Effects of MgO, \(\gamma\)-Al\(_2\)O\(_3\), and TiO\(_2\) Nanoparticles at Low Concentrations on Interfacial Tension (IFT), Rock Wettability, and Oil Recovery by Spontaneous Imbibition in the Process of Smart Nanofluid Injection into Carbonate Reservoirs

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1. INTRODUCTION

According to available sources, at least 50% of the primary oil is trapped in oil reservoirs after initial production and thus is not produced for various reasons.\(^1\) The water injection method in secondary and tertiary recovery operations shows improved performance.\(^2\) In the chemically improved water injection, dissolved components are engineered and managed to achieve the best performance in the presence of reservoir fluid and rock. This engineered water method adjusts the type and concentration of water-soluble ions to achieve the highest recovery factor. Wettability alteration is known as a major result of low-salinity water injection.\(^3\)–\(^5\) However, the regulation of ions also affects the reduction of interfacial tension (IFT). Some additives, such as nanoparticles, can improve the performance of injection water in enhanced oil recovery (EOR) process. A nanofluid consists of a fluid and nanoparticles dispersed in that fluid. The properties and efficiency of nanofluids in EOR depend on various parameters such as the size and type of the dispersed nanoparticles.\(^6\)–\(^8\) The behavior of pressure drop in nanofluids is different from that in common fluids. Nanoparticles dispersed in nanosuspensions are normally in the size range of 1–100 nm.\(^9\)–\(^11\) The small sizes of the nanomaterials increase their effective surface areas that will change some of the properties of the fluids containing these particles, such as heat transfer, viscosity, and activity of the particles on the surface.\(^12\)–\(^15\) So far, the most important mechanisms studied in EOR by nanofluids include pore channel plugging, pressure disjoining, increased viscosity of the injected phase, reduced oil–water IFT, wettability alteration and deformability, and prevention of asphaltene precipitation.\(^16\)–\(^19\) Esfandyari et al. reviewed some published articles from 2010 to 2014. The most commonly used nanoparticles include zinc, aluminum oxide, silica, titanium dioxide, and zirconium oxide.\(^20\) Some researchers have also used MgO and Fe\(_2\)O\(_3\) nanoparticles in nanofluids.\(^21\) Ogolo et al. evaluated some nanofluids with water, ethanol, saline water, and gasoline as the dispersion phase and the nano-oxides of aluminum, zinc, tin, silicon, nickel, zirconium, iron and, magnesium as the dispersed phase for enhanced oil recovery and obtained similar results from the increase in oil recycling.\(^22\) Jalilian et al. used zirconium oxide nanopowder in emulsion flooding and achieved a recovery factor of up to 60%.\(^23\) Cheraghian and Khalili Nezhad applied clay nanoparticles with an anionic surfactant. In addition to a 52% increase in heavy oil recovery, they observed a decrease in...
surfactant adsorption. In another study, they showed that clay nanoparticles could also reduce polymer adsorption. The use of Al₂O₃ nanoparticles showed that these materials are very useful in improving the foam behavior of the injected fluid. Ehtesabi et al. used a TiO₂ nanofluid and did not report fundamental changes in viscosity and interfacial tension. However, they reported a recovery factor of over 55%. In an investigation by Hendraningrat et al., TiO₂ nanoparticles did not show a significant impact on interfacial tension but showed a better performance in wettability alteration. Metal oxide nanoparticles showed a better performance in the reduction of interfacial tension. Nazari Moghaddam et al. estimated the efficiency of CaCO₃ and SiO₂ nano fluids on altering wettability and oil recycling from carbonates. They stated an increase of 8–9% in oil recycling and wettability alteration to hydrophilic. Li et al. performed some experiments on IFT and contact angle using a sample of crude oil and nanofluid containing 7 nm silica particles and studied enhanced oil recovery in a glass micromodel and sandstone cores. Their results show a significant difference in the IFT and contact angle reduction, which was related to the concentration of nanoparticles in the saline water-based suspensions. Water-based, saline-water, and ethanol-based nano suspensions have been used in most studies. Smart water in the real sense has been used in a few studies so far. Sadatshojaei et al. reported the interplay of these methods and their effects on wettability alteration of dolomite. They dispersed SiO₂ nanoparticles with different concentrations in four diluted seawater samples. They found that increasing water salinity leads to reduced variations in the contact angle while increasing the concentration of SiO₂ nanoparticles at any given salinity increases the variations in this angle. It seems that both management of ions at low concentrations and the nanoparticles will improve the performance of smart water more than that achieved by each method separately and there is a gap in the literature that requires an evaluation of the combination of these methods. This is studied in detail in this research work. It should be noted that nanoparticles, even those of Al₂O₃, form stable suspensions only at low enough concentrations. The combination of two EOR methods makes it possible, in one operation, to benefit the mechanisms of the two methods for the residual oil reduction. In addition, by optimizing the concentrations of ions in injected water, one can find the best performance of the smart water with stable nanoparticles, thus closer to an ideal process. Reduction of interfacial tension and wettability alteration are considered as the main mechanisms of chemical EOR. In addition, the formation of stable emulsions of the injection phase and oil and foam and oil swelling as a result of mass transfer of the injection phase or part of it into oil are also considered in some processes. Interfacial tension is directly related to capillary pressure in cavities and its reduction reduces capillary pressure. Altering the wettability of the rock to hydrophilicity activates the imbibition process. Hydrophilicity allows injected water to surround the rock surface and creates a passageway for trapped oil.

