Impact of Gelation pH, Rock Permeability, and Lithology on the Performance of a Monomer-Based Gel

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Summary. Resorcinol/formaldehyde gels are used to show that gel performance in porous rocks depends critically on the pH at which gelation occurs. The gels generally reduced the permeability of low-permeability sandstone more than in high-permeability sandstone. However, residual resistance factors can be greater in sandstones than in less permeable carbonate cores. A simple mathematical model is used to assess whether pH effects can be exploited to optimize gel placement in injection wells.

Introduction

Ideally, gel treatments should reduce fluid channeling through high-permeability, watered-out flow paths without damaging oil-productive zones. In most applications, however, the gelant penetrates to some extent into low-permeability, oil-productive zones. A gel treatment can enhance or harm oil production, depending on how the gel's performance in low-permeability rock compares with that in the "thief" zone.[1-4]

This paper reports results from an experimental investigation of the effects of gelation pH, rock permeability, and lithology on the performance of a resorcinol/formaldehyde gel. This gel was chosen for study because its placement in porous media is not complicated by some factors that influence placement of polymeric gelants. In particular, before gelation, aqueous resorcinol/formaldehyde solutions (1) are Newtonian, (2) exhibit nearly the same viscosity as water, and (3) can propagate through sandstone or carbonate rocks without being retained significantly. Insights obtained by studying this relatively simple resorcinol/formaldehyde gel may be valuable when assessing the performance of more complex gels in fluid diversion.

Resorcinol and formaldehyde are small molecules that are very soluble in water. Resorcinol and formaldehyde will polymerize, as shown in Fig. 1. This polymerization is similar to that during the formation of phenol-formaldehyde resins.[5] These gels have been used in field applications.[6-9]

The terms "gelant" and "gelling agent" here refer to the liquid formulation before gelation. Resistance factor, F_r, is defined as water mobility divided by gelant mobility. It is equivalent to the effective viscosity of the gelant in porous media relative to that of water. Residual resistance factor, F_{rr}, is defined as water mobility in the absence of gel divided by water mobility in the presence of gel. F_{rr} is a measure of the permeability reduction caused by gel.

All gelant formulations throughout this study contained 3 wt% resorcinol (0.27 *M*), 3 wt% formaldehyde (1 *M*), and 0.5 wt% KCl (0.067 *M*). All chemicals were reagent-grade. All core experiments and gelation studies were performed at 41°C.

pH Dependence of Gelation

The product formed by the reaction of resorcinol with formaldehyde depends on pH. At pH=9, a strong gel is formed that is clear and red. No free water remains after gelation. However, as the initial pH is decreased, gel formation becomes less perfect. With an initial pH=7, an opaque orange-white gel is formed, and some free water remains after the reaction. The gelation time (at 41°C) is about 4 hours at pH=9 and is 5 to 7 hours when the initial pH=7. As initial pH is decreased below 7, the gelation time and the final ratio of free water to gel increase.

As the reaction between resorcinol and formaldehyde proceeds, the pH tends to decrease. For example, for a gelant at an initial pH=7, the pH gradually declines to 5.1 over the course of 5 hours. Under similar conditions, the pH remains stable at 7 for solutions of resorcinol without formaldehyde or of formaldehyde without resorcinol.

Resorcinol and formaldehyde have very little capacity to buffer the pH of a solution (Fig. 2). Thus, acid generated during the resorcinol/formaldehyde reaction can decrease pH and affect the final nature of the product. Because gelation is sensitive to pH, all factors that affect pH should be of concern during determination of the nature and performance of the gel. Rock minerals also can have an important influence on solution pH. For example, clays can reversibly exchange cations (e.g., Na^+ and Ca^{2+}) with hydrogen ions in solution.[10] Clays also can react irreversibly with hydrogen or hydroxide ions.[11] Dissolution and precipitation of minerals also can change pH.[12-14] Thus, the reaction products formed in beaker tests may differ from those formed in porous media. Furthermore, during laboratory corefloods with unbuffered gelants, a gradient of pH values may exist in the core. Because the nature and performance of gels vary considerably with pH, coreflood results with unbuffered gelants may be difficult to scale to field applications.

We examined the use of buffers to maintain constant pH. Carbonate, bicarbonate, phosphate, and acetate buffers were used at concentrations of 0.05 M. At pH=9, gel time, strength, and appearance with a carbonate buffer were identical to those without the buffer.

At an initial pH=7, the gelation time ranged from 5 to 7 hours with or without a phosphate buffer. Also, the gel product had the same color (opaque orange-white) with or without phosphate. With phosphate, no free water remained after gelation. Without the phosphate buffer, however, free water remained after the reaction, and the "gel" appeared as a grainy precipitate. Without phosphate, the final ratio of free water to "gel" ranged from 5:1 to 1:10 during several replicate experiments. Thus, there is variability that is not currently understood. In contrast, results were reproducible when buffers were used. This provides another argument for using buffers during laboratory experiments.

For gelants buffered with bicarbonate at pH=6, no free water formed but the gel was grainier in appearance than with phosphate at pH=7. For gelants buffered with acetate at pH=5, free water in contact with a grainy precipitate was formed (ratio of ≈3:1, respectively). We cannot eliminate the possibility that the buffers interfere with the resorcinol/formaldehyde reaction by some means other than by affecting pH. However, we suspect that pH is the dominant factor.

We also determined the inherent permeability of gel formed at pH=9. Gel was allowed to form in a glass "micromodel" that had internal dimensions of 10.35×0.21×0.0178 cm. Before the gel was placed, the effective "permeability" of the micromodel was 893 darcies. After gelation, the permeability to brine was 6.2 μd.

