Effect of Low Salinity Water Injection on Capillary Pressure and Wettability in Carbonates

Farzin Vajihi, Pedro Diaz, Ivy Sagbana, Hassan Zabihi, Arash Farhadi, Saham Sherhani London South Bank University

This paper was prepared for presentation at the International Symposium of the Society of Core Analysts held in Vienna, Austria, 27 August – 1 September 2017

ABSTRACT

In the past decade, much attention has been pointed toward Low Salinity Water Injection (LSWI) as an efficient oil recovery technique. Despite compelling laboratory evidence of LSWI and smart water potential, the underlying mechanisms causing the incremental oil recovery in carbonate rocks are still controversial. Several studies have indicated that wettability alteration is the primary mechanism for LSWI. However, high temperature was required to observe this wettability alteration in majority of cases. This paper presents the effect of LSWI and smart water on the wettability of limestone at ambient conditions at the laboratory scale.

An ultra-centrifuge was used to measure the capillary pressure curve prior and after LSWI on four limestone core samples at ambient conditions. The end point from the imbibition capillary pressure data were used to calculate incremental oil recovery. U.S. Bureau of Mines (USBM) method was deployed to calculate wettability of the limestone core samples from forced drainage and imbibition capillary pressure curve. The effect of brine salinity and ionic composition was investigated by diluting seawater and altering concentration of sodium chloride (NaCl) and sulphate (SO_4^2 -).

The result from imbibition capillary pressure data indicated a reduction in residual oil saturation as the salinity was reduced. Twenty times diluted seawater enriched with four times sulphate lead to an incremental oil recovery of 7% compared to twenty times diluted seawater. Moreover, depletion of NaCl in the low salinity brine enriched with sulphate lead to 1.6% additional oil recovery. Reducing salinity of the injected brine resulted in a more water-wet condition. The highest wettability index alteration towards water-wet condition was observed when sulphate was spiked in low salinity brine. The result obtained in this work provided direct evidence that LSWI could change the wetting condition of the rock toward a more water-wet state. It was concluded LSWI could be an effective oil recovery technique, which could be improved by altering ionic composition of the brine on limestone core samples.

INTRODUCTION

Low salinity water injection is an emerging oil recovery technique. The chemistry of injected water can be reformed by dilution (i.e. LSWI) or selectively modifying the concentration of individual ions (i.e. Smart Water) presented in the brine. Majority of the researchers have reported a positive response to LSWI and wettability alteration is believed to be the primary reason for incremental oil recovery in carbonate cores [1, 4 and 10].

Yousef et al. [9] conducted coreflooding experiments to study the effect of LSWI on oil recovery and wettability alteration for carbonate rocks at reservoir conditions. The incremental oil recovery by injection of diluted seawater was up to 18% of the OOIP. Putervold et al. [6] investigated the concentration ratio between NaCl and SO₄²⁻ in the injection brine that is required to improve oil recovery in chalk core sample. The results suggest 90% depletion of NaCl and enrichment of sulphate concentration by 3-4 times in the brine was required in order to achieve maximum oil recovery. A successful design of waterflooding to alter the wettability of the carbonate rock depends on optimum salinity and ionic concentration of the injected brine. However, very limited attention has been given to effect of salinity and ionic composition of injected water on capillary pressure.

Capillary pressure (P_c) data are vital in modelling heterogeneous carbonate reservoirs. In general, capillary pressure data from drainage process is used to determine Original Oil in Place (OOIP) and imbibition capillary pressure is used to design recovery characteristic of hydrocarbons in secondary and tertiary flooding [5]. Webb et al. [8] investigated the effect of formation water free of sulphate and seawater with high concentration of sulphate on capillary pressure curves and oil recovery of carbonate core samples at reservoir condition. An incremental oil recovery of 15% was observed when seawater was injected compared to formation water in forced imbibition test. Wang and Alvarado [7] investigated the effect of low salinity brine on capillary pressure hysteresis using an improved quasi-static porous plate method at 30°C. The core samples were not aged in this work to reduce the possibility of wettability alteration and isolate the effect of interfacial viscoelasticity caused by LSWI. Results indicated less hysteresis and an incremental oil recovery 15% OOIP for low salinity compared to high salinity.

