

Enhanced oil recovery using nanoparticle-stabilized oil/water emulsions

Hanam Son^{*,***}, Hyuntae Kim^{*}, Geunju Lee^{**,†}, Jinwoong Kim^{**}, and Wonmo Sung^{***}

^{*}Korea Institute of Geoscience and Mineral Resources, Daejeon 305-350, Korea

^{**}Department of Applied Chemistry, Hanyang University, Ansan 426-791, Korea

^{***}Department of Natural Resources and Environmental Engineering, Hanyang University, Seoul 133-791, Korea

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Abstract—We experimentally investigated nanoparticle-stabilized emulsions for enhanced oil recovery (EOR) applications. The emulsions were injected into a silica bead column containing mineral oil, and the oil recovery was calculated using a mass-balance approach. The experiments were carried out as follows: 1) The emulsions were injected into a column with 100% water saturation to investigate the mobility of the water and emulsions, 2) Water flooding was then carried out at initial oil and water saturation, and the emulsion flooding was injected to calculate the enhancement in the oil recovery rate. The results indicate that the nanoparticle-stabilized emulsions increased the oil recovery rate by 11% after water flooding. The mechanism for this is attributed to a greater pressure difference across the porous medium, leading to oil remaining in the pores being produced via a piston effect. These results indicate that nanoparticle-stabilized emulsions may be effective EOR agents.

Keywords: Nanoparticle-stabilized Emulsions, Oil-in-water Emulsions, Enhanced Oil Recovery (EOR), Water Flooding, Silica Bead Column

INTRODUCTION

Nanoparticle-stabilized emulsions have attracted much recent research interest as emulsifiers for enhanced oil recovery (EOR) applications with advantages over conventional emulsions stabilized by surfactants or by colloidal particles. For example, solid nanoparticles can be attached to the oil/water interface and form a rigid nanoparticle monolayer on the surface of the droplet, which induces a highly stable emulsion [1-4] that can withstand harsh environmental conditions [5]. Emulsions stabilized using nanoparticles can travel greater distances than emulsions stabilized using colloidal particles [3,4].

Recently, detailed characterizations of the properties of emulsions stabilized by nanoparticles have been reported. The influence of the nanoparticle wettability, particle concentration, initial location (i.e., whether dispersed in water or in oil), and the properties of the oil on the emulsion system have been studied, and detailed reviews are available [6-10]. In addition, flooding experiments have been carried out using silica beads, sand packs, and sandstone to evaluate how effective nanoparticle-stabilized emulsions are as a displacing fluid for EOR [3,11,12]. These studies report the possibility of substantial additional recovery over conventional water flooding. However, an accurate assessment of the potential for nanoparticle-stabilized emulsion flooding requires a detailed analysis of aspects such as the pressure difference under various flow phase conditions.

Our objective was to investigate the effect of nanoparticle-stabilized emulsions in EOR applications: specifically, to analyze the flow

of the emulsions in a porous medium and to investigate the movement at the fluid interfaces, as well as to investigate the oil recovery rate and pressure difference with water flooding and with emulsion injection.

EXPERIMENTAL MATERIALS

1. Nanoparticle-stabilized Emulsions

Oil-in-water emulsions were prepared using *n*-decane and deionized water as the oil and water phases, and hydrophilic silica nanoparticles were used to stabilize the emulsions. The nanoparticles were ordered from Evonik industries and consist of silicon dioxide (SiO₂) 99%. A silane coupling agent (SCA) and polyvinyl alcohol (PVA) were used to improve the adsorption of nanoparticles at the water/*n*-decane interface. The materials used in the preparation of the emulsions are listed in Table 1.

The procedure for fabrication was as follows. First, *n*-decane, deionized water, silica, and SCA were mixed using a homogenizer (ULTRA TURRAX T25 basic) for 2 minutes at 19,000 rpm. During the mixing, the SCA facilitated a coupling reaction between the hydroxyl groups and alkyl chains at the surface of the silica.

