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Novel Coupling Smart Water-CO₂ Flooding for Sandstone **Reservoirs**

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<code>Novel</code> Coupling Smart Water-CO₂ Flooding for Sandstone Reservoirs $^{\rm 1}$

Hasan N. Al-Saedi^{2, 3} and Ralph E. Flori²

ABSTRACT

CO₂ flooding is an environmentally friendly and cost-effective EOR technique that can be used to unlock residual oil from oil reservoirs. Smart water is any water that is engineered by manipulating the ionic composition, regardless of the resulting salinity of the water. One CO₂ flooding mechanism is wettability alteration, which meets with the main smart waterflooding function. Injecting $CO₂$ alone increases the likelihood of an early breakthrough and gravity override problems, which have already been solved using water-alternating-gas (WAG) using regular water. WAG is an emerging enhanced oil recovery process designed to enhance sweep efficiency during gasflooding. In this study, we propose a new method to improve oil recovery via synergistically smart brine with $CO₂$. This new method takes advantage of the relative strengths of

INTRODUCTION

 The injected water ionic composition has surprising and interesting effect on the efficiency of waterflooding. Previously, we reported that the concentration of Ca^{2+} and Mg^{2+} affects the wettability alteration of sandstone reservoirs (Al-Saedi et al., 2019a, 2019b). In this study, we investigate NaCl removal from the brine and combine the resulted optimum smart water with immiscible CO₂ flooding to propose a new water-alternating-gas (WAG) process instead of using regular water that used in WAG to provide more oil recovery from heavy-oil reservoirs. We also studied replacing regular water used in WAG with low-salinity (LS) water to attain more oil recovery by altering the sandstone wettability and enhancing gas sweep efficiency (Al-Saedi et al., 2019b).

 Recently, the interest in WAG has increased noticeably to enhance the gas sweep efficiency. The produced gas has been employed in pressure maintenance and enhanced oil recovery (EOR) by contacting the unswept zones, improving gas mobility, and improving microscopic sweep efficiency. The environmental issues, taxes on $CO₂$, and the regulations

both processes. We hypothesized that brine depleted in NaCl provides more oil recovery. We also determined that depleting NaCl in brine is not the end of the story; diluting divalent cations/anions in the brine depleted in NaCl provides higher oil recovery. Injecting smart brine depleted in NaCl with diluted Ca^{2+} and CO_2 resulted in a high oil recovery percentage among the other scenarios. Thus, the above water design was applied as a WAG in three cycles, which resulted in a much higher oil recovery of 24.5% of the OOIP. This improved heavy-oil recovery is a surprising and promising result. The spontaneous imbibition agreed with the oil-recovery results. This study sheds light on how manipulating ions in the water used in WAG can significantly enhance oil recovery.

of gas flaring are other advantages of reinjecting the gas (Christensen et al., 1998).

The main functions of injecting CO_2 are (1) oil swelling, (2) viscosity reduction, and (3) wettability modifications. The third function works synergistically with smart water in wettability alteration towards being more water-wet. Wettability plays a significant role in the performance of EOR methods. Rock wettability can be determined by the thickness of the water film between the rock surface and the crude oil (Hirasaki, 1991). Wettability can be determined by various methods, such as Amott-Harvey, contact angle, the United States Bureau of Mines (USBM), chromatographic separation method for carbonate, and chromatographic separation method for sandstone (Amott, 1959; Donaldson et al., 1969; McCaffery, 1972; Anderson, 1986; Strand et al., 2006; Al-Saedi et al., 2018a). Numerous studies have shown that using smart water can alter the rock wettability and increase oil recovery in both carbonate and sandstone reservoirs (RezaeiDoust et al., 2009, 2011; Strand et al., 2009; Fathi et al., 2010, 2011; Austad, 2013; Ghosh et al., 2016; Strand and Puntervold, 2018; Al-Saedi et al., 2018c). Other than the multifunctional features that CO_2 provides,

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rock-wettability alteration is one of the main advantages (Stalkup, 1987; Grigg and Schechter, 1998; Grigg, 1999; Ghedan, 2009; Salem and Moawad, 2013).

