Improvement of Relative Permeability and Wetting Condition of Sandstone by Low Salinity Waterflooding

Falan Srisuriyachai 1, Monrawee Pancharoen 2, Rapheepan Laochamroonvorapose 2, Pattraporn Juckthong 2, Arisara Kukiattikoon 2, Boonpipop Sirirojrattana 1

1 Department of Mining and Petroleum Engineering, Chulalongkorn University, Phayathai Road, Pathumwan, Bangkok 10330, Thailand
2 PTT Exploration and Production Public Company Limited, Vibhavadi-Rangsit Road, Chatuchak, Bangkok 10900, Thailand

falan.s@chula.ac.th

Abstract. Waterflooding is generally performed to maintain reservoir pressure and as a consequence, production period is extended. However, conventional waterflooding may be not suitable for every reservoir. Low Salinity Waterflooding (LSW) which is recently the most mentioned technique is therefore, considered. Although clear explanation of oil recovery mechanism is not available, it is believed that the key mechanism is Multi-component Ion Exchange (MIE). This study aims to assess improvement of relative permeability and wetting condition of sandstone formation from oilfield in Thailand, through the MIE mechanism. The study is divided into two major parts. The first part is laboratory study including core and fluid preparations, imbibition test, coreflooding test and ion-exchange detection. After laboratory data including fluid production rate and pressure difference versus time are obtained, core simulation using reservoir simulation program called STAR® commercialized by Computer Modelling Group (CMG) is performed to study the change of wetting condition through the shifting of relative permeability. Obtaining results would help verifying suitability of the implementation of this technique in oilfield. Results from imbibition test showed that LSW yields higher oil recovery factor compared to formation water. Diluted formation water at 5,000 ppm which is approximately one-third of formation water, is the best water formulation, yielding the fastest rate of imbibition in this study. From ion-exchange detection test, results showed the variation of divalent ion concentrations compared to injected water and moreover, presence of calcium and magnesium ions in oil phase supports the occurrence of MIE during the displacement mechanism. The theoretical model matching with physical data using reservoir simulation program indicates that LSW slightly affects the original wetting condition. Water wetness is lessened as can be observed from the increment of relative permeability to water at the end point saturation. Moreover, LSW reduces residual oil saturation and at the same time, increases relative permeability to oil. From the detection of MIE together with the observation of wetting condition through core simulation, it can be concluded that LSW is a promising technique for oilfield in Thailand. As produced water must be reinjected back into reservoir based on zero discharge regulation of Thai government, this low-cost technique of diluting water salinity prior to reinjection would fulfil the requirement of government and at the same time helps increasing oil recovery of the total field.
1. Introduction

Waterflooding also known as secondary recovery is a technique associated with injection of water into reservoir to maintain reservoir pressure after primary depletion. However, this technique potentially succeeds in reservoir with appropriate rock and fluid properties. In recent years, Low Salinity Waterflooding (LSW) is highly mentioned and it is intensively studied due to cost effectiveness as well as ability to increase oil recovery. However, the technique is still questionable and oil recovery mechanisms are not completely understood since there are many explanations describing how additional oil recovery can be obtained. Hence, major affecting key factor remains unclear. Nevertheless, wettability alteration, with many evidences, is expected to be the major mechanism.

Many oil recovery mechanisms by LSW have been proposed over decades. Tang and Morrow [1] discovered that additional oil recovery was related to clay content. However, the explanation cannot fit in most of the following experiments. Austad et al. [2] proposed different oil recover mechanism occurring from changing of pH value during LSW. Local increment of pH value was observed, causing chemical reaction between adsorbed organic acid and organic base with hydroxide ions and resulting in liberation of these materials together with oil phase. Again, increment of pH value was not always observed together with increment of oil recovery by means of LSW. The most commonly mentioned oil recovery mechanism was proposed by Lager et al. [3]. Cation exchange was detected together with increasing of oil recovery during LSW. Reduction of ionic strength in injected water changes equilibrium between rock surface and fluid. Dissolution of divalent ions linking between rock surface and organic materials occurs and monovalent ion replaces the bridging site. Eventually adsorbed organic materials are liberated together with oil phase, leaving surface to become more water-wet. The overall process was called Multi-component Ion Exchange (MIE). However, reduction of total salinity of injected water was not the only key of success for LSW. Nasralla [4] discovered that using sodium chloride solution to represent low salinity water showed better performance compared to solutions of calcium chloride and magnesium chloride. Therefore, reduction of divalent ion in injected water seemed to be answer for both studies. Additional oil recovery mechanism was added to MIE. Myint and Firoozabadi [5] focused on a mechanism called Double-Layer Expansion (DLE). Low salinity water causes an increase in electrostatic repulsion within a water film between rock surface and adsorbed oil layer. Water film is then expanded and adsorption strength of hydrocarbon onto rock surface is reduced, facilitating oil recovery mechanism by MIE.

