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High-Temperature Stability of Aqueous Foams as Potential Waterless Hydrofracking Fluid for Geothermal Reservoir Stimulation

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ABSTRACT

Hydraulic fracturing is the process of fracturing rock formations with high-pressure water-based fluids. In Enhanced Geothermal Systems (EGS) hydraulic fracturing is carried out by injecting high-pressure fluids into the Hot Dry Rocks (HDR) under carefully controlled conditions. The fluid used for fracturing is an important component for EGS, not only concerning the technical approch but also environmental impact. Recent research has been carried out to develop waterless fracturing technologies for EGS, including foam-based hydrofracking, where foams are mixtures of gas and liquid fluids. Foam fracturing fluids have potential benefits over water-based fluids because of less water consumption, less damage in water sensitive formations, and less liquid to recover and handle after fracturing process. One challenge for implementing foam fracturing in EGS is to achieve stable foams at high temperatures, as the foam stability tends to decay with increase in temperature.

This research is focused on investigating the stability of foams at high temperatures. Preliminary results show that 1) N_2 foams are more stable compared to CO_2 foams, 2) foams containing only surfactants were not stable at high temperatures, and 3) addition of different stabilizing agents increased the thermal stability of all the foams. It was observed that different stabilizing agents interacted differently with anionic, nonionic, and cationic surfactants. It was further shown that the crosslinking agent with a base solution of pH 6 and graphene oxide dispersion was the most effective stabilizing agent for anionic surfactant AOS, while bentonite clay effectively enhanced thermal stability for another anionic surfactant SDS. SiO_2 nanoparticles showed limited improvement in thermal stability at high temperatures compared to other stabilizing agents.

1. INTRODUCTION

Geothermal energy is clean, and renewable, which can be found in abundance in our planet. This vast store of thermal energy is largely contained in Hot Dry Rocks (HDR), which are present within 5-6 miles underneath the earth's surface. In recent years hydrofracking of HDR has become a growing research area in Enhanced Geothermal Systems (EGS). EGS utilizes artificial reservoirs created by injecting high-pressure fluids into the HDR under carefully controlled conditions. Fracturing fluids are typically water-based,which can enter the formation and cause damage and harm the environment due to high volume of water usage by contaminating surface water resources, and usage of additives (Gandossi L., 2016). Hence, new waterless fracturing technologies could help to address these concerns. Research has been conducted to develop non-water based fracturing fluids, particularly gas-based fluid and foam-based fluids, with little water consumption that can effectively deliver the preferred hydraulic pressure into the fracture zone (Yekeen et al., 2018). Among all the waterless fracturing, foam-based fracturing has gained much interest due to its unique attributes, including higher proppant carrying capacity, lower water and chemical usage, more efficient and easier fluid flow back and less environmental damage (Wanniarachchi et al., 2017). In particular, foams have the capacity to reduce about 10-20 times water usage during hydraulic fracturing.

Foams are complex mixture of liquids with gaseous phase, where the liquid phase act as an ambient phase and gas as the dispersed phase. Its rheological properties foam are influenced by many factors including gaseous phase, surfactant, stabilizing agent, foam quality, temperature, pressure, bubble texture, shear rate, and viscosity. Many researchers have developed laboratory-scale experimental setups to study the foam rheological properties at downhole conditions. A circulating foam loop was design to study foam stability at 400°F and 2000 psi by evaluating two rheological techniques, a standard fluid-stability test and temperature sweep test influenced by additives, temperature, and pressure. These tests allowed to measure foam stability with time, determine temperature limitations for a particular foam fluid, and allow direct comparison of different foamers, additives, or gelling agents (Miller, M.J., 2005). Study for foam-based fracturing fluid at high temperature up to 120°C for CO_2 water-based foams containing different ethoxylated amine surfactant showed stabilized carbon water foams with high salinity brine base solution up to 182g/L at 120°C and 3,400 psi and high foam quality (Chen et al., 2014). Also, decrease in alkyl tail for trimethylammonium cationic surfactant foams with the increase in temperature up to 120°C was unusually stabilized (Chen et al., 2016). Cationic surfactant showed better stability compared to ethoxylated amine surfactant at lower concentration of dissolved brine solution. One of the important early experiments for high temperature (300°F) foam stability was carried out by Harris, who showed rheological behavior of nitrogen-based foam fracturing fluids with the addition of stabilizing agent guar gum using a recirculating loop viscometer. It was observed that foam fluids did not thin as rapidly as gel fluid and foam stability tends to depend on surfactant concentration not the gelling agent (Harris et al., 1987). Also, high temperature borate cross-linked fracturing fluid rheology for foam stability was investigated. Borate ions form a complex cross-link pair with stabilizing agent guar 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 better stable foams. Additives like gel-stabilizer, polymer and high pH crosslinked-fluid showed increase in temperature range for fracturing fluids upto 300°F (Harris, 1993). Borate crosslinked fluids for use above 200°F requires adequate control of delay time by controlling pH or the availiblity of broate ions or both by using of low soluble calcium borate salts (Ainley B. R.,1993). Another gelling agent bentonite clay was studied which reported that clay was found to improve foam rheology at a reduced concentration of anionic surfactant, including improvement of apparent viscosity, viscoelasticity, and thermal stability (Verma. A., 2017). The mechanism for improved thermal stability by the gelling agent is due to the adsorption of a polymer layer of surfactant onto the gelling agent (guar/bentonite clay) particle surface which results in better stabilization of bubbles. Foam stability at high pressure and temperature, experimental results showed that the performance of CO_2 foams was greatly dependent on the type of surfactant and its hydrophilic-lipophilic balance (HLB) value i.e. cationic or nonionic surfactants. They observed a synergic effect of different surfactants improving the CO_2 foam performance at high temperatures (Wang Y. et al., 2017).

