The effect of foam quality, particle concentration and flow rate on nanoparticle-stabilized CO2 mobility control foams

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CO2 foam is regarded as a promising technology and widely used in the oil and gas industry, not only to improve oil production, but also to mitigate carbon emissions through their capture. This paper describes a series of nanoparticle-stabilized CO2 foam generation and foam flow experiments under reservoir conditions. Stable CO2 foam was generated when CO2 and a nanosilica dispersion flowed through the core sample under 1500 psi and 25 °C. The foam changed from a fine-texture foam to a coarse foam as the foam quality increased from 20% to 95%. Foam mobility increased slightly with the increasing foam quality from 20% to 80% and then rapidly from 80% to 95%. A stable CO2 foam was generated as the nanosilica concentration increased to 2500 ppm. Foam mobility and resistance factor increased with the increasing nanosilica concentration. As the injection flow rate increased to 60 ml h⁻¹, stable and fine-texture CO2 foam was obtained. Foam mobility was observed to remain almost constant as the injection flow rate increased from 60 ml h⁻¹ to 150 ml h⁻¹.

1. Introduction

Carbon dioxide (CO2) injection is presently one of the most commonly used approaches in The Enhanced Oil Recovery (EOR) application. CO2 can be used either as an immiscible or a miscible displacing agent based on the reservoir conditions and the composition of crude oils. Injection of CO2 can benefit production by mobilizing more oil trapped in the pores of the reservoir rock. However, the lower viscosity of CO2 compared to crude oil induces an unfavorable mobility ratio. In addition, the heterogeneity of the reservoir formation results in an early breakthrough and a poor oil sweep efficiency. The use of surfactant is one way to rectify the drawbacks associated with CO2 flooding. It helps to reduce the viscosity difference between the displacing and displaced fluids by restricting the flow of CO2 through high permeability zones. Today, the major challenges for surfactant EOR are high surfactant retention in porous media and unstable foam properties under high-temperature reservoir conditions.

Recently, a new generation of CO2 foam using nanotechnology to create lasting foams has been studied, and this new technology has been attracting more and more attention due to the long-term stability of foams under harsh reservoir conditions. Dickson et al. first reported generating CO2 foam with nanosilica particles. Nanosilica particles were dispersed in water and then sheared through an orifice with supercritical CO2. CO2 foam was generated and observed through a view cell. They observed that foam stability increased with the increasing particle concentration, CO2 density, and shear rate. Later, Espinoza et al. proposed the generation of nanoparticle-stabilized supercritical CO2 foams (CO2 in water foam) for potential mobility control applications by using commercial surface-modified silica particles. The foams were generated by co-injecting CO2 and an aqueous dispersion of the nanoparticles through a glass-bead pack. They demonstrated that supercritical CO2 foams could be generated by nanoparticles with a concentration as low as 0.05 wt%. Andrew et al. conducted foam generation experiments focused on nanoparticles with different surface coatings and demonstrated that the larger size of 50% SiOH nanoparticles resulted in stronger stable CO2 foams compared to those generated with PEG-coated silica particles. Singh and Mohanty investigated the process of foam stabilized by in situ surface-activated nanoparticles in bulk and porous media. Alumina-coated silica nanoparticles were mixed with different concentrations of propyl gallate (PG) and the particle hydrophilic surface was converted to partially hydrophobic by anchoring PG molecular to the particle surface. They observed a strong foaming tendency with surface-modified nanoparticles (SMNPs). The bubble texture of foam stabilized by SMNPs was finer than that with surfactants. A synergic interaction between surfactant and nanoparticles was observed to generate stable foam. For
example, Worthen et al.\textsuperscript{12} reported the generation of viscous and stable CO\textsubscript{2} foams with fine texture by use of bare silica nanoparticles and zwitter-ionic surfactant, when neither of these species could stabilize foam independently. More recently, nanoparticle-stabilized CO\textsubscript{2} foam flow behavior was studied by Prigiobbe et al.\textsuperscript{13} A two-phase flow mechanistic model combining the mass conservation law and the population balance equation was implemented to analyze the CO\textsubscript{2} foam transport in porous media. Their results indicated that the two-phase flow model described well the experiments when a strong high-quality foam was generated.

