ASP design for the Minnelusa formation under low-salinity conditions: Impacts of anhydrite on ASP performance

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HIGHLIGHTS

- We designed ASP blends based only on fluid–fluid interactions and phase behavior.
- We compared recovery from model rock (less reactive) with rock containing anhydrite.
- Geochemical observations and modeling show why anhydrite affects water chemistry.
- Our results explain why NaOH should be used in contrast with Na$_2$CO$_3$ in Minnelusa rock.

ABSTRACT

Alkali–surfactant–polymer (ASP), surfactant–polymer (SP) and alkali–polymer (AP) flooding have been recognized as potentially effective Chemical Enhanced Oil Recovery (EOR) techniques. The alkali in ASP or AP flooding blends interacts with formation minerals, markedly with anhydrite in the case of eolian deposits. As a result, water chemistry after the injection of an engineered chemical blend is unlikely to be governed only by fluid–fluid interactions at reservoir conditions. To investigate rock-fluid interactions, Berea and available rock samples from an oil-bearing Minnelusa reservoir in Wyoming, an eolian formation, are used in coreflood experiments. Further, a robust ASP blend at optimal salinity was designed for the DC Minnelusa crude oil. Secondary waterflooding, tertiary ASP injection, polymer drive and finally a brine flush are subsequently completed in coreflood experiments. Oil recovery, pressure drop, surfactant concentration, pH, and viscosity are measured during or immediately after each experiment; water chemistry is analyzed in effluent samples. Findings show the potential of the chemical blends to improve oil recovery significantly under low-salinity conditions (<12,000 ppm) of the DC formation at present. Also, rock type recovery dependence highlights the importance of rock-fluid interactions. The results of this study can be applied to reservoirs at low salinity conditions and/or where anhydrite is present.

1. Introduction

Alkali–surfactant–polymer (ASP) flooding owes its success to the synergy of the individual components of Enhanced-Oil Recovery (EOR) blends. Alkali offers several benefits including promoting crude oil emulsification, increasing aqueous-phase ionic strength leading to regulation of phase behavior of the injected surfactant, and lowering interfacial tension (IFT) to ultralow values in presence of surfactant. Alkali can also reduce costs by limiting the amount of surfactant needed in two ways. First, alkali reduces surfactant adsorption by increasing the rock surface's negative charge density, making it preferentially water-wet [1–3]. Second, alkali reacts with the acids in the crude oils to produce in situ soaps, which in turn broadens the optimal salinity range. This is the key to extending the three-phase region (or ultra-low IFT region), because the soap generated creates a micro-emulsion phase that can coexist with oil and water [3–6].

Surfactants work in ASP flooding to lower the IFT between trapped oil and brine, to aid to mobilize and contribute to the formation of oil banks. IFT reduction lowers capillary forces and allows for the oil bank to flow more freely without renewed trapping [4,6–8].

Polymer increases the viscosity of the aqueous phase as well as reduces water permeability due to mechanical entrapment, consequently resulting in more favorable mobility ratio. With a more viscous phase, the collected oil bank can be more easily moved through the reservoir and eventually into the producing well [9]. Polymer flooding alone helps to accelerate oil production over secondary waterflooding. With ASP flooding, reservoir productive life is extended and significantly more oil can be produced 1.
general, ASP flooding is an approach that synergizes the advantages of alkali, surfactant, and polymer in order to increase in situ capillary number. This results in the favorable scenario of decreased residual oil saturation [10].

The first ASP field pilots were conducted in the Minnelusa formation. The first test was carried out in the West Kiehl Field located in Crook County of Wyoming. In this case, no injectivity problems were detected and 23% of the original oil in place (OOIP) was recovered [10]. The incremental cost (chemicals, facilities, implementation, etc.) was estimated at 2.13 $/bbl and no formation damage was observed [11]. Next came the Cambridge field, a Minnesusa field located contiguous to the Kiehl field. In this case, ASP flooding increased recovery by 28% of OOIP (1,143,000 bbls) and incremental costs were estimated at 2.42 $/bbl. In the case of the Kiehl field, the ASP blend featured Sodium Carbonate (Na₂CO₃) and 0.1 wt.% Petrostep B-100 [12]. Later, these techniques were implemented in other fields such as Tanner field, Mellott Ranch, and Driscoll Creek. The Tanner field formulation contained 1 wt.% Sodium Hydroxide (NaOH) and 0.1% active ORS-41HF. The projected incremental OOIP was 17%, based on experiments and results from pilot tests [13].

Other successful field projects have taken place in Oklahoma and in China [14]. Results from the Daqing oil field in China indicated that surfactant did not produce ultra-low water–oil IFT values. However, the addition of 1 wt.% NaOH enabled them to reach this condition. Another ASP project designed through phase behavior analyses, coreflooding, and single well pilots took place in Oman. In this case, the blend was made up of 0.3 wt.% manufactured surfactant and 1 wt.% Na₂CO₃ [15].

