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**Nanoparticle-Stabilized Supercritical CO₂ Foams for Potential Mobility
Control Applications**

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**Nanoparticle-Stabilized Supercritical CO₂ Foams for Potential Mobility
Control Applications**

by

David Ryan Espinosa, B.S.P.E.

Thesis

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Dedication

To my Mom for showing me how to be compassionate; raising me to be strong,

My Dad for showing me an example of who I am supposed to be,

Raul for being the oldest brother, who led the way and set the bar high,

Andrew for always looking out for me and teaching me how to be loyal,

And Alex, who has always been there to support me and has made me a better person.

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Nanoparticle-Stabilized Supercritical CO₂ Foams for Potential Mobility Control Applications

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The University of Texas at Austin, 2011

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Abstract

The petroleum industry has been utilizing surfactant stabilized foams for mobility control and enhanced oil recovery applications. However, if surface-treated nanoparticles were utilized instead of surfactants, foams stabilized with such particles could have a number of important advantages. The solid-stabilized foams are known to have a much better stability than the surfactant-stabilized foams, because the energy required to bring nanoparticles to, and detach from the foam bubble surface is much larger than that of surfactants, and thus the resulting foam will be more stable. Since nanoparticles are the stabilizing component of the foam and are solid, they have potential to stabilize foam at high temperature conditions for extended periods of time. Since they are inherently small, nanoparticles, as well as the foam that they stabilize, can be transported through rocks without causing plugging in pore throats.

Stable supercritical carbon dioxide-in-water foams were created using 5 nm silica-core nanoparticles whose surface had short polyethylene-glycol chains covalently bonded to it. The foams were made by injecting CO₂ and an dispersion of with surface-treated

nanoparticles simultaneously through a glass-bead pack. The fluids flowing through this permeable media created shear rates in the range of 10^3 to 10^4 sec^{-1} . Nanoparticle concentration, nanoparticle coating, water salinity, volume ratios between CO_2 and water, temperature and shear rates were systematically varied in order to define the range of conditions for foam generation. Using de-ionized water to dilute the nanoparticle concentration, we were able to generate stable foams at nanoparticle concentrations as low as 0.05 weight percent. Among the different surface coatings tested PEG coatings were the only type that was able to stabilize foam. As the salinity of the aqueous phase increased, the nanoparticle concentration required to maintain foam also increased; for example, 0.5 weight percent nanoparticles were required for 4 weight percent NaCl brine. Foam stability was weakly correlated with volume ratios as foams were made across ratios from two to fourteen, and the normalized mixture viscosity increased with the increase of the phase ratio. Foams were created at temperatures up to 95 degrees Celsius. Foam generation was also determined to require a critical shear rate, which increased with temperature. When foam was stabilized by the nanoparticles, the foam exhibited an increase of between two and twenty times in the resistance of flow compared to the two fluids flowing without nanoparticles.

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Chapter 1: Introduction

The petroleum industry has always been looking for new ways to further science in an attempt to extract more oil out of the ground. Petroleum engineers have been looking at breakthroughs in other industries in order to manipulate and apply their science toward the petroleum industry's goals. Nanotechnology is a fast growing research field, and the petroleum industry is now seeking to apply the nanotechnology advances. This thesis relates to utilizing the advances in nanotechnology, to create and stabilize carbon dioxide (CO₂) foams for both enhanced oil recovery (EOR) and CO₂ sequestration proposes.

This thesis is divided into five chapters and an accompanying appendix. The first chapter introduces the advances in nanotechnology that allow for and influence this research path. There is also a literature review which discusses the utilization of nanoparticles in the oilfield. The second chapter deals with the materials that are used in the experiments; this chapter is divided into two sections, one describing the nanoparticles used and the other describing the apparatus development. The third chapter discusses the results and their implications from the experiments run using the materials from the second chapter. The fourth chapter gives possible implications from the results of the third chapter. The last chapter details the conclusions that can be drawn from our results and suggestions for future work.

1.1 Background

CO₂ floods are used in the upstream oil industry as one method of enhanced oil recovery. CO₂ floods can improve oil recovery by two means. The CO₂ can become miscible with the oil, leading to better displacement efficiency. CO₂ also aids recovery by reducing the oil's viscosity. The flood can also help with pressure maintenance, which adds energy to the reservoir and produces more oil.

One of the problems with CO₂ floods is the low viscosity of CO₂. Viscosity is a key factor when determining the mobility ratio of the two fluids that are involved in a flood. Mobility ratio determines how effective the flood will be, because sweep efficiency and breakthrough time depend on mobility ratio.

Thus the key to an effective flood is making the mobility shift toward a more favorable value. When performing a CO₂ flood this can be accomplished by turning the CO₂ into foam which has a higher viscosity than the pure CO₂. This higher viscosity lowers the mobility of the CO₂ phase, which positively influences the efficiency of the flood and the decreases the breakthrough time. Traditionally, the foam was created and stabilized with the aid of surface active chemicals. The idea behind the research in this thesis is to determine whether nanoparticles can be used as an alternative to these surfactants.

1.2 Nanoparticles and their use in the petroleum industry

Nanotechnology has been experiencing exciting continuous growth across a variety of fields in the past few decades. The experiments reported here involve trying to utilize this growth and apply it to my specific goal: the long lasting stability of CO₂ foams using

nanoparticles as an alternative to or in addition to surfactants, to help each other obtain this goal. Nanoparticles have higher adhesion energy to the fluid interface than the surfactants (Dickson *et al.*, 2004). This gives the potential for the nanoparticles to stabilize longer lasting foams, as nanoparticles would require more energy to destabilize the foam. This means that even if there was a water phase depleted of nanoparticles present in concurrence with the foam phase, the nanoparticles adsorbed to droplet surfaces would not release from the interface. Thus the foam would remain stable. The nanoparticles are solid which raises the possibility that surface modified nanoparticle stabilized foams could be more resilient to harsh reservoir conditions (e.g. high salinity, temperature). Surface modified nanoparticles also appear to be well suited for flooding with little retention. While the nanoparticle-to-rock adsorption mechanism is not fully understood yet, the early results average between 10-15 percent for retention (Rodriguez *et al.*, 2009; Caldelas *et al.*, 2011). Nanoparticles appear to have one more possible advantage when it comes to stabilizing CO₂ foams because the coating can be designed to have a better CO₂ solvation capability than that of surfactants (Espinosa *et al.*, 2010). Beyond the scope of these studies, but still relevant, is that nanoparticles can also potentially have other advantages. For example, if the nanoparticles have paramagnetic properties, the nanoparticles could be transported by applying an external magnetic field.

1.3 Literature review

1.3.1 Solid Particle-Stabilized Emulsions/Foams

Solid stabilized emulsions, or Pickering emulsions, have recently been of interest in the petroleum industry because of their ability to remain stable for months and also because

the stabilizing solid can carry additional functionalities, such as paramagnetism. The mechanisms for stabilizing emulsions using nanoparticles instead of surfactants have been investigated extensively by many researchers, (Binks 2002). These emulsions have also drawn interest because solid particles are accepted as more stable in high temperature and high salinity environments than surfactants. Recent improvements in nanoparticle technology have allowed for nanoparticles to be produced economically in larger quantities and with desired properties, such as uniform size distribution, surface coating, et cetera. The ability to adjust the nanoparticle surface “wettability” by means of the surface coating is a key step in foam stabilization. The solid particles should be able to stabilize foam in harsher conditions than surfactants, but also allow for increased functionality. For example, if nanoparticles are paramagnetic and in a viscous emulsion, a large electromagnetic field can be applied, and reveal the stress orientation by forcing the emulsion into the fractures.

Surfactants and solid particles have been compared for their ability to stabilize foams/emulsions (Binks 2002, Horozoy 2008). While Horozoy’s study investigated CO₂-in-water foams, Binks studied both emulsions and foams, that were stabilized using nanoparticles. As with surfactants, the chemical structure that interacts with the fluid controls the type of foam/emulsion made. If a particle’s coating is hydrophilic, than there will be a CO₂-in-water foam created, and a water-in-CO₂ foam if the coating is hydrophobic. These tests showed that the nanoparticle concentration, the volume ratio between the phases, the salinity of the aqueous phase, and the pH of the fluids involved can predict the stability of the created foams/emulsion.

Nanoparticle stabilized emulsions using an aqueous phase and oil have been developed and studied within our research group (Zhang *et al.*, 2011, Zhang *et al.*, 2010, Zhang *et al.*, 2009). These emulsions have several potential applications, ranging from conformance control to enhanced recovery of heavy oils. Oil-in-water and water-in-oil emulsions were able to be stabilized using surface coated silica nanoparticles. The surface coating of these nanoparticles determined the type of emulsion created. These emulsions were stabilized for several months, lending credit to the theory that nanoparticle stabilized emulsions can improve long term stability. Experiments were set up to test the emulsion phase behavior and the effects of water to oil ratio, salinity of the aqueous phase, nanoparticle concentration, and the coating wettability. These tests show that emulsion stabilization required a critical concentration.

During CO₂ flooding, surfactants have been sometimes added to the aqueous phase in order to generate foam and thereby to increase the apparent viscosity and enhance the mobility of these displacing CO₂ phase. This enhancement of the mobility improves the volumetric sweep efficiency of the foam (Rossen, 1996; Kim *et al.*, 2005). These surfactant-stabilized foams, however, exhibit critical weaknesses in their ability to stabilize foams for long periods of time, especially when in the presence of high salinity and high temperature. As outlined in the previous studies, nanoparticle dispersions are able to stabilize foams that can withstand the harsh conditions that would destabilize surfactant-stabilized foams.

1.3.2 Nanoparticle-stabilized CO₂ foams

The work done for this thesis involves the generation and characterization of nanoparticle stabilized CO₂ foams for CO₂ flood. Recent research has been conducted on supercritical CO₂ in water foam (Dickson *et al.*, 2004) as well as water in supercritical CO₂ foam by (Adkins *et al.*, 2007). The Dickson study involved mixing an aqueous phase containing up to 50 weight percent silica nanoparticles with a CO₂ phase. These experiments were conducted at a constant temperature of 25 degrees Celsius and under pressure varying from 34 to 700 bars. These experiments were intended to test the effects of particle concentration, phase volume fractions, the nanoparticle coating, and the CO₂ density on foam stability. There were two key conclusions from Dickson's experiments. If the nanoparticle concentration was increased the foam stability increased. And when holding all other parameters constant, the nanoparticle coating's hydrophilicity increased the foam's stability. The Adkins study differed from the above in that it involved using nanoparticles smaller than 10 nm in diameter, and that the nanoparticle surface was hydrophobic instead of hydrophilic. This coating inverted the foam to be water-in-CO₂. These foams were very stable, which led to the conclusion that the nanoparticles were forming a dense layer between the fluids' interface. These foams were shown to be stable under harsh, reservoir conditions like high temperature and high salinity.

1.4 Research objectives

The primary motivation for this research is making the mobility ratio of carbon dioxide floods more favorable for enhanced oil recovery by CO₂ injection. The major drawback to using CO₂ is the poor volumetric sweep efficiency prevalent in CO₂ floods. CO₂'s low density also compared to the reservoir fluid density causes the CO₂ floods to experience

gravity segregation. To combat this, surfactant-stabilized CO₂ foams have been proposed. The foams viscosify the CO₂; this increase of viscosity enhances the mobility ratio of the CO₂ flood, making the flood more effective. These surfactant stabilized foams do have some drawbacks; primarily, their long term stability is difficult to maintain. This instability is further compounded when the foam encounters oil in the reservoir. Even with some of the high cost, specialty designed surfactants, the foams tend to degrade before the long term goal of the project is realized.

The main objective of this thesis research is to remedy the above described weaknesses of the surfactant-stabilized foams, by developing foams that are stabilized with nanoparticles. To achieve the above main goal, the conditions that are required to generate foams that have long-term stability were investigated in a systematic manner, by using silica nanoparticles with different surface coatings, and by varying CO₂/water volume ratios, and temperature.

Chapter 2: Experimental Methods and Materials

2.1 Materials used:

Silica nanoparticles with four different types of surface coatings were received from 3M Co, St. Paul MN, and Nyacol Nano Technologies Inc., Ashland, MA. The 3M particles have two different coatings, designated as “Hydrophilic PEG” and “Salt Tolerant”. The hydrophilic PEG-coated particles have a silica core of 5 nm and were coated by covalently bonding polyethylene glycol to the silica. These particles were received dispersed in de-ionized water with a pH of 7. The dispersion is received as a 23.04 wt% concentration, and the fluid has a viscosity of about 2 cP. Another hydrophilic nanoparticle dispersion had a 20 nm core with a similar polyethylene glycol coating bonded to the silica. This gave the nanoparticle an effective size of 25 nm, which was otherwise similar to the previous 5 nm dispersion. The dispersion is received as an 18.64 wt% concentration and had a similar viscosity of about 2 cP. The Salt Tolerant particles have the 5 nm silica core, however, its coating is believed to have more of the polyethylene glycol, but the coating not revealed because it is a trade secret. The Nyacol nanoparticles consisted of a silica core of unknown diameter, with a covalently bonded organic –OH functionality coated to this silica core. The rest of the information about the core is proprietary, but the effective diameter of the core plus the coating was listed by the provider as 20 nm. Most of the experiments used the hydrophilic PEG coated nanoparticles with a silica core of 5 nm, unless noted otherwise.

Each of the particles received had a similar physical schematic, illustrated in **Figure 1**.

There is a silica core with an outer coating that was covalently bonded to the core. For the

Figure 1: Schematic of nanoparticle and coating

nanoparticles to stabilize foam, the nanoparticle dispersion and CO₂ must be sheared to produce droplets, and allow the nanoparticles to adsorb to the droplet surfaces. The nanoparticles keep the foam stable by preventing the droplets

from coalescing into their original phases. The coating plays a

vital role in foam stabilization. The coating determines the

wettability of each particle, and thus its ability to be dispersed, to stabilize the foam, and

to determine whether the foam is CO₂ in water or water in CO₂. The coating determines

the foam type by preferentially orienting a particle at an interface into one fluid versus

the other. Hydrophilic particles can be used to disperse CO₂ bubbles into water, with

CO₂-philic doing the opposite. As discussed above there were four different particles that

were tested. As the results described in Chapter 3 show, the most successful were the 5

nm silica core PEG coated particles from 3M. The other particles yielded inconclusive

results. In the subsequent sections and subsections (starting with effect of concentration,

section 3.1), the term “nanoparticle solution” refers to 5 nm silica core PEG coated

nanoparticles, unless noted otherwise.

The water used to dilute the dispersions is de-ionized water obtained from our lab using a

recirculating pump and a Barnstead filter. The salt used was reagent grade sodium

chloride (NaCl). For the experiments that tested salinity, the nanoparticle brine phase is

prepared separately before injecting the fluid.

