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State-of-the Art Low Salinity Waterflooding for Enhanced Oil Recovery

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Summary

Low salinity waterflooding (LSW) is an emerging enhanced oil recovery technique in which the salinity of the injected water is controlled to improve oil recovery vs. conventional, higher salinity waterflooding. Despite significant growing interest in LSW, a consistent mechanistic study has not yet emerged, and the mechanisms behind the LSW process have been debated for the last decade due to the complexity of the crude oil-brine-rock interactions. The intent of this paper is to:

- Provide a concise review of the current understanding of LSW mechanism and prediction methods;
- Address the current development and challenges of LSW modeling and numerical simulation;
- Summarize and highlight the success and failur of LSW implementation in pilot tests;
- Discuss the potential of a Hybrid LSW in the current and future projects.

Introduction

Waterflooding is currently accepted worldwide as a simple, reliable, and economic technique; most of conventional oil reservoirs have been, are being, or will be considered for waterflooding during secondary recovery. Unquestionably, waterflooding will continue to be applied to unlock huge hydrocarbon reserves left behind by primary recovery.

In most waterflooding projects, especially in offshore oil fields, the injected brine is normally chosen to be compatible with the existing reservoir brine so that damage to the formation does not occur. However, several authors have reported that injecting low salinity brine can increase oil recovery, compared to conventional high salinity waterflooding in sandstone reservoirs.

The original ideas of LSW came from Morrow and his research colleagues at the University of Wyoming in the early 1990's during their experiments to determine the interactions and effects of brine, crude oil, and mineralogy on wettability (Morrow, etal., 1998). Subsequently, numerous evaluations in laboratories and in the fields have proven the possibility of higher oil recovery factor by LSW. Although people widely agree with this point, the underlying mechanisms of additional oil recovery are still being debated. Several hypotheses have been proposed during last two decades including fines migration, wettability alteration, multi-component ionic exchange (MIE), pH modification, desorption, and double layer effects. Up to now, the mechanism responsible for increased oil recovery is poorly understood with many contradictory published results.

Nonetheless, LSW has a promising future since 50% of the world's conventional petroleum reservoirs are found in sandstones, and most of these reservoirs contain clays minerals, which is indicative as the favorable condition for LSW. Additionally, it could achieve considerable recovery potential with a relatively low operation cost and less formation damage compared to other chemical EOR techniques. LSW can also be considered for secondary recovery, or combined with other EOR approaches such as CO_2 miscible flooding, polymer, and surfactant-polymer for a higher oil recovery factor in tertiary mode.

Discussion on Underlying Mechanisms of LSW

In the 1990s, Jadhunandan et al. (1995) and Yildiz et al. (1996) published papers on the influence of brine composition on oil recovery which opened the window to optimize a waterflooding process with a simple modification of brine salinity. Then, numerous laboratory experiments by Morrow and his research colleagues (Morrow, et al., 1998; Tang, et al., 1999; Zhang, et al., 2007; Buckley, et al., 2010; Lohardjo, et al., 2010; Morrow, et al., 2011) and also by researchers at BP (Lager, et al., 2007, 2008; Webb, et al., 2004; McGuire, et al., 2005; Jerauld, et al., 2008) have confirmed that EOR can be obtained when performing a tertiary low salinity waterflood. The salinity in these tests is in the range of 1,000-2,000 ppm.

Migration of Fines

The first explanation for LSW effects was from “migration of fines” by Tang and Morrow in 1999. Theoretically, less saline brine promotes the dispersion of clay and silt in the formation where these fine materials become mobile and follow in the high permeability paths. The mobile clays become lodged in smaller pore spaces of these paths, and the injected water is forced to go to lower permeability zones. Tang and Morrow (1999) observed that fines (mainly kaolinite clay fragments) were released from the rock surface and an increase of spontaneous imbibition recovery with a decrease in salinity for different sandstone cores. The total dissolved solids (TDS) in their experiment changed from 35,960 to 1,515 ppm for reservoir brine, sea water and low saline brine. They found that the oil recovery factor increases significantly in the case of Berea sandstone core with more clay content. However, oil recovery is independent of brine salinity when cores were fired and acidized to stabilize fines and saturated with refined mineral oil rather than crude oil. From their results, they suggested that the mobilization of fines resulted in exposure of underlying rock surfaces, which increased the water wetness of the system.