Table 1. Materials used to prepare the emulsions

Component	Materials	Content (wt%)
Nanoparticles	Hydrophilic silica (12 nm)	3
Oil	<i>n</i> -Decane	17
Water	Deionized water	80
Silane coupling agent (SCA)	Hexadecyl-trimethoxy-silane	3
Polyvinyl alcohol (PVA)	Polyvinyl alcohol (PVA)	0.5

[†]To whom correspondence should be addressed.

E-mail: dreamerj@gmail.com

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Table 2. The characteristics of the silica-bead-filled column

Length	30 cm
Diameter	2.54 cm
Porosity	36.8%
Pore volume	56 mL
Permeability	60 Darcy

Second, PVA was added to the emulsions, which was then mixed again for 1 minute to improve the stability of the emulsions. The properties of the emulsions are as follows. The viscosity was in the range of 20-3,000 cp and the shear rate was in the range of 0.01-200 s^{-1} ; the emulsions exhibited shear-thinning across the entire range of shear rates. Furthermore, the average diameter of the oil droplets was 33 μm .

2. Oil and the Porous Medium

Mineral oil was supplied by Sigma-Aldrich industries (M-3516). The viscosity was measured at 30 cp using a Brookfield viscometer (LV DV-1 prime) at 22 °C. A cylindrical column was filled with the 1 mm silica beads; the parameters of the column are listed in Table 2.

EXPERIMENTAL FLOODING PROCEDURE

1. Experimental Apparatus

The nanoparticle-stabilized emulsions were injected as a recovery agent following water flooding at room temperature (i.e., 22 °C). Fig. 1 shows a schematic diagram of the experimental apparatus.

The water was injected using a pump through a 1/8-inch-diameter tube to push a piston plate located inside the vessel. The piston plate also separated different fluids while avoiding mixing (Furthermore, injecting emulsions directly using the pump may be harmful to the piston of the pump.). A cylindrical container was installed with a piston plate inside. The containers were filled with the emulsions above the piston. Valves were installed at the inlet and outlet of the container to regulate the fluid flow. The influent flow lines from the container were connected to the porous medium (silica bead column). Fluids flowed through the pores of the silica beads and were collected using a measuring cylinder. Cooling water was circulated around a column to ensure a constant temperature, and a filter with 150- μm -diameter pores was attached at the inlet and outlet of the cell to prevent the silica beads from leaking out. During fluid flow in the porous medium, the pressure difference between the inlet and outlet of a column was monitored. An electronic balance and optical imaging were used to measure the production. The measured data were logged on a personal computer (PC).

2. Flooding Experiments

The experiments were carried out as follows: 1) the emulsions were injected into the porous medium with 100% water saturation; 2) water flooding with initial and oil saturation; 3) emulsion flooding following water flooding. In experiment 2), the following steps were carried out to prepare the initial state of the porous medium. First, water was injected into the silica beads, and then the mineral oil was injected into the water-saturated medium until no more water was produced. Second, the initial water and oil saturation were calculated from the amount of water produced. The injection of emul-

