The Study to Improve Oil Recovery through the Clay State Change during Low Salinity Water Flooding in Sandstones

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ABSTRACT: Low salinity water flooding is a low-cost enhanced oil recovery (EOR) technology. The mechanism of EOR in a sandstone reservoir is still controversial, and there are many influencing factors. In this study, the effects of salinity (2000, 4000, 8000, and 100,000 ppm), pH (5.5 acidic, 7.0 neutral, and 8.0 alkaline), cation type (Na+ and Ca2+), and clay content (A rock 6.04%, B rock 11.94%) on zeta potential and recovery related to clay swelling were studied. The results showed that the absolute value of zeta potential increased with the decrease of salinity, cation changes from divalent to monovalent, and an increase of the pH value or clay content. The results of the SEM test before and after displacement and the continuous increase of displacement pressure after low salinity water injection show that low salinity water will cause clay swelling and the absolute value of zeta potential increased. The extreme value of recovery appears in the rocks with a high clay content: In neutral and alkaline NaCl solutions, $R_I$ and $PEOR$ of rock B first increase and then decrease with the decrease of salinity. When the salinity is 4000 ppm, $R_I$ and $PEOR$ were 8.16 and 34.13% in the neutral state, and 8.50 and 25.00% in the alkaline state, respectively. $R_I$ and $PEOR$ of other experimental groups increased with the decrease of salinity. The study showed that the displacement pressure increases with the decrease of salinity, which indicates that the proper expansion of clay can improve the recovery of a sandstone reservoir, while the excessive expansion of clay will damage the reservoir and reduce the recovery. Based on the experimental results, the factors and indexes involved in the experiment were analyzed by multiple variance analysis. The result showed that the salinity, cationic type, and pH value have a significant effect on the zeta potential. All factors in the experiment have a significant effect on $R_I$, salinity, and cationic type, and the clay content have a significant effect on PEOR. The conclusion of this study could guide the design of low-salinity water flooding technology in oil fields.

1. INTRODUCTION

At present, most oil fields in the world have been developed by water injection. The injected water largely originates from produced water, which has inorganic salt with high salinity after its separation and treatment. Scaling and blockage are caused by incompatibility between the injected water and formation water; the formation of blockages is caused by the content of suspended particles being exceeded. This phenomenon can lead to poor sewage treatment, reduced formation permeability due to water sensitivity, reduced pore throat radius values for the water injection channel caused by excessive clay swelling, and pipeline corrosion and blockage issues caused by the high salinity of the injected water. To prevent such problems, oil fields usually use bactericides, antiswellling treatments, anticorrosion treatments, and other methods to improve the quality of the sewage water. For wells with such problems, oil field companies usually use acidification and fracturing measures to resolve the problems. These measures might increase the economic cost of water injection. The best way to solve the problems is to utilize knowledge of the problems to find the favorable low-cost measures.

Low-salinity water flooding (LSWF) is a new low-cost technology that has been used to improve oil recovery in the oil industry in recent years. The salinity of LSWF is usually lower than 10,000 ppm. Some old fields have improved oil recovery after introducing LSWF technology. In North Slope reservoirs, the low-salinity enhanced oil recovery (EOR) benefits ranged from 6−12% OOIP (original oil in place), resulting in an increase in water flood recovery of 8−19% (McGuire PL 2005). Webb et al. compared the baseline residual oil saturation between high-salinity brine and low-salinity water.
salinity brine. The results were in line with those of previous laboratory tests from other fields and showed a 25–50% reduction in residual oil saturation when flooded with low salinity water. In the Syrian Omar field, the wettability modification caused by the injection of low-salinity water led to an associated incremental recovery of 10–15% of the stock tank oil initially in place (STOIIP).

The research on LSWF has attracted wide attention because LSWF has achieved good effects in improving oil recovery in oil fields. The main mechanisms of LSWF for EOR in sandstone are clay swelling and migration, electric double layer expansion, and wettability alteration. The EOR of LSWF was affected by various factors, such as the salinity, cationic type, pH value, and clay content. For this reason, much research has been conducted on the effects of these factors on EOR using LSWF.

During an experiment, while the brine changed from high to low salinity, Berg et al. observed the crude oil released from the clay particles with flow cell equipment. A massive release of crude oil (up to 80%) was observed when the brine was at a very low salinity condition. However, the decomposition of the montmorillonite clay minerals occurred in the process of oil release, which resulted in a damaged formation. The factors in this study included the brine composition, clay type, and salinity. Their research shows that while the release of oil was seen in low salinity where also clay deflocculation and formation damage occurs, at least for montmorillonite clays, there is a regime of intermediate salinity where still oil is released but the clays stay intact ("controlled formation damage"). Al-Sarihi et al. considered the clay content and salinity to improve oil recovery. The clay fines migrate into filled water pores due to the decreased attraction force. Therefore, the diversion of the water flux into the trapped oil pores occurs, which displaces the residual oil in these pores. These results show a permeability decline with the injection of low-salinity water in the single phase tests of clay-rich cores accompanied by the production of fine particles and an increase in pH.

