

EFFECT OF ROCK PERMEABILITY  
ON GEL PERFORMANCE IN FLUID-DIVERSION APPLICATIONS

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ABSTRACT

This paper describes an experimental investigation of the effects of rock permeability and lithology on the performance of several gels, including those formed from resorcinol-formaldehyde, colloidal silica, Cr(III) chloride-xanthan, and Cr(III) acetate-polyacrylamide. During core experiments, the "strongest" gels were found to reduce the permeability of all cores to approximately the same value (in the low microdarcy range). Tracer studies indicated that these gels occupied most of the available pore space. Flow experiments were performed in rectangular micromodels to determine whether these gels have some inherent permeability to water. The permeabilities for five gels were found to be less than or equal to 60  $\mu$ d.

For "weaker" gels (i.e., those leaving a significant permeability), residual resistance factors generally decreased with increased rock permeability. Tracer studies indicated that these gels occupied a small fraction of the pore space in a core. Experiments revealed that gelation in the porous rock was often far less complete than that in a bottle. For unbuffered gelants in porous rocks, the pH at which gelation occurs may be determined more by rock mineralogy than by the pH of the injected gelant. Thus, the buffering action of reservoir rocks should be considered when evaluating gel performance in the laboratory. The immense buffering capacity of limestone can effectively preclude the propagation of unbuffered Cr(III) chloride-xanthan gelants or CrCl<sub>3</sub> solutions through porous limestone.

INTRODUCTION

Ideally, gel treatments should reduce channeling of fluids through high-permeability, watered-out flow paths without damaging oil-productive zones. However, in most applications, the gelant penetrates to some extent into low-permeability, oil-productive

TABLE 1  
Gelant Compositions and Properties (at 41°C)

Gelant Composition	pH	Gelation time, hrs.	Gel-strength code <sup>8</sup>
3% resorcinol, 3% formaldehyde, 0.5% KCl, 0.42% NaHCO <sub>3</sub>	6.0-6.5	6	*
3% resorcinol, 3% formaldehyde, 0.5% KCl, 0.42% NaHCO <sub>3</sub>	9.0	4	I
4% colloidal silica, 0.7% NaCl	7.0	15	I
10% colloidal silica, 0.7% NaCl	8.2	5	J
0.4% xanthan, 154-ppm Cr(III) (as CrCl <sub>3</sub> ), 0.5% KCl	4.3	10	I
0.4% xanthan, 154-ppm Cr(III) (as CrCl <sub>3</sub> ), 0.5% KCl, 0.3% CH <sub>3</sub> COOH	4.5-4.8	10	F-G
1.39% polyacrylamide, 212-ppm Cr(III) [as Cr <sub>3</sub> (OH) <sub>2</sub> (CH <sub>3</sub> COO) <sub>7</sub> ], 1% NaCl	5.9	15	H
1.39% polyacrylamide, 636-ppm Cr(III) [as Cr <sub>3</sub> (OH) <sub>2</sub> (CH <sub>3</sub> COO) <sub>7</sub> ], 1% NaCl	5.9	7	I

\* Product could be described better as a precipitate than as a gel.

zones. A gel treatment can either enhance or harm oil production, depending on how the gel's performance in low-permeability rock compares with that in the "thief" zone.<sup>1-5</sup>

This paper describes an experimental investigation of the effects of rock permeability and lithology on the performance of several gels. During our experiments, particular attention was paid to (1) the importance of pH to gelation, (2) gel performance as a function of fluid velocity, and (3) the use of tracers to assess the fraction of the pore space that was occupied by gel. The effects of oil and wettability on gel performance can be found in Ref. 6.

## GELANTS AND GELANT PLACEMENT PROCEDURES

### Gelants Studied

In this work, experiments were performed with four different gelants, including resorcinol-formaldehyde, colloidal silica<sup>7</sup> (DuPont's Ludox SM<sup>®</sup>), Cr(III) chloride-

xanthan, and Cr(III) acetate-polyacrylamide<sup>8-10</sup> (Marathon's MARCIT®). Eight different formulations were investigated. The compositions of these formulations are listed in Table 1. The two resorcinol-formaldehyde gelants had the same composition, except that one was buffered at pH=9, while the other was buffered at pH=6.0 to 6.5. The two different pH values were chosen because gel performance was radically different at these pH values. For the other gelants, the pH was selected based on recommendations of the vendor or developer of the gelant (to provide the "strongest" gel for that composition). DuPont supplied the colloidal silica, and Pfizer provided the xanthan<sup>11</sup> (Flocon 4800®). Marathon provided the polyacrylamide (HPAM), characterized by a molecular weight of about 2 million daltons and a degree of hydrolysis of 2 percent. All other chemicals were reagent grade.

Approximate gelation times and gel-strength codes are listed in Table 1. Gelation times were estimated by observing the fluidity of gelant in bottles. Gelation times for the eight gels ranged from four hours to fifteen hours. The system for assessing gel strength was taken from Ref. 8. In this system, the codes range alphabetically from A to J, with code A representing a fluid liquid, code J representing a rigid, ringing gel, and code F representing a highly deformable nonflowing gel. Code E corresponds to the sol-gel transition.

### Rocks Used

Three types of rock were used during our core experiments, including (1) a high-permeability Berea sandstone, (2) a low-permeability Berea sandstone, and (3) an Indiana limestone. Porosities for the three types of rock averaged 0.22, 0.19, and 0.19, respectively. Table 2 lists permeabilities of the cores. Each core was about 14-cm long with a cross-sectional area of 10 cm<sup>2</sup>. The cores were cast in a metal alloy (Cerrotro®). Each core had one internal pressure tap that was located approximately 2 cm from the inlet rock face. The first core segment was treated as a filter, whereas the second core segment (12-cm length) was used to measure mobilities and residual resistance factors. The cores were not fired.

### Coreflood Sequence

The sequence followed during our core experiments is listed in Table 3. The cores were saturated with brine and porosities were determined at ambient conditions (Step 1

TABLE 2  
Rock Permeabilities

Gelant to be injected	Permeability, md		
	High-k Berea sandstone	Low-k Berea sandstone	Limestone
Resorcinol-formaldehyde, pH=6.0-6.5	704	61	7.4
Resorcinol-formaldehyde, pH=9	570	49	7.4
4% colloidal silica	546	67	13.4
10% colloidal silica	630	50	12.0
Unbuffered Cr(III)-xanthan	728	68	15.3
Cr(III)-xanthan buffered with acetate	840	93	—
Cr(III) acetate-HPAM, 212-ppm Cr(III)	746	74	10.7
Cr(III) acetate-HPAM, 636-ppm Cr(III)	662	65	11.0

of Table 3). All subsequent steps were performed at 41°C. When saturating a given core, the brine composition was the same as that used in preparing the gelant formulation.

