

# SPE 169027

# Field vs Laboratory Polymer Retention Values for a Polymer Flood in the Tambaredjo Field

R.N. Manichand, Staatsolie Maatschappij Suriname N.V., and R.S. Seright, New Mexico Tech

Copyright 2014, Society of Petroleum Engineers

This paper was prepared for presentation at the SPE Improved Oil Recovery Symposium held in Tulsa, Oklahoma, USA, 12–16 April 2014.

This paper was selected for presentation by an SPE program committee following review of information contained in an abstract submitted by the author(s). Contents of the paper have not been reviewed by the Society of Petroleum Engineers and are subject to correction by the author(s). The material does not necessarily reflect any position of the Society of Petroleum Engineers, its officers, or members. Electronic reproduction, distribution, or storage of any part of this paper without the written consent of the Society of Petroleum Engineers is prohibited. Permission to reproduce in print is restricted to an abstract of not more than 300 words; illustrations may not be copied. The abstract must contain conspicuous acknowledgment of SPE copyright.

# Abstract

During a polymer flood, polymer retention can have a major impact on the rate of polymer propagation through a reservoir, and consequently, on oil recovery. A review of the polymer-retention literature revealed that iron and high-surface-area minerals (e.g., clays) dominate polymer retention measurements in permeable rock and sand (>100 md). A review of the literature on inaccessible pore volume revealed inconsistent and unexplained behavior. A conservative approach to design of a polymer flood in high-permeability (>1 darcy) sands would assume that inaccessible pore volume is zero. Laboratory measurements using fluids and sands associated with the Sarah Maria polymer flood in Suriname suggested polymer retention and inaccessible pore volume values near zero. A procedure was developed using salinity-tracer and polymer concentrations from production wells to estimate polymer retention during the Sarah Maria polymer flood in the Tambaredjo reservoir. Field calculations indicated much higher polymer retention values than lab tests, typically ranging from ~50 to 250  $\mu g/g$ . Field cores necessarily represent an extremely small fraction of the reservoir. Because of the importance of polymer retention, there is considerable value in deriving polymer retention from field results, so that information can be used in the design of project expansions.

# Introduction

Since 2008, Staatsolie's Sarah Maria polymer flood pilot project (with three injectors and 10 producers) has been underway in the Tambaredjo field in Suriname (Moe Soe Let *et al.* 2012, Manichand *et al.* 2013). Low-salinity water [500-ppm (parts per million) TDS] with polymer was injected to displace viscous oil, where the formation water salinity was 4700-ppm TDS. Because no waterflood was implemented between primary production and the polymer flood, produced water salinity could be used as a tracer. This paper demonstrates that by monitoring salinity and polymer concentration in the produced water, polymer retention could be estimated in different portions of the pilot project. The paper first discusses the importance of polymer retention during a polymer flood. Next, the literature is reviewed for laboratory methods of measuring polymer retention and factors affecting polymer retention and inaccessible pore volume. Then, results of laboratory retention measurements are presented using the polymer, sand, water, and temperature associated with the Sarah Maria polymer flood. Finally, results from the field project are analyzed to establish field polymer retention values for different patterns of the Sarah Maria polymer flood.

# **Importance of Polymer Retention**

Polymer retention delays polymer propagation through porous media. Consequently, high polymer retention can substantially delay oil displacement and recovery during polymer flooding and other chemical flooding processes. To illustrate this point, consider the range of polymer retention levels reported in the literature—9 to 700 µg/g (Green and Willhite 1998)—and the range of polymer concentrations used in polymer floods—500 to 3000 ppm. Given the rock density ( $\rho_{rock}$ , 2.65 g/cm<sup>3</sup> for quartz), porosity ( $\phi$ ), polymer retention in µg/g ( $R_{prel}$ ), and polymer concentration ( $C_{inj}$ ) in mg/L (or ~ppm), Eq. 1 can be used to calculate the delay ( $PV_{ret}$ , additional pore volumes of polymer solution that must be injected to contact one pore volume). *IAPV* is inaccessible pore volume, which will be discussed shortly.

 $PV_{ret} = \left[\rho_{rock} \left(1 - \phi\right)/\phi\right] \left[R_{pret}/C_{inj}\right] - IAPV \dots (1)$ 

Using this equation and the parameters mentioned above, Fig. 1 shows delay factors, assuming IAPV=0. With a very low

retention level of 10  $\mu$ g/g and a polymer concentration of 2000 ppm, the delay factor is only about 0.03 (3%) of one pore volume. With a moderate polymer retention value of 100  $\mu$ g/g and a polymer concentration of 1240 ppm, the delay factor is 0.5 (50%)—meaning that 50% more polymer must be injected to reach a target distance in the formation, relative to the case for no polymer retention. For values greater than 200  $\mu$ g/g, polymer retention can have a serious impact on oil displacement rate and the economics of polymer flooding.



Fig. 1—Polymer bank delay factors associated with polymer retention.

#### Methods of Measuring Polymer Retention

Several methods have been proposed to measure polymer retention and inaccessible pore volume (API RP63 1990, Dawson and Lantz 1972, Szabo 1975, 1979, Dominguez and Willhite 1977, Gupta and Trushenski 1978, Castagno *et al.* 1987, Huh *et al.* 1990, Mezzomo *et al.* 2002, Zhang and Seright 2013). Several of them advocate injection of a slug of polymer solution, followed by brine, and performing a mass balance on the polymer (i.e., retention = polymer injected minus polymer produced). Key problems with this type of method are (1) recovery of the polymer may require an extended period of brine injection because of the unfavorable displacement and (2) cumulative errors associated with measurements of low polymer concentrations in the produced fluid can introduce considerable uncertainty to the mass balance.

Static methods have also been used to measure polymer adsorption/retention (API RP63 1990, Chiappa, *et al.* 1999). In this method, polymer concentration is measured before and after exposure to sand. Polymer adsorption is assessed by dividing the loss of mass from the solution by the weight of the exposed sand. One criticism of this method is that it relies heavily on only two measurements of polymer concentration, so errors in those measurements have a substantial impact on the calculated adsorption value. A second criticism is that if rock must be pulverized to make the sand, surface area and minerals may be exposed that might not be available during dynamic experiments (where polymer solutions flow through the porous rock). Further, the method does not account for polymer that may be mechanically entrapped.

We prefer the method used by Lotsch *et al.* (1985), Hughes *et al.* (1990), and Osterloh and Law (1998). In this method, a bank of polymer solution is injected into a core or sand pack with a tracer. After the effluent concentrations for both polymer and tracer reach the injected concentrations, many (e.g., ~100) pore volumes of brine are injected to displace all mobile polymer and tracer. Subsequently, a second bank of polymer solution is injected with the tracer. Polymer retention and inaccessible pore volume 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. Inaccessible pore volume (*IAPV*) is determined during the second injection cycle from the difference in area between the polymer breakout curve and the tracer breakout curve. Specifically, Eq. 2 is used.

$$IAPV = \Sigma \left[ (C_{poly}/C_{polyo} * \Delta PV) - (C_{trac}/C_{traco} * \Delta PV) \right] \dots (2)$$

Next, polymer retention is determined during the first injection cycle from the difference in area between the polymer breakout curve and the tracer breakout curve. Specifically, Eq. 3 is used.

$$R_{pret} = \{ \left[ \sum \left[ (C_{poly}/C_{polyo} * \Delta PV) - (C_{trac}/C_{traco} * \Delta PV) \right] + IAPV \} * C_{polyo} * PV / M_{rock} \dots (3) \} \}$$

Here,  $C_{poly}$  is effluent polymer concentration,  $C_{trac}$  is effluent tracer concentration,  $C_{polyo}$  is the injected polymer concentration,  $C_{traco}$  is the injected tracer concentration, PV is the volume in one pore volume,  $\Delta PV$  is pore-volume increment, and  $M_{rock}$  is the rock mass in the core.

# **Components of Polymer Propagation**

Polymer propagation through porous media is governed by polymer retention and inaccessible pore volume. Inaccessible pore volume will be discussed in more detail later, but basically, it accelerates polymer flow through porous rock (relative to the rate of solvent propagation) because large polymer molecules cannot penetrate into all pore space that is available to the solvent (Dawson and Lantz 1972).

**Polymer Adsorption.** Polymer retention is comprised of polymer adsorption and mechanical entrapment (Gogarty 1967). Polymer adsorption is the adhesion of the polymer molecules onto the rock surface. Because EOR polymers have high molecular weights and extended chains, many polar groups along the polymer chain will attach to many different polar points on the rock surface. Consequently for practical purposes, polymer adsorption is irreversible (Lee and Fuller 1985, Green and Willhite 1998). Although a given polar group of a polymer may detach from the rock, other points of attachment will stay in place. By the time additional polar groups detach, it is likely that the previously detached group will reattach to the rock. It is statistically very unlikely that a polymer molecule would release all points of attachment at the same time.

**Mechanical Entrapment.** Because of their large size, polymer molecules may become physically trapped in porous media. Several mechanisms have been offered for these trapping processes, including hydrodynamic retention (Maerker 1973, Dominguez and Willhite 1977), "straining", deep-bed filtration, trapping in dead-end pores (Szabo 1975, 1979, Huh *et al.* 1990), and bridging adsorption (Zitha and Botermans 1998, Zitha *et al.* 1998). Some aspects of mechanical entrapment are reversible (such as hydrodynamic retention), while others are not. Based on seven experiments in 100-to-130-md Berea sandstone, Huh *et al.* (1990) indicated that about half of xanthan retention was attributed to adsorption and half was due to mechanical entrapment.