Water-wet condition is originally occurred during rock deposition as rock is firstly in contact with water. Once oil migrates into reservoir rock, charged organic compounds induce the water-wet surface to oil-wet by means of wettability alteration mechanisms. Ion binding is one of the four mechanisms that changes wettability of water-wet rock to a more oil-wet condition [6]. A process can be simply explained by sandstone surface containing negative charge at reservoir pH condition. The surface is then linked with organic acid containing negative charge in oil through the bridging of divalent ions such as calcium ion and magnesium ion. By reducing salinity of injected water, divalent cations that previously link between sandstone surface and oil layer will desorb, leading to liberation of adsorbed oil and the sandstone surface returns to a more water-wet condition. At the same time, oil recovery is increased.

This study aims to investigate physicochemical reaction by means of LSW in Sirikit oilfield or so-called S1. The S1 oilfield is located in the Phitsanulok Basin of central Thailand and the production of this oilfield was started in December 1982. The produced oil is light with around 40 °API and contains high wax content (15-20 %wt) which leads to high pour point temperature of about 35 °C. Lithologically, S1 oilfield is sandstone with high portion of clay content (up to 40 percent) where majority is illite. Due to discovery of acid number in crude oil together with divalent ions in formation water and large surface from clay content, this sandstone is believed to be oil-wet at in-situ condition by ion binding mechanism.

Obtained result from this study will lead to identifying appropriate formulation of injected water. By assessing oil recovery factor and detection of divalent ion in effluents, effects of each water formulation are revealed. Moreover, an assist of CMG STAR®, reservoir simulation program, will be useful to match experimental data with reservoir simulation. A change of relative permeability is expected after injection
of LSW. Corey’s exponents which is a value determining curvature of relative permeability will be varied in order to match cumulative oil production as well as pressure difference across core sample. Finally, this simulation would provide relative permeability curves from LSW process by matching collecting data and simulated data. An obtained relative permeability curves and study of wettability will confirm the feasibility of this technique to be performed in S1 oilfield.

2. Methodology

The study is divided into two parts consisting laboratorial experiment and core simulation. The laboratorial experiment is performed in order to select the best formulation of injected water by observe the increment of oil recovery factor. Moreover, evidence of Multi-Component Ion Exchange (MIE) occurred during the displacement mechanism. After results are obtained from coreflooding experiment, simulation study is performed to provide the best fit relative permeability curves for low salinity waterflooding process to observe wettability alteration. Details of each section are as follow.

2.1. Core and fluid preparation

2.1.1. Core preparation. Core samples are firstly cleaned by solvent extraction using Soxhlet apparatus. Heavy hydrocarbon is removed by Toluene whereas light hydrocarbon is cleaned by Methanol. Each cleaning process takes approximately 24 hours. Part of core sample is crushed into powder for the measurement of grain density using pycnometer. Cleaned core samples are then measured for effective porosity and absolute permeability, using coreflood apparatus. In addition, to ensure that carbonate is absent in rock sample, testing by soaking rock sample in hydrochloric acid is quickly performed. The test of carbonate content is to ensure the effect of LSW since oil recovery mechanism by means of LSW is different in sandstone and carbonate formations. Restoration of core samples is performed by fully saturating by formation water followed by crude oil. Once irreducible water saturation is attained the data is taken and initial oil saturation can be calculated. Samples are aged for 2 weeks to allow wettability alteration mechanism at 70 ºCelsius. Ionic composition of formation water is summarized in table 1.

