EXPERIMENTAL INVESTIGATION OF THE ROLE OF DIFFERENT CLAYS IN LOW
SALINITY WATERFLOODING

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ABSTRACT

Various studies have demonstrated that Low Salinity Water Flooding (LSWF) can enhance oil recovery effectively, and its typical recovery mechanisms have been recognized. However, there is still a significant debate on the functions of clay during LSWF. This study investigates the impact of different clays, including montmorillonite, illite, and kaolinite, on the performance of LSWF.

The zeta potentials of sand, montmorillonite, illite, and kaolinite in the presence of high salinity water (HSW) and low salinity water (LSW) were first examined. Then, the swelling factors of the three clay minerals in the HSW and LSW were measured in succession to determine their swelling characteristics. Subsequently, coreflooding experiments were conducted using one clay-free sand pack column and five sand pack columns respectively containing 10 wt% of montmorillonite, 10 wt% of illite, 10 wt% of kaolinite, compound clays (5 wt% of montmorillonite + 2.5 wt% of illite + 2.5 wt% of kaolinite), and 5 wt% of montmorillonite and the cumulative oil production and pressure drops were recorded.

A produced crude oil sample with the American Petroleum Institute (API) gravity of 34° and viscosity of 14 cP (60°F) was used in the experiments. The total dissolved solids (TDS) of the HSW and LSW are 27,501 mg/L, and 2,485 mg/L respectively. It has been found that LSW could generate more negative zeta potential values for sand, montmorillonite, illite, and kaolinite, which made them more water-wet and thus favor oil recovery. Montmorillonite obviously swelled in HSW, and it could further swell significantly by contacting LSW. Although illite showed some

swelling in HSW, LSW could not further expand it. Kaolinite did not swell in both HSW and LSW. The results from six coreflooding experiments showed that after high salinity waterflooding, the subsequent LSWF could generally further improve the oil recovery. The sand pack columns containing montmorillonite showed higher incremental oil recovery during LSWF (17.42% from sand pack column with 10 wt% of montmorillonite, 10.27% from sand pack column with compound clay, and 8.90% from sand pack column with 5 wt% of montmorillonite). Also, LSWF could improve oil recovery for the clay-free sand pack column, the sand pack column with kaolinite, and the sand pack column with illite by 0.73%, 0.83%, and 1.03%, respectively.

Therefore, clay minerals would play an important role in determining oil recovery performance in LSWF, and the more swelling there is in clay in LSW, the more favorable it is in LSWF. This study proved that both clay swelling and wettability alteration could attribute to the improved oil recovery by LSWF.

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NOMENCLATURE

ANS	Alaska North Slope
API	American Petroleum Institute
BPR	Back Pressure Regulator
CEC	Cation-Exchange Capacity
cP	Centipoise
DI	De-Ionized
DLE	Double Layer Expansion
EOR	Enhanced Oil Recovery
HSW	High Salinity Water
ID	Inner Diameter
L	Liter
LSW	Low Salinity Water
LSWF	Low Salinity Waterflooding
LVDT	Linear Variable Displacement Transducer
mD	Millidarcy
meq	Milliequivalents
mg	Milligram
min	Minute
mL	Milliliter
OOIP	Original Oil In Place

psi Pounds Per Square Inch

PV Pore Volume

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Chapter 1 Introduction

1.1 Background

At the early development stage of an oilfield, natural pressure from the reservoir helps push the fluid to the surface, which is known as primary recovery. However, with the natural pressure beginning to decline over time, secondary and/or tertiary recovery methods are usually employed. The most commonly applied secondary recovery methods are waterflooding and gas injection (Ahmed 2010). But as water cut and gas ratio increase during production, the field reaches an economic threshold. When this happens, other artificial methods are implemented known as tertiary or enhanced oil recovery (EOR).

Waterflooding has drawn attention as an emerging process that could increase oil recovery for decades. Recently, low salinity waterflooding (LSWF), an EOR technique using injection water containing modified composition to improve oil recovery, has been extensively studied in attempts to increase oil recovery (Tang and Morrow 1997; Austad et al. 2010; Awolayo et al. 2018; Nasralla et al. 2014). The technology of LSWF has been proposed to improve oil recovery in several projects globally. Laboratory experiments and field pilot applications have shown that there is improved oil recovery corresponding to LSWF, compared to conventional waterflooding implementations. However, there is still no agreement on the principal mechanism of LSWF for enhanced oil recovery.

1.2 Problem definition

The absence of a single reasonable common mechanism to describe how LSWF can improve oil recovery in both laboratory experiments and field pilot projects has increased the interests of

several researchers. There is no understanding as to why it works better than the conventional waterflooding. Nevertheless, several experimental studies for LSWF set out conditions for how low salinity water (LSW) works (Tang and Morrow 1999; McGuire et al. 2005; Lager et al. 2006).

The conditions are:

- 1) Porous reservoir rock contains clay.
- 2) Oil composition contains polar components.
- 3) Divalent cations must be present in the connate water.

However, some of the conditions reported being essential for the occurrence of LSWF-such as the presence of clay-have lately been questioned (Sohrabi et al. 2015; Al-Saedi et al. 2018). Fjelde et al. (2014) found that the clay content plays a vital role in LSWF; not only could the concentration of the clay, but also its distribution influence the EOR performance of LSWF. Shehata and Nasr-El-Din (2017) also investigated the effect of clay content. They concluded that instead of overall clay fraction, the amount and surface area of each type of clay affects the additional oil recovery by LSWF.

1.3 Research objectives

The objective of this study is to gain a better understanding of the functions of clay during LSWF on enhanced oil recovery in sandstone reservoirs. This study investigates the impact of different clays including montmorillonite, illite, and kaolinite on the performance of LSWF.

The objectives of the study are as follows:

- 1) To evaluate the zeta potential of pure sand, montmorillonite, illite, and kaolinite individually in the presence of high salinity water (HSW) and LSW, respectively;

- 2) To examine the swelling properties of montmorillonite, illite, and kaolinite in the presence of HSW and LSW in succession;
- 3) To investigate the effect of montmorillonite, illite, and kaolinite on the recovery of incremental oil by LSWF.

1.4 Brief description of chapters

Chapter 2 reviews the literature which includes the fundamental theories of oil recovery. It also explains the significance of LSWF in EOR processes. Furthermore, Chapter 2 discusses the various underlying proposed mechanisms of LSWF. At the end of this Chapter, the necessary conditions for LSWF are discussed.

Chapter 3 introduces clay, the properties of various clay contents, and includes a literature review on authors finding clay as necessary as well as counterevidence on the relevance of clay in LSWF.

Chapter 4 describes the experimental work including all the materials, apparatuses, and procedures used in the zeta potential measurement, swelling test, and coreflooding experiment.

Chapter 5 analyzes the results obtained from the experiments. It quantifies the changes in the surface charges caused by the brine salinity change, the swelling of each clay mineral with the swelling test, and results from the coreflooding experiment. It also illustrates the predominant mechanism(s) supporting the importance of montmorillonite, illite, and kaolinite in LSWF.

Chapter 6 presents the conclusion statement based on this research. It shows the relevant observation of the relationship between LSWF and the importance of various clay contents. Besides, it presents some recommendations for future work.

Chapter 2 Literature Review

This chapter reviews the fundamental concepts of LSWF and its effect on oil recovery. The purpose is not to elaborate the details in all subjects, but to provide the basic foundation that introduces most terms required to understand the subject in this thesis adequately. This chapter also presents the proposed principal mechanisms of LSWF from other studies conducted.

2.1 Oil recovery processes

The oil recovery processes are divided into three stages: primary, secondary, and tertiary recovery or EOR (Green and Willhite 2008). **Figure 2.1** shows a schematic illustration of the oil recovery stages.

Figure 2.1–Progressive stages of oil recovery (Alvarez 2017)

2.1.1 Primary recovery

In the primary recovery, the natural energy existing in the reservoir is used as the main source of energy for displacing hydrocarbons. Green and Willhite (2008) specified that the principal natural energy sources are as follows:

- 1) Solution-gas drive
- 2) Gas-cap drive
- 3) Natural water drive
- 4) Fluid and rock expansion
- 5) Gravity drainage

Depending on the reservoir drive mechanism and hydrocarbons properties, only around 5-15% of the original oil-in-place (OOIP) can be recovered from this primary method.

2.1.2 Secondary recovery

Secondary recovery, which is used for augmentation of the natural energy, is introduced when natural reservoir energy is depleted to the extent that there is not enough energy to lift fluids economically (Green and Willhite 2008). This method involves the injection of water or gas, which will displace the oil. This is typically effective in targeting an incremental 30% of the oil reserves.