The carbon dioxide used in these experiments is greater than 99.99% pure carbon dioxide as received from Praxair Distribution Inc. as a liquid. This liquid is then compressed further into an accumulator that is held at higher pressure by using a water pump which can displace the CO₂ into the foam generation apparatus as needed.

2.2 CO₂ foam generation experimental setup

Two apparatuses were used in these experiments, the schematics for which are given in **Figures 4** and **6**, respectively. The second apparatus was created because of safety concerns with the ageing first apparatus. While the mixing principle is the same, several key features are different. The first apparatus will be outlined and then the differences in the second apparatus will be highlighted.

The first apparatus is set up to test the concept of stabilizing foam with nanoparticles. This apparatus is shown in **Figure 4**. To inject the nanoparticle laden water phase there is an ISCO 500-D Teledyne syringe pump. The CO₂ is first charged into the upper portion by use of a Haskel air powered fluid pump. The CO₂ is then displaced from the high pressure accumulator by flowing de-ionized water through a Beckman 100-A HPLC pump into the bottom of the accumulator. Both of these pumps feed directly into the foam generating apparatus. The phase volume ratio is the ratio of the two flow rates when the flow rates are leaving the accumulator (CO₂) and the pump (nanoparticle solution). Each fluid will flow in a coiled 1/8th inch OD tube that is submersed in hot water-bath powered by a MGW Lauda temperature controller. This coiled tubing allows the fluid enough time for the heat transfer to raise the temperature of the fluids inside to be at equilibrium with

the fluid in the hot water bath. The increase in temperature increases the phase volume ratio, as the CO₂ density decreases and the aqueous phase density changes only slightly. The coil of tubing is not represented accurately in the schematic drawing, **Figure 4**, so a closer view is provided in **Figure 2**, below. The water-bath temperature is verified by two thermocouples, one that runs into the **T-joint 1** to measure the temperature before fluids enter the sand pack and one thermocouple that independently verifies the hot water bath fluid temperature. This redundancy allows for three way temperature verification. The hot water-bath has one temperature output and a thermocouple that measures the water temperature. When these two temperatures match, as well as the second thermocouple in a T-joint, as shown in **Figures 2** and **4**, then the experimental temperature can be assured.

Figure 2: Close up of temperature verification set-up.

Each fluid phase flows from its respective sources through the coiled tube to allow the fluid to warm up to the temperature of the water bath. Downstream of the coiled tubes, the fluids meet in T-joint 1 (Fig. 2), which has a thermocouple that measures the fluid mixture temperature. Once the temperature is verified, the fluids flow into a high pressure (HIP) column. The column is 10.2 cm in length with a 0.386 cm ID high pressure tubing that is filled with 180 micron diameter glass beads.. A typical total flow rate ($q_{\text{CO}_2} + q_{\text{H}_2\text{O}}$), while at ambient temperature, of an experiment was around 6 mL/min, which yields a shear rate within the HIP column of about 1430 sec⁻¹. The shear rate is

determined by using Equation 6 in Section 2.10.1. The experiments had a residence time of about 5 seconds inside the HIP column.

Because shear rate turns out to be a critical parameter for foam generation, it is important to know the shear rate in the flow line between the T-junction 1 and the HIP column, Figure 2. The shear rate leading up to the column is smaller than the shear rate inside the HIP column, about 600 sec^{-1} at the highest flow rates used in experiments at ambient temperature. For experiments that were run at higher temperatures, the shear rate in the tube was higher. For example, at 90 degrees Celsius, the highest shear rate in the tubing was about 2950 sec^{-1} . Even at the highest flow rate conditions, the calculated Reynolds number was 3200, using a viscosity of 0.32 cP, the viscosity of water at 90 degrees Celsius. For these calculations we use the definition of shear rate for laminar flow of a single phase Newtonian fluid in a tube. For these Reynolds number calculations, the fluid properties assumed to be the same as water. Shear rate is defined as:

$$\dot{\gamma} = \frac{8v}{d}$$

Equation 1: Definition of shear rate in pipe

where

$\dot{\gamma}$ is the shear rate in reciprocal seconds,

v is the linear fluid velocity in meters per second, and

d is the inside diameter of the pipe in meters.

After leaving the HIP column, the foam and any residual fluids move into a capillary tube (length = 200 cm, ID = 0.0508 cm). The differential pressure across this length of tubing is continuously measured using a Validyne pressure transducer model 363-42 and a Validyne carrier model MCI-20. After leaving the capillary tube, the foam flows into a

Figure 3: Macroscopic view cell example.

macroscopic view cell. This view cell is used to make observations about the foam quality and the bubble size. The view cell cylinder is 1.5 cm in diameter and is 1.25 cm thick. The fluids can enter and exit through 0.06 cm tubing located on opposite sides of the view cell. **Figure 3** is a sample photograph

of the foam during an experiment. The view cell observations are mostly qualitative and used to compare the different foams to correlate the pressure drop results with visual observations.

The foam effluent can be collected in a waste accumulator or a secondary accumulator. When foam flows into the waste accumulator the foam will displace water through a back pressure valve, which maintains the desired pressure for the entire experiment. If desired, the foams could be directed to the secondary accumulator that would displace water and keep the pressure of the experiment in similar manner to the waste accumulator. The difference is that the secondary accumulator also had plumbing that allowed for the foam to be flowed back through the capillary tube part of the apparatus. This allows the pressure drop data to be taken (as a reverse value) a second time. This allowed for testing of foam stability as the foam aged. This was accomplished by allowing the foam to remain in the accumulator for a given period of time, and then flowing water into

accumulator, displacing the foam and measuring the pressure drop data again after aging. The schematic and photograph of this apparatus is shown below, in **Figures 4** and **5**, respectively.

Figure 4: Schematic of first generation experimental set-up for CO₂ foam generation.

Figure 5: Photograph of first generation experimental set-up for CO₂ foam generation. Arrows indicate a) HIP column; b) view cell; c) capillary tubing for viscosity measurement; d) water bath.

The second generation of the foam creation apparatus (**Figure 6**) had differences in the design in order to upgrade the safety of the apparatus and to make the apparatus more flexible in order to run different tests. The primary update was a large panel of perforated steel (similar to pegboard). This panel is the shape of a 36 in square and is 1/4 inch thick. The hole spacing is 1 inch by 1 inch in a square pattern and was machined by the

McNicols Co. The panel provides key upgrades to the previous design: easier visualization of the testing procedure, increasing safety by enabling secure tie-down of parts of the apparatus, improving the general facility design and easier changing of parts. The panel aids visualization by placing every part in a more organized, linear fashion. Previously, all the parts of the apparatus were held in place by two vertical posts or were suspended in open space (as seen in **Figure 5**, above). This older design was prone to tubes becoming tangled and thus the visualization became complicated. The new design allowed for every tube and almost every other part to be bolted down to the perforated steel in an orderly way. This reduced the tangling of tubes, made it easier to visualize the experiment, but also had other key advantages. With the bolting of parts to the steel perforated board, safety was also greatly increased. Previously, only large volume parts of the apparatus were bolted down, which left the smaller tubes suspended mid-air. If there was a failure in one of these tubes, the force of the gas exiting could cause the tubes to whip around with no hope of controlling them until the gas finished expanding. With the steel panel, the length of tube that could turn into a whip is greatly reduced, thus reducing the potential damage by reducing both the potential damage area and force the tube could strike with. Another safety upgrade is that the points more vulnerable to failure are covered with a poly-methyl methacrylate blast shield to protect observers. This blast shield currently covers the view cell and the majority of the 1/16 inch tubing. The shield can be moved and resized to cover more or different parts as the user sees fit. The key advantage this panel provided was the upgrade flexibility. Previously with the disorganized tangle of tubing, changing out parts could take some time. With the new set up, changing parts is more analogous to changing components on a motherboard, which

has drastically reduced the downtime. The schematic of the updated profile is shown below in **Figure 6**. After **Figure 6**, there is a picture, **Figure 7**, of the updated apparatus, showing the perforated board and new setup.

Figure 6: Schematic of second generation experimental set-up for CO₂ foam generation.

Figure 7: Photograph of second generation experimental set-up for CO₂ foam generation. Arrows indicate a) ISCO pump; b) water bath; c) view cell; d) capillary tubing for viscosity measurement; e) PEG board; f) HPLC pump

2.3 Experimental pprocedure

Several different procedures need to be followed in order to successfully run an experiment. Two different experimental procedures are included in the sections titled “2.11 Flow” and “2.11.1 Flow in second apparatus” for the two different set-ups, each briefly discussing the procedure and the differences between them.

2.4 Waste accumulator

Before running an experiment, the accumulators that will be used to hold the foam after the foam leaves the apparatus need to be set to the proper starting position. During an

experiment, all injected fluids eventually enter the accumulators, which displace water through a back pressure regulator in order to maintain the pressure of the experiment. For both apparatuses the procedure for the accumulator is essentially the same. The first step is to make sure that the system is not at pressure. This is accomplished by venting the system by opening valves that open to the atmosphere. Once there is no pressure difference between the atmosphere and the internal pressure of the apparatus, the accumulator can be disconnected. Before removing an accumulator from the apparatus system, the valve that is upstream of the accumulator, relative to the back pressure valve, valve D in **Figure 8**, needs to be closed. This ensures that if there is any residual pressure in the apparatus, that pressure would not be able to cause flow. Next detach the accumulator from the apparatus plumbing, making sure to unscrew the fitting slowly, to allow any pressure in the accumulator to escape before the accumulator removed. If the previous experiment was run with nanoparticles (or any chemical) the drained fluid must be disposed in the appropriate manner. The next step is to push the floating piston inside the accumulator all the way down to the opposite side of its position at the end of an experiment. A close up schematic of the waste accumulator set-up is shown in **Figure 8**, located below. The cylindrical figure inside the waste accumulator is the floating piston that needs to be reset.

Figure 8: Set-up of waste accumulator for CO₂ foam

This resetting of the piston to its original position will help minimize nanoparticles leaking into the waste water through the back pressure regulator. Keeping which end

receives the nanoparticles consistent between experiments reduces the chance of residual nanoparticles leaving the accumulator. Once the piston is reset to its original position, fill the void in the accumulator with water. Screw in both end pieces until tight, and reattach the accumulator with the piston facing the apparatus and the water column facing the back pressure accumulator. This process can be repeated for the secondary accumulator if it is needed. Here the caution on keeping the accumulator orientation consistent is again important.

2.5 CO₂ charging

The CO₂ used in these experiments is kept in a large accumulator donated by Occidental Petroleum Corporation. The accumulator enables storage of large amounts of CO₂ in the liquid state safely and conveniently. The CO₂ is kept at pressure by pumping in water to the lower portion of the accumulator. From time to time this accumulator requires maintenance in order to operate at acceptable conditions. The maintenance involves the O-ring around the piston in the accumulator and keeping the accumulator charged.

The O-ring around the piston has two functions. First the O-ring allows the piston to move up and down the accumulator, and thereby to displace the CO₂. The O-ring also prevents the CO₂ and water from mixing, which is important for safety and for the integrity of the experiment. Typically, these O-rings are made out of thermoset synthetic rubbers. While the O-ring allows the piston to move up and down, this piston movement can cause mechanical damage to the O-ring. The damage can degrade the seal, and thus compromise the ability to run experiments. The O-ring also is subjected to high pressure

CO₂, which can attack the material and cause the material to crack. When the accumulator can no longer hold pressure despite compressing more CO₂ into the upper part of the accumulator or pumping water into the lower part, the O-ring has likely failed, and needs to be replaced. Maintenance can be performed by venting the pressure in the accumulator, then disconnecting the accumulator from the system. Next, empty the bottom section of the accumulator, to make sure there is neither water nor CO₂ present. After the accumulator is empty, the top and bottom seals can be removed in order to retrieve the piston. Once the piston is out of the accumulator, the old O-ring must be removed, and a new O-ring can be installed in its place. When the new O-ring is in place, the piston can be returned to the accumulator and checked to make sure the piston can freely slide down the accumulator. The last step is to seal and reconnect the accumulator to the system.

The CO₂ inside of the accumulator can be depleted by running experiments, intentional venting of the system, and unintentional CO₂ leakage. To refill the accumulator with CO₂ is a streamlined process. The CO₂ charging system is represented with **Figure 9**. First empty the bottom portion of the accumulator of any water present. Care should be taken because this section often is under some pressure, and can cause spills of water. Once the water is drained, the CO₂ compressor can be utilized. First turn the 3 way valve E to make the flow direction into the accumulator. Then open valve 7, and 6; valve 7 controls the flow in a line that delivers high pressure air to provide the energy needed run the compressor. Once these valves are open, turn the accumulator on, and this will initiate the flow from a larger CO₂ tank into the accumulator. The compressor will need to run until

the accumulator pressure is at least 1500 psia. Once this pressure is met, the valves need to be reset in reverse order. Once the valves are reset, reconnect the accumulator to the apparatus system, and the CO₂ tank is ready to be used to run experiments again.

Figure 9: Set-up for recharging experimental CO₂ accumulator.

2.6 Dilution

The nanoparticles that are used are received as a stabilized suspension, often at a much higher concentration than needed for experiments. For example, the 5 nm silica core PEG coated nanoparticles are received at a concentration of 18.64 weight percent, but foams were successfully created at concentrations as low as 0.05 weight percent. Thus dilution is needed in order to prepare solutions with small concentrations of nanoparticles. In order to make any nanoparticle concentration lower than the concentration that is received, **Equation 2** below is used to determine dilution volumes:

$$V_i = V_m * \frac{C_m}{C_i}$$

$$V_w = V_m - V_i$$

where

V_m is the volume mixture in mL,

C_m is the target concentration mixture as a weight percent,

V_i is the original volume sample in mL,

C_i is the original sample concentration as a weight percent, and

V_w is the volume of de-ionized water in mL

Equation 2: Nanoparticle dilution formula

The procedure for diluting the particles is as follows. First select the values needed for the experiment. Most experiments used $V_m = 250$ mL. Next select the target concentration (C_m) for the experiment. Then, since C_i is known, using **Equation 2**, solve for V_i , and then V_w . With V_i known, measure this volume from the nanoparticle solution stock using a graduated cylinder and pipette, discarding any leftover sample. Next measure V_w from the de-ionized water stock using a separate graduated cylinder and pipette. Combine both V_i and V_w into a flask and place on a magnetic mixing plate. Insert a stirrer bar, cover the sample, and turn on the plate. After a period of no less than 15 minutes, the two fluids should be adequately mixed.

2.6.1 Changing the salinity

Some of the experiments were run to test the effect of salinity on foam stabilization. In order to change the salinity for the nanoparticle solution, the procedure for dilution, the preceding section, was followed. After the desired concentration was achieved, the NaCl was added into the nanoparticle solution as if the nanoparticle solution were fresh water,

until the desired NaCl concentration was achieved as a weight percent. The NaCl mass values were taken from table 2.5, page 52 in Applied Drilling Engineering (Society of Petroleum Engineers, 1986, Adam T. Bourgoyne, *et al.*). Changing the salinity of the solution was accomplished by adding lab grade sodium chloride (NaCl) distributed by Fisher Scientific.