In this study, the performances of smart water containing different concentrations of MgSO₄ and CaCl₂ and 500 ppm of TiO₂, γ-Al₂O₃, and MgO nanoparticles were separately investigated by measuring IFT using the pendant drop method. Also, the contact angle experiments were performed to measure the capability of the nano fluids to alter the wettability of carbonate rocks. Finally, the imbibition tests with optimum nanosolutions were conducted to obtain oil recovery.

2. MATERIALS

MgSO₄ and CaCl₂ supplied by MP Biomedical (The Netherlands) with the specifications given in Table 1 were used. Formation water and dead oil were sampled from the Gachsaran oil field in Iran. Crude oil analysis is shown in Table 2. Nano-γ-alumina (γ-Al₂O₃), TiO₂ and MgO from US Nano Co. were used. The characteristics of the nanoparticles are shown in Table 3. The properties listed in Table 3 are specific to the materials used. For example, nanoparticles were synthesized in different sizes. In addition, their physical shapes and effective surfaces are different in different synthesis methods. Changing these properties along with the assay of the material may change some of the EOR parameters; for example, as the size of the TiO₂ decreases, the IFT decreases further. Many nanoparticles that have been used in EOR so far are mentioned in the Introduction section. The nanoparticles used in this study were selected according to their production on the industrial scale and their characteristics such as their small sizes and significant effective surfaces. In addition, except for some nanoparticles such as SiO₂, few studies have been done on them so far. Carbonate rock containing 61% dolomite and 39% calcite from an outcrop of the Asmari formation located in the southwest Iran was sampled. X-ray diffraction (XRD) and scanning electron microscopy (SEM) analyses of the rock are shown in Figure 1.

3. EQUIPMENT

3.1. IFT and Contact Angle Measurement Equipment.

The main equipment used in this study is IFT400 manufactured by Fars EOR Company (Iran). The contact angle and IFT tests can be done by this device using the pendant drop method. This method is one of the most common and simplest methods for measuring the interfacial tension of two immiscible liquids. It has high accuracy and is highly dependent on the cleanliness of the measuring device and equipment. However, due to the stability conditions of the droplet and bulk system, it is not recommended for very small values of interfacial tension and application for viscous fluids (the spinning drop method can be used as an alternative to water and oil interfacial tension tests if the interfacial tension values are close to zero). The main parts include a high-pressure steel enclosure with two resistant glass windows, in which a droplet needle and rock cross-section support are implemented, three heat elements embedded in the enclosure body, two high-pressure manual pumps, a high-pressure liquid transmission line, a 2 megapixel high-definition couple-charged device (HD CCD) camera with an adjustable position base, an adjustable light source, three pressure gauges, a temperature indicator and regulator, and a computer equipped with corresponding software. To calculate the IFT between two fluids in this device, a droplet of the fluid is suspended in an
immiscible bulk fluid. The high-pressure cell is filled with a manual pump from the bulk fluid and the droplet is hung from the needle tip in the bulk fluid by another pump. The pressure is increased by manual pumps and controlled by the pressure gauges embedded in the pump outlets and that attached to the cell. The camera connected to the computer regularly takes photographs of the contents of the cell and sends them to the software, and the software calculates the small and large diameters of the device to calculate the interfacial tension using the input defaults from eq 1.34

\[
\sigma = \frac{\Delta \rho g d_e^2}{H}
\]  

(1)

where \(\Delta \rho\) is the density difference between two immiscible phases in g/cm\(^3\) (e.g., water–gas or oil–water), \(g\) is the acceleration of gravity in cm/s\(^2\), \(d_e\) is the minimum horizontal diameter of the droplet in cm, \(H\) is the droplet shape factor as a function of \(S = \frac{d_r}{d_e}\), where \(d_r\) is the measured droplet diameter at the distance \(d_e\) from the top.

The same procedure was used to do the contact angle test in an aqueous medium. The oil droplet is released onto the rock. The software draws two tangential lines on both sides of the droplet. Based on the line separating the rock surface and fluid determined by the user, the left and right and average contact angles are reported. Figure 2 shows a schematic of IFT400. The basis for selecting and using this device is the convenience of performing tests in terms of physicality, easy cleaning, and the possibility of performing both interfacial tension tests and contact angle tests. In addition, the software of this device with the capability to analyze the drops simultaneously during the test automatically increases the speed of the tests. Calculating the interfacial tension and contact angle online and automatically is another advantage of using this device. Manual analysis devices can cause serious error results.

4. METHODS

The experimental method includes the preparation of solutions and nanosuspensions, interfacial tension tests, contact angle tests, and production under optimal fluid imbibition. Figure 3 shows these steps in a flowchart. Each of them is described in detail below. It should be noted that in these tests, each experiment was repeated three times to consider reproduc-

Table 2. Crude Oil Analysis

| component | C\(_2\) | C\(_3\) | iC\(_4\) | nC\(_4\) | iC\(_5\) | nC\(_5\) | C\(_6\) | C\(_7\) | C\(_8\) | C\(_9\) | C\(_{10}\) | C\(_{11}\) | C\(_{12+}\) | total |
|-----------|--------|--------|---------|---------|---------|---------|--------|--------|--------|--------|--------|--------|--------|-------|
| percent, molar | 0.08 | 0.73 | 0.72 | 2.22 | 1.10 | 1.10 | 8.66 | 9.32 | 6.60 | 7.14 | 5.36 | 5.01 | 51.96 | 100.00 |

\(M_c = 247 \text{ g/mol}\)
\(C_{12+}, M_c = 380 \text{ g/mol}\)
\(C_{12+}, \text{ Sp. Gr (@ 15.55 °C)} = 0.9369\)