Tracer studies were routinely performed to characterize pore volumes and dispersivities of the cores. These studies involved injecting a brine bank that contained potassium iodide as a tracer. The tracer concentration in the effluent was monitored spectrophotometrically at a wavelength of 230 nm. Usually, four replicates were performed for each tracer study. Also, the replicates included studies performed at different injection rates. For all of the tracer studies described in this work, an error-function solution<sup>12</sup> fit the tracer curves fairly well.

For a given core, many pore volumes of gelant (typically, 10 PV) were injected to ensure that the cores were saturated (i.e., most of the chemical retention sites in the rock were occupied). Thus, in field applications, the gel properties reported in this study are more relevant to the region behind (upstream of) the front of the gel bank than to the region at the front of the gel bank. While injecting the gelants, resistance factors were continuously monitored in both segments of the core. Effluent properties were also

TABLE 3  
Sequence Followed During Core Experiments

<u>Step</u>	
1.	Saturate core with brine and determine porosity.
2.	Perform tracer study to confirm the pore volume ( $V_{po}$ ) and to determine the core dispersivity ( $\alpha_o$ ).
3.	Determine absolute brine permeability and mobility.
4.	Inject gelant using a superficial velocity of 15.7 ft/d.
5.	Shut in core for several days to allow gelation to occur.
6.	Inject brine to determine residual resistance factor ( $F_{rrw}$ ) as a function of superficial velocity ( $u$ ).
7.	Perform tracer study to determine the fractional pore volume remaining ( $V_p/V_{po}$ ) and the relative dispersivity ( $\alpha/\alpha_o$ ).

monitored, including pH, viscosity, composition, appearance, gelation time, and final gel strength. Detailed results from the experiments are documented in Refs. 13 through 16.

#### Chromium Propagation Without Polymer

Several experiments were performed to assess how well chromium propagates through porous rock. Fig. 1 shows results from six corefloods where solutions containing 154-ppm Cr(III) (as either chromium acetate or chromium chloride) were injected (at 15.7 ft/d) to displace brine. (These solutions did not contain polymer.) The effluent from corefloods was analyzed for chromium using atomic absorption spectrometry. Fig. 1 plots the chromium concentration in the effluent relative to the injected chromium concentration. After injecting 10 PV of chromium solution, in no case did the effluent chromium concentration reach the injected concentration. For a given type of rock, chromium propagation was significantly more rapid when the counterion was acetate rather than chloride. Also, for a given counterion (i.e., acetate or chloride), chromium propagation was more rapid in the Berea sandstone cores than in the Indiana limestone cores. In fact, no chromium was detected in the effluent after injecting 10 PV of chromium chloride solution through a limestone core (bottom of Fig. 1). Of course, the latter observation raises concern about the ability of chromium chloride to propagate through carbonate reservoirs.

The propagation of Cr(III) through porous rock can be related to the pH dependence of chromium chemistry. Although controversy still exists about the exact forms of

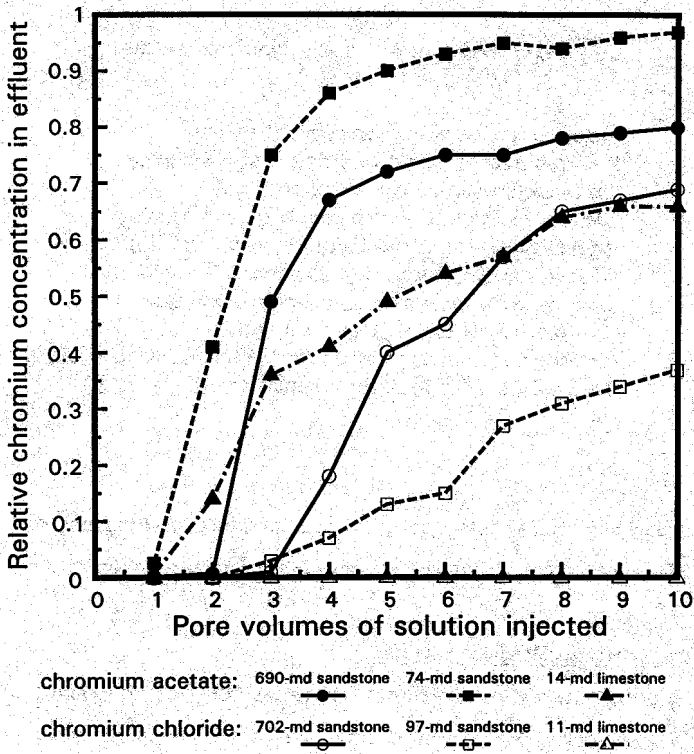


FIG. 1. Chromium propagation through cores. Injected solutions contain 154-ppm chromium.

chromium that participate in gelation,<sup>17-22</sup> there is agreement that Cr(III) is most soluble at acidic pH values and that chromium association is promoted as pH is increased—ultimately leading to the formation of a colloid or a precipitate at neutral or alkaline pH values. If an unbuffered chromium solution (e.g., one containing  $\text{CrCl}_3$ ) is injected at low pH, rock minerals can raise the pH and induce formation of colloidal chromium (i.e., insoluble chromium hydroxide). Deposition in or filtration by the porous medium may then inhibit propagation of the colloidal chromium. In contrast, a buffered chromium solution (e.g., one containing acetate) will resist pH changes, and the soluble chromium will propagate through porous rock more effectively than a colloid. Formation

of chromium-carboxylate complexes may also promote chromium solubility at pH values of 6 or higher.<sup>19,20</sup> Adsorption of the hydrated Cr(III) ion is also capable of explaining the observed behavior.<sup>23</sup> Differences in chromium propagation and effluent pH in the different cores may also be influenced by differences in rock surface area.

The above ideas are supported by the effluent pH values that accompanied our chromium propagation data.<sup>15,16</sup> For the unbuffered chromium-chloride solutions, the effluent pH can be correlated with chromium propagation. The pH was 3.35 for the unbuffered chromium-chloride solution before injection. After injecting 10 PV, the pH values were 4.89, 5.05, and 7.03, for effluent from the high-permeability sandstone, the low-permeability sandstone, and the limestone, respectively. For the chromium-chloride solutions, Fig. 1 shows that the effluent chromium concentrations after 10 PV were greatest for the high-permeability sandstone and least for the limestone.