The electric double layer expansion could be explained by the thickness of the water film becoming thicker as the salinity decreased, which was used by Lee et al. to explain the increase in the displacement efficiency. The investigation of Nasralla and Nasr-El-Din showed that the major mechanism of LSWF-enhanced oil recovery was electric double layer expansion. In this study, they considered EOR to be affected by factors such as the salinity, pH value, and cationic type. In a NaCl solution, a low-salinity environment could increase the negative charge at the rock/brine and oil/brine interfaces in experiments with the zeta potential. In addition, the electric double layer expanded with the increasing pH. This caused an increase in repulsive forces between the oil and rock surfaces; therefore, the electric double layer expanded, and the wettability of the formation changed to water-wet conditions. The change of salinity will cause the expansion of the double layer, which means the change of the clay state. Rivet et al. and Fjelde et al. explained the adsorption capacity of the cations in clay and other cations due to the negative charge on the clay surface. The different cations that affect the adsorption capacity are as follows:

\[
\text{H}^+ > \text{Ba}^{2+} > \text{Sr}^{2+} > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{Cs}^+ > \text{Rb}^+ > \text{K}^+ > \text{Na}^+ > \text{Li}^+
\]

Xie et al. researched the effects of LSWF for EOR and found that divalent cations and low salinity caused the high negative zeta potential. At a reservoir condition, due to the acidic gases the pH of formation water was about 5. However, the low-salinity water injection would create a local increase in pH close to the brine clay. In this situation, the oil recovery increased.

Among the many mechanisms of LSWF for EOR, the change in wettability caused by the various chemical or physical changes is usually considered to enhance oil recovery. Many researchers have indicated that the LSWF proved to be more effective than using high-salinity brine and increased oil recovery via the wettability alterations. For unconventional shale, the shale rocks were very sensitive to water salinity, the low-salinity water will also cause clay mineral swelling in the shale and cause shale fragmentation and fracturing. The oil recovered from water imbibition was in line with the degree of shale fragmentation and fracturing. Therefore, it is necessary to explore the interaction mechanism between shale and low-salinity water.

According to the research findings, clay swelling, migration, and electric double layer expansion would increase the EOR in sandstone due to the change in the clay state. For this study, the outcrop sandstone rock samples of our experiment come from the Xinjiang oil field, and the LSWF has strong water-wet conditions. Therefore, the wettability change is not considered. Low-salinity water flooding enhanced oil recovery of sandstone reservoir affected by many factors. However, the comprehensive effect of the combination of factors was few. In this work, the comprehensive effect of salinity, cationic type, pH value, and clay content on clay and recovery of the sandstone reservoir were investigated. The types of clay were determined by XRD. The change rules of the clay double layer state, recovery, and displacement pressure under the action of four factors were explored by the zeta potential experiment and displacement experiment. The clay state before and after displacement was observed by SEM. The influence of four factors on the clay state and the relationship between the clay state and recovery were reported. The influence degree of factors on the clay charge and the recovery factor was determined by multiple variance analysis.

2. EXPERIMENTAL SECTION

2.1. Materials. The crude oil sample used in these experiments was from the Baikouquan block of the Xinjiang oil field. The viscosity at 25 °C of the crude oil was 5.00 mPa·s. The pH value of the water in oil was 6.4 and was measured by a pH meter. The density was 0.873 g/cm³, which was measured at normal atmospheric pressure and 25 °C. The crude oil component was analyzed and the results were 6.56% wax, 9.47% resin, and 0.96% asphaltene. The asphaltene, resin, and wax were tested by a NanoBrook Zetapals (U.S.A.). The
test theory used was the high-sensitivity analysis based on the dynamic light scattering principle. The accuracy of the zeta potential experiment was 0.01 mV. X-ray diffraction (XRD) was recorded using an X’Pert Pro MPD (PANalytical, Netherlands). The SEM experiment is conducted with a FEI Quanta 650 FEG (U.S.A.). The displacement experiment system included a distilled water container, constant flux pump, intermediate container, six-way valve, pressure gauge (three valves were standby valves), core holder, and a confining pressure pump. When the core was put into the core holder, the confining pressure pump added the distilled water in the interlayer of the core holder to build the confining pressure. The accuracy of recording pressure was 0.01 MPa. Then, the distilled water was pumped into the bottom of the intermediate container by a constant flux pump (the range of the flux pump rate was 0.01–9.99 mL/min (the accuracy of the flux pump rate was 0.01 mL/min). To carry out the displacement experiment, the brine from the top of the intermediate container was pushed to the core holder through the six-way valve by distilled water. The displacement pressure was measured by a pressure gauge (The accuracy of recording pressure was 0.01 MPa), which was connected on the six-way valve. The core was held by the core holder with the confining pressure. The displacement experiment system is shown in Figure 1.

