Experimental Core Flooding Investigation of New ZnO–γAl₂O₃ Nanocomposites for Enhanced Oil Recovery in Carbonate Reservoirs

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ABSTRACT: Generally, crude oil production in mature oil reservoirs is difficult. In this regard, some nanoparticles have been used to upgrade injected water into oil reservoirs. These nanoparticles can be used in a variety of injectable waters, including smart water (SMW) with special salinity. This study aims to evaluate the performance of the injection of SMW with ZnO–γAl₂O₃ nanoparticles in enhanced oil recovery (EOR). The performance of SMW with ZnO–γAl₂O₃ nanoparticles in regard to contact angle (CA), interfacial tension (IFT) reduction, and oil production with core flooding tests was investigated. The newly prepared ZnO–γAl₂O₃ structure was characterized by energy dispersive X-ray (EDX), Fourier transform infrared (FT-IR) spectroscopy, transmission electron microscopy (TEM), scanning electron microscopy (SEM), and X-ray diffraction (XRD) analyses in this research. The effects of different concentrations of nanofluids on zeta potential (ZP) and conductivity were investigated. The ZP test confirmed the results of the stability tests of the developed nanofluids in water-based solutions. After the introduction of ZnO–γAl₂O₃ nanoparticles into the formation of brine and SMW solutions, oil–water (O/W) IFT was reduced. Based on the results, the IFT decreased more when nanoparticles and ions were present in the system. The results of the present study showed that at the concentration of SW+300 ppm ZnO–γAl₂O₃, the IFT value reached 11 mN/m from 27.24 mN/m. The results of the CA tests showed that improving the capabilities of salt water in the presence of nanoparticles has resulted in a very effective reduction. Also, in this regard, very hydrophilic wettability was achieved using SMW with stable nanoparticles. Moreover, the results of the present study showed that at the concentration of SMW+300 ppm ZnO–γAl₂O₃ nanoparticles, the CA value reached 31 from 161°. In the end, the solution of SW+300 ppm ZnO–γAl₂O₃ improved the OR by 15 and 24%. This research indicated that it is possible to develop and implement different nanoparticles by combining SMW to manage reservoir rock wettability and maximize OR from carbonate reservoirs. Thus, this combination as an effective agent could significantly increase reservoir sweep efficiency. Thus, as a result, using the established hybrid technique has distinct advantages over using SMW flooding alone.

1. INTRODUCTION

After oil production from reservoirs, oil cannot be recovered using conventional methods, and it must be extracted by chemical methods. In some research, chemical-enhanced oil recovery (CEOR) methods have been used to solve this problem by providing mechanisms such as interfacial tension (IFT) reduction and wettability alteration (WA). Nano-technology in the oil industry has significant capacity and potential in oil reservoirs to meet growing energy needs. Nanoparticles in enhanced oil recovery (EOR) processes in oil reservoirs are an emerging technique, and their impact on oil reservoirs is increasing rapidly. The use of nanoparticles can be prominent in many fields. Several nanoparticles (such as Al₂O₃ and SiO₂) have been studied in EOR, and some nanoparticles have shown acceptable potential in EOR processes. Recently, ZnO nanoparticles have been able to help oil production by various mechanisms to reduce oil viscosity and change wettability. However, the reported results regarding using ZnO in the direction of IFT are still controversial. In this regard, some studies claim that ZnO nanoparticles increase the IFT, and, on the other hand, some reports claim that ZnO reduces IFT. This issue should be discussed for the stability of the nanoparticle suspension. Ideally, a nanoparticle suspension should be stable. Suspensions that are less stable experience particle deposition, affecting physical properties such as IFT. In this regard, it has been shown in most reports that the stability of nanoparticle suspensions in the presence of surfactants can be increased. In the case of zinc oxide nanoparticles, anionic surfactants such as sodium dodecyl sulfate are generally...
Table 1. Integration of Nanoparticle Propagation Methods

| references | mechanisms | materials | result |
|------------|------------|-----------|--------|
| 68 CA      | imbibition | ZrO₂      | reduced CA dramatically adsorption of ZrO₂ nanoparticles was shown through SEM; in this regard, the adsorption process on the surface was slow |
| 69 WA      | IFT       | NiO/SiO₂  | reduced costs and damages improved swept efficiency increased OR by up to 50% |
| 70 WA      | IFT       | F–SiO₂−F | changed the wettability of CR from OW to WW |
| 71 WA      | IFT       | SiO₂/NiO | changed the wettability from OW to WW minor effect of time and salinity on IFT results |
| 72 IFT     | SiO₂      | surfactant together with WW nanoparticles at low concentrations of nanoparticles reduced the IFT at low concentrations of nanoparticles by an adsorption process removed the surfactant from the aqueous phase at high concentrations of nanomaterials |
| 73 IFT     | SiO₂      | bivalent ions performed better than monovalent ions because they have equal ZP and lower ionic strength nanoparticles increased OR by about 4% more than water at low salinity by increasing SiO₂ to 5 wt % |
| 74 WA      | viscosity | SMW/silica addition of SMW to silica nanoparticles improved the WA mechanism the results showed that the highest OR was obtained by injecting smart water with a high concentration of SO₄²⁻ ions along with a concentration of 0.1 wt % with silica nanoparticles adding SMW to silica nanoparticles increased the sweep efficiency and fluid viscosity |
| 75 CA      | SMW       | the CA decreased from 91.0° to 67.8° in relation to the seawater in the Persian Gulf as a result of the elimination of NaCl and the surface wettability was altered micromodel flooding results showed that Persian Gulf seawater without NaCl could increase OR by 10.12% in comparison to Gulf seawater reduced CA dramatically increasing OR by up to 50% reduced costs and damages improved swept efficiency increased OR by up to 50% changed the wettability of CR from OW to WW |
| 76 micromodel flooding | OR increased by 7.34% compared to Persian Gulf seawater when the Na₂SO₄ concentration in Persian Gulf seawater tripled depending on the conditions, Persian Gulf seawater may be used to improve OR efficiency by increasing the concentration of Na₂SO₄ three times or by removing NaCl |

