Reduction of Gas and Water Permeabilities Using Gels

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Summary

We investigated how different types of gels reduce permeability to water and gases in porous rock. Five types of gels were studied, including (1) a "weak" resorcinol-formaldehyde gel, (2) a "strong" resorcinol-formaldehyde gel, (3) a Cr(III)-xanthan gel, (4) a Cr(III)-acetate-HPAM gel, and (5) a colloidal-silica gel. For all gels, extensive coreflood experiments were performed to assess the permeability-reduction characteristics and the stability to repeated water-alternating-gas (WAG) cycles. Studies were performed at pressures up to 1,500 psi using either nitrogen or carbon dioxide as the compressed gas. We developed a coreflood apparatus with an in-line high-pressure spectrophotometer that allowed tracer studies to be performed without depressurizing the core. We noted several analogies between the results reported here and those observed during a parallel study of the effects of gel on oil and water permeabilities.

Introduction

In recent years, gel treatments have been applied to reduce channeling in high-pressure gas floods[1-3] and to reduce water production from gas wells! Laboratory work has also been performed to assess the ability of various gels to divert CO_2.[5,6] With increasing interest in the use of gels to reduce channeling during high-pressure gas floods, the question arises, How do the mechanisms for gas diversion differ from those for water diversion?

This paper reports the results from an experimental investigation of how different types of gels reduce permeability to water and to compressed gases (i.e., carbon dioxide and nitrogen). Studies were performed at 900 psi and 1,500 psi using a specially developed core apparatus that allowed a comprehensive sequence of experiments to be performed without depressurizing the core. Since water-alternating-gas (WAG) cycles are often used in high-pressure gas floods, we were especially interested in how well gels withstand exposure to multiple WAG cycles. We also performed tracer studies at various stages during the experiments to estimate the fraction of the pore space that was occupied by gel.

Finally, we compared the results from these gas/water experiments with those from a parallel study that investigated how gels affect permeability to oil and water.[7] We hope that these studies will ultimately help explain why some gels can selectively reduce permeability to one phase more than to another. This property is critical to the success of gel treatments in production wells if zones cannot be isolated during gelant placement.[8-10]

Experimental Procedures

Gelants Studied. We investigated several types of gels, including (1) a "weak" resorcinol-formaldehyde gel that was buffered and formed at pH = 6.5, (2) a "strong" resorcinol-formaldehyde gel formed at pH values from 8.3 to 9.0, (3) a Cr(III)-xanthan gel, (4) a Cr(III)-acetate-HPAM gel, and (5) a colloidal-silica gel. The compositions of the five formulations are listed in **Table 1.** Pfizer provided the xanthan (Flocon 4800®); Marathon provided the polyacrylamide or HPAM (used in the gel, MARCIT®[11]); and DuPont supplied the colloidal silica (Ludox SM®[12]).

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Core Preparation. In all core experiments, we used high-permeability Berea sandstone cores. Typically, each core was 14-cm long with a cross-sectional area of 10 cm^2. The cores were cast in a metal alloy (Cerrotru®). 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, while the second core segment (12-cm length) was used to measure mobilities and residual resistance factors. The cores were not fired.

The sequence followed during our core experiments is listed in **Table 2.** First, at ambient conditions, the cores were saturated with brine and porosities were determined (Step 1 of Table 2). All subsequent steps were performed at 41°C. Most experiments were performed at 900 psi (61 atm), but three floods were performed at 1,500 psi (102 atm). The gels investigated at 1,500 psi included resorcinol-formaldehyde (formed at pH = 9) and Cr(III)-acetate-HPAM. When saturating a given core, the brine composition was the same as that used in preparing the gelant formulation. Unless stated otherwise, the core was mounted so that the flow was horizontal.

Steps 1 through 6 were performed to characterize permeabilities, porosities, and brine and gas mobilities. Detailed results from these characterizations can be found in Ref. 10. The rock properties were similar for the different core experiments. Brine permeability averaged 650 md, and porosity averaged 0.21. During injection with back pressures of 900 or 1,500 psi, the mobility of brine was the same as that at atmospheric pressure.

Tracer studies were routinely performed to characterize pore volumes and dispersivities of the cores. These studies involved injecting a brine bank containing potassium iodide as a tracer. The tracer concentration in the effluent was monitored spectrophotometrically at a wavelength of 230 nm. Detailed descriptions of the tracer studies can be found in Refs. 9 and 10.

Our coreflood apparatus included an in-line high-pressure spectrophotometer that allowed tracer studies to be performed without depressurizing the core. Thus, after the initial saturation of a given core with brine, experiments were conducted entirely at high pressure. Maintenance of a high pressure minimizes complications introduced by gas expansion when cores are depressurized.