Implementation of an optimum ASP blend can be difficult at times due to many uncertainties, i.e. heterogeneities, interference from adjacent wells, surface facilities, mixing of blend, rock-fluid interactions, mineralogy, clay content, and other reservoir complexities [15]. More specifically, ASP flooding is unlikely to work for all Minnelusa reservoirs. Limitations include high water hardness, high reservoir temperature, and chemical consumption properties of reservoir rock [16,17]. However, one study of 120 Minnelusa fields revealed that 130 million barrels of incremental oil could potentially be recovered using ASP formulations [1].

In this paper, static (bottle tests) and dynamic tests (coreflooding) are carried out to develop an ASP blend for the conditions of the DC field. This Minnelusa reservoir has two important characteristics that impact the blend selection. First, the formation is likely to contain a significant amount of anhydrite that is typical of most Minnelusa fields in Wyoming. Second, the formation current relative low salinity water (< 12,000 ppm), resulting from fresh water injection. The challenges of the ASP design for this field are sustaining high pH conditions and finding a surfactant with optimum salinity at low ionic strength, also able to tolerate a high calcium concentration. Finally, we also investigate the impact of alkali type and speculate on reasons why NaOH works better than Na₂CO₃.

2. Experiments

2.1. Rheology

A rheological analysis of polymer and alkaline–surfactant–polymer (ASP) solutions is carried out with an ARES Rheometer in parallel plate geometry using 50-mm plates. Blend viscosity is measured as a function of shear rate from 5–100 Hz.

2.2. Interfacial tension

The crude oil–brine interfacial tension is measured using the Spinning Drop Tensiometer SITE100. Crude oil form the DC field in Wyoming is used in all the experiments. Two types of experimental conditions are set for IFT determination:

- Alkali weight fraction sweeps at constant surfactant and NaCl concentrations.
- NaCl weight fraction sweep at constant surfactant and alkali concentrations.

These experiments were done to compare IFT values with visual phase behavior results. All the IFT measurements were completed at 48 °C and at 5000 rpm.

2.3. Surfactant concentration

Surfactant concentration is measured through titration. First, a titration standard is generated using 1 wt.% total surfactant at the same brine composition as the ASP flooding design. To carry out the titration, 1 mL of standard sample is added to deionized water, di-methyl blue indicator and chloroform. Then, the titrating solution, 0.04 M Hyamine, is added until the solution reached the titration point. The volume of spent titrant (Hyamine) is recorded and used as the standard titration volume. To measure the surfactant concentration of effluent samples, 1 mL aliquots are taken from each effluent sample. Then, recorded titration volumes of the samples are divided by the standard titration volume to give the surfactant concentration.

2.4. Screening procedure to find suitable surfactant and alkali agents

Prior to experimentation, considerable research efforts went into designing a robust ASP blend. The main goal when designing the surfactant blend was to find a combination that would work well at lower salinities. Table 1 shows the DC field produced water chemistry. The target salinity when screening for surfactants was set between 2000 and 12,000 ppm based on the TDS value from Table 1.

From the literature review, it was concluded that surfactants with a larger carbon chain length, increased branching, and multiple Propylene Oxide groups (PO groups) would work ideally for lowering optimal salinity [18–21].

Increasing branching and molecular weight of surfactants can have multiple benefits. High molecular weight sulfonates can be properly balanced to match the brine-oil system and thus be more effective oil recovery agents. Further, chain length can tailor the surfactant to a specific crude oil, i.e. longer carbon chains make it more compatible with hydrophobic crude oils than do alcohol-based surfactants with lower carbon numbers. The greatest benefit from increasing the length the chain for this application is the result lowering of optimal salinity. Evidence of this lies in increasing chain length from C15–18 to C20–24 results in an optimal salinity decrease for internal olefin sulfonates (IOS) [18].

The reason high carbon number IOS surfactants display desirable phase behavior is not solely due to the relationship with low IFT, but is also due to branched hydrophobic structures preventing ordered arrays and viscous phases from forming. This branching is ideal when the double bond occurs internally rather than at the end of the surfactant molecule, which is a characteristic of IOS. Other important attributes of IOS is that they are good at high and low temperatures [19]. Researchers at the University of Texas at Austin

<table>
<thead>
<tr>
<th>Ion</th>
<th>Na⁺</th>
<th>K⁺</th>
<th>Ca²⁺</th>
<th>Mg²⁺</th>
<th>HCO₃⁻</th>
<th>Cl⁻</th>
<th>SO₄²⁻</th>
<th>pH</th>
<th>TDS</th>
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<tbody>
<tr>
<td>Conc. (ppm)</td>
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<td>71</td>
<td>456</td>
<td>63</td>
<td>509</td>
<td>30</td>
<td>3,400</td>
<td>7.95</td>
<td>6,174</td>
</tr>
</tbody>
</table>

Table 1

DC synthetic reservoir brine.
also discuss favorable tolerance as well as reduced adsorption for highly branched surfactants [20]. Based on all of this, and the fact that IOS are low in cost due to large scale manufacturing, it was decided that IOS would be the optimal co-surfactant.