very promising in stabilizing the suspension. IFT reduction is caused by surfactants such as sodium dodecyl sulfate, making sodium dodecyl sulfate solutions an excellent choice for EOR processes. The potential applications of nanoparticles for WA in EOR have been shown in many studies. Nanoparticles, due to their nanodimensions, can pass through the micropores of the reservoir rock. The volume-to-surface ratio of nanoparticles is very low. On the other hand, the ratio of atoms to their surfaces is very high. In this regard, they have high surface energy, and their absorption on the rock surface causes the surface energy of the rock to change. In most studies, nanoparticles for WA are applied in sandstone core rocks. Despite the importance of carbonate reservoirs, the application of nanoparticles to these oil reservoirs has not been well studied. On the other hand, SMW can be defined as the water engineered by manipulating the ionic composition (removing or adding ions) regardless of the resulting salinity. An alternative that simultaneously embodies a sustainable environmental and economic EOR flooding method is SMW injection. The enhanced ionic content of the injected water enhances initial wetting toward more WW conditions, which enhances the displacement efficiency due to greater capillary forces. SMW improves OR by WA in both carbonate and sandstone reservoirs. Seawater is the main injection brine offshore, and when it is enriched in divalent ions such as Ca²⁺ and SO₄²⁻ and deficient in Cl⁻ and Na⁺, it is considered SMW in carbonates. SMW has an ion composition and salinity different from formation water and can alter the established equilibrium between crude oil, formation water, and pore surface minerals, thereby modifying the wetting properties of reservoirs. Generally, SMW is produced by merely adding salts to the water. The majority of salt compounds found in nature are the byproducts of acid—base processes; they are pH-neutral and release their ions when dissolved in water. These active ions also change the reservoir rock's wettability. They significantly reduce the IFT between oil and water. SMW injection techniques and the accompanying EOR operations are founded on this concept. This method's minimal costs are one of its benefits. According to Puntervold et al., reducing more than 90% of the NaCl concentration and increasing the SO₄²⁻ ion concentration by around three to four times increased the SW efficiency. They attributed the double layer near the positively charged surface of CRs as the cause for the decrease in ionic density. However, Seyyedi et al. found that dilute seawater injection, either as secondary or tertiary recovery, led to WA and an additional OR in the spontaneous imbibition, although any modification in the potential-determining ions (i.e., Mg²⁺, SO₄²⁻, Ca²⁺) in seawater cannot improve its performance. Numerous mechanisms, such as rock dissolution, WAX, and IFT reduction, have been proposed in the literature for low-salinity water (LSW)/SMW injection in carbonates. The WA of the rock surface is a reliable indicator, despite the fact that the underlying mechanisms are almost debatable.

Hosseini et al. investigated the effect of dispersed silica and alumina nanoparticles on IFT. Their studies showed that nanoparticles change the wettability of carbonate and sandstone rocks from OW to WW. Al-Anssari et al. altered the wettability of carbonate reservoir rock using a combination of nanoparticles and surfactant flooding. Their research showed that the formulation of sodium dodecyl sulfate and silica nanoparticles could change the OW capability of calcite cores from OW to WW. Giraldo et al. by Al₂O₃ nanoparticles, investigated the change in wettability of sandstone cores at concentrations of 100–10,000 ppm in an anionic surfactant. By increasing the optimum concentration of 100 ppm alumina
nanoparticles through CA measurements and adsorption experiments, they observed significant WA from OW to WW. By changing the wettability of rock in the presence of nanoparticles and a surfactant, Suleimanov et al. concluded that this solution leads to an improvement of rheological properties and increases the OR. Suleimanov et al. investigated LSW flooding and nanofluid flooding of oil reservoirs to enhance OR. They concluded that using these reagents led to WA of the rock pore walls, reduced oil viscosity, decreased IFT, and increased disjoining pressure. The developed nanofluids could increase OR by 15–20%.

Rasooli-Manesh et al. studied the potential role of γ-Al₂O₃ nanoparticles in EOR. They increased OR by 4% by adding 0.3 wt % Al₂O₃ nanoparticles to the base fluid. The injection of the nanofluid into the reservoir converted the wettability of the rock surface from OW to WW, thereby facilitating the movement of oil within the reservoir porous media. Table 1 presents the most up-to-date studies on EOR mechanisms using nanoparticles and SMW.

Considering that OR results from displacement efficiency and sweep efficiency, LSW/SMW injection increases OR by merely enhancing the displacement efficiency while having no impact on oil sweep efficiency. Water potential in light oil reservoirs is generally higher than in medium and heavy oil reservoirs due to its low specific gravity. In light of these shortcomings, several researchers suggested that LSW/SMW may occasionally have a limited or even harmful effect. A more economical and efficient way to overcome the constraints of using LSW/SMW is created when coupled with other EOR techniques. Some researchers have confirmed the excellent efficiency of combining LSW/SMW with chemical EOR (CEOR) technologies. Surfactants and polymers are the most popular compounds utilized for this purpose. However, due to the high cost of these chemicals, a hybrid of nanoparticles with LSW/SMW is a unique EOR approach in carbonate reservoirs that can address a number of issues in the oil and gas sector. Generally, two new EOR techniques are nanofluids and SMW flooding. Despite some efforts to examine the advantages of each technique, it is necessary to weigh the benefits and drawbacks of their combined use. SMW flooding is a useful method to increase OR for field applications in oil reservoirs. Numerous authors have studied SMW injection as an EOR technique. There have not been many investigations into SMW nanomaterial injection in carbonate reservoirs in the past.