Gas and Water Flow Before Gelant Placement. We addressed several questions concerning the effects of gas and water injection before gelant placement. Detailed results for each of these experiments are documented in Ref. 10. The first question was, Does either continued gas injection or multiple WAG cycles erode the properties of the core (e.g., by increasing porosity or permeability)? Results from our experiments indicated that our Berea sandstone cores did not experience irreversible changes. Specifically, reproducible permeabilities and porosities were observed for the cores before and after injecting many cycles of gas (either CO_2 or N2) and brine and more than 100 PV of both gas and brine.

A second question was, Would the results from our experiments be significantly different if wet gases (gases saturated with water prior to injection) were used in place of dry gases? We found that the endpoint mobilities for wet and dry CO_2 were fairly constant during the first 40 PV of gas injection. Thereafter, significant mobility increases were observed as the gas de-watered the core.

A third question was, Do endpoint mobilities for gas (CO_2 or N2) and brine depend on whether flooding occurs horizontally or vertically? In our experiments, we found that endpoint mobilities could depend on core orientation during flooding. However, the differences were not large, and they were not significant enough to change the basic conclusions from our gel experiments.

TABLE 1—GELANT COMPOSITIONS

Gelant Composition	pH
3% resorcinol, 3% formaldehyde, 0.5% KCl, 0.42% $NaHCO_3$	6.5
3% resorcinol, 3% formaldehyde, 0.5% KCl, 0.42% $NaHCO_3$	8.3-9.0
0.4% xanthan, 0.0154% Cr(III) (as $CrCl_3$), 0.5% KCl	3.8
1.39% HPAM, 0.0212% Cr(III) (as acetate), 1% NaCl	5.3-5.9
10% colloidal silica, 0.7% NaCl	8.2

TABLE 2—SEQUENCE FOLLOWED DURING CORE EXPERIMENTS

Step	
1.	Saturate core with brine and determine porosity.
2.	Determine absolute brine permeability and mobility.
3.	Perform tracer study to confirm the pore volume (V_{po}) and to determine the core dispersivity (α_o).
4.	Inject gas to determine gas mobility at residual water saturation.
5.	Inject brine to determine brine mobility at residual gas saturation.
6.	Perform tracer study to determine the fraction of the original pore volume remaining (V_p/V_{po}) and the change in dispersivity (α/α_o).
7.	Inject gelant using 15.7 ft/d superficial velocity.
8.	Shut in core to allow gelation.
9.	Inject brine to determine brine residual resistance factor (F_{rrw}).
10.	Perform tracer study *to* determine V_p/V_{po} and α/α_o.
11.	Inject gas to determine gas residual resistance factor (F_{rrgas}).
12.	Inject brine to determine F_{rrw}.
13.	Perform tracer study to determine V_p/V_{po} and α/α_o.
14.	Inject gas to determine F_{rrgas}.
15.	Inject brine to determine F_{rrw}.
16.	Perform tracer study to determine V_p/V_{po} and α/α_o.
17.	Inject gas to determine F_{rrgas}.
18.	Inject brine to determine F_{rrw}.
19.	Perform tracer study to determine V_p/V_{po} and α/α_o.

Gelant Placement in the Cores. Gelant was injected into a given core (Step 7 in Table 2) using a superficial velocity of 15.7 ft/d. In each case, several pore volumes of gelant (typically 10 PV) were injected to ensure that the cores were saturated with gelant. Thus, in field applications, the gel properties reported in this study are more relevant to the region upstream of the front of the gel bank than to the region at the front of the gel bank.

Effluent samples were collected during gelant injection. The samples were allowed to gel, and final gel strength was compared with a gelant that had not been injected into the core. In all cases, the last gelant effluent from the core before shut-in had final gel strengths similar to the non-injected formulations. The Cr(III)-xanthan gelant and the resorcinol-formaldehyde gelant at pH 6.5 formed very "weak" gels, while the others formed relatively "strong" gels (see Ref. 10 for a more quantitative characterization).

The resorcinol-formaldehyde gelants, with viscosities near that of water, were the least viscous of the formulations. Viscosities for the colloidal-silica gelant and the Cr(III)-acetate-HPAM gelant were **2.0** cp and 33 cp (at 11 s^{-1}, 41°C), respectively. These gelants were found to be Newtonian. The Cr(III)-xanthan gelant was the most viscous; its viscosity was 253 cp at 11 s^{-1}. The viscosity exhibited a strong shear-thinning character. Gelation times were estimated by observing the fluidity of gelant in bottles. Gelation times for the gels ranged from 2.4 hours to 18 hours. For gelant that had been forced through a core, gelation times were approximately the same as those for a gelant that was not injected. After injecting a given gelant, the core was shut in for three to five days. In all cases, the gelation times were substantially less (by factors ranging from 5 to 40) than the shut-in times. More detailed gelant placement data can **be** found in Refs. **9** and 10.

