

A NOVEL EOR POLYMER (II) ——INVESTIGATION ON IN-SITU GELATION OF SMRF SYSTEM IN BEREA CORE

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ABSTRACT

In-situ gelation of aqueous sulfomethylated resorcinol formaldehyde (SMRF) system in Berea core has been investigated. Two sets of displacement experiments were conducted with this system (containing 5% NaCl, 0.036% $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$). The brine permeabilities of the cores were reduced significantly from about 600 to 0.1 md. The in-situ gelation in Berea core occurred a little bit earlier than gelation anticipated from bulk test in the experiments. The gel time was easier to control at initial pH between 6 and 8. During injection of SMRF system, the apparent viscosity was less than 1 mPa · s at 41 °C.

INTRODUCTION

Primary and secondary oil recovery together only 25—50% recovery of the oil originally in place in a reservoir can be obtained. A major reason for low oil recovery efficiency in waterflooding and other displacement processes is poor performance due to reservoir heterogeneities. Volumetric sweep efficiency of displacement processes can be improved significantly by using gelled polymers to modify in-situ permeability. This process, which is typically referred to as polymerflooding, is among several methods known as enhancing oil recovery (EOR) techniques applied to extract additional oil beyond primary and secondary productions.

Gel treatment technology is a technique used to block high permeable zones. When high permeability zones are blocked, injected solutions will flow through the previously , unswept low permeable zones resulting in an

increase in oil recovery. In-situ gelation refers to development of a region of high resistance due to the gelation process taking place inside of a porous medium when gel solution is injected. Berea cores are used to study the gelation of the gel forming solution in the laboratories.

The primary objective in the present work was to study the gelation process of a novel EOR polymer, aqueous sulfomethylated resorcinol formaldehyde system, as it occurred in-situ in the Berea cores.

EXPERIMENTAL

The system is shown schematically in Fig. 1. All solutions to be injected into the Berea cores were filtered through a 0.22 micron filter. During the experiments, a Berea core was initially saturated with brine (5% NaCl), then injected with a gel solution at a fixed pump setting and lastly shut-in. Both the Berea core and the gel solution were located in a constant temperature water bath. Pressure distribution along the length of the core during a displacement was measured with transducers connected through a demodulator to a minicomputer. The general behavior of the gelation in the Berea core was inferred from interpretation of the pressure data and analysis of effluents that were collected manually.

Gel solution

Aqueous sulfomethylated resorcinol formaldehyde (SMRF) gel solution # 1 (2.5 wt. % R, mol ratio of SMRF : F_2 (F_2 molal quantity of formaldehyde added in polycondensation of sulfomethylated resorcinol) : F_1 (F_1 molal quantity of formaldehyde added in sulfomethylation of resorcinol) : S (S molal quantity of sodium sulfite added) : R (R molal quantity of resorcinol added) = 1.4 : 0.75 : 0.5 : 1, Brine D : 5% NaCl, 0.036% $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$) was made as described in Part (I)^[1]. The gel solution was prepared just before investigation. Initial pH of this gel solution was adjusted to 6.00 or 8.00 (System I or system II).

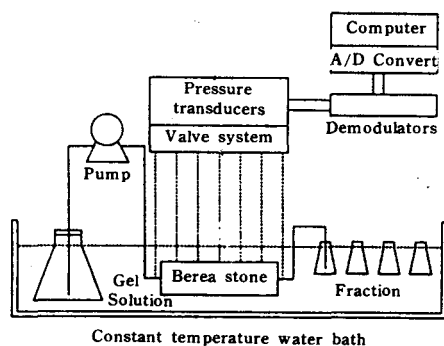


Fig. 1 Experimental apparatus for in-situ gelation studies

Berea core

30.48 cm long, 5.08 cm ID and 6 sections Berea cores were used. The inlet and outlet fittings were in place, and the pressure-port tubings were capped. The cores were covered with a resin coating. The cores were unfired.

The pore volumes were determined from measurements of core weights with the fittings before and after saturation, brine density and the dead volumes of the tubings. The pore volumes were confirmed by dispersion experiments. The outlet of the core was connected to the sample inlet of the differential refractometer Waters R401. 7.25% K_2SO_4 solution was taken as a reference solution. 5%, 5.2% and 5% NaCl solution were displaced through the core respectively. At a constant flow rate of about 2 g/min, differential refractive indices were recorded, then converted to dimensionless concentration.

Permeabilities for each section and the total length of cores were determined from pressure-drop measurements with brine as the flowing fluid at several constant flow rates. The brine permeabilities were calculated from Darcy's Law.