Some suggest that adsorption may be the dominant mechanism for polymer retention in high-permeability sands (Huh *et al.* 1990), while mechanical entrapment dominates in low-permeability rock (Szabo 1975, 1979, Dominguez and Willhite 1977, Huh *et al.* 1990). In contrast, in a 5.6-darcy silica pack, Cohen and Christ (1986) suggested that adsorption accounted for 35.2% of the HPAM retention, while mechanical entrapment and hydrodynamic retention accounted for the remainder. It is worth noting that most current large polymer floods are in reservoirs with high-permeability sands or sandstones (Daqing: 800 md; Pelican Lake: 1-3 darcys; Mangala: 5 darcys; Marmul: 15 darcys, Dalia: >1 darcy; Tambaredjo: 4-12 darcys).

# **Review of Factors Affecting Polymer Retention**

**Polymer Charge.** Next, we discuss the relative importance of several variables for polymer retention. **Table 1** summarizes these effects. In a brine with 2.2% TDS, MacWilliams *et al.* (1973) reported that HPAM adsorption onto Miocene sand was around 30  $\mu$ g/g if the degree of hydrolysis was between 25% and 70%. However, as the degree of hydrolysis was reduced from 15% to 2%, HPAM adsorption increased from ~60  $\mu$ g/g to ~700  $\mu$ g/g. It was presumed that adsorption was reduced by charge repulsion between the polymer's acrylate groups and anionic groups on the quartz. Based on this logic, most HPAM polymers used for chemical flooding contain at least 20% anionic monomers. However, subsequent work has raised doubts about the importance of the degree of hydrolysis to polymer retention. In unconsolidated sand packs, Martin and Sherwood (1975) noted a modest increase in retention as the degree of hydrolysis increased from 0 to 15%. Also, Meister *et al.* (1980) observed that retention in Berea sandstone was about the same for an acrylamide homopolymer (10.2  $\mu$ g/g) as for HPAM with 22% degree of hydrolysis (8.3  $\mu$ g/g)—in brine with 0.5% NaCl. Meister *et al.* also observed that the acrylamide homopolymer showed significantly lower retention (1.9  $\mu$ g/g) in Baker dolomite than the HPAM (8.4  $\mu$ g/g).

During static adsorption studies, Chiappa, *et al.* (1999) found adsorption on to quartz sand was two to four times higher for a cationic (degree of cationicity not reported) polyacrylamide than for an anionic (23% degree of hydrolysis) HPAM. On pure quartzite with 1%-5% KCl, they found HPAM adsorption to be comparable to that for a weakly anionic polyacrylamide (i.e., near zero degree of hydrolysis). However, with no added KCl (i.e., distilled water), HPAM adsorption was about 5 times lower than that for PAM. Skauge (2013) suggested that sulfonate incorporation can dramatically reduce HPAM retention.

**Salinity.** Martin *et al.* (1983) compared polymer retention for seven commercial HPAM polymers (with 25-35% hydrolysis) in 350-to-550-md Berea sandstone. In a given brine, these polymers showed retention values of  $15.5\pm3 \mu g/g$  in 0.1% NaCl and  $25.1\pm2.1 \mu g/g$  in 2% NaCl. Under the same conditions, retention values for three commercial xanthans were less than half those of the HPAM polymers. In contrast to the work of Martin *et al.* (1983), Mungan (1969) did not observe a consistent difference in adsorption for HPAM in distilled water versus in 2% NaCl solution—i.e., values in sands (Ottawa sand, silica powder, and disaggregated Berea sandstone) ranged from 270 to 880  $\mu g/g$  in distilled water versus from 70 to 675  $\mu g/g$  in 2% NaCl. Interestingly, both Mungan and Martin *et al.* examined Dow Pusher 500 and 700 HPAMs during their studies. In 2% NaCl, Mungan's retention values were typically about ten times higher than those of Martin *et al.*—possibly reflecting differences in experimental technique.

During static adsorption studies, Chiappa, *et al.* (1999) found adsorption on quartzite for a cationic polyacrylamide to be nearly independent of salinity, between 0% and 13% KCl (~610  $\mu$ g/g). For HPAM (with 23% degree of hydrolysis), they noted adsorption on quartzite increased from ~60  $\mu$ g/g with no CaCl<sub>2</sub> present to ~750  $\mu$ g/g with 8% CaCl<sub>2</sub> in the brine. To explain this behavior, they proposed calcium bridging from the anionic rock to the anionic polymer. Consistent with their hypothesis, they also noted that adsorption of cationic polyacrylamide was nearly independent of CaCl<sub>2</sub> content.

Table 1—Summary of polymer retention effects.							
	Polymer	Retention, µg/g	Reference				
MINERALOGY and POLYMER TYPE: Clay and Iron are VERY important!							
montmorillonite	CPAM	180,000	Chiappa <i>et al</i> .				
quartzite with 8% montmorillonite	CPAM 14500		Chiappa et al.				
quartzite	CPAM	610	Chiappa et al.				
kaolinite	Xanthan	16900	Hughes et al.				
siderite	Xanthan	15600	Hughes et al.				
kaolinite	HPAM	1500-8000	Chauveteau et al.				
kaolinite	HPAM	339-1217	Meister et al.				
Berea (350-550 md)	HPAM	22 ± 6	Martin <i>et al</i> .				
Berea (350-550 md)	Xanthan	10.7 ± 3	Martin et al.				
calcium carbonate	HPAM	20-100	Szabo				
Baker dolomite	HPAM	1.9-17.8	Meister et al.				
99% quartz	HPAM	15	Zaitoun & Kohler				
DEGREE OF HYDROLYSIS: Conf	licting message	e, but generally m	inor importance.				
Berea, 0% hydrolysis PAM	PAM	10.2	Meister et al.				
Berea, 22% hydrolysis HPAM	HPAM	8.3	Meister et al.				
Miocene sand, 0% hydrolysis	PAM	~700	MacWilliams et al.				
Miocene sand, 25-70% hydrolysis	HPAM	~30	MacWilliams et al.				
POLYMER CONCENTRATION: De	epends on conc	entration regime					
10 ppm to 6000 ppm	HPAM	20-420	Zhang & Seright				
20 ppm to 1000 ppm	HPAM	21-30	Green & Willhite				
250 ppm to 1500 ppm	HPAM	40-58	Zheng et al.				
50 ppm to 200 ppm	Scleroglucan	8.2-11.7	Huang & Sorbie				
SALINITY: NaCl content not so in	nportant. Calciu	um content may b	e important.				
0.1% to 2% NaCl	HPAM	15-25	Martin et al.				
quartzite, 0% CaCl <sub>2</sub>	HPAM	60	Chiappa et al.				
quartzite, 8% CaCl <sub>2</sub>	HPAM	~750	Chiappa <i>et al</i> .				
OIL SATURATION: Minor effect.							
quartz sand with or without oil	HPAM	~35	Brosetta et al.				
Reservoir core without oil	xanthan	~75	Hughes et al.				
Reservoir core with oil	xanthan	30-55	Hughes et al.				
Berea sandstone without oil	xanthan	nthan 31 Huh et a					
Berea sandstone with oil	xanthan	49-72	Huh <i>et al</i> .				
PERMEABILITY: Very important below 100 md. Less important above 200 md.							
2100-md Vosges sandstone	HPAM	155	Zaitoun & Kohler				
520-md Vosges sandstone	HPAM	140	Zaitoun & Kohler				
137-md reservoir sandstone	HPAM	12	Vela <i>et al.</i>				
12-md reservoir sandstone	HPAM	~130	Vela et al.				

Table 1—Summar	y of	poly	ymer r	etenti	on ef	fect	S
----------------	------	------	--------	--------	-------	------	---

Polymer Concentration. HPAM retention was usually reported as modestly sensitive to polymer concentration. Green and Willhite (1998) noted retention in Berea sandstone increasing from  $21-24 \ \mu g/g$  at ~20-ppm polymer to ~30  $\ \mu g/g$  at ~1000ppm polymer. Zheng et al. (2000) observed HPAM retention in Berea increasing from 40  $\mu$ g/g at 250 ppm to 58  $\mu$ g/g at 1500 ppm. For six sets of experiments in silica flour, Szabo (1979) reported adsorption increased from 35% to 70% as polymer concentration increased from 150 ppm to 1200 ppm. Friedmann (1986) saw no effect of polymer concentration on retention (in Berea sandstone) between 200- and 1,000-ppm HPAM. Huang and Sorbie (1993) observed that scleroglucan retention (in Ballotini glass bead packs) increased from 8.21  $\mu$ g/g at 50 ppm to 11.71  $\mu$ g/g at 200 ppm. During experiments with HPAM concentrations ranging from 10 to 6000 ppm, Zhang and Seright (2013) reported three regimes of retention behavior: (1) relatively low retention (but concentration-insensitive) at low polymer concentrations (e.g., ~20 µg/g between 10 and 100 ppm), (2) retention increasing with increased polymer concentration at intermediate polymer concentrations (e.g., rising to  $\sim 200 \ \mu g/g$  between 100 and 1000 ppm), and (3) relatively high retention (but concentration-insensitive) at high polymer concentrations. They proposed a conceptual model to explain this behavior.

