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An Experimental Investigation of the Catalytic Effect of Fe_2O_3 Nanoparticle on Steam Injection Process of an Iranian Reservoir

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Abstract

Nanotechnology has the potential to introduce revolutionary changes to several areas of oil and gas industry such as exploration, production, enhanced oil recovery, and refining. In this paper, the effect of different concentrations of Fe_2O_3 nanoparticles as a catalyst on the heavy oil viscosity at various temperatures is studied. Furthermore, the effect of a mixture of Fe_2O_3 nanoparticles and steam injection on heavy oil recovery is studied in laboratory. The experimental tests show that some of these nanoparticles decrease the heavy oil viscosity less than 50% at certain concentrations at different temperatures. The reason for this viscosity reduction is that, similar to a catalyst, these nanoparticles activate some reactions. Our results of steam injection tests show that the injection of a Fe_2O_3 nanoparticle mixture increases heavy oil recovery because of cracking reactions which crack the C-S, C=C, and C≡C bonds of the heavy components of heavy oil and change them to light components.

Keywords: Steam Injection, Fe_2O_3 Nanoparticles, Heavy Oil Recovery

1. Introduction

As the world's supply of light, sweet crude oil is depleted, the stocks of heavy oils and bitumen become more and more important as a component in supplying the demand for fuels and petrochemical feedstock (Maneeintr et al., 2010).

Thermal processes used in enhanced oil recovery (EOR) tend to decrease the viscosity of the fluid and can be classified as thermal drives or stimulation treatments (Lashanizadegan et al., 2008). Steam injection is one of the commercial technologies widely used to produce oil from heavy oil reservoirs as well as light oil reservoirs (Shuhong et al., 2008).

In many of the studied researches, recovery by steam is greater for lighter oil. With increasing temperature, oil recovery increases and residual oil saturation decreases in steam injection and hot-water flooding. In the steam injection process, the effect of matrix relative permeability is less important. After its reaction with steam, the amount of the saturated and aromatic hydrocarbons increases which results in a reduction of viscosity of the heavy oil.

With reduced oil viscosity as well as gravity stability, recovery increases in both oil-wet and water-wet fractured porous media. At an optimum temperature, the steam quality is the most important parameter in the steam injection process.

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Nanotechnology has already contributed significantly to the technological advances in several industries such as biomedical, materials and manufacturing, and more recently in the oil industries. Nanotechnology has the potential to introduce revolutionary changes to several areas of oil and gas industries such as exploration, production, enhanced oil recovery, and refining (Shahi, 2009). In high-temperature steam injection applications, steam is injected into a reservoir to provide the heat for visbreaking of heavy oil/bitumen (Omole et al., 1999).

Fan et al. (2004) investigated the catalytic effects of minerals on aqua-thermolysis of heavy oils. They found that heavy oil of Liaohe oilfield could undergo aqua-thermolysis in the steam stimulation process and the viscosity and molecular weight of heavy oils could be reduced. Their results showed that the reservoir rock had a catalytic role in aqua-thermolysis. Furthermore, by adding 10 wt.% reservoir rock to the reaction system, they observed that the heavy oil viscosity decreased from 88.5 to 55.8 Pa.s at a reservoir rock concentration of 36.9 wt.% and the average molecular reduced from 587 to 475at a reservoir rock concentration of 19.1 wt.% (Fan et al., 2004).

Fan et al. (2009) experimentally studied using ionic liquid to upgrade heavy oil. They found that ionic liquid, i.e. [(Et)NH][AlCl], could decrease the viscosity, average molecular weight, and asphaltene content of heavy oil. Their results showed that the bonds which were formed between ionic liquids and organic sulfur in heavy oil were very weak due to the weakness of C-S bonds (Fan et al., 2009).

Li et al. (2007) studied the effect of nickel nanocatalyst on the viscosity reduction of Liahoextra-heavy oil by aqua-thermolysis reaction. They observed that the viscosity, resin content, and asphaltene content of extra-heavy oil were effectively reduced (Li et al., 2007)

Hacker et al. (2008) investigated the effect of micron-sized iron particles on heavy oil viscosity without steam treatment. They reported a noticeable viscosity reduction (Hacker et al., 2008).