Although they indicated that the possibility of fine migration during LSW, Zhang and Morrow (2007) later reported LSW oil recovery improvement without fine production. There are other authors who reported no LSW improvement despite great quantity of clay production (Boussour, et al., 2009) and those who reported low salinity improvement without fine production (Lager, et al., 2006). Based on these results, the link between fines migration and increased oil recovery was called into question. The differences of lithology and minerals inside the cores used by Morrow and other researchers could explain the conflicting results. The Berea sandstone used by Morrow and his staffs for many of their experiments had predominantly kaolinite clay and quartz. A number of studies have shown that kaolinite is easily wetted by crude oil.

pH Contribution

An increase of pH is usually observed during LSW (McGuire, et al., 2005; Zhang, et al., 2007). Thus a local pH increase has been proposed as the alternative driving mechanism for LSW improvement. McGuire et al. (2005) suggested that the EOR mechanisms of LSW appear similar to those of alkaline flooding by generation of in-situ surfactants, changes in wettability, and reduction in the interfacial tension. They also proposed the saponification mechanism of elevated pH and removal of harmful multivalent cations due to low salinity injection by the following chemical reactions:

$$\underset{\text{fat}}{(RCOO)_3C_3H_5} + \underset{\text{alkali}}{3\ NaOH} \rightarrow \underset{\text{soap}}{3\ (RCOONa)} + \underset{\text{glycerol}}{C_3H_5(OH)_3} \tag{1}$$

$$\underset{\text{soap}}{2\ (RCOONa)} + \underset{\text{“hardness”}}{Ca(HCO_3)_2} \rightarrow \underset{\text{insoluble soap curd}}{(RCOO)_2Ca + 2\ (NaHCO_3)} \tag{2}$$

Alternatively, Lager (2007) had another explanation for the increase in pH:

- Cation exchange between clay minerals and invading water. This reaction is relatively fast. The mineral surface will exchange H^+ present in the liquid phase with cations previously adsorbed, thereby resulting in an increase in pH.
- Dissolution of carbonate (calcite and dolomite), which results in an excess of OH^- and an increase in pH. The dissolution reactions are slower and dependent on the amount of carbonate material present in the rock:

$$CaCO3 \leftrightarrow Ca^{++} + CO_3^{--}CaCO \tag{3}$$

$$CO_3^{--} + H_2O \leftrightarrow HCO_3^{-} + OH^{-} \tag{4}$$

Nevertheless, the acid number of crude oil should be larger than 0.2 mg KOH/g in order to generate in-situ surfactant; but most of crude oil samples that were used had an acid number of less than 0.05 mg KOH/g. Additionally, the increase and final value of pH after LSW is quite small; therefore, it is difficult to conclude that additional oil recovery is due mainly to in-situ surfactant generation.

Since there is lack of evidence on the effects of in-situ surfactant, Austad et al. (2010) proposed a hypothesis of desorption by pH increase. In his statement, desorption of initially adsorbed cations onto the clay is the key process in increasing pH of water at the clay surface. At the beginning, both basic and organic materials are adsorbed onto the clay together with inorganic cations, especially Ca^{2+} from the formation water. Then a net adsorption of cations occurs as low salinity water is injected into a reservoir. Proton H^+ will be exchanged with cation Ca^{++}, leading to a local increase in pH close to the clay surface. The local increase in pH close to the clay surface causes reactions between adsorbed basic and acidic material as in an ordinary acid-base proton transfer reaction (Austad, et al., 2010). A fast reaction between OH^-, the adsorbed acidic and basic material will cause desorption of organic material from the clay surface. Thus the water wetness of the rock is improved. The mechanism of this theory is described in the following chemical reactions:

- Clay-Ca^{++} + H_2O = Clay-H^+ + Ca^{++} + OH^- (5)
- Clay-NHR_3+ + OH^- = Clay + R_3N + H_2O (6)
- Clay-RCOOH + OH^- = Clay + $RCOO^-$ +H_2O (7)

The source of OH- mainly comes from injected water; however, the concentration of OH- in the reservoir conditions is relative small and it can be easily precipitated by combining with the other divalent ions such as Mg^{++} instead of exchanging with clay surfaces. It is also difficult to use this hypothesis for explaining the strong dependence of the incremental oil recovery on the divalent ion concentrations such as Ca^{++} and Mg^{++} in the injected brine.

Salting-in Effect

Austad et al. (2008) and RezaeiDoust et al. (2009) suggested another hypothesis which is named a salting-in effect. This idea is related to changes in the solubility of polar organic components in the aqueous phase, described as salting in and out effects. The salting-out effect is defined by decrease in the solubility of organic material in water by adding salt to the solution; whereas, the salting-in effect is an increase in the solubility of organic material in water by removing salt from the water. When water is injected into the reservoir with a lower salinity than the initial formation water, the salting-in effect happens and partially contributes to desorption of some organic materials loosely bonded to the clay surface. However, this hypothesis could not explain some important observations during LSW such as local pH increase, variance of ion concentrations, and the dependence on mineral composition.

