

High Temperature Stability of Aqueous Foams for Potential Application in Enhanced Geothermal System (EGS)

Viren Thakore^a, Fei Ren^{a,*}, Josh Voytek^a, Hong Wang^b, Jy-An John Wang^b, and Yarom Polsky^c

^aTemple University, 1947 North 12th Street, Philadelphia, PA 19122

^bMaterials Science & Technology Division, Oak Ridge National Laboratory, PO Box 2008, MS 6069, Oak Ridge, TN 37831

^cElectrification & Energy Infrastructure Division, Oak Ridge National Laboratory, PO Box 2008, MS 6075, Oak Ridge, TN 37831

*Email: renfei@temple.edu

Keywords: Enhanced geothermal system, aqueous foams, high temperature, high pressure, surfactant, stabilizing agent, half-life, stability.

ABSTRACT

Enhanced Geothermal Systems (EGS) are typically constructed by injecting high-pressure water into the deep hot dry rocks (HDR) under carefully controlled conditions to create new or re-open existing fractures, which usually utilizes an immense quantity of water. Alternatively, aqueous foam-based fracturing fluids may offer potential advantages over conventional water-based fracturing fluid, including reduced consumption of water and environmental impact. Although foam-based fracturing has shown promising results in oil and gas industries, its applicability to EGS is unknown. Foams are complex mixtures of liquids with gaseous phases that are thermodynamically unstable. Their stability will decrease over time due to liquid drainage, bubble coarsening, and coalescence. Therefore, it is essential to stabilize foam fluids at high temperatures for EGS related applications such as fracking of HDRs.

This paper is focused on investigating high-temperature stability of N₂-in-water or N₂ foams containing different surfactants and stabilizing agents. Foam stability was characterized by the half-life, which is defined as the time a foam decreases to 50% of its original height due to drainage. Surfactants with various concentrations dissolved in deionized water were investigated, including alfa olefin sulfonate (AOS), sodium dodecyl sulfonate (SDS), TergitolTM (NP – 40), and cetyltrimethylammonium chloride (CTAC). Also, the effects of other stabilizing agents, including guar gum, bentonite clay, crosslinker, graphene oxide (GO) dispersion on foam stability were tested. Initial results showed that foam stability decreased dramatically as temperature increased. On the other hand, foams became relatively more stable as pressure increased. Certain stabilizing agents, such as guar gum and crosslinker, can enhance foam stability at a wide range of temperatures. Our results indicate that it may be possible to obtain stable foams at high-temperature, high-pressure conditions with appropriate stabilizing agents.

1. INTRODUCTION

Geothermal energy is a clean, renewable source of energy. Hydraulic fracturing is sometimes used to generate new or to enhance existing reservoirs to create an enhanced geothermal system (EGS). EGS involves deep drilling into the earth's crust with the injection of high-pressure water under carefully controlled conditions into hot dry rocks (HDRs), which are typically present 5-6 miles underneath the earth's surface and contain vast stored thermal energy. The water injected for hydraulic fracturing is usually in huge quantity, which may also damage the environment by contaminating water resources. Therefore, it is highly desired to develop waterless fracturing technologies for EGS applications. Waterless fracturing has been practiced in oil and gas industries for some years, which covers a range of mechanical, electrical, and chemical fracturing methods (Olasolo et al. 2016; Gandossi 2016; Moridis, 2017). Among all the waterless fracturing, foam-based fracturing is considered a good candidate for EGS due to its unique attributes, including higher proppant carrying capacity, lower water consumption, less chemical usage, and less environmental damage (Wanniarachchi et al., 2017; Wang et al., 2019).

Foam fracturing has been practiced by many oil and gas industries to fracture low permeability reservoirs to extract shale gas. The first foam-based fluid fracturing application was conducted in 1975 at Devonian shale (Ohio), which showed that foam-based fracturing was less expensive and more effective compared to water-based fracturing (Frohne K., 1976). A large scale gas production at lower Huron shale fairway (Appalachian Basin) showed that performance and effectiveness of foam-based fracturing fluid could be significantly enhanced using ultra high-quality foams (Brannon H. et al., 2009). Oussoltsev et al. in 2008 reported that foam-based fracturing in western Siberia increased gas production and had high fracture conductivity comparing to water-based fracturing due to foam rheology properties and high gas-phase factor (Oussoltsev D., 2008). Wilk K. (2019) conducted laboratory work in combination with 3D simulation, showed that foam fluid had suitable viscosity which allowed opening the fracture, and transporting the proppant into the fracture, providing successful fracture openings. Preliminary work by this group (Wang et al. 2020, 2021) also demonstrated foam fracturing of cement and granite materials with and without pulsed pressure control.

Foams are complex mixtures of liquids with a gaseous phase, where the liquid phase act as an ambient phase and gas as the dispersed phase. Foam rheological properties are influenced by many factors including the gaseous phase, surfactants, stabilizing agents, the foam quality, the bubble texture, and the temperature, pressure, and shear rate. For EGS applications, the foam performance, including its thermal ability is extremely influenced by the downhole condition that involves high temperatures and high pressures. Several researchers have developed laboratory-scale experimental setups to study the foam rheological properties to enhance foam stability at downhole

conditions. Ahmed, S. et al. (2018) investigated the effects of temperature and pressure on apparent viscosity for supercritical carbon dioxide (sCO₂) foams using a foam rheometer. They tested sCO₂ foams at a temperature range of 40-120°C and pressure range of 1000-2500 psi and found that the foams exhibited shear-thinning behavior. The apparent viscosity of foam decreased as the temperature increased, whereas an increase in pressure stabilized the lamella and increased the foam viscosity. Wang H. et al. (2017) reported an experiment with 10 different surfactants using FoamScan® equipment to measure the half-life of the foam at a maximum temperature of 65°C. They showed that the half-life of all the surfactants decreased with an increase in temperature. At higher temperatures, viscosity is believed to be the main influence causing rapid liquid drainage. Anionic surfactants were found to be the best foaming agent in terms of foam stability compared to cationic and non-ionic surfactants. Wang Y. et al. (2017) tested different ionic surfactants with CO₂ as foaming agents using a visualized foam meter at high pressure (3600 psi) and high temperature (160°C). The experimental results showed that CO₂ foams at high temperatures was greatly influenced by the types of surfactants used depending up on their hydrophilic-lipophilic balance (HLB). There was an optimal HLB value corresponding to the most stable foam for the surfactant with similar molecular structure at certain temperature and pressure range, non-ionic surfactants the optimum HLB value was around 17. The thermal stability of foams of non-ionic surfactant was improved with the addition of ethylene oxide, while anionic surfactant had much better thermal stability compared to non-ionic surfactants. Also, they showed that combining different surfactants had a synergistic effect that could significantly improve the performance of CO₂ foams and increase the foam's stability at high temperatures.

The viscosity of the liquid phase directly affects the foam stability, the higher the viscosity, the longer lasting, and more stable foams are. Therefore, one way to enhance the stability of liquid foams is by the addition of stabilizing agents. Early experiments for high temperature (300°F) foam stability were carried out by Harris P.C. et al. (1987) to understand the rheological behavior of nitrogen-based foam fracturing fluids with the addition of stabilizing agent guar gum. It was observed that foam fluids did not thin as rapidly as gel fluid under similar conditions. They also studied the stability of foams containing crosslinking agent borate. Borate ions can form a complex cross-link pair with stabilizing agent guar gum giving an increase in viscosity of the base fluid. The addition of cross-linker increased fluid stability at high temperatures up to 250°F at pH 10. An increase in pH allows enough active borate ions to form crosslink with the gelling agent that increases the viscosity of foam fluid resulting in more stable foams. Additives like gel-stabilizer, polymer, and high pH crosslinker showed increased foam stability in the temperature range for fracturing fluids up to 300°F (Harris, 1993). Zhang and coworkers investigated CO₂ foams stabilized with viscoelastic surfactant at high temperature (160°C) and high pressure (1800 psi) using foam-meter testing equipment (Zhang P. et al., 2019). Experimental results showed that viscoelastic surfactants had a high-temperature tolerance up to 160°C due to the high bulk viscosity of the viscoelastic surfactant that led to lower drainage velocity in the foam film. Another gelling agent bentonite clay was studied by Verma A. (2017). They showed that foam rheological properties with microscopic study improved the apparent viscosity, viscoelasticity, thermal stability, and morphology of foam on the addition of bentonite clay. Addition of bentonite clay also showed reduced formation damage due to low doses of polymer with similar proppant suspension capacity.