The Berea core was first flooded with more than 10 PV's of Brine D (5% NaCl, 0.036% $CaCl_2 \cdot 2H_2O$) with pH adjusted to 6.00 or 8.00. The core was then flushed with Brine D with a pH value that was the same as the initial pH of gel solution. The Berea core was ready for use and was used immediately.

RESULTS AND DISCUSSION

Bulk tests

Some additional bulk tests were done primarily to complement the data taken in the core experiments. Samples were placed in jars under static conditions in a 41°C water bath. A sample was periodically removed and its viscosity was measured in the microviscometer (Brookfield Digital Viscometer, Model LVTDCP, 0.8°) at a shear rate of 22.5 sec^{-1} . Fig. 2 presents a plot of viscosity vs. time for the gel solution #1 with initial pH 6.00 and 8.00. The initial viscosity was quite low (0.87 mPa · s) and changed significantly over a period of time. The gel times for them were found to be about 64 hours and 39 hours, respectively. Variations of pH with time during gelation were shown in Fig. 3.

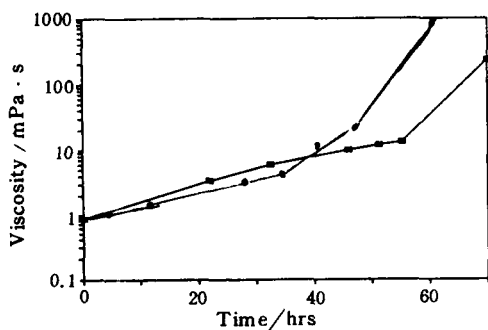


Fig. 2 Viscosity/time behavior for gel solution
 ■ initial pH 6.00; ● initial pH 8.00

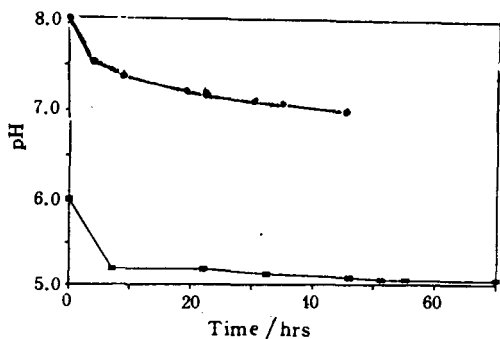


Fig. 3 pH/time behavior for gel solution
 ■ initial pH 6.00; ● initial pH 8.00

Displacement experiments

Two sets of displacement experiments were conducted with gel solution # 1. Injection of gel solution began right after the solution was prepared. Three pore volumes of SMRF gel-forming solution # 1 were injected at about 2 g/min. Effluent pH was monitored. Due to the action of Berea core, effluents of Brine D had higher pH than flushed Brine D. When pH of flushed Brine D were 6.00 and 8.00, pH of the effluent was 8.75—8.79 or 8.79—8.85 respectively. When the third volume of gel solution was injected, the effect of the core on pH change of the gel system was quite small (Figs. 4, 5). The pore volumes injected for effluent sample 16 #, 18 # and 20 # were 2.27, 2.56 and 3.15 respectively. A comparison between the displacement gel time of 35 hours and the beaker gel time of 39 hours indicates that gelation occurred a little bit earlier in the Berea core than in a beaker (Fig. 6).

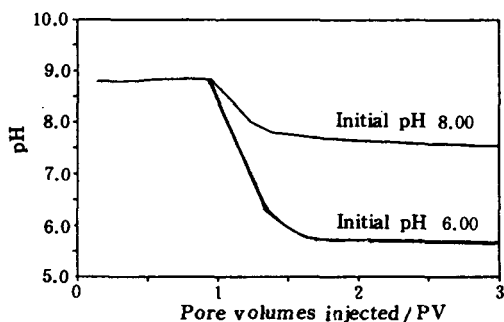


Fig. 4 pH variation with pore volumes of gel solution

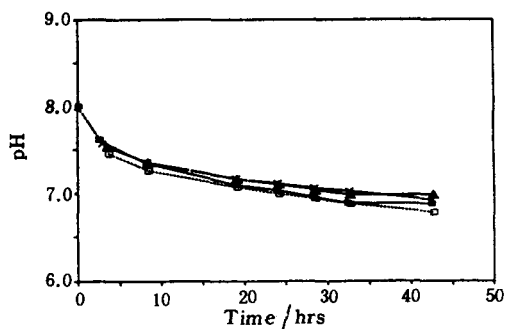


Fig. 5 pH of effluent samples in gel solution (initial pH 8.00) displacement experiment
 ■ 16 #; × 18 #; ▲ 22 #; □ 0 #

