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Surfactant and a Mixture of Surfactant and Nanoparticles Stabilized- CO₂/Brine Foam for Gas Mobility Control and Enhanced Oil Recovery

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Abstract

Injecting carbon dioxide (CO₂) into oil reservoirs has the potential to enhance oil recovery (EOR) and mitigate climate change by storing CO₂ underground. Despite successes in using CO₂ to enhance oil recovery, mobility control remains a major challenge facing CO₂ injection projects. The objective of this work is to investigate the potential of using surfactant and a mixture of surfactant and nanoparticles (NPs) to generate foam to reduce gas mobility and enhanced oil recovery.

A newly developed anionic surfactant and a mixture of the surfactant and surface modified silica NPs 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 NPs at 90% quality. The coreflood experiments were conducted using non-fractured and fractured sandstone cores at 1550 psi and 50°C.

Surfactant alone and mixtures of surfactant and NPs were able to generate foam in porous media and reduce 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 NPs 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 (OOIP). Using surfactant brought the oil recovery to 76% of the OOIP. The addition of NPs to surfactant resulted in a higher oil recovery still, 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.

Large amounts of oil remain underground following 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 NPs may provide a solution to stabilize CO₂-brine foam at harsh reservoir conditions and, therefore, reduce gas mobility, consequently enhancing oil recovery.

Introduction

The remaining oil underground following traditional recovery mechanisms is considerable (Hirasaki, Miller, and Puerto 2011). Typically, fields can produce about 45 to 50 % of the original oil in place (OOIP) following primary and secondary oil production mechanisms (Sandrea and Sandrea 2007). As a result, oil production 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 used extensively to enhance 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, Holder, and Morsi 1988, Bayraktar and Kiran 2000). Despite the reported successes of CO₂ injection, a major challenge facing this technique is poor volumetric sweep efficiency. Major factors that contribute to this problem are 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). 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 often reported and applied approaches are: water alternating gas (WAG); generation of foams; and increasing gas viscosity by adding thickening agents (Christensen, Stenby, and Skauge 1998, Chkravarthy, et al. 2004, Enick 1998, Dalland and Hanssen 1996, Enick and Olsen 2012, Dandge and Heller 1987, Heller, J. 1994). The use of foam has the potential to reduce the gas mobility in petroleum reservoirs by increasing the gas apparent viscosity and reducing the gas relative permeability and, hence, improve the volumetric sweep efficiency (Falls et al. 1988, Kovscek 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, Schramm, and Novosad 1993, Al-Hashim, H.S. et al. 1988, Figdore 1982, Grigg and Bai 2005).

Nanoparticles (NPs) have been used to stabilize CO₂/brine emulsions at reservoir conditions (Espinoza et al. 2010, Al Otaibi et al. 2013, Worthen et al. 2013). The use of specially designed surfactants and the synergistic effects of surfactant and NPs may help to stabilize CO₂/brine foams at harsh reservoir conditions and, therefore, reduce gas mobility, consequently enhancing oil recovery. For instance, Worthen et al. (2013) 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. Similarly, 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. Binks et al. (2015) reported a stable foam by mixing calcium carbonate (CaCO₃) particles and sodium stearyl lactylate surfactant (SSL). Finally, 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 $30 \text{ nm} \pm 1$. 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 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.

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	-

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, **figure 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 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 and 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 generated foam to reduce gas mobility and enhanced 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 were 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 NP solutions were stirred separately overnight to ensure homogeneity. The NPs were then added to the surfactant solution slowly, in stepwise fashion, to avoid aggregation of NPs. The size of NPs was measured before and after the mixing to verify that no extensive aggregation occurred during mixing. The concentration of surfactant and NPs used was 0.50 wt%. The brine was prepared with 1 wt% NaCl.

