Application of DLVO Modeling to Study the Effect of Silica Nanofluid to Reduce Critical Salt Concentration in Sandstones

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Abstract. Critical salt concentration (CSC) is the minimum salt concentration of injected water used for different oil recovery operations, below which fines migration initiates within sandstone reservoirs having clay contents and could be one of the potential causes of formation damage. This paper estimated CSC for Berea sandstone-NaCl brine system experimentally and by using DLVO modeling based on Van der Waals and electric double layer (EDL) surface forces. Furthermore, the effectiveness of silica nanofluid to reduce CSC and control fines migration was investigated. At different salinities of the injected fluid, the experimental CSC was determined by performing corefloods and analyzing effluent turbidity and absorbance. Attractive (van der Waals) and repulsive (EDL) forces were estimated by DLVO theory to predict the value of CSC. The experimental data were used to validate the model. The application of silica nanoparticles (NPs) was studied by injecting 0.1 wt% silica nanofluid and the resultant reduction in CSC was observed. During the injection of brines at different salinities ranging from 0.2 M to 0.05 M into the sandstone porous media, fines production was detected in the effluent after the injection of 0.1M NaCl solution, indicating that the CSC was 0.1M for this sand-fine-brine (SFB) system. The zeta potentials for SFB systems of different salinities were measured by zeta-sizer and were in the range of -32 mV to -24 mV. DLVO model based on attractive and repulsive forces was then used to predict the CSC, at which the total DLVO energy shifts from negative to positive and was around 0.1M for NaCl solution. The model prediction was in close agreement with the experimental results. Both the experiment and DLVO model showed the efficiency of silica nanofluid to mitigate fines migration as no fines production was observed for 0.1M NaCl case after the treatment with nanofluid. The estimation of CSC is critical to avoid formation damage during many oil recovery processes, included but not limited to low salinity waterflooding and alkaline flooding. The utilization of nanofluid provided promising results in controlling fines migration and reducing CSC. The proposed model based on DLVO theory can work as a useful tool to predict CSC without the need for extensive experimental work.

1. Introduction

Oil-containing sandstone reservoirs are a huge source of energy worldwide and consist of about 60% of the world’s petroleum reservoirs [1]. Due to low salinity waterflooding, a decrease in ionic strength and change in ionic composition of formation water with different cations and anions can cause fines migration and permeability impairment in porous and permeable sandstones containing different types of clay minerals. These minerals are a part of rock bulk volume and reside in the pores either in the form of clusters or as fines covering the sand grains. Clay minerals are primarily composed of alumino-
silicates with a platelet configuration. The chemical composition of clay minerals incorporates silicon oxide, aluminum oxide, and compounds of magnesium. Kaolinite, illite, and montmorillonite are the three most commonly found clay minerals [2]. The fine particles remain in equilibrium in a high salinity formation water environment as the electric double layers around fine and sand grain are contracted because of the presence of high charge density in the system. However, when system salinity decreases due to the injection of low salinity water, both electric double layers expand, and because of high repulsion, fine particles are released and migration starts within the reservoir even at a low flow rate [3]. Released fines can block the pore throats and cause productivity and injectivity problems due to high pressure drop requirements [4, 5]. Fines can be released because of three conditions: (1) if the system salinity is less than a critical salt concentration (2) production or injection velocity is higher than a critical velocity and, (3) pH of the system is greater than a critical pH [6].

The use of nanotechnology to control the fines migration has gained considerable importance in the petroleum industry in recent years. NPs are very small particles with a size ranging between 1–100 nanometers and having a high specific surface area due to their extremely small size. The adsorption of NPs onto the rock surface changes the surface potential. Various types of NPs with different chemical nature (composition, water solubility, and stability) and distinctive properties (size, shape, and specific surface area) have been utilized to mitigate fines migration e.g. silicon oxide (SiO$_2$) [7, 8], magnesium oxide (MgO) [9], and aluminum oxide (Al$_2$O$_3$) [10]. Derjaguin, Landau, Verwey, and Overbeek (DLVO) presented a theory that is a useful tool to model the dynamics of a sand-fine-brine system and study the effect of various critical parameters on fine migration initiation [11-13]. It describes the total potential ($V_T$) of the system by integrating all the effective surface forces which include van der Waals attractive potential ($V_V$), electric double layer potential ($V_E$), and Born repulsion ($V_B$). This theory considers that the $V_V$, $V_E$, and $V_B$ do not depend on each other, and hence can be summed up for the particle-plate configuration, to quantify the total potential as a function of separation distance. The DLVO-based total potential of a system containing a fine particle and a pore surface is presented as Equation-1 which is a superposition of all the energies. In this research work, the application of nanoparticles to reduce CSC was examined experimentally and modeled by the analysis of surface forces using DLVO theory.

$$V_T = V_V + V_E + V_B.$$

\[1\]

2. Methodology

2.1. Brines.
To replicate the reservoir conditions, high salinity formation water (FW) of 7.7 wt% ionic strength was used to saturate the core samples in the experimental phase. NaCl brines of 0.2, 0.15, and 0.1 molarities with pH 7-7.5 were used to determine the CSC for the given SFB system. The ionic compositions of the brines are given in Table 1.