For the above cases, the experimental behavior did not appear to be consistent with the Langmuir isotherm. Ironically, most chemical flooding simulators use the Langmuir isotherm to describe polymer retention (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 polymer retention (1) approaches zero at low polymer concentrations and (2) is reversible. Both of these assumptions have generally been proven false (Green and Willhite 1998). As the main author with exceptions, Szabo (1975, 1979) reported several adsorption experiments of HPAM on silica sand and calcium carbonate powder that appeared to follow Langmuir isotherms. Use of the Langmuir isotherm for polymer adsorption was introduced by Dawson and Lantz in 1972-without experimental justification. Apparently, they assumed that polymers would follow the same adsorption behavior as surfactants.

Chauveteau *et al.* (1987) reported that HPAM adsorption on sodium kaolinite was between 1,500 and 8,000  $\mu$ g/g, depending on salinity and degree of hydrolysis. For a given salinity, they found that HPAM adsorption was independent of degree of hydrolysis between 20% to 50%. Adsorption increased as degree of hydrolysis decreased from 20% to 0%—by 30% with 24% NaCl brine and by a factor of five with 0.2% NaCl brine. Also, for HPAM polymers with more than 20% degree of hydrolysis, adsorption on kaolinite was about four times greater in 24% NaCl brine as in 0.2% NaCl brine.

In a 2.9-darcy sand with 99% quartz, Zaitoun and Kohler (1987) observed xanthan adsorption of 15  $\mu$ g/g; whereas in a 790-md sand with 50% quartz, 10% carbonate, and 15% clay, they noted adsorption of 90  $\mu$ g/g.

Szabo (1979) typically observed HPAM adsorption values from 20 to 100  $\mu$ g/g on calcium carbonate powder, depending on the polymer and salinity. Based on field data, Zettlitzer and Volz (1992) found HPAM retention values from 8 to 15  $\mu$ g/g in the German Hankensbuettel-Sued oil field—a 2-to-4-darcy sand with 5% clay.

During static adsorption studies, Chiappa, *et al.* (1999) found adsorption for a cationic polyacrylamide (in 2% KCl) to be 610  $\mu$ g/g on quartzite, 14,500  $\mu$ g/g on quartzite with 8% clay (Wyoming montmorillonite), and 180,000  $\mu$ g/g on pure Wyoming montmorillonite.

**Oil Saturation**. Broseta *et al.* (1995) examined polyacrylamide retention in a water-wet 5-to-6-darcy quartzitic natural sand pack with/without a residual saturation (16% dodecane). They found retention values of ~ 35  $\mu$ g/g for both cases—suggesting that non-wetting oil did not significantly affect retention. In a water-wet system (with a mineral oil in a silica sand pack), Szabo (1975) found that HPAM retention at residual oil saturation was 40% to 100% of that with no oil present—suggesting that the presence of residual oil may reduce HPAM retention somewhat. Similarly, Kolodziej (1988) found that xanthan retention in 600-md Berea sandstone with a residual oil saturation was about half that for a core without oil. Similarly, Hughes et al. (1990) measured retention values of 30 to 55  $\mu$ g/g in the presence of residual oil and about 75  $\mu$ g/g at zero oil saturation. They also found that the *IAPV*'s were 30% at residual oil and 20-25 % at zero oil saturation.

Huh *et al.* (1990) studied xanthan retention in 100-to-130-md Berea cores with/without residual oil (dodecane). The Berea sandstone was found to contain 85% quartz and 5% clay. Xanthan retention with no oil present (127-md Berea) was calculated to be 31  $\mu$ g/g. When residual oil saturation was present, the endpoint permeability to water was 25-41 md, and retention values ranged from 49 to 71.5  $\mu$ g/g, depending on xanthan source and concentration. Thus, in contrast to the above studies, polymer retention was actually greater at the residual oil saturation than in the absence of oil. Huh *et al.* attributed this finding to greater trapping of the polymer with decreased effective permeability of the core.

Broseta *et al.* (1995) reported that the presence of a residual oil (iso-octane) saturation increased HPAM retention in oilwet cores. However, since silane treatments were used to achieve hydrophobic wetting, doubts arise about the generality of this latter suggestion. In contrast using PAM and cationic polyacrylamide, Chiappa *et al.* (1991) found adsorption on oil-wet quartzite (aged in the presence of crude oil) was about half that on water-wet quartzite.

**Permeability Dependence of Polymer Retention.** For the discussion to this point, we have focused on relatively high porous media—generally of 500 md or more. In a given type of high-permeability porous media, polymer retention is generally insensitive to permeability. For example, Zaitoun and Kohler (1988) observed polyacrylamide retention values of 140  $\mu$ g/g in 0.52-darcy Vosges sandstone and 155  $\mu$ g/g in 2.1-darcy Vosges sandstone. (This sandstone contained 7% clay, mainly illite.)

For less-permeable rock, polymer retention typically increases dramatically with decreasing permeability. In reservoir cores at residual oil saturation, Vela *et al.* (1976) found HPAM (Pusher 700) retention values increased from ~12  $\mu$ g/g in 137-md sandstone to ~130  $\mu$ g/g in 12-md sandstone. Along with this increase in polymer retention, resistance factors and residual resistance factors increased by factors from 13 to 20. Hirasaki and Pope (1974) noted HPAM (Pusher 700) retention in sandstone was twice as high in an 80-md core as in a 359-md core.

As mentioned above, Huh *et al.* (1990) observed that xanthan retention in 100-to-130-md Berea sandstone at residual oil saturation (making the effective permeability 25-41 md) was about twice that in a 127-md Berea core without oil.

Length Dependence of Polymer Retention. Depending on the polymer and porous medium, a length-dependence was seen for polymer retention. At least two types of length dependence have been reported. In one form, a fraction of the polymer is clearly stripped from the solution at the sand face. Fletcher *et al.* (1991) reported two cases of this type—one with scleroglucan and one with xanthan. In a 157-md Brent core, they calculated 39  $\mu$ g/g retention of scleroglucan within the core and the equivalent of 17  $\mu$ g/g was filtered by the core face during the experiment. Similarly, in a 253-md Brent core, 36.5  $\mu$ g/g retention of xanthan was calculated within the core and the equivalent of 7  $\mu$ g/g was filtered by the core face.

In calcium-carbonate packs (12-cm long), Szabo (1979) found retention of Polymers 454 (HPAM) and 340 (acrylamide-AMPS copolymer) were independent of distance between 4 and 12 cm. However, retention at the core inlet was typically more than twice that at 4 cm.

In the second form of length dependence, polymer retention decreases somewhat gradually with distance into the porous

medium—suggesting that deep-bed filtration removes a high-molecular-weight component of the polymer. For example, in a 1,200-md sandpack, Szabo (1979) noted that "Polymer 454" HPAM (with 18% degree of hydrolysis) retention dropped gradually from 24  $\mu$ g/g near the core inlet to 7  $\mu$ g/g at a distance 24 cm into the pack. In contrast, for "Polymer 340" acrylamide-AMPS copolymer, retention was 1-2  $\mu$ g/g throughout the 24-cm-long sandpack.

Several authors have reported a "long tail" as the polymer effluent from the core gradually approaches the injected concentration (Szabo 1975, Martin and Sherwood 1975, Dominguez and Willhite 1977, Gupta and Trushenski 1978, Huang and Sorbie 1993). Several explanations have been offered for this behavior, including (1) high-molecular weight polymers/microgels propagating slowly through the core, (2) slow establishment of an equilibrium in adsorption and/or mechanical entrapment for the various polymer species in a molecular weight distribution, (3) heterogeneity within the core requiring extended flushing to displace fluid from the low-permeability path(s), and (4) chemical alteration of the injection composition (e.g., salinity, hardness, pH, etc.) causing an interference with the polymer detection method.

In 100-to-130-md Berea sandstone, Huh *et al.* (1990) concluded that flow through about 1 ft of core was needed to achieve equilibrium during polymer retention tests.

**Flow-Rate Dependence of Polymer Retention (Hydrodynamic Retention).** Maerker (1973) observed evidence that xanthan retention increased with increase fluid velocity in a 121-md Berea core. This phenomenon was also observed with HPAM in a Berea core. Maerker suggested that a significant pressure gradient causes polymer molecules to deform and become trapped within the core, in particular in relatively small pores. When flow stops or is reduced in rate, these molecules relax to a random coil configuration and subsequently diffuse to larger pore channels—temporarily increasing polymer concentration until the excess polymer is flushed from the core. Many have referred to this reversible phenomenon as "hydrodynamic retention." Maerker did not quantify the magnitude of this retention, as a function of flow rate.

Huh *et al.* (1990) concluded that xanthan retention in 100-to-130-md Berea (at residual oil saturation) was only 6% greater when determined at a velocity of 1/ft than at 0.333 ft/d. In separate experiments with a different xanthan in similar cores, polymer retention was 40% greater at 5 ft/d than at 1 ft/d.

