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 (0 +/- 20 µg/g for retention and 0 +/- 10% PV for IAPV). 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 µg/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 ($\rho_{\text{rock}}$, 2.65 g/cm$^3$ for quartz), porosity ($\phi$), polymer retention in µg/g ($R_{\text{pret}}$), and polymer concentration ($C_{\text{inj}}$) in mg/L (or ~ppm), Eq. 1 can be used to calculate the delay ($PV_{\text{ret}}$, 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.

$$PV_{\text{ret}} = \left[\frac{\rho_{\text{rock}} (1-\phi)}{\phi}\right] \left[\frac{R_{\text{pret}}}{C_{\text{inj}}}\right] - IAPV$$ .................................................................................... (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 µg/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 µg/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 µg/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.](image-url)
LITERATURE REVIEW OF POLYMER RETENTION

1. Clay (high-surface-area materials) and iron in the rock dominate polymer retention.
2. Polymer retention can increase dramatically with decreasing permeability, especially below 100 md. Most current polymer floods are applied in very permeable formations (> 500 md).
3. Most (but not all) polymer retention data suggests that use of the Langmuir isotherm is inappropriate. Ironically, most commercial simulators use the Langmuir isotherm.
4. Retention of xanthan is usually less than that of HPAM.
5. The most reliable current means to measure polymer retention is the double-polymer/tracer-bank method.
6. Retention in the presence of residual oil is ~1/2 half that without $S_{or}$. Wettability has not been established as a key factor in polymer retention.
Several methods have been proposed to measure polymer retention and inaccessible pore volume (Dawson and Lantz 1972, Szabo 1975, 1979, Dominguez and Willhite 1977, Gupta and Trushenski 1978, Castagno et al. 1987, API RP63 1990, 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 (Green and Willhite 1998) 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 (Zaitoun and Kohler 1987).

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 breakthrough curve and the tracer breakthrough curve. Specifically, Eq. 2 is used.

\[
IAPV = \sum [(C_{poly}/C_{polyo} * \Delta PV) - (C_{trac}/C_{traco} * \Delta PV)]
\]

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

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

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.

**Literature Review: Components of Polymer Propagation**

Polymer propagation through porous media is governed by polymer retention and inaccessible pore volume. Inaccessible pore volume 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).

In concept, precipitation and partitioning (into another phase) could also contribute to polymer retention, although these phenomena are not normally associated with flow of conventional water-soluble polymers through porous media.

Literature 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 µg/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 µg/g to ~700 µg/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 µg/g) as for HPAM with 22% degree of hydrolysis (8.3 µg/g)—in brine with 0.5% NaCl. Meister et al. also observed that the acrylamide homopolymer showed significantly lower retention (1.9 µg/g) in Baker dolomite than the HPAM (8.4 µg/g).
During static adsorption studies, Chiappa, *et al.* (1999) found adsorption on 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. Vermolen *et al.* (2011) and Skauge (2013) reported that incorporation n-vinyl pyrrolidone or sulfonate 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±3 µg/g in 0.1% NaCl and 25.1±2.1 µg/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 µg/g in distilled water versus from 70 to 675 µg/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 µg/g). For HPAM (with 23% degree of hydrolysis), they noted adsorption on quartzite increased from ~60 µg/g with no CaCl2 present to ~750 µg/g with 8% CaCl2 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 CaCl2 content.

**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 µg/g at ~20-ppm polymer to ~30 µg/g at ~1000-ppm polymer. Zheng *et al.* (2000) observed HPAM retention in Berea increasing from 40 µg/g at 250 ppm to 58 µg/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 µg/g at 50 ppm to 11.71 µg/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 ~200 µg/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.
Table 1—Summary of polymer retention effects.