Although some researches were performed on nanoparticle-stabilized CO\textsubscript{2} foam generation, field tests with high pressure CO\textsubscript{2} foam indicated that field application of CO\textsubscript{2} foam was a technically viable process for improved oil recovery.\textsuperscript{14} An efficient evaluation of candidate reservoirs for possible CO\textsubscript{2} foam application requires a fundamental understanding of information on CO\textsubscript{2} foam behavior under various foam test conditions. In our previous studies, the effects of different ions and temperature on nanosilica-stabilized CO\textsubscript{2} foam generation were studied.\textsuperscript{15} More CO\textsubscript{2} foam was generated as the NaCl concentration increased from 1.0\% to 10\%. Also the foam texture became finer and foam stability improved with the NaCl concentration increase. In this paper, the effects of foam quality, particle concentration, and flow rate on nanoparticle-stabilized CO\textsubscript{2} foam generation, foam texture, foam stability, and foam flow behavior in a porous medium were investigated.

2. Experimental

2.1 Materials

Silica nanoparticles were obtained from Akzo Nobel Pulp and Performance Chemicals Inc. as an aqueous dispersion and diluted with 2.0\% NaCl to the desired concentration. Particle size and morphology were characterized by dynamic light scattering (DLS) and transmission electron microscopy (TEM). Berea sandstone core samples were purchased from Cleveland Quarries. The core was cut and polished to a diameter of 2.12 in. and a length of 8.3 in. Then the core was loaded into a core holder with an overburden pressure of 3500 psi. The initial brine permeability and the porosity of the core were measured as 33.0 mD and 17.4\%, respectively. The pore volume (PV) of the core was calculated as 100.4 ml.

2.2 Experiment devices

Fig. 1 shows the experimental apparatus for CO\textsubscript{2} foam generation. First, CO\textsubscript{2} and nanosilica dispersion were stored in two floating piston accumulators, respectively. Two TEMCO Back Pressure Regulators (BPR) were used to maintain the accumulator under required operating pressure. During the CO\textsubscript{2} foam generation, two ISCO syringe pumps (model 260D) were used to inject distilled water into the CO\textsubscript{2}/nanosilica dispersion accumulators, forcing nanosilica dispersion and CO\textsubscript{2} flow out from the accumulator under operating pressure. The injected high pressure CO\textsubscript{2} and nanosilica dispersion were mixed in the core sample, providing the shear energy to drive the nanosilica particles to adsorb into the interface between CO\textsubscript{2} and water. A sapphire observation cell was installed behind the core holder to estimate the foam morphology and bubble size. Pressure drop along the core was measured with a Honeywell 3000 differential pressure transducer connected to a Daq56 data acquisition system. After the observation cell, another accumulator was used to collect the CO\textsubscript{2} and nanosilica mixture. The third BPR was installed after the accumulator to control the operation pressure in the core sample and observation cell. The entire apparatus, except for the syringe pumps, was placed in an air bath.
air bath to maintain a constant temperature throughout the experiment.

All the core-flooding tests were conducted at 25 °C and 1500 psi. To evaluate the effect of nanosilica on CO₂ foam generation and mobility control, baseline experiments were first performed by simultaneously injecting CO₂ and brine into the core at different volumetric injection ratios without nanosilica particles. Each baseline experiment lasted until a steady-state pressure drop was achieved.

2.3 Characterization

2.3.1 Foam mobility. The foam mobility in this study is defined as the total mobility of CO₂/nanosilica dispersion. The mobility can be evaluated by eqn (1):

\[ \lambda = \frac{qL}{A\Delta P} \]  

where \( q \) (ml s⁻¹) is the flow rate; \( A \) (cm²) and \( L \) (cm) are the cross-area and length of the core, respectively; \( \Delta P \) (atm) is the pressure drop along the core; \( \lambda \) is the mobility with the unit of D cP⁻¹.

2.3.2 Foam resistance factor. The foam resistance factor here is defined as the ratio of the total mobility of CO₂/brine divided by the foam mobility (total mobility of CO₂/nanosilica dispersion) at the same flow rate and phase ratio. In this study, the same sandstone core was used for all tests. The calculation of the foam resistance factor is as follows:

\[ \gamma = \frac{\Delta P_{\text{CO}_2-\text{NPs}}}{\Delta P_{\text{CO}_2-\text{brine}}} \]  

where \( \Delta P_{\text{CO}_2-\text{NPs}} \) is the pressure drop across the core with CO₂/nanoparticle dispersion injection and \( \Delta P_{\text{CO}_2-\text{brine}} \) is the pressure drop during baseline experiments with brine and CO₂ injection.