Table 3. Properties of Nanoparticles Used in Smart Water with Stable Nanoparticles

| nanoparticle | APS (nm) | SSA (m\(^2\)/g) | morphology | density (g/cm\(^3\)) |
|--------------|----------|-----------------|------------|---------------------|
| TiO\(_2\) (anatase) | 20 | 200–240 | spherical | 3.9 |
| \(\gamma\)-Al\(_2\)O\(_3\) | 20 | >138 | nearly Spherical | 3.890 |
| MgO | 20 | >60 | polyhedral | 3.58 |

| certificate of analysis (ppm) | TiO\(_2\) | Al | Mg | Si | Ca | S | Nb |
|------------------------------|---------|----|----|----|----|---|----|
| >990 000 | ≤19 | ≤67 | ≤116 | ≤75 | ≤128 | ≤82 |
| \(\gamma\)-Al\(_2\)O\(_3\) | V | Cl | Na | Ca | S | Mn | Co |
| >990 000 | ≤5 | ≤280 | ≤30 | ≤20 | ≤5 | ≤5 |
| MgO | K | Na | Ca |
| >980 000 | ≤227 | ≤2109 | ≤1815 |

Figure 1. XRD and SEM analyses of the rock.

Figure 2. IFT400 Schematic.
bility and the final result was reported as an average of three values obtained from each experiment.

4.1. Preparation of the Solutions and Nanosuspensions. Smart water was prepared by dissolving various concentrations of CaCl₂ and MgSO₄ in deionized water as the base fluid. The salt powder and nanoparticles were weighed by a JA-120-HR scale (Japan) with an uncertainty of 0.0010. Concentrations were expressed in ppm based on the solvent and solute weights. Ultrasonic waves with a power of 400 W (UP400 Ultrasonic Mixer, Hielser, Germany) were used for 5 h to prepare stable nanosuspensions. The density of solutions at the desired temperature (75 °C) was measured by a floating pycnometer (HP-HT-Pycnometer-91-201, Fars EOR Technologies Co., Iran).

4.2. Experimental Procedure. The main experiments of this work included measurements of contact angle, IFT and oil production by spontaneous imbibition in carbonate plugs. In another study, we measured the IFT of smart water containing MgSO₄ and CaCl₂ at different concentrations and an oil sample at ambient pressure and 75 °C. Interfacial tension and wettability are highly dependent on oil, rock, and injection phase compositions. In our previous study, we used the same fluids, additives, and rocks. Also, the experiments were performed under similar conditions. For this reason, the data were used in this study. In case of any discrepancies in the composition and conditions of the obtained data, they cannot be compared and generalized. Mg²⁺, SO₄²⁻, and Ca²⁺ are stronger ions in the mechanism of using smart water, and other soluble ions in injected water have less effective on smart water mechanisms, especially ion exchange and wettability alteration, so these ions were selected on this basis. The interfacial tension experiments were performed by adding 500 ppm of nanoparticles to these solutions in the same situation. Experiments were conducted with the same materials and equipment under the same conditions. Then, the contact angles of the oil droplets on cross-sections aged in smart solutions in the absence and presence of dispersed nanoparticles were measured. For this purpose, 1 inch carbonate cross-sections of 5 mm thickness were cut and cleaned by nitrogen gas flow. Then, they were kept in toluene to eliminate fatty acids from the surfaces. The cleaned sections were then dried and placed in crude oil in a suitable container. The sections were aged for 7 days at 75 °C in an oven. The hydrophobic sections were soaked in the desired nanofluids at 75 °C for three days. In this way, the sections were prepared for contact angle measurements to investigate the carbonate rocks’ wettability alteration.

In a similar study, we reported the contact angles for different concentrations of CaCl₂ and MgSO₄ with the same materials and methods. Here, these experiments were continued by adding nanoparticles to smart solutions to investigate and compare the effects of nanoparticles. After conducting the contact angle tests, the optimal concentrations were determined in terms of minimum contact angles. In the next step, production under spontaneous imbibition in the carbonate plugs was studied using smart fluids and nanofluids selected from contact angle tests. Since the alteration of wettability is the most important mechanism of using smart water, it is logical to select optimal fluids with minimum contact angles. However, there are many factors involved in a chemical oil recovery operation and several mechanisms control the quality and ability of the injectable fluid to enhance oil recovery.

The production tests with imbibition were carried out at 75 °C and ambient pressure in a container known as the Amott cell. Spontaneous imbibition is a major mechanism of oil recovery in fractured reservoirs. These experiments were continued to achieve constant production in the plugs with no significant changes. The oil produced from the carbonate plugs was collected by buoyancy force in the narrow scaled cylinder of the Amott cell. The cylinder body was transparent, and the gradual production volumes under spontaneous imbibition were observed and recorded at 2 day intervals. The total cumulative production of oil from the carbonate plugs was obtained. The total cumulative production is a fraction of the primary oil in place, which is obtained using the spontaneous imbibition factor. The carbonate plugs in spontaneous imbibition experiments were used without limiting their boundaries to simulate the matrix and surrounding fractures.