The most common secondary recovery technique used to recover oil is waterflooding. Conventionally, the waterflooding technique has been performed mainly in light- and medium-oil reservoirs. Advantages of waterflooding include the availability of water sources, satisfactory mobility ratio, good sweep efficiency, and low cost associated with handling produced water.

However, waterflooding is insufficient, especially in viscous and heavy oil reservoirs due to viscous fingering, which results in low oil recovery (Targac et al. 2005; Cheng 2018).

2.1.3 Tertiary recovery/EOR

The way to further increase oil production is through tertiary recovery or EOR. EOR technology enhances fluid flow within the reservoir by adding heat, solvent/miscible gas, or chemicals. This improves the interaction between the injected fluid and the reservoir fluids, promotes the mass transfer process, and/or alters the oil properties which can result in enhancing oil movement through the reservoir.

2.1.3.1 Thermal injection

It involves the introduction of heat (such as steam) to lower the viscosity and improve the fluid's flowing ability through the reservoirs. This method has been considered the most efficient for viscous and heavy reservoirs with shallow zones. However, thermal recovery is not viable in some places such as Alaska North Slope (ANS), due to the thawing of the permafrost when the subsurface temperature increases (Attanasi and Freeman 2014).

2.1.3.2 Miscible flood

This recovery method involves injecting gases that are miscible with oil resulting in the generation of a homogenous low viscosity mixture into the reservoir to produce additional oil to the wellbore. This method requires an available cheap source of gases and a high reservoir pressure to operate efficiently. Initially, CO₂ and produced natural gas were selected as viscosity reducing and swelling agents for improving oil recovery (Targac et al. 2005). Recently, CO₂ enriched with

natural gas liquid has been used since miscibility is more likely to be achieved, and oil viscosity can be reduced significantly with enriched gas (McGuire et al. 2005; Cheng 2018).

2.1.3.3 Water-alternating-gas (WAG)

This technique improves recovery by combining water and gas injection. The use of both gas and water alternately helps provide better sweep efficiency and reduce gas channeling, making it more effective and efficient for oil displacement. The WAG technique is particularly a more effective way of producing heavy oil reservoirs since near-wellbore viscosity can be reduced considerably (McKean et al. 1999). A viscosity-reducing agent such as hydrocarbon gases or CO₂ reduces the viscosity from viscous and heavy oil reservoirs up to 90%, leading to an extra recovery of up to 20% (McGuire et al. 2005; Targac et al. 2005; Paskvan et al. 2016; Cheng 2018).

2.1.3.4 Chemical injection

Chemical injection involves the injection of chemicals into reservoirs to help reduce interfacial tension and aid mobility. Chemicals such as detergent-like surfactants could be used to help lower interfacial tension, allowing the flow of oil. Other chemicals such as polymer could increase the efficiency of waterfloods by increasing water viscosity. Microbial injection is also considered as a part of chemical injection but is rarely used, due to its high cost and the fact that its development is not yet broadly established.

2.1.3.5 Cold heavy oil production with sand (CHOPS)

This is a new recovery technique that is used in viscous and heavy oil production from poorly consolidated and unconsolidated sandstone reservoirs where the production of sand is allowed

(Young et al. 2010; Nassir et al. 2015; Cheng 2018). CHOPS involves the deliberate initiation of sand influx during the completion procedure, thereby increasing the permeability of the reservoir and allowing heavy oil to flow. Although CHOPS is a promising technology for viscous and heavy oil reservoirs, it is not widely accepted due to high sand production.

Many EOR techniques have been proposed and practiced over the years. However, the economic feasibility and practical applicability of most of these recovery techniques drive researchers into improving and reforming these techniques.

2.2 LSWF

LSWF, which has been known as a promising and rapidly evolving EOR technology, can improve oil recovery by lowering the salinity of the injected water (Sorop et al. 2013; Chandrashegaran 2015). It has several potential benefits, such as a relatively low cost compared to other EOR techniques. Moreover, it can be implemented in new and ongoing waterflood projects both in sandstone and carbonate reservoirs. Also, it can be used as a stand-alone recovery method or in conjunction with other EOR techniques, such as polymer flooding. It can also address problems of scale formation associated with conventional waterflooding.

LSWF has been considered to be an economical method that can significantly increase oil recovery with experimental studies (Tang and Morrow 1997; Zhang et al. 2007; Austad et al. 2010; Yousef et al. 2011; Al-Saedi et al. 2018; Cheng 2018). Likewise, field applications of LSWF also show enhancement of oil recovery (Buikema et al. 2012; Webb et al. 2004; Robertson 2007; Lager et al. 2008; Vledder et al. 2010).

Although the EOR performance of LSWF has been confirmed by numerous lab experiments and field pilot tests, no mechanism has been widely accepted yet as the principal mechanism in the LSWF process due to the complex interaction between crude oil, brine, and rock. The various low salinity mechanisms which have been proposed include the following.

2.2.1 Mechanisms of LSWF

2.2.1.1 Wettability alteration

Wettability is the inclination of one fluid to preferentially adhere to a solid surface in the presence of a second fluid (Green and Willhite 2008). Wettability alteration has been reported by many researchers and observed with additional oil recovery in LSWF (Rezaeidoust et al. 2009; Tang and Morrow 1997; Jadhunandan and Morrow 1995; Buckley et al. 1998; Nasralla et al. 2013; Austad et al. 2010). This mechanism involves alteration of the rock surface from being oil-wet to becoming more water-wet. Due to this change, additional oil is released and allowed to flow out of the rock surface. Alotaibi et al. (2010) studied low salinity behavior via contact angle (a measure of wetness) measurement. As the salinity decreases, the contact angle also tends to decrease, though different crude oil/rock/brine systems wet differently. Fjelde et al. (2013) observed that in the case of a more water-wet rock, there was later breakthrough, faster oil production, and a decrease in residual oil saturation. However, for a less water-wet rock case, slower oil production and earlier breakthrough were observed, but residual oil saturation also decreased with several pore volumes (PVs) of injected water. In this manner, it is beneficial to change the wettability from oil-wet to water-wet or mixed-wet. **Figure 2.2** shows the example of wettability alteration leading to the enhancement of oil recovery.

Figure 2.2–Schematic sketch of low salinity flooding wettability effect change in a porous sandstone rock (Mahani et al. 2015)

LSWF mechanism leading to wettability change has been shown to depend on (Rezaeidoust et al. 2009; Jackson et al. 2016),

- 1) pH and water composition
- 2) clay content in the reservoir
- 3) crude oil properties
- 4) reservoir temperature, and
- 5) characteristics of mineral surfaces

Moreover, most researchers have reported that injection water containing a higher concentration of sulfate SO_4^{2-} could lead to wettability alteration (Rezaeidoust et al. 2009; Al-adasani et al. 2012). Recently, another mechanism causing wettability change was reported by Mahani et al. (2015), which is the electrostatically-induced repulsive force formed between the reservoir rock and the injected brine as well as between the injected brine and crude oil.

2.2.1.2 Multi-ion exchange (MIE)

MIE is another LSWF mechanism assumed to improve oil recovery further. This mechanism was first presented by Lager et al. (2006), who stated that the polar components were bonded to the rock surface by divalent ions (Lager et al. 2008).

On an oil-wet surface, organo-metallic complexes form from multivalent cations on a rock surface bonding to polar compounds present in the oil phase. At the same time, the oil wetness of the rock surface is enhanced due to some organic polar compounds adsorbed directly to the mineral surface. In relation to low salinity, MIE will take place, removing directly adsorbed organic compounds and organo-metallic complexes from the surface and substituting them with uncomplexed cations. This results in improved oil recovery from the desorption of organic matter, and change in the wetness of the rock surface. Lager et al. (2008) also reported that the removal of divalent cations like Ca^{2+} and Mg^{2+} from the rock surface led to higher recovery. Thus, injection of LSW containing a reduced concentration of divalent cations results in additional oil recovery. This is significant because for the first time they experienced that in a clastic reservoir where the mineral structure was preserved, no improved oil recovery was observed with LSW containing divalent ions of Ca^{2+} and Mg^{2+} . **Figure 2.3** shows the example of MIE leading to hydrocarbon release.

Figure 2.3—Illustration of the effect of MIE for desorption of organic oil components (Cotterill 2014)

2.2.1.3 Fine migration

Fine migration is another mechanism of LSWF that occurs when brine of low salinity containing a low concentration of Ca^{2+} and Mg^{2+} is injected. The injection of LSW results in fine grains migrating and filling the pore spaces, therefore forcing the injected brine to flow through the unswept zone (Rivet et al. 2010).