Residual Resistance Factors

F_{rrw} Values During First Brine Injection. Following the shut-in period, brine was injected (Step 9 in Table 2) to determine the residual resistance factor for brine (F_{rrw}). These F_{rrw} values were determined by dividing brine mobility (at residual gas saturation) before gel placement by brine mobility after gel placement. Whenever possible, we determined residual resistance factors as a function of injection rate. **Table 3** summarizes most of the residual resistance factors from this study. In all cases, these residual resistance factors apply to the second core segment.

For the resorcinol-formaldehyde gel that was formed at pH = 6.5, the F_{rrw} value was 140 upon first brine injection (at 0.785 ft/d) after shut-in (see **Fig. 1).** The F_{rrw} value decreased each time the superficial velocity was raised to successively higher values. In particular, F_{rrw} values were 24.7, 21.8, 13.7, and 6.5 for injection velocities of 1.57 ft/d, 3.14 ft/d, 6.28 ft/d, and 31.4 ft/d, respectively. When the injection rate was subsequently decreased, F values remained at approximately 7. This behavior is consistent with that reported earlier.[13,14] Earlier studies suggested that upon first exposure to a given fluid velocity, a certain amount of resorcinol-formaldehyde gel breaks down to allow additional flow paths through the porous medium. Flow of brine through this porous medium then appears more or less Newtonian until the previous maximum in fluid velocity is exceeded.

TABLE 3—SUMMARY OF RESIDUAL RESISTANCE FACTORS FOR BRINE (F_{RRW}) AND COMPRESSED GAS (F_{RRGAS})

Core	1	2	3	4	5	6	7	8	9
Gelant	Cr(III)-Xanthan	Resorcinol-Formaldehyde				Cr(III)-Acetate-HPAM			Colloidal Silica
pH	3.8	6.5	8.3	9.0	9.0	5.3	5.9	5.9	8.2
Gas used	CO_2	C02	CO_2	N_2	C02	CO_2	N_2	CO_2	CO_2
System pressure, psi	900	900	900	900	1,500	900	1,500	1,500	900
F during 1st WAG	417 $u^{-0.38}$	7	21,600	10,400	19,600	272,000	170,000	4,970 $u^{-0.72}$	32,000
F_{rrgas} during 1st WAG	12	2	101	126	17	500	284	148	400
F_{rrw} during 2nd WAG	23	5	570	520	23	1,720 $u^{-0.72}$	3,440 $u^{-0.55}$	472 $u^{-0.48}$	3,800
F_{rrgas} during 2nd WAG			60	64	14	50	103	64	380
F_{rrw} during 3rd WAG			400	484	18	549 $u^{-0.58}$	1,750 $u^{-0.45}$	177 $u^{-0.43}$	2,600
F_{rrgas} during 3rd WAG			57	61	11	13	81	34	290
F during 4th WAG			361	370	20	131 $u^{-0.47}$	1,440 $u^{-0.48}$	94 $u^{-0.43}$	1.800

Note u is superficial velocity of brine in units of ft/d

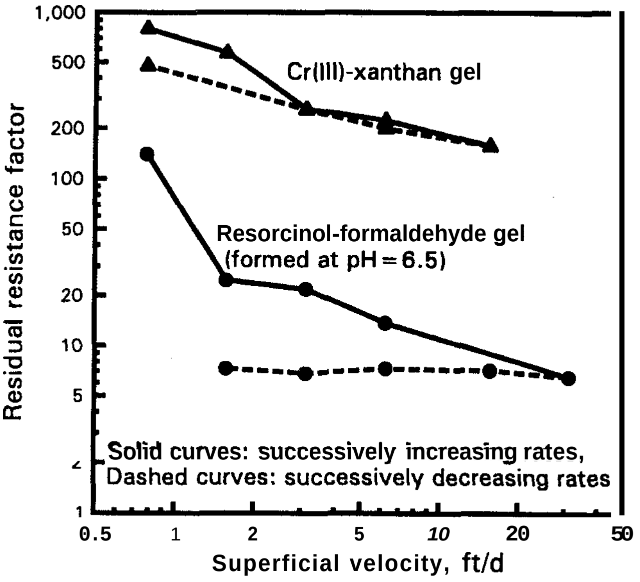

Fig. 1—Effect of brine injection velocity on Cr(III)-xanthan and resorcinol-formaldehyde gels.