5. RESULTS AND DISCUSSION

5.1. IFT. The IFT of water with stable nanoparticles and the oil was determined upon reaching a constant value (equilibrium IFT). Table 4 shows the values obtained from IFT tests. Figure 4 shows the IFT of a stable oil droplet in the nanofluid containing MgSO₄ at different concentrations and nano-MgO, -TiO₂, and -γ-Al₂O₃ at Ambient Pressure and 75 °C.
nanoparticles at 2000 ppm of CaCl2. Given the interfacial tension of the 2000 ppm CaCl2 solution in the absence of any nanomaterial, the interfacial tensions for nanofluids with MgO, TiO2, and γ-Al2O3 were 11.637, 12.165 and 10.679 mN/m, respectively. For the smart suspensions containing different concentrations of MgSO4, the interfacial tensions were reduced less than those obtained with CaCl2. However, the ultimate interfacial tensions in the presence of TiO2 and MgO were lower. Moreover, the interfacial tensions in the absence of nanoparticles with 2000 ppm of CaCl2 and MgSO4 for a crude oil sample were 19.081 and 18.122 mN/m, respectively. The minimum IFT obtained by 500 ppm of TiO2 particles was 7.362 mN/m at 2000 ppm of MgSO4 at ambient pressure and 75 °C. The minimum IFT obtained by 500 ppm of MgO nanoparticles was 4.684 mN/m at 2000 ppm of MgSO4 at ambient pressure and 75 °C. The minimum IFT obtained by 500 ppm of γ-Al2O3 nanoparticles was 9.650 mN/m at 2000 ppm of MgSO4 at ambient pressure and 75 °C. The reduction in IFT by nanoparticles dispersed in smart solutions is obvious in Figures 4 and 5. As shown, the curve for nanofluids is above that for the smart solution containing only CaCl2 and MgSO4 at all concentrations of salts and the constant concentration of nanoparticles. The lowest interfacial tension of 4.684 mN/m was obtained by the nanofluid containing 500 ppm of MgO nanoparticles and 2000 ppm of MgSO4 at ambient pressure and 75 °C. According to the IFT diagrams, the salinity and type of salt effects on IFT at constant concentrations of dispersed nanoparticles can be investigated. As shown in Figure 5, the smart solution containing 500 ppm of TiO2 nanoparticles at various concentrations of CaCl2, the interfacial tension decreases to 8.173 mN/m by increasing salt concentration up to 2000 ppm at 75 °C and ambient pressure. There is an increase in the interfacial tension at 500 ppm of MgO and γ-Al2O3 nanoparticles. According to Figure 5, the same trend is observed for the nanofluids containing MgO and γ-Al2O3 nanoparticles so that the lowest interfacial tension of 7.645 mN/m was recorded for MgO nanoparticles dispersed in the bulk fluid at 2000 ppm of CaCl2 at ambient pressure and 75 °C. The IFT increased at 10 000 ppm of CaCl2. The lowest interfacial tension of 9.131 mN/m was obtained with nano-γ-Al2O3 at 2000 ppm of CaCl2 at ambient pressure and 75 °C. The interfacial tension increased at a concentration of 10 000 ppm of CaCl2. The same trend is observed for the nanofluid containing MgSO4 so that the lowest interfacial tensions of 7.362, 4.684, and 9.650 mN/m were obtained at 2000 ppm of salt in the presence of MgO, TiO2, and γ-Al2O3 nanoparticles, respectively, at ambient pressure and 75 °C. A similar trend has also been reported in studies on smart water techniques.34 According to Alotaibi et al., interfacial tension reaches a minimum value at a specific salt concentration in most cases.37 According to the results, the presence of MgO, TiO2, and γ-Al2O3 nanoparticles maintains smart water performance in interfacial tension variations. Although the salt concentration at the minimum interfacial tension may vary, the interfacial tension decreases at each salt concentration. The ability to reduce the IFT by soluble ions and nanoparticles dispersed in nanofluids was also studied separately. Figure 6 shows the interfacial tensions obtained from different smart water samples with stable nanoparticles separately. The concentration of nanoparticles in these experiments was 500 ppm. The IFTs of CaCl2 and MgSO4 solutions and oil in Figure 6 were obtained for 2000 ppm of salts. As shown, the

![Figure 4](https://example.com/fig4.png)

**Figure 4.** IFT of the oil and nanofluid containing MgSO4 and 500 ppm of MgO, TiO2, and γ-Al2O3 at ambient pressure and 75 °C (●, based on ref 34).

![Figure 5](https://example.com/fig5.png)

**Figure 5.** IFT of the oil and nanofluid containing CaCl2 and 500 ppm of MgO, TiO2, and γ-Al2O3 at ambient pressure and 75 °C (●, based on ref 34).

![Figure 6](https://example.com/fig6.png)

**Figure 6.** Interfacial tensions of the oil and one-component smart water with 500 ppm of the stable nanoparticles and 2000 ppm of salts at ambient pressure and 75 °C (●, based on ref 34).
interfacial tension is lower than the distilled water–oil IFT with nanoparticles or salts in the bulk fluid. The IFT is higher than that obtained for the nanofluid containing both nanoparticles and salts. This shows the higher ability of smart water with stable nanoparticles containing ionic compounds and nanoparticles in the reduction of IFT than any of them alone. In other words, modification of the injectable fluid by nanoparticles increases the ability of low-salinity of water with dissolved ions in the nanofluid in the reduction of IFT, meaning that each factor plays a complementary role for the other. Based on a mechanism reported by Dahle et al. 38 and Li et al.,39 the IFT changes are related to the formation of a nanofilm by particles at the interface. This mechanism is very similar to the accumulation mechanism of IFT reduction by nanoparticles is related to the nanoparticles is represented by eq 2.42

\[ \Pi_{NP} = \Delta E \times \Gamma_{NP} \]  

where \( \Delta E \) is the change in the oil–water interface energy and \( \Gamma_{NP} \) is the surface excess of nanoparticles at the interface. Equation 3 expresses the change in the oil–water interface energy by the wettability of nanoparticles with the radius \( r \) adsorbed at the interface.41

\[ \frac{\Delta E}{\text{particle}} = -\pi r^2 \gamma_{OW} (1 \pm \cos \theta_{OW})^2 \]  

where \( \gamma_{OW} \) and \( \theta_{OW} \) represent the IFT and the contact angle between oil and aqueous phases, respectively.