Various attempts have been made to explain this mechanism. Vaidya and Fogler (1992) showed that a sudden reduction in the salinity to extremely low saline brine and a high pH could be the prime cause of the fine release. Tang and Morrow (1997) noticed that during the LSWF on the Berea core samples, kaolinite fines were mainly being eluted, so they came to the conclusion that fine mobilization was obtained from the exposure of underlying surfaces and increased water wetness of the system. Also, Tang and Morrow (1997) reported a reduction in permeability when the injected fluid had a salinity lower than 1,550 mg/L.

2.2.1.4 pH change

Studies have shown that a rise in pH during LSWF has contributed to the success of LSWF. The increase in pH is a result of two concurrent reactions: carbonate dissolution and cation exchange. The amount of carbonate present is significant because a release of excess OH^- and cation exchange occurs between the clay minerals and the invading LSW.

However, some conflicting evidence has thrown doubts on this effect. Al-Saedi et al. (2018) reported that an increase in pH with the change to LSWF showed little recovery. This shows that despite the earlier proof, pH is an effect of LSWF but might not be responsible for the additional oil from the LSW injection. **Figure 2.4** shows an increase in pH with an injection of LSW.

Figure 2.4—Indication of a rise in pH with the change to LSWF (Chen et al. 2018)

2.2.1.5 Double-layer expansion (DLE)

DLE attributes the success of LSWF to the reduction of the total salinity content of water, rather than just a decrease in divalent cation concentration (Ligthelm et al. 2009). During LSWF, as the salinity of water decreases, the double layer expands due to lower attractive force resulting from the reduced ionic strength. Therefore, the thickness of the water layer which is adjacent to the surface is increased. This drives the rock surface to become more water-wet, and thus more oil is recovered. Ashraf et al. (2010) stated that as the salinity of the electrolyte decreases, the thickness of the electrical double layer and electrostatic repulsiveness increase, which ultimately helps in releasing oil from the pore of the rock surface. Nasralla and Nasr-El-Din (2011 and 2012) and Nasralla et al. (2011a and 2011b) also conducted studies that support the DLE mechanism. The researchers explained that correlating the zeta potential measurements to coreflooding shows that the DLE, which results from the forces between oil and rock, could be a dominant mechanism in improving oil recovery by LSWF. **Figure 2.5** shows a simple schematic of an electrical double layer.

2.2.2 Necessary conditions for LSWF and factors affecting its process

It has been extensively acknowledged that LSWF can lead to higher oil production in the field (Lager et al. 2006; Webb et al. 2004; Tang and Morrow 1999). Nevertheless, LSWF may not be applied to all oil reservoirs as an EOR technique.

Figure 2.5–Schematic of electrical double layer (Nasralla and Nasr-El-Din 2011).

Based on the experimental observations of earlier researchers on LSWF and proposed LSWF mechanisms explained in the above section, some of the conditions that are necessary for an effective application of LSWF can be summarized:

- 1) Clay must exist in the sandstone core (Tang and Morrow 1997).
- 2) Crude oil must contain organic materials. Since improved oil recovery in LSWF was not observed when synthetic oil (white oil) was used, the oil should contain polar crude oil components (Tang and Morrow 1997).
- 3) Presence of connate water (Lager et al. 2008).
- 4) Formation brine contains divalent cations with high salinity (Lager et al. 2008; Ligthelm et al. 2009; Austad et al. 2010; Emadi and Sohrabi 2013).

- 5) The rock is an intermediate-wet or weakly water-wet system (Emadi and Sohrabi 2013).
- 6) Brine injected is Ca^{2+} free (Nasralla and Nasr-El-Din 2011).
- 7) pH of water is about 5 (Austad et al. 2010).

Notwithstanding meeting the above requirements, there have been some disappointing results in coreflood studies and pilot field tests (Zhang and Morrow 2006; Rezaeidoust et al. 2010; Skrettingland et al. 2011). These disappointing results have led to questions as to how true each of these conditions holds. It further shows that a lot is still not understood about the potential of LSW despite the interest that it has generated (Morrow and Buckley 2011).

For this research, we focused on the first condition, which is on the importance of clay in sandstones. About 50% of the world's petroleum reservoirs are found in sandstones, and most of these reservoirs contain clay minerals. Questions on whether clay necessarily has to be present for successful recovery have been asked, as well as how much and what type should be present for additional recovery with LSW.

Chapter 3 Clay and Its Properties

3.1 Introduction of clay

Sandstone constitutes about 10-20% of the sedimentary rocks in the Earth's crust and is the second most commonly existing sedimentary rock after shale (Britannica 2010). It is composed mostly of sand-sized minerals as well as matrix and cement. Matrix is the fine-grained material that is present within the interstitial pore space between the framework grains. Cement is the mineral matter that binds the siliciclastic framework grains together. The cement materials are mostly calcite, quartz (silica), clays, and gypsum (Alden 2017).

Clay is a general term commonly used to describe sediments, soils, or rocks consisting of extremely fine-grained mineral particles and organic matters (M-I Swaco 1998). They are often soft and plastic when wet but become hard when dry. Clay is also used as a group term for particles with a size of less than $2\text{ }\mu\text{m}$ in diameter, which includes most of the clay minerals. Clay exists in nature with a stacked or layered structure; each clay layer is highly flexible, very thin, and has a huge surface area. An individual clay particle can be visualized as being much like a sheet of paper with each unit layer roughly 10 angstroms ($\text{\AA}$) thick. **Figure 3.1** shows a typical structure of a clay platelet.

Figure 3.1–Shape, size, and charge of a typical clay platelet in the reservoir (Lei 2020)

The groups of clay minerals are as follows:

- 1) Kaolinite group, which includes kaolinite, dickite, nacrite, halloysite, and nacrite. It is formed by the decomposition of orthoclase feldspar (e.g., in granite);
- 2) Illite group, which includes hydrous micas, phengite, brammalite, and celadonite. It is formed by the decomposition of feldspars and micas;
- 3) Smectite group, which includes montmorillonite, bentonite, nontronite, hectorite, saponite, and sauconite. It is formed by the alteration of mafic igneous rock rich in calcium and magnesium;
- 4) Glauconite is an iron potassium phyllosilicate mineral characterized by green color, very low weathering resistance, and is very friable (Odin 1988);
- 5) Vermiculite is a hydrous phyllosilicate mineral that undergoes expansion when heated. It is formed by weathering or hydrothermal alteration of biotite or phlogopite (Potter 2000).

Table 3.1 shows a breakdown of the various clay content mentioned in the literature, by researchers who had investigated the EOR performance of LSWF in the presence of clay. **Table 3.2** shows different reservoirs' clay contents from various locations. Although it shows that the clay composition varies across different reservoirs in various proportions, commonly naturally occurring clay minerals in sandstone reservoirs are kaolinite, illite/mica, montmorillonite, and smaller contents of chlorite (Grim 1942 and 1953; Hughes 1950; Civan 1990). Therefore, in this study, three main types of clay minerals, including kaolinite, illite, and montmorillonite, were investigated. **Table 3.3** below describes the different properties of kaolinite, illite, and montmorillonite.

Table 3.1–Clay composition of clay content used in literature

Source/Paper	Clay %	Clay Composition		
		Kaolinite	Illite	Montmorillonite
Rezaeidoust et al. (2009)	7-16	3.5	0	0
Austad et al. (2010)	9.9-10.3	0	8.4-8.7	0
Cissokho et al. (2010)	9.2	0	2-7.7	0
Rezaeidoust et al. (2010)	8-16	3-3.4	2.7-10.3	0
Nasralla and Nasr-El-Din (2011)	14	5	1	0
Hadia et al. (2011)	3-7	1.5-6	0	0
Fjeldo et al. (2012)	13	NR	NR	NR
Hadia et al. (2012)	7.5	6.5	0	0
Shehata and Nasr-El-Din (2014)	5-14	2-6	2-10	2
Ramanathan et al. (2015)	13	6	2	0
Rezai-Gomari et al. (2015)	5-15	5-15	5-15	0
Pinerez et al. (2016)	11	0	8.2	0
Sohrabi et al. (2017)	5.9	3.4	1.9	0
Al-Saedi et al. (2018)	5-20	2.5-20	2.5-20	0
*NR = Not Reported				

Table 3.2—Reservoirs clay content in different locations (Hosterman et al. 1990)

Location	Formation	Clay %	Clay Composition		
			Kaolinite %	Illite %	Montmorillonite %
Alaska	Endicott Formation	13	95	Trace	0
California	Pismo Formation	8	25	27.5	47.5
Kentucky	Lower Pennsylvanian Caseyville Formation	12.2	95	5	0
Utah	Eocene Green River Formation	9	21	79	0
Alberta	Frontier Sands	9.6	4	7	26

Table 3.3—Basic properties of kaolinite, illite, and montmorillonite (International Drilling Fluids 1982)

Group	Structure	Cation exchange capacity (CEC) (meq/100g)	Exchange cation
Montmorillonite	2:1 layer	80-150	Na ⁺ , Ca ²⁺ , K ⁺ , Mg ²⁺
Illite	2:1 layer	10-40	K ⁺
Kaolinite	1:1 layer	3-15	None

3.2 Structure of clay

Each plate-like clay particle comprises a stack of parallel unit layers. Each unit layer is a combination of tetrahedral arranged silica sheets and octahedral arranged alumina or magnesia sheets. Clays are usually either of the two-layer type or three-layer type (Srivastava 1968).