Chen et al. (2009) conducted a study on the viscosity reduction of nano-keggin-$K_3PMo_{12}O_{40}$ in catalytic aqua-thermolysis of heavy oil. They found that nano-keggin-$K_3PMo_{12}O_{40}$ was changed in oxygen-containing groups mainly during the catalytic aqua-thermolysis (Chen et al., 2009).

Hamedi et al. (2010) worked on the effect of nanosized metal on the viscosity reduction of heavy oil/bitumen during thermal applications. They used different metal types such as iron, nickel, and copper with different sizes. Their results showed that nanosized particles had a remarkable effect on heat transfer through heavy oil (Hamidi and Babadagli, 2010).

Most of the reported studies on the effect of temperature and pressure on the recovery of the steam injection process have been carried out with sandstone and there is very little published data on carbonate rocks especially for heavy oil. Moreover, the effects of nanoparticles on the viscosity in bulk systems have been studied. There is limited published data on the effect of nanoparticles on the recovery of heavy oil, and the application of mixed steam-nanoparticle injection in the process of oil recovery has not particularly investigated yet.

The purpose of this study is investigating the effect of Fe_2O_3 nanoparticles on the recovery of heavy oil from the real core sample by the steam injection process.

2. Experimental study

2.1. Rock sample

A type of carbonate rock was used in this study and the cores were limestone; plugs were cylindrical with a diameter of 3.8 cm and a length of 7-7.5 cm. The cores used were from real heavy/medium oil Iranian reservoirs (Kuh-e-Mond). After cutting, the samples were washed completely with toluene over 10 days and dried in an oven at a temperature higher than 150 °C for at least 24 hrs to remove possible oil and fine materials from rocks. A helium porosimeter and air permeameter were used for porosity and absolute permeability measurements. The absolute permeability of the samples was determined to be 0.1 mD for carbonate and the porosity was 19%. Table 1 shows the measured porosity and absolute permeability of each sample. After washing and drying the core samples, they were saturated with the oil phase without prewetting the medium with water phase. Table 1 shows the properties of the rock samples used in the experiments.

Table 1
Properties of the cores used in the experiments.

Core name	Type	Absolute Permeability (mD)	Porosity (%)	Pore volume (ml)
KM1	Lime stone	0.1	18.6	15.58

2.2. Fluids

The oil samples used in this study were heavy oil of Kuh-e-Mond reservoir from Iranian fields. Its properties are given in Table 2. Figure 1 shows that oil viscosity changes with increasing the temperature of the heavy oil sample used in the experiments. Table 3 lists the stock tank crude oil composition of the heavy oil sample.

Table 2
Properties of the oil used in experiments.

Name	Oil density (API)	Dead oil viscosity (at 38 °C) (cP)	Thermal expansion factor (from 20 to 66 °C) (C^{-1})	Compressibility (psi^{-1})
KM	12	16000	7.20×10^{-4}	4.67×10^{-6}

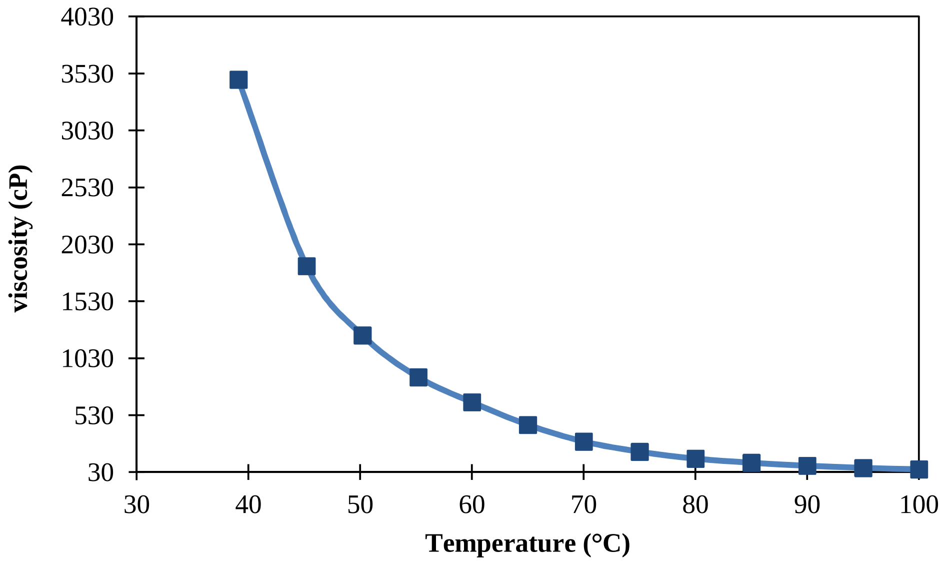

Figure 1
Oil viscosity–temperature relationship of the oil samples used in this study.