Propylene oxide groups decrease optimal salinity in that they make the surfactant more hydrophobic [21]. In addition to lowering optimal salinity, adding these PO groups will higher solubilization, broaden the ultralow IFT region and increase calcium tolerance and affinity. The mechanism works in that adding PO groups to the surfactant chain helps to increase interface affinity of the molecules which in turn increases the breadth of the salinity region where high solubilization and ultralow IFT occur. When PO and EO (Ethylene oxide groups) are added between hydrophobic and hydrophilic groups, further extension in aqueous and oleic phases can occur. However, EO groups are not desirable here because they increase optimal salinity and decrease solubility ratio [19]. Thus, one of the major advantages of PO groups is that they allow for ultra-low IFT’s at a wide range due to high oil solubilization [8].

The following commercial surfactants were screened for research purposes (all from Stepan): NEODOL-67-7PO-Sulfate (PS1), IOS C15–18 (PS2), IOS C20–24 (PS3-B), 16–17Alcohol-13PO-Sulfate (PS13-D), Alky Xylene Sulfonate (A6). Of these surfactants, the two Alcohol Ether Sulfates (PS1 and PS13-D) and the Xylene Sulfonate (A6) were used as main surfactants. The other two internal Olefin Sulfonates (PS2 and PS3-B) were used as co-surfactants. The main difference between PS1 and PS13-D is that PS1 has 7 PO groups whereas PS13-D has 13 PO groups. Additionally, the hydrophobic parts of these two surfactants are different: the hydrophobe of PS1 is 16–17 carbon, branched, NEODOL product whereas S13D is a 13 carbon, isostearic product. The difference between PS2 and PS3-B is that PS-B has a longer chain length/molecular weight. The ratio of main surfactant to co-surfactant is 3:1. Initially 1.5 wt.% of main surfactant was used with 0.5 wt.% of co-surfactant. The following combinations were tested:

- **Blend 1**: 1.5 wt.% PS13-D, 0.5 wt.% PS3-B.
- **Blend 2**: 1.5 wt.% PS1, 0.5 wt.% PS2.
- **Blend 3**: 1.5 wt.% PS1, 0.5 wt.% PS3-B.

All of these combinations were tested over salinity scans from 5000–35,000 ppm NaCl at a 1:1 aqueous phase to oil ratio. (Note: All experimental phase behavior tests were run at a 1:1 ratio). Once the optimal blend was discovered (Blend 1), this amount was cut in half to 0.75 wt.% and 0.25 wt.% and will be referred to as Blend 5. At this point A6 was also tested with PS3-B:

- **Blend 4**: 0.75 wt.% A6, 0.25 wt.% PS3-B (0–20,000 ppm NaCl).
- **Blend 5**: (Blend 1) 0.75 wt.% PS13-D, 0.25 wt.% PS3-B (0–2,000 ppm NaCl).

Using Xylene Sulfonate (A6) in Blend 4 revealed poor solubility, so it was decided to continue on with Blend 5 as the optimal blend. Research at Rice University indicates that a similar surfactant/co-surfactant combination to Blend 5 worked very effectively. However, favorable results only occurred when both are used together rather than individually. Another study by Lin et al. showed promising results with a similar surfactant blend again along with the addition of Na2CO3 [8]. This leads to the effect of alkali, which was tested on all surfactant blends, but only results from Blend 5 are presented. Both NaOH and Na2CO3 were tested. Both alkalis were also tested with DC crude oil alone in the absence of surfactant. All of these blends were screened from the NaCl weight fraction range of 0–20,000 ppm.

In order to test solubility and stability of Blend 5 with alkali, a cloud point test was used. In this test, ran from 0–20,000 ppm NaCl, all components are dissolved into an aqueous solution and placed in an oven at reservoir temperature for one week. Cloudiness is then determined through visual observation.

### 2.5. Experimental setup

DC reservoir temperature, 48 °C, corresponding to the shallow reservoir depth for Minnelusa was set in all experiments. Synthetic DC formation brine composition from Table 1 was also used. The typical source of injection water in the Powder River Basin, where most of the Minnelusa reservoirs are located, is the Fox Hills formation. To mimic the injection water source, 1600 ppm NaCl brine is used for waterflooding and preparing chemical solutions. DC oil is collected and used in these experiments after filtering and centrifuging to remove fines. This oil has a viscosity of 83 cP (at 48 °C) and an acid number of 0.43 mg KOH/gr oil.

