# Wettability Alteration of Oil- Wet and Water-Wet of Iranian Heavy Oil Reservoir by CuO Nanoparticles

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ABSTRACT: The petroleum industry requires the best materials to reverse the rock wettability to water-wet state which give significantly improved oil recovery. Nanoparticles is suggested as enhanced oil recovery potential agents to decrease viscosity and alter the wettability of reservoir towards more water-wet. This study provides new insights into CuO nanoparticles effects on wettability alteration of different core types (sandstone and carbonate) and increases oil recovery. The first objective of this research is to determine the potential of CuO nanoparticles to imbibe through spontaneous imbibition cell and raise the oil recovery experimentally. The second goal is to prove that CuO nanoparticles have the ability to alter wettability of sandstone and carbonate cores quantitatively. Laboratory tests were conducted in two experiments on four cylindrical core samples taken from Iranian heavy oil reservoir. In the first experiment, core samples were saturated by crude oil and in the second test, nanoparticles were flooded, and then saturated by crude oil, immersed in distilled water and the amount of recovery was monitored during 30 days. Experimental results show that oil recoveries for sandstone cores change from 20.74, 4.3 and 3.5% of OOIP without nanoparticles to 31.77, 17.3 and 14.42% of OOIP with CuO nanoparticles, respectively. The oil recoveries for carbonate core vary from zero without nanoparticles to 6.92% of OOIP with nanoparticles, respectively. By investigation of relative permeability curve, the crossover-point is shifted to the right by adding CuO nanoparticles which means nanoparticles succeed in altering the wettability to more water- wet for sandstone and even carbonate cores.

KEYWORDS: Nano Particles; Carbonate reservoir; Wettability alteration; Relative permeability.

## INTRODUCTION

When petroleum companies abandon an oil well, more than half the reservoir's oil is usually left behind as too difficult to recover. Whereas, much of the residual oil can be recovered. Oil to be recovered is confined in tiny pores within rock, often sandstone. Oil recovery becomes more complicated when it copes with carbonate reservoirs.

Carbonate reservoirs are categorized as oil-wet with low permeability. Hence, applying some technologies to decrease heavy oil viscosity and alter wettability to more water wet state is one of recent important issues[1]. Nanotechnology provides essential improvement potentials for development of both conventional energy and renewable

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energy sources. Breakthroughs in nanotechnology open up the possibility of moving beyond our current alternatives for energy supply by introducing more efficient, inexpensive and environmentally sound technologies [2-4]. Nanoparticles are able to travel long distances in the porous reservoir. Smart particles open for detailed control of benefits such as viscosity reduction, wettability alternation and interfacial tension reduction of oil and water [1].

When nanoparticles enhanced water reaches a tunnel opening, it will accelerate faster than the particles behind to accumulate and plug the tunnel entrance and ultimately, sealing the tunnel. This forces the following water to take other paths through the rock's pores and passages, which is forced out with water flow. The result is that more oil extracted from the production well and higher profits for the petroleum companies [5]. The probable mechanism of four different hydrophilic silica nanoparticles are studied to disperse in porous media, expel oil and enhance oil recovery through flooding method in Egyptian sandstone formation. The results show that nanoparticles are the main reason of increased oil recovery from 36 to 65% of the IOIP [6]. The reversible and irreversible adsorption are the main nanoparticles dispersion mechanism through porous media. Nanoparticles dispersion mechanism depends on several parameters such as nanoparticle type, the condition of dispersion, injected nanoparticles concentration, porous media and flow rate [7].

The transportation and distribution mechanism of Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, and SiO<sub>2</sub> metal oxide nanoparticles are studied through porous media. It is shown that nanoparticles cause higher oil mobility and higher oil recovery [8].

In some researches it has been reported that heavy oil viscosity is further reduced when metal is added [9, 10]. The mechanism of activity, selectivity and stability of nanoparticles in dehydrogenation of cyclohexane and methyl cyclohexane process are studied [11]. It has been also shown that the micron sized iron particles influence on heavy oil viscosity without heating process [12, 13]. Ionic liquid decreases viscosity, average molecular weight and asphaltene content of the heavy oil [14]. The weak bond formation between the ionic liquids and organic sulfur in heavy oil is the main cause of viscosity reduction [15]. By inserting solid particles such as copper

and zinc, thermal conductivity of liquid such as water can be improved. The main reason of this event is related to the nanoparticles effect on transport properties and heat transfer ability [16].