3.2.1 Montmorillonite

Montmorillonite, as shown in **Figure 3.2** and the picture at the right side of **Figure 3.3**, is a 2:1 clay that is built of unit layers composed of two tetrahedral sheets on either side of one octahedral sheet which are held together by weak O-O van der Waals force.

3.2.2 Illite

Illites, like the montmorillonites, have the fundamental structural pattern of a 2:1 clay. That is, one unit consists of three sheets where the octahedral aluminum layer lies between two tetrahedral silica layers.

3.2.3 Kaolinite

Kaolinite, which is shown on the left side of **Figure 3.3**, is characterized as a 1:1 clay consisting of one tetrahedral silica layer and one octahedral aluminum layer. Additionally, the unities are bonded together by strong hydrogen bonds (M-I Swaco 1998).

Figure 3.2–Montmorillonite structure of two silica tetrahedral and one alumina sheet (M-I Swaco 1998)

Figure 3.3–Layer structure of a 1:1 and 2:1 clay (Craig 2005)

3.3 Surface charge of clay

Clay minerals behave as colloid particles and typically negatively charged. The net negative charge is compensated by the adsorption of cations on the unit layer surfaces, both on the interior and the exterior surfaces of the stack.

3.3.1 Montmorillonite

Montmorillonites have two types of electric charges: a variable charge from the proton adsorption/desorption reactions on the surface of hydroxyl groups and a structural negative charge from isomorphous substitutions around the clay structure. As a result of this negative potential, montmorillonite has negative electrophoretic mobility and high cation adsorption and cation exchange properties (Avenai 1998). **Figure 3.4** shows the structural negative charge from the isomorphous substitution around the clay.

Figure 3.4—Substitution of Mg²⁺ for Al³⁺ causing a negative-charged particle (M-I Swaco 1998)

3.3.2 Illite

Illite has the same basic structure as montmorillonites, but instead of the substitution of Mg²⁺ for Al³⁺ as in montmorillonite, illite has a substitution of Al³⁺ for Si⁴⁺. This still gives a negative charge since the compensating cations are primarily the potassium ion (K⁺).

3.3.3 Kaolinite clay

Kaolinite does not contain interlayer cations or surface charges, and there is little or no substitution in either tetrahedral or octahedral sheets. However, some slight charges can come from broken bonds or impurities. Therefore, kaolinite has a relatively low CEC.

3.4 Swelling capacity of clay

The swelling-dependent property of clay varies proportionally and is a function of hydration. However, not all clays swell when hydrated.

3.4.1 Montmorillonite

Montmorillonite, on hydration, absorbs water and cations to surfaces between layers in its crystalline structure and on its external surfaces. Therefore, the ability of montmorillonite to adsorb water is much greater than other clay minerals.

Depending on the cation saturating the montmorillonite, there are two forms of montmorillonite: sodium montmorillonite and calcium montmorillonite. In the presence of an aqueous phase, sodium montmorillonite swells considerably more than calcium montmorillonite. This is because calcium is a divalent cation; and divalent cations such as Ca^{2+} and Mg^{2+} increase the attractive force between platelets, thus reduce the amount of water that can be absorbed. Monovalent cations such as Na^+ give rise to a smaller attractive force and allow more water to penetrate between the platelets. In this study, the sodium montmorillonite was used to conduct the analysis. **Figure 3.5** shows the difference in the swelling capacity for the various montmorillonite.

Figure 3.5—Comparison of swelling for calcium and sodium montmorillonite (M-I Swaco 1998)

3.4.2 Illite

The swelling property of illite, on hydration, falls between montmorillonite and kaolinite, but are in general, closer to kaolinite than to montmorillonite in their increase in volume. This is due to the fact that the exchangeable ion on the illite surface is K^+ . The size and shape of the K^+ fit between the layers, and it pulls them closer together.

3.4.3 Kaolinite

Kaolinite consists of broken edges on its outer surfaces and a lack of ions between the sheets. Due to both these reasons, the dissociation of the cations does not pry the clay particles apart into their constituent units and therefore there is no swelling in the presence of aqueous phase.

3.5 Influence of clay on LSWF EOR performance

Clay minerals in sandstone are thought to be a necessary criterion for successful LSWF, but in the past few years, there has been a lot of debate surrounding the importance of clay. This section reviews details of different authors' researches, both supporting and contradicting the importance of clay in LSWF.

3.5.1 Supporting evidence

Jerauld et al. (2006) concluded that incremental oil recovery from LSW is a function of kaolinite content and a reasonably strong correlation between incremental oil recovery and kaolinite content was obtained. Seccombe et al. (2008) further confirmed that the EOR performance of LSWF improves with the increasing clay content of kaolinite. Later, Cissokho et al. (2010) presented experiments dealing with tertiary and secondary recovery tests performed on an outcrop sandstone containing 9.2 wt% clays (2-7.7 wt% illite) and concluded that, compared to kaolinite, the presence of illite yielded 10% more oil recovery by injecting LSW. Rezaeidoust et al. (2010) conducted coreflooding experiments with cores containing clay content ranging from 8 to 16 wt% with illite and kaolinite being the majority of the clay constituents. The authors concluded that the oil recovery decreased from 6% to about 2% when the clay content of the core material decreased from 16 to 8 wt%. Then, Hadia et al. (2011) evaluated the LSWF performance using core plugs

containing 3 to 7 wt% clay content, which consists mainly of kaolinite (1.5-6 wt%) and found that 8% additional oil recovery was obtained.

3.5.2 Contradicting evidence

Soraya et al. (2009) stated that rock containing kaolinite was not a necessary condition to obtain additional oil gain by LSW injection; on the contrary, very positive results were observed with kaolinite-free sandstone. Shehata and Nasr-El-Din (2014) injected low salinity brine to cores from Bandera, Parker, Grey Berea, and Buff Berea sandstone formation containing 6 to 22 wt% clay content (2 to 6 wt% kaolinite, 2 to 10 wt% illite, and 2 wt% montmorillonite). They found that there was no direct relation between the clay contents and oil recovery, while the sandstone rock quality and mineral distribution appeared to play critical roles in the effectiveness of LSWF. Sohrabi et al. (2017) further evaluated the effect of clay by performing LSWF on the clay-free core as they observed significant additional oil recovery compared to HSW injection in the clay-free porous medium. Al-Saedi et al. (2018) conducted several coreflooding experiments on clay-free cores and cores containing 5-20 wt% kaolinite and illite, and the authors concluded that clay is not absolutely needed.

Based on the aforementioned literature survey, kaolinite, illite, and montmorillonite have been shown to be the three major clays contained in sandstone reservoirs (Grim 1942 and 1953; Hughes 1950; Civan 1990). However, most researchers have focused on kaolinite and illite without the investigation of montmorillonite. Besides, there are also conflicting results of the influence of kaolinite and illite on LSWF. Herein lies the purpose of this research, which is to evaluate the

respective potential of montmorillonite, illite, and kaolinite on LSWF by conducting zeta potential measurements, swelling tests, and coreflooding experiments.

Chapter 4 Experimental Methodology

4.1 Experimental materials

4.1.1 Brine sample

Synthetic brines of both high and low salinity were used in the experiments. The HSW and LSW were obtained by mixing various salts in de-ionized (DI) water in proper proportion. Exact quantities of each salt were weighed using a scale sensitive to 1 ten-thousandth of a gram. These quantities were calculated based on 1 liter of DI water, and the salts were then added to the water. The detailed compositions of the HSW and LSW are shown in **Table 4.1** below.