Chemical Transport in Porous Media

For an aqueous solution that contains 3 wt% resorcinol, 3 wt% formaldehyde, and 0.5 wt% KCl, the viscosity at 41°C (before gelation) is 0.75 cp—nearly the same as that of a brine that contains 0.5% KCl (0.65 cp). During flow through cores, all resistance factors for resorcinol/formaldehyde solutions (again, before gelation)

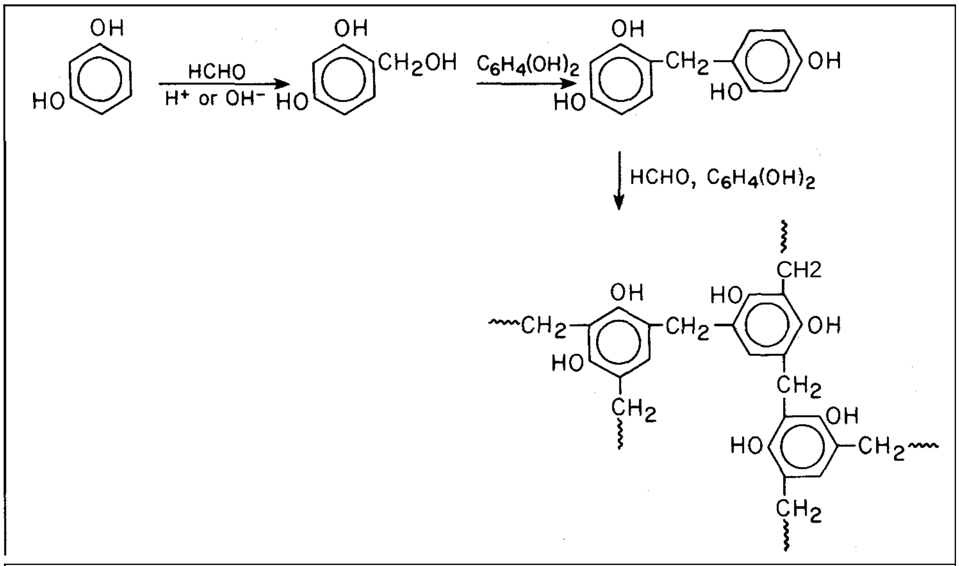

Fig. 1—Reaction of resorcinol with formaldehyde.

were observed to be near unity. This was noted in both sandstone and carbonate cores with permeabilities ranging from 7 to 700 md.

Previous work[15] demonstrated that propagation of formaldehyde is not retarded during flow through reservoir rock. Using corefloods where a continuous bank of 3 wt% resorcinol was injected to displace brine from 288-md Berea core, we found no retention of resorcinol.

Coreflood Procedures

In each coreflood performed during this work, the porosity and permeability to brine were determined first. The cores typically were about 15 cm long and 3.6 cm in diameter. All cores had one internal pressure tap 1.2 to 2.5 cm from the inlet rock face. The core materials used included Berea sandstone and Indiana limestone. None of the cores were fired. Tracer studies were performed to find the dispersivity of the core and to confirm the PV determination. 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.

Then, 3 PV of resorcinol/formaldehyde gelant were injected using a flux of 15.7 ft/D. Resistance factors were monitored in the two core sections. We also continuously monitored pH values in the effluent. Effluent samples were collected and monitored to determine whether the gelation characteristics of the effluent differed from those of gelant that had not been injected. After injection of the gelant, cores were shut in for 3 to 4 days (at 41°C).

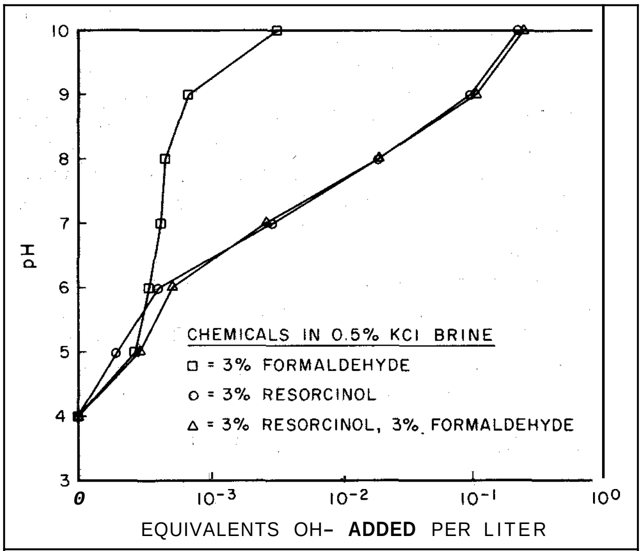

Fig. 2—Buffer capacities of resorcinol and formaldehyde.

After shut-in, brine was injected to determine F_{rr}. Low injection rates were used first. The F_{rr} values reported here were measured with the second segment (≈ 12.5 cm) of the core. Note was made of how rapidly F_{rr} 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_{rr} values changed at lower rates. This process was repeated with successively higher rates. The objective of this procedure was to determine the apparent rheology of the gel in porous media and whether gel mobilization or breakdown occurred at a particular flow rate or pressure gradient.

After the F_{rr} values had been determined, additional tracer studies were performed to determine the final PV that was occupied by the gel and the final dispersivity of the core.

Permeability Reduction After Gelation

In each core experiment, F_{rr} was determined during brine injection over a range of fluid velocities. In many cases, F_{rr} values decreased significantly upon exposure to successively higher brine flow rates. **Table 1** lists F_{rr} data for a resorcinol/formaldehyde gel that was buffered at pH = 7 in 63-md Berea sandstone. (The data are listed in the order in which they were collected.) F_{rr} decreased from 1,735 after first exposure to a fluid flux of 0.025 ft/D to 1,120 after exposure to a flux of 0.393 ft/D. However, when flow rates were subsequently reduced, the F_{rr} values remained fairly constant. The results suggest that, upon first exposure to a given fluid velocity, a certain amount of gel breaks down to allow a flow path 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 2 provides an example of a gel that was buffered at pH = 9 in 49-md Berea sandstone. With this gel, F_{rr} values experienced a more dramatic decrease upon exposure to successively higher injection rates. This is also shown in Fig. 3. (Interestingly, gel was not observed in the effluent during these experiments.) Upon subsequent reduction of injection rates, a mild shear-thinning character was observed for the gel at pH = 9. Equations relating F_{rr} values to flux values are included in Table 2. Similar data from other core experiments are listed in Appendix D of Ref. 16. **Table** 3 summarizes these data. To determine each F_{rr} relation in Table 3, the core was first exposed to an injection rate that resulted in the maximum pressure gradient and Darcy velocity specified. Then, F_{rr} values were determined at a number of lower rates. In these F_{rr} relations, u is superficial velocity in feet per day.