| Ion                | ppm  | mole/L | %mole |
|-------------------|------|--------|-------|
| Sodium            | 5,076| 220.79 | 47.78 |
| Potassium         | 84   | 2.15   | 0.46  |
| Calcium           | 255  | 6.36   | 1.38  |
| Magnesium         | 28   | 1.15   | 0.25  |
| Hydrogen Carbonate| 522  | 8.55   | 1.85  |
| Chloride          | 7,910| 223.13 | 42.48 |
| **Total**         | 13,875| 462.14| 100   |

2.1.2. Fluid preparation. Injected water is prepared in four formulations including formation water (around 14,000 ppm), diluted formation water (5,000 ppm), 10,000 ppm potassium chloride solution (KCl), and 5,000 ppm KCl solution. As potassium ion is found to be more effective than sodium ion during MIE mechanism, the test for sodium chloride (NaCl) solution is not performed in this study. Moreover, due to high percentage of clay content, potassium ion will yield benefit as clay control agent. Density and viscosity of prepared water and crude oil are detected at different temperatures as the date are important for several calculations. Acid number of crude oil is also performed by color titration to confirm alteration of wettability to oil-wet condition through ion-binding.

2.2. Imbibition test

An imbibition test of different injected water is conducted to compare imbibition potential of each into a rock specimen. Faster rate of imbibition indicates high potential in wettability alteration that could be related to MIE mechanisms. Detection of imbibition is performed by measuring sample weight. The
experiment is terminated once sample weight is constant. Selection of injected water is based on how fast imbibition occurs and maximum oil recovery. Moreover, the selection must also consider the sensitivity of clay, inexpensiveness of adding salts, availability of salts, and compatibility of fluids. Four core samples after aging are soaked in formation water at 70 ºC. Weight of each core is measured daily until the weight becomes constant. Then, core samples are switched to soak in four different water formulations to compare the increment of oil recovery factor. Weight measurement is re-performed until constant weight is attained. Finally, water saturation and oil recovery factor of each core can be calculated.

2.3. Coreflood experiment
This step is performed to simulate to gather necessary data including oil recovery factor, difference pressure, fluid production rates and also to collect effluent for core simulation and MIE study. First, formation water is injected to perform conventional waterflooding until oil production is no longer observed. Pressure difference, cumulative oil production, and cumulative water production are recorded throughout the test. Moreover, five cm³ of effluent sample is collected. After that, selected water formulation is injected to perform low salinity waterflooding. Again, similar data are detected. However, effluent samples are collected every five cm³ in order to observe concentration of divalent ion to observe results from MIE mechanism.

2.4. Determination of divalent ion by complexometric titration
Effluent sampled are titrated with Ethylene Diamine Tetra-acetic Acid (EDTA) to detect number of divalent ions which are calcium ion and magnesium. Using different color indicators, total hardness and concentration of calcium ion can be determined. The difference of these two values indicates concentration of magnesium ion. These two cations are related to oil recovery obtained from LSW. Higher concentration of divalent ion together with high oil recovery factor would ensure MIE mechanism as potassium ion replaces calcium ion or magnesium ion that link sandstone surface and oil layer.

2.5. Matching of theoretical model with results from coreflood experiment
Core simulation is performed to proceed history matching including fluid productions and pressure differences with data obtained from coreflooding experiment in order to acquire relative permeability curves. Core simulation is performed by reservoir simulation program called CMG STAR®. The assumptions in this study are that rock sample is homogeneous and there is no liberation of solution gas throughout the experiment. First, grid model is created by dividing core into 40 grid blocks of 20×1×2 respectively in x-, y-, z- directions. Black oil PVT component and rock-fluid type are then imported. Relative permeability curves for both conventional waterflooding and low salinity waterflooding are assumed. Next, initial condition, time step control, well constraints, and perforation data are also added. Fluid production and pressure difference are reported after running simulation. The data from core simulation and experiment are compared. If simulated results do not fit the experimental data, input relative permeability curves are adjusted in order to obtain the best fit relative permeability curves.