Table 4.1–Compositions of HSW and LSW

Water source	NaCl (mg/L)	CaCl ₂ (mg/L)	MgCl ₂ (mg/L)	KCl (mg/L)	Salinity (mg/L)
HSW	25,640	605	1,103	153	27,501
LSW	2,173	269	34	8	2,484

4.1.2 Crude oil

The representative oil obtained from ANS with an American Petroleum Institute (API) gravity of 34° was used in this study. The viscosity of the crude oil was measured using Brookfield viscometer at a temperature ranging from 40°F to 140°F with a shear rate of 7.92 s⁻¹. The viscosity changes with temperature are described in **Figure 4.1**.

Figure 4.1–Viscosity change of ANS oil with temperature

4.1.3 Sand and clay

Sand and clays (montmorillonite, illite, and kaolinite) used in this study, were all commercial grade. Commercial sand was screened with sieves to a mesh size between 65 and 80 meshes using a mechanical shaker and washed thoroughly. Screened sand was washed with distilled water to make sure all clay minerals were removed and then dried in an oven at a temperature of 70°C.

4.2 Experimental facilities

4.2.1 Brookfield programmable DV-II viscometer

The Brookfield viscometer (**Figure 4.2**) was used to measure viscosity at given shear rates. The principle of operation for the DV-II is to drive a spindle (immersed in the crude oil) through a

calibrated spring. The viscous drag of the fluid against the spindle is measured by the spring deflection.

Figure 4.2—Photographic representation of the Brookfield programmable DV-II viscometer

4.2.2 Hydraulic compactor

A hydraulic compactor unit was employed to prepare the mineral wafer for placement inside the transfer stand. 5 grams of the desired clay were put inside the compactor cell and high pressure of 6,000 psi was applied to the compactor cell assembly to form a consolidated wafer using a 10,000-psi rated Enerpac hand pump (**Figure 4.3**).

Figure 4.3—Photographic representations of the OFITE compactor, Enerpac hand pump, and the compactor cell assembly

4.2.3 Zeta potential measurement apparatus

Zeta potentials of sand and the three types of clay particles at the presence of HSW and LSW were measured individually using a phase-analysis light-scattering technique (ZetaPALS potential analyzer). It is an instrument that uses electrodes coated with palladium and a He-Ne laser as a light source to determine the zeta potential by measuring the electrophoretic mobility of charged colloidal suspensions. **Figure 4.4** shows an image of the zeta potential measurement apparatus used in this study. The zeta potential value of this equipment ranges from -220 to 220 mV with an accuracy of $\pm 1\%$.

**Figure 4.4—Image of the zeta potential measurement apparatus
(photographed at Research Institute of Petroleum Exploration and Development, China)**

4.2.4 Swelling test apparatus

The swelling properties of montmorillonite and illite were tested using a Dynamic Linear Swellmeter. The schematic view of the swelling test apparatus is depicted in **Figure 4.5**. The swelling test apparatus consists of a wafer container which can expose the clay wafer to the prepared HSW/LSW, a swell cup which is to contain brines, and a Linear Variable Differential Transducer (LVDT) which is connected to the data acquisition system to record the expansion of the clay wafer in the vertical direction with an accuracy of 0.1%.

The swell property of kaolinite was measured using the standard method of Free Swell Index, which is the increase in the volume of clay mineral on submergence in the prepared water sources without any external constraints.

Figure 4.5–Schematic view of the swelling test apparatus

4.2.5 Coreflooding

4.2.5.1 AFS-300 reservoir conditions coreflooding system

Coreflooding experiments were conducted using a computer-controlled coreflooding system, designed by Core Lab, as shown in **Figure 4.6**. The equipment is designed to function at a temperature as high as 430°F (200°C). The differential pressure is measured with an accuracy of ± 0.03 psi, and the volume measurement has an accuracy of ± 0.01 cc.

This coreflooding system primarily consists of the following three units – injection unit, production unit, and data acquisition unit. The injection unit involves three accumulators with a capacity of 1,000 mL, which were respectively filled with HSW, ANS oil sample, and LSW. A high-precision syringe pump (which is capable of delivering fluid at a constant flow rate or constant pressure) is connected to the injection unit. The production unit composes of a sand pack column that has a 1-inch ID (inner diameter) by 6-inch long uniform rough internal surface, a

differential pressure transducer (with the capability of reading differential pressure up to 600 psi) which is used to record the pressure drop along the length of the compacted sand pack, and an automatic fraction collector which is to continuously record the produced liquid volumes. The data acquisition unit is used to control the coreflooding system and continuously record the pressure drop across the sand pack column.

Figure 4.6–Schematic view of the coreflooding experimental setup

4.2.5.2 Sand pack column

The sand pack column is a 1-inch diameter by 6-inch long horizontally positioned cylindrical stainless steel column with injection and production ports located at each end of the column, as shown in **Figure 4.7**.

Figure 4.7–Photographic representation of sand pack column

4.2.5.3 Spectra/Chrom CF-2 fraction collector

The Spectra/Chrom CF-2 fraction collector was used for the collection of liquid fractions from the sand pack column (**Figure 4.8**). Produced fluids are collected based on time intervals (20 minutes or 40 minutes). The fraction collector has a maximum tube capacity of 116 tubes with an external diameter of 18 mm.

Figure 4.8–Photographic representation of Spectra/Chrom CF-2 fraction collector

4.3 Experimental procedure

4.3.1 Zeta potential measurement

The detailed procedure is described as follows:

- 1) Crush and ground quartz to very fine particles and screened with a 200-mesh sieve;
- 2) Prepare a colloidal suspension sample by adding 1 wt% of quartz powder into aqueous solution. This is achieved by mixing 0.2 gram of solid powder of particle size below 75 μm with 20 grams of HSW/LSW;
- 3) After the sample is fully mixed, transfer 1.2 mL of sample solution to a cuvette slowly and remained undisturbed for about 15 minutes prior to performing zeta potential measurements;
- 4) Subsequently, preheat the sample in the cuvette for 5 minutes and then place a parallel-plate electrode into the cuvette;
- 5) At last, measure the electrophoretic mobility of the sample at 77°F, from which the zeta potential can be calculated;
- 6) Repeat **Step 1-5** for montmorillonite, illite, and kaolinite.

A total of five runs were conducted for each sample, and the presented results are the average of these measurements.

4.3.2 Swelling test

4.3.2.1 Swell meter

In quantifying the swelling property of montmorillonite and illite, the swelling test was conducted using the OFITE swell meter. The detailed procedure is described as follows:

- 1) Pour 5 grams of montmorillonite into the wafer maker;

- 2) Apply 6,000 psi on the top of the wafer maker using the hydraulic compactor to ensure that a wafer sample with a thickness of about 0.5 inches can be obtained;
- 3) Assemble the wafer samples in a dynamic liner swell meter cup assembly;
- 4) Place a Linear Variable Differential Transducer (LVDT) on top of the cup sample. This enables the swell meter to record and quantify the percentage swell with time. Note that the swell percent is measured with an accuracy of $\pm 1\%$;
- 5) Soak the wafer sample in the HSW and start recording the swelling properties of the wafer sample until no more swelling is observed;
- 6) Stop recording the swelling property of the wafer sample, drain the HSW and soak the wafer sample in the LSW;
- 7) Restart recording the swelling properties of the wafer sample till the end of the test;
- 8) Repeat **Step 1-7** for illite.

4.3.2.2 Free Swell Index Method

The swelling of kaolinite was determined by Free Swell Index method. Due to the inability of kaolinite to form smooth surface wafers, the Free Swell Index method with kerosene was used to quantify the swell (**Figure 4.9**). The detailed procedure is described as follows:

- 1) Pour three representative samples of 20 grams of kaolinite in a 100 ml capacity graduated cylinder;
- 2) Fill each sample to the 100ml mark with kerosene, HSW, and LSW, respectively. Remove entrapped air in the cylinder by gentle shaking and stirring with a glass rod;
- 3) Allow samples to settle in all cylinders for 24 hours to attain equilibrium in their state of volume without any further change in volume of clay;

- 4) Monitor and record the volume of kaolinite in each cylinder every 24 hours until the 96th hour.