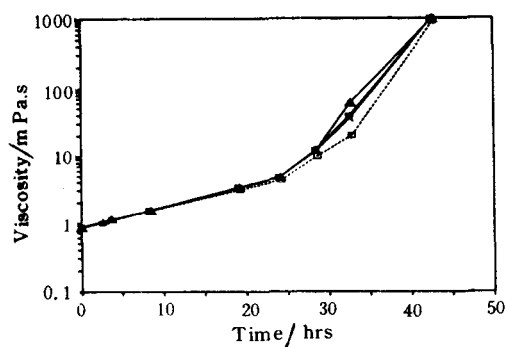


Fig. 6 Viscosity of effluent samples in gel solution (initial pH 8.00) displacement experiment)

■ 16#; × 18#; ▲ 22#; □ 0#

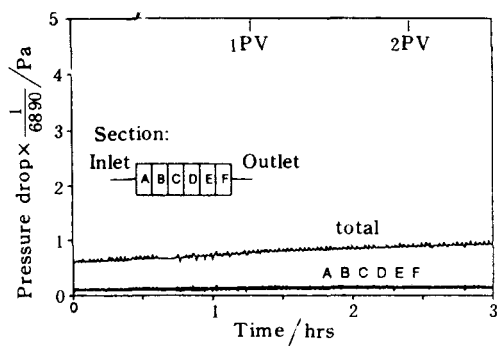


Fig. 7 Pressure drop across total core and each section in displacement experiment Gel solution #1, initial pH 8.00

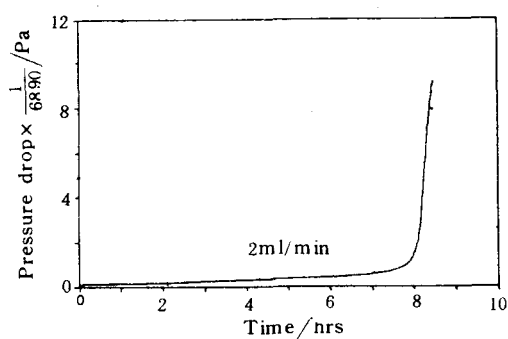


Fig. 8 Pressure drop for gel solution in filter experiment Gel-forming solution (containing 3% NaCl) initial pH 6.00

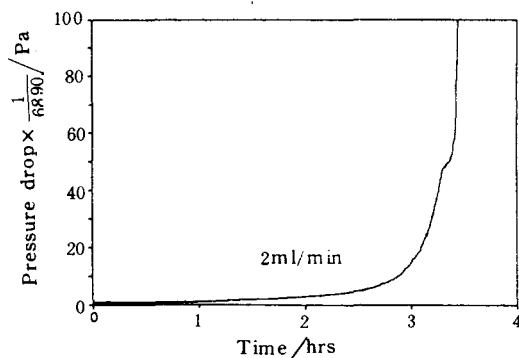


Fig. 9 Pressure drop for gel solution in filter experiment Gel-forming solution (containing Brine D) initial pH 6.00

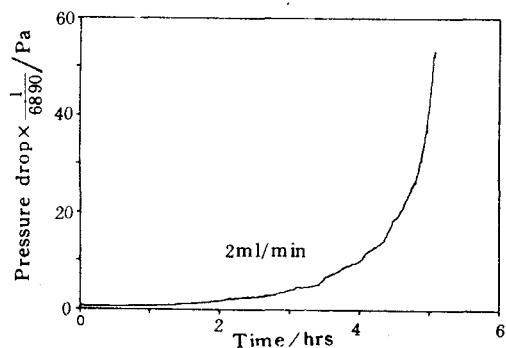


Fig. 10 Pressure drop for gel solution in filter experiment Gel-forming solution (containing Brine D) initial pH 8.00

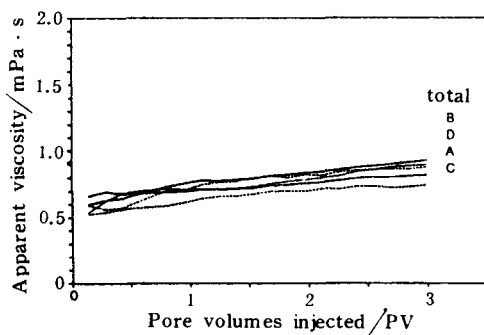


Fig. 11 Apparent viscosity across total core and several sections in displacement experiment

Fig. 7 shows the pressure drop across the total core and in each section. The pressure drop was increased a little during injection. The increasing speed depended on the composition and pH of gel solution.