This paper presents effect of salinity and ionic composition of the injected water on capillary pressure and wettability at ambient condition by deploying multi-speed centrifuge technique which has not been used previously in this field.

EXPERIMENTAL PROCEDURES Material

Various laboratory tests were conducted to select Indiana limestone outcrop core plugs with similar petrophysical properties. This includes routine core analysis such as porosity, gas permeability, and dimensions measurements. X-ray Diffraction (XRD) analysis indicated the mineralogy of the rock is composed of 98wt% calcite. The petrophysical properties of the limestone core samples are presented in Table 1. Dead crude oil from

North Sea was mixed with heptane in ratio of 60:40, respectively. The Total Acid Number (TAN) of the synthetic oil was 0.18 mg KOH/g measured by ASTM D-664 method. The oil properties used in this work are presented in Table 2.

Synthetic brine was prepared in laboratory from distilled water reagent grade chemical. Four types of brines were prepared I) formation water, II) seawater, and III) diluted seawater, and IV) seawater selectively modified ionic composition. Table 3 indicates the formulation of the brines used in this work. In this paper, formation water is referred as FW and seawater (SW), ten times diluted seawater (0.1xSW), ten times diluted seawater doped with 4 times sulphate $(0.1xSWx4SO_4^{2-})$ and ten times diluted seawater depleted in sodium chloride (0.1xSWx0NaCI).

Description of Equipment and Procedures

A refrigerated centrifuge apparatus was used in this work to measure both forced drainage and imbibition capillary pressure curves at ambient condition. A schematic diagram of the centrifuge forced drainage and imbibition is provided in Figure 1. The average saturation detected by the centrifuge camera was used to measure the local capillary pressure at the inlet of the core sample. Three different interpretation methods I) Hassler-Brunner, II) Forbes Continuous, and III) Forbes + Spline were used in multi-speed centrifuge experiment to convert the average capillary pressure curve to local capillary pressure curve.

Core preparation

To minimise the wettability alteration of the rock, core samples were injected with distilled water to remove any dissolvable sulphate. Toluene and methanol were used to clean the core plugs before drying in oven. Then, the core samples were saturated with formation brine using vacuum pump and centrifuge. Primary drainage P_c experiment was conducted using the centrifuge to measure the irreducible water saturation. Forced imbibition and secondary drainage experiments were performed to measure the capillary pressure curve for high salinity FW which was followed by low salinity imbibition and drainage P_c curve. The purpose of this experiment was conducted at ambient conditions and the core samples were not aged after the primary drainage which minimised the possibility of wettability alteration in the core samples.

RESULTS AND DISCUSSION

Salinity Effect

The experimental results indicated an increase in oil recovery as the salinity of the imbibing brine is reduced. The highest oil recovery and wettability alteration is observed using twenty times diluted seawater in secondary flooding mode. The results are comparable with previous experimental work by Yousef et al. [9]. Figure 2 shows that the oil recovery and

wettability are not a linear function of salinity and more than 95% reduction in salinity is required to obtain reasonable oil recovery. The irreducible water saturation (S_{wi}) was increased as the S_{wi} is a function of wettability and pore-size distribution. It worth mentioning that the experimental work presented here were performed at ambient conditions to minimise the wettability alteration. Majority of research has reported positive effect of LSWI in carbonates at high pressure and temperature. This is due to the increase in reactivity of potential determining ions (Ca^{2+} , Mg^{2+} , and SO_4^{2-}) at higher temperature [4, 9 and 10]. Knowing the effect of temperature, additional oil recovery and further change in wetting condition toward a more water wet state can be expected.

