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COPPER OXIDE NANO-FLUID STABILIZED BY IONIC LIQUID FOR ENHANCING THERMAL CONDUCTIVITY OF RESERVOIR FORMATION: APPLICABLE FOR THERMAL ENHANCED OIL RECOVERY PROCESSES

Article Highlights

- Three conventional surfactants and one ionic liquid type are used as stabilizing agents
- 1-dodecyl-3-methylimidazolium chloride ([C_{12}mim] [Cl]) was used as a new kind of surfactant
- Thermal conductivity of base fluid was increased up to 48% using nanoparticles of copper oxide

Abstract

Since oil reservoirs are limited and energy demand is increasing, seeking for high efficient EOR processes or enhancing the efficiency of current proposed EOR methods for producing trapped oil from reservoirs are highly investigated. As a way out, it is possible to couple the EOR and nanotechnology to utilize the efficiency of both methods together. Regarding this possibility, in the present study, in the first stage of investigation stable and uniform water-based solution of nano-sized particles of copper oxide with different concentrations (0.01-0.05 M) were prepared and then injected into the core samples. In the first stage, the effects of different surfactants with respect to their concentrations were investigated. Then, different scenarios of using nano-fluid as a thermal conductivity modifier were examined. The obtained results clearly demonstrate that changing concentration of nanoparticles of copper oxide from 0.01 to 0.05 M is able to enhance the thermal conductivity of rocks from 27 to 48% compared with the thermal conductivity of dry core.

Keywords: thermal conductivity, nano-fluid, copper oxide, enhanced oil recovery, ionic liquids.

A considerable amount of crude oil remains unrecoverable underground after the primary and secondary oil recovery processes, which is the target of more oil recovery as the demand for energy increases rapidly [1]. These techniques are gaining more momentum as the giant oil reserves are being rapidly depleted and the search for new oil reserves is becoming more expensive [2]. Hence, over the past decades, many research studies have examined methods called enhanced oil recovery (EOR) to find the most suitable methods to extract larger amount of trapped oil from the oil reservoirs [3-10]. Among the different EOR methods, the thermal method is one of the most favorable methods examined over the past three decades due to the several advantages. Thermal EOR methods are generally applicable to heavy, viscous crudes, and involve the introduction of thermal energy or heat into the reservoir to raise the temperature of the oil and reduce its viscosity. However, the main limitations of thermal methods are the low thermal conductivity of the reservoir rock and consequent heat loss during the thermal process affecting low reservoir area by the heat transfer process [11,12]. For example, Kiasari *et al.* [13] have reported that as the thermal conductivity of the rock reduced, less heat was conducted into farther distances from steam chamber in the core.

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Generally, it can be concluded that in the case of thermal EOR processes, it is well established that the effective thermal conductivity (ETC) not only has a direct effect on the efficiency of the thermal EOR processes, but also measuring and estimation of ETC of the dry or fluid-saturated porous materials are essential for several other applications [14-31].

In other words, accurate knowledge of ways that can enhance the ETC for certain purposes is crucial, since heat transfer and temperature distributions resulting from heat conduction in the solid matrix are the basis of most of the above-mentioned applications.

In this regard, it was a great interest of many researchers in the world to measure the experimental value of ETC and investigate the effect of different parameters, which can modify this parameter toward a desired status [32-38]. As a way out, there are two options to eliminate these limitations: a) injecting the steam or other heat transferring fluid into a reservoir with shallow depth and thick pay zone or b) using method that it is able to deliver the heat into the larger area of reservoir [38]. Among these, since the first one seems applicable, several methods are proposed to modify this parameter, especially the injection of nanoparticles that introduce unique features.

During the past ten years, nanotechnology has paved its way as a novel technique that can contribute to more efficient, less expensive, and more environmentally friendly technologies through different industries including oil and gas industries [39,43]. For example, Hascakir *et al.* [10] added three different iron powders including iron (Fe), ferric oxide (Fe_2O_3), and ferric chloride ($FeCl_3$) into the heavy crude oil. They reported that not only was iron oxide able to increase the thermal conductivities, but it was also able to assist in decreasing the percentage of polar component in the oil, resulting in a reduction in the viscosity of the oil caused by hydrogen bonding reduction, consequently enhancing the oil recovery.

In addition, Onyekonwu *et al.* [41] reported that it is possible to alter the wettability of rock surfaces using three kinds of polysilicon nano-fluids including lipophobic and hydrophilic PSNP (LHPN), hydrophobic and lipophilic PSNP (HLPN) and neutrally wet PSNP (NWPN). They claimed that NWPN and HLPN introduced good capability to enhance oil recovery by two different mechanisms, namely alteration of rock wettability and reduction of interfacial tension [41].

Furthermore, Roustaei *et al.* [43] have reported that using lipophilic polysilicon and naturally wet polysilicon (NWP) nanoparticles led to a change toward less water-wet conditions and a drastic decrease in oil-water interfacial tension from 26.3 to 1.75 mN/m and 2.55 mN/m, respectively. Moreover, they reported that oil recoveries increased by 32.2 and 28.57%, respectively, when 4 g/L HLP and NWP nano-fluids were injected into the core samples [43].

A point worth mentioning is that although the nano-fluids are greatly used in different areas of oil and gas industries, especially EOR methods as aforementioned [40-47], no application of nano-fluids for thermal EOR processes has yet been reported.

Due to this shortcoming and the possibility of utilizing this technology in this area, in the current work metal-based nano-fluid of copper oxide has been examined to if it is possible to enhance the thermal conductivity of the rocks or not. The other novelty of this work is the application of new kind of surfactants, namely ionic liquid (IL)-based surfactant utilized for the first time, to the best knowledge of the authors, for stabilizing the nano-fluid solution. The idea behind this novelty was raised from the recent work performed by Hezave *et al.* [48-50], which introduced the ILs as a new kind of surfactants for oil industries with special focus on EOR purposes.

In brief, the applications of ILs have been crucially increased due to their unique physicochemical properties such as high thermal stability, large liquids range, high ionic conductivity, high solvating capacity, negligible vapor pressure, and non-flammability which make them a very good candidate to replace by the conventional solvents in the different fields of chemical engineering industries [48-50].

Based on these unique advantages, the effectiveness of using copper oxide nanoparticles to enhance the thermal conductivity of rocks was investigated. Thus, besides the effect of 1-dodecyl-3-methylimidazolium chloride [C_{12}mim] [Cl] on the stability of the nano-fluid solution, the effects of different parameters including nanoparticles concentration in the range of 0.01-0.05 M were investigated.