2.3. Experiment and Evaluation. 2.3.1. Rock Sample and Brine Preparation. The rock samples were used for the zeta potential and displacement experiments. To prevent clay swelling in rock samples, all the rock samples were cut as cores without using water; the rock fragment was cleaned with inert gas during the process of core cutting. The cores of the displacement experiment were cylindrical (height 100 mm, diameter 25 mm). A total of 30 cores (15 cores of A and 15 cores of B) were used for displacement experiments. The remaining rock samples were used for the zeta potential, XRD, and SEM experiments.

Part of these rock samples were ground into rock powder by a ceramic grinder. These rock powders were filtered through a 400 mesh filter screen. Every 30 g of rock powder was mixed with 100 mL of anhydrous ethanol. Each group was ground for 48 h in ceramic pots of a planet ball mill. After grinding, the powder samples were dried in a vacuum environment at room temperature. The rock powder particle size was measured by a NanoBrook Zetapals 190 plus. The results are shown in Table 1.

![Figure 1](image1.png)

**Figure 1.** Schematic diagram of the displacement experimental system.

| Sample | Clay Content | Quartz | Orthoclase | Plagioclase | Calcite | Dolomite |
|--------|--------------|--------|------------|-------------|---------|----------|
| A      | 6.04         | 91.91  | 0.56       | 0.64        | 0.4     | 0.44     |
| B      | 11.94        | 56.38  | 1.68       | 22.96       | 4.09    | 2.96     |

**Table 2. Clay and Other Mineral Percentages of Rocks A and B**

Rock: The results show that there was lower clay content in rock A than rock B and a higher quartz content in rock A. The clay content in rock B was nearly twice as much as that in rock A. The subtype clays montmorillonite, illite, and kaolinite were found in both rocks A and B.

Brine: The brine sample used was made by adding NaCl or CaCl₂ salt crystals to deionized water. Rock B has many calcite and dolomite in it, which should change the pH of the solutions, particularly the acidic one. However, in an actual engineering situation, there is a slight change in the pH value. In subsequent experiments (zeta potential experiment and displacement experiment), this change can be ignored. The brine was regulated by HCl and NaOH to different pH values (The accuracy of the pH value was 0.01). Every 500 mL of brine was titrated with 2 M of HCl or NaOH using a needle tube. The pH value of the brine was measured using a pH meter.

![Figure 2](image2.png)

**Figure 2.** Analysis of Rock A and B’s XRD.
The composition, pH value, and salinity of the brine are shown in Table 3.

Table 3. Composition of the Experimental Brine

| Ionic type | pH value | Salinity (ppm) |
|------------|----------|----------------|
| NaCl       | 5.5      | 2000, 4000, 8000, 10,000 |
| CaCl₂      | 7.0      | 2000, 4000, 8000, 10,000 |

"The density of brine with different salinity are 1.001 g/mL (2000 ppm), 1.002 (4000 ppm), 1.004 (8000 ppm), and 1.005 (10,000 ppm).

2.3.2. The Clay Evaluation Procedure. The variables in the zeta potential and displacement experiments were the salinity, cationic type, pH value, and clay content. Considering that CaCl₂ easily precipitates into Ca(OH)₂ in alkaline conditions, the test in the CaCl₂ solution was not included in the high pH value test. All results of each group after 10 repeats of the zeta potential experiments were averaged to approach the real clay state of each group and reduce the error. The rock powder that was already ground and dried was added into the high-salinity brine, as shown in Table 3. To prevent the clays from aggregating, the brine and powder were mixed with an ultrasonic mixer (Elmasonic E 60 H, 37 kHz, 500 W) for 10 min at room temperature. After waiting for 1 day, the brine and powder were mixed with an ultrasonic mixer (Elmasonic E 60 H, 37 kHz, 500 W) for 10 min at room temperature. All zeta potential experiments were performed immediately within 10 min after mixing. The zeta potential experiment is a microscopic experiment. There are many random situations in each test, and the ideal state is difficult to achieve. Thus, each measurement cannot be very accurate. The SEM experiment was performed after the processing of gold plating on the fresh section of the rock.

2.3.3. The Displacement Procedure. The purpose of the core displacement experiments is to explore the values of Rₑ and PEOR affected by the different salinities, cationic types, pH values, and clay contents. Usually, when conventional water flooding is inefficient or is oil-free over a longtime duration, low-salinity water flooding can be used as a low-cost technology to increase oil production. To simulate the conventional water flooding process, the displacement experiment with the brine at 1.0 × 10⁻⁶ ppm salinity and neutral conditions was continued until an inefficient and oil-free state appeared after a longtime duration. Then, the brine at one of the following salinities, namely, 8000, 4000, or 2000 ppm, was used to simulate low-salinity water flooding.

