



Surfactant flooding characteristics of dodecyl alkyl sulfate for enhanced oil recovery



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ABSTRACT

Surfactant-enhanced oil recovery is a type of enhanced oil recovery (EOR), a method to produce residual oil by injecting surfactant solution into the reservoir. The application of surfactant EOR requires knowledge of the phase behavior for more efficient production of residual oil.

In this study, the relationship between dodecyl alkyl sulfate and some specific crude oils was examined through phase behavior test. It was found that the branched surfactant was more effective than the linear surfactant. The system was stable at salinities <3 wt%. On adding a small amount of co-surfactant, the emulsion activity was increased.

The gravity drainage flooding test (GDFT) was performed to determine the potential of dodecyl alkyl sulfate to produce residual oil in porous media. It was found that the solution could be flooded at temperatures of 60 °C or higher. In the core flooding test, injecting one pore volume of 2 wt% surfactant solution with 3 wt% salinity produced 26.6% more oil after water flood. With the addition of only 0.01 wt% co-surfactant, oil production increased by 1.6%. Contrary to the phase behavior test, the linear surfactant produced 1.3% more oil than the branched surfactant in the core flooding test.

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1. Introduction

Enhanced oil recovery (EOR) is a general term for any technique used to increase oil production after the primary and secondary production periods. EOR has been receiving much more attention since the last decade [1], mainly because of the increasing price of oil and the massive market value of the residual oil in reservoirs. The petroleum industry has typically used mechanical (steam/CO₂) and chemical (polymer/surfactant) EOR processes to increase production in oil and gas reservoirs [2]. Polymer injection helps in propagating the oil bank formed by surfactant injection by increasing the sweep efficiency [3]. Heavy oil recovery by alkali-polymer flooding using polyacrylamide (HPAM) solution with the addition of NaOH could be more effective in improving sweep efficiency than polymer flooding [4]. Bo et al. showed the potential of utilizing Gemini surfactants in harsh reservoir conditions for EOR applications. Gemini surfactant molecules have excellent

aqueous stability even in high salinity and properties that are lower maximum adsorption densities than the conventional single chain surfactants [5].

In this study, surfactant EOR, one of the chemical EOR processes, was investigated. The application of surfactant EOR improves the recovery of residual oil from known deposits by using a surface-active agent to reduce interfacial tension (IFT) to mobilize the residual oil. The surfactant needed to obtain good phase behavior and ultra-low IFT varies greatly with oil characteristics and reservoir conditions [6]. Low IFT can be obtained with a wide variety of surfactants, but the best surfactant depends on the crude-oil and reservoir conditions and must also satisfy several other stringent requirements [7]. When water is injected into the reservoirs during the secondary production period, the capillary forces gradually become larger as compared to the viscous forces. Generally, 50–70% residual oil is still trapped in the reservoir by the capillary forces [8].

Four primary mechanisms are used to enhance oil recovery with the help of surface-active additives: (1) the generation of very low IFT (<10^{−3} mN/m) between the oil and the water flooding solution, (2) the spontaneous emulsification or microemulsification of the trapped oil, (3) the reduction of the interfacial rheological properties at the oil–aqueous solution interface, and (4) controlling the wettability of rock pores to optimize the oil displacement [9].

Abbreviations: ASP, alkaline-surfactant polymer; CMC, critical micelle concentration; EOR, enhanced oil recovery; GDFT, gravity drainage flooding test; IFT, interfacial tension; PV, pore volumes; SEAR, surfactant-enhanced aquifer remediation.

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This study was primarily conducted to design an alkaline-surfactant-polymer (ASP) process for application in a reservoir at $>60^{\circ}\text{C}$. A screening method that utilizes the knowledge of the surfactant structure and the results of the phase behavior test was used to understand the complexities of ASP. The information obtained from the phase behavior test was then used to design and optimize a laboratory-scale flood. Laboratory tests were described by Levitt et al. which starts with the screening and optimization of surfactant formulations by phase behavior experiments incorporating co-surfactants, alkali and then advances to core flood testing with the most promising formulations [10,11]. These techniques were built on the enormous amount of information accumulated from research conducted over the past 40 years, because of the well-established relationship between the micro-emulsion phase behavior and IFT. It is common in the industry to screen surfactants and their formulations for low IFT through laboratory-based oil/water phase behavior tests [10,12]. Particularly the research on surfactant-enhanced aquifer remediation (SEAR) by Jayanti et al. at the University of Texas at Austin [13] and the chemical EOR research by Levitt et al. [14] and Jackson et al. [15].

