

Rheology of a New Sulfonic Associative Polymer in Porous Media

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Summary

For hydrophobically associative polymers, incorporating a small fraction of hydrophobic monomer into a hydrolyzed polyacrylamide (HPAM) polymer can promote intermolecular associations and thereby enhance viscosities and resistance factors. In this paper, we investigate the behavior of a new associative polymer in porous media. The tetra-polymer has low hydrophobic-monomer content and a molecular weight (Mw) of 12–17 million g/mol. Total anionic content is 15–25 mol%, including a few percent of a sulfonic monomer. This polymer is compared with a conventional HPAM with 18–20 million g/mol Mw and 35–40% anionic content. Rheological properties (viscosity vs. concentration; and shear rate and elastic and loss moduli vs. frequency) were similar for the two polymers [in a 2.52% total dissolved solids (TDS) brine at 25°C]. For both polymers in cores with permeabilities from 300 to 13,000 md, no face plugging or internal-filter-cake formation was observed, and resistance factors correlated well using the capillary-bundle parameter. For the HPAM polymer in these cores, low-flux resistance factors were consistent with low-shear-rate viscosities. In contrast, over the same permeability range, the associative polymer provided low-flux resistance factors that were two to three times the values expected from viscosities. Moderate shear degradation did not eliminate this effect—nor did flow through a few feet of porous rock. Propagation experiments in long cores (up to 157 cm) suggest that the unexpectedly high resistance factors could propagate deep into a reservoir—thereby providing enhanced displacement compared with conventional HPAM polymers. Compared with HPAM, the new polymer shows a significantly higher level of shear thinning at low fluxes and a lower degree of shear thickening at high fluxes.

Introduction

In polymer floods or chemical floods in which polymer is needed for mobility control, the cost-effectiveness of the polymer is a major concern. Cost-effectiveness is determined by the polymer cost and the resistance factor provided by the chosen polymer solution at conditions found deep within a reservoir (i.e., low fluid velocities and at reservoir temperature). Resistance factor is the effective viscosity of the polymer solution in porous media, relative to water (i.e., water mobility divided by polymer-solution mobility). HPAM and xanthan polysaccharides have been the dominant polymers used in enhanced oil recovery (EOR). If polymers are identified that are more cost-effective than these traditional EOR polymers, field applications of chemical floods could become much more widespread.

Associative polymers have been investigated as a possible substitute for HPAM polymers in EOR applications (Evani 1984; Bock et al. 1988; McCormick and Johnson 1988; Taylor and Nasr-El-Din 1998, 2007; Buchgraber et al. 2009; Dupuis et al. 2011). In particular, Taylor and Nasr-El-Din (1998, 2007) extensively reviewed the literature for synthesis and performance of associative polymers. For hydrophobically associative polymers, incorporation of a small fraction of hydrophobic monomer into an HPAM polymer is intended to promote intermolecular associations and

thereby enhance viscosities and resistance factors. At moderate concentrations (e.g., 0.05% to 0.5%), these polymers (with 0.1–7% hydrophobic monomer) can provide substantially higher viscosities than equivalent-Mw polymers without hydrophobic groups (Bock et al. 1988; McCormick and Johnson 1988).

A number of issues have inhibited widespread application of associative polymers for EOR. In some cases, the increase in viscosity with increasing polymer concentration is abrupt (Bock et al. 1988; McCormick and Johnson 1988)—leading to concerns about controlling the performance of the polymer during flooding operations. If small changes in concentration cause large changes in viscosity, small operational errors could accentuate injectivity problems if polymer concentrations are higher than the target and could provide insufficient mobility control if polymer concentrations are low.

A second concern is the ability of associative polymers to penetrate deep into a reservoir. Compositions have been identified that show a maximum in plots of viscosity vs. shear rate (Bock et al. 1988; Kujawa et al. 2004; Maia et al. 2009). Apparently, within a certain range of shear rates, the polymer becomes sufficiently extended to promote intermolecular interactions over intramolecular interactions. The polymer complexes that form by associative polymers certainly enhance viscosity and can provide high resistance to flow for a short distance in porous media. However, an important unresolved issue with many associative polymers is whether the enhanced viscosity characteristics can be propagated deep into a reservoir. Most previous studies of these polymers have used short cores with no internal pressure taps for their evaluations of behavior in porous media: 1.3–2.54 cm for Bock et al. (1988), 2.54 cm for Evani (1989), 13 cm for Dong and Wang (1995), 7 cm for Kun et al. (2004), and 9 cm for Maia et al. (2009). With such short cores (and no internal pressure taps), resistance factors that appear high may simply reflect plugging.

Argillier et al. (1996) and Volpert et al. (1997) concluded that hydrophobically associative polymers show multilayer adsorption on clays and siliceous minerals. Consistent with this finding, Maia et al. (2009) observed that resistance factors for an associative polymer increased continuously with increased throughput in sandstone cores. Kun et al. (2004) and Lu et al. (2008) provided evidence of velocity- and history-dependent retention and resistance factors for associating polymers in sandpacks. Several authors (Eoff et al. 2005; Zhao et al. 2006) proposed using highly adsorbing associating polymers to reduce rock permeability for acid diversion and conformance improvement. During a study of associative polymers in 10-cm-long cores with two internal pressure taps, Dupuis et al. (2011) noted a “minority polymeric species” that provided high resistance factors but that propagated very slowly through the cores. They felt that their observations were inconsistent with the classic view of multilayer adsorption of a polymer. Of course, if an associative polymer complex is removed (either by adsorption or mechanical entrapment) after flowing a short distance in a porous medium, its mobility-reduction benefits cannot be expected to materialize far from a wellbore where most oil is displaced. Work is needed in longer cores to assess whether the beneficial properties of associative polymers can be propagated deep into a porous medium.

In this paper, we examine the rheology (both in a viscometer and in porous media) for a new sulfonic hydrophobically associative polymer. This sulfonated polymer has a lower hydrophobe content (and higher Mw) than most associative polymers that

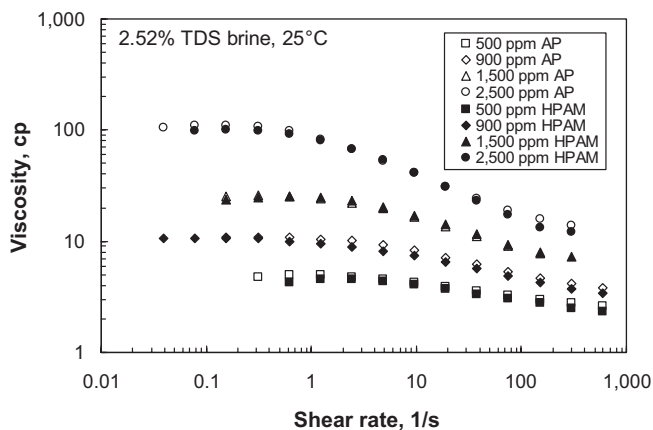


Fig. 1—Viscosity vs. shear rate and concentration.

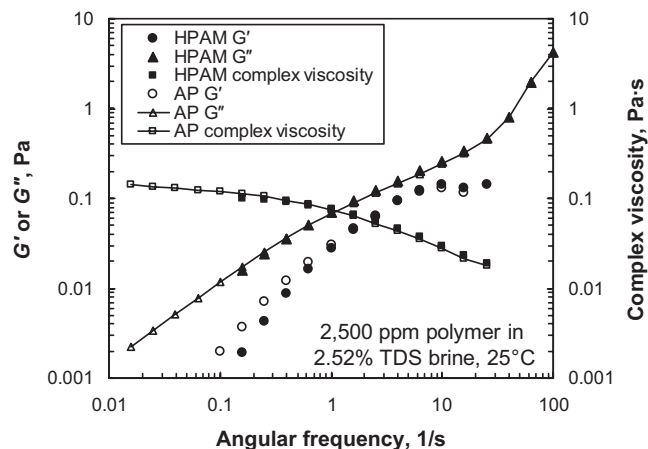


Fig. 2— G' , G'' , and complex viscosity.

were investigated previously for EOR. Consequently, it does not exhibit viscosities that are noticeably higher than those for the HPAM analog. Nevertheless, as will be shown, it provides significantly higher resistance factors in porous media than HPAM. Furthermore, its associative properties are not so great that polymer propagation through porous media is impaired. For studies in porous media in this work, a wide range of flux (0.1 to 100 ft/D), polymer concentration (500–2,500 ppm), and core permeability (300–13,000 md) is investigated. Throughout this study, comparisons are made with the performance of a commercially available HPAM. Our goals were to establish (1) whether the associative polymer provided superior resistance factors, compared with HPAM; (2) whether these enhanced resistance factors are expected to propagate deep into a reservoir; and (3) the resistance of the associative polymer to mechanical degradation, compared with HPAM.

Polymers Examined and Viscosity Behavior

The new hydrophobically associative polymer was provided by SNF Floerger: Superpusher DP/C1205, Lot GC 2882/6 (hereafter called AP or the “associative polymer”). This polymer is an anionic-polyacrylamide-based tetra-polymer that has associative properties as described by Gaillard et al. (2010). Typically, the hydrophobic monomer content ranges from 0.025 to 0.25 mol%. Mw ranges from 12 to 17 million g/mol, and the total anionic content is between 15 and 25 mol%. Less than 8 mol% sulfonic monomer is present. The associative polymer was made by a process derived from micellar polymerization, but the “hydrophobic” monomer used was amphiphilic and dissolved very well in water. A slight amount of surfactant was used as a process aid, but the

final amount of remaining surfactant did not exceed 0.25% of the final polymer product, and for the solutions prepared here, it had a concentration in brine of less than 10 ppm—well below any critical micelle concentration.

During our studies, the brine contained 2.52% total dissolved solids (TDS), specifically with 2.3% NaCl and 0.22% NaHCO_3 . The studies were performed at 25°C. This brine and temperature are representative of those associated with a large polymer flood in Canada. Comparisons will be made with the performance of a conventional HPAM, SNF Flopaam 3830S (Lot X 1899). This polymer has an Mw of 18–20 million g/mol and a degree of hydrolysis of 35–40%. Hereafter in this paper, we call this polymer “HPAM.” Polymer solutions were prepared using the standard method for preparing laboratory HPAM solutions. A vortex was established in a beaker of brine using a magnetic stir bar. The polymer powder was sprinkled onto the vortex shoulder to individually wet the polymer particles. After adding the polymer, the stir rate was reduced but kept at a level sufficient to keep the hydrating polymer particles suspended and separated. Compared with the HPAM, the associative polymer generally took longer to dissolve in the 2.52%-TDS brine (which contained no divalent ions). In a brine that contained calcium (2.3% NaCl, 0.23% CaCl_2), the dissolution time for the associative polymer was approximately 30% longer than that without calcium. (However, this time could be reduced by optimizing the polymer composition for a calcium-containing brine.) The associative polymer solutions could exhibit viscosities that depend on mixing time and shear history during the dissolution period.

For both polymers, viscosity (determined using an Anton Paar Physica MCR 301 viscometer) vs. shear rate and polymer concentration is plotted in Fig. 1. For polymer concentrations of 500, 900, 1,500, and 2,500 ppm in 2.52%-TDS brine, viscosity vs. shear rate was quite similar for the HPAM and associative polymers. Fig. 2 demonstrates that the elastic modulus (G'), loss modulus (G''), and complex viscosity behavior were also very similar for the two polymers.

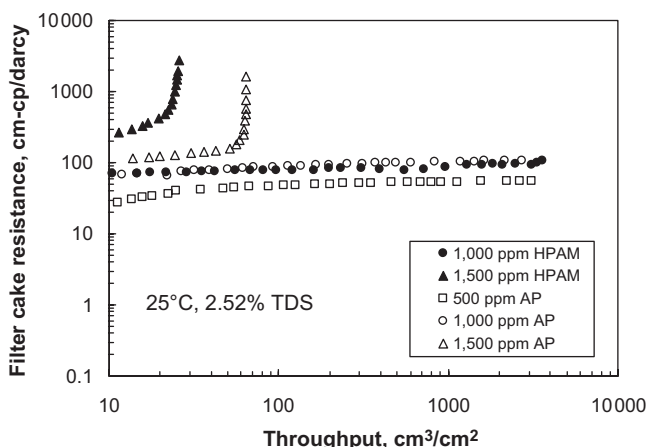


Fig. 3—Filter-test results.

Face Plugging

Filter Tests. Our previous work (Seright et al. 2009) identified a filter test that allows comparison of the face-plugging characteristics for polymers. In this test, a Millipore AP10™ filter pad is placed in a filter holder upstream of a 10- μm polycarbonate (Sterlitech Track Etch™) membrane filter (both 13 mm in diameter). Using a fixed pressure drop across the filter holder, we record filter-cake resistance (calculated using the Darcy equation, with units of cm-cp/darcy) vs. throughput (volume of fluid injection per filter area, in cm^3/cm^2 .) Fig. 3 compares filtration results for HPAM (solid symbols) and the associative polymer (open symbols). Notice that both polymers show excellent filterability at lower concentrations (1,000 ppm or lower), but plugged within 70- cm^3/cm^2 throughput at higher concentrations (1,500 ppm). Plugging characteristics of

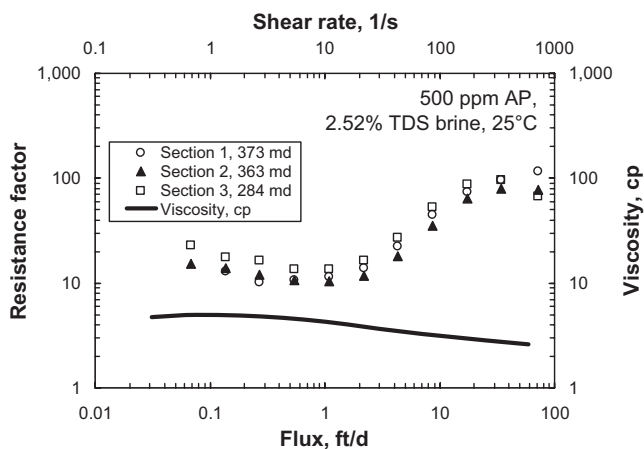


Fig. 4—500-ppm associative polymer viscosity and resistance factor in Berea sandstone.

the associative polymer appear to be no worse than those of HPAM. The fact that plugging behavior for both polymers was severe with 1,500-ppm polymer, but not with lower concentrations, may be explained using the bridging-adsorption concepts described by Zitha et al. (2001).

Core-Face Plugging. Several experiments examined the level of face plugging that occurred during injection of large volumes of associative polymer solutions through a 363-md Berea sandstone core and through a 12,313-md porous polyethylene core. Both of these 13- to 14-cm-long cores had two internal pressure taps that divided the cores into three sections. By monitoring pressure drops and resistance factors in the various core sections we could assess the level of face plugging as a function of polymer solution throughput. After injecting 97 pore volumes (PV) or 580 cm³/cm² of the associative polymer-solutions (with concentrations up to 2,500 ppm) through the 12,313-md core, resistance factors in the first core section were no higher than in the second or third core sections. Similarly, after injecting 51 PV or 248 cm³/cm² of associative polymer solutions (again with concentrations up to 2,500 ppm) through the 363-md core, resistance factors in the first core section were no higher than in the second or third core sections. Thus, no significant face plugging was observed for the associative polymer solutions. Details of these tests can be found in Seright (2010).

Pore Plugging

Resistance Factor vs. Flux and Concentration. Fig. 4 plots resistance factor as a function of flux in each of the three core

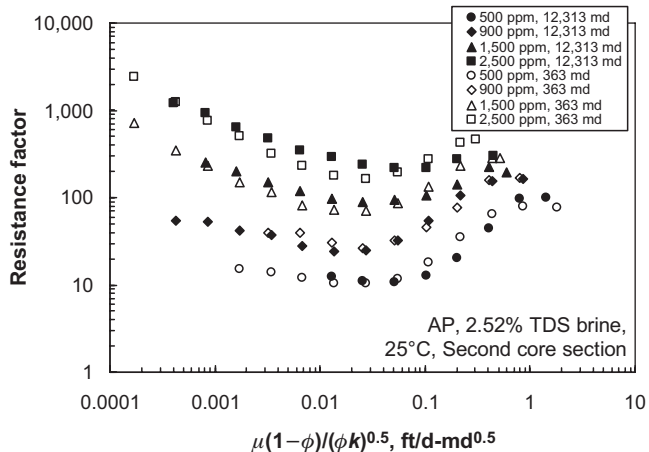


Fig. 6—AP resistance factor vs. capillary-bundle parameter.

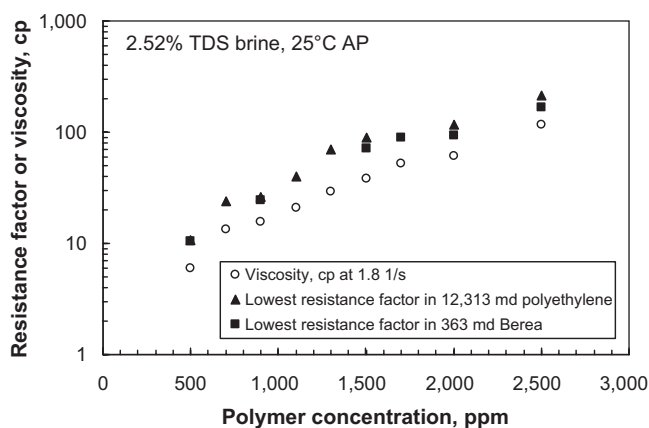


Fig. 5—AP resistance factors and viscosities vs. concentrations.

sections for injection of 500-ppm associative polymer in a Berea sandstone core. [Details of our equipment and methods can be found in Seright et al. (2011) and Seright (2010). At a given flux, the resistance factors were reasonably consistent in the three core sections. The resistance factors were somewhat higher in the third core section, which argues against plugging of the inlet face. Consistent with normal HPAM behavior (Seright et al. 2011), a strong shear thickening was seen at moderate-to-high flux values and Newtonian or a slight shear-thinning behavior was seen at low flux values.

Fig. 4 also plots viscosity vs. shear rate for 500-ppm associative polymer (solid curve). Note that at all flux values, resistance factors were considerably greater than values expected from viscosity measurements. This behavior was noted in both Berea and porous polyethylene for all (fresh) associative polymer concentrations tested. It is interesting that for conventional HPAM and xanthan polymers, resistance factors at low fluxes were reasonably consistent with values expected from viscosity measurements unless a pore-plugging effect occurred (Seright et al. 2011) (e.g., if the permeability was too low to accommodate the size of the highest-Mw species within the polymer).

Fig. 5 confirms that for other associative polymer concentrations in 363-md Berea and 12,313-md polyethylene, the lowest resistance factors were noticeably greater than (roughly twice) the highest measured viscosity (i.e., viscosity at 1.8 s⁻¹). If this result was caused by large polymer adsorption or retention, we might have expected different resistance factors in the hydrophilic 363-md Berea than in the hydrophobic 12,313-md polyethylene. Fig. 6 also supports the idea that the higher-than-expected resistance factors may not be caused by polymer adsorption or retention. In Fig. 6, resistance factors for selected concentrations (500, 900, 1,500, and 2,500 ppm) are plotted against the capillary-bundle parameter, $u(1-\phi)/(\phi k)^{0.5}$, where u is flux in ft/d, k is permeability in md, and ϕ is porosity. For all four associative polymer concentrations, the behavior in 363-md Berea correlated well with that seen in 12,313-md polyethylene. For a given x -axis value, resistance factors should have been different in 363-md Berea than in 12,313-md polyethylene if polymer retention was important.

If we assume that 363-md Berea has smaller pores and pore throats than 12,313-md polyethylene, we might expect pore plugging to be more severe in the less-permeable core—because particles of a given size should be more likely to plug small pores than large pores. Fig. 6 demonstrates that this expectation was not met. Ironically, Berea sandstone and porous polyethylene have very similar pore structures (Seright et al. 2006). Although the porosity and permeability for Berea sandstone and porous polyethylene are quite different, the pore size, pore-throat size, and pore-aspect-ratio distributions are very similar. These facts may explain the similarity of behavior seen in Fig. 6 for the different porous media.

If a polymer particle (i.e., a polymer aggregate) was responsible for the higher-than-expected resistance factors, one might expect larger particles and/or a higher concentration of particles as the

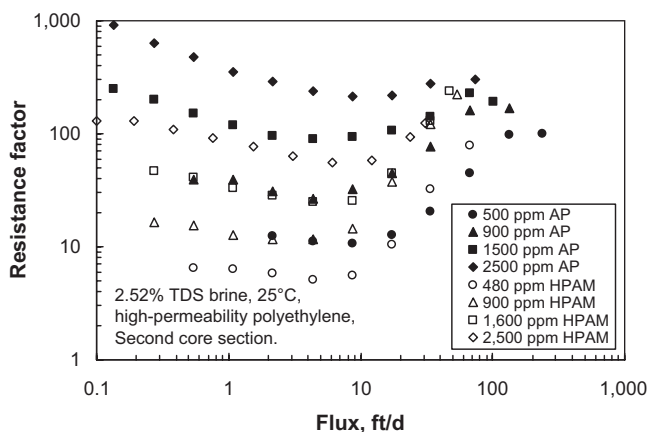


Fig. 7—Resistance factors in polyethylene: AP vs. HPAM.

polymer concentration is increased. In turn, this occurrence should cause a higher ratio of resistance factor to viscosity as polymer concentration rises. This expectation was met at low fluid velocities. At a $u(1-\phi)/(\phi k)^{0.5}$ value of 0.0017, the ratio of resistance factor (from Fig. 6) to zero-shear viscosity (from Fig. 1) ranged from 3 for 500-ppm associative polymer to 5 for 2,500-ppm polymer. This ratio reached as high as 22 for 2,500-ppm polymer at a $u(1-\phi)/(\phi k)^{0.5}$ value of 0.00017. Interestingly, the ratio decreased substantially with increased velocity in porous media. When the $u(1-\phi)/(\phi k)^{0.5}$ value was raised to 0.027, the ratio was roughly 2 for all polymer concentrations between 500 and 2,500 ppm (see Figs. 5 and 6). Apparently, flow through porous media at intermediate velocities disrupted polymer aggregates that form from hydrophobic associations.

Fig. 7 compares resistance factors in porous polyethylene for associative polymer vs. HPAM. For all four concentration levels examined (≈ 500 , 900, $\approx 1,500$, and 2,500 ppm), resistance factors (at a given flux) were substantially greater for associative polymer than for HPAM. Specifically, 500-ppm associative polymer (solid circles) acts similar to 900-ppm HPAM (open triangles), and 900-ppm associative polymer (solid triangles) acts similar to 1,600-ppm HPAM (open squares).

Residual Resistance Factors. At the end of associative polymer injection, many PVs of brine were injected to determine residual resistance factors in the Berea and polyethylene cores. After injecting 109 PV of brine into the polyethylene core, residual resistance factors were 1.9, 2.1, and 1.3 in the first, second, and third sections, respectively. This result is consistent with a suggestion of little to no significant pore plugging in the 12,313-md polyethylene core. However, after injecting 170 PV of brine into the Berea core, residual resistance factors were 13.0, 19.3, and 15.3 in the first,

second, and third sections, respectively. This result suggests that some pore plugging or higher polymer retention may have occurred in the 363-md Berea core. In both cores, residual resistance factors were not sensitive to flow rate.

Mechanical Degradation

In previous work (Seright et al. 2011) when xanthan or HPAM resistance factors were higher than expected at moderate-to-low flux values, the effect was shown to be a result of high-Mw polymer species. For both xanthan and HPAM, this species was removed by flow through a few feet of porous rock. For HPAM, the species was readily destroyed by mechanical degradation. Either way, the species was not expected to propagate deep into a reservoir to provide low-flux resistance factors that were substantially higher than expectations from viscosity measurements. During a study of a hydrophobically associative polymer, Dupuis et al. (2011) concluded that it contained a low-mobility (high-resistance-factor), high-Mw species that propagated significantly more slowly than other components of the polymer. We wondered whether mechanical degradation would reduce the high resistance factors that we observed.

We examined the effects of mechanical degradation by first forcing 6.4 L of a 500-ppm associative polymer solution through a 13-cm-long 347-md Berea core using a flux of 292 ft/D (resulting in a pressure gradient of 2,500 psi/ft). The effluent from this experiment was then reinjected (using a wide range of flow rates) into a new 78.2-cm-long polyethylene core that had four equally spaced internal pressure taps. The porosity of this core was 44%, and the PV was 390.6 cm³. The permeabilities of the five 15.64-cm-long core sections were 8,316, 11,554, 11,105, 11,222, and 10,370 md, respectively. Thus, the average permeability was 10,365 md. We repeated this experiment using 900-, 1,500-, and 2,500-ppm associative polymer solutions (in the same cores), where the pressure gradient was 2,500 psi/ft when forcing the solutions through the 347-md Berea core.

Because a 2,500-psi/ft pressure gradient was a fairly extreme level of mechanical degradation, additional work with a lower level of mechanical degradation was performed. For these cases, the pressure gradient was 235 psi/ft when forcing the solutions through the 347-md Berea core. The effluent from this core was then injected into the polyethylene core using a range of flow rates. The same polymer concentrations and range of rates were used. All of these procedures were repeated using HPAM. Details of the results can be found in Seright (2010).

Comparison of Viscosity and Resistance-Factor Losses. Table 1 lists viscosity and resistance factor losses experienced by HPAM and associative polymer solutions after being forced through the 347-md Berea sandstone core at either 235 psi/ft or 2,500 psi/ft. The third and fourth columns in this table list the percent of the original viscosity that was lost, as measured at a shear rate of 7.3 s⁻¹ and 25°C. The fifth and sixth columns in this table list the

TABLE 1—LOSSES AFTER BEING FORCED THROUGH A BERE A CORE AT GIVEN PRESSURE GRADIENT					
Polymer	Concentration (ppm)	Viscosity Loss (% of original at 7.3 s ⁻¹)		Resistance Factor Loss (% of original at 1 ft/d)	
		235 psi/ft	2,500 psi/ft	235 psi/ft	2,500 psi/ft
HPAM	500	1	11	4	31
Associative polymer	500	6	35	39	53
HPAM	900	2	17	0	24
Associative polymer	900	5	19	31	64
HPAM	1,500	0	10	15	41
Associative polymer	1,500	3	27	36	64
HPAM	2,500	1	5	0	9
Associative polymer	2,500	8	23	45	71

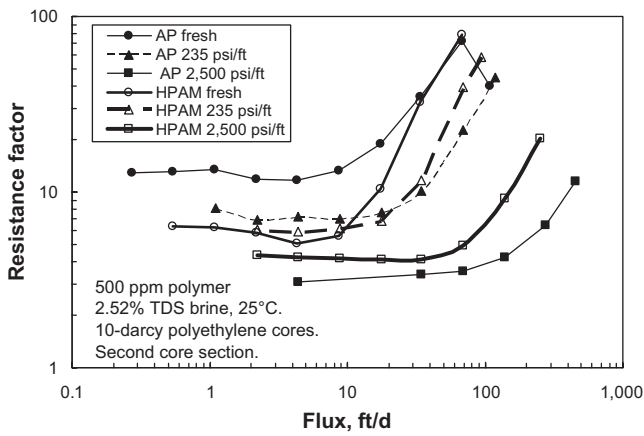


Fig. 8—Resistance factors for 500-ppm polymer: AP vs. HPAM.

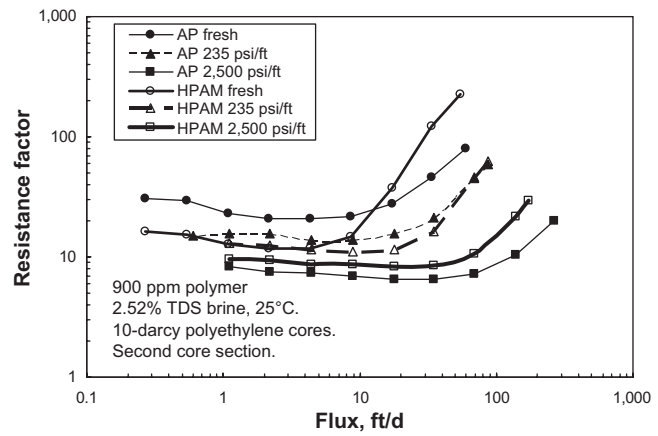


Fig. 9—Resistance factors for 900-ppm polymer: AP vs. HPAM.

percent of the original resistance factor that was lost, as measured at a flux of 1 ft/d (in the middle section of the polyethylene core) and 25°C. For both polymers at all concentrations, exposure to 235 psi/ft resulted in very little viscosity loss—from 0 to 8% of the original viscosity. Resistance-factor losses for HPAM were modest (0–15%) after exposure to 235 psi/ft. However, resistance-factor losses for the associative polymer were significant after exposure to 235 psi/ft—from 31 to 45%. For HPAM after exposure to 2,500 psi/ft, viscosity losses ranged from 5 to 17%. For the associative polymer after exposure to 2,500 psi/ft, viscosity losses were higher, ranging from 19 to 35%. Similarly, after exposure to 2,500 psi/ft, resistance-factor losses were much greater for the associative polymer (53–71%) than for HPAM (9–41%).

Figs. 8 through 11 compare resistance factor (in the middle polyethylene core section) vs. flux for the associative polymer and HPAM at various polymer concentrations and levels of mechanical degradation. In all four figures (i.e., at 500-, 900-, 1,500-, and 2,500-ppm polymer, respectively), the low-flux resistance factors for fresh associative polymer (solid circles) were considerably greater than (typically twice) those for fresh HPAM (open circles). Second, for all but the highest concentration, low-flux resistance factors for associative polymer that was degraded using 235 psi/ft (solid triangles) were approximately the same as those for fresh HPAM (open circles). Third, for all four concentrations, the low-flux resistance factors for associative polymer that was degraded using 2,500 psi/ft (solid squares) were the same as or less than those for HPAM that was degraded using 2,500 psi/ft (open squares). Fourth, the shear-thickening behavior (i.e., increase in resistance factors) at moderate-to-high flux values for fresh and 235-psi/ft-degraded HPAM was more pronounced than that for fresh and 235-psi/ft-degraded associative polymer.

For the HPAM cases (fresh, 235 psi/ft, and 2,500 psi/ft), the low-flux resistance factors were usually the same as or just slightly greater than expectations from the low-shear-rate viscosities. To quantify this point, **Fig. 12** plots the ratio of resistance factor at 1 ft/d flux in the middle polyethylene core section to shear rate at 7.3 s^{-1} for the two polymers, with different polymer concentrations and different levels of mechanical degradation. For all cases with HPAM concentrations up to 1,500 ppm, the low-flux resistance factor was only 0 to 33% greater than the low-shear-rate viscosity. For all cases (fresh, 235 psi/ft, and 2,500 psi/ft) with 2,500-ppm HPAM, the resistance factor at 1 ft/d was approximately twice the viscosity at 7.3 s^{-1} . However, a more detailed examination of the resistance-factor-vs.-flux curves and the viscosity-vs.-shear-rate curves [which can be found in Figs. 49, 53, and 55 of Seright (2010)] revealed that the low-flux resistance factors were actually just slightly above the low-shear-rate viscosities. Similarly, for cases with associative polymer concentrations up to 1,500 ppm that had been exposed to 2,500 psi/ft, the low-flux resistance factor was only 0 to 32% greater than the low-shear-rate viscosity. For associative polymer solutions that were exposed to 235 psi/ft, the low-flux resistance factors were 1.6 to 3.3 times greater than the low-shear-rate viscosity. For fresh, undegraded associative polymer solutions, the low-flux resistance factors were 2.5 to 5.6 times greater than the low-shear-rate viscosity. Thus, even after exposure to 235 psi/ft, associative polymer solutions provided low-flux resistance factors that were significantly greater than expectations from viscosity values.

Table 1 and Figs. 8 through 12 reveal that the associative polymer was more sensitive to mechanical degradation than the HPAM. For comparison, after being forced through a 1.3-cm-long Berea core at high rates, Bock et al. (1987) found that 1,500-ppm associative

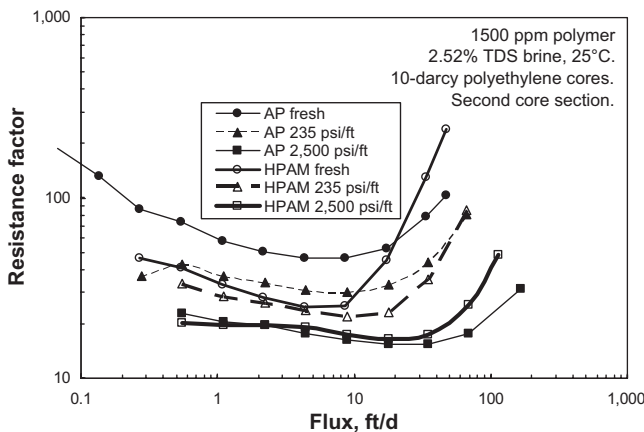


Fig. 10—Resistance factors for 1,500-ppm polymer: AP vs. HPAM.

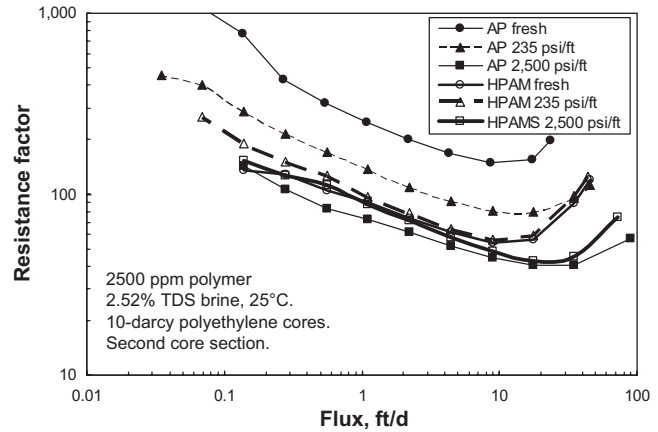


Fig. 11—Resistance factors for 2,500-ppm polymer: AP vs. HPAM.

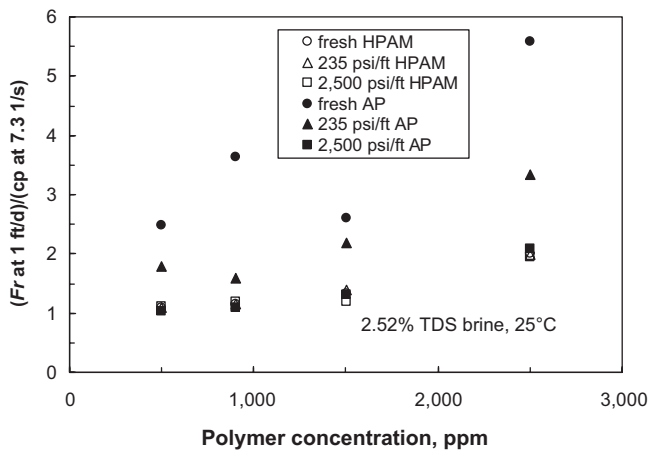


Fig. 12—Low-flux resistance factors relative to low-shear-rate viscosities.

polymer with 0.75% hydrophobic monomer (octylacrylamide) and 20–30% 2-acrylamido-2-methylpropane sulfonic acid (AMPS) (in brine with 3.3% TDS) experienced a significantly smaller loss of viscosity than a normal HPAM. Compared with Bock, their polymer, our associative polymer had less than one-third the hydrophobe and sulfonic monomer content. For an associative polymer with 0.1% hydrophobic monomer, Dong and Wang (1996) found that the level of shear degradation (as judged by viscosity loss induced by a Waring™ blender) was approximately the same as for other HPAM solutions.

Will the High Resistance Factors Propagate Deep Into Porous Rock?

Cores With Lengths up to 78 cm. In previous work, no permeability dependence of resistance factors was noted for HPAM in 13- to 15-cm-long Berea sandstone cores with permeabilities of 269 md or above (Seright 2009). In permeable polyethylene cores, we did not observe any length dependence of resistance factors for any concentration or level of mechanical degradation when using HPAM [see Figs. 46 through 53 of Seright (2010)]. This point is, perhaps, made most effectively in Fig. 13, which plots resistance factors for a fresh 2,500-ppm solution of HPAM in the five sections of the 78.2-cm-long 10-darcy polyethylene core. In short (13–14 cm) Berea sandstone or porous polyethylene cores, we also saw no length dependence of resistance factors for the associative polymer [see Figs. 28, A-1, and A-3 through A-13 of Seright (2010)].

A set of experiments was performed in a 78.09-cm-long porous polyethylene core. In this case, the porosity was 0.377, and the PV was 343 cm³. The core had two internal pressure drops that divided the core into three sections of equal length (i.e., 26.03 cm each). The section permeabilities were 7,295, 10,144, and 8,717

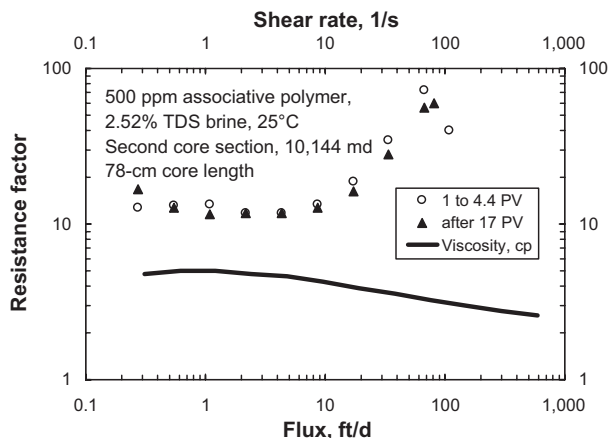


Fig. 14—500-ppm associative polymer resistance factors at beginning vs. end of the experiment.

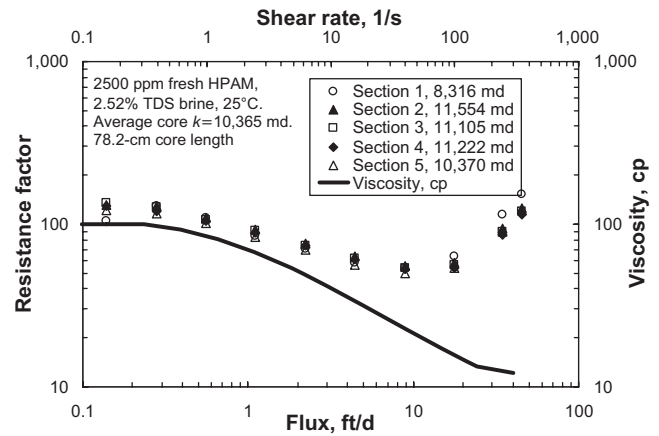


Fig. 13—Resistance factors for fresh 2,500-ppm HPAM.

md, respectively. After saturating with brine, we injected 1 PV of 500-ppm associative polymer at 108 ft/D. Over the next 3.4 PV, we determined resistance factor for progressively lower flux values. Then, 13.2 PV more of polymer solution was injected, where resistance factor vs. flux was determined at the end of the injection process. Fig. 14 demonstrates that 500-ppm associative polymer showed the same behavior for the entire course of this experiment. So whatever phenomenon caused the resistance factors to be two to three times the value expected from viscosity measurements (solid curve in Fig. 14), it did not seem to change the rheology in porous media over the course of injecting many PV of polymer solution.

Propagation in a 157.5-cm-Long Polyethylene Core. An experiment was performed in a 157.5-cm-long porous polyethylene core that had five equally spaced internal pressure taps. These taps divided the core into six sections, each with 26.25-cm length. The last two sections were combined to make one 52.5-cm-long section, thus reducing the total number of core sections to five. The permeabilities of these five sections were 12.25, 16.56, 9.59, 10.58, and 10.11 darcies, respectively. The composite average permeability of the core was 11.2 darcies. The core cross-sectional area was 11.04 cm², and the core PV was 754 cm³. We injected 15.7 PV of 500-ppm AP polymer (in 2.52%-TDS brine) using a fixed flux of 7.13 ft/D. Subsequently, we injected 110 PV (83 L) of brine to flush the polymer from the core. Then, 8 PV of 500-ppm AP polymer was injected again using a fixed flux of 7.13 ft/D. This procedure allowed determination of polymer retention and inaccessible PV for the core.

Fig. 15 plots resistance factors in the five core sections as a function of volume for the first 15.7 PV of polymer solution injected. Fig. 16 amplifies the first 2 PV of Fig. 15. Examination

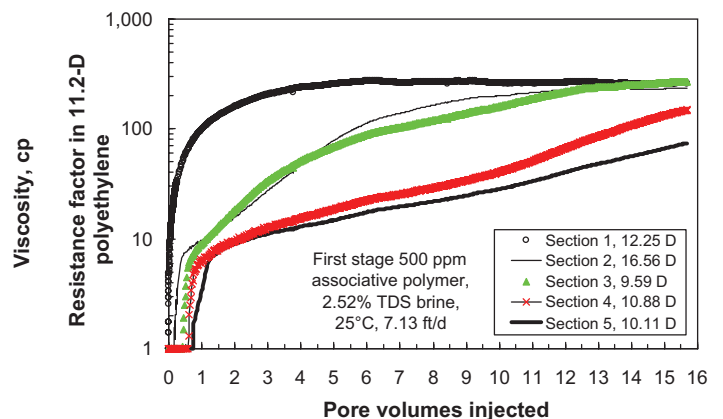


Fig. 15—Resistance factors during first injection of 500-ppm AP at 7.13 ft/D into 11.2-darcy polyethylene.

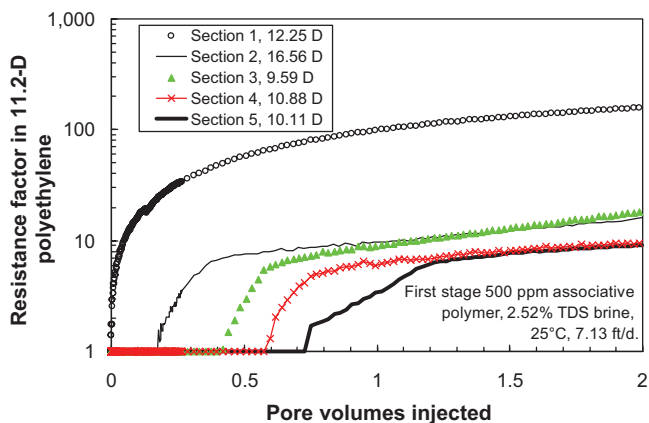


Fig. 16—Closer look at the first 2 PV of Fig. 15.

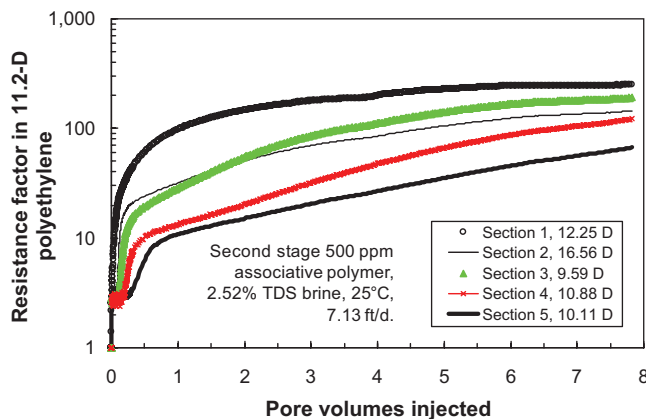


Fig. 17—Resistance factors during second injection of 500-ppm AP at 7.13 ft/D into 11.2-darcy polyethylene.

of the curves suggests that two species of polymer propagated through the core—a fast species that arrived at the end of the first core section after 0.23 PV and a much slower species that caused resistance factors to increase steadily for many PV. This concept is consistent with that proposed by Dupuis et al. (2011). The first polymer species provided a resistance-factor plateau of 7–8 after 1 PV. The second species ultimately provided a resistance factor of 260 (more than 60 times the value expected from viscosity measurements). After the first stage of polymer injection, 110 PV of brine was injected—resulting in ultimate residual resistance factors of 1.8, 3.6, 3.3, 2.8, and 2.4 in the five core sections, respectively. We suspect that the residual resistance factors could have been driven to lower values with more brine throughput.

Fig. 17 plots resistance factors in the five core sections as a function of volume for the second stage (8 PV) of polymer-solution injection. Just as with the first polymer injection, a fast polymer species and a slow polymer species appeared to propagate through the core. The fast species arrived at the end of the core before 1 PV—where it provided resistance factors ranging from 10 in the fifth core section to more than 20 in the second core section. During both the first and second stages of polymer injection, resistance factors in all core sections were at least twice the viscosity value after 1 PV of polymer injection. This result indicates that the higher-than-expected resistance factors can propagate effectively.

Fig. 18 plots viscosities of the effluent during the two stages of polymer injection. During both stages, the effluent viscosity reached only 3.3–3.4 cp (i.e., 20% less than the 4.2 cp of the injected concentration). Apparently, passage through the core at low velocity either disrupted or removed some of the associative polymer species. Fig. 18 indicates that the viscous polymer front (associated with the fast polymer species) reached the end of the core after 1.24 PV during the first stage of polymer injection and after 0.72 PV during the second stage. Assuming that

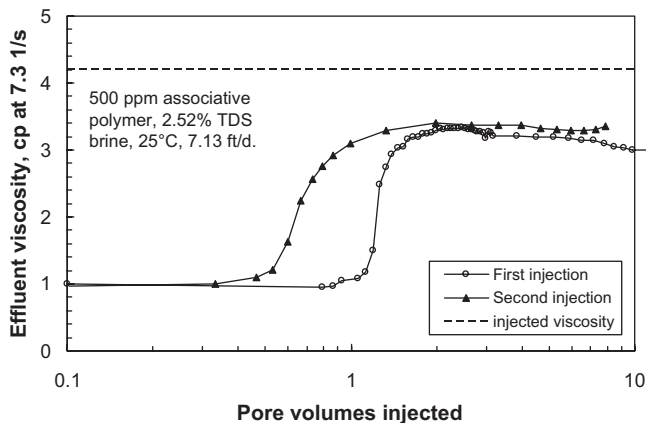


Fig. 18—Effluent viscosities.

polymer-retention sites were occupied during the second stage of polymer injection, the front arrival at 0.72 PV indicates an inaccessible-PV value of 0.28 (i.e., 1–0.72). The difference between the front arrivals during the first and second stages of polymer injection gives an indication of polymer retention (at least for the fast species)— $(1.24 - 0.72 \text{ PV}) \cdot (500 \times 10^{-6} \text{ g polymer/cm}^3) \cdot (754 \text{ cm}^3/\text{PV}) / (1002.11 \text{ g of core}) = 196 \text{ } \mu\text{g/g}$. A careful examination of the front arrivals in Figs. 15 through 18 indicates that the retention and inaccessible-PV values were fairly consistent through all five core sections (i.e., the level of polymer retention did not depend on distance travelled). The observed retention level was comparable with that for HPAM. These observations provide hope that the fast species and the higher-than-expected resistance factors can propagate deep into a reservoir.

For the second, slower polymer species, ≈ 4 PV of injection was required for the resistance factors in the first core section (i.e., the first 1/6 of the core) to level out during both stages of polymer injection (Figs. 15 and 17), suggesting that approximately 24 PV of injection is required for the slow species to fill the core. This result can be used to estimate a retention level of $9,000 \text{ } \mu\text{g/g}$ —more than 40 times greater than that for the fast species. The ultimate resistance factor associated with this slow species was approximately 260. Upon first consideration, this high value seems inconsistent with the resistance factor of 12 that was observed at the same flux after 17 PV in Fig. 14. However, note that Figs. 15 through 17 report values measured at a fixed flux over a wide range of polymer throughput. In contrast, the values in Fig. 14 were determined within a short range of throughput, during which fluid velocities varied over a wide range. Conceivably, exposure to high flux values (in Fig. 14) may have disrupted polymer structures that might form during a constant low flux of 7.13 ft/D. In other words, the polymer-retention level (and therefore resistance-factor values) might vary with fluid velocity. Future work will be needed to establish whether the high resistance factors that develop at low flux values will present problems with injectivity and polymer transport.

Although the coreflood results could be interpreted to indicate that two polymer species exist in the associative polymer, some information is inconsistent with this view. The associative polymer is not a mixture of two different macromolecules. The product is obtained by radical polymerization, and because of the manufacturing process, drift of compositions can occur. Each macromolecule contains the four monomers used as raw materials for the synthesis. However, the percentage of each monomer can differ from one molecule to the next owing to differences in reactivity. Also, Mw differs from one molecule to the next. Thus, a continuous distribution of polymer compositions and structures can exist. This view is consistent with the gradual rise in resistance factors (with increasing PV throughput) in Figs. 15 through 17. If only one slow species was present, step changes in resistance factors might be expected (e.g., at 6, 12, 18 PV).

One might expect that size exclusion chromatography (SEC) could distinguish whether the associative polymer contained one,

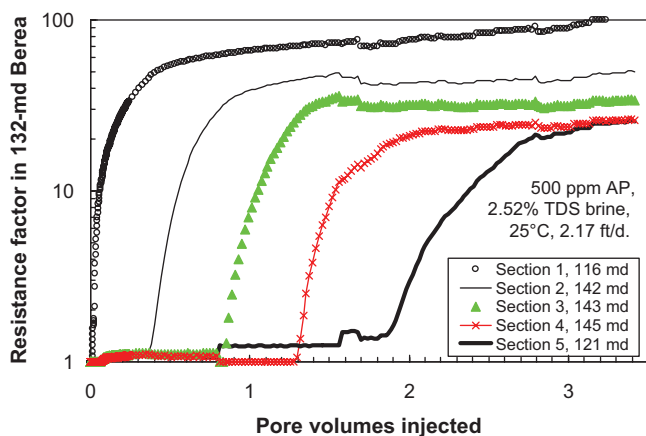


Fig. 19—Resistance factors during injection of 500-ppm AP at 2.17 ft/D into 132-md Berea.

two, or multiple polymer species. However, the associative polymer has a very high Mw (near 12–15 million g/mol by intrinsic viscosity measurement). To our knowledge, there is no standard column for SEC to handle such polymers.

Propagation in a 122-cm-Long Berea Sandstone Core. An experiment was performed in a 122-cm-long Berea sandstone core that had four equally spaced internal pressure taps. These taps divided the core into five sections, each with 24.4-cm length. The permeabilities of these five sections were 116, 142, 143, 145, and 121 md, respectively. The composite average permeability of the core was 132 md. The core cross-sectional area was 14.52 cm², and the core PV was 329.7 cm³. We injected 3.5 PV of 500-ppm AP (in 2.52%-TDS brine) using a fixed flux of 2.17 ft/D. Fig. 19 plots resistance factors in the five core sections as a function of volume injected. Fig. 19 indicates polymer arrival at the end of the five core sections after 0.42, 0.84, 1.29, 1.90, and 2.7 PV injected. This rate of AP propagation was noticeably slower than that in 11.2-darcy polyethylene (Figs. 15 and 16). Nevertheless, it still suggests that the AP may have the ability to penetrate deep into the porous rock of a reservoir. Note in the last two core sections that the resistance factors levelled out at a resistance factor of 25, which is 6 times the value expected from viscosity measurements. (We planned to inject brine and another polymer bank to determine retention and inaccessible PV. Unfortunately, the core broke.)

Conclusions

This investigation compared the hydrophobically associative polymer, C1205, and the conventional HPAM, 3830S, for potential use in polymer flooding.

1. Rheological properties (viscosity vs. concentration and shear rate, elastic modulus vs. frequency, loss modulus vs. frequency) were similar for the two polymers (in a 2.52%-TDS brine at 25°C).
2. Both HPAM and the associative polymer show excellent filterability at lower concentrations (1,000 ppm or lower), but plugged within 200-cm³/cm² throughput at higher concentrations (1,500 ppm).
3. In cores with multiple sections, we saw no evidence of face plugging for either polymer at any concentration. This was true in both 347-md Berea sandstone and 10- to 12-darcy porous polyethylene.
4. Plots of resistance factor vs. flux (after normalization for permeability using the capillary-bundle correlation) matched well for a broad range of permeability.
5. In Berea sandstone and porous-polyethylene cores, low-flux resistance factors for fresh associative polymer were at least twice those for HPAM.
6. Both polymers showed modest (0–8%) viscosity losses (at 7.3 s⁻¹) after exposure to 235-psi/ft pressure gradient in a core. However, associative polymer solutions experienced 31–45% loss in low-flux resistance factor, whereas HPAM solutions

experienced only 0–15% loss. After 235 psi/ft, low-flux resistance factors for associative polymer solutions were often similar to those for fresh HPAM solutions.

7. After exposure to 2,500-psi/ft pressure gradient, associative polymer solutions experienced 19–35% viscosity loss, whereas HPAM solutions experienced 5–17% viscosity loss. After 2,500 psi/ft, low-flux resistance factors for associative polymer solutions were the same as or less than those for HPAM solutions.
8. Results from propagation studies in long polyethylene and sandstone cores suggest that higher-than-expected resistance factors (typically at least twice the values expected from viscosity measurements) can propagate deep into a reservoir.
9. Consistent with previous research (Dupuis et al. 2011), the associative polymer appears to contain a species that propagates through porous rock at rates comparable to those for HPAM and a second species (or perhaps multiple species) that moves much more slowly and creates much higher resistance factors.

Nomenclature

- F_r = resistance factor (water mobility/polymer-solution mobility)
 k = permeability, darcies [μm^2]
 u = flux, ft/D [m/d]
 Δp = pressure difference, psi [Pa]
 μ = viscosity, cp [mPa·s]
 ϕ = porosity

Acknowledgments

We gratefully acknowledge financial support of this work from the US Department of Energy (Award No. DE-NT000655), ConocoPhillips, CP Kelco, SNF Floerger, and Statoil.

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SI Metric Conversion Factors

cp × 1.0*	E-03 = Pa·s
ft × 3.048*	E-01 = m
in. × 2.54*	E+00 = cm
psi × 6.894 757	E+00 = kPa

*Conversion factor is exact.

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