

# Effect of Concentration on HPAM Retention in Porous Media

Guoyin Zhang, SPE, and, R.S. Seright, SPE, New Mexico Petroleum Recovery Research Center

## Summary

This paper investigates the effect of hydrolyzed polyacrylamide (HPAM) polymer concentration on retention in porous media by use of both static and dynamic measurements. Consistent results by use of these two methods show that different polymer-retention behaviors exist in dilute, semidilute, and concentrated regions. In both the dilute and concentrated regions, polymer retention has little dependence on concentration. In contrast, in the semidilute region, polymer retention is concentration dependent. If a porous medium is first contacted sufficiently with dilute polymer solution to satisfy the retention, no significant additional retention occurs during exposure to higher HPAM concentrations. On the basis of the experimental results, a concentration-related retention mechanism is proposed that considers the orientation of the adsorbed polymer molecules and the interaction between molecular coils in solution. By use of this model, we explain why polymer retention does not show much dependence on concentration in the dilute and concentrated regimes. Further, in the semidilute region, we explain how moderate coil interactions lead to mixed adsorbed-polymer orientation and magnitude on rock surfaces, and retention becomes concentration dependent. In field applications of polymer and chemical floods, reduced polymer retention may be achieved by first injecting a low-concentration polymer bank.

## Introduction

When water-soluble, high-molecular-weight polymers are used for enhanced oil recovery (EOR), polymer retention retards propagation into the formation. The presence of the polymer is needed to provide high viscosity and low mobility levels—which in turn are needed to improve oil displacement and sweep efficiency. Consequently, high polymer retention can substantially delay oil displacement and recovery. To illustrate this point, consider the range of polymer-retention levels reported in the literature—9 to 700  $\mu\text{g/g}$  (Green and Willhite 1998)—and the range of polymer concentrations used in polymer floods—500 to 3,000 ppm. Given the rock density ( $\rho_{\text{rock}} = 2.65 \text{ g/cm}^3$  for quartz), porosity ( $\phi$ ; e.g., 0.3), polymer retention in  $\mu\text{g/g}$  ( $R_{\text{ret}}$ ), and polymer concentration in ppm ( $C_{\text{poly}}$ ), Eq. 1 can be used to calculate the delay [ $PV_{\text{ret}}$ , or pore volume (PV) delay per PV injected]:

$$PV_{\text{ret}} = [\rho_{\text{rock}}(1 - \phi)/\phi][R_{\text{ret}}/C_{\text{poly}}] \quad (1)$$

By use of Eq. 1 and the previously discussed parameters, Fig. 1 shows delay factors. With a very low retention level of 10  $\mu\text{g/g}$  and a polymer concentration of 2,000 ppm, the delay factor is only approximately 3% of 1 PV. In contrast, for a high retention of 500  $\mu\text{g/g}$  and a polymer concentration of 500 ppm, the delay factor is more than 6 PV. For more-typical values of 150  $\mu\text{g/g}$  for retention and a polymer concentration of 1,500 ppm, the delay factor is approximately 0.6 PV. For this latter combination, a 20% difference in retention would mean an extra 12% PV polymer bank needed (if the retention is higher) or not needed (if the retention is lower) to accomplish a given objective. In one 40-acre, five-spot pattern with a height of 20 ft and a porosity of 0.3, 0.12

PV of 1,500 ppm HPAM (costing USD 1.5/lbm) would represent a polymer cost of approximately USD 176,000.

From another viewpoint, the mass of rock in the previously discussed 40-acre pattern is  $40 \times 43,560 \times 20 \times (12 \times 2.54)^3 \times 2.65 \times (1 - 0.3)/0.3 = 6.10 \times 10^{12} \text{ g}$ . Given the retention levels of 10, 50, 120, 150, 180, and 500  $\mu\text{g/g}$ , and an HPAM cost of USD 1.5/lbm, the polymer costs required to satisfy the retention requirements of the rock would be USD 201,777, 1,008,883, 2,421,320, 3,026,650, 3,631,980, and 10,088,835, respectively.

Of course, the delay in polymer propagation also delays oil recovery. Fig. 2 illustrates this point by use of fractional-flow calculations (Seright 2010). For these calculations, we assumed oil viscosity of 1,000 cp, water viscosity of 1 cp, and that the reservoir was initially at connate-water saturation ( $S_{\text{wr}} = 0.3$ ). The reservoir was then flooded with 1 PV of water (before continuous polymer flooding with 100-cp polymer); one homogeneous layer was present; flow was linear; and the following relative permeability curves were used:

$$k_{\text{rw}} = 0.1 \times [(S_{\text{w}} - 0.3)/(1 - 0.3 - 0.3)]^2, \quad (2)$$

$$k_{\text{ro}} = 1 \times [(1 - 0.3 - S_{\text{w}})/(1 - 0.3 - 0.3)]^2. \quad (3)$$

In Fig. 2, the term IAPV refers to inaccessible PV, which is defined as the fraction of the pore space that is inaccessible to the large polymer molecules but accessible to the small solvent and salt molecules and ions. IAPV accelerates polymer propagation, whereas polymer retention ( $PV_{\text{ret}}$ ) retards it. Three different levels were considered in Fig. 2: where retention and IAPV were perfectly balanced to cause no delay in polymer propagation (i.e.,  $PV_{\text{ret}} + \text{IAPV} = 0$ ); where retention and IAPV caused a 1-PV delay (i.e.,  $PV_{\text{ret}} + \text{IAPV} = -1$ ); and where retention and IAPV caused a 2.5-PV delay (i.e.,  $PV_{\text{ret}} + \text{IAPV} = -2.5$ ). Fig. 2 illustrates that the delay in the arrival of the oil bank is directly proportional to the delay in polymer propagation. Consequently, high polymer retention is economically detrimental because of increased cost for polymer and delayed oil recovery.

It is widely accepted that polymer retention comprises polymer adsorption on the rock surface and mechanical entrapment in small throats and pores (Gogarty 1967). A third type of retention is related to the hydrodynamic force acting on polymer molecules, and this flow-induced retention is called hydrodynamic retention (Marker 1973; Dominguez and Willhite 1977; Aubert and Tirrell 1980; Zaitoun and Kohler 1987; Huh et al. 1990).