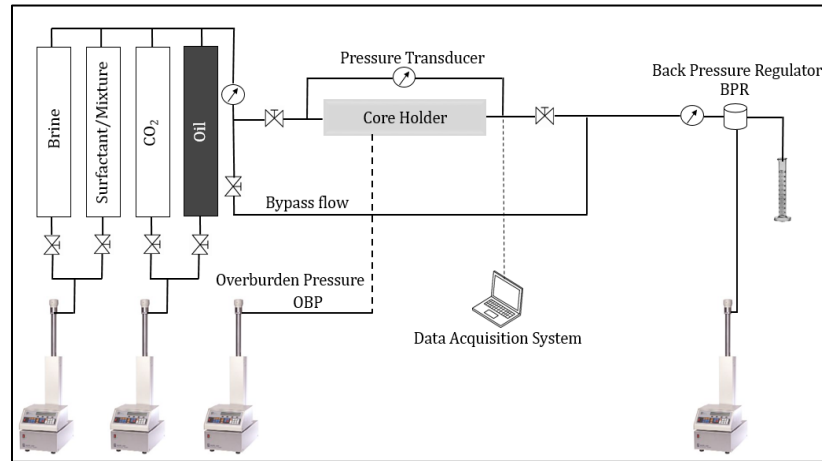


Figure 1: Experimental Setup

Results and Discussion

Dynamic Foam Tests

Comparisons here were based on recorded pressure drops across core samples and calculated MRF (steady state pressure drop/ steady state pressure drop for baseline experiment) 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 **figure 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 **figure 2**. The surfactant has 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 **figure 3**, 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 permeability of the rocks used here was about 1.5 Darcy, so these reported values are still acceptable. The MRF values 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.

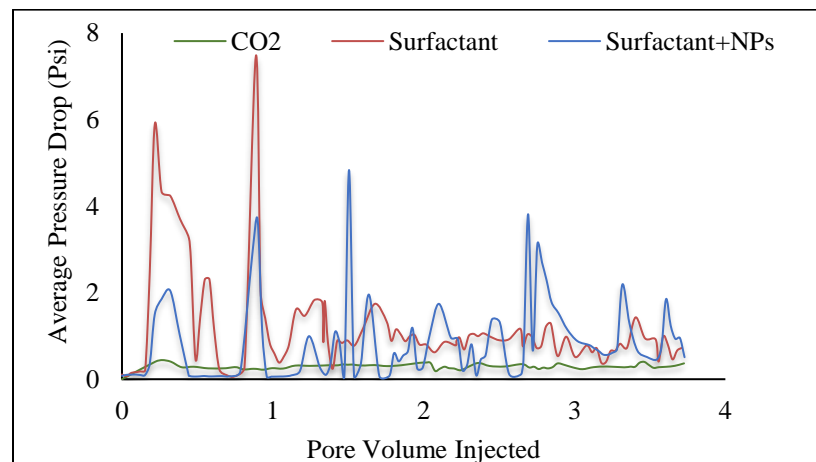


Figure 2: Average pressure drop across the Bentheimer sandstone for baseline, 0.50 wt% surfactant and a mixture of 0.50 wt% surfactant and 0.50 wt% NPs at 50°C using CO₂

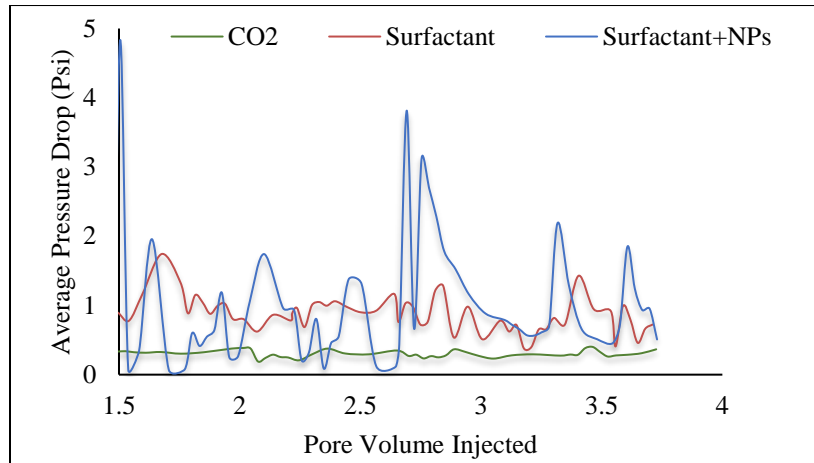


Figure 3: Average pressure drop after 1.5 PVs of the co-injection across the Bentheimer sandstone for baseline, 0.50 wt% surfactant and a mixture of 0.50 wt% surfactant and 0.50 wt% NPs at 50°C using CO₂

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 4** 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 3.5 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, 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.