Table 1. Composition of formation water and NaCl brines.

| Ions  | FW  | 0.2M NaCl | 0.15M NaCl | 0.1M NaCl |
|-------|-----|-----------|------------|-----------|
|       | [ppm]|           |            |            |
| Na$^+$| 23426| 4600      | 3450       | 2300      |
| Ca$^{2+}$ | 4448 | -         | -          | -         |
| Mg$^{2+}$ | 1300 | -         | -          | -         |
| Cl$^-$ | 47781| 7093      | 5320       | 3547      |
| Total | 76955| 11693     | 8770       | 5847      |

2.2. Rock Samples.
Berea sandstone outcrop cores were used for the experimental part. The mineral composition of the Berea sandstone as obtained from scanning electron microscopy - energy dispersive spectroscopy...
Four core samples were cut, each with 3 in length and 1.5 in dia. The samples were initially oven dried and then saturated with formation water using Vinci manual saturator. The wet weights were measured and porosities for each sample were calculated. Each sample was then flooded with FW using the Vinci SRP30 coreflood system to measure absolute permeabilities. Table 2 shows the properties of each sample. The core samples were then used for different experiments.

Table 2. Properties of sandstone cores.

| Sample ID | Diameter [mm] | Length [cc] | Pore volume [%] | Porosity [%] | Permeability [md] |
|-----------|---------------|-------------|-----------------|--------------|-----------------|
| 1         | 38.12         | 75.98       | 17.40           | 19.21        | 295.3           |
| 2         | 38.12         | 76.45       | 16.77           | 19.22        | 303.5           |
| 3         | 38.12         | 76.20       | 17.05           | 19.65        | 320.1           |
| 4         | 38.12         | 74.70       | 16.65           | 19.53        | 312.1           |

2.3. Nanofluid.
To study the effect of nanoparticles on CSC, silica nanoparticles of 20 nm size were used provided in the form of a 25 wt% concentrated dispersion by Glantero Ltd. Ireland. The reason for selecting these nanoparticles is their hydrophilic nature, high stability, low toxicity, and better performance in controlling fines migration in sandstones [14]. Moreover, 0.1 wt% nanofluid was prepared by diluting the dispersion using 0.15M NaCl brine.

2.4. Coreflooding.
Three corefloods were performed by injecting brines of different molarities at a flow rate of 0.2 cc/min (0.82 ft/day) and pressure drop was monitored to estimate the fines migration initiation. Effluent absorbance was measured by UV-Vis-Spectrophotometer and turbidity was obtained by turbidity meter to confirm fines presence and determine CSC for NaCl solution. A fourth coreflood was conducted by injecting 0.1 wt% silica nanofluid at the observed CSC to analyze the effectiveness of NPs in controlling fines migration and reducing the CSC.

2.5. Zeta Potential Measurements.
Sand-brine and sand-nanofluid zeta potentials were required as input for DLVO modeling. For this purpose, a core sample was crushed using a cone crusher and sieved to 40 um size of sand grains. The sieved sample was washed with a sequence of distilled water, acetone and again distilled water to remove any impurities on the sand grains. The crushed sand was dispersed in different brines and nanofluid with an ultrasonic homogenizer and the zeta potentials were measured using Malvern zeta sizer.

2.6. Fines Analysis.
The effluents from coreflood tests were oven-dried to collect the in-situ fines and the shape and average size of a fine particle were obtained using SEM. Furthermore, SEM-EDS was performed to obtain information regarding the chemical composition of fines.

2.7. DLVO Modeling.
Measured zeta potentials, the average size of fine particles, and ionic strength of the brines were used as input for DLVO modeling, and surface forces were calculated based on available models mentioned in our previous study [15]. CSC was determined using the DLVO model and was compared with the experimentally obtained CSC to validate the proposed approach. In addition, the model was used to check the efficacy of nanofluid in altering the surface forces and minimizing the fines movement.
3. Results and Discussion

3.1. CSC from Corefloods.

The first objective of coreflood tests was to determine the CSC for NaCl brine-sandstone system. The pressure drop versus pore volume data was recorded for each case and a high pressure drop was observed during the 0.1M NaCl injection scenario as compared to 0.2M and 0.15M brines injection. This high pressure drop was the indication of fines release and migration in the system at 0.1M ionic strength. However, the other two scenarios showed a relatively low and stable pressure drop during the experiment, indicating 0.1M was the CSC for the SFB system under study. Moreover, turbidity analysis (Fig. 1a) and UV-spectrophotometry results (Fig. 1b) also showed that the effluent produced during 0.1M NaCl injection had high turbidity and more light absorbance due to the presence of a high concentration of fine particles. Effluent received after 0.1M NaCl injection had high turbidity of 25.6 NTU whereas 0.15M and 0.2M effluents showed turbidities of 2.51 and 1.71 NTU respectively, which could be because of some mineral dissolution in the cores. Similarly, the same effluent of 0.1M injection resulted in light absorbance of 0.458 ABS, and the other two effluents showed negligible light absorbance of 0.05 and 0.019 ABS. These experimental results collectively confirmed the fines migration after 0.1M brine injection. Hence, the CSC from the experimental results was around 0.1M.

