Literature Review and Experimental Observations of the Effects of Salinity, Hardness, Lithology, and ATBS Content on HPAM Polymer Retention for the Milne Point Polymer Flood

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Summary

At the Milne Point polymer flood (North Slope of Alaska), polymer retention is dominated by the clay, illite. Illite, and kaolinite cause no delay in polymer propagation in Milne Point core material, but they reduce the effective polymer concentration and viscosity by a significant amount (e.g., 30%), thus reducing the efficiency of oil displacement until the full injected polymer concentration is regained [which requires several pore volumes (PVs) of throughput]. This work demonstrates that polymer retention on illite is not sensitive to monovalent ion concentration, but it increases significantly with increased divalent cation concentration. The incorporation of a small percentage of acrylamido tertiary butyl sulfonic acid (ATBS) monomers into hydrolyzed polyacrylamide (HPAM) polymers is shown to dramatically reduce retention. The results are discussed in context with previous literature reports. Bridging adsorption was proposed as a viable mechanism to explain our results. Interestingly, an extensive literature review reveals that polymer retention (on sands and sandstones) is typically only modestly sensitive to the presence of oil. Extensive examination of the literature on inaccessible pore volume (IAPV) suggests the parameter was commonly substantially overestimated, especially in rock/sand more permeable than 500 md (which comprises the vast majority of existing field polymer floods).

Introduction

Depending on the magnitude and form of the polymer retention function, polymer retention can have a major impact on the technical feasibility and economics of a field-scale polymer flood (Manichand and Seright 2014; Wang et al. 2020; Seright and Wang 2022). Various mechanisms could contribute to polymer retention, including adsorption, mechanical entrapment (in various forms), hydrodynamic retention, and precipitation (Manichand and Seright 2014).

In previous work (Wang et al. 2020; Seright and Wang 2022, 2023), we identified and characterized a "tailing" phenomenon during studies of HPAM polymer retention in Milne Point core material (in support of polymer flooding field trials on the North Slope of Alaska). In these experiments, polymer propagated through Milne Point (Schrader Bluff) core material without any delay (relative to a water tracer), but the effluent polymer concentration typically achieved only about 70% of the injected concentration upon initial arrival at the end of the core. Subsequently, the effluent polymer concentrations gradually increased ("tailed") over the course of many PVs before finally reaching the injected polymer concentration (see the green curve of **Fig. 1**). From a practical viewpoint, this behavior means that polymer retention (at Milne Point) will not delay propagation of the polymer bank (and consequently, the displaced oil bank), but the mobility ratio and efficiency of oil displacement will be less than if no polymer retention occurred. (Although IAPV can easily be incorporated into the calculations associated with **Fig. 1**, it was intentionally not included here for reasons that will be detailed in the literature review—basically because IAPV is zero for these floods in permeable sand and rock.)

Use of three independent methods of polymer detection demonstrated that the "tailing" phenomenon was not an experimental artifact (Wang et al. 2020; Seright and Wang 2022). Over practical ranges of conditions found in the field, the "tailing" effect was not sensitive to flow rate, polymer concentration, polymer molecular weight (MW), core length, core permeability, core heterogeneity, or whether the core was preserved, in its native state, cleaned of oil, cleaned and resaturated with oil, or cleaned, resaturated, and aged with oil. Illite was identified as the mineral that was primarily responsible for the "tailing" phenomenon in Milne Point core material. The effect was not noted in bead packs that excluded illite but did include dolomite, limestone, siderite, pyrite, chlorite, montmorillonite, or calcium sulfate. All of the previous work was performed using HPAMs in "Milne Point injection water," which contained 2,435 ppm total dissolved solids (TDS), including 128 ppm calcium and 11 ppm magnesium. The current work expands the study of the "tailing" phenomenon to include salinities from 2,400 ppm TDS to 27,600 ppm TDS, divalent cation concentrations from 0 ppm to 6,000 ppm, and ATBS content of the polymer from 0% to 25%. We also examined the effect of the degree of hydrolysis/anionicity of the polymer (from 10% to 30%). We further examined the tailing effect in the presence of kaolinite, dolomite, and limestone.

Before reporting our experimental results, there is value in reviewing important previous reports concerning polymer retention and IAPV in the petroleum literature. Our review notes a reasonable consensus of views about trends in polymer retention. However, we point out serious discrepancies on the topic of IAPV.

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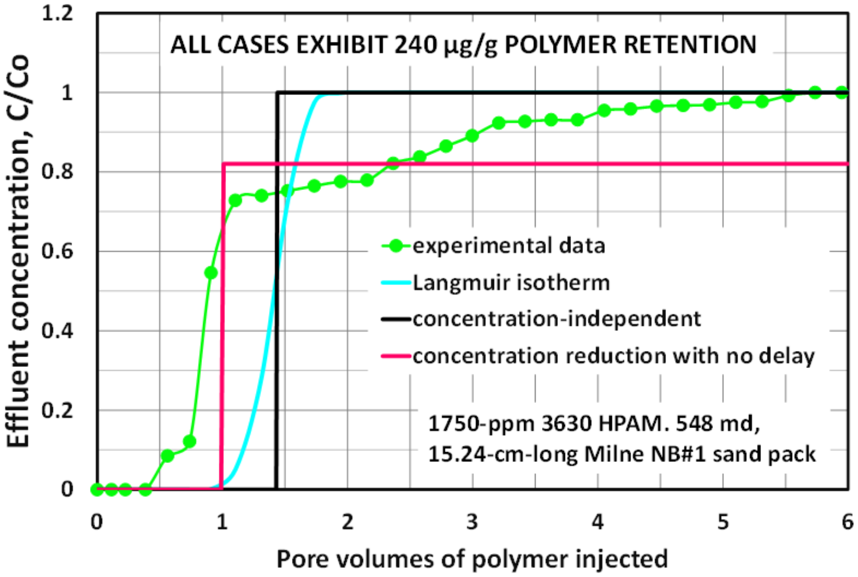

Fig. 1—Various forms of the polymer retention function.

Polymer Retention in the Petroleum Literature

Forms of the Retention Function. A number of different forms have been assumed for the polymer retention function. **Fig. 1** plots predictions for the various cases, where the total retention is fixed at 240 µg/g. For each case, **Fig. 1** plots the predicted effluent polymer concentration vs. PVs of polymer injected into a linear core. In fractional flow calculations, polymer retention is assumed to be a fixed value (Green and Willite 1998). The black curve in **Fig. 1** shows the predicted behavior for this case. With a polymer retention value of 240 µg/g, effluent polymer concentration remains at zero until 1.44 PV of polymer is injected; then, the effluent concentration abruptly increases to the injected value. Thus, retention delays propagation of the polymer bank (and the displaced oil bank), but after polymer breakthrough, the effluent reaches its full concentration and viscosity (as was injected). Others (Surtek 2020) assume that polymer retention causes no delay in polymer propagation but immediately reduces the polymer concentration and viscosity. This case is shown by the red curve in **Fig. 1**. This case predicts no delay in the development and movement of an oil bank from polymer flooding, but the polymer is less efficient in displacing the oil (because the polymer viscosity is lower). Most chemical flooding simulators assume that the Langmuir isotherm is valid (Satter et al. 1980; Vossoughi et al. 1984; Camilleri et al. 1987; Yuan et al. 2010; Dang et al. 2011). The Langmuir isotherm assumes that retention is zero at zero polymer concentration but rises linearly with concentration until reaching the maximum value (240 µg/g in our example). This case is illustrated by the blue curve in **Fig. 1**. As with the assumption of concentration-independent retention (i.e., for fractional flow calculations), the Langmuir isotherm predicts a delay in propagation of the polymer bank (in proportion to the retention value), but once breakthrough occurs, effluent polymer concentration rises rapidly to the injected value. The Langmuir isotherm forecasts a more dispersed polymer front than is predicted by the concentration-independent case. For comparison, the green curve in **Fig. 1** shows actual effluent polymer concentrations from a dynamic retention experiment in Milne Point core material (Wang et al. 2020; Seright and Wang 2022).

Effect of Permeability. Table 1 summarizes the effects of many factors, as reported in recent literature. Our table includes a reference to Manichand and Seright (2014, Table 1), which summarizes similar information for literature before 2014. Many researchers reported that polymer retention increased with decreased permeability, especially in rock with permeability less than 100 md (Jewett and Schurz 1970; Jennings et al. 1971; Hirasaki and Pope 1974; Vela et al. 1976; Zaitoun and Kohler 1987, 1988; Huh et al. 1990; Seright 1992). Also, many previous researchers (Szabo 1975, 1979; Dominguez and Willhite 1977; Huh et al. 1990) suggested that retention is dominated by mechanical entrapment in low-permeability rock (<130 md), while adsorption primarily dictates retention in moderate- to high-permeability sand and rock. These suggestions make sense since the dimensions (typically 0.1–0.5 µm radius, depending on MW and salinity) of high-MW enhanced oil recovery (EOR) polymers could approach the size of pore throats in low-permeability rock or minerals (Sorbie 1991; Jouenne and Levache 2020). Although Ghosh et al. (2021) and Song et al. (2022) noted that polymer flooding could be feasible in less-permeable reservoirs, the vast majority of recent polymer floods are applied in sands or sandstones with an average permeability above 500 md (Daqing, Shengli, Bohai Bay, Mangala, Baghyam, Pelican Lake, Cactus Lake, Seal, Mooney, Rapdan, Milne Point, Captain, Matzen, Patos Marinza, Bockstedt, Dalia, Marmul, Tambaredjo, Palogrande, Kalamkas, Diadema, Grimbeek, Los Perales, Rayoso, and El Corcobo) (Sagyndikov et al. 2022). X-ray computed microtomography of a 470-md sandstone revealed that pores are highly connected, and 98% of the pores have an effective diameter greater than 26 µm and a pore throat diameter greater than 6.7 µm (Seright et al. 2006, 2009). Consequently, mechanical entrapment of polymers is not anticipated to be significant in most polymer floods with an average permeability greater than 500 md (Maerker 1973; Huh et al. 1990; Zhang and Seright 2015). Of course, polymer solutions must be fully dissolved before injection into reservoir rock—otherwise, the undissolved polymer could be removed by filtration at the injection sandface. For previous studies in Milne Point core material using an 18 million g/mol HPAM (Flopaam 3630S) in 2,435 ppm TDS water, we noted no correlation between polymer retention and permeability between 15 md and 10 darcies (Dandekar et al. 2021).

MINERALOGY: Clay and high-surface-area minerals are very important.	
For quartz or clean outcrop sands/sandstones, HPAM retention is low (typically <50 µg/g) if permeability is >100 md and the temperature is not high (<60°C).	Pre-2014 literature review in Manichand and Seright (2014)
HPAM retention is high (339–8000 µg/g) on kaolinite. Tailing phenomenon observed.	Pre-2014 literature review in Manichand and Seright (2014); Seright and Wang (2022)
HPAM retention is high (~1100 µg/g) on illite. Tailing phenomenon observed.	Seright and Wang (2022)
HPAM retention is moderate (<100 µg/g) on carbonate and dolomite if permeability is >100 md and temperature is not high (<60°C).	Pre-2014 literature review in Manichand and Seright (2014); Wan and Seright (2017); Seright and Wang (2022)
HPAM retention on iron minerals (e.g., siderite) is high (>545 µg/g).	Pre-2014 literature review in Manichand and Seright (2014); Wan and Seright (2017); Seright and Wang (2022)
PERMEABILITY: Very important below 100 md; less important above 200 md.	
Retention increases substantially with decreasing permeability below 100 md (depending on polymer MW). Retention tends to be fairly independent of permeability above 200 md.	Pre-2014 literature review in Manichand and Seright (2014); Dandekar et al. (2021)
OIL SATURATION and WETTABILITY: Mixed but generally moderate effect.	
For HPAM, retention with an S_{or} may be less (as much as half), the same, or greater than retention without oil. Wettability has not been shown to have a definitive effect. Applies to both sandstones and carbonates.	Pre-2014 literature review in Manichand and Seright (2014); Masalmeh et al. (2019); Wang et al. (2020, 2021); Alfazazi et al. (2021); Sebastian et al. (2022); Song et al. (2022); Seright and Wang (2022)
Only one unambiguous case showed that an oil saturation dramatically reduced HPAM retention in a carbonate core. A second report also claimed this with sands but is arguable.	Wever et al. (2018); Souayeh et al. (2022)
POLYMER CONCENTRATION: Depends on the concentration regime.	
Most studies show little dependence of retention on polymer concentration but have examined a limited concentration range. Over a wide range of concentrations, HPAM retention on Berea was constant and low (~20 µg/g) below 1,000 ppm and constant and higher (~200 µg/g) above 100 ppm. Most studies were performed with sands or sandstones.	Pre-2014 literature review in Manichand and Seright (2014)
POLYMER MW: May be complex.	
Most previous studies indicate that HPAM MW is primarily a factor for polymer retention in low-permeability rocks.	Pre-2014 literature review in Manichand and Seright (2014)
HPAM MW had a minor impact in retention on illite.	Seright and Wang (2022)
Two papers suggest retention on carbonates may be reduced as MW increases.	Dupuis et al. (2017); Souayeh et al. (2022)
HPAM DEGREE OF HYDROLYSIS: Conflicting message but generally of minor importance.	
All but one previous paper showed a minor effect of the degree of hydrolysis on HPAM retention on sandstones. Vast majority of previous studies performed with HPAM on sandstones.	Pre-2014 literature review in Manichand and Seright (2014); this work
SALINITY AND DIVALENT ION CONTENT: Monovalent ions have little effect but divalent cations have a major effect.	
Monovalent ions have little effect, but divalent cations have a major effect. Most studies used HPAM on sands/sandstones at low temperatures (<60°C).	Pre-2014 literature review in Manichand and Seright (2014); this work
ATBS CONTENT: ATBS can substantially reduce retention, but the reasons why are not known.	
Many previous studies indicate that incorporating some level of ATBS into HPAM reduces retention (for sands, illite, and carbonates at low temperatures), but the reasons are not clear.	Pre-2014 literature review in Manichand and Seright (2014); Beteta et al. (2021); Sebastian et al. (2022); Song et al. (2022); this work
TEMPERATURE: Few studies have examined this variable.	
Studies of various synthetic polymers in hard brines at high temperatures (>70°C) in carbonates show varied but generally high retention (84–911 µg/g).	Masalmeh et al. (2019); Wang et al. (2020, 2021); Alfazazi et al. (2021); Seright et al. (2021); Sebastian et al. (2022): Song et al. (2022)
Laboratory and field data (at Mangala) suggest that hydrolysis and precipitation may accentuate HPAM retention at elevated temperatures (>65°C).	Shankar et al. (2022)

Table 1—Summary of effects on polymer retention reported in the literature

Effect of Polymer Charge, Salinity, Divalent Ion Content, and Alternative Monomer Units. Some have suggested that polymer adsorption should decrease with an increased degree of hydrolysis for HPAM and with decreased salinity (Smith 1970). The logic behind this suggestion was that negatively charged rock surfaces should repel negatively charged polymers. Increased salinity should screen this repulsion and therefore increase polymer adsorption. MacWilliams et al. (1973) presented some evidence to support this view, as

HPAM's degree of hydrolysis decreased from 15% to 2%. However, their work showed no significant effect on retention for degrees of hydrolysis between 25% and 75%. Martin and Sherwood (1975) did not find that polymer retention in Berea sandstone decreased as HPAM degree of hydrolysis increased from 0% to 15%. Meister et al. (1980) also found that polymer retention on Berea sandstone was about the same for 0% and 22% degree of hydrolysis. Our work in this paper will also indicate that HPAM retention (on illite) is not greatly sensitive to the degree of hydrolysis between 10% and 30%.

At low to moderate salinities, most previous researchers found that HPAM retention was not sensitive to the monovalent ion content of the water. Martin et al. (1983) found similar HPAM retention on Berea sandstone between 0.1% and 2% NaCl. Mungan (1969) did not observe a consistent difference in HPAM adsorption in distilled water vs. 2% NaCl. Chiappa et al. (1999) found polymer adsorption on quartzite was nearly independent of salinity between 0% and 13% KCl. Smith (1970) reported a modest dependence of HPAM retention on silica for NaCl concentrations below 3%. However, he observed dramatically higher retention above 10% NaCl. Chauveteau et al. (1988) also reported that HPAM adsorption on kaolinite was four times greater with 24% NaCl than with 0.2% NaCl. We wonder if the high retention observed at very high salinities might be related to HPAM solubility/cloudpoint rather than the charge repulsion arguments. If charge repulsion was the dominant factor, one would expect the greatest variation in polymer retention to occur at the lowest salinities. In reality, the greatest retention variations in clastic cores have been observed at the highest salinities (Smith 1970). Interestingly, in Indiana limestone cores, Souayeh et al. (2022) reported that the retention of an ATBS polymer was 2.5 times greater with a salinity of 0.196% TDS than with a salinity of 19.6% TDS (using the same ratio of monovalent to divalent cations).

Chiappa et al. (1999) found that polymer adsorption on quartzite was substantially higher with 8% $CaCl_2$ in the brine vs. when no $CaCl_2$ was present. Our work in this paper will reveal that HPAM retention on illite is influenced dramatically more by divalent cations than monovalent cations.

Vermolen et al. (2011), Skauge (2013), and Beteta et al. (2021) reported that incorporation of *n*-vinyl pyrrolidone (NVP) or sulfonate can substantially reduce HPAM retention. In this paper, evidence will be presented to support this finding. In carbonate cores with less than 50 md, Song et al. (2022) reported much lower retention for the ATBS-polyacrylamide copolymer (32% ATBS) than for HPAM. Sebastian et al. (2022) reported low to modest retention values (24–56 µg/g) for an ATBS polymer (SNF SAV10) in ~250 md Indiana limestone cores (at 25°C) over a very broad range of salinity (425 ppm TDS to 167,114 ppm TDS). Of course, the incorporation of ATBS into the polymer will increase the polymer price to some extent.

Effect of Oil Saturation and Wettability. Intuitively, one might expect polymer retention to be lower (perhaps even radically lower) when oil is present during the retention measurement than when no oil is present (because oil restricts polymer access to the rock surface) (Smith 1970; Dean et al. 2022). Further, one might expect water-wet rock to exhibit higher polymer adsorption than oil-wet rock. However, most researchers reported only a modest effect of oil presence on polymer retention—sometimes modestly lower (e.g., as much as half) than with no oil (Szabo 1975; Kolodziej 1988; Chiappa et al. 1999; Masalmeh et al. 2019; Wang et al. 2020; Alfazazi et al. 2021; Sebastian et al. 2022; Seright and Wang 2022; Song et al. 2022), sometimes about the same (Huh et al. 1990; Wang et al. 2020; Seright and Wang 2022; Song et al. 2022), and sometimes higher (Huh et al. 1990; Broseta et al. 1995; Wang et al. 2021; Song et al. 2022; Seright and Wang 2022). As an interesting exception, Wever et al. (2018) found a case where retention on sand from an Oman reservoir was 10 times greater without oil than in the presence of oil. However, this case is clouded because the core without oil had a substantially lower permeability than that with oil. Souayeh et al. (2022) reported a case where retention of an ATBS polymer (SAV10) in ~250 md carbonate cores with residual oil was 16% of that with no residual oil. Over the course of 30 core experiments with Milne Point core material, we found no clear relation between HPAM retention and wettability or the presence/absence of oil (Wang et al. 2020; Seright and Wang 2022). One possible explanation for why retention is not greatly affected by the presence of oil is that polymer adsorption increases the water-wet character of rock (Zaitoun and Kohler 1987, 1988; AlSofi et al. 2019; Li et al. 2020; Souayeh et al. 2022). As in other chemical flooding processes, added chemicals may release oil that was previously adsorbed to the rock surfaces, thus increasing the fraction of the rock that directly contacts the aqueous phase. We acknowledge that most previous work was performed with sands and sandstones. More work is needed to establish trends in carbonates.

Effects of Clay Content, Carbonates, and Iron. Several authors reported polyacrylamide, HPAM, and xanthan retention values on kaolinite, with values ranging from 339 µg/g to 16,900 µg/g (Meister et al. 1980; Chauveteau et al. 1988; Hughes et al. 1990). During one experiment with 9% kaolinite in 200-µm glass beads, Seright and Wang (2022) found 845 µg of HPAM retained per gram of kaolinite. For comparison, our previous work with illite in 200-µm bead packs (16 separate experiments with illite fractions ranging from 4.5% to 36%) yielded average HPAM retention values on illite around 1100 µg/g (Seright and Wang 2022). We found that experiments with pure clay were difficult to assess because their low permeability (<1 md) led to severe mechanical entrapment of the polymer and subsequent extremely high retention values during flooding experiments. These high values would not be representative of polymer retention where the clay comprised a modest fraction of the reservoir rock. We suspect that this issue may have contributed to the extremely high retention values (>10,000 µg/g) reported by some authors with pure clays (Hughes et al. 1990; Chiappa et al. 1999). This point may also be relevant to a report of 15 600 µg/g retention in siderite ($FeCO_3$) by Hughes et al. (1990). In a bead pack with 9% siderite, we found HPAM retention to be only 545 µg/g, when retention was expressed as polymer retention per gram of siderite present.

At low temperatures (e.g., 25°C) in brines with low salinity, most reports of polymer retention on carbonates or in carbonate (dolomite or calcium carbonate) cores or packs indicate modest HPAM retention values (typically 100 µg/g or less) (Szabo 1979; Meister et al. 1980; Wan and Seright 2017; Seright and Wang 2022). At higher temperatures (60–130°C) in high-salinity, high-hardness brines, retention of synthetic polymers (especially containing ATBS or NVP) in carbonate cores varied over a wide range—from 84 µg/g to 911 µg/g, with values from 200 µg/g to 300 µg/g being the most common (Gaillard et al. 2014; Alfazazi et al. 2021; Alsofi et al. 2017; Masalmeh et al. 2019; Seright et al. 2021; Song et al. 2022). More work is needed to sort out the effects of temperature on polymer retention in sands, carbonates, and other minerals. We note the work of Shankar et al. (2022), who convincingly demonstrated substantial retention of HPAM through hydrolysis and precipitation associated with prolonged contact with divalent cations during propagation through the Mangala reservoir at 65—74°C. It is conceivable that this mechanism may have contributed to some of the high retention measurements reported by others in hard brine at elevated temperatures (in either carbonates or sandstones).

Effects of Polymer Concentration and MW. The Langmuir isotherm assumes that polymer retention increases linearly with increased polymer concentration at low values, but plateaus at a fixed value at higher concentrations. Most polymer-flood simulators assume this behavior (Satter et al. 1980; Vossoughi et al. 1984; Camilleri et al. 1987; Yuan et al. 2010; Dang et al. 2011), but only Szabo (1975, 1979) presented experimental data to support it. Most others report a weak (or no significant) dependence of retention on polymer concentration

(Friedmann 1986; Huang and Sorbie 1993; Zitha et al. 1998; Green and Willite 1998; Zheng et al. 2000). During experiments with HPAM concentrations ranging from 10 ppm to 6,000 ppm, Zhang and Seright (2014) reported three regimes of retention behavior: (1) relatively fixed and low retention at low polymer concentrations (e.g., ~20 µg/g between 10 ppm and 100 ppm), (2) increasing retention at intermediate HPAM concentrations (e.g., rising to ~200 µg/g between 100 ppm and 1,000 ppm), and (3) relatively high and fixed retention at high HPAM concentrations. Ferreira and Moreno (2020) reported similar behavior. Wang et al. (2020) reported that HPAM retention was insensitive to polymer concentration and MW in Milne Point core material. In studies with 9% illite in bead packs, Seright and Wang (2022) also found little dependence of retention on HPAM polymer concentration and MW, except at very low values (i.e., 200 ppm polymer or <2.7 million g/mol MW).

Concerning the effect of polymer MW on retention in sandstones, many authors suggest that mechanical entrapment may substantially increase polymer retention as polymer MW increases (Jewett and Schurz 1970; Jennings et al. 1971; Manichand and Seright 2014). In contrast, in carbonate cores over a limited range of polymer MW values, Dupuis et al. (2017) and Souayeh et al. (2022) suggested that polymer adsorption could actually decrease with increased MW. Much more work is needed on retention in carbonates to clarify any differences in behavior between sandstones and carbonates.

Effect of Flow Rate. As mentioned in the Introduction, Wang et al. (2020) and Seright and Wang (2022) reported a pronounced "tailing" phenomenon associated with HPAM retention during studies involving core materials associated with the Milne Point polymer flood. In particular, effluent polymer concentrations arrived at the core outlet at a time indicating little or no polymer retention, then rapidly rose to about 70% of the injected concentration **(Fig. 1)**. Thereafter, the effluent HPAM concentration gradually increased ("tailed") up to reach the injected concentration over the course of many PVs. Illite was identified as the mineral that was primarily responsible for this phenomenon (Seright and Wang 2022). A reasonable guess is that diffusion or dispersion might be responsible for the effect. For perspective, diffusion is estimated to allow movement to translate at about 1 cm/d for small molecules (like our iodide tracer) and about 0.03 cm/d for our HPAM (Seright 1991). The influence of rate effects was extensively investigated in Wang et al. (2020) and Seright and Wang (2022) by performing identical dynamic retention experiments but with different rates—ranging from 0.31 ft/D to 12.4 ft/D (Darcy velocity). They found that rate had no discernable effect on the initial polymer breakthrough volume or the ultimate volume to reach the injected concentration. However, between 1 PV and 2.5 PV, effluent HPAM concentrations rose to higher values with increased rate—resulting in decreased polymer retention with increased rate (i.e., 152 µg/g at 0.31 ft/D to 99 µg/g at 12.4 ft/D). Rate had no discernable effect on effluent concentrations associated with the potassium iodide tracer used in these experiments. These results imply that polymer diffusion (and time of exposure) had a modest effect on the HPAM-illite interaction. Seright and Wang (2022) further explored this possibility by varying HPAM MW (from 0.1 g/mol to 18 million g/mol), HPAM concentration (from 200 ppm to 1,750 ppm), and core length (from 15.24 cm to 61 cm). Many different mechanisms were considered to explain the results. Several mechanisms that could not explain the results were (1) HPAM imbibition into the clay, (2) IAPV arguments, and (3) flocculation (Seright and Wang 2022). A correlation was developed that accounted well for all polymer propagation data using Flopaam 3630S (MW = 18 million g/mol) in packs with 9% illite—including polymer concentrations from 200 ppm to 1,750 ppm, Darcy velocities from 0.31 ft/D to 12.4 ft/D, core lengths from 15.24 cm to 61 cm, and illite with different particle sizes. This correlation introduced an exposure parameter, Lp that is defined by Eq. 1:

$$Lp = (t - t_{bt})\, u\, C^{0.5}, \tag{1}$$

where t is the time since the start of polymer injection (seconds), t_{bt} is the time of first polymer arrival at the end of the core (seconds), u is the Darcy velocity (cm/s), and C is the injected polymer concentration (weight fraction). The units for Lp are cm-(wt. fraction)$^{0.5}$. The effluent polymer concentration, relative to the injected value, C/Co, was predicted quite well using Eq. 2.

$$C/Co = 1 - 0.7\, \mathrm{e}^{-Lp/0.03} - 0.3\, \mathrm{e}^{-Lp/0.25}. \tag{2}$$

To rationalize this correlation, we suggested that polymer retention depends on the total time ($t - t_{bt}$) of polymer exposure to illite. This time difference is multiplied by the injection rate, u, to reflect that slow rates cause longer exposure times for a given fluid element. This product is then multiplied by the square root of the polymer concentration. One might anticipate that lower HPAM concentrations could show reduced reaction rates. However, the source of the dependence on the square root of concentration is not obvious.

In Eq. 2, the two exponential terms suggest that two exposure-dependent processes occurred at the same time. The middle term reveals that ~70% of the concentration change was due to a relatively short process (with an exposure constant of 0.03), while the third term indicates that ~30% of the concentration change was ascribed to the longer process (with an exposure constant of 0.25). Although the correlation expressed in Eq. 2 describes the retention data extremely well, it does not identify the detailed mechanism behind the correlation. Thus, we felt that additional studies were needed—as pursued during the experimental work associated with the current paper.

Summary. As a summary of important views concerning polymer retention, we note the following consensus. First, polymer retention can increase greatly with increased divalent ion content in the brine. Second, monovalent ion content has little effect on polymer retention, except possibly at very high salinities. Third, depending on polymer MW, mechanical entrapment can substantially increase polymer retention as permeability decreases, especially in low-permeability sandstones. However, in reservoirs with average permeabilities above 500 md (which comprise the vast majority of existing polymer floods), mechanical entrapment is not significant. Fourth, considerable interest has occurred recently for polymer flooding applications in carbonate reservoirs, which tend to have lower permeabilities and sometimes multimodal pore size distributions. Fifth, although many authors reported polymer retention to be modestly lower (by as much as half) with oil present vs. without, many other cases were noted where polymer retention was the same or greater without oil present vs. with. Only two cases were noted (one in a carbonate core and another in sands) where polymer retention was dramatically lower (i.e., 6–10 times lower) with oil present vs. without. Sixth, incorporation of some ATBS into HPAM-type polymers can dramatically lower retention. Seventh, HPAM degree of hydrolysis has only a minor effect on polymer retention. Finally, it has been reported that retention is fairly insensitive to polymer concentration under most EOR flooding conditions. Two authors (who examined retention over a wide concentration range) reported low (but fixed) retention values at low concentrations and notably higher (but fixed) values at higher concentrations, with a transition in retention values in between. Again, we emphasize that most previous work was performed with sands and sandstones, so some of the above-mentioned observations may need to be qualified as more work is done with carbonates.

IAPV in the Petroleum Literature

Inconsistency of Previous Reports. IAPV is expected to accelerate polymer flow through porous rock (relative to the rate of solvent propagation) because large polymer molecules cannot penetrate into all the pore space that is available to the solvent (Dawson and Lantz 1972). In contrast to the relative consensus on findings and beliefs regarding polymer retention, IAPV reports and beliefs are plagued by serious inconsistencies. The importance of excluded volume effects in chromatography is not doubted here. Further, it makes sense that low-permeability rocks may possess a significant fraction of pores that are not accessible by high-MW polymers, especially carbonates that have a bimodal pore size distribution. As an example, Souayeh et al. (2022) reported IAPV values up to 68% in 200–300-md Indiana limestone where 56% of the pores were smaller than 1 µm. As an interesting contrast, Song et al. (2022) reported IAPV values were only 0–11% in Edwards Yellow limestone cores with less than 50 md but with 90% of the pore throats between 1 µm and 10 µm. Even in significantly more permeable rock and sand, critical inconsistencies exist concerning IAPV in the petroleum literature. Manichand and Seright (2014) extensively reviewed prior literature and noted no correlation between IAPV and permeability or polymer MW. Further, they noted that X-ray computed microtomography and other data show that virtually all pores in moderate- to high-permeability (i.e., greater than 500 md) rock and sand should be quite accessible to typical HPAM molecules (Seright et al. 2006, 2009). They suggested that experimental challenges associated with the measurement of IAPV might be responsible for the literature's inconsistencies, especially in moderate- to high-permeability rock and sand. Gilman and MacMillan (1987) also pointed out that caution must be exercised when translating observed polymer breakthrough times to IAPV values if heterogeneities exist in the porous media. Wang et al. (2020) demonstrated that IAPV values will appear misleadingly high if not enough brine is flushed through the core after the first polymer slug of a dynamic retention experiment in a core. Curiously, even today, researchers rarely report how much brine was flushed between the polymer banks in these experiments. Most who did report the brine volume flushed stated 10 PV or less (Manichand and Seright 2014).

Akbari et al. (2019) extensively reviewed methods for assessing IAPV. They concluded that the best method for the determination of IAPV was the double tracer-laden polymer method of Lotsch et al. (1985). In this method, a bank of polymer solution is injected into a core or sandpack with a tracer. After the effluent concentrations for both polymer and tracer reach the injected concentrations, many PVs (e.g., >100) of brine must be injected to displace all mobile polymer and tracer. Subsequently, a second bank of polymer solution is injected with the tracer. Polymer retention and IAPV are assessed only using the front part of the effluent curves during the two injection stages, thereby eliminating the problems and uncertainties associated with viscous fingering and extended production of low-concentration fluids. IAPV is determined during the second injection cycle from the difference in area between the polymer breakout curve and the tracer breakout curve. Although Akbari et al. (2019) provided an excellent review, three critical concepts were missing or not sufficiently emphasized from their considerations. The first was that many PVs (e.g., ~100 or more) of brine must be flushed after the first polymer bank. If only ~10 PV of brine is flushed, viscous fingering will leave behind a substantial amount of nonadsorbed polymer that will be misinterpreted as IAPV during the subsequent polymer flush (as discussed extensively in Wang et al. 2020). Second, they did not consider the clear inconsistencies (of no relation between IAPV and permeability/pore size or MW) in previous literature reports (as discussed in Manichand and Seright 2014). Third, they advocated flawed depletion-layer concepts without a critical analysis of the basis of those concepts, as presented in the petroleum literature. That point will be amplified in the next paragraph.

Critique of the "Depletion-Layer" Concept. Some argued that a "depletion layer" contributes to the IAPV (Chauveteau et al. 2002; Sorbie 1991; Stavland et al. 2010; Akbari et al. 2019; Skauge et al. 2021; Dean et al. 2022). To explain, if the polymer does not adsorb onto the rock surface, the center of mass for a large polymer molecule may not approach the rock surface as closely as a small solvent molecule or ion. Consequently, the fluid closest to the rock is depleted of polymers and has a lower viscosity than the fluid in the center of the pore. Because the depleted layer is accessible to the solvent but not to the polymer, the polymer can propagate through porous media more rapidly than the solvent. Akbari et al. (2019) distinguished this depletion layer volume as "excluded pore volume" or EPV, which they advocate is a part of the total IAPV in a porous medium.

The depletion-layer concept loses credibility if polymers adsorb onto the rock surface. Advocates of the depletion layer argue that the adsorbed polymer layer simply moves the effective surface out toward the flow stream. However, adsorbed polymer is not a smooth, hard layer, like a rock surface. It is fuzzy with polymer strands sticking out into the flow stream—on average about the diameter of a polymer molecule (De Gennes 1979).

Also, polymer concentrations in EOR applications are well above the critical overlap concentration, so the center of mass of a polymer molecule is not the appropriate basis for the depletion-layer thickness. Instead, the radius of an average overlap-polymer-blob segment (De Gennes 1979) should be used—a far smaller distance. Thus, one would expect that if measurements of IAPV could be made precisely, IAPV (especially due to a depletion layer) should decrease with increased polymer concentration. Liauh et al. (1979) argued that even with the maximum possible depletion layer, hydrodynamic exclusion could not provide an IAPV greater than 9%.

The most concerning aspect of the depletion-layer or EPV concept is the method by which it was measured and reported in the petroleum literature. Advocates of the depletion-layer effects flush water through the core after polymer injection to determine the permeability reduction or residual resistance factor (Chauveteau et al. 2002; Sorbie 1991; Stavland et al. 2010; Skauge et al. 2021). Typically, they do not specify how much water was flushed. Since they often observed relatively high residual resistance factors, we suspect that they did not displace all of the mobile (nonadsorbed) polymer. Seright (2017) demonstrated that more than 100 PV of brine flush may be needed to achieve a true residual resistance factor. The resistance factor during polymer injection is then divided by the residual resistance factor to determine the apparent polymer viscosity in porous media and/or IAPV/EPV. Unfortunately, several experimental factors can lead to the incorrect measurement of high residual resistance factors, which in turn leads to the calculation of unexpectedly low apparent polymer viscosities in porous media and excessively large depletion layers. These factors could include insufficient brine flushed through the core before recording the brine mobility, face plugging during brine injection, air injection, or any other factor that causes an excess pressure drop during the measurement of post-polymer brine mobility. The bottom line is that it is doubtful that a significant region exists in moderate to large pores where polymers cannot reach (i.e., there is no significant depletion layer). Previous measurements of depletion layers and significant IAPV values in moderate- to high-permeability sand and rock may be experimental artifacts. As mentioned in several publications, the conservative and most appropriate assumption for IAPV values is zero in moderate- to high-permeability rock (Manichand and Seright 2014; Seright 2017; Wang et al. 2020; Sagyndikov et al. 2022b).

Other IAPV Methods. Fedorov et al. (2021) proposed a mathematical method (based on the theory of multicomponent transport in porous media) for determining polymer adsorption-retention constants and IAPV. However, there are concerns about how viscous fingering affects the validity of this method.

Dean et al. (2022) advocated the method of to determine IAPV. Recognizing the problem of water viscous fingering in the method of Lotsch et al. (1985), Dean et al. (2022) and Shook et al. (2009) proposed injecting a bank with moderate polymer concentration/viscosity, followed by a bank with higher polymer concentration/viscosity. Each polymer bank must be of sufficient size that the effluent concentration reaches the injected polymer concentration. After normalizing the baselines for the two banks, IAPV was determined by the second-(high-concentration)-bank polymer breakout curve. The method assumes that polymer retention and IAPV are not sensitive to polymer concentration. The method appears very promising in its simplicity and avoidance of viscous-fingering issues that plague other methods of IAPV determination. However, substantially more testing of this method is needed before acceptance. At present, we are only aware of one published test (Dean et al. 2022), and the permeability and character of the rock were not specified. Measuring IAPV is very time-consuming, and the results may not be very accurate. Even for the method proposed by Dean et al., there is an inherent simplifying assumption that the first bank is dominated by adsorption and the second by IAPV. We understand that simulators are tempted to use history matching of corefloods and field projects as an easy method to estimate IAPV and other parameters. However, because multiple adjustable parameters are involved during these history matches, the solutions are often not unique, and we urge caution when using history matching. If the parameters obtained from the history match are unusual (e.g., high IAPV values or high-permeability reduction values), independent experiments should be performed before accepting these parameters.

Summary. In contrast to the case for polymer retention, a review of IAPV in the petroleum literature reveals serious discrepancies. Contrary to expectations, petroleum literature reports of IAPV do not reveal a trend where IAPV increases with increased polymer MW or decreased rock permeability. Further, wide variations in IAPV values have been reported under a given set of conditions. Measurements can substantially overestimate IAPV if not enough brine is flushed (e.g., ~100 PV) between the first and second polymer slugs in the IAPV determination. Many previous measurements used only 5–10 PV of brine flush, while most others did not report how much brine was flushed. This situation may be largely responsible for the inconsistencies associated with previous IAPV reports/observations. At a minimum, future IAPV reports should include the brine flush volume to be credible. For most existing polymer floods, where average permeability is greater than 500 md (in sands or sandstones), IAPV should be effectively zero—especially considering the ratio of polymer size in solution relative to the size of pore throats and pore bodies. Consequently, when designing a polymer flood in reservoirs with moderate to high permeabilities (>500 md), IAPV should be assumed to be zero. In low-permeability rocks, especially carbonates, IAPV is expected to be more important.

Materials and Methods

In our experimental work, we examine how various factors affect polymer retention under conditions associated with the Milne Point polymer flood. As mentioned earlier, many factors were covered in our previous work (Wang et al. 2020; Seright and Wang 2022). That previous work noted that the clay illite dominated polymer retention behavior at Milne Point and that bead packs containing illite were useful in studying retention in a reproducible manner. The current paper expands previous work to explore the effects of salinity, hardness, degree of HPAM hydrolysis, and polymer ATBS content on retention behavior.

Details of the materials and methods used in this work can be found in Wang et al. (2020) and Seright and Wang (2022). Here, we summarize the main points of our experimental methods. Dynamic polymer retention studies were performed in sandpacks that were 15.24 cm long and 2.54 cm in diameter. One case (in this particular work) contained native-state sand from the Schrader Bluff Nb Formation, while the others used packs consisting of 91% (by weight) of 200-µm glass beads and 9% of a given mineral, such as illite, kaolinite, dolomite, and calcium carbonate. A pack of the 200-µm glass beads by themselves (no added minerals) has a permeability of 7 darcies. Pack preparation procedures were described in the two earlier publications. The packs were contained in a Hassler cell with 500-psi overburden pressure. Polymer solutions (in the brine specified in a given figure in this paper) contained 1,750 ppm of a specified polymer and 20 ppm potassium iodide (KI; as a water tracer). Each pack was saturated with brine (without KI tracer) before being flooded with ~10 PV of polymer solution at a Darcy velocity of 1.86 ft/D. New sandpacks were used for each experiment (i.e., none were reused). All experiments were performed at room temperature (21°C). In the current experiments, the cores were completely water-saturated (i.e., no residual oil was present). **Table 2** summarizes the experimental conditions.

Temperature	21°C
Sandpack diameter	2.54 cm
Sandpack length	15.24 cm
Core confining pressure	500 psi
Oil saturation	0
Were packs reused?	No
Flood rate (Darcy velocity)	1.86 ft/D
Water tracer	20 ppm KI
Polymer	1,750 ppm Flopaam 3630S
HPAM MW	18 million g/mol
Effluent collection increment	3–4 cm^3
Polymer detection method	Chemiluminescent nitrogen

Table 2—Summary of experimental conditions.

Effluent from packs was analyzed by several methods. Routinely, we monitored a water tracer (20 ppm KI) using a Genesys 2™ spectrophotometer at a wavelength of 230 nm. Effluent polymer concentration was monitored by three methods—total organic carbon, total nitrogen, and viscosity. For total organic carbon, a Shimadzu TOC-L™ was used. We recognize that this measurement might be influenced by the presence of oil. Total nitrogen was measured using chemiluminescence with a Shimadzu TNM-L™ unit. Viscosity was measured at 7.3 s^{-1} (25°C) using proRheo LS-300™ and/or Vilastic VE™ rheometers. The previous measurements were made at 3–4 cm^3

increments for each effluent sample. For most figures in this paper, effluent concentrations are reported relative to the injected values. Also, because nitrogen detection is the most reliable measure of polymer concentration in our case, all effluent polymer concentrations reported in this paper are based on that method.

Polymer retention values were determined from the area between the effluent tracer and polymer concentrations, as described in Wang et al. (2020) and Seright and Wang (2022). For reasons detailed in these previous publications, the IAPV was assumed to be zero (basically because the polymer molecules were small enough to access all of the relatively large pore throats and pore bodies in our high-permeability porous media). Thus, Eq. 3 (from Manichand and Seright 2014) provides a means for the retention determination:

$$R_{pret} = \left\{\left[\sum\left[(C_p/C_{po} * \Delta\mathrm{PV}) - (C_t/C_{to} * \Delta\mathrm{PV})\right]\right] + \mathrm{IAPV}\right\} * C_{po} * \mathrm{PV}/M_{\mathrm{rock}}, \qquad (3)$$

where R_{pret} is the polymer retention, C_p is the effluent polymer concentration, C_{po} is the injected polymer concentration, C_t is the effluent tracer concentration, C_{to} is the injected tracer concentration, PV is the volume in 1 PV, ΔPV is the PV increment, and M_{rock} is the rock mass in the sandpack.

Results

Effect of Salinity and Hardness for Polymer Retention on Illite. We examined the effect of salinity and hardness (divalent cation content) on polymer retention. These experiments used 1,750 ppm Flopaam 3630S in packs with 9% illite. Polymer retention results are shown in **Fig. 2,** while **Fig. 3** shows viscosity vs. shear rate (determined using a Vilastic V-E rheometer) for the solutions examined. The solid black curve in **Fig. 2** illustrates the typical retention tailing phenomenon that we have observed previously in bead packs with 9% illite when the brine was our “Milne Point injection brine” (composition indicated in the figure legend). The total polymer retention was 125 µg/g when the brine contained 0.22% NaCl, 0.027% $CaCl_2$, and 0.0034% $MgCl_2$. The dashed black curve shows that similar tailing and retention were noted (114 µg/g) for a similar salinity but with no magnesium (0.18% NaCl, 0.06% $CaCl_2$). When synthetic Milne Point formation brine was used (solid green curve: 2.56% NaCl, 0.065% $CaCl_2$, and 0.11% $MgCl_2$), polymer retention was modestly greater (145 µg/g)—even though salinity was about ten times greater and hardness was about six times greater than for the Milne Point injection brine case (solid black curve). The solid green curve exhibited about the same retention tail as the solid black curve, but a significant delay in polymer arrival was noted for the green curve, whereas the delay was not seen for the solid black curve.

When using 2.76% NaCl with no divalent cations (the solid blue curve in **Fig. 2**), polymer retention was much lower (38 µg/g). Thus, it appears that much of the polymer retention on illite is tied to the presence of divalent cations. To further test this idea, experiments were performed using a brine with 1.8% NaCl and 0.6% $CaCl_2$ (dashed green curve in **Fig. 2**). This case had roughly the same total salinity as the Milne Point formation brine (solid green curve) and the 2.76% NaCl brine (solid blue curve), but the calcium content was much higher and a substantially greater polymer retention was seen (248 µg/g). We tried to prepare polymer solutions with even higher calcium concentrations, but the HPAM would not dissolve fully in those brines. Another case was tested with 0.9% NaCl and 0.3% $CaCl_2$, leading to a polymer retention of 281 µg/g (dashed red curve in **Fig. 2**). For these last two cases, note that retention is higher primarily because of the delay in arrival of the HPAM. The retention “tail” is not greatly different from most of the other cases in **Fig. 2**. The overall conclusion here is that HPAM retention on illite is dominantly dictated by divalent ion content—much more so than salinity, injection rate, polymer concentration, polymer MW, degree of hydrolysis, polymer solution viscosity, presence/absence of residual oil, or wettability state (from our previous studies: Wang et al. 2020; Seright and Wang 2022). In Milne Point injection brine, Seright and Wang (2022) demonstrated that retention in bead packs with 9% illite was not sensitive to viscosity or polymer concentration between 200 ppm and 1,750 ppm HPAM (3630S)—corresponding to viscosities (at 7.3 s^{-1}) between 4 cp and 45 cp.

Effect of Polymer ATBS Content for Polymer Retention on Illite. We also examined the effect of ATBS content on polymer retention on illite. ATBS is a monomer that is much more resistant to hydrolysis and precipitation than acrylamide and can impart substantial long-term stability to HPAM-type polymers (see Seright et al. 2021). A comparison of the solid blue and black curves in **Fig. 4** reveals that inclusion of only 3–7% ATBS into HPAM dramatically reduced polymer retention on illite with Milne Point injection water (0.22% NaCl, 0.027% $CaCl_2$, and 0.0034% $MgCl_2$)—from 125 µg/g for Flopaam 3630 S to only 14 µg/g for Flopaam 5205XV.

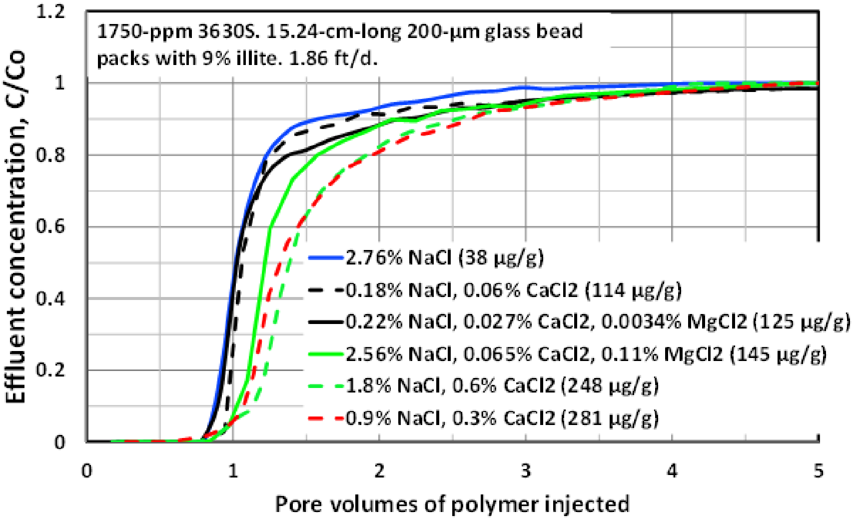

Fig. 2—Divalent cations accentuate HPAM retention.

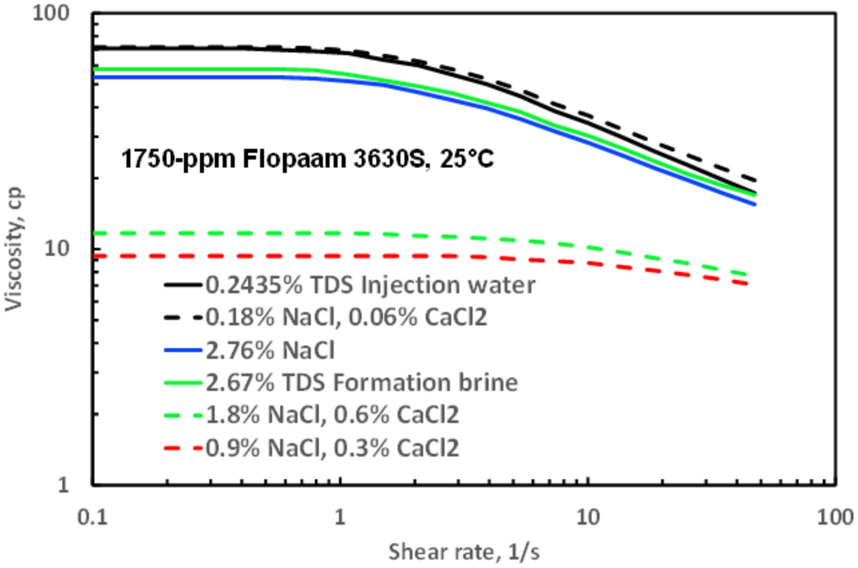

Fig. 3—Viscosity vs. shear rate for HPAM in various brines.

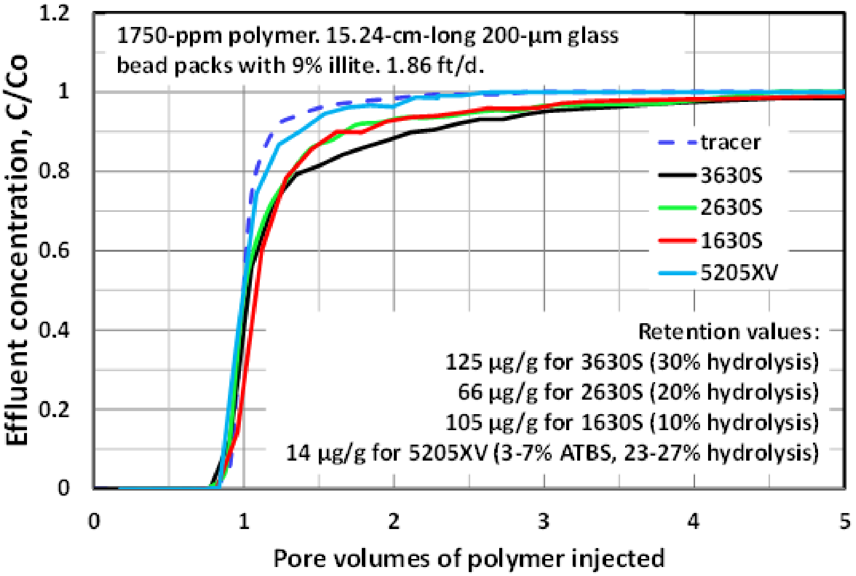

Fig. 4—Polymer retention on illite using Milne injection water.

Based on our results in **Fig. 4**, we performed additional studies to examine the effect of ATBS content on polymer retention on illite in brine with 1.8% NaCl and 0.6% $CaCl_2$. We guessed that any retention differences would be accentuated using this high-hardness brine. **Fig. 5** confirms that polymer retention decreased substantially with increased ATBS content—from 248 μg/g with Flopaam 3630S (0% ATBS) to 70 μg/g with Flopaam 5205XV (3–7% ATBS) to only 3 μg/g for AN125 (25% ATBS). These results suggest that polymer retention (at least on illite) could be dramatically reduced in hard brines by using a polymer with some ATBS in it. (For the various polymers, viscosities at 7.3 s^{-1} were roughly 45 cp in **Fig. 4** and 11 cp in **Fig. 5**.)

Further confirmation is provided in **Fig. 6,** which compares retention in Milne Point (Schrader Bluff) NB1 sand for 1750 ppm SNF Flopaam 5205XV (3–7% ATBS) with the same concentration of Flopaam 3630S (0% ATBS). (Both solutions and experiments used Milne Point injection brine.) Polymer retention was effectively zero for Flopaam 5205XV but was 336 μg/g for Flopaam 3630S.

Effect of Mineralogy on Polymer Retention in a High-Hardness Brine. Additional experiments were performed to examine the impact of other mineralogy (besides illite) on polymer retention. Again, 1,750 ppm Flopaam 3630S was used. These studies focused on the high-hardness brine (1.8% NaCl and 0.6% $CaCl_2$) to accentuate differences in retention. All studies used 9% of the chosen mineral in 200-μm glass bead packs. **Fig. 7** provides the results. A comparison of the dashed and solid green curves reveals that kaolin exhibits the same behavior as illite (215 μg/g vs. 248 μg/g total retention). Retention on 9% dolomite or 9% $CaCO_3$ exhibited similar behavior in that (1) total retention values (45 μg/g and 59 μg/g, respectively) were much less than on either 9% kaolin or illite (215 μg/g and 248 μg/g, respectively) and (2) retention tailing was far less evident than on kaolin or illite. Although the retention curves for dolomite (solid red curve) and $CaCO_3$ appear notably different in **Fig. 7**, this occurred primarily because the water-tracer breakout curves were substantially

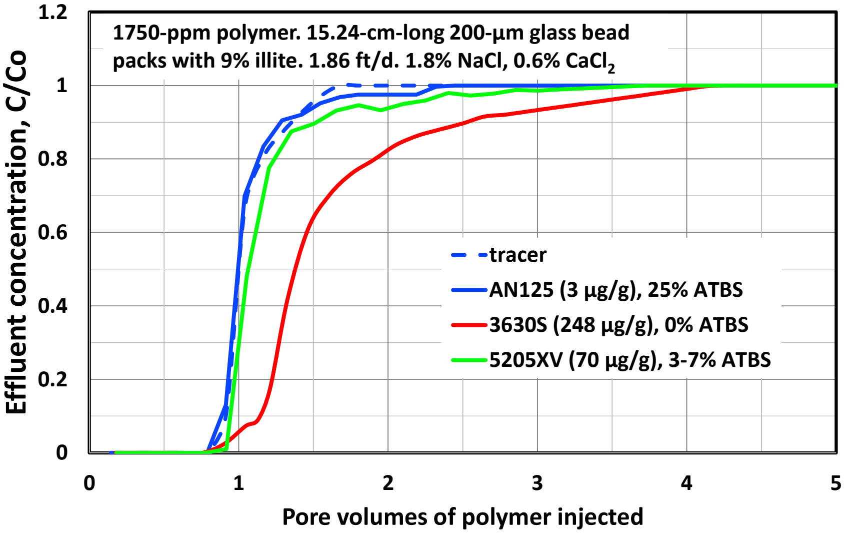

Fig. 5—Effect of ATBS content on polymer retention with a hard brine.

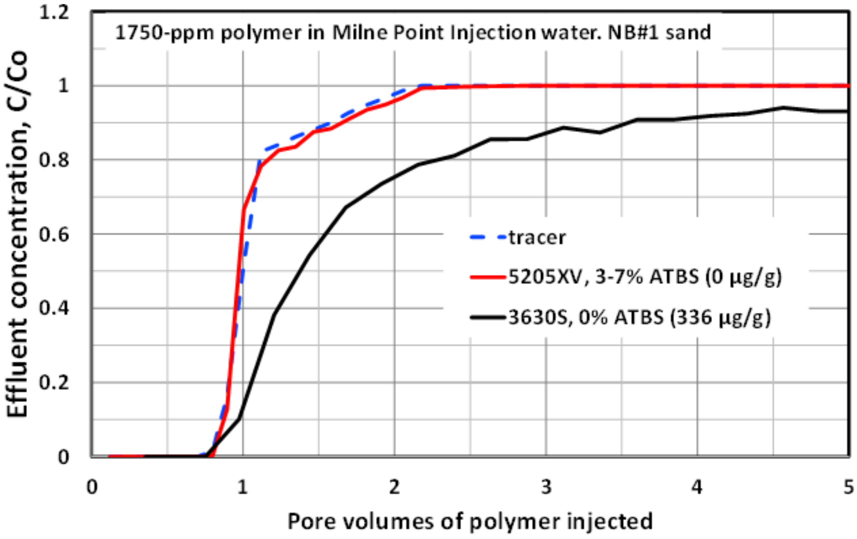

Fig. 6—A small amount of ATBS reduces polymer retention in NB1 sand.

different. The tracer (and polymer) curves for 9% $CaCO_3$ were more spread out than normal because the pack was more heterogeneous than normal for our bead-pack experiments.

In summary, **Fig. 7** reveals that HPAM retention is significantly greater on kaolin and illite than on dolomite or limestone ($CaCO_3$). Also, consistent with our earlier studies (Seright and Wang 2022), the retention tailing effect occurs dominantly with kaolin and illite rather than with other minerals.

Bridging Adsorption as a Proposed Mechanism

At this point, we suggest a mechanism to explain our observations in this paper, along with those made in Wang et al. (2020) and Seright and Wang (2022). As mentioned in the discussion associated with Eqs. 1 and 2, we earlier established a correlation to account for many of the previous findings. Eq. 2 indicates that two exposure-dependent exponential terms are needed to describe HPAM retention on illite, but the equation does not actually reveal a mechanism for the retention process. In this section, we propose bridging adsorption as a mechanism to explain our results. Bridging adsorption was introduced as a mechanism for HPAM retention by Zitha et al. (1998) and Zitha and Botermans (1998). They noted that flexible polymers in solution (like HPAM) adsorb onto grains in a serpentine fashion, as illustrated in **Fig. 8.** In high-permeability sands, as we commonly use, most pore-throat radii are too large (>5 μm) for normal HPAM molecules (0.1–0.5 μm) to bridge. However, for very small pores associated with very low-permeability porous media, the intergrain distance may be small enough to allow some polymer strands to bridge. Usually, EOR polymer solutions are well above the critical overlap concentration. However, the temporary entanglements of different polymer molecules do not constitute a bridge between grains. An adsorption bridge must involve a single polymer molecule. In our case, where we have clay (e.g., illite) dispersed on sand or glass bead surfaces in a very permeable porous medium, bridging adsorption could occur across the small clay pores or pore throats.

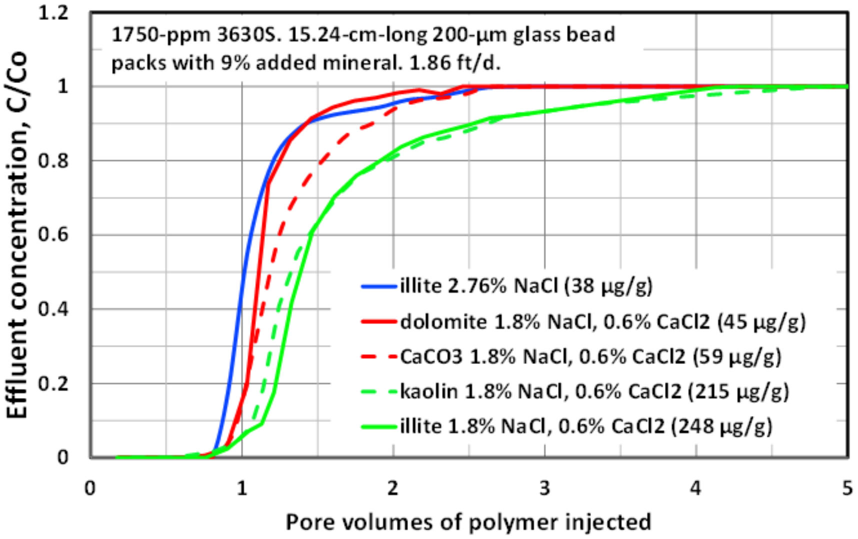

Fig. 7—Impact of mineralogy on HPAM retention with a hard brine.

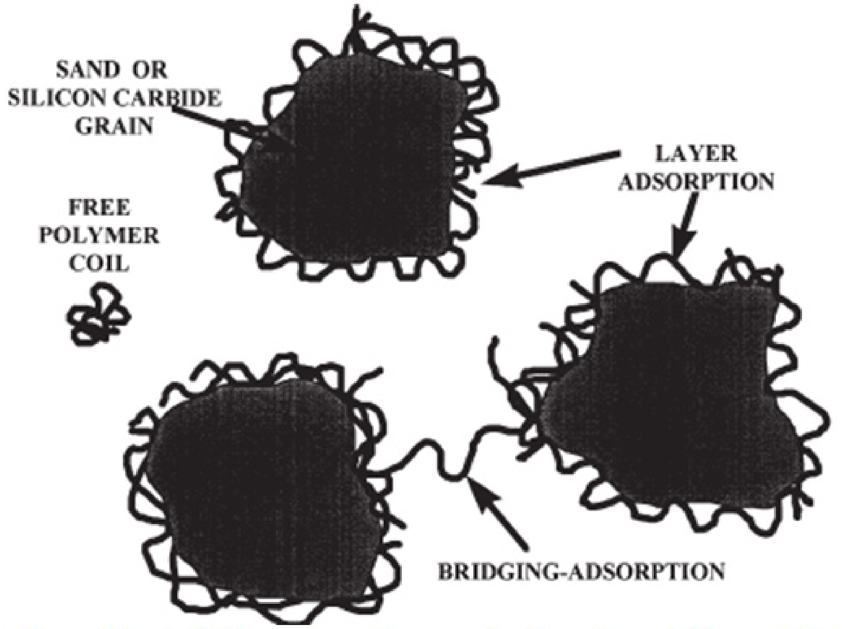

Fig. 8—Illustration of the bridging-adsorption mechanism (from Zitha and Botermans 1998).

How well does this model explain our results? First, it accounts for the existence of the "tailing" effect. The first exponential in Eq. 2 describes normal polymer adsorption on any surfaces present. The second exponential in Eq. 2 describes the retention "tail"—which in the bridging mechanism would be the more gradual process of long high-MW polymers attaching between clay grains. This concept is consistent with the observation that pressure drops across the cores always stabilized quickly during the retention experiments (i.e., pressure drops did not gradually increase as might be expected when associated with the retention tail). (Some advocate that polymer retention is directly tied to an increase in pressure gradient during flow through cores.) Bridging the adsorption of polymer between clay grains would not block flow along the main pore channels that dominate the permeability.

Also, the slight dependence on flow rate/time for the "tail" part of retention can be rationalized. **Fig. 9** (from Seright and Wang 2022) shows that between 1 PV and 2.5 PV, effluent polymer concentrations were lower for the lower flood rates. In this period, flooding at reduced rates may allow the bridging mechanism to remove more polymer from the solution than at higher rates.

Strong support for the bridging-adsorption mechanism is provided by the MW-dependence of HPAM retention on illite, as shown in **Fig. 10.** This figure (data from Seright and Wang 2022) plots effluent concentrations when injecting 1,750 ppm HPAM with 30% degree of hydrolysis but with differing MW values, ranging from 0.3 million to 18 million g/mol. With the largest polymer (18 million g/mol), the most prominent retention tail is observed, while no retention tail is seen for the smallest polymer (0.3 million g/mol). Presumably, the smallest polymer is too small to bridge between clay grains. Also, the larger the HPAM molecule, the more bridging adsorption that occurs.

To explain the dependence of polymer retention on HPAM degree of hydrolysis **(Fig. 4)**, one can rationalize that the acrylate groups are most likely to contribute to polymer-surface bonding. HPAM with a 30% degree of hydrolysis (black curve in **Fig. 4**) contains the most

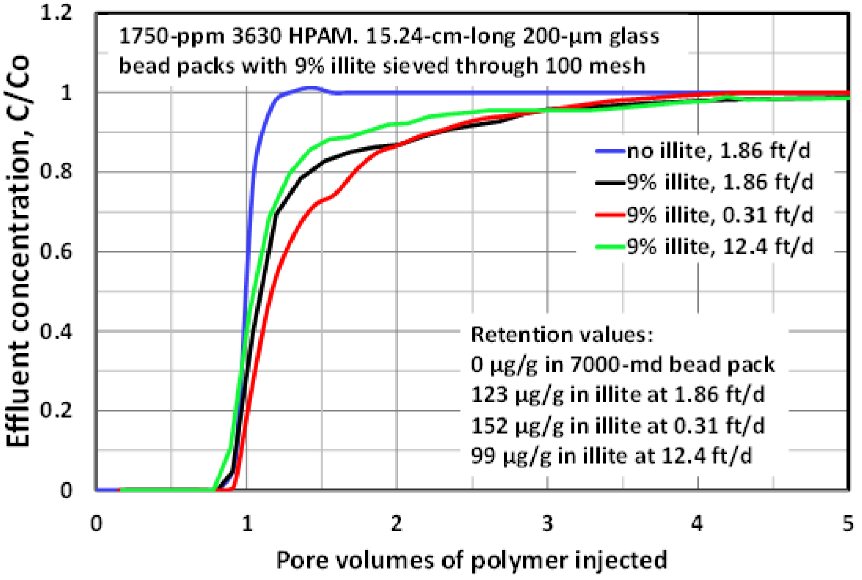

Fig. 9—Tailing phenomenon in 9% illite vs. flooding rate (from Seright and Wang 2022).

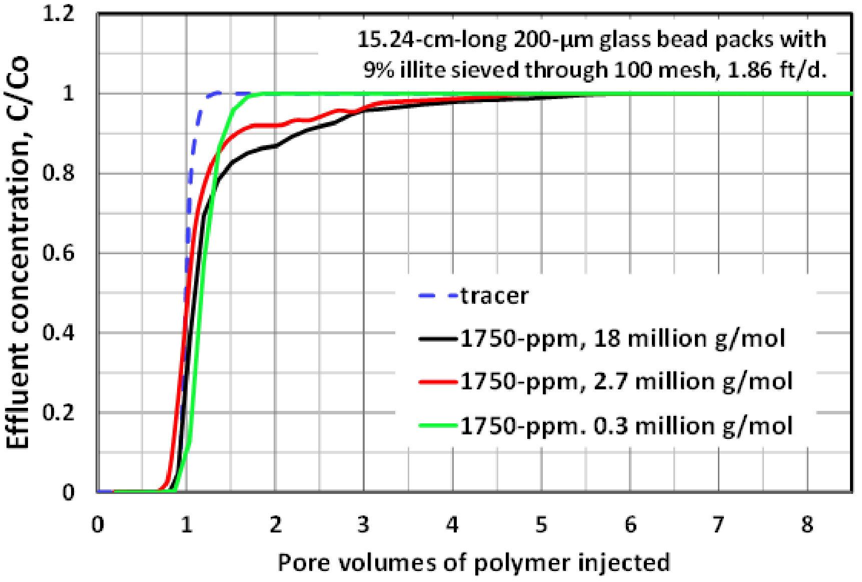

Fig. 10—Tailing phenomenon in 9% illite vs. flooding rate. Data from Seright and Wang (2022).

carboxylate groups and is therefore most likely to participate in bridging adsorption and exhibit the most prominent tail. The sulfonate groups (in ATBS copolymers) are much less likely to bond with the clay surface and apparently disrupt polymer-surface bonding and bridging adsorption (blue curve in **Fig. 4**, blue and green curves in **Fig. 5**, and red curve in **Fig. 6**). The increased retention associated with increasing divalent cation content **(Figs. 2 and 7)** can also be rationalized. Divalent cations are known to form strong interactions with acrylate groups—so much so that hydrolysis and precipitation are major problems for HPAM polymers at elevated temperatures (Seright et al. 2021). (Of course, it is well known that incorporation of ATBS groups into HPAM polymers reduces this problem, because the ATBS sulfonate groups do not interact strongly with divalent cations.) If divalent cations accentuated the bridge between the HPAM carboxylate groups and the clay surface (i.e., forming a carboxylate-cation-surface bond), that would be consistent with the high retention values and prominent retention tails seen for kaolinite and illite in **Fig. 7** (i.e., the green curves). Clays are commonly known for exhibiting ion exchange involving monovalent and divalent cations. This phenomenon supports the idea that the bridging of divalent cations between the clay and HPAM carboxylate groups may play an important role in the sensitivity of polymer retention to divalent cation concentration.

Conclusions

1. In reviewing the literature before 2023, a consensus appears concerning several aspects of polymer retention in porous media. One aspect of the review that may surprise some is that polymer retention is typically not greatly affected by the presence of residual oil. Although many authors reported polymer retention to be modestly lower (by as much as half) with oil present vs. without, many other

cases were noted where polymer retention was the same or greater without oil present vs. with. Only two cases were noted where polymer retention was dramatically lower (i.e., 6–10 times lower) with oil present vs. without.

2. In contrast to the case for polymer retention, a review of IAPV in the petroleum literature reveals serious discrepancies. The many inconsistencies in reported IAPV values may be due to incomplete and inconsistent volumes of brine flushed during IAPV measurements. When designing a polymer flood in reservoirs with moderate to high permeabilities (>500 md), IAPV should be assumed to be zero.
3. Laboratory retention studies in this work demonstrated that HPAM retention on illite (the dominant clay at the Milne Point polymer flood) was not sensitive to HPAM degree of hydrolysis or monovalent cation concentration. However, HPAM retention on illite increased significantly with increased divalent cation concentration.
4. HPAM retention on kaolinite showed very similar behavior to that on illite.
5. Retention on illite and Milne Point core material was found to be substantially lower for polymers containing ATBS than for normal HPAM polymers.
6. Bridging adsorption was proposed as a viable mechanism to explain our results.

Nomenclature

C = effluent concentration, mg/L or ~ppm (μg/g)
C_o = injected concentration, mg/L or ~ppm (μg/g)
C_p = effluent polymer concentration, mg/L or ~ppm (μg/g)
C_{po} = injected polymer concentration, mg/L or ~ppm (μg/g)
C_t = effluent tracer concentration, mg/L or ~ppm (μg/g)
C_{to} = injected tracer concentration, mg/L or ~ppm (μg/g)
C^* = polymer critical overlap concentration, mg/L or ~ppm (μg/g)
k = permeability, darcies (μm^2)
k_{wsor} = permeability to water at residual oil saturation, darcies (μm^2)
L_p = exposure parameter in Eqs. 1 and 2, cm-(wt. fraction)$^{0.5}$
M_{rock} = mass of rock in the sandpack, g
MW = polymer molecular weight, g/mol [daltons]
ΔPV = pore volume difference
R_{pret} = polymer retention, μg/g
S_{or} = residual oil saturation
t = time, seconds
t_{bt} = polymer breakthrough time in Eq. 2, seconds
u = Darcy velocity, cm/s

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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
md×9.869 233	E−04 = μm^2
psi×6.894 757	E+00 = kPa

* Conversion is exact