TABLE 1—RESULTS FROM BRINE INJECTION AFTER GEL PLACEMENT IN 63-md BEREA SANDSTONE—GELANT CONTAINS 3% RESORCINOL, 3% FORMALDEHYDE, 0.5% KCl, 0.05 *M* PHOSPHATE, pH = 7 $\phi = 0.192$, $\mu_w = 0.70$ cp, 105°F

Flux (ft/D)	Pressure Gradient (psilft)	Final k (md)	F_{rr}	
0.025	76.2	0.0363	1,735	
0.050	140.5	0.0394	1,600	$\overline{F}_{rr} = 1{,}620$
0.025	71.8	0.0385	1,635	
0.100	259	0.0427	1,475	$\overline{F}_{rr} = 1{,}520$
0.025	68.5	0.0404	1,560	
0.201	494	0.0450	1,400	
0.100	267	0.0414	1,520	$\overline{F}_{rr} = 1{,}420$
0.025	58.4	0.0474	1,330	
0.393	773	0.0563	1,120	
0.202	415	0.0538	1,170	$\overline{F}_{rr} = 1{,}150$
0.100	211	0.0525	1,200	
0.025	48.3	0.0573	1,100	

TABLE 2—RESULTS FROM BRINE INJECTION AFTER GEL PLACEMENT IN 49-md BEREA SANDSTONE—GELANT CONTAINS 3% RESORCINOL, 3% FORMALDEHYDE, 0.5% KCl, 0.05 *M* $NaHCO_3$, pH = 9 $\phi = 0.200$, $\mu_w = 0.67$ cp/C, 105°F

Flux	Pressure Gradient (psilft)	Final k (md)	F_{rr}	
0.025	466	0.0057	8,600	
0.050	471	0.0113	4,350	$F_{rr} = 3{,}793\,u^{-0.05}$
0.025	243	0.0109	4,490	
0.126	622	0.0214	2,280	
0.025	156	0.0170	2,890	$F_{rr} = 1{,}688\,u^{-0.15}$
0.050	313	0.0184	2,660	
0.251	690	0.0385	1,270	$F_{rr} = 1{,}017\,u^{-0.16}$
0.025	100	0.0266	1,840	
0.628	748	0.0889	550	
0.126	199	0.0670	730	$F_{rr} = 515\,u^{-0.16}$
0.025	50	0.0531	920	

Is there a threshold velocity or pressure gradient for gel breakdown in a given rock? The data in Tables **1** and 2 suggest that there may not be a single threshold. Instead, additional gel breakdown occurs each time the pressure gradient achieves a new high. In other cases, no threshold was observed. For example, consider the case for gel formed at pH = 6.5 with 0.05 M phosphate in 28-md Berea (see Table 3 or Table **D4** of Ref. 16). In this case, one relationship ($F_{rr} = 24.4\,u^{-0.26}$) describes all experimental data for all injection rates from 0.025 to **16 ft/D**. Also, no gel breakdown was observed as pressure gradients were increased from 8 to 930 psi/ft.

Because F_{rr} values depend on current and previous fluid velocities, there is some doubt about the best way to compare F_{rr} values from one core experiment to another. Fig. **4** plots initial F_{rr} values vs. gelation pH. In this figure, the F_{rr} values are the first values measured during brine injection after gelation. Because of the way our experiments were performed, these F_{rr} values were measured at low velocities.

Fig. **4** shows that, for a given lithology and permeability, the highest F_{rr} values were observed for gels formed at pH = 9. This was anticipated because the most rigid gels are formed at pH = 9 during beaker tests. For gels that were buffered at pH ≥ 7, F_{rr} values were also very high. In fact, these values were so high that a rock matrix treated by these gels would be effectively plugged. Thus, when these gels are placed in a reservoir, caution should be used to prevent damage to oil-productive zones.

For gels buffered at pH ≤ 6, F_{rr} values were near unity, indicating that the "gel" had little or no effect. Thus, the range of pH (6 to 7) over which F_{rr} values will change from unity to very high values is fairly narrow.

For gels buffered at a given pH in Berea sandstone, F_{rr} values generally remained about the same or increased with decreasing permeability. This is shown in Table **4,** where the values in parentheses indicate the pressure gradients at which the F_{rr} values were measured. (In Table 3, F_{rr} values in Berea at pH ≈ 6.5 appear to decrease with decreasing permeability. However, this may be an artifact because different buffers were used and because the results were very sensitive to pH in this region.)

For some data observed in limestone cores, F_{rr} values were less than those in more permeable Berea cores (see Table **4).** Thus, F_{rr} values can be affected by both permeability and lithology.

For gels that were injected at pH ≈ 7 but were not buffered, we are less certain about the actual pH at which the gelation reaction occurred. From the F_{rr} values, we suspect that reaction pH values were between 6 and 7. However, it is quite possible that the reaction pH values were different in the three unbuffered cases, especially in the sandstone cores vs. the carbonate core.