To simulate the actual reservoir environment, the cores were dried at 80 °C in a vacuum environment, and the weight of the dry core was recorded as W_dry. The brine used in the displacement experiments has two cationic types: NaCl and CaCl₂. These cores, which use the NaCl solution as the displacement brine, were saturated with a 1.0 × 10⁻⁶ ppm NaCl solution in neutral (pH value equal to 7.0) conditions. Others cores were saturated with a 1.0 × 10⁻⁶ ppm CaCl₂ solution in neutral conditions. The process of saturated core is to immerse the core completely in the brine, which needs to be saturated in the vacuum saturation tank, keeping the vacuum saturation for 72 h under the pressure of -0.10 MPa.

After saturation, the weight of the core was recorded as W_water. The pore volume is marked V_p and it can be expressed as

\[ V_p = \frac{W_{water} - W_{dry}}{\rho_{brine}} \]  

(1)

Next, the core was placed into the core holder. The measuring cylinder was placed at the outlet end of the core holder. The outlet end of the intermediate container was connected to the inlet end of the core holder. The inlet end of the intermediate container was connected to the outlet end of the constant flow pump. The upper part of the intermediate container was filled with oil. The lower part was pumped with distilled water by a constant flow pump. The oil was put into the core by the distilled water pumped through the partition in the intermediate container. The confining pressure of the whole displacement process was kept at 5.00 MPa, the temperature was kept within 65 °C, and the rate of displacement was kept at 0.10 mL/min.

The pore volumes and porosity of 30 rock samples, which were used for the experiment, were calculated. The pore volume and porosity range of all rocks were 3.5–8.7 cm³ and 7–18%, respectively, among which, the pore volume and porosity range of rocks A and B were 5.4–8.7 cm³ and 11–18%, and 3.5–5.7 cm³ and 7–12%, respectively. After pumping 20 V_2 of oil, the pump was stopped, and the volume of the water that was displaced in the measuring cylinder was recorded as V_water. The volume of crude oil V_oil in the core can be expressed as

\[ V_{oil} = V_{water} \]  

(2)

After the oil displacement, the state of the core was close to that of the actual reservoir environment. To calculate the original oil recovery of these cores, conventional water flooding experiments were performed. After pumping 20 V_oil of the 1.0 × 10⁻⁶ ppm brine at neutral conditions, the pump was stopped, and the volume of the oil that was displaced in the measuring cylinder was recorded as V_oil. The original recovery Rₑ can be expressed as

\[ R_e = \frac{V_{oil-2}}{V_{oil}} \]  

(3)

The effects of improved oil recovery by LSWF can be observed in the comparison of the original recovery and the recovery after LSWF. The LSWF experiments were based on conventional water flooding. After calculating Rₑ, low-salinity water was used for the injection water. The low-salinity water has three kinds of variables, including the salinity, cationic type, and pH value.

The salt type of this LSWF was the same as the brine in conventional water flooding in each displacement experiment group. The salt types, included NaCl and CaCl₂; the pH values represented neutral, acidic, and alkaline conditions (neutral pH value equal to 7.0; acidic pH value equal to 5.5; and the alkaline pH value equal to 8.0), and the low salinity included concentrations of 8000, 4000, and 2000 ppm. The oil volume displaced by LSWF was recorded in a measuring cylinder as V_oil-3. The final recovery R_{EOR} can be expressed as

\[ R_{EOR} = \frac{V_{oil-2} + V_{oil-3}}{V_{oil}} \]  

(4)
Compared with the $R_O$ and $R_{EOR}$, the improved recovery $R_I$ can be expressed as

$$R_I = R_{EOR} - R_O$$  \hspace{1cm} (5)$$

The clay content and permeability of rocks A and B are different, and the proportion of $R_I$ on $R_O$ (PEOR) is introduced to explain the effect of LSWF, which can be expressed as