Results from our experiments using chromium acetate are consistent with reports that chromium solubility at neutral pH values is increased by the presence of carboxylate compounds.<sup>19,20</sup> For the chromium-acetate solution, the pH was 5.90 before injection. After injecting 10 PV, the pH values were 6.01, 5.65, and 5.92, for effluent from the high-permeability sandstone, the low-permeability sandstone, and the limestone, respectively. Thus, the acetate effectively buffered the solutions in the porous rock. Also, in spite of a pH value near 6, chromium propagation in all three types of rock was as good or better with the acetate than that for chromium-chloride solutions with lower pH values.

#### Chromium Propagation With Polymer

Propagation of chromium in the presence of 0.4% xanthan is illustrated in Fig. 2. In all four cases shown, the 154-ppm chromium was added as  $\text{CrCl}_3$ . In one case, 0.3% acetic acid was added as a buffer. As expected, chromium propagated most rapidly for the gelant that contained the acetate buffer. For the three gelants that did not contain acetate, chromium propagation was most rapid in the high-permeability sandstone and least rapid in the limestone. This ordering was the same as that observed for chromium-chloride propagation without xanthan. Again, the rate of chromium propagation for the unbuffered solutions can be correlated with effluent pH values. After injecting 10 PV

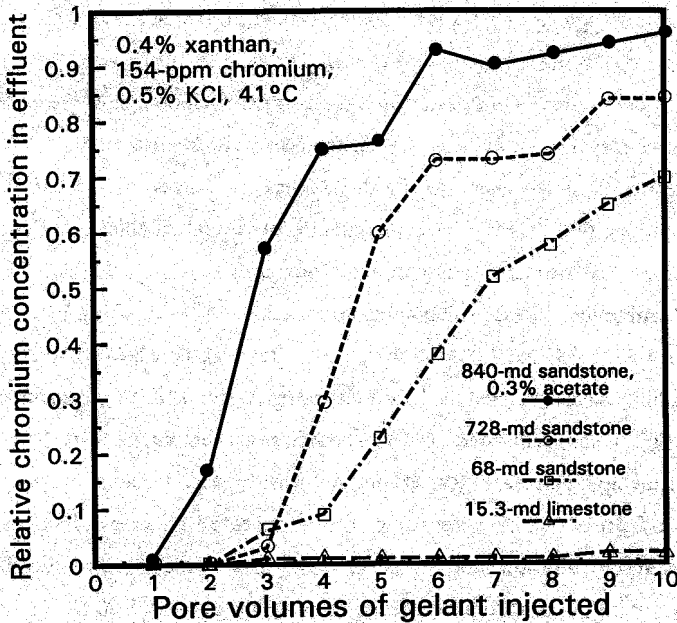


FIG. 2. Chromium propagation for solutions that contain 0.4% xanthan and 154-ppm chromium (as chromium chloride).

of gelant, the effluent pH values were 4.38, 4.55, and 6.57, for effluent from the high-permeability sandstone, the low-permeability sandstone, and the limestone, respectively. The pH value was 4.3 before injection.

A close comparison of Figs. 1 and 2 suggests that the rate of chromium propagation for unbuffered chromium-chloride solutions is greater in the presence of 0.4% xanthan than in its absence. This observation was made for all three rock types. We note that Garver *et al.*<sup>24</sup> suggested the opposite possibility. However, the apparent difference in interpretation can readily be explained. In the experiments of Garver *et al.*, injection rates were relatively low, so gelation could occur during gelant injection. As Garver *et al.* noted, filtration of gel by the core probably caused very high chromium retention in the presence of polymer. In our experiments, injection rates were relatively high, so gelation and filtration of gel particles occurred to a lesser extent during gelant injection. (Filtration of gel particles is also discussed in Refs. 25 and 26.)



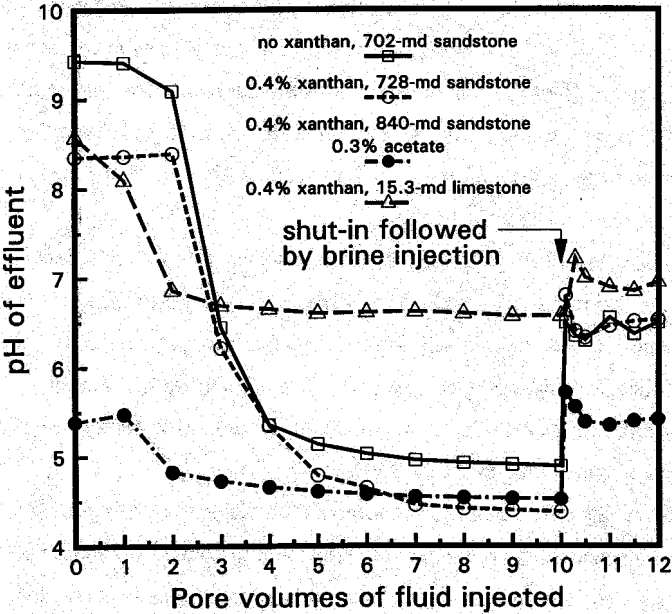


FIG. 3. Effluent pH during gelant injection. 154-ppm chromium (as chloride), 0.5% KCl.

Fig. 3 illustrates effluent pH values during the course of injecting four solutions. For the three solutions without acetate, the first effluent from the cores had pH values between 8.3 and 9.4. This observation requires explanation. Before gelant injection, the cores were saturated with 0.5% KCl brine. Even though the KCl brine was injected at a pH value between 6 and 7, it emerged from the core at a pH value between 8.3 and 9.4. Previous workers<sup>27</sup> showed that this behavior occurs because dissolution of carbonates in the rock leads to a pH increase. If the brine had contained divalent cations, the increased pH may not have occurred because dissolution of carbonates could have been suppressed.

As discussed earlier, the effluent pH decreased to pH values between 4.38 and 5.05 during the course of injecting 10 PV of unbuffered chromium-chloride formulation into Berea sandstone. During injection of an unbuffered gelant into limestone, the pH only decreased to 6.57 after 10 PV.

For the formulation with 0.3% acetate, the core was first saturated with brine buffered at pH=4.8. At the start of gelant injection, the pH of the effluent was 5.39. Presumably, the effluent pH was greater than 4.8 because reaction with rock minerals neutralized some of the acid. Even so, the buffering action of the acetate prevented the pH from rising to the values observed for the unbuffered brines. Also, the pH remained low during injection of 10 PV of gelant.

