Is Polymer Retention Different Under Anaerobic vs. Aerobic Conditions?

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Summary

This paper examines whether retention of partially hydrolyzed polyacrylamide (HPAM) is different under anaerobic vs. aerobic conditions. Both static (mixing with loose sand) and dynamic methods (corefloods) were used to determine HPAM retention. There are both advantages and disadvantages associated with determining polymer retention with static tests vs. dynamic tests and with aerobic vs. anaerobic conditions. From static-retention measurements, polymer-adsorption values on pure silica sand or Berea sandstone were small, and they showed little difference between experiments conducted aerobically or anaerobically. For both aerobic and anaerobic conditions, HPAM retention increased significantly with increased pyrite or siderite content. Static retention under anaerobic conditions ranged from 45 to 75 µg/g with 1% of either pyrite or siderite to 137–174 µg/g for 10% pyrite or siderite to 1161–1249 µg/g for 100% pyrite or siderite.

If iron minerals are present, the most representative polymer-retention results are obtained (for both static and dynamic tests) if conditions are anaerobic. Retention values (from static measurements) under aerobic conditions were commonly twice those determined under anaerobic conditions. If iron minerals are present and retention tests are performed under aerobic conditions, total organic carbon (TOC) or some similar method should be used for polymer detection. Viscosity detection of polymer may provide retention values that are too high (because oxidative degradation can be misinterpreted as polymer retention). For a broad range of siderite content, retention from static tests did not depend on whether dissolved oxygen was present. However, for a broad range of pyrite content, HPAM retention was significantly lower in the absence of dissolved oxygen than under aerobic conditions. These results may be tied to iron solubility. When polymer solutions were mixed with 100% pyrite over the course of 12 hours, 360–480 ppm of iron dissolved into polymer solutions under both aerobic and anaerobic conditions, whereas with 100% siderite, only 0.0–0.6 ppm of iron dissolved. If dynamic methods (i.e., corefloods) are used to determine polymer retention under aerobic conditions, flow rates should be representative of the field application. Rates that are too high lead to underestimation of polymer retention. With 10% pyrite, dynamic retention was 211 µg/g at 6 ft/D vs. 43.2 µg/g at 30 ft/D. In contrast, retention values were fairly consistent (40.6–47.8 µg/g) between 6 and 33 ft/D under anaerobic conditions.

Introduction

In polymer flooding, polymer retention is defined to include the combined effects of polymer adsorption on rock and mechanical entrapment of polymer in pores. Polymer retention can have a major impact on polymer-slug propagation and economics. Manichand and Seright (2014) calculated that a 1,240-ppm polymer solution exhibiting a retention value of 100 µg/g would require injection of 50% more polymer to reach a target distance in a formation (relative to the case for no polymer retention). They also reported field polymer (HPAM) retention values ranging from 50 to 250 µg/g for the Tambaredjo polymer flood in Suriname. In our laboratories with clean sands (Zhang and Seright 2014, 2015), some very low retention values (<10 µg/g) have been measured. On the other hand, we have also occasionally witnessed polymer-retention values up to 1000 µg/g in multidarcy rock and sand from oil reservoirs. In concept, any process that removes polymer could affect measurement of polymer retention, including precipitation, partitioning between phases, and degradation. For example, if viscosity was used to detect produced-polymer concentration, any polymer degradation (and consequent viscosity loss) that occurred during contact with the rock could be interpreted as polymer retention.

Most oil reservoirs exist under anaerobic conditions (Xu et al. 2000; Hartog et al. 2002). In contrast, most laboratory studies of chemical enhanced-oil-recovery (EOR) processes take place with ambient oxygen present. Wang (1993) found that surfactant-retention values were significantly lower in reservoir anaerobic conditions than in laboratory aerobic conditions, because the redox state affects surface-charge density and potential. Rajapaksha et al. (2014) noted higher polymer degradation and poor polymer transport in an ankerite-rich carbonate core. Hughes et al. (1990) reported a polymer (xanthan) retention value of 15 600 µg/g in unfired siderite. Consequently, we wonder whether redox condition may affect polymer retention—primarily by affecting the state of any iron present and its interaction with polymer.

