Why Do Gels Reduce Water Permeability More Than Oil Permeability?

Jenn-Tai Liang, SPE, **Haiwang Sun,** and **R.S. Seright,** SPE, New Mexico Petroleum Recovery Research Center

Summary

A capacity to reduce water permeability much more than oil permeability is critical to the success of gel treatments in production wells if zones cannot be isolated during gel placement. Although several researchers have reported polymers and gels that provide this disproportionate permeability reduction, the explanation for the phenomenon was unclear. In this paper, we examine several possible explanations for why some gels reduce water permeability more than oil permeability. Our experimental results indicate the disproportionate permeability reduction is not caused by gravity or lubrication effects. Results also indicate that gel shrinking and swelling are unlikely to be responsible for the phenomenon. Although wettability may play a role in the disproportionate permeability reduction, it does not appear to be the root cause for water permeability being reduced more than oil permeability. Results from an experiment with an oil-based gel suggest that segregation of oil and water pathways through a porous medium (on a microscopic scale) may play the dominant role in the disproportionate permeability reduction. However, additional work will be required to verify this concept.

Introduction

Several researchers[1-5] reported that polymers or gels can reduce permeability to water much more than to oil. This property is critical to the success of gel treatments in production wells if zones cannot be isolated during gel placement.[6,7] We have demonstrated that this disproportionate permeability reduction is not an experimental artifact caused by hysteresis of relative permeabilities or by gel breakdown.[6,8] This property is observed not only with polymers and "weak" polymer-based gels but also with a monomer-based gel (resorcinol/formaldehyde) and with "strong" polymer-based gels.[8]

In this paper, we examine several possible explanations for the disproportionate permeability reduction, including (1) gravity effects, (2) lubrication effects, (3) gel swelling and shrinking, (4) water and oil pathway constrictions, (5) wettability effects, and (6) segregated water and oil pathways. A series of experiments has been performed to assess the relative importance of these mechanisms.

Experimental Procedures

Gelants Studied. The study included four types of gels: (1) resorcinol/formaldehyde, (2) Cr(III) acetate/partially hydrolyzed polyacrylamide (HPAM), Marcit supplied by Marathon Oil Co., **(3)** glyoxal/cationic polyacrylamide (CPAM), Floperm 500 supplied by Pfizer Chemical Co., and (4) 12-hydroxystearic acid/Soltrol 130 (an oil-based gel)—2% 12-hydroxystearic acid obtained from Johnson Wax Co. Two formulations of the oil-based gel were examined. **Table 1** lists the compositions of these gelants. The HPAM had a molecular weight of ≈ **2** million daltons and a 2% degree of hydrolysis. The other chemicals used in this study were reagent grade.

Coreflood Sequence. In each coreflood, the core was saturated with brine and the porosity and permeability determined. Then, the core went through a cycle of oilflooding followed by waterflooding (Flow Direction 1). The endpoint oil and water permeabilities were determined at the irreducible water saturation after the oilflood and at the irreducible oil saturation after the waterflood, respectively. A constant pressure drop was maintained across the core during the process. To simulate the "pump-in, pump-out" sequence during gel treatments in production wells, the gelant was injected into the core from one direction (Flow Direction 1). After a 5-day shut-in period, residual resistance factors, F_{rr}, were measured in the opposite direction (Flow Direction 2). F_{rr} is defined in this study as the mobility before gel treatment divided by the mobility after gelation. Water- and oil-tracer studies were routinely performed to characterize PV's and dispersivities. All experiments were performed at 105°F. Table 2 of Ref. 1 summarizes our general coreflood sequence, and Ref. 9 gives a more detailed description of the core experiments.

High-permeability Berea sandstone cores were used in all core experiments. Most cores were strongly water-wet, and none of the cores were fired. The cores had a nominal absolute permeability to brine of 800 md. Typically, each core was 5.5 in. long and 1.4 in. diameter. All cores had at least one internal pressure tap located ≈ 0.8 in. from the inlet rock faces. The first core segment was treated as a filter, and the second core segment was used to measure mobilities and F_{rr}. A refined oil, Soltrol-130 (Oil A), was usually used as the oil phase. This oil had a viscosity of 1.05 cp and a density of 0.76 g/cm^3 at 105°F. Banco IC46980 paraffin oil (Oil B), with a viscosity of 31.6 cp and density of 0.88 g/cm^3 at 105°F, was used as the viscous oil in conjunction with Oil A to study lubrication effects. For a given core experiment, the brine used to saturate the core had the same composition as that used for gelant preparation. All brines had viscosities of 0.67 cp at 105°F.