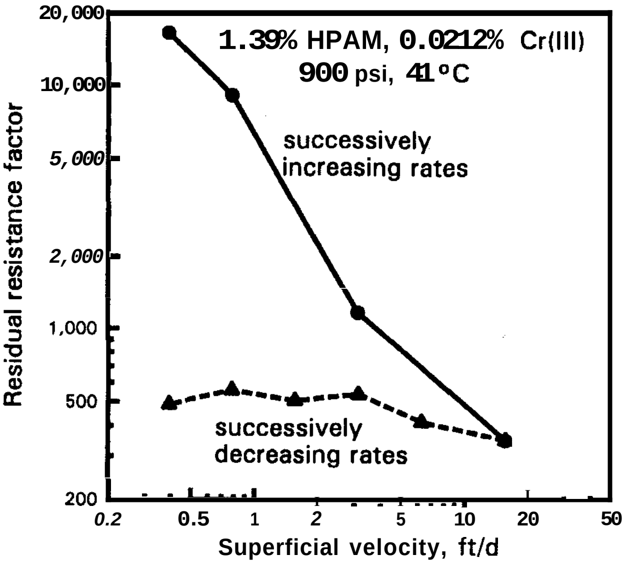

Fig. 2—Effect of fluid velocity on residual resistance factors during CO_2 injection.

For the Cr(III)-xanthan gel, F values also experienced a significant decrease with increased injection rate (Fig. 1). When injection rates were subsequently reduced, the curve associated with decreasing rates (the dashed curve) was slightly lower than that for increasing rates (the solid curve). This observation suggests that the Cr(III)-xanthan gel experienced a small degree of breakdown upon exposure to higher fluid velocities. However, the F values still increased noticeably with decreasing brine velocity. The latter data could be described by Eq. 1,

$$F_{rrw} = 417\ u^{-0.38} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

where u is superficial velocity in units of ft/d. 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. We observed this behavior earlier with Cr(III)-xanthan gels.[14,15]

More or less Newtonian behavior was observed for the resorcinol-formaldehyde gels and the colloidal-silica gel (data associated with Cores 2, 3, 4, 5, and 9 in Table 3). However, an apparent shear-thinning behavior was observed during brine injection for the Cr(III)-acetate-HPAM gel that was placed in Core 8. For two of the Cr(III)-acetate-HPAM gels (Core listings 6 and 7 in Table 3) during first brine injection after gelation, the F_{rrw} values (272,000 and 170,000, respectively) were so high that experiments could be performed only at one very low injection rate (0.025 ft/d). Shear-thinning behavior might have been observed if we could have varied the injection rate.

For all core experiments, the highest residual resistance factors were obtained during the first brine injection after gelation. In agreement with our previous work,[13-15] relatively low residual resistance factors were found for the Cr(III)-xanthan gel and the resorcinol-formaldehyde gel formed at pH = 6.5. Extremely high residual resistance factors were obtained for the resorcinol-formaldehyde gels formed at pH values from 8.3 to 9.0, the Cr(III)-acetate-HPAM gels, and the colloidal-silica gel. These very high F values were anticipated based on previous work.[11-14]

The reader should recognize that very high pressure gradients (up to 1,300 psi/ft) accompanied the highest residual resistance factors. In field applications in unfractured wells where the gelant has penetrated many feet radially into the rock matrix, the high residual resistance factors simply mean that the gel will effectively stop flow. In fractured wells, very high residual resistance factors can have a more practical function than in unfractured wells. In particular, if the gelant leaks off a very short distance from a fracture face, a moderate or small reduction in the matrix flow capacity can occur even though the residual resistance factor is high.[10] These observations should be kept in mind if our data are to be applied to field situations.

For the resorcinol-formaldehyde gels that were formed at pH 8.3 to 9.0 (associated with Cores 3, 4, and 5 in Table 3), the first F_{rrw} values ranged from 10,400 to 21,600. Some variations in the first F_{rrw} values were also noted for the Cr(III)-acetate-HPAM gels (associated with Cores 6, 7, and 8). These experiments used different combinations of system back-pressure (900 or 1,500 psi) and residual gas (CO_2 or N_2). However, during the first brine injection after gel placement, we are not convinced that variations in the F values can necessarily be attributed to differences in system pressure or the type of residual gas.

F_{rrgas} Values During First Gas Injection. After determining F values, compressed gas was injected to determine the residual resistance factors for gas (F_{rrgas}). These F_{rrgas} values were determined by dividing gas mobility (at residual water saturation) before gel placement by gas mobility after gel placement. These values were also measured as a function of injection rate.

Table 3 shows that for all gels, the residual resistance factors decreased sharply when gas was injected. During CO_2 or N_2 injection, F_{rrgas} values sometimes decreased with increased injection rate. For example, **Fig. 2** shows this behavior for a Cr(III)-acetate-HPAM gel in Core 6. When $CO2$ (at 900 psi) was first injected after gelation, the F_{rrgas} values decreased from 16,500 to 354 as fluid velocity was increased from 0.393 to 15.7 ft/d. However, when velocities were subsequently reduced, the F_{rrgas} values appeared more or less Newtonian. F_{rrgas} values ranged from 354 at **15.7** ft/d to 490 at 0.393 ft/d, and no trend was evident with changing velocity. This suggests that the decrease in F_{rrgas} with increasing velocity may be a result of gel breakdown.