Foam stability with the addition of nanoparticles has also been investigated at high temperatures. The presence of nanoparticle aggregates to stop free drainage of foam by trafficking plateau border of foam bubbles. It is worth understanding the nanoparticle stability which is important for foam fracturing for EGS. Several experiments were conducted to study foam stability at high temperature with surface treated hydrophilic silicon dioxide (SiO2) nanoparticles in presence of an anionic surfactant Sodium dodecyl benzenesulfonate (SDBS), it was observed that stability and thermal adaptability of the SDBS foam increased when SiO_2 nanoparticles were added to the base solution at high temperature up to 90°C (Lv Q., et al., 2015). They also reported proppant carrying capacity of SiO_2/SDBS foams was slightly larger than SDBS foam and gel/SDBS foams. Moreover, laboratory-based experiments were performed to understand optimal concentration of the surfactant and nanoparticles for CO_2 based foam stability at high temperature (212°F/100°C) and pressure (800 psi). Temperature and pressure showed opposite effects on foam stability when an anionic solution was used, however nanoparticles improved the foam stability for nonionic surfactant, surfactant with guar gum and viscoelastic surfactant (Emrani, A. S. et al., 2017). In addition to SiO_2 nanoparticles, graphene oxide (GO) was also considered to be a foam additive for enhanced oil recovery. GO is considered to adhere by a lower interfacial energy which acts like a surfactant (Cote, L., et al., 2010). Research showed that GO can be used as a surfactant sheet to emulsify organic solvents with water and disperse insoluble materials in water; also GO sheets were also found to be capable of stabilizing oil-water interface to form the particles-stabilized emulsions. Some other studies showed that GO appeared as amphiphile sheets with hydrophilic edges and a more hydrophobic basal plane which is a single molecule as well as a colloidal particle; this duality makes it behave like a molecular and colloidal surfactant (Kim et al., 2010). Experimental studied showed graphene oxide foam are more stable compared to nanographene and partially reduced graphene oxide. This shows that graphene oxide has good hydrophilicity and the highest interfacial activity that enabled stabilizing CO_2 foams (Barrabino, A. et al., 2018).

Beyond the laboratory research, efforts to develop waterless stimulation technologies have been practiced for decades in the oil and gas industries. Waterless simulation has been tried historically in regions where formations are water sensitive or water is unavailable or limited (Koshshou et al., 2017). It covers a wide range of methods from mechanical, electrical, foam, cryogenic, to explosive and propellant fracturing (Lu S., 2018; Moridis G., 2017). Currently, various types of non-water hydraulic fracturing fluids are used in the oil and gas industries, including foams, gases, and hydrocarbons and each has advantages and limitations (Olasolo, P. et al., 2016). A few field work had used foam as the fracturing fluid. The first documented foam-based fracturing fluid application was in Youngs town, Ohio, USA in 1975, where foam was generated by mixing water and nitrogen. It was shown that foam fracturing had better performance compared to conventional hydraulic fracturing. Later, a large-scale foam fracturing operation was successfully performed in Devonian shale well in Jackson County, USA. The foam was made up of CO_2 (liquid) and N_2 (gas) for hydro fracturing (Riedel, E. F., 1981). Foam based fracturing fluid has also been tested in Russia, western Siberia basin using water/nitrogen foam and successful production from depleted mid-permeable oil wells was achieved (Oussoltsev, D. et al., 2008).