Table 3
Three tank system parameters.

Name	IC4	NC4	IC5	NC5	C6	C7+
KM	1.53	3.76	3.95	2.31	2.85	85.60

The water phase for the injection of all the experiments was distilled water with a viscosity of 1 cP under ambient conditions. In some of the experimental tests, we used Fe_2O_3 nanoparticles mixed with distilled water.

2.3. Materials

To study the effect of nanoparticles on the steam injection process, iron (III) oxide was selected. These metal oxides were selected because of their role as a catalyst in cracking reaction and their heat properties.

Table 4 shows the specifications of the nanoparticles; the nanoparticles were supplied by Notrino Company.

Table 4

Three tank system parameters.

Particle type	Formula	Form	Purity (wt.%)	APS	SSA	Appearance
Iron (III) oxide	Fe_2O_3	nanopowder	99%	<30 nm	<30 m^2/g	Red powder

2.4. Equipment

A DBR electromagnetic viscometer was used for viscosity measurement. This apparatus determines the viscosity using electromagnetic waves by imposing a constant force on a piston inside the measurement chamber. The motion of the piston is impeded by viscous flow in the annulus between the piston and the measurement chamber wall. This chamber is covered by a jacket and supplied with a liquid bath. This system is supplied with the Cambridge ViscoPro 2000 electronic package and can measure the viscosity of oil at various temperatures continuously (operation manual DBR, 2000).

Figure 2 shows a schematic representation of the displacement apparatus used in this study. This apparatus includes three sections, namely injection, core holder, and production. Water was injected using a nitrogen pressure on the cylinder containing water. This positive pressure pump can inject water to the steam generator in a pressure range from 150 to 4000 psi. Steam generator heats water with an electrical element to vaporize water and injects the steam by the nitrogen pressure pump at a constant pressure. A temperature controller is used to inject the hot fluid at constant temperatures (Operation manual of COREXPORT).

The core holder was built from stainless steel which was capable of loading overburden pressure up to 10000 psi and operating at temperatures up to 500 °C. Nitrogen was used as the overburden fluid and the overburden pressure was always 250 psi higher than the core pressure. The core holder and measurement tools were placed in a thermostatic oven as shown by dotted line in Figure 2. The effluent was collected in graduated cylinders for analysis and separation of oil and water in the system output. The produced fluid was cooled in a condenser before collection; glass cylindrical vessels with a small diameter were used to minimize the measurement error.

Pressure, temperature, and pump calibrations were checked before each experiment. The accuracy of the pressure transducers, thermocouples, and production fluid were 10 psi, 2 °C, and 0.05 ml respectively.

For adding and distributing nanoparticles to the crude oil, an ultrasonic lab device well suited for all general ultrasonic applications on small and medium scales (UP200S, Hielscher Ultrasonics, 200W, 24 kHz) was used.