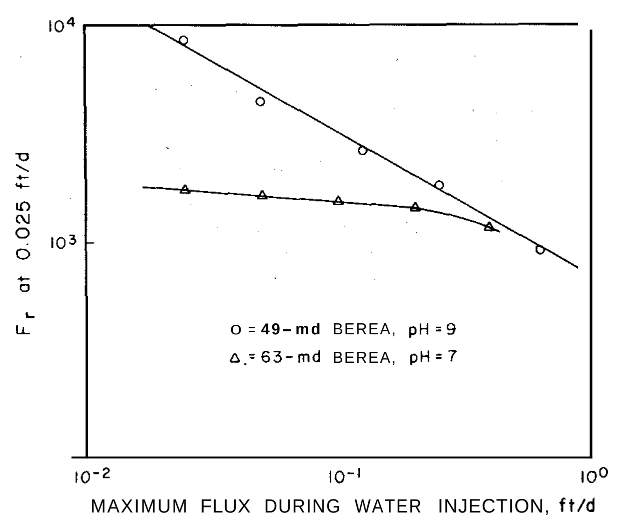

Fig. 3—F_{rr} value at 0.025 ft/D after injecting brine *at* the maximum flux specified on the abscissa.

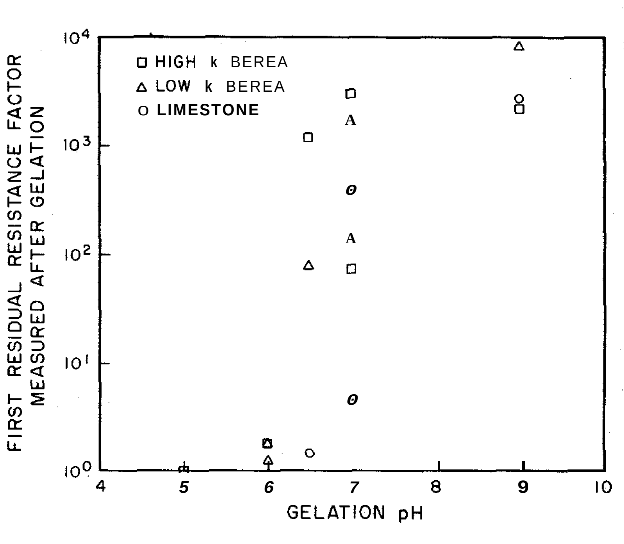

Fig. 4—Effect of gelation pH on residual resistance factors.

TABLE 3—SUMMARY OF RESULTS FROM BRINE INJECTION AFTER GELATION"
GELANT CONTAINS 3% RESORCINOL, 3% FORMALDEHYDE, 0.5% KCl, 41°C

				Maximum			
Rock**	pH	Buffer	F_{rr}†	psi/ft	ft/D	V_{pf}/V_{pi}	α_f/α_i
570-md BS	9	0.05 *M* $NaHCO_3$	2,170	251	0.62		
			1,250	750	3.10	0.09	106
49-md BS	9	0.05 *M* $NaHCO_3$	3,793 $u^{-0.05}$	471	0.05		
			1,688 $u^{-0.15}$	622	0.13		
			1,017 $u^{-0.16}$	690	0.25		
			515 $u^{-0.16}$	748	0.63	0.13	11.5
7.4-md LS	9	0.05 *M* $NaHCO_3$	1,594 $u^{-0.16}$	1,006	0.025	0.01	2.9
455-md BS	7	0.05 *M* phosphate	970 $u^{-0.11}$	56	0.20		
			662 $u^{-0.19}$	74	0.39		
			500 $u^{-0.17}$	100	0.79		
			386 $u^{-0.10}$	147	1.57		
			286	1,103	15.7	0.12	5.2
63-md BS	7	0.05 *M* phosphate	1,735	76	0.025		
			1,620	141	0.05		
			1,520	259	0.10		
			1,420	494	0.20		
			1,150	773	0.39	0.73	94
7-md LS	7	0.05 *M* phosphate	404	160	0.025		
			365	283	0.05		
			355	534	0.10		
			326	910	0.20	0.66	4.4
390-md BS	7	None	83.1 $u^{-0.05}$	298	15.7	0.13	64
57-md BS	7	None	128	160 to 2,130	0.6 to 9	1.0	29
13-md LS	7	None	4.7 $u^{-0.04}$	24 to 504	0.6 to 16	0.98	0.35
28-md BS	6.5	0.05 *M* phosphate	24.4 $u^{-0.26}$	8 to 930	0.025 to 16	0.39	9.0
288-md BS	6.5	0.05 *M* $NaHCO_3$	417 $u^{-0.28}$	29	0.10		
			404 $u^{-0.19}$	41	0.20		
			242 $u^{-0.31}$	48	0.39		
			248	69	0.79		
			153	169	3.14		
			123	629	15.7	0.99	1.5
7.4-md LS	6.5	0.05 *M* $NaHCO_3$	1.5 $u^{-0.07}$	1 to 29	0.4 to 16	0.99	1.5
704-md BS	6	0.05 *M* NaHCO,	1.8	1 to 8	3 to 31	0.87	5.1
61-md BS	6	0.05 *M* NaHCO,	2.1 $u^{-0.14}$	5 to 41	1 to 29	1.0	1.0
77-md BS	6	0.05 *M* phosphate	1.3	3 to 27	1 to 16	0.93	1.4
573-md BS	5	0.05 *M* acetate	1.0	2.5 to 5	16 to 31	0.97	1.3

*Data summarized from Ref. 16.
**BS = Berea sandstone, LS = Indiana limestone.
†u = superficial velocity in feet per day.

Tracer studies provide interesting insights about the fraction of the total PV occupied by gel. In Table 3, V_{pf}/V_{pi} refers to the fraction of the original PV sampled by the iodide tracer after gel placement (as determined by the 50% tracer-concentration level in the effluent). For gels at pH = 9, the gel apparently occupied 87% to 99% of the pore space. Generally, as the gelation pH was reduced, a smaller fraction of the PV was occupied by the gel. This is shown in Table 3 and **Fig. 5.** In one case (unbuffered gel at pH = 7 in 57-md Berea), the gel reduced permeability by a factor of 128, apparently without reducing the PV. In other cases (gel buffered at pH = 7 in 63-md Berea and in 7-md limestone), large F_{rr} values were associated with fairly small reductions in PV (27% to 34%). We can speculate how a small volume of gel could cause large permeability reductions. Perhaps small gel particles lodge in pore throats, thereby dramatically reducing brine permeability without occupying much volume.