Partially HPAM undergoes degradation by redox cycles when both Fe^{2+} and oxygen are present (Pye 1967; Shupe 1981; Ramsden and McKay 1986; Levitt et al. 2011; Seright and Skjevrak 2015). Seright and Skjevrak (2015) compared stability of HPAM in the presence of varying initial dissolved oxygen (0–8000 ppb), Fe^{2+} (0–220 ppm), and Fe^{3+} (0–172 ppm). For 2,000 ppm of HPAM at 23 and 90°C, no significant viscosity loss was observed after 1 week when less than 200 ppb of dissolved oxygen was present. Above that level, significant viscosity losses were seen and increased with Fe^{2+} concentration. At 23°C with 8,000 ppb initial oxygen, a 75% loss occurred for HPAM with 30 ppm of Fe^{2+}. Oxidative degradation of HPAM has been attributed to radical species, generated by redox cycling of transition metal ions. These radicals reportedly cleave the acrylic backbone of the polymer, leading to reduction of molecular weight and a corresponding drop of viscosity (Pye 1967; Shupe 1981; Ramsden and McKay 1986; Levitt et al. 2011).

HPAM can be quite stable in the presence of Fe^{2+} (up to 220 ppm) if no dissolved oxygen is present (Seright and Skjevrak 2015). However, any Fe^{3+} that is present can complex with the polymer to form a gel, regardless of whether dissolved oxygen is present (Seright and Skjevrak 2015). After polymer crosslinking occurs and gel particles grow to approach the size of pore throats, they will no longer flow through porous rock at a practical rate (Seright 1995; Ranganathan et al. 1998). This seems a possible mechanism for HPAM retention to be investigated.

Wang (1993) showed that surfactant retention on natural kaolin clays can be reduced (from 990 to 400–650 µg/g) by using dithionite-containing brine prewash to have surface iron reduced to the ferrous state, whereas dithionite-containing brine prewash had no effect on surfactant retention for the pure synthetic kaolin clay without iron impurities. Also, Wang and Guidry (1994) found that Berea-core wettability can be changed from strongly water-wet to mixed-wet under conventional aerobic condition after aging for 54 days. However, wettability altered at a slower rate (196 days) when cores were exposed to reducing conditions, and no wettability change was detected when surface iron in cores

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Sand Composition	Surface Area (m^2/g)
100% Quartz	0.244
100% Pyrite (FeS_2)	1.312
100% Siderite ($FeCO_3$)	8.004
1% Pyrite, 99% Quartz	0.271
10% Pyrite, 90% Quartz	0.873
1% Siderite, 99% Quartz	0.581
10% Siderite, 99% Quartz	1.136
Crushed Berea Sand	0.722

Table 1—Surface area of sand composition.

was removed by sodium dithionite. Transition metals (e.g., iron) were suggested as attracting and complexing anionic surfactants to polar surfaces or to polar molecules in crude oils.

Experimental

Two types of experiments were performed to evaluate retention of HPAM in or onto rock materials: static-adsorption experiments and retention during flow through porous media (dynamic-retention experiments). For a given set of experiments, one part was conducted in the presence of ambient oxygen (i.e., aerobic), whereas a second part was conducted with no atmospheric or dissolved oxygen present (anaerobic). Oxygen-free solutions were prepared and sealed inside an anaerobic chamber (Forma Scientific Model 1025^{TM}), which was filled with an anaerobic gas (10–15% hydrogen and 85–90% nitrogen) that was continuously circulated through a palladium catalyst. Oxygen level was regularly checked with a colorimetric method (CHEMet^{TM}). The oxygen levels in aqueous solutions were less than 5 ppb.

Brine and Polymer. The brine used for making polymer solutions contained 2.52% total dissolved solid (0.22% calcium chloride and 2.3% sodium chloride). It was filtered through 0.45-µm filters after preparation. The polymers used in our tests were SNF Flopaam^{TM} 3230S and 3630S. They are acrylamide-acrylate copolymers; 3230S has molecular weight of approximately 6 to 8 million daltons and 30% degree of hydrolysis; 3630S has molecular weight of approximately 18 million daltons and 30% degree of hydrolysis. During dynamic-retention measurements, polymer solutions also contained 40 ppm of potassium iodide (KI) as a tracer.

