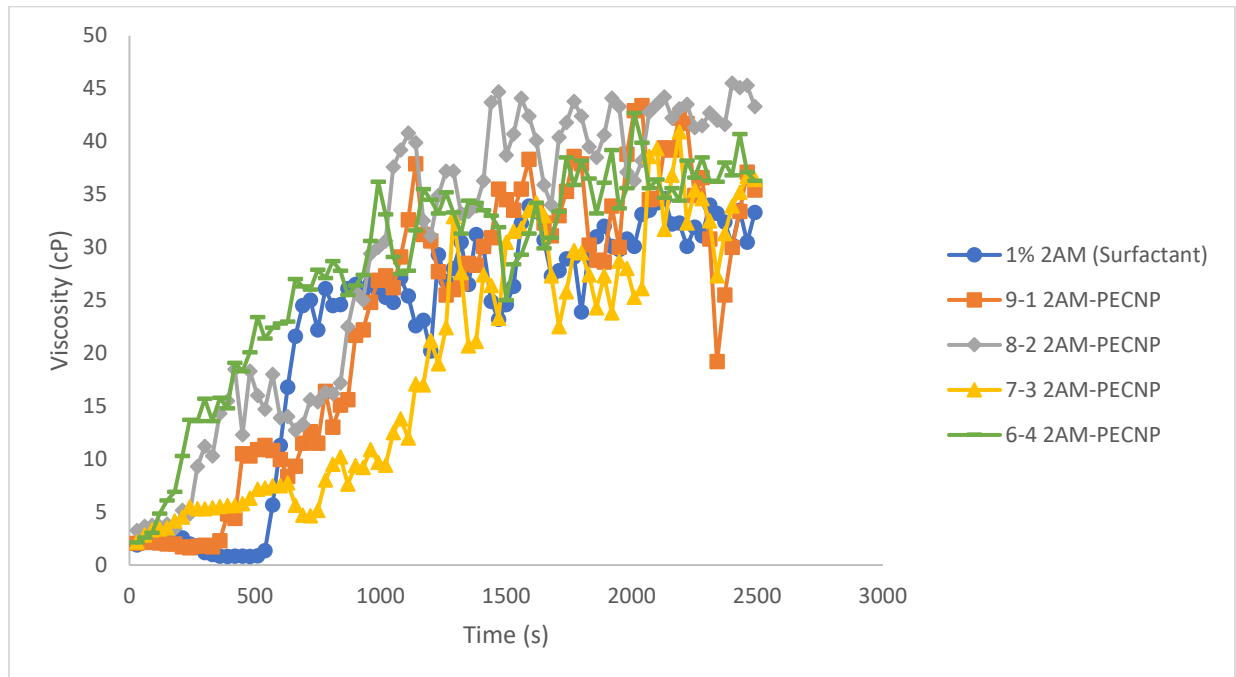


Figure 8. Viscosity vs time for different surfactant-PECNP systems at 95% foam quality with supercritical CO₂ as the discontinuous phase

Different surfactant-PECNP systems plus supercritical CO₂ foam systems at 70%, 80%, 90% and 95% foam quality are compared in the Figure 5 to Figure 8. These graphs clearly shows that addition of surfactant-PECNP system resulted in a significant increase in viscosity compared to just surfactant (1% 2AM) generated foam and the optimum system of PECNP-surfactant is 8:2 2AM: PECNP for 70%, 80% and 95% foam quality and 9:1 2AM: PECNP for 90% foam quality. In Figure 9 viscosity versus time was plotted for the best surfactant-PECNP system under each foam quality and it clearly demonstrates that increase in foam quality increased the viscosity.