EXPERIMENTAL

Materials

Copper oxide particles were supplied from Merck, Germany with purity of >99.99%. The ionic liquid under the name of 1-dodecyl-3-methylimidazolium chloride ([C_{12}mim] [Cl]) was synthesized as previously described [50]. In brief, 1-methylimidazole, 1-chlorododecyl and diethyl ether were supplied from Merck/Fluka and used without any further purification. According to the previously reported procedure the IL 1-dodecyl-3-methylimidazolium chloride ([C_{12}mim] [Cl]) was synthesized by reacting 1-methylimidazolium with excess amount of the 1-chlorododecane without any additional solvent in a round bottomed flask fitted with a reflux condenser (heating and stirring at 70 °C for 48-72 h). The resulting viscous liquid was cooled to room temperature and was washed by diethyl ether. After drying overnight at 100 °C, the purity of the products was assessed by HNMR. In addition, the used cores in this investigation were prepared from outcrop rocks of southern Iran cores for core-flooding tests were prepared from samples in a similar formation. The majority content of the rocks was recognized to be dolomite (see Table 1).

Table 1. Properties of the used cores; length: 3.0 cm, diameter: 7.0 cm

No	Porosity (φ)	Permeability, mD
1	19.5	101.1
2	20.6	117.7
3	16.3	141.0
4	20.4	138.8
5	18.2	48.6

Preparation of nano-fluid

In the first stage of this study, copper oxide nano-fluids with different concentrations were prepared to find the effect of copper oxide nanoparticles on the thermal properties of the core. It is worth mentioning that two different base fluids were used to prepare the nano-fluid – water and ethylene glycol. In this way, ionic liquid as a surface-active agent (surfactant) was used to stabilize the nanoparticles of copper oxide in the solution by modifying the scattering factor. In fact, a layer that was coated around the nanoparticles with the surfactant caused electrostatic repulsion between double layer particles, so the nanoparticles were dispersed into the base fluid. Because of this phenomenon, adhesion and aggregation of particles was prevented.

IL was used as a surfactant since it has been proven that this kind of surfactant is able to tolerate harsh temperature conditions without any breakdown, decomposition and degradation at high temperatures, while common surfactants such as C_{16}TAB corrupted and lost their functionality at temperatures above 40 °C. In the light of above facts, IL seems a suitable candidate for stabilizing nano-fluids for thermal applications. After finding the optimum surfactant concentration, optimum pH and exposure time solution under ultrasonic irradiation, consistent nano-fluid copper oxide was synthesized. Finally, the stability of prepared nano-fluids was examined by performing sedimentation tests for at least one month to investigate the possible aggregation of the particles [51]. To investigate the effects of other surfactants in thermal conductivity of core, CuO nano-fluids were prepared with different kinds of surfactants and then injected to core samples. The C_{16}TAB, SDS and PVP were used for this purpose. After that, the CuO nano-fluids with several kinds of surfactants (PVP, SDS, C_{16}TAB and IL) at different concentrations were synthesized and then their stability and thermal influences were compared to each other. Moreover, the experiments were designed in way that allowed investigating the effects of base fluids, including water and ethylene glycol, in preparing the nano-fluid as the nano-fluid IL was used as the stabilizer.

Thermal conductivity measurement

After measuring the porosity (He-Porosimeter 32351, Vinci, France) and permeability (Coreval700 32372, Vinci, France) of cores, In order to measure the thermal conductivity of rocks with different status (dry, water-saturated and nano-fluid saturated) a homemade thermal conductivity measurement apparatus worked based on the steady state method was used (Figure 1). This apparatus designed in a way that allowed measuring the thermal conductivity at ambient pressure and elevated temperature up to 180 °C. A brief description of the used apparatus is as follows. At first, the core was placed into the core holder made of polytetrafluoroethylene (PTFE). The core holder consisted of three different sections demonstrated in Figure 1. As it is clear in this figure, there is a section made of copper, which was used as a reference for calculation of heat transmission. Further, the apparatus was equipped with four different temperature sensors controlled by PID protocol with accuracy of 0.1 °C to measure the temperature through the apparatus (reference section and core plug). In more detail, these four sensors as shown in Figure 1 were used to measure the temperature of beginning and end of reference copper and core plug. The required heat in this apparatus was generated using three electric heaters symmetrically placed before the reference section made of copper. Since there were two different kinds of materials (copper as a reference section and core plug as the under investigation section) that are contacted to each other, contact resistance had a significant role, which can face the experiments with large order of error. To overcome this problem, a silicon thermal compound slot was used to minimize the resistance between two different sections. The effectiveness of the used silicon thermal compound slot was evaluated by measuring the temperature of two sides. In addition, con-

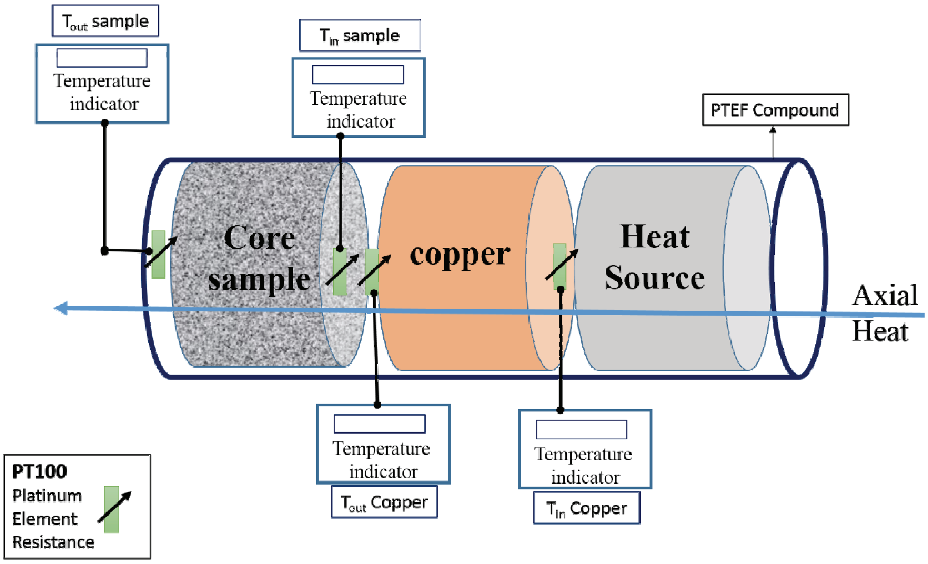

Figure 1. Thermal conductivity measurement apparatus.

struction of the core holder using PTFE minimized the heat loss through the system by reducing the convective heat transfer. It should be noted that that besides the internal temperature sensors, four external temperature sensors have been used to ease calculation of radial heat loss. On the other hand, recording ambient temperature fluctuations is a crucial parameter necessary for calculating the thermal conductivity.