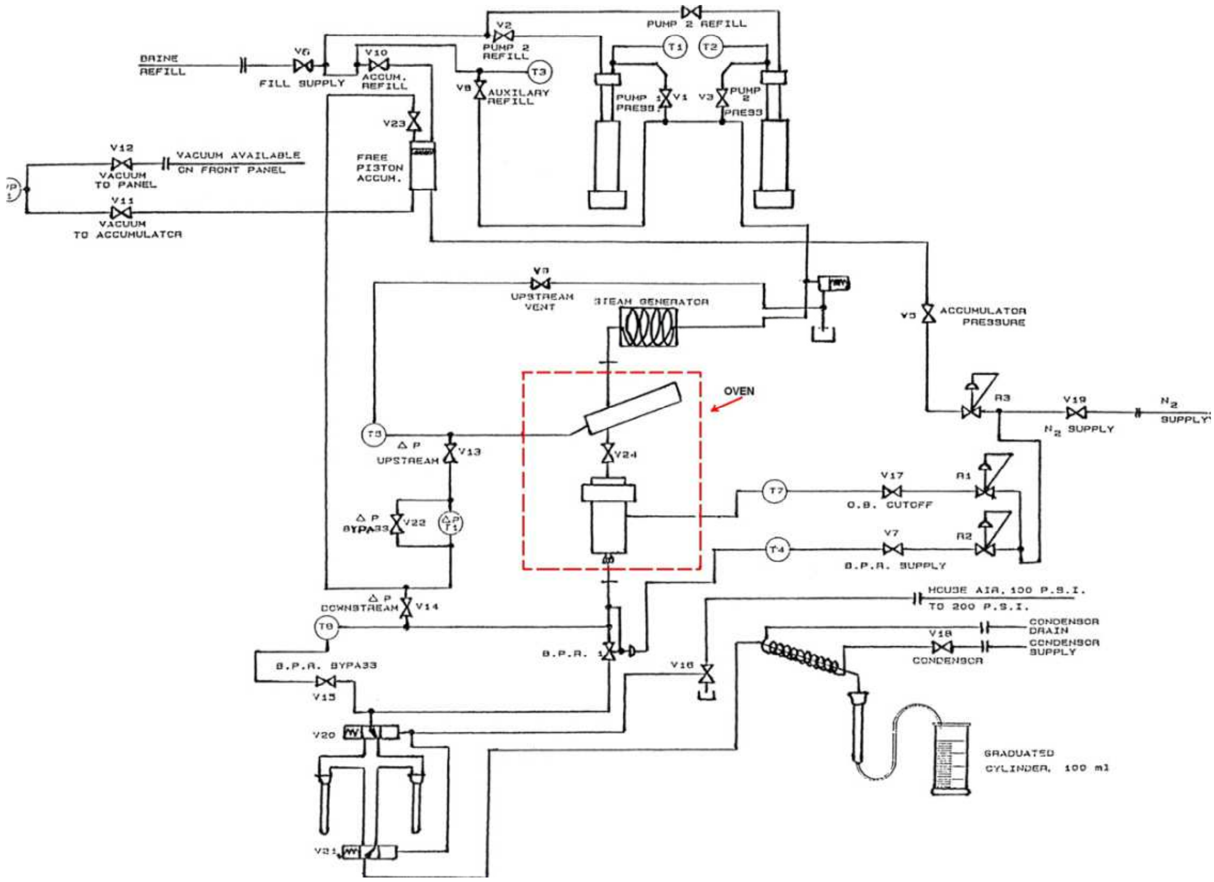

Figure 2
A schematic representation of experimental apparatus.

2.5. Procedure

The experiments of viscosity determination were implemented in a way that our mixtures (heavy oil and nanoparticles) are prepared first; a definite amount of nanoparticles was added to the heavy oil sample and the mixtures were then exposed to ultrasonic at 100% power and 1 cycle in each second for 10 minutes to mix well. In the next stage, the mixture was imported to DBR electro-magnetic viscometer and its temperature was then adjusted at the desired value; after a short time, the viscosity of the mixture could be read on the device.

Four concentrations, including 0.2, 0.5, 1, and 2 wt.% of each nanoparticle were used and the viscosity of each mixture was measured at four temperatures of 40, 50, 80, and 100 ºC.

After saturating the samples with 100% oil phase, each core sample was placed into the core holder. The oven and steam generator temperatures were fixed at the selected set points. For the injection steam, the pressure of back cylinder was set based on the core type sample.

When the system became steady state, oven and steam generation temperature and injection pressure were set and water changed to steam in a vent tube. The test of the steam injection process was then started. The steam injection was stopped when the oil fraction of the produced fluid decreased below 1%. All the production fluids were collected in calibrated graduated cylindrical tubes and then a few drops of a demulsifier were added to them and they were centrifuged at 6000 rpm for 30-70 minutes.