Dispersivity values for cores before exposure to gel were roughly the same in high- and low-permeability Berea (= 0.1 cm).[16] However, dispersivity values for Indiana limestone were typically 5 to **10** times greater than those for Berea.[16]

Table 3 also lists dispersivity results obtained during tracer studies. The quantity α_f/α_i refers to the final dispersivity during tracer injection after gelation divided by the initial dispersivity value before gel placement. The effluent tracer curves were usually fit quite well with the error-function solution.[17] **Figs. 6a through 6c** show several tracer curves that were obtained before and after gel placement. **Fig. 7** plots relative dispersivities as a function of gelation pH.

In most cases, the presence of gel increased dispersivity. At pH > 6, dispersivity values in Berea were 5 to 106 times greater after gel placement than before gel placement. Gel-induced dispersivity changes in Indiana limestone were generally less than those in Berea sandstone. Qualitatively, the increased dispersivity values indicate 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.

When the tracer studies were performed at very low injection rates, tracer curves sometimes showed signs of an exchange of iodide between the gel and the mobile brine. We observed that the degree of "tailing" exhibited by the tracer curve increased with decreasing injection rate. As injection rate decreased, there was *a* greater need to use a capacitance model (e.g., a Coats-Smith model[18]) to describe the tracer data. Further evidence of iodide exchange between the gel and the brine was found when brine was used to flush tracer from the core. After injection of many PVs of brine at a high rate to displace tracer, no iodide was detected in the effluent. However, if the core was shut in for a day and then additional brine injected, iodide was detected in the first PV of effluent.

Exploiting pH To Optimize Gel Placement

We have shown that residual resistance factors provided by a resorcinol/formaldehyde gel depend on the pH at which gelation occurs. This is especially true over the pH range from 6 to 7. For gelation pH values between 6 and 7, F_{rr} can change from 1 to more than 1,000.

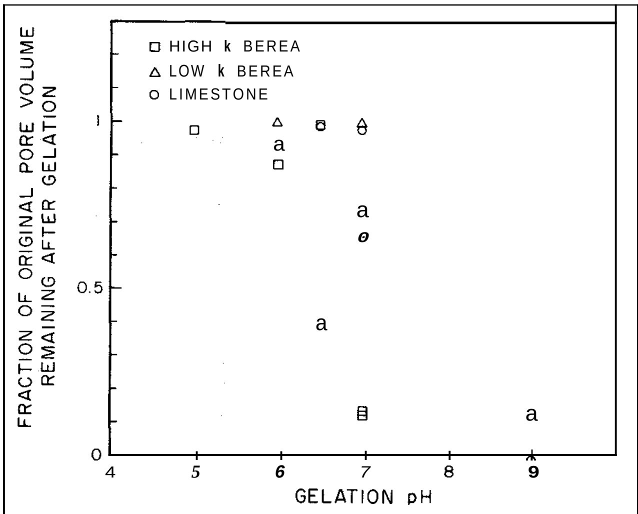

Fig. 5—PV remaining after gelation vs. gelation pH.

TABLE 4—F_{rr} VALUES FOR RESORCINOUFORMALDEHYDE GELS

Gelation pH	High-*k* Berea	LOW-k Berea	Indiana Limestone
9	2,170 (251)*	8,600 (466)	2,800 (1,006)
7	770 (74)	1,735 (76)	404 (160)
7**	74 (298)	138 (771)	4.8 (24)

'Values in parentheses show pressure gradients in psi/ft.
**Unbuffered.

Can this pH dependence of gelation be exploited to optimize gel placement? Certainly this behavior could be useful if a high-pH preflush were injected only into the "thief" zones, or if a low-pH preflush were injected only into the less permeable zones. But can the pH dependence of gelation be exploited to eliminate the need for zone isolation completely? In concept, ion exchange and other reactions with rock minerals could retard the movement of a pH front more in one zone than in another zone. Perhaps different rates of propagation of pH fronts could be exploited to attain high F_{rr} values in the most-permeable zones but low F_{rr} values in less permeable zones.

Previous researchers[10,19] described the propagation of buffered and unbuffered fluid banks through porous media. As with any species, the propagation of H^+ or OH^- through porous media depends on (1) the injected concentration of the species, (2) the volume of fluid injected, (3) the number of sites available for adsorption or exchange, and (4) any reactions or equilibria that involve the species.

A parameter a, is defined here as the number of PV's of a chemical formulation that must be injected to satisfy all available retentive sites in 1 PV of the porous medium. To evaluate a,,

$$a, = n_f/n_s. \quad\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \quad (1)$$

Here, n_f is the amount of a specific chemical that is removed by the rock from a certain PV of fluid under a particular set of conditions. The parameter n_s is the amount of the species of interest in solution per unit of volume of the injected formulation. When considering changes in H^+ or $OH-$ concentrations, both n_f and n_s can be expressed in units of equivalents per liter of PV.

The capacity of a given rock to retard a pH front is related to the quantities and specific types of clays and other minerals that are present. The ion exchange capacity, n_{max}, provides a measure of the number of sites that can reversibly exchange cations or hydrogen ions. Berea, which is considered a relatively clean sandstone, has an ion-exchange capacity around **5** meq/kg of rock.[20] For reservoir rocks, ion-exchange capacities from 4 to 70 meq/kg have been reported.[20]

Eq. 2 allows ion exchange capacities, expressed in meq/kg of rock, to be converted to n_f values, with units of meq/L of PV.[10]

$$n_f = n_{max}\rho_r(1-\phi)/\phi. \quad\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \quad (2)$$

To derive this equation, n_{max} first is multiplied by rock density, ρ_r, and $(1-\phi)$. This product is the maximum number of milliequivalents that can be exchanged per volume of porous rock. Dividing this product by the porosity, ϕ, provides n_f, the maximum number of milliequivalents that can be exchanged per PV of porous rock. To illustrate the use of Eq. 2, consider a sandstone with a porosity of 0.2, a rock density of 2.65 g/cm^3, and an ion-exchange capacity of 10 meq/kg. From Eq. 2, n_f is calculated to be 10 meq/kg$\times10^{-3}$ kg/g$\times$2.65 g/cm$^3\times10^3$ cm^3/L$\times(1-0.2)/0.2$. Thus, in this case, $n_f = 106$ meq/L or 0.106 eq/L.