<table>
<thead>
<tr>
<th>MINERALOGY and POLYMER TYPE: Clay and Iron are VERY important!</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymer</td>
</tr>
<tr>
<td>montmorillonite</td>
</tr>
<tr>
<td>quartzite with 8% montmorillonite</td>
</tr>
<tr>
<td>quartzite</td>
</tr>
<tr>
<td>kaolinite</td>
</tr>
<tr>
<td>siderite</td>
</tr>
<tr>
<td>kaolinite</td>
</tr>
<tr>
<td>kaolinite</td>
</tr>
<tr>
<td>Berea (350-550 md)</td>
</tr>
<tr>
<td>Berea (350-550 md)</td>
</tr>
<tr>
<td>calcium carbonate</td>
</tr>
<tr>
<td>Baker dolomite</td>
</tr>
<tr>
<td>99% quartz</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>DEGREE OF HYDROLYSIS: Conflicting message, but generally minor importance.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymer</td>
</tr>
<tr>
<td>Berea, 0% hydrolysis PAM</td>
</tr>
<tr>
<td>Berea, 22% hydrolysis HPAM</td>
</tr>
<tr>
<td>Miocene sand, 0% hydrolysis</td>
</tr>
<tr>
<td>Miocene sand, 25-70% hydrolysis</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>POLYMER CONCENTRATION: Depends on concentration regime.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymer</td>
</tr>
<tr>
<td>10 ppm to 6000 ppm</td>
</tr>
<tr>
<td>20 ppm to 1000 ppm</td>
</tr>
<tr>
<td>250 ppm to 1500 ppm</td>
</tr>
<tr>
<td>50 ppm to 200 ppm</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>SALINITY: NaCl content not so important. Calcium content may be important.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymer</td>
</tr>
<tr>
<td>0.1% to 2% NaCl</td>
</tr>
<tr>
<td>quartzite, 0% CaCl₂</td>
</tr>
<tr>
<td>quartzite, 8% CaCl₂</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>PERMEABILITY: Very important below 100 md. Less important above 200 md.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymer</td>
</tr>
<tr>
<td>2100-md Vosges sandstone</td>
</tr>
<tr>
<td>520-md Vosges sandstone</td>
</tr>
<tr>
<td>137-md reservoir sandstone</td>
</tr>
<tr>
<td>12-md reservoir sandstone</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>OIL SATURATION: Minor effect.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymer</td>
</tr>
<tr>
<td>quartz sand with or without oil</td>
</tr>
<tr>
<td>Reservoir core without oil</td>
</tr>
<tr>
<td>Reservoir core with oil</td>
</tr>
<tr>
<td>Berea sandstone without oil</td>
</tr>
<tr>
<td>Berea sandstone with oil</td>
</tr>
</tbody>
</table>
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.

Iron, Clay Content, Carbonates. Retention is strongly affected by the iron and clay content of the porous medium. In sodium kaolinite, Meister et al. (1980) noted PAM and HPAM retention values from 339 to 1217 µg/g, whereas values in Berea sandstone and Baker dolomite ranged from 1.9 to 17.8 µg/g. Hughes et al. (1990) reported xanthan retention values of 16,900 µg/g in unfired Georgia clay (mostly kaolinite) and 15,600 µg/g in unfired siderite (FeCO₃).

Chauveteau et al. (1987) reported that HPAM adsorption on sodium kaolinite was between 1,500 and 8,000 µg/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 µg/g; whereas in a 790-md sand with 50% quartz, 10% carbonate, and 15% clay, they noted adsorption of 90 µg/g.

Szabo (1979) typically observed HPAM adsorption values from 20 to 100 µg/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 µg/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 µg/g on quartzite, 14,500 µg/g on quartzite with 8% clay (Wyoming montmorillonite), and 180,000 µg/g on pure Wyoming montmorillonite.

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 µg/g in 0.52-darcy Vosges sandstone and 155 µg/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 µg/g in 137-md sandstone to ~130 µg/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.

**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 µg/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 µg/g in the presence of residual oil and about 75 µg/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 µg/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 µg/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 oil-wet 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.

**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 µg/g retention of scleroglucan within the core and the equivalent of 17 µg/g was filtered by the core face during the experiment. Similarly, in a 253-md Brent core, 36.5 µg/g retention of xanthan was calculated within the core and the equivalent of 7 µg/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—sugesting 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 µg/g near the core inlet to 7 µg/g at a distance 24 cm into the pack. In contrast, for “Polymer 340”
acrylamide-AMPS copolymer, retention was 1-2 µg/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/d 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.

Literature Review: 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.