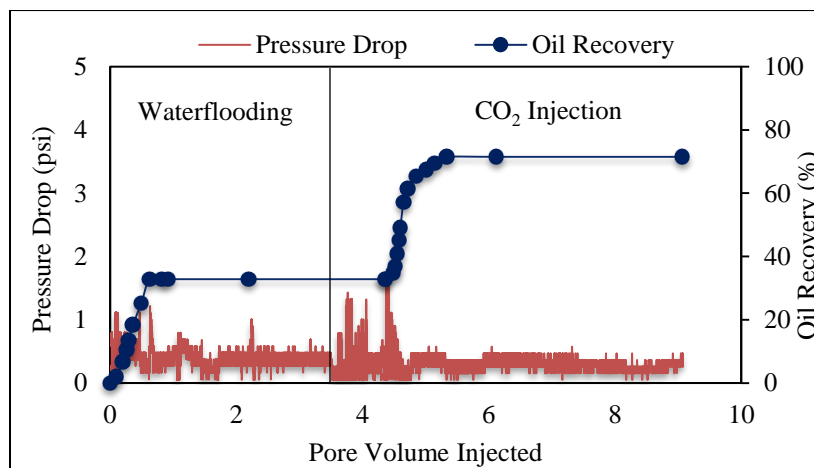


Figure 4: Oil recovery following waterflooding and CO₂ injection, Non-fractured rock

Figure 5 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 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 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 CO₂ alone.

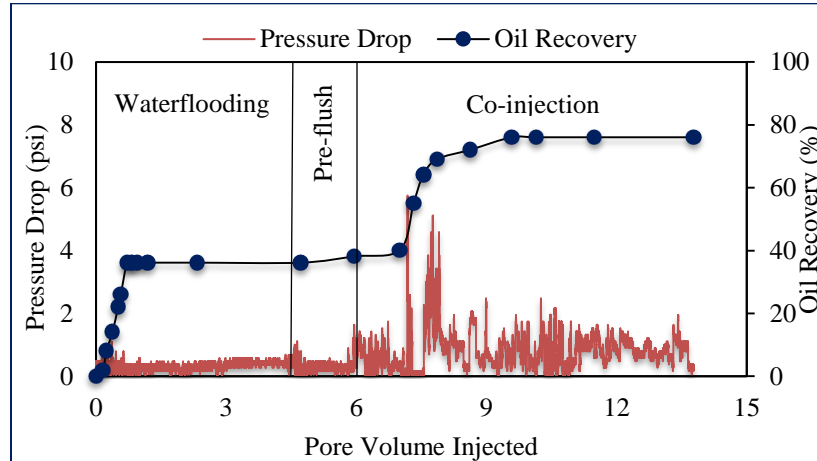


Figure 5: Oil recovery following waterflooding and foam injection for surfactant, Non-fractured rock

The next experiment, as shown in **figure 6**, 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.

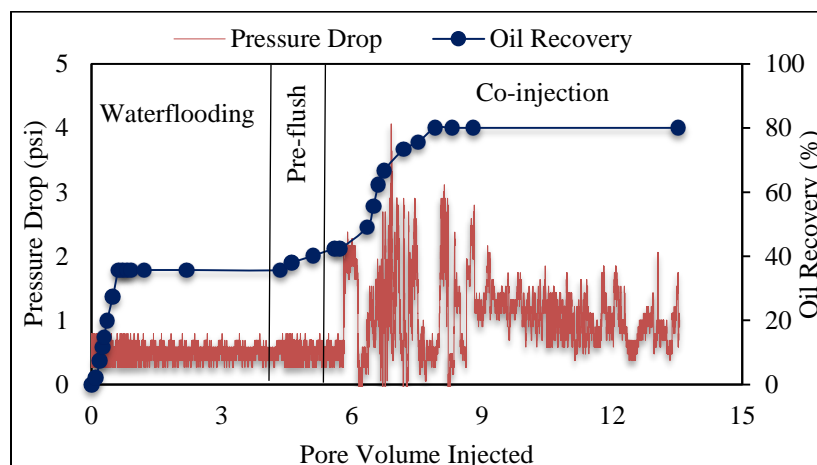


Figure 6: Oil recovery following waterflooding and foam injection for a mixture of surfactant and NPs, Non-fractured rock

A comparison between the three cases is presented in **figure 7**. The highest oil recovery was reported for the mixture while the lowest was for CO₂. The high oil recovery 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.