Prior to any test, the accuracy of the data was evaluated by measuring the thermal conductivity of known samples such as aluminum and copper rods. The measured thermal conductivities revealed that there was less than 3% difference between the results of the obtained thermal conductivities and those reported in literature (Table 2).

Table 2. Thermal conductivity of the calibration set

Sample	Length mm	Thermal conductivity, W/mK [53]	Calculated thermal conductivity, W/mK
Copper	48.5	400	405.8
Aluminum	72.4	250	246.67

Considering the measured temperatures and utilizing Fourier's law (Eq. 1) it is possible to calculate the rock thermal conductivity as:

$$Q = KA\Delta T \quad (1)$$

where K is the thermal conductivity (W/mK), A is the area (m^2) and ΔT is the temperature difference (°C). If the above equation utilizes for constant heat transfer between the copper section and core section, it is possible to calculate the core thermal conductivity as follows:

$$Q = K_{Cu} A_{Cu} \Delta T_{Cu} \quad (2)$$

$$k_{Core} = \frac{Q}{A_{Core}\Delta T_{Core}} \quad (3)$$

where K_{Cu} is the copper conductivity, A_{Cu} is the surface area of copper cylinder faced with heat transfer, ΔT_{Cu} is the temperature difference of two faces of the copper cylinder, k_{Core} is core conductivity, A_{Core} is the surface area of core and ΔT_{Core} is the temperature difference of two faces of the core.

Core flooding procedures

In this study, the core-flooding apparatus (Figure 2) was used to flood the core plugs with the prepared nano-fluid solutions to measure the conductivity of the treated cores.

The core flooding system, previously described in detail [48], was used to conduct the core flooding experiments. In brief, after porosity and permeability measurements, the core plugs were placed in the core-holder. Then, the cores were saturated by injecting several pore volumes (PV) of nano-fluids at the injection rate of 0.3 mL min^{-1} while the effluent solution was monitored. It is noteworthy that at the start of injection stage, the effluent was completely clear. In other words, at first it seemed that the core plug was acting like a filter, but after injecting several pore volumes of nano-fluid, the same effluent was produced, which indicated that the rock was fully saturated with the nano-fluids and further injection of nano-fluid into the core could be halted. Then, the saturated core was placed into the thermal conductivity measurement apparatus for further processing. Figure 3 shows the status of the effluent nano-fluid solutions at different time periods.

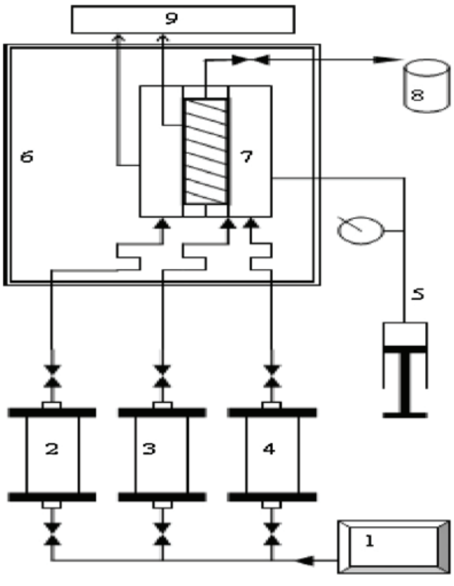

Figure 2. Schematic of the used core flooding apparatus (1 - HPLC pomp, 2 - chemicals cylinder,3 - brine cylinder, 4 - oil cylinder, 5 - confining pressure, 6 - oven, 7 - core holder, 8 - outlet fluids tube, 9 - pressure transducer).

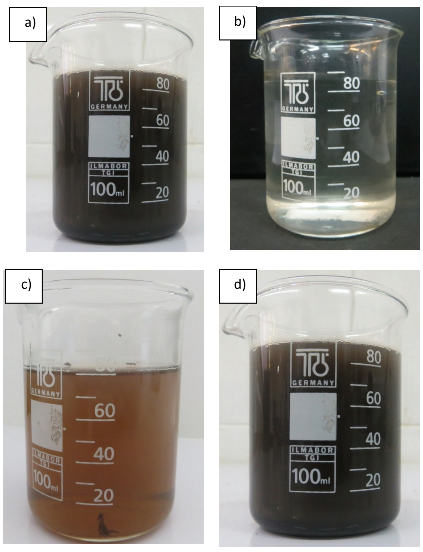

Figure 3. a) Fluid inlet; b) effluent after injection of 5 PV; c) effluent after 10 PV; d) effluent after 13 PV.

RESULTS AND DISCUSSION

Effect of nano-fluid injection on thermal conductivity of core

In the first stage, the effect of nano-fluid injection on the enhancement of thermal conductivity was examined using copper oxide as nanoparticle at a concentration of 0.01 M. Then, the obtained results were compared with the thermal conductivity of dry core and saturated core by distilled water. The obtained results demonstrated in Figure 4 revealed that injection of water can reduce the temperature difference along to the core to the value of 12.4 °C, which means higher thermal conductivity of rock compared to dry status (13.1 °C). This obtained result can be explained based on the fact that the dry core utilizes the porous media occupied by air, which acts as an insulation, thereby reducing the thermal conductivity of core. However, if the dry core is saturated with distilled water, the air will be replaced by distilled water, which has a higher thermal conductivity compared to air; consequently, lower temperature difference between the two sides of the core will be observed.

Also, measuring the temperature difference of two sides of the core saturated with nano-fluids of copper oxide revealed that injection of nanoparticles had a great effect on the thermal conductivity compared with two previously examined statuses. In other words, injection of nano-fluid of copper oxide into the core reduced the temperature different from to 10.1 °C, which is lower than 13.1 °C (for dry core) and 12.4 °C (for core saturated with distilled water). This reduction can be related to the presence of metallic based particles in the fluid which can be oriented into the pores in a way that increases the thermal conductivity by making a continuous conductive path.

Also, a closer examination in Figure 4 revealed that the temperature variation profile is consisted of two different areas named A and B. The B section is the steady zone while the A section is a zone which the temperature variation experienced a fluctuation can rise from the two different parameters including movement and settlement of the particles and the steadiness of transferred heat into the core. Finally, to observe the sole effect of nanoparticles on the thermal conductivity of the core, nano-fluid-saturated core was dried at ambient temperature for a week. After that, the temperature difference along to the core was measured again and it was found that the presence of nanoparticles in the core can reduced the temperature difference about 1 °C, which was 8% higher than the temperature difference when only water was injected into the core.