2.7 Apparatus calibration

The experimental apparatus is set up to determine the change in pressure across a capillary tube as the fluids exiting the HIP column flow through the tube. This change in pressure can be related to the apparent viscosity of the fluids if the apparatus has been calibrated and when two assumptions are made. The assumptions are that the fluid is a single phase whose flow is laminar. So Reynolds numbers were also calculated for each test in order to make sure the laminar flow condition was met. In each case calculated Reynolds number was lower than the accepted threshold between laminar and turbulent flow of 2300. Therefore all the calibration tests should also be conducted under laminar flow conditions. The single phase flow assumption is valid for the calibration test, because the fluid tested is only water. When foam is generated, there are two phases present, one suspended in the other, and excess phases not incorporated in the foam may also be present. For this reason, the flow through the capillary yields an apparent viscosity, not a true viscosity. The calibration tests are outlined in **Table 1**, below.

Flow Rate (ml/min)	Measured Pressure Drop (psia)	Theoretical Pressure Drop (psia)	Reynolds Number
20	105	59.2	835.5
18	95.4	53.2	751.9
16	83.4	47.3	668.4
14	71.3	41.4	584.8
12	59.5	35.5	501.3
10	48.15	29.6	417.7
9	42.7	26.6	376.0
8	37.4	23.7	334.2
7	32.3	20.7	292.4
6	27.55	17.7	250.6
5	23	14.8	208.9
4	18.6	11.8	167.1
3	14.5	8.9	125.3
2	10.3	5.9	83.5
1	5.1	3.0	41.8

Table 1: Apparatus calibration experiment summary.

De-ionized water was the fluid choice because the viscosity is well documented as 1.002 cP at the 20 degrees Celsius and atmospheric pressure (<http://www.engineeringtoolbox.com>). The tests were run with a series of flow rates. The comparison between the measured pressure drop and the flow rates is shown below in **Figure 10**.

Figure 10: Apparatus calibration curve fit.

As discussed below, the measured pressure drop is considerably larger than expected from theory. Thus to use the capillary tube as a viscometer, the data in Figure 10 are treated as a calibration curve. The data fit line is set to only the data that covers the experimental range of 1 to 10 mL per minute. This is adequate for all the experiments conducted at ambient temperature. For the experiments conducted at elevated temperature, the flow velocity through the tubing is in the range 14-25 mL per minute. The calibration in this range is quadratic expression located in Figure 10, which covers the range 5 to 25 mL/min.

The equation for the calibrated pressure drop as a function of flow rate for a fluid of constant viscosity $\mu = 1$ cP at moderate flow rates is shown as **Equation 3**. This linear

equation was used in favor of the quadratic because of simplicity and because the early experiments never reached the higher flow rates. Since the flow rates stayed low until experiment 40b, there was never a need for using the higher flow rate equation.

$$\Delta P = 4.7143 * 1 \text{ cP} * Q$$

where

ΔP is the change in pressure in psia, and

Q is the flow rate, in mL/min

Equation 3: Apparatus calibration equation

Manipulating this equation, we get **Equation 4**. This equation yields the apparent viscosity of the fluids given the data measured in the experiments (flow rate, pressure drop):

$$\mu = \frac{\Delta P}{4.7143 * Q}$$

where

μ is viscosity in cP,

ΔP is change in pressure in psia, and

Q is flow rate in mL/min,

Equation 4: Correlation between apparent viscosity of fluid phase(s) in capillary tube given measured flow rate and pressure drop.

Table 1 also shows theoretical pressure drops calculated using the Hagen Poiseuille equation for laminar flow in a pipe (**Equation 3**) (length = 200 cm, ID = 0.0508 cm). The measured pressure drop was 1.5 to 2 times larger than the theoretical value. The discrepancy could have been caused by a number of sources. This pressure drop

calculation did not take into account pinch points or fittings in the apparatus that can be located where the pressure transducers connect to the capillary tube. At these points there is switch between tubing diameters (from Swagelok 1/8th inch OD tubing to HIP 1/16th inch OD tubing) that requires conversion fittings as well as provides a convenient point for the pressure transducer to be in communication with the apparatus. The reason for the discrepancy remains unclear, but the correction embodied in the calibration curves yields good estimates of the apparent viscosity. In any case, viscosity is not a well-defined concept for the simultaneous flow of foam and excess CO₂ and/or excess aqueous phases in the capillary. Thus a measure of relative resistance to flow is the best that can be obtained from the apparatus. The calibration procedure is reliable for this purpose.

2.8 DP cell Calibration

In between runs, the DP cell might slightly deviate from the accepted calibration values. Using a small screwdriver, the “R” value can be adjusted on the Validyne pressure transducer module case. The pressure transducer readings are taken using the program LabVIEW. This program will display the values from the pressure transducer graphically on the computer screen and can be used to aid daily maintenance. This maintenance involves adjusting the “R” value while looking at the LabVIEW output for the pressure transducer. Using the LabVIEW output, the adjustment can be made to the “R” value so that the graph output shows the pressure difference is zero. This adjustment ensures that data acquisition in each experiment is started at the same point. In order to make sure the calibration is still acceptable; an experiment with only water can be run and compared to known values.

2.9 Charging ISCO pump

Once the nanoparticle solution is prepared for an experiment, the solution needs to be placed into the ISCO pump. To charge the ISCO pump, first make sure the three way valve directs flow into the pump and not into the apparatus. Then place the end of the plastic tube into the prepared nanoparticle solution. Activate the pump by pressing the “Refill” button. Depending on how much of the nanoparticle solution has been prepared, the pump can either be cut off early by pressing the “Stop” button, or the pump will cut itself off when the pump is at full capacity. For example, for Experiments 1-28, a full pump capacity’s worth of nanoparticle solution was prepared, and the pump was filled. For subsequent experiments, the observation was made that about 150 mL had been injected in an experiment when the waste accumulator grew full. Thus, for the remaining experiments, the prepared solution was reduced to 200 mL. Once the refilling process has been stopped, remove the plastic tube from the nanoparticle solution container. There will be a small level of air that needs to be evacuated. To do this, hold the plastic tube above the exit point for the ISCO pump, and press “Run.” The pump will push all of the air out first and once the nanoparticle solution starts to be depleted from the pump, press “Stop” again. Switch the three way valve back towards flow to the apparatus, and the pump is set to begin the experiment.

2.10 Packing a bead pack

The shear provided by a High Pressure (HIP) column filled with glass beads, or a glass bead pack, generates the foam. For testing the effect of shear rate on foam generation, the

bead pack can be changed in order vary the shear rate. Since this procedure is more intensive and long, it will be listed line by line. The procedure is found below:

1. Run DI water through entire flow line until fully saturated with DI water.
2. Remove bead pack from flow line (will need to bleed pressure of entire flow line, this is why we saturated with water in step 1).
3. Use vise to open bead pack.
4. Flush old sand out of bead pack and rinse well with DI water.
5. In the ends, attach pieces of mesh to prevent beads from exiting into rest of flow line (This would be disastrous and will take large amounts of time and effort to undo!) To attach mesh, use epoxy to hold the mesh in place. Attach one end with mesh and close with vise.
6. Fill with a small amount of beads and then tap the side vigorously to pack sand. Repeat this until bead pack is full and will not pack any more compactly.
7. Attach mesh to other end and close.
8. Connect bead pack to influx side of flow line.
9. Flow water through bead pack at a slow flow rate and tap the side vigorously to remove as much air as possible.
10. Attach other end of bead pack to flow line.

2.10.1 Bead pack properties

The bead pack is a critical part of the apparatus. It provides the shear and energy to disperse one fluid into another, as well as to force the nanoparticles to adsorb to the interface between the two fluids once dispersed. The bead pack properties are related to

the particle diameter of the glass beads. The bead diameter determines the permeability of the bead pack, and the permeability determines the shear rate achieved in the bead pack. For every experiment in this thesis, 180 micron glass beads were used for the bead pack. The equation that describes the relationship between the glass bead diameter and the permeability of the bead pack is below in **Equation 5**. For this equation, the porosity is estimated as 38%, the median value for dense disordered packing of spherical grains in a tube. The tortuosity is estimated as 25/12. These assumptions and **Equations 5** and **6** were taken from “Enhanced Oil Recovery” (Prentice Hall, Larry W. Lake, 1996).

$$k = \frac{1}{(72 * \tau)} * \frac{(\phi^3 * D_p^2)}{(1 - \phi)^2}$$

where

k is permeability in D,

τ is the path tortuosity,

ϕ is porosity and dimensionless, and

D_p is bead diameter in microns.

Equation 5: Permeability correlation

Once the permeability of the bead pack has been determined, the next step is to calculate the shear rate. This relationship is described by **Equation 6**, located below.

$$\dot{\gamma} = \frac{4 * Q}{(A * \sqrt{8 * k * \varphi})}$$

Where

$\dot{\gamma}$ is the shear rate in reciprocal seconds,

Q is the flow rate in cubic centimeters per second,

A is the cross sectional flow area in centimeters squared,

k is the permeability in centimeters squared, and

φ is the porosity and is dimensionless.

Equation 6: Shear rate correlation

2.11 Flow

Once the nanoparticle solution is at the proper dilution and the apparatus setup has been completed, the experiment is ready to be run. There are two different flow procedures, one for each of the apparatus set ups.

The time at which each action is performed is noted. This enables relating all the data acquired (pressure, pictures, etc.) correctly.

1. Complete/double check all set-up procedure
2. If this is first time running in a while, pre-flush with DI water.
3. Pressure will need to be built up in the apparatus before injecting CO₂. A good way of doing this is closing valve J and injecting water until ISCO pump pressure reaches approximately 1200 psia. Then open valve J and continue injecting until pressure equilibrates (should be around 1350 psia). Then open CO₂ to flow.
4. CO₂ needs to be pressured up as well. Open valve 2 and maintain valve 3 closed with 3-way A towards CO₂ accumulator. Turn on HPLC pump (at any flow rate,

6. Set desired flowrates in ISCO and HPLC pumps as per experiment plan. Open valves 1 and 2.
7. Pressure in ISCO pump and HPLC pump should settle to the pressure that the back pressure valve is set to. Every experiment was run with the back pressure valve set to about 1350 psia. Waste line should start flowing at this time (only DI water comes out of waste line).
8. Check view cell and pressure drop across capillary for foam status. For a good pressure drop reading, try to get a stabilized value for a minute or two. Common sense should be carefully used in this step. Good notation of steps completed will allow for troubleshooting.
9. To isolate view cell, switch 3-ways B&C. This isolates view cell to check for foam stability; take pictures of foam progress with time.
10. To sample foam, switch 3-ways D&E. To stop sampling, switch them back.
11. While sampling foam and isolating view cell valve arrangement should as shown in **Figure 12**:
12. To finish run, close valves 1, 3, 4, and 5, and then turn off the pumps
13. To perform backflow, see next section
 - Back Flow

Figure 12: Final valve arrangement in experimental procedure for the first generation apparatus

1. After step 12 in previous section:

- Turn off ISCO pump
- Shut off valve 1
- Shut off valve 2 and 3

- Switch 3-way A
 - Switch 3-ways F&G
 - Close valve 5
2. Set flow rate on HPLC pump to desired back flow (the entire rate will be set by this pump).
 3. Monitor pressure drop across capillary; small pressure drop corresponds to CO₂ and large pressure drop corresponds to water. If there are larger pressure drops than expected if the fluid was only water, then there is likely foam present.
 4. When sample in sampling accumulator runs out, HPLC pump will reach maximum pressure almost instantly. This means the piston has reached the end, there is no more sample. Then switch valves D&E to flush with water again.

2.11.1 Flow in second apparatus

The procedure for the second apparatus is fundamentally the same, but there are some slight differences because this apparatus has considerably fewer valves in order to simplify operations. The main difference is that to build up pressure, only valve D is closed and opened in the pressure build-up and subsequent start of the foam generation.

In the second apparatus, the starting position is to have valves 3 and C closed to flow. The HPLC pump that pumps water into the CO₂ accumulator should be turned on with the flow rate for the experiment already set. Then the ISCO pump is turned on, and allowed to build pressure in the apparatus until the pressure reaches about 1200 psia. Then open valve C, and let the pump continue to build pressure, which should settle around 1350 psia, what the back pressure valve is set to. Once this pressure is open valve

3 to allow the CO₂ to flow. This apparatus does not have the capability for backflow.

After the experiment is run, flush the apparatus with water.

2.11.2 Viscosity measurements

After the experiment has started and the foam is flowing through the apparatus, the pressure drop measurements can be made. These pressure drop readings often vary wildly in the early stages. **Figure 13** is a sample of the change in pressure measurements taken during the experiment, with notes of different time periods of the experiment.

Figure 13: Example pressure drop data for foam flow in the capillary tube. The experiment was run at 21 degrees Celsius, 1350 psia, a shear rate of 1430 sec⁻¹, and a nanoparticle concentration of 0.1 weight percent using the 5 nm silica core PEG coated nanoparticles from 3M. The green region indicates steady flow of stable foam, and the average pressure drop in this region is used to calculate the apparent viscosity.

This graph is of experiment 28. The conditions for the experiment were: 0.1 weight percent nanoparticles in the aqueous phase, a phase ratio (defined below) of 11, and a shear rate of approximately 1430 sec⁻¹, ambient temperature, no salinity, and the

nanoparticles were 5 nm silica core coated with polyethylene glycol. The phase ratio is the volumetric flow rate of CO₂ divided by the volumetric flow rate of the aqueous phase. There are three distinct zones that are designated by different colors. The first zone is in red, and this is the initial build-up of pressure using just the nanoparticle solution. At the transition between the red and yellow zones, the CO₂ flow was initiated, and explains the brief drop in the change in pressure in the data. The yellow zone denotes when the flow was trying to stabilize, but still oscillating around a stable value. The end of the yellow zone shows that data converging towards a stable value in the green zone. The green zone shows a steady value which is a representative pressure drop for this foam. Once this stable zone has been observed, the pressure drop data from this zone is averaged, and the pressure drop and flow rate that the experiment is run at is used in **Equation 4** to determine an average apparent viscosity.

2.11.3 Setting up a baseline

All viscosity calculations are based on the pressure drop across a capillary tube, Equation 4. These calculations treat all cases encountered in the experiments (water calibration; CO₂ and water mixture; foam + excess phase) as if a single continuous phase were passing through the capillary in laminar flow. To focus on the effect of the nanoparticles, a baseline set of multiphase flow experiments was conducted. These baseline experiments were run under the same conditions that the foam generation experiments were run at (pressure at 1350 psia, temperature at 21 degrees C, and shear at 1430 sec⁻¹), but included no nanoparticles in the aqueous solution. The aqueous solution was only water. At these conditions the viscosities of water and of CO₂ are 1 cP and 0.07 cP, respectively. The experiments are summarized in **Table 2** and **Figure 14** below.