Petroleum literature review shows that among the factors influencing polymer retention, polymer concentration is controversial. Some researchers suggested that polymer retention in the porous media is concentration dependent or fits the Langmuir isotherm (Mungan 1969; Dawson and Lantz 1972; Szabo 1975, 1979; Deng et al. 2006). Close examination of these reports reveals that most measurements were performed using a static method. The Langmuir adsorption model, which is well-known to describe reversible adsorption, is currently used in most chemical-flooding simulators to describe polymer retention in porous media (Satter et al. 1980; Vossoughi et al. 1984; Camilleri et al. 1987; Yuan et al. 2010; Dang et al. 2011). Ironically (and in contrast), most experimentalists regard adsorption of high-molecular-weight polymers on surfaces to be largely irreversible. Results from most researchers show polymer concentration is a minor factor for polymer retention (Shah et al. 1978; Green and Willhite 1998; Zheng et al. 1998). Generally, these studies used dynamic

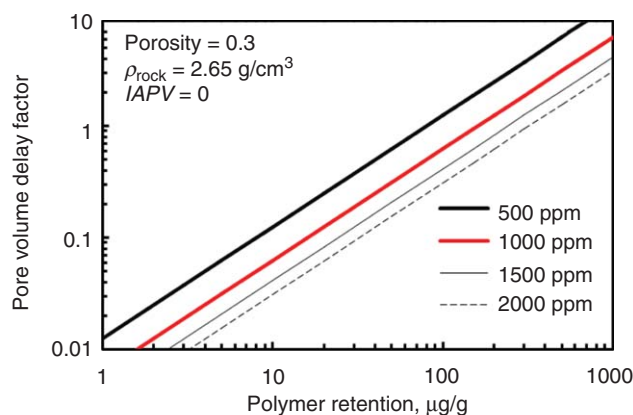


Fig. 1—Polymer-bank delay factors associated with polymer retention.

measurements, and the same cores were used repeatedly in the tests. Specifically, a given core was flooded first with a low-polymer concentration; retention was assessed; then a higher polymer concentration was injected into the same core to assess whether any further retention occurred. Although Zheng et al. (1998) claimed their data fit the Langmuir isotherm, their retention values increased from 40 µg/g at 250 ppm to only 58 µg/g at 1,500 ppm. Only a few studies used new cores or sandpacks for each concentration; these studies demonstrated moderate concentration dependence for retention (Szabo 1975; Huang and Sobie 1993).

Results from different literature studies are comparable only if measurements were conducted under similar conditions. This is especially true when comparing results from static measurements with those from dynamic measurements. In this paper, a series of tests was designed to clarify literature discrepancies concerning how polymer concentration affects retention in porous media. Several types of experiments were performed, including static measurements of polymer retention on fresh sand for each concentration case, and dynamic measurements of polymer retention in new sandpacks with similar permeability and porosity for different HPAM concentrations. We also examined polymer-retention measurements in which a single sand, sandpack, or sandstone core was exposed to successive solutions with increasing polymer concentration. HPAM-polymer solutions with a broad concentration range (from 10 to several thousand ppm) were used.

## Materials and Methods

**Polymer and Brine.** SNF Flopaam 3230S, a partially HPAM polymer, was used in our tests. It was provided by the manufacturer as a white granular powder with an estimated molecular weight of 6 to 8 million daltons and degree of hydrolysis of approximately 30%. After the polymer was dissolved by use of the magnetic-stirrer vortex method, the solution was filtered through a 10-µm filter to remove any microgels and debris. Two brines were used: One was 2% NaCl for the static measurements and coreflooding by use of sandpacks, whereas the other brine contained 2.52% total dissolved solids (2.3% NaCl and 0.22% NaHCO<sub>3</sub>) when consolidated sandstone cores were used. Both brines were filtered through 0.45-µm filters before application.

**Sand Preparation.** Sand grains with particle sizes between 106 and 180 µm were prepared as the adsorbent by crushing and sieving Berea sandstone. To reduce the presence of very fine particles, special processes were undertaken for the treatment of these disaggregated sands. First, the sand was put into a bottle with brine and rotated at 300 rev/min for 8 hours. Then, the muddy liquid phase was separated from the sand. Next, the sand was washed with distilled water to remove newly generated fine particles and residual salt until the upper water phase was clear. Finally, the sand was dried at 110°C.

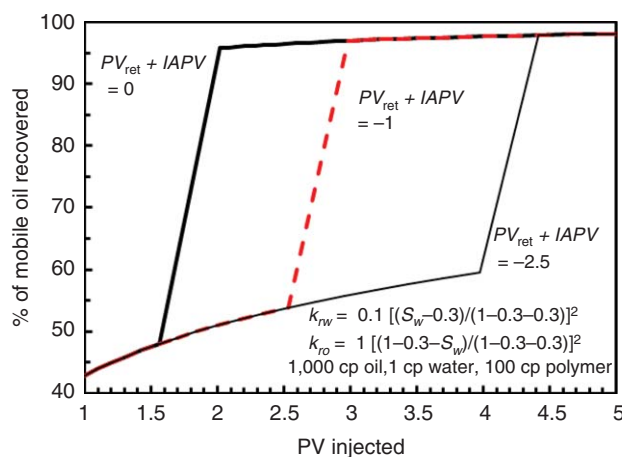


Fig. 2—Delay in oil recovery caused by retention.

**Porous Media.** Disaggregated sands prepared as described previously were used for static adsorption measurements. To determine dynamic polymer retention in porous media, both sandstone cores and sandpacks were used. The Dundee sandstone core had a permeability of 347 md and porosity of 0.23. This rectangular core (with 15-cm length and a 14.5-cm<sup>2</sup> cross section) was cast in epoxy. Sandpacks with relatively similar permeability and porosity were prepared from the same sands used for static measurements. Sandpacks were 6.35 cm long and 14.5 cm<sup>2</sup> in cross section.