Figure 4.9–Photographic representation of the free index swelling

4.3.3 Coreflooding procedure

4.3.3.1 Sand pack compaction procedure

A total of six sand pack columns were created to conduct the corresponding displacement experiments. The detailed procedure is described as follows:

- 1) Screen sand to mesh sizes of 65 – 80 mesh using a mechanical shaker;

- 2) Wash the screened sand with distilled water to make sure all clay minerals are removed and then dry the sand in an oven at a temperature of 70°C;
- 3) Place a certain amount of sand and clay sample in a container based on experimental design and shake the container properly to ensure uniform distribution;
- 4) Compact the sand pack column using a three-segment-method. Different pressures were applied to the various sand pack columns in order to get similar nitrogen permeability;
- 5) Attach fine papers and filter nets to each end of the column to prevent any fine production along the column during coreflooding experiments;
- 6) Measure gas permeability using nitrogen as the injecting gas at different flow rate ranging from 1,320 mL/sec to 4,320 mL/sec and record corresponding pressure drops across the sand pack columns. Calculate the nitrogen permeability using the following formula (**Equation 1**);

$$K_a = \frac{2000 p_a \mu L q_a}{A(P_2^2 - P_1^2)} \dots \dots \dots (Equation 1)$$

where

- k_a = nitrogen permeability, md
- p_a = atmospheric pressure, atm
- p_1 = upstream pressure, atm
- p_2 = outlet pressure, atm
- L = length, cm
- μ = viscosity of nitrogen, cP
- q_a = flow rate of nitrogen at atmospheric pressure, mL/sec
- A = cross-sectional area, cm²

The nitrogen permeability was non-Klinkenberg corrected; to that effect, they would be 3-10 times higher compared to those of water due to gas slippage effect (Aftab 2017). However, due to the chalky nature of kaolinite, the gas permeability of the sand pack column with kaolinite was smaller than the water permeability.

4.3.3.2 Displacement procedure

After the sand pack gas permeability was measured within a reasonable range, it was now ready for the displacement experiment. Each sand pack was flooded with the HSW and LSW successively, and the oil recovery factors and incremental oil recovery after each flooding were determined. The detailed procedure is described as follows:

- 1) Place the sand pack column into the coreflooding system and purge air out of the system by vacuuming the sand pack. The presence of air in the system would have amplified the fluctuations in pressure measurement;
- 2) Fill the HSW, crude oil, and LSW into accumulators A, B, and C, respectively;
- 3) Connect accumulator A (HSW) to the sand pack column and set the syringe pump at a constant flow rate of 0.1 mL/min to inject the HSW into the sand pack column;
- 4) Calculate the PV of the sand pack column using the following formula (**Equation 2**);

$$PV = V_{inj} - V_{prod} \dots \dots \dots (Equation 2)$$

where

- V_{inj} = Volume of water injected, cc
- V_{prod} = Volume of water produced, cc

- 5) Determine the porosity of the sand pack column using the following formula (**Equation 3**);

$$Porosity = \frac{PV}{Bulk Volume} * 100\% \dots \dots \dots (Equation 3)$$

- 6) Remain the sand pack column for 12 hours prior to measuring absolute permeability to HSW;
- 7) Determine the absolute permeability to HSW with various flow rates (0.1, 0.3, 0.5, 0.7, and 1 mL/min) and corresponding pressure drops. Calculate the absolute permeability to HSW using Darcy's law (**Equation 4**);

$$k = \frac{Q * \mu * L}{A * dP} \dots \dots \dots (Equation 4)$$

where

- k = absolute permeability to HSW, Darcy
- Q = flow rate, mL/sec
- dp = pressure drop across the sand pack column, atm
- L = length, cm
- μ = viscosity of HSW, cP
- A = cross-sectional area, cm²

- 8) After measuring the absolute permeability, connect accumulator B (containing the crude oil) to the sand pack column and saturate the sand pack column with crude oil at a flow rate of 0.1 mL/min;

- 9) Determine the initial oil saturation using the following formula (**Equation 5**);

$$S_{oi} = \frac{V_w}{PV} \dots \dots \dots (Equation 5)$$

where

- S_{oi} = Initial oil saturation
- V_w = Volume of displaced water, cc

- 10) Age the sand pack column for 2 days;

- 11) Connect accumulator A (HSW) to the sand pack column and start HSW waterflooding at 0.1 mL/min for 9 PVs to ensure no more additional oil production. During the displacement, the software was used to monitor and record the experimental data including oil production and differential pressure;
- 12) After HSW waterflooding, disconnect accumulator A (HSW) and connect accumulator C (LSW) to the sand pack column.
- 13) Continue to flood the sand pack column using LSW at 0.1 mL/min for 9 PVs to ensure no more additional oil production while oil production and differential pressure are being monitored and recorded;
- 14) Determine the oil recovery factors and incremental oil recoveries.

Chapter 5 Results and Discussion

In this chapter, the results of zeta potential measurement, swelling test, and coreflooding experiments are presented and discussed. Zeta potentials of quartz and each clay mineral at the presence of HSW and LSW were first examined respectively to indicate the change of wettability. Then the swelling characteristics of clay minerals including montmorillonite, illite, and kaolinite at the presence of HSW and LSW were analyzed in succession to quantify the swelling capacity. Subsequently, coreflooding experiments were conducted using a 1-inch diameter and 6-inch long sand pack column to study the influence of different types of clay minerals on oil recovery during LSWF. Finally, based on the analysis of the experimental data, combined with literature research, the functions of clay minerals on affecting LSWF EOR performance are discussed.

5.1 Zeta potential study

The zeta potential of various solid/brine systems was determined to quantify the changes in the surface charges caused by the brine salinity change. In general, surface zeta potential can indicate its wettability. Nasralla and Nasr-El-Din (2014) demonstrated that the electrokinetic potential of clay surfaces and oil-water interfaces (zeta potential) becomes more negative with the decreasing total salinity. This means that at lower salinity, the balance between positive and negative electrical surface charges at sand/brine and clay/brine interfaces shifts to more negative values. And such increase in the magnitude of the negative surface charge would be expected to lead to a favorable wettability alteration due to the fact that the stronger negatively charged solid/brine interface could affect the potential at the shear plane of the electrical double layer and therefore increase the double

layer thickness at the interface which contributed to a more stable water thin film resulting in a more water-wet state of the solid surface.

Figure 5.1 presents the zeta potentials of sand, montmorillonite, illite, and kaolinite in HSW and LSW, respectively, and the results showed negative electric charges for all samples, except sand in HSW. The HSW resulted in a positive charge with a value of 5.1 mV on the sand particle surface. In comparison, the electric charges at the interfaces of HSW and clay minerals were negative, with values ranging from -11.5 mV to -19 mV. This implies that, in the presence of HSW, the sand surface tends to be more oil-wet compared with montmorillonite, illite, and kaolinite. However, in the presence of LSW, the zeta potential of the sand surface was altered to be moderately negative (from 5.1 mV to -12.4 mV). Also, the presence of LSW augmented zeta potential on the surfaces of montmorillonite (from -19 mV to -20.5 mV), illite (from -13.3 mV to -23.4 mV), and kaolinite (from -11.5 mV to -17.2 mV). Thus, reducing the salinity from HSW of 27,501 mg/L to LSW of 2,484 mg/L could promote the negative zeta potential on the surfaces of sand, montmorillonite, illite, and kaolinite, making their surface more water-wet. This effect is one of the reasons that lead to the improvement of oil recovery by LSWF.

Figure 5.1–Comparison of zeta potential of sand, montmorillonite, illite, and kaolinite in HSW and LSW

5.2 Swelling test study

The swelling properties of the three clay minerals (montmorillonite, illite, and kaolinite) were investigated at the presence of HSW and LSW in succession. **Figure 5.2** demonstrated the swelling test results for montmorillonite, illite, and kaolinite. As can be seen, montmorillonite swelled by almost 180% due to hydrating after soaking in the HSW. Since the montmorillonite used in this study was sodium-based, Na^+ , which was originally adsorbed on the interlayers, could be replaced by divalent cations such as Ca^{2+} and Mg^{2+} by immersing in the HSW. Obviously, by replacing the HSW with LSW, montmorillonite further swelled significantly by contacting LSW. This phenomenon may result from the fact that Na^+ in the LSW re-replaced a large amount of Ca^{2+} and Mg^{2+} which were absorbed onto the interlayers during the soaking period of HSW due to the salinity change effect. Thus, the attractive force between the interlayers was reduced, resulting in

more expansion of the space between the interlayers. That is why montmorillonite could further swell in the presence of LSW after soaking in the HSW.