Multicomponent Ionic Exchange

Relating to the cations exchange in reservoir conditions, Lager (2007) proposed another idea about Multicomponent Ionic Exchange (MIE) as the basis for geochromatography. MIE involves the competition of all the ions in pore fluids for the mineral exchange sites. Lager found that Mg^{++} concentration sharply decreased in the effluent analysis of Alaska reservoir's corefloods. From this result, Lager stated that four mechanisms, i.e., cation exchange, ligand bonding, cation bridging and water bridging, have strong effects during LSW. Besides that, protonation, anion exchange, hydrogen bonding, and Van der Waals interaction also contribute to the overall ionic exchange. Lager assumed that Ca^{++} and Mg^{++} may act like a bridge between the negatively charged clay surface and the carboxylic material. The organic material was supposed to be removed by cation exchange between the mineral surface and the invading low salinity brine. Expansion of the electrical double layer due to low salinity flooding enables desorption of polar compounds from the surface (Lager, et al., 2007). However, Lager did not consider precipitation of $Mg(OH)_2$ which could explain the decrease of the cation Mg^{++} concentration in the effluent. Additionally, there are no chemical reasons why the strongly hydrated Mg^{++} ion should have a superior reactivity toward the active sites on the clay surface compared to Ca^{++} (Melberg, 2010). Also, Ca^{++} is typically expected to be stronger adsorbed on the clay mineral instead of desorption during the course of LSW as the explanations from Appelo and Postma (2005).

Ligthelm et al. (2009) discussed the double layer effect, which is the expansion of the ionic electrical double layer between the clay and oil interfaces and increases in the absolute level of the zeta potential. This in turn yields increased electrostatic repulsion between the clay particle and the oil, leading to desorption of oil components from the surface and increase in water wetness. They believed that the mechanism of LSW in a sandstone reservoir primarily relies on the expansion of electrical double layers and to a lesser extent on the cation exchange process. Nevertheless, Austad et al. (2010) pointed out that polar oil components adsorb onto clay minerals without a bridge of divalent cations, and hence the effect of electrical double layers may not be significant.

Wettability Alteration

Wettability alteration, toward increased water-wetness during the course of LSW, is the most frequently suggested cause of increased recovery (Morrow, et al., 2011). The effects of low salinity brine on wettability modification have been reported by several authors. First, Tang et al. (1997) proposed wettability modification as microscopic mechanism, and then Drummond et al. (2002) observed wettability change based on pH and salinity for silicate surfaces. Buckley et al. (1998) explained wettability modification as a result from interactions between crude oil components and reservoir rock. Berg et al. (2010) provided direct experimental evidence that wettability alteration of clay surfaces is the microscopic mechanism for LSW. They concluded that emulsification, IFT reduction, fines migration and selective plugging of water-bearing pores via clay swelling are the most important reasons for higher oil recovery during LSW. Ramez et al. (2011) investigated the wettability properties of sandstone under LSW in different ranges of pressure and temperature (500-1000 psi, and 140-250^{o}F). They found that high salinity showed high contact angles, while low salinity water decreased the contact angles significantly for the two types of crude oil in their experiments. It shows that low salinity water could alter the wettability to more water-wet. Zhang et al. (2007) and Zekri et al. (2011) pointed out that LSW can also alter the wettability in carbonate formation. Vledder et al. (2010) documented a proof of wettability alteration during LSW in field scale from spontaneous imbibitions experiments in core material and a single well Log-Inject-Log test. From their field observations, wettability has changed to more water wetness, leading to an associated incremental recovery of 10-15% of the Stock Tank Oil Initially in Place.

Among the proposed hypotheses, wettability alteration towards increased water wetness during the course of LSW is the widely suggested case of increased oil recovery. It has been experimentally found that the low salinity brine has a significant effect on the shape and the end points of the relative permeability curves (Webb et al., 2004; Kulkarni and Rao, 2005; Rivet, 2009; Fjelde et al., 2012), resulting in a lower water relative permeability and higher oil relative permeability. Buckley et al. (1998) and Suijkerbuijk et al. (2012) reported the important role of divalent ions on wettability alteration that usually happens in the course of LSW. This phenomenon could be physically explained by the ionic exchange between the injected brine and formation water, and mineral dissolution/precipitation in LSW. The ionic exchange during this process leads to the adsorption of divalent ions, promotes the mineral dissolution, and changes the ionic composition of formation water and the wettability condition.

Modeling and Numerical Simulation of LSW

While extensive experimental studies of LSW have been reported, modeling work is rarely found in the literature. One of the earlier studies on modeling of LSW was presented by Jerauld et al. (2008). They developed a new model for LSW with some modifications from the traditional waterflooding model. In their model, salt was modeled as an additional single-lumped component in the aqueous phase; relative permeability and capillary pressure are made a function of salinity, and include the effect of connate water, hysteresis between imbibitions and secondary drainage water relative permeability, and dispersion phenomena. However, this model used a simple linear salinity dependence on residual oil saturation, which is not appropriate for real cases.

Rueslatten et al. (2008) performed a LSW experiment on a North Slope core sample. Then a model using the geochemical code, PHREEQC, was created to simulate the LSW. This model gave only an approximation of the pH variation as the mechanism of LSW. Subsequently, Sorbie and Collins (2010) extended their work by introducing a semi-quantitative model that describes the multicomponent ion exchange process at the pore scale. This model attempts to show the consequences of the change in the electrical double layers and the adsorption of polar organic species. However, further experimental studies are required to confirm this mechanism.