 The resulting residual oil saturation after the WAG process $(CO_2$ alternating with LS water) is lower than the residual oil saturation from waterflooding alone and CO₂ flooding alone (Wylie and Mohanty, 1999). The remaining oil saturation after WAG by LS water is lower than that in WAG using formation water (FW) (Al-Saedi and Flori, 2019). We believe that smartening the water will provide a lower residual oil saturation. To our knowledge, no experimental studies have been performed to consider brine composition manipulation combined with CO₂ flooding. A series of coreflooding experiments and spontaneous imbibition tests have been carried out to investigate the proposed study. Heavy crude oil and reservoir sandstone core plugs were used to apply the mentioned theory. It is worth mentioning that all CO₂ flooding in this study was carried out in the immiscible state.

 The brine was prepared at our laboratory, and we manipulated its composition. Smart brine depleted in NaCl means the NaCl is zero ppm. This study investigates smartening brine and combines it with $CO₂$ in the areas close to the brine due to the cost issues. However, we can smarten the FW produced from Bartlesville reservoir the same way we did with brine and combine it with CO_2 .

EXPERIMENTAL METHODOLOGY

 In order to evaluate our new proposed method, several successively coreflood experiments of smart water and CO₂ were conducted. The coreflood experiments include injection

of the brine, smart brine sequentially, and ultimately $CO₂$ in reservoir sandstone cores taken from Bartlesville Sandstone reservoir (eastern Kansas). The coreflood experiments provided promising results that could change the traditional EOR methods.

The cores were delivered fully saturated with reservoir fluids and well coated with plastic wrap. Because the cores were bearing heavy oil, the following procedure was carried out:

- 1. The cores were cleaned by injecting kerosene until a clear effluent was observed.
- 2. Toluene was then pumped to displace the kerosene and to achieve extra cleaning.
- 3. Water with 3,000 ppm NaCl replaced toluene and for dissolving formation water (FW) fluids.
- 4. The cores were then transferred to a Soxhlet extractor for further cleaning.
- 5. The cores spent one day drying in the oven at 80°C.

 The cores were then transferred to a vacuum container for evacuation purposes. A 1-day vacuum was performed on all the cores; after that, synthetic FW with salinity of 104,000 ppm was presented to the cores under vacuum. FW basically consists of NaCl, CaCl₂, MgCl₂, Na₂SO₄, and KCl. Brine contains the same salts except for KCl; the brine description is shown in Table 1. The XRD test on the reservoir core fragments indicated that the abundant minerals are quartz followed by clays. Crude oil was delivered from the same reservoir with a viscosity around 600 cP and 0.83 g/cm³ density. The crude oil was diluted with heptane in a 10/90 heptane/oil ratio. The resulting oil properties after dilution are shown in Table 2.

Table 1—Composition of the Injected Brine (mg/l)

| Compound | FW | Brine | B-0NaCl | SMB1 0 NaCl- d_{5Ca} | | \mid SMB2 0NaCl—d _{5Mg} \mid SMB3 0NaCl—d _{5SO4} |
|---------------------------------|-----------|--------------|----------------|--------------------------|-------|--|
| NaCl | 81,000 | 25,000 | | | | |
| CaCl ₂ | 17.000 | 2.000 | 2,000 | 400 | 2,000 | 2,000 |
| MgCl ₂ | 5.000 | 10.500 | 10.500 | 10.500 | 2.100 | 10,500 |
| Na ₂ SO ₄ | | 4.900 | 4.900 | 4.900 | 4.900 | 980 |
| KCI | 1.000 | | | | | |
| TDS | 104,000 | 43,400 | 18,400 | 15,800 | 9.000 | 13,480 |

SMB - smart brine

Table 2—Crude Oil Properties

| Viscosity | Density | TAN | TBN |
|-----------|----------------------|------------|------------|
| (cP) | (a/cm ³) | (mq KOH/q) | (mg KOH/g) |
| 150 |).821 | .01 | |

TAN – total acid number; TBN – total base number.

 Porosity was measured by the weight difference between dry and wet weight. To saturate FW in the cores, a high injection pressure of 1,000 psi was applied with an injection rate of 0.25 ml/min. FW was injected into the core to measure permeability using different flow rates. The criteria for changing the flow rate was obtaining a constant pressure. The FW was then displaced by 3 pore volumes (PVs) crude oil in both directions to establish the irreducible water saturation $S_{\mu\nu}$ taking the same permeability measurement criteria in addition to no water observation in the effluent. To saturate crude oil in the cores, the same FW saturation procedure was performed. The cores were then aged in the crude oil for 3 weeks at 90°C to bring back the initial wettability.