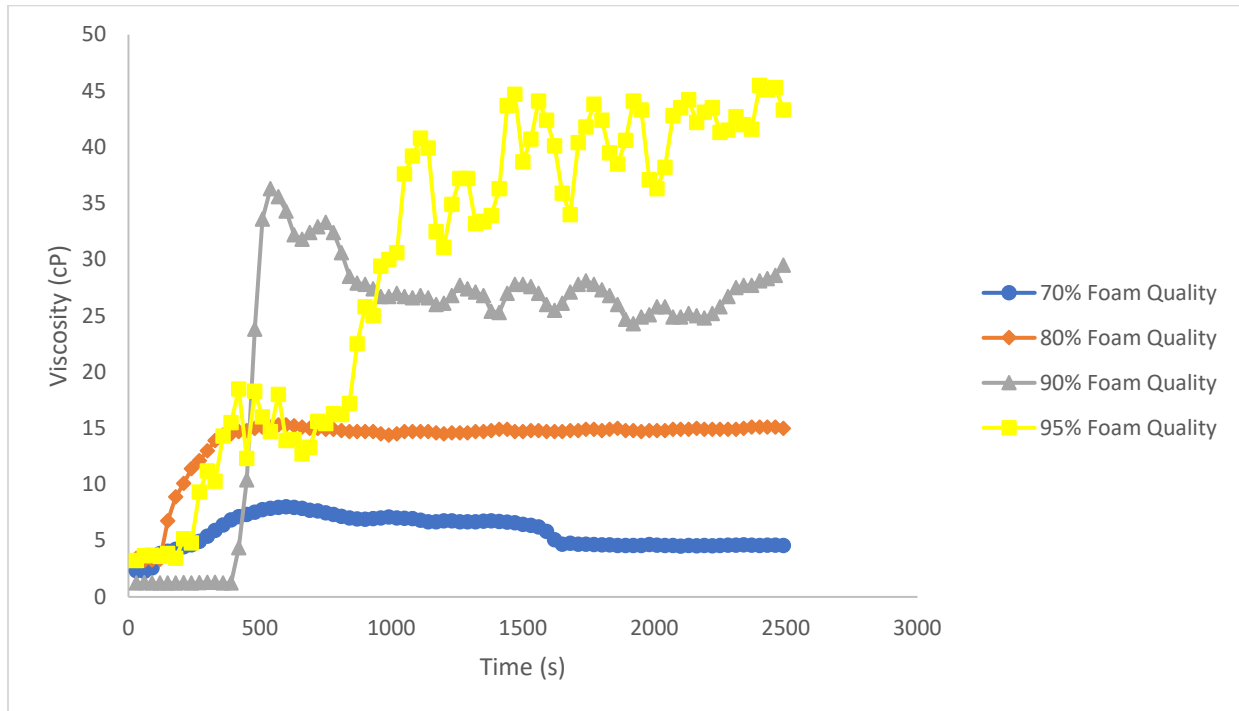


Figure 9. Viscosity vs time for optimal surfactant-PECNP systems in each of the four different foam quality conditions

Static Test

Figure 10 shows viscosity vs time for the optimal PECNP-surfactant system under each foam quality and it shows that viscosity increases with increase in foam quality.