### 2.6. Coreflooding experiments

Based on phase behavior results, Blend 5 was selected for three corefloods. In the first two, everything was kept the same, except for the rock to investigate the impact of rock-fluid interaction on the performance of the ASP blend. A Berea core was used in the first experiment and a sample of Minnelusa core was used in the second. In the third coreflooding test, another sample Minnelusa formation plug was used. In this test, the concentrations of surfactant and alkali were 50% of the values in the first two tests.

To begin the coreflooding procedures, the cores were first characterized (porosity, permeability, weight dry, weight wet, length, diameter, and total pore volume). The cores were then vacuum saturated for one day and allowed to age to age in the synthetic DC formation brine within the core holder at 48 °C and under 500 psi confining pressure for a week. The core plugs were water-saturated with this same brine. To measure connate brine permeability, the injection flow rate was varied from 0.5–0.7 ml/min and the pressure drop along the core was recorded. The cores were flooded with DC oil at a rate of 0.5 ml/min (2.16 ft/day) for 2.5 pore volumes (PVs). Effluent samples were collected using an automated fraction collector to determine initial water and oil saturations within the core through material balance calculations. After aging a minimum of 10 days, cores were waterflooded with injection brine containing 1600 ppm NaCl for 8 PVs to establish residual oil saturation. Before initiating the tertiary chemical flooding, permeability was measured at residual oil saturation. The cores were then injected with 1 PV of the ASP blend followed by a 1 PV polymer (P) slug consisting of the injection brine and 1000 ppm Flopaam 3330S. To complete the coreflood, a 5 PV waterflood of injection brine was run. At the conclusion of the final waterflood, the permeability of the core was again measured. Pressure drop was recorded for all flooding activities and plotted along with oil recovery. Flow rates for waterflooding and chemical flooding were held constant at 0.5 ml/min.

For the first two experiments, the chemical ASP blend contained Blend 5: (0.75% PS13-D and 0.25%PS3-B), 1 wt.% NaOH, and 2000 ppm Flopaam 3330S prepared in 1600 ppm NaCl brine. For the third ASP flooding test, the chemical blend contained 0.375% PS13-D and 0.125% PS3-B, 0.5 wt.% NaOH and 2000 ppm Flopaam 3330S prepared in 1600 ppm NaCl brine.

### 3. Results and discussion

#### 3.1. Phase behavior and optimum salinity (bottle tests)

The phase behavior of 1 wt.% total surfactant solution versus NaCl weight fraction is shown in Fig. 1. It can be noticed that the
optimum salinity of Blend 5 in this study without alkali is higher than 35,000 ppm of NaCl, a value greater than formation salinity.

The phase behavior of Blend 5 + 1 wt.% Na₂CO₃ while varying NaCl weight fraction is shown in Fig. 2. The presence of Na₂CO₃ yields somewhat lower optimum salinity at approximately 30,000 ppm of the total salinity (NaCl + Na₂CO₃), though it is still not in the range of formation salinity. Keeping everything else the same, Na₂CO₃ was replaced with NaOH to investigate the effect of alkali type on phase behavior. In this situation, generated in situ soaps impact on changing optimum salinity to lower values is observed (Fig. 3). NaOH reduces the optimum salinity significantly and into the range of the DC formation. It also broadens the desirable phase behavior region (Type III and Type II⁻) of the mixture of surfactant and soap.

To investigate the role of alkali in lowering optimum salinity in more detail, an additional set of phase behavior screening tests was performed without surfactant. The phase behavior of DC oil and 1 wt.% Na₂CO₃ at varying salinities is shown in Fig. 4. Here, Na₂CO₃ emulsifies oil at salinity lower than 35,000 ppm of NaCl. The optimum phase behavior takes place at roughly 32,500 ppm of NaCl, which is higher than the formation salinity. NaOH, on the other hand, emulsifies a significant amount of DC oil, shows favorable phase behavior in terms of lowering optimum salinity, and also displays a wider type III and II⁻ region (Fig. 5).

The optimum salinity of the mixture can be obtained as follows [22]:

\[
\log(\text{Opt}_{\text{mix}}) = x_{\text{soap}} \log(\text{Opt}_{\text{soap}}) + (1 - x_{\text{soap}}) \log(\text{Opt}_{\text{surf}})
\]

where \(x_{\text{soap}}\) is the mole fraction of generated soap by alkali-organic acid interaction. Eq. (1) shows that the optimum salinity of mixture lowers if the generated soap has a lower optimum salinity than surfactant. This explains why the blend of 1 wt.% Surfactant + 1 wt.% NaOH yields a lower optimum salinity as compared to 1 wt.% surfactant alone or 1 wt.% surfactant + 1 wt.% Na₂CO₃. Generated soaps by NaOH appear to have lower optimum salinity values than those from Na₂CO₃ (Figs. 4 and 5). Hence, for DC crude oil at reservoir conditions, it is more efficient to use NaOH as an alkaline agent (more information is provided in Appendix A).

Fig. 1. Phase behavior of DC oil and 1 wt.% surfactant with varying NaCl weight fraction (at 48 °C).