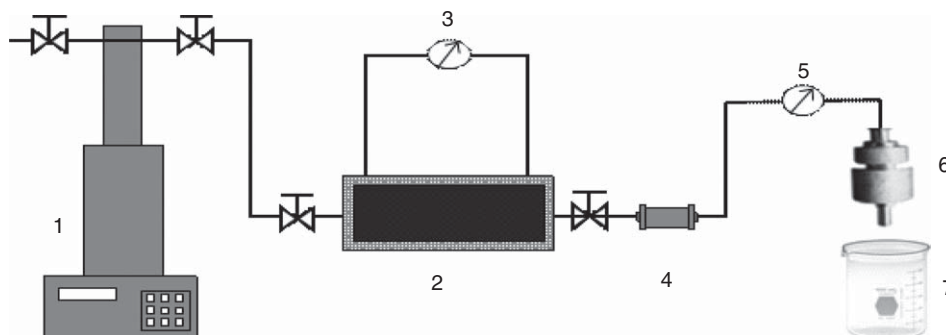
**Polymer-Concentration Determination.** For static measurements, the concentration of the initial and equilibrium polymer solutions was determined by use of a total-organic-carbon (TOC) analyzer (Shimaduz model TOC-V\_CSH). If a polymer solution was too viscous, dilutions were made before measurement. When dynamic measurements were performed, polymer concentration in the effluent was determined on the basis of fluid viscosity. When flowing through a 10-µm filter combination (Seright et al. 2009) connected to the outlet of the core, reliable pressure drops were detected even for HPAM concentrations as low as 25 ppm (Seright et al. 2011). By use of this method, the effluent polymer concentration could be monitored continuously.

**Static Adsorption Measurements.** Bottles containing sand and polymer solution (of known mass) were fastened to a roller, which rotated at a speed of 6 rev/min for 1 hour. The 1-hour contact was considered sufficient because the polymer adsorption on the rock surface is believed to be instantaneous (adsorption kinetics will be discussed later). After rotation, the upper polymer solution was transferred to a plastic tube to be centrifuged at 3,000 rev/min to settle any sand particles. Equilibrium polymer concentration was determined by a TOC analyzer. Polymer adsorption for each concentration was calculated by use of Eq. 4 (on the basis of a mass balance):

$$R_{\text{pret}} = (C_0 - C_{\text{eq}}) \times V_p / W_{\text{sg}}, \quad \dots \dots \dots (4)$$

where  $R_{\text{pret}}$  is polymer adsorption in µg/g sand and  $C_0$  and  $C_{\text{eq}}$  are initial and equilibrium polymer concentrations, respectively, in ppm.  $V_p$  is polymer volume in cm<sup>3</sup>, and  $W_{\text{sg}}$  is sand weight in g. Both polymer and brine density were assumed to be 1 g/cm<sup>3</sup>.

**Dynamic Retention Measurements.** Several methods were proposed to measure polymer retention in porous media (Dawson and Lantz 1972; Szabo 1975, 1979; Dominguez and Willhite 1977; Gupta 1978; Castagno et al. 1987; API 1990; Huh et al. 1990; Mezzomo et al. 2002). Several of them call for injection of a slug of polymer solution, followed by brine, and then performing a mass balance on the polymer (i.e.: retention = polymer injected minus polymer produced). Key problems with this type



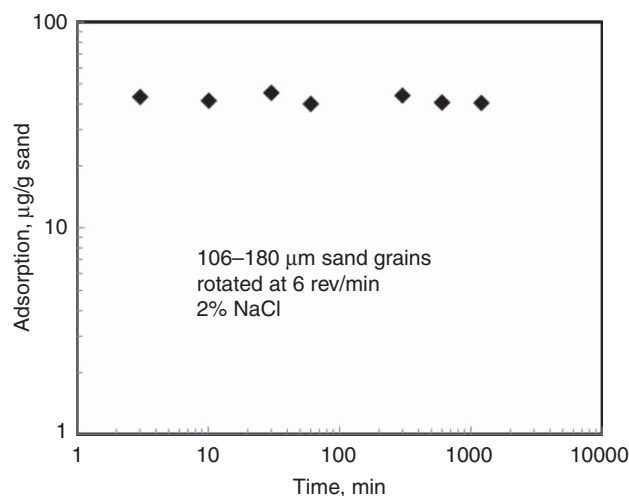
**Fig. 3—Schematic of polymer-retention-determination system. (1) Isco syringe pump (Model 500D); (2) sandstone core or sand-pack; (3) Pressure Transducer No. 1; (4) 7- $\mu$ m Swagelok filter; (5) Pressure Transducer No. 2; (6) 10- $\mu$ m millipore filter combination, and (7) beaker.**

of method are that recovery of the polymer may require an extended period of brine injection because of the unfavorable displacement, and cumulative errors associated with measurements of low polymer concentrations in the produced fluid can introduce considerable uncertainty to the mass balance.

We prefer the method used by Lotsch et al. (1985), Hughes et al. (1990), and Osterloh and Law (1998). In this method, two banks of polymer solution are injected and are separated by a brine slug. Polymer retention can be determined by the plot of the two effluent polymer-concentration profiles vs. PV injected. Fig. 3 shows a schematic of our experimental unit to determine polymer retention in porous media. It should be noted that any reversibly retained polymer should be flushed from the core during the extensive brine injection. The reoccurrence of this retention during the following polymer injection will make the second effluent concentration profile shift closer to the first one. As a consequence, reversible retention is excluded, or only irreversible retention is measured by means of this dynamic method.

## Results and Discussions

**Adsorption Kinetics.** The kinetics of polymer adsorption was first analyzed by mixing 100 ppm polymer solution with sand. Samples of the polymer solution were taken periodically for polymer-concentration determination. The results of adsorption vs. time are plotted in Fig. 4. Adsorption reached the maximum (approximately 40  $\mu$ g/g sand) within approximately 3 minutes and then leveled off. This indicates polymer adsorption on the sand surface can be considered instantaneous. In our tests, the contact of polymer solution and sand lasted 1 hour to ensure adsorption equilibrium.