Based on the laboratory experimental data and field practice results, it was believed that foam was promising as a potential fracking fluid in enhanced geothermal applications (Wang, H. et al., 2019). Among many parameters, several foam characteristics are considered to be critical for EGS hydrofracking including viscosity, density, and stability. In particular, the stability of foams at high temperatures (> 150^{o}C) is not well understood partly because most existing applications, such as those used in the oil and gas industries, only involve services at relatively low temperatures (below 150^{o}C). The stability of foams depends on slowing down three major phenomena taking part in the foam bubbles. These are described as coarsening, coalescence, and drainage. Coalescence occurs due to equilibrium liquid volume fraction which causes rupture of bubble film separating the bubbles until they fully disappear with respect to time. Coarsening has the same origin as the phenomenon referred to as Oswald ripening, where gas diffuses from smaller to larger bubbles due to pressure difference. During the coarsening bubbles move relative to each other, changing their topology and shape while liquid moves within the border region separating the bubbles (Gilberto L., 2015). Drainage is the downward flow of liquid between the plateau borders of bubbles due to gravity. Foams are more stabilized by reducing drainage by the addition of surface-active particles, gelling agents, or surfactants. Controlling drainage in the foam films could be an important means to enhance the foam stability for EGS applications.

This paper is focused on the thermal stability study of water foams as a function of temperature. Using a home-made apparatus, the thermal stability of N_2-in-water and CO_2-in-water foams were measured between room temperature and 180^{o}C. The effect of surfactants, gelling agents, and nanoparticles will be presented and discussed.

2. EXPERIMENTAL METHOD

2.1 Apparatus for foam generation

A laboratory setup was designed to study thermal foam stability, which includes the following components, as shown in figure 1: gas tank (CO_2 and N_2), the base solution container, a foam generator tube, a water bath, an oil bath, a view cell, and various flow meters, pressure gauges, and valves. The base solution is pressurized using the gas tank. The foam generator contains a stainless steel mesh. The water bath is used to preheat the foam to approximately 80°C, and the oil bath is used to heat the foam to the final target temperature. In the current setup, the heating oil can be used up to 180°C. A high-temperature oil can also be used, which is capable of heating to 250°C. The view cell is a sealed stainless cube with a sapphire window. The foam height is observed through the window by a digital camera. Temperatures of the water and the oil baths are measured and controlled by thermocouples. An infrared camera is also used to monitor the temperature inside the view cell when it is in equilibrium with the oil bath temperature. Due to the limitation of the base solution tank, the pressure in the system was kept at around 10 psi. The foam quality is controlled by adjusting the flow rates of the gaseous phase and the liquid phase. In this study, the quality of the foams was maintained around 95% (5 vol.% of the water in foams), representing a 20 times water deduction.

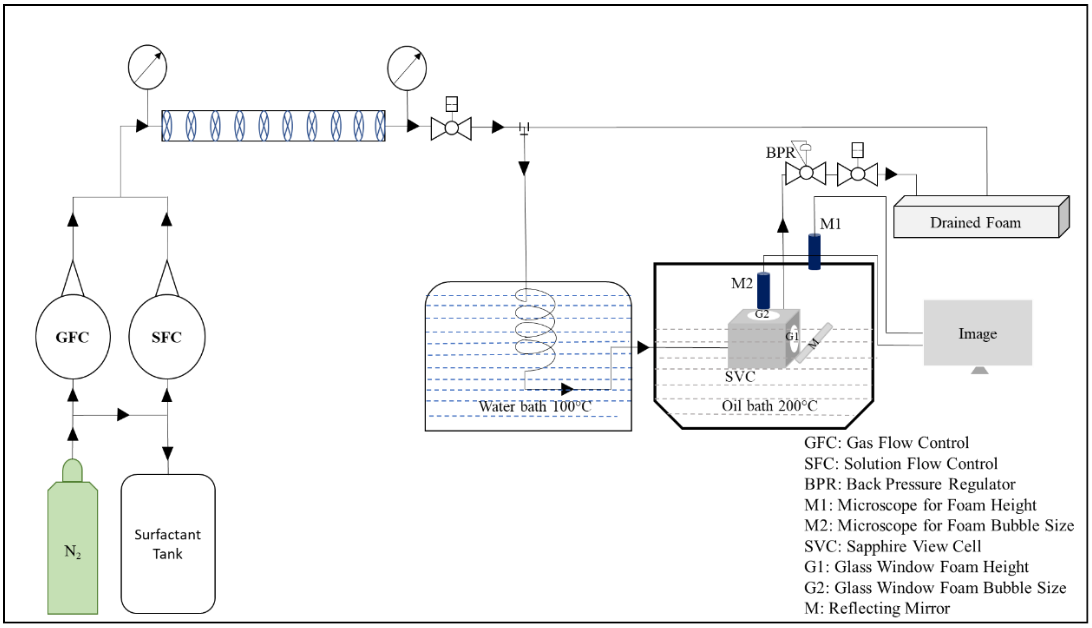


Figure 1: Schematic of the foam study setup.