### LITERATURE REVIEW OF INACCESSIBLE PV (IAPV)

1. **Reported IAPV values are VERY inconsistent, especially with respect to permeability dependence.**

2. **The available theories for the IAPV phenomenon cannot explain the magnitude and odd variations of IAPV with changes in permeability.** Experimental limitations?

3. **More work is needed to understand IAPV phenomenon.**

4. **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).**

5. **A conservative approach to design of a polymer flood would assume that inaccessible pore volume is zero, especially in multi-darcy sands**

### 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 µm (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 µm and a pore throat diameter over 6.7 µm (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 (de Gennes 1979).

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 (de Gennes 1979) 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).

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

1 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.
3 IAPV was the same with/without a 30% residual oil saturation.
4 28-35% residual oil saturation.
**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 partly responsible for the observed variations. We do not deny the existence of excluded volume effects when polymers flow through porous media—especially low-permeability rock. However, reports of high *IAPV* values in high-permeability rock require more support to be credible. 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.

**Laboratory Measurement of Polymer Retention**

<table>
<thead>
<tr>
<th>REVIEW OF POLYMER RETENTION METHODS</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>1. Mass balance on polymer: Polymer slug followed by water.</strong></td>
</tr>
<tr>
<td>a. Unfavorable displacement during water injection after polymer –requiring MANY PV of water.</td>
</tr>
<tr>
<td>b. Significant errors accumulate from measuring low polymer concentrations.</td>
</tr>
<tr>
<td><strong>2. Static method: Sand mixed with polymer solution.</strong></td>
</tr>
<tr>
<td>a. Relies on only two measurements of polymer concentration.</td>
</tr>
<tr>
<td>b. Exposes extra mineral area for crushed rock.</td>
</tr>
<tr>
<td>c. Does not account for mechanically entrapped polymer.</td>
</tr>
</tbody>
</table>

**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 3630STM, which is an acrylamide-acrylate copolymer with a molecular weight of ~19 million g/mol and ~30% degree of hydrolysis (as stated by the manufacturer). 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 (i.e., 12.4% PV) 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 µm 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 $IAPV = 0$ (within our experimental error).

In Fig. 5, a small difference between the two curves between 1 and 1.5 PV, where the tracer concentration is higher than the polymer concentration. This might suggest additional polymer retention, even though it is the second cycle of polymer injection. However, we did not generally observe this phenomenon, and we do not have a physical explanation—other than to suggest possible limitations of the measurement technique. Considering our experimental errors, our error bars were generally around +/- 10% PV for the IAPV values.

![Fig. 2—Retention during 1st injection of HPAM into T1 sand.](image)
Fig. 3—Retention during 2nd injection of HPAM into T1 sand.

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

\[
C = \frac{\text{(injected concentration)}}{\text{[(capillary reading)-1]}}/\frac{\text{[(capillary reading @ 3 PV)-1]}}{\text{..............(4)}
\]

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 µg/g for Fig. 1 (HPAM in T1 sand) and 2 µg/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, within our experimental error) on the T1 and T2 sand samples that we examined. Considering our experimental error bars, we assign the retention values of 0 +/- 20 µg/g.

<table>
<thead>
<tr>
<th>Polymer Retention and IAPV from Laboratory Studies</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tambaredjo Sands, Sarah Maria Polymer Flood, Suriname</td>
</tr>
<tr>
<td>Retention, µg/g</td>
</tr>
<tr>
<td>-----------------</td>
</tr>
<tr>
<td>T1 Sand</td>
</tr>
<tr>
<td>T2 Sand</td>
</tr>
</tbody>
</table>

What is the best source of reservoir sand?

a. Coring?
b. From the shale shaker during drilling?
c. Sand production from a production well?
d. Synthetic sand?
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 field mandates that polymer injection is preferred over water injection. Produced oils range in viscosity from 1,260 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.

- **Laboratory polymer retention measurements use/represent a VERY small part of the reservoir.**
- **Can field measurements be used to obtain more representative polymer retention values?**
- **Data would be helpful for scale up to a larger project.**

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 (determined using the starch-iodide method) 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.

- Injected salinity: 500-ppm TDS.
- Formation water salinity: 4700-ppm TDS.
- Polymer flood started right after primary production.
- Produced water salinity can act as a tracer.