Subsequently, Wu et al. (2009) presented a general mathematical model to quantify the LSW process. Salt is also treated as an additional component in the aqueous phase that is transported by advection and diffusion. The relative permeability is assumed to be a function of fluid saturation and salt concentration, which cannot account correctly for wettability changes.

Omekeh et al. (2012) presented a black-oil type model with ion exchange and mineral solubility in LSW. They considered two-phase flow of oil and brine that contains Na^+, Mg^{++}, SO_4^{--}, and Cl^-. Cations are involved in a fast ion exchange process with the negative clay surface, X^-. In this model, the total release of divalent cations from the rock surface gives rise to change of the relative permeability such that more oil is mobilized, which agrees with the desorption of divalent ions being the main mechanisms for LSW. However, divalent ions such as Ca^{++} and Mg^{++} are expected to be adsorbed on the clay mineral during the course of LSW (Appelo, 2005) and the wettability alteration happens with the adsorption of divalent ions only (Suijkerbuijk, et al., 2012).

It would be more advantageous to model the process in a compositional simulator with full geochemical reactions. Dang et al. (2013) introduced a comprehensive ion exchange model with geochemical processes including intra-aqueous and mineral reactions. It has been coupled to the multi-phase multi-component flow equations in an equation-of-state compositional simulator which was introduced by Nghiem et al. (2004). This model captures most of the important physical and chemical phenomena that occur in LSW, including intra-aqueous reactions, mineral dissolution/precipitation, ion exchange and wettability alteration. The focus of this model is on the widely agreed mechanism that is the wettability alteration from preferential oil wetness to water wetness of formation rock surfaces due to ion exchange and geochemical reactions. With this model, Dang et al. (2013) were able to match accurately the ion-exchange phenomena from PHREEQC and the observed improved oil recovery and pH change, evolutions of multiple ions from LSW experiments by Fjelde et al. (2012) and Rivet (2009).

Pilot Test and Field Implementation

McGuire et al. (2005) and Lager et al. (2008) reported tests performed by BP in four areas using water injection salinity ranges between 1,500 to 3,000 ppm. Their single well chemical tracer tests (SWCTT) were performed in Alaska and the benefits of LSW EOR range from 6 to 12% OOIP, resulting in an increase in waterflooding recovery of 8 to 19%. In a log-inject-log test, typically 0.1 to 0.15 pore volume of high-salinty brine was injected first into the volume of interest to obtain the baseline residual oil saturation. This was followed by sequences of more dilute brine followed by high-salinity brine. Multiple log passes were conducted during each brine injection. At least three further passes were run to ensure that a stable saturation value had been established after injection of each type of brine. Results from the log-inject-log test (Webb, et al., 2004) showed 25-50% reduction in residual oil saturation by LSW.

Table 1: Summary of LSW Implementation in the Field

Author	Reservoir	Injected Brine (ppm)	Formation Damage	Incremental Oil Recovery (%)
Webb (2004)	Sandstone	3,000/ 220,000	No	20% -50%
McGuire (2005)	Sandstone <Alaska North Slope>	150-1,500 /15,000	No	13%
Robertson (2007)	Sandstone <West Semlek Reservoir> <North Semlek Reservoir> <Moran Reservoir>	10,000/60,000 3,304/42,000 7,948/128,000	No	Recovery tends to decrease as the salinity ratio increases.
Lager (2008)	Sandstone <Alaskan Oil Field>	2,600/ 16,640	No	10%
Veledder (2010)	Sandstone <Omar Oil Field> <Isa Oil Field>	2,200/ 90,000	No	10% - 15%
Seccombe (2010)	Sandstone <Endicot Oil Field>	12,000/ --	No	13%
Skrettingland (2010)	Sandstone <Snorre Oil Field>	500/50,000	No	No significant change.

Another successful application of LSW from SWCTT was given by Seccombe et al. (2010) in a mature offshore oil field located on the North Slope of Alaska. Recovery of residual oil between wells separated by 1,000ft was reported in their study. Additionally, historical field evidence in the Powder River basin of Wyoming reported by Robertson (2010) also showed that oil recovery tended to increase by about 12.4% as the salinity of injection brine decreases. Thyne and Gamage (2011) published a comprehensive evaluation of the effect of LSW for 26 field trials in Wyoming. Shell and Statoil have also reported the results of an unintended LSW field trial in a Middle Eastern oil field after they injected the water from a low saline river into this reservoir. The results showed that LSW led to a significant increase in the oil production and extended the potential of LSW application to adjacent fields (Veldder, et al., 2012; Mahani, et al., 2011; Suijkerbuijk, et al., 2012). However, one sandstone reservoir in North Sea oil fields that met the necessary conditions for LSW did not achieve a higher oil recovery factor in both the laboratory and field tests (Skrettingland, et al., 2010).