Eq. 2 assumes that retention of the species is independent of concentration and that no reactions other than irreversible retention involve the species. However, adsorption of the species often will be governed by a Langmuir-type isotherm[10] so that n_f will be less than the value given by Eq. 2.

Concerning n_s, equilibria may exist between components in solution so that a species may be replenished as it is removed by adsorption. For example, in a buffered solution, loss of hydrogen ion by ion exchange will cause the buffer to replenish the H^+. Thus, the denominator in Eq. 1 often will be underestimated by use of the existing concentration of the species.

From Fig. 2, we note that 0.107 eq/L of H^+ is required to change the pH from 9 to 7 for our resorcinol/formaldehyde gelant. Only another 0.00223 eq/L of H^+ is needed to change the pH from 7 to 6. Thus, if $n_f \leq 0.106$ and if a gelant is injected at pH=9, we can estimate the maximum a, value associated with the rock changing the gelant pH to 6. That is, $a_r < 1$ [i.e., $0.106/(0.107+0.00223)$]. Similarly, if a gelant is injected at pH=7, the maxi-

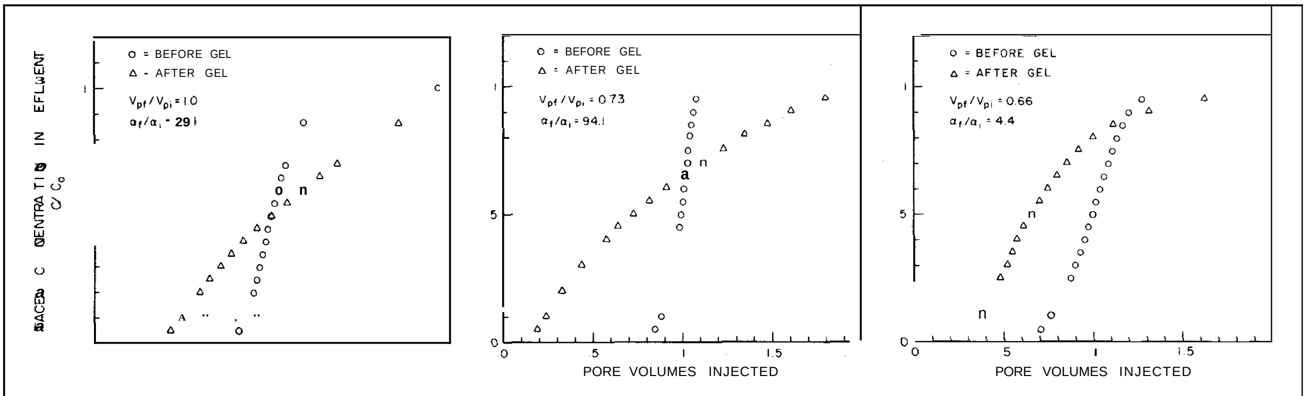

Fig. 6—Tracer results during brine injection before vs. after gel placement: (a) 57-md Berea, no buffer, initial gelant pH = 7; (b) 63-md Berea, phosphate buffer, gelant pH = 7; and (c) 7-md limestone, phosphate buffer, gelant pH = 7.

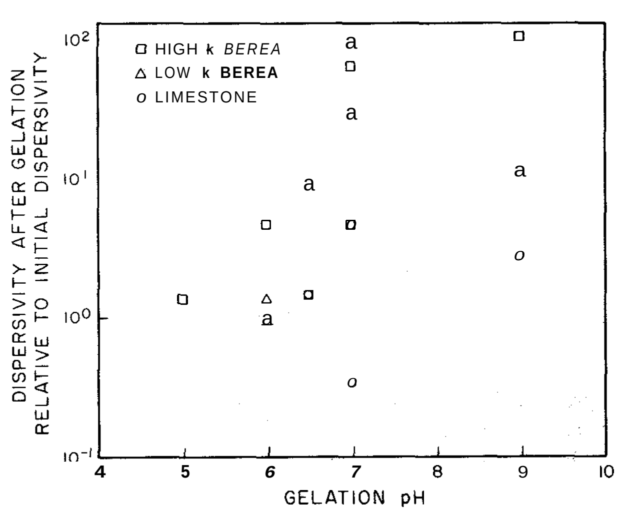

Fig. 7—Relative dispersivity after gelation vs. gelation pH.

mum a, value associated with the rock changing the gelant pH to a value of 6 is about 48 (i.e., 0.106/0.00223). If the gelant contains a buffer, the a, values could be significantly lower because n_s could be considerably greater than the values used in these examples.