For all gels tested, the apparent rheology during gas injection was generally Newtonian in the absence of gel breakdown. That is, when injection velocities were successively decreased (as in the dashed curve of Fig. 2), F_{rrgas} values were fairly independent of injection rate.

F_{rr} Values During Reinjection of Water and Gas. When water was reinjected to displace gas, residual resistance factors were less than the preceding F_{rrw} values. This was noted for all gels (see Table 3). Apparently, the gels experienced substantial breakdown during the first WAG cycle. This behavior was also observed during earlier studies.[5,6] The decrease in F_{rrw} values was most dramatic for those gels with the highest initial residual resistance factors. Additional WAG cycles were performed for most of the gels. With each new WAG cycle, both F and F_{rrgas} values decreased, indicating further gel breakdown.

One of the most interesting findings of this study was that the F values obtained during Step 12 (from Table 2) were significantly

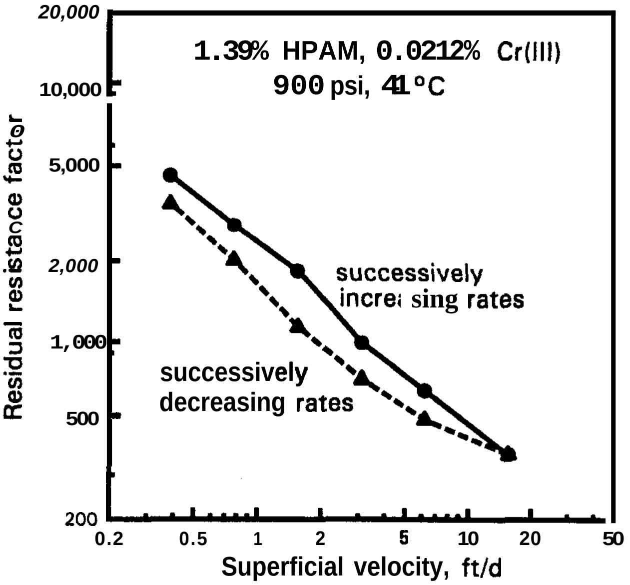

Fig. 3—Effect of fluid velocity on residual resistance factors during brine injection.

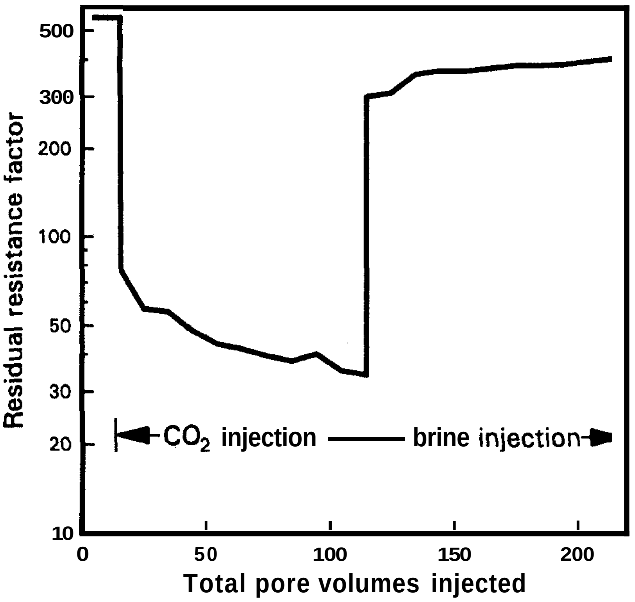

Fig. 4—Effects of injecting 100 PV of gas and brine on the residual resistance factors for a resorcinol-formaldehyde gel (900 psi, 41°C.

greater than the F_{rrgas} values from Step 11. This was noted for all gels (see Table 3). The results indicate that several different types of gels can reduce permeability to water more than to gas. Table 3 reveals that this behavior persists through multiple WAG cycles.

