



Surfactant and a mixture of surfactant and nanoparticles to stabilize CO₂/brine foam, control gas mobility, and enhance oil recovery

Zuhair A. Al Yousef¹ · Mohammed A. Almobarky² · David S. Schechter³

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Abstract

Injecting carbon dioxide into oil reservoirs has the potential to serve as an enhanced oil recovery (EOR) technique, mitigating climate change by storing CO₂ underground. Despite the successful achievements reported of CO₂ to enhance oil recovery, mobility control is one of the major challenges faced by CO₂ injection projects. The objective of this work is to investigate the potential of using surfactant and a mixture of surfactant and nanoparticles to generate foam to reduce gas mobility and enhance oil recovery. A newly developed anionic surfactant and a mixture of the surfactant and surface-modified silica nanoparticles were used to assess the ability of generating a stable foam at harsh reservoir conditions: sc-CO₂ and high temperature. Dynamic foam tests and coreflood experiments were conducted to evaluate foam stability and strength. To measure the mobility of injected fluids in sandstone rocks, the foam was generated by co-injection of sc-CO₂ and surfactant, as well as a mixture of surfactant and nanoparticles at 90% quality. The coreflood experiments were conducted using non-fractured and fractured sandstone cores at 1550 psi and 50 °C. The use of surfactant and mixture was able to generate foam in porous media and reduce the CO₂ mobility. The mobility reduction factor (MRF) for both cases was about 3.5 times higher than that of injecting CO₂ and brine at the same conditions. The coreflood experiments in non-fractured sandstone rocks showed that both surfactant and a mixture of surfactant and nanoparticles were able to enhance oil recovery. The baseline experiment in the absence of surfactant resulted in a total recovery of 71.50% of the original oil in place. However, the use of surfactant was able to bring oil recovery to 76% of the OOIP. The addition of nanoparticles to surfactant, though, resulted in higher oil recovery, 80% of the OOIP. In fractured rocks, oil recoveries during secondary production mechanisms for the mixture, the surfactant alone, and sc-CO₂ alone were 12.62, 8.41, and 7.21% of the OOIP, respectively. Huge amount of oil remains underground following the primary and secondary oil production schemes. CO₂ has been widely used to enhance oil recovery. However, its high mobility might result in unfavorable and unsuccessful projects. The use of specially designed surfactants and the synergistic effect of surfactant and nanoparticles may provide a solution to stabilize CO₂/brine foam at harsh reservoir conditions and, therefore, reduce the gas mobility and, consequently, enhance oil recovery.

Keywords Surfactant · Nanoparticles · Gas mobility · Enhanced oil recovery

Introduction

The remaining oil underground following traditional recovery mechanisms is considerably huge (Hirasaki et al. 2011). Typically, fields can produce about 45–50% of the original oil in place (OOIP) following primary and secondary

oil production mechanisms (Sandrea and Sandrea 2007). As a result, the oil produced is coming up short in meeting the ever-increasing global energy demand (EIA 2011). Enhanced oil recovery (EOR) techniques are needed to recover this huge amount of residual oil. CO₂ is extensively applied for enhancing oil recovery. Technically, it can promote swelling, reduce oil viscosity, vaporize, and extract portions of crude oil. Moreover, the easy solubility of CO₂ in oil makes it an ideal gas for EOR applications (Slobod and Koch 1953; Enick et al. 1988; Bayraktar and Kiran 2000). Despite the reported successes of CO₂ injection, a major challenge faced by this technique is poor volumetric sweep efficiency. Major factors that contribute to this problem are

✉ Zuhair A. Al Yousef
zuhair.yousif@aramco.com

¹ Saudi Aramco, Dhahran, Saudi Arabia

² King Saud University, Riyadh, Saudi Arabia

³ Texas A&M University, College Station, USA

the low density and viscosity of CO₂ relative to reservoir fluids, as well as reservoir heterogeneity such as high permeability and heavily fractured zones (Campbell and Orr 1985; Chakravarthy et al. 2004; Masalmeh et al. 2010). To solve this issue, either conformance control or mobility control techniques might be applied (Seright 1997; Choi et al. 2010; Pu et al. 2018; Torrealba and Hoteit 2018; Enick et al. 2012). Some researchers recommended the use of both techniques to overcome the poor sweep efficiency challenge. They recommended to start first with the use of gel, as an example, for conformance control and then the CO₂ foam for in-depth mobility control (Enick et al. 2012). The focus of this work will be on the mobility control of CO₂ during EOR processes.