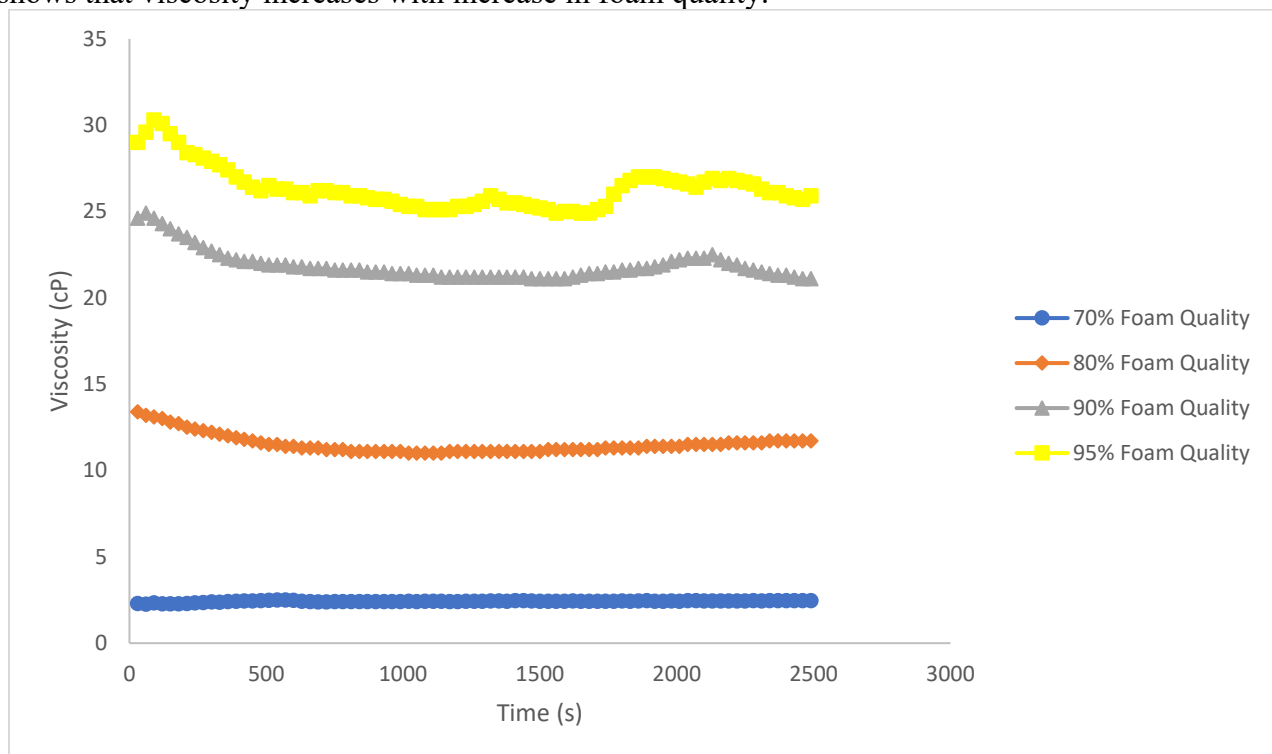


Figure 10. Viscosity vs time for optimal surfactant-PECNP systems in each of the four different foam quality conditions

Ramp Test

In this test, shear sweep was performed on different foam systems. Power-law model (Ostwald-de Waele equation) was used to find the flow consistency index (K) and flow behavior index (n).

$$\mu_{\text{eff}} = K \dot{\gamma}^{n-1} \dots\dots\dots \text{Equation 1}$$

Table 3-Table 6 summarizes the flow consistency index and flow behavior index for 70%, 80%, 90%, 95% foam quality. As the flow behavior index value was less than one for all the foam systems, they are pseudo-plastic (shear-thinning). Foam consistency index increased with increasing foam quality and it was higher for the surfactant-PECNP system compared to just surfactant foam (1% 2AM). Surfactant-PECNP systems with the highest flow consistency index in each table from Table 3 to Table 6 are highlighted. Compared to the surfactant generated foam the percentage increase in flow consistency index for the most optimized surfactant-PECNP generated foams are 117.47 %, 52.95 %, 18.91 % and 81.59 % for 70 %, 80 %, 90 % and 95 % CO₂ foam quality.

Foam System	n	K	R ²
1% 2AM-Reference	0.544	22.715	0.979
9:1 2AM:PECNP	0.549	43.084	0.965
8:2 2AM:PECNP	0.468	49.399	0.978
7:3 2AM:PECNP	0.518	44.881	0.955
6:4 2AM:PECNP	0.609	19.339	0.992

Table 3. Flow behavior index and flow consistency index for different surfactant-PECNP systems of 70% foam quality

Foam System	n	K	R ²
1% 2AM-Reference	0.568	296.68	0.993
9:1 2AM:PECNP	0.516	364.29	0.981
8:2 2AM:PECNP	0.487	453.77	0.993
7:3 2AM:PECNP	0.536	352.34	0.997
6:4 2AM:PECNP	0.533	353.21	0.994

Table 4. Flow behavior index and flow consistency index for different surfactant-PECNP systems of 80% foam quality

Foam System	n	K	R ²
1% 2AM-Reference	0.569	389.59	0.998
9:1 2AM:PECNP	0.569	463.26	0.998
8:2 2AM:PECNP	0.575	397.58	0.997
7:3 2AM:PECNP	0.568	431.13	0.995
6:4 2AM:PECNP	0.563	415.32	0.994

Table 5. Flow behavior index and flow consistency index for different surfactant-PECNP systems of 90% foam quality

Foam System	n	K	R ²
1% 2AM-Reference	0.691	321.68	0.998
9:1 2AM:PECNP	0.568	429.42	0.978
8:2 2AM:PECNP	0.549	584.17	0.998
7:3 2AM:PECNP	0.468	487.37	0.998
6:4 2AM:PECNP	0.543	525.16	0.995

Table 6. Flow behavior index and flow consistency index for different surfactant-PECNP systems of 95% foam quality

View Cell Test

Foam height vs time was monitored in an isolated view cell. Figure 11-Figure 14 show the height of a static foam column vs time for the surfactant and surfactant-PECNP systems for 70%, 80%, 90% and 95% foam quality respectively. Based on the performance of different surfactant-PECNP systems in rheology test (dynamic, static and ramp) and view cell test, the optimal systems of PECNP-surfactant are 8:2 2AM: PECNP for 70%, 80% and 95% foam quality and 9:1 2AM: PECNP for 90% foam quality. Note that a very similar behavior for foam systems prepared using 8:2 ratio and 9:1 ratio of 2AM: PECNP was observed.