In each experimental test, the oven temperature was fixed at the desired level and the systems were allowed to reach a thermal equilibrium. The volumes of oil and water produced during this process were monitored. At the end of the runs, several pore volumes of hot toluene were injected to wash the core and core properties were measured again. The experiment tests were done again by injecting the mixture of nanoparticles and water as a mixing steam to the core sample. For each test, all the particles were exposed to 90 minutes of ultrasonication at 100% power and 1 cycle in each second at a concentration of 0.2%.

3. Experimental results and analysis

The experimental results are divided into two parts, namely the effect of nanoparticles on viscosity and on the steam injection process, which are reported in part 1 and part 2 respectively.

3.1. Effect of Fe_2O_3 nanoparticles on heavy oil viscosity

The results of the viscosity measurement are presented in Table 5 and Figure 3. The measurements for each sample were repeated at least three times to confirm the results. Values given in Table 5 are the deviation percent ($(\mu-\mu_0)/\mu_0\times100\%$).

Table 5
The percentage of viscosity deviation at different temperatures using different types of nanoparticles at various concentrations.

Nanoparticle type	Concentration of particles (wt.%)	Percent of viscosity deviation at 40 °C	Percent of viscosity deviation at 50 °C	Percent of viscosity deviation at 80 °C	Percent of viscosity deviation at 100 °C
Fe_2O_3	0.2	-38.71	-43.75	-54.96	-64.78
	0.5	-32.78	-40.39	-54.24	-64.88
	1	0.64	-17.65	-48.45	-54.85
	2	-37.86	-32.00	-34.36	-35.28

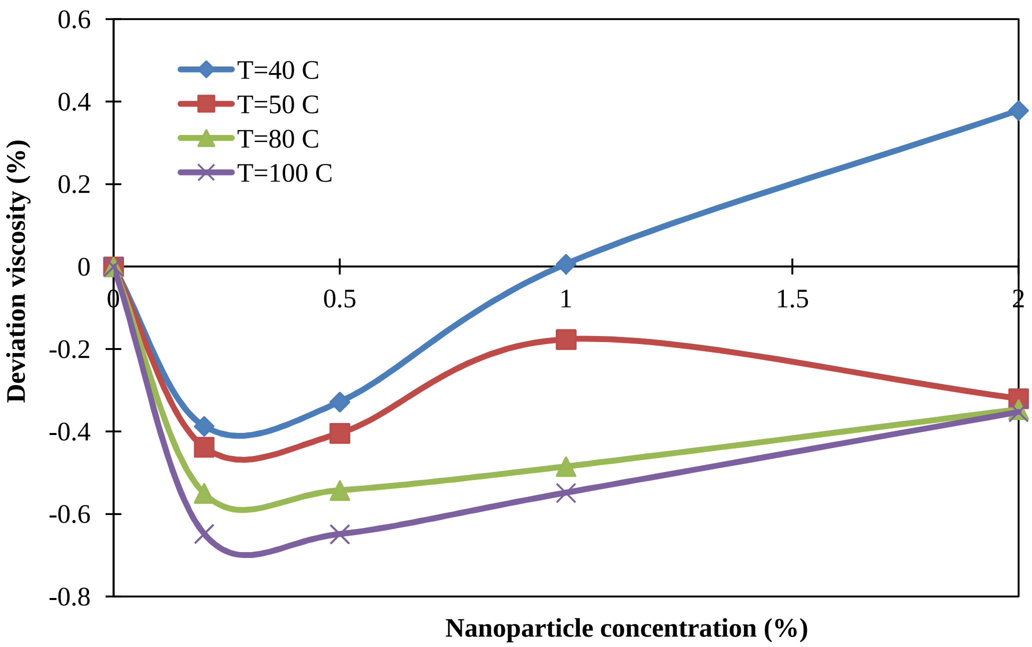

Figure 3
Effect of the Fe_2O_3 nanoparticles on the percentage of the viscosity deviation versus concentration at 40, 50, 80, and 100 ºC.

Investigating the overall effect of nanoparticles on the sample viscosity leads to an optimum concentration of the particles, at which the viscosity reduction is maximized. The viscosity of heavy oil samples versus concentration of different nanoparticles at different temperatures are compared in Figure 3. It is obvious that the highest reduction in viscosity happens at the lowest concentration of nanoparticles, because the nanoparticles act as catalysts in cracking reaction; therefore, heavy oil samples crack to the lighter components. Previous studies indicated that Fe acts as a catalyst in cracking of C-S, C=C, and C≡C bonds of heavy components of heavy oil at low temperatures. This effect is explained by referring to the catalytic effect of metal particles on the breaking of the C-S bonds in the aqua-thermolysis process (Hamidi and Babadagli, 2010).