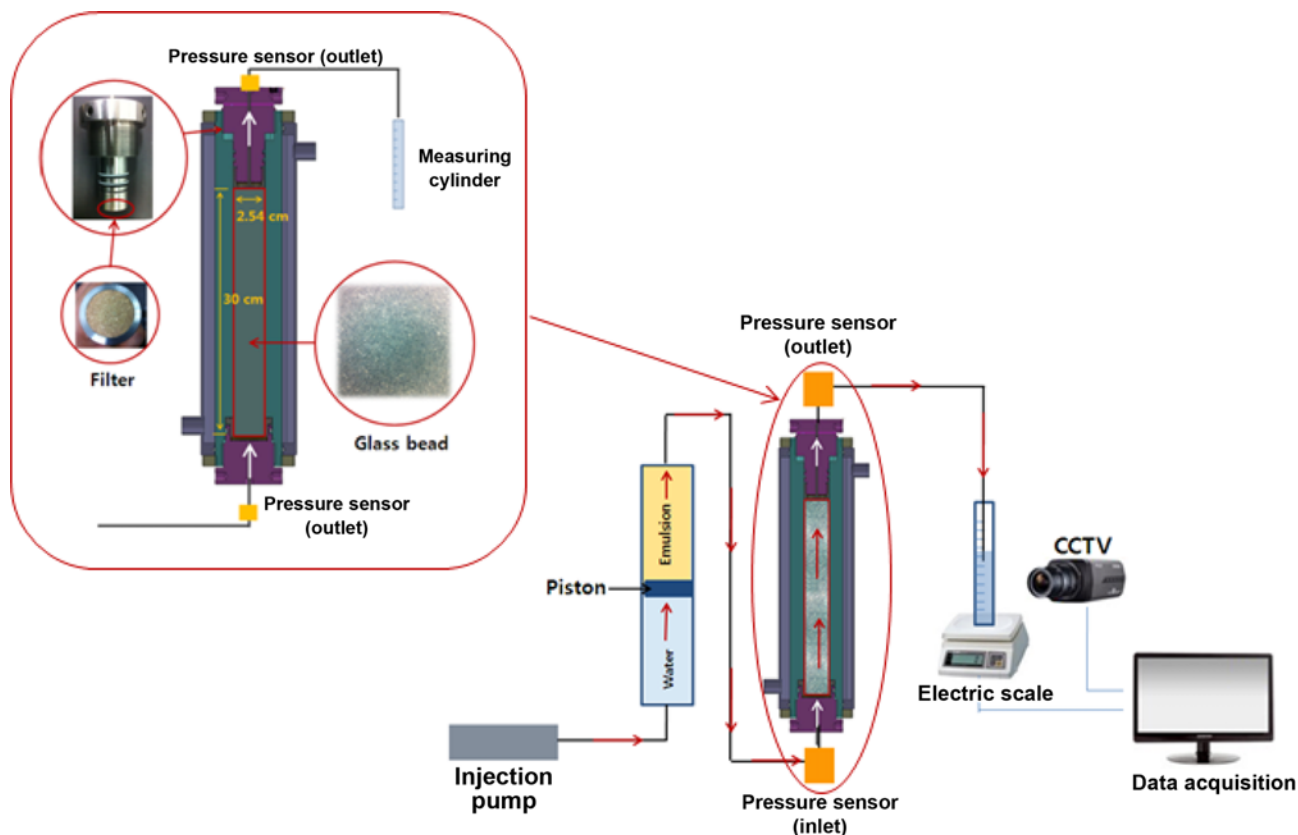


Fig. 1. Schematic diagram showing the flooding apparatus.

sions and water in all experiments was carried out at a flow rate of 1 mL/min.

RESULTS AND DISCUSSION

1. Emulsions Flow with Fully Water Saturated

Flooding with the emulsions makes it possible to observe the flow in the porous medium when saturated with water. This is a significant advantage in the characterization of the movement at the interfaces between the water and the emulsions. Before the emulsions reached the silica beads, the average flow rate in tubing was 1.02 mL/min. The emulsions were introduced into the pores between beads and flowed as pushing residual water. Water was immediately produced following injection, and the flow in the porous medium reached a steady state, with a production rate of 1 mL/min. After

56 minutes, the color of the measuring cylinder changed, as shown in Fig. 2. Also, the mass rate in the measuring cylinder changed from 1 g/min to 0.8-0.9 g/min, as shown in Fig. 3. The breakthrough time of the emulsion was therefore 56 minutes, and the water saturation was predicted to be approximately 13.5%, based on the material balance calculations shown in Table 3. The emulsion slug displaced the initial water via a piston effect.

