

Wettability Alteration of Sandstone and Carbonate Rocks by Using ZnO Nanoparticles in Heavy Oil Reservoirs

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Abstract

Efforts to enhance oil recovery through wettability alteration by nanoparticles have been attracted in recent years. However, many basic questions have been ambiguous up until now. Nanoparticles penetrate into pore volume of porous media, stick on the core surface, and by creating homogeneous water-wet area, cause to alter wettability. This work introduces the new concept of adding ZnO nanoparticles by an experimental work on wettability alteration and oil recovery through spontaneous imbibition mechanism. Laboratory tests were conducted in two experimental steps on four cylindrical core samples (three sandstones and one carbonate) taken from a real Iranian heavy oil reservoir in Amott cell. In the first step, the core samples were saturated by crude oil. Next, the core samples were flooded with nanoparticles and saturated by crude oil for about two weeks. Then, the core samples were immersed in distilled water and the amount of recovery was monitored during 30 days for both steps. The experimental results showed that oil recovery for three sandstone cores changed from 20.74, 4.3, and 3.5% of original oil in place (OOIP) in the absence of nanoparticles to 36.2, 17.57, and 20.68% of OOIP when nanoparticles were added respectively. Moreover, for the carbonate core, the recovery changed from zero to 8.89% of OOIP by adding nanoparticles. By the investigation of relative permeability curves, it was found that by adding ZnO nanoparticles, the crossover-point of curves shifted to the right for both sandstone and carbonate cores, which meant wettability was altered to water-wet. This study, for the first time, illustrated the remarkable role of ZnO nanoparticles in wettability alteration toward more water-wet for both sandstone and carbonate cores and enhancing oil recovery.

Keywords: Spontaneous Imbibition, Nanoparticles, Wettability Alteration, Oil Recovery

1. Introduction

It is documented that close to 50% of the world proven petroleum reserves are located in carbonates and are strongly oil-wet. Carbonate reservoirs are quite different from sandstone reservoirs. Carbonate rock has a low permeability and very different surface properties compared to sandstone. Generally,

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carbonates tend to be more oil-wet than sandstones. About 80-90% of the world carbonate reservoirs have a negative capillary pressure and usually show a rather low oil recovery factor (less than 30%). The EOR potential of these oil-wet carbonate reservoirs is high. Spontaneous imbibition (SI) has long been recognized as an alternative enhanced oil production strategy capable of recovering a portion of some trapped oil through a replacement mechanism which exchanges water for oil. The effectiveness of this process depends on several parameters, including permeability and rock wettability. It is found that SI rate is highly sensitive to wettability. However SI rate increases as the water-wetness improves.

One of the newborn methods to create wettability alteration is adding certain surface-active materials, including nanoparticles. Nanotechnology has the potential to introduce revolutionary changes in several areas of oil and gas industry, for example exploration, production, enhanced oil recovery, and refining (Shah, 2009). Nanoparticles are defined as surface active agents, because they have a very small particle size, which helps them penetrate into the pore volume of porous media, stick on the core surface, and, by creating homogeneous water-wet area, increase surface energy more than the surface tension of water. Thus the wettability is altered to water-wet and oil is pulled out from the core surface. Recently, only a few studies have been carried out and still a lot of questions on the influence of nanoparticles on SI, wettability alteration, and the possible improvement of oil recovery have been remained unanswered. Clark et al. (1990) found that when an aqueous metal was added into the process, the heavy oil viscosity was further reduced. Cacciola et al. (1993) reported that nanoparticles have a benign activity, selectivity, and stability for the dehydrogenation of cyclohexane and methylcyclohexane. Ali et al. (2004) and Temple et al. (2005) investigated the effect of nanoparticles on lowering the permeability of shale in drilling fields. Nanoparticles succeeded in blocking water invasion and decreasing the strength of shale wall. When nanoparticles are passed through porous media, there is no straining of nanoparticles (Zhang, 2010). Fan et al. (2009) studied experimentally using ionic liquids to upgrade heavy oil. They found that ionic liquids could decrease the viscosity, average molecular weight, and asphaltene content of the heavy oil. Chen et al. (2009) studied the viscosity reduction of nanoparticles in the catalytic aqua-thermolysis of heavy oil. Yu et al. (2010) found nanoparticles are roughly 2 orders of magnitude smaller to be able to pass through porous media. Rodriguez et al. (2010) and Caldelas et al. (2011) proved that nanoparticles showed stabilized emulsions, and if surface has coated with nanoparticles with an acute contact angle, their retention and aggregation in porous media are decreased. Fletcher et al. (2011) compared the use of nanotechnology with other forms of EOR processes and showed nanotechnology effects on several parameters like oil viscosity reduction. Sunjay et al. (2011) reported that nanoscience can contribute in wide fields to be more effective, less expensive, and more economic. Nanoparticles can improve recovery between 80-90% of original oil in place (OOIP). Ogolo et al. (2012) reported that depending on the type of nanoparticles, wettability can be changed. These particles alter the chemical interactions in interfacial tension. Ayatollahi et al. (2012) tested several compounds in surface conditions, including mainly alumina oxide and iron oxide. Generally, alumina oxide showed the best results in terms of altering wettability. They showed that the contact angle of the fluids and phase behavior can be altered by adding alumina oxide. The main characteristic of alumina oxide is to change the wettability of rock surface to more water-wet. Parvazdavin et al. (2012) investigated the effect of adding water-based nanoparticles on the hysteresis of oil and water relative permeability curves. They used SiO₂ nanoparticles and showed that, by using nanoparticles, the hysteresis of both oil and water phases decreased and the hysteretic behavior of relative permeability curves was reduced. This paper introduces a novel concept, which ZnO nanoparticles have the ability to modify the wettability of reservoir rock and enhance oil recovery rates oil via SI.