The interesting point is that measuring the temperature difference between the two sides of the core (dried after saturating by distilled water) revealed temperature variation similar to when the core was dry from the beginning. However, in the nano-fluid saturated case, after evaporation of base fluid during one week, the particles remained on the surface of the

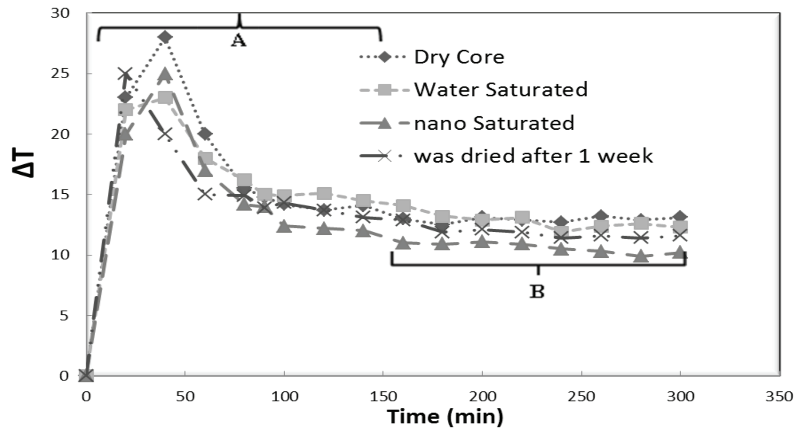

Figure 4. Temperature difference variation along the core for different cases.

rock, consequently decreasing the temperature difference compared to the dry core state.

Based on the obtained results, it can be concluded that the highest thermal conductivity enhancement can be achieved while the nanoparticles and base fluid (distilled water) injected concurrently.

In the next stage of this investigation, the obtained results of temperature variations converted to thermal conductivity demonstrated an interesting behavior. A close examination of the results depicted in Figure 5 revealed a transient behavior of thermal conductivity can be related to the existence of vapor in the core holder chamber produced by introducing heat into the core sample.

In more detail, because of time passing, vapors started to be produced under the effect of heat passing through the system. In light of the produced vapor, the thermal conductivity experienced a fluctuation, which faded away after a while, when the produced vapor escaped from the system. The results depicted in Figure 5 show that the presence of nanoparticles of copper oxide significantly increased the thermal conductivity of rock up to 33%. As aforementioned, this trend can be related to the fact that the injected fluid enters into the core pores and produces a continuous conductive pass full of nano-fluid copper oxide, increasing the thermal conductivity of the core toward a more conductive state.

The calculated thermal conductivity of different cases including dry core, water-saturated core and nano-fluid-saturated core are given in Table 3. As can be seen, injection of only distilled water enhances the thermal conductivity of core about 6% while injection of copper oxide nano-fluid solution with concentration of 0.01 M enhances the thermal conductivity up to 26%. In other words, injection of copper oxide nano-fluid even with low concentration of 0.01 M can significantly affect the thermal conductivity of the rock.

Effect of nano-copper oxide particles concentration on thermal conductivity

In the last section of this study, the effect of copper oxide nanoparticles on the thermal con-

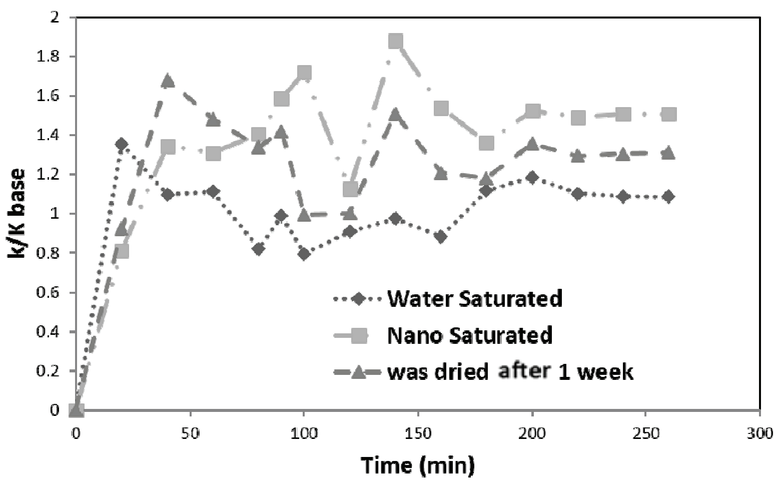

Figure 5. Changes of sample thermal conductivity compares to base case (dry) as a function of time for 4 different cases.

ductivity of core was investigated. In this regard, the concentration of nano-fluid of copper oxide was ranged between 0.01 to 0.05 M (0.01, 0.02, 0.03, 0.04 and 0.05 M) while the other operational conditions including pH, sonication time, temperature and injection rate were kept constant.

Table 3. Thermal conductivity of rock at injection of copper oxide nano-fluid solution with concentration of 0.01 M

Test	Thermal conductivity, W/mK	Enhancement on the thermal conductivity, %
Dry core	1.5	-
Water saturated core	1.59	6
Nano-fluid saturated core	1.88	25.91

The obtained results demonstrated in Figure 5 revealed that as the concentration of copper-oxide nanoparticles increased from 0.01 to 0.05 M, the final temperature difference between the two ends of the core decreased from 10.1 to 8.8 °C, corresponding to 47% enhancement in thermal conductivity. It should be mentioned that as the concentration of nano-fluid increases, the required time for stabilization of temperature difference decrease, resulting in higher effectiveness of nano-fluid injection at higher concentration. The reason behind this trend can be related to the fact that as the concentration of the nanoparticles increases, a denser continues convective path for heat transfer through the porous media will be produced, therefore faster and higher heat transfer through the core occur. In addition, comparing the thermal conductivity of the dried cores after nano-fluid injection (see Figure 6) revealed that although the thermal conductivity of the samples for all of the concentrations were lower than the saturated cores by nano-fluids, they leads to the higher thermal conductivity compared with thermal conductivity of cores saturated only by distilled water. Finally, the obtained thermal conductivities enhancement for different cases were demonstrated in Figure 6 revealed that thermal conductivity of nano-fluid saturated cores were higher compared with those cores which were dried after nano-fluid injection.

The point is completely obvious is that injection of nano-fluid solution in both cases of before and after drying leads to a significant increase in the thermal conductivity enhancement compared with saturated core with distilled water. In more details, when the core was dried for one week at room temperature, the thermal conductivity of the core reduced since water was evaporated from the pores and the continuity of the conductive path was reduced compared with the initial status. However, the dried saturated core with nano-fluid was still more conductive than the core saturated by distilled water, due to the considerable effect of copper oxide nanoparticles on the thermal conductivity considering its metallic nature.