Foam stability is also improved with the addition of nanoparticles. The presence of nanoparticle can slow down the drainage of foam by clustering the lamella of foam bubbles. Espinoza et al. (2010) studied different anionic surfactants with addition of silicon dioxide (SiO₂) nanoparticles and found that foams stabilized with laurylamidopropyl betaine (LAPB) surfactant and silica nanoparticles, with and without partially hydrolyzed polyacrylamide (HPAM) were stable for hours to days. The adsorbed nanoparticles at the interface of lamella are shown to slow down Ostwald ripening (with or without polymer added) and increase foam stability (Xue Z., 2016). Emrani, A. S. (2017) conducted a foam test which showed that alpha olefin sulfonate (AOS) surfactant with SiO₂ nanoparticles can generate stable foams. It was found that AOS solution with nanoparticles was more stable than viscoelastic surfactant, and nanoparticles tended to improve the stability of foams stabilized with guar gum. Lv et al. studied the foam stability at temperatures up to 90°C and observed that the thermal stability of sodium dodecyl benzenesulfonate (SDBS) foam was increased when surface-treated hydrophilic silicon dioxide (SiO₂) nanoparticles were added to the base solution (Lv Q., et al., 2015). In addition to SiO₂ nanoparticles, graphene oxide (GO) was also considered. Cote, L. et al. (2010) found that GO could act as a surfactant to lower the interfacial energy and thus help emulsify organic solvents with water and disperse insoluble materials in water. Besides, GO sheets were found to be capable of stabilizing the oil-water interface to form particle-stabilized emulsions.

A few researchers have experimentally investigated the influence of pressure and showed a positive effect on foam stability. Szabries M. et al. (2019) investigated foam stability at pressure of 35 MPa and temperature up to 120°C using a High Pressure Foam Analyzer (HPFA). They studied foam height and mean bubble size of nitrogen foams at high pressure and found the foams were slightly more stable compared to low pressure, which can be explained by an increase in the Marangoni effect which allows liquid to flow from areas with lower surface tension to areas with higher surface tension. Wang Y. et al. (2017) experimentally investigated the stability of CO₂ foam at high pressure (2000 psi) and high temperature (110°C) and showed that the performance of foams at high temperatures was greatly dependent on the type of surfactant used. Pressure had a positive influence on the stability of CO₂ foams but was also dependent on the type of surfactant used. It was reported that half-life of NP-21 stabilized foam increase gradually with the increase of pressure, while pressure has a negative effect on the stability performance of NP-15 and NP-10 foams. Also, for anionic surfactant pressure showed positive effect with increase in half-life of sodium dodecyl sulfate (SDS) and sodium dodecyl sulfonate (SDS') surfactants due to their higher HLB values. In a previous work (Thakore V. et al., 2020), our preliminary results showed at a temperature of 100°C slight increase in pressure could increase the half-life of N₂ foams stabilized with several surfactants.

To date, there is very limited information on the thermal stability of liquid foams at elevated temperatures (e.g., 150°C and above), which are typical in EGS environments. In this paper, we will discuss the thermal stability of N₂/water foams under the influence of temperature and pressure. The N₂ foams were studied previously for Oil & Gas production (Harris and Reidenbach, 1987) and in this project as one category of foam candidates for EGS application (Thakore et al., 2020). But these previous studies were limited in temperature and pressure ranges. A laboratory setup was constructed to measure foam stability for temperature ranging between room temperature (~25°C) and 200°C and pressures up to 400 psi. The effect of four different surfactants, three types of gelling agents, and two different nanoparticles are presented along with discussion. Our results will show that while temperature decreases the foam half-life, pressure can

enhance its stability. Among the various compositions, foams stabilized with AOS surfactant and gelling agent guar gum or GO nanoparticles exhibit the best overall performance under the current testing conditions.

2. EXPERIMENTAL METHOD

2.1 Apparatus for foam generation

A laboratory setup was designed to study the foam stability as shown in Figure 1. In a typical experiment, the base solution (the liquid phase) store in a stainless steel tank is pressurized by an air-driven pump. The pressurized liquid flows passing an accumulator, which is used to stabilize the liquid pressure, into a foam generator. Meanwhile, high-pressure gas (N_2) was injected into the foam generator. The pressure of the gas phase is adjusted by the tank regulator to match the pressure of the liquid phase. The quality of the foam is calculated from the densities of the liquid and the gas phases along with their flow rates, which are controlled by flow meters. In this study, the quality of the foams is maintained around 95% (5 vol.% of the water in foams). The foam generator is a $\frac{1}{4}$ " diameter and 6" long tube that contains a wire mesh. Two pressure gauges are installed on both sides of the foam generator to monitor pressure drop. The heating section consists of a water bath for pre-heating and a high-temperature oil bath. The water bath and oil bath can heat up to 100°C and 250°C , respectively. The generated foam is injected into a sealed stainless-steel cube with sapphire windows (view cell). The view cell is completely immersed inside the oil bath. The generated foam flows through the pre-heated water bath and is stored inside the view cell. The pressure of the view cell is controlled by a back pressure regulator. Our setup can generate liquid pressure up to 2800 psi. However, due to the pressure ratings of other components, this study focused on testing at 400 psi or below. The foam height is observed through the window by a digital camera. An infrared camera is also used to monitor the temperature of the view cell when it is in equilibrium with the oil bath.

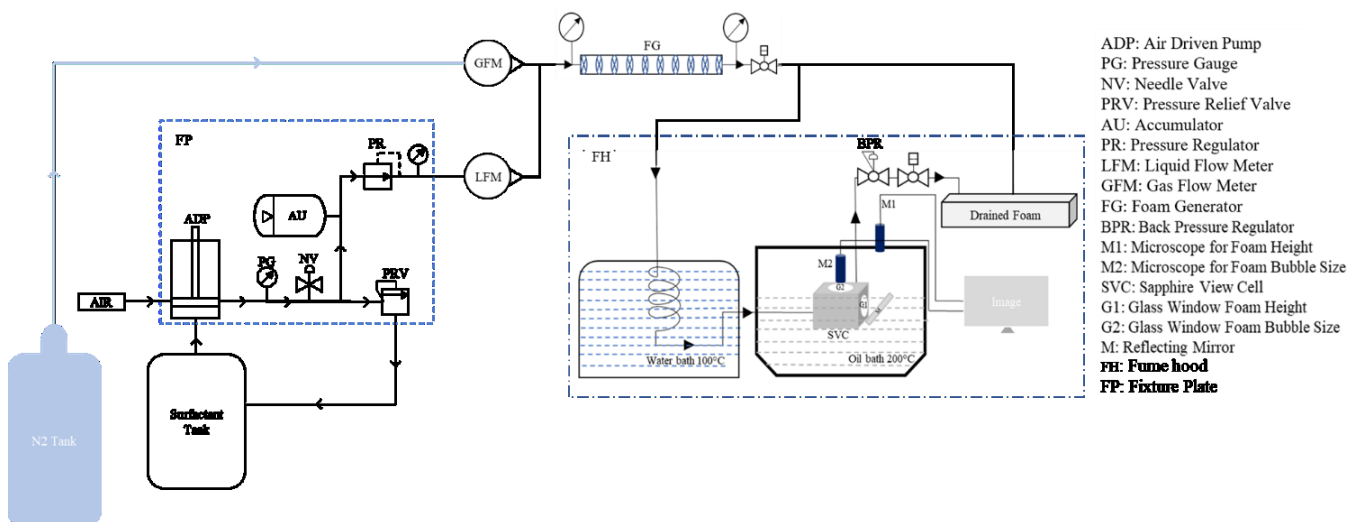


Figure 1: Schematic of high pressure and high-temperature foam study setup.