2. Methodology

2.1. Rock samples

Laboratory tests were conducted on four cylindrical core samples taken from a real Iranian heavy oil reservoir. To verify the wettability characteristics of all the four cores, core analysis and contact angle methods were conducted. It was identified that core A was water-wet ($\theta = 27^\circ$), core B was intermediate water-wet ($\theta = 58^\circ$), core D was intermediate water-wet ($\theta = 71^\circ$), and core C was oil-wet ($\theta = 120^\circ$). After cutting, the cores were washed in Soxhlet apparatus using methanol and toluene for around two weeks and dried in oven at around 150°C for one day. The dimensions, porosity, and permeability of each core sample were measured by helium porosimeter and air permeameter respectively. Table 1 shows the measured porosity, absolute permeability, and dimension of each sample.

Table 1
Properties of the cores used in the experiments.

Core name	Type	K_a (md)	Porosity (%)	L (cm)
A	Sandstone	122.36	22.705	5.910
B	Sandstone	107.44	22.579	7.138
C	Carbonate	0.309	11.539	7.362
D	Sandstone	6.038	26.124	6.390

2.2. Materials

The oil used in this study was taken from Iranian heavy oil fields. Its properties are tabulated in Table 2. ZnO nanoparticles used in all the experiments were bought from Notrino Company with the specifications showed in Table 3. Dealing with heavy oil with high viscosity was one of the challenging issues. The temperature of all the experiments was 50°C . Selecting the best concentration at this temperature was a very important factor. Figure 1 shows the effect of different concentrations of ZnO nanoparticles on viscosity at different temperatures. As shown, by increasing temperature, the effect of different concentrations of ZnO nanoparticles is small. But at a low temperature, especially around the temperature of our experiments (50°C), a ZnO nanoparticles concentration of 0.2 wt.% has a better influence on decreasing viscosity compared to the other ones. Therefore, the concentration of 0.2 wt.% selected for the current study is less than the values reported by others, which helps to cope with heavy oil during the experiments.

Table 2
Properties of the oil used in the experiments.

Name	API degree	Oil viscosity(cP)	Compressibility (psi ⁻¹)
KM	13	16000	4.67×10^{-6}

Table 3
Specifications of ZnO nanoparticles used in the experiments.

Particle type	Formula	Form	Purity (wt.%)	APS	SSA	Appearance
Zinc oxide	ZnO	Nanopowder	99	<50 nm	>60 m ² /g	White power

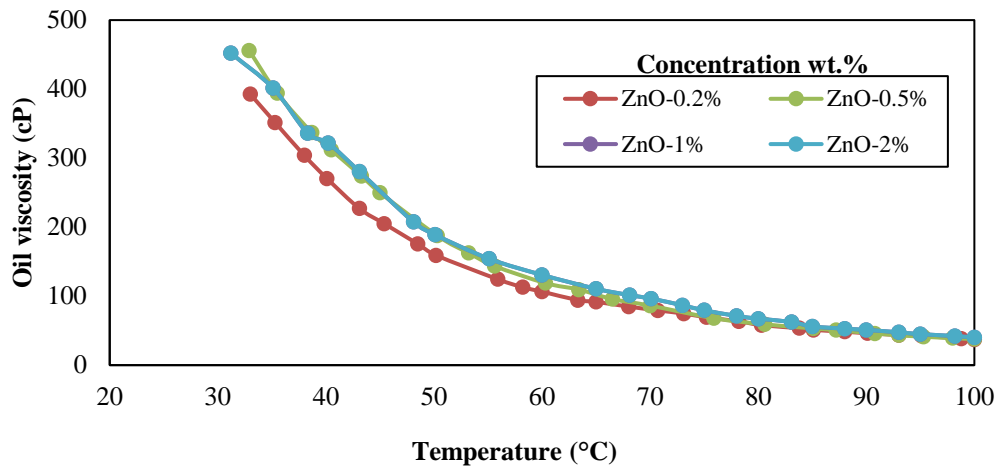


Figure 1

The effect of ZnO nanoparticles concentration on oil viscosity.

2.3. Experimental procedure

a. SI test without ZnO nanoparticles

The procedure for SI tests without nanoparticles was as follows:

- 1- Wash the cores in Soxhlet apparatus using methanol and toluene for around two weeks and dry in oven at around 150 °C for one day;
- 2- Saturate core samples with crude oil after two weeks;
- 3- Clean excess oil;
- 4- Determine the weight of oil saturated cores for the calculation of the oil volume in the core;
- 5- Place the oil saturated cores in Amott-cell;
- 6- Add distilled water up to the special level on the burette;
- 7- Seal the top of the burette and the top seal of the junction of the burette;
- 8- Monitor the volume of oil expelled by the core and determine the oil recovered as the percentage of original oil in place (OOIP) versus time for 30 days at 50°C.

In all the experiments, the initial water saturation was zero.

b. SI test with ZnO nanoparticles

Preparing the homogeneous nanoparticles solution was one of the most important challenging issues in this section. ZnO nanoparticles tend to be disposed after around 7 hours. There have been three methods to study the effect of nanoparticles, namely saturating the clean cores with oil and nanoparticles, adding nanoparticles to distilled water inside the SI cell, and flooding the cores with nanoparticles. The problem of first method is that by adding nanoparticles to oil in a saturation cylinder one cannot assure that the nanoparticles are able to fill porous media. The problem of the second method is the time of the experiment. The SI test usually takes 30 days; so it is necessary to pay attention to avoid disposing nanoparticles and, at least, there is some doubt that nanoparticles are

able to diffuse to core or not, especially about carbonate core. Finally, the best decision is flooding, which is the reliable routine method for materials like surfactant, nanoparticles, or some other disposed materials. 7 hours disposing time was enough for our experiment to let the nanoparticles diffuse. For avoiding this problem and assuring that the nanoparticles affected cores directly, after washing the cores, the core holder was first vacuumed and the cores were then flooded with ZnO nanoparticles for around 3 hours as shown in Figures 2(a) and 2(b) respectively. In the middle of flooding, the nanoparticles cylinder was shaken and the outlet of the core holder was monitored to be clean. It was the reliable evidence to assure that nanoparticles were displaced inside the pore volume as shown in Figure 3, and the cores were then saturated with crude oil for around two weeks. The weights of the clean core, the core saturated by crude oil in the absence of nanoparticles, and the cores saturated by crude oil in the presence of nanoparticles are reported in Table 4. The complete saturation was not important. The most important point was that the saturation conditions (the applied temperature and pressure) for all the experiments were the same. The rest of steps were similar to the SI tests in the absence of nanoparticles.