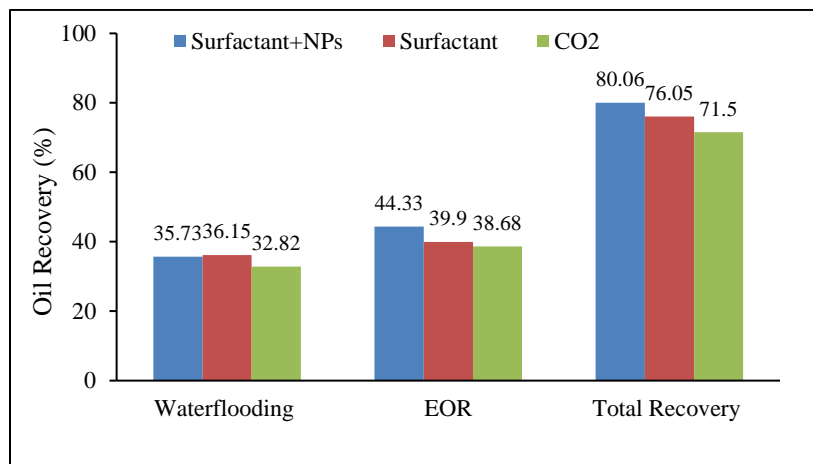


Figure 7: Oil recovery following waterflooding, CO₂ and foam injection, Non-fractured rocks

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 8** 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 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 18.28% 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.

The next run, as shown in **figure 8**, 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.

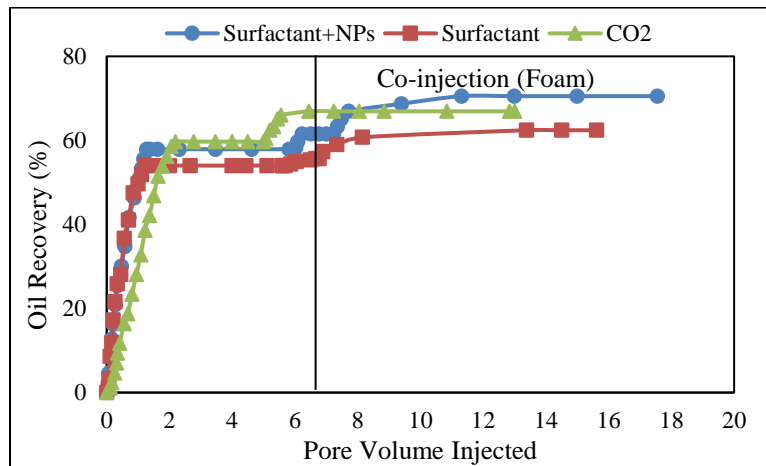


Figure 8: Oil recovery following waterflooding, CO₂ and foam injection, fractured rock

A comparison among the three cases is presented in **figure 9**. 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 and, hence, to improve 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, thus improving the sweep efficiency and, hence, recovering more oil. The summary of the performance of waterflooding and secondary recovery schemes can be found in **figure 9**.

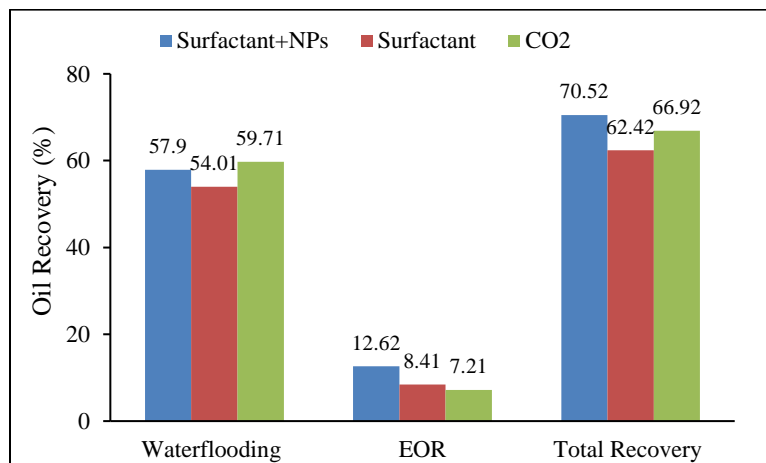


Figure 9: Summary of coreflood experiments, fractured rocks

Conclusion

Anionic surfactant and a mixture of anionic surfactant and surface modified silica NPs 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 surfactant and the mixture to generate foam in porous media and to reduce CO₂ mobility. Core flood experiments were performed in Bentheimer non-fractured and fractured sandstone rocks to examine the ability of generated foam to reduce gas mobility and to enhance oil recovery. Based on the results of dynamic foam tests and coreflood experiments:

- At harsh reservoir conditions, both surfactant and the 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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