2.2 Foam base solutions

Four different surfactants and five additives were investigated in this study. Alfa olefin sulfonate (AOS) and sodium dodecyl sulfate (SDS) are commonly used anionic surfactants, while TergitolTM (NP-40) and cetyltrimethylammonium chloride (CTAC) are nonionic and cationic surfactants, respectively. Guar gum and bentonite clay are used as gelling agents, borate salt as a cross-linker for the gelling agent guar gum, and SiO₂ and graphene oxide as nanoparticle additives. All these chemicals were purchased from commercial sources and diluted to the specific concentration to make the base solutions (Table 1). In the current study, all surfactants were tested at 1 wt.% concentration, which was a common value used in many literature works. It has been shown when the concentration of the surfactant was above an optimal value, no significant increase in stability could be observed (Simjoo M., 2012; Azdarpour A., 2013).

All the liquid phases were prepared in deionized (DI) water. Surfactants of appropriate amounts were added to 2500 ml of DI water and the solution was mixed with a mechanical stirrer at 1100 rpm for 5 min while avoiding the formation of bubbles in the base solution. For the preparation of the guar/clay-containing solution, both were slowly added to the DI water which was constantly stirred at 800 rpm until all the powder was homogeneously dispersed without the formation of agglomeration. Then, surfactants were added to the guar suspension and mixed for about 5 min. Additional DI water was then added under constant stirring at 1100 rpm to avoid the formation of any foam. For the preparation of the crosslinked base solution, borate salt (crosslinker) was added into guar-containing solution with constant stirring at 1100 rpm to avoid thickening of base solution due to active cross-linking between guar polymer and borate ions. Then, the surfactant was added to the crosslinked solution and mixed for 10 mins. Additional DI water was added to complete the solution with the required concentration. Graphene oxide base solution was prepared by simply adding the required amount of GO water dispersion to the DI water, followed by the addition of the surfactants and stirring at 800 rpm to ensure homogenous mixing of the solution. Additional DI water was added to adjust the GO concentration to 0.05 wt.%.

Table 1 Surfactants and additives used in this study.

Additive	Characteristics	Vendor	Concentration in the base solution (wt.%)
AOS	Anionic surfactant	Chemistry Connection, PA, USA	1
SDS	Anionic surfactant	Sigma-Aldrich, USA	1
NP-40	Nonionic surfactant	Sigma-Aldrich, USA	1
CTAC	Cationic surfactant	Sigma-Aldrich, USA	1
Guar gum	Gelling agent	Sigma-Aldrich, USA	0.36
Bentonite clay	Gelling agent	Sigma-Aldrich, USA	0.36
Borate salt	Cross-linker	Sigma-Aldrich, USA	0.1
Graphene oxide	Nanoparticle, 4-30 μm	Graphenea, Spain	0.05

2.3 Foam thermal stability measurement

To study the foam stability, the foam life is measured inside the view cell at a given temperature and pressure condition. Before the foam is injected, the view cell is first heated to reach the oil bath temperature, which is checked with an IR camera. The foam quality is controlled by adjusting the flow rates of gaseous and liquid phases and foam injected pressure is controlled by pressure regulators. It is important to note that the injection of foams into the view cell would slightly reduce the temperature of the view cell due to the lower temperature of the foams. This phenomenon may represent a potential temperature drop in the hot dry rocks because of the injection of ambient-temperature fluid. This “quenching” effect in the view cell was partially mitigated by preheating the foam using the water bath.

After the foam is injected into the view cell, the height of the foam is monitored by a digital camera as shown in Figure 2. By measuring the foam height as a function of time, the half-life of the foam, i.e. the time needed to reduce to 50% of original foam height, can be determined (Figure 2b). For each testing condition, three experiments were conducted, and the average values were reported.

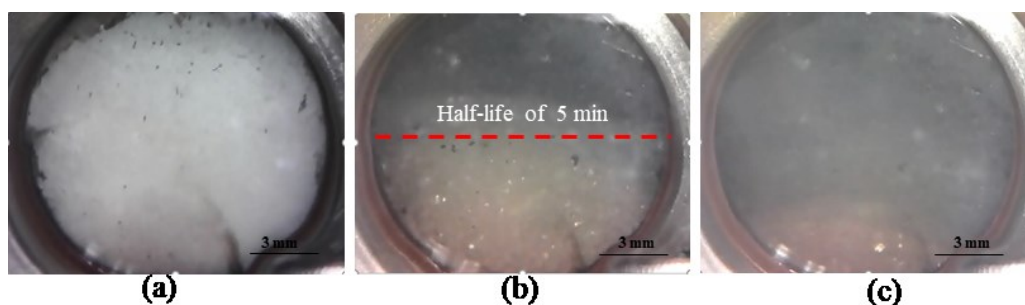


Figure 2: Digital images were taken during a foam testing of AOS+Guar foams at 180°C and 400 psi condition. The three images represent foam (a) after the injection, (b) at 50% height, and (c) at end of the test.

3. RESULTS

In this section, experimental results will be reported. We will focus on surfactants, and then foams with and without stabilizing agents including guar, crosslinker, GO and clay. The temperature and pressure effects will be discussed, and the performance of these agents at the condition 200°C and 400 psi will be highlighted.

3.1 Foams containing Alfa Olefin Sulfonate (AOS)

Alfa olefin sulfonate is an anionic surfactant commonly included in foam base fluids used by oil and gas industries. Figure 3 shows the half-life of various foams stabilized with AOS at different temperatures and pressures. For all compositions, it is observed that foam half-life decreases with an increase in temperature. On the other hand, the half-life is increased with an increase in pressure. For example, at 100 psi, the half-life of AOS+ Crosslinker foam decreased from 3600 sec (60 min) to 48 sec (0.8 min) when the temperature increased from 100°C to 200°C (Figure 3A). Whereas, with the increase in pressure from 100 psi (Figures 3A) to 200 psi (Figures 3B), the half-life of AOS foam is observed to increase from 27 sec (0.45 min) to 60 sec (1 min) at 200°C. Addition of other stabilizing agents further enhanced the thermal stability of AOS foams, which is more prominent at pressures above 200 psi. Crosslinking agent (borate salts) and graphene oxide nanoparticles generated the most stable AOS foams, which showed similar thermal stability at high temperature and pressure, their half-life was found to be around 540 sec (9 min) at 200°C and 400 psi (Figure 3D). Gelling agent guar gum also enhanced thermal stability for AOS foams, which recorded stable foams for approximate 275 sec (4.5 min) at 200°C and 400 psi (Figure 3D). At 400 psi and 200°C, the foam half-life was measured to be about 180 sec (3 min) with addition of bentonite clay (Figure 3D), which among all the stabilizing agents was least effective and showed similar thermal stability behavior to that of only AOS foams.