2. Experimental procedure

In this study, an experiment was performed to analyze the oil recovery by using dodecyl alkyl sulfate through phase behavior analysis and core flooding system. The core flooding system was set horizontally to simulate oil recovery after injecting the surfactant into the system (Fig. 1). Two 500-mL syringe pumps were used to inject the fluids (brine, oil, and surfactants); a 1000-mL syringe pump was used to maintain the overburden pressure inside the core holder. The water circulating around the core holder was heated using the heat circulator to establish the required testing conditions.

The experimental temperature and pressure data were collected from the core flooding system with the help of a computer. The effluent fluids were collected in the separator. The amount of the recovered oil was measured 30 h after the collection of the effluent fluids began.

2.1. Microemulsion phase behavior

A microemulsion phase behavior test was performed to investigate the performance of the surfactant formulation with the specific crude oil. Due to the complexity of the crude oil

composition, the surfactant had to be tested with specific crude oil to find the one that could be used to generate a microemulsion system. The commonly observed Winsor type system indicates that the microemulsion can remain in equilibrium with excess oil, excess water, or both and that affect the phase change between different types of system and physicochemical properties include salinity, temperature, molecular structure and water–oil ratio [16–19].

The procedure of the microemulsion phase behavior test is simple, similar to that of aqueous solubility tests. The test consists of combining and blending crude oil, brine, the surfactant, and electrolytes, and then waiting for a phase change depending on the concentrations of the surfactant and the brine. The surfactant and the brine were blended beforehand so that the surfactant was completely dissolved in the brine. The volume of the aqueous solution was recorded and the crude oil was blended into the solution. Small amounts of aqueous components were gradually poured into a glass tube, which was then kept at room temperature in order to observe the phase change of the microemulsion. Microemulsion phases are changed from Winsor type I to Winsor type II through Winsor type III by variation of salinity at a certain temperature and pressure [20,21].

2.2. Core flooding

The core flooding procedure included core preparation, assembly, saturation, and aging with brine or crude oil; brine flooding, oil flooding, water flooding, and surfactant flooding; collection and analysis of the effluent samples for cumulative oil recovery; and surfactant retention and adsorption [22].

2.2.1. Brine flooding

After core preparation, core flooding assembly, and aging, the core was flooded with brine. The main purpose of this brine flooding was to determine the absolute permeability. About two pore volumes (PV) of brine were injected into the core at a flow rate of 0.5–1.0 mL/min until the pressure stabilized. The pressure drop was recorded to determine the average absolute brine permeability of the core.

2.2.2. Oil flooding

After the brine flooding, oil flooding was conducted at 60°C . The main purpose of the oil flooding was to determine the initial water saturation, effective oil permeability, and relative oil permeability. The oil flooding was conducted under a constant pressure to saturate the pores with oil and to accurately obtain the initial water saturation. Considering the different densities of oil and water approximately 1.5 PV of the oil was injected into the top end. The effluent fluids were collected in a separator, and the volume of the displaced water was acknowledged as the volume of oil retained in the core. The oil flooding was continued until the water cut reached $<1\%$ and the pressure stabilized. The pressure drop was recorded during oil flooding to determine the oil permeability.

2.2.3. Water flooding

Water flooding with filtered brine was performed after oil flooding to determine the residual oil saturation, effective water permeability, and relative water permeability. Approximately 0.8 PV of brine was injected into the core at a low constant flow rate of 0.4–0.5 mL/min to achieve natural residual oil saturation after the water flooding. The effluent fluids were collected in a separator. The water flooding was stopped when the water cut reached 99% and the pressure was stabilized. The residual oil saturation was estimated by the oil volume in the separator. The effective brine permeability was calculated from the pressure drop across the core.