$$PEOR = \frac{R_I}{R_O}$$  \hspace{1cm} (6)$$

3. RESULTS

3.1. Zeta Potential Experiment. Usually, the clay state can be reflected by a zeta potential value. The clay colloid suspension system with a higher absolute value of zeta potential is more stable, which also indicates the expansion of the electric double layer. There are four factors involved in the experiment: salinity, pH value, cation type, and clay content. Figure 3 shows the zeta potential trend under different salts, pH, and clay content in NaCl solution, and Figure 4 shows the zeta potential trend under different salts, pH, and clay contents in CaCl$_2$ solution.
The change rule of zeta potential in the CaCl₂ solution is similar with that in the NaCl solution group when the salinity is 4000 and 2000 ppm. The absolute value of zeta potential increased (zeta potential value decreased) with the change of pH from acidic to neutral. Also, the difference in zeta potential of the same core in acidic and neutral conditions becomes larger with the decrease of salinity. However, for core A and core B with salinity of 1.0 \times 10^4 and 8000 ppm, respectively, zeta potential shows the opposite phenomenon with low salinity of the CaCl₂ and NaCl solution environment, which zeta potential in the acidic condition is smaller than that in the neutral condition. The interpretation of this phenomenon is that Ca²⁺ is easier to neutralize with the negative charge on the clay surface than Na⁺ in a high-salinity environment. The effect of Ca²⁺ concentration and clay content on zeta potential is much greater than that of pH because the change from the pH value of 5.5 in the acidic condition to the pH value of 7.0 in the neutral condition is small. Ca²⁺ is completely adsorbed on the clay surface in a high-salinity environment, which greatly compresses the double layer. In addition, a possible reason is the excessive concentration of Ca²⁺ in the neutral condition forms micro precipitation on the clay surface, which reduces the contact between the clay and the solution and prevents the expansion of the double layer. In an acidic condition, this kind of micro precipitation will not form. Although the double electric layer is compressed, the clay surface is still in contact with the solution, such that the double layer still has expansion, which is larger than that in the neutral environment. This difference of the double layer state between acidic and neutral conditions was minimal, thus the zeta potential has a small difference. However, the smaller clay content it is, the larger the proportion of clay is covered by this kind of micro precipitation, which leads to the greater difference between the expansion of the double layer, thus the zeta potential has a greater difference. The results show that the zeta potential difference of core A with the low clay content in a 1.0 \times 10^4 ppm CaCl₂ solution in neutral and acidic conditions is larger than that of core B with high clay content. In an 8000 ppm solution, the zeta potential difference of core A under neutral and acidic conditions is smaller than that under a 1.0 \times 10^4 ppm solution. For core B with high clay content, the effect of calcium ions on the formation of micro precipitation is very small, indicating a normal rule.

3.2. Scanning Electron Microscope Experiment. The change in the clay state can be observed directly by SEM. Combining the results of other experiments, the most
representative samples were used in the SEM experiment, and their results are shown in Figure 5.

Figure 5 shows that rock B is in the original state in the 1.0 × 10^4 ppm neutral NaCl solution and 2000 ppm neutral solution conditions. Evidently, the clay (montmorillonite) heavily swelled in the low salinity condition. However, in the high salinity condition, the clay state has no large change compared to the clay in the original state. Combining the results of the zeta potential experiments, displacement experiments, and the variation in the injection pressure, it is not difficult to find that the regularity and limit value of the clay are related to the degree of clay expansion.

3.3. Displacement Experiment. There are four factors involved in the experiment: salinity, pH value, cation type, and clay content. Figure 6 shows the recovery trend under different salinity, pH value, and clay content in the NaCl solution; and Figure 7 shows the recovery trend under different salinity, pH value, and clay content in the CaCl_2 solution.

The displacement experiment results are shown in Figure 6. We can see that in any situation, when the salinity is decreased, the \( R_I \) of core A increased and reached its maximum at the
minimum salinity of 2000 ppm. However, in the neutral and alkaline conditions, the R_i of core B first increased and then decreased with the decrease in salinity. It reaches its maximum value at 4000 ppm. While the salinity is decreased from 8000 to 2000 ppm in neutral conditions, the R_i of core A increases from 3.77 to 8.00% (8000 to 4000 ppm) and then decreases from 8.00 to 6.98% (4000 to 2000 ppm). In acidic conditions, the R_i of core A increased from 2.27 to 18.18% (8000 to 2000 ppm). The recovery efficiency of both core A and B basically follows the trend: alkaline > neutral > acid.

Figure 7 shows the corresponding recovery improvement of core A and core B in a CaCl_2 solution environment with two values of pH and four concentrations of salinities. As the CaCl_2 solution salinity decreased, the R_i of both core A and B increased, and R_i reached a maximum at a minimum salinity of 2000 ppm. As the salinity decreased from 8000 to 2000 ppm, in neutral conditions, the R_i of core A increased from 2.27 to 6.82% and that of core B increased from 2.44 to 6.67%; in acidic conditions, the value for core A increased from 2.13 to 4.65% and that for rock B increased from 2.38 to 2.00%. The recovery efficiency of both cores A and B basically follows the trend: neutral > acidic.

In the same salinity condition, the R_i values of rocks A and B are close. Except when the CaCl_2 solution salinity is equal to 2000 ppm in neutral conditions, the R_i of rock A is larger than...
that of rock B; in other situations, the enhanced recovery of rocks A and B is contrary.

The displacement dynamic record of core An-2 in 4000 ppm NaCl solution at pH = 7.0 is taken as an example of all displacement experiments and is shown in Figure 8. During the first step (conventional water flooding), the oil recovery of An-2 increased by 41.29% with the high-salinity water injection and remained stable. In the process of the first five pore volume (PV) injections, the recovery of the An-2 core increased rapidly. During the low-salinity injection process, the oil recovery of An-2 increased from 41.29 to 45.68%, and the PEOR recovery was enhanced from 4.39 to 10.64% at pH = 7 and with a 4000 ppm NaCl solution injection. In the process of LSWF, the recovery of core An-2 steadily increased.