3. Results and discussion
The measured grain density by pycnometer is 2.593 g/cm³ showing that rock sample is sandstone with presence of clay which is matched with data obtained from oilfield that illite and kaolinite are majority of clay content found in S1 oilfield. From observing reaction with hydrochloric acid, it is found that core samples are absent by carbonate compounds. Porosities for cores are in a range between 10-20% while absolute permeabilities are extremely varied from 1-181 md. Most homogeneous cores are selected for coreflooding experiment and the rests are used for imbibition test. For properties of hydrocarbon, it is found that acid number is very small (less than 0.1). However, increasing amount of acid is observed when flowing n-dodecane through clean core sample. This indicates that organic acid is attached onto rock surface and it is not cleaned by solvent extraction. Therefore, sandstone surface will be easily
altered to oil-wet condition when any crude oil is injected into core samples. The crude oil used in this study is a light oil and it possesses low viscosity and high pour point temperature.

3.1. Imbibition test
As the imbibition test is conducted, daily weight of each core sample is detected and used for calculation of oil recovery factor. Once the detected weight is obviously constant, imbibition process is switched to perform using low salinity water. Both increment of oil recovery factor and rate of increment in oil recovery showed that diluted formation water at 5,000 ppm is the best formulation for LSW in this test. As shown in figure 1, diluted formation brine of 5,000 ppm can increase oil recovery factor up to 27.79% over the testing period of eight days, while the increment of recovery factor by other fluids is less than 15%. It can be observed that additional oil is recovered when imbibed water is changed to formation water to lower salinity water. As potassium ion is found to be active monovalent ion in replacing divalent ions capturing oil on rock surface through ion binding, presence of only potassium ion in low salinity water yields less oil recovery factor compared to the result obtained from diluted formation water. It could be explained that the occurrence of MIE requires collaboration of several ions including both monovalent ions and divalent ions. Small amount of divalent ion in injected brine may favor dissolution process of calcium ions and magnesium ions and at the same time, certain number of divalent ions will need to form carboxylate complex with organic acid. To balance the charge of sandstone surface, monovalent ions will replace the site of divalent ions after dissolution. Hence, presence of both monovalent and divalent ions yields benefit to the MIE mechanisms.

3.2. Coreflood experiment
From imbibition test, diluted formation water at salinity of 5,000 ppm is selected for coreflood experiment. The testing temperature is 70 °C and injection rate is constant at 0.5 cm³/min. Formation water at 14,000 is firstly injected and at about 2.6 pore volume, the injected process is stopped as no additional oil recovery is observed. The oil recovery factor at this stage is 84.06%. Most of oil is produced before water breakthrough and only a few percent of oil are recovered after that. Meanwhile, pressure difference is gradually decreased and becomes constant at the same time when no additional oil is recovered. After that, diluted formation water is followed. Sudden drop of pressure is detected due to transition of injecting water. No additional oil is recovered until 0.87 pore volume of low salinity water enters core sample. Additional amount of oil after LSW is recovered in a form of emulsion, resulting in total oil recovery of 93.12%. Pressure difference during LSW decreases compared to that obtained during conventional waterflooding, indicating an increasing of effective permeability. The results showed that LSW can increase oil recovery factor about 9.03% beyond conventional waterflooding.
3.3. Determination of divalent ion by complexometric titration

Amounts of calcium ion and magnesium ion obtained during injection of both formation water and dilute formation water at 5,000 ppm are summarized in figure 2.

From figure 2, it can be seen that concentrations of divalent ions from the first collected sample obtained from formation water are higher than that of the period of low salinity water. This can be explained that major number of divalent ions undergoes desorption and accumulation at the flood front. After that, concentrations of divalent ions from effluent start to decline. In case of magnesium ion, the concentration from effluent is higher than that of injected due to MIE mechanism during injection of formation water. On the other hand, concentration of calcium ion in effluent is less than the concentration in injected fluids. It could be explained that part of calcium ion reacts with carboxylic acid in oil, forming calcium carboxylate complex and this explanation could be responsible for reduction of calcium ion in effluent. The difference in magnitude of calcium ion and magnesium ion can in this period may reflects to difficulties of dissolution process of different divalent ions. During injection of low salinity water, concentration of both ions is less than initial concentration in injected water.
Concentration of calcium ion is slightly greater than that of magnesium ion. This could be explained that low salinity water can cause dissolution of calcium ion remaining from the first period and at the same time, portion of calcium ion in injected water is higher than that of magnesium ion. However, amount of both ions is less than initial concentration in injected water. As concentration of divalent ions is small, both are consumed to create carboxylate complex. Zahid et al. [7] concluded that at elevated temperature, magnesium ion can also form carboxylate complex. Recovered oil from low salinity process is then collected to stirred with distilled water. Both calcium ion and magnesium ion are found in the effluent as expected.