Additionally, these investigations were conducted in a setting very dissimilar from the circumstances of a genuine reservoir. Not enough has been done to understand how WA caused by ZnO–γ-Al₂O₃ nanoparticles fully and SMW concurrently works. As a result, systematic research on the impact of nanoparticles in the presence of SMW in EOR is lacking. In this study, we aim to simultaneously investigate the effect of SMW and new nanoparticles in EOR. In this study, by investigating WA and OR during the displacement process, the performance of SMW with nanoparticles is elucidated. In addition, the performance of ZnO–γ-Al₂O₃ nanoparticles dispersed in SMW was investigated in terms of wettability modification, quantified by CA measurements and displacement efficiency with injection into two cores. The core of our experiments included examining the stability of 300 ppm ZnO–γ-Al₂O₃ in SMW, measuring CA at varying concentrations, and, finally, evaluating the oil displacement efficiency of SMW+300 ppm ZnO–γ-Al₂O₃ nanofluids by injecting them into the core through the core flooding device. On the other hand, by analyzing O/W IFT during the injection of SMW+300 ppm ZnO–γ-Al₂O₃, we showed how the presence of SMW+300 ppm ZnO–γ-Al₂O₃ could reduce the amount of O/W IFT. This study analyzed the synthesized structure of ZnO–γ-Al₂O₃ by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), UV–vis spectrophotometry, and energy dispersive X-ray (EDX) analyses. To the best of the authors’ knowledge, there is no similar study examining all EOR-related parameters. Therefore, as an innovation to alter the wettability of the CR, this new SMW+300 ppm ZnO–γ-Al₂O₃ can be effective in the EOR.

2.1. Materials. In this study, new nanoparticles were synthesized. These nanoparticles can be an effective agent in CEOR. To synthesize these ZnO–γ-Al₂O₃ nanoparticles, isopropanol, 2-propanol, propionic acid, nitric acid, nonhydrated aluminum nitrate, potassium bicarbonate, aluminum nitrate, sodium hydroxide, and a high-quality acid from Merck (Germany) were used. All reagents are of analytical grade and used without further purification. The inoculation method was used to synthesize ZnO–γ-Al₂O₃. The precursors used in the synthesis of ZnO–γ-Al₂O₃ by inoculation included γ-alumina powder (γ-Al₂O₃) as the base of ZnO–γ-Al₂O₃ and zinc nitrate Zn(NO₃)₂·6H₂O in the role of a phase supplier. The starting material of the active phase in ZnO–γ-Al₂O₃ prepared by the sol–gel method was the same zinc nitrate used in the inoculation method. Other materials used in this method were aluminum nitrate (Al(NO₃)₃·9H₂O purchased as a base supply precursor and citric acid as a gelling agent.

2.2. Methods. 2.2.1. Characterization of Synthesized ZnO–γ-Al₂O₃. For better analytical characterization of this newly synthesized ZnO–γ-Al₂O₃, tests were conducted after synthesis, including Fourier transform infrared (FT-IR), SEM, EDX, and XRD.

2.2.2. Synthesis of ZnO–γ-Al₂O₃. The present study shows the synthesis steps of ZnO–γ-Al₂O₃ by an inoculation method, as shown in Figure 1. As shown in the figure, the initial mixture was prepared via inoculation by mixing γ-Al₂O₃ and Zn(NO₃)₂·6H₂O powder in distilled water for 5 h at 60 °C. The mixture was dried in air for 15 h at 110 °C. The final powder was
formed after ZnO–γAl₂O₃ calcination at 550 °C for 4 h. Then, ZnO–γAl₂O₃ was prepared for rock wettability evaluations with the prepared powder.

2.3. Preparation of the Fluids. In this research, the oil sample used was prepared from one of the oil reservoirs in western Iran. Formation water was sampled from the Asmari oil field in Iran. The sample of dead oil was light, and its properties were μ = 15.41 cp, API = 38.7, and ρ = 0.831 g/cm³ values. Table 2 presents the characteristics of the carbonate cores used in this research. SMW was prepared by dissolving various concentrations of Na₂SO₄, MgSO₄, and CaCl₂ in deionized water (DIW) as the base fluid. Salts used to produce smart solutions were provided by Merck, Germany and were of high purity. Table 3 reports the properties of the salts used. During the experiment, a pH value of 6 was selected.

ZnO–γAl₂O₃ nanoparticles with fixed concentrations of 300 ppm were utilized in all experiments after a screening process was conducted, which considered the potential of the suspensions for IFT reduction, a low-cost operational process, and a lower risk of nanoparticle aggregation. To prepare a mild nanometer suspension, ZnO–Al₂O₃ nanoparticles were mixed with salt water. These two solutions were stirred using a magnetic stirrer, and then, the prepared solution was subjected to ultrasound. Also, SARA analysis was performed to characterize the crude oil better. The results of the SARA analysis of the crude oil are displayed in Figure 2. These ions were chosen because, in general, Mg²⁺, SO₄²⁻, and Ca²⁺ are stronger ions in the SMW mechanism, while other soluble ions in the water injection have little impact on SMW mechanisms, particularly ion exchange and WA. In the same circumstance, 300 ppm of nanoparticles was added to these solutions to conduct the IFT studies. The ideal concentrations were established in terms of minimum CAs after the CA tests were conducted.

The next phase involved using smart fluids and nanofluids chosen from CA testing to study production during core flooding tests in carbonate plugs. The best fluids with the fewest CAs are chosen because changing wettability is the main way to use SMW. However, numerous variables are at play during a chemical OR procedure, and several mechanisms control the efficacy and capability of the injectable fluid to improve OR.