The high surface-to-volume ratio of nano fluids lead to improve thermal properties. The surface-to-volume ratio of nanoparticles may be 1000 times greater than micro particles. A variety particle sizes and types tested to find the best particle suited for plugging the rock pores, which turned out to be elastic nanoparticles made of polymer threads that retract into coils [17].

Nano fluid distributes through porous media by several mechanisms. It is found that the wettability of rock may be changed by absorption of nanoparticles on rock surface. It is reported that absorption of nano silica particle concentration on the rock surface decreases silica particle concentration in the reservoir. Van der Waals attraction between the silica particle and the pore wall is the main reason of detaching on it. This is what causes the attractive forces between nanoparticles atoms and the pore wall [18]. By intensifying the particles repulsive forces, the stability and aggregation of suspensions are avoided [19].

Different compounds including alumina oxide and iron oxide alter the wettability to more water wet through changing of contact angle of the fluids and phase behavior. SiO<sub>2</sub> nanoparticles is applied to decrease the hysteresis behavior of both oil and water phases and the hysteretic behavior of relative permeability curves [20]. The potential enhanced oil recovery of nano fluids, 4-5% increasing recovery, is compared to brine in the core flooding procedure. The experimental results show that the IFT between water phase and oil phase can be reduced by nano fluids and the wettability of solid surface alters to more water wet. It shows that releasing oil drops by increasing capillary pressure is completely obvious [21].

The hydrophilic or hydrophobic monolayer role of Silica nanoparticles fluid in water-wet sandstone in the pore spaces is investigated. It is found that adsorption of SNPs can help to alter reservoir wettability [22].

The capability of ferrofliud on overcoming capillary pressure, expel trapped oil and finally enhance oil recovery are investigated numerically. Nanoparticle-based EOR application in wettability alteration, oil viscosity reduction of foam or emulsions stabilization and interfacial tension decrease are discussed. It is suggested

that nanoparticles can be used as inhibiting hydrate and wax deposition [23]. The potential of ZnO nanoparticles is investigated to alter the wettability for both sandstone and carbonate cores in heavy oil reservoir. It is completely obvious from relative permeability curves, ZnO nanoparticles shift the crossover point, critical saturation, end point of water and end point of oil to the rightward which means that the wettability alters to more water wet area [24].

In this study, the influence of CuO nanoparticles on wettability alteration of oil-wet carbonate core, waterwet sandstone core and enhancing oil recovery rates experimentally and numerically are assessed. Experimental results show the noticeable influence of CuO nanoparticles effect on improved oil recovery. Numerical results provide the reasonable proof to alter the wettability using CuO nanoparticles by investigation of relative permeability curves.

## **EXPERIMENTAL SECTION**

Laboratory tests were conducted on four cylindrical core samples taken from real Iranian heavy oil reservoir. Three cores were sandstone and one core was carbonate (limestone). To verify the wettability characteristics of all four cores, core analysis and contact angle method were conducted. It was identified 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 ethanol 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 samples are measured as shown in Table 1.

The oil used in this study was taken from Iranian heavy oil fields. Its properties are given in Table 2. CuO nanoparticles were bought from Notrino Company with specifications which show in Table 3 are used.

Selection of the best concentration of nanoparticles is one of the challenging issues. Fig. 1 shows the effect of different concentrations of CuO nanoparticles on heavy oil viscosity at different temperatures. As shown in Fig. 1, by increasing temperature, the viscosity decreases. Because high temperature improves the physical properties of heavy oil. It seems that by adding nanoparticles and its concentration reduction, viscosity reduction happens more. It is presumed that the main

reason of this viscosity reduction can be related to the catalytic characteristics of nanoparticles on breaking the carbon and sulfur bonds in a chemical reaction. The most viscosity reduction happens at the lowest concentration of nanoparticles (0.2-0.5% wt). It is widely assumed that micelle such as cluster forms in the asphaltene molecules in oil agglomerate. By breaking these agglomerates apart, viscosity will be reduced. Nanoparticles are identified as surface active agent which have larger contact area with oil phase in comparison with other scale. Hence, nanoparticles stick between the oil layers and lead to move fluid layers on each other easily. The exothermic chemical reaction between nanoparticles and oil phase provides the required energy to break big molecules bonds, like asphaltene. Therefore, it seems that decreasing nano concentration has an essential role on increasing breaking down the asphaltene agglomerates and deeper viscosity reduction. Therefore, heavy oil samples crack to the lighter components. This result is similar to the obtained results of [5-20]. Finally as shown in Fig. 1, 0.2wt% of CuO nanoparticles concentration is chosen as selective concentration.