Possible Mechanisms for Disproportionate Permeability Reduction

Gravity Effects. We wondered whether the disproportionate permeability reduction could be caused by gravity (i.e., by gravity influencing the location of gel particles in pores). For a water-based gel, the density of the gel is similar to that of the brine. During waterflooding, gel particles floating freely in the water phase can be caught easily in the pore throats, thereby reducing water permeability. However, during oilflooding (if the fluid velocity is low enough), the density difference between the water-based gel particles and the oil could cause the gel particles to settle away from the pore throats, thereby allowing higher permeabilities for oil. While we recognized that this theory was unlikely to provide a valid explanation of the disproportionate permeability reduction simply because each core contains a large number of pores with random orientations, we proceeded to test this concept. We performed oil/water experiments to test whether the disproportionate permeability reduction was sensitive to changes in core orientation and flow direction.

Glyoxal/CPAM gels with **0.3%** CPAM and 0.114% glyoxal were used in these core experiments. The experiments were performed with three different combinations of core orientation and flow direction. Water and oil residual resistance factors, F_{rrw} and F_{rro}, respectively, first were measured with the core oriented horizontally. Then, the core was oriented vertically and water or oil was injected into the bottom of the core. Finally, the experiment was repeated with oil or water injection into the top of the core.

Results showed that the F_{rrw} and F_{rro} values were not sensitive to flow direction or core orientation; averaging 4,990 ± 110 for F_{rrw} and 7 ± 0.1 for F_{rro}. (Table 3 of Ref. 1 gives detailed results.) Through the water/oil injection cycles, the gel consistently reduced water permeability substantially more than oil permeability, which suggests that the disproportionate permeability reduction was not caused by a gravity effect.

Lubrication Effects. Two concepts that have some elements in common are Sparlin and Hagen's[2] "hydrophilic-film theory" and the Zaitoun and Kohler's[3] "lubrication effect." Both concepts apply to strongly water-wet cores where a layer of polymer or gel is ad-

Original SPE manuscript received for review May 12, 1994. Revised manuscript received July 31, 1995. Paper peer approved Aug. 3 1995. Paper (SPE 27829) first presented at the 1994 SPU DOE Symposium on Improved Oil Recovery, Tulsa, OK, April 1994

TABLE 1—GELANT COMPOSITIONS AND VISCOSITIES

Gelant Composition	pH	p at 11 seconds-’ (cp)
3% resorcinol, 3% formaldehyde, 0.5% KCl, 0.42% $NaHCO_3$	6.5	0.67
1.39% HPAM, 0.0212% Cr(III) as acetate, 1% NaCl	6.0	33
0.3% CPAM, 0.114% glyoxal, 2% KCl	7.3	5.4
4% 12-hydroxystearic acid in Oil A		1.05
2% 12-hydroxystearic acid in Oil A		1.05

All tests run at 105°F

TABLE 2—EFFECT OF μ_o ON ENDPOINT PERMEABILITIES BEFORE GEL TREATMENT

Oil	μ_o (cp)	S_{wr}	k_o^o (md)	S_{wr}*	k_o^o* (md)
A	1.05	0.28 ± 0.02	503 ± 5	0.26rt0.00	522 ± 17
B	31.6	0.24 ± 0.02	561 ± 5	0.23rt0.01	588 ± 16
A	1.05	0.24 ± 0.02	537 ± 9	0.23rt0.01	561 ± 19
1% NaCl Brine					
	μ_w (cp)	S_{or}	k_w^o (md)	S_{or}*	k_w^o* (md)
	0.67	0.34rt0.01	112 ± 3	0.35 ± 0.00	124 ± 1

All tests done in strongly water-wet Berea sandstone core at 105°F.
*Flow-direction reversed.

orbed onto pore walls. For different reasons, the two theories suggest that the presence of the hydrocarbonladsorbed-polymer interface effectively “lubricates” the flow of oil or gas through the center of pores. These ideas appear to be an extension of Odeh’s[10] theory for the effect of oillwater viscosity ratio on relative permeabilities.