The results of the PEOR in NaCl solution is shown in Table 4 and the PEOR in CaCl₂ is shown in Table 5.

Table 4 shows that in the NaCl solution environment in alkaline conditions, the Rᵢ of rock A reaches 7.55% at 2000 ppm, and the PEOR reaches 21.05%. The Rᵢ of rock B reaches the largest value of 8.51% at 4000 ppm, and the PEOR reaches 25.00%; with the salinity decrease at 2000 ppm, the Rᵢ and PEOR of rock B both decreased. In neutral conditions, the Rᵢ of rock A reaches 8.00% at 2000 ppm, and the PEOR reaches 21.05%. The Rᵢ of rock B reaches its largest value of 8.16% at...
4000 ppm, and the PEOR reaches 34.13%; with the salinity decrease at 2000 ppm, the EOR and PEOR of rock B both decreased. In acidic conditions, the \( R_I \) of rock A reaches 6.25% at 2000 ppm, and the PEOR reaches 15.15%. The \( R_I \) of rock B reaches its largest value 6.35% at 2000 ppm, and the PEOR reaches 23.53%.

Table 5 shows that in the CaCl\(_2\) solution environment and in neutral and alkaline conditions, the \( R_I \) and PEOR of rocks A and B both reach the largest value with a salinity of 2000 ppm. The \( R_I \) of rock A reached the largest values of 6.82 and 4.65% in neutral and alkaline conditions and the PEOR reached 16.67 and 11.11% in neutral and alkaline conditions, respectively. The \( R_I \) of rock B reached the largest values of 6.67 and 5.00% and the PEOR reached 30.02 and 18.18%.

In the displacement experiment, the core in each group was used with the low-salinity water to be displaced after the displacement of the 1.0 \( \times \) 10\(^3\) ppm brine. The variation in the injection pressure between high-salinity and low-salinity brine can show the permeability changes that can be used to evaluate the effect of profile control on LSWF. The permeability test result is shown in Figure 9. The variation in the injection pressure of each displacement experiment group is shown in Figure 10.

Figures 9 and 10 show that permeability decreased and the injection pressure increases when the salinity of the injection water changes from high to low. Comparing the values of the permeability difference and the variation injection pressures of rocks A and B, the variation in the injection pressure of rock B is higher than that for rock A, the proportion of the permeability difference in initial permeability is that rock B bigger than rock A, which means that the relationship between the clay content and the variation in the injection pressure is proportional to the same extent. The results show that most of the variation in the injection pressure in rocks A and B increased as the salinity decreased. The low-salinity water causes reduced permeability.

### 3.4. Multivariate Analysis of Variance

We regulated the factors and the experimental result indexes (dependent variable). We used Statistical Product and Service Solutions (SPSS) to analyze the multivariate linear model of those data. In the multivariate model, the dependent variables are the zeta potential, \( R_I \), and PEOR. The fixed factors are the salinity, cationic type, pH value, and clay content. Before the analysis of the multivariate model, the homogeneity of variances was tested. The test result is shown in Table 6.

#### Table 6. Test of Homogeneity of Variances

| factors       | indexes | Levene statistic | df1  | df2  | Sig  |
|---------------|---------|-----------------|------|------|------|
| salinity      | \( R_I \) | 0.690           | 2.22  | 0.512|
|               | PEOR    | 0.467           | 2.68  | 0.632|
|               | zeta potential | 1.775  | 3.28  | 0.175|
| cationic type | \( R_I \) | 0.030           | 2.79  | 0.863|
|               | PEOR    | 0.049           | 2.68  | 0.827|
|               | zeta potential | 3.873  | 2.55  | 0.008|
| pH value      | \( R_I \) | 2.562           | 2.57  | 0.097|
|               | PEOR    | 5.766           | 2.23  | 0.009|
|               | zeta potential | 1.229  | 3.53  | 0.305|
| clay content  | \( R_I \) | 0.101           | 2.79  | 0.740|
|               | PEOR    | 0.769           | 2.77  | 0.388|
|               | zeta potential | 0.327  | 2.93  | 0.572|

From Table 6, the test level of homogeneity of variances is mostly bigger than 0.05, which indicates that the analysis of the multivariate model can be carried out.

In the specific model, we use the main effects and type III sum of squares. A statistical analysis of those data yielded the results for tests of between-subject effects and is shown in Table 7.

From Table 7, the type III sum of squares, df, mean square, \( F \), and Sig (use the \( F \) value to judge whether factors have significant effects on indexes (\( R_I \), PEOR, and zeta potential)) show the degree of dispersion and statistical significance among the data. While the \( P \) value is smaller than 0.05, the factor has a significant effect on the index.\(^{27}\) The SPSS model analysis calculates the estimated marginal means graphic, which shows the effect of each factor on each dependent variable.

### 4. DISCUSSION

#### 4.1. The Effect of Salinity

Figure 11 shows the estimated marginal means graphic of salinity (independent factor) for the different indexes (\( R_I \), PEOR, and zeta potential).