Previous work[1] has quantified the impact of retention (a,) and inaccessible PV (V_{pin}) on the degree of penetration of gelant into a given zone in reservoirs with noncommunicating layers. For Newtonian fluids in linear flow, &. 3 relates the depth of penetration, L_{p1}, for a species in the most permeable layer (with properties designated with the subscript 1) to the depth of penetration, L_{p2}, in a given less permeable layer (with properties designated with the subscript 2).

$$(1+a_{r1}-V_{pin1})(\phi_1/k_1)[(F_r-1)L_{p1}^2/2+(\Delta p_{D1}+1)L_{pm}L_{p1}]$$
$$=(1+a_{r2}-V_{pin2})(\phi_2/k_2)[(F_r-1)L_{p2}^2/2+(\Delta p_{D2}+1)L_{pm}L_{p2}]. \quad \ldots\ldots (3)$$

Eq. **4** provides the analogous relation for Newtonian fluids in radial flow (with r_{p1} and r_{p2} designating radii of penetration in a given layer):

$$(1+a_{r1}-V_{pin1})(\phi_1/k_1)\{r_{p1}^2[F_r\ln(r_{p1}/r_w)+\ln(r_{pm}/r_{p1})$$
$$+(1-F_r)/2+\Delta p_{D1}\ln(r_{pm}/r_w)]-r_w^2[(\Delta p_{D1}+1)\ln(r_{pm}/r_w)$$
$$+(1-F_r)/2]\}$$
$$=(1+a_{r2}-V_{pin2})(\phi_2/k_2)\{r_{p2}^2[F_r\ln(r_{p2}/r_w)+\ln(r_{pm}/r_{p2})$$
$$+(1-F_r)/2+\Delta p_{D2}\ln(r_{pm}/r_w)]-r_w^2[(\Delta p_{D2}+1)\ln(r_{pm}/r_w)$$
$$+(1-F_r)/2]\}. \quad \ldots\ldots (4)$$

Eqs. 5 and 6 provide the analogous relations for non-Newtonian fluids in linear flow and radial flow, respectively:

$$(1+a_{r1}-V_{pin1})(\phi_1/k_1)\mathrm{f}(L_{p1})=(1+a_{r2}-V_{pin2})(\phi_2/k_2)\mathrm{f}(L_{p2}). \quad \ldots\ldots (5)$$

$$(1+a_{r1}-V_{pin1})(\phi_1/k_1)\mathrm{f}(r_{p1})=(1+a_{r2}-V_{pin2})(\phi_2/k_2)\mathrm{f}(r_{p2}). \quad \ldots\ldots (6)$$

In Eqs. 5 and 6, $\mathrm{f}(L_{p1})$, $\mathrm{f}(L_{p2})$, $\mathrm{f}(r_{p1})$, and $\mathrm{f}(r_{p2})$ are independent of any depth of penetration other than the parameter indicated.

For propagation of H^+ or $OH-$ fronts, the inaccessible PV terms (V_{pin}) can be neglected. Then, close examination of Eqs. 3 through 6 reveals that the $(1+a_r)$ terms will cancel if a, $\ll$ 1 or if a, values are the same in all layers. Thus, retention values must be significantly different in different layers to have a strong impact on the relative depth of penetration.

Now, we examine whether pH effects can be exploited to optimize gel placement in an unfractured (radial flow) injection well with two noncommunicating layers. A gelant will be injected without zone isolation until the gelant penetrates to a radius of 50 ft in the most permeable layer (Layer 1). (The wellbore radius, r_w, is 0.5 ft.) We focus on the "best-case" situation. In particular, a_{r1} is assumed to be zero in the most-permeable layer. Thus, there is no retention of the gelant in Layer 1, and the pH front (i.e., the pH of the injectant) coincides with the final radius of the gelant bank (50 m). All the gelant that enters this layer can form gel at the optimum pH. Also, the resistance factor of the gelant is assumed to be one. This ensures that the depth of penetration of gelant in the less permeable layer (Layer 2) will be minimized.[1,2] For simplicity, dispersion is neglected.[3]

In the less-permeable layer, the gelant front and the pH front are retarded to the extent determined by the factor a_{r2}. After gelant placement, the well is shut in to allow gelation. The gel is allowed to form only upstream of the pH front. Thus, gel with an F_{rr} is formed to a radius of 50 ft in Layer 1. In both layers, no gel is formed downstream of the pH front ($F_{rr}=1$).

During brine injection after gelation, we are interested in how the injection profile has changed. Figs. **8a** and **8b** illustrate how the value for a_{r2} affects injection profiles in a reservoir with two noncommunicating layers. This is shown as a function of permeability ratio, k_1/k_2, for the two layers. In the label for the y axis in Figs. 8a and 8b, q_2/q_{20} is the water injectivity in Layer 2 after the gel has formed, relative to water injectivity before gel placement. Similarly, q_1/q_{10} is the water injectivity in Layer 1 after the

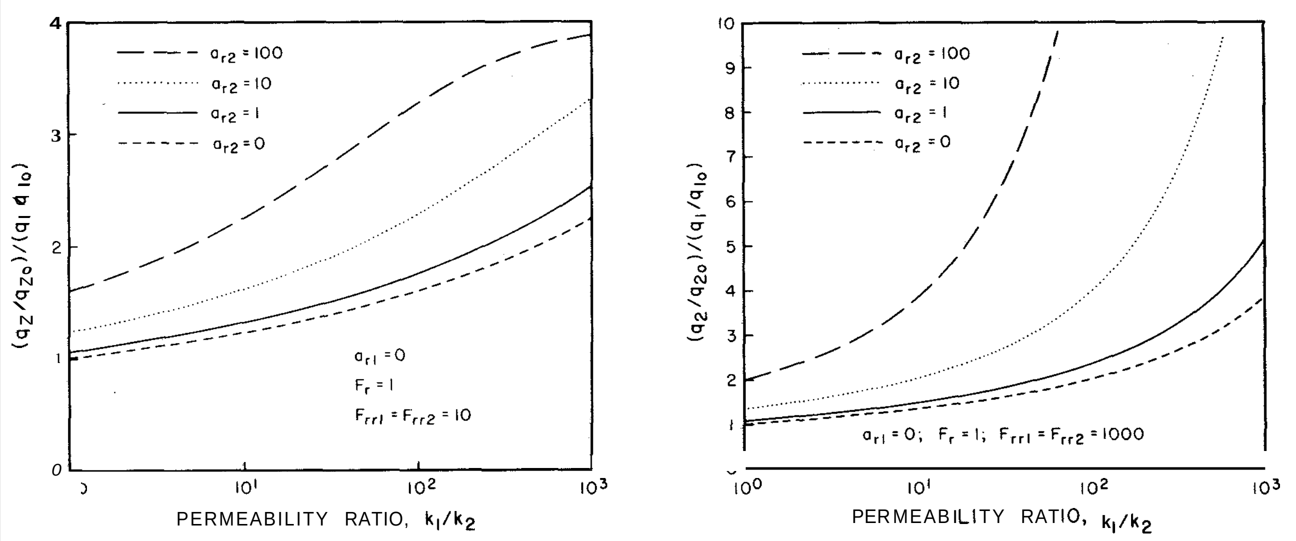

Fig. 8—Best-case profile improvement in radial flow: (a) weak gel ($F_{rr}=10$) and (b) strong gel ($F_{rr}=1{,}000$).