On the basis of Zaitoun and Kohler’s[3] and Odeh’s[10] ideas, we expect residual resistance factors to vary with oil viscosity during core experiments with gels present. Therefore, we investigated the lubrication effect in a strongly water-wet Berea sandstone core using two oils with different viscosities. At 105°F, Oils A and B had viscosities of 1.05 and 31.6 cp, respectively. After saturating the core with brine, Oil A was injected to determine oil permeability at the residual water saturation. Then, Oil A was displaced by Oil B, and oil permeability was measured again. Oil B was then displaced by Oil A, and oil permeability was determined once more. Next, brine was injected to determine water permeability at the residual oil saturation. This procedure was repeated three times. Two sets of measurements were performed with the original flow direction and two sets with flow through the core in the reverse direction. **Table 2** provides average endpoint permeability values (and standard deviations) for the different fluids. If a lubrication effect was important, the apparent oil permeability should have been much greater for Oil B than for Oil A.[10] Given the similarity of the permeabilities for Oils A and B (Table 2), no significant lubrication effect was evident before placing gel in the core.

Next, 6 PV of Cr(III) acetate/HPAM gelant, containing 1.39% HPAM, 0.0212% Cr(III) as acetate, and 1% NaCl, was injected into the core. After the core was saturated with the gelant and shut in for 5 days, water was injected. **Table 3** shows that F_{rrw} was > 35,000. The core then was oilflooded to establish a residual water saturation, and F_{rro} for both oils were determined. Next, the core was waterflooded, and F_{rrw} were redetermined. These last values can be described by the equation $F_{rrw} = 1{,}430u^{-0.44}$.

F_{rro} for both oils were measured at two residual water-plus-gel saturations (Table 3). At a given saturation, the F_{rro} values for the two oils were essentially the same. Thus, no lubrication effect was apparent. Through the water/oil injection cycle, the gel reduced water permeability substantially more than oil permeability. These observations suggest that the disproportionate permeability reduction was not caused by a lubrication effect. Oils A and B had densities of 0.76 and 0.88 g/cm^3, respectively. Table 3 shows that, at a given saturation, the F_{rro} values did not vary with oil density. This finding is consistent with our earlier conclusion that gravity effects did not cause the disproportionate permeability reduction.

Gel Shrinking and Swelling. Sparlin and Hagen[2] proposed that water-based gels swell in water and shrink in oil. This property should result in constricted pathways for water and more-open pathways for oil in the porous media. The validity of the shrinking/swelling argument is not obvious because it requires that the hydrophilic gel give up water to the hydrophobic oil. The most obvious method to test for shrinking/swelling effects is to observe volume changes in a gel when it comes into contact with water or oil. In visualization studies with Cr(III) acetate/HPAM and resorcinol/formaldehyde gels (at atmospheric pressure), we observed no volume changes on alternating exposure of the gels to brine and oil (Oil A). Similar experiments were performed with these gels at 1,500 psi that showed no significant macroscopic changes during multiple alternating exposures of the gels to brine, oil, and compressed CO_2.[11] These findings argue against the importance of shrinking and swelling effects.

To examine the shrinking/swelling mechanism further, we performed core experiments at various pressures ranging up to 1,500 psi. If the shrinking/swelling mechanism is valid, an increase in system pressure should favor a smaller volume state for the gel. The logic in this argument parallels that explaining the effect of pressure on surfactant aggregation in solution. One might expect liquids to be so incompressible that no significant volume changes occur during liquid-phase reactions. However, the volume change associated with micelle formation is enough for the critical micelle concentration to increase with increased pressure.[12,13] The partial molal volume of a surfactant molecule solvated individually in water is less than that inside a micelle. Thus, increased pressure drives the micelle equilibrium toward individually solvated surfactant molecules (i.e., toward a smaller volume state).