Hybrid LSW-Chemical Flooding

LSW has a great advantage since it can be combined with other classical EOR approaches such as polymer flooding, surfactant flooding and CO_2 miscible flooding. This is a very important aspect for the future development of LSW. A new hybrid LSW-EOR is getting wider attention in research centers and the oil industry because it is more cost-effective and has better performance in hostile reservoir conditions.

High viscosity of the injected fluid is a key requirement to ensure good volumetric sweep efficiency for secondary or tertiary recovery of oil. Typically, polymers are used to increase the viscosity of the displacing fluid, thereby reducing its mobility and effectively suppressing viscous channeling in heterogeneous oil reservoirs. One of the most widely used polymers for mobility control is partially-hydrolyzed polyacrylamide (HPAM). It is a water-soluble polyelectrolyte with negative charges along its chain; the repulsion between the negative charges contributes to the chain extension, thereby resulting in high viscosity.The use of low salinity polymer solution in polymer flooding has significant benefits because considerable lower amount of polymer is required to make the solution reach the target viscosity. Low salinity polymer flooding can also increase oil recovery by lowering residual oil saturation and achieve faster oil recovery by improving sweep efficiency. Kozaki (2011) demonstrated the synergy of LSW and polymer flooding in mixed-wet Berea sandstone cores. All the core samples were aged with a crude oil at 90°C for 30-60 days before the test. All the polymer floods were conducted in the tertiary mode. Synthetic formation brine (33,800 ppm) was chosen as high salinity water and NaCl brine (1,000 ppm) as low salinity water. Medium molecular weight HPAM polymer, FlopaamTM 3330S was used due to the low/moderate permeability of the Berea sandstone cores in this study. Coreflood tests indicate that injection of low salinity polymer solution reduces residual oil saturation by 5-10% over that of the high salinity waterflood. A part of the residual saturation reduction is due to low salinity and this reduction is achieved in less pore volumes of injection in the presence of polymers.

Alagic et al. (2010) reported that considerable amount of remaining oil is recovered from short core plugs when the selected surfactant formulation is introduced in pre-established low salinity environment. Alagic et al. (2011) extended their previous work by using two selected surfactants to evaluate surfactant ability to remobilize and produce remaining oil left behind after LSW. They injected high and medium surfactant concentration in both aged and un-aged Berea sandstone cores with the same permeability range. The experimental results indicated that continuous injection of LSW-surfactant resulted in higher incremental oil recovery from two aged cores (79.1% and 47% for high and medium surfactant concentration injection, respectively) compared to the un-aged cores (60.8% and 39.3%). It is important to note that they observed a strong ion exchange (between Mg^{++}, Ca^{++} and Na^{+}) and mineral reactions from effluent ion analysis. Elevated temperature, such as during the ageing step, is expected to promote ion exchange between the connate water brine and clays. High temperature will also increase the rate of calcite dissolution, which may be a source of Ca^{++} in the effluent. Increased levels of Ca^{++} in the water phase will promote adsorption of Ca^{++} on negatively charged clay surfaces, and play an important role on altering wettability towards more water wetness (Buckley, et al., 1998; Suijkerbuijk, et al., 2012). These important observations are well modeled in the LSW model proposed by Dang et al. (2013).

Hybrid LSW-Miscible CO_2 Flooding

Not only limited to chemical flooding, several investigations have been conducted to evaluate the potential of a combination of LSW and Water-Alternating-Gas (WAG). One of the first works in this area was reported by Kulkarni et al. (2004). In their experiment, miscible floods were conducted using rock-fluids systems consisting of Berea cores, n-Decane and two different brines (5% NaCl solution and another being the multi-component reservoir brine). The experimental results showed a significant decrease in oil recovery by WAG when the connate brine was changed from 5% NaCl to the lower salinity reservoir brine. It is possible to explain the observed trend by considering the injected ion composition of the two brines and the rock properties. They used strong water wetness sandstone core samples with very low clay content. These reasons have eliminated the advantages of LSW. Unfortunately, another research was lately reported by Jiang et al. (2010) with similar limitations in their experiments.