a)



b)

**Figure 2**

(a) Vacuuming the core holder; (b) Flooding the cores with ZnO nanoparticles.

**Figure 3**

Saturated cores with ZnO nanoparticles after flooding.

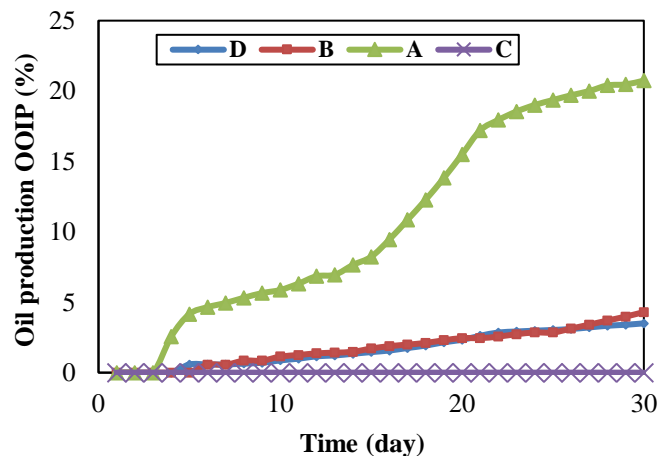
Table 4
The weight of the core samples.

Core name	Clean core	Oil saturated cores in the absence of nanoparticles	Oil saturated cores in the presence of nanoparticles
A	137.866	149.83	151.30
B	166.904	181.512	183.87
C	199.567	206.642	208.72
D	143.0963	159.86	161.106

3. Results and discussion

The oil recovery percentages for the four core samples without ZnO nanoparticles during 30 days are shown in Figure 4(a). The final oil recoveries in the absence of nanoparticles were 20.74, 4.3, and 3.5% of OOIP for A, B, and D sandstone cores respectively and 0% of OOIP for the carbonate core (core C). Figure 4 (b) shows the SI Amott cell for the four cores in the last day. By using core analysis and contact angle method, it was identified that core A was water-wet, cores B and D were intermediate water-wet, and core C was oil-wet. In the oil-wet core C, the non-wetting phase has an affinity toward the core. Hence capillary pressure was negative and there was no response to SI without any additives. Therefore, the core did not allowed water to imbibe and oil recovery was 0% of OOIP during 30 days.

a)



b)



Figure 4

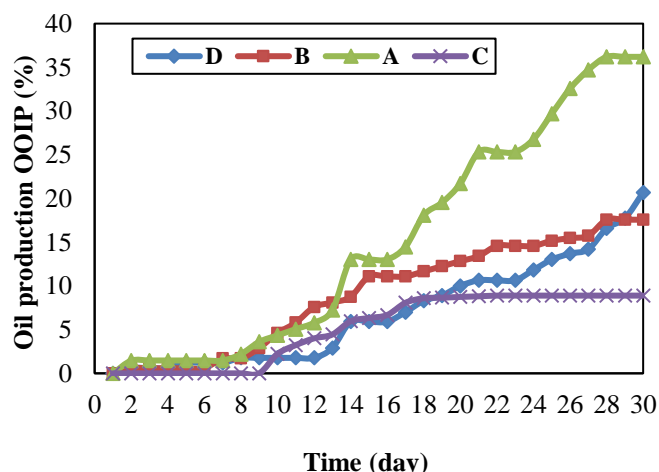
(a) The oil recovery percentage for the four core samples during 30 days; (b) Amott cell in the last day without ZnO nanoparticles.

There was no initial water inside the sandstone cores, and thus, in the early days, the water moved to the core until the water saturation rose to the critical value. After this point, when water saturation was present, oil production started. In the water-wet core A, the wetting phase had an affinity toward the core; so after 5 days, oil recovery started. The wettability influenced the oil recovery through capillary pressure and relative permeability. In water-wet core A, oil is generally displaced with water more efficiently than in intermediate water-wet and oil-wet cores. In water-wet rocks, oil did not imbibe, unless the capillary pressure exceeded the entry pressure. Then, the capillary pressure increased as the

water saturation decreased. The general trend was that as wettability varied from water-wetness to oil-wetness, the water relative permeability and the residual oil saturation increased, while the oil relative permeability and the initial water saturation decreased. Therefore, the water displacement was more favorable in core A and thus the oil recovery was greater than the other ones (20.74% of OOIP). Intermediate-wet cores B and D did not have a strong affinity toward either water or oil. Therefore, it took more time to let water imbibe and water saturation reached the critical water saturation. Hence oil recovery started for cores B and D after 6 and 4 days respectively. With time passing, the wetting phase occupied the small pore volume and influenced the flow paths, capillary pressure, and relative permeability. As water imbibition increased, capillary pressure rose. Thus the wettability of the intermediate core was critical to determine recovery. Therefore, ultimate oil recovery was 4.3 and 3.5% of OOIP for cores B and D respectively, which was lower than water-wet core A.