If gels swell in water and shrink in oil (on a pore level), then increased system pressure might inhibit the gel from swelling in the presence of water. Thus, as the system pressure is raised, F_{rrw} should decrease (and decrease more than that for oil, which has already forced the gel into a smaller volume state). To investigate this concept, oil/water experiments were performed in a high-permeability Berea core at different backpressures with a Cr(III) acetate/HPAM gel, with 1.39% HPAM and 0.0212% Cr(III) as acetate.

To establish baselines for the effect of changing system pressure on the F_{rr}, endpoint mobility measurements were made at different backpressures (0, 500, 1,000 and 1,500 psi). Results from our experiments showed that mobilities were independent of system pressure; averaging 1,144 ± 7 md/cp for the brine at $S_w = 1.0$, 545 ± 21 md/cp for the oil at $S_{wr} = 0.24$, and 249 ± 20 md/cp for the brine at $S_{or} = 0.31$. (Table 6 in Ref. 1 summarizes detailed results.)

Five PV of gelant was injected into the core at residual water saturation. After gelant injection, the core was shut in for 5 days. Then, oil was injected and residual resistance factors were measured at the four backpressures (0, 500, 1,000, and 1,500 psi). During the process, water- and oil-tracer studies were performed at 0 and 1,500 psi.

TABLE 3—EFFECT OF μ_o ON F_{rr}

Fluid injected	$S_{wr}+S_{gel}$	S_{or}	F_{rro}	F_{rrw}
1% NaCl brine		0.35		> 35,000
Oil A	0.50		50	
Oil B	0.46		20	
Oil A	0.46		20	
Oil B	0.43		10	
Oil A	0.43		10	
1% NaCl brine		0.44		$1{,}430u^{-0.44}$

Gelant: 1.39% HPAM/0.0212% Cr(III) as acetate.
Oil A: μ_o=1.05 cp and ρ_o=0.76 g/cm^3.
Oil B: μ_o=31.6 cp and ρ_o=0.88 g/cm^3.
All tests run at 105°F.

TABLE 4—EFFECT OF SYSTEM PRESSURE ON F_{rr}

Backpressure (psi)	F_{rro}	F_{rrw}
0	9	$18u^{-0.18}$
500	9	$16u^{-0.26}$
1,000	11	$18u^{-0.31}$
1,500	11	$15u^{-0.24}$

Gelant: 1.39% HPAM/0.212% Cr(III) as acetate.
All tests run at 105°F.

The tracer breakthrough curves were insensitive to system pressure, indicating no detectable shrinking or swelling of the gel. **Table 4** shows that the F_{rro} values were Newtonian and insensitive to system pressure. The core was then waterflooded, and F_{rrw} were measured. As Table 4 shows, the F_{rrw} values exhibited a strong apparent shear-thinning behavior where the relationship between F_{rrw} and superficial velocity, ***u***, can be described with a power-law equation. Table 4 shows that the F_{rrw} values also are insensitive to system pressure. Gel breakdown was observed during the early stage of oil injection and during the water- and oil-tracer studies.[9] To confirm these results, we measured F_{rro} and F_{rrw} again at the same four backpressures using a constant flow velocity. Our results showed that, at a constant flow velocity of 3.15 ft/D, values for both F_{rro} and F_{rrw} were insensitive to system pressure; averaging 2 ± 0.1 and 7.6 ± 0.5, respectively. (Table 8 of Ref. 1 gives detailed results.) The lower F_{rro} values were caused by the gel breakdown, which occurred during the oilflooding process after the previous F_{rrw} measurements. During the oil/water injection cycles, the gel reduced water permeability significantly more than oil permeability. Our results suggest that gel shrinking and swelling effects are unlikely to be responsible for the disproportionate permeability reduction.