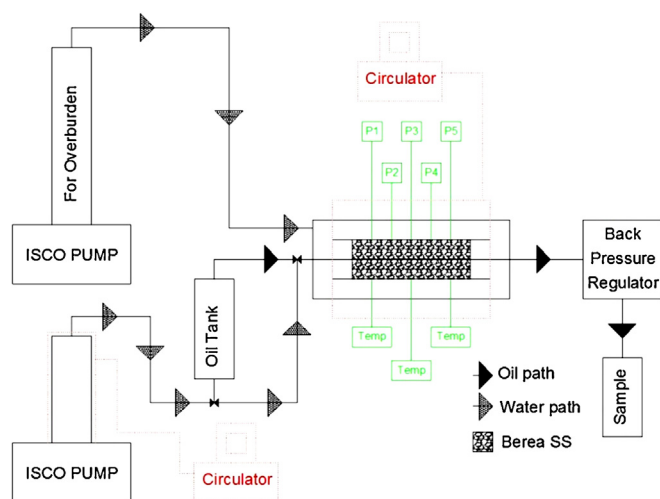


Fig. 1. Schematic design of the system for core flooding experiment.

2.2.4. Surfactant flooding

The surfactant solution was injected after the water flooding to check the performance of the solution for tertiary recovery of the residual oil in the core. A surfactant solution with 2.2 PV was injected into the core at 60 °C. The surfactant flooding was performed at a constant flow rate of 0.4–0.5 mL/min, and it was continued until emulsion production stopped. The effluent fluids were collected in a centrifuge tube for further analysis. The oil recovery and the residual oil saturation after the surfactant flooding were determined by measuring the volume of the produced oil according to the material balance approach.

3. Results and discussion

3.1. Microemulsion phase behavior

It is generally impossible to visualize the critical micelle concentration (CMC) without using an interfacial tension meter. The activation of the surfactant can be estimated by the change in color; however, this can be done when the concentration of the surfactant is slightly increased with zero salinity followed by increasing salinity with the selected concentration of the surfactant. It is reported that the interfacial tension does not change once the CMC is reached; however, the solubilization ratio increases as the concentration of the surfactant increases [23]. In this study, three different types of surfactants and two different crude oils were used, as shown in Tables 1 and 2, respectively. The surfactant used in this study is an anionic surfactant. The OSR 100 surfactant is dodecyl alkyl sulfate and the OSP 600 co-surfactant is polyoxyalkylene glycol. The chemical structures of alkyl sulfate (a) and polyoxyalkylene glycol (b) are represented in Fig. 2. The phase behavior tests of various concentrations of surfactants are shown in Table 3.

The results of the phase behavior test at various concentrations of surfactants, sodium chloride and co-surfactant are shown in Tables 4–6. The tables contain the results of the phase behavior test using Crude A that are used in flooding test. From the phase behavior test, it was found that the D-type surfactant requires a lower concentration than the L-type surfactant in order to reach the CMC. The D-type surfactant also formed emulsions at higher salinity (up to 4 wt%); however, both surfactants broke the emulsion phase at a salinity of 5 wt%. Therefore, a salinity of 3 wt% was used in the core flooding experiment to stabilize the emulsion system. In addition, Crude A and B showed similar responses in the phase behavior test; therefore, only Crude A was used in the core flooding.

3.1.1. Small-scale gravity drainage flooding test (GDFT)

Before the core flooding, the potential of the surfactant to permeate the porous media was investigated. To check the

Table 1
Surfactant types used in the experiment.

Surfactant	Product name	Content (%)	Remarks
L-type	Dodecyl alkyl sulfate	100	Linear
D-type			Branched
Co-type	Polyoxyalkylene glycol	95	Co-surfactant

Table 2
Crude oil types used in the experiment.

Crude oil	API	SG [60°/60 °F]	Viscosity
Crude A	30.6°API	0.873	11.5 cP@60 °C
Crude B	17.1°API	0.952	355.5 cP@71 °C

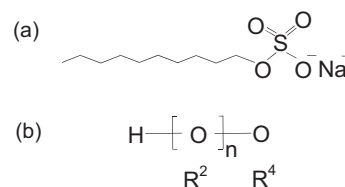


Fig. 2. The chemical structures of alkyl sulfate (a) and polyoxyalkylene glycol (b).

capacity using GDFT, 80–100 mesh glass beads were compacted in a plastic tube with a tiny hole at the bottom. As a result, the brine formed a precipitate at room temperature, as shown in Fig. 3.