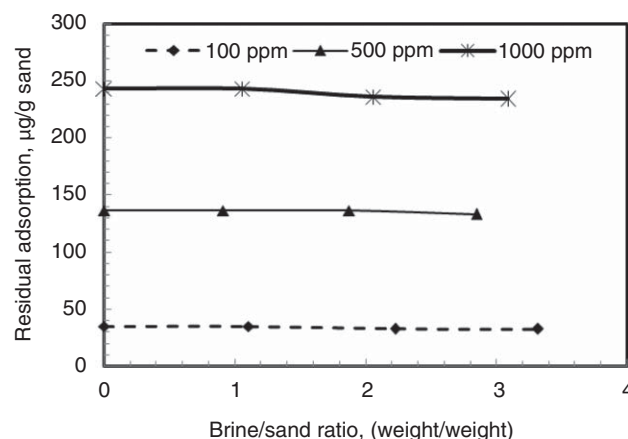


**Fig. 4—Kinetics of polymer adsorption on sand.**

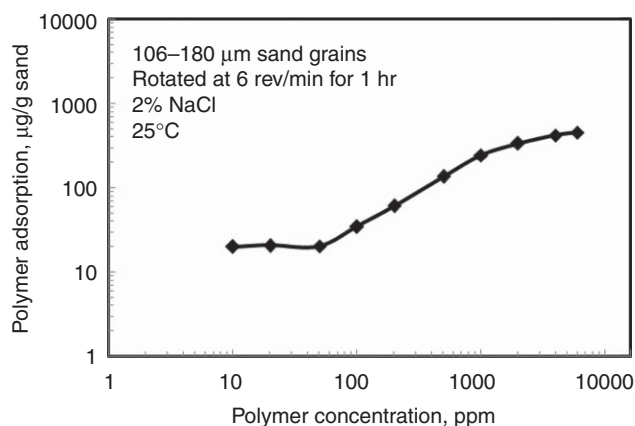
**Desorption Test.** After adsorption, desorption tests were carried out to estimate the amount of polymer that can be removed. In this test, excess polymer solution was decanted from the top of the sand. Fresh brine was then added, and again the bottle containing both sand and brine was rotated at 6 rev/min for 1 hour. When the sands settled, the upper-phase solution was sampled for polymer-concentration determination. The residual polymer adsorption was calculated by use of mass balance. This procedure was repeated until no more desorbed polymer was detected. Fig. 5 shows the results for 100, 500, and 1,000 ppm HPAM. Calculations show that the percentage of the reversible adsorption for these three cases was 6.6, 2.4, and 2.9%, respectively. This result was similar to that from Deng et al. (2006). 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. It is statistically very unlikely that a polymer molecule would release all points of attachment at the same time. Therefore, polymer adsorption on the sand surface can be treated as almost irreversible.

**Effect of Polymer Concentration.** To investigate the effect of polymer concentration on retention, polymer solutions were examined with concentrations from 10 to 6,000 ppm. The results are illustrated in Fig. 6, which suggests three distinct concentration-related retention behaviors. First, in the low-concentration region (from 10 to approximately 100 ppm), polymer retention stabilized approximately at a value of 20  $\mu$ g/g. In the intermediate-concentration region (from 100 to approximately 4,000 ppm), polymer retention increased from 35 to 420  $\mu$ g/g, increasing almost linearly with polymer concentration. In the high-concentration region (more than 4,000 ppm), nearly constant retention (approximately 420  $\mu$ g/g) was achieved.

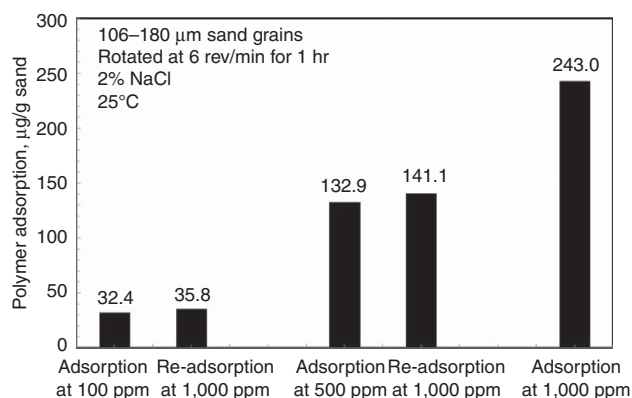
These results (especially the concentration-dependent observation) agree with previous findings, in which most of the



**Fig. 5—Desorption tests for 100, 500, and 1,000 ppm HPAM.**



**Fig. 6—Adsorption isotherm of HPAM by use of the static method.**



**Fig. 7—Comparison of retention on fresh sands and used sands.**

**TABLE 1—DYNAMIC RETENTION IN SANDPACKS**

Sandpack Number	Length, cm	Area, cm <sup>2</sup>	Weight of Sand, g	Pore Volume, cm <sup>3</sup>	Porosity	Permeability, darcies	Polymer Concentration, ppm	Retention, µg/g Sand
1	6.25	14.19	140.4	39.1	0.441	5.51	2,000	27.8
2			139.7	39.0	0.440	5.04	1,000	14.3
3			140.2	38.7	0.436	4.88	500	10.2
4			141.4	38.3	0.432	4.69	100	5.71
5			141.0	38.7	0.436	5.03	50	4.85
6			140.6	39.1	0.441	5.37	20	4.63

measurements were made in the intermediate-concentration region (Mungan 1969; Espinasse and Siffert 1979). Our findings indicate that polymer retention does not fit the Langmuir isotherm, which is commonly used to describe the reversible adsorption of small molecules such as surfactants and gas. For EOR polymers with high molecular weights and extended chains, adsorption on rock shows little reversibility (Fig. 5). It is postulated that at very low concentration, polymer molecules continue to be adsorbed until the maximum coverage is reached. During this process, few adsorbed polymer molecules are likely to detach from the surface. Therefore, unlike the adsorption described by the Langmuir isotherm, polymer adsorption at low concentration approaches a constant nonzero value.

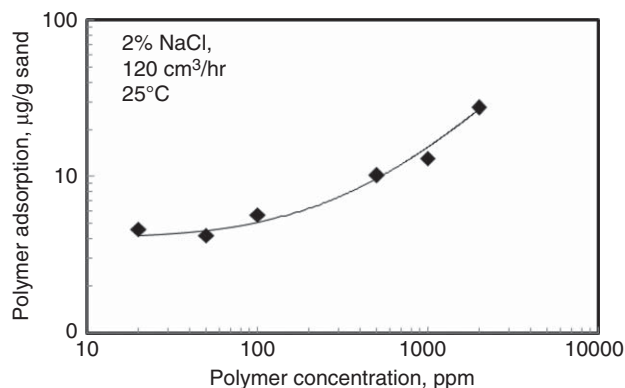
**Readsorption Test.** Fresh sands were used for each case to generate the adsorption isotherm shown in Fig. 6, which illustrates the concentration-related adsorption behaviors. After the desorption

tests in Fig. 5, 1,000 ppm polymer solution was added to the sands previously contacted with 100 and 500 ppm polymer solution to check if polymer readsorption occurred. Little additional polymer was adsorbed onto the used sands. For instance, for the 100-ppm concentration case, the retention increased from 32.4 to 35.8 µg/g, increasing by 10.3%. For the 500-ppm case, retention rose from 132.9 to 141.1 µg/g, merely a 6.1% increase. Compared with the adsorption at a concentration of 1,000 ppm (243 µg/g, as shown in Fig. 7), a large retention difference existed between the fresh sand and sand for which retention was satisfied by low-concentration polymer solution. Apparently, even though polymer adsorption was relatively small at low concentration, the surface was already fully covered by adsorbed polymer molecules, and no vacant sites were available for further attachment.