2.2 Base solutions

Four different types of surfactants and five additives were investigated in this study. Alfa olefin sulfonate (AOS) and Sodium Dodecyl Sulfate (SDS) are commonly used anionic surfactants, while tergitol (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, and SiO_2 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 work. 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 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 waere 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 crosslinked foam base solution, borate salt was added into guar-containing solution with constant stirring at 1100 rpm to avoid thickening of base solution due to active cross-link 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 and maintain the pH of the crosslinker solution at 6. For the preparation of the suspension containing the SiO_2 nanoparticles, SiO_2 powder was ultra-sonicated in DI water at 150 W. This homogenized nanoparticle suspension was then added to the required surfactant solution under constant stirring. Graphene oxide base solution was prepared by simply adding the required amount of GO 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 0.05wt%. Figure 2 shows some example pictures of the base solutions prepared in this study.

Table 1 Surfactants and additives used in this study

Chemical Name	Characteristics	Vendor	Concentration in the base solution (wt.%)
AOS	Surfactant	Chemistry Connection,PA, USA	1
SDS	Surfactant	Sigma-Aldrich, USA	1
NP-40	Surfactant	Sigma-Aldrich, USA	1
CTAC	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
SiO_2	Nanoparticle, 50-70 nm	US research nanomaterials, USA	0.1
Graphene oxide	Nanoparticle, 4-30 µm	Graphenea, Spain	0.05

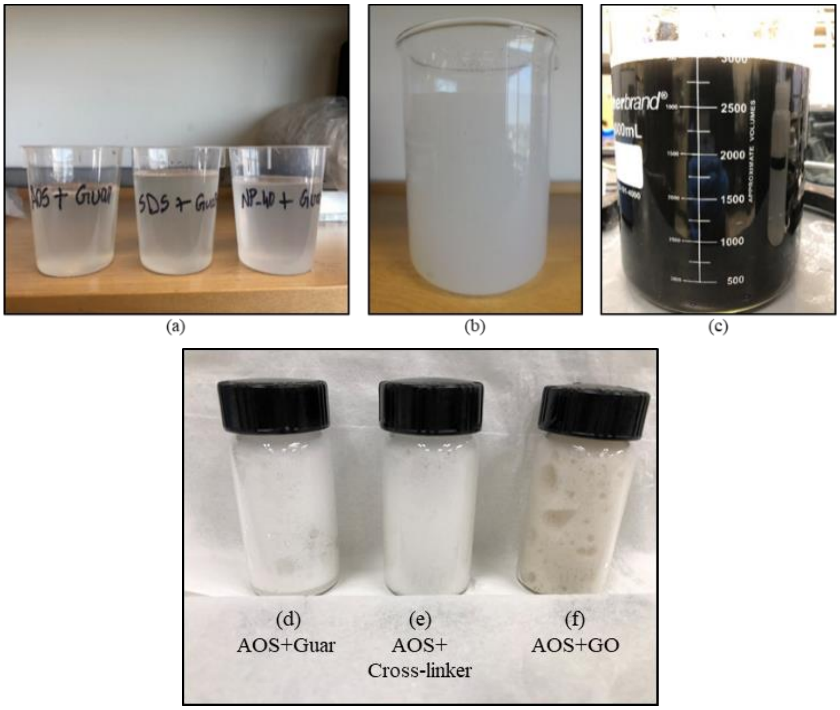
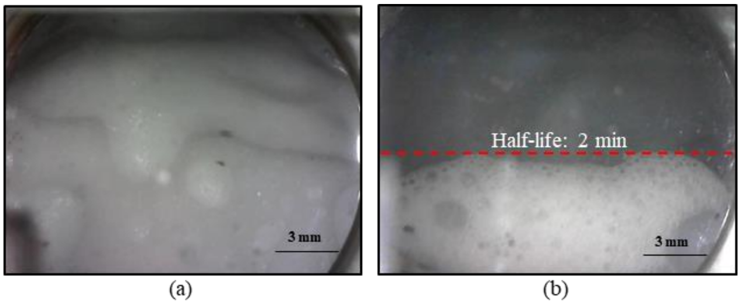


Figure 2: Picture showing (a) base solution with various surfactants and the gelling agent guar, (b) base solution containing suspended 0.1wt% SiO_2 nanoparticles with 1 wt% of SDS, and (c) 0.05 wt% GO base solution with 1wt% AOS as the surfactant. Pictures (d), (e) and (f) represent N_2 based foams made from AOS+Guar, AOS+Crosslinker, and AOS+GO foam at room temperature, respectively.