A closer examination of Table 4 reveals an interesting point that the percentage of reduction in the thermal conductivity after drying of core saturated by nano-fluid solution is equal to the increase of core thermal conductivity if saturated by distilled water. In other words, it can be concluded that thermal conductivity of core experienced an increase of about 6% in the presence of water, which is similar to the percentage of thermal conductivity reduction if the injected nano-fluid was dried. This trend was consistently observed for all of the examined cores with

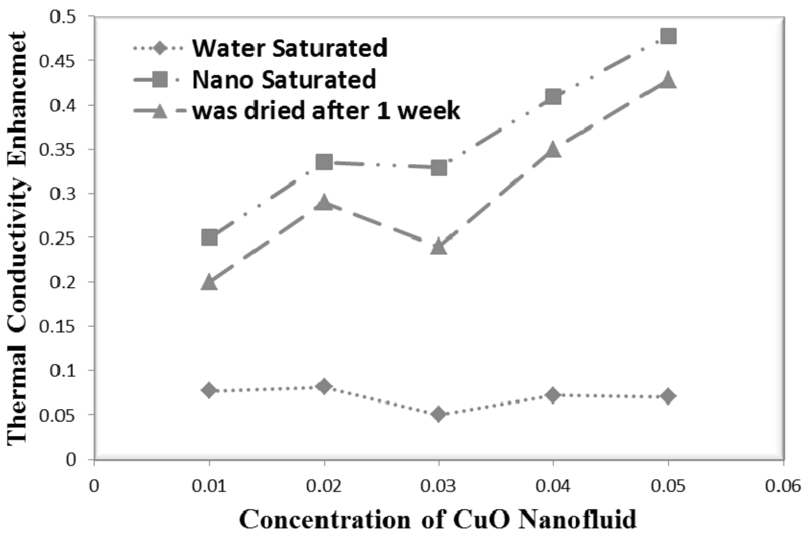

Figure 6. Changes in thermal conductivity increases as a function of nanoparticle concentration of the injected fluid.

Table 4. Percentage of enhancement of cores' thermal conductivity (W/mK)

Concentration of Nano-fluid, M	Water saturated, %	Nano-saturated, %	Dried after 1 week, %
0.01	7.69	25	20
0.02	8	33.5	28.9
0.03	5	32.94	24
0.04	7.14	40.9	35
0.05	6.9	47.82	42.8

different concentrations of copper oxide nanoparticles. Hence, it can be concluded that the great portion of the thermal conductivity enhancement during injection of nano-fluid solution into the core can rise from the presence of the metallic-based nanoparticles of copper oxide.

Finally, SEM analysis was used to find the effect of the injected nanoparticles of copper oxide on the surface alteration of the core samples. As it can be seen from Figure 7, the injected nanoparticles of the copper oxide are deposited on the surface of the rock, and thus increase the thermal conductivity of rock.

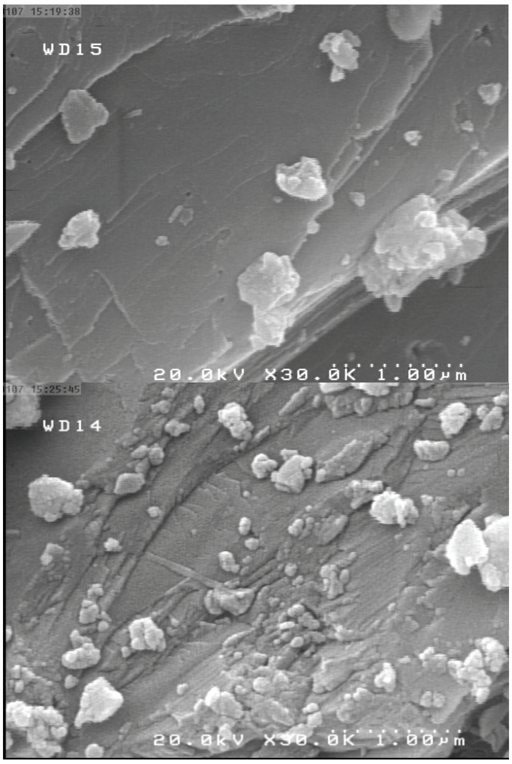

Figure 7. SEM image of core saturated with CuO nano-fluid: a) blank sample; b) sample treated with nano-fluid.

Effect of the base fluid on the thermal conductivity of the core

In the previous step, the effect of water-based CuO nano-fluid was investigated and the results was determined. But the other crucial parameter influences the effectiveness of the nano-fluids is the used base fluid. Regarding this fact, in the current section the effect of using another fluid, namely ethylene glycol, was investigated. For this purpose, ethylene glycol-based CuO nano-fluid was prepared and injected in to the core and the temperature differences between its two end caps was measured. The obtained results demonstrated that the used nano-fluid decreases the temperature differences and increased thermal conductivity of core. However, the obtained temperature differences using ethylene glycol were higher than the values obtained the water-based fluid. This means the ethylene glycol-based CuO nano-fluid caused less increase in thermal conductivity compared to the water-based CuO nano--fluid.

As it is clear from Figure 8, preparing the solution using ethylene glycol reduces the temperature difference about 1.4 °C and enhances the thermal conductivity about 15%. Comparing the obtained results by the experiments performed with water and those performed with ethylene glycol, one can conclude that ethylene glycol is not only unable to modify the thermal conductivity, but also reduces the thermal conductivity to some extent. The reason behind this observed trend can be related to the lower thermal conductivity of ethylene glycol compared with water. In other words, since the thermal conductivity of ethylene glycol is lower than water, injection of solution with ethylene glycol reduces the thermal conductivity. Based on the obtained results in this section, it can be concluded that in the way of choosing the best base fluid for preparation of the nano-fluid, one must consider the thermal conductivity of the base fluid. In other words, higher thermal conductivity of base fluid leads to better results for preparing the nano-fluid for thermal conductivity enhancement purposes.

According to Figure 9, the lower increase in thermal conductivity of 17% in the case of ethylene glycol can be due to lower thermal conductivity of ethylene glycol, as compared to water.