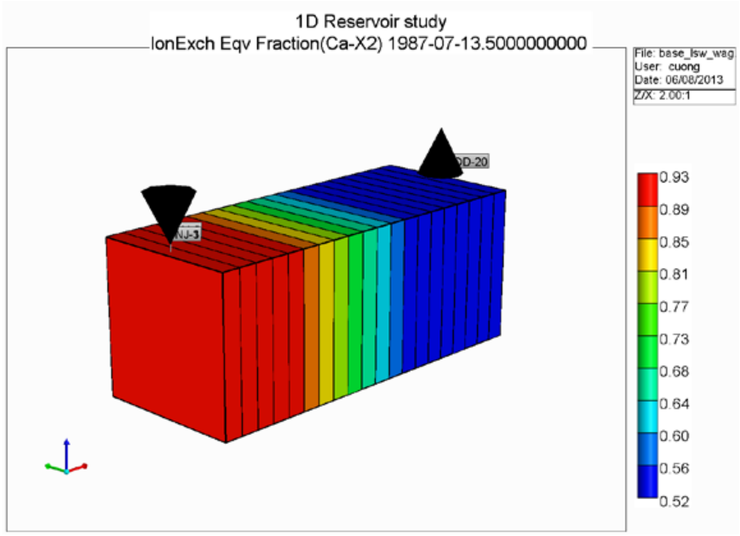

Figure : 1D Linear Model of LSW - CO_2 WAG

However, LSW is expected to improve the performance of WAG in the preferential oil wet and mixed wet reservoirs. Theoretically, LSW-WAG has a faster and higher oil recovery factor and better mobility control compared to the traditional WAG by promoting ion exchange and wettability alteration. This section reports preliminary results of LSW - CO_2 WAG in a mixed wet reservoir by coupling the LSW model introduced by Dang et al. (2013) with a comprehensive geochemical model (Nghiem, et al., 2004). A one-dimensional model was setup in order to simulate this process. Figure 1 shows the 1-D linear model for simulation of LSW and LSW - CO_2 WAG with the main properties shown in Table 2. A synthetic brine composition was used in this model where the salinity was similar to the formation water salinity in the high salinity waterflooding and diluted to 10 times lower in the low salinity waterflooding simulation. The clay content in the rock was about 20% volume of the bulk sample. In this model, we considered the reversible ion exchange between calcium and sodium as well as aqueous and mineral reactions.

The reactions that are modeled are:

$$CO_2(aq) + H_2O \leftrightarrow H^+ + HCO_3^- \tag{8a}$$

$$H^+ + OH^- \leftrightarrow H_2O \tag{8b}$$

$$\text{Calcite} + H^+ \leftrightarrow Ca^{2+} + HCO_3^- \tag{8c}$$

$$\frac{1}{2}Ca^{2+} + Na-X \leftrightarrow \frac{1}{2}Ca-X_2 + Na^+ \tag{8d}$$

Table 2: Basic Reservoir Properties for Base Case

Parameter	**Value for Base Case**
Grid blocks system	20 x 1 x 1
Grid block sizes	$\Delta x = 3.66$ m, $\Delta y = 30.48$ m, $\Delta z = 15.24$ m
Horizontal permeabilities	2000 mD
Vertical permeabilities	2000 mD
Porosity	0.2
Initial water Saturation	0.3
Cation Exchange Capacity (CEC)	50 eq/ft^3 of pore volume
Selectivity coefficient	0.4 at 25^{o}C (From Appelo, 1994)
Clay volume fraction	0.2

The dissolution of Calcite is a very important reaction in LSW. It provides a Ca^{++} source for ion exchange that affects the reservoir wettability. Buckley et al. (1998), Lebedeva and Fogden (2010), and Suijkerbuijk et al. (2012) indicated that the Ca^{++} concentration is important in determining wettability. In the one-dimensional model, we used two relative permeability sets that are represent mixed and preferential water wet conditions. Several scenarios were performed to compare LSW-CO_2 WAG with the other injection approaches as shown in Table 3.

Table 3: Injection Schemes for Numerical Simulation

Run	Water Injection (0.4 Pore Volume)		Water Alternating Gas (0.8 Pore Volume)								Chase Water (0.6 Pore Volume)		
A	HSW	HSW	HSW	HSW	HSW	HSW	HSW	HSW	HSW	HSW	HSW	HSW	HSW
B	LSW	LSW	LSW	LSW	LSW	LSW	LSW	LSW	LSW	LSW	LSW	LSW	LSW
C	HSW	HSW	CO_2	HSW	CO_2	HSW	CO_2	HSW	CO_2	HSW	HSW	HSW	HSW
D	HSW	HSW	CO_2	LSW	CO_2	LSW	CO_2	LSW	CO_2	LSW	LSW	LSW	LSW
E	LSW	LSW	CO_2	LSW	CO_2	LSW	CO_2	LSW	CO_2	LSW	LSW	LSW	LSW
F	HSW	HSW	CO_2	CO_2	CO_2	CO_2	-	-	-	-	LSW	LSW	LSW

(red)	HSW
(green)	LSW
(yellow)	CO_2

First, we consider the effect of LSW (Run A) on the oil recovery compared to the conventional high salinity waterflooding (Run B). Figure 2 indicates that LSW has a great advantage on oil recovery. This benefit is due to ion exchange and mineral reactions, which were discussed in detail in Dang et al. (2013). When the high salinity brine was injected, no wettability alteration occurred since the injected brine composition is similar to formation water composition. On the contrary, the adsorption of Ca^{++} during LSW altered the original mixed wetness to preferential water wetness, leading to a significant increase in the oil recovery.