**Key Observations for Polymer Retention.** Our review of the polymer retention literature revealed several key observations. First, clay and iron content in the rock or sand dominate polymer retention. Therefore, determining how much of these minerals are present in the target formation(s) is important prior to polymer flooding. Second, depending on the polymer type and molecular weight, polymer retention can increase dramatically with decreasing permeability, especially below 100 md. Most current polymer floods are applied in very permeable formations (greater than 500 md). Third, most (but not all) data suggests that the Langmuir isotherm does not appropriately describe polymer retention. Ironically, most commercial chemical flooding simulators use the Langmuir isotherm. Fourth, retention of xanthan is usually significantly less than that of HPAM. Fifth, the most reliable current means to measure polymer retention is the double-polymer/tracer-bank method used by Lotsch *et al.* (1985), Hughes *et al.* 1990, and Osterloh and Law (1998). Finally, studies to date suggest that polymer retention in the presence of residual oil is roughly half that in the absence of residual oil. Wettability has not been established as a key factor in polymer retention.

#### **Inaccessible Pore Volume**

Dawson and Lantz (1972) noted that polymer molecules propagated through sandstones more rapidly than salt ions in the solvent. They attributed this effect to a fraction of the pore space being inaccessible to the large polymer molecules but accessible to the small solvent and salt molecules and ions. In 470-md Berea sandstone, they concluded that HPAM (Pusher 700) experienced a 22% inaccessible pore volume (*IAPV*). In 681-md Berea, xanthan experienced an *IAPV* of 35%. In 2,090-md Bartlesville sandstone, HPAM experienced a 24% *IAPV*. By examining molecular weight distributions of HPAM effluent from cores, He *et al.* (1990) provided evidence that larger polymer molecules transit porous media faster than small polymer molecules.

**Small Pores and Pore Throats.** Several mechanisms can be envisioned to explain inaccessible pore volume for polymers (Liauh *et al.* 1979, van Domselaar and Fortmuller 1992). First, pores or parts of pore spaces may be large enough to accommodate small molecules (such as solvent, salts or tracers) but too small to allow entry of polymer molecules (Dawson and Lantz 1972). For perspective, the diameter of an EOR HPAM in a 3% NaCl brine is typically 0.5-0.8  $\mu$ m (Sorbie 1991). Also, an XMT analysis of 470-md Berea sandstone revealed that pores were highly connected and 98% of the pores had an effective diameter greater than 26  $\mu$ m and a pore throat diameter over 6.7  $\mu$ m (Seright *et al.* 2006, 2009). So a typical EOR HPAM molecule in solution is small compared to the pore and throat sizes and should have access to most spaces in moderate-to-high-permeability porous media. However, clay minerals present an obvious exception to the previous statement. The fraction of clay present could directly contribute to inaccessible pore volume, if small molecules can freely penetrate the clay but polymers cannot. For the samples used by Dawson and Lantz, Berea cores of that era typically had clay content around 5%. Further, unless the displacement is conducted very slowly, there is doubt that even small molecules would have time to sufficiently sample the clay (and therefore materialize as *IAPV*). Thus, some other mechanism appears needed to explain the 22%-35% *IAPV* values that they reported.

**Hydrodynamic Exclusion or "Depletion Layer".** Chauveteau (1981) and Sorbie (1991) argued that part of the observed *IAPV* phenomenon might be due to a "depletion layer". In concept, if the polymer does not adsorb onto the rock surface, then the center of mass for a large polymer molecule cannot get as close to the rock surface as a small solvent molecule or ion. Consequently, the region of fluid closest to the rock surface is depleted of polymer (and has a lower viscosity than 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.

The depletion-layer concept loses some credibility if polymers can adsorb on the rock surface. Advocates of the depletion layer argue that the adsorbed polymer layer simply moves the pore surface out towards the flow stream. However, the 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.

Further, in EOR applications, polymer concentrations are well above the critical overlap concentration, so the center of mass of a polymer molecule is not the appropriate basis to use for the depletion-layer thickness. Instead, the radius of an average overlap-polymer-blob segment should be used—a far smaller distance. In qualitative agreement with this concept, Shah *et al.* (1978) reported that *IAPV* (for a 5-million-dalton HPAM (Pusher 700) in 277-md Berea sandstone) decreased from 24% to 18.7% as HPAM increased from 51.5 to 1070 ppm. Kolodziej (1988) reported qualitatively similar results for xanthan. Liauh *et al.* (1979) argued that even with the maximum possible depletion layer, hydrodynamic exclusion could not provide an *IAPV* more than 9%.

**Thermodynamic Equilibrium.** Thermodynamic arguments have also been made, indicating that entropic effects will tend to push polymers away from solid boundaries (even in the absence of flow), toward the middle of pores (Dimarzio 1965, Meier 1967, Casassa 1967, Huh *et al.* 1990). However, if polymers adsorb onto a surface, the thermodynamics of that adsorption process must have already overcome these entropic effects.

**Experimental Results. Table 2** lists *IAPV* values that were reported in the literature. One might expect *IAPV* to increase with decreasing permeability. However, that trend was not observed. Using Pusher 700 HPAM, Dawson and Lantz (1974) observed about the same *IAPV* in 470-md Berea (22%) as in 2090-md Bartlesville sandstone (24%). Using Pusher 500 HPAM, Dabbous (1977) noted an *IAPV* value of 19% in 761-md Berea with no residual oil. In contrast, for the same polymer in Berea with a 28-35% residual oil, the permeability to water ranged from 49 to 61 md, and *IAPV* ranged from 17% to 37%. Why should *IAPV* values in a given rock remain in the same ball park when the presence of residual oil reduced permeability by factors of 12-16? One would think that a radical decrease in permeability would increase *IAPV*. Osterloh and Law (1998) reported *IAPV* values up to 48% in sand packs with permeabilities up to 11 darcys. However, they acknowledged the experimental difficulties of accurately determining *IAPV* values. Using a controversial method, Pancharoen *et al.* (2010) suggested *IAPV* values from 20%-40% in a 12-darcy sandpack. One wonders whether experimental difficulties are responsible for the wide, unexplained variation of *IAPV* values in Table 2.

Similarly for xanthan in reservoir sandstones with permeabilities ranging from 300 to 2400 md—with and without a residual oil saturation—*IAPV* values only ranged from 25% to 29% (Hughes *et al.* 1990). Qualitatively similar results were reported for xanthan by Kolodziej (1988).

As mentioned above, theoretical arguments raise questions about why the observed *IAPV* values were so high. Gilman and MacMillan (1987) pointed out that caution must be exercised when translating observed polymer breakthrough times to *IAPV* values if heterogeneities exist in the porous media.

Views differ concerning whether or not inaccessible pore volume is a benefit. For polymer flooding, many consider *IAPV* as a benefit because it accelerates polymer propagation into the formation and counteracts the retarding effects of polymer retention. In contrast, for surfactant floods, concern was expressed that accelerated polymer from the chase polymer bank will penetrate the surfactant bank and create a low-mobility polymer phase that compromises mobility control (Trushenski *et al.* 1974, Kolodziej 1988).

**Key Observations for Inaccessible Pore Volume.** A limited number of inaccessible pore volume values have been reported in the literature. The range of values reported is troubling, considering the conditions of the experiments. For example with a single polymer (Pusher HPAM) in Berea sandstone, *IAPV* values range from 0-4% in 90-to-120-md rock (Knight *et al.* 1974) to 19% in 761-md rock without residual oil (Dabbous 1977) to 17-37% in 49-to-61-md rock with residual oil (Dabbous 1977). The available theories for the *IAPV* phenomenon cannot explain the magnitude and odd variations of *IAPV* with changes in permeability (in Table 2). It seems likely that experimental errors and limitations are responsible for the observed variations. Thus, more work is needed to understand the *IAPV* phenomenon. A conservative approach to design of a polymer flood would assume that inaccessible pore volume is zero, especially in multi-darcy sands.

Porous medium	<i>k</i> , md	polymer	Salinity,% TDS	IÁPV, %	Reference
Berea	90-120	Push. 700 HPAM	0.05	0-4	Knight <i>et al.</i>
Berea	277	Push. 700 HPAM	2	18.7-24 <sup>1</sup>	Shah et al.
Berea	470	Push. 700 HPAM	1-2	22	Dawson & Lantz
Bartlesville	2090	Push. 700 HPAM	1-2	24	Dawson & Lantz
Reservoir sand	30-453	Push. 700 HPAM	13.3	32-37	Vela et al.
Teflon	86	Push. 700 HPAM	2	19	Dominguez
Berea	49-61 <sup>4</sup>	Push. 500 HPAM	1.2	17-37	Dabbous
Berea	761	Push. 500 HPAM	1.2	19	Dabbous
Sand pack	12600	3630 HPAM	-	35	Pancharoen et al.
Sand pack	2500-11000	HPAM	1.3	18-48	Osterloh & Law
Berea	681	xanthan	1-2	35	Dawson & Lantz
Sandstone with 10-12% clay	300-2400	xanthan	3-4	25-31 <sup>2</sup>	Hughes et al.
Berea	450-680	xanthan	3	18-41	Gupta & Trushenski
Brent	157-253	xanthan/scleroglu	7.4	14-22	Fletcher et al.
Bentheim	1600-2000	xanthan	9	10 <sup>3</sup>	Lotsch et al.
Bentheim	1600-2000	scleroglucan	9	11 <sup>3</sup>	Lotsch et al.
Ballotini glass	1270	scleroglucan	2	~20	Huang & Sorbie
Berea	300	dextran	-	11	Liauh <i>et al.</i>

Table 2—Literature inaccessible pore volume (IAPV) values.