2.4. Evaluation of Stability. In this section, the suspension stability of SMW (base fluid) and ZnO–γAl₂O₃ was determined. Stability is an effective and acceptable parameter in evaluating the performance of nanofluids. On the other hand, ZP is one of the best ways to evaluate and measure nanofluids’ stability. Thus, ZP analysis was performed on different concentrations of SMW+ZnO–γAl₂O₃ to identify the most stable nanofluid. This work was done to quantify the stability of colloidal dispersions of seven concentrations of ZnO–γAl₂O₃ (100, 300, 500, 700, 900, 1100, and 1300 ppm) with SMW. The prepared suspensions were then stirred with an ultrasonic bath for 60 min to reduce nanoparticle agglomeration. By measuring the amount of adsorption with an ultraviolet–visible spectrometer, the stability of the prepared suspensions at 720 nm was quantitatively evaluated and visually observed for two weeks. A NanoZ Zetasizer (Malvern Instruments Ltd., Malvern, U.K.) was used for these measurements. So, after measurement, the SMW+300 ppm ZnO–γAl₂O₃ showed better stability. Observations of the ionic forms of the solutions were performed using Inola Cond7110 conductivity measurements.

In this study, using SEM equipped with EDX, the obtained nanopowder was investigated. The crystal structure was analyzed by X-ray diffraction (Ultima IV XRD model). To test the wettability of the fabricated nanofluids, the CA between water and a thin film of SMW+300 ppm ZnO–γAl₂O₃ was measured using the sessile drop method. Also, the IFT between water and oil was measured using the pendant drop method.

Core flooding testing, IFT tests, CA tests, and solution preparations are all a part of the experimental process. A flowchart of these procedures is shown in Figure 3. It should be mentioned that each test experiment was carried out three times to examine repeatability. In this regard, the three values obtained from each experiment were averaged to produce the final result.

2.5. Contact Angle (CA) and IFT Measurement. In this research, a CA measuring device has been used to investigate the variability of rock wettability. Its schematic is shown in

| Table 2. Core Characteristics |
|--------------------------------|
| number | core length, cm | core diameter, cm | porosity, % | permeability, mD |
|-------|----------------|-------------------|------------|-----------------|
| 1     | 5.105          | 3.799             | 17.491     | 0.262           |
| 2     | 5.110          | 3.800             | 22.613     | 0.483           |

Figure 2. Crude oil SARA fractions.

Figure 3. Flowchart of the experimental method.
Figure 4. This device contains equipment such as a glass cell, a light source, and a camera. So, between the light source and the camera is this glass cell. A carbonate plate was placed on the cell poles. Then, a drop of oil was poured on the rock surface with a syringe. The camera then provided a high-quality image of falling drops on the rock surface on the computer connected to it. Finally, the CA between the oil droplets and the rock surface was accurately measured by ImageJ software. CA was measured at four different positions for each sample, and the CA average was well reported. Since there is more than one liquid in the pores of the porous media of the reservoir, it can be said that, in this regard, the tendency for surface adhesion of each fluid is different. This activity creates competitive conditions where fluids adhere to the surface with different intensities and make other CA with the surface, making the rock conditions strongly WW or strongly OW. Various techniques are used to measure CA. Drop shape analysis has recently been developed, and this analysis is currently the most widely used. Generally, a common type of drop shape analysis is performed in EOR studies; this effective method is known as a sessile drop. In this study, this method was used to measure the CA of the rock surface in the presence of SMW+300 ppm ZnO–γAl$_2$O$_3$ and crude oil. For this purpose, the CRs were prepared, and then, several tabletlike pellets of rocks were cut into thin sizes and polished to be completely smooth.

The pellets were then thoroughly washed with toluene and DIW. Afterward, the pellets were placed in a pile full of crude oil. Following the procedure, a pressure of 1000 psi was applied to the accumulator. The pellets were then aged in an accumulator furnace for 20 days to closely resemble underground conditions. The oven temperature was fixed at 80 °C. In each experiment, the measuring cell was filled with SMW+300 ppm ZnO–γAl$_2$O$_3$. In the next step, a drop of oil was injected from the needle, dropped into the container containing SMW+300 ppm ZnO–γAl$_2$O$_3$, and placed on the underside of the rock pellet. An image of the deposited oil was captured by placing a light behind the cell and a powerful camera in the front. After at least 3 h, the CA was extracted from the recorded images. In this experiment, the measurement is based on Young’s formula as follows:

$$\sigma_{so} = \sigma_{sw} + \sigma_{wo} \cos \theta$$

(1)

where $\sigma_{so}$ is the surface energy between the solid and oil, $\sigma_{sw}$ is the surface energy between water and oil, and $\theta$ is CA at the solid/water/oil boundary.

Figure 5. Schematic of IFT measurement instruments (1, pressure indicators; 2, cylinder inlet valves (for importing the fluid (oil)); 3, cylinder outlet valves; 4, valve-connected pistons; 5, nanofluid inlet valve to the bottom of the container; 6, oil line to the bottom of the container; 7, oil inlet valve to the top of the container; 8, nanofluid inlet valve to the top of the container; 9, thermometer; 10, camera; 11, computer program; 12, oil line to the bottom of the container; 13, nanofluid line to the top of the container; 14, oil drop; 15, container; 16, needles; 17, table.
On the other hand, IFT measurements were performed using the pendant drop method. In this study, IFT700-32175 was used to measure IFT. The device includes a transparent cell, an injection system responsible for injecting colloidal solutions and petroleum samples, an observation system for droplet illumination, and software for collecting and processing data at the output in the form of a pendant drop. In this test, a drop of oil was injected into the aqueous solution (SMW+300 ppm ZnO−γAl₂O₃) with a needle, and after a while, the oil drop was fixed at the tip of the needle. With the help of a digital camera, the data collection system recorded images of the oil droplets at different stages when they reached the stabilization state. This software uses the Young–Laplace equation to fit the theoretical surface shapes produced by the curve fitting method. Finally, the IFT value was determined with time. Figure 5 indicates the schematic of the IFT setup.