3. Results and discussions

3.1 CO₂ foam generation in Berea sandstone core

The diluted nanosilica dispersion (5000 ppm) had an average particle size around 17 nm as measured by DLS and TEM. Fig. 2 shows the CO₂ foam images from the observation cell in the presence and absence of nanosilica particles (CO₂ : brine = 3 : 2) and the pressure drops along the core. Due to the low viscosity of CO₂ and high interfacial tension between CO₂ and brine, no stable foam lamella was formed in the absence of nanoparticles. The generated CO₂ bubble were prone to collapse and merge into a CO₂ slug (on the top of Fig. 2a). However, a large volume of CO₂ foams with a small bubble size was formed as the CO₂ and nanosilica dispersion flowed through the core. This suggests that when nanoparticles were introduced to the CO₂/brine system, they were adsorbed at the interfaces between CO₂ and brine, stabilizing the foam by mitigating processes such as coalescence and Ostwald ripening.¹¹

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Fig. 2  Images of CO₂ foam with brine and CO₂ (a); nanosilica and CO₂ (b) and pressure drop along the core in CO₂/brine flood (c); in CO₂/nanosilica dispersion core flood (d). (Total flow rate is 150 ml h⁻¹, nanosilica concentration: 5000 ppm, and CO₂/brine phase ratio is 3 : 2.)
Fig. 2 also displays the pressure drops along the core in CO$_2$/brine and CO$_2$/nanosilica dispersion core-flooding tests. In the CO$_2$/nanosilica dispersion core test, nanosilica dispersion was diluted with 2.0% NaCl solution to the particle concentration of 5000 ppm. The results of the pressure drop along the core indicated that, as nanosilica was introduced, the pressure...
The higher pressure drop in the presence of nanosilica implied that CO₂ foam was generated in the core, resulting in a more “viscous” CO₂ fluid. Here, it is necessary to emphasize that the core was flooded with brine after the test, and the core permeability was observed to be almost the same before and after the test, indicating no particle plugging during the test. On the other hand, Fig. 2c and d also show that much more injection volumes were required to reach the steady state in the CO₂/nanosilica dispersion core flood test. For example, it took 8–10 PVs of CO₂/nanosilica dispersion to reach the steady state in CO₂/nanosilica dispersion core flood test, while it reached the pressure equilibrium as 1.5 PVs of CO₂/brine were injected in CO₂/brine core flood test. The requirement of high PV injection to reach steady state has also been observed by other researchers and currently is not well understood. The experiments of Ettinger suggested that the slow increases in pressure were caused by the propagation of a capillary end effect from the back of the core to the front of the core.

Further investigations of the foam stability is shown in Fig. 3, which displays the height of CO₂ foam at different times after core-flooding. The inserted images in Fig. 3 show the foam pictures being observed in the observation cell in Fig. 1 with different standing times. The generated CO₂ foam, when left at room temperature and 1500 psi, displayed very good stability. Less than one-third of the foams collapsed after standing at room temperature for five days. The half life-time, here is defined as the time elapsed when the foam reaches its half of its initial height, was measured around 168 hours. Similarly, Martinez et al. also observed nine months lifetime for nanosilica-stabilized N₂ foam. Worthen et al. and Binks et al. reported long-term stable CO₂/air foams generated by nanoparticles.

The long-term stability of nanoparticle-stabilized CO₂ foam is attributed to the high adsorption energy of nanosilica particles at the CO₂/brine interface. Horozov reported that particles in a foam existed at the interface in three ways: a monolayer bridge, a bilayer, and a gel inside the liquid lamellae. Binks proposed to estimate the adsorption energy of nanoparticles at nanoaqueous/aqueous interface as

$$\Delta G_{ad} = \pi \alpha^2 \gamma_{ow}(1 - |\cos \theta|)^2,$$

where \(\alpha\) is the particle radius; \(\gamma_{ow}\) is the interfacial tension, and \(\theta\) is the contact angle through the aqueous phase. An estimation of the adsorption energy in this study with \(\gamma_{CO_2/brine} = 25.15 \text{ mN m}^{-1}\) \(\theta = 75^\circ\) is 763 kₜ/ₜ, which is much larger than the adsorption energy for a typical surfactant molecule at an oil–water interface (which is of the order of several kₜ/ₜ). This high adsorption energy favors irreversible adsorption of the nanoparticles to the CO₂/brine interface and to the formation of solid-like surface layers. Together with the resistance of the interfaces to collapse, this prevents the CO₂ bubbles from coarsening and coalescence, resulting in highly stable CO₂ foams.