## Dynamic Method

**Retention in Sandpacks.** Dynamic measurements were performed in sandpacks made from the same sand source that was used for static measurements. For each concentration, a new sandpack was used. As shown in Table 1, these sandpacks had very similar properties. Permeability ranged from 4.69 to 5.51 darcies, and porosity ranged from 0.432 to 0.441. Because of the high permeability, we suggest that polymer adsorption dominated the retention (Szabo 1975; Huh et al. 1990). Polymer solutions with concentrations of 20, 50, 100, 500, 1,000, and 2,000 ppm were investigated by use of an injection rate of 120 cm<sup>3</sup>/h (6.6-ft/D flux). The retention is shown by both Table 1 and Fig. 8. Retention was approximately 5 µg/g at low concentrations from 20 to 100 ppm. With the increase of concentration from 100 to 2,000 ppm, retention increased from 5.71 to 27.8 µg/g, increasing by a factor of nearly five.

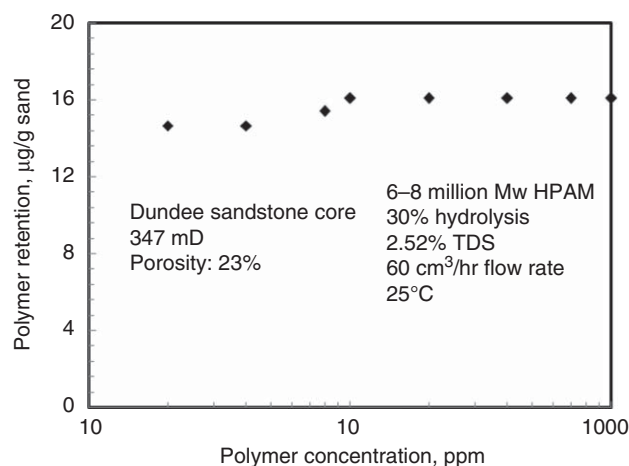
After completion of measurements for 100- and 500-ppm cases (Sandpacks 4 and 3 in Table 1, respectively), 1,000-ppm solution was injected. Retention increases of 5.6 and 7.3% were detected in these two used sandpacks, respectively. This result agrees with the static measurement on used sands, which also



**Fig. 8—Adsorption isotherm by use of the dynamic method (new sandpacks were used for each concentration).**

**TABLE 2—DYNAMIC RETENTION IN DUNDEE SANDSTONE CORES AT INJECTION RATE OF 60 cm<sup>3</sup>/h or 3.3 ft/D**

Core Number	Length, cm	Section Area, cm <sup>2</sup>	Pore Volume, cm <sup>3</sup>	Porosity, %	Permeability, md	Polymer Concentration, ppm	Retention, µg/g
1	15	14.5	49	22	347	20 through 1,000	16.1
2			51	23	449	1,000	56.5



**Fig. 9—Adsorption isotherm on 347-md Dundee sandstone core (the same core was used for all concentrations).**

confirms that the adsorbed molecules occupy almost all the vacant sites on the sand surface and prevent further attachment.

**Retention in Dundee Sandstone Cores.** In addition to the disaggregated sands and highly permeable sandpacks, retention was also measured in two consolidated Dundee sandstone cores. As shown in **Table 2**, these two cores had similar properties of permeability and porosity. Two distinct strategies were used. For Core 1, polymer solutions with concentrations from 20 through 1,000 ppm were injected sequentially to determine retention for each concentration. In contrast, for Core 2, only 1,000-ppm solutions were injected. The result from Core 1 is shown in **Fig. 9**. Retention was approximately 15 to 16 µg/g. When polymer concentration was greater than 100 ppm, the retention reached a plateau, with the maximum retention of approximately 16 µg/g. In contrast, the retention for Core 2 was as high as 56.5 µg/g rock, 3.5 times higher than that for the first core (Table 2). These results agree with our findings mentioned previously. The result from Core 1 was also consistent with other studies in which the same core was repeatedly used (Shah et al. 1978; Zheng et al. 1998).

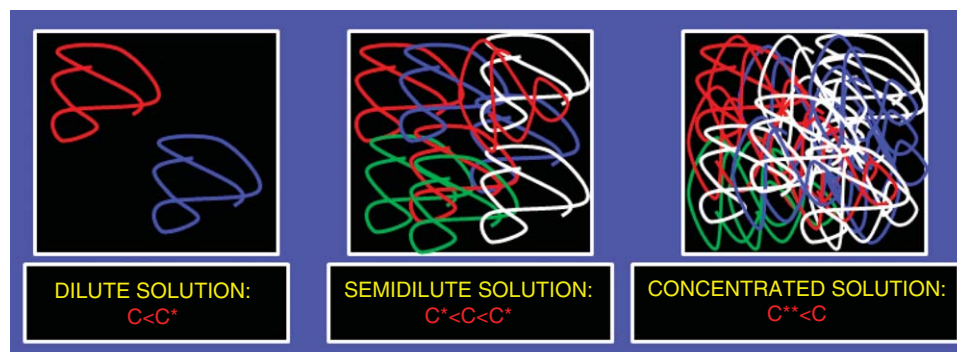
When static and dynamic retention are compared, we found at the same polymer concentration that static measurement gives much higher retention. For instance, at a concentration of 2,000

ppm, static retention of 335 µg/g is detected on disaggregated sand grains (Fig. 6). Nevertheless, Table 1 shows dynamic retention is only approximately 27.8 µg/g in 5.51-darcy sandpack. The unusually high retention from static measurement is attributed to the larger surface area exhibited by disaggregated sands. Compared with the 27.8-µg/g retention in 5.51-darcy sandpack, the dynamic retention in 449-md fresh sandstone core is approximately 56.5 µg/g at concentration of 1,000 ppm (Core 2 in Table 2). The difference between these two dynamic retention rates can be explained by the effect of rock permeability. Research shows that polymer retention strongly depends on the permeability of porous media. Polymer retention usually increases with decrease of rock permeability (Vela et al. 1976).