Figure 6. Schematic diagram of the step-by-step core flooding test.

According to Figure 5, the equatorial diameter, \( d_e \), and the diameter \( d_s \) at a distance \( d_e \) from the top of the drop are two characteristics of the pendant drop that are determined experimentally. In this regard, the IFT is then determined using eq 2.

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

where \( g \) and \( \Delta \rho \) represent the acceleration of gravity and the difference in densities of an aqueous solution and a drop of crude oil, respectively. The shape parameter \( (H) \) is influenced by the shape factor’s value \( (S = d_s/d_e) \).

2.6. Displacement Tests. The core flood system includes two pressure cylinders to transport the fluid. These fluids can be oil and 300 ppm ZnO−γAl₂O₃ with SMW. In this regard, in Figure 6, the process of core flooding is reported step by step.
3. RESULTS AND DISCUSSION

3.1. Structural and Morphological Properties of ZnO–γAl₂O₃ Nanoparticles. FT-IR spectra were performed to confirm the synthesis of the ZnO–γAl₂O₃ nanoparticles. The results of FT-IR analysis for the synthesized ZnO, γAl₂O₃, and ZnO–γAl₂O₃ nanoparticles are shown in Figure 7a–c, respectively. The ZnO FT-IR spectrum is shown in Figure 7a. In this figure, the signals observed in the range of 1050 cm⁻¹ are related to Zn–O bonds. Also, the C–O stretching vibration is related to the signal in the range of 1358 cm⁻¹. The O–H bonds of water correspond to the 3200–3500 cm⁻¹ signals. In fact, this range indicates that ZnO particles have been adsorbed on the surface of water molecules. The 2988 cm⁻¹ signal is the vibrational traction of Al–O–H, which corresponds to the typical absorption peak shown in Figure 7b. On the other hand, the signal at 1533 cm⁻¹ is due to O–H bending, which is attributed to adsorbed water molecules. Due to Al–O vibrations, absorption bands at 491, 616, and 878 cm⁻¹ have been observed, which are related to γAl₂O₃ nanoparticles. The comparison of Figure 7a,b shows that the signals at 3468.2, 1383.79, and 535.1 cm⁻¹ occurred due to zinc oxide in ZnO–γAl₂O₃ nanoparticles.

On the other hand, the XRD diagrams of the synthesized γAl₂O₃, ZnO, and ZnO–γAl₂O₃ nanoparticles are shown in Figure 8a–c, respectively. It was observed that ZnO and ZnO–γAl₂O₃ nanoparticles had corresponding diffraction peaks at 31.6, 34.3, 56.6, and 62.8°. Also, in Figure 9, the size and surface morphology of the synthesized nanoparticles were studied by SEM analysis. In a complete nanometer form, the presence of ZnO nanoparticles on the surface of γAl₂O₃ is shown in Figure 9. In this regard, microcubic γAl₂O₃ in Figure 9 had a wide size distribution range. In the next step, a single-point analysis of scattered X-ray spectroscopy was performed to confirm further the successful synthesis of ZnO–γAl₂O₃ and the possibility of its elemental energy analysis.

In Figure 10, the TEM image of ZnO–γAl₂O₃ sheets in the form of exfoliated structures is shown in the dimension of 50 nm. Figure 11 shows the atomic and weight percentages and the presence of elements O, C, Zn, and Al in the sample structure. Also, Figure 12 shows a qualitative elemental mapping image of the synthesized ZnO–γAl₂O₃. It indicates that elements Zn, O, Al, and C are present in the synthesized ZnO–γAl₂O₃ sample. The rock used in this study is carbonate, and calcite is their primary constituent material. SEM-equipped EDX analysis is performed to identify the CR...
minerals. The elements in the CR structure are listed in Table 4.

### 3.2. Stability of SMW-ZnO−γAl₂O₃

In this study, pH was measured for each of the different concentrations prepared from SMW+ZnO−γAl₂O₃ (100, 300, 500, 700, 900, 1100, and 1300 ppm). Figure 13 indicates the ZP of nanofluid SMW+300 ppm ZnO−γAl₂O₃. According to Figure 13, the values of the ZP make it possible to identify the electric potential conditions of the slipping plane (interfacial double layer) in the bulk liquid that is far from the interface. Regardless of its sign, increasing this value means increasing the potential difference. This is the potential difference between the fluid fixed layer attached to SMW+300 ppm ZnO−γAl₂O₃ nanoparticles and the dispersion medium. This trend in SMW+300 ppm ZnO−γAl₂O₃ leads to an acceptable stability condition. Generally, 35 mV of ZP can be used as a separation value to distinguish between highly charged and lowly charged surfaces (independent of their sign).³³ As shown in Figure 13, the SMW+300 ppm ZnO−γAl₂O₃ concentration has convincing stability.

![Figure 10. TEM image of 300 ppm ZnO−γAl₂O₃ nanoparticles in the dimension of 50 nm.](image)

![Figure 11. EDX spectrum result for the synthesized ZnO−γAl₂O₃.](image)

![Figure 12. EDX mapping images of (a) Zn, (b) O, (c) Al, and (d) C.](image)

![Figure 13. Measurement schematic of the ZP of SMW+ZnO−γAl₂O₃.](image)

| Element | wt % |
|---------|------|
| K       | 0.15 |
| C       | 28.72|
| O       | 46.93|
| Ti      | 0.16 |
| Al      | 0.31 |
| Fe      | 0.41 |
| Si      | 0.60 |
| Au      | 22.71|