Figure 5.2–Swelling test result for the various clay samples

Also can be seen, illite showed some swelling in the HSW, but it could not further swell in the LSW, which could attribute to the fact that the exchangeable ion on the illite surface is K^+ . The K^+ fits between the layers, pulling them together tightly. And the K^+ becomes trapped between the layers, which could not be replaced by other ions, such as Ca^{2+} and Mg^{2+} . Water cannot invade into the interlayers of illite. Thus, although illites have the same basic 2:1 structure as montmorillonites, they do not show interlayer swelling. Although some K^+ on the outer surfaces of illite could be replaced by Ca^{2+} and Mg^{2+} , the amount is minimal due to the lower CEC. As a result, there is only limited hydration on the external surfaces of illite particles, resulting in much

smaller swelling than montmorillonite. Subsequently, by replacing the HSW with LSW, no more cation exchange may occur on the outer surfaces of illite due to the small CEC, so illite could not be further hydrated in the LSW. Accordingly, illite did not further swell in the LSW. Since the unit layers of kaolinite bound tightly together by hydrogen bonding, water is unable to penetrate the interlayers. Besides, kaolinite does not contain interlayer cations or surface charges, so its CEC is extremely low as described earlier. Therefore, kaolinite cannot be hydrated, and thus it is a kind of non-swelling clay. Our experimental test showed the same result that kaolinite could not swell in the HSW and the subsequent LSW.

5.3 Coreflooding study

A total of six sand pack columns were created for coreflooding experiments and detailed properties are shown in **Table 5.1**. **Table 5.2** summarizes the oil recovery performance of the six coreflood runs. Note that for each test, the conventional waterflooding (HSW flooding) is regarded as the baseline to determine the incremental oil recovery of LSWF. The incremental oil recovery is defined as the difference in oil recovery factors between LSWF and conventional waterflooding, measured at residual oil saturation after each displacement. For example, the ultimate oil recovery of Test #1 is 37.9%, so compared to conventional waterflooding, the incremental oil recovery for LSWF is 0.73% (i.e., 37.9%-37.17%). As can be seen from **Table 5.2**, not all six runs yielded a significant improvement in oil recovery by LSWF. In particular, sand pack columns containing montmorillonite (Test #2, #5, and #6) showed considerable enhancement of oil recovery after the injected water was switched from HSW to LSW.

Table 5.1—Properties of compacted sand pack columns for coreflooding tests

Sand pack column #	Sand (wt%)	Montmorillonite (wt%)	Illite (wt%)	Kaolinite (wt%)	Porosity (%)	Absolute permeability to N ₂ (mD)	Absolute permeability to HSW (mD)	Initial oil saturation (%)
1	100	0	0	0	37.26	1,274	541.3	69.5
2	90	10	0	0	48.60	1,298	33.5	40.3
3	90	0	10	0	46.08	1,312	345.4	53.5
4	90	0	0	10	51.12	495	2,000	42.0
5	90	5	2.5	2.5	48.73	1,205	118	42.8
6	95	5	0	0	42.30	1,281	70	52.3

Table 5.2–Oil recovery performance of the sand pack columns containing various types of clay minerals

Test #	Experiment scenarios	Recovery factor after HSW flooding, %	Recovery factor after LSWF, %	Incremental oil recovery, %
1	100% quartz	37.17	37.90	0.73
2	90 wt% quartz + 10 wt% montmorillonite	35.91	53.33	17.42
3	90 wt% quartz + 10 wt % illite	41.47	42.50	1.03
4	90 wt% quartz + 10 wt% kaolinite	38.27	39.10	0.83
5	90 wt% quartz + 5 wt% montmorillonite + 2.5 wt % illite + 2.5 wt% kaolinite	37.21	47.48	10.27
6	95 wt% quartz + 5 wt% montmorillonite	37.48	46.38	8.90

5.3.1 Test #1: clay-free sand pack column

Sand pack #1 was successively flooded with HSW and LSW, and the corresponding oil recovery performance and pressure drop across the sand pack were recorded in **Figure 5.3** below. As can be seen, the injection of 9 PVs of HSW yielded an oil recovery of 37.17% and the 9 PVs injection of LSW improved the oil recovery slightly by 0.73%. Also, the pressure drop during HSW flooding decreased gradually and eventually stabilized at 0.7 psi, but the pressure drop increased after 0.5 PV of LSW injection and reached the value of 1 psi at the end of LSWF. It is observed that during the first 2 PV injections of LSW, there was no incremental oil production while the pressure drop began to increase. Analyzing coreflooding results and zeta potential measurement results (**Figure 5.1**), the slightly improved oil recovery and increased pressure drop during the LSWF period may result from the fact that the wettability of sand surface was altered to a more water-wet state by injecting LSW.

Figure 5.3–Coreflooding performance for Test #1: oil recovery and pressure drop profile

5.3.2 Test #2: sand pack column with 10 wt% of montmorillonite

Figure 5.4 shows the oil recovery performance and pressure drop profile. As can be observed, 35.91% OOIP was produced after injecting 9 PVs of HSW, and the pressure drop first increased and then decreased, and eventually stabilized at 24 psi. The subsequent 9 PVs of LSW injection improved oil recovery to 53.33% while the pressure drop jumped to about 300 psi. Compared with LSWF in Test #1, the pressure drop in Test #2 increased immediately and dramatically after introducing LSW into the sand pack column. As can be seen from **Figure 5.1**, the LSW could enhance the water-wet state of sand and montmorillonite, which may be one of the reasons for increasing pressure drop and improved oil recovery. The significantly increased pressure drop and improved oil recovery primarily resulted from the swelling of montmorillonite in the presence of LSW, causing the increase of the local pressure gradient and hydrodynamic force to remobilize the trapped residual oil.

Figure 5.4—Coreflooding performance for Test #2: oil recovery and pressure drop profile

5.3.3 Test #3: sand pack column with illite

The production and pressure curves of Test #3 are depicted in **Figure 5.5** below. As is shown, 9 PVs of HSW injection produced 41.47% OOIP and, the pressure drop plateaued at 1.45 psi. The subsequent 9 PVs of LSW injection improved the oil recovery up to 42.50% (i.e., an additional oil recovery of 1.03%) and, the pressure drop stabilized at 3.23 psi. Since the LSW could not further swell illite after HSW, as shown in **Figure 5.2**, the underlying reason for the increase of pressure drop and improved oil recovery in LSWF was attributed to the fact that the LSW could alter the sand and illite to be more water-wet, as shown in **Figure 5.1**.

Figure 5.5—Coreflooding performance for Test #3: oil recovery and pressure drop profile

5.3.4 Test #4: sand pack column with kaolinite

The oil recovery performance and pressure drop profile of Test #4 were illustrated in **Figure 5.6**. It can be seen that injecting 9 PVs of HSW yielded 38.27% OOIP with the pressure drop stabilizing

at 0.35 psi, while injection of 9 PVs of LSW improved oil recovery by 0.83% with pressure drop increasing up to 1.2 psi. Since there was no swelling for kaolinite in both HSW and LSW, the increasing pressure drop and improved oil recovery resulted from the fact that the LSW altered the sand surface and kaolinite to be more water-wet. Besides some similarities with previous tests, the main difference was that there was a more intense fluctuation of pressure drop in Test #4 than those in Tests #1, #2, and #3. Another apparent phenomenon in Test #4 was that although the pressure drop in LSWF continued to increase until the end of the injection, the oil recovery quickly plateaued, which resulted from the clay particle migration during flooding since sand pack column with kaolinite was much more unconsolidated and associated with larger porosity and water permeability than the sand pack columns with montmorillonite and illite.

Figure 5.6—Coreflooding performance for Test #4: oil recovery and pressure drop profile

5.3.5 Test #5: sand pack column with compound clay

The oil recovery and pressure drop of Test #5 were shown in **Figure 5.7**. As can be noted, the injection of 9 PVs of HSW yielded an oil recovery of 37.21%, and the pressure drop stabilized at around 9 psi. The subsequent 9 PVs of LSW injection improved oil recovery by 10.27% and the pressure drop increased to 70 psi. It was not surprising to observe that its performances fell between Test #1 and Tests #2, #3, and #4 due to their composite effect. Also, compared with Tests #1, #2, and #3, there was more intense pressure drop fluctuation, which resulted from kaolinite clay particle migration.