The high mobility of injected gas may lead to early breakthrough of gas, leaving most of the residual/trapped oil untouched and increasing the gas-to-oil ratio (GOR). To solve the CO₂ injection issues, several approaches have been tested. The most reported and applied approaches are: water alternating gas (WAG), generation of foams, and increasing gas viscosity by adding thickening agents (Christensen et al. 1998; Chakravarthy et al. 2004; Enick 1998; Dalland and Hanssen 1997, Enick et al. 2012; Dandge and Heller 1987; Heller 1994). The use of foam has the potential to reduce the gas mobility in a petroleum reservoir by increasing the gas apparent viscosity and reducing the gas relative permeability and, hence, improve the volumetric sweep efficiency (Falls et al. 1988; Kovsky and Radke 1994). However, the generation and stabilization of foam at reservoir conditions are major challenges. The major contributors to foam destabilization in porous media are the harsh conditions such as reservoir temperature and salinity, surfactant adsorption to the rock, and the presence of crude oil (Mannhardt et al. 1993; Al-Hashim et al. 1988; Figdore 1982; Grigg and Bai 2005).

Nanoparticles (NPs) were used to stabilize CO₂/brine emulsion at reservoir conditions (Espinoza et al. 2010; Al Otaibi et al. 2013; Worthen et al. 2013a, b). Also, the use of specially designed surfactants and the synergistic effect

of surfactant and NPs may provide a solution to stabilize CO₂/brine foam at harsh reservoir conditions and, therefore, reduce the gas mobility and, consequently, enhance oil recovery (AlYousef et al. 2017a). Worthen et al. 2013a, b used non-modified silica NPs and caprylamidopropyl betaine (CAPB) surfactant. The mixture produced a stable and viscous CO₂-in-water foam when neither of these materials could stabilize foam individually at experimental conditions. Singh et al. 2015 used fly ash powder and three types of surfactants: anionic, cationic, and nonionic. In the presence of NPs, anionic and nonionic surfactants produced foam with smaller bubble size. In porous media, NPs and anionic surfactant produced a stable foam. AlYousef et al. 2017a, b also reported a stable foam when they mixed anionic surfactant and coated silica NPs. Binks et al. 2015 reported a stable foam by mixing calcium carbonate (CaCO₃) particles and sodium stearyl lactylate surfactant (SSL). Xue et al. 2016 found that mixing silica NPs and laurylamidopropyl betaine (LAPB) surfactant produced a viscous foam with small bubble sizes.

The objective of this study is to investigate foam strength using a newly developed anionic surfactant and the mixture of the surfactant and surface-modified silica NPs. Importantly, this study reports the CO₂ mobility reduction factor (MRF) and oil recovery factors as a result of using the surfactant and the mixture at 1550 psi and 50 °C.

Materials

The surfactant used in this study is a complex nanofluid (CNF) anionic surfactant. The NPs used are surface-modified silica nanoparticles received in aqueous form from Nyacol Chemicals (DP 9711). The size of the particles was measured using dynamic light scattering (DLS) and found to be 30 nm ± 1. Brine was prepared using deionized water (DI) (ASTM Type II, Lab Chem) and sodium chloride (99%, Cole-Parmer). The cores used in this study were

Table 1 Properties of rock samples

Sample #	Length (in)	Diameter (in)	Type of rock	Porosity (%)	Pore volume (ml)	Permeability (D)
1	12	1	Non-fractured	21.76	33.61	1.50
2	12	1	Non-fractured	21.44	33.11	1.55
3	12	1	Non-fractured	21.20	32.74	1.72
4	12	1	Non-fractured	21.20	32.74	1.76
5	12	1	Non-fractured	21.84	33.74	1.77
6	12	0.96	Fractured	20.68	29.74	–
7	12	0.95	Fractured	19.90	27.74	–
8	12	0.95	Fractured	19.90	27.74	–

non-fractured and fractured Bentheimer sandstone from Kocurek Industries. Table 1 summarizes the properties of these cores. The oil used in this study was North Burbank Unit (NBU) oil with an average viscosity of 3.2 cp at 50 °C.