Table 3. Results of emulsion injection with fully saturated water

Initial water saturation	100%
Injection fluid	Emulsion
Water saturation after emulsion injection	13.5%
Emulsion breakthrough time	56 min

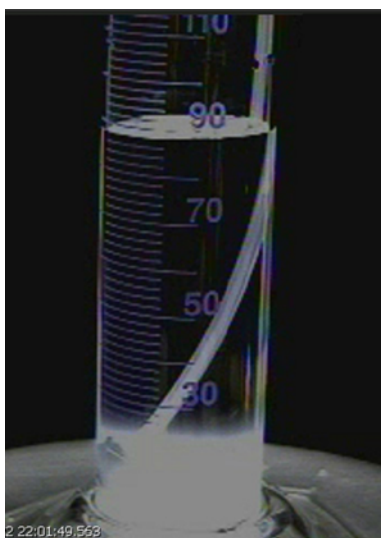


Fig. 2. Emulsions produced in the measuring cylinder.

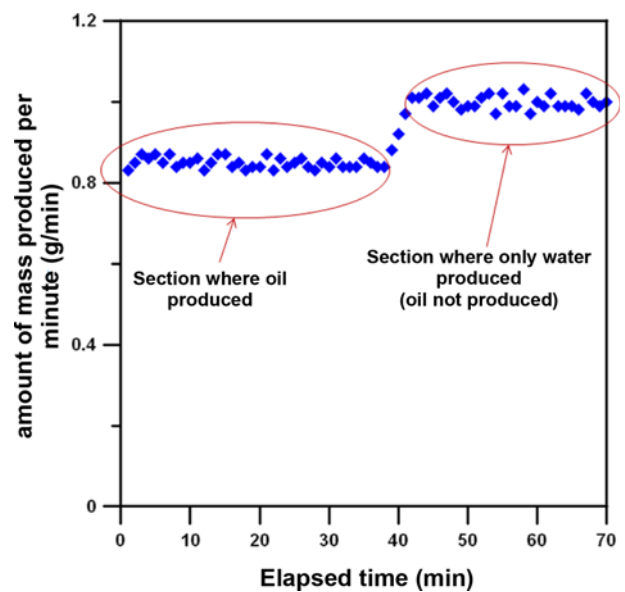


Fig. 4. Flow rate of oil and water.

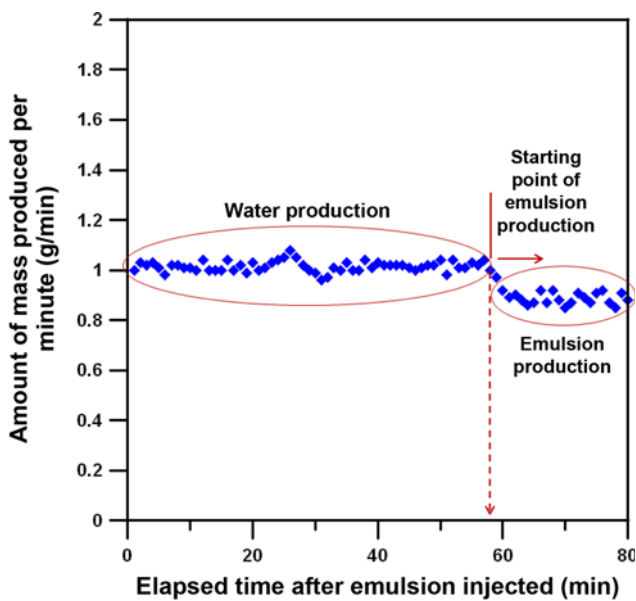


Fig. 3. Mass flow rate of emulsions and water in the measuring cylinder.