Water and Oil Pathway Constrictions and Wettability Effects. To estimate the permeability reduction after a polymer or gel treatment, Zaitoun and Kohler[14] proposed the equation

$$F_{rr} = \left(1 - \frac{\delta}{r}\right) , \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots \quad (1)$$

where F_{rr} is the permeability reduction (residual resistance factor). According to Eq. 1, increasing the thickness of the adsorbed layer, 6, and/or reducing the pore radius, ***r***, would increase the permeability reduction. Zaitoun and Kohler proposed that in a strongly water-wet system, the presence of residual oil droplets at the center of the pores can significantly reduce the effective r during waterflooding. In contrast, no such constriction exists during oilflooding. Therefore, for a given 6, the permeability reduction for water during waterflooding is greater than that for oil during oilflooding. Using this reasoning, we expect the disproportionate Permeability reduction to be most evident in strongly water-wet cores (if hydrophilic polymers or gels are used). For less water-wet cores, polymers and gels should adsorb on pore walls to a lesser extent, and consequently, should be less likely to restrict water flow. Thus, we expect the disproportionate permeability reduction to be less apparent in cores of intermediate wettability.

In an earlier study,[8] we performed core experiments with both strongly water-wet cores and cores of intermediate wettability. **Table 5** shows that the disproportionate permeability reduction was observed in systems of intermediate wettability as well as in strongly water-wet systems. Surprisingly, for a resorcinol/formaldehyde gel, the disproportionate permeability reduction was actually more evident in a core of intermediate wettability than in a strongly water-wet core. For a Cr(III)/xanthan gel, no effect of wettability on disproportionate permeability reduction was evident. Obviously, the effect of wettability on gel performance varied with the gel. Although wettability may play a role in the disproportionate permeability reduction, it does not appear to be the root cause for water permeability being reduced more than oil permeability.

Zaitoun and Kohler[4] speculated that the stretching of coiled macromolecules in the adsorbed polymer or gel layer under elongational flow could make the pore throats more constricted at higher water rates. They also speculated that higher oil rates might reduce the apparent thickness of the polymer or gel layer, thereby reducing the resistance to oil flow. In our standard coreflood procedure, F_{rrw} are determined as a function of injection rate to determine the apparent rheology of gels in porous media. **Fig. 1** shows that for a Cr(III) acetate/HPAM gel, the flow of brine in a strongly water-wet Berea sandstone core exhibited a strong apparent "shear-thinning" behavior after treatment, where the F_{rrw} values actually decreased with increasing superficial velocity. In this case, the F_{rrw} can be described by a power-law equation, $F_{rrw} = 105u^{-0.55}$. In contrast, the flow behavior of oil in the porous medium after treatment was Newtonian.

Segregated Oil and Water Pathways. White *et al.*[5] suggest that the disproportionate permeability reduction might be caused by water and oil following segregated pathways. As **Fig. 2** illustrates, during high water fractional flow, water flows through most of the open pathways while some of the open pathways remain connected by oil and inaccessible to water. On a microscopic level, if a water-based gelant follows primarily the pathways available to water, then many of the oil pathways could remain connected and gel-free after treatment. In this way, the water-based gel could reduce water permeability more than oil permeability. Following the same logic, if an oil-based gelant follows primarily the pathways available to oil, then many of the water pathways could remain connected and gel-free after treatment. Therefore, if this concept is valid, an oil-based gel should reduce oil permeability more than water permeability.

To investigate this theory, we used an oil-based gel consisting of 12-hydroxystearic acid and Oil A (Soltrol-130). In this case, the gelation reaction is triggered by lowering the temperature. Above 149°F, 12-hydroxystearic acid is soluble in Oil A; however, an opaque gel forms if the temperature is lowered below 140°F. The gelation reaction can be reversed by raising the temperature above the gelation temperature.

For the oil-based gel, we used two formulations of different final gel strength in the core experiments. During each experiment, 10 PV of the gelant was injected into a high-permeability Berea sandstone core at residual water saturation at 176°F. After gelant injection, the core was shut in at 105°F for — 3 days. After shut-in, for the gelant that contained 2% 12-hydroxystearic acid in Oil A, F_{rr} were determined at different flow rates. The flow behavior was Newtonian for both water and oil. **Table 6** shows that the gel reduced oil permeability more than water permeability. However, severe gel breakdown occurred during the oil/water injection cycles. The core experiment was repeated with a stronger gel containing 4% 12-hydroxystearic acid in Oil A. To minimize gel breakdown, F_{rr} were determined at a single flow rate (0.787 ft/D). The F_{rro} was determined immediately after shut-in. Then, brine was injected at the same flow rate (0.787 ft/D) until a steady state was reached. After brine injection, oil was reinjected again to verify that the disproportionate permeability reduction was not caused by gel breakdown. As Table 6 shows, the gel reduced oil permeability significantly more than water permeability. This result suggests that a significant portion of the water pathways remained gel-free and open to water flow after treatment. The