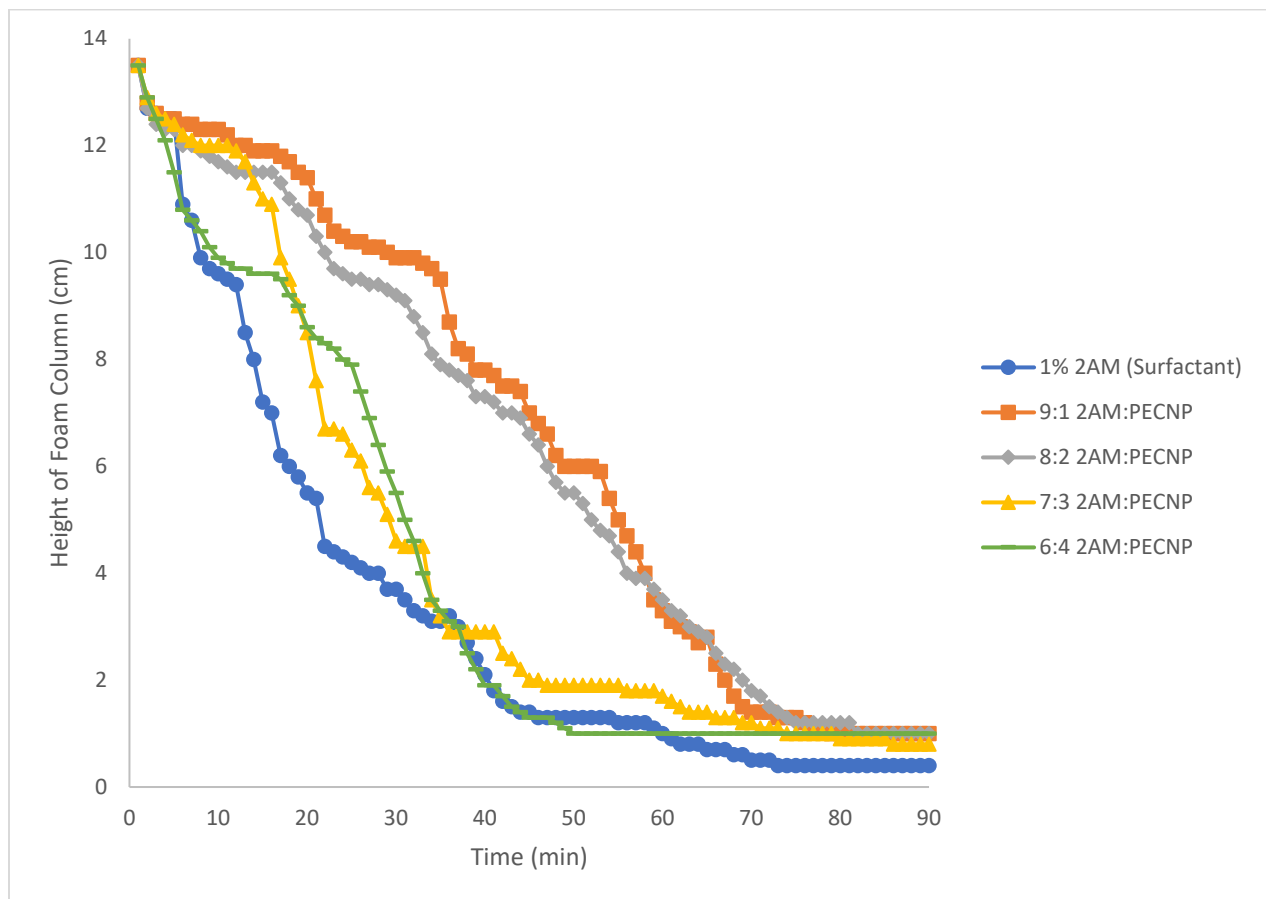


Figure 11. Height of foam column vs time for the surfactant and different surfactant-PECNP systems at 70% foam quality