After pre-aging duration has completed, the cores were then flooded with 2 PVs brine followed by 3 PVs smart brines (SMB) (SMB are described in Table 1), and then 5 PVs of $CO₂$ at 50°C. Brine and SMB were injected into the cores until no more oil was produced and the stabilized pressure was observed. The reservoir cores were flooded using the following scenarios:

- 1. RC16a was flooded with $CO₂$ only.
- 2. RC17a was flooded with brine followed by $CO₂$.
- 3. RC17b was flooded with brine followed by B-0NaCl and $CO₂$.
- 4. RC17c was flooded with brine followed by SMB1 and $CO₂$.
- 5. RC17d was flooded with brine followed by SMB2 and $CO₂$.
- 6. RC17e was flooded with brine followed by SMB3 and $CO₂$.

7. RC17e was flooded with brine followed by SMB3 and $CO₂$ but in shorter cycles using our proposed design for low-salinity-alternating-steam-flooding (LSASF) (Al-Saedi et al., 2018b), which was $0.5 \text{ PV } CO_2 + 0.5$ ${\rm SMB3 + 0.5~PV~CO_2 + 0.5~PV~SMB3 + 0.5~PV~CO_2 +}$ 0.5 PV SMB3.

The pressure across the core during coreflooding experiments was recorded using a pressure transducer on both sides of the core holder. A confining pressure 600 psi higher than injection pressure was applied on the sandstone reservoir core plugs. The entire experimental equipment was installed inside the dispatch oven, which was set on 50°C (Fig. 1). The minimum miscible pressure (MMP) was above 2,000 psi. The backpressure regulator was established at 1,200 psi, which provides immiscible $CO₂$ conditions.

Contact-Angle Measurements

The same brines that were used in the coreflooding experiments were also used for this test. The core substrates were cut and sanded on two sides using fine sandpaper. The substrates were treated with air to remove mineral fins and were then rinsed with deionized water and treated again with air. The wet substrates were mounted in the oven to dry. The substrates were then attached to the glass platelet by glue. The specified brine was poured into the test chamber, and the entire glass platelet and the substrate were immersed inside the chamber until the substrate was immersed completely in the brine. The oil droplet was initiated via needle underneath the substrate until the droplet attached to the substrate surface. The light source and digital camera in the Ramé-

Fig. 1–Schematic of the coreflooding system.

hart advanced goniometer 500-F1 were used to measure contact angle using the pendant-drop method.

Spontaneous Imbibition Test

 For further wettability investigation of our proposed procedure, an imbibition test was conducted using the Amott cell. The cores that were used in the coreflooding experiments were cleaned as described previously and used in a spontaneous imbibition test. This was performed to limit the measurements' uncertainty due to mineralogy. Five brines were used, brine, B–0NaCl, SMB1, SMB2, and SMB3. Cores RC17a, RC17b, RC17c, RC17d, and RC17e were immersed in an Amott cells filled with brine, B–0NaCl, SMB1, SMB2, and SMB3, respectively. The cores were immersed in the imbibing fluid for 20 days.

RESULTS AND DISCUSSION

CO2 Flooding

 The results of this experiment are plotted vs. injected PVs in Fig. 2. In this experiment, only CO_2 was injected to compare our findings with injecting gas only. RC16a was allotted for this experiment. The total injected pore volumes were 5 PVs. No oil recovery was observed at the beginning of CO₂ flooding. The oil produced out the core after injecting 0.25 PV CO₂. The pressure drop started at zero and kept increasing until reaching 7.4 psi after injecting 0.7 PV $CO₂$; thereafter, the pressure declined. The inclination of the pressure to decline began when the CO_2 breakthrough occurred, which is marked by the red point on the oilrecovery curve. The oil recovery increased linearly until the gas breakthrough. The oil recovery at the gas breakthrough point was 38%. The gas breakthrough causes oil recovery

to reduce before injecting one complete PV (as usually happens when injecting water). However, the oil recovery increased slowly from the 0.7 PV point until injecting a total of 2.1 PV $CO₂$. At this point, the oil stopped flowing out of the system until all 5 PVs CO_2 was injected. The total oil recovery was 45.8% of the original oil in place (OOIP). The pressure dropped from 7.4 psi at the breakthrough until reaching 0.1 psi. As can be seen from this experiment, an early breakthrough occurred because of the low $CO₂$ density.