![Fig. 7—Produced water salinities for wells of interest.](image)
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.
Procedure to Estimate Polymer Retention from Field Data

1. Assume IAPV = 0.
2. For each producer, use the stabilized salinity data to establish the fraction of water flow coming from a nearby injector. \( f_{wtrac} = B/A \).
3. Use salinity to assign a swept volume between an injector producer pair. \[ V_{swept} = (f_{wtrac}) \sum [\Delta V_{tracprod} \cdot (1 - \frac{C_{trac}}{C_{trac0}})] \]

Procedure to Estimate Polymer Retention from Field Data

4. Estimate the rock mass in the swept area:

\[ M_{rock} = V_{swept} [(1-\phi)\phi] \rho_{rock} \]

5. Estimate polymer retention:

\[ R_{pret} = \left\{ C_{poly} \sum [\Delta V_{polyprod} \cdot (1 - \frac{C_{poly}}{C_{poly0}})] \right\} / M_{rock} \]
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 uncertainty 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. Further, even if the polymer had degraded, the starch-iodide method used at the time should have detected the polymer. 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.

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

(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. 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, \( C_{\text{trac}}/C_{\text{traco}} \) 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, \( C_{\text{trac}}/C_{\text{traco}} = (2500-4737)/(1291-4737) = 0.649 \). For Production Well 1N11, recall that \( f_{\text{wtrac}} \) was 0.813. For Production Well 1N11, the calculated value for \( V_{\text{swept}} \) 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. Among the wells in the pilot project, polymer and water breakthrough was noted earliest for Well 1N11—because this area included the most permeable part of the pilot project. Well 1N11 was shut-in December 11, 2012, because of the high water cut. Our analysis indicated that high water cuts in this well were due to flow through very permeable sand—not through a fracture. If a fracture had been responsible for channeling, the polymer retention associated with this part of the field should have been quite low. Instead, retention was estimated to be between 160 and 517 \( \mu g/g \)—the highest range of values among the six wells. The fact that the retention values associated with Well 1N11 were not low is qualitatively consistent with flow through porous rock.

Because polymer retention denudes polymer from the first part of the injected aqueous bank, a bank of water propagates ahead of the polymer bank. The volume swept by the water could be less than that swept by the subsequent polymer. Consequently, the swept volume may be conservatively low. This fact will tend to inflate the calculation of polymer retention.

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

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

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

Finally, polymer retention is estimated using Eq. 7.

\[
R_{\text{pret}} = \{ C_{\text{polyo}} \sum \left[ \Delta V_{\text{polyprod}} \ast (1-C_{\text{poly}}/C_{\text{polyo}}) \right] \}/ M_{\text{rock}} \tag{7}
\]

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, \( \Delta V_{\text{polyprod}} \), is multiplied by \( (1- C_{\text{poly}}/C_{\text{polyo}}) \) and summed. Here, \( C_{\text{poly}} \) is the produced polymer concentration at a given time. Choices exist for the parameter, \( C_{\text{polyo}} \). One choice is the stabilized polymer concentration after breakthrough. Alternatively, one could argue that \( C_{\text{polyo}} \) should be given by the injected polymer concentration multiplied by \( f_{\text{wtrac}} \). 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.

<table>
<thead>
<tr>
<th>Production well</th>
<th>1N11</th>
<th>1I25</th>
<th>1N06</th>
<th>1M05</th>
<th>1M09</th>
<th>1N01</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starting salinity, ppm TDS</td>
<td>4737</td>
<td>4686</td>
<td>4657</td>
<td>4432</td>
<td>4707</td>
<td>3998</td>
</tr>
<tr>
<td>Ending salinity, ppm TDS</td>
<td>1291</td>
<td>1692</td>
<td>1684</td>
<td>2531</td>
<td>2281</td>
<td>1769</td>
</tr>
<tr>
<td>Ending polymer, ppm</td>
<td>634</td>
<td>550</td>
<td>375</td>
<td>226</td>
<td>216</td>
<td>395</td>
</tr>
<tr>
<td>$f_{\text{wtrac}}$</td>
<td>0.813</td>
<td>0.708</td>
<td>0.715</td>
<td>0.483</td>
<td>0.577</td>
<td>0.637</td>
</tr>
<tr>
<td>$f_{\text{wpoly}}$</td>
<td>0.634</td>
<td>0.554</td>
<td>0.349</td>
<td>0.195</td>
<td>0.203</td>
<td>0.381</td>
</tr>
<tr>
<td>Range of retention values, µg/g</td>
<td>160-517</td>
<td>129-247</td>
<td>53-125</td>
<td>14-337</td>
<td>45-99</td>
<td>50-168</td>
</tr>
</tbody>
</table>