After injecting 10 PV of gelant, the core was shut in for several days. After this shut-in period, brine was reinjected. Fig. 3 shows that the pH of the first effluent after the shut-in period was significantly higher than that just before shut-in. Evidently, reactions with rock minerals increased the gelant pH during the shut-in period. As expected, the pH increase in Berea sandstone during the shut-in period was less for the buffered gelant than for the unbuffered gelant.

The preceding observations raise concerns about the practice of injecting unbuffered gelants. During laboratory corefloods and, especially, in field applications, a pH gradient will form in the rock when injecting an unbuffered gelant. This pH gradient will depend upon the gelant composition, the injection rate, and the rock mineralogy. For gelation reactions that are sensitive to pH, the pH gradient and the performance of the gel treatment may be difficult to predict. In contrast, for buffered gelants, gelation should be more predictable and controllable.

### RESIDUAL RESISTANCE FACTORS

After injecting a given gelant, the core was shut in for three to six days. In all cases, the gelation times were substantially less (by factors ranging from 12 to 40) than the shut-in times. Following the shut-in period, brine was injected to determine residual resistance factors ( $F_{rrw}$ ). These  $F_{rrw}$  values were determined by dividing brine mobility before gel placement by brine mobility after gelation. Residual resistance factors were determined as a function of injection rate. Low injection rates were used first. A note was made of how rapidly  $F_{rrw}$  values stabilized and whether any gel was forced from the core along with the effluent. After stabilization, brine injection rates were increased, and the observations were repeated. Then, the injection rate was decreased to determine whether  $F_{rrw}$  values at lower rates had changed. This process was repeated with successively higher injection rates. The objectives of this procedure were to (1)

TABLE 4  
Comparison of Residual Resistance Factors for Several Gels (41°C)

Gel	Residual resistance factor		
	High-k Berea sandstone	Low-k Berea sandstone	Indiana Limestone
Resorcinol-formaldehyde, pH=6.0-6.5	1.8	2.1	1.5
Resorcinol-formaldehyde, pH=9	2,170	3,800	1,600
4% colloidal silica	6,100	1,400	102
10% colloidal silica	23,200	3,810	819
Unbuffered Cr(III)-xanthan	$43.8 u^{-0.31}$	$57.7 u^{-0.44}$	--
Cr(III)-xanthan buffered with acetate	$3.6 u^{-0.095}$	$8.1 u^{-0.14}$	--
Cr(III) acetate-HPAM, 212-ppm Cr(III)	$34,700 u^{-0.46}$	$200 u^{-0.53}$	$49.7 u^{-0.46}$
Cr(III) acetate-HPAM, 636-ppm Cr(III)	187,000	44,600	5,810

$u$  is superficial velocity in ft/d

determine whether gel mobilization or breakdown occurred at a particular flow rate or pressure gradient and (2) determine the apparent rheology of the gel in porous media. Detailed listings of the residual resistance factors (as a function of fluid velocity) are documented in Refs. 14, 15 and 16. All of the residual resistance factors reported in this paper apply to the second segment ( $\approx 12$  cm) of the core.

Table 4 provides a summary and a comparison of residual resistance factors for the eight gels that were studied. This information is not meant to suggest that one gel is better or worse than another. The residual resistance factors provided by a given gel can be increased or decreased by adjusting the composition of the gelant. The primary purpose of Table 4 is to illustrate the effects of permeability and lithology on gel performance.

### Cr(III)-Xanthan Gels

Residual resistance factors for Cr(III)-xanthan gels can decrease significantly with increased injection rate. This behavior can have a reversible component and an

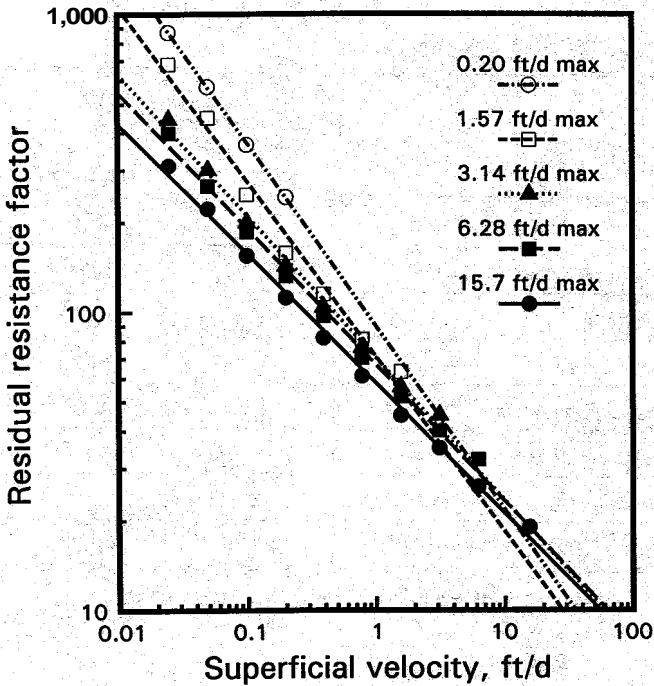


FIG. 4. Residual resistance factors for an unbuffered chromium-xanthan gel in 68-md Berea sandstone. 0.4% xanthan, 154-ppm chromium, 0.5% KCl.

irreversible component. Fig. 4 shows  $F_{rrw}$  values for an unbuffered Cr(III)-xanthan gel in 68-md Berea sandstone. When brine was first injected at 0.2 ft/d,  $F_{rrw}=243$ . When the velocity was decreased to 0.1 ft/d, 0.05 ft/d, and 0.025 ft/d,  $F_{rrw}$  values increased to 365, 571, and 870, respectively. As indicated by the first entry in Table 5 and by the open circles in Fig. 4, these data can be described very well using Eq. 1.

$$F_{rrw} = 89.8 u^{-0.62} \quad (1)$$

When brine was subsequently injected at 1.57 ft/d,  $F_{rrw}=63$ . Then, when the velocity was decreased, the  $F_{rrw}$  data could be described using Eq. 2.

$$F_{rrw} = 71.0 u^{-0.59} \quad (2)$$

TABLE 5  
 $F_{rrw}$  Relations Shown in Fig. 4

Maximum superficial velocity, ft/d	Maximum pressure gradient, psi/ft	Residual resistance factor relation	Correlation coefficient
0.20	74	$F_{rrw} = 89.8 u^{-0.62}$	0.999
1.57	150	$F_{rrw} = 71.0 u^{-0.59}$	0.984
3.14	215	$F_{rrw} = 70.6 u^{-0.48}$	0.994
6.28	305	$F_{rrw} = 66.6 u^{-0.46}$	0.994
15.7	453	$F_{rrw} = 57.7 u^{-0.44}$	0.997

The above procedure was repeated using successively higher injection velocities. As shown in Fig. 4 and in Table 5, each set of data could be described quite well using a power-law relation. With each successive exposure to a new high in velocity (or pressure gradient), the power-law exponent increased (became less negative), and the velocity coefficient decreased. This behavior suggests that (1) the gel physically breaks down with exposure to higher velocities and pressure gradients and (2) the gel exhibits a reversible "shear-thinning" character during brine injection. Of course, brine is a Newtonian fluid, so this apparent shear-thinning behavior must be attributed to the gel in the core rather than to the brine.