## Experimental procedure

Spontaneous Imbibition (SI) test without nanoparticles

The procedure for SI test without nanoparticles is as follows; a) core samples were saturated in saturating cell with heavy oil for about four weeks, b) removed from saturating cell and cleaned excess oil, c) weighted the oil saturated cores for calculation of the oil volume in the core, d) immersed in Amott- cell which was filled with distilled water through to the special level on the burette. e) monitored the volume of expelled oil for 30 days at 50°C and determined the recovered oil as percentage of Original Oil in Place (OOIP) versus time. In all experiments, the initial water saturation was zero.

# SI test with nanoparticles

Water was selected as base fluid. By using ultrasonic device, the homogeneous nanoparticles solution was made. But, keeping the homogeneous solution during the experiment is one of the most important challenging issues in this section. Nanoparticles tend to be disposed after around 7h. There have been three methods to study the effect of nanoparticles; a) saturate the clean cores

Table 1: Properties of the cores used in experiments.

Core name	Туре	Absolute permeability (md)	Porosity (%)	Length (cm)
A	Sandstone	122.36	22.705	5.910
В	Sandstone	107.44	22.579	7.138
С	Carbonate	0.309	11.539	7.362
D	Sandstone	6.038	26.124	6.390

Table 2: Properties of the oil used.

Name	Oil density (API)	Dead oil viscosity (at 7.158 °C) (cp)	Compressibility (psi <sup>-1</sup> )	Thermal expansion factor (from 4 to 12.421 °C) (°C -1)
Kohe Mond	13	16000	4.67× 10⁻⁶	4.00 × 10 <sup>-4</sup>

Table 3: Specifications of CuO nanoparticles used.

Particle type	Formula	Form	Purity	Absolute particle size	Specific surface area	Appearance
Copper oxide	CuO	Nano powder	99%	<50 nm	>60 m <sup>2</sup> /g	Black powder

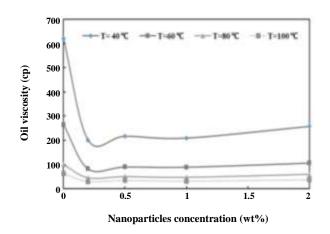


Fig. 1: The effect of different concentrations of CuO nanoparticles on heavy oil viscosity.

with oil and nanoparticles, b) add nanoparticles to distilled water inside the SI cell, c) flood the cores with nanoparticles. By using the first method there is no any evidence to ensure that the nanoparticles are able to fill porous media or not. The problem of second one is the time of experiment. The SI test takes 30 days therefore, it is necessary to pay attention to avoid disposing nanoparticles and at least there has been 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 studying materials such as surfactant, nanoparticles or some other disposed materials. For assuring that the nanoparticles

affect on cores directly, after washing the cores and vacuuming the core holder, they are flooding with nanoparticles around 3h. In the middle of flooding, the nanoparticles accumulator vibrates and monitors the outlet of the core holder is clean. Then they dry for about 48h to remove water. Finally the cores are ready for heavy oil saturation. The rest of steps are the same as SI test without nanoparticles.

# RESULTS AND DISCUSSION

The oil recovery percentages for four core samples without nanoparticles during 30 days are shown in Fig. 2(a). The final oil recoveries are 20.74, 4.3 and 3.5% of OOIP for A, B and D sandstone cores, respectively and zero% of OOIP for carbonate one (C). Fig. 2(b) shows SI Amott cell for four cores in the last day. Generally in oil-wet core (core C), the non-wetting phase has affinity toward it. Capillary pressure is negative and there is no any response to SI without any additives. Hence, the core does not let to imbibe water and oil recovery was zero% of OOIP during 30 days. There is no initial water inside the sandstone cores. Therefore, in the early days the water moves to the core and the water saturation is increased up to critical water saturation. After this point, when water saturation is present, oil production starts. In water-wet core A, the wetting phase has affinity toward it. Accordingly, after 5 day oil recovery starts. The wettability influences the oil recovery through capillary pressure and