Methodology

This study consists mainly of dynamic foam tests and coreflood experiments for CO₂, surfactant, and the mixture of surfactant and silica NPs. The dynamic foam was generated using a coreflood apparatus, as shown in Fig. 1, and the CO₂ mobility was evaluated in rock samples at 1550 psi, 50 °C, and 90% quality (the gas fractional flow in the co-injection process). At least five pore volumes (PVs) of 1 wt% brine were injected at 5 ft/day to ensure the sample was 100% saturated with brine. The BPR was set to be 1550 psi. The baseline experiment was conducted through a co-injection of sc-CO₂ and brine at 90% quality. For other experiments, the samples were pre-flushed with a surfactant or a mixture of surfactant and NPs at 5 ft/day for 1 PV before starting the co-injection. Then, the co-injection of sc-CO₂ and surfactant/mixture was conducted also at 90% quality and the drop in pressure was recorded for each case. The same setup at the same conditions, except that water was injected at 3 ft/d during waterflooding process, was used to conduct coreflood experiments to assess the ability of the generated foam to reduce gas mobility and enhance oil recovery. Non-fractured rocks were used to run the mobility tests, while fractured and non-fractured rocks were used to conduct the coreflood experiments. For fractured rocks, the sample was initially 100% saturated with crude oil. Fractures were created through the horizontal axis by cutting the rocks from the center.

During sample preparation, the diluted surfactant and NPs solutions were stirred separately overnight to ensure homogeneity. The NPs were then added to the surfactant solution slowly, in a stepwise fashion, to avoid aggregation

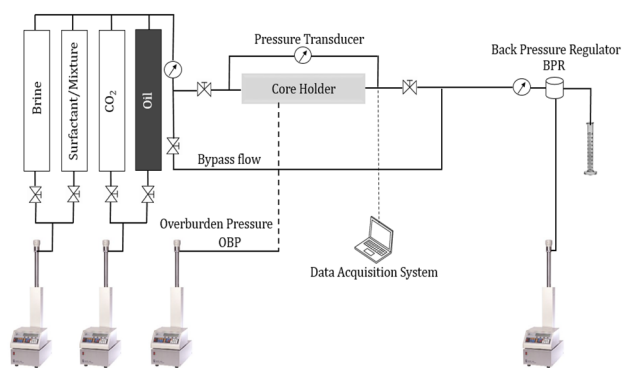


Fig. 1 Experimental setup

of NPs. The size of NPs was measured before and after the mixing to verify that no extensive aggregation occurs during mixing. The concentration of surfactant and NPs used was 0.50 wt%. The brine was prepared with 1 wt% NaCl.

Results and discussion

Dynamic foam tests

Comparisons here were based on recorded pressure drops across core samples and calculated MRF for the three cases: baseline, surfactant, and mixture of surfactant and NPs. Rock sample #1 was used to conduct the baseline experiment. The results, as shown in Fig. 2, showed that the steady-state pressure drop for the baseline experiment was about 0.29 psi. Bentheimer sample #2 was used to conduct the experiments in the absence and presence of NPs. In the absence of NPs, the foam behavior was excellent at the first PVs injected. After that, it had a sudden drop in the pressure values and it produced a foam with a steady-state pressure drop of 0.88 psi, as shown in Fig. 2. These results reflect the stability rather than the foamability. Surfactants have the ability to reduce the CO₂/water IFT and generate foams, but the stability is challenging. In the presence of NPs, the behavior was similar to that in the absence of NPs. However, it had a lower foam generation ability in the first PVs injected. After 1.5 PVs of the co-injection process, as shown in Fig. 2, the mixture resulted in a slightly higher steady-state pressure drop, 1 psi, than the surfactant case. This is an indication of the ability of NPs to produce a more stable foam in porous media. The foamability (the ability of a material to generate foam) might be higher for the surfactant case; however, the foam stability is much better in the case of the mixture. The permeability of the rocks used here was about 1.5 Darcy, so these reported values are still acceptable. The MRF values