Fig. 2. Phase behavior of DC oil and 1 wt.% surfactant + 1 wt.% Na₂CO₃ with varying NaCl weight fraction (at 48 °C).
To explore the potential of a more economical blend, i.e. lower concentration of alkali and surfactant, the concentration of NaOH was screened at both 1 and 0.5 wt.% surfactant. Results are shown in Figs. 6 and 7. As shown in Figs. 6 and 7, there seems to be an interval for the concentration of NaOH to operate at optimum conditions (here from 2000 to 10,000 ppm) at both 1 and 0.5 wt.% surfactant. This indicates that a certain amount of NaOH in solution is necessary to generate sufficient soap and to increase the mole fraction of the soap, as per Eq. (4). On the other hand, the concentration of alkali should be less than a threshold value, because it can suppress optimum conditions and cause phase behavior to transition from type III to type II* [4,23]. Additionally, as discussed before, Na₂CO₃ does not contribute to lowering optimum salinity. In addition to the aforementioned advantages of NaOH, other results involving rock-fluid interactions obtained by Kazempour et al. [17] showed that in the presence of anhydrite, pH buffering of the injected alkali is significant. Used as a typical alkali in EOR, NaOH is a better candidate to overcome the pH buffering problem and raise the pH to the required level for saponification. However, this alkali can cause secondary mineral precipitation [17]. Based on all the evidence presented, NaOH was selected as the alkali for coreflooding experiments.

Fig. 3. Phase behavior of DC oil and 1 wt.% surfactant + 1 wt.% NaOH with varying NaCl weight fraction (at 48 °C).

Fig. 4. Phase behavior of DC oil and 1 wt.% Na₂CO₃ with varying NaCl weight fraction (at 48 °C).
3.2. Fluids and interfacial properties

Results from rheological analysis show that the polymer solutions all exhibit bulk shear-thinning behavior, i.e. the viscosity decreases with increasing shear rate. As shown in Fig. 8, the viscosity of ASP blend is higher than the viscosity of polymeric solution at different shear rates which is mainly due to the higher concentration of polymer in ASP blend (2000 compared to 1000 ppm). The results of IFT measurements at different NaCl and alkali weight fractions are depicted in Fig. 9. As shown (top figure), Blend 5 with the weight fractions of NaOH and Na₂CO₃ kept constant and NaCl varied, results provide ultra-low IFT between DC crude oil and brine in a wide range of salinity. The minimum IFT for both alkalis occurs at approximately 10,000 ppm of NaCl, although the minimum value for NaOH (point A) is somewhat lower than Na₂CO₃ (point B) which agrees with the visual phase behavior. Fig. 9 (bottom figure) shows that at constant NaCl weight fraction and varied amounts of NaOH and Na₂CO₃, even 1 wt.% surfactant alone can reduce IFT significantly and adding alkali enhances IFT reduction. Also using NaOH allows for lower IFT values as compared to using Na₂CO₃, though not significantly. It should be pointed out that at higher weight fractions of NaCl (15,000–30,000-region M in Fig. 9), the IFT values between oil and aqueous phases for both Na₂CO₃ and NaOH become closer and their corresponding visual phase behavior becomes quite similar as well [Fig. 9-top].

3.3. ASP flooding experiments

Pressure drop across the core was acquired and plotted with oil recovery for each of the three coreflooding experiments. The results of the first ASP flood on the Berea core are shown in Fig. 10. Here, the injection of the ASP blend in tertiary mode recovered almost all of the residual oil left behind after secondary waterflooding. As shown, the generated oil bank by ASP was produced...
mostly during polymer drive and subsequent post brine flooding. Note that recovery factors in all coreflooding experiments are estimates with approximately 5% error. De-emulsifiers or emulsion breakers could have been used to reduce this error, but in order to accurately measure surfactant concentration, they were not used. Produced emulsions types were identified through optical microscopy. It was observed that W/O emulsions in this experiment were not stable and turned into O/W emulsions after one day.

Surfactant concentration and pH (Fig. 10) show that the injected amount of surfactant and alkali were high enough to sustain favorable conditions for chemical flooding in this test. Additionally, even after switching to a 4 PV post waterflood, the pH of effluent remained higher than 10. This indicates no active mechanism to irreversibly buffer pH under this test's conditions. Effluent samples also displayed traces of surfactant even after 4 PVs of waterflooding lending to favorable surfactant retention. As mentioned earlier, permeability of oil and water at different steps were calculated and are reported in Table 2.