<sup>1</sup> IAPV decreased from 24% to 18.7% as HPAM increased from 51.5 to 1070 ppm.

 $^{2}$  IAPV was 25% with no residual oil and 29% with residual oil.

<sup>3</sup> *IAPV* was the same with/without a 30% residual oil saturation.

<sup>4</sup> 28-35% residual oil saturation.

# Laboratory Measurement of Polymer Retention

**Sand.** Laboratory measurements of polymer retention were performed using sand from polymer flooded intervals of the Tambaredjo formation in Suriname: the T1 and T2 sands. Both sands were clean and large-grained, with a minimum of fines.

Sand samples were taken at the shale shaker during the drilling process for Well 30CX11 and Well 30HW25. Sidewall cores were not used because they provided very insufficient volumes of formation sand and were extremely contaminated with drilling fluid. Coring in other wells in the past had a very poor sample recovery. Therefore, gathering sand during the drilling process was considered the quickest, next best option that could provide sufficient sample. Well 30CX11 was sampled at the T sand plus Cretaceous interval of 800-880 ft. The T1 sand at 830-840 ft and the T2 sand at 800-820 ft are the main polymer flood targets. Well 30HW25 was sampled at the T sand interval of 980-1050 ft. The T1 sand at 1040-1050 ft and the T2 sand at 980-1028 ft are the main polymer flood targets. The samples were rinsed with water. No extraction was done on the sand, and no chemicals were used. The chemical compositions of the sands in these specific wells were not determined. However, in general, the formation is large-grained with about 80% quartz (average of XRD 74-86%) sand. One analysis indicated 11% kaolinite and 1.7% pyrite.

The two sand packs used in this work were 0.90 cm in inside diameter and 30.5 cm in length. One sand pack contained 36.90 g of T1 sand, with a porosity of 0.284 and permeability to water of 877 md. The second sand pack contained 38.66 g of T2 sand, with a porosity of 0.249 and permeability to water of 401 md. After packing, the sand packs were saturated with synthetic Sarah Maria water. Two liters of Sarah Maria water were flushed through the packs to condition the sand—especially to achieve stabilized baselines of viscosity and spectral absorbance for the effluent from the packs.

**Brine and Polymer Solution.** The synthetic Sarah Maria water contained 200-ppm magnesium sulfate, 120-ppm sodium sulfate, 100-ppm sodium chloride, and 80-ppm calcium chloride, for a salinity of 500-ppm total dissolved solids (TDS). This water is representative of the water that was used to make up polymer solutions during the field polymer flood. The polymer solution used in the field polymer flood and in this test was SNF Flopaam  $3630S^{TM}$ , which is an acrylamide-acrylate copolymer with a molecular weight of ~19 million g/mol and ~30% degree of hydrolysis. In our retention tests, we used 1000-ppm HPAM solutions—the same concentration as used during the first part of the field polymer flood (Moe Soe Let *et al.* 2012, Manichand *et al.* 2013). The polymer solutions also contained 40-ppm potassium iodide (KI) as a tracer.

**Flooding and Polymer Detection.** After preparation and saturation with brine, we injected polymer solution at a fixed rate (4 ft/d, using an ISCO 500D pump) at the reservoir temperature of 38°C. Brine tracer (KI) was detected using an in-line spectrophotometer, with wavelength detection set at 230 nm. (The spectrophotometer also provided a secondary means to detect the HPAM.) We detected polymer concentrations primarily by viscosity measurements using a small-diameter capillary tube that was located at the end of the sand packs. A very accurate digital pressure transducer (reading to 0.001 psi) measured pressure drops across the capillary. Polymer/tracer solution was injected until the readings from the capillary tube reached the value associated with the injected composition.

For each polymer retention test, we injected two cycles or banks of polymer solution that contained 1000-ppm HPAM and 40-ppm potassium iodide tracer. **Figs. 2 and 4** plot tracer and polymer effluent concentrations for the first cycle of traced polymer injection for the T1 and T2 sands, respectively. **Figs. 3 and 5** plot tracer and polymer effluent concentrations for the second cycle of traced polymer injection for the T1 and T2 sands, respectively.

**Calculation Method.** For Figs. 3 and 5 (i.e., the second cycle of polymer injection), the difference in areas between the tracer curve and the polymer curve determines the inaccessible pore volume (*IAPV*) for the polymer, as described by Eq. 2 above. These values were 0.124 for the T1 sand (Fig. 3) and zero for the T2 sand (Fig. 5). Generally, these inaccessible pore volume values are small or zero, which is the expected result for multi-darcy sand. Polymer molecules are on the order of 0.5  $\mu$ m in diameter, which should be able to access more than 99% of the pore space in our sand packs. Consequently, the most appropriate assumption for inaccessible pore volume for our cases is *IAPV* = 0.



Fig. 2—Retention during 1st injection of HPAM into T1 sand.



Fig. 4—Retention during 1st injection of HPAM into T2 sand.



Fig. 3-Retention during 2nd injection of HPAM into T1 sand.



Fig. 5—Retention during 2nd injection of HPAM into T2 sand.

Assuming that inaccessible pore volume is zero, polymer retention is given by the difference in area between the tracer and polymer curves—especially the set of curves associated with the first cycle of polymer injection (Figs. 2 and 4). Eq. 3 above was used for this calculation.

The polymer concentration was obtained from a given curve in Figs. 2-5 by assuming that the effluent capillary viscometer value during the early part of polymer injection (i.e., a value of 1) reflects brine flow (i.e., the same viscosity as water or zero-ppm polymer). Independent analysis of the effluent by viscosity and total organic carbon analysis confirmed that the polymer concentration in the effluent had reached the injected concentration by 3 PV. Consequently, the effluent capillary viscometer value at 3 PV was assigned the injection concentration (i.e., 1000 ppm). Intermediate polymer concentrations were assigned in direct proportion to the capillary viscometer reading, as indicated in Eq. 4:

C = (injected concentration)\*[(capillary reading)-1]/[(capillary reading @ 3 PV)-1]....(4)

Similarly, tracer concentrations were assigned in direct proportion to the spectrophotometer readings, between KI-free brine, and KI concentration in the injected solution.

Using the above method, the calculated polymer retention values were  $-12 \mu g/g$  for Fig. 1 (HPAM in T1 sand) and  $2 \mu g/g$  for Fig. 4 (HPAM in T2 sand). If there were no experimental error, a negative polymer retention number simply means that inaccessible pore volume was greater than polymer retention. Since IAPV is zero (within our experimental error), the key message is that polymer retention was very low (effectively zero) on the T1 and T2 sand samples that we examined.

# **Field Measurement of Polymer Retention**

**Reservoir Description.** Staatsolie's Sarah Maria polymer flooding pilot project in the Tambaredjo field (**Fig. 6**) currently has three injection wells (1M101, 1N062, and 1M052) with nine offset production wells (1M09, 1M10, 1N06, 1M051, 1N11,1N061, 1M04, 1M05, and 1I25). Solution gas drive and compaction were largely responsible for the 20% original oil in place recovery factor associated with primary recovery in the pilot area. No active water drive in this part of the field is evident, and no waterflood has been implemented. A combination of rock and fluid expansion and reservoir compaction (associated with decreased pore pressure) appear to be responsible for most formation water produced from the project area. Average permeabilities for the T1 sand (the main productive interval) range from ~4 darcys to ~12 darcys. A significant level of heterogeneity exists in the Tambaredjo reservoir—with a 12:1 permeability contrast observed for the ~20-ft thick T1 layer and the overlying ~15-ft thick T2 layer. No significant flow barriers exist between the two layers. To supplement the compaction and solution gas drive mechanisms, polymer injection is being evaluated. High oil viscosity in the Tambaredjo to 3,057 cp, with an average of 1,728 cp. Water viscosity at reservoir temperature (100°F, 38° C) is about 0.7 cp.



Fig. 6—Sarah Maria polymer pilot project.

**Polymer Injection and Breakthrough.** Polymer injection into Well 1M101 began in September 2008. Injection rate varied between 160 and 450 BPD (September 2008 – December 2013). As of December 2013, 458,728 bbl of polymer solution had been injected into Well 1M101. Polymer injection into Well 1N062 began in May 2010 and has continued with rates between 200 and 320 BPD. As of December 2013, 346,832 bbl of polymer solution had been injected into Well 1N062. Polymer injection in a third well, 1M052, began in June 2011. As of December 2013, 224,766 bbl had been injected at rates varying between 200 and 380 BPD. Considering the pore volume of all three injection patterns, approximately 36.5% PV of polymer solution had been injected as of December 2013. Between September 2008 and November 2, 2011, 1000-ppm HPAM (45-cp) was injected. Between November 2, 2011 and February 4, 2013, 1350-ppm HPAM (85 cp) was injected. Subsequently, 2300-ppm HPAM (125 cp) was injected. Oil and water cut responses to polymer injection can be found in Moe Soe Let *et al.* 2012 and Manichand *et al.* 2013.

During the Sarah Maria polymer flood in the Tambaredjo reservoir, produced water salinity was continually monitored in the production wells. Fig. 7 shows produced water salinities for six relevant wells in the pilot area. Polymer concentration was also monitored, although on a less frequent basis. Fig. 8 shows produced polymer concentrations for the same six wells. This information can be used to estimate polymer retention in the pilot project. For this calculation, the salinity is used as a tracer for water. (In other polymer floods where extensive waterflooding occurred before polymer injection, a tracer should intentionally be added to the injected polymer to make our method work.) Polymer retention is estimated from the difference in breakthrough volumes for the polymer and tracer (i.e., salinity) curves.