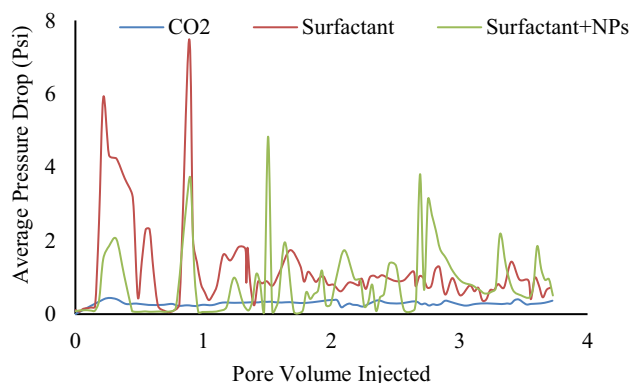


Fig. 2 Average pressure drop across the Bentheimer sandstone for baseline, 0.50 wt % surfactant, and a mixture of 0.50 wt % surfactant and 0.50 wt % NPs at 50 °C using CO₂

calculated for both the surfactant and mixture were found to be 3.04 and 3.45, respectively. This means that both the surfactant and the mixture were able to reduce the CO₂ relative permeability and increase the gas apparent viscosity, thereby reducing gas mobility.

Coreflood experiments

Two sets of experiments were conducted to assess the ability of foam to enhance oil recovery, one in non-fractured rocks (3–5) and the other in fractured rocks (6–8).

Non-fractured rocks

Coreflood experiments showed that both conditions, with and without NPs, improved oil recovery during foam injection processes, with higher recovery in the presence of NPs. Figure 3 shows the results of coreflood experiments following waterflooding and CO₂ injection. Oil recovery following the waterflooding process was about 32.82% of the OOIP. At least 4 PVs of water were injected to ensure that no more oil could be recovered in this process and to diminish any capillary end effects that might exist. Then, CO₂ was injected at 5 ft/d and total oil recovery reached 71.50% of the OOIP. This means that CO₂ was able to produce about 38.68% of the OOIP and 57.58 of the remaining oil in place. The average pressure drop during CO₂ injection was about 0.36 psi.

Figure 4 shows the results of coreflood experiments when surfactant was used. Oil recovery following the waterflooding process was about 36.15% of the OOIP. As before, at least 4.5 PVs of water were injected to ensure that no more oil could be recovered in this process and to diminish any capillary end effects that might exist. Then, 1 PV of surfactant was injected as a pre-flush step. The objective of this step was to minimize the adsorption that might occur during the co-injection processes. There was no significant amount of oil produced during the pre-flush step. The surfactant foam was able to produce about 39.90% of the OOIP

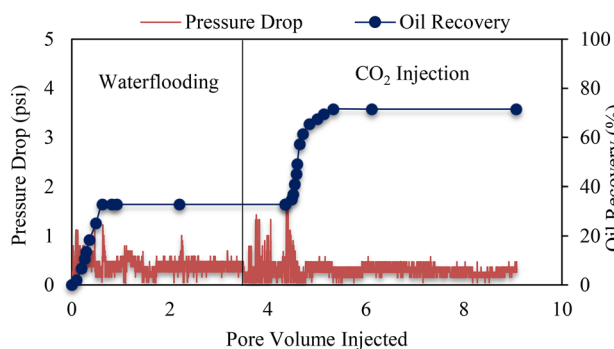


Fig. 3 Oil recovery following waterflooding and CO₂ injection, non-fractured rock

and 62.50% of the remaining oil in place. This brought the total oil recovery to around 76.06% of the OOIP. This is 4.56% higher than injecting CO₂ alone. The average pressure drop during the co-injection process of CO₂ and surfactant was about 0.71 psi. This is almost double that of injecting only CO₂.

The next experiment, as shown in Fig. 5, was for the mixture of surfactant and NPs. The same procedures used in the previous experiment were used in this run. Oil recovery following the waterflooding process was about 35.73% of the OOIP. The pre-flush with the mixture was not able to significantly recover any additional oil. During the co-injection processes, the mixture was able to produce about 44.33% of the OOIP and 68.97% of the remaining oil in place. The total oil recovery following the mixture foam process was around 80.05% of the OOIP. This is around 4% higher than the previous experiment where only surfactant was used and 8.55% higher than CO₂. The average pressure drop during the co-injection process of CO₂ and the mixture was about 1.16 psi. This is higher than both the surfactant and CO₂ cases.