The second ASP flooding experiment was done keeping everything the same, except rock type. Here the experiment was performed on a Minnelusa core plug, which is known to contain anhydrite. From Fig. 11, the proposed ASP formulation is shown to perform well, yielding 30% incremental recovery after secondary waterflooding.
There are some interesting differences between the first and second ASP experiments resulting from the mineralogical differences. In the second ASP experiment, both O/W and W/O emulsions were produced. The emulsions turned out very stable when compared to the first ASP flooding test results (not shown). The apparent more stable W/O emulsions here could be attributed to the higher concentration of calcium ion in the second test. As shown in published work [17], when anhydrite is present there is always a certain amount of calcium in the aqueous phase that depends on pH. A relationship between W/O emulsion stability and calcium concentration has been observed with crudes from Wyoming at low brine salinity [24]. In contrast with the results with the Berea core, pH at effluent decreased down to 8 (Fig. 11) during the post waterflood on the Minnelusa core. This indicates an irreversible sink for OH\textsuperscript{-} under the conditions of this test. This sink might result from precipitation of secondary minerals [17].

<table>
<thead>
<tr>
<th>Description</th>
<th>Permeability (mD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial brine permeability ($S_w = 1$)</td>
<td>55.5</td>
</tr>
<tr>
<td>Oil permeability at $S_w = 1$</td>
<td>218.7</td>
</tr>
<tr>
<td>Brine permeability at $S_w$</td>
<td>24.1</td>
</tr>
<tr>
<td>Brine permeability at the end of the test</td>
<td>27.4</td>
</tr>
</tbody>
</table>

Fig. 12 visually compares the collected effluent samples of the first and second ASP tests. It can be observed that the designed ASP blend performed better in the Berea as compared to the Minnelusa core, which is attributed to the different mineralogy, particularly anhydrite. Unlike the first ASP flood on Berea, during the second ASP flooding test, some particles accumulated in the collected samples tubes (Fig. 13). This might be a sign of fine migration or secondary mineral precipitation under the conditions of the second ASP flood. The fines were analyzed to find out their origin. Fig. 13 indicates that the accumulated particles in the sample tubes were mainly calcite, generated by rock-fluid interaction during the NaOH invasion in presence of anhydrite and dolomite as reported [17].

The distribution of anhydrite along the core after ASP flooding is depicted in Fig. 14. This shows two important facts, first, anhydrite is distributed all throughout the core and secondly, anhydrite dissolution took place mainly in the inlet section and partially in the mid-section of the core. Permeability of oil and water at different steps of this test were calculated as well and are reported in Table 3.

The results of the third ASP flood using another Minnelusa core are shown in Fig. 15. As aforementioned, the main difference between second and third experiments is a 50% decrease in the concentration of surfactant and alkali. It can be observed that an even smaller amount of designed surfactant blend and NaOH is able to improve recovery factor, although the incremental recovery after...
secondary waterflooding of this test is not as significant as second coreflood (15% compared to 30%).

3.4. Effect of Ca$^{2+}$ ion on the performance of the designed ASP blend

As speculated earlier, the recovery from the injection of the ASP blend in the Minnelusa plug was lower than that in Berea likely due to the presence of anhydrite. To test this hypothesis, a specific bottle test was carried out to investigate the presence of calcium ion on the performance of the ASP blend. For each bottle, different amounts of CaCl$_2$.2H$_2$O were added to the blend of 1 wt.% NaOH + 1500 ppm of NaCl + 1 wt.% surfactant and mixed thoroughly. After one hour in the oven at 48°C precipitation was observed. The solution was extracted through a filter in 6 mL aliquots into pipettes for the representative aqueous phase. Next, 6 mL of DC crude oil was added to complete the bottle test exper-
iment (as sketched in Fig. 16). It should be mentioned that at each step, the added amount of calcium chloride was selected to keep the salinity constant, shown in Fig. 3. The purpose for this sequence was to mimic the effect that anhydrite plays in reacting with NaOH to cause calcium precipitation. However, some calcium still exists in the system, which can have a detrimental effect on the phase behavior of the surfactant-soap system as shown in Fig. 17. It can be observed that the presence of calcium ion in the aqueous phase inhibits the ASP blend from performing well by reducing its ability to emulsify oil. At a high concentrations of calcium (above 700 ppm), the designed ASP blend in this study might not improve oil recovery as well as expected.

Further investigation into harmful effects that Calcium ions caused on the surfactant-soap system are shown in Table 4. Here, surfactant concentration was tracked at various amounts of Ca\(^{2+}\) following the appointment procedure. Results show that surfactant weight fraction was only reduced from 8–14% after CaCl\(_2\).2H\(_2\)O was added, indicating that Ca\(^{2+}\) was not causing significant surfactant dropout. It could be conjectured that Ca\(^{2+}\) causes unfavorable phase behavior to either the generated in situ soaps or the surfactant synthetic. As a result, the surfactant-soap system becomes ineffective.

Cloud point test results reveal that at reservoir temperature, the aqueous phases with 1 wt.% surfactant and 1 wt.% NaOH at salinity above 15,000 ppm of NaCl showed poor solubility and stability. This should not affect the ASP flooding design, as the DC formation is less the 12,000 ppm TDS.

Appendix B presents forward simulation results that indicate that the selected ASP blend could improve oil recovery significantly at field scale.