Brine and CO₂ Flooding

 This experiment was conducted on RC17a. Contrary to the previous experiment, the core was flooded initially with brine in the secondary recovery mode, and then followed with $CO₂$ in the tertiary recovery mode. As discussed earlier in the methodology section, 2 PVs of brine were injected initially, followed with 5 PVs $CO₂$. This experiment was conducted in order to illustrate what would happened if we inject water before $CO₂$ in contrast to the previous experiment. The oil recovery due to injecting 2 PVs brine was 43.64% of the OOIP. This recovery percentage was lower than injecting $CO₂$ alone. Despite poor sweep efficiency, $CO₂$ has multiple functions in improving oil recoveries, such as oil swelling and viscosity reduction. However, upon switching to $CO₂$ flooding, the oil recovery improved to 47.64% of the OOIP, meaning that injecting 5 PVs of $CO₂$ after brine provided 4% of the OOIP. The results of this experiment are shown in Fig. 3. The injected PVs in this experiment are larger than 2 PVs, but the oil recovery stopped to increase after injecting less than 2 PVs of CO_2 . Thus, the PV differences cannot be considered as an influencing factor. As a result, the total oil recovery from this experiment is higher than the previous one that injected CO_2 only. It is obvious that injecting brine

Fig. 2—Oil recovery factor and pressure drop across RC16a after injecting 5 PVs of CO₂ only (Al-Saedi et al, 2019a).

Fig. 3—Oil recovery factor for RC17a after injecting 2 PVs of brine as a secondary recovery mode and 5 PVs of CO₂ as a tertiary recovery mode.

before CO_2 was able to improve the CO_2 sweep efficiency, and in turn, the oil recovery was improved too.

Brine, B-0NaCl, and CO2 Flooding

 In this experiment, the effect of NaCl depletion in brine was investigated. The coreflooding procedure was injecting 2 PVs brine in the secondary recovery mode followed by 3 PVs B–0NaCl and then 5 PVs $CO₂$. By injecting 2 PVs brine the oil recovery was 43.4% of the OOIP, which was similar to that in the previous experiment $(43.4 \text{ vs. } 43.64\%)$. This indicated that the reservoir cores and the experimental conditions were similar. The next experiment injected 3 PVs of B–0NaC, which provided 2.85% of the OOIP, meaning that removing NaCl from brine can be more beneficial than injecting brine as it is. This result of B–0NaCl can be applied in waterflooding, WAG or any EOR method. However, the injected fluid was then switched to $CO₂$, and the oil recovery resulting from injecting 5 PVs of CO_2 was 6.45% of the OOIP. The improved oil recovery in this experiment was higher than the previous one and the CO_2 -only experiment. This higher recovery occurs from injecting the brine depleted in NaCl. Removing NaCl from brine can alter sandstone wettability towards water-wet status (see imbibition and contact-angle tests). The active cations that affect EOR performance in sandstone were discussed in previous studies (Al-Saedi et al., 2019a, 2019b). We found that Ca^{2+} and Mg^{2+} are the most effective cations, Ca²⁺ the most effective. In this experiment, the noneffective ions (i.e., NaCl) are investigated, and it seems to influence oil recovery. However, this will be explained in imbibition and contact-angle results. The total number of injected PVs was not effective since dead injected volume was the most abundant, as discussed in the previous experiment. The results are plotted in Fig. 4.

SMART WATER BRINES AND CO₂

 The objective of the following experiments was to verify if modified brine could enhance oil recovery, so that they can be merged with $CO₂$.

Brine, SMB1 and CO₂

 A similar secondary recovery mode was conducted by injecting brine as that in the previous experiments. The experimental procedure was injecting 2 PVs brine, 3 PVs SMB1, and 5 PVs CO_2 . SMB1 is B-0NaCl with diluting $Ca²⁺$ five times. The oil recovery due to brine flooding was also similar to that in the previous experiments, which means the conditions are the same for all the experiments. Injecting brine resulted in 44.2% of the OOIP. An additional 6.1% of the OOIP was observed after injecting SMB1. Diluting $Ca²⁺$ in the B-0NaCl added additional positive effect on the brine EOR flooding. It is clear that manipulating the brine composition affects the oil recovery. The improved oil recovery in this experiment was higher than the previous one (6.1 vs. 2.85%).

 The additional oil recovery from sandstone reservoirs is mostly due to wettability alteration towards being more water-wet. Diluting Ca^{2+} five times triggers the wettability of the sandstone core plug to be altered towards water-wet. This water-wet condition is also a favorable condition that must be present before CO₂ flooding to obtain a higher oil recovery. For that, the oil recovery after injecting 5 PVs of $CO₂$ provided an additional oil recovery of 13.15% of the OOIP, which was undoubtedly the highest among the previous experiments. This higher recovery can be explained by the decreased solubility of the $CO₂$ in brine as the divalent cations decreased. This low solubility in brine redirects CO₂

Fig. 4—Oil recovery factor for RC17b after injecting 2 PVs of brine as a secondary recovery mode and 3 and 5 PVs of B–0NaCl and CO₂ as a tertiary recovery mode, respectively.