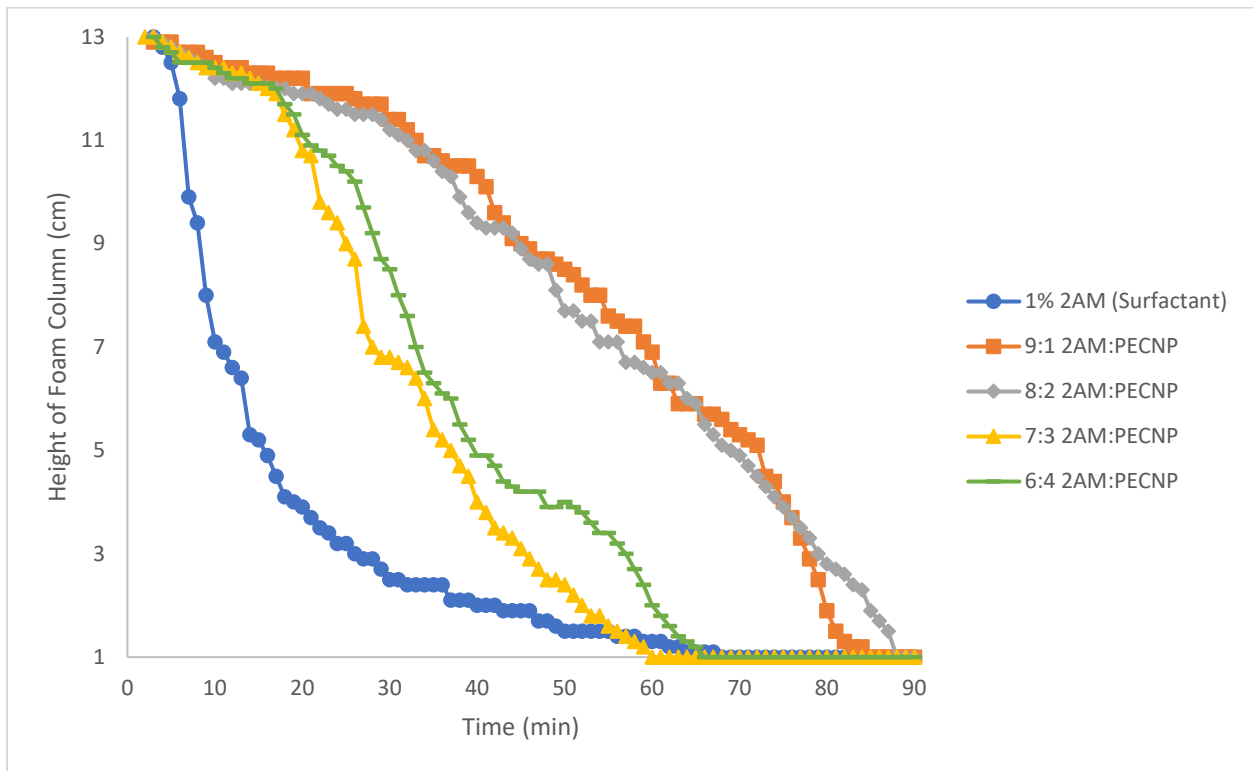


Figure 12. Height of foam column vs time for the surfactant and different surfactant-PECNP systems at 80% foam quality