Table 3
Permeability values for oil and water at different steps (second ASP test).

<table>
<thead>
<tr>
<th>Description</th>
<th>Permeability (mD)</th>
</tr>
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<tbody>
<tr>
<td>Initial brine permeability (Sw = 1)</td>
<td>152</td>
</tr>
<tr>
<td>Oil permeability at Swi</td>
<td>429</td>
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<tr>
<td>Brine permeability at Sor</td>
<td>42.5</td>
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<tr>
<td>Brine permeability at the end of the test</td>
<td>78.8</td>
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</table>

Fig. 14. Anhydrite distribution along the Minnelusa core after the second ASP flooding test: (a) inlet section of the core, (b) midsection of the core, and (c) outlet section of the core (light-gray color represents anhydrite).

Fig. 15. Pressure drop and oil recovery data obtained from third ASP flood in Minnelusa sandstone (top) and measured pH and surfactant concentrations at effluent (bottom).
4. Conclusion

1. The proposed ASP formulation, resulting from blending a surfactant with the appropriate cosurfactant, turns out to be effective under low salinity conditions. This was demonstrated in phase-behavior and coreflooding experiments.

2. Secondary mineral precipitation during ASP treatment is inferred from our observations, most likely as a result of anhydrite dissolution. This can lead to permeability reduction (injectivity loss), particularly in low-permeability formations and also fine accumulation in production facilities.

3. The type of alkali agent and its initial concentration are paramount to achieve optimum phase behavior in the surfactant-soap system. In this study, NaOH with a concentration between 0.5 and 1 wt.% is suggested. The speculated effects of alkali type are adequate natural surfactants and sufficiently high pH for the case of NaOH in contrast with Na₂CO₃.

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Table 4
Surfactant in presence of Ca²⁺:

<table>
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<tr>
<th>Ca²⁺ (ppm)</th>
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<th>728.3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surf. (wt.%)</td>
<td>1</td>
<td>0.915</td>
<td>0.901</td>
<td>0.90</td>
<td>0.859</td>
</tr>
</tbody>
</table>

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![Fig. 16. The schematic diagram showing the steps taken in the new bottle test experiment (effect of Ca²⁺ on the ASP blend performance).](image1)

![Fig. 17. Phase behavior of DC oil and 1 wt.% surfactant + 1 wt.% NaOH with varying CaCl₂/H₂O weight fraction (at 48 °C).](image2)

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Appendix A. Phase-behavior

Additional experiments were carried out to identify different impacts of NaOH and Na2CO3 on oil emulsification and partitioning of organic matter from the DC crude oil into the aqueous phase. In this test, nine beakers were filled with 40 mL of 1600 ppm NaCl brine plus various amounts of alkali (NaOH or Na2CO3), and then 40 mL of DC crude oil were poured in. Before adding the oil, a hollow glass tube (for pH measurement) and a small magnetic stir bar were placed in the aqueous phase. The concentrations of alkali were varied as follows: 0, 200, 500, 1000 and 1500 ppm of both NaOH and Na2CO3. Each beaker was put in the oven at 48 °C for three days while the aqueous phase was gently mixed. The pH of this phase was measured every day and is reported in Fig. A.18. All the trends show a decrease in pH as compared to the initial values showing the migration of acidic material from oil phase into the aqueous phase. Physical observation of the phase-behavior and the value of total organic carbon (TOC) of the aqueous phase are plotted in Fig. A.19. This clearly shows that the TOC values at this phase was measured every day and is reported in Fig. A.18. This clearly shows that the TOC values at this phase was measured every day and is reported in Fig. A.18. This clearly shows that the TOC values at this phase was measured every day and is reported in Fig. A.18. This clearly shows that TOC values and phase behavior of different alkali solutions after 3 days.

Appendix B. Numerical simulation

The pseudo-compositional simulator CMG-STARS (with CMOST) [25,26] was used to complete an assisted history match of the two-phase flow experimental results (ASP2). The coreflood model consists of a 1D Cartesian model. Three relative permeability curves are initially assigned for water, ASP and final polymer floods. The choice of relative permeability set is governed by a Capillary Number (CN) threshold which varies with each step of the flood. In situ CN is calculated internally by the simulator using Eq. (B.1) under flooding conditions:

\[ N_c = \frac{\nu \mu}{\sigma} \]  

where \( \nu \) is Darcy velocity, \( \mu \) is the viscosity of displacing fluid and \( \sigma \) is the interfacial tension (IFT) between displaced and displacing fluids.