Figure 5.7–Coreflooding performance for Test #5: oil recovery and pressure drop profile

5.3.5 Test #6: sand pack column with 5 wt% of montmorillonite

The oil recovery and pressure drop of Test #6 were shown in **Figure 5.8**. As can be noticed, the injection of 9 PVs of HSW yielded an oil recovery of 37.48%, and the pressure drop stabilized at

around 11 psi. The subsequent 9 PVs of LSW injection improved oil recovery by 8.9% and the pressure drop increased to 250 psi. As can be seen from **Figure 5.8**, the oil production and pressure drop profiles during LSWF were similar to those of Tests #2 and #5, which was due to the swelling of montmorillonite after injecting LSW. However, the incremental oil recovery and pressure drop were both lower than those of Test #2, since the content of montmorillonite in Test #6 was lower. Moreover, although the pressure drop in Test #6 was higher than that in Test #5, the incremental oil recovery was lower which was due to the fact that the sand pack column used in Test #6 was free of illite and kaolinite. Therefore, compared to the sand pack column used in Test #5, the wettability of the sand pack column used in Test #6 was less-water wet during LSWF, resulting in lower incremental oil recovery.

Figure 5.8—Coreflooding performance for Test #6: oil recovery and pressure drop profile

5.4 Reiteration

To ensure the reproducibility of the coreflooding experiments, a second sand pack column containing 10 wt% montmorillonite was compacted and flooded with HSW and LSW successively.

Table 5.3 shows the properties of the two sand pack columns. **Table 5.4** presents the oil recoveries from the two coreflooding experiments, and **Figure 5.9** shows the results of the recovery factor and the pressure profile (d_p) from both tests.

Table 5.3—Properties of compacted sand pack columns containing 10% montmorillonite

Properties	1 st Core flooding	2 nd Core flooding
Pore Volume (PV) (cc)	38.57	35.57
Porosity, (%)	48.60	44.82
Absolute permeability to N ₂ (mD)	1,298	1,279
Absolute permeability to HSW (mD)	33.50	22.70
Initial oil saturation (%)	40.32	39.50

Table 5.4—Oil recovery performance of the sand pack columns containing 10% montmorillonite

Experiment scenarios	Recovery factor after HSW flooding, %	Recovery factor after LSWF, %	Incremental oil recovery, %
1 st Core flooding	35.91	53.33	17.42
2 nd Core flooding	36.44	52.98	16.54

Figure 5.9—Coreflooding performance for 10% montmorillonite: oil recovery and pressure drop profile

As can be seen from **Table 5.4**, the recovery factor of the 2nd coreflooding experiment had a similar result as the 1st coreflooding. During the HSW flooding, a recovery of 36.44% OOIP was obtained from the 2nd coreflooding test, which is a difference of 0.53%, compared with the 1st coreflooding test. After switching the injection fluid to LSW, an additional oil recovery of 16.54% OOIP was gained from the 2nd core flooding, demonstrating that there was a 0.88% incremental oil recovery difference between the two core flooding experiments. Therefore, it is believed that our experimental tests have reliable repeatability.

5.5 Discussion

Figure 5.10 shows the comparison of the recovery performance for all six coreflood runs. One of the mechanisms that explain the additional oil recovery by LSWF is the clay swelling effect. During the displacement process in the reservoir, the clay swelling may result in formation damage (i.e., permeability reduction) by blocking the pore throat, which may reduce the injectivity. Simultaneously but in contrast, there may exist several potential advantages of in-situ clay swelling for oil production. The swelled clay may block the high permeability water flow channels in the reservoir, diverting the injected water to relatively low permeability and unswept oil zones, to improve the sweep efficiency and eventually enhance the oil recovery.

Figure 5.10–Recovery results for all coreflooding tests

As for the studied reservoirs, which were unconsolidated and associated with high permeability, the potential advantages of clay swelling in the displacement process weigh more than its disadvantages. Compared with LSWF in Tests #1, #3, and #4, the pressure drop in Tests #2, #5, and #6 increased immediately and dramatically after introducing LSW into the sand pack column, as shown in **Figure 5.11**. The significantly increasing pressure drop and improved oil recovery primarily resulted from the swelling of the montmorillonite in the presence of LSW, causing the increase of the local pressure gradient.

Figure 5.11–Pressure drop profile for all coreflooding tests

The wettability alteration is another mechanism contributing to improved recovery during the LSWF process. In a rock/oil/brine system, both the negatively charged oil/water interface and the clay surfaces will have associated double layers. The thickness of the double layer is relatively small in a brine of high ionic strength. This allows the oil and the clay to get physically close enough for interaction with the active oil components, allows adsorption, and allows a change to a more oil-wet state. With the reduction in salinity, the ionic strength is decreased and results in a reduction of attractive force. The increase of repulsive force between the similarly charged oil/water interface and clay surface overcomes the binding force between the oil and clay surface. Therefore, the double-layer expands resulting in oil desorption and a change to a more water-wet surface.

In this research, the injection of LSW slightly improved oil recovery from all three montmorillonite-free sand pack columns due to the reason that LSW could promote the negative zeta potential on the surfaces of sand and kaolinite/illite resulting in more water-wet surface. Thus, more oil was desorbed and produced.

In general, LSWF can further improve oil recovery after HSW injection, and the existence of clay in the reservoir can promote the EOR performance of the LSWF. The incremental oil recovery during LSWF generally increases with the clay content, especially the montmorillonite content owing to its more significantly swelling characteristics in LSW. **Figure 5.12** shows the additional recovery from LSWF with the increase in montmorillonite clay content.

Figure 5.12–Incremental oil recovery for montmorillonite clay content

5.6 Validation

Shehata and Nasr-El-Din (2014) investigated the influence of clay on LSWF with cores from different formations: Buff Berea, Grey Berea, Bandera, and Parker Formation. They concluded that the presence of clay was not necessarily the primary mechanism in LSWF experiments. This conclusion resulted from the fact that the clay proportion was not directly related to additional oil recovery with LSWF. **Table 5.5** presents the composition of the various sandstone cores used in the experiment, and **Figure 5.13** shows the additional recoveries by LSWF and the quantities of various clay minerals.

Figure 5.13—Additional recoveries for cores in Buff Berea, Grey Berea, Bandera, and Parker Formation (Shehata and Nasr-El-Din 2014)

Table 5.5—Composition for cores in Buff Berea, Grey Berea, Bandera, and Parker Formation

Buff Berea		Grey Berea		Bandera		Parker	
Clay	Concentration (wt %)	Clay	Concentration (wt %)	Clay	Concentration (wt %)	Clay	Concentration (wt %)
Kaolinite	3	Kaolinite	6	Kaolinite	3	Kaolinite	2
Montmorillonite	2	Illite	2	Chlorite	1	Illite	4
				Illite	10	Mica	2
TOTAL	5		8		14		8

While their conclusion is a representation of the actual results, they did not analyze the results from the aspect of clay composition. From the composition of the individual formation, the Buff Berea had the least clay content but yielded the highest additional recovery during LSWF; note that it was the only formation containing montmorillonite. On the other hand, although the Bandera Formation had the highest clay content, the additional oil recovery was lower due to the absence of montmorillonite. This further validates the point that the presence of montmorillonite is favorable for additional oil recovery with LSWF, as seen in **Figure 5.14**.

Figure 5.14—Incremental oil recoveries during LSWF from six coreflood runs

Chapter 6 Conclusions and Recommendations

6.1 Conclusions

This study reveals the influence of clay mineral composition on LSWF and can provide more guidance and improve the understanding of conventional and unconventional oilfield applications of LSWF technology. While there is no exact primary mechanism behind LSWF, wettability alteration, multi-component ion exchange, fine migration, and pH are widely discussed in the literature.

The debate around the function of clay on the EOR performance of LSWF is still a topic for discussion. This experimental work allows us to understand better the effect of different clays in control of the LSWF EOR performance in sandstone reservoirs.

The following conclusions were drawn from the results of this work:

- 1) Compared with HSW, LSW could generate more negative zeta potential values for sand, montmorillonite, illite, and kaolinite, resulting in favorable wettability alteration.
- 2) Montmorillonite showed obvious swelling in HSW, and it could further swell significantly by contacting LSW due to multi-ion exchange and high negative electric charge at brine/montmorillonite-particle interface. Illite showed some swelling in HSW, but LSW could not further swell it. Kaolinite did not swell in both HSW and LSW.
- 3) The coreflooding experiments results could prove that clay minerals would play an important role in determining the oil recovery performance in LSWF. In general, the more swelling the clay in LSW, the more favorable the clay is in LSWF. The non-swell clay,

such as kaolinite, may migrate during the LSWF process, resulting in the continuous increase of pressure drop with no further oil recovery improvement.

- 4) Finally, we could confirm that both wettability alteration and clay swelling could attribute to the improved oil recovery in LSWF.

6.2 Recommendations

It is recommended that, in the future, the following be investigated:

- 1) Due to the discrepancies in the kaolinite permeability, the kaolinite influence needs more detailed investigation;
- 2) Conducting a displacement test using constant injection pressure, to see the influence of swelling on injectivity.

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