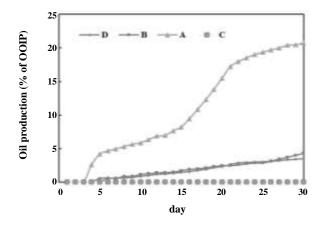




Fig. 2: (a) The oil recovery percentages for four core samples during 30 days without any nanoparticles (b) Amott cell in the last day.

relative permeability. In water- wet core A, oil is generally displaced with water more efficiently than intermediate water-wet and oil-wet cores. In water-wet rocks, oil does not imbibe unless the capillary pressure exceeds the entry pressure. Therefore, the water displacement is more favorable in core A and the oil recovery is greater (20.74% of OOIP). Intermediate-wet core B and D have neither a strong affinity toward water nor oil. Thus, it takes more time to let water imbibe and saturation reaches to critical water saturation. For core B and D, oil recovery starts after 6 and 4 days, respectively. By passing the time, the wetting phase occupies the small pore volume and influences the flow paths, capillary pressure and relative permeability. As water imbibition increases, capillary pressure raises. Thus, the wettability of intermediate core is critical to determine recovery. Ultimately oil recovery is 4.3 and 3.5% of OOIP for core B and D, respectively which are lower than waterwet core A.

The oil recovery percentages for four core samples with CuO nanoparticles during 30 days are illustrated in Fig. 3(a) and final day of SI Amott cell system shows in Fig. 3(b). As shown in Fig. 3(a), the final oil recoveries are 31.77, 17.3 and 14.24% of OOIP for A, B and D (sandstone cores), respectively and 6.92% of OOIP for carbonate one (C). By using CuO nanoparticles, the appropriate time needs to reach to critical water saturation decreases and initial delay time for starting oil recovery reduces. After 3, 4, 2 and 10 days for core A, B, D and C expelling oil starts, respectively. All experimental conditions are the same as previous test. Thus, it is assumed that wettability alteration by flooding of CuO nanoparticles is the only reason which causes to decrease the time. Core A is water- wet and has suitable porosity to let nanoparticles to stick on the pores and good permeability let them diffuse easily during nano flooding. All these positive parameters (permeability, porosity and length) help more to alter wettability to more water- wet and final oil recovery is greater than other cores (31.77% of OOIP). This condition is valid for core B and D. Suitable porosity of both cores help nanoparticles to occupy more pore volume and wettability alteration of cores are obvious through SI mechanism. Final oil recoveries are 17.3 and 14.24% of OOIP for core B and D, respectively. As shown in Fig. 3(a), wettability alteration of oil- wet carbonate core C to more water- wet is completely obvious. Despite low permeability, flooding of CuO nanoparticles helps to decrease oil- wet wettability. This event causes to have oil recovery 4.92% of OOIP whereas oil recovery is zero % in without nanoparticles condition. The experimental results show that CuO nanoparticles appeare to have an important role to improve oil recovery for intermediate water-wet and preferential oil-wet rocks. It causes the affinity of cores towards water- wetness increases and ultimate oil recovery raises.

By comparison between the results of all experiments, it is completely obvious that by using nanoparticles, oil recovery is increased. There has been one vague question that among viscosity reduction and wettability alteration by adding CuO nanoparticles, which one has the sensible and important effect on improved oil recovery? Investigation of relative permeability curves is a reasonable

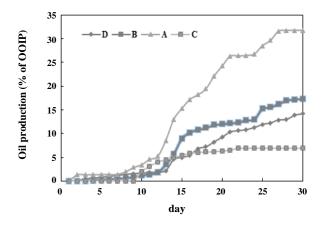




Fig. 3: (a) The oil recovery percentages for four core samples during 30 days with CuO nanoparticles (b) Amott cell in the last day.

evidence to jump to conclusion. Because relative permeability curve shifting by temperature changes is inconsiderable. Therefore, the main factor which has noticeable influence on relative permeability curve characteristics is wettability alteration. As another aspect, by flooding of nanoparticles into cores before saturation by crude oil, we can assure that wettability alteration is the main reason of these oil recoveries in comparison with viscosity reduction possibilities. For proving this claim, Burdin correlation is selected to study the numerical modeling of relative permeability curves of oil and water for each core.