gel has formed, relative to water injectivity before gel placement. Thus, they axis represents the injectivity retained in the less permeable layer relative to the injectivity retained in the most permeable layer. If $(q_2/q_{20})(q_1/q_{10}) > 1$, then the flow profile is improved by the gel treatment. In contrast, if the expression is less than one, the flow profile is impaired.

Fig. 8a illustrates the case where a "weak" gel is formed (i.e., $F_{rr}=10$), while Fig. 8b illustrates the case where a "strong" gel is formed (i.e., $F_{rr}=1{,}000$). These figures show that, even under the best circumstances, very high a_{r2} values and very high permeability ratios are required to improve the injection profile significantly. Under more realistic conditions, ion-exchange capacities and retention levels for H^+ and OH^- may not be radically different in different strata. Thus, our results suggest that pH effects usually will not help much in eliminating the need for zone isolation during gel placement in unfractured injection wells (radial flow) with noncommunicating zones.

Conclusions

The following conclusions were reached during a study at 41°C of a gelant containing 3 **wt%** resorcinol, 3 **wt%** formaldehyde, and ***0.5*** wt% KCl.

1. The product formed by the reaction of resorcinol with formaldehyde depends on pH. During studies of gelation in beakers, the strongest resorcinol/formaldehyde gels are formed at pH=9. The inherent permeability to water for this gel (no rock) was found to be 6 μd.

2. As the initial pH is decreased, gel formation becomes less perfect. With an initial pH=7, an opaque orange-white gel is formed during beaker tests, and some free water remains after the reaction. As the initial pH value is decreased below 7, the final ratio of free water to gel increases.

3. During core experiments, residual resistance factors are very high (1,000 to 10,000) for gelants buffered and formed at pH=9. Tracer studies reveal that this gel occupies 87% to 99% of the available PV.

4. As pH decreased during core experiments, the gelation reaction is inhibitied. In particular, as gelation pH decreases from 7 to 6, residual resistance factors decrease sharply from high to low values (e.g., from ≈ 1,000 to 1). Tracer studies show that the fraction of the PV occupied by the gel generally decreases over this pH range.

5. In many core experiments, the results suggest that upon first exposure to a given fluid velocity, a certain amount of gel breaks down to allow a flow path 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.

6. F_{rr} generally increased with decreased permeability. However, F_{rr} values can be significantly higher in sandstones than in less-permeable carbonate cores.

7. A simple mathematical model was used to assess whether pH effects can be exploited to optimize gel placement in injection wells. Our results suggest that pH effects usually will not help much in eliminating the need for zone isolation during gel placement in unfractured injection wells with noncommunicating zones.

Nomenclature

a, = dimensionless retention of a given species (PV's of formulation injected to satisfy the retentive sites in 1 PV of rock)
f( ) = function describing degree of penetration
F_r = resistance factor (brine mobility before gel placement divided by gelant mobility before gelation)
F_{rr} = residual resistance factor (brine mobility before gel placement divided by brine mobility after gel placement)
k = permeability, A, md [μm^2]
k_i = aqueous-phase permeability of Layer *i*, A, md [μm^2]
L_{pi} = distance the chemical species has propagated in a linear core or from the face of a vertical fracture (into the rock matrix) in Layer *i*, L, ft [m]
L_{pm} = maximum distance that the gelant will propagate from the fracture face in the most-permeable core, L, ft [m]
n_f = amount of a specific chemical that is removed by the rock from a certain PV of fluid under a particular set of conditions, m/V, eq/L
n_{max} = ion-exchange capacity, m/m, eq/kg
n_s = amount of the species of interest in solution per unit of volume of the injected formulation, m/V, eq/L
Δp_{Di} = pressure drop between r_{pm} (or L_{pm}) and production well divided by pressure drop between injection well and r_{pm} (or L_{pm}) in Layer *i*
q_i = injectivity in Layer *i* after gel placement, V/t, B/D [m^3/s]
q_{i0} = injectivity in Layer i before gel placement, V/t, B/D [m3/s]
r_{pi} = radius of penetration of a chemical species in Layer *i*, L, ft [m]
$r_{p\max}$ = maximum radius of penetration of gelant in the most-permeable layer, L, ft [m]
r, = wellbore radius, L, ft [m]
u = flux or Darcy velocity, L/t, ft/D [m/s]
V_{pf} = apparent remaining PV, V, cm3
V_{pi} = initial PV of core, V, cm^3
V_{pin} = inaccessible PV
α_f = dispersivity at given stage in experiment, L, cm
a, = initial dispersivity of core, L, cm
μ_w = viscosity of brine, m/Lt, cp [mPa·s]
ρ_r = rock density, m/V, g/cm^3
ϕ_i = effective aqueous-phase porosity of Layer i

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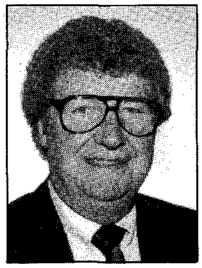

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SI Metric Conversion Factors

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
$in.^3$	×	1.638706	E+01	= cm^3
md	×	9.869233	E−04	= μm^2

*Conversion factor is exact.

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