Sand. Polymer adsorption was studied with four different materials: quartz powder, iron sulfide (pyrite) powder, iron carbonate (siderite) powder, and crushed Berea sandstone. The Berea sandstone was prepared by crushing and sieving to make grain sizes between 106 and 180 µm. Sands were washed with distilled water before use to remove extra-fine particles generated during the crushing process. The quartz powder was BDH9274 Ottawa sand; it was pure quartz with particle sizes between 420 and 590 µm. This sand was used as received. We also mixed Ottawa sand with pyrite (FeS_2) and siderite ($FeCO_3$) mineral powders to the desired mineral concentration to study the effect of iron and oxygen on polymer retention. Surface area of each composition is listed in **Table 1.** For comparison, surface area of Berea sandstone measured by Wang (1993) was 0.3 to 0.6 m^2/g.

Sandpacks. The sandpacks used in this work had 0.88-cm inside diameter and were 30.48 cm long. Each sandpack contained either crushed Berea sandstones or quartz with different mineral concentrations. After packing, the total weight of the sand inside each sandpack was determined, as well as its porosity and permeability to brine. Then, 2 L of brine was flushed through the packs to condition the sand.

Static-Equilibrium Adsorption. The static-adsorption tests were performed on different sets of sand particles. The 1500-ppm polymer solutions (3230S) were added to clean, dry sands with a liquid/solid ratio of approximately 1:2. Then, the mixtures were stirred for 15 minutes to ensure adequate contact, and left quiescent for 12 hours thereafter. Next, the supernatant was decanted from the mixtures and centrifuged at 300 rev/min for further separation. Then, the fully separated polymer solutions were tested for TOC. The retention level (R) was determined by the concentration change ($C_{\text{polyo}}-C_{\text{poly}}$), volume of polymer solution (M_{poly}/ρ_p), and the mass of sand (M_{sand}), as shown in Eq. 1:

$$R = \frac{(C_{\text{polyo}} - C_{\text{poly}}) \times M_{\text{poly}}}{\rho_p \times M_{\text{sand}}}. \qquad (1)$$

Dynamic-Retention Experiments. Three sets of polymer-retention experiments were conducted with sandpacks to test the effect of redox state on polymer retention: one set under aerobic conditions, a second by extensive flushing with oxygen-free brine (in which oxygen was removed by bubbling anaerobic gas through the brine), and a third by preflushing with brine containing sodium dithionite ($Na_2S_2O_4$, a water-soluble oxygen scavenger). We examined HPAM polymer retention in silica sandpacks mixed with 1, 10, and 15% siderite and 1, 10, and 20% pyrite.

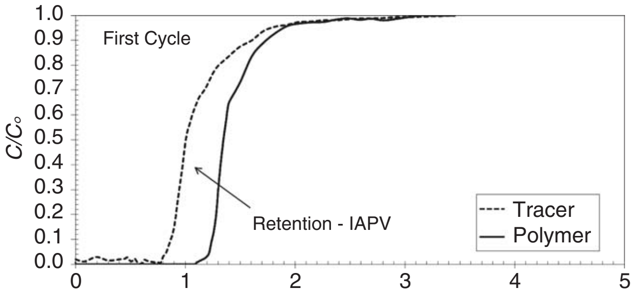
During the restoration process, approximately 60 pore volumes (PV) of oxygen-free synthetic brine (with or without sodium dithionite) was injected before retention measurements. Those injected brines were deoxygenated by purging with hydrogen and nitrogen gas inside the anaerobic chamber. Oxygen level was regularly monitored to make sure it was totally removed. Brine containing sodium dithionite had an E_H value of approximately –580 mV (meter reading; –370 mV after adjustment to standard conditions). Oxygen-free brine without dithionite had an E_H value of approximately –210 mV (standard conditions). A special coreflood arrangement was prepared that allowed fluids to flow from the anaerobic chamber through the test core and back into the anaerobic chamber. Flushing with brine that contained sodium dithionite resulted in a significant amount of iron removal from the sandpacks. The iron concentration in the effluent slowly decreased from 10 to 8 ppm over 60 PV of brine injection. In contrast, injecting brine without sodium dithionite resulted in zero iron concentration in the effluent. After the iron level in the effluent decreased to less than 10 ppm, the sandpack was flooded with synthetic brine to remove the sodium dithionite. The dissolved-oxygen concentration and E_H of effluent were constantly measured until no oxygen was detected, and E_H level was the same as that of injected brine to make sure the rock surface was in an anaerobic, reduced state. After that, a polymer solution with tracer was injected to measure the polymer retention. All experiments were conducted at room temperature.

For each test, two cycles of polymer solution were injected and separated by a 20-PV brine slug. During each cycle, polymer solution was injected until the readings reached injected concentrations for both polymer and tracer. Polymer retention can be determined from the difference in area between the polymer-breakout curve and tracer-breakout curve during the first-injection cycle **(Fig. 1a)** and is calculated as shown in Eq. 2:

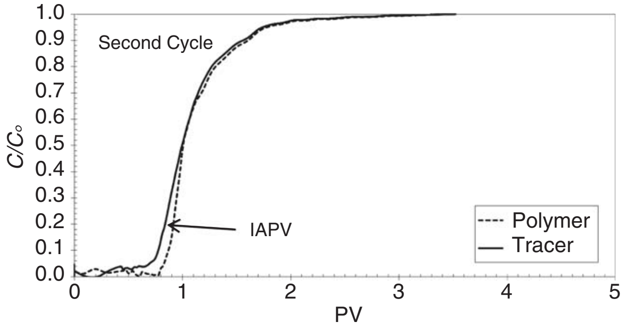
$$R = \left(\left\{ \sum \left[\left(\frac{C_{\text{poly}}}{C_{\text{polyo}}} \times \Delta\text{PV} \right) - \left(\frac{C_{\text{trac}}}{C_{\text{traco}}} \times \Delta\text{PV} \right) \right] \right\} + \text{IAPV} \right) \times C_{\text{polyo}} \times \text{PV}/M_{\text{sand}}. \qquad (2)$$

Similarly, inaccessible PV (IAPV) is determined from the difference in area between the polymer-breakout curve and the tracer-breakout curve during the second-injection cycle (Fig. 1b) and calculated by Eq. 3:

$$IAPV = \sum \left[(C_{\text{poly}}/C_{\text{polyo}} \times \Delta\text{PV}) - (C_{\text{trac}}/C_{\text{traco}} \times \Delta\text{PV}) \right]. \qquad (3)$$



(a) First-Injection Cycle



(b) Second-Injection Cycle

Fig. 1—Effluent-concentration curve of polymer and tracer for computation of polymer retention and IAPV: (a) first-injection cycle and (b) second-injection cycle.

Results and Discussion

Polymer Adsorption on Iron Minerals. ***Effect of Oxygen.*** Results of static adsorption tests are summarized and plotted as shown in **Tables 2 and 3** and **Fig. 2.** For the crushed Berea sandstone, removal of oxygen had no discernible effect on polymer adsorption. Polymer-adsorption results from experiments conducted inside and outside the anaerobic chamber were roughly the same (Table 2). The chemical analysis for the Berea sand that was washed and dried showed that it was mainly composed of quartz and feldspars, with very-low clay content (less than 1%) and no iron. Also, adsorption increased with increased polymer concentration, which was consistent with previous research by Zhang and Seright (2015) that showed polymer retention is concentration-dependent in the semidilute region.

For pure silica sand, because of its low surface area, polymer-adsorption values were small, and showed little difference between experiments conducted inside and outside of the anaerobic chamber (Table 3). For a broad range of siderite contents, retention did not definitively depend on whether dissolved oxygen was present. However, for a broad range of pyrite content, HPAM retention was consistently lower in the absence of dissolved oxygen than under aerobic conditions.

Effect of Iron Mineral. From Fig. 2, silica sands mixed with pyrite generally induced higher polymer retention than those mixed with siderite. Pure pyrite under aerobic conditions exhibited the highest retention, and retention for pure pyrite under anaerobic conditions was similar to retention for pure siderite under both aerobic and anaerobic conditions.

Discussion. **Table 4** shows pH, E_H, and iron concentration of the 1,500-ppm 3230S solutions after mixing with pure pyrite or siderite minerals for 12 hours. The total dissolved-iron concentrations were measured by colorimetric-iron test strips (Iron VACUettes^{TM} kit). Note that pyrite contact resulted in 360–480 ppm of iron released into polymer solutions under both aerobic and anaerobic conditions, whereas siderite contact induced only 0.0–0.6 ppm of dissolved iron. Also, polymer solutions that contacted pyrite rendered lower pH than solutions that contacted siderite. Those results are consistent with Levitt et al. (2011), who emphasized that iron solubility is especially low at high-pH values if carbonate/bicarbonate is present, and that iron solubility increases as pH and E_H decrease (Hem and Stumm 1961). From visual observations, the supernatant decanted from sands mixed with aerobic pyrite condition acquired a yellow-orange tint **(Fig. 3a),** whereas the supernatant decanted from sands mixed with anaerobic pyrite was clear (Fig. 3b).

The literature consistently states that HPAM experiences degradation when ferrous iron reacts with dissolved oxygen (Pye 1967; Shupe 1981; Ramsden and McKay 1986; Levitt et al. 2011; Seright and Skjevrak 2015). If increased polymer degradation resulted in less polymer detected, we might conclude that oxidative degradation was an important contributor to the observed HPAM adsorption values. However, TOC analysis should detect degraded (low-molecular-weight) HPAM as well as undergraded (high-molecular-weight) HPAM. Consequently, an alternative mechanism or mechanisms must be envisioned for the polymer loss.

On the basis of our results, we envision that multiple mechanisms are involved in polymer retention. First, a basic affinity of HPAM for pyrite and siderite must be important. This fact is evident because adsorption increased substantially with increased iron-mineral content, both with pyrite and siderite and during both aerobic and anaerobic conditions (Table 3 and Fig. 2). Surface area could make part of the contribution to the total increase, because surface area increases with increased iron-mineral content (Table 1). However, the effect of iron mineral is more prominent, because sand with pyrite that has lower surface area induced higher retention than sand mixed with siderite under the same iron content. Second, the presence of ferric iron (Fe^{3+}) appears to play a role. We suggest that aerobic pyrite results in generation of ferric iron (Fe^{3+}) in the solution (Table 4). As observed by Seright and Skjevrak (2015), this Fe^{3+} complexes with and removes HPAM from solution. In contrast, for anaerobic pyrite, even though a large concentration of ferrous iron (Fe^{2+}) dissolves (Table 4), Fe^{2+} does not crosslink with HPAM, so less polymer is lost (compared with the aerobic case). For the cases with siderite, the iron is bound so tightly by the carbonate that very little iron enters solution (Table 4)—so no iron reacts with oxygen to form Fe^{3+}, and no additional polymer losses are attributed to complexation with Fe^{3+}. Third, increased salinity associated with iron dissolution may decrease the hydrodynamic polymer size—allowing more polymer molecules to adsorb on a given surface (as shown by Zhang and Seright 2014), and ultimately resulting in higher retention.

	Adsorption Results (μg/g)					
Sand	Aerobic	Anaerobic	C_o (ppm)	Solid/Liquid Ratio	Sand (g)	Polymer (g)
Berea Sand	60	44.6	1535	2.4	30	12.5
	29.3	48.5	1526	2	30	15
	53.3	46.9	1526	2	50	25
	18.4	22.2	469	2	30	15

Table 2—Berea-sand static adsorption for 3230S HPAM.

Sand	Adsorption Results (µg/g) Aerobic	 Anaerobic
Pure Quartz (SiO_2)	29	38
1% Pyrite + 99% Silica	148	61
	135	75
10% Pyrite + 90% Silica	291	174
100% Pyrite	2154	1189
1% Siderite + 99% Silica	34	45
	51	47
10% Siderite + 90% Silica	128	137
100% Siderite	1185	1249
	1211	1161

Table 3—Static adsorption for 1500-ppm 3230S.

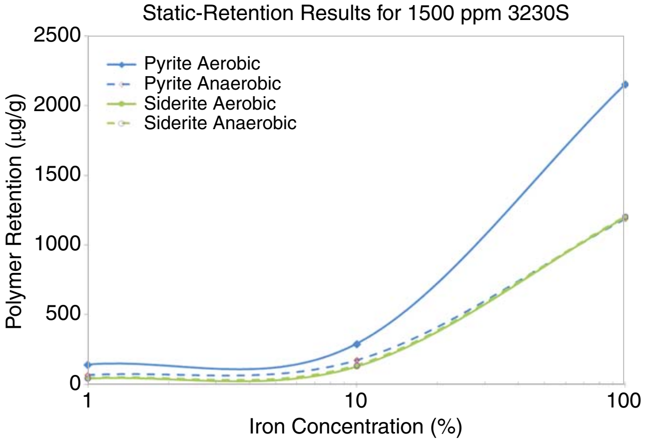


Fig. 2—Effects of iron-mineral concentration and oxygen on HPAM static retention at 23°C.