Three filter experiments were conducted. In these experiments, Berea core was emplaced with a 0.22 micron filter. As filtered brine was pumped through the filter, the pressure drop was almost constant. When the gel solution containing lower salinity (3% NaCl) was pumped through the filter, the pressure drop increased slower, because of its slower reaction of gel-forming solution (Fig. 8 and 9) and less particles bigger than 0.02 μm were built up on the filter paper during the same period of time. Although the reaction of system II was faster than that of system I, but the solubility of the products formed during the reaction was better, so the speed of building up was slower (Figs. 9 and 10). The increasing pressure drop depended on the rate of building up.

Prior to gelation, the aqueous solution of the reactive monomers is a low viscosity fluid which can be pumped as easily as water, and may be injected at relatively high rates so that they can be easily emplaced into the reservoir sufficiently far from the well-bore so as to be effective. In the displacement experiment, the apparent viscosity was less than 1 mPa. s (Fig. 11).

After injection of gel solution, the core was shut-in for a period of time, then Brine D with the same initial pH of the gel solution was injected to measure the brine permeability of the core again (e. g. Fig. 12). The permeabilities at that time were listed in Table 1.

Table 1 Permeability of section A

Permeability (md.) *	Berea Core #2 System I	Berea Core #4 System I
Initial	719.47	702.36
7 days later	0.03	
9 days later		0.004
85 days later	0.03	

* md; milli darcy, unit of permeability of porous medium

When the gelation was completed thoroughly, the Berea core was sliced. Some particles were built up on the first surface of the core near the inlet during the injection of gel solution in the Berea core, each sliced section was

flushed with Brine D before the final brine permeability was measured. The brine permeability of the core had reduced significantly from about 600 to 0.1 md. (Table 2).

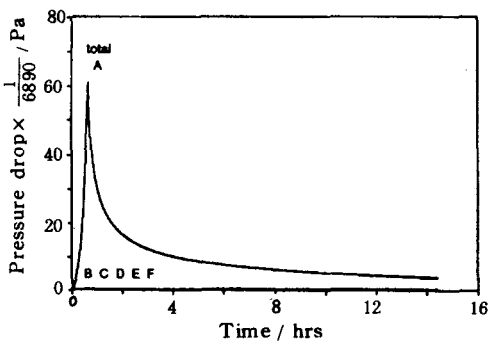


Fig. 12 Pressure drop across total core and each section after 85 days
Brine D injected, initial pH 6.00
Pump setting: 0.05 ml/min and 0 ml/min

Table 2 Permeability of Berea core #2

System 1		
Section	Initial (md.)	3 Months later (Sliced) (md.)
A	719.47	0.14
B	594.25	0.16
C	583.88	0.11
D	559.12	0.03
E	575.93	0.10
F	617.07	0.28

CONCLUSIONS AND RECOMMENDATIONS

- 1. Aqueous sulfomethylated resorcinol formaldehyde gel solution reduced the permeability of the Berea core significantly. This gel system could be used in the brine with higher salinity and hardness.
- 2. pH affected the gelation of this gel system. Due to the action of Berea core, pH of effluent samples were a little bit higher than that of bulk

sample. The gel times of effluent samples were a little bit shorter than that of bulk samples under this experimental condition. The in-situ gelation in Berea core occurred a little bit earlier than gelation anticipated from bulk test in the experiment.

When the third pore volume of gel solution was injected, the effect of the core on pH change of the system was quite small. The in-situ gelation time along the Berea core was not changed greatly. If initial pH of the gel system was between 6 and 8, the gel time was easier to control.

3. During injection of gel solution in the experiment, the apparent viscosity was less than $1 \text{ mPa} \cdot \text{s}$. The aqueous solution of the reactive monomers might be injected at relatively high rates so that they could be easily emplaced into the reservoir sufficiently far from the well-bore so as to be effective.

4. During injection, some particles were built up on the first surface of the core near the inlet. Long core was suggested to test.

Keywords:

In-situ gelation; EOR polymer; Oil recovery; Sulfomethylated resorcinol formaldehyde

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REFERENCES

- [1] Zhuang, Y. F.; Stanley McCool, G. Paul Willhite and Don W. Green, *Chinese J. Polym. Sci.* **1995**, 13 (1) 59.