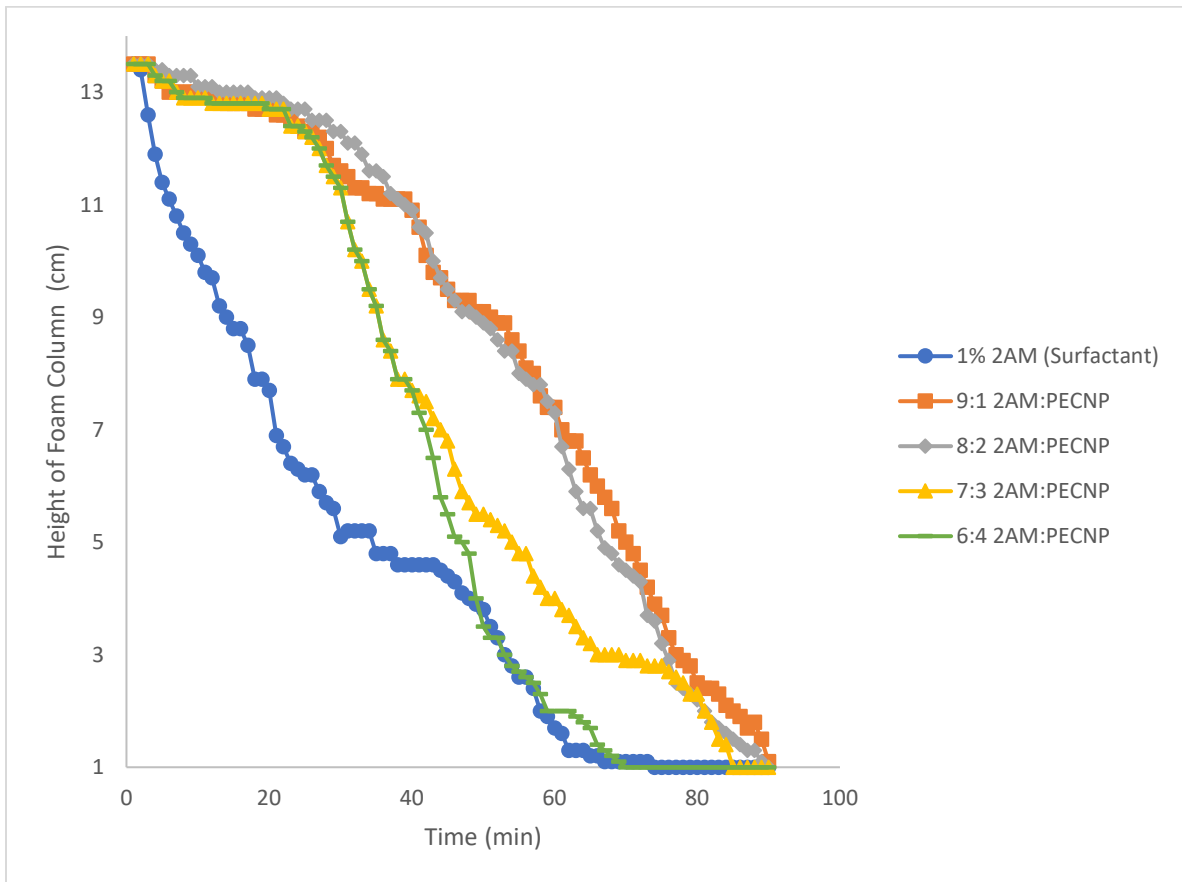


Figure 13. Height of foam column vs time for the surfactant and different surfactant-PECNP systems at 90% foam quality

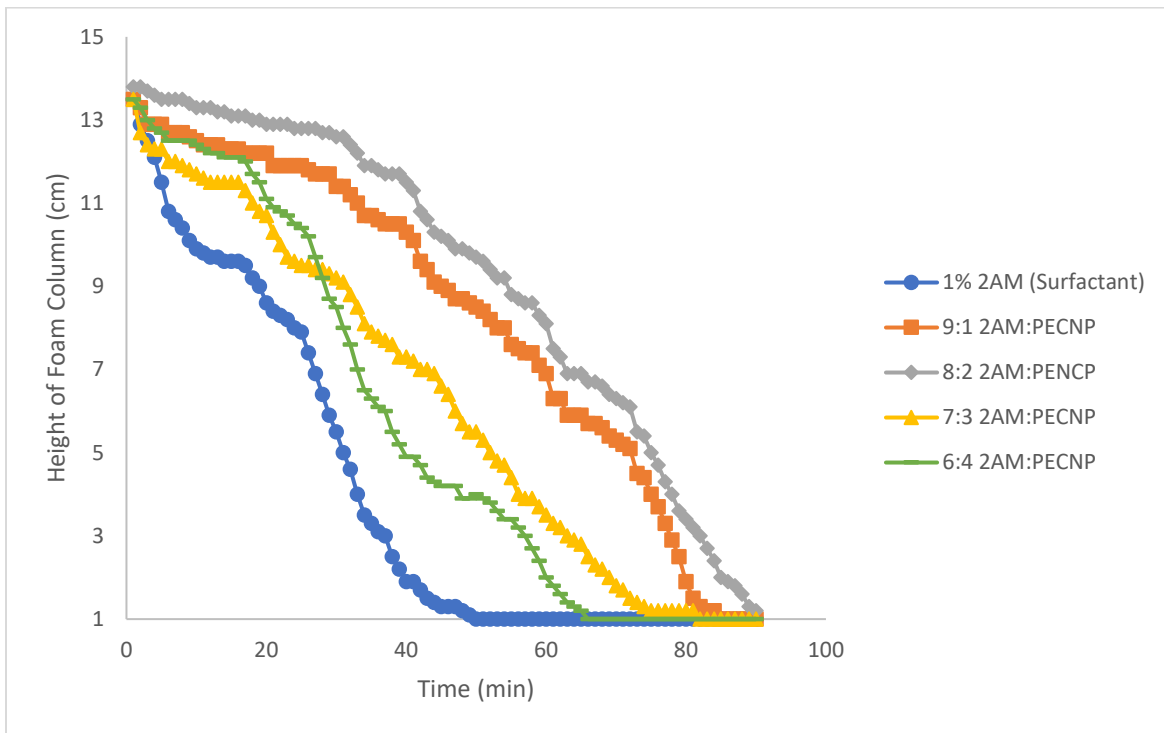


Figure 14. Height of foam column vs time for the surfactant and different surfactant-PECNP systems at 95% foam quality