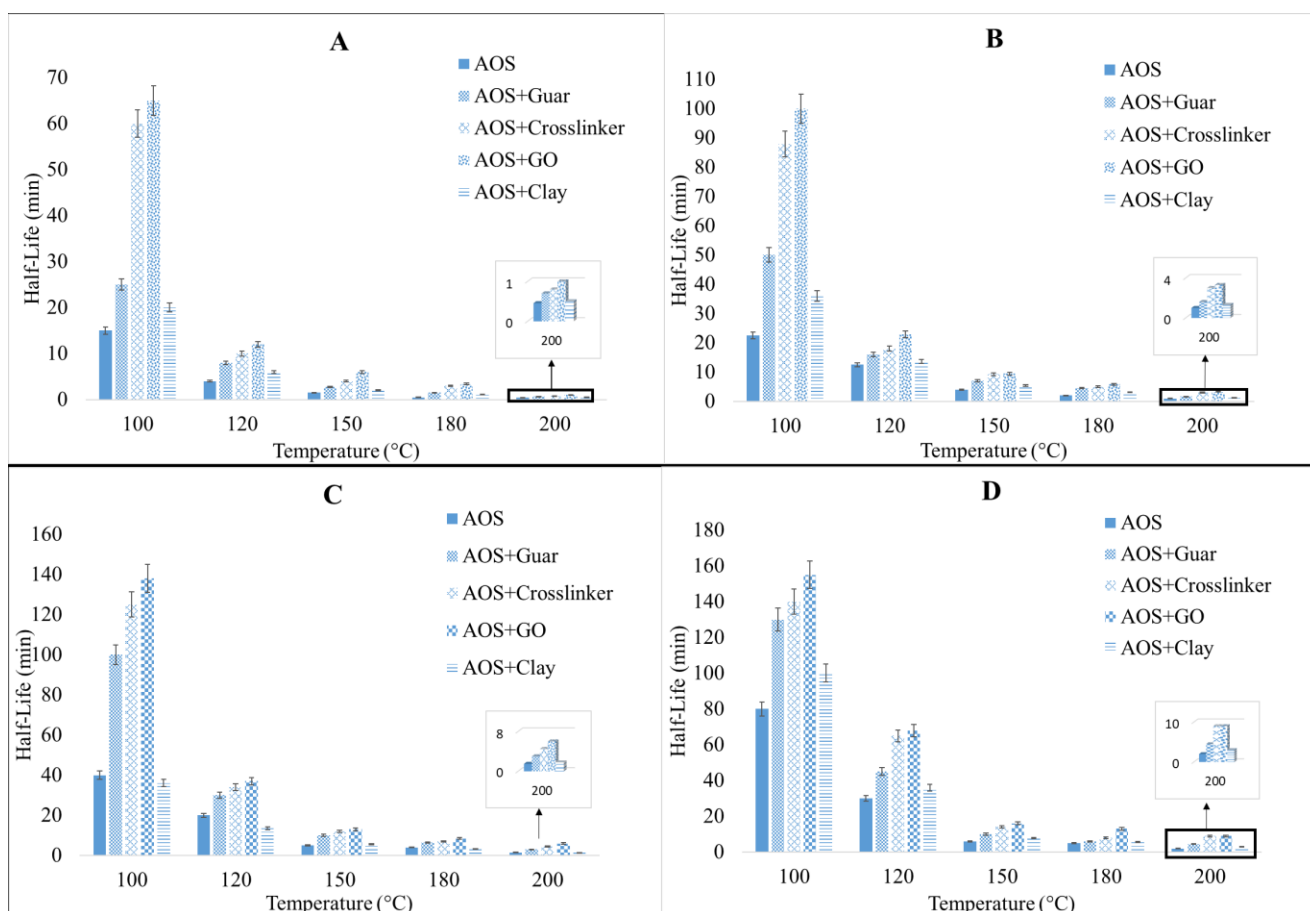


Figure 3: Thermal stability of AOS foams with different stabilizing agents at (A) 100 psi, (B) 200 psi (C) 300 psi, and (D) 400 psi.

3.2 Foams containing Sodium Dodecyl Sulfate (SDS)

Sodium dodecyl sulfate is another anionic surfactant that is capable to generate long-lasting room temperature foams. As shown in Figure 4, the thermal stability of SDS foam decreased with increase in temperature, and a drastic reduction in half-life is observed for temperature above 120°C. At 200°C, the half-life of SDS foam increased from ~8 sec at 100 psi (Figure 4A) to ~25 sec at 400 psi (Figure 4D). On the other hand, at 400 psi, SDS foam's half-life plunged by 33% with an increase in temperature from 100°C to 200°C (Figure 4D). The addition of gelling agent guar gum showed enhanced thermal stability comparing to only SDS foams at 100°C, which recorded a 23% increase at 100 psi (Figure 4A) compared to a 16% increase at 400 psi (Figure 4D). SDS+Guar foams showed the least thermal stability with a half-life of only 30 sec at 200°C and 400 psi. SDS foam with addition of graphene oxide showed the best stability at the temperature of 100°C under all pressure ranges. SDS+GO foam's half-life at 100°C was recorded at 600 sec (Figure 4A) and increased to 1380 sec with an increase in pressure from 100 psi (Figures 4A) to 400 psi (Figures 4D). GO foams recorded a half-life of 50 sec at 200°C and 400psi (Figure 4D). Bentonite clay was also seen to improve the thermal stability of SDS-only foams, which showed a half-life similar to GO foams (Figure 4D). SDS+clay foam's half-life was recorded at 45 sec for 400 psi and 200°C (Figure 4D). Crosslinking agent borate salt showed the least stable foams at 200°C for pressure up to 300 psi (figure 4C). However, with an increase in pressure to 400 psi this foam showed a similar half-life as of GO and clay foams (Figure 4D).

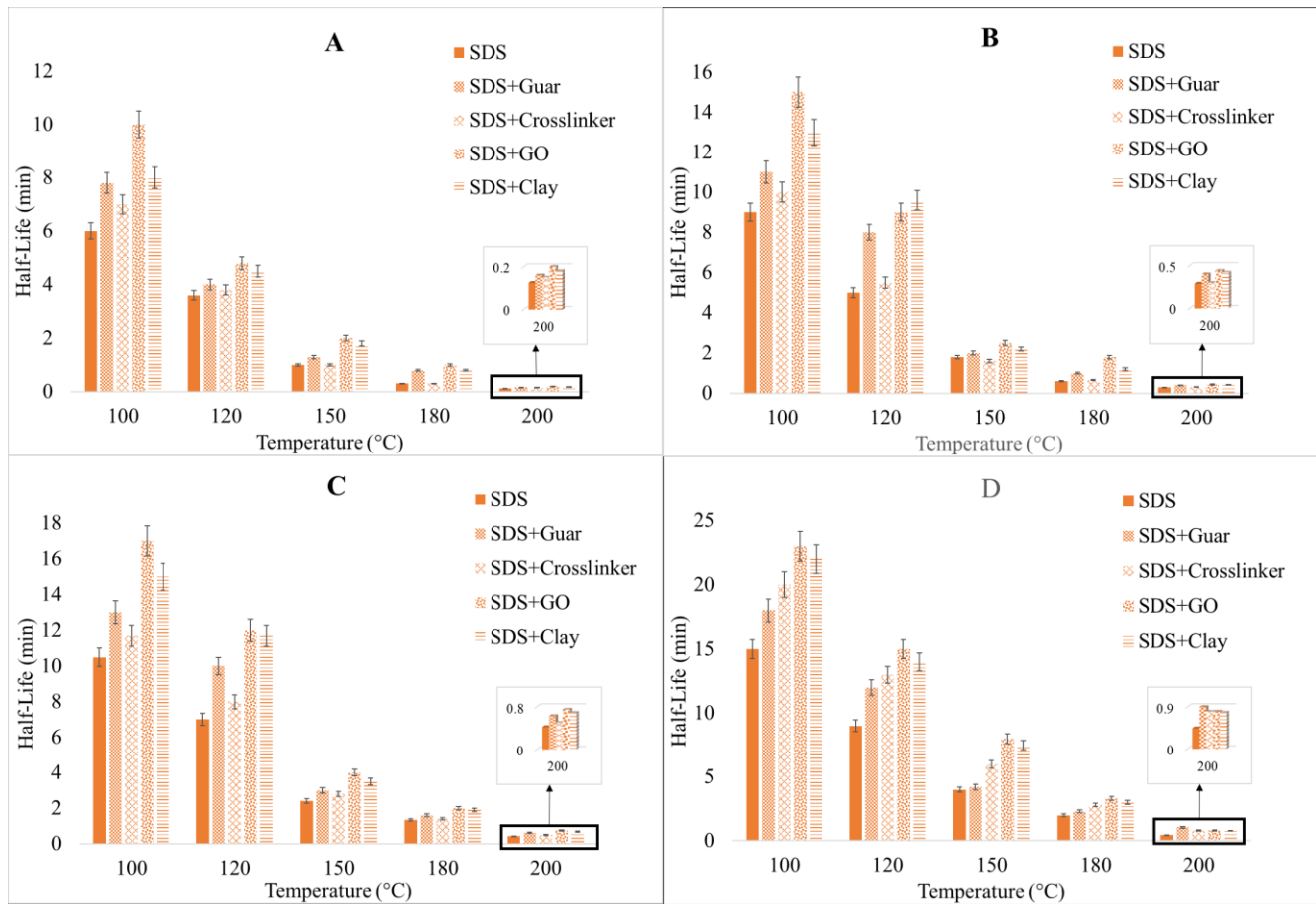


Figure 4: Thermal stability of SDS foams with different stabilizing agents at (A) 100 psi, (B) 200 psi (C) 300 psi, and (D) 400 psi.