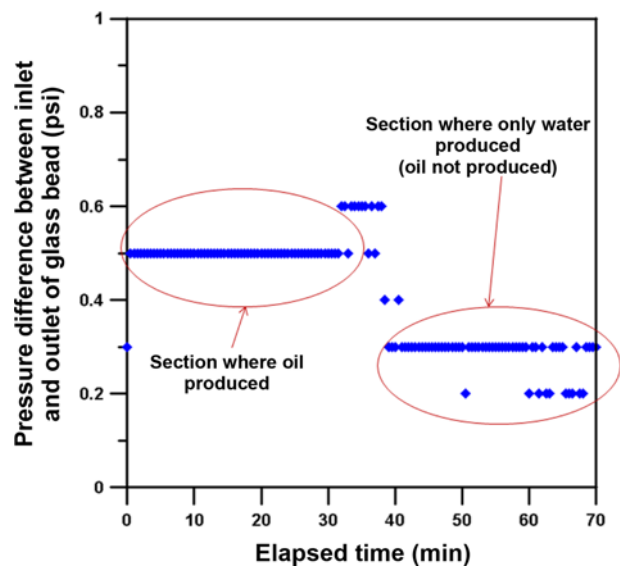


Fig. 5. Pressure difference between the inlet and outlet during water flooding.

Table 4. Oil recovery using water flooding

Initial saturation	Water saturation	23.13%
	Oil saturation	69.87%
Injection fluid		Water
Saturation after water injection	Water saturation	78.91%
	Oil saturation	21.09%
Oil recovery		72.21%
Water breakthrough time		39 min

2. Water Flooding

The porous medium was saturated with 23.13% water and 69.87% oil. Water was then injected into the porous medium at a rate of 1.0 mL/min until oil was no longer produced. The initial mass flow rate from the column was 0.83-0.88 g/min, and the pressure difference between the inlet and outlet was 0.5 psi (see Figs. 4 and 5). After 39 minutes, water was produced. The pressure difference between inlet and outlet of the silica bead column was 0.2-0.3 psi as lowering during water production (Fig. 5), it was because viscosity of water (1 cp at 22 °C) is lower than oil (30 cp at 22 °C). The recovery rate was 72.2% (see Table 4). The breakthrough time was shorter than that of the two-phase flow of the emulsions and water. It appears that displacement was less sharp at the oil/water interface compared with the emulsions/water interface, which is attributed to viscous fingering.

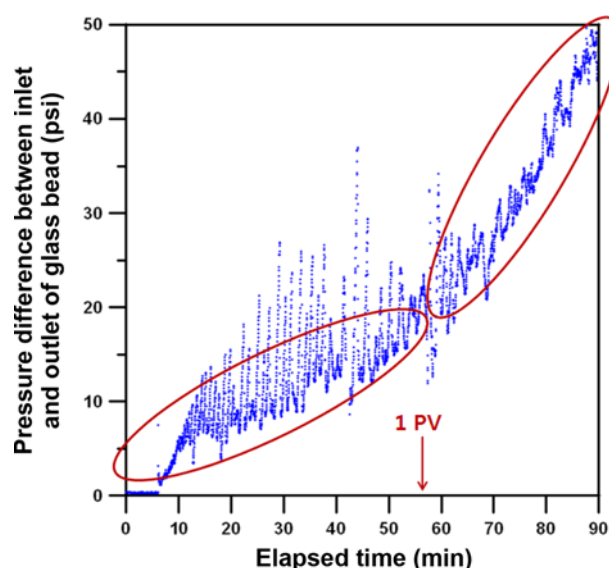
3. Emulsion Flooding

The emulsions were injected after water flooding; the initial water saturation was 78.91%, and the initial oil saturation was 21.09%. As a result of experiment, the increase in the oil recovery rate was 11.57%, and 41.67% of the residual oil could be recovered (see Table 5).