3.4. Matching of theoretical model with results from coreflood experiment

History matching of oil production and pressure difference is constructed to compared with data obtained from coreflood experiment to study the alteration of wetting condition through by adjusting relative permeability curves for both formation water injection period and low salinity water injected period. Figure 3 illustrates the best history matching. Matching result of pressure difference deviates from laboratory data at the beginning during injection of formation water because pressure difference from model gradually increases from zero at the start, whereas inlet pressure of core holder is already built prior starting of the process. Moreover, early drop of pressure difference from model at the beginning during low salinity waterflooding is due to a sudden change of injected fluid in simulation while there is a delay of pressure difference dropping in laboratory data.

![Figure 3. Cumulative oil production and pressure difference versus time from laboratory data and core simulation data.](image)

Relative permeability curves as a result of history matching indicates that residual oil saturation is reduced and relative permeability for both water and oil slightly increases as shown in figure 4. Wetting condition during low salinity water moving toward neutral wet condition or rock tends to be less water-wet. Nevertheless, the modification of relative permeability curves only occurs at high water saturation. The improvement of both oil and water flow ability could be explained that MIE would remove and mobilize oil drops blocking flow paths, relative permeability to water is therefore slightly increased.
Figure 4. Comparison of relative permeability curves obtained from best history matching during injection of formation water and during low salinity waterflooding.

4. Conclusions
Low salinity waterflooding shows ability to improve oil recovery from S1 Oilfield. As initial condition of reservoir contains divalent ions from clays, linking crude oil onto rock surface, this condition allows low salinity water to liberate bridging divalent ion. From this study, diluted formation water at 5,000 is chosen as best water formulation. Comparing results obtained from the solution of potassium chloride at the same concentration, it could be possible that MIE is triggered by collaboration of many ions in injected water. The evidence of calcium ion and magnesium ion attached in oil phase supports the forming of carboxylate complex which is one of the mechanism during MIE. Wetting condition of sandstone surface is slightly changed toward neutral wet condition. Both relative permeability to oil and water are slightly improved at high water saturation.

References
[1] G.Q. Tang, and N. R. Morrow, “Salinity, temperature, oil composition, and oil recovery by waterflooding,” SPE Reservoir Engineering, vol. 12, pp. 269-279, 1997.
[2] T. Austad, A. Rezaeidoust, and T. Puntervold “Chemical mechanism of low salinity waterflooding in sandstone reservoirs,” Proceedings of the SPE Improved Oil Recovery Symposium, Tulsa, Oklahoma, USA, 2010.
[3] A. Lager, K. J. Webb, C. J. J. Black, M. Singleton, and K. Sorbie, “Low salinity oil recovery: An experimental investigation 1,” Petrophysics, vol. 49, pp. 28-35, 2008.
[4] R. A. Nasralla, and H. A. Nasr-El-Din, “Coreflood study of low salinity water injection in sandstone reservoirs,” Proceeding of the SPE/DGS Saudi Arabia Section Technical Symposium and Exhibition, Al-Khobar, Saudi Arabia, 2011.
[5] P. C. Myint, and A. Firoozabadi, “Thin fluid film in improved oil recovery from low salinity brine,” Current Opinion in Colloid & Interface Science, vol. 20, pp. 105-114, 2015.
[6] J. S. Buckley, Y. Liu, and S. Monsterleet, “Mechanisms of wetting alteration by crude oils, SPE Journal vol. 3(1), pp. 54-61, 1998.
[7] A. Zahid, A. Shapiro, and A. Skauge, “Experimental studies of low salinity waterflooding in carbonate reservoirs,” Proceeding of EOR Conference at Oil and Gas West Asia, Muscat, Oman, 2012.