The apparent shear-thinning character was noted for both buffered and unbuffered Cr(III)-xanthan gels in both low- and high-permeability Berea sandstone. This is illustrated in Fig. 5. Power-law equations describing the relations between residual resistance factors and superficial brine velocities are also shown. For both buffered and unbuffered gels, the velocity coefficient and the absolute value of the power-law exponent are both greater in low-permeability sandstone than in high-permeability sandstone. For a given gel at a fixed superficial velocity, the residual resistance factor in low-permeability Berea sandstone is greater than that in high-permeability Berea sandstone. Using the procedures described in Refs. 14 and 28, calculations can be made to show that the apparent shear-thinning character will not aid in profile modification in field applications.

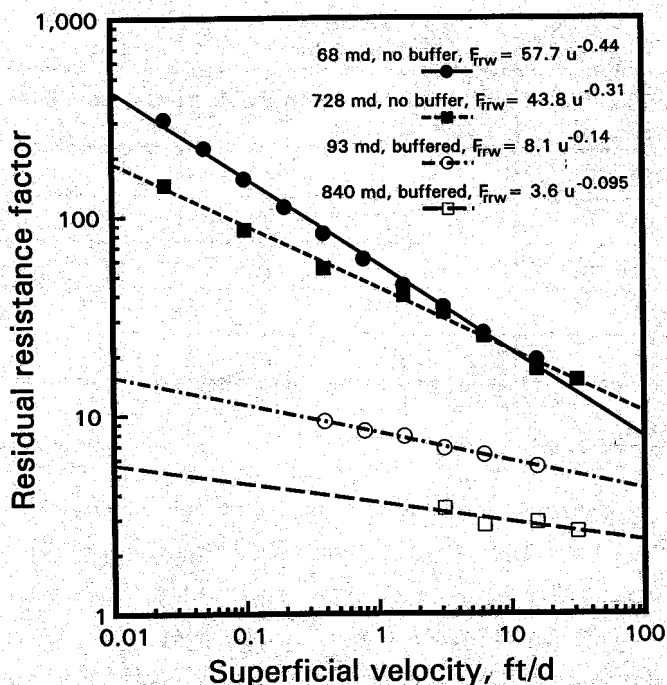


FIG. 5. Velocity dependence of residual resistance factors in Berea sandstone. Gel: 0.4% xanthan, 154-ppm chromium, 0.5% KCl.

The residual resistance factors for the buffered gel were significantly lower than those for the unbuffered gel. This observation is interesting. Originally, we expected the acetate buffer to allow stronger gels to form in the porous media because the average pH during gelation was lower than that for the unbuffered gelant. Therefore, we expected to find residual resistance factors that were much higher than those for the unbuffered gel. However, since dissolved acetate or carboxylate groups on the polymer molecule compete for Cr(III), the acetate apparently caused Cr(III)-xanthan gels to be weaker or less rigid than analogous gels formed when acetate was not present. During gelation studies in bottles, we noted that the unbuffered Cr(III)-xanthan formulations formed more rigid gels than the buffered formulations.

### Resorcinol-Formaldehyde Gels

For the resorcinol-formaldehyde gels, a much more detailed description of our studies can be found in Refs. 13 and 14. Although residual resistance factors for these gels can show a slight shear-thinning character, their behavior is essentially Newtonian. As with most gels, residual resistance factors for resorcinol-formaldehyde formulations are sensitive to gelation pH. Table 4 shows that  $F_{rrw}$  values are very high for gels formed at pH 9 and are very low for gels formed between pH 6.0 and 6.5. In Berea sandstone,  $F_{rrw}$  values increased with decreased permeability. However,  $F_{rrw}$  values can be higher in Berea sandstone than in less-permeable limestone cores. Like the Cr(III)-xanthan gels, resorcinol-formaldehyde gels can experience physical breakdown upon exposure to successively higher fluid velocities.<sup>13,14</sup>

### Colloidal-Silica Gels

For the 10%-colloidal-silica gel, residual resistance factors averaged 23,200 in 630-md Berea sandstone, 3,810 in 50-md Berea sandstone, and 819 in 12-md Indiana limestone (Table 4). Thus, residual resistance factors decrease significantly with decreased permeability. Considered another way, the final permeabilities after gelation average 27  $\mu\text{d}$  in 630-md Berea sandstone, 13  $\mu\text{d}$  in 50-md Berea sandstone, and 15  $\mu\text{d}$  in 12-md Indiana limestone. Thus, the colloidal-silica gel reduced the permeability of consolidated porous media to between 10 and 30  $\mu\text{d}$ , regardless of the initial permeability of the rock. This conclusion is consistent with the findings of Jurinak *et al.*<sup>7</sup> We observed a similar behavior for the 4%-colloidal-silica gel (see Table 4). For 4% colloidal silica, the final permeability after gelation was roughly 100  $\mu\text{d}$ —somewhat higher than that for 10% colloidal silica.

In one sense, the above permeability dependence of the  $F_{rrw}$  values could be very desirable. All gel-contacted portions of a heterogeneous reservoir could be altered to have nearly the same permeability. However, with the colloidal-silica gels that we tested, the permeability is so low that flow is effectively stopped. In order to eliminate the need for zone isolation during gel placement, the residual permeability after gelation should be much higher than 100  $\mu\text{d}$ . It may be worthwhile to search for a gel with higher residual permeabilities. (Detailed results from our experiments with colloidal silica can be found in Refs. 15 and 16.)