Non-active Ions and Sulphate

Twenty times diluted SW spiked with 2 and 4 times sulphate and depleted in NaCl was used as the imbibing fluid to determine the capillary pressure curve, oil recovery and wettability index. The results presented in Figure 5 and 6 indicate a reduction in residual oil saturation as the sulphate was increased. This confirms that SO_4^{2-} can lead to an expansion of EDL even at low temperature (24°C). Depletion of NaCl had less effect on oil recovery compared to SO_4^{2-} . An incremental oil recovery of 7% and 1.6% was obtained when 4 times sulphate was added and NaCl was depleted in low salinity water, respectively.

Non active ions (Na⁺, Cl⁻) are not part of the inner Stern layer in Electrical Double Layer (EDL), which can lead to reducing the influence of potential determine ions [2]. High affinity of sulphate toward the rock surface leads to adsorption of calcium due to reduced electrostatic repulsion. Removal of NaCl from imbibing fluid provides better access for calcium and magnesium ions in double layer to get closer to surface of the rock which leads to expansion of EDL. However, the incremental oil recovery obtained after depletion of NaCl did not have any effect on wettability. Wang and Alvarado [7] reported the incremental oil recovery is due to interfacial viscoelasticity which leads to suppression of snap-off and continuity of oil recovery.

CONCLUSIONS

Significant incremental oil recovery has been reported by reducing salinity, NaCl, and increasing SO_4^{2-} at reservoir condition. In this paper the effect of salinity, non-active salt, and SO_4^{2-} on oil recovery and wettability at ambient condition has been investigated. Low salinity water and sulphate enriched brine successfully improved the wettability and oil recovery of limestone rock at ambient conditions. Marginal oil recovery was observed by depletion of NaCl but the wetting condition was not changed. The incremental oil recovery achieved by depletion of NaCl was result of liquid-liquid interaction and not wettability alteration. In summary:

• The capillary pressure data confirms that both LSWI and smart water are able to modify wettability of the limestone core samples from a mix-wet state toward a more water-wet state.

- Forced imbibition tests by centrifuge indicated an incremental oil recovery up to 8% by modifying the ionic concentration and salinity of the SW.
- The increase in oil recovery is not a linear function of salinity. Over 95% of SW's total dissolved salts were removed prior to any noticeable incremental oil recovery.
- Increasing concentration of SO₄²⁻ by 2-4 times altered the wettability toward waterwet condition. Whereas, depletion of NaCl resulted in reducing the residual oil saturation but had no effect on wettability.

ACKNOWLEDGEMENTS

The authors acknowledge the London South Bank University for financial support.

REFERENCES

- 1. Austad, T., Shariatpanahi, S.F., Strand, S., Black, C.J.J., Webb, K.J., 2012. "Conditions for a low-salinity enhanced oil recovery (EOR) effect in carbonate oil reservoirs". Energy Fuels 26 (1), 569–575.
- 2. Fathi, J.S., Austad, T., Strand, S. 2012. "*Water-Based Enhanced Oil Recovery* (*EOR*) by Smart Water In Carbonate Reservoirs". Paper SPE 154570, Presented at the SPE EOR Conference at Oil and Gas West Asia, Muscat, Oman, 16-18 April.
- 3. Fernø,, M.A., Grønsdal, R.J., Nyheim, A.M., Berge, M., and Graue, A., 2011. "Use of Sulfate for Water Based Enhanced Oil Recovery during Spontaneous Imbibition in Chalk". Paper Energy & Fuels, 25(4): 1697-1706.
- Gupta, R., Griffin, S., Willingham, T.W., Casico, M.L., Shyeh, J.J., Harris, C.R. 2011. "Enhanced Waterflood for Middle East Carbonate Cores – Impact of Injection Water Composition". Paper SPE 142668 presented at SPE Middle East Oil and Gas Show and Conference, 25-28 September, Manama, Bahrain.
- Masalmeh, S.K., Jing, X.D., 2006. "Capillary Pressure Characteristics of Carbonate Reservoirs: Relationship between Drainage and Imbibition Curves". Paper SCA2006-16 Presented at the SCA International Symposium, Trondheim, Norway, 12 – 16 September
- 6. Puntervold, T., Strand, S., Ellouz, R., Austad, T., 2015. "Modified Seawater as a Smart EOR Fluid in Chalk". Journal of Petroleum Science and Engineering 133, 440-443.
- 7. Wang, X. and Alvarado, V., 2016. "*April. Effects of Low-Salinity Waterflooding on Capillary Pressure Hysteresis*". Paper SPE-179562 Presented at SPE Improved Oil Recovery Conference, Tulsa, Oklahoma, USA, 11-13 April.
- Webb, K.J., Black, C.J.J., and Tjetland, G., 2005. "A Laboratory Study Investigating Methods for Improving Oil Recovery in Carbonates". Paper SPE 10506, SPE International Petroleum Technology Conference, Doha, Qatar, 21 – 23 November
- 9. Yousef, A.A., Al-Saleh, S., Al-Kaabi, A.O., and Al-Jawfi, M.S. 2010. "Laboratory Investigation of Novel Oil Recovery Method for Carbonate Reservoirs". Paper