Figure 15 shows the foam decay versus time for the best surfactant-PECNP system for each foam quality and it shows that foam durability and stability increases with increase in foam quality. This demonstrates the capability of the foam system to perform at higher foam quality.

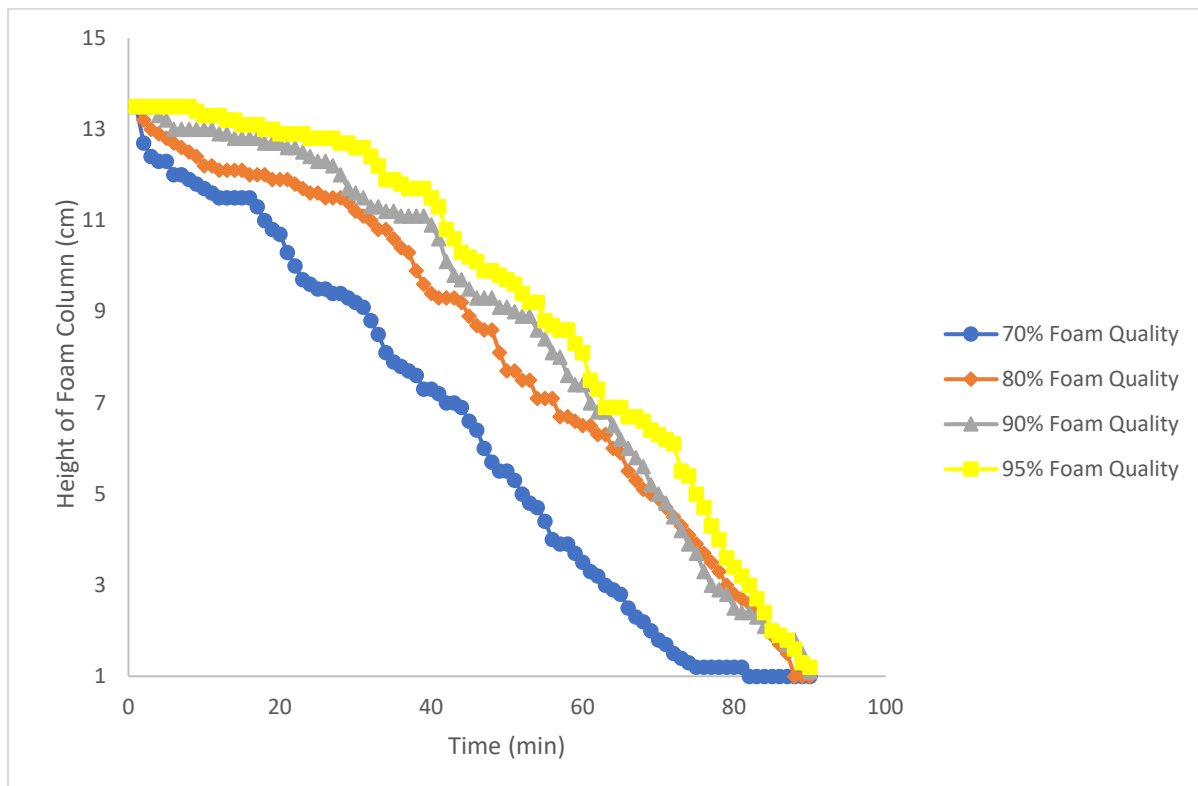
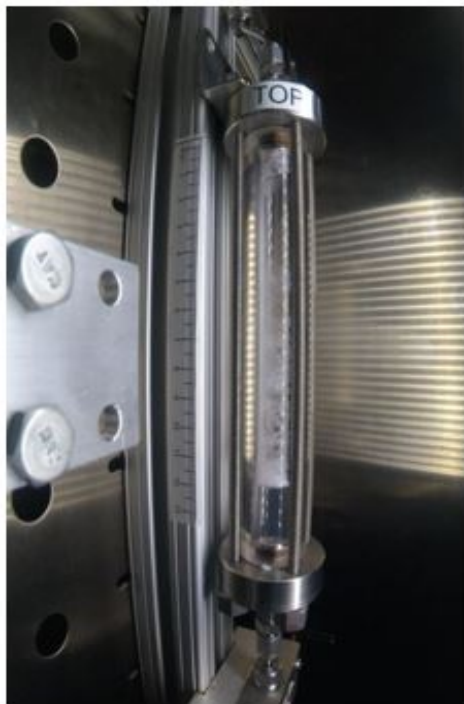