One part of the increase in thermal conductivity is caused by the fluid and depends on the thermal

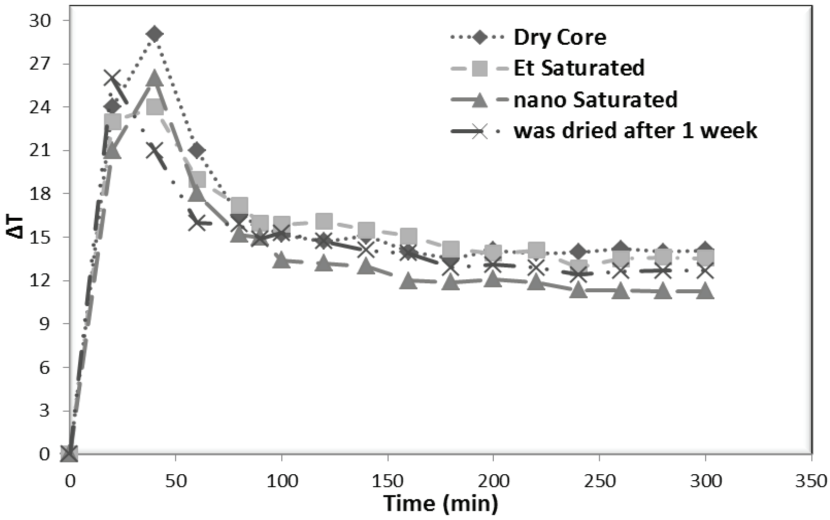

Figure 8. Temperature difference variation along the core for different cases in ethylene glycol-based fluid.

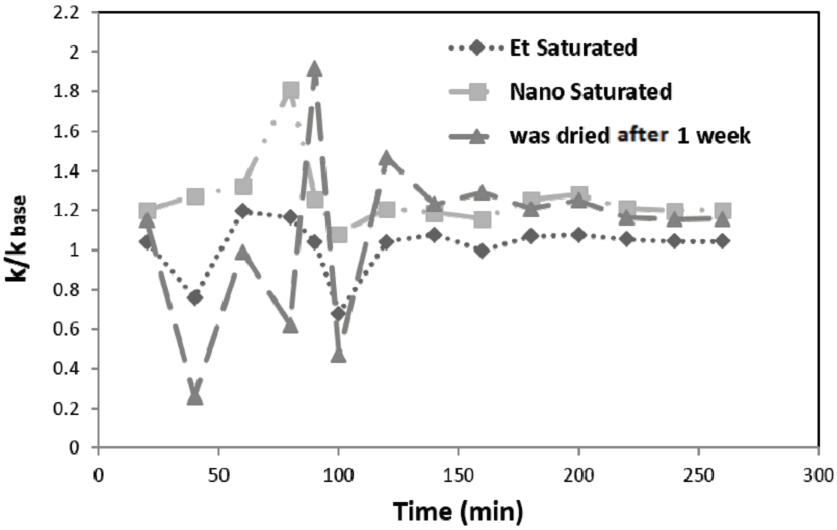

Figure 9. Changes of sample thermal conductivity compare to base case (dry) as a function of time for 4 different cases in ethylene glycol-based fluid.

conductivity of the base fluid. So this part is lower in the case of ethylene glycol because of its lower thermal conductivity [53]. Finally, a comparison with the use of water-base fluid, ethylene glycol is more appropriate and enhances the heat transfer increases.

Effect of surfactant type on stability of nano-fluids and the thermal conductivity of core

Four different surfactants, namely ionic liquid, SDS (sodium dodecyl sulfate), C_{16}TAB (cetyl trimethylammonium bromide) and PVP (polyvinylpyrrolidone) were used as stabilizer agents.

After preparation of the solutions, they were injected into the cores and the effects of the solutions were investigated through two stages. In the first stage, the effect of injected nano-solution on the thermal conductivity of rock samples was investigated spontaneously after injection (see Figure 9). A glance into Figure 9 reveals that injection of nano-CuO fluid into cores leads to an increase in the thermal conductivity of core samples for all of the used surfactants. This observed trend can be related to the presence of the nanoparticles of CuO occupying the pores, which enhances the effective path for heat transfer.

A closer examination in Figure 10 also demonstrated that although all of the used surfactants enhance the thermal conductivity of core samples, the ionic liquid introduced a significant effect on the thermal conductivity compared with the other used surf-

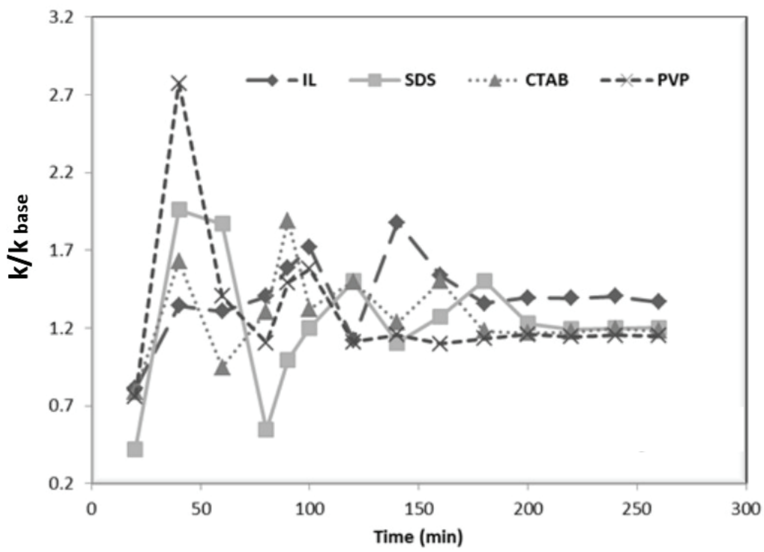

Figure 10. Changes of sample thermal conductivity compare to base status (dry) as a function of time for 4 different kind of surfactants after nano-fluid injection.

actants. In other words, utilization of IL had the highest effect on the thermal conductivity enhancement.

The reason for this observed trend arises from the structure of the ionic liquid. The IL used in this study comprises of a hydrophilic section with a benzene ring, which distribute the electrical charges through the IL molecules. Due to this distribution, the surfactant molecules have many opportunities to orient on the surface of the nanoparticles of copper oxide in order to introduce proper repulsion force between the nanoparticles. Because of these repulsion forces, double layers form, enhancing the stability of nanoparticles suspension in the solution. Due to the produced repulsion forces, agglomeration and coagulation of nanoparticles are reduced to a level that considerably increases stability [54].

Furthermore, the required concentration of IL for efficient stabilization is significantly lower than the conventional surfactant utilized in the current study including PVP, C_{16}TAB and SDS. The reason of this observed trend can be also be related to the structure of the IL which enhances the active sites for occupation by nanoparticles with no steric hindrance, consequently increasing the stability of the nano-fluid and heat transfer capability (see Figure 11).

According to Figure 10, between SDS and C_{16}TAB, SDS (12 carbons) is more efficient for increasing the thermal conductivity since its carbon chain is shorter than C_{16}TAT (16 carbons). As the carbon chain of surfactant increases the steric hindrance, it thus reduces the effectiveness of the nanofluid for thermal conductivity modification.