### 3.2 CO₂ foam generation with different phase ratios

It has been reported that the foam quality (vol_CO₂ : vol_CO₂-brine) is one of the controversial parameters affecting foam flow behavior. Core-flooding tests of different CO₂/nanosilica dispersion phase ratios were conducted to investigate the effects of volumetric phase ratio on CO₂ foam behavior such as foam generation and foam mobility. Fig. 4 displays the CO₂ foam images at different foam qualities. At low foam quality regime such as Fig. 4a and b, collisions and interactions between bubbles are infrequent and weak, and the possibility of bubble collapse decreases. The generated CO₂ foams were fine-textured with uniform bubble size. In addition, the low foam quality implied high brine content, which could produce more stable liquid lamellae and supply sufficient nanoparticles around the foam bubbles, resulting in more stable CO₂ foams. The results in Fig. 4 indicated that the CO₂ foam with a foam quality of 20% displayed fine-texture structure with excellent foam stability. The height of the foam did not change after standing for four days. At intermediate foam quality regime such as Fig. 4c–e, the generated CO₂ foam displayed larger bubble size compared with that of low foam quality. More bubble collisions and interactions might occur and result in slightly more coarse foams. However, the generated CO₂ foam still displayed very good stability. The height of the foam remained almost unchanged after 48 hours. The further increase of CO₂ phase ratio to a higher foam quality regime

![Fig. 5 CO₂ foam mobility versus foam quality. (Total flow rate is 150 ml h⁻¹; nanosilica concentration: 5000 ppm.)](image1)

![Fig. 6 Foam resistance factor versus foam quality. (Total flow rate is 150 ml h⁻¹; nanosilica concentration: 5000 ppm.)](image2)
resulted in more coarse \( \text{CO}_2 \) foams (Fig. 4f and g). Foam coarsening and coalescence were enhanced and resulted in the deterioration of foam stability. For example, the lifetime of the \( \text{CO}_2 \) foam was several hours as the foam quality was 95% (Fig. 4g).

Fig. 5 shows the changes of foam mobility with foam quality. The results clearly indicate that, in the presence of nanosilica particles, the \( \text{CO}_2 \) foam mobilities are lower than those of \( \text{CO}_2 \)/brine with the same phase ratio. The low foam mobility greatly benefits \( \text{CO}_2 \) mobility control in \( \text{CO}_2 \) EOR operation. Fig. 6 also shows that the \( \text{CO}_2 \) foam mobility increased slightly as foam quality increased from 20% to 80% and then increased rapidly from 80% to 95%. The effect of foam quality on foam flow behavior has been widely investigated with surfactant as the \( \text{CO}_2 \) foam stabilizer. For example, Lee and Heller\(^{25}\) reported that \( \text{CO}_2 \) foam mobility increased with the increasing foam quality from 60% to 90%. De Vries and Wit\(^{26}\) performed a series of tests and concluded that a critical point (breakpoint) for foam mobility existed at an imposed total flow rate; beyond that point, foam mobility increased with foam quality. The results in Fig. 5 indicated that the foam quality of 80% might be the critical point, beyond which the foam mobility quickly increased. In addition, \( \text{CO}_2 \) foam images in Fig. 4 also indicated that more coarse foams were generated as the foam quality was higher than 80%, which was consistent with the foam mobility change.

Fig. 6 shows the foam resistance factor versus foam quality. The results display that foam resistance factor slightly increases with the increasing foam quality from 20% to 60% and then decreases as foam quality further increases. There appeared to be a maximum foam resistance factor obtained at a foam quality of around 60%.

### 3.3 Effect of nanosilica concentration on foam mobility

The effect of nanosilica concentration on foam flow behavior in sandstone was investigated. Tests were conducted at a foam quality of 60% and a total flow rate of 150 ml h\(^{-1}\) with varying nanosilica concentrations.

![Fig. 7](image1.png) Foam mobility versus particle concentration. (Total flow rate is 150 ml h\(^{-1}\), and \( \text{CO}_2 \)/brine is 3 : 2.)