3.3 Foams containing Tergitol™ (NP-40)

Tergitol™ is a commercially available non-ionic surfactant, which is studied by several researcher (Goswami, R. et al., 2018, Wang, Y. et al., 2017) as potential foaming agents for fracturing fluids. Foams containing only NP-40 showed a radical decrease in thermal stability with increase in temperature above 120°C. NP-40 foam showed an 83% increase in half-life with an increase in pressure at 100°C (Figure 5A), while at 200°C, NP-40 foams recorded an 85% increase with an increase in pressure from 100 psi (Figure 5A) to 400 psi (Figure 5D). Moreover, it was noted that half-life for NP-40 foams was decreased with an increase in temperature from 100°C to 200°C by 57% at 100 psi (Figure 5A) compared to a 12% decrease at 400 psi (Figure 5D). All the stabilizing agents improved thermal stability compared to NP-40 only foams. At the pressure range of 100 psi and 200 psi, all stabilizing agents showed comparable thermal stability. With the increase in pressure, NP-40+GO generated the most stable foams. At 200°C, NP-40+GO foam's half-life was recorded at 30 sec, 36 sec, 108 sec, and 168 sec (2.8 min) under pressures of 100 psi, 200 psi, 300 psi, and 400 psi, respectively (Figure 5). On the other hand, bentonite clay was the least effective stabilizing agent with an increase in pressure with a half-life of 46 sec and 90 sec at 200°C at 100psi (Figure 5A) and 400 psi respectively (figure 5D). The half-life of foams with guar and crosslinker stabilizing agent was recorded at 102 sec (1.7 min, Figure 5a) and 120 sec (2 min, Figure 5D) at 200°C and 400 psi, respectively.

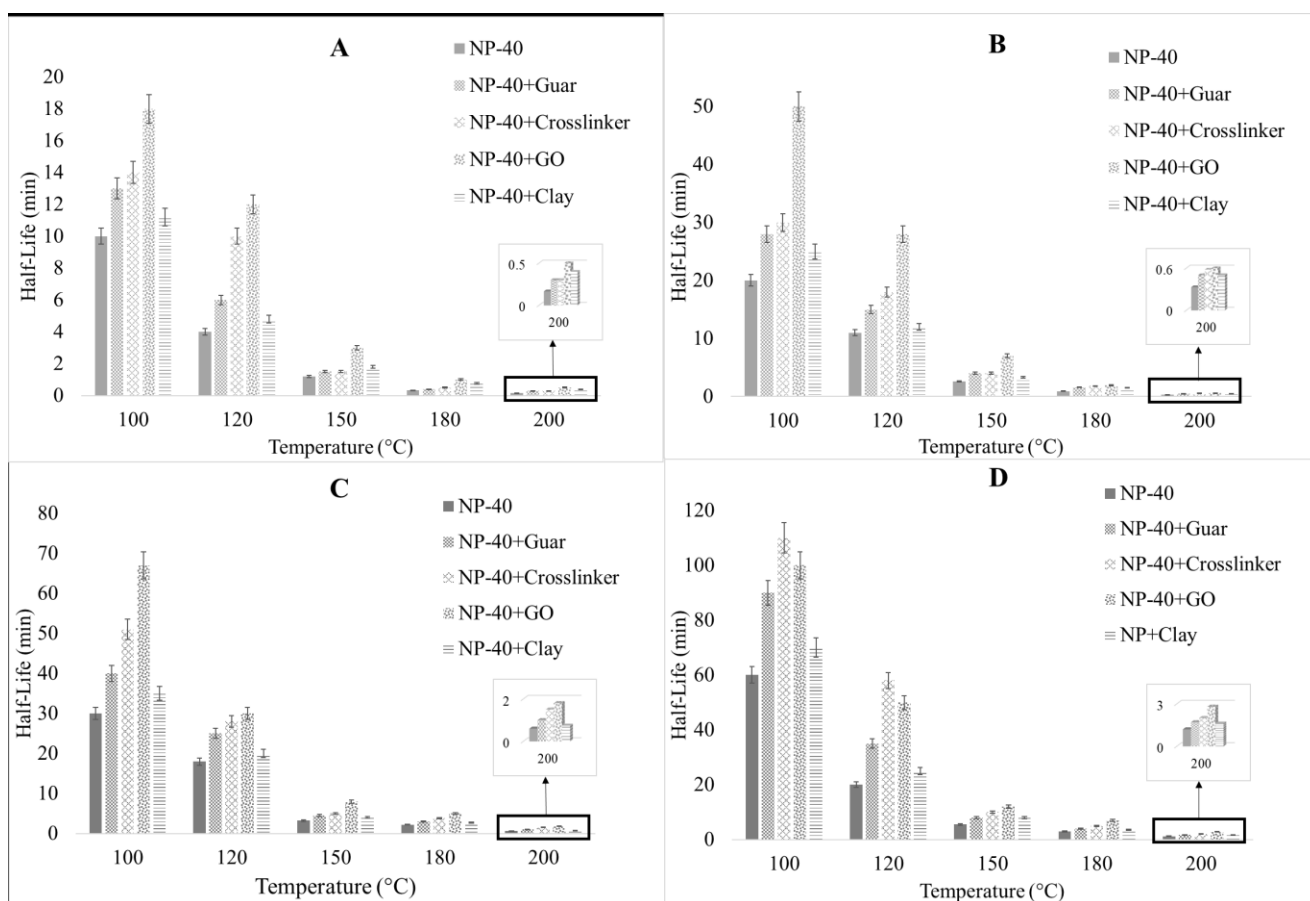


Figure 5: Thermal stability of NP-40 foams with different stabilizing agents at (A) 100 psi, (B) 200 psi (C) 300 psi, and (D) 400 psi.

3.4 Foams containing cetyltrimethylammonium chloride (CTAC)

CTAC is a cationic surfactant widely used in many different fields, such as cosmetics, textile, and petrochemical industries. As shown in Figure 6, a drastic decrease in half-life is observed with an increase in temperature above 120 °C for all CTAC foams. Contrastingly, the half-life increased with increase in pressure from 100 psi to 400 psi. Stabilizing agent guar gum can significantly stabilize CTAC foams at a temperature of 100-120 °C but is observed to be the least stable at a higher temperature above 150 °C. Crosslinker agent was the most effective stabilizing agent for all the pressure ranges, however, thermal stability rapidly decreased with an increase in temperature with a half-life of 2400 sec at 100 °C (Figure 6A) which was then reduced to 130 sec at 200 °C at 400 psi (Figure 6D). Graphene oxide enhanced thermal stability for CTAC foam at 200 °C, with a half-life of 27 sec, 36 sec, 50 sec, and 150 sec for 100 psi, 200 psi, 300 psi, and 400 psi. Also, stabilizing agent bentonite clay showed a drastic increase in stability at high temperature and pressure. It was observed that the thermal stability of CTAC foam was significantly enhanced with the addition of clay and GO stabilizing agents showing an 80% increase in half-life at 200 °C compared to CTAC-only foams.