A comparison between the three cases is presented in Fig. 6. The highest oil recovery was reported for the mixture, while the lowest was for CO₂. The high oil recovery

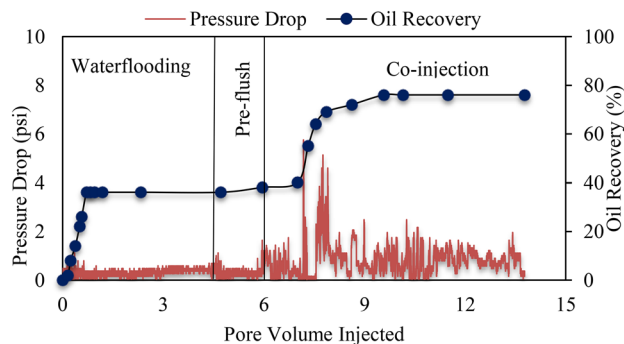


Fig. 4 Oil recovery following waterflooding and foam injection for surfactant, non-fractured rock

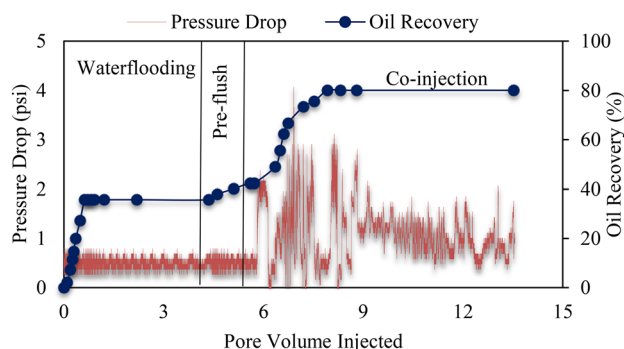


Fig. 5 Oil recovery following waterflooding and foam injection for a mixture of surfactant and NPs, non-fractured rock

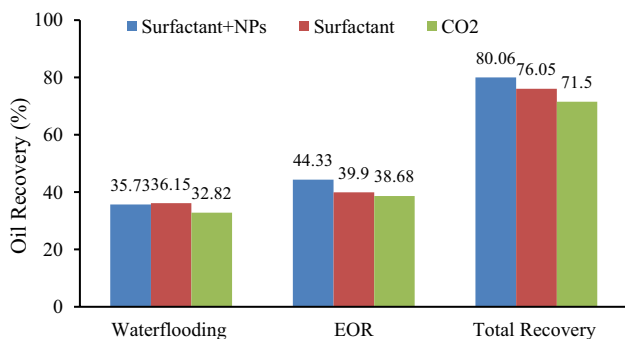


Fig. 6 Oil recovery following waterflooding, CO₂ and foam injection, non-fractured rocks

produced for CO₂ was because the experiment was conducted at or near the minimum miscibility pressure (MMP) of CO₂ in NBU oil. The higher oil recovery reported for surfactant compared to CO₂ demonstrates the ability of foam flooding to reduce gas mobility and enhance oil recovery. Also, the higher recovery of the mixture compared to that of surfactant demonstrates the ability of the presence of NP to further reduce gas mobility, improving the gas sweep efficiency and, therefore, recovering more oil.

Fractured rocks

Similar to the previous experiments, the results of coreflood experiments here on non-fractured rocks showed improved oil recovery during the foam injection processes, with higher recovery when NPs were used. Figure 7 shows the results of coreflood experiments for the baseline case, surfactant, and the mixture.

For the baseline experiment, the oil recovery following the waterflooding process was about 59.71% of the OOIP. At least 4 PVs of water were injected at 3 ft/d to ensure that no more oil could be recovered in this process and to

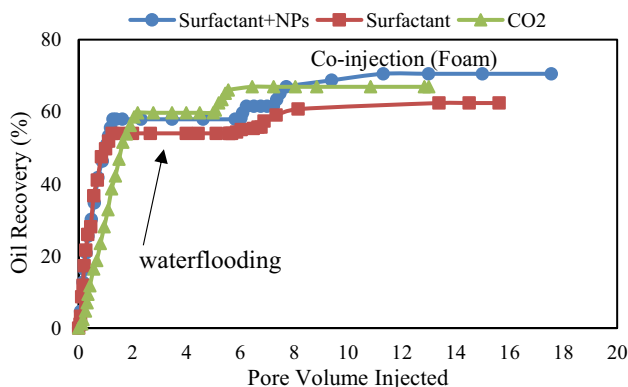


Fig. 7 Oil recovery following waterflooding, CO₂ and foam injection, fractured rock

diminish any capillary end effects that might exist. Then, CO₂ was injected at 5 ft/d and the total oil recovery reached 66.92% of the OOIP. This means that the CO₂ was able to produce about 7.21% of OOIP and 17.90% of the remaining oil in place.