The oil recovery percentages for the four core samples with ZnO nanoparticles during 30 days are illustrated in Figure 5(a) and the final day of SI Amott cell system is shown in Figure 5(b). As shown in Figure 5(a), the ultimate oil recoveries are 36.2, 17.57, and 20.68% of OOIP for cores A, B, and D (sandstone cores) respectively and 8.89% of OOIP for the carbonate core (core C). By using ZnO nanoparticles, the appropriate time needed to reach the critical water saturation decreased and thus the initial delay in starting oil recovery was reduced. Expelling oil for cores A, B, D, and C started after 3, 4, 2, and 10 days respectively. All the experimental conditions were the same as the previous test; the only reason caused a decrease in the time was wettability alteration by ZnO nanoparticles. Core A was water-wet and had suitable porosity to let nanoparticles stick on the pores and good permeability to allow the nanoparticles to diffuse easily during nanoflooding. Therefore, all these positive parameters (permeability, porosity, and length) helped more to alter wettability to more water-wet and thus its final oil recovery was greater than the other cores (36.2% of OOIP). This condition was valid for cores B and D too. The suitable porosity of both cores helped nanoparticles to occupy more pore volume and the wettability alteration of the cores were obvious through SI mechanism. Hence the final oil recovery was 17.57 and 20.68% of OOIP for cores B and D respectively.

a)



b)



Figure 5

(a) The oil recovery percentage for the four core samples during 30 days; (b) Amott cell in the last day with ZnO nanoparticles.

The interesting point was that the final oil recovery of core D was higher than that of core B. This behavior was related to the smaller length and higher porosity of core D. High porosity let the

nanoparticles penetrate further; so wettability alteration happened in a better situation. This factor in addition to a smaller length helped to speed up oil expelling and oil recovery. As shown in Figure 5(a), the wettability alteration of oil-wet carbonate core C to more water-wet was completely obvious. Despite low permeability, the flooding of ZnO nanoparticles helped to decrease oil-wet wettability. This event caused an oil recovery of 8.89% of OOIP, whereas oil recovery was 0% in the absence of nanoparticles. The experimental results showed that adding ZnO nanoparticles appeared to be an important improved oil recovery method for intermediate water-wet and preferentially oil-wet rocks. They caused the affinity of the cores towards water-wetness to increase and thus the ultimate oil recovery improved.

For proving the claim that the main reason for increasing oil recovery was wettability alteration, it was better to study the numerical modeling of relative permeability curves of oil and water for each core. The mathematical formulation and solution procedure used in the modeling is briefly outlined as follows.

Mass conservation of a flowing phase is given by Equation 1:

$$\frac{d \int_{\Omega} \phi \rho_l S_l d\Omega}{dt} + \int_{\Gamma} \rho_l v_l d\Gamma = \int_{\Omega} q_l d\Omega \quad (1)$$

The porosity and mass densities are given by:

$$\phi = \phi_{init}(1 + c_r(P_O - P_{init})) \quad (2)$$

$$\rho_l = \rho_{l,init}(1 + c_l(P_O - P_{init})) \quad (3)$$

Darcy's law provides the average flow velocity in a porous medium as reads:

$$v_l = -K \frac{k_{r,l}}{\mu_l} \nabla \phi_l \quad (4)$$

The gradient of the flow potential is presented by:

$$\nabla \Phi_l = \nabla P_l + \rho_l \left(gz - \frac{\omega^2}{2} x^2 \right) \quad (5)$$

where, z is the elevation and x is the distance from the axis of rotation. Gravity was only applied to a vertically oriented core plug, in which there was not centrifugal acceleration.

Saturations and pressures are related by:

$$S_O + S_W = 1 \quad (6)$$

$$S_W^* = \frac{S_W - S_{Wi}}{1 - S_{Wi}} \quad (8)$$

For each cell, the discrete residual of the mass conservation equation is:

$$r_{i,l}^{n+1} = V_i \phi_i \rho_{i,l}^n \left(\frac{S_{i,l}^{n+1} + S_{i,l}^n}{\Delta t} \right) + \sum_{j \in M_i} \lambda_{up,l}^{n+1} T_{i,j} \Delta \Phi_{i,l} - Q_{i,l}^{n+1} \quad (9)$$

The summation is over the two neighboring cells, except at the two boundaries. The potential difference is given by:

$$\Delta \Phi_{i,l} = \Delta P_l^{n+1} + \rho_l^{-n} (g \Delta z - w^2 x \Delta x) \quad (10)$$

The phase mass density is the simple arithmetic average of the densities in the two adjacent cells, and is treated explicitly. The upstream mobility is evaluated in the cell from which the phase is flowing, which is in turn taken from the sign of the potential difference between cells i and j :

$$\lambda_{up,l} = \rho_l^n \frac{k_{r,l}^{n+1}}{\mu_l} \quad (11)$$

The upstream cell is the one with the largest potential at time step n . The transmissibility between adjacent cells is calculated by a harmonic average:

$$T_{i,j} = \frac{2A}{\frac{\Delta x_i}{K_i} + \frac{\Delta x_j}{K_j}} \quad (12)$$

The cross sectional area is given by:

$$A = \pi \frac{d^2}{4} \quad (13)$$

The initial pressure is hydrostatic for the specified mobile phase:

$$P_l(z) = P_{init} + g \rho_l (z - z_{ref}) \quad (14)$$

The initial saturation is constant. Pressure for the water phase is corrected by adding the capillary pressure, if any. The flow calculations at the boundary are handled as a normal flow, except for a half-length transmissibility:

$$T_f = \frac{AK_f}{\Delta X_f} \quad (15)$$

The cross sectional area, the permeability in the cell adjacent to the boundary, and the distance from the face to the center of the inside cell are included.