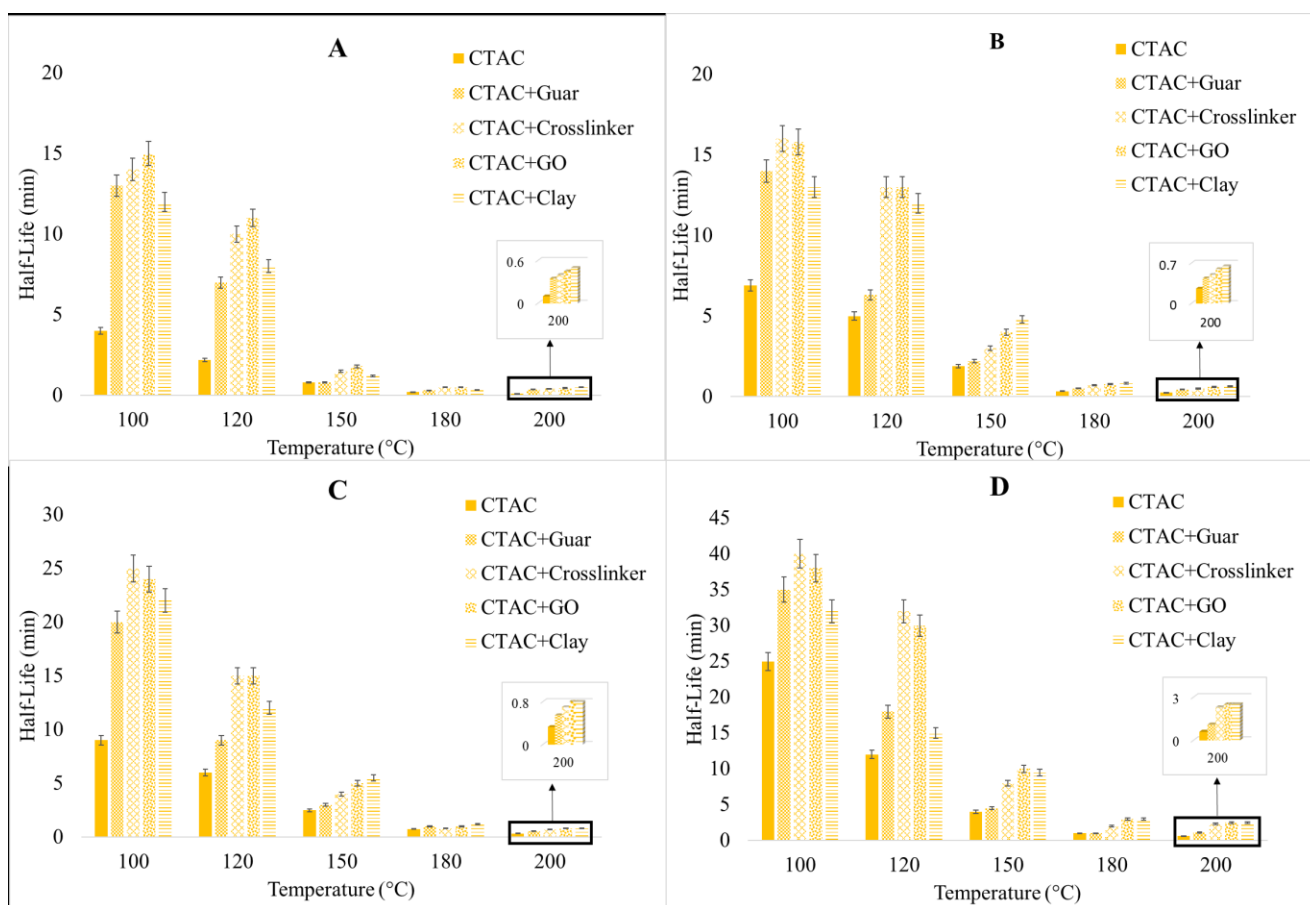


Figure 6: Thermal stability of CTAC foams with different stabilizing agents at (A) 100 psi, (B) 200 psi (C) 300 psi, and (D) 400 psi.

4. DISCUSSION

4.1 Effect of stabilizing agents

In general, stabilizing agents can enhance the thermal stability of foams at elevated temperatures. However, as shown in Tables 2-5, their effect differs depending on the type of the surfactants, as well as the temperature and pressure. With the addition of guar gum half-life of AOS, SDS, NP-40, and CTAC foams at 200°C and 400 psi were recorded as 270 sec, 30 sec, 100 sec, and 65 sec, respectively. An approximately 80% increase of half-life is observed at 200°C for all the surfactants with increase in pressure from 100 psi to 400 psi (Table 2). For all foams containing gelling agent guar, AOS foams showed the best thermal stability at high temperatures. Addition of crosslinker agent borate salt showed more enhancement in thermal stability for AOS and NP-40 foams than SDS and CTAC foams. AOS foams with crosslinker were most stable at 200°C and 400 psi with a half-life of 540 sec. SDS was least affected by the addition of the crosslinking agent. An average 88% increase of half-life is observed at 200°C for all the surfactants with the addition of crosslinker by increase in pressure from 100 psi to 400 psi (Table 3). For bentonite clay, at lower pressure and high temperature of 200°C, CTAC foams showed the most enhanced thermal stability compared to other surfactants. AOS foams with addition of clay was most stable at 100°C, however a drastic reduction on half-life was observed with increase in temperature above 150°C. Approximately an average of 76% increase of half-life is observed at 200°C for all the surfactants with addition of bentonite clay by increase in pressure from 100psi to 400psi (Table 4). When GO was used in addition to various surfactants, AOS foams were most stable compared to any other surfactants. AOS foam's half-life recorded at 200°C for 100 psi was 60 sec and 540 sec for 400 psi. With GO as a stabilizing agent, ~ 86% increase in half-life was observed at 200°C with increase in pressure from 100 psi to 400 psi for all the surfactants (Table 5).

Table 2. Half-life of Guar gum foams at 200°C							
Liquid Phase Composition	Half-Life (sec) for respective pressure (psi)						
	100	150	200	250	300	350	400
AOS+Guar	42 ±2	70 ±3	96 ±2	135 ±2	180 ±6	240 ±4	270 ±5
SDS+Guar	9 ±3	16 ±2	24 ±2	30 ±5	38 ±6	54 ±3	63 ±3
NP40+Guar	18 ±3	22 ±3	30 ±2	40 ±5	60 ±4	84 ±2	102 ±5
CTAC+Guar	21 ±2	34 ±5	27 ±6	30 ±3	35 ±5	43 ±7	66 ±3

Table 3. Half-life of Crosslinker foams at 200°C							
Liquid Phase Composition	Half-Life (sec) for respective pressure (psi)						
	100	150	200	250	300	350	400
AOS+ Crosslinker	48 ±2	150 ±5	180 ±6	216 ±3	270 ±5	390 ±5	540 ±3
SDS+ Crosslinker	9 ±5	14 ±2	18 ±2	27 ±3	30 ±2	36 ±8	50 ±5
NP40+ Crosslinker	18 ±2	21 ±4	35 ±5	38 ±3	90 ±2	105 ±5	120 ±2
CTAC+ Crosslinker	24 ±5	28 ±4	32 ±3	40 ±2	45 ±3	50 ±2	138 ±5

Table 4. Half-life of Bentonite clay foams at 200°C							
Liquid Phase Composition	Half-Life (sec) for respective pressure (psi)						
	100	150	200	250	300	350	400
AOS+ Clay	30 ±2	60 ±5	78 ±3	102 ±2	108 ±9	162 ±10	180 ±6
SDS+ Clay	11 ±2	17 ±1	25 ±4	36 ±3	40 ±5	42 ±3	47 ±2
NP40+ Clay	24 ±3	28 ±2	30 ±5	40 ±6	45 ±4	60 ±4	96 ±3
CTAC+ Clay	30 ±2	36 ±2	40 ±7	45 ±6	48 ±3	80 ±4	150 ±3