This energy reduction is due to the replacement of nanoparticles at the fluid–fluid interface, which form a contact angle at the interface and its maximum is 90°.41,43 In this case, considering the nanoparticles with a spherical shape, half of each particle is in the aqueous phase and the other half is in the oil phase. In other words, when exactly half of each particle is hydrophilic and the other half is hydrophobic, the nanoparticles are adsorbed at the interface with the largest chord. This occupies the interface and forms a thin film with the least possible number of nanoparticles. The surface pressure (\( \Pi_{NP} \)) depends on the adsorption and interactions of the particles at the interface, which are controlled by the nature, surface charge, and synthesis manner of the particles. These are the factors that affect the wettability of particles. Another mechanism of IFT reduction by nanoparticles is related to the adsorption of asphaltenes by nanoparticles. When nanoparticles are added to the injected water, the relative penetration of the nanoparticles into the crude oil phase causes the adsorption of polar asphaltene particles near the interface. As a result, the interface changes. Adsorption of asphaltenes by nanoparticles increases the relative solubility of crude oil in the nanofluid and reduces interfacial tension due to the reduction of surface friction forces.46 Since each type of nanoparticle adsorbs different amounts of polar asphaltenes particles according to their properties, they will have the variable capabilities to reduce interfacial tension. These properties are controlled by the size, surface area, and nature of the nanoparticles. In addition to particles, ions also play a role in the interface. The presence of ions at the interface, which makes the surface excess concentration positive, consequently lowers the IFT according to the Gibbs adsorption isotherm.7 Ions are adsorbed at the interface due to the presence of polar components and natural surfactants in crude oil. These polar components include resins and asphaltenes. Adsorption of ions at the interface and the formation of a thin film reduce the interfacial tension. However, the tendency of ions to attract polar components is not the same. For example, the Mg2+ dependence on resins molecules is higher than Ca2+, while Ca2+ dependence on asphaltenes molecules is higher than Mg2+.48 A competition for adsorption is formed between them. Repulsive–repulsive interaction occurs between ions and particles that equilibrate over time, and the film structure eventually stabilizes.49,50 The repulsion–repulsion interactions between ions and nanoparticles occur when nanoparticles and even ions are considered solid particles without reacting with each other. In fact, in this case, competition is formed between ions and nanoparticles to occupy the interface, in which particles with more kinetic energies and, of course, higher concentrations succeed in adsorbing at the interface. In this case, the synergistic effect between ions and nanoparticles is ignored and only the interactions of the two with the components in crude oil are considered. However, there are interactions between active ions and nanoparticles. In a different mechanism, nanoparticles adsorb ions51 and as charged particles pair with polar components in crude oil such as asphaltenes. In this case, ions and nanoparticles, which now form more active particles, contribute to the formation of the thin film. As a result, the thin film is reinforced and the interfacial tension changes will be more noticeable. Moreover, the electrostatic force of attraction increases the oppositely charged components at the interface, leading to an increase in surface excess and thereby a decrease in the IFT.52

5.2. Contact Angle. The values obtained from the contact angle tests show the significant ability of nanofluids used in this study in wettability alteration of the carbonate rock. Nevertheless, for correct generalization of the contact angle results in wettability alteration in porous media, the factors affecting the contact angle should be studied. The contact angle test for the wettability of reservoir rocks is a well-established and accepted experiment in the literature. Table 5 shows the contact angles of crude oil droplets on the carbonate sections aged in smart water with stable nanoparticles at different concentrations of MgSO4 and CaCl2 and 500 ppm of MgO, TiO2, and γ-Al2O3 nanoparticles at 75 °C and ambient pressure. Figures 7 and 8 show the results reported in Table 5 as curves for smart water with stable nanoparticles containing MgSO4 and CaCl2. The lowest contact angle of 18.52° showing a hydrophilic rock was
Table 5. Oil Droplet Contact Angles on Aged Carbonated Sections in Smart Water with Stable Nanoparticles at Different Concentrations of MgSO\(_4\) and CaCl\(_2\) and 500 ppm of MgO, TiO\(_2\), and \(\gamma\)-Al\(_2\)O\(_3\) Nanoparticles at Ambient Pressure and 75 °C

| Nanoparticles | Contact Angle (Degree) ± 0.02 |
|---------------|-------------------------------|
| MgSO\(_4\) conc. (ppm) | TiO\(_2\) | MgO | \(\gamma\)-Al\(_2\)O\(_3\) |
| 500           | 21.73 | 25.06 | 28.79 |
| 1000          | 21.07 | 22.57 | 20.26 |
| 2000          | 19.65 | 22.41 | 20.96 |
| 10 000        | 18.52 | 20.14 | 18.33 |
| CaCl\(_2\) conc. (ppm) | 25.34 | 29.62 | 31.24 |
| 500           | 23.86 | 29.31 | 26.36 |
| 1000          | 20.14 | 25.54 | 23.17 |
| 10 000        | 18.78 | 21.49 | 22.69 |

Figure 7. Contact angle values for different concentrations of MgSO\(_4\) and 500 ppm of MgO, TiO\(_2\), and \(\gamma\)-Al\(_2\)O\(_3\) nanoparticles at ambient pressure and 75 °C (●, based on ref 35).