According to the SPSS results, the salinity has a significant effect on the indexes (the factor of salinity was analyzed independently). The absolute zeta potential value decreases when the salinity decreases. The high absolute zeta potential value indicates that the electric double layer of the clay expands considerably. Combining the estimated marginal means of salinity for the indexes, the \( R_I \) and PEOR increase with decreasing salinity. In the solution with one cationic type, the cations have a low concentration when the salinity is low, which means that the cation distribution is relatively dispersed. The cations on the clay surface will go into the solution. The Gouy layer range will increase, the electric double layer of the clay will swell, and the absolute zeta potential value will increase. In deionized water, this phenomenon will be amplified. The clay will overhydrate and swell. It will cause formation damage. In the high-salinity solution, the cation concentration is high. The interaction force between cations is large. It can cause the cation groups to be compressed, the Gouy layer range to be decreased, the electric double layer of the clay to be compressed, and the absolute zeta potential value to be decreased. The clay swelling is inhibited. The clay colloidal suspension system is unstable. The clay swelling becomes more serious when the degree of electric double layer expands. The clay swelling will make the main rock pore be partially blocked. This phenomenon will cause profile control and improve oil recovery. According to the Berg experiment,\(^{12}\) when clay swelling occurs, the force balance between clay and crude oil will be broken. The crude oil will drop off from clay easier.

#### 4.2. The Effect of a Cationic Type

Figure 12 shows the estimated marginal means graphic of the cationic type (independent factor) for the different indexes. According to the SPSS results, there are significant effects of the salinity factors on the indexes.

In the independent analysis of the cationic type factor, the absolute zeta potential value estimated for the marginal means of Na\(^+\) is larger than that for Ca\(^{2+}\). The result is the same for the \( R_I \) and PEOR. Based on the negative charge on the clay surface, Rivet et al.\(^{17}\) and Fjelde et al.\(^{18}\) concluded that the adsorption capacity between the clay with different cations can be concluded as follows:
### Table 7. Tests of Between-Subjects Effects

| factors     | indexes | type III sum of squares | df | mean square | F     | Sig (P value) |
|-------------|---------|-------------------------|----|-------------|-------|---------------|
| salinity    | RI      | 0.024                   | 3  | 0.008       | 85.827| 0             |
|             | PEOR    | 0.219                   | 3  | 0.073       | 33.958| 0             |
|             | zeta potential | 763.902          | 3  | 254.634     | 17.481| 0             |
| cationic type | RI   | 0.001                   | 1  | 0.001       | 9.190 | 0.005         |
|             | PEOR    | 0.017                   | 1  | 0.017       | 8.143 | 0.008         |
|             | zeta potential | 1384.695        | 1  | 1384.695    | 95.064| 0             |
| pH value    | RI      | 0.001                   | 2  | 0           | 5.150 | 0.012         |
|             | PEOR    | 0.004                   | 2  | 0.002       | 1.021 | 0.372         |
|             | zeta potential | 789.145         | 2  | 394.573     | 27.089| 0             |
| clay content| RI      | 0                       | 1  | 0           | 4.504 | 0.042         |
|             | PEOR    | 0.062                   | 1  | 0.062       | 28.819| 0             |
|             | zeta potential | 8.492           | 1  | 8.492       | 0.583 | 0.451         |

**Figure 11.** Estimated marginal means graphic of salinity for the indexes.

**Figure 12.** Estimated marginal means graphic of the cationic type for the indexes.

**Figure 13.** Estimated marginal means graphic of the pH value for the indexes.
Figure 14. Estimated marginal means graphic of the clay content for the indexes.

$H^+ > Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+} > Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$

The adsorption capacity of $Ca^{2+}$ to clay is larger than that of Na$. It can be said that $Ca^{2+}$ is easier to aggregate and Na$^+$ is easier to disperse in the same cation concentration (same salinity) solution due to the different adsorption capacities. This caused the different zeta potentials between Na$^+$ and $Ca^{2+}$. The Na$^+$ can increase the Gouy layer range, cause the expansion of the electric double layer of the clay, and cause clay swelling. $Ca^{2+}$ has less impact. Compared with deionized water, $Ca^{2+}$ can compress the electric double layer more easily than Na$. The different cationic types can cause different $R_I$ values, and the PEOR is improved in the estimated marginal means graphic. The theory of this phenomenon is the same as that for the salinity factor.

4.3. The Effect of the pH Value. Figure 13 shows the estimated marginal means graphic of the pH value (independent factor) for the indexes. The pH value shows a significant effect on the indexes of the $R_I$ and zeta potential and has a nonsignificant effect on the index of PEOR from the results of the tests of between-subjects effects.