Table 5. Half-life of Graphene oxide foams at 200°C							
Liquid Phase Composition	Half-Life (sec) for respective pressure (psi)						
	100	150	200	250	300	350	400
AOS+ GO	60 ±1	168 ±3	190 ±5	240 ±2	360 ±5	420 ±8	540 ±4
SDS+ GO	12 ±1	20 ±3	25 ±2	32 ±4	45 ±6	48 ±2	50 ±3
NP40+ GO	30 ±5	35 ±4	38 ±2	85 ±6	108 ±3	120 ±2	160 ±5
CTAC+ GO	27 ±4	33 ±6	36 ±3	42 ±2	48 ±5	73 ±6	150 ±2

4.2. Effect of temperature

Good thermal stability is essential for foams to be utilized as a hydrofracturing fluid in EGS reservoir stimulation applications. However, our results as well as many literature data showed that temperature had strong and negative influence on foam stability. The poor thermal stability at elevated temperatures may be attributed to the accelerated liquid phase drainage and gaseous phase diffusion. First of all, the reduced foam stability may be due to lower viscosity of the liquid phase at higher temperature, which resulted in more rapid liquid drainage and hence lower foam stability. A literature review on foam fracturing fluid by M. Gu, K.K. Mohanty (2015) suggested that temperature lowered the viscosity of foams by decreasing the liquid phase viscosity and stability of bubbles. In addition, the foam included in this study had high quality of ~ 90-95%. Harris et al. (1996) reported that high quality foams were highly unstable with either N₂ or CO₂ gaseous phases, as these foams were usually a mixture of very small and very large gas bubbles, which could lead to faster bubble coalescence.

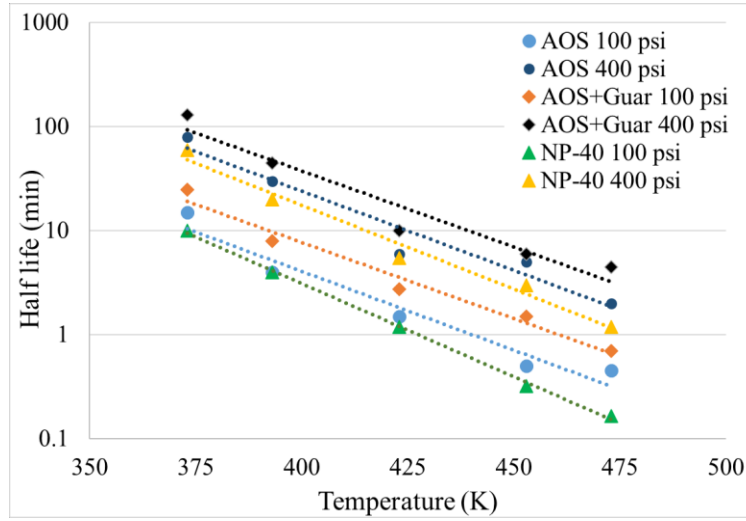
Our preliminary analysis showed that for a given foam composition at a given pressure, the half-life, t , may be described by the following relationship

$$t = t_0 \exp(-aT) \quad (1)$$

where T is temperature in Kelvin, and t_0 and a are fitting parameters. Figure 7 shows some fitting examples to this exponential decay function. The corresponding quantitative fitting results are given in Table 6. These preliminary analysis shows that t_0 depends on the pressure such that an increase in the pressure will lead to an increase in t_0 (Table 6). In addition, t_0 may also be a function of the type of the foam composition (Table 6). On the other hand, parameter a may be considered as the decay rate, which is dependent on the foam composition and pressure. A higher value of a indicates a higher dependency of the foam stability on temperature. As shown in Table 6, foams generated with AOS had smaller a value than the foam stabilized with NP-40, implying that the thermal stability of AOS foams was less susceptible to temperature than NP-40 foam. More detailed analysis of the temperature effect on foam stability is ongoing and will be reported in the future.

Table 6. Fitting results of data included in Figure 7 to Eq. (1).

Data set	t_0 (min)	a (1/K)	R^2
AOS foam at 100 psi	4.67×10^6	3.4×10^{-2}	0.951
AOS foam at 400 psi	2.93×10^7	3.5×10^{-2}	0.940
AOS+guar foam at 100 psi	5.48×10^6	3.7×10^{-2}	0.974
AOS+guar foam at 400 psi	2.61×10^7	3.3×10^{-2}	0.936
NP-40 foam at 100 psi	4.56×10^7	4.1×10^{-2}	0.998
NP-40 foam at 400 psi	4.98×10^7	3.7×10^{-2}	0.970

**Figure 7.** Temperature dependence of foam half-life for selected data. The dotted lines represent exponential fitting of experimental data to Eq. (1).

4.3. Effect of pressure

In contrast to the effect of temperature, pressure shows a positive effect on the foam stability, which is both observed in this study as well as in other literature work. Szabries M. et al. (2019) experimentally showed that mean bubble size were significantly constant at high pressure than at lower pressure and foam stability was increased with increase in pressure. They argued that this was due to the increased Marangoni effect which allowed liquid to flow from areas with lower surface tension to areas with higher surface tension. Coalescence of bubbles is caused by diffusion of the gaseous phase from smaller bubbles, where the surface tension is higher, to larger bubbles, where the surface tension is lower. Therefore, an enhanced Marangoni effect would countereffect coalescence in foams and thus extend the foam longevity.

In this study, pressure showed positive effect on foam stability for all surfactants at various temperatures. Figure 8 shows a few examples of pressure dependency of experimental data, where increasing trends are observed for different testing condition. Although our preliminary analysis showed that different sets of experimental data might be better fit to various mathematical equations (e.g., exponential, power law, polynomial, etc.), the overall trend indicated that increase in pressure would lead to increased thermal stability of all foams. Our future work will extend the testing pressure to higher pressures, which will provide more information on the dependence of foam stability on pressure conditions.

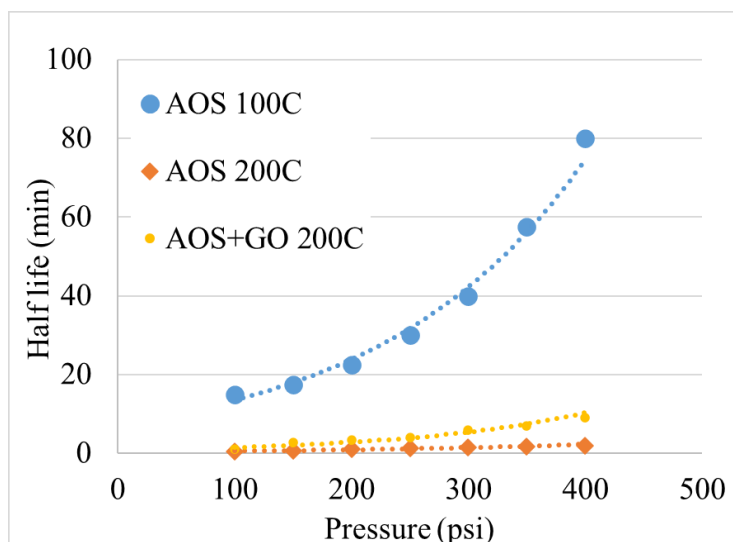


Figure 8. Pressure effect on foam half-life for selected data. The dotted lines are not fitting curves but trend lines.

5. CONCLUSIONS

In this work, a laboratory setup was constructed to study thermal stability of aqueous nitrogen foams in the temperature range between 100°C and 200°C, while the pressure was varied between 100 psi and 400 psi. Foams stabilized with four surfactants and other stabilizing agents were examined, including guar gum, bentonite clay, crosslinker, and GO. Results indicated that foam stability decreased dramatically as temperature increased. On the other hand, foams became relatively more stable as pressure increased. Anionic surfactant AOS and non-ionic surfactant NP-40 showed the best overall performance with relatively stable foams within the temperature and pressure ranges included in this study. In contrast, foams generated using another anionic surfactant SDS or cationic surfactant CTAC were less stable. Crosslinking agent and graphene oxide were most effective stabilizing agents which significantly enhanced foam half-life for all surfactants, while bentonite clay was least effective. Addition of guar gum also showed long lasting foams for temperature below 120°C. Finding from this study indicates that with appropriate selection of surfactants and stabilizing agent it is possible to obtain more stable foams as potential fracturing fluids for EGS applications.