Figure 8. Contact angle values for different concentrations of CaCl\(_2\) and 500 ppm of MgO, TiO\(_2\), and \(\gamma\)-Al\(_2\)O\(_3\) nanoparticles at ambient pressure and 75 °C (●, based on ref 35).

obtained for the nanofluid containing 500 ppm of TiO\(_2\) nanoparticles dispersed in smart water containing MgSO\(_4\) at 75 °C and ambient pressure. The concentration of MgSO\(_4\) in this experiment was 10 000 ppm. The contact angle increased to 20.14° by adding MgO nanoparticles to the system at 75 °C and ambient pressure. The contact angle decreased to a minimum value of 18.33° for the nanofluid containing \(\gamma\)-Al\(_2\)O\(_3\) at 75 °C and ambient pressure. The nanoparticles dispersed in smart water showed a similar performance when CaCl\(_2\) was dissolved in solution instead of MgSO\(_4\). In this case, when 500 ppm of MgO, TiO\(_2\), and \(\gamma\)-Al\(_2\)O\(_3\) nanoparticles were dispersed separately in smart water, the lowest contact angles of 18.78, 21.49, and 22.69° were obtained, respectively, at 75 °C and ambient pressure. Considering hydrophobicity, hydrophilicity, and moderate hydrophilicity ranges, these contact angles indicate significant hydrophilicity for EOR and imbibition oil production.

Here, the smart nanofluid contains the dissolved and dispersed components, i.e., ions (salts) and nanoparticles. The wettability alteration mechanisms for carbonate rocks have been developed using a solution of ions in smart water. According to Strand et al., Ca\(^{2+}\) and SO\(_4^{2-}\) are the most effective ions in the wettability alteration of calcareous rocks. Based on the results of chromatography experiments and by presenting a model for the behavior of ions on the surface of carbonate rocks, Zhang et al. studied the effects of Mg\(^{2+}\) and Ca\(^{2+}\) concentrations, temperature, and flow rate of the injectable fluid. According to their results, wettability alteration is due to the removal of adsorbed fatty acids from the surface of the rock. According to their findings, SO\(_4^{2-}\) reduces the positive charges on the surface and increases the capability of cations to approach carboxylic acids adsorbed on the calcareous rocks. By increasing the concentration of Mg\(^{2+}\) ions in smart water, the capability of cations to remove carboxylic acid increases. SO\(_4^{2-}\) anions on the carbonate rock decrease the positive charges of the rock surface. As a result, bivalent cations can easily approach the surface of the carbonate rock and adsorb acids. They claimed that the reaction between Ca\(^{2+}\) and carboxylic group adsorbed on the surface of the rock releases the former, consequently leading to the substitution of Mg\(^{2+}\) in the Ca\(^{2+}\) carboxylate complex. In addition, Ca\(^{2+}\) may react at both high and low temperatures, while Mg\(^{2+}\) only reacts at high temperatures. According to Lager et al., bivalent cations adsorbed on the surface of carbonate rock are replaced with monovalent cations. The polar molecules of oil are bonded to divalent cations and dispersed in the medium leading to a hydrophilic rock. This effect is known as multi-ion exchange. The temperature of 75 °C is based on the temperature of the reservoir from which the test oil was extracted. In addition to weakening ion exchange with carbonate rocks, lowering the temperature can reduce the solubility of hydrocarbon components in water and change the results of interfacial tension and wettability. According to RezaeiDoust et al., sulfate ions are hydrated due to hydrogen bonds in water. The reactivity of SO\(_4^{2-}\) ions increases at high temperatures due to the break of hydrogen bonds on the surface of carbonate rock. As a result, SO\(_4^{2-}\) ions are adsorbed more strongly on the surface of the rock, which leads to a reduction in the repulsive forces between the positive charges on the rock surface and cations. This, in turn, increases the capability of cations to adsorb carboxylic acid.

It should be mentioned that these mechanisms have been developed mainly for smart water at high concentrations. For the mechanism of wettability alteration of the carbonate rock by smart water at low concentrations, the mechanism reported by Lashkarbolooki et al. can be used. They attributed the latter
mechanism to the reactions that cause the dissolution of rock, which release OH\textsuperscript{−} ions, according to eqs 4 and 5.\textsuperscript{58}

\[
\text{CaCO}_3(s) \rightleftharpoons \text{Ca}^{2+}(aq) + \text{CO}_3^{2−}(aq) \quad (4)
\]

\[
\text{CO}_3^{2−}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{HCO}_3^−(aq) + \text{OH}^{−}(aq) \quad (5)
\]

It should be noted that CaCO\textsubscript{3} solubility in water is very low unless a low-pH aqueous solution is used. Dissolution of CaCO\textsubscript{3} as a mechanism might be valid for very long periods. Although hydrophilicity is achieved by smart solutions in the absence of nanoparticles, comparing the contact angles of smart water lacking nanoparticles with that containing 500 ppm of MgO, TiO\textsubscript{2}, and γ-Al\textsubscript{2}O\textsubscript{3} nanoparticles shows the improved performance of the injectable phase in the reduction of the contact angle by dispersing nanoparticles in smart water. To compare the performance of nanoparticles and soluble ions in smart water, contact angle tests were performed for an oil droplet on sections aged in nano fluids containing 500 ppm of MgO, TiO\textsubscript{2}, and γ-Al\textsubscript{2}O\textsubscript{3} and the results were compared with those in ref 35. The results are shown in Table 6. Figure 9 shows a better understanding of this comparison.

Table 6. Oil Droplet Contact Angles on the Aged Carbonate Sections in Nanosuspensions Containing 500 ppm of Nanoparticles in the Absence of Salts at Ambient Pressure and 75 °C

| nanoparticles | TiO\textsubscript{2} | MgO | γ-Al\textsubscript{2}O\textsubscript{3} |
|---------------|-------------------|-----|-----------------|
| contact angle (degree) ± 0.02 | 27.71 | 36.59 | 31.46 |

Figure 9. Comparison of smart water and nanofluid ability in the reduction of contact angle at ambient pressure and 75 °C (●, based on ref 35).