2.3 Thermal stability measurement

To measure the foam stability at a given temperature, the view cell was pre-heated to a pre-determined temperature. The foam was then generated by passing the gaseous phase and the liquid phase through the foam generator and directed into the view cell. The foam quality was adjusted by controlling the flow rates of the gaseous and liquid phases, while the pressure of the foam inside the view cell was controlled by adjusting the back-pressure regulator. Foam stability was studied by measuring the foam height as a function of time, from which the half-life of the foam was determined (Figure 3). Three measurements were taken from each testing condition. 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 as a result of the injection of ambient-temperature fluid. This "quenching" effect in the view cell was partially reduced by preheating the foam using the water bath. Figure 4 shows some example data for N_2 foams, where the normalized foam height as a function of time was plotted at various temperatures. The half-life of the foam was determined by finding the time corresponding to the 50% of the initial foam height (see the red dotted line as an example).



(a) (b)

Figure 3: Pictures showing the decay of foam height as a function of time: (a) immediately after the foam injection, and (b) reduced to approximately 50% of the original height. These images were taken at 100°C for an N_2 based foam made with AOS and crosslinker.

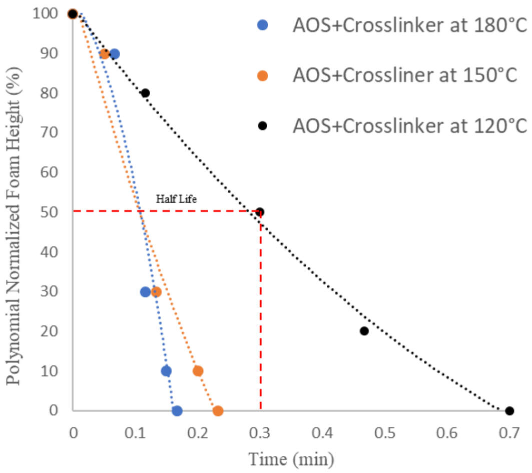


Figure 4: Foam Height measurement with respect to time for AOS + Crosslinker foams at various temperatures.

3. RESULTS AND DISCUSSION

3.1 Thermal Stability of Foams Containing Only Surfactants

Figure 5 compares the half-life between room temperature and 100°C for both N_2 and CO_2 foams made with various surfactants. The four surfactants used in this study showed similar results. It can be seen that with an increase in temperature, thermal stability drastically decreases for all the surfactants. No stable foams were observed above 100°C. AOS showed slightly better thermal stability at 100°C compared to other surfactants. Foams made with N_2 had half-lives greater than 50 min. at room temperature while CO_2 foams had half-lives around 10 min. This result, along with the data to be discussed in the next sections, indicates N_2 foams are more stable than CO_2 foams made in this study.

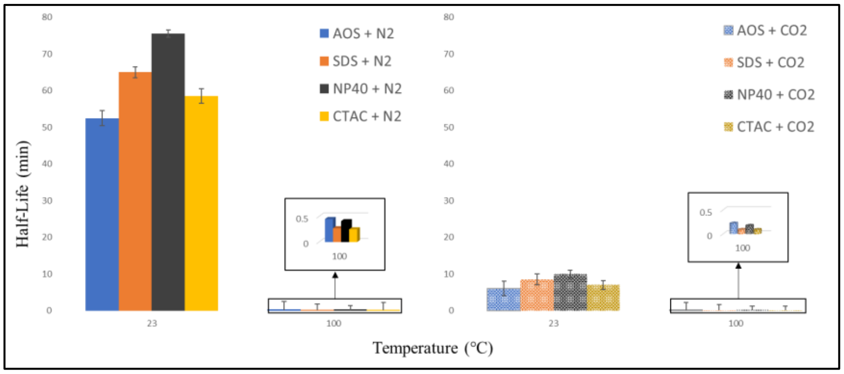


Figure 5: Thermal stability of nitrogen (left) and carbon dioxide (right) foams for different surfactants.

3.2 Thermal Stability of Foams Containing Surfactants and Stabilizing Agents

To improve the thermal stability at high temperatures, several stabilizing agents were added to the base solution in addition to the surfactants. These stabilizing agents function differently in order to reduce drainage in foam films. It was observed that foams were more stable with stabilizing agents when compared to individual surfactants. Both N_2-water-foams and CO_2-water-foams were studied with all four different surfactants and five different stabilizing agents.