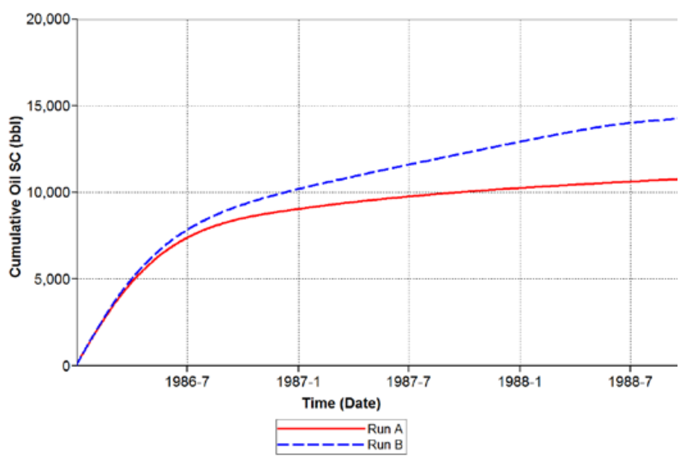

Figure 2: Cumulative Oil Recovery from Runs A and B

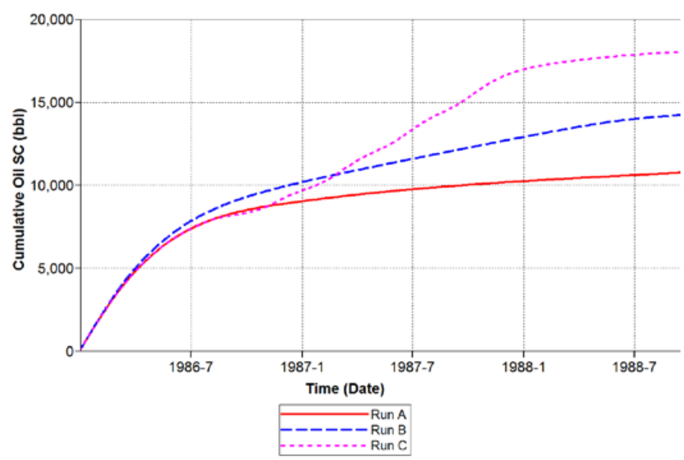

Figure 3: Cumulative Oil Recovery from Runs A, B and C

Although LSW has higher oil recovery than the conventional high salinity waterflooding, large amount of oil is still trapped in the reservoir. High Salinity WAG (Run C) was considered to increase oil recovery. In this run, about 0.4 pore volumes of high salinity brine was first injected into the reservoir, followed by 4 cycles of high salinity WAG, and finally buffered by 0.6 pore volumes of high salinity brine. Figure 3 shows that oil recovery by high salinity WAG increases by 28.7% and 15% of the original oil in place (OOIP) compared to the high salinity waterflooding and low salinity waterflooding, respectively. The additional oil recovery comes from the effects of CO_2 miscible flooding.