	Total Flow Rate (mL/min)	Volumetric Phase Ratio (mL/min)/(mL/min)	Viscosity Apparent (cP)
Exp 11	6.5	12.0	0.29
Exp 12	7	6.0	0.33
Exp 13	7.5	4.0	0.48
Exp 14	8	3.0	0.44
Exp 15	5.5	10.0	0.35
Exp 16	6	5.0	0.39
Exp 17	6.5	3.3	0.41
Exp 18	7	2.5	0.46
Exp 19	4.5	8.0	0.38
Exp 20	5	4.0	0.36
Exp 21	5.5	2.7	0.38
Exp 22	6	2.0	0.46
Exp 23	3.5	6.0	0.41
Exp 24	4	3.0	0.46
Exp 25	4.5	2.0	0.47
Exp 26	5	1.5	0.59
Exp 33	6	11.0	0.36

Table 2: Summary of the baseline experiments and results. There were no nanoparticles in any of these tests, and the conditions were 21 degrees Celsius, zero salinity, and varying shear rates based on Equation 6.

Figure 14: Comparison of the results of the baseline experiments. There were no nanoparticles in any of the tests, and the conditions were 21 degrees Celsius, zero salinity, and varying shear rates based on equation 6.

Figure 14 shows that the lower the phase ratio (and thus more water, less CO₂) the greater the apparent viscosity. Normalized mixture viscosity is defined as the ratio of apparent viscosity when an experiment is run with nanoparticles in the aqueous phase to apparent viscosity for the corresponding baseline experiment. The normalized mixture viscosity thus measures directly the contribution of nanoparticles to reducing the fluids' mobility.

Chapter 3: Results

Experiments were run at a wide variety of conditions, both to quantify the foam's stability characteristics and to test the ability to generate and stabilize foams in different field conditions. The parameters varied were temperature, salinity of the brine phase and flow velocity (shear rate). There were also some constant environmental factors: pressure at around 1350 psia, and the grain size of the bead pack at 180 micron. Regarding the nanoparticles, the experimental parameters varied include the coating of the nanoparticles themselves, and the concentration of nanoparticles in water. The other operational parameter varied was the phase volume ratio (CO_2 volumetric flow rate divided by aqueous phase volumetric flow rate at accumulator conditions of 1350 psia and 21°C). How these parameters influence the creation and stabilization of foam was quantified.

The parameters and their value ranges are located below in **Table 3**.

Parameter	Values tested
Temperature	21, 50, 75, 90 C
Total flow rate	3, 4.5, 5, 6 mL/min
Phase ratio	1 to 24
Salinity	0, 2, 4 weight percent
Nanoparticle concentration	0.01 through 10 weight percent
Nanoparticle coating	PEG, Salt Tolerant, Organic -OH

Table 3: Summary of experimental parameters tested.

Several different nanoparticle coatings were tested for their ability to generate foam. Experiments were conducted with different particles holding other conditions same, studies the effect of nanoparticle coating on foam stabilization. Different nanoparticles were never used in mixed combination, to isolate the effects of the nanoparticle coating. One set of experiments studied the effect of the concentration of nanoparticles; another similar set tested the effect of salinity of the water in the nanoparticle solution. The concentrations were adjusted by adding de-ionized water to the nanoparticle dispersion as described in Chapter 2. The salinity was changed by adding lab grade sodium chloride to the prepared solution, based on a weight percentage. **Table 4** lists all the experiments that were carried out, for reference. The details of the individual experiments are subsequently described in this chapter.

Experiment ID	Particle Type	Nanoparticle Concentration (wt%)	Salinity (wt%)	Temperature (Degrees Celsius)	Total Flow Rate* (mL/min)	Volumetric Phase Ratio* (mL/min)/(mL/min)	Section where results are given
Exp 1	PEG	10	0	21	6	2	3.2
Exp 2	PEG	10	0	21	5	4	3.2
Exp 3	PEG	5	0	21	6	2	3.2
Exp 4	PEG	5	0	21	3	2	3.2
Exp 5	PEG	1	0	21	6	2	3.2
Exp 6	PEG	1	0	21	4.5	2	3.2
Exp 7	PEG	1	0	21	6	1	3.2
Exp 8	PEG	1	0	21	6	3	3.2
Exp 9	PEG 5nm	1	0	21	6	5	3.1
Exp 10	PEG 5nm	2	0	21	6	11	3.2
Exp 11	N/A	0	0	21	6.5	12	2.11
Exp 12	N/A	0	0	21	7	6	2.11
Exp 13	N/A	0	0	21	7.5	4	2.11
Exp 14	N/A	0	0	21	8	3	2.11
Exp 15	N/A	0	0	21	5.5	10	2.11
Exp 16	N/A	0	0	21	6	5	2.11
Exp 17	N/A	0	0	21	6.5	3.3	2.11
Exp 18	N/A	0	0	21	7	2.5	2.11
Exp 19	N/A	0	0	21	4.5	8	2.11
Exp 20	N/A	0	0	21	5	4	2.11
Exp 21	N/A	0	0	21	5.5	2.7	2.11
Exp 22	N/A	0	0	21	6	2	2.11
Exp 23	N/A	0	0	21	3.5	6	2.11
Exp 24	N/A	0	0	21	4	3	2.11
Exp 25	N/A	0	0	21	4.5	2	2.11
Exp 26	N/A	0	0	21	5	1.5	2.11
Exp 27	PEG 5nm	0.1	0	21	6	5	3.1
Exp 28	PEG 5nm	0.1	0	21	6	11	3.2
Exp 29	PEG 5nm	0.05	0	21	6	5	3.1
Exp 30	PEG 5nm	0.05	0	21	6	11	3.2
Exp 31	PEG 5nm	0.01	0	21	6	5	3.1
Exp 32	PEG 5nm	0.01	0	21	6	11	3.2
Exp 33	N/A	0	0	21	6	11	2.11
Exp 34	PEG 5nm	0.025	0	21	6	11	3.2
Exp 35	PEG 5nm	0.025	0	21	6	5	3.1
Exp 36	PEG 5nm	0.025	0	21	6	3	3.2

Table 4: Experiment conditions examined in this thesis. Entries in red indicate no foam formed.

Exp 37	PEG 5nm	0.025	0	21	6	2	3.2
Exp 40	PEG 5nm	0.5	2	21	6	5	3.4
Exp 40b	PEG 5nm	0.5	0	50	6	5	3.5
Exp 40c	PEG 5nm	0.5	0	75	6	5	3.5
Exp 40d	PEG 5nm	0.5	0	95	6	5	3.5
Exp 41	PEG 5nm	0.5	2	21	6	11	3.4
Exp 42	PEG 5nm	0.05	2	21	6	5	3.4
Exp 43	PEG 5nm	0.05	2	21	6	11	3.4
Exp 44	PEG 5nm	0.1	2	21	6	5	3.4
Exp 45	PEG 5nm	0.1	2	21	6	11	3.4
Exp 46	PEG 5nm	0.05	4	21	6	11	3.4
Exp 47	PEG 5nm	0.05	4	21	6	5	3.4
Exp 48	PEG 5nm	0.1	4	21	6	11	3.4
Exp 49	PEG 5nm	0.1	4	21	6	5	3.4
Exp 50	PEG 5nm	0.5	4	21	6	11	3.4
Exp 51	PEG 5nm	0.5	4	21	6	5	3.4
Exp 52	PEG 5nm	0.5	0	21	6	11	3.2
Exp 53	PEG 5nm	0.5	0	21	6	5	3.1
Exp 54	PEG 5nm	0.05	0	21	6	14	3.2
Exp 55	PEG 5nm	0.05	0	21	6	19	3.2
Exp 56	PEG 5nm	0.05	0	90	6	29	3.2
Exp 57	PEG 5nm	0.5	0	90	2.05	1.05	3.6
Exp 58	PEG 5nm	0.5	0	90	3.5	2.5	3.6
Exp 59	PEG 5nm	0.5	0	90	2.35	3.7	3.6
Exp 60	PEG 5nm	0.5	0	90	4.7	3.7	3.6
Exp 61	PEG 5nm	0.5	0	90	6	5	3.6
Exp 62	PEG 5nm	0.5	0	90	7	2.5	3.6
Exp 63	PEG 5nm	0.5	0	90	4.1	1.05	3.6
Exp 64	PEG 5nm	0.5	0	75	2.19	2.19	3.6
Exp 65	PEG 5nm	0.5	0	75	2.35	2.35	3.6
Exp 66	PEG 5nm	0.5	0	75	3.5	3.5	3.6
Exp 67	PEG 5nm	0.5	0	75	6	6	3.6
Exp 68	PEG 5nm	0.5	0	75	4.38	4.38	3.6
Exp 69	PEG 5nm	0.5	0	75	4.7	4.7	3.6
Exp 70	Salt Tolerant	0.05	0	21	6	5	3.4

Table 4 (cont.) 1

Exp 71	Salt Tolerant	0.05	0	21	6	11	3.4
Exp 72	Salt Tolerant	0.1	0	21	6	5	3.4
Exp 73	Salt Tolerant	0.1	0	21	6	11	3.4
Exp 74	Salt Tolerant	0.5	0	21	6	5	3.4
Exp 75	Salt Tolerant	0.5	0	21	6	11	3.4
Exp 76	Nyacol	0.5	0	21	6	5	3.4
Exp 77	Nyacol	0.5	0	21	6	11	3.4
Exp 78	Nyacol	1	0	21	6	5	3.4
Exp 79	Nyacol	1	0	21	6	11	3.4
Exp 80	Nyacol	5	0	21	6	5	3.4
Exp 81	Nyacol	5	0	21	6	11	3.4

Table 4 (cont.) 2

In this chapter the term “external properties” refer to changes made to the experiment that were not made to the fluid or the nanoparticles themselves. These involve adjusting the phase volume ratio, the temperature of the experiment, and the shear rate in the bead pack. The phase volume ratio is the volumetric flow rate ratio of the two fluids in the experiment, at 21 degrees Celsius and about 1350 psia, effectively making this a mass flow rate ratio. Changing the flow rates of each pump allows setting desired ratios. The temperature was controlled by submersing part of the apparatus into MGW Lauda hot water-bath. The shear rate can be changed by three different ways, by adjusting the flow rate, by changing the bead diameter of the bead pack, and increasing the temperature of the experiment.

The matrix of experiments was set up such that only one parameter would be varied at a time. In each subsequent section of this chapter the description will follow a general order. First the method will be explained as to how each of the parameters was tested.

Next, the results are reported in tabulated summaries of the data collected. Comments about specific tests follow, in which any irregular data are explained or more general discussions about the tests. Lastly a plot summarizes the results.

3.1 Effect of concentration

The first intrinsic property of the nanoparticle solution to test was the concentration of the nanoparticles. This series of tests were conducted with the 3M PEG coated nanoparticles with a 5 nm silica core. The tests correspond to Experiments 9, 27, 29, 31, 35, and 53 in **Table 5**. Concentration is the most easily adjusted parameter, as it just involves using **Equation 1**, in **Chapter 2**, and adding de-ionized water. The experiments in **Table 5** were run in order to find the lower limit of the concentration that stabilizes foam. The phase ratio, shear rate, salinity, and temperature were kept the same for these experiments at values of 5 mL/min CO₂ per 1 mL/min nanoparticle solution, 1430 sec⁻¹, zero salinity in the brine phase, and 21 degrees Celsius, respectively. The viscosity of liquid CO₂ at 1350 psia and 21 degrees Celsius is approximately 0.07 cP, and the viscosity of water is approximately 1 cP. The baseline apparent viscosity of CO₂/water at the 5:1 phase ratio was measured to be 0.39 cP. The run summary of the experiments testing the effect of concentration is found in **Table 5** located below.

	Total Flow rate (mL/min)	Volumetric Phase Ratio (CO ₂ mL/min)/(H ₂ O mL/min)	Nanoparticle Concentration (wt%)	Viscosity Apparent (cP)	Normalized Mixture Viscosity
Exp 9	6	5	1	2.20	5.66
Exp 27	6	5	0.1	2.16	5.55
Exp 29	6	5	0.05	1.23	3.17
Exp 31	6	5	0.01	NO FOAM	1
Exp 35	6	5	0.025	NO FOAM	1
Exp 53	6	5	0.5	6.15	15.82

Table 5: Effects of nanoparticle concentration using 5 nm silica core PEG coated nanoparticles near the threshold for foam generation.

The data marked in red (experiments 31 and 35) indicate failure to make stable foam. This was inferred from the pressure drop across the capillary tube measurements (value same as corresponding baseline experiment without nanoparticles) and the evidence from the macroscopic viewing cell. Even at small concentration the foam has large viscosity compared to the same fluids without nanoparticles. This is evidenced by the normalized mixture viscosity. The results of the plots are summarized below in **Figure 15**.

Figure 15: The effect of nanoparticle concentration on foam stabilization and viscosity. These experiments were run using the 5 nm silica core PEG coated nanoparticles. They were run at a phase ratio of 5, temperature of 21 degrees Celsius, and a shear rate of 1430 sec^{-1}

Concentrations as small as 0.05 weight percent, or 500 parts per million can cause a viscosifying effect of about 3 times what would be expected if there were just two phase flow. The threshold concentration for foam generation at these temperature, pressure, and shear rates is somewhere between 0.025 and 0.05 weight percent. The concentration that yields the best results for increasing the viscosity appears to be around the 0.5 weight percent concentration.

3.2 Effect of phase volume ratio

The first operating parameter that was varied was the phase ratio. The nanoparticles used for these experiments were the 3M PEG coated nanoparticles with a 5 nm silica core. The

phase volume ratio is determined by the displacing flow rates from the two pumps. These experiments were run at a constant 21 degrees Celsius, so the phase ratio in the HIP column is the same as the phase ratio at accumulator conditions. These experiments somewhat overlapped the experiments of section 3.1 because both the phase volume ratio and the nanoparticle concentration determine the amount of nanoparticles available to stabilize the foam. But there is a key difference, because the phase volume ratio tests not just how many nanoparticles are delivered but also the amount of water available in which the CO₂ droplets (or bubbles) can be dispersed. So these experiments were run in parallel to the tests that determined the minimum nanoparticle concentration. The concentrations were varied somewhat, but the shear rates, the temperatures, and the salinities were kept the same.

To do this several series of experiments were run under the exact same parameters, except for adjusting the flow rate of CO₂ and the nanoparticle solution by the same increment, but in opposite directions. For example, consider Experiments 29, 30, 54, 55, and 56. Each of these experiments was run at the same pressure (1350 psia), temperature (21 degrees Celsius), and shear rate (1430 sec⁻¹). The one thing that did vary was the flow rate ratios. Since the shear rate remains constant the total flow rate is constant at 6 mL/min. The difference between **Experiments 30** and **54** is that the CO₂ flow rate increased from 5.5 mL/min in Experiment 30 to 5.6 mL/min in **Experiment 54**. To keep the total flow rate the same, the nanoparticle solution flow rates were decreased from 0.5 mL/min in **Experiment 30** to 0.4 mL/min for **Experiment 54**. This similar process of increasing CO₂ flow rates while decreasing the nanoparticle solution flow rate by the

same increments was continued for **Experiments 55** and **56**. **Table 6** shows an overview of the experiments run to test the effect of phase ratio. Experiments reported in **Table 4** are included in **Table 6**.