3.2.1 Guar gum

Guar gum is a plant-based polymer commonly used in oil and gas enhanced industries. Addition of guar increases the viscosity of the base solution for all the surfactants. The temperature effect on half-life of guar-based foams for both CO_2 and N_2 as the gaseous phase is shown in Table 2. It was noticed that with an increase in temperature, the thermal stability decreased for all the guar-based foams. It was clearly observed that CO_2-based foams showed less stable performance when compared to N_2-base foams, likely due to the faster transfer of CO_2 gas across foam bubble films (lamella). Nonionic surfactant, NP-40 showed the best performance of thermal stability at 90°C and 100°C for both N_2 and CO_2 based foams. However, its half-life reduced drastically for higher temperature up to 180°C, whereas, AOS foams with guar showed better thermal stability at high temperature ranges. CTAC does not show a drastic reduction in thermal stability but were observed less stable when compared to AOS guar-based foams. SDS foams were the least stable with addition of guar for all the temperatures and its half-life monotonically decreased with an increase in temperature.

Table 2a Half-Life of N_2 foam with Guar.

Liquid Phase Composition	Half-Life (sec) fro respective temperature (°C)				
	90	**100**	**120**	**150**	**180**
AOS+Guar	72 ±3	57 ±2	45 ±6	9 ±4	3 ±1
SDS+Guar	39 ±5	30 ±3	7 ±2	4 ±2	2 ±1
NP40+Guar	187 ±2	63 ±6	15 ±6	4 ±2.2	2 ±1
CTAC+Guar	86 ±4	48 ±2	21 ±5	8 ±3	3 ±2

Table 2b Half-Life of CO_2 foam with Guar.

Liquid Phase Concentration	Half-Life (sec) fro respective temperature (°C)				
	90	**100**	**120**	**150**	**180**
AOS+Guar	34 ±5	22 ±2	15 ±3	3 ±1	2 ±0.5
SDS+Guar	29 ±2	16 ±5	6 ±3	2 ±1	3 ±2
NP40+Guar	61 ±2	42 ±2	7 ±1	4 ±1	1
CTAC+Guar	53 ±4	16 ±1	10 ±2	6 ±3	1

3.2.2 Bentonite clay

The addition of bentonite clay did not increase the viscosity of base solution as it did for guar, however it showed improved performance in half-life for some surfactants (Table 3). It was observed that both N_2 and CO_2 based foams showed a similar trend in foam half-life for all the surfactants. AOS was the most stable at 90°C but showed worst stability at 180°C for both the gaseous phase. It was observed that CTAC showed the best thermal stability performance at 180°C compared to other nonionic and anionic surfactants for both gaseous phases. There is no drastic reduction in half-life for SDS foam with increase in temperature as it is for other surfactants with addition of clay in both gaseous phases. At high temperature of 180°C both N_2 and CO_2 foams showed similar half-life for all the surfactants.

Table 3a Half-Life of N_2 foam with clay.

Liquid Phase Composition	Half-Life (sec) fro respective temperature (°C)				
	90	**100**	**120**	**150**	**180**
AOS+Clay	72 ±1	33 ±3	15 ±2	4 ±2	2 ±1.5
SDS+Clay	21 ±2	14 ±5	6 ±2	4 ±1	1
NP40+Clay	30 ±2	16 ±5	9 ±3	3 ±0.5	2 ±1

Table 3b Half-Life of CO_2 foam with clay.

Liquid Phase Concentration	Half-Life (sec) fro respective temperature (°C)				
	90	**100**	**120**	**150**	**180**
AOS+Clay	78 ±3	40 ±2	18 ±3	5 ±3	2
SDS+Clay	45 ±1	27 ±2	13 ±5	7 ±4	4 ±2
NP40+Clay	49 ±8	22 ±5	10 ±2	4 ±3	3 ±1

CTAC+Clay	30 ±1	18 ±2	13 ±4	4 ±1.5	3 ±1

CTAC+Clay	43 ±1	24 ±3	11 ±5	6 ±5	5 ±1.5

3.2.3 Crosslinking Agent

Boric acid was used as a crosslinking agent. Borate ions can crosslink with guar polymer to increase the viscosity of the base solution. Table 4 shows thermal stability with crosslinking agent in addition of guar at pH 6 of base solution for both CO_2 and N_2. The anionic surfactant AOS showed good thermal stability performance compared to other surfactant for all temperatures, however radical change in foam stability from 90°C to 180°C is observed. Crosslinker did not enhance the performance of SDS as a surfactant which was observed to have poor thermal stability at 90°C and least stable to high temperature of 180°C. The cationic surfactant CTAC showed thermal stability similar to AOS at 180°C, while the least effect of cross linker was observed with NP40 as a surfactant at high temperature.

Table 4a Half-Life of N_2 foam with crosslinker.