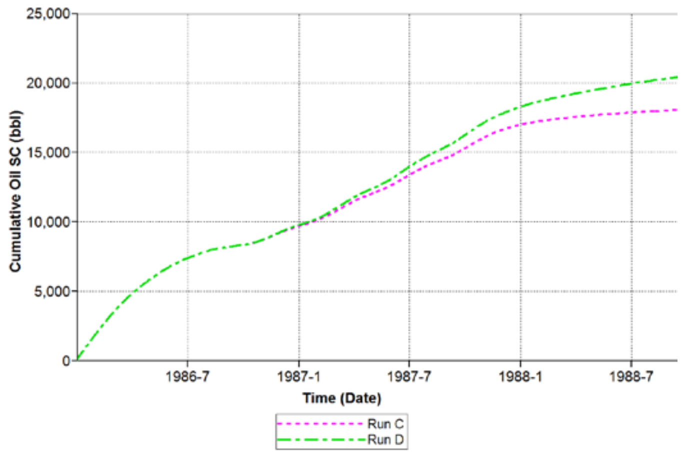

Figure 4: Cumulative Oil Recovery from Runs C and D

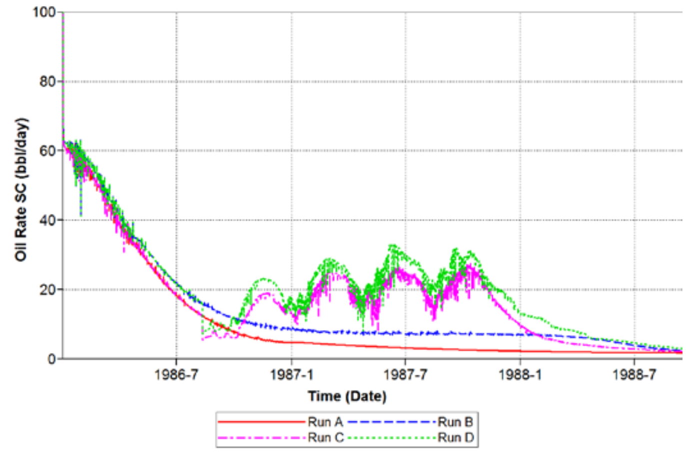

Figure 5: Oil Rate from Runs A, B, C and D

Figure 4 addresses the difference in oil recovery as the low salinity brine is used in the four WAG cycles and the buffering water slug (Run D) instead of high salinity brine in Run C. The final oil recovery factor increase further by about 9% of the OOIP in Run D compared to Run C, which could be inferred from mineral reactions and wettability alteration. Injection of CO_2 increases the dissolution of calcite, provides a source of Ca^{++} for ion exchange and promotes the wettability alteration towards more water wetness. Figure 5 indicates the variance of the oil rate in the first four simulations. It shows that WAG improved the recovery over waterflooding and that LSW-WAG has a higher oil rate than the high-salinity WAG.

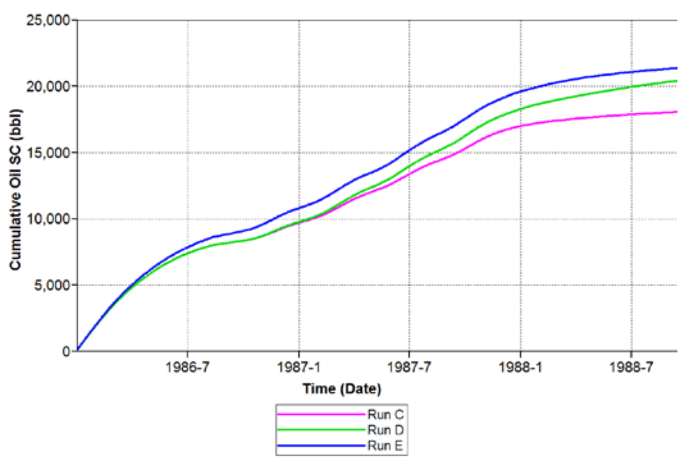

Figure 6: Cumulative Oil Recovery from Runs C, D, and E

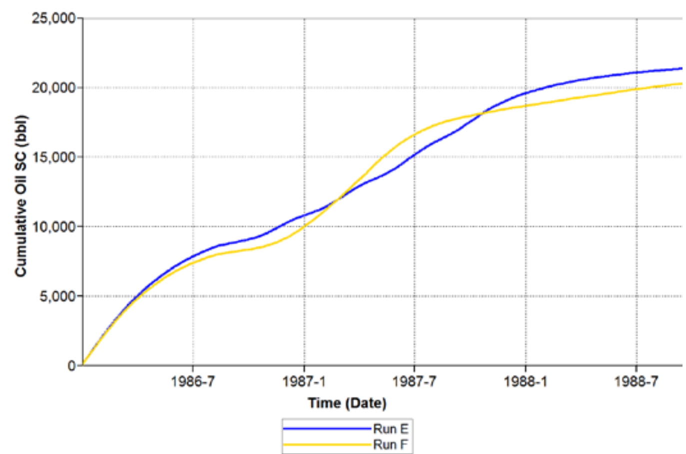

Figure 7: Cumulative Oil Recovery from Runs E and F

Subsequently, LSW is used in the first 0.4 pore volume instead of high salinity brine, followed by four cycles of low salinity brine WAG and 0.6 pore volume of low salinity buffering water as similar as the one in Run D. Figure 6 shows that this injection scheme has the highest ultimate oil recovery factor compared to Runs C and D. This is an important observation since late production is one of the main disadvantages of conventional high salinity WAG. It sometimes prevents the application of WAG in the field scale because of economic issues. However, this challenge could be overcome by using LSW-WAG. Finally, we compare the LSW-WAG with continuous CO_2 flooding. Note that the same amount of CO_2 about 0.4 pore volumes were used in these two runs. The simulation result in Figure 7 indicates that LSW-WAG still has higher ultimate oil recovery than continuous CO_2 injection.

Conclusions

This paper presents a review of LSW research achievements during last two decades and provides suggestions for new applications of LSW. The following remarks are consolidated from our experiences, previous studies, and industrial keynotes:

- LSW yields higher oil recovery in comparison with conventional waterflooding.
- Wettability alteration towards more water wetness during the course of LSW due to ion exchange and mineral reactions is the most important mechanism that leads to higher recovery.
- Most of pilot tests proved that LSW is a promising method for EOR in full field scale.
- LSW would be considered for both secondary and tertiary modes. Alternatively, LSW can be combined with other chemical flooding and WAG processes for better recovery. From the simulation results, LSW - CO_2 WAG yields higher ultimate oil recovery factor compared to high/low salinity waterflooding and high salinity CO_2 WAG.

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