Table 4. EDX Analysis Results for the Used CR Samples
3.3. Effect of SMW+ZnO−γAl₂O₃ on IFT. IFT is a known parameter to increase OR. In this study, the electrical conductivity (EC) of prepared SMW with different concentrations of ZnO−γAl₂O₃ (100, 300, 500, 300, and 700 and 100, 300, 500, 700, and 100) was measured. As shown in Figure 14, a linear conductivity versus concentration pattern was obtained at a concentration of SMW+300 ppm ZnO−γAl₂O₃. So, the conduction line against the concentration is shown as an orange line. That is, the conductivity of the solution increases with increasing concentration of SMW+ZnO−γAl₂O₃. According to the above interpretations, abnormal behavior was well observed at the concentration of SMW+300 ppm ZnO−γAl₂O₃. In Figure 14, the leading trend line is a green anomaly line. This nanoscale incompatibility occurs due to the effective EC of colloidal suspensions in fluids. This represents a complex mode of dependence on ion release, volume fraction, EDL properties, and other physicochemical properties that standard models do not accurately capture. The trend of increasing state in the conductivity of SMW+300 ppm ZnO−γAl₂O₃ was related to the electrical interactions of the two layers and the effect of the net charge of solid particles. Therefore, at this concentration value, these interactions occurred strongly. These mechanisms created an abnormal signal in the conductance against the concentration process at the concentration of SMW+300 ppm ZnO−γAl₂O₃. Therefore, the solution (SMW+300 ppm ZnO−γAl₂O₃) achieved a strong negative charge concentration, as determined by the EC and ZP tests. In this regard, the IFT values of the fluid and crude oil, as well as SMW+300 ppm ZnO−γAl₂O₃, are shown in Figure 15. In the presence of different concentrations (100, 300, 500, 700, 900, 1100, and 1300 ppm) of ZnO−γAl₂O₃ with SMW, the IFT values were 13, 11, 15, 18, 20, 27, and 24 mN/m, respectively. Therefore, according to Figure 15, SMW+300 ppm ZnO−γAl₂O₃ had the lowest amount of IFT. This amount of IFT was detected due to abnormal behavior compared to other concentrations. Therefore, the SMW+300 ppm ZnO−γAl₂O₃ nanofluid had high stability and also showed lower IFT than other concentrations. Therefore, this concentration was used in the CA test.

IFT reduction is mainly used in oil reservoirs with surfactants that reduce IFT levels to very low. However, with this difference, SMW+300 ppm ZnO−γAl₂O₃ used in this study proved that it could reduce IFT from the initial value of 27.24 to 11 mN/m. Thus, SMW+300 ppm ZnO−γAl₂O₃ can reduce IFT. In this regard, along with other methods of EOR from oil reservoirs, it can be used with surfactants. This structure acts as an intermediate and reduces the amount of IFT between immiscible liquids, as surfactants reduce IFT. Individual nanoparticles of ZnO and γAl₂O₃ illustrate synergistic integration effects on reducing IFT. As expressed by Kazemzadeh et al., this synergistic effect can be deduced from the simultaneous effects that appeared among the individual factors that make up FeO/SiO₂. Based on the results of previous studies, WA and IFT may be achieved by using synergistic materials, in the form of FeO/SiO₂, instead of single nanoparticles. However, it has been reported widely that the reduction of IFT is not, compared to other CEOR mechanisms, the primary mechanism of nanofluid injection. Generally, in this regard, the gravitational forces between the nanoparticles intensify at high pressures and cause nanoparticles to accumulate on the joint surface of O/W. This is due to their close packaging arrangement. Higher pressures create a stronger and harder interface due to the deposition of nanoparticles on the surface. As a result, ambient pressures are good for getting the lowest IFT values. This is another reason why decreasing IFT is not the main driver of nanoparticle displacement in the challenging reservoir conditions.

3.4. Effect of SMW+300 ppm ZnO−γAl₂O₃ on Contact Angle (CA). In this section, it was observed that the oil droplet was instantly spread on the O/W carbonate plates, which means that the CA of the oil droplet placed onto the rock surface was zero, implying that the rock has a strong OW condition initially. CRs, after being washed and dried, were prepared for CA tests. The oil CA in the initial conditions for carbonate samples subjected to aging is 161° (Figure 16a). Additionally, Figure 16b–d shows the measurement of the oil CA on the carbonate surface to determine the WA of carbonate pellets aged at various SMW+100 ppm ZnO−γAl₂O₃, SMW+300 ppm ZnO−γAl₂O₃, and SMW+300 ppm ZnO−γAl₂O₃ concentrations. Figure 16c indicates the CA of the solid surface of the carbonate in the SMW+300 ppm ZnO−γAl₂O₃ nanofluid. The ZnO−γAl₂O₃ nanofluid in the concentrations of 100, 300, 500, 700, 900, 1100, and 1300 ppm with SMW resulted in angles of 110, 31, 45.03, 70, 120, 130, and 138°, respectively. The lowest CA was obtained for the SMW+300 ppm ZnO−γAl₂O₃ nanofluid, 31°. In general, the change in the CA of the rock in the presence of SMW+300 ppm ZnO−γAl₂O₃ nanofluid from the initial value of 161 to 31° may be due to the synergistic and harmonized effects of SMW and 300 ppm ZnO−γAl₂O₃ nanofluids. This can

![Figure 14. Conductivity values of the SMW+300 ppm ZnO−γAl₂O₃ solution (μS/cm) against concentration.](image1)

![Figure 15. IFT of the oil and nanofluid.](image2)
significantly increase oil recovery. The oil CA increased after treatment of the plates with SMW+300 ppm ZnO−γAl₂O₃, which indicates that the WA was altered from an OW to a WW state. Also, increasing the concentration above SMW+300 ppm ZnO−γAl₂O₃ leads to instability of SMW+300 ppm ZnO−γAl₂O₃, which is not desirable. Therefore, the results showed that the MSW+300 ppm ZnO−γAl₂O₃ nanofluid has high stability.