According to the results, the ion-free nanofluids have also a significant ability to reduce contact angles, although not as much as nanofluids containing ions. In general, the most important factors affecting wettability alteration and contact angle reduction by nanofluids include the concentration of nanoparticles,\textsuperscript{50,59} concentration and type of ions dissolved in nanofluid,\textsuperscript{59} aging time,\textsuperscript{60} the type of nanoparticles,\textsuperscript{61,62} and the particle size.\textsuperscript{2} The mechanisms of wettability alteration by nanoparticles in nanofluids are not yet well known. These mechanisms include three major approaches in the application of nanocatalysts, nanoemulsions, and nanofluids.\textsuperscript{63} As mentioned earlier, nanoparticles dispersed in nanofluids have dimensions of 1–100 nm. Nanofluids can create a film on a solid surface. Further, nanoparticles dispersed in nanofluids remove materials from the surface because of their high adsorption capacity.\textsuperscript{64} According to McElfresh et al., the film propagated on the rock surface can separate oil, paraffin, water, and gas from the surface, leading to a hydrophilic surface by removing materials, causing the hydrophobic nature of the rock.\textsuperscript{65,66} This capability is dependent on the nanofluid properties and the surface of each nanoparticle. Also, the arrangement of the nanoparticles in the wedge layer applies a disjoining pressure on the surface of the rock, which overcomes the adhesion force between crude oil and solid surface. This detaches the crude oil droplet from the rock surface.\textsuperscript{61,60} The vertex of wedge film keeps moving forward when structural disjoining pressure is stronger than the adsorption force between the oil droplet and rock pore surface.\textsuperscript{67} In the simultaneous presence of ions and nanoparticles, ions are adsorbed on the surface of nanoparticles. A negatively charged particle forms when anions surround the nanoparticles. The carbonate surface has a positive charge and adsorbs a negatively charged particle. This interaction can enhance the formation of a wedge-shaped film on the carbonate surface. In the formation of a wedge film, when only nanoparticles are present in the system, only the energy of the nanoparticles is involved, while in the presence of ions, the difference between the surface charge of the particles and the carbonate also plays an important role.

In this study, the role of pressure is neglected by assuming complete discharge of the reservoir pressure as a result of initial production. However, pressure may affect the process of dissolution of carbonate rock in water with low salinity as one of the mechanisms of wettability alteration. It may also increase the dissolution of petroleum components in water, thereby altering the results of interfacial tension.

5.3. Spontaneous Imbibition. The nanofluids with a higher capability in the reduction of contact angle were selected for spontaneous imbibition tests. This makes them the optimal fluids in imbibition experiments due to the depend-

Table 7. Specifications of the Carbonated Plugs (without Initial Water Saturation for All Samples)

| plug no. | permeability (mD) ± 0.01 | porosity (%) ± 0.01 | length (cm) | V\textsubscript{p} (cm\textsuperscript{3}) | mass of dry plug (g) ± 0.0001 | mass of oil-saturated plug (g) ± 0.0001 | S\textsubscript{a} (%) | OOIP (cm\textsuperscript{3}) | solids dissolved and diffused in the imbibition fluid |
|----------|------------------|------------------|--------------|-------------|-----------------|---------------------------|-------|-------|----------------------------------|
| 1 13.45  | 23.14            | 7.50             | 19.77        | 191.6712    | 203.7384        | 70.12                     | 13.87 | MgSO\textsubscript{4}         |
| 2 13.16  | 22.74            | 7.50             | 19.43        | 192.1386    | 204.8235        | 75.02                     | 14.58 | CaCl\textsubscript{2}        |
| 3 14.01  | 23.17            | 7.49             | 19.77        | 189.1523    | 201.8198        | 73.64                     | 14.56 | MgSO\textsubscript{4} + TiO\textsubscript{2} |
| 4 13.74  | 23.65            | 7.50             | 20.21        | 189.1174    | 203.4205        | 81.35                     | 16.44 | MgSO\textsubscript{4} + MgO |
| 5 12.33  | 24.41            | 7.51             | 20.89        | 191.2351    | 204.7813        | 74.54                     | 15.57 | MgSO\textsubscript{4} + γ-Al\textsubscript{2}O\textsubscript{3} |
| 6 13.85  | 22.87            | 7.48             | 19.49        | 189.1413    | 202.6614        | 79.76                     | 15.54 | CaCl\textsubscript{2} + TiO\textsubscript{2} |
| 7 13.02  | 23.50            | 7.50             | 20.08        | 190.3470    | 204.3978        | 80.42                     | 16.15 | CaCl\textsubscript{2} + MgO |
| 8 13.76  | 23.27            | 7.51             | 19.91        | 191.2562    | 204.8111        | 78.23                     | 15.58 | CaCl\textsubscript{2} + γ-Al\textsubscript{2}O\textsubscript{3} |
ence of spontaneous imbibition on the wettability of the reservoir rock. In this way, six nanofluids were selected: three containing 10 000 ppm of MgSO4 and three containing 10 000 ppm of CaCl2. In these nanofluids, MgO, TiO2, and γ-Al2O3 nanoparticles were dispersed separately. For a better comparison of the results, spontaneous imbibition tests were performed using smart solutions containing 10 000 ppm of MgSO4 and CaCl2 separately in the absence of nanoparticles. Thus, the effects of MgO, TiO2, and γ-Al2O3 nanoparticles on smart water were compared by performing eight spontaneous imbibition tests on the carbonate plugs. The specifications of the plugs used are shown in Table 7. Gradual production was recorded at specified intervals (every 2 days) until the production in the plugs was stopped. Figure 10 shows the percentage of recovery in gradual and cumulative production.