The same experiment was carried out by increasing 10 °C from 30 to 80 °C, respectively. A minimum temperature of 60 °C was required for the surfactant solution to completely permeate the porous media. Accordingly, the core flooding was tested at 60 °C.

During the GDFT, an aqueous solution of the surfactant was formed, thereby producing a microemulsion while passing through the porous media. This experiment showed that the surfactant required a concentration of at least 2% to economically produce crude oil from a porous media. However, crude oil shows different properties in different fields; therefore, more phase behavior tests are needed.

3.2. Core flooding

The D-type surfactant requires lower concentration of the surfactant in lighter oil with salinity <3 wt%, which will otherwise make the microemulsions unstable in both D- and L-type surfactants. The temperature during the core flooding experiment is >60 °C. In accordance with these results, the core flooding system stabilized the surfactant in the porous media.

3.2.1. Flooding preparation

The gas permeability of the sandstone core that was used in this study ranged from 75 to 125 mD, as marked by the supplier. The measured average liquid permeability of the four cores was 115 mD, as shown in Table 7.

In the oil flooding process known as drainage, oil was injected until the water cut was <1%. After 30 h of aging in the reservoir conditions, the oil was assumed to be adsorbed on the pore surfaces of the core.

In the water flooding process called imbibition, an average of 0.62 PV brine was injected into the core. The same brine was injected until the water cut reached 99%. The performances of oil recovery by water flooding were described in Fig. 4. The average oil production was 25.1%, which is the normal oil production rate by water flooding in sandstones with a permeability of 100 mD.

3.2.2. Surfactant flooding

Aqueous surfactant solutions were injected into each of the different cores, as shown in Table 8. From the phase behavior test, the concentration of the aqueous solution was determined at 2 wt%. A surfactant with 1.99 wt% concentration and a co-surfactant with 0.01 wt% concentration were applied to cores 3 and 4, respectively. In this process, an average of 2.2 PV of the aqueous solution was injected into the cores. It was found that the L-type surfactant was more effective than the D-type. Since the

Table 3

Surfactant and salinity concentrations in the phase behavior test.

Test no.	Surfactant types	Surfactant concentrations (%)	Co-surfactant concentrations (%)	Salinity concentrations (%)	Crude oil
1	L	0.01–10	–	–	Light and heavy
2	D	0.01–10	–	–	Light and heavy
3	D and L	0.5–2.5	–	–	Light
4	D and L	2	–	0.5–5.0	Light
5	D and L	2	–	0.5–5.0	Heavy
6	D and L	2	0.01–0.3	3.0	Light

Table 4

Phase behavior test without salinity in light oil.

Test no.	Primary surfactant	Surfactant concentration (wt%)	Water w/NaCl (wt%)	Surfactant reaction (cm)	Winsor
1	OSR 100L	0.50	–	0	Type I
2	OSR 100L	0.70	–	0	
3	OSR 100L	0.90	–	0	
4	OSR 100L	1.00	–	0	
5	OSR 100L	1.10	–	0.2	Type III (brownish color)
6	OSR 100L	1.30	–	0.5	
7	OSR 100L	1.50	–	2	
8	OSR 100L	1.70	–	4.3	
9	OSR 100L	2.0	–	Completely	Type II
10	OSR 100L	2.2	–		
11	OSR 100D	0.50	–	0	Type I
12	OSR 100D	0.70	–	0	Type I (oil and water contact getting flat)
13	OSR 100D	0.90	–	1	Type III (brownish color)
14	OSR 100D	1.00	–	3	
15	OSR 100D	1.10	–	5	
16	OSR 100D	1.30	–	Completely	Type II
17	OSR 100D	1.50	–		

Table 5

Phase behavior test with salinity in light oil.