### Proposed Adsorption Model

On the basis of the experimental results, a polymer-concentration-related retention model is proposed that accounts for the observed retention behavior. It is well-known that polymer molecules may interact with each other in solution and the degree of interaction depends greatly on polymer concentration. Three concentration regimes were proposed (de Gennes 1979; Ying and Chu 1987) as dilute ( $c < c^*$ ), semidilute ( $c^* < c < c^{**}$ ), and concentrated ( $c^{**} < c$ ), where  $c^*$  is the overlap concentration crossover from the dilute to the semidilute regime and  $c^{**}$  is the overlap concentration crossover from the semidilute to the concentrated regime. More specifically, as shown in **Fig. 10**, in the dilute regime, polymer molecules exist in solution as free coils where little interaction occurs. In the semidilute regime, where polymer concentration is greater than the overlap concentration,  $c^*$ , macromolecules start to contact each other and intermolecular interactions occur. With further increase in concentration (especially when the concentration is more than  $c^{**}$ ), the intermolecular entanglements dominate the interaction, resulting in the formation of a network structure (Ferry 1948). For our HPAM, brine, and temperature, we measured  $c^*$  to be 300 ppm and  $c^{**}$  to be 3,000 ppm. When dealing with polymer retention on sand surfaces, this concentration-based interaction among polymer molecules in solution may be used to explain the adsorption mechanism.

In the dilute regime, polymer molecules exist in solution as free coils but tend to take a flat orientation when they adsorb onto the rock surface. In this configuration, most, if not all, of the molecular segments are in contact with the surface. It was called 2D adsorption (Peterson and Kwei 1961). In this regime, 2D adsorption dominates retention, and polymer molecules continue to be adsorbed until the maximum coverage is reached. As shown by



**Fig. 10—Polymer-molecule interaction at different concentrations.**



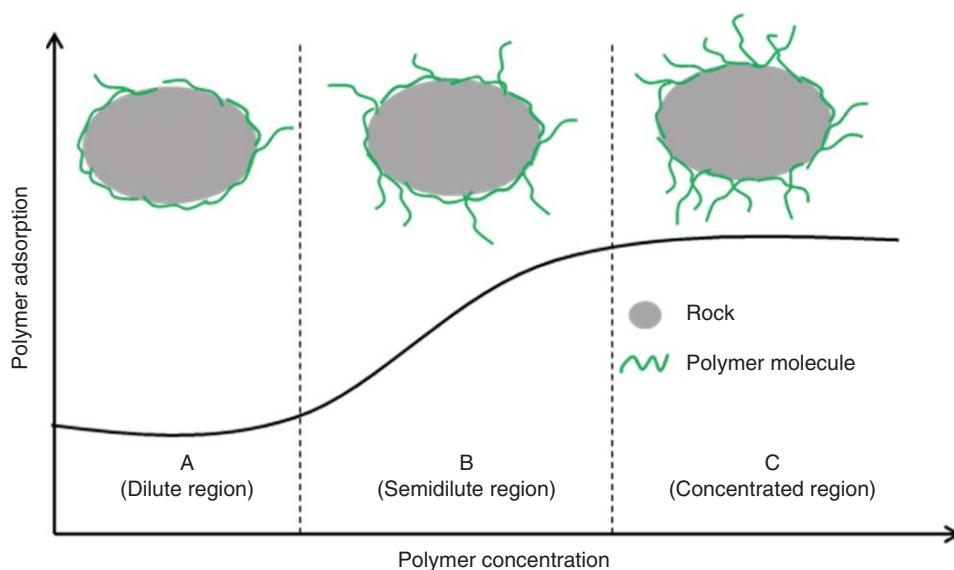


Fig. 11—Proposed polymer-adsorption mechanism on the rock surface.

Region A in Fig. 11, adsorption is independent of polymer concentration. For practical purposes, the retention in the dilute regime indicates the minimum amount of polymer needed to occupy the available vacant sites. In field applications of polymer and chemical floods, reduced polymer retention may be achieved by first injecting a low-concentration polymer bank.

In the semidilute regime, the intermolecular interaction in solution will result in a mixed adsorption (i.e., some molecules will be adsorbed with all the segments in contact with the surface, whereas others will be adsorbed with only partial segments in contact with the surface). The latter orientation will be labeled as 3D adsorption. Increasing the polymer concentration will increase the 3D adsorption as well as the total adsorption, as shown by Region B in Fig. 11. Polymer retention is concentration dependent in the semidilute regime.

In the concentrated regime, the molecular entanglement in solution causes the 3D adsorption to dominate (i.e., most polymer molecules are adsorbed with segments partially attached to the rock surface). Put another way, only one end of the polymer molecule is attached to the surface, whereas the majority of the molecule dangles free in the solution. In this case, almost no additional polymer molecules can be adsorbed with increasing concentration because all sites are taken. As shown by Region C in Fig. 11, the adsorption is concentration independent.

This model also explains why no significant adsorption occurred during exposure to a high-concentration solution after sand was first contacted with dilute polymer solution. After the surface maximum coverage is achieved, no more vacant sites are available.

This explanation accounts for the dependence of adsorption on polymer concentration. Nevertheless, besides adsorption on rock surface, mechanical entrapment occurs simultaneously in pore-throat constrictions and dead-end spaces when consolidated cores are used (Huh et al. 1990; Ranjbar et al. 1991). The impact of polymer concentration on mechanical entrapment should hence also be addressed. On the basis of the experimental results depicted by Fig. 9, polymer retention that encompasses both adsorption and entrapment shows concentration-independent behavior. Because additional adsorption proves to be insignificant when used sands are used (Fig. 7), the mechanical entrapment—at least the irreversible accumulation of polymer molecules in small pores and dead-end spaces—shows little variation with increase of polymer concentration. In other words, suppose two identical fresh cores are used. If a high polymer concentration is injected, this will result in a higher adsorption relative to low-concentration injection.

## Discussion

This research focused on the effect of polymer concentration on retention, and measurements were carried out in monophasic conditions (in the absence of oil phase). Previous work shows polymer retention is usually lower with residual oil saturation than without oil present—suggesting that the presence of residual oil may reduce HPAM retention (Szabo 1975; Hughes et al. 1990; Broseta et al. 1995). Polymer retention causes rock-permeability reduction by forming a thin layer on rock surface (residual resistance factor). The residual resistance factor increases with decrease of permeability (Jennings et al. 1971; Hirasaki and Pope 1974; Seright 1993). In the future, the dependence of permeability reduction and oil saturation on polymer concentration should be investigated further, especially with regard to the concentration dependence of polymer retention that was reported in this paper.

As mentioned earlier, field applications may be interested in our finding that polymer retention is low if the rock is first contacted with a low polymer concentration. Polymer losses caused by retention may be reduced considerably if a dilute polymer bank precedes the main mobility-control bank. Whether this approach is practical will depend on economics, timing, and the specific polymer-retention levels that occur in the particular field application.