For the Cr(III)-acetate-HPAM gel, we observed shear-thinning behavior during the second cycle of brine injection. For example, after obtaining the results during CO_2 injection that were described in Fig. 2, brine was reinjected to obtain the results illustrated in **Fig. 3.** As the brine velocity increased from 0.393 to 15.7 ft/d, the F_{rrw} value decreased from 4,560 to 365. Then, as the brine velocity was reduced from 15.7 to 0.393 ft/d, the F_{rrw} values increased from 365 to 3,520. Thus, some gel breakdown apparently occurred during this procedure (because the two curves in Fig. 3 do not overlap); however, a shear-thinning character stands out in spite of the breakdown. In Fig. 3, the data associated with decreasing rates could be described using Eq. 2.

$$F_{rrw} = 1,720\ u^{-0.72} \quad \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

Throughout the various WAG cycles, we consistently observed shear-thinning behavior during brine injection and Newtonian behavior during gas injection for the Cr(III)-acetate-HPAM gel (see Table 3). At present, we do not understand why this difference in rheology occurs. However, in a parallel study of the effects of gel on oil and water permeabilities,[7] we noted shear-thinning behavior during brine injection and Newtonian behavior during oil injection for Cr(III)-acetate-HPAM gels. We suspect that the explanations for the results from the gas/water and the oil/water experiments are related.

Effects of WAG Versus Continuous Injection on Gel Breakdown. While performing the experiments described in Table 3, we noted that gel breakdown (i.e., irreversible loss of residual resistance factor) was more sensitive to the process of switching from brine injection to gas injection than it was to continuous injection of either fluid. This behavior was particularly evident during the first WAG cycle. To demonstrate this finding more clearly, we performed an experiment using a resorcinol-formaldehyde gelant with the same composition and under the same experimental conditions as those indicated under Core 3 in Table 3.

When brine was first injected after the shut-in period, F values were stable at 29,000 during injection of 2.3 PV. Then, one PV of CO_2 was injected, followed by 11 PV of brine. During the first 0.4 PV of the latter brine injection, F_{rrw} stabilized at a value of 550. Thus, a single WAG cycle involving only one PV of CO_2 was enough to reduce F_{rrw} from 29,000 to 550.

After injecting the second cycle of brine (i.e., 11 PV), 100 PV of CO_2 was injected, followed by 100 PV of brine. The residual resistance factors observed during this WAG cycle are shown in **Fig. 4** as a function of pore volumes injected. As the number of pore volumes of CO_2 injected increased from 1 to 10 to 100, CO_2 residual resistance factors decreased from 76.6 to 57.2 to 34.6, respectively. One possible explanation for this decrease could be gel breakdown during CO_2 injection. Another explanation is that the large volume of continuous CO_2 injection gradually shrank the gel by extracting water. The latter explanation is more consistent with the behavior noted while injecting the subsequent 100 PV of brine. As the second part of Fig. 4 shows, the brine residual resistance factor increased from 302 to 312 to 412, as the number of pore volumes of brine injected increased from 1 to 10 to 100, respectively. Perhaps this increase occurs because the gel is rehydrating and expanding during the prolonged period of brine injection.

Performance Using CO_2 Versus N_2. We conducted two sets of experiments to compare gel performance during CO_2 injection versus that during N_2 injection. One set was performed using a resorcinol-formaldehyde gel at 900 psi. The results are associated with Cores 3 and 4 in Table 3. Note the similarity in behavior. After the first brine injection, the F and F_{rrgas} values during the multiple WAG cycles were virtually identical for the CO_2 experiment and the N_2 experiment. The similarity in results suggests that the observed behavior is not sensitive to the type of gas used during this experiment with the resorcinol-formaldehyde gel. To expand on this point, (1) for both compressed CO_2 and compressed N_2, the gel reduced brine permeability significantly more than gas permeability, (2) multiple WAG cycles degraded the residual resistance factors to about the same extent for CO_2 as for N_2, and (3) Newtonian behavior was observed during both brine and gas injection. These results are especially interesting considering the corrosive nature of CO_2 and the inert nature of N_2.

The second set of experiments that compare gel performance during CO_2 versus N_2 injection are associated with Cores 7 and 8 in Table 3. These experiments used a Cr(III)-acetate-HPAM gel at 1,500 psi. There were many similarities in the results from the two experiments. First, for both experiments, the gel reduced brine permeability significantly more than gas permeability. Second, Newtonian behavior was observed during gas injection. Third, an apparent shear-thinning behavior was observed during brine injection. In summary, the performance of the gels during CO_2/water experiments was not greatly different than that during N_2/water experiments.

One might expect gel formation and stability to be altered by a low pH environment that was created by the presence of CO_2. For most gels, gelation is sensitive to pH.[13,14] However, our tracer results[10,16] revealed that the gas saturations were very low when the gelants were placed in the core, so the buffering capacity of the rock probably overwhelmed the influence of the CO_2 on pH. Also, during high-pressure pH measurements at 41°C, we found that pH (of water in the presence of CO_2 at 1,500 psi) was between 4.4 and 5.1 in the absence or presence of rock (sandstone, limestone, or dolomite).[17]

Effect of Pressure on Performance. Most of our experiments were performed at 900 psi. This pressure was selected because the upper pressure limit for our in-line spectrophotometer was stated by the manufacturer to be 1,000 psi. However, we were concerned that CO_2 behavior at 900 psi (where CO_2 density is 0.156 g/cm^3) might be much different than that at 1,500 psi (where CO_2 density is 0.641 g/cm^3). Therefore, we performed three experiments at 1,500 psi—one using a resorcinol-formaldehyde gel (at pH = 9) and two using a Cr(III)-acetate-HPAM gel.