	Total Flow rate (mL/min)	Volumetric Phase Ratio (mL/min)/(mL/min)	Nanoparticle Concentration (wt. %)	Viscosity Apparent (cP)	Normalized Mixture Viscosity
Exp 1	6	2	10	3.74	8.14
Exp 10	6	11	2	3	8.37
Exp 27	6	5	0.1	2.16	5.55
Exp 28	6	11	0.1	2.7	7.54
Exp 29	6	5	0.05	1.23	3.17
Exp 3	6	2	5	2.8-3.7	6.1-8.1
Exp 30	6	11	0.05	0.74	2.05
Exp 31	6	5	0.01	NO FOAM	1
Exp 32	6	11	0.01	NO FOAM	1
Exp 34	6	11	0.025	NO FOAM	1
Exp 35	6	5	0.025	NO FOAM	1
Exp 36	6	3	0.025	NO FOAM	1
Exp 37	6	2	0.025	NO FOAM	1
Exp 5	6	2	1	1.25	2.72
Exp 52	6	11	0.5	4.76	13.3
Exp 53	6	5	0.5	6.15	15.82
Exp 54	6	14	0.05	2.5	N/A
Exp 55	6	19	0.05	1.5	N/A
Exp 56	6	29	0.05	NO FOAM	1
Exp 7	6	1	1	1.25	N/A
Exp 8	6	3	1	1.5	3.99
Exp 9	6	5	1	2.2	5.66

Table 6: Effect of Phase Ratio on Apparent Viscosity when the phase volume ratio is varied when using 5 nm silica core nanoparticles coated with PEG. All experiments conducted at 21 degrees Celsius and at 1350 psia.

Once again the red text denotes when no stabilized foam formed. We first examine a smaller group, in this case **Experiments 29, 30, 54, 55, and 56**. These experiments were all run at the smallest nanoparticle concentration known to stabilize foam. Starting at smaller phase volume ratios, increasing the CO₂ flow rate incrementally and decreasing

the nanoparticle solution flow rate by the same increment kept the shear rate constant while varying the phase ratio. The interesting result is that even at the lowest known concentration to stabilize foam a large phase ratio is able to sustain foam. In this case, at 0.05 weight percent foam can survive if there is 19 times more CO₂ than water; and the foam has a viscosity that appears to be higher than water. There were no baseline experiments run at the higher phase volume ratio experiments, so the normalized mixture viscosity is not available for these experiments. **Figure 16** shows the full scale of the experiments run giving a picture of the lower boundary of foam generation for these experiments, which were run at 1350 psia, 1430 sec⁻¹, and 21 degrees Celsius. **Figure 17** shows the same experiments with their normalized viscosity results. The trend from these results is that there seems to be a threshold concentration (0.5 wt%) in which the PEG coated 5 nm nanoparticles when run at 1350 psia, 1430 sec⁻¹, and 21 degrees Celsius.

Figure 16: At ambient temperature and a pressure of 1350 psia and a shear rate of 1430 sec^{-1} , CO_2 foam generation requires a threshold nanoparticle concentration using 5 nm silica PEG-coated ; the data also suggest an upper bound of phase volume ratio. In these experiments the nanoparticles were dispersed in deionized water.

Figure 17: At ambient temperature and a pressure of 1350 psia, zero salinity, and a shear rate of 1430 sec^{-1} , CO_2 foam generation requires a threshold nanoparticle concentration using 5 nm silica PEG-coated. The data suggests a that a nanoparticle concentration of 0.5 wt% creates the largest normalized mixture viscosity.

3.4 Effect of coating

3.4.1 Polyethylene-glycol coating

Two types of polyethylene glycol coated nanoparticles were tested. Both types had a silica core coated by a short 5nm polyethylene glycol chains. The difference is that the core size changes the effective diameter. The 20 nm core did show some potential to stabilize foam as there was a brief set of successful experiments with these particles. The supply of 20 nm core nanoparticles was extremely limited, and only two tests were run. In Experiments 1-8, the nanoparticle coating was PEG coated nanoparticles. The core size was not known, but at these core sizes, the coating is more important to foam stabilization than particle diameter. The summary of experiments run using the 5 nm core can be found in **Appendix A.1**. A plot of all the experiments run using the 5 nm core

PEG coated nanoparticles can be found in **Figure 15**. This plot shows a wide array (or a foam generating envelope) of experiments run, but also illustrates the versatility of these nanoparticles in creating foam.

3.4.2 Other types of coating

The other types of coated nanoparticles were a Salt Tolerant coated nanoparticle from 3M and another nanoparticle from Nyacol. Both of these particles were used in experiments over a range of conditions that are known to create stable and high quality foams when using the 5 nm PEG coated nanoparticles. Both of these types of nanoparticles were tested using the same procedure as the PEG coated nanoparticles. The concentrations were 0.05, 0.5, and 1.0 weight percent for the Salt Tolerant coated nanoparticles, and 0.5, 1.0, and 5.0 weight percent for the Nyacol particles. Each of these experiments was run at two different phase ratios of 5 and 11. All of the experiments were run at a constant 1430 sec^{-1} shear rate. These experiments are summarized in **Table 7**.

Experiment number	Nanoparticle Coating	Nanoparticle concentration (wt %)	Phase Volume Ratio (mL/min)/(mL/min)	Foam Created?
Exp 70	Nyacol	0.5	5	No
Exp 71	Nyacol	1	5	No
Exp 72	Nyacol	5	5	No
Exp 73	Nyacol	0.5	11	No
Exp 74	Nyacol	1	11	No
Exp 75	Nyacol	5	11	No
Exp 76	Salt Tolerant	0.05	5	No
Exp 77	Salt Tolerant	0.5	5	No
Exp 78	Salt Tolerant	1	5	No
Exp 79	Salt Tolerant	0.05	11	No
Exp 80	Salt Tolerant	0.5	11	No
Exp 81	Salt Tolerant	1	11	No
Exp 7	PEG	1	1	Yes
Exp 5	PEG	1	2	Yes
Exp 3	PEG	5	2	Yes
Exp 1	PEG	10	2	Yes
Exp 8	PEG	1	3	Yes
Exp 29	PEG	0.05	5	Yes
Exp 27	PEG	0.1	5	Yes
Exp 9	PEG	1	5	Yes
Exp 53	PEG	0.5	5	Yes
Exp 30	PEG	0.05	11	Yes
Exp 28	PEG	0.1	11	Yes
Exp 10	PEG	2	11	Yes
Exp 52	PEG	0.5	11	Yes
Exp 54	PEG	0.05	14	Yes
Exp 55	PEG	0.05	19	Yes
Exp 56	PEG	0.05	29	No
Exp 32	PEG	0.01	11	No
Exp 34	PEG	0.025	11	No
Exp 37	PEG	0.025	2	No
Exp 36	PEG	0.025	3	No
Exp 31	PEG	0.01	5	No
Exp 35	PEG	0.025	5	No

Table 7: Summary of experimental results using Nyacol, Salt Tolerant, and PEG coated nanoparticles. All experiments were run at a shear rate of 1430 sec^{-1} and at 21 degrees Celsius.

For the all experiments with Nyacol or the Salt Tolerant coatings, no foam was sustained. The salt tolerant coating produced a small film of foam visible in the view cell between the CO_2 – water interface. These thin layers of foam did not increase the resistance of flow, so the normalized mixture viscosity was not significantly increased. It

may be that the Salt Tolerant and Nyacol particles could stabilize foam at larger shear rates or at larger particle concentration than tested here. Recall however that the PEG coated particles did stabilize foam in the range of conditions used for these other particles. Figure 16 summarize the experiments run, including the successful foam generation envelope reported in Section 3.4.1 for the 5 nm core PEG coated particles.

Figure 18: Experimental results for testing the Nyacol, Salt Tolerant and PEG nanoparticle coating. These experiments were run at a shear rate of 1430 sec^{-1} and at 21 degrees Celsius. Experiments that yielded stable foam are marked as green triangles.

3.4 Effect of salinity

Salinity will always be encountered in petroleum reservoirs, and can cause instability with surfactant stabilized foams. The nanoparticles used for these experiments were the PEG coated 5 nm silica core provided by 3M. The nanoparticle brine was diluted in the

previously described manner to obtain the appropriate nanoparticle concentration. As with the experiments that tested the effect of nanoparticles concentration, section 3.4, care was taken in order to ensure that salinity was the only parameter was changing. This means that temperature, pressure, and shear rates were kept constant (21 degrees Celsius, 1350 psia, and 1430 sec^{-1} , respectively). Since the effects of concentrations were known, three concentrations that stabilized foam well within the foam generating envelope shown in **Figure 14** were selected and tested at three different salinity levels. The phase ratio was also adjusted to test two phase ratios, to see if the salinity had a notable effect when there were different relative amounts of each fluid present. The two phase volume ratios tested were 5 and 11. In **Tables 8** and **9** the outline of these tests are shown. The phase volume ratios for **Table 8** and **Table 9** are 5 and 11, respectively.

	Total Flow rate (mL/min)	Nanoparticle Concentration (wt. %)	Salinity (wt. %)	Viscosity Apparent (cP)	Normalized Mixture Viscosity
Exp 29	6	0.05	0.0	1.23	3.17
Exp 42	6	0.05	2.0	0.81	2.09
Exp 47	6	0.05	4.0	NO FOAM	1
Exp 27	6	0.1	0.0	2.16	5.55
Exp 44	6	0.1	2.0	4.30	11.1
Exp 49	6	0.1	4.0	2.16	5.56
Exp 53	6	0.5	0.0	6.15	15.8
Exp 40	6	0.5	2.0	2.50	6.42
Exp 51	6	0.5	4.0	6.99	18.0

Table 8: Effect of salinity on normalized mixture viscosity when the phase volume ratio is 5 using 5 nm SiO₂ PEG coated particles at three concentrations. Experiments were run at 21 degrees Celsius, 1350 psia, and a shear rate of 1430 sec^{-1} .

	Total Flow rate (mL/min)	Nanoparticle Concentration (wt. %)	Salinity (wt. %)	Viscosity Apparent (cP)	Normalized Mixture Viscosity
Exp 30	6	0.05	0.0	0.74	2.05
Exp 43	6	0.05	2.0	NO FOAM	1
Exp 46	6	0.05	4.0	NO FOAM	1
Exp 28	6	0.1	0.0	2.70	7.54
Exp 45	6	0.1	2.0	1.90	5.30
Exp 48	6	0.1	4.0	NO FOAM	1
Exp 52	6	0.5	0.0	4.76	13.3
Exp 41	6	0.5	2.0	2.92	8.14
Exp 50	6	0.5	4.0	NO FOAM	1

Table 9: Effect of salinity on normalized mixture viscosity when the phase volume ratio is 11 using 5 nm SiO₂ PEG coated particles. Experiments were run at 21 degrees Celsius, 1350 psia, and a shear rate of 1430 sec⁻¹.

As with previous tables, the data marked in red indicate when no foam was observed in the macroscopic view cell and when there was no noticeable change in pressure drop across the capillary tube compared to the corresponding baseline experiment. Experiment 45, whose results are recorded in blue, is interesting because it showed the destabilizing effect of the salinity very clearly. Originally there was stable foam 1.90 cP viscosity. The foam remained stable for a brief time interval after which, the foam broke and was no longer observed.

In these experiments the normalized mixture viscosity is computed using the baseline experiments reported in **Table 2** described above. The aqueous fluid in the baseline experiments has zero salinity. This is because these specific experiments are designed to show the effect of *salinity and nanoparticles* on foam qualities. If the baseline experiments had salinity included to match the tests at different salinities, the results would be similar to the baseline results when both experiments had zero salinity (i.e. testing only the effect of the nanoparticles). **Figures 19** and **21** show how the normalized

mixture viscosity is affected by the salinity of the aqueous phase at phase ratios of 5 and 11, respectively. **Figures 20** and **22** show how the foam generation envelope is influenced by salinity at phase ratios 5 and 11, respectively.

Figure 19: Normalized mixture viscosity vs. nanoparticle concentration at different salinities and a constant phase ratio of 5. These experiments were run at 21 degrees Celsius, 1350 psia, and 1430 sec⁻¹.

Figure 20: Foam stability vs. salinity and nanoparticle concentration using 5 nm silica core PEG coated nanoparticles for a CO₂/brine phase ratio of 11. These experiments were run at 21 degrees Celsius, 1350 psia and a shear rate of 1430 sec⁻¹

Figure 21: Normalized mixture viscosity vs. nanoparticle concentration at different salinities and a constant phase ratio of 11. These experiments were run at 21 degrees Celsius, 1350 psia, and 1430 sec⁻¹.

Figure 22: Foam stability vs. salinity and nanoparticle concentration using 5 nm silica core PEG coated nanoparticles for a CO₂/brine phase ratio of 11. These experiments were run at 21 degrees Celsius, 1350 psia and a shear rate of 1430 sec⁻¹

When the phase ratio is 5, **Figure 20**, there is more water than when the phase ratio is 11, **Figure 22**, to deliver the nanoparticles to the CO₂ – water interface. The increase in water, vs. the experiments in **Figure 20**, does provide more of one of the key building blocks of the foam, water. Thus better stability is expected in these experiments. The graphs show just that: in **Figure 22** there is a large foam generating envelope, and none of the experiments had the foam destabilize mid-experiment. The only time there was no foam generated is when the salinity was at its highest value tested (4 weight percent) and the nanoparticle concentration at its lowest (0.05%) This nanoparticle concentration value is also the lowest value known to stabilize foam without salinity. When the phase ratio is increased to 11, the stabilizing effects of the nanoparticles are weakened. There is no

stable foam at the highest salinity for any of the nanoparticle concentrations tested. At the lowest concentration of nanoparticles (0.05 weight percent), salinity of 2 weight percent was enough to prevent foam stabilization.

The **Tables 8** and **9**, as well as **Figures 19** and **21** that accompany these experiments show two general trends. First, salinity does have some destabilizing effects on nanoparticle based foams. This effect is more pronounced when there are fewer nanoparticles present to counteract the salinity (i.e. higher phase ratio and lower concentrations). The second general trend is while the salinity does have a destabilizing trend, increasing the salinity also increases the viscosity of some foams, given the right parameters. For example, between experiments 27 and 44 there is a large increase in apparent viscosity, and the only thing that changed is the salinity, which increases from zero to 2 weight percent.