Should our model and results replace the existing Langmuir-isotherm formulations for polymer retention in simulators? The Langmuir isotherm was always incorrect mechanistically for polymer retention (because most polymer retention is irreversible), so one could argue that it should never have been used. However, to be more supportive of previous simulators, the use of the Langmuir isotherm may not result in grossly incorrect predictions if the Langmuir plateau is set to be reached at a very low polymer concentration, if the polymer front is sufficiently sharp, and if the injected-polymer concentration is relatively high. If these conditions are not met, there should be value in incorporating our model into the polymer-flooding simulator.

## Conclusions

1. HPAM-polymer adsorption on a rock surface can be considered instantaneous and irreversible.
2. Different polymer-retention behaviors are observed in dilute, semidilute, and concentrated regions in the absence of oil saturation. In both dilute and concentrated regions, polymer retention is basically concentration independent. In contrast, in the semidilute region, polymer retention is concentration dependent.

3. If a porous medium is first contacted with dilute HPAM solution to satisfy the retention, no significant additional retention occurs when exposed to higher concentrations. In field applications of polymer and chemical floods, reduced polymer retention may be achieved by first injecting a low-concentration polymer bank.
4. On the basis of the experimental results, a concentration-related retention mechanism is proposed that considers the orientation of the adsorbed-polymer molecules and the interaction between molecular coils in solution.

## Nomenclature

$c^*$  = polymer overlap concentration crossover from the dilute to the semidilute regime  
 $c^{**}$  = polymer overlap concentration crossover from the semidilute to the concentrated regime  
 $C_0$  = initial polymer concentration, ppm  
 $C_{eq}$  = equilibrium polymer concentration, ppm  
 $C_{poly}$  = polymer concentration, ppm  
 $k_{ro}$  = relative permeability to oil  
 $k_{rw}$  = relative permeability to water  
 $PV_{ret}$  = PV delay per PV injected  
 $R_{pret}$  = polymer adsorption,  $\mu\text{g/g}$  sand  
 $S_{wr}$  = residual water saturation  
 $V_p$  = volume of polymer solution,  $\text{cm}^3$   
 $W_{sg}$  = weight of sand, g  
 $\rho_{rock}$  = rock density,  $\text{g/cm}^3$   
 $\phi$  = porosity

## Acknowledgments

We thank Statoil for financially supporting this work.

## References

- API. 1990. *API RP 63 Recommended Practices for Evaluation of Polymers Used in Enhanced Oil Recovery Operations*. American Petroleum Institute, Washington, D.C. (June 1990).
- Aubert, J. H. and Tirrell M. 1980. Flows of Dilute Polymer Solutions through Packed Porous Chromatographic Columns. *Rheol. Acta* **19** (4): 452–461. <http://dx.doi.org/10.1007/BF01524018>.
- Broseta, D. Medjahed, F., Lecourtier, J., et al. 1995. Polymer Adsorption/Retention in Porous Media: Effects of Core Wettability and Residual Oil. *SPE Advanced Technology Series* **3** (1): 103–112. <http://dx.doi.org/10.2118/24149-PA>.
- Camilleri, D., Engelsens, S., Lake, L. W., et al. 1987. Description of an Improved Compositional Micellar/Polymer Simulator. *SPE Res Eng* **2** (4): 427–432. <http://dx.doi.org/10.2118/13967-PA>.
- Castagno, R. E., Shupe, R. D., Gregory, M. D., et al. 1987. Method for Laboratory and Field Evaluation of a Proposed Polymer Flood. *SPE Res Eng* **2** (4): 452–460. <http://dx.doi.org/10.2118/13124-PA>.
- Dang, C. T. Q., Chen, Z., Nguyen, N. T. B., et al. 2011. Development of Isotherm Polymer/Surfactant Adsorption Models in Chemical Flooding. Paper SPE 147872 presented at the SPE Asia Pacific Oil and Gas Conference and Exhibition, Jakarta, Indonesia, 20–22 September. <http://dx.doi.org/10.2118/147872-MS>.
- Dawson, R., and Lantz, R. B. 1972. Inaccessible Pore Volume in Polymer Flooding. *SPE J.* **24** (5): 448–452. <http://dx.doi.org/10.2118/3522-PA>.
- de Gennes, P. G. 1979. *Scaling Concepts in Polymer Physics*. Ithaca, New York: Cornell University Press.
- Deng, Y., Dixon, J. B. and White, G. N. 2006. Adsorption of Polyacrylamide on Smectite, Illite, and Kaolinite. *Soil Sci. Soc. AM. J.* **70** (1): 297–304. <http://dx.doi.org/10.2136/sssaj2005.0200>.
- Dominguez, J. G. and Willhite, G. P. 1977. Retention and Flow Characteristics of Polymer Solutions in Porous Media. *SPE J.* **17** (2): 111–121. <http://dx.doi.org/10.2118/5835-PA>.
- Espinasse, P., and Siffert, B. 1979. Acetamide and Polyacrylamide Adsorption onto Clays: Influence of the Exchangeable Cations and the Salinity of the Medium. *Clay. Clay. Miner.* **27** (4): 279–284. <http://dx.doi.org/10.1346/CCMN.1979.0270406>.
- Ferry, J. D. 1948. Viscoelastic Properties of Polymer Solutions. *J. Res. Nat. Bur. Stand.* **41** (1): 53–62. <http://dx.doi.org/10.1007/BF01974775>.
- Gogarty, W. B. 1967. Mobility Control with Polymer Solutions. *SPE J.* **7** (2): 161–173. <http://dx.doi.org/10.2118/1566-PA>.
- Green, D. W., and Willhite, G. P. 1998. *Enhanced Oil Recovery*, Vol. **6**, 107–110. Richardson, Texas: Textbook Series, SPE.
- Gupta, S. P. 1978. Micellar Flooding: The Propagation of the Polymer Buffer Bank. *SPE J.* **18** (1): 5–12. <http://dx.doi.org/10.2118/6204-PA>.
- 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. <http://dx.doi.org/10.2118/4026-PA>.
- Huang, Y., and Sobie, 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 SPE International Symposium on Oilfield Chemistry, New Orleans, Louisiana, 2–5 March. <http://dx.doi.org/10.2118/25173-MS>.
- Hughes, D. S., Teeuw D., Cottrell, C. W., et al. 1990. Appraisal of the Use of Polymer Injection to Suppress Aquifer Influx and to Improve Volumetric Sweep in a viscous Oil Reservoir. *SPE Res Eng* **5** (1): 33–40. <http://dx.doi.org/10.2118/17400-PA>.
- Huh, C., Lange, E. A., and Cannella, W. J. 1990. Polymer Retention in Porous Media. Paper SPE 20235 presented at the SPE/DOE Enhanced Oil Recovery Symposium, Tulsa, Oklahoma, 22–25 April. <http://dx.doi.org/10.2118/20235-MS>.
- Jennings, R. R., Rogers, J. H. and West, T. J. 1971. Factors Influencing Mobility Control by Polymer Solutions. *J. Pet. Tech.* **23** (3): 391–401. <http://dx.doi.org/10.2118/2867-PA>.
- Lotsch, T., Muller, T., and Pusch, G. 1985. The Effect of Inaccessible Pore Volume on Polymer Core Experiments. Paper SPE 13590 presented at the SPE Oilfield and Geothermal Chemistry Symposium, Phoenix, Arizona, 9–11 April. <http://dx.doi.org/10.2118/13590-MS>.
- Marker, J. M. 1973. Dependence of Polymer Retention on Flow Rate. *J. Pet. Tech.* **25** (11): 1307–1308. <http://dx.doi.org/10.2118/4423-PA>.
- Mezzomo, R. F., Moczydlower, P., Sanmartin, A. N., et al. 2002. A New Approach to the Determination of Polymer Concentration in Reservoir Rock Adsorption Tests. Paper SPE 75204 presented at the SPE/DOE Improved Oil Recovery Symposium, Tulsa, Oklahoma, 13–17 April. <http://dx.doi.org/10.2118/75204-MS>.
- Mungan, N. 1969. Rheology and Adsorption of Aqueous Polymer Solutions. *J. Cdn. Pet. Tech.* **8** (2): 45–50. <http://dx.doi.org/10.2118/69-02-01>.
- Osterloh, 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, Oklahoma, 19–22 April. <http://dx.doi.org/10.2118/39694-MS>.
- Peterson, C. and Kwei, T. K. 1961. The Kinetics of Polymer Adsorption onto Solid Surfaces. *J. Phys. Chem.* **65** (8): 1330–1333. <http://dx.doi.org/10.1021/j100826a013>.
- Ranjbar, M., Rupp, J. and Pusch, G. 1991. Influence of Pore Radi Distribution on Polymer Retention in Natural Sandstones. Oral presentation given at 6th European Symposium on Improved Oil Recovery, Stavanger, Norway, 21–23 May.
- Satter, A., Shum, Y. M., Adams, W. T., et al. 1980. Chemical Transport in Porous Media with Dispersion and Rate-controlled Adsorption. *SPE J.* **20** (3): 99–104. <http://dx.doi.org/10.2118/6847-PA>.
- Seright, R. S. 1993. Effect of Rock Permeability on Gel Performance in Fluid-Diversion Applications. *In Situ*. **17** (4): 363–386.
- Seright, R. S. 2010. Reservoir Sweep Improvement. <http://baervan.nmt.edu/randy/>.
- Seright, R. S., Fan, T., Wavrik, K., et al. 2011. New Insights into Polymer Rheology in Porous Media. *SPE J.* **16** (1): 35–42. <http://dx.doi.org/10.2118/129200-PA>.
- Seright, R. S., Seheult, M., and Talashek T. 2009. Injectivity Characteristics of EOR Polymers. *SPE Res Eval & Eng* **12** (5): 783–792. <http://dx.doi.org/10.2118/115142-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 Fall Technical Conference and Exhibition, Houston, Texas, 1–3 October. <http://dx.doi.org/10.2118/7586-MS>.
- Szabo, M. T. 1979. An Evaluation of Water-Soluble Polymers for Secondary Oil Recovery – Part 2. *J. Pet. Tech.* **31** (5): 561–570. <http://dx.doi.org/10.2118/6601-PA>.