For the resorcinol-formaldehyde gel, a comparison of the results from Cores 3 and 5 in Table *3* suggests that gel breakdown during the first WAG cycle was more severe at 1,500 psi than at 900 psi. However, gel breakdown at 1,500 psi was less evident during subsequent WAG cycles. At both pressures, residual resistance factors for water were consistently greater than those for gas.

For the Cr(III)-acetate-HPAM gel, a comparison of the results from Cores 6 and 8 in Table **3** reveals many similarities in behavior at the two pressures. At both pressures, (1) Newtonian behavior was observed during CO_2 injection: (2) an apparent shear-thinning behavior was observed during brine injection; *(3)* resistance factors were consistently greater for brine than for CO_2; and (4) residual resistance factors decreased during multiple WAG cycles. Although some differences exist in F_{rrw} and F_{rrgas} values during the multiple WAG cycles, the overall behavior at 1,500 psi was not radically different from that at 900 psi.

High-pressure Visualization Experiments

We performed high-pressure visualization experiments to determine whether macroscopic changes in the gels could be observed during exposure to water, oil (Soltrol 130®), and CO_2 at 1,500 psi. Two gels were studied during these experiments—a resorcinol-formaldehyde gel (formed at pH = 9) and a Cr(III)-acetate-HPAM gel (formed at pH = 5.8). Compositions of these gels are indicated in Table 1. For the Cr(III)-acetate-HPAM case, 60 ml of gelant was placed in a high-pressure visualization cell (– 100 ml total volume) and allowed to gel for several days at 41°C. After gelation, the cell was pressurized with water to 1,500 psi. The gel shrank very slightly during this pressurization. After observing the gel for 24 hours, the water was replaced by oil without depressurization. The gel was then observed for another day at 1,500 psi and 41°C. This procedure was repeated using the following sequence of fluids to contact the gel: brine, oil, brine, oil, CO_2, brine, CO_2, oil. The gel showed no significant changes during these procedures. When the cell was depressurized, gas boiled out from the gel, causing the gel to fracture. We observed similar results during exposure of the resorcinol-formaldehyde gel to brine-CO_2 cycles. In summary, no significant macroscopic changes were observed for the gels when exposed to brine, CO_2, or oil at 1,500 psi.

Results From Tracer Studies

Tracer studies provide interesting insights about the fraction of the total pore volume occupied by gel and/or gas. An extensive set of pore volume and dispersivity data was collected during our experiments. This information is documented and analyzed in Refs. 10 and 16.

Analogy With Oil/Water Experiments

We noted a number of analogies between the results reported here and those observed during a parallel study of the effects of gels on oil and water permeabilities.[7] **Table 4** summarizes one set of oil and water residual resistance factors reported in Ref. 7. These data apply to a Cr(III)-acetate-HPAM gel with the same composition as that reported in Table 1. The rock (Berea sandstone), temperature, brine, and gelant placement technique were identical to those used in this study. However, the oil/water experiments were performed at atmospheric pressure using a refined oil (Soltrol 130®) instead of compressed gas.

TABLE 4—RESIDUAL RESISTANCE FACTORS FOR BRINE (F_{rrw}) AND OIL (F_{rro}) FOR THE Cr(III)-ACETATE-HPAM GEL FROM TABLE 1. (0 psig, 41°C. DATA FROM REF. 7.)

Injection cycle:	1	2	3	4
F_{rrw}	**53,000**	**972** $u^{-0.50}$	**357** $u^{-0.49}$	**105** $u^{-0.55}$
F_{rro}	50	**25**	**14**	

By comparing the data in Table 4 with that associated with Cores 6, 7, and 8 in Table 3, one can see several striking similarities between the results from the gas/water experiments and the oil/water experiments. First, in both sets of experiments, very high F_{rrw} values were observed when brine was first injected after gelation. Second, oil residual resistance factors (F_{rro}) were substantially less than water residual resistance factors—just as F_{rrgas} values were substantially less than F_{rrw} values. Third, F_{rrw} and F_{rro} values degraded during multiple cycles of water and oil injection—just as F_{rrw} and F_{rrgas} values degraded during multiple cycles of water and gas injection. Fourth, an apparent shear-thinning behavior was noted during brine injection, but Newtonian behavior was observed during oil or gas injection.