According to the interpretations provided in the above sections, at a concentration of SMW+300 ppm ZnO−γAl₂O₃, a strong negative charge caused the stretched nanofluid to act as an electrolyte. On the other hand, the surface loads on carbonate core rocks are positive. Therefore, a gravitational force was created between the positively charged rock surface and the highly negatively charged nanofluid. On the other hand, minimizing the free surface energy of Gibbs was due to the adsorption phenomenon. The electrolytic behavior of the nanofluid and the surface causes the adsorption of the nanofluid to be the dominant mechanism for changing the wettability of CRs, despite the disjoint pressure (as shown in Figure 17). The CA value of the rock reached its minimum at a concentration of SMW+300 ppm ZnO−γAl₂O₃. Increasing the concentration above SMW+300 ppm ZnO−γAl₂O₃ increased the system’s entropy; this increase was also due to disjoint pressure. This increased entropy caused a conflict with minimizing the use of Gibbs’s free energy for surface adsorption as a dominant mechanism of WA. As presented in the above interpretation, the prepared composition showed extraordinary potential as a good candidate for changing the surface wettability of carbonated OW rock. The charge is completely positive Ca²⁺, and the charge negative is CO₃⁻ on CR surfaces; on the other hand, there is a positive and negative partial charge in the water molecule. Also, there is a negative surface charge in SMW+300 ppm ZnO−γAl₂O₃ and the hydroxyl groups of Zn−OH and Al−OH are formed in contact with water. On the surface of the CR, these SMW+300 ppm ZnO−γAl₂O₃ are easily adsorbed and thus in contact with water form more hydroxyl groups.

According to the findings of the previous section, 300 ppm of ZnO−γAl₂O₃ was added to the SMW at pH 6 to create all of the nanofluids. The concentration and valency of the existing ions and their effects on the ZP of the rock surface are key factors in the WA by SMW process. The presence of potential-determining ions in SMWs causes partial detachment of oil carboxylic components from the rock surface in the absence of 300 ppm ZnO−γAl₂O₃ nanoparticles. Given the positive surface charge of 300 ppm ZnO−γAl₂O₃ nanoparticles at pH 6, the repulsive forces between the Ca²⁺ and Mg²⁺ ions have a favorable impact on the stability of the 300 ppm ZnO−γAl₂O₃ nanoparticles (Figure 18a). However, even at lower concentrations than MSWs, the SO₄²⁻ ions in SMWs might partially neutralize the positive charge of ZnO−γAl₂O₃ nanoparticles, leading to their aggregation (Figure 18b).

### 3.5. Core Flooding Experiments

In this experimental study, core flooding tests were conducted using SMW and

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**Figure 16.** (a) Process of determination of the CA of an oil droplet on the rock plate in an aging condition. CA of the oil droplet on OW thin slices surrounded by (b) SMW+100 ppm ZnO−γAl₂O₃, (c) SMW+300 ppm ZnO−γAl₂O₃, and (d) SMW+500 ppm ZnO−γAl₂O₃.

**Figure 17.** CAs of SMW+ZnO−γAl₂O₃ droplets and CR.

**Figure 18.** Effect of (a) Ca²⁺ and Mg²⁺ and (b) SO₄²⁻ ions on the surface charge of ZnO−γAl₂O₃ nanoparticles at pH 6.
SMW+300 ppm ZnO–γAl₂O₃ respectively. The results of SMW and SMW+300 ppm ZnO–γAl₂O₃ flooding tests are presented in Figure 19. Thus, the breakthrough in the flooding process with SMW for the first and second core plugs was 48 and 46.5%, respectively. The calculated values of the OR ratio after SMW and SMW+300 ppm ZnO–γAl₂O₃ flooding to the overall OR are presented in Table 5. It can be observed that 24% and 15% of the recovered oil in cores 1 and 2, respectively, are due to using SMW+300 ppm ZnO–γAl₂O₃.

3.6. ZnO–γAl₂O₃ Nanoparticles’ Mechanism in the Presence of SMWs. The dispersed flow of prepared SMW+ZnO–γAl₂O₃ in the reservoir is schematically shown in Figure 20. When SMW+300 ppm ZnO–γAl₂O₃ nanoparticles enter the porous media, some particles may be adsorbed on the CRs surface and alter the rock’s wettability. Thus, SMW+300 ppm ZnO–γAl₂O₃ nanoparticles are absorbed in the O/W interface, thereby significantly reducing the amount of IFT.

In the absence and presence of each potential-determining ion, 300 ppm ZnO–γAl₂O₃ nanoparticles behave differently, resulting in a different WA mechanism. The underlying mechanism in the case of divalent cations is the adsorption of 300 ppm ZnO–γAl₂O₃ nanoparticles onto the oil components and transportation through the porous media, which also decreases nanoparticle deposition (Figure 20a). In these circumstances, greater oil mobility results in better oil component transportation and more OR. The mobility of nanoparticles through a porous media is greatly influenced by a number of important factors, including the nanoparticles' surface charge and stability as well as the surface charge and grain surface roughness of the porous media. The adsorption of nanoparticles on the rock surface diminishes when the surface charge signs of the nanoparticles and porous media are similar, and increased mobility is attained because of the nanoparticles’ excellent stability against deposition.

The presence of uneven dents and bumps on the grain surface makes it rough, and this could trap the nanoparticles in the porous media. The deposition of the nanoparticles takes place in the presence of divalent anions and their high concentration, particularly in the absence of other potential-determining ions, and their retention on the rock surface result in the formation of a uniform layer due to the structural disjoining pressure. Rock surface retention of the nanoparticles gradually separates the oil droplets from the initially OW rock surface, causing WA toward WW and more OR (Figure 20b).