Field values for HPAM retention ranged from 14 µg/g to 517 µg/g, depending on the pattern in the polymer flood and the $f_w$ and $C_{\text{polyo}}$ 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 µg/g). Most retention numbers in Table 3 fall between 50 and 250 µg/g. An average of all 12 numbers listed in the last row is 162 µg/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 µg/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/represent the reservoir sand: (a) coring, (b) from the shale shaker during drilling (as we did in this study), (c) sand production from a production well, or (d) formulation of synthetic sand based on mineralogical analysis? Perhaps, for the most appropriate method: when obtaining reservoir cores for laboratory retention studies, drilling/coring procedures should not use high-surface area materials.

In Table 3, Well 1N01 was outside the immediate pilot area. Nonetheless, this well experienced polymer breakthrough—probably because the well was in the most-permeable area of this portion of the field and was adjacent to the pilot. All wells surrounding the pilot were produced by primary mechanisms (compaction and solution gas drive; no gas cap or aquifer drive). No unusual activities were conducted outside the pilot area.

Wang (1993) suggested that surfactant retention values from laboratory studies in aerobic cores were higher than those in anaerobic rock in the reservoir. Conceivably, the redox state of iron
minerals may affect surfactant retention. By extension, the redox state of the sand or rock may also affect polymer retention. We are actively investigating this possibility.

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. Our method may be of value in determining retention for surfactants or other chemicals during field chemical flooding processes. Our application was fortunate in that the produced salinity acted as a natural tracer. If a waterflood is applied between primary production and the chemical flooding process, a separate tracer (or set of tracers) must be used.

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 (0 +/- 20 µg/g for retention and 0 +/- 10% PV for IAPV).
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 ~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

\[ C = \text{polymer concentration, mg/L or ~ppm} \ [\mu g/g] \]
\[ C_{\text{inj}} = \text{injected polymer concentration during a retention study, mg/L or ~ppm} \ [\mu g/g] \]
\[ C_{\text{poly}} = \text{produced polymer concentration, mg/L or ~ppm} \ [\mu g/g] \]
\[ C_{\text{polyo}} = \text{injected polymer concentration or stabilized produced polymer concentration, mg/L or ~ppm} \ [\mu g/g] \]
\[ C_{\text{trac}} = \text{produced tracer concentration minus zero-baseline tracer concentration, mg/L or ~ppm} \ [\mu g/g] \]
\[ C_{\text{traco}} = \text{injected tracter concentration or stabilized produced tracer concentration minus zero-baseline tracer concentration, mg/L or ~ppm} \ [\mu g/g] \]
\[ f_{\text{wpoly}} = \text{fraction of produced water originating from an offset injection well, based on polymer flow} \]
\[ f_{\text{wtrac}} = \text{fraction of produced water originating from an offset injection well, based on tracer flow} \]
\[ IAPV = \text{inaccessible pore volume} \]
\[ M_{\text{rock}} = \text{mass of rock in the core or polymer contacted portion of the reservoir, g} \]
\[ PV = \text{pore volumes of fluid injected} \]
$PV_{ret}$ = 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 [$m^3$]

$\Delta V_{polyprod}$ = incremental produced volume associated with polymer, bbl [$m^3$]

$\Delta V_{polytrac}$ = incremental produced volume associated with tracer, bbl [$m^3$]

$\phi$ = porosity

$\rho_{rock}$ = rock density, g/cm$^3$

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


448–452.


Zheng, C.G., Gall, B.L., Gao, H.W., Miller, A.E., and Bryant, R.S. 2000. Effects of Polymer