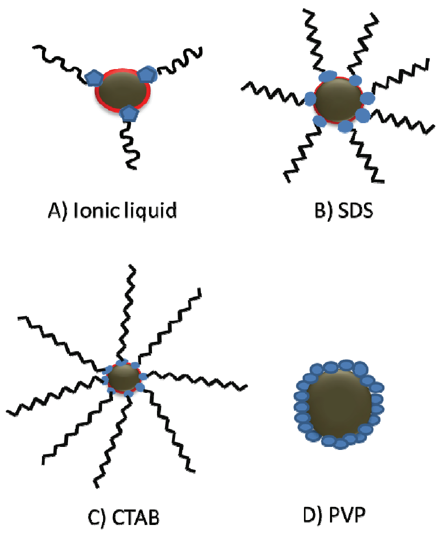

Figure 11. Schematic of nanoparticles coating by different kind of surfactants.

Among all of the examined surfactants, PVP exhibited the poorest results, which can rise from its different structure. In more details, PVP is a polymer-like molecule that surrounds the nanoparticles and introduces a shielding effect on them; consequently, the heat transfer capability via nanoparticles reduces.

Moreover, it can be seen in Figure 10 that, compared to other surfactants used in this study, PVP is the last in ranking of increasing heat transfer. This is because of different its structure and its ability to create a layer around the nanoparticles, strengthening the double-layer repulsion between the nanoparticles.

On the other hand, the polymer layer acted as an insulator layer, in addition to reducing nano-sized active participation, and prevented the formation of a conductive surface for heat transfer. Therefore, the heat transfer performance of PVP was the weakest relative to other surfactants.

The other investigated case was the sole effect of nanoparticles on the thermal conductivity. For this purpose, after the injection of nano-fluid into the core samples, the core was left at the room temperature to let the water evaporate. After that, the thermal conductivity was measured, which can be considered as the sole effect of nanoparticles. The obtained results based on this procedure revealed that the thermal conductivity of dried samples was lower than in the case when the system was flooded by nano-fluid. In other words, drying the cores leads to lower thermal conductivity. This observed trend can be related to the fact that as the water evaporated, the effect of base fluid (water) on the thermal conductivity enhancement was eliminated, which reduced the overall thermal conductivity enhancement. On the other hand, the nanoparticles settled on the rock surfaces and the role of surfactants will be motivated. Also, IL due to its structure and low concentration, results in a lower steric hindrance, which leads to higher available active sites for orientation of nanoparticles, modifying the thermal conductivity.

Figure 12 shows results after injection of nanofluids that have been prepared with different surfactants. The core is given time to dry about one week, which allowed the tangible effects of nanoparticles to be exhibited. The results showed that after a week of drying, the heat transfer process was unchanged, but the percentage increase in thermal conductivity compared to the previous state (immediately after injection) was lower. This is due to the evaporation of the base fluid (water). On the other hand, nanoparticles are adsorbed onto the surface of core and the effect of surfactants on the absorption will be highlighted. In addition, IL due to the mobility of charge on its hydrophilic head and its lower required concentration, does not prevent the nanoparticles from participating in the heat transfer surface. Therefore, a greater area of the nanoparticles is in contact with the rock and increases the heat transfer.

SDS possesses concentrated electrical charges on its hydrophilic head, which increases its required concentration for a certain thermal conductivity enhancement compared with the other surfactants. In addition, $C_{16}TAB$ has a low efficiency due to its long chain, which increases the steric hindrance for nanoparticles and reduces the active surfaces necessary for interaction between nanoparticles and the rock surfaces. Lastly, utilization of PVP produces a layer around the nanoparticles, which reduces the thermal conductivity (see Figure 13).

Effect of concentration of CuO nanoparticles regarding different kind of surfactant on the thermal conductivity of core

In this section, the functionality of thermal conductivity to concentration and type of surfactants has been investigated (see Figure 14). As it is obvious, among the used surfactants, IL showed the best results for enhancing the thermal conductivity of rock. On the other hand, it can be observed that as the concentration of nanoparticles increases, the thermal conductivity increases, while an increase in the concentration of surfactant leads to a reduction of thermal conductivity. This observed trend can be related to two different phenomena. As the concentration of

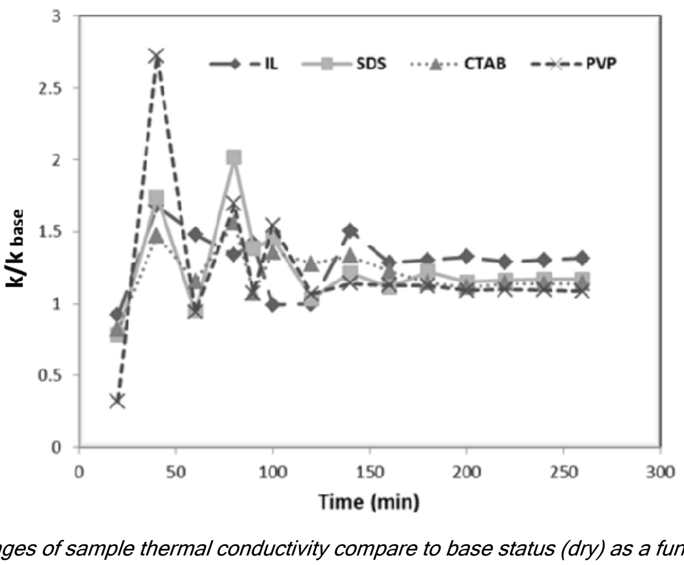

Figure 12. Changes of sample thermal conductivity compare to base status (dry) as a function of time for 4 different kind of surfactants for dried core.

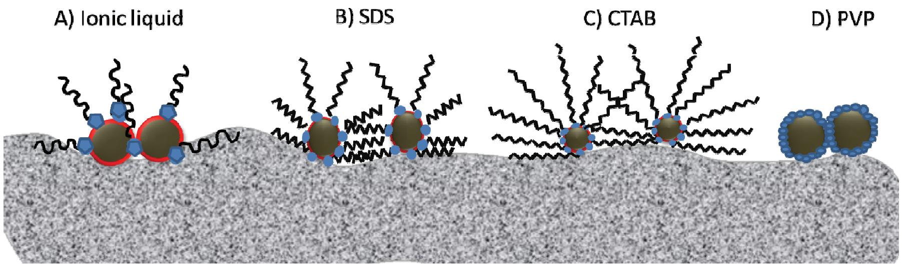

Figure 13. Schematic of nanoparticles adsorbed on the surface of the core with different kind of surfactants.