### Cr(III) Acetate-Polyacrylamide Gels

For the Cr(III) acetate-polyacrylamide gels, one set of experiments was performed using 212-ppm Cr(III). A second set of experiments was performed using 636-ppm Cr(III). As expected, a stiffer gel was formed using the higher chromium concentration (gel code I, compared with H for the lower concentration). Using the higher chromium concentration, residual resistance factors averaged 187,000 in 662-md Berea sandstone, 44,600 in 65-md Berea sandstone, and 5,810 in 11-md Indiana limestone (Table 4). Considered another way, the final permeabilities after gelation average  $3.5 \mu\text{d}$  in 662-md Berea sandstone,  $1.5 \mu\text{d}$  in 65-md Berea sandstone, and  $1.9 \mu\text{d}$  in 11-md Indiana limestone. Thus, the gel reduced the permeability of consolidated porous media to between 1 and  $4 \mu\text{d}$ , regardless of the initial permeability of the rock. This behavior parallels that for the colloidal-silica gels. Because the residual resistance factors were so high, experiments could only be performed at a single, low injection rate. Thus, we were not able to determine how  $F_{\text{rrw}}$  varied with injection rate for this gel.

For the experiments performed using Cr(III) acetate-polyacrylamide gels with 212-ppm Cr(III),  $F_{\text{rrw}}$  values were lower than those for gels with 636-ppm Cr(III) (see Table 4). For the gel with 212-ppm Cr(III), it is somewhat surprising that the  $F_{\text{rrw}}$  values in 74-md sandstone were significantly less than those in 746-md sandstone. In both cores, the relationship between  $F_{\text{rrw}}$  and  $u$  values can be described using power-law equations where the velocity exponent is near -0.5 (see Table 4). However, the velocity coefficient is more than 100 times greater for gel in the 746-md rock than in the 74-md rock. During brine injection after gelation, the first PV of effluent from the 74-md core had a viscosity of about 20 cp and a chromium concentration that was 7% of the injected value. This suggests that a significant amount of uncrosslinked or lightly crosslinked polymer was displaced from the core after the shut-in period. Since washout of the gel was not observed in the 746-md core and was rarely observed in our experiments with other gels, further work will be needed to explain why gel washout occurred in the case with 74-md sandstone.

Two core experiments were performed using gels containing 1.39% polyacrylamide in 11-md Indiana limestone. The Cr(III) concentrations in the gels were 212 ppm and 636 ppm. During placement in the cores, only 0.9 and 1.2 PV of gelant were injected, respectively, before excessive pressure gradients mandated that



injection be stopped. Because these cores may not have been completely saturated with gelant, the corresponding properties listed in Tables 4 and 6 should be viewed with caution. If this type of gelant is intended to penetrate a significant distance into a low-permeability rock matrix, it may be appropriate to use a polymer with a lower molecular weight (i.e., less than 2 million daltons). More detailed results from our experiments with Cr(III) acetate-polyacrylamide gels can be found in Ref. 16.

### RESULTS FROM TRACER STUDIES

After measuring  $F_{rrw}$  values, tracer studies were performed to determine (1) the fraction of the pore volume that remained available to flow and (2) the new dispersivity of the core. The results from our tracer studies are listed in Table 6. In Table 6,  $V_p/V_{po}$  refers to the fraction of the original pore volume that was sampled by the iodide tracer during a given tracer study. The difference,  $1-V_p/V_{po}$ , provides an indication of the fraction of the original pore volume that was occupied by gel. The original pore volume of a given core ( $V_{po}$ ) was typically about 30 cm<sup>3</sup>.

For the 10%-colloidal-silica gel and the resorcinol-formaldehyde gel formed at pH=9, Table 6 indicates that the gels occupied most (i.e., from 73% to 99%) of the original pore space. This seems qualitatively consistent with the high  $F_{rrw}$  values that were observed for these gels (see Table 4). Resistance to flow is expected to be high when most of the pore space is occupied by gel. The behavior of the resorcinol-formaldehyde gel formed at pH=6.0 to 6.5 can also be rationalized using this logic. In particular, the gel provided low  $F_{rrw}$  values (Table 4) and occupied no more than 1% of the pore space (Table 6).

In contrast, the unbuffered Cr(III)-xanthan gel provided fairly high  $F_{rrw}$  values but apparently occupied no more than 13% of the pore space. Perhaps, small gel particles lodge in pore throats—thereby, dramatically reducing brine permeability without occupying much volume. Experiments performed using 154-ppm Cr(III) without xanthan indicate that this behavior was not due to the chromium alone. These chromium solutions had no significant effect on the apparent pore volume, the dispersivity, or the permeability of the cores.

For most cases when Cr(III) acetate-polyacrylamide gels were used, the flow rates were so low during brine injection after gelation that tracer studies could not be

TABLE 6  
Results from Tracer Studies

Gel	$V_p/V_{po}$			$\alpha/\alpha_0$		
	High-k sandstone	Low-k sandstone	Limestone	High-k sandstone	Low-k sandstone	Limestone
Resorcinol-formaldehyde, pH=6-6.5	0.99	1.00	0.99	1.5	1.0	1.5
Resorcinol-formaldehyde, pH=9	0.09	0.13	0.01	106	11.5	2.9
4% colloidal silica	0.18	0.42	0.78	3.0	4.0	1.8
10% colloidal silica	0.18	0.27	--	8.5	5.3	--
Unbuffered Cr(III)-xanthan	0.92	0.90	0.87	9.9	8.3	1.6
Cr(III)-xanthan buffered with acetate	0.87	0.90	--	1.2	2.7	--
154-ppm Cr(III) (no xanthan)	1.00	1.00	0.98	1.0	1.0	1.0
Cr(III) acetate-HPAM, 212-ppm Cr(III)	--	0.89	0.87	--	0.5	1.7

performed. In view of the very high residual resistance factors (Table 4), we suspect that these gels occupied most of the pore space. However, in two cases (using gelant with 212-ppm Cr(III)),  $F_{rrw}$  values were low enough so that tracer studies were performed. In these cases, the gel apparently occupied from 11% to 13% of the pore space (see Table 6). For the case using 74-md sandstone, the tracer result (11% PV occupied by gel) is qualitatively consistent with the washout of polymer noted in the previous section. For the case using 10.7-md limestone, the tracer result (13% PV occupied by gel) could be attributed to either polymer washout or insufficient gelant injection during the process of gelant placement (as discussed in the previous section).

Table 6 also lists dispersivity results obtained during the tracer studies. The quantity,  $\alpha/\alpha_0$ , refers to the final dispersivity during tracer injection after gelation divided by the initial dispersivity value before gel placement. Initial dispersivity values ( $\alpha_0$ ) for the Berea cores were approximately 0.1 cm. Dispersivity values for cores before exposure to gel were roughly the same in high-permeability Berea sandstone as in low-permeability Berea sandstone ( $\approx 0.1$  cm). However, dispersivity values for Indiana limestone were typically five to ten times greater than those for Berea sandstone.