The transmission rate of additives such as surfactant, polymer and alkali is affected by fluid-rock interactions. CMG-STARS handles these interactions through mechanistic models. In this study, a Langmuir isotherm is used in the following form (B.2):

\[ Ad_i = \frac{a_i}{1 + b_i z_i} \]  

where \( z_i \) is the concentration of species in the solution and, \( a \) and \( b \) are constant values for each species and generally are temperature dependent. The adsorption of alkali, surfactant and polymer, determined through static adsorption tests, are 55, 11 and 7 mg gr of rock respectively (based on static adsorption tests). History-match parameters include: endpoint values and exponents of the Corey relative permeability parameters for oil and water in each set, the maximum adsorption values of surfactant and polymer, reversibility degree of adsorption isotherm for each adsorbed species, flexibility in permeability of the rock values, and the resistance factor of polymer. This resistance factor links local absolute permeability with local adsorption level. It is assumed that only one-phase paths are altered. For instance, water phase permeability reduction factor is defined as (B.3):

\[ RKW = 1.0 + (RRF_i - 1) \frac{Ad_i}{Ad_{MAX_i}} \]  

where \( RKW \) is the water permeability reduction factor, \( RRF \) is the resistance factor of species iAdi is the amount of adsorbed species calculated from Eq. (B.2) and AdMAXi is the maximum adsorption level of species i from static adsorption tests. The objective function corresponds with a combination of cumulative oil recovery factor, pressure drop, and surfactant concentration at effluent.

Fig. A.19. TOC values and phase behavior of different alkali solutions after 3 days.

Fig. A.18. Trends for pH with different alkali solutions after aging 3 days in contact with DC crude oil (at 48 °C).
The results of the second ASP flood were history-matched in two different scenarios and the best-matched cases were used for forward simulations to forecast the performance of the proposed ASP blend in a field scale situation.

As a first step, sensitivity analysis was performed to find the weight factor of each manipulating variable on each term of the objective function. In this sensitivity analysis, the objective function had three terms: cumulative oil recovery, pressure drop, and surfactant concentration. It turns out that the most dominant parameters affecting oil recovery are the curvature of the oil relative permeability curve at high CN, the endpoint value of the water relative permeability curve at high CN, and also the resistance factor of polymer. For pressure drop, the degree of reversibility of surfactant adsorption, the endpoint value of the water relative permeability curve at high CN, and the adsorption of polymer and its degree of reversibility are the most important conditions. Additionally, the amount of adsorbed surfactant and its degree of reversibility are the key parameters which impact produced surfactant concentration. Further, the results of sensitivity analysis were used to build an appropriate influence matrix.

In the first scenario, the objective function is cumulative oil recovery factor. Results of the automated history match process shown in Fig. B.20 reveal that the history matching of oil recovery

![Fig. B.20. Results of history match process of first scenario.](image1)

![Fig. B.21. Results of history match process for second scenario.](image2)
factor was successful and the error of objective function compared to experimental data was 2.4%.

In the second scenario, the objective function has two equally weighted terms, cumulative oil recovery factor and pressure drop. Additionally, in this case, the surfactant concentration was selected as a monitoring parameter. This scenario yields a larger error compared to the first one, although it is more representative (Fig. B.21). The best matched case has 9.96% error compared to experimental data. The observed larger error in this case can be attributed to the generation of emulsions and microemulsions and their mobilization in porous media, which can possibly affect both pressure drop and oil recovery under the conditions of this test.

In the next step, the optimum solutions from scenario one and two were taken to forward simulation to predict the efficiency of the found blend on a field scale. This hypothetical field case is a 3D model corresponding a heterogeneous quarter of a 5-spot pattern containing five layers with vertical communication. The 3D model is $288 \times 288 \times 20$ m ($x \times y \times z$) in size with $100 \times 100 \times 5$ Cartesian grid blocks along the $x$, $y$, and $z$ directions, respectively. The permeability in the $x$ and $y$ directions are the same and vertical permeability is one tenth of the lateral permeability. Each layer has different permeability and thickness which varies from top to bottom as follows: 80, 90, 100, 110, 120 mD and 4, 5, 4, 5, 2 m respectively. The injection rate was kept constant during flooding steps at 909 m$^3$/day and the producing well worked at a minimum bottom hole pressure of 500 psi. The flooding sequence was as follows: 4 PV injection of water, 0.3 PV injection of ASP blend, 0.3 PV injection of polymeric solution, and 2 more PV of re-injected water. The chemical composition of ASP and polymeric blends were kept the same as the ones used in the first two ASP flooding tests of this study.

The results of the forward simulation on the basis of the obtained optimum solution in the first scenario are plotted in Fig. B.22. Fig. B.22 shows that eventually ASP flooding can recover significant amounts of oil compared to waterflooding alone, although, there is a large lag time between ASP injection and oil bank generation. The results of forward simulation on the basis of obtained optimum solution in the second scenario are plotted in Fig. B.23. Results of forward simulation using the best matched case in the first scenario.

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in Fig. B.23. Similar to the results of the first scenario, the results of the second one reveals that the ASP injection yields significant oil recovery compared to just waterflooding. In contrast to the first forward simulation, oil bank generation took place right after switching to post brine flooding indicating that there is no large delay.

References


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