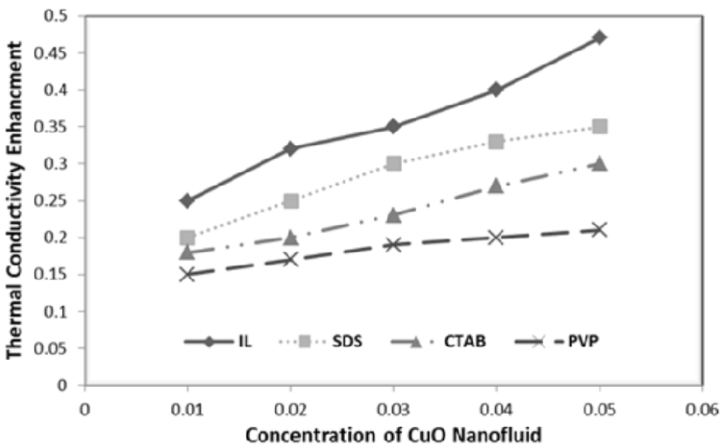

Figure 14. Changes of sample thermal conductivity compare to base status (dry) as a function of time for 4 different kind of surfactants after injection of nano-fluid solution.

nanoparticles increases, the active surface for heat transfer related to the nanoparticles increases, while as the concentration of the surfactant increases, the steric hindrance increases, which reduces the functionality of the nano-fluid. In other words, it is the net effect of these two competing factors that dictates whether the thermal conductivity increases or decreases.

A close examination of Figure 14 revealed that these two competing factors are more obvious for PVP surfactant, while they can barely be realized for IL. In conclusion, it is obvious that the PVP surfactant introduces no significant change on the thermal conductivity.

In the next step, the cores saturated by CuO nano-fluid were dried for one week at ambient conditions. The results of these experiments (Figure 15) revealed that after one week, the increase in thermal conductivity was the highest for IL and the lowest for PVP. However, in these conditions, tangible effects of

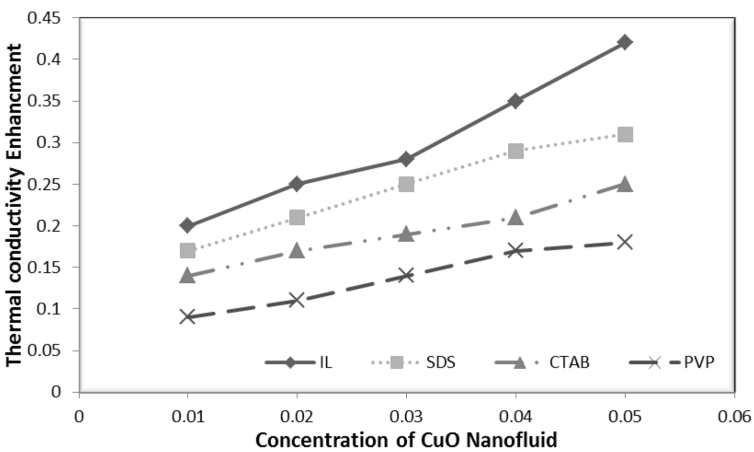

Figure 15. Changes of sample thermal conductivity compare to base status (dry) as a function of time for 4 different kind of surfactants as the cores were dried after one week.

nanoparticles and surfactant are seen after vaporization of the base fluid. According to Figure 15, increasing the concentration of nano-fluid prepared by PVP has a slight effect on the thermal conductivity.

CONCLUSION

In the present study, a homemade thermal conductivity measurement apparatus was used to investigate the effect of copper oxide nanoparticles on the thermal conductivity of the core. Different solutions of copper oxide nanoparticles, using 1-dodecyl-3-methylimidazolium chloride ([C_{12}mim] [Cl]), sodium dodecyl sulfate (SDS) C_{16}TAB and PVP as stabilizing agents, were used to prepare nano-fluids necessary for injecting into the core. The obtained results revealed that injection of copper oxide nanoparticles prepared in water with different concentrations of 0.01 to 0.05 M was able to enhance the thermal conductivity of the cores up to 48%. In addition, the obtained results revealed that the thermal conductivity of core saturated by distilled water is significantly lower than the thermal conductivity of a core saturated by nano-fluid of copper oxide, since the presence of metallic base particles of copper oxide prove a conductive path through the core by orienting in the pores. In addition, the results revealed that type of base fluid for preparation of the nano-fluid is a crucial parameter for enhancing the thermal conductivity.

Finally, based on the obtained results it can be concluded that injection of metallic-base nanoparticles of copper oxide is an applicable and feasible method to enhance the thermal conductivity of cores especially since stabilized by 1-dodecyl-3-methylimidazolium chloride ([C_{12}mim] [Cl]), which is a new kind of surfactant that can tolerate harsh temperature conditions. Although the results in this study revealed the potential of copper oxide nanoparticles for thermal EOR methods, the application of nanoparticles needs further systematic investigations.

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NAUČNI RAD

NANO FLUID SA BAKAR OKSIDOM STABILIZOVAN JONSKOM TEČNOŠĆU ZA POVEĆANJE TOPLOTNE PROVODLJIVOSTI STENA LEŽIŠTA: PRIMENA U TERMALNIM PROCESIMA SA POVEĆANIM ISKORIŠĆENJEM NAFTNIH LEŽIŠTA

Pošto su rezerve nafte ograničene, a potražnja za energijom u porastu, nalaženje novih efikasnih ili poboljšanje efikasnosti postojećih metoda za povećanja iskorišćenja naftnih ležišta (EOR) je predmet brojnih istraživanja. Kao izlaz iz ovog problema moguća je kombinovana upotreba EOR metoda i nanotehnologija metoda da bi se iskoristile efikasnost obe ove metode. U potrazi za takvom mogućnošću u prvom delu ovog rada pripremljeni su stabilni vodeni rastvori sa nano česticama bakar oksida različitih koncentracija (0,01-0,05 M), koji su zatim ubrizganu u uzorke stena. Analiziran je efekat koncentracije različitih površinski aktivnih komponenti. Zatim su proučavani različiti scenariji korišćenja nano fluida kao modifikatora toplotne provodljivosti. Dobijeni rezultati jasno pokazuju da se promenom koncentracije nano čestica bakar oksida u opsegu od 0,01 do 0,05 M može da poboljša toplotna provodljivost stena od 27 do 48% u poređenju sa suvim stenama.

Ključne reči: toplotna provodljivost, nano-fluid, bakar-oksid, povećanje iskorišćenja naftnih ležišta, jonske tečnosti.