Fig. 7—Produced water salinities for wells of interest.



Fig. 8—Produced water polymer concentrations for wells of interest.

**Procedure for Estimating Field Polymer Retention Values.** This section details our method for estimating polymer retention values, based on field data. Zettlitzer and Volz (1992) used a mass balance on polymer injected and polymer produced to estimate polymer retention in the Hankensbuettel-Sued field. Many correction factors were required. In addition, their method suffers from the same problem that plagues laboratory mass-balance methods for determining polymer retention. Specifically, (1) recovery of the polymer may require an extended period of brine injection because of the unfavorable displacement and (2) cumulative errors associated with measurements of low polymer concentrations in the produced fluid can introduce considerable uncertainty to the mass balance.

Our method effectively uses the combined polymer/tracer bank method that we used to determine polymer retention in our laboratory work (i.e., Figs. 2-5). In our case, low-salinity water (used to make the polymer solution) was our tracer. For the first step in our method, each production well of interest must assign the fraction of the produced water that originates from a near-by polymer injection well versus the fraction that comes from other sources (e.g., water from outside the polymerflood pattern). This assignment is based on either the final stabilized salinity or the final stabilized produced polymer concentration. For example, for Production Well 1N11, the produced water salinity averaged 4737-ppm TDS before July 1, 2010 (black circles in Fig. 7). Subsequently, produced water salinity dropped and stabilized, averaging 1291-ppm TDS after September 1, 2011. The salinity drop was associated with injecting polymer solution with 500-ppm-TDS in Injection Well 1N062 (Fig. 6). The final stabilized produced water salinity should have been 500 ppm if Injector 1N062 was the only water

source feeding Producer 1N11. Since the actual stabilized salinity was higher (i.e., 1291-ppm TDS), the fraction of water ( $f_{wtrac}$ ) coming from Injector 1N062 was assigned (4737-1291)/(4737-500) = 0.813.

Alternatively, this assignment could have come from the stabilized produced polymer concentration. In Production Well 1N11, no polymer was detected on or before August 5, 2010. On February 1, 2011, 563-ppm HPAM was detected. Somewhat of a plateau was noted in produced polymer concentrations between February 1, 2011 and February 10, 2012— averaging 634 ppm (Fig. 8). Thereafter, the produced polymer concentration jumped to 896 ppm, associated with the increase in injected concentration to 1350-ppm polymer beginning November 2, 2011. If the 634-ppm polymer concentration is accepted as the plateau in Fig. 8, the assigned fraction of water ( $f_{wpoly}$ ) for Producer 1N11 coming from Injector 1N062 would be (634-0)/(1000-0) = 0.634. This number is notably lower than the 0.813 value calculated from salinity numbers. For several reasons, a significantly greater uncertainly is associated with the polymer calculation. First, polymer concentration was measured far less frequently than salinity (compare Figs. 7 and 8). Second, the injected polymer concentration changed on two occasions during the pilot, whereas the injected salinity remained constant. Third, the viscous polymer may sweep a larger part of the reservoir volume than the low-viscosity tracer—i.e., some of the water (that was stripped of polymer by retention) channeled through to the production well. As another point, one might suggest the possibility of polymer degradation reducing the produced polymer concentration. However, our earlier work (Manichand *et al.* 2013) demonstrated that the HPAM propagated through the formation without degradation. At any rate, salinity may provide the preferred basis to assign the fraction of water arriving at a production well that is sourced from a polymer injector.

The next step involves estimating an effective swept volume ( $V_{swept}$ ) in the path between the injector and the producer. That information comes from the tracer (salinity data, Fig. 7) analysis based on Eq. 5.

$$V_{swept} = (f_{wtrac}) \Sigma \left[ \Delta V_{tracprod} * (1 - C_{trac}/C_{traco}) \right].$$
(5)

In Eq. 5, the summation begins the first day of polymer/tracer injection. For every subsequent time increment, the differential volume of water produced from the target production well,  $\Delta V_{tracprod}$ , is multiplied by (1-  $C_{trac}/C_{traco}$ ) and summed.  $C_{trac}$  is produced tracer concentration minus zero-baseline tracer concentration.  $C_{traco}$  is stabilized produced tracer concentration minus zero-baseline tracer concentration.  $C_{traco}$  is stabilized produced tracer concentration minus zero-baseline tracer concentration. Here,  $C_{trac}/C_{traco}$  is ratioed by the produced water salinity at a given time between the initial produced salinity (before polymer injection) and the final stabilized salinity after breakthrough. For Production Well 1N11,  $C_{trac}/C_{traco}$  is zero when the produced water salinity is 4737-ppm TDS and is one when the produced water salinity reaches 1291-ppm TDS. As an intermediate example, if salinity is 2500-ppm TDS,  $C_{traco} = (2500-4737)/(1291-4737) = 0.649$ . For Production Well 1N11, recall that  $f_{wtrac}$  was 0.813. For Production Well 1N11, the calculated value for  $V_{swept}$  was significantly lower than the pore volume of the quarter pattern volume between Injector 1N062 and Producer 1N11 in Fig. 6. This result occurs because of heterogeneity within the pattern and especially because of the unfavorable mobility ratio associated with water and/or 45-cp polymer solution displacing the very viscous oil.

The effective rock mass associated with the swept volume is estimated using Eq. 6.

$$M_{rock} = V_{swept} \left[ (1 - \phi)/\phi \right] \rho_{rock}.$$
(6)

In this formation, porosity ( $\phi$ ) was 0.273, and rock (quartz) density ( $\rho_{rock}$ ) was 2.65 g/cm<sup>3</sup>.

Finally, polymer retention is estimated using Eq. 7.

$$R_{pret} = \{C_{polyo} \Sigma \left[ \Delta V_{polyprod} * (1 - C_{poly} C_{polyo}) \right] \} / M_{rock}$$
(7)

In Eq. 7, the summation begins the first day of polymer/tracer injection. For every subsequent time increment, the differential volume of water produced from the target production well,  $\Delta V_{polyprod}$ , is multiplied by  $(1 - C_{poly}/C_{polyo})$  and summed. Here,  $C_{poly}$  is the produced polymer concentration at a given time. Choices exist for the parameter,  $C_{polyo}$ . One choice is the stabilized polymer concentration after breakthrough. Alternatively, one could argue that  $C_{polyo}$  should be given by the injected polymer concentration multiplied by  $f_{wtrac}$ . We used both approaches as a means to reflect the uncertainty in our calculation of retention. Table 3 lists calculated parameters for the six production wells.

Table 3—Parameters for the calculations of polymer retention in the Sarah Maria pilot.

Production well	1N11	1125	1N06	1M05	1M09	1N01
Starting salinity, ppm TDS	4737	4686	4657	4432	4707	3998
Ending salinity, ppm TDS	1291	1692	1684	2531	2281	1769
Ending polymer, ppm	634	550	375	226	216	395
f <sub>wtrac</sub>	0.813	0.708	0.715	0.483	0.577	0.637
f <sub>wpoly</sub>	0.634	0.554	0.349	0.195	0.203	0.381
Range of retention values, µg/g	160-517	129-247	53-125	14-337	45-99	50-168

Field values for HPAM retention ranged from 14  $\mu$ g/g to 517  $\mu$ g/g, depending on the pattern in the polymer flood and the  $f_w$  and  $C_{polyo}$  values used in the calculation. The last row of Table 3 suggests significant uncertainty in our retention calculations (typically, with two-three-fold variation). Even so, the field retention numbers were significantly greater than those observed during our laboratory retention studies (~0  $\mu$ g/g). Most retention numbers in Table 3 fall between 50 and 250  $\mu$ g/g. An average of all 12 numbers listed in the last row is 162  $\mu$ g/g. Within a given range of the listings, we tend to believe the lower numbers, because those were calculated using the  $f_w$  value associated with the tracer. As is evident from Figs. 7 and 8, much more salinity data was collected than produced polymer data. (This observation points out the need for more frequent collection and analysis of produced polymer samples during a pilot project.) If only the lower numbers are averaged for the ranges listed at the bottom of Table 3, the average field retention value is 75  $\mu$ g/g. Of course, we expect mineralogical variations through the reservoir, so different retention values are not unexpected for the different patterns in the pilot.

A number of points may account for the discrepancy between the lab and field data. The sand used during our laboratory studies was taken from the shale shaker during drilling and was extensively washed. Consequently, high-surface-area minerals may have been washed away during this process. Other analyses reported that the Tambaredjo formation contains ~11% kaolinite and 1.7% pyrite—which should result in significant polymer retention values. Perhaps, the sand samples used in during our lab study fortuitously were lacking in these minerals. Ironically, in separate studies, we noted very high polymer retention for reservoir cores—which we suspect occurred because of contamination by high-surface-area minerals (e.g., bentonite, silica flour) that are associated with drilling/coring fluids. This presents a dilemma for collection of reservoir material for evaluation of retention for a polymer flood. What is the best way to obtain the reservoir sand: (a) coring, (b) from the shale shaker during drilling (as we did in this study), or (c) sand production from a production well? When obtaining reservoir cores for laboratory retention studies, drilling/coring procedures should not use high-surface area materials.