Figure 15. Height of foam column vs time for the best surfactant-PECNP system at different foam qualities

Figure 16 and Figure 17 shows the picture of supercritical CO₂ foam generated by optimal surfactant-PECNP systems at each foam quality.

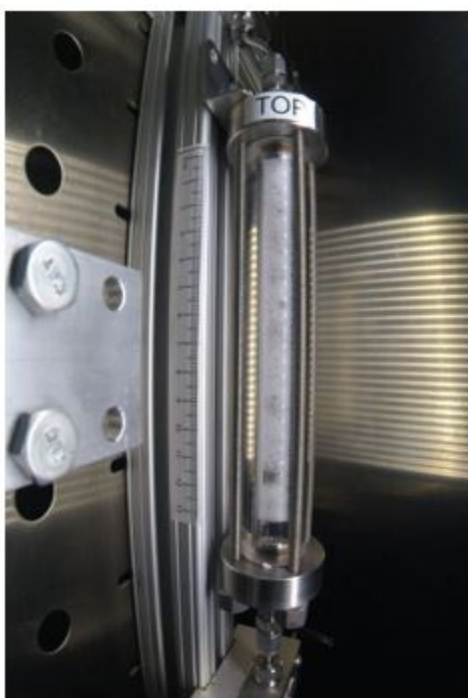


A

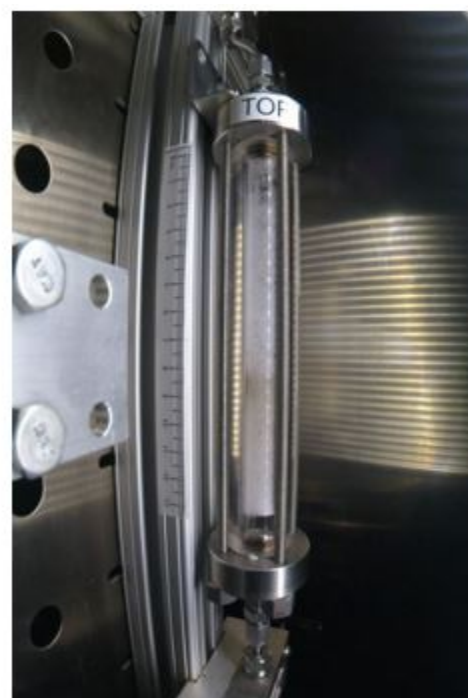


B

Figure 16. Static supercritical CO₂ foam at A) 70% B) 80% foam quality after 40 minutes



A



B

Conclusions

Addition of PECNP to the surfactant solution for generating a more stable supercritical CO₂ foam and effect of foam quality on its rheological properties, stability and durability was investigated. PECNPs were optimized for colloidal stability on the basis of minimizing size and maximizing absolute zeta potential. One PECNP formulation at each foam quality was examined for its effects on dynamic and static foam viscosity, and on static foam longevity under supercritical conditions.

- 1) PECNP formulation of 3:1:0.1 (PEI:DS:2% NaCl) and surfactant-PECNP ratios of 9:1, 8:2, 7:3 and 6:4 were found to be the most favorable ratios based on the particle size and zeta potential test. These tests showed that adding PECNP to surfactant solution improved the zeta potential by stabilizing the foam lamellae.
- 2) Rheology tests showed that adding PECNP to surfactant significantly improved the viscosity and flow consistency index of the foam over a range of foam qualities. Increasing foam quality resulted in better rheological performance.
- 3) View cell tests indicated that adding PECNP to surfactant significantly improved foam stability and durability compared to the foam systems generated using surfactant alone. Moreover, increasing the foam quality improved foam stability and durability.

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Nomenclature

μ_{eff}	: Effective viscosity, cP
K	: Flow consistency index
n	: Flow behavior index
γ	: Shear rate, s ⁻¹
τ	: Shear stress

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