Table 6 demonstrates that the gels usually increase dispersivity in the cores. Qualitatively, these data mean that the gels broaden the range of flow paths through the porous medium. Gels could create some short pathways simply as a consequence of filling the pore space. On the other hand, longer flow paths could result if the gel acts as a medium that is permeable to the brine (either because of more tortuous flow paths through the gel or because of reversible adsorption or entrapment of the tracer).

#### INHERENT PERMEABILITY TO WATER FOR GELS

Many EOR gelant formulations produce rigid gels when the gelation reaction occurs in a beaker. Viewing these gels leaves an impression that they should completely prevent flow through any porous medium that they occupy. However, after these gels are placed in a porous medium, some level of permeability is usually retained. Rock minerals can change the pH of gelant formulations such that gelation is less complete than that observed in a beaker.<sup>13,14,28</sup> Also, tracer studies reveal that gels often occupy only a fraction of the available pore space. Thus, flow paths around the gel are often available in porous media.

TABLE 7  
Inherent Permeability to Water for Several Gels

Gel	Permeability, $\mu\text{d}$
3% resorcinol, 3% formaldehyde, 0.5% KCl, pH=9	6.2
10% colloidal silica, 0.7% NaCl, pH=8.2	60
0.4% xanthan, 154-ppm Cr(III) (as $\text{CrCl}_3$ ), 0.5% KCl, pH=4	50
1.39% polyacrylamide, 360-ppm Cr(III) (as acetate), 1% NaCl, pH=6	42
2.8% polyacrylamide (Cyanamid Cyanagel 100 <sup>®</sup> ), 500-ppm $\text{Na}_2\text{Cr}_2\text{O}_7$ , 1500-ppm $\text{Na}_2\text{S}_2\text{O}_4$ , 0.5% KCl, pH=5	30

We tried to determine if gels have some inherent permeability so that water can flow through the gel matrix. **Two-dimensional glass micromodels** were fabricated using the procedures described in Ref. 14. The internal dimensions for these rectangular micromodels were 10.3 cm x 0.2 cm x 0.02 cm. Before placing gelant in the models, the "permeability" to water was found to be about 900 darcies. The direction of flow was perpendicular to the 0.2-cm x 0.02-cm face.

The five gelants described in Table 7 were prepared, placed in a micromodel, and allowed to gel at 41°C. All of the formulations produced rigid gels upon gelation. After gelation, brine was injected using a fixed pressure drop. Pressure drops between 5 psi and 25 psi were applied. In all cases, the brine had the same composition as that used to prepare the gel. The flow rate was determined by timing the movement of the brine/air interface in a capillary tube (0.019-cm inner radius) that was connected to the outlet of the micromodel. Because of the low permeabilities that were observed, days or weeks were usually required to perform an experiment. Studies were conducted to confirm that water evaporation at the brine/air interface did not influence the results.

Permeabilities to water were calculated using the Darcy equation, and the results are listed in Table 7. To obtain gel permeabilities, injected water must not fracture the gel, and the gel must not pull away from the walls of the glass micromodel. For the gels listed in Table 7, the gel structure in the clear micromodels appeared intact. However, the possibility remains that the observed permeabilities were influenced by undetected

fractures or by flow around the gel. Therefore, the values listed in Table 7 should be viewed as possible upper limits on the inherent permeability to water.

Note that all permeabilities listed in Table 7 are very low—ranging from 6  $\mu\text{d}$  to 60  $\mu\text{d}$ . For practical purposes in typical secondary and tertiary oil recovery operations, these values are equivalent to total shutoff of flow. Thus, unless a gel treatment reduces the permeability of a porous medium to the microdarcy level, it is unlikely that gel occupies all of the aqueous-phase pore volume. This supports results from our other experiments indicating that gelation is often less complete in a porous rock than that observed in a beaker.

### CONCLUSIONS

1. During injection of gelants that contained Cr(III), chromium propagation was significantly more rapid when the counterion was acetate rather than chloride. For a given counterion, chromium propagation was more rapid in Berea sandstone cores than in Indiana limestone cores. The large buffering capacity of limestone can effectively preclude the propagation of unbuffered Cr(III) chloride-xanthan gelants or  $\text{CrCl}_3$  solutions through porous limestone.
2. During core experiments, the "strongest" gels were found to reduce the permeability of all cores to approximately the same value (in the low microdarcy range). Tracer studies indicated that these gels occupied most of the available pore space.
3. Flow experiments performed in rectangular micromodels indicated that the permeabilities (to water) for five gels were less than or equal to 60  $\mu\text{d}$ .
4. For "weaker" gels (i.e., those leaving a significant permeability), residual resistance factors decreased with increased rock permeability in Berea sandstone. Tracer studies indicated that these gels occupied a small fraction of the pore space in a core. Experiments revealed that gelation in the porous rock was often far less complete than that in a bottle. For unbuffered gelants in porous rocks, the pH at which gelation occurs may be determined more by rock mineralogy and surface area than by the pH of the injected gelant. Thus, the buffering action of reservoir rocks should be considered when evaluating gel performance in the laboratory.
5. Residual resistance factors for Cr(III)-xanthan and Cr(III) acetate-polyacrylamide gels exhibited a reversible shear-thinning character that was described using power-law

relations. In contrast, residual resistance factors for the resorcinol-formaldehyde gels were generally Newtonian.

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### NOMENCLATURE

- $F_{rrw}$  = brine residual resistance factor (brine mobility before gel placement divided by brine mobility after gelation)
- $u$  = superficial or Darcy velocity, ft/d [m/s]
- $V_p$  = apparent remaining pore volume,  $\text{cm}^3$
- $V_{po}$  = initial pore volume of the core,  $\text{cm}^3$
- $\alpha$  = core dispersivity after gelation, cm
- $\alpha_o$  = initial dispersivity of the core, cm
- $\gamma$  = shear rate,  $\text{s}^{-1}$
- $\mu$  = viscosity, cp [mPa-s]

### REFERENCES

1. Seright, R.S.: "Placement of Gels to Modify Injection Profiles," paper SPE/DOE 17332 presented at the SPE/DOE Enhanced Oil Recovery Symposium, Tulsa, OK (April 17-20, 1988).
2. Liang, J., Lee, R.L., and Seright, R.S.: "Placement of Gels in Production Wells," paper SPE/DOE 20211 presented at the SPE/DOE Enhanced Oil Recovery Symposium, Tulsa, OK (April 22-25, 1990).