This result obtained herein is similar to those obtained by Hamidi et al. (Hamidi and Babadagli, 2010) and Hascakir (Hascakir et al., 2008). This issue is due to the larger surface area of nanoparticles, which causes an increase in the contact area of the particles with the oil phase (Hamidi and Babadagli, 2010). Furthermore, when nanoparticles are added to the oil, they are placed between the oil layers and lead to the easy movement of fluid layers (Ettefaghi et al., 2013).

Fe_2O_3, at high concentrations, increases the crude oil viscosity, which is attributed to the interaction between oil and nanoparticles and the consequent increased resistance against the movement.

At higher temperatures, the addition of Fe_2O_3 decreases oil viscosity at all concentrations; but the drop of viscosity is more considerable at low nanoparticle concentrations of 0.2 and 0.5%.

3.2. Effect of Fe_2O_3 nanoparticles on steam injection process

Two sets of steam injection experiments of one type of rock was provided and analyzed. Table 6 summarizes these experiments and operation conditions. In this set of experiments, a constant temperature displacement was conducted under reservoir conditions followed by the experiments at a pressure of 1100 psi. The temperature was selected so that water was transformed into saturated vapor (at 295 °C).

Table 6

Specification of cores and crude oils in experiments under operation conditions.

No. test	Core name	Total oil (gr)	Pressure (psi)	Fluid injection	Total oil recovery
1	KM1	9.65	1100	Seam	38.31
2	KM1	9.97	1100	Mixture of nano-Fe_2O_3 and steam	68.41

Each experimental test was stopped when the oil fraction of the produced fluid decreased below 1%. The volume of recovery (water and oil) in producing fluid versus time was monitored.

For the investigation of each parameter varying, the other parameters of the experimental tests and core conditions are chosen the same. The parameter chosen for studying in this paper is the injection of a mixture of Fe_2O_3 nanoparticles with the distillate.

To compare the results, two tests were carried out with same parameters such as absolute permeability and pressure. In these comparative tests, the carbonate cores (KM1) were used at 1100 psi pressure; also, steam was injected in one test and, in the other test, a mixture of nano-Fe_2O_3 (0.2% wt) and steam was injected. The core contained 9.65 gr of heavy oil.

Figures 4 and 5 show the results of the comparison. Heavy oil recoveries in the processes injecting steam and injecting a mixture of nano-Fe_2O_3 and steam were 28.18 and68.41% respectively at 500 minutes of the experiment; the total recovery values after 1756 minutes were 38.34 and 69.53% for steam injection and injecting a mixture of steam and nanoparticles respectively.

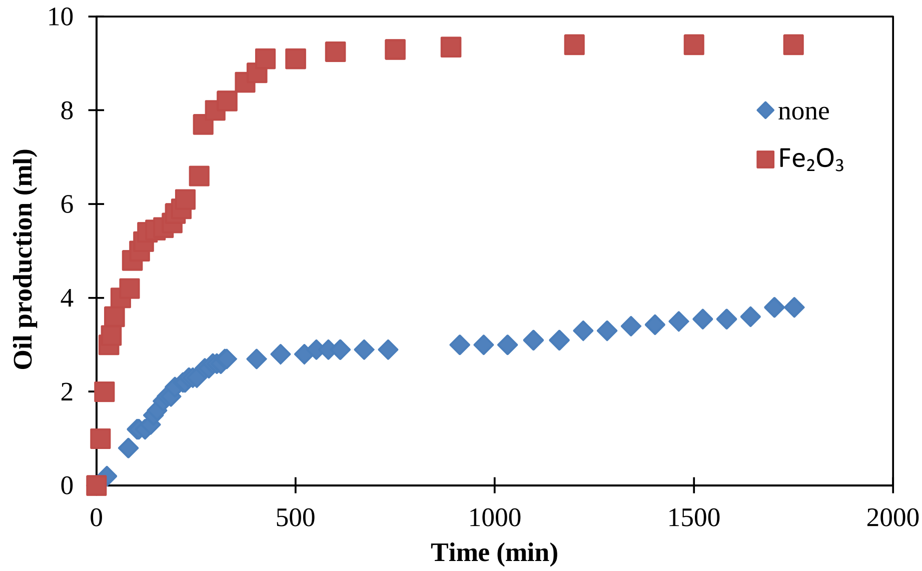

Figure 4
Effect of injecting a mixture of nano-Fe_2O_3 and steam on heavy oil production.