3.5 Effect of temperature

The temperature of oil reservoirs increases with depth because of the geothermal gradient. In order to emulate reservoir conditions, a series of experiments were conducted using parameters that reliably yielded foam at ambient temperature: nanoparticle concentration 0.5 weight percent, zero salinity, and a phase ratio of 5. In the first tests, the temperatures were 50, 75, and 95 degrees Celsius. These experiments were labeled Experiments 40b, 40c, and 40d, respectively, shown in **Table 10**.

	Total Flow Rate* (mL/min)	Volumetric Phase Ratio* (mL/min)/(mL/min)	Volumetric Phase Ratio at HIP Column Conditions (mL/min)/(mL/min)	HIP Column Temperature (°C)
Exp 40b	5	5	14.8	50
Exp 40c	5	5	21.0	75
Exp 40d	5	5	24.6	95

Table 10: Temperature experiments experiments using 5 nm silica core, PEG coated nanoparticles at 0.5 weight percent nanoparticle concentration.

* Accumulator conditions (21 C, 1350 psia)

The experiments were successful in that they were able to create and stabilize foam. However, there was a key oversight that caused difficulties, and we could not measure viscosity data. The higher temperature reduced the density of the CO₂ in the HIP column. This caused the waste accumulator to fill faster for the same nominal flow rate. For example, for **Experiment 40b** in **Table 10**, the temperature was set at 50 degrees Celsius. The pressure was set at about 1350 psia with a total flow rate of 6 mL/min (5 mL/min CO₂ + 1 mL/min nanoparticle dispersion) at accumulator conditions (T = 21°C). The density of the CO₂ entering the bead pack at 50 degrees Celsius was a factor of 3 smaller than in the accumulator. Thus the volumetric rate of CO₂ in the HIP column was 15 mL/min. (Density calculations were made with property calculator from the Duan research group, from the Chinese Academy of Sciences (<http://www.geochem-model.org/>). During experiments run at 1350 psia, 21 degrees Celsius, and the same 6 mL/min total flow rate, the accumulator required approximately 60-75 minutes to fill. Thus at least 60 minutes were available to observe a stable pressure drop across the capillary tube. The reduction of density decreased the available time to get this reading at 50 degrees Celsius to about 20-25 minutes. Note also that the effective phase volume

ratio at bead pack conditions was 15:1 not the 5:1 at accumulator conditions. The pressure drop data from **Experiments 40b** and **40c** are shown below in **Figure 23** and **Figure 24**, respectively. **Figure 23** shows how short the period for data collecting was and what happened when the accumulator was filled. **Figure 24** shows results when the experiment was repeated but the temperature increased to 75 degrees Celsius.

Figure 23: Pressure drop across the capillary tube during the Experiment 40b. Experiment was run at 50 degrees Celsius, with a nanoparticle concentration of 0.5 weight percent of the 5 nm silica core nanoparticles coated with PEG. The phase ratio at accumulator conditions for the experiment was 5 but was 14.8 in the HIP column where foam was generated.

Figure 24: Experiment 40c pressure drop data. Experiment was run at 75 degrees Celsius, with a nanoparticle concentration of 0.5 weight percent of the 5 nm silica core nanoparticles coated with PEG. The phase ratio at accumulator conditions for the experiment was 5 but was 21 in the HIP column where foam was generated.

There are a few things to note from **Figures 23** and **24**. First, in Experiment 40b, the experiment ended abruptly before stabilizing, because the waste accumulator ran out of space for the incoming CO₂. Second, in Experiment 40c, the experiment ended before the pressure stopped climbing. The pressure drop measurements increased throughout the experiment until the accumulator filled up. Finally, there are no results for 40d. At this temperature the water bath overtaxed the circuit breakers. This caused the all the electronics in the area to shut off. For safety reasons the next experiments were run at slightly decreased temperature (90 degrees Celsius).

When adjusted for the increased volumetric flow rate at temperature, the apparent viscosity for experiment 40b is estimated to be 3.53 cP (using a pressure drop of 350 psia from Fig 19). Taking a typical pressure drop of 225 psi for experiment 40c, the apparent

viscosity is estimated to be 2.08 cP. Baseline experiments to determine the apparent viscosity without nanoparticles were not conducted at elevated temperature. . However it is possible to bound the apparent viscosity from the pure phase viscosities. **Figure 25** show the temperature dependence of the phase viscosities.

Figure 25: How the viscosity of CO₂ varies with temperature at 1350 psia. The calculations were made with the Peng-Robinson equation of state, using the WebGasEOS calculator from Berkley Lab (<http://triton.lbl.gov/gaseos/gaseos.html>). Also shown is how H₂O viscosity varies with temperature, at atmospheric pressure. These values were taken from water tables at Engineering Toolbox (<http://engineeringtoolbox.com>)

The measured apparent viscosity is significantly larger than the viscosities of either component. In experiment 40b the apparent viscosity was about 3.53 and the corresponding component viscosities are about 0.55 cP for water and about 0.016 cP for CO₂. In experiment 40c the apparent viscosity was about 2.08 and the corresponding component viscosities are about 0.35 cP for water and about 0.018 cP for CO₂. The baseline experiments at ambient temperature show that the apparent viscosity of two phase flow is somewhere in between (normally closer to the viscosity of the fluid with

the greatest volume present) viscosities of the two independent phases. The minimum value for the normalized mixture viscosity can be obtained by assuming the CO₂/brine mixture viscosity equal to the viscosity of water at experimental temperature. For experiments 40b and 40c this lower bound on the normalized mixture viscosity was 6.4 and 5.9, respectively. Thus the foam stabilized by nanoparticles increases the resistance to flow by at least an order of magnitude at elevated temperatures. This strong mobility reduction is being achieved at large phase ratios, 15 to 20 CO₂:H₂O.

3.6 Effect of shear rate

In order for the nanoparticles to be introduced to the CO₂ and water interface, there needs to be some sort of mixing of the two phases. The mixing for our experiments is accomplished by co-injecting the fluids through a bead pack. The shear rates in the rest of the apparatus are below that achieved in the HIP column. There were two methods for changing the shear rate, the glass bead diameter could be changed (a long and tedious process not used in this thesis) or the pump flow rates could be adjusted (operational range of available pumps provide a limited ability). The experiments at temperature reported in previous section produced foam at large phase ratios but steady foam production was difficult to achieve in the short time before the accumulator filled.

To allow experiments at elevated temperature to run longer, the overall flow rates were decreased while keeping the phase volume ratio the same. The tests are outlined in **Table 11** and **12**. The increase of temperature increased the volumetric flow rate through the HIP column, and thus increased the shear rate (as shown in **Equation 6**). For these

experiments the salinity was zero and nanoparticle concentration was kept at 0.5 weight percent, while phase ratio and overall flowrates were adjusted independently and together in order to test for a critical shear rate. For example, Experiments 60-66 were run in order to test for a shear rate that at 90 degrees Celsius would create foam. In Experiments 67-71 foam was not generated except when the shear rate for the experiment exceeded approximately 4000 sec^{-1} . The phase ratio was varied at 90 degrees Celsius but did not affect whether foam was generated. As long as the shear rate at the HIP was 4000 sec^{-1} or greater, foam was generated and observed, not only with the increase in the resistance to flow, but also in the view cell. Experiments 57-67 were testing only whether foam was made (i.e. visual confirmation of foam as well as increased resistance to flow) and not foam quality. No measurements of the pressure drop across the capillary tube were made, and thus no observations about the apparent or normalized viscosity are available for these experiments. **Tables 11 and 12**, and **Figures 26 and 27** below show the parameters and results for Experiments 57-69.

	Total Flow Rate* (mL/min)	Volumetric Phase Ratio* (mL/min)/(mL/min)	Volumetric Phase Ratio at HIP Column Conditions (mL/min)/(mL/min)	Shear Rate in HIP Column (sec^{-1})	Foam?
Exp 64	2.19	1.19	5.0	2000	No
Exp 65	2.35	3.7	15.6	2140	No
Exp 66	3.5	2.5	10.5	3190	Yes
Exp 67	6	5	21.04	5470	Yes
Exp 68	4.38	1.19	5.09	3990	Yes
Exp 69	4.7	3.7	15.6	4290	Yes

Table 11: Shear rate experiments for 75 degrees Celsius using 5 nm silica core, PEG coated nanoparticles at 0.5 weight percent nanoparticle concentration.

* Accumulator conditions (21 °C, 1350 psia)

Figure 26: Effect of shear rate on foam generation at 75 degrees Celsius. A threshold shear rate exists, below which foam is not generated using 5 nm silica core, PEG coated nanoparticles at 0.5 weight percent nanoparticle concentration.

	Total Flow Rate* (mL/min)	Volumetric Phase Ratio* (mL/min)/(mL/min)	Volumetric Phase Ratio at HIP Column Conditions (mL/min)/(mL/min)	Shear Rate in HIP Column (sec ⁻¹)	Foam?
Exp 57	2.05	1.05	4.99	2110	No
Exp 58	3.5	2.5	11.9	3610	No
Exp 59	2.35	3.7	17.6	2420	No
Exp 60	4.7	3.7	17.6	4840	Yes
Exp 61	6	5	23.8	6180	Yes
Exp 62	7	2.5	11.9	7210	Yes
Exp 63	4.1	1.05	4.99	4220	Yes

Table 12: Shear rate experiments for 90 degrees Celsius using 5 nm silica core, PEG coated nanoparticles at 0.5 weight percent nanoparticle concentration.

* Accumulator conditions (21 °C, 1350 psia)

Figure 27: Effect of shear rate on foam generation at 90 degrees Celsius. A threshold shear rate exists, below which foam is not generated using 5 nm silica core, PEG coated nanoparticles at 0.5 weight percent nanoparticle concentration.

These results reinforce the idea that there is a threshold energy that is required to force the nanoparticles to adsorb to the CO₂ – water interface. The critical shear rate seems to increase with increasing temperature. While tests at ambient temperature conditions were mostly conducted at a constant shear rate of 1430 sec⁻¹, there is evidence that the critical shear rate is be lower. Experiments 2, 4, and 6 were all run at lower flow rates, and thus at lower shear rates, and there was both a foam observed in the view cell and an increase in the pressure drop across the capillary tube. At 75 °C, the critical shear rate is about 2500 to 3000 sec⁻¹, and at 90 °C, it is about 4000 sec⁻¹.

Chapter 4: Discussion

4.1 Proof of concept

Using nanoparticles to stabilize CO₂ and water foams is not new (Binks 2002). The results reported in Chapter 3 are original in that the foams were created during flow through a porous medium as opposed to mixing bulk phases together. The ability to generate foam simply by co-injecting these fluids into reservoir formation greatly facilitates the application of this concept to the field. Field application could potentially be as simple as up-scaling the equipment (at least two pumps for each fluid, a large vessel to hold a nanoparticle solution).

4.2 Critical parameters

4.2.1 Nanoparticle coating

Four different nanoparticles were tested to for their ability to create foam. Two of the nanoparticles tested did create and stabilize foam. Both were coated with PEG. The chemical natures of the two nanoparticle coatings that did not create foam are unknown. While the salt tolerant coated 3M particles did create a small film of foam, there was no increase in resistance to flow. The Nyacol organic coated particles produced no evidence of foam at 1350 psia, 1430 sec⁻¹, and 21 degrees Celsius for particle concentrations ranging from 0.5 to 5.0 weight percent..

4.2.2 Salinity

The effect of salinity was investigated to determine potential field applicability at different reservoirs. The test were run with the PEG coated 5nm silica core nanoparticles

from 3M. The nanoparticle concentrations were varied from 0.05, 0.1, and 0.5 weight percent. The aqueous fluid salinities were varied between 0, 2, and 4 weight percent. All experiments were performed at the same pressure, 1350 psia, 1430 sec⁻¹, and 21 degrees Celsius. Two different phase volume ratios were tested as well, at 5 and 11. The salinity tests revealed two observations. First, the salinity has a destabilizing effect on foams. Second, that salinity did seem to have a viscosifying effect on the foams. This might be useful in creating a more favorable mobility ratio in CO₂ foam floods.

4.2.3 Shear rate

Shear rate is inherently important to the foam generation process because there has to be mixing in order for the nanoparticles to be attached at the CO₂/water interface. From a series of shear rate experiments, we established the critical shear rate for different temperatures. All experiments used PEG-coated 5 nm silica-core nanoparticles provided from 3M. The tests were performed at 1350 psia. The phase ratios and shear rates were varied by adjusting the overall flow rates and the individual flow rates. The nanoparticle concentrations were varied for the 21 degrees Celsius experiments, but kept constant at 0.5 weight percent for the experiments run at 75 and 90 degrees Celsius. At 21 degrees Celsius the experiments were all run at a constant shear rate, so the critical shear rate is not established, but the lowest known shear rate at which foam was generated was around 720 sec⁻¹ for 21 degrees Celsius.

4.3 Applications

4.3.1 Fractures

Fractures exacerbate mobility control problems in a CO₂ flood. This is because fractures are essentially infinite permeability compared to the surrounding reservoir, and thus the CO₂ will preferentially flow through the fractures whenever it is possible. There are two potential research problems to study, to see if the nanoparticle stabilized foams can be used to remediate the above problem. First would be an experimental set-up to quantify the conditions for generation in a fracture. The second experiment would be to see what happens if the foam were to be created in a bead pack, as in the experiments reported here, and then allowed to flow through a fracture. Both experiments could give insight into the foam's potential success in a fractured reservoir.

When looking at the geometry of a fracture, it is helpful to consider the fracture walls two plates that are stationary. If there are two fluids flowing between the plates, the fluid interface will experience a shear force. The proposed experiment would be to machine a series of cylinders. One would be hollow (the HIP column that housed the bead pack could be used) and of a fixed diameter. The next set of columns would need to be machined to be slightly smaller in diameter, as shown in **Figure 28**. There would also have to be another cylinder machined, as thin as the annular size desired for the experiment. These two cylinders would be set up as shown in the figure, and the offsetting smaller cylinder would create an annular space for the two fluids to flow. This annular space would be varied to test the effects of shear on the foam.

Figure 28: Experimental set-up for CO₂ foams in fractures. In this figure, the red circle is the solid cylinder that blocks fluid flow. The yellow circle is wire that will hold the fracture propped open. The green crescent shape is annular space designed to simulate a fracture.

While the tests on shear rate for foam have been performed using a bead pack, the shear rate tests for a fracture would be slightly different. This shear is purely at a fluid interface, and the fracture does not provide a tortuous path. These tests would provide insight to the foam generation process, lending evidence to whether the generation is based on only shear, or shear and other forms of mixture.

4.3.2 Contact with oil

The next set of experiments would test the effects of an oil phase upon the foam. These foams are meant to sweep oil out of a reservoir. So a set-up that allows the foam to come

in contact with the foam to determine the foam's stability when there are three phases present would be imperative. The experimental set-up is shown in **Figure 29**.