Fig. 5—Oil recovery factor for RC17c after injecting 2 PVs of brine as a secondary recovery mode and 3 and 5 PVs of SMB1 (B–0NaCl—d_{sca}) and $CO₂$ as a tertiary recovery mode, respectively.

to be more soluble in the crude oil, which helps to swell the oil and reduce its viscosity. We conducted CO_2 solubility in different brines, and as a result lower solubility of $CO₂$ was observed in the brine containing a lower Ca^{2+} concentration. It is worth mentioning that although the salinity of SMB1 is higher than SMB2 and SMB3, it produced more oil. The results are shown in Fig. 5.

Brine, SMB₂ and CO₂

 Completing the investigation of depleting NaCl in brine with manipulating other ions, this experiment was performed the same way as the previous one, but instead of diluting Ca^{2+} , this time Mg²⁺ was diluted five times. The initial 2 PVs of injected brine resulted in recovery of 42.55% of the OOIP, which was also similar to the previous experiments. After that, the SMB2 was injected. The injected 3 PVs of SMB2 resulted in a 4% improved oil recovery. This improved recovery percentage is lower than the previous experiment when Ca^{2+} was diluted five times because Ca^{2+} can get closer to the oil and mineral surfaces than Mg^{2+} and have a more significant effect. The explanation for the more substantial $Ca²⁺$ effect can be found in Al-Saedi et al. (2019c). A lower Mg^{2+} effect is undoubtedly influencing the CO₂ flooding as explained in the previous experiment. As was expected, the

improved oil recovery by CO_2 was lower than the previous experiment, which was 8.1% of the OOIP. The ultimate enhanced oil recovery of this experiment was 12.1% of the OOIP. Compared to the previous experiment, the improved oil recovery was 12.1 vs. 19.25%. The experimental results are shown in Fig. 6.

Brine, SMB3 and CO₂

 RC17e was allotted for this experiment. This experiment is the final investigation of manipulating ions in the brine depleted in NaCl. Similar to all previous experiments, 2 PVs of injected brine produced 42.6% of the OOIP. Upon switching to SMB3, the improved oil recovery was 3.8%, which was similar to that in SMB2 and way below SMB1. The SMB3 alters the wettability towards more water-wet, but SMB1 does not. The improved oil recovery due to $CO₂$ flooding provided 9.43% more of the OOIP. Results of this study are illustrated in Fig. 7.

 Up to this point, the highest oil recovery was observed when flooding RC17c with SMB1. SMB1 was clearly able to increase water-wetness more than the other smart water brines. So, the design published in Al-Saedi et al. (2018b) was applied using SMB1 to obtain a higher oil recovery from sandstone reservoirs bearing heavy oil.

Fig. 6—Oil-recovery factor for RC17d after injecting 2 PVs of brine as a secondary recovery mode and 3 and 5 PVs of SMB2 (B–0NaCl—d_{aMa}) and CO_2 as a tertiary recovery mode, respectively.

Fig. 7—Oil-recovery factor for RC17e after injecting 2 PVs of brine as a secondary recovery mode and 3 and 5 PVs of SMB3 (B–0NaCl—d_{5SO4}) and $CO₂$ as a tertiary recovery mode, respectively.