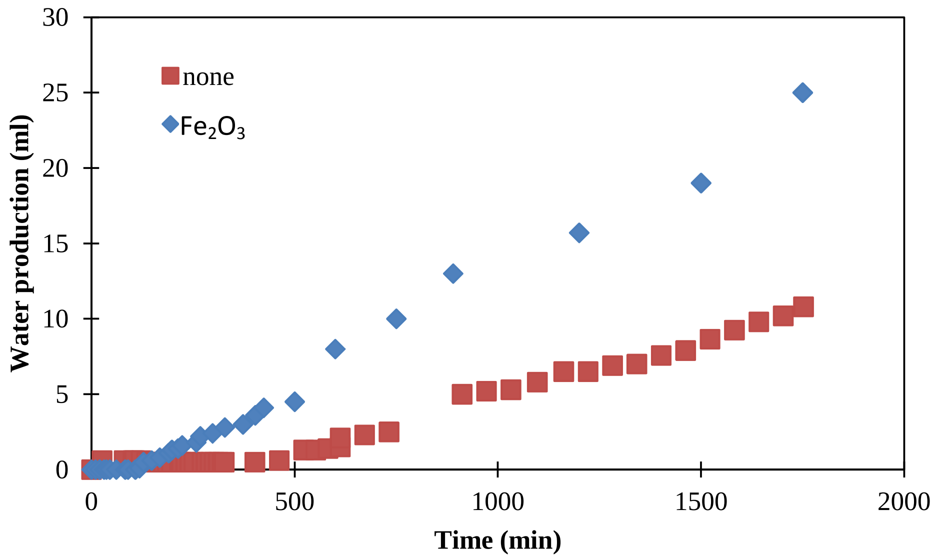

Figure 5
Effect of injecting a mixture of nano-Fe_2O_3 and steam on water production.

The results show that injecting a mixture of nano-Fe_2O_3 and steam increases recovery and reduces time to complete the experiment. In this test, the core contained 9.97 gr of heavy oil.
The observations show that during the experiment of injecting a mixture of nano-Fe_2O_3 and steam oil flows more easily due to reduced oil viscosity in the vicinity of the nanoparticles. In addition to reducing the viscosity, nanoparticles cause the injected fluid viscosity to increase and raise the amount of oil swept from the core pores.

4. Conclusions

In the current study, the effect of nanoparticles on heavy oil viscosity is investigated experimentally. The obtained viscosity data show the effect of Fe_2O_3 nanoparticles at different concentrations and temperatures. Heavy oil viscosity could be decreased by adding Fe_2O_3 nanoparticles even at different temperatures. The catalytic reaction and heat transfer properties may be the reason for this reduction. Fe_2O_3 nanoparticles, as a cracking catalyst, crack the C-S, C=C, and C≡C bonds of heavy components of heavy oil and decreases the heavy oil viscosity. The optimum Fe_2O_3 nanoparticle concentrations are obtained to 0.2 and 0.5% and the maximum reduction in heavy oil viscosity is achieved at high temperatures. Increasing of heavy oil viscosity at high concentrations of nanoparticles occurs at different temperatures for all the types of nanoparticles. Several experiments were performed by injecting steam and injecting a mixture of nanoparticles and steam using one type of core (carbonate). Saturated steam was injected at a pressure of 1100 psi in all the experiments (295 °C). Moreover, a comparison was made between the results of the two injection processes. It was found out that injecting a mixture of nanoparticles and steam decreases the oil viscosity. In fact, the nanoparticles cause a reduction in the viscosity of the injected fluid, and as a result, the amount of oil swept from the core pores increases. Therefore, a higher oil recovery and shorter experiment time are achieved.

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