3. Seright, R.S.: "Effect of Rheology on Gel Placement," *SPE Reservoir Eng.* **6**, No. 2, 212 (1991). *Transactions AIME* **291**.
4. Seright, R.S.: "Impact of Dispersion on Gel Placement for Profile Control," *SPE Reservoir Eng.* **6**, No. 3, 343 (1991).
5. Sorbie, K.S. and Seright, R.S.: "Gel Placement in Heterogeneous Systems with Crossflow," paper SPE/DOE 24192 presented at the SPE/DOE Enhanced Oil Recovery Symposium, Tulsa, OK (April 21-24, 1992).
6. Liang, J., Sun, H., and Seright, R.S.: "Reduction of Oil and Water Permeabilities Using Gels," paper SPE/DOE 24195 presented at the SPE/DOE Enhanced Oil Recovery Symposium, Tulsa, OK (April 21-24, 1992).
7. Jurinak, J.J., Summers, L.E., and Bennett, K.E.: "Oilfield Application of Colloidal Silica Gel," paper SPE 18505 presented at the SPE International Symposium on Oilfield Chemistry, Houston, TX (Feb. 8-10, 1989).
8. Sydansk, R.D.: "A New Conformance Improvement Treatment Chromium (III) Gel Technology," paper SPE/DOE 17329 presented at the SPE/DOE Enhanced Oil Recovery Symposium, Tulsa, OK (April 17-20, 1988).
9. Sydansk, R.D. and Smith T.B.: "Field Testing of a New Conformance-Improvement Treatment-Chromium (III) Gel Technology," paper SPE/DOE 17383 presented at the SPE/DOE Enhanced Oil Recovery Symposium, Tulsa, OK (April 17-20, 1988).
10. Sydansk, R.D.: "Acrylamide-Polymer/Chromium(III)-Carboxylate Gels for Near Wellbore Matrix Treatments," paper SPE/DOE 20214 presented at the SPE/DOE Enhanced Oil Recovery Symposium, Tulsa, OK (April 22-25, 1990).
11. Avery, M.R., Burkholder, L.A., and Gruenenfelder, M.A.: "Use of Crosslinked Xanthan Gels in Actual Profile Modification Field Projects," paper SPE 14114 presented at the SPE International Meeting on Petroleum Engineering, Beijing, China (March 17-20, 1986).
12. Perkins, T.K. and Johnston, O.C.: "A Review of Diffusion and Dispersion in Porous Media," *Soc. Pet. Eng. J.* **3**, No. 1, 70 (1963).
13. Seright, R.S. and Martin, F.D.: "Impact of Gelation pH, Rock Permeability, and Lithology on the Performance of a Monomer-Based Gel," *SPE Reservoir Eng.* **8**, No. 1, 43 (1993).
14. Seright, R.S. and Martin, F.D.: "Fluid Diversion and Sweep Improvement with Chemical Gels in Oil Recovery Processes," first annual report (DOE/BC/14447-8), U.S. DOE, 10-25 and 151-158 (June 1991).
15. Seright, R.S. and Martin, F.D.: "Fluid Diversion and Sweep Improvement with Chemical Gels in Oil Recovery Processes," second annual report (DOE/BC/14447-10), U.S. DOE, 3-25 and 121-127 (Nov. 1991).

16. Seright, R.S. and Martin, F.D.: "Fluid Diversion and Sweep Improvement with Chemical Gels in Oil Recovery Processes," final report (DOE/BC/14447-15), U.S. DOE, 3-27 and 100-109 (Sept. 1992).
17. Shu, P.: "The Gelation Mechanism of Chromium(III)," *American Chemical Society Symposium Series* 33, No. 1, 43 (1989).
18. Mumallah, N.A.: "Chromium (III) Propionate: A Crosslinking Agent for Water-Soluble Polymers in Hard Oilfield Brines," *SPE Reservoir Eng.* 3, No. 1, 243 (1988).
19. Tackett, J.E.: "Characterization of Chromium(III) Acetate in Aqueous Solution," *Applied Spectroscopy* 43, No. 3, 490 (1989).
20. Lockhart, T.P.: "Chemical and Structural Studies on  $\text{Cr}^{3+}$ /Polyacrylamide Gels," paper SPE 20998 presented at the SPE International Symposium on Oilfield Chemistry, Anaheim, CA (Feb. 20-22, 1991).
21. Kolnes, J., Stavland, A, and Thorsen, S.: "The Effect of Temperature on the Gelation Time of Xanthan/Cr(III) Systems," paper SPE 21001 presented at the SPE International Symposium on Oilfield Chemistry, Anaheim, CA (Feb. 20-22, 1991).
22. Willhite, G.P. *et al.*: "Gelled Polymer Systems for Permeability Modification in Petroleum Reservoirs," final report (DOE/ID/12846-6), U.S. DOE (Sept. 1991).
23. Woods, C.L. *et al.*: "A Numerical Modelling Study of the Mechanisms of Gelation in Porous Media," *In Situ* 15, No. 4, 347 (1991).
24. Garver, F.J., Sharma, M.M., and Pope, G.A.: "The Competition for Chromium Between Xanthan Biopolymer and Resident Clays in Sandstones," paper SPE 19632 presented at the SPE Annual Technical Conference and Exhibition, San Antonio, TX (Oct. 8-11, 1989).
25. McCool, C.S., Green, D.W., and Willhite, G.P.: "Permeability Reduction Mechanisms Involved in In-Situ Gelation of a Polyacrylamide/Chromium(VI)/Thiourea System," *SPE Reservoir Eng.* 77 (Feb. 1991).
26. Jousset *et al.*: "Effect of High Shear Rate on In-Situ Gelation of a Xanthan/Cr(III) System," paper SPE/DOE 20213 presented at the SPE/DOE Enhanced Oil Recovery Symposium, Tulsa, OK (April 22-25, 1990).
27. Kia, S.F., Fogler, H.S., and Reed, M.G.: "Effect of pH on Colloidally Induced Fines Migration," *J. Colloid & Interfac. Sci.* 118, No. 1, 158 (1987).
28. Seright, R.S. and Martin, F.D.: "Effect of  $\text{Cr}^{3+}$  on the Rheology of Xanthan Formulations in Porous Media: Before and After Gelation," *In Situ* 16, No. 1, 1 (1992).