The mathematical formulation and solution procedure use in the modeling is briefly outlined. Mass conservation of a flowing phase is given by the equation:

$$\frac{\mathrm{d}\int_{0}^{\Omega}\phi\rho_{1}\mathrm{S}_{1}\mathrm{d}\Omega}{\mathrm{d}t} + \int_{0}^{\Gamma}\rho_{1}\mathrm{v}_{1}\mathrm{d}\Gamma = \int_{0}^{\Omega}\mathrm{q}_{1}\mathrm{d}\Omega \tag{1}$$

The porosity and mass densities are given by:

$$\phi = \phi_{\text{init}} \left( 1 + c_r \left( P_o - P_{\text{init}} \right) \right) \tag{2}$$

$$\rho_{l} = \rho_{l,init} \left( 1 + c_{l} \left( P_{o} - P_{init} \right) \right) \tag{3}$$

Darcy's law provide the average flow velocity in a porous medium:

$$v_l - K \frac{k_{r,l}}{\mu_l} \nabla \phi_l \tag{4}$$

The gradient of the flow potential is given by:

$$\nabla \Phi_1 = \nabla P_1 + \rho_1 \left( g z - \frac{w^2}{2} x^2 \right)$$
 (5)

Here, z is the elevation and x is the distance from the axis of rotation. Gravity only applies for a vertically oriented core plug, in which case there is not centrifugal acceleration. Saturations and pressures are related by:

$$S_O + S_W = 1 \tag{6}$$

$$P_C = P_{nW} - P_W \tag{7}$$

$$S_{W}^{*} = \frac{S_{W} - S_{Wi}}{1 - S_{Wi}} \tag{8}$$

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

$$r_{i,l}^{n+l} = V_i \phi_i \rho_{i,l}^n \left( \frac{S_{i,l}^{n+l} + S_{i,l}^n}{\Delta t} \right) + \tag{9}$$

$$\textstyle \sum_{j \in M_i}^{\infty} \lambda_{up,l}^{n+1} T_{i,j} \Delta \Phi_{i,l} - Q_{i,l}^{n+l}$$

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

$$\Delta\Phi_{i,l} = \Delta P_l^{n+l} + \rho_l^{-n} \left( g\Delta z - w^2 x \Delta x \right) \tag{10} \label{eq:deltaplace}$$

The phase mass density is the simple arithmetic average of the densities in the two adjacent cells, and is treated explicitly. The upstream mobility;

$$\lambda_{up,l} = \rho_l^n \frac{k_{r,i}^{n+1}}{\mu_l} \tag{11}$$

is evaluated in the cell, which is in turn taken from the sign of the potential difference between cells i and j. 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:

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

The cross sectional area is given by:

$$A = \pi \frac{d^2}{4} \tag{13}$$

The initial pressure is hydrostatic for the specified mobile phase:

$$P_{l} = P_{init} + g \rho_{l} \left( z - z_{ref} \right)$$
 (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 normal flow, except for a half-length transmissibility:

$$T_{f} = \frac{AK_{f}}{\Delta X_{f}} \tag{15}$$

Included are 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.

There are three types of possible boundary conditions; a) fixed boundary pressure, b) constant injection rate, c) specified total production rate. For inlets, the phase mobility used is the total phase mobility:

$$\lambda_{\text{total}} = \lambda_{\text{w}} + \lambda_{\text{o}} \tag{16}$$

The quantities are all evaluated on the inside of the core. 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:

$$q_{l} = q_{total} \frac{\lambda_{l}}{\lambda_{w} + \lambda_{o}}$$
 (17)

Boundary face pressures are calculated from 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 are 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. Relative permeability can be described with functional relationships, in addition to tabular formats. Such as other numeric minimization algorithms, the Levenberg-Marquardt algorithm is an iterative procedure. To start a minimization by initial guess of Swi and Sor. 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:

$$S = \frac{S_{W} - S_{Wi}}{1 - S_{ro} - S_{Wi}}$$
 (18)

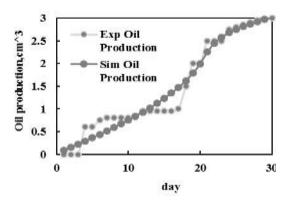
Burdine correlation is as below:

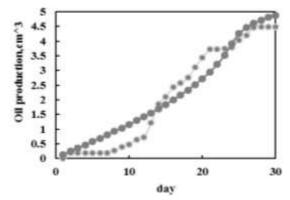
$$k_{rW} = k_{rW}^{o} \left( S^{\frac{2+3\lambda}{\lambda}} \right)$$
 (19)

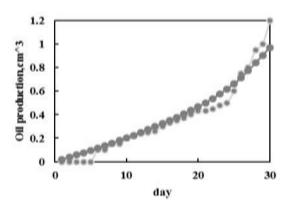
$$k_{rO} = k_{rO}^{o} (1-S)^{2} (1-(1-S))^{\frac{2+\lambda}{\lambda}}$$
 (20)

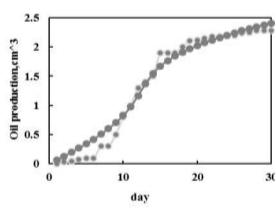
As shown in Fig. 4(a), there is a reasonable matching between experimental and simulated oil production rate for all cores without nanoparticles condition. As shown in Fig. 4(b), the matching between experimental and simulated oil production rate are also valid with CuO nanoparticles condition for all carbonate and sandstone cores, respectively. There is just one except related to the carbonate core without nanoparticles condition. Due to reasonable matching in nanoparticles section, it can be ignored that differences. Generally, by these matching, Burdine correlation can be chosen as a base correlation for relative permeability curves.

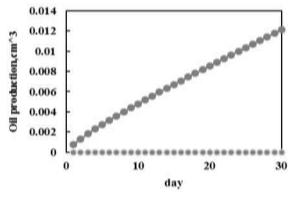
Relative permeability curves for core A, B, C and D are shown in Fig. 5 as without nanoparticles and with CuO nanoparticles conditions. Table. 4 and 5 show the characteristics of Fig. 5 (relative permeability curves)

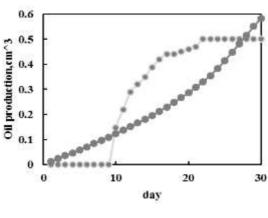


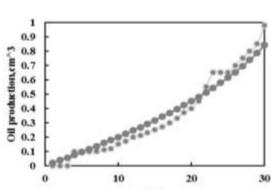












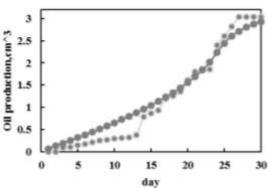


Fig. 4: The matching between experimental and simulated oil production rate (a) without CuO nanoparticles (b) with CuO nanoparticles for all cores.

Table 4: The characteristics of relative permeability curves in without nanoparticles condition.

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

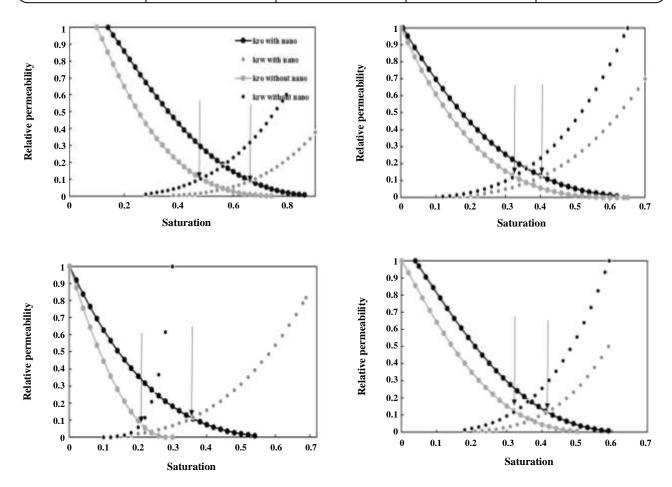


Fig. 5: Relative permeability curves in without nanoparticles and with CuO nanoparticles for core A, B, C and D.