Figure 29: Experimental set-up for studying CO₂ foams in contact with oil

This set-up could test the stability of the foam when it comes in contact with oil. Also, if the core has sufficient dimensions, the test can be run in concurrence with a CO₂ flood experiment to determine the effects the foam generation has on flood efficiency. These experiments could also provide other inside to the nanoparticle behaviors. It has been shown that a similar set-up to the foam generation can generate emulsions using a similar nanoparticle solution. It would be an interesting study to see what exactly happens when there are three phases present. The nanoparticles could potentially move from the foam to the oil and create an emulsion between the oil and water or the foam could sweep the oil more effectively than a pure CO₂ flood would.

4.3.3 Nanoparticle core material

These studies have used nanoparticles with a silica core and focused on the outside coating. One topic that is currently being discussed for its current stabilization potential is using different materials for the cores – specifically using fly ash or a clay particle, both of which are inexpensive by-products of other processes.

4.3.4 CO₂ sequestration

The current research was focused on using the CO₂ foams in order to help improve mobility in CO₂ floods for oil reservoirs. An analogous problem would be the storage of CO₂ for sequestration purposes. The first idea involves creating CO₂ foam similar to the ones created with these experiments.

CO₂ sequestration has a term that is similar to sweep efficiency, named storage efficiency. The storage efficiency is the ability of the reservoir to effectively store CO₂. The CO₂ foams would help with sequestration the same way that the foams would help with and EOR flood, by improving the mobility ratio. An example of how the foam could help with storage efficiency. **Figure 31** is an example reservoir where foam could potentially help. This reservoir is 3 cylinders that sit on top each other. Each cylinder has a different permeability, labeled in the figure. The calculations are based on a few assumptions: the flood is at steady flow, the injection pressure is 500 psi above reservoir pressure, wellbore radius is 3 inches, reservoir radius is 5260 feet, each zone height is 10 feet (a total of 30 feet for all 3 layers), μ_{foam} is 2 cP, $\mu_{\text{no-foam}}$ is 0.4 cP, skin is 2, and temperature is 90 degrees Celsius.

Figure 30: Example reservoir with no nanoparticles in aqueous phase.

Based on these assumptions and using Darcy's law, the reservoir's ability to allow for the CO₂ and water to flow is dominated by the top layer. This layer takes 72% of the total flow of the CO₂. If the water phase included the PEG coated 5 nm silica core nanoparticles the storage efficiency would be much different. Based on the same assumptions, only this time with a nanoparticles concentration of 0.5 weight percent, the flood would look more like **Figure 31**.

Figure 31: Example reservoir with nanoparticles in aqueous phase.

The different permeabilities create different shear rates. In this case the top layer provides enough shear for the foam to be generated. This means the fluid in highly permeable zone

(1000mD) will have a viscosity of 2 cP, instead of 0.4 cP. Consequently flow into the most permeable layer decreases from 72% of the total flow rate to 34%. The rate into the middle reservoir is the same absolute value but its portion of the total flow rate increases to 50% of the total flow rate. This effect could potentially double the storage capacity. The third layer also would have modest gains.

Chapter 5: Conclusion

This chapter summarizes the findings extracted from the experimental data described in the above Results chapter. The experiments tested the effects on foam generation of nanoparticle coating, nanoparticle concentration, salinity, phase volume ratio, temperature, and shear rate. The key findings from these experiments are discussed first, and then recommendations for future work are provided.

5.1 Key findings

There are two key findings from all of these experiments: First, we demonstrated that nanoparticle-stabilized CO₂-water foams can be generated by co-injecting the fluids into a porous medium. Second, we identified a list of parameters that critically affect the foam stabilization, which are described in detail below.

5.2 Critical parameters

The experiments were designed in order to test a variety of parameters to simulate the field conditions, such as the coating of the nanoparticle, the concentration of the nanoparticles, the salinity of the aqueous phase, and the phase volume ratios of the fluids that make the foam, the temperature, and the shear rate.

- **Nanoparticle coating** is critical for foam generation. Nanoparticles coated with poly-ethylene glycol by 3M (5 nm and 20 nm silica cores) stabilized CO₂/water and CO₂/brine foams at a wide range of conditions. The salt tolerant particles from 3M made a thin bubbly film between the CO₂ and aqueous phases in the

view cell. These experiments we run at varying nanoparticle concentrations (0.05, 0.5, and 1.0 weight percent, 21 degrees Celsius, 1350 psia, zero salinity, and shear rate 1430 sec^{-1} . This film did not increase the resistance to flow. The salt tolerant particles did not make foam at any salinity (0%, 2%, and 4%). The Nyacol particles did not make foam at any of the conditions tested: zero salinity, shear rate of 1430 sec^{-1} , varying nanoparticle concentrations (0.5, 1.0 and 5.0 weight percent), 21 degrees Celsius and phase ratios of 5 and 11.

- **Nanoparticle concentration** has a threshold which allows for foam generation. That threshold is in between 0.025 and 0.05 weight percent for the PEG coated 5 nm particles when the tests were run at 1350 psia, 1430 sec^{-1} , and 21 degrees Celsius.
- The **optimal concentration** of 5 nm silica core nanoparticles coated with PEG (with respect to viscosity of foam) appears to be at 0.5 weight percent for 1350 psia, 1430 sec^{-1} , and 21 degrees Celsius.. The other particles were not tested for a threshold concentration or critical shear rate, but rather were tested at concentrations and shear rates at which that 3M 5 nm SiO_2 PEG coated particles made high quality foams.
- The largest **phase volume ratio** (CO_2 to brine) at which foam could be formed at 21 degrees Celsius was 19. Foams were observed at phase ratios of 14.9 at 50 degrees Celsius, 21.0 at 75 degrees Celsius, and 23.8 at 90 degrees Celsius, but

the upper limit for foam generation was not tested at elevated temperatures. These limits apply at pressure of 1350 psia and a range of shear rates of 1430 sec^{-1} to 6400 sec^{-1} using PEG coated 5 nm silica core nanoparticles from 3M.

- At the lowest nanoparticle concentration that successfully stabilized foam, 0.05 weight percent of 3M PEG coated 5 nm SiO_2 particles, the highest phase ratio at which stable foam was generated was 19.
- **Salinity** has a destabilizing effect on the foam. The experiments with a phase volume ratio of 5 were able to stabilize foam except when at the highest salinity and lowest concentration (Experiments 46-47). When the phase volume ratio was 11, the foam was much less stable, and foam was formed only for 2 weight percent salinity, and at 0.1 and 0.5 weight percent nanoparticle concentration.
- When salinity did not prevent foam generation, the foam was usually of larger viscosity.
- Foams were created at **temperatures** of 50, 75, and 95 degrees Celsius with the PEG coated 5 nm silica core nanoparticles provided from 3M at 1350 psia, and a phase volume ratio of 5 at accumulator conditions.
- The **critical shear rate** at 21 C is less than 720 sec^{-1} , at 75 degrees Celsius is about 2800 sec^{-1} . and at 90 degrees Celsius is about 4000 sec^{-1} . The critical shear

rate increased with increasing temperature, but was independent of phase volume ratio.

- The viscosity of foams is influenced by nanoparticle concentration, the phase volume ratio and the salinity in the aqueous phase. At 21°C the presence of nanoparticles increased the viscosity of the fluids by up to 18 times what would be expected if the two fluids were co-injected without nanoparticles present. At elevated temperature, the nanoparticles increased apparent viscosity by at least a factor of ten.

5.3 Recommended future work

- Fractures
 - Fractures often plague CO₂ floods because fractures provide paths of almost infinite permeability in comparison to the surrounding rock. If the nanoparticles are able to stabilize a foam in fractures, this could improve the sweep efficiency of the flood. Also, if fractures are able to generate foam with the fluids flowing through them, this could provide solutions to the fracture problem. The foam should be tested for two properties: whether foam can be generated in a fracture at a given shear rate, and whether a foam will remain stable when it encounters a fracture.

- Contact with Oil
 - Using these foams for EOR means the foam stability needs to remain in the presence of oil. Experiments that test the effects of oil contact when the three phases are present are therefore needed. Experiments should be run with an oil saturated core to test the sweep efficiency and foam stability in the core.

- CO₂ Sequestration
 - The nanoparticles show the potential for increasing the chances of a successful sequestration operation by creating foam in permeable rock formations and increasing the formation's storage capacity. Also, if foam is able to be created, and stabilized in fractures, this could greatly benefit the sequestration operations. The fracture experiments could provide some useful data for sequestration. Experiments should also be set up with heterogeneous flow media to provide insight into whether the preferential generation of nanoparticle stabilized foam occurs in the high-permeability region of the medium.

Appendices

A.1 Summary of experiments

	Total Flow Rate (mL/min)	Nanoparticle Concentration (wt%)	Volumetric Phase Ratio (mL/min)/(mL/min)	Salinity (wt%)	Shear Rate (sec ⁻¹)	Viscosity Apparent (cP)	Normalized Mixture Viscosity
Exp 1	6	10	2	0	1430	3.74	8.14
Exp 2	5	10	4	0	1200	1.60	4.44
Exp 3	6	5	2	0	1430	2.8-3.7	6.1-8.1
Exp 4	3	5	2	0	715	1.5-2.3	N/A
Exp 5	6	1	2	0	1430	1.25	2.72
Exp 6	4.5	1	2	0	1100	1.14	2.42
Exp 7	6	1	1	0	1430	1.25	N/A
Exp 8	6	1	3	0	1430	1.50	3.99
Exp 9	6	1	5	0	1430	2.20	5.66
Exp 10	6	2	11	0	1430	3.00	8.37
Exp 11	6.5	0	12	0	1550	0.29	BASELINE
Exp 12	7	0	6	0	1670	0.33	BASELINE
Exp 13	7.5	0	4	0	1790	0.48	BASELINE
Exp 14	8	0	3	0	1910	0.44	BASELINE
Exp 15	5.5	0	10	0	1310	0.35	BASELINE
Exp 16	6	0	5	0	1430	0.39	BASELINE
Exp 17	6.5	0	3.3	0	1550	0.41	BASELINE
Exp 18	7	0	2.5	0	1670	0.46	BASELINE
Exp 19	4.5	0	8	0	1100	0.38	BASELINE
Exp 20	5	0	4	0	1200	0.36	BASELINE
Exp 21	5.5	0	2.7	0	1300	0.38	BASELINE
Exp 22	6	0	2	0	1430	0.46	BASELINE
Exp 23	3.5	0	6	0	830	0.41	BASELINE
Exp 24	4	0	3	0	950	0.46	BASELINE
Exp 25	4.5	0	2	0	1070	0.47	BASELINE

Exp 26	5	0	1.5	0	1190	0.59	BASELINE
Exp 27	6	0.1	5	0	1430	2.16	5.55
Exp 28	6	0.1	11	0	1430	2.70	7.54
Exp 29	6	0.05	5	0	1430	1.23	3.17
Exp 30	6	0.05	11	0	1430	0.74	2.05
Exp 31	6	0.01	5	0	1430	NO FOAM	NO FOAM
Exp 32	6	0.01	11	0	1430	NO FOAM	NO FOAM
Exp 33	6	0	11	0	1430	0.36	BASELINE
Exp 34	6	0.025	11	0	1430	NO FOAM	NO FOAM
Exp 35	6	0.025	5	0	1430	NO FOAM	NO FOAM
Exp 36	6	0.025	3	0	1430	NO FOAM	NO FOAM
Exp 37	6	0.025	2	0	1430	NO FOAM	NO FOAM
Exp 40	6	0.5	5	2	1430	2.50	6.42
Exp 40b	6	0.5	5	0	3900	N/A	N/A
Exp 40c	6	0.5	5	0	5500	N/A	N/A
Exp 40d	6	0.5	5	0	6400	N/A	N/A
Exp 41	6	0.5	11	2	1430	2.92	8.14
Exp 42	6	0.05	5	2	1430	0.81	2.09
Exp 43	6	0.05	11	2	1430	NO FOAM	NO FOAM
Exp 44	6	0.1	5	2	1430	4.30	11.06
Exp 45	6	0.1	11	2	1430	1.90	5.30
Exp 46	6	0.05	11	4	1430	NO FOAM	NO FOAM
Exp 47	6	0.05	5	4	1430	NO FOAM	NO FOAM
Exp 48	6	0.1	11	4	1430	NO FOAM	NO FOAM
Exp 49	6	0.1	5	4	1430	2.16	5.56
Exp 50	6	0.5	11	4	1430	NO FOAM	NO FOAM
Exp 51	6	0.5	5	4	1430	6.99	17.97

Exp 52	6	0.5	11	0	1430	4.76	13.30
Exp 53	6	0.5	5	0	1430	6.15	15.82
Exp 54	6	0.05	14	0	1430	N/A	N/A
Exp 55	6	0.05	19	0	1430	N/A	N/A
Exp 56	6	0.05	29	0	1430	NO FOAM	NO FOAM
Exp 57	2.05	0.5	1.05	0	2110	NO FOAM	NO FOAM
Exp 58	3.5	0.5	2.5	0	3610	NO FOAM	NO FOAM
Exp 59	2.35	0.5	3.7	0	2420	NO FOAM	NO FOAM
Exp 60	4.7	0.5	3.7	0	4840	N/A	N/A
Exp 61	6	0.5	5	0	6180	N/A	N/A
Exp 62	7	0.5	2.5	0	7210	N/A	N/A
Exp 63	4.1	0.5	1.05	0	4220	N/A	N/A
Exp 64	2.19	0.5	2.19	0	2000	NO FOAM	NO FOAM
Exp 65	2.35	0.5	2.35	0	2140	NO FOAM	NO FOAM
Exp 66	3.5	0.5	3.5	0	3190	N/A	N/A

**Denotes at accumulator conditions*

The next appendix figures are the experimental data taken from the successful experiments, assuming that the data could be taken. For example, Experiments 56-69 did not have any graphs to represent their data because their experiments were only to determine if there was foam created, not the foam viscosity.

A.2 Experiment 1

This experiment was run at a 5 nm silica core PEG coated nanoparticle concentration of 10 weight percent. The phase volume ratio was 2, the temperature was 21 degrees Celsius, salinity was 0 weight percent, and the shear rate was 1430 sec^{-1} . This foam was recorded as an average apparent viscosity of 3.74 cP, and a normalized mixture viscosity of 8.14.

A.3 Experiment 2

This experiment was run at a 5 nm silica core PEG coated nanoparticle concentration of 10 weight percent. The phase volume ratio was 4, the temperature was 21 degrees Celsius, salinity was 0 weight percent, and the shear rate was 1192 sec^{-1} . This foam was recorded as an average apparent viscosity of 1.60 cP, and a normalized mixture viscosity of 4.37.

A.4 Experiment 3

This experiment was run at a 5 nm silica core PEG coated nanoparticle concentration of 5 weight percent. The phase volume ratio was 2.00, the temperature was 21 degrees Celsius, salinity was 0 weight percent, and the shear rate was 1430 sec^{-1} . This foam was recorded as an average apparent viscosity of 2.80 cP, and a normalized mixture viscosity of 6.09.