Finally, cores necessarily represent an extremely small fraction of the reservoir. Because of the importance of polymer retention (see Fig. 1), deriving polymer retention values from field results are valuable for designing of project expansions.

## Conclusions

- 1. A review of the polymer-retention literature revealed that iron and high-surface-area minerals (e.g., clays) dominate polymer retention measurements in permeable rock and sand (>100 md).
- 2. A review of the literature on inaccessible pore volume revealed inconsistent and unexplained behavior. A conservative approach to design of a polymer flood in high-permeability (>1 darcy) sands would assume that inaccessible pore volume is zero.
- 3. Laboratory measurements using fluids and sands associated with the Sarah Maria polymer flood in Suriname suggested polymer retention and inaccessible pore volume values near zero.
- 4. A procedure was developed using salinity-tracer and polymer concentrations from production wells to estimate polymer retention during the Sarah Maria polymer flood in the Tambaredjo reservoir.
- 5. Field calculations indicated much higher polymer retention values than lab tests, typically ranging from  $\sim$ 50 to 250 µg/g.
- 6. Field cores necessarily represent an extremely small fraction of the reservoir. Because of the importance of polymer retention, there is considerable value in deriving polymer retention from field results, so that information can be used in the design of project expansions.

#### Nomenclature

- $C = \text{polymer concentration, mg/L or ~ppm [}\mu\text{g/g]}$
- $C_{inj}$  = injected polymer concentration during a retention study, mg/L or ~ppm [µg/g]
- $C_{poly}$  = produced polymer concentration, mg/L or ~ppm [µg/g]
- $C_{polyo}$  = injected polymer concentration or stabilized produced polymer concentration, mg/L or ~ppm [µg/g]
- $C_{trac}$  = produced tracer concentration minus zero-baseline tracer concentration, mg/L or ~ppm [µg/g]
- $C_{traco}$  = injected tracter concentration or stabilized produced tracer concentration minus zero-baseline tracer concentration, mg/L or ~ppm [µg/g]
- $f_{wpoly}$  = fraction of produced water originating from an offset injection well, based on polymer flow
- $f_{wtrac}$  = fraction of produced water originating from an offset injection well, based on tracer flow
- *IAPV* = inaccessible pore volume
- $M_{rock}$  = mass of rock in the core or polymer contacted portion of the reservoir, g
- PV = pore volumes of fluid injected
- $PV_{ret}$  = additional pore volumes of polymer solution that must be injected to contact one pore volume
- $\Delta PV$  = pore volumes difference
- $R_{pret}$  = polymer retention,  $\mu g/g$
- $V_{swept}$  = swept volume, bbl [m<sup>3</sup>]
- $\Delta V_{polyprod}$  = incremental produced volume associated with polymer, bbl [m<sup>3</sup>]
- $\Delta V_{polytrac}$  = incremental produced volume associated with tracer, bbl [m<sup>3</sup>]

 $\phi$  = porosity

 $\rho_{rock}$  = rock density, g/cm<sup>3</sup>

#### References

API Recommended Practice 63 (RP63) American Petroleum Institute, Washington, DC (June 1, 1990) 67-74.

- Broseta, D. Medjahed, F., Lecourtier, J., and Robin, M. 1995. Polymer Adsorption/Retention in Porous Media: Effects of Core Wettability and Residual Oil. SPE Advanced Technology Series 1(1) 103-112.
- Camilleri, D., Engelsen, S., Lake, L.W., Lin, E.C., Ohno, T., Pope, G., Sephehrnoori, K. 1987. Description of an Improved Compositional Micellar/Polymer Simulator. SPE Reservoir Engineering (November 1987) 427-432.
- Casassa, E.F. 1967. Equilibrium Distribution of Flexible Polymer Chains Between a Macroscopic Solution Phase and Small Voids. *Polymer Letters* **5**: 773-778.
- Castagno, R.E., Shupe, R.D., Gregory, M.D., and Lescarboura, J.A. 1987. Method for Laboratory and Field Evaluation of a Proposed Polymer Flood. SPE Reservoir Engineering (November 1987) 452-460.
- Chauveteau, G. 1981. Molecular Interpretation of Several Different Properties of Flow of Coiled Polymer Solutions Through Porous Media in Oil Recovery Conditions. Paper SPE 10060 presented at the SPE Annual Technical Conference and Exhibition, San Antonio, Texas, USA, 4–7 October. doi: 10.2118/10060-MS.
- Chauveteau, G., Lecourtier, J., and Lee, L.T. 1987. Reduction of Polymer Adsorption on Reservoir Rocks. Presented at the 4<sup>th</sup> European Symposium on Enhanced Oil Recovery. Hamburg. 27-29 October, 1987.
- Chauveteau, G., Denys, K., and Zaitoun, A. 2002. New Insight on Polymer Adsorption under High Flow Rates. Paper SPE 75183 presented at the 2002 SPE/DOE Improved Oil Recovery Symposium. Tulsa, OK. 13-17 April.
- Chiappa, L., Mennella, A. Lockhart, T.P., Burrafato, G. 1999. Polymer Adsorption at the Brine/Rock Interface: The Role of Electrostatic Interactions and Wettability. J. of Petroleum Science and Engineering 24(1999) 113-122.
- Cohen, Y., and Christ, F.R. 1986. Polymer Retention and Adsorption in the Flow of Polymer Solutions through Porous Media. SPE Reservoir Engineering (March 1986) 113-118.
- Dang, C.T.Q., Chen, Z., Nguyen, N.T.B., Bae, W., and Phung, T.H. 2011. Development of Isotherm Polymer/Surfactant Adsorption Models in Chemical Flooding. Paper SPE 147872 presented at the 2011 SPE Asia Pacific Oil and Gas Conference and Exhibition. Jakarta, Indonesia. 20-22 September.
- Dabbous, M.K. 1977. Displacement of Polymers in Waterflooded Porous Media and Its Effects on a Subsequent Micellar Flood. SPE Journal (October) 358-368.

Dawson, R., and Lantz, R.B. 1972. Inaccessible Pore Volume in Polymer Flooding. SPEJ 12 (5): 448-452.

- Dimarzio, E.A. 1965. Proper Accounting of Conformations of a Polymer near a Surface. J. Phys. Chem. 42: 2101-2106.
- Dominguez, J.G. and Willhite, G.P. 1977. Retention and Flow Characteristics of Polymer Solutions in Porous Media. SPE Journal (April) 111-121.
- Fletcher, A.J.P., Flew, S.R.G., Lamb, S.P., Lund, T., Bjornestad, E., Stavland, A., and Gjovikli, N.B. 1991. Measurements of Polysaccharide Polymer Properties in Porous Media. Paper SPE 21018 presented at the 1991 SPE International Symposium on Oilfield Chemistry. Anaheim, CA. 20-22 February.
- Friedmann, F. 1986. Surfactant and Polymer Losses. SPE Reservoir Engineering (May 1986) 261-271.
- Gilman, J.R. and MacMillan, D.J. 1987. Improved Interpretation of the Inaccessible Pore-Volume Phenomenon. SPE Formation Evaluation (December 1987) 442-448.
- Gogarty, W.B. 1967. Mobility Control with Polymer Solutions. SPE J. 7 (2): 161–173. SPE-1566-PA. doi: 10.2118/1566-PA.
- Green, D.W., and Willite, G.P. 1998. Enhanced Oil Recovery. Textbook Series, SPE, Richardson, Texas 6: 100–185.
- Gupta, S.P. and Trushenski, S.P. 1978. Micellar Flooding-Propagation of the Polymer Buffer Bank. SPE Journal (February 1978) 5-12.
- He, Q., Young, T.S., Willhite, G.P., and Green, D.W. 1990. Measurement of Molecular Weight Distribution of Polyacrylamides in Core Effluents. SPE Reservoir Engineering (August 1990) 333-338.
- Hirasaki, G.J. and Pope, G.A. 1974. Analysis of Factors Influencing Mobility and Adsorption in the Flow of Polymer Solution Through Porous Media. SPE J. 14 (4): 337–346. SPE-4026-PA. doi: 10.2118/4026-PA.
- Huang, Y., and Sorbie, K.S. 1993. Scleroglucan Behavior in Flow through Porous Media: Comparison of Adsorption and In-Situ Rheology with Xanthan. Paper SPE 25173 presented at the 1993 International Symposium on Oilfield Chemistry. New Orleans, LA. 2-5 March.
- Hughes, D.S., Teew, D., Cottrell, C.W., and Tollas, J.M. 1990. Appraisal of the Use of Polymer Injection to Suppress Aquifer Influx and to Improve Volumetric Sweep in a Viscous Oil Reservoir. SPE Reservoir Engineering (February 1990) 33-40.
- Huh, C., Lange, E.A., and Cannella, W.J. 1990. Polymer Retention in Porous Media. Paper SPE 20235 presented at the SPE/DOE Symposium on Enhanced Oil Recovery. Tulsa, OK. 22-25 April.
- Knight, B.L., Jones, S.C., and Parsons, R.W. 1974. Discussion. SPE Journal (December) 643-644.
- Knight, B.L. and Rudy, J.S. 1977. Recovery of High-Viscosity Crudes by Polymer Flooding. JPT (December 1977). 46-55.
- Kolodziej, E.J. 1988. Transport Mechanisms of Xanthan Biopolymer Solutions in Porous Media. Paper SPE 18090 presented at the 1988 SPE Annual Technical Conference and Exhibition. Houston, TX. (2-5 October).
- Lee, J., and Fuller, G.G. 1985. Adsorption and Desorption of Flexible Polymer Chains in Flowing Systems. *Journal of Colloid and Interface Science* **103**(2) (February 1985) 569-577.
- Liauh, W.C., Duda, J.L., and Klaus, E.E. 1979. An Investigation of the Inaccessible Pore Volume Phenomena. Paper SPE 8751. 20 August.
- Lotsch, T., Muller, T., Pusch, G. 1985. The Effect of Inaccessible Pore Volume on Polymer Core Experiments. Paper SPE 13590 presented at the International Symposium on Oilfield and Geothermal Chemistry. Phoenix, AZ. 9-11 April.
- MacWilliams, D.C., Rogers, J.H., and West, T.J. 1973. Water Soluble Polymers in Petroleum Recovery in *Water Soluble Polymers*. N.M. Bikales (ed.) Plenum Press. New York City, NY (1973) 105-126.
- Maerker, J.M. 1973. Dependence of Polymer Retention on Flow Rate. J Pet Technol 25 (11): 1307–1308. SPE-4423-PA. doi: 10.2118/4423-PA.
- Manichand, R.N., Moe Soe Let, K.P., Gil, L., Quillien, B., Seright, R.S.. 2013. Effective Propagation of HPAM Solutions through the Tambaredjo Reservoir during a Polymer Flood. *SPE Production & Operations* (November 2013) 358-368.
- Martin, F.D. and Sherwood, N. 1975. The Effect of Hydrolysis of Polyacrylamide on Solution Viscosity, Polymer Retention, and Flow Resistance Properties. Paper SPE 5339 presented at the 1975 Rocky Mountain Regional Meeting. Denver, CO. 7-9 April.