During the various cycles of fluid injection, the magnitude and trends for the F; values were surprisingly similar for the two sets of experiments. Also, the magnitude and trends for the F_{rro} values in the oil/water experiments were surprisingly similar to those for the F_{rrgas} values in the gas/water experiments. Thus, we suspect that the explanation for the behavior during our gas/water experiments will be closely related to that during our oil/water experiments. At present, we do not fully understand why gels should reduce water permeabilities much more than either gas or oil permeabilities. However, we recognize the importance of these phenomena in field applications of gels. Therefore, we have an extensive research program underway to determine why these phenomena occur.

Significance in Field Applications

An ability for gels to reduce the permeability of one phase more than that of another phase is critical to the success of gel treatments in many applications. For example, in oil production wells with excess water production, gel treatments are often applied without confining the gelant to the water-source zone. Since aqueous gelants can penetrate a significant distance into all open zones, oil-productive zones could be seriously damaged unless the gel maintains a high permeability to oil.[7-9] Thus, an ability to reduce water permeability much more than oil permeability could (under the right circumstances[8,9]) eliminate the need for zone isolation during gelant placement.

Using the same logic, the gas/water permeability-reduction properties of gels that were observed in this study could be exploited during treatment of gas wells with excess water production (e.g., from water coning). Because these gels can reduce water permeability much more than gas permeability, there is a reduced risk of damage to gas-productive zones during gelant placement.

An important question that remains unanswered is, Can gels be used to reduce excess gas production (e.g., gas coning) from oil wells? In this case, we want a gel that reduces gas permeability much more than it reduces oil permeability. To our knowledge, no experiments have been performed to test this property for gels. Thus, this topic remains an important area for future research.

Our original motivation for this study was to assess the use of gels as a means to reduce fluid channeling in CO_2 floods. Since WAG cycles are often used in high-pressure gas floods, we were interested in how well gels withstand exposure to multiple WAG cycles. Our experiments suggest two important deficiencies for gels in this type of application. First, WAG cycles (especially the first **WAG** cycle) can significantly degrade gel properties. Second, in our experiments, the gels always reduced water permeability much more than they reduced gas permeability. Since gas mobility is usually significantly greater than water mobility, we would like a gel that reduces gas permeability at least as much as it reduces water permeability for applications to control gas channeling in CO_2 injection wells. Martin *et al.*[5,6] found some cases where gels reduced CO_2 permeability more than water permeability. Additional work will be required to establish why gels disproportionately reduce permeabilities to different phases.

Conclusions

We investigated how different types of gels reduce permeability to water and gases in porous rock. Five types of gels were studied, including (1) a "weak" resorcinol-formaldehyde gel, *(2)* a "strong" resorcinol-formaldehyde gel, (3) a Cr(III)-xanthan gel, **(4)** a Cr(III)-acetate-HPAM gel, and (5) a colloidal-silica gel. The following conclusions were reached:

1. In Berea sandstone, all five types of gels can reduce permeability to water much more than they reduce permeability to CO_2.

2. All five types of gels experienced some breakdown (i.e., permanent loss of residual resistance factor) during WAG cycles. Gel breakdown was more severe during exposure to a WAG cycle (especially the first WAG cycle) than during prolonged injection of either brine or gas.

3. An apparent shear-thinning behavior was observed for the polymer-based gels during brine injection.

4. The apparent rheology in porous media was more or less Newtonian for all five gels during gas injection.

5. For a resorcinol-formaldehyde gel and a Cr(III)-acetate-HPAM gel, the behavior during CO_2/water experiments had many similarities to that during N_2/water experiments.

6. For resorcinol-formaldehyde and Cr(III)-acetate-HPAM gels, the behavior at 1,500 psi (where C02 density is 0.641 g/cm^3) was not radically different from that at 900 psi (where CO_2 density is 0.156 g/cm^3).

7. No significant macroscopic changes were observed for a resorcinol-formaldehyde gel or a Cr(III)-acetate-HPAM gel when exposed to brine, CO_2, or oil during visualization experiments at 1,500 psi.

Nomenclature

F_{rrgas} = gas residual resistance factor (gas mobility at residual water saturation before gel placement divided by gas mobility at residual water saturation after gelation)
F_{rro} = oil residual resistance factor (oil mobility at residual water saturation before gel placement divided by oil mobility at residual water saturation after gelation)
F_{rrw} = brine residual resistance factor (brine mobility at residual gas saturation before gel placement divided by brine mobility at residual gas saturation after gelation)
u = superficial or Darcy velocity, ft/d [m/s]
V_p = apparent remaining pore volume, cm3
V_{po} = initial pore volume of the core, cm^3
a = core dispersivity after gelation, cm
α_o = initial dispersivity of the core, cm

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SI Metric Conversion Factors

'Conversion factor is **exact.**

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