There are three types of possible boundary conditions:

1. Fixed boundary pressure;
2. Constant injection rate;
3. Specified total production rate;

For the inlets, the phase mobility used is the total phase mobility:

$$\lambda_{total} = \lambda_w + \lambda_o \quad (16)$$

The quantities are all evaluated on the inside of the core. The outlets use the respective phase mobility in the grid block adjacent to the boundary.

When a total production rate is specified, individual phase rates are allocated based on mobility:

$$q_l = q_{total} \frac{\lambda_l}{\lambda_w + \lambda_o} \quad (17)$$

Boundary face pressures are calculated from the given rates using Darcy's law.

The parameter estimation problem is solved using the popular Levenberg-Marquardt (LMA). The method is implemented as described by Nocedal and Wright. Modifications have been made to easily cater for linear constraints. The LMA interpolates between the Gauss-Newton algorithm (GNA) and the method of gradient descent and is used to solve non-linear least squares problems. Using forward differences, $n+1$ simulation runs are needed. The parameter estimator uses threads, and runs as many threads simultaneously as there are processors available. The relative permeability can be described with functional relationships in addition to tabular formats. Like other numeric minimization algorithms, the Levenberg-Marquardt algorithm is an iterative procedure. To start a minimization by the initial guess of S_{wi} and S_{or} , the algorithm converges to the global minimum, only if the initial guess is already somewhat close to the final solution.

The normalized water saturation is used as given by:

$$S = \frac{S_w - S_{wi}}{1 - S_{ro} - S_{wi}} \quad (18)$$

Burdine equation is as given below:

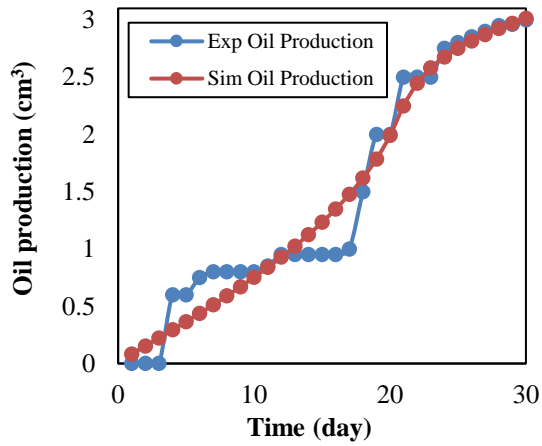
$$k_{rw} = k_{rw}^0 \left(S \frac{2+3\lambda}{\lambda} \right) \quad (19)$$

$$k_{ro} = k_{ro}^0 (1 - S)^2 (1 - (1 - S)^{\frac{2+\lambda}{\lambda}}) \quad (20)$$

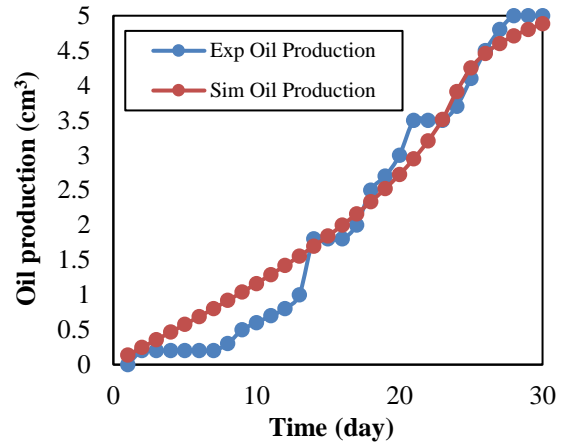
Famous relative permeability equations like Corey, Sigmund & McCaffery, Parcell, and Burdine are used for matching the obtained experimental data. Among these equations, just Burdine is able to match the experimental recovery data as shown in Figure 6(a) in the absence of nanoparticles and Figure 6(b) in the presence of nanoparticles. As shown in Figure 6(a), there is a sufficient matching between the experimental and simulated oil production rate for all the sandstone cores (cores A, B, and D). As shown in Figure 6(a), it seems there is a difference between the experimental and simulated matching for the carbonate core (core C). Because the amount of the simulated oil production rate is under 0.01, it could be ignored. It is completely obvious from Figure 6(b) that there is a reasonable matching between the experimental and simulated oil production rate for all the sandstone and carbonate cores in the presence of nanoparticles. Therefore, Burdine correlation is selected for the investigation of relative permeability curves.

A

a)

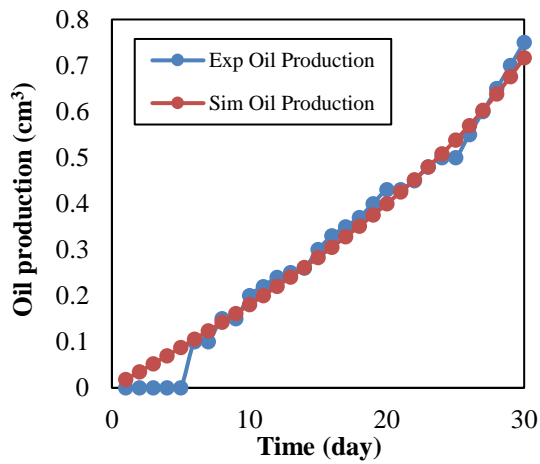


b)

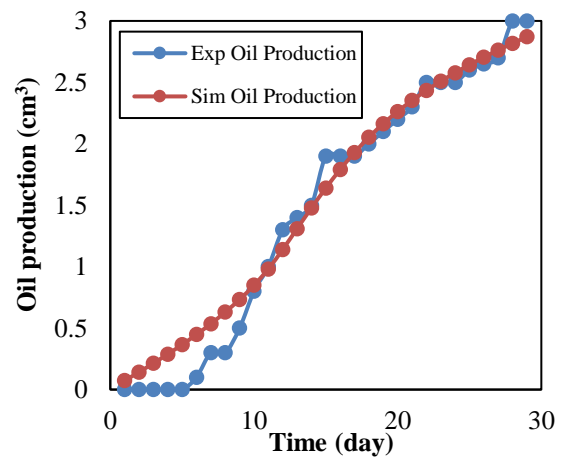


B

a)