- Szabo, M. T. 1975. Some Aspects of Polymer Retention in Porous Media Using a C14-Tagged Hydrolyzed Polyacrylamide. *SPE J.* **15** (4): 323–337. <http://dx.doi.org/10.2118/4668-PA>.
- 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. <http://dx.doi.org/10.2118/5102-PA>.
- Vossoughi, S., Smith, J. E., Green, D. W., et al. 1984. A New Method to Simulate the Effects of Viscous Fingering on Miscible Displacement Processes in Porous Media. *SPE J.* **24** (1): 56–64. <http://dx.doi.org/10.2118/10970-PA>.
- Ying, Q., and Chu, B. 1987. Overlap Concentration of Macromolecules in Solution. *Macromolecules* **20** (2): 362–366. <http://dx.doi.org/10.1021/ma00168a023>.
- Yuan, C., Delshad, M., and Wheeler, M. F. 2010. Parallel Simulations of Commercial-Scale Polymer Floods. Paper SPE 123441 presented at the SPE Western Regional Meeting, Anaheim, California, 27–29 May. <http://dx.doi.org/10.2118/132441-MS>.
- 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, 4–6 February. <http://dx.doi.org/10.2118/16274-MS>.
- Zheng, C. G., Gall, B. L., Gao, H. W., et al. 1998. Effects of Polymer Adsorption and Flow Behavior on Two-Phase Flow in Porous Media. Paper SPE 39632 presented at SPE/DOE Improved Oil Recovery Symposium, Tulsa, Oklahoma, 19–22 April. <http://dx.doi.org/10.2118/39632-MS>.

## SI Metric Conversion Factors

ft × 3.048*	E–01 = m
in. × 2.54*	E+00 = cm
lbm × 4.535 9237	E–01 = kg
md × 9.869 233	E–01 = μm <sup>2</sup>

\*Conversion factor is exact.

**Guoyin Zhang** is a PhD candidate in petroleum engineering at New Mexico Tech (NMT), Socorro, New Mexico. He holds a bachelor's degree from China University of Petroleum and a master's degree in petroleum engineering from NMT. Before his study at NMT, he worked for the EOR department of Daqing Exploration & Development Research Institute (PetroChina) for more than 10 years.

**Randall Seright** is a senior engineer at the New Mexico Petroleum Recovery Research Center at NMT, where he has worked since 1987. He holds a bachelor's degree in chemical engineering from Montana State University and a PhD degree in chemical engineering from the University of Wisconsin. Seright was awarded the SPE/DOE IOR Pioneer Award in 2008.