Brine and Wag of SMB1 and CO₂

 As stated previously, this experiment exploited the design in Al-Saedi et al. (2018b) to enhance the steam sweep efficiency. Three cycles of SMB1 and $CO₂$, 0.5 PV each in each cycle were conducted on RC17f. The secondary recovery mode, by injecting 2 PVs of brine, produced 43.4% of the OOIP, which was also similar to all coreflooding experiments conducted in this study. The pressure drop across this core was recorded to monitor the pressure behavior during the WAG process. The pressure drop across RC17f during brine flooding increased slowly until stabilizing at more than 4 psi. The first cycle of $SMB1-CO₂$ increased oil recovery noticeably. The observed improved oil recovery was 11.3% of the OOIP. Only 1 PV of SMB1-CO₂ produced oil more than B-0NaCl and CO_2 with many PVs. The second cycle resulted in another 8.15% OOIP. The first and second cycles both improved the oil recovery up to 19.45%, which represents the highest oil recovery of all the experiments conducted in this study with injecting only 2 PVs of SMB1 and $CO₂$. The improved oil recovery during the third cycle reached 5.5% of the OOIP. The total improved oil recovery from the WAG process was 24.5% of the OOIP. Only 3 PVs of SMB-CO₂ provided 24.5% of the OOIP. The optimum ion composition with the right selection of flooding design could extract vast quantities of heavy crude oil with fewer injected pore volumes and at lower cost. Injecting the first 0.5 PV of SMWS1 did not significantly affect the pressure-drop profile, but during CO₂ flooding, the pressure drop decreased dramatically due to its low density. The pressure profile maintained the same behavior of increasing and decreasing while injecting

SMB1 and $CO₂$ until the flooding was terminated at 5 PVs. The results of oil recovery and pressure drop versus injected pore volume are plotted in Fig. 8. The continuous

increase in pressure occurred after injecting 0.3 PVs of water injection might be due to fines migration, which blocked the pore throats and led to increasing pressure.

WETTABILITY INVESTIGATION

The same brines that were used in the coreflooding experiments were used in this test. The procedure is illustrated in the methodology section. The results of this test are shown in Fig. 9. As can be seen in Fig. 9, the lowest contact angle was observed with SMB1, confirming the vital role of depleting NaCl in brine in addition to diluting Ca^{2+} . The importance of depleting NaCl in brine can be seen from the contact-angle difference between brine and B–0NaCl. The other smart water brines showed a low contact angle but higher than SMB1.

 On the other hand, spontaneous imbibition test results agreed with the contact angle and coreflooding experiments results. The brines imbibed into the cores and the oil released from the core in an average 15 days. The imbibition observation was terminated after 20 days, when there was no more oil floating in the Amott cell. As expected, the highest oil recovery was observed in the core imbibed in SMB1. This observation confirms the role of SMB1 in altering wettability of the sandstone core plug into a water-wet condition. The same was observed for both SMB2 and SMB3 but at lower oil recovery percentage. As expected, the oil recovered from the core imbibed in the B–0NaCl was higher than that in the brine. Depleting NaCl in brine triggers wettability alteration of the sandstone core plug towards more water-wet. The imbibition test results are shown in Fig. 10. Even though the salinity of SMB1 is higher than SMB2 and SMB3, the extracted oil from the core imbibed in SMB1 is greater.

Fig. 8—Oil recovery factor for RC17f after injecting 2 PVs of brine as a secondary recovery mode and three cycles of SMB3 (B–0NaCl—d_{5Ca}) and $\text{CO}_2^{\text{}}$ (3 PVs total, each cycle 0.5 PV of each) as a tertiary recovery mode, respectively.

Fig. 9—Contact-angle results of the brines used in this study.

Fig. 10—Oil recovery results from imbibition test.

CONCLUSIONS

 This study was presented with the purpose of extracting more oil from sandstone reservoirs bearing heavy oil. Usually, heavy-oil reservoirs are treated with thermal EOR methods, which are considered expensive and have technical difficulties, such as heat loss in the reservoir and require the presence of a thick pay zone. However, we propose different chemical compositions of brine be injected with $CO₂$ instead of regular water, which provides only sweep efficiency enhancement. Brine could be more beneficial than regular water if its composition is engineered perfectly. Depleting NaCl in brine was one of our solutions and provided 10% more OOIP than brine with $CO₂$. We also manipulated the depleted brine in NaCl in order to extract as much heavy oil as possible. The results of this study indicate that if brine is depleted in NaCl and then the concentration of Ca^{2+} is diluted five times, the improved oil recovery could reach 19.25% of the OOIP. The results also show that if the same water mentioned above is alternated with CO_2 in smaller slug size, the improved oil recovery can reach 24.5% of the OOIP. The other ion manipulation resulted in a higher oil recoveries of 12.1 and 13.23%. It is worth mentioning that the total injected pore volumes of SMB1 alternating $CO₂$ were lower

than the entire experiments in this study. Thus, this design provided a higher heavy-oil recovery and lower operational cost at the same time. Also, SMB1 salinity is higher than in SMB2, and SMB3 indicated that salinity reduction does not always provide higher recovery. We believe that further investigation of diluting/depleting Ca^{2+} and/or the other divalent cations/anions in brine could result in higher oil recovery than what we observed in this study.

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