Liquid Phase Composition	Half-Life (sec) fro respective temperature (°C)				
	90	**100**	**120**	**150**	**180**
AOS+ Crosslinker	150 ±1	117 ±3	21 ±2	6 ±1	4 ±0.8
SDS+ Crosslinker	30 ±2	25 ±2	18 ±5	5 ±2	2 ±0.5
NP40+ Crosslinker	120 ±1	102 ±3	24 ±2	5 ±0.4	3 ±1
CTAC+ Crosslinker	144 ±2	108 ±2	30 ±5	6 ±2	3 ±0.5

Table 4b Half-Life of CO_2 foam with crosslinker.

Liquid Phase Concentration	Half-Life (sec) fro respective temperature (°C)				
	90	**100**	**120**	**150**	**180**
AOS+ Crosslinker	120 ±2	52 ±2	14 ±4	5 ±3	4 ±1
SDS+ Crosslinker	21 ±2	14 ±3	6 ±1	4 ±0.5	1
NP40+ Crosslinker	84 ±2	48 ±5	15 ±4	5 ±4	2 ±1
CTAC+ Crosslinker	96 ±3	36± 2	12 ±6	5 ±2.5	4 ±2

3.2.4 Silicon dioxide nanoparticles

SiO_2 nanoparticles reduces the drainage time by blocking the lamella border between foam bubble (Hunter T. et al., 2007). Table 5 shows thermal stability effect of SiO_2 nanoparticles with different surfactants for both N_2 and CO_2 gaseous phases. Both gaseous phases showed a similar trend for half-life with respect to temperature with N_2 foams being more thermally stable. Silicon dioxide was most effective with nonionic surfactant NP40 at high temperature of 180°C. AOS foams were observed to be most stable at 90°C and least stable at 180°C for both gaseous phases.

Table 5a Half-Life of N_2 foam with SiO_2 nanoparticles.

Liquid Phase Composition	Half-Life (sec) fro respective temperature (°C)				
	90	**100**	**120**	**150**	**180**
AOS+SiO_2	39 ±2	19 ±5	10 ±2	6 ±3	2 ±0.5
SDS+SiO_2	30 ±3	12 ±3	9 ±2	4 ±2	3 ±2
NP40+SiO_2	33 ±2	15 ±5	10 ±4	6 ±3	3 ±1
CTAC+SiO_2	36 ±3	16 ±3	9 ±4	4 ±1	2

Table 5b Half-Life of CO_2 foam with SiO_2 nanoparticles.

Liquid Phase Concentration	Half-Life (sec) fro respective temperature (°C)				
	90	**100**	**120**	**150**	**180**
AOS+SiO_2	17 ±4	13 ±2	9 ±3	4 ±8	2 ±0.5
SDS+SiO_2	13 ±2	9 ±2	6 ±1	3 ±5	2 ±1
NP40+SiO_2	15 ±2	10 ±1	7 ±2	3 ±6	3 ±0.5
CTAC+SiO_2	16 ±3	12 ±2	6 ±3	3 ±5	2 ±1

3.2.5 Graphene oxide dispersion

As shown in Table 6, graphene oxide (GO) dispersion tends to enhance foam stability at high temperature for all the surfactants. SDS was seems as the most stable at 90°C and least at 180°C. It was observed that all the surfactants had similar foam half-life at high temperatures. The cationic surfactant CTAC and anionic surfactant AOS had better half-life at 180°C compared to other two surfactants. Both gas foams showed a similar trend for thermal stability with all the surfactants being the most effective with GO dispersion and SDS the least effective. CO_2 foams with GO dispersion showed poor thermal stability compare to N_2 foams.

Table 6a Half-Life of N_2 foam with GO.

Liquid Phase Composition	Half-Life (sec) fro respective temperature (°C)				
	90	**100**	**120**	**150**	**180**
AOS+GO	30 ±2	24 ±1	10 ±2	6 ±2	4 ±2
SDS+GO	40 ±2	22 ±3	7 ±4	5 ±2	4 ±2
NP40+GO	33 ±2	27 ±4	9 ±2	6 ±1	4 ±1
CTAC+GO	60 ±3	52 ±1	18 ±4	7 ±5	5 ±2

Table 6b Half-Life of CO_2 foam with GO.