without and with nanoparticles conditions, respectively. By comparison of Table 4 and 5 results, it concludes that the crossover point of core A changes from 0.47 to 0.66, critical saturation changes from 0.28 to 0.38, end points of water changes from 0.79 to 0.99 and end points of oil changes from 0.72 to 0.86. These rightward shifting of crossover point, critical saturation and endpoints of water and oil relative permeability curve of water-wet core A are completely obvious by adding CuO nanoparticles. Therefore, it is a good proof that the main reason of

improved oil recovery is wettability alteration. It seems that this condition is valid for intermediate water-wet cores. The crossover point changes from 0.36 and 0.32 to 0.4 and 0.41, the critical saturation changes from 0.12 and 0.17 to 0.18 and 0.21, end points of water changes from 0.7 and 0.65 to 0.98 and 0.7 and end points of oil changes from 0.62 and 0.57 to 0.62 and 0.6 for core B and D, respectively. Hence, wettability alteration is a reasonable cause for increasing oil recovery of intermediate waterwet cores. The interesting finding is about oil-wet core C,

Core name Crossover point Critical saturation End points of water End points of oil 0.38 Α 0.66 0.99 0.86 B 0.4 0.18 0.78 0.62 C 0.14 0.36 0.68 0.54 D 0.41 0.21 0.7 0.6

Table 5: The characteristics of relative permeability curves in with CuO nanoparticles condition.

because the crossover point changes from 0.21 to 0.36, the critical saturation changes from 0.1 to 0.14, end points of water changes from 0.3 to 0.68 and end points of oil changes from 0.3 to 0.54. It is definitely clear that by adding CuO nanoparticles, wettability alteration happens and causes to expel oil. Finally as shown in Fig. 5, this rightward shifting in crossover point, critical saturation and end points for all (carbonate and sandstone) cores are the clear evidence that wettability alters to more water-wet by adding CuO nanoparticles which helps to enhance oil recovery.

#### CONCLUSIONS

This study shows the potential of CuO nanoparticles to alter wettability and expel oil through SI process. By adding nanoparticles, viscosity reduction happens more. Whereas the viscosity reduces with decreasing nano concentration. The catalytic chemical reaction between nanoparticles and carbon and sulfur bonds to break molecular bond is assumed the main reason of viscosity reduction. The most viscosity reduction happens at the lowest concentration of nanoparticles (0.2-0.5% wt). Flooding of nanoparticles is a useful method to study their effect on wettability alteration. CuO nanoparticles which alter the wettability toward more water-wet regime, give higher recovery rates. As the wettability alteration increases, the oil recovery rate raises. SI test in carbonate core yields an improvement in oil recovery from zero of OOIP% without nanoparticles to 6.92% of OOIP for CuO nanoparticles, respectively. Also SI test with nanoparticles in sandstone cores favorably alters the rock surface wettability and enhanced oil recovery from 20.74, 4.3 and 3.5% of OOIP without nanoparticles to 31.77, 17.3 and 14.24% of OOIP for CuO nanoparticles, respectively. By investigation of relative permeability curve, it is completely clear that by adding CuO nanoparticles, crossover point of curve shifts to right which means the main reason of wettability alteration

to more water- wet for both carbonate and sandstone cores is nanoparticles rather than other possibilities like viscosity reduction. Totally, experimental results show CuO nanoparticles have the ability of viscosity reduction and wettability alteration. Therefore, by considering these two important features, CuO nanoparticles can be applied thermal processes and wettability mechanisms to enhance oil recovery.

### **Nomenclature**

Nomenciature	
ф	Porosity
1	Phase index, can be oil or water
$S_1$	Phase saturation
$\rho_l$	Phase mass density
$\nu_l$	Darcy average velocity
$q_l$	Phase mass source
$C_{r}$	Rock compressibility
$C_l$	Phase compressibility
K	Absolute (base) permeability
$K_{r,l}$	Relative phase permeability
$\mu_{l}$	Phase viscosity
$\Phi_l$	Phase flow potential
$P_l$	Phase pressure
$P_c$	Capillary pressure
$P_{W}$	Capillary pressure of wetting phase
$P_{n,W} \\$	Capillary pressure of non-wetting phase
g	Gravity acceleration constant
Z	Elevation distance
w	Centrifuge rotation speed
X	Distance from centrifuge rotation axis
$V_{i}$	Bulk volume of a grid cell
$S_{\mathrm{wi}}$	Initial water saturation
$S_{\rm ro}$	Residual oil saturation
$T_{i,j} \\$	Transmissibility between cells
t	Time
λ	Mobility
d	Diameter
A	Surface area

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