A.5 Experiment 4

This experiment was run at a 5 nm silica core PEG coated nanoparticle concentration of 5 weight percent. The phase volume ratio was 2.00, the temperature was 21 degrees Celsius, salinity was 0 weight percent, and the shear rate was 715 sec^{-1} . This foam was recorded as an average apparent viscosity of 1.5-2.3cP, and a normalized mixture **viscosity of n/a.**

A.6 Experiment 5

This experiment was run at a 5 nm silica core PEG coated nanoparticle concentration of 1 weight percent. The phase volume ratio was 2.00, the temperature was 21 degrees Celsius, salinity was 0 weight percent, and the shear rate was 1430 sec^{-1} . This foam was recorded as an average apparent viscosity of 1.25, and a normalized mixture viscosity of 2.72.

A.7 Experiment 6

This experiment was run at a 5 nm silica core PEG coated nanoparticle concentration of 1 weight percent. The phase volume ratio was 2.00, the temperature was 21 degrees Celsius, salinity was 0 weight percent, and the shear rate was 1073 sec^{-1} . This foam was recorded as an average apparent viscosity of 1.14, and a normalized mixture viscosity of 2.42.

A.8 Experiment 7

This experiment was run at a 5 nm silica core PEG coated nanoparticle concentration of 1 weight percent. The phase volume ratio was 1.00, the temperature was 21 degrees Celsius, salinity was 0 weight percent, and the shear rate was 1430 sec^{-1} . This foam was recorded as an average apparent viscosity of 1.25, and a normalized mixture viscosity of n/a.

A.9 Experiment 8

This experiment was run at a 5 nm silica core PEG coated nanoparticle concentration of 1 weight percent. The phase volume ratio was 3.00, the temperature was 21 degrees Celsius, salinity was 0 weight percent, and the shear rate was 1430 sec^{-1} . This foam was recorded as an average apparent viscosity of 1.50, and a normalized mixture viscosity of 3.99.

A.10 Experiment 9

This experiment was run at a 5 nm silica core PEG coated nanoparticle concentration of 1 weight percent. The phase volume ratio was 5.00, the temperature was 21 degrees Celsius, salinity was 0 weight percent, and the shear rate was 1430 sec^{-1} . This foam was recorded as an average apparent viscosity of 2.20, and a normalized mixture viscosity of 5.66.

A.11 Experiment 10

This experiment was run at a 5 nm silica core PEG coated nanoparticle concentration of 2 weight percent. The phase volume ratio was 11.00, the temperature was 21 degrees Celsius, salinity was 0 weight percent, and the shear rate was 1430 sec^{-1} . This foam was recorded as an average apparent viscosity of 3.00, and a normalized mixture viscosity of 8.37.

A.12 Experiment 27

This experiment was run at a 5 nm silica core PEG coated nanoparticle concentration of 0.1 weight percent. The phase volume ratio was 5.00, the temperature was 21 degrees Celsius, salinity was 0 weight percent, and the shear rate was 1430 sec^{-1} . This foam was recorded as an average apparent viscosity of 2.16, and a normalized mixture viscosity of 5.55.

A.13 Experiment 28

This experiment was run at a 5 nm silica core PEG coated nanoparticle concentration of 0.10 weight percent. The phase volume ratio was 11.00, the temperature was 21 degrees Celsius, salinity was 0 weight percent, and the shear rate was 1430 sec^{-1} . This foam was recorded as an average apparent viscosity of 2.70, and a normalized mixture viscosity of 7.54.

A.14 Experiment 29

This experiment was run at a 5 nm silica core PEG coated nanoparticle concentration of 0.05 weight percent. The phase volume ratio was 5.00, the temperature was 21 degrees Celsius, salinity was 0 weight percent, and the shear rate was 1430 sec^{-1} . This foam was recorded as an average apparent viscosity of 1.23, and a normalized mixture viscosity of 3.17.

A.15 Experiment 30

This experiment was run at a 5 nm silica core PEG coated nanoparticle concentration of 0.05 weight percent. The phase volume ratio was 5.00, the temperature was 21 degrees Celsius, salinity was 0 weight percent, and the shear rate was 1430 sec^{-1} . This foam was recorded as an average apparent viscosity of 1.23, and a normalized mixture viscosity of 3.17.

A.16 Experiment 40

This experiment was run at a 5 nm silica core PEG coated nanoparticle concentration of 0.5 weight percent. The phase volume ratio was 5.00, the temperature was 21 degrees Celsius, salinity was 2 weight percent, and the shear rate was 1430 sec^{-1} . This foam was recorded as an average apparent viscosity of 2.50, and a normalized mixture viscosity of 6.42.

A.17 Experiment 41

This experiment was run at a 5 nm silica core PEG coated nanoparticle concentration of 0.5 weight percent. The phase volume ratio was 11.00, the temperature was 21 degrees Celsius, salinity was 2 weight percent, and the shear rate was 1430 sec^{-1} . This foam was recorded as an average apparent viscosity of 2.92, and a normalized mixture viscosity of 8.14.

A.18 Experiment 42

This experiment was run at a 5 nm silica core PEG coated nanoparticle concentration of 0.05 weight percent. The phase volume ratio was 5.00, the temperature was 21 degrees Celsius, salinity was 2 weight percent, and the shear rate was 1430 sec^{-1} . This foam was recorded as an average apparent viscosity of 0.81, and a normalized mixture viscosity of 2.09.

A.19 Experiment 44

This experiment was run at a 5 nm silica core PEG coated nanoparticle concentration of 0.10 weight percent. The phase volume ratio was 5.00, the temperature was 21 degrees Celsius, salinity was 2 weight percent, and the shear rate was 1430 sec^{-1} . This foam was recorded as an average apparent viscosity of 4.30, and a normalized mixture viscosity of 11.07.

A.20 Experiment 45

This experiment was run at a 5 nm silica core PEG coated nanoparticle concentration of 0.10 weight percent. The phase volume ratio was 11.00, the temperature was 21 degrees Celsius, salinity was 2 weight percent, and the shear rate was 1430 sec^{-1} . This foam was recorded as an average apparent viscosity of 1.90, and a normalized mixture viscosity of 5.30 before the foam broke.

A.21 Experiment 49

This experiment was run at a 5 nm silica core PEG coated nanoparticle concentration of 0.10 weight percent. The phase volume ratio was 5.00, the temperature was 21 degrees Celsius, salinity was 4 weight percent, and the shear rate was 1430 sec^{-1} . This foam was recorded as an average apparent viscosity of 2.16, and a normalized mixture viscosity of 5.56.

References

- Adkins, S.S., G., Dhiren, J.L., Dickson, S.E., Webber and K.P., Johnston, Water-in-Carbon Dioxide Emulsions Stabilized with Hydrophobic Silica Particles, *Phys. Chem. Chem. Phys.*, 9, 1-11 (2007).
- Binks, B.P., Particles as Surfactants — Similarities and Differences, *Current Opinion in Colloid & Interface Science*, 7, 21-41 (2002).
- Binks, B.P., and T.S., Horozov, Aqueous Foams Stabilized Solely by Silica Nanoparticles, *Angew. Chem. Int. Ed.* 44, 3722-3725 (2005).
- Binks, B.P., and S.O., Lumsdon, Stability of Oil-in-Water Emulsions Stabilized by Silica Particles, *Phys. Chem. Chem. Phys.*, 1, 3007-3016 (1999).
- Binks, B.P., and S.O., Lumsdon, Influence of Particle Wettability on the Type and Stability of Surfactant-Free Emulsions, *Langmuir*, 16, 8622-8631 (2000a).
- Binks, B.P., and S.O., Lumsdon, Effect of Oil Type and Aqueous Phase Composition on Oil-Water Mixtures Containing Particles of Intermediate Hydrophobicity, *Phys. Chem. Chem. Phys.*, 2, 2959-2967 (2000b).
- Binks, B.P., and S.O., Lumsdon, Transitional Phase Inversion of Solid-Stabilized Emulsions Using Particle Mixtures, *Langmuir*, 16, 3748-3756 (2000c).
- Binks, B.P., and S.O., Lumsdon, Catastrophic Phase Inversion of Water-in-Oil Emulsions Stabilized by Hydrophobic Silica, *Langmuir*, 16, 2539-2547 (2000d).
- Binks, B.P., and R., Murakami, Phase Inversion of Particle-Stabilized Materials from Foams to Dry Water, *Nature Materials*, 5, 865-869 (Nov. 2006).
- Binks, B.P., J., Philip, and J.A., Rodrigues, Inversion of Silica-Stabilized Emulsions Induced by Particle Concentration, *Langmuir*, 21, 3296-3302 (2005).
- Binks, B.P., and J.A., Rodrigues, Influence of Surfactant Structure on the Double Inversion of Emulsions in the Presence of Nanoparticles, *Colloids and Surfaces A*, 345, 195-201 (2009).
- Binks, B.P., and C.P., Whitby, Nanoparticle Silica-Stabilized Oil-in-Water Emulsions: Improving Emulsion Stability, *Colloids and Surfaces A*, 253, 105-115 (2005).
- Bragg, J.R., and Varadaraj, R., Solids -Stabilized Oil-in-Water Emulsion and a Method for Preparing Same, World Intellectual Property Organization, WO 03/057793 (July 17, 2003).
- Caldelas, F.M., Experimental Parameter Analysis of Nanoparticle Retention in Porous Media, Thesis, The University of Texas – Austin (2010).
- Choy, C.C., M., Wazne, and X., Meng, Application of an Empirical Transport Model to Simulate Retention of Nanocrystalline Titanium Dioxide in Sand Columns, *Chemosphere*, 71, 1794-1801 (2008).
- Cortis, A., T., Harter, L., Hou, E.R., Atwill, A.I., Packman, and P.G., Green, Transport of *Cryptosporidium Parvum* in Porous Media: Long-Term Elution Experiments and Continuous Time Random Walk Filtration Model, *Water Resources Research*, 42, W12S13 (2006).
- Espinosa, D., F., Caldelas, K., Johnston, S.L., Bryant and C., Huh, Nanoparticle-Stabilized Supercritical CO₂ foams for Potential Mobility Control Applications, SPE paper 129925, presented at SPE Improved Oil Recovery Symposium, Tulsa, OK (2010).

- Frelichowska, J., M-A., Bolzinger, and Y., Chevalier, Pickering Emulsions with Bare Silica, *Colloids and Surfaces A*, 343, 70-74 (2009).
- Gu, C.Y., and Q.F., Di, Slip Velocity Model of Porous Walls Absorbed by Hydrophobic Nanoparticles SiO₂, *Journal of Hydrodynamics*, 19, 365-371 (2007).
- Horozov, T.S., Foams and Foam Films Stabilized by Solid Particles, *Current Opinion in Colloid & Interface Science*, 13, 134-140 (2008).
- Ju, B., T., Fan, and M., Ma, Enhanced Oil Recovery by Flooding with Hydrophobic Nanoparticles, *China Particuology*, 4, 41-46 (2006).
- Kim, J.S., Dong, Y., and Rossen, W.R., Steady-State Flow Behavior of CO₂ Foam, *Soc. Petrol. Eng. J.*, 405-415 (Dec., 2005).
- Lecoanet, H.F., J.-Y., Bottero, and M.R., Wiesner, Laboratory Assessment of the Mobility of Nanomaterials in Porous Media, *Environ. Sci. Technol.*, 38, 5164-5169 (2004).
- Li, Y., Y., Wang, K.D., Pennell, and L.M., Abriola, Investigation of the Transport and Deposition of Fullerene (C₆₀) Nanoparticles in Quartz Sands under Varying Flow Conditions, *Environ. Sci. Technol.*, 42, 7174-7180 (2008).
- McDowell-Boyer, L.M., J.R., Hunt, and N., Sitar, Particle Transport Through Porous Media, *Water Resources Research*, 22, 1901-1921 (1986).
- Pride, S.R., Governing Equations for the Coupled Electromagnetics and Acoustics of Porous Media, *Physical Review B*, 50, 15678-15696 (1994).
- Prodanovic, M., S., Ryoo, A.R., Rahmani, R., Kuranov, C., Kotsmar, T.E., Milner, K.P., Johnston, S.L., Bryant, and C., Huh, Effect of Magnetic Field on the Motion of Multiphase Fluids Containing Paramagnetic Particles in Porous Media, SPE paper 129850, presented at SPE Improved Oil Recovery Symposium, Tulsa, OK (2010).
- Rodriguez, E., M.R., Robert, H., Yu, C., Huh, and S.L., Bryant, Enhanced Migration of Surface-Treated Nanoparticles in Sedimentary Rocks, SPE paper 124418, presented at SPE Annual Technical Conference and Exhibition, New Orleans, LA (2009).
- Rossen, W.R., Foam in Enhanced Oil Recovery, in Foams, Theory, Measurements, and Applications, Prud'homme, R.K., and Khan, S.A., eds., Chapter 11, 413-464, Marcel Dekker (1996).
- Ryoo, S., A.R., Rahmani, K.Y., Yoon, M., Prodanovic, C., Kotsmar, T.E., Milner, K.P., Johnston, S.L., Bryant, and C.,
Huh, Theoretical and Experimental Investigation of the Motion of Multiphase Fluids Containing Paramagnetic Nanoparticles in Porous Media, SPE paper 134879, presented at SPE Annual Technical Conference and Exhibition, Florence, Italy (2010).
- Thompson, A.H., Electromagnetic-to-Seismic Conversion: Successful Developments Suggest Viable Applications in Exploration and Production, 75th SEG Annual Meeting Expanded Abstracts, Houston, TX (2005).
- Wang, Y., Y., Li, J.D., Fortner, J.B., Hughes, L.M., Abriola, and K.D., Pennell, Transport and Retention of Nanoscale C₆₀ Aggregates in Water-Saturated Porous Media, *Environ. Sci. Technol.*, 42, 3588-3594, (2008a).
- Wang, Y., Y., Li, and K.D., Pennell, Influence of Electrolyte Species and Concentration on the Aggregation and Transport of Fullerene Nanoparticles in Quartz Sands, *Environmental Toxicology and Chemistry*, 27, 1860-1867 (2008b).

- Yu, H., C., Kotsmar, K.Y., Yoon, D.R., Ingram, K.P., Johnston, S.L., Bryant, and C., Huh, Transport and Retention of Aqueous Dispersion of Paramagnetic Nanoparticles in Reservoir Rocks, SPE paper 129887, presented at SPE Improved Oil Recovery Symposium, Tulsa, OK (2010).
- Zhang, T., M.R., Robert, S.L., Bryant, and C., Huh, Foams and Emulsions Stabilized with Nanoparticles for Potential Conformance Control Applications, SPE paper 121744, presented at SPE International Symposium on Oilfield Chemistry, Woodlands, TX (2009).
- Zhang, T., A., Davidson, S.L., Bryant and C., Huh, Nanoparticle-Stabilized Emulsions for Applications in Enhanced Oil Recovery, SPE paper 129885, presented at SPE Improved Oil Recovery Symposium, Tulsa, OK (2010).

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