![Fig. 8](image2.png) Images of the \( \text{CO}_2 \) foam generation at different nanosilica concentrations. (Total flow rate = 150 ml h\(^{-1}\); \( \text{CO}_2 \)/brine = 3 : 2; images captured as the foam flowed in the observation cell.)
particle concentration ranging from 100 ppm to 5000 ppm. A plot of foam mobility versus nanosilica concentration is shown in Fig. 7. Foam mobility was reduced as the nanosilica concentration increased. The foam mobility decreased sharply from 14.2 mD cP⁻¹ to 3.78 mD cP⁻¹ as the nanosilica concentration increased from 100 ppm to 1000 ppm, then decreased slowly as the particle concentration increased from 2500 ppm to 5000 ppm. This could be attributed to the formation of lamellae in the pore spaces between CO₂ and brine, which becomes more stable as the nanosilica concentration increased. Stability of the lamellae improved the foam’s resistance to coalescence and allowed more CO₂ to flow through the core sample. Foam images in Fig. 8 indicated that the foam height increased with the increasing nanosilica concentration from 100 ppm to 5000 ppm, which was consistent with the results of foam mobility. In addition, the foam texture was observed to be finer as the nanosilica concentration increased, indicating more stable foam generated at a higher concentration of nanosilica dispersion. The role of particle concentration in foam stability can be rationalized by surface coverage. To generate stable foam, the foam bubbles surface should be sufficiently covered by particles to resist coalescence. Assuming the maximum particle surface concentration (Γ) is Γmax = 50 mg m⁻² and bubble radii are of 25 μm, Río estimated that a minimum particle concentration of 0.7% was required to generate stable foams with the particle size of 10 nm. Our results indicated that stable CO₂ foam was generated as the nanosilica concentration was 0.25%, which was close to Río’s estimation. The dependence of the foam resistance factor on particle concentration is plotted in Fig. 9. The resistance factor was 2.9 for a particle concentration as low as 100 ppm. As the nanosilica concentration was increased from 100 ppm to 1000 ppm, the resistance factor increased to 10.7, and then slowly increased to 16.8 as the nanosilica concentration increased to 5000 ppm.

3.4 Effect of flow rate on foam mobility

A plot of foam mobility vs. flow rate at a particle concentration of 5000 ppm and a foam quality of 60% is shown in Fig. 10. The total foam mobility was reduced from 9.6 mD/cp to 2.3 mD/cp as the flow rate increased from 20 ml h⁻¹ to 60 ml h⁻¹. The significant mobility reduction can be explained by the increasing shear rate from the flow rate increase, which in turn facilitates silica nanoparticle attachment at the water-CO₂ interface, resulting in more stable CO₂ foam as in Fig. 11. Further increase of the flow rate from 60 ml h⁻¹ to 150 ml h⁻¹ did not result in noticeable mobility change, indicating that stable CO₂ foam could be obtained at a flow rate of 60 ml h⁻¹. It should be noted that, in some studies with CO₂ foam, foam mobility increased with flow rate increase or called shear-thinning, and in other studies, foam mobility decreased with flow.
rate increase or called shear-thickening. Here we believe that the foam texture and stability need to be considered in understanding foam flow behavior. Fig. 11 shows the images of foam generation at different injection rates with a foam quality of 60% and a nanosilica concentration of 5000 ppm. It shows that finer and more stable CO₂ foams were obtained as the flow rate increased from 20 ml h⁻¹ to 60 ml h⁻¹. It is expected that the finer and stable foam can decrease the foam mobility as it flow through a porous medium.

A similar result emerges from the relationship between the foam resistance factor and the flow rate in Fig. 12. The resistance factor slightly increased from 3.2 to 3.3 as the flow rate increased from 20 ml h⁻¹ to 30 ml h⁻¹, and then jumped to 14.3 as the flow rate further increased to 60 ml h⁻¹. Then, the resistance factor slowly increased from 14.3 to 17.9 as the flow rate increased from 60 ml h⁻¹ to 150 ml h⁻¹. It is well-known that foam propagation in porous media is a process of breaking and reforming the lamellae of the foam. The more

Fig. 11 Images of CO₂ foam generated at different flow rates. (Nanosilica concentration: 5000 ppm; CO₂/brine is 3 : 2; images captured as the foam flowed in the observation cell.)

Fig. 12 Foam resistance factor versus flow rate. (Nanosilica concentration: 5000 ppm, and CO₂/brine is 3 : 2.)
stable the lamellae, the higher the resistance factor of the foam. Our results indicate that stable lamellae start to form when the flow rate is around 60 ml h$^{-1}$.

4. Conclusions

(1) A stable CO$_2$ foam was generated when CO$_2$ and nanosilica dispersion flowed through a core sample.

(2) Foam mobility slightly increased with the increasing foam quality from 20% to 80% and then rapidly increased as the foam quality increased from 80% to 95%.

(3) With the increase of nanosilica concentration, foam mobility decreased and the foam resistance factor increased. The threshold concentration required to generate a stable CO$_2$ foam was 2500 ppm under the experimental conditions herein.

(4) Foam mobility decreased with the increasing flow rate from 20 ml h$^{-1}$ to 60 ml h$^{-1}$ and then slightly changed as the flow rate increased from 60 ml h$^{-1}$ to 150 ml h$^{-1}$.

Conflicts of interest

There are no conflicts to declare.

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