Test no.	Primary surfactant	Surfactant concentration (wt%)	Water w/NaCl (wt%)	Surfactant reaction	Comment
1	OSR 100L	2.0	0.5	Stable	
2	OSR 100L	2.0	1.0	Stable	
3	OSR 100L	2.0	1.5	Stable	
4	OSR 100L	2.0	2.0	Milky	Still stable
5	OSR 100L	2.0	3.0	Separating	Start to break the emulsion
6	OSR 100L	2.0	4.0	Separating	Break slowly
7	OSR 100L	2.0	5.0	Completely	Completely break
8	OSR 100D	2.0	0.5	Stable	
9	OSR 100D	2.0	1.0	Stable	
10	OSR 100D	2.0	1.5	Stable	
11	OSR 100D	2.0	2.0	Stable	
12	OSR 100D	2.0	3.0	Milky	Still stable
13	OSR 100D	2.0	4.0	Separating	Start to break the emulsion
14	OSR 100D	2.0	5.0	Completely	Completely break

Table 6

Phase behavior test with 3 wt% salinity and OPS 600 co-surfactant in light oil.

Test no.	Primary surfactant	Surfactant concentration (wt%)	Co-surfactant concentration	Surfactant reaction	Comment
1	OSR 100L	2.0	0.01	Stable	
2	OSR 100L	2.0	0.05	Stable	
3	OSR 100L	2.0	0.10	Stable	Increased emulsion phase then previous case
4	OSR 100L	2.0	0.15	Stable	
5	OSR 100L	2.0	0.20	Stable	
6	OSR 100L	2.0	0.25	Stable	No more effects
7	OSR 100L	2.0	0.30	Stable	
8	OSR 100D	2.0	0.01	Stable	
9	OSR 100D	2.0	0.05	Stable	Increased emulsion phase then previous case
10	OSR 100D	2.0	0.10	Stable	
11	OSR 100D	2.0	0.15	Stable	
12	OSR 100D	2.0	0.20	Stable	
13	OSR 100D	2.0	0.25	Stable	No more effects
14	OSR 100D	2.0	0.30	Stable	Decreased emulsion phase then previous case



Fig. 3. Precipitate formed after gravity drainage flooding test (GDFT) at room temperature conditions.

Table 7

Absolute permeability and porosity determined by brine flooding.

Core no.	Absolute permeability (md)	Porosity (%)	Pore volume (mL)
Core no. 1	114	18.4	63.00
Core no. 2	116	18.8	63.46
Core no. 3	116	18.8	63.43
Core no. 4	115	18.4	62.11

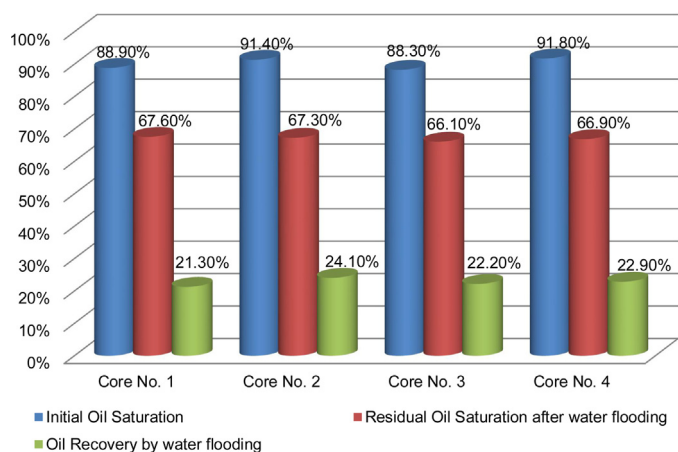


Fig. 4. Oil saturation before injecting surfactant.

co-surfactant was non-ionic, it improved the behavior of the surfactant system, thereby slightly improving the oil production. However, the non-ionic surfactant is not cost-effective for the petroleum industry. Because of this, the use of a large amount of co-surfactant is avoided.

3.2.3. Recovery factor and tertiary recovery

The recovery factor and the tertiary recovery were determined based on the test results. Tertiary recovery is dimensionless and is

Table 8

Residual oil saturation and oil recovery.

Core no. and surfactant type	Residual oil saturation		Total oil recovery	
	Water flooding	Surfactant flooding	Water flooding	Surfactant flooding
Core no. 1 With D-type	67.6%	30.8%	23.9%	65.4%
Core no. 2 With L-type	67.3%	25.2%	26.4%	72.4%
Core no. 3 With D- and Co-type	66.1%	27.4%	25.2%	68.9%
Core no. 4 With L- and Co-type	68.9%	23.7%	24.9%	74.2%

Table 9

Tertiary recovery factor (RF) after surfactant flooding.