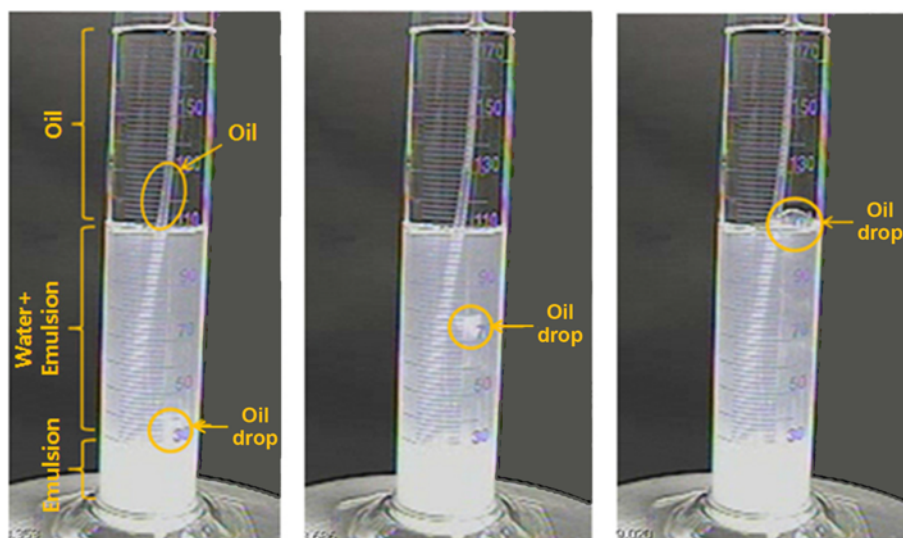
During emulsion injection, oil was not produced until the emulsions were injected by one pore volume (1 PV); however, additional oil could be produced following PV injection. In addition, the pressure difference increased following the injection of PV, as shown in Fig. 6. This may be explained by analyzing the flow rate of the produced oil and the pressure drop. Before emulsion flood-

Table 5. Oil recovery by emulsion flooding

Total pore volume	56.89 mL
Volume of injected emulsions	85.33 mL (1.5 PV)
Oil saturation before emulsion injection	21.09%
Oil saturation after emulsion injection	12.3%
Oil recovery enhanced by emulsion injection	11.57%
Oil recovery by water and emulsion flooding	83.78%

**Fig. 6. Pressure difference between the inlet and outlet during emulsion flooding.**

ing, the porous medium was saturated with residual oil (21.09%) and plenty of water (78.91%), and then only water was produced into measuring cylinder until 1 PV injection since emulsion injection was started. The reason, only water had been produced, was because almost producible oil was already produced by water flood-

**Fig. 7. Production of oil in the measuring cylinder during emulsion flooding.**

ing, and a greater pressure was required to recover the additional oil. Furthermore, emulsions were not injected into all the pores until 1 PV injection of the emulsions; thus, a significant amount of water was still saturated in the pores. Because of this, residual water was easily produced, and the pressure drop increased more slowly than 1-1.5 PV injection. However, in the case of 1-1.5 PV, the pressure drop increased rapidly because the emulsions (with a higher viscosity than water) filled the porous medium, and most of the water had already been recovered. When the pressure increased sufficiently, oil remaining in the pores was produced with the emulsions, as having the mobility caused by a piston effect. Thus, the pressure drop between the inlet and outlet increased, and additional oil could be recovered.

Fig. 7 shows that oil was recovered after 1 PV. After the oil passed through the porous medium and tubing, the oil formed droplets, which traveled from the bottom to the top of the measuring cylinder. These results show that nanoparticle-stabilized emulsions are effective as recovery agents and supply additional pressure to the porous medium.

CONCLUSIONS

Based on the results of this study, the following conclusions may be drawn:

1. In water flooding, the breakthrough time was shorter than emulsion injection in the porous medium with fully saturated water. These results mean that water could not push sharply oil at the oil/water interface due to viscous fingering. However, an emulsion slug could displace water sharply at the emulsion/water interface.

2. Flooding using nanoparticle-stabilized emulsions can increase oil recovery by 11% after water flooding, and nanoparticle-stabilized emulsions can be used as EOR agents. They result in an increased mobility of the oil in the pore network.

3. The recovery of oil using nanoparticle-stabilized emulsions was due to the supply of additional pressure to the porous medium,

which led to recovery of the residual oil in the pores via a piston effect when the pressure was increased.

ACKNOWLEDGEMENTS

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