For the surfactant case, the oil recovery following the waterflooding process was about 54.01% of the OOIP. At least 5.5 PVs of water were injected at 3 ft/d to ensure that no more oil could be recovered in this process and to diminish any capillary end effects that might exist. Then, 1 PV of surfactant was injected at 1.5 ft/d as a pre-flush step. There was no significant amount of oil produced during the pre-flush step. The co-injection process was conducted at 5 ft/d and 90% quality. The surfactant foam was able to produce about 8.41% of the OOIP and 15.28% of the remaining oil in place. This brought the total oil recovery to be around 62.42% of the OOIP. Even though the total oil recovery of CO₂ was higher than surfactant, the recovery factor during foam injection was higher than the CO₂ case. The surfactant produced 8.41% following waterflooding, whereas the CO₂ recovered 7.21% of the OOIP. Also, the recovery factor during the waterflooding for the CO₂ case was higher than the surfactant case, 59.71% for CO₂ versus 54.01% for surfactant. This resulted in a higher total recovery for CO₂ compared to surfactant.

The next run, as shown in Fig. 7, was for the case where the mixture of surfactant and NPs was used. The same procedure as in the previous experiment was used in this run. The oil recovery following the waterflooding process was about 57.90% of the OOIP. A small amount of oil was produced during the pre-flush process. During the pre-flush and co-injection processes, the mixture was able to produce about 12.62% of the OOIP and 29.98% of the remaining oil in place. The total oil recovery following the mixture foam process was around 70.52% of the OOIP. This is around 8.10% higher than the previous experiment in which only surfactant was used and 3.60% higher than CO₂.

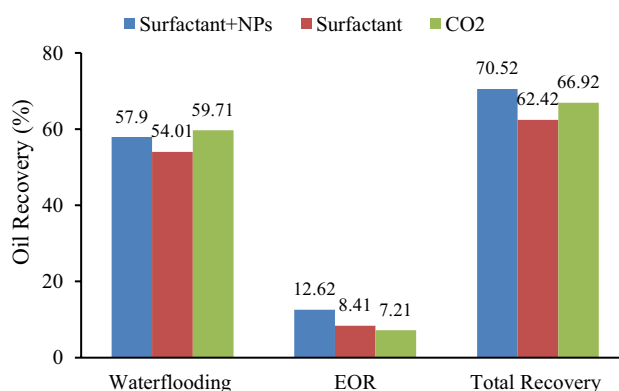


Fig. 8 Summary of coreflood experiments, fractured rocks

A comparison between the three cases is presented in Fig. 8. The highest oil recovery was reported for the mixture, while the lowest was for surfactant. However, the results reported for surfactant compared to CO₂ are already discussed above. The high oil recovery reported for all cases was because the experiments were conducted at or near the minimum miscibility pressure (MMP) of CO₂ in NBU oil. Also, the rock samples were 100% saturated with oil. The higher oil recovery reported for surfactant compared to CO₂, at the secondary recovery scheme, demonstrates the ability of foam flooding to reduce gas mobility, hence improving oil recovery. Also, the higher recovery of the mixture compared to that of surfactant and CO₂ demonstrates the ability of NPs to further reduce gas mobility, improving the sweep efficiency and, therefore, recovering more oil. The summary of the performance of waterflooding and secondary recovery schemes can be found in Fig. 8.

Conclusion

Anionic surfactant and a mixture of anionic surfactant and surface-modified silica nanoparticles were used in this study to assess the ability of the surfactant and the mixture to stabilize CO₂/brine foam at reservoir conditions. Dynamic foam tests were conducted to test the ability of the surfactant and the mixture to generate foam in porous media and reduce CO₂ mobility. Coreflood experiments were performed in Bentheimer non-fractured and fractured sandstone rocks to examine the ability of the generated foam to reduce gas mobility and enhance oil recovery. Based on the results of dynamic foam tests and coreflood experiments:

- At harsh reservoir conditions, both surfactant and mixture were able to reduce the sc-CO₂ mobility about 3–4 times.
- Using non-fractured rocks, the mixture of surfactant and NPs recovered about 80.05% of the OOIP. This is around 4% higher than surfactant and 8.55% higher than sc-CO₂.
- Using fractured rocks, the presence of NPs was able to improve the oil recovery compared to the surfactant and pure sc-CO₂ injection cases. The oil recoveries during secondary production mechanisms for CO₂, surfactant, and mixture were 7.21, 8.41, and 12.62% of the OOIP, respectively.

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