TABLE 5—WETTABILITY EFFECT ON GEL PERFORMANCE

Gelant	Core Wettability	F_{rrw}	F_{rro}	F_{rrw}/F_{rro}
3% resorcinol/3% formaldehyde	Strongly water wet	49	11	4.5
	Intermediate	510	26	20
0.4% xanthan/0.0154% Cr(III)	Strongly water wet	a	5	1.6
	Intermediate	22	14	1.6

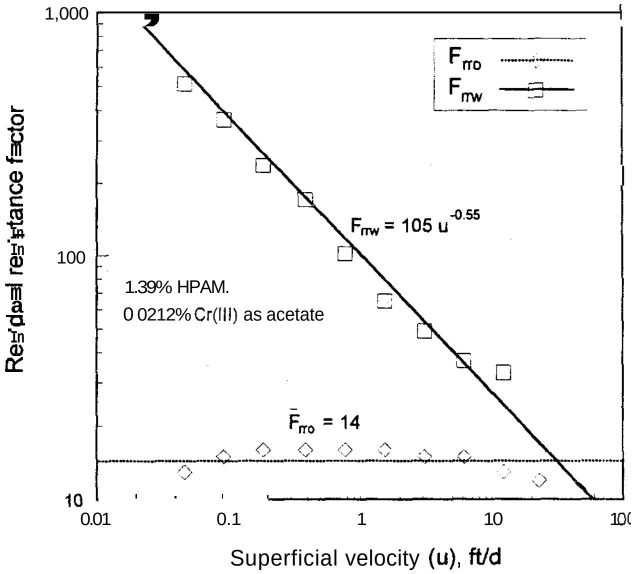

Fig. 1—Apparent rheology during oil and water injection.

TABLE 6—F_{rro} AND F_{rrw} FOR AN OIL-BASED GEL			
Gelant	First Oilflood F_{rro}	First Waterflood F_{rrw}	Second Oilflood F_{rro}
2% 12-hydroxystearic acid, Oil **A**	26	1	3
4% 12-hydroxystearic acid and Oil **A**	36*	**2***	**18***

All tests run on strongly water-wet Berea sandstone core at 105°F.
'Measured at a single flow rate (0.787 WD).

number of oil pathways open to oil flow, however, was reduced by the gel after treatment.

Our results suggest that segregation of oil and water pathways through a porous medium may play the dominant role in disproportionate permeability reduction. However, additional work is required to verify this concept. We must emphasize that this concept of segregated flow paths is not valid on a macroscopic scale. In field applications, aqueous gelants will flow into hydrocarbon zones? We certainly recognize that the mechanism responsible for the disproportionate permeability reduction may be one other than those discussed in this paper; therefore, further research is needed to elucidate the correct mechanism. By determining why certain materials reduce permeability to water more than that to oil, we hope that a means will be found to maximize this phenomenon.

Conclusions

1. The disproportionate permeability reduction was insensitive to core orientation and fluid-density differences, suggesting that gravity effects did not cause the phenomenon.
2. The disproportionate permeability reduction was insensitive to the nonwetting-phase viscosity (from 1 to 31 cp), indicating that lubrication effects are not responsible for the phenomenon.
3. In visualization studies with Cr(III) acetate/HPAM and resorcinol/formaldehyde gels, no volume changes were observed on alternating exposure of the gels to brine and oil. Also, core experiments performed between 0 and 1,500 psi showed no significant effect of pressure on gel performance. These results suggest that the disproportionate permeability reduction is probably not caused by gel swelling/shrinking effects.
4. We observed the disproportionate permeability reduction in both intermediate-wet and strongly water-wet systems. The effect of wettability varied with the gel. Although wettability effects may play a role in the disproportionate permeability reduction, they do not appear to be the root cause for water permeability being reduced more than oil permeability.
5. Results from our experiments suggest that segregation of oil and water pathways through a porous medium (on a microscopic scale) may play the dominant role in the disproportionate permeability reduction. However, additional work is required to verify this concept.