In the independent analysis of the factor of pH value, the neutral pH (pH value equal to 7) was used as the contrast standard. In the alkaline environment, there is OH$^-$ present in the solution. A negative charge on the clay surface will cause the OH$^-$ to diffuse away from the clay. Moreover, there is an adsorption capacity between OH$^-$ and the cations on the clay surface. This adsorption capacity will counteract the adsorption capacity between the clay and cation. This condition will make the cation distribution more dispersed. This causes the Gouy layer range to increase, the absolute zeta potential value to increase, the electric double layer expansion, and clay swelling. In the acidic environment, there are many H$^+$ in the solution. H$^+$ increases the concentration of cations in the solution, and H$^+$ has a strong adsorption capacity on the clay surface. The consequences of this condition are contrary to the alkaline environment. The theory of the pH value factor affects the $R_I$ and the PEOR trend is the same as that for the salinity factors and cationic type.

4.4. The Effect of the Clay Content. Figure 14 shows the estimated marginal means graphic of the salinity (independent factor) for the indexes ($R_I$, PEOR, and zeta potential). The clay content has a significant effect on the indexes of $R_I$ and PEOR and a nonsignificant effect on the zeta potential.

In the independent analysis of the clay content, the effect of clay content on the zeta potential is less obvious than that for other factors. However, the effect of the clay content on $R_I$ and PEOR is obvious. The zeta potential experiment uses rock powder. The rock powder cannot reflect the difference in the clay content. The different clay contents (rock A has 6.04%; rock B has 11.94%) cause different coverage areas in the rock pores. When the clay swells (including montmorillonite), the higher clay content rock has a larger pore-blocked area. If the clay swelling is small, the higher clay content rock provides a better profile control effect. However, if the clay swelling is excessive, the higher clay content rock would cause formation damage. Rock A has a low clay content and high permeability, and rock B is the opposite. This means that the original recovery of rock A is higher than that of rock B. The PEOR of rock B has higher odds than that of rock A. The SPSS results also show the significant effect of the clay content on the PEOR.

4.5. Extreme Point Values of the $R_I$ Analysis. Considering the displacement experiment results, we find that rock B in a 4000 ppm NaCl solution in neutral and alkaline environments have extreme values. The $R_I$ and PEOR values corresponding to these two extreme points are also the highest in all the experimental results. The results were shown in Figure 15. After the independent analysis of each factor, the results show that low salinity, Na$^+$ (monovalent cation, except H$^+$), high pH value, and high clay content can control the profile and can break the force balance between the clay and crude oil, thereby improving the oil recovery. However, while

Figure 15. Extreme $R_I$ values of rock B.
each factor is in the state that can cause maximum clay swelling, the clay will exhibit over swelling, formation damage occurs, and the rock permeability decreases. From Figure 15, the injection pressure corresponding to those extreme points has a large difference from that for other points.

For these four factors, there is a combination that can make the clay swelling reach an optimum state and the \( R_I \) reach an extremum value. This state is similar to "the controlled formation damage state" proposed by Berg et al. Through our experiments, the zeta potential can be used to determine the clay state. In our experiment, these four factors are the main factors affecting the clay state. However, other factors can affect the clay state. This is a subject that our team needs to research and discuss in the future.

5. CONCLUSIONS

Three Conclusions are listed as following from the presented experiments:

In the zeta potential experiment, when the salinity is at 4000 and 2000 ppm, the changes of the two rocks in NaCl and CaCl\(_2\) solutions were the same: the absolute value of zeta potential increased with pH changing from acidic to neutral. However, the change of Zeta potential was different in the case of high salinity.

The SEM results before and after displacement and the continuous increase of displacement pressure after low-salinity water injection in the displacement experiment indicated that the injection of low-salinity water will cause clay swelling. Combined with the zeta potential experiment, the absolute value of zeta potential increased after low-salinity water is injected, which indicates that the clay will expand in low salinity, high pH value, Na\(^+\) ion water injection, and high clay content situation.

Rock B has an extreme value of recovery in the process of displacement: the maximum \( R_I \) and PEOR values of rock B were found in 4000 ppm of NaCl with neutral and alkaline conditions: \( R_I = 8.16\% \), PEOR = 34.13\% in a neutral condition, and \( R_I = 8.50\% \), PEOR = 25.00\% in an alkaline condition. In the same condition, no extremum \( R_I \) and PEOR was observed in rock A; no extreme \( R_I \) and PEOR was observed in an acidic condition when other conditions remained unchanged; no extreme \( R_I \) and PEOR was observed in CaCl\(_2\) solution when other conditions remained unchanged. It can be concluded that the extremum \( R_I \) and PEOR appeared in the condition of monovalent cation, low salinity, neutral and alkaline solutions, and high clay content by analyzing the conditions of the \( R_I \) and PEOR. The corresponding results of these conditions in zeta potential showed that the clay state was expanded. The displacement pressure increased in the process of displacement, which indicated that the proper expansion of clay can improve the recovery of sandstone reservoir, and the excessive expansion of clay will damage the reservoir, resulting in the decline of oil recovery.

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Notes

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