CSUG/SPE 137634, presented at the Canadian Unconventional Resources & International Petroleum Conference, Calgary, Alberta, Canada, 19-21 October.

 Zhang, P., Tweheyo, M.T., Austad, T., 2007. "Wettability alteration and improved oil recovery by spontaneous imbibition of seawater into chalk: Impact of the potential determining ions: Ca²⁺, Mg²⁺ and SO4²⁻". Colloids Surf. A: Physicochem. Eng. Asp. 301, 199–208.

Sample	Length (Inch)	Diameter (Inch)	Gas Perm. (mD)	Porosity (%)
L1	4	1	60	17.2
L2	4	1	75	19
L3	4	1	72	18.7
L4	4	1	54	16.9

Table 1: Indication of core samples petrophysical properties

Table 2: Oil Properties

Oil	Density (g/cm ³) at 20°C	Viscosity (cp) at 20°C	TAN (mg KOH/g)
Synthetic Oil	0.862	18	0.18

Salts(g/l) Brine	NaCl	CaCl ₂ .2H ₂ O	KC l	MgCl ₂ .6H ₂ O	Na ₂ SO ₄	NaHCO ₃	Total Dissolved Salts (TDS), g/l
Formation Water (FW)	67.56	14.7	0.52	4.47	0	0.34	87.59
Seawater (SW)	26.30	1.91	0.75	9.15	3.41	0.17	41.68

Table 3: Indication of brine formulation

.

Seawater diluted 10 times (0.1xSW)	2.63	0.19	0.07	0.91	0.34	0.02	4.17
Seawater diluted 20 times (0.05xSW)	1.31	0.10	0.04	0.46	0.17	0.01	2.08
20Xdiluted SeawaterX2times Sulphate (0.05xSWx2SO4 ⁻²)	1.31	0.10	0.04	0.46	0.34	0.01	2.25
20Xdiluted SeawaterX4times Sulphate (0.05xSWx4SO4 ⁻²)	1.31	0.10	0.04	0.46	0.68	0.01	2.60
20Xdiluted SeawaterX2times SulphateX0NaCl (0.05xSWx2SO4 ⁻ ² x0NaCl)	0.00	0.10	0.04	0.46	0.34	0.01	0.94
20Xdiluted SeawaterX4times SulphateX0NaCl (0.05xSWx4SO4 ⁻ ² x0NaCl)	0.00	0.10	0.04	0.46	0.68	0.01	1.28



Figure 1: Indication of Centrifuge core holder setup, forced drainage and imbibition cycle





Figure 4: Formation Water and twenty times diluted Seawater capillary pressure curve for Limestone 4



Figure 5: Formation Water, twenty times diluted Seawater enriched with twice sulphate with/without sodium chloride capillary pressure curve for Limestone 1



Figure 6: Formation Water, twenty times diluted Seawater enriched with four times sulphate with/without sodium chloride capillary pressure curve for Limestone 2