As shown in Figure 10, the oil production of plugs 1–8 was 59.95, 53.49, 67.99, 66.30, 67.50, 65.01, and 64.10% of the primary oil in place, respectively. Oil production under spontaneous imbibition with smart water with stable nanoparticles showed a significantly higher than that obtained by smart water only in the presence of salts in the fluid. The highest oil production of 70.68% of the primary oil in place was obtained from plug 5 under imbibition with the nanofluid containing 10 000 ppm of MgSO4 and 500 ppm of γ-Al2O3 nanoparticles. Regardless of the type of nanoparticles dispersed, different nanoparticles achieved the same performance. The increase in the recovery factor by imbibition with these nanofluids is dependent on the contact angle reduction. Both smart water and smart fluids showed a proper performance in reducing contact angle and increasing the recovery factor under spontaneous imbibition. Figure 11 shows the dependence of the contact angle and the recovery factor in the imbibition experiments by smart water and smart water with stable nanoparticles. As shown in Figure 11, there is a significant relationship between the contact angle and the final oil production under imbibition as the contact angle decreases, the hydrophilicity becomes stronger, and the oil production increases. For example, nanofluids containing γ-Al2O3 and MgSO4 with the lowest contact angle of 18.33° caused higher oil production. This is while the lowest oil production is related to the solution containing CaCl2 without the presence of nanoparticles, the highest contact angle of which is 27.02°.

Sources of error in experiments are related to computational errors and device uncertainties. For example, errors in density calculations affect interfacial tension results. Peripherals such as thermometers, barometers, scales, and measuring software can also be considered as sources of errors. Any impurity in materials such as salts and nanoparticles may cause errors compared to the use of pure materials, although such errors are not so serious.

6. CONCLUSIONS

Smart water containing MgSO4 and CaCl2 salts in combination with MgO, TiO2, and γ-Al2O3 nanoparticles at low concentrations was used to reduce the interfacial tension and contact angle and enhance oil production under imbibition. Based on the results, the combination of nanoparticles and smart water reduces the IFT and contact angle further than both nanofluids and smart water alone. The lowest interfacial tension of 4.684 mN/m was obtained by the nanofluid containing 500 ppm of MgO nanoparticles and 2000 ppm of MgSO4 at ambient pressure and 75 °C. The highest oil production of 70.68% was obtained under imbibition of the nanofluid containing 10 000 ppm of MgSO4 and 500 ppm of γ-Al2O3 nanoparticles. The lowest contact angle of 18.33° indicates that a hydrophilic rock was obtained using the nanofluid containing 500 ppm of γ-Al2O3 nanoparticles dispersed in smart water containing MgSO4 at 75 °C and ambient pressure. The results of contact angle and oil production under imbibition are significantly related to each other as nanofluids containing γ-Al2O3 and MgSO4 with the lowest contact angle of 18.33° caused higher oil production. These results indicated the capability of combined engineered water and dispersed nanoparticles in spontaneous imbibition operation. Three nanomaterials were dispersed in smart water at low concentrations. The nanoparticles modified and improved the reduction of oil–water interfacial tension by soluble ions to some extent. However, the interfacial tensions may have an insignificant impact on the capillary pressure and may not lead to strong emulsification. This is expected according to the literature on IFT reduction by nanoparticles and smart water. Smart water and nanofluids and their combination showed a significant performance in reducing the contact angle.
and changing the carbonate rock wettability. The contact angles obtained by nano-MgO, TiO₂, and γ-Al₂O₃ showed the highly hydrophilic behavior of the rock.

These nanofluids are good candidates for EOR operations considering the compatibility of these nanoparticles with the formation of water. In this study, the nanoparticles were used at low concentrations (500 ppm). The results showed that nanofluids at low concentrations have good performance in the modification of EOR mechanisms, resulting in the reduction of nanoparticle and nanofluid costs. Due to their low concentration in the injectable fluid, the use of nanoparticles can be justified as compared to most EOR methods. The long-term stability of nanoparticles in smart nanosuspensions provides the grounds for this mechanism. In this study, a recovery factor of 64.10–68.70% was obtained for imbibition using smart water with stable nanoparticles. Comparing these values with those obtained in imbibition experiments with nanoparticle-free smart water containing 10 000 ppm of MgSO₄ salt (56.95%) and a fluid containing 10 000 ppm of CaCl₂ (53.49%) indicates that in addition to the effect of nanoparticles on increased oil production under imbibition, nanofluids can improve and enhance oil production by imbibition.

The use of nanoparticles has some limitations at high concentrations due to the instability of nanofluids. Also, the use of expensive nanoparticles and their inefficiency in the reservoirs with very low permeability rocks due to blockage of the bottlenecks could be another issue. However, the effects of nanoparticles on optimizing the EOR parameters will be of interest to continue research. It is suggested that other nanoparticles be used in future research. Other methods such as injection of polymers and surfactants in combination with nanoparticles be used in future research. Other methods such as injection of polymers and surfactants in combination with nanoparticles can be tested. Natural resources for the synthesis of nanoparticles can be identified and used. In addition, the structure of nanoparticles can be purposefully modified and nanocomposites with polymeric properties and more surface activity can be used.

Nanoparticles are a good alternative to traditional additives such as surfactants and polymers due to their special properties. Chemical stability at high salinity, temperature, and pressure distinguishes nanoparticles. Most of the oil reservoirs often have a useful life and have reached the stage of bottlenecks could be another issue. However, the effects of nanoparticles on optimizing the EOR parameters will be of interest to continue research. It is suggested that other nanoparticles be used in future research. Other methods such as injection of polymers and surfactants in combination with nanoparticles can be tested. Natural resources for the synthesis of nanoparticles can be identified and used. In addition, the structure of nanoparticles can be purposefully modified and nanocomposites with polymeric properties and more surface activity can be used.

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