3.7. Economic Feasibility of SMW+300 ppm ZnO–γAl₂O₃ Nanofluids. An alternative that simultaneously exemplifies a sustainable environmental and financially advantageous EOR flooding approach is SMW injection. The improved initial wetting toward more WW states is made possible by the injection of a water-adjusted ionic composition, and the displacement efficiency is enhanced as a result of greater capillary forces. In both sandstone and carbonate reservoirs, SMW enhances OR by WW. The primary injection brine used offshore is seawater, which is regarded as SMW in the formation water, crude oil, and pore surface minerals can be changed by SMW since it has a different ion content and salinity from formation water. This can change how well reservoirs moisten. Simultaneous injection of nanoparticles and SMW have efficient effects due to a very small concentration of nanoparticles in reservoir. The use of these compounds is very affordable due to their very low concentration, and they are known as effective and environmentally friendly nanofluids to increase OR. Every stage of

![Figure 19. OR factor vs PV injected for CRs.](image)

![Figure 20. Mechanism of OR by ZnO–γAl₂O₃ nanoparticles.](image)

Table 5. OR Factor of Nanofluid Flooding

| Number | Nanofluid | OR percent after | Overall OR | OR to overall OR ratio after |
|--------|-----------|-----------------|------------|-----------------------------|
|        |           | SMW flooding    | SMW+300 ppm ZnO–γAl₂O₃ flooding | SMW+300 ppm ZnO–γAl₂O₃ flooding |
| 1      | (SMW+300 ppm ZnO–γAl₂O₃) | 48              | 8.8        | SMW flooding                | 85 | 15 |
| 2      | (SMW+300 ppm ZnO–γAl₂O₃) | 46.5            | 15.1       | SMW+300 ppm ZnO–γAl₂O₃ flooding | 75 | 24 |
design, implementation, and evaluation must be completed for an EOR technique to be successful. A combination chemical agent known as the SMW+300 ppm ZnO–γAl2O3 nanofluid was used in this paper. Here, the experimental findings demonstrated that CA was effectively reduced at a very low concentration of SMW+300 ppm ZnO–γAl2O3. As a result, this level of concentration is extremely economical. Expenses for the preparation of nanomaterials are not involved in the initial stages of evaluation and design steps. However, it takes center stage during the implementation phase. The synthesis of nanoparticles theoretically entails significant costs for the last step, but from the perspective of experimentation, setting up a production line for mass production justifies the economic aspect of the approach. In addition, the aforesaid is demonstrated in very small quantities by the created SMW+300 ppm ZnO–γAl2O3 nanofluid. The IFT of O/W was generally decreased in this study after a very tiny concentration of the ZnO–γAl2O3 nanofluid was added. The OR was enhanced by this process. Nanomaterials can typically produce OR at relatively low doses. They are reasonable in contrast to surfactants and other materials. The main practical benefit of nanomaterials is their ability to achieve high OR in the reservoir at relatively low concentrations. As a result, there is a decrease in the overall cost of field-scale implementation of nanomaterials.

4. CONCLUSIONS
The application of nanoparticles in the reservoir can modify reservoir properties such as rock wettability and IFT. In this paper, first, ZnO–γAl2O3 was synthesized. In the next step, SMW was prepared. Then, various static experiments and tests of stability, IFT, and CA were conducted. The properties of synthesis ZnO–γAl2O3 were determined using FT-IR, EDX, SEM, and XRD analyses. The presence of the Zn, O, Al, and C elements in the ZnO–γAl2O3 structure was confirmed by FT-IR and EDX analyses. This study presented an effective method of WA of OW carbonate rocks to a WW condition using SMW+300 ppm ZnO–γAl2O3. The CA tests showed that SMW+300 ppm ZnO–γAl2O3 adsorption is responsible for WA. The stability of SMW+300 ppm ZnO–γAl2O3 was tested over time. SMW+300 ppm ZnO–γAl2O3 was stable for two weeks. In this regard, the ZP of SMW+300 ppm ZnO–γAl2O3 is in the vicinity of –30 mV, indicating a stable colloidal condition. The IFT test of the most stable suspension SMW+300 ppm ZnO–γAl2O3 showed a reduction in the IFT from 27.24 mN/m to 11 mN/m. IFT measurements showed that SMW+300 ppm ZnO–γAl2O3 is the effective concentration to reduce the IFT. The shift in wettability and the reduction in IFT were attributed to the disjoining pressure exerted by SMW+300 ppm ZnO–γAl2O3. On the other hand, a concentration of SMW+300 ppm ZnO–γAl2O3 resulted in a significant reduction of CA. In particular, it reduced the contact angle of the rock from the initial 161° to 31°. Thus, the effective mechanism of oil displacement using SMW+300 ppm ZnO–γAl2O3 is attributed to the WA. Also, this new combination improved the understanding of different recovery mechanisms and rock/fluid and fluid/fluid interactions. Generally, this nanofluid represents a strong WA toward WW conditions for OW carbonates. SMW+300 ppm ZnO–γAl2O3 nanofluids tend to be adsorbed on the rock surface. In this regard, the 300 ppm nanofluid solution showed a pronounced effect by adsorbing on the solid surfaces, resulting in more WW states. The applicability of the nanofluid for EOR was evaluated using a core flooding test. In this regard, at a concentration of SMW+300 ppm ZnO–γAl2O3, flooding tests were also conducted. Nanofluid flooding using SMW+300 ppm ZnO–γAl2O3 improves the OR by 15% and 24%. Our findings through CA, IFT, and flooding tests indicate that the dominant mechanism in increasing OR by the nanofluid is WA. Generally, more research is needed to determine whether using SMW+300 ppm ZnO–γAl2O3 nanoparticles can improve OR from carbonate oil reservoirs; nonetheless, this research can serve as a starting point for future efforts to put the suggested technique into practice through pilot studies.

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NOMENCLATURE
CA contact angle
CR carbonate rocks
DIW deionized water
EOR enhanced oil recovery
IFT interfacial tension
OW oil-wet
OR oil recovery
PV pore volume
SMW smart water
WA wettability alteration
WW water-wet
ZP zeta potential

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