ACKNOWLEDGEMENT

This research was sponsored by the US Department of Energy, Assistant Secretary for Energy Efficiency and Renewable Energy, Geothermal Technologies Office, as part of the Enhanced Geothermal Systems Program under Contract No. DE-AC05-00OR22725 with the US Department of Energy.

REFERENCES

- Aarra MG, Skauge A, Solbakken J, Ormehaug PA (2014) Properties of N₂- and CO₂-foams as a function of pressure. *J Petrol Sci Eng* 116:72–80.
- A. Azdarpour, O. Rahmani, E. Mohammadian, M. Parak, A. R. M. Daud and R. Junin: The effects of polymer and surfactant on polymer enhanced foam stability, *IEEE Business Engineering and Industrial Applications Colloquium (BEIAC)*, Langkawi, 2013, 97-102.
- Ahmed, S.; Elraies, K.A.; Hashmet, M.R.; Alnarabiji, M.S. Empirical Modeling of the Viscosity of Supercritical Carbon Dioxide Foam Fracturing Fluid under Different Downhole Conditions. *Energies* **2018**, *11*, 782.
- Brannon H, Kendrick D, Luckey E, Stipetich A (2009) Multi-stage fracturing of horizontal wells using ninety-five quality foam provides improved shale gas production. *SPE Eastern regional meeting proceedings*. Paper (vol 124767).
- Emrani, A. S., & Nasr-El-Din, H. A. (2017, April 1). Stabilizing CO₂ Foam by Use of Nanoparticles. *Society of Petroleum Engineers*. 2017, April 1) 174254-PA.
- Espinoza, D. A., Caldelas, F. M., Johnston, K. P., Bryant, S. L., & Huh, C. (2010, January 1). Nanoparticle-Stabilized Supercritical CO₂ Foams for Potential Mobility Control Applications. *Society of Petroleum Engineers*. 2010, April 24).
- Frohne K: "Comparison of conventional hydraulic and water/nitrogen foam fracturing in two Ohio Devonian shale gas wells". *Energy Research and Development Administration*, Morgantown, WV (USA). Morgantown Energy Research Center (1976).
- Gandossi, L.: State of the Art Report on Waterless Stimulation Techniques for Shale Formations, *EUR 28189 EN*, Luxembourg: Publications Office of the European Union, (2016).

- Goswami, R., Chaturvedi, K.R., Kumar, R.S., B.H. and Sharma, T., Effect of ionic strength on crude emulsification and EOR potential of micellar flood for oil recovery application in high saline environment. *Journal of Petroleum Science and Engineering*, 170, pp.49-61.
- Harris, P.C.: Chemistry and Rheology of Borate-Crosslinked Fluids at Temperatures to 300°F, *J. Petroleum Technology*, (1993), 24339-PA
- Harris, P. C., Reidenbach, V. G.: High-Temperature Rheological Study of Foam Fracturing Fluids, *J. Petroleum Technology*, (1987), 613-619
- Lv, Q., Li, Z., Li, B., Li, S., & Sun, Q.: Study of Nanoparticle–Surfactant-Stabilized Foam as a Fracturing Fluid. *Industrial & Engineering Chemistry Research*, **54**, (2015), 9468-9477.
- M. Gu, K.K. Mohanty, Rheology of polymer-free foam fracturing fluids, *Journal of Petroleum Science and Engineering*, Volume 134, 2015, Pages 87-96, ISSN 0920-4105.
- M. Simjoo, T. Rezaei, A. Andrianov, P.L.J. Zitha,: Foam stability in the presence of oil: Effect of surfactant concentration and oil type, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **438**, 2013, 148-158.
- Moridis, G.: Literature Review and Analysis of Waterless Fracturing Methods, Lawrence Berkeley National Laboratory, Berkeley, CA 94720 (2017).
- Olasolo, P., Juárez, M.C., Morales, M.P., D’Amico, S., Liarte, I.A.: Enhanced Geothermal Systems (EGS): A Review, *Renewable and Sustainable Energy Reviews*, 56, (2016), 133-144.
- Oussoltsev D, Fomin I, Butula KK, Mullen K, Gaifullin A, Ivshin A, Senchenko D, Faizullin I (2008): “Foam fracturing: new stimulation edge in Western Siberia (in Russian)”. *SPE Russian oil and gas technical conference and exhibition*.
- Szabries M., Sergelius S., Kordts A., Jonsson Marlitt (KRUS): Foam Stability and Foam Structure under High Pressure for Terriary Oil Prodction. *Enhanced Oil Recovery*, Aplication Report AR290, 06/2019.
- Thakore, V., Ren, F., Voytek, J., Xi, J., Wang, H., Wang, J.-A.J., Polsky, Y.: High-Temperature Stability of Aqueous Foams as Potential Waterless Hydrofracking Media for Enhanced Geothermal Systems (EGS), *Proceedings*, 45th Workshop on Geothermal Reservoir Eng., Stanford U., Stanford, CA, Feb. 10-12, 2020, SGP-TR-216.
- Verma, A., Chauhan, G., and Ojha, K.: Synergistic effects of polymer and bentonite clay on rheology and thermal stability of foam fluid developed for hydraulic fracturing. *Asia-Pac. J. Chem. Eng.*, **12**, (2017), 872– 883.
- Wang, Hong, Wang, Jy-An John, Polsky, Yarom, & Ren, Fei. Research Considerations for Foam Fracturing in Stimulation Development for Enhanced Geothermal Systems. *Proceedings*, 44th Workshop on Geothermal Reservoir Eng., Stanford U., Stanford, CA, Feb. 10-12, 2020, SGP-TR-216.
- Wang, Hong, Wang, Jy-An John, Polsky, Yarom, Ren, Fei, Li, Haoqi, Thakore, Virensinh, & Xi, Jiaxin. Study of Foam Fracturing for Enhanced Geothermal Systems Using Model Material. *Proceedings*, 45th Workshop on Geothermal Reservoir Eng., Stanford U., Stanford, CA, Feb. 10-12, 2020, SGP-TR-216.
- Wang, H., Guo, W., Zheng, C. *et al.* Effect of Temperature on Foaming Ability and Foam Stability of Typical Surfactants Used for Foaming Agent. *J Surfact Deterg* **20**, 615–622
- Wanniarachchi, W.A.M., Ranjith, P.G., Perera, M.S.A. *et al.*: Current opinions on foam-based hydro-fracturing in deep geological reservoirs, *Geomech. Geophys. Geo-energ. Geo-resour.* **1**, (2015), 121–134.
- Wilk, K. Experimental and Simulation Studies of Energized Fracturing Fluid Efficiency in Tight Gas Formations. *Energies* **2019**, *12*, 4465.
- Yanqing Wang, Yang Zhang, Yanmin Liu, Liang Zhang, Shaoran Ren, Jun Lu, Xiaohui Wang, Na Fan: The stability study of CO2 foams at high pressure and high temperature, *Journal of Petroleum Science and Engineering*, **154**, 2017, 234-243.
- Zhang, Pan & Ren, Shaoran & Shan, Yu & Liang, Zhang & Liu, Yizhe & Huang, Lijuan & Pei, Shufeng. (2019). Enhanced stability and high temperature-tolerance of CO 2 foam based on a long-chain viscoelastic surfactant for CO 2 foam flooding. *RSC Advances*. 9. 8672-8683. 10.1039/C9RA00237E
- Zheng Xue, Andrew Worthen, Ali Qajar, Isaiah Robert, Steven L. Bryant, Chun Huh, Maša Prodanović, Keith P. Johnston, Viscosity and stability of ultra-high internal phase CO2-in-water foams stabilized with surfactants and nanoparticles with or without polyelectrolytes, *Journal of Colloid and Interface Science*, Volume 461, 2016, Pages 383-395, ISSN 0021-9797.