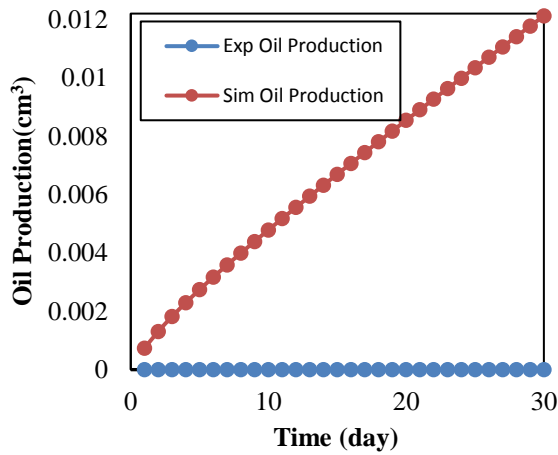


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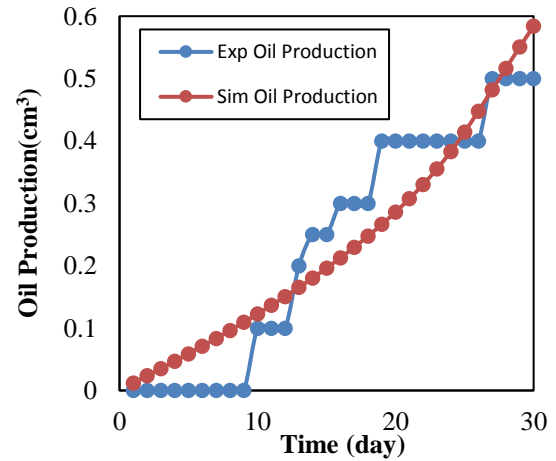


C

a)

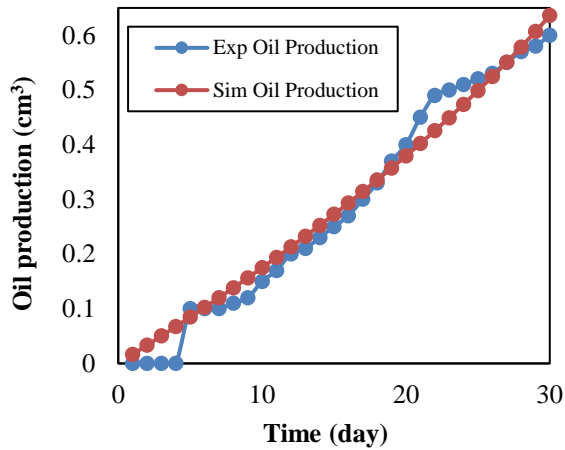


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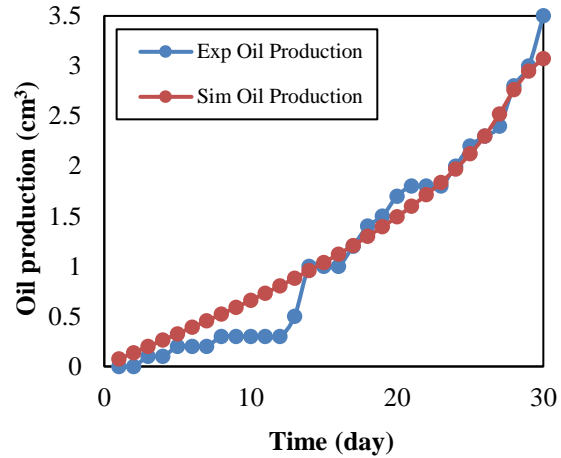


D

a)



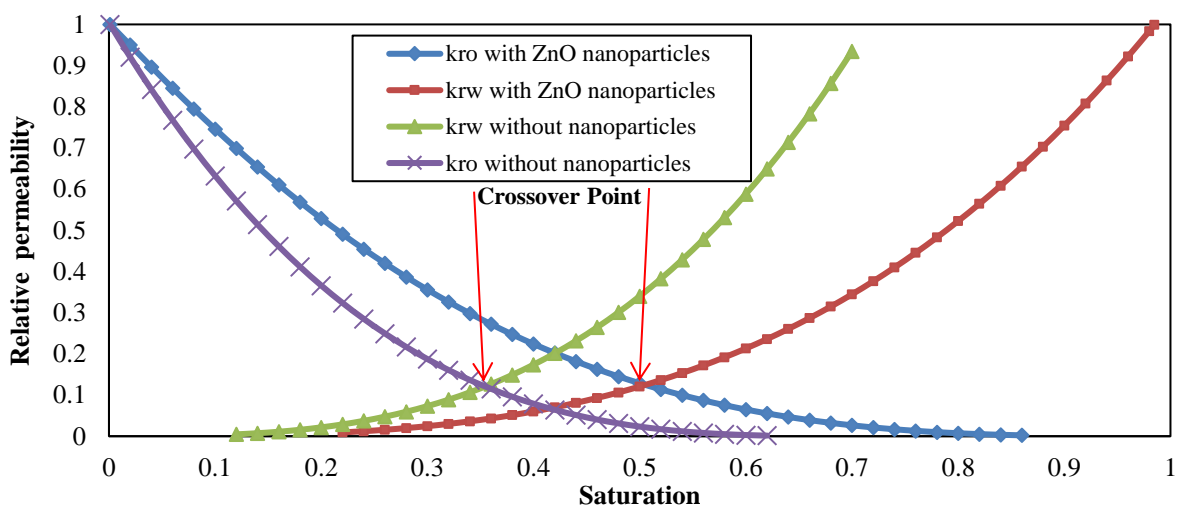
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**Figure 6**