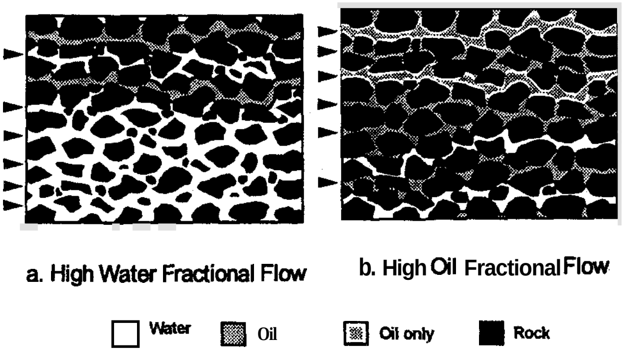

Fig. 2—Segregated water and oil pathways.

Nomenclature

F_{rr} = residual resistance factor (mobility before gel placement divided by mobility after gelation)
F_{rro} = oil residual resistance factor
F_{rrw} = water residual resistance factor
k_o^o = endpoint oil permeability, L^2, md
k_w = absolute permeability to water, L^2, md
k_w^o = endpoint water permeability, L^2, md
r = pore radius, L, in.
S_{gel} = gel saturation (fraction of PV occupied by gel)
S_{or} = irreducible oil saturation
S_w = water saturation
S_{wr} = irreducible water saturation
u = superficial or Darcy velocity, L/t, ft/D
δ = adsorbed polymer or gel layer thickness, L, in.
μ = viscosity, m/Lt, cp
μ_o = oil viscosity, m/Lt, cp
ρ_o = oil density, m/L^3, g/cm^3

Acknowledgments

This work was financially supported by the U.S. DOE, the New Mexico Dept. of Energy & Minerals, Arco E&P Technology, British Petroleum, Chevron Petroleum Technology Co., Conoco Inc., Exxon Production Research Co., Marathon Oil Co., Mobil R&D Corp., Phillips Petroleum Co., Texaco, and Unocal. This support is gratefully acknowledged. We thank John Hagstrom for performing some of the core experiments.

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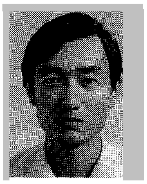
SI Metric Conversion Factors

cp × 1.0* E − 03 = Pa · s
ft × 3.048* E − 01 = m
°F (°F − 32)/1.8 = °C
in. × 2.54* E + 00 = cm
md × 9.869 233 E − 04 = μm^2
psi × 6.894 757 E + 00 = kPa

*Conversion factor is exact.

SPERE

Jenn-Tai Liang is a senior research associate at the New Mexico Petroleum Recovery Research Center in Socorro. His main research interests are experimental and theoretical studies *of* improved techniques for water shutoff and fluid diversion in oil recovery processes. Liang holds a BS degree in chemistry from Tamkang U. in Taiwan, an MS degree in mineral engineering from the U. of Alabama, and a PhD degree in petroleum engineering from the U. of Texas at Austin. **Haiwang (Tom) Sun** is an environmental engineer with Geoscience Consultants Ltd. in Albuquerque, NM. He holds a BS degree in drilling engineering from Daqing Petroleum Inst. and MS and PhD degrees in petroleum engineering from Montana Tech and New Mexico Tech, respectively. **Randy Seright** is a senior engineer at the New Mexico Petroleum Recovery Research Center. He holds a BS degree from Montana State U. and a PhD degree from the U. *of* Wisconsin-Madison, both in chemical engineering. Seright is a member of the Editorial Review Committee, Program Chairman of the *1995* Symposium on Oilfield Chemistry, and Chairman of the 1995 SPE Emerging/Peripheral Technology Technical Committee. He was a 1993–94 Distinguished Lecturer. Currently the chairman of the SPE Roswell Section, he has served in many section offices.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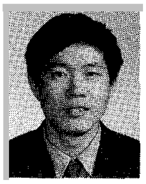
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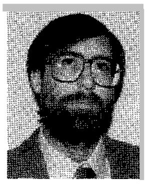
Seright