3.2. Fines Characterization.

The fines recovered from the coreflood effluent were analyzed by SEM and SEM-EDS and the results are presented in Figure 2.

![Figure 1](image1.png)

Figure 1. Results of effluents (a) Turbidity, and (b) Absorbance as a function of ionic strength.

![Figure 2](image2.png)

Figure 2. (a) SEM image of kaolinite fines, and (b) SEM-EDS results for fines composition.
Based on the SEM-EDS and X-ray diffraction (XRD) analysis, the fine particles were composed of mainly kaolinite clay ($\text{Al}_2\text{Si}_2\text{O}_5\text{(OH)}_4$), and the average size of these particles was around 800-900 nm.

### 3.3. CSC by DLVO Modeling.

Zeta potentials were measured for different systems being studied and were found to be in the range of -32 mV to -24 mV for the brine salinity range of 0.1M to 0.2M (Fig. 3a). The measured zeta potentials were in close agreement with the developed correlations in our previous study [15]. An increase in zeta potential towards the negative side was observed with decreasing brine salinity, indicating the dominance of repulsive forces in the system. The measured zeta potentials, ionic strength of each brine, and the average size of fine particles were used to calculate surface forces between fine and sand grain, and then the total interaction energy of each system was calculated using DLVO modeling as shown in Figure 3b. The total interaction energy is the sum of attractive and repulsive forces. In the high salinity environment, as in the case of 0.2M NaCl solution, attractive forces dominate the repulsive forces because of compacted electric double layers on fines and sand grains and the total energy comes out to be negative, which indicates there would not be any fines migration in the system. The same results were obtained for 0.2M, and 0.15M brine environments with the total interaction energy in the negative region. However, for 0.1M brine, the total interaction energy shifted from negative to positive indicating the dominance of repulsive forces in the system at this separation distance. This can be attributed to the expansion of electric double layers around fines and sand grains under low salinity conditions. Based on the DLVO model results, it was inferred that 0.1M was less than CSC, and CSC was in between 0.15M and 0.1M NaCl brines for the SFB system under investigation. Thus, the DLVO model validated the experimental results and can be successfully used to predict CSC for a certain brine-rock system.

![Figure 3](image)

**Figure 3.** (a) Zeta potentials for different systems, and (b) CSC prediction from DLVO model.

### 3.4. Effect of Nanoparticles on CSC.

In the last coreflood test, 0.1 wt% silica nanofluid was injected in the core at an injection rate of 0.02 cc/min after FW injection. This low injection rate was set to provide more time for the NPs to interact with the sandstone surface and alter the surface forces. After injecting 4 PVs of nanofluid, 24 hrs soaking period was given followed by injection of 0.1M NaCl solution at the rate of 0.2 cc/min. The turbidity analysis showed no presence of fine particles in the effluent as the turbidity value was only 1.39 NTU after injecting 4 PVs of low salinity water (Fig. 1a). The UV spectrophotometry results also confirmed the absence of fine particles in the effluent as the measured absorbance was very low (0.07 ABS). This test showed the effectiveness of nanotechnology in mitigating fine migration problems during low salinity waterflooding operations. The DLVO model was also used to further validate the experimental data in the case of nanofluid. For this purpose, the zeta potential of the sand-nanofluid system was measured and is plotted in Figure 3a along with sand-brine zeta potentials. As expected, nanoparticles decreased the absolute value of sand-brine zeta potential, implying higher attractive forces. The DLVO
model was then run for the sand-nanofluid system and the results are presented in Figure 3b with the sand-brine cases. It is clear from Figure 3b that the silica nanoparticles successfully altered the surface potential, causing an increase in the attractive forces. Hence, fine particles remained attached to the sandstone surface in the presence of nanofluid, indicating that the CSC for this system was now reduced to a lesser value than 0.1M.

4. Conclusions

The estimation of CSC is necessary to avoid formation damage during many oil recovery processes, particularly in low salinity waterflooding and alkaline flooding. From core-flood experiments and effluent analysis, the CSC for sandstone-NaCl brine was in between 0.15M and 0.1M which was also validated through the analysis of surface forces and DLVO modeling. DLVO model results were in close agreement with the experimental results and this tool can be used to estimate the CSC without extensive experimentation. The effect of nanoparticles on fine migration control was also studied and it was found that nanoparticles altered the surface potential and reduced repulsive forces in the SFB system, thereby mitigating the fines migration issue and lowering the CSC. Both the experimental results and DLVO model outcome proved that nanotechnology has the potential to improve the performance of enhanced oil recovery methods by controlling fines production and overcoming productivity and injectivity issues.

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