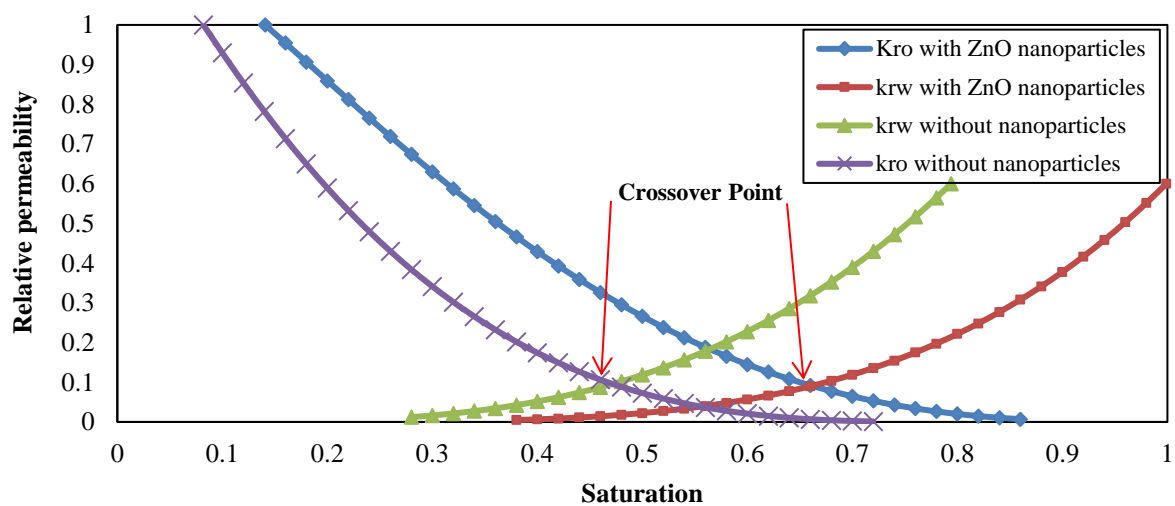
The matching between the experimental and simulated oil production rate: (a) without ZnO nanoparticles and (b) with ZnO nanoparticles for all the cores.

The relative permeability curves for core A, B, C, and D are shown in Figure 7 in the presence and absence of nanoparticles. Tables 5 and 6 show the characteristics of Figure 7 (relative permeability curves) in the absence and in the presence of ZnO nanoparticles respectively. By comparison of Tables 5 and 6, it is concluded that the crossover point of core A is changed from 0.47 to 0.66, its critical saturation is changed from 0.28 to 0.38, its end point of water is varied from 0.79 to 0.99, and its end point of oil is increased from 0.72 to 0.86. These rightward shiftings of the crossover point, critical saturation, and the endpoints of water and oil relative permeability curve of the water-wet core A by adding ZnO nanoparticles are completely obvious. Thus one may reach a conclusion that the main reason for improved oil recovery is wettability alteration. It seems this condition is also valid for intermediate water-wet cores. Based on the results of Tables 5 and 6, for core B, the crossover point is changed from 0.36 to 0.5, the critical saturation is increased from 0.12 to 0.22, the end point of water is varied from 0.7 to 0.98, and the end point of oil is changed from 0.62 to 0.86. For core D, the crossover point is changed from 0.32 to 0.43, the critical saturation is varied from 0.17 to 0.23, the end point of water is increased from 0.65 to 0.7, and the end point of oil is changed from 0.57 to 0.59. Therefore, wettability alteration is a reasonable cause for increasing the oil recovery of intermediate water-wet cores. The interesting finding is about oil-wet core C. Because the crossover point is changed from 0.21 to 0.36, the critical saturation is varied from 0.1 to 0.16, the end point of water is increased from 0.3 to 0.68, and the end points of oil is changed from 0.3 to 0.6, it is definitely clear that by adding ZnO nanoparticles, wettability alteration happens and causes oil to expel in comparison with the condition which no additives are added. Finally, as shown in Figure 7, these rightward shiftings in crossover point, critical saturation, and the end points for all the carbonate and sandstone cores are the clear evidence that wettability is altered to more water-wet by adding ZnO nanoparticles, which helps to enhance oil recovery. The second feature of Figure 7 is that the bands of relative permeability curves are also longer and wider by adding nanoparticles for all the four cores, which corresponds to higher recoveries. This behavior is the positive factor to affect the wider area of cores and help to expel more oil from different points of cores.

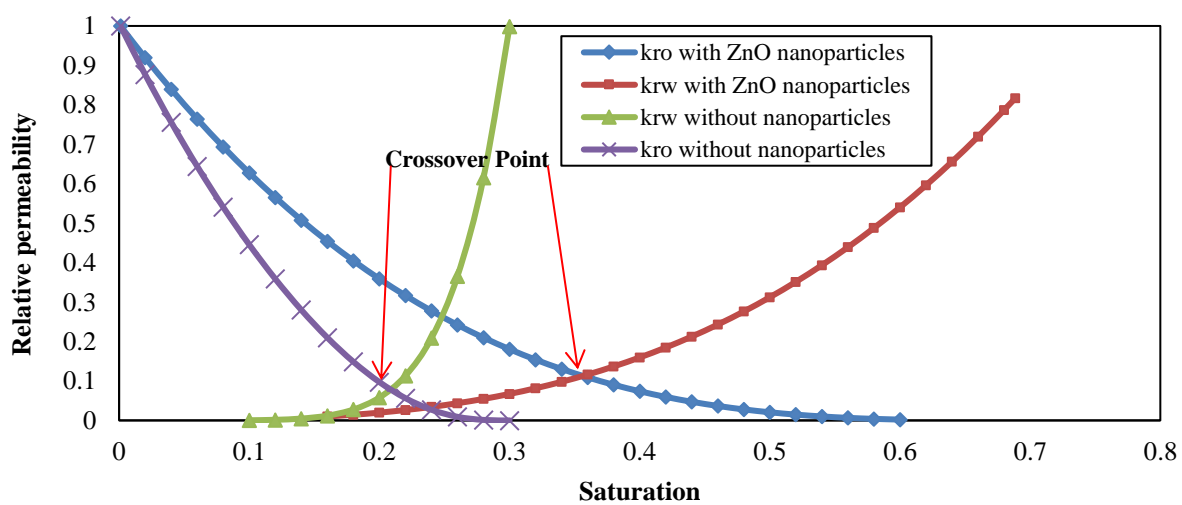
a)