Core no. and used surfactant type	Tertiary RF	Tertiary RF per PV ^a (unitless)
Core no. 1 With D-type	54.5%	25.9
Core no. 2 With L-type	62.5%	27.2
Core no. 3 With D- and Co-type	58.5%	27.8
Core no. 4 With L- and Co-type	65.7%	28.5

^a PV, pore volume.

Table 10

The absolute permeability and the permeability after the test.

Core no. with used surfactant type	Absolute permeability	Permeability after the test	Permeability change, %
Core no. 1 With D-type	114 mD	101 mD	–11%
Core no. 2 With L-type	116 mD	104 mD	–10%
Core no. 3 With D- and Co-type	116 mD	108 mD	–7%
Core no. 4 With L- and Co-type	115 mD	110 mD	–4%

represented by the total oil production divided by the PV of the injected surfactant solution [24]. As shown in Table 9 and Fig. 5, the co-surfactant improved the oil production per PV of aqueous solution by an average of 1.6%. However, the L-type surfactant was more effective than the D-type surfactant, contrary to the results of the phase behavior test. Brine flooding was again performed with each core to check the absolute permeability after the surfactant flooding test. The permeability reduced after surfactant flooding, as shown in Table 10. This result showed that as the aqueous solution was injected into the core, brine precipitated, thereby disturbing the permeable path of the core, as was seen in the GDFT.

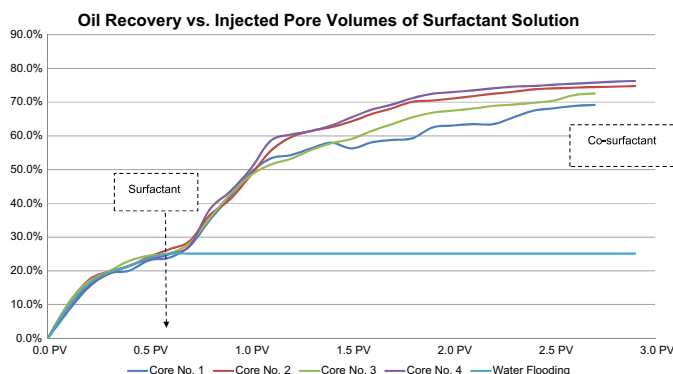


Fig. 5. Oil recovery vs. injected pore volumes of surfactant solution.

4. Conclusions

In this study, branched and linear dodecyl alkyl sulfates were compared through the phase behavior test and the core flooding test. The phase behavior test must be performed before applying the surfactant EOR in order to find the optimal surfactant conditions. The phase behavior test was performed with variable surfactant concentrations in light and heavy oils. The results show that a similar reaction occurs in both oils; however, the heavy oil requires a higher surfactant concentration to form the micro-emulsion system. In addition, the phase change of the micro-emulsion from Winsor type I to type II, and finally to type III was observed. The D-type surfactant reached the CMC earlier in each crude oil.

The phase behavior test was performed with various salinity concentrations in light and heavy oils. Surfactant with 2 wt% concentration was used. The emulsion system was stable within a salinity concentration of 3 wt%, and began to break at salinity concentrations above 5 wt%. The same phase behavior test was performed as previously by adding a very low concentration of the co-surfactant. It was found that addition of the co-surfactant increased the emulsion activity; however, adding the co-surfactant at salinity concentrations of 0.25 wt% or higher did not cause any change in the emulsion formation.

To gauge the possibility of producing residual oil with dodecyl alkyl sulfate in porous media, the GDFT was performed with the salinity at 3 wt% and surfactant at 2 wt%, based on the phase behavior tests. It was found that the solution could be flooded in porous media only at temperatures of 60 °C or higher. If the temperature is <60 °C, the aqueous solution formed precipitates that disturbed the microemulsion system.

In the core flooding test injecting with 3 wt% saline solution and 2 wt% surfactant solution into the core, 26.6% more oil was produced on average through the use of 1 PV surfactant solution. Co-surfactant with 0.01 wt% concentration was used to investigate the possibility of increasing oil production with a small amount of co-surfactant. The result showed that oil production was increased by 1.6% after adding only 0.01% of co-surfactant. Contrary to the phase behavior test, the linear surfactant produced more oil than the branched by 1.3% in the core flooding test. However, the D-type surfactant formed precipitates on contact with brine, which disturbed the porous media system.

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