Liquid Phase Concentration	Half-Life (sec) fro respective temperature (°C)				
	90	**100**	**120**	**150**	**180**
AOS+GO	21 ±2	13 ±6	9 ±2	4 ±3	3 ±2
SDS+GO	28 ±1	9 ±2	7 ±3	3 ±2	2 ±0.5
NP40+GO	12 ±2	11 ±2	7 ±1	4 ±1	3 ±1
CTAC+GO	30 ±1	18 ±3	13 ±2	4 ±1	3 ±2

AOS based foams showed better thermal stability performance for temperature range up to 120°C for all stabilizing agents, especially with guar and the crosslinking agent. However, at 180°C foams were only stable for 10-12 seconds. Even though crosslinker and GO dispersion foams were observed to be more stable than all the other stabilizing agents, they were only stable for a few seconds. Silicon dioxide and bentonite clay were observed to be least effective stabilizing agents with AOS as the surfactant. For SDS foams, guar was less effective as the stabilizing agent with increase in temperature. The two most effective stabilizing agents for SDS foams were bentonite clay and GO dispersions. The cross-linking agent showed good thermal performance at 100°C and 120°C, however half-life reduced by 80% when increased to 180°C. Silicon dioxide nanoparticles foams showed poor thermal stability performance, having similar half-life as guar at 180°C. Tergitol foams were very unstable at 100°C and no stability data were recorded above 100°C for NP-40 without addition of stabilizing agent. Tergitol foams showed improved half-life with crosslinker at intermediate temperatures of 100°C and 120°C compared to other stabilizing agents, but at high temperature of 150°C and above it was observe to have poor thermal stability performance. Bentonite clay and GO dispersions had almost same half-life at 180°C which were the best stabilizing agent for NP-40 for high temperature. SiO_2 and guar foams with NP-40 showed least thermal stability data with poor half-life with almost no foams at high temperatures. Foam half-life decreased rapidly with increase in temperature for all of the stabilizing agents studied for NP-40. Cationic surfactant CTAC was most effective to achieve high temperature stability with addition of bentonite clay and GO dispersion. The stabilizing agent showed less reduction on half-life with increase in temperature up to 180°C. Crosslinking agent foams showed half-life of 1.8 min at 90°C but decreased to 4 sec at 180°C. SiO_2 foams were least effective with CTAC for all the temperature range from 90°C to 180°C.

Good thermal stability is essential for foams to be utilized as a hydrofracturing fluid in EGS reservoir stimulation applications. The data obtained in this study showed a significant impact of temperature on the foam stability. At high temperatures of 180^{o}C, the foams were only stable for seconds. This poor thermal stability may be related to a couple of factors. First of all, the quality of the foams included in this study were approximately 95%. It was reported that high quality foams were highly unstable with both N_2 and CO_2 gaseous phases, as these foams are usually a mixture of very small and very large gas bubbles (Harris et al., 1996). Another yet more important reason, may be the pressure. The preliminary data presented in this study were recorded at pressures around 10 psi. At this pressure, the boiling temperature of water is approximately 115^{o}C, implying the liquid phase would be very unstable at high temperatures. Some literature data showed enhanced thermal stability with increase in pressure. The half-life of different ionic surfactant foams at 2000 psi and 120°C, which showed half-life for both CO_2 and N_2 foams increased with increase in pressure, howerer no study has been recorded at lower pressure (Wang et al., 2017). It was also studied that CO_2 foams were less stable than N_2 foam, which may be explained by the higher solubility of CO_2 that can lead to faster transport across the bubble films resulting in faster drainage and thus shorter half-life (Rio, E. et al., 2014). Our recent data showed that at 100^{o}C, the half-life of AOS-guar foam was increased from 2.5 min at 10 psi to 5 min when the pressure was increased to 30 psi (Table 7). This results implies that the high-temperature foam stability could be improved by increasing the pressure.

Table 7 Half-life data of N_2 Foam as a function of pressure.

Foam Base Solution	Temperature (°C)	Pressure (psi)	Half-life (min)
AOS+Guar	100	10	2.5
AOS+Guar	100	20	4.3

AOS+Guar	100	30	5.0

4. CONCLUSIONS

In this study, a laboratory setup was constructed to study the high-temperature thermal stability of aqueous foams by monitoring the time-dependent foam height. Foams made with four types of surfactants with five different stabilizing agents were examined between room temperature and 180^{o}C. Results show that N_2 foams were more stable than CO_2 foams, likely due to the lower solubility of N_2 in water. The addition of gelling agent guar showed some improvement for up to 120°C however drastic reduction in foam half-life with further increase in temperature was observes. Crosslinker (boric acid) and GO dispersion showed good thermal stability for most of the surfactants, while bentonite clay was very effective with CTAC and SDS foams. Silicon dioxide nanoparticles improved thermal stability for nonionic surfactant NP40. The addition of stabilizing agents could improve stability; however, half-life monotonically decreases with an increase in temperature. New strategies of high-pressure foam injection and addition of combination of stabilizing agents can be adopted to enhance high temperature foam stability. Future studies will focus on the examination of the pressure effect on foam stability at high temperatures.

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