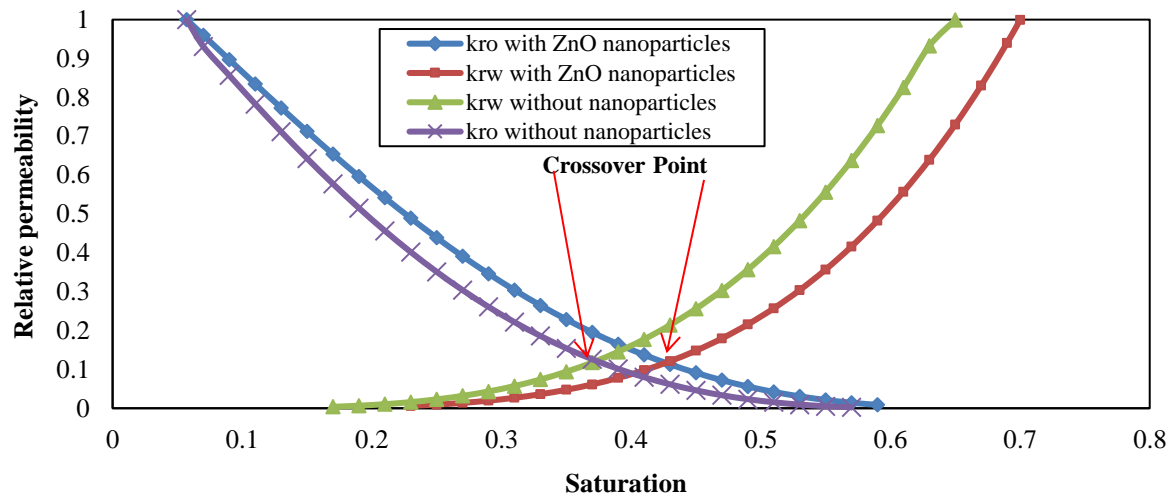
b)



c)



d)

**Figure 7**

Relative permeability curves in the absence and in the presence of ZnO nanoparticles for (a) core A, (b) core B, (c) core C, and (d) core D.

Table 5

The characteristics of relative permeability curves in the absence of nanoparticles.

Core name	Crossover point	Critical saturation	End points of water	End points of oil
A	0.47	0.28	0.79	0.72
B	0.36	0.12	0.7	0.62
C	0.21	0.1	0.3	0.3
D	0.32	0.17	0.65	0.57

Table 6

The Characteristics of relative permeability curves in the presence of nanoparticles.

Core name	Crossover point	Critical saturation	End points of water	End points of oil
A	0.66	0.38	0.99	0.86
B	0.5	0.22	0.98	0.86
C	0.36	0.16	0.68	0.6
D	0.43	0.23	0.7	0.59

4. Conclusions

This study showed the capability of ZnO nanoparticles to alter wettability and expel oil through a SI process.

- Carbonate core is classified to be neutral-wet or preferentially oil-wet. SI in the carbonate core sample was a very slow process regardless of its permeability. This core did not respond to SI by distilled water solution without any additives, which confirms its strong wettability by oil;

- SI tests with nanoparticles in the carbonate core yielded an improvement in oil recovery (compared to the base fluid with no nanoparticles) from zero to 8.89% of OOIP;
- SI tests with nanoparticles in the sandstone cores favorably altered the wettability of the rock surface and enhanced oil recovery from 20.74, 4.3, and 3.5% to 36.2, 17.57, and 20.68% of OOIP respectively for cores A, B, and C;
- The power of nanoparticles to decrease surface tension and wettability alteration is the most important vague question dealt with herein. By the investigation of relative permeability curves, it was completely clear that by adding ZnO nanoparticles crossover point of curve shifted to right, which meant wettability altered to water-wet for both carbonate and sandstone cores;
- In the presence of ZnO nanoparticles, the delay time of oil recoveries was reduced, which meant that the time of reaching critical water saturation was decreased and the starting time of oil recovery took place in a shorter period of time;
- The experimental results showed that ZnO nanoparticles had the ability of viscosity reduction and wettability alteration. Thus, by considering these two important features, ZnO nanoparticles could be applied to EOR thermal processes and wettability alteration mechanisms to enhance oil recovery.

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Nomenclature

C_l	: Phase compressibility
C_r	: Rock compressibility
g	: Gravity acceleration constant
K	: Absolute (base) permeability
$k_{r,l}$: Relative phase permeability
l	: Phase index for either oil or water
P_c	: Capillary pressure
P_l	: Phase pressure
P_{nW}	: Capillary pressure of non-wetting phase
P_W	: Capillary pressure of wetting phase
q_l	: Phase mass source
S	: Saturation
S_l	: Phase saturation
$T_{i,j}$: Transmissibility between cells
V_i	: Bulk volume of a grid cell
w	: Centrifuge rotation speed
x	: Distance from centrifuge rotation axis

Z	: Elevation distance
Greek	
\emptyset	: Porosity
Φ_l	: Phase flow potential
ρ_l	: Phase mass density
μ_l	: Phase viscosity
v_l	: Darcy average velocity

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