- Martin, F.D., Hatch, M.J., Shepitka, J.S., and Ward, J.S. 1983. Improved Water-Soluble Polymers for Enhanced Oil Recovery. Paper SPE 11786 presented at the SPE International Symposium on Oilfield and Geothermal Chemistry. Denver, CO. 1-3 June.
- Meier, D.J. 1967. Theory of Polymeric Dispersants. Statistics of Constrained Polymer Chains. J. Chem. Phys. 71: 1861-1868.
- Meister, J.J., Pledger, H., Hogen-Wsch, T.E., and Butler, G. 1980. Retention of Polyacrylamide by Berea Sandstone, Baker Dolomite, and Sodium Kaolinite during Polymer Flooding. Paper SPE 8981 presented at the 1980 International Symposium on Oilfield and Geothermal Chemistry. Stanford, CA. 28-30 May.
- Mezzomo, R.F., Moczydlower, P., Sanmartin, A.N., and Araujo, C.H.V. 2002. A New Approach to the Determination of Polymer Concentration in Reservoir Rock Adsorption Tests. Paper SPE 75204 presented at the 2002 SPE/DOE Symposium on Improved Oil Recovery. Tulsa, OK. 13-17 April.
- Moe Soe Let, K.P., Manichand, R.N., and Seright, R.S. 2012. Polymer Flooding a ~500-cp Oil. Paper SPE 154567 presented at the Eighteenth SPE Improved Oil Recovery Symposium held in Tulsa, Oklahoma, USA, 14–18 April 2012.
- Mungan, N. 1969. Rheology and Adsorption of Aqueous Polymer Solutions. *Journal of Canadian Petroleum Technology* (April-June 1969) 45-50.
- Osterioh, W.T., and Law, E.J. 1998. Polymer Transport and Rheological Properties for Polymer Flooding in the North Sea Captain Field. Paper SPE 39694 presented at the SPE/DOE Improved Oil Recovery Symposium. Tulsa, OK. 19-22 April.
- Pancharoen, M., Thiele, M.R., and Kovscek, A.R. 2010. Inaccessible Pore Volume of Associative Polymer Floods. Paper SPE 129910 presented at the SPE Improved Oil Recovery Symposium. Tulsa, OK. 24-28 April.
- Satter, A., Shum, Y.M., Adams, W.T., and Davis, L.A. 1980. Chemical Transport in Porous Media with Dispersion and Rate-Controlled Adsorption. SPE Journal (June 1980) 129-138.
- Skauge, Arne. 2013. EOR Introduction. Presented at the FORCE-EOR Competence Building seminar, Stavanger, Norway. 6-7 November. http://www.force.org/Global/Seminars/2013/EOR%20Competence%20Building%20workshop/Presentations/1\_Intro\_EOR%20introduc tion\_Arne\_Skauge.pdf
- Seright, R.S., Prodanovic, M., and Lindquist, W.B. 2006. X-Ray Computed Microtomography Studies of Fluid Partitioning in Drainage and Imbibition Before and After Gel Placement. SPE J. 11 (2): 159–170. SPE-89393-PA. doi: 10.2118/89393-PA.
- Shah, B.N., Willhite, G.P., and Green, D.W. 1978. The Effect of Inaccessible Pore Volume on the Flow of Polymer and Solvent through Porous Media. Paper SPE 7586 presented at the SPE Annual Technical Conference and Exhibition. Houston, TX. 1-3 October.
- Sorbie, K.S. 1991. Polymer-Improved Oil Recovery. Blackie and Son. Glasgow. 50.
- Szabo, M.T. 1975. Some Aspects of Polymer Retention in Porous Media Using a C<sup>14</sup>-Tagged Hydrolyzed Polyacrylamide. SPE Journal (August 1975) 323-337.
- Szabo, M.T. 1979. An Evaluation of Water-Soluble Polymers for Secondary Oil Recovery-Part 2. J. Petroleum Technology (May 1979) 561-570.
- Trushenski, S.P., Dauben, D.L., and Parrish, D.R. 1974. Micellar Flooding—Fluid Propagation, Interaction, and Mobility. SPE Journal (December) 633-645.
- Van Domselaar, H.R., and Fortmuller, C. 1992. On the Transport Properties of a Rod-Type Polymer in Sand Packs. Paper SPE 25073 presented at the European Petroleum Conference. Cannes, France. 16-18 November.
- Vela, S., Peaceman, D.W., and Sandvik, E.I. 1976. Evaluation of Polymer Flooding in a Layered Reservoir with Crossflow, Retention, and Degradation. SPE J. 16 (2): 82–96. SPE-5102-PA. doi: 10.2118/5102-PA.
- Vossoughi, S., Smith, J.E., Green, D.W., and Willhite, G.P. 1984. A New Method to Simulate the Effects of Viscous Fingering on Miscible Displacement Processes in Porous Media. *SPE Journal* (February 1984) 56-64.
- Yuan, C., Delshad, M., and Wheeler, M.F. 2010. Parallel Simulations of Commercial-Scale Polymer Floods. Paper SPE 123441 presented at the 2010 SPE Western Regional Meeting held in Anaheim, California. 27-29 May.
- Zaitoun, A. and Kohler, N. 1987. The Role of Adsorption in Polymer Propagation Through Reservoir Rocks. Paper SPE 16274 presented at the SPE International Symposium on Oilfield Chemistry, San Antonio, Texas, USA, 4–6 October. doi: 10.2118/16274-MS.
- Zaitoun, A., and Kohler, N. 1988. Two-Phase Flow through Porous Media: Effect of an Adsorbed Polymer Layer. Paper SPE 18085 presented at the SPE Annual Technical Conference and Exhibition. Houston, TX. 2-5 October.
- Zaitoun, A., and Chauveteau, G. 1998. Effect of Pore Structure and Residual Oil on Polymer Bridging Adsorption. Paper SPE 39674 presented at the 1998 SPE/DOE Improved Oil Recovery Symposium. Tulsa, OK. 19-22 April.
- Zettlitzer, M., and Volz, H. 1992. Comparison of Polyacrylamide Retention in Field Application and Testing. Paper SPE 24121 presented at the 1992 SPE/DOE Symposium on Enhanced Oil Recovery. Tulsa, OK. 22-24 April.
- Zhang, G. and Seright, R.S. 2013. Effect of Concentration on HPAM Retention in Porous Media. Paper SPE 166265 presented at the SPE Annual Technical Conference and Exhibition, New Orleans, LA, 30 September–2 October.
- Zheng, C.G., Gall, B.L., Gao, H.W., Miller, A.E., and Bryant, R.S. 2000. Effects of Polymer Adsorption and Flow Behavior on Two-Phase Flow in Porous Media. SPE Reservoir Evaluation & Engineering 3(3) (June 2000). 216-223.
- Zitha, P.L.J., and Botermans, C.W. 1998. Bridging Adsorption of Flexible Polymers in Low-Permeability Porous Media. SPE Production & Facilities (February 1998) 15-20.
- Zitha, P.L.J., van Os, K.G.S., and Denys, K.F.J. 1998. Adsorption of Linear Flexible Polymers during Laminar Flow through Porous Media: Effect of the Concentration. Paper SPE 39675 presented at the 1998 SPE/DOE Improved Oil Recovery Symposium. Tulsa, OK. 19-22 April.

#### **SI Metric Conversion Factors**

cp x 1.0*	E-03	$= Pa \cdot s$
ft x 3.048*	E-01	= m
in. x 2.54*	E+00	= cm
md x 9.869 233	E-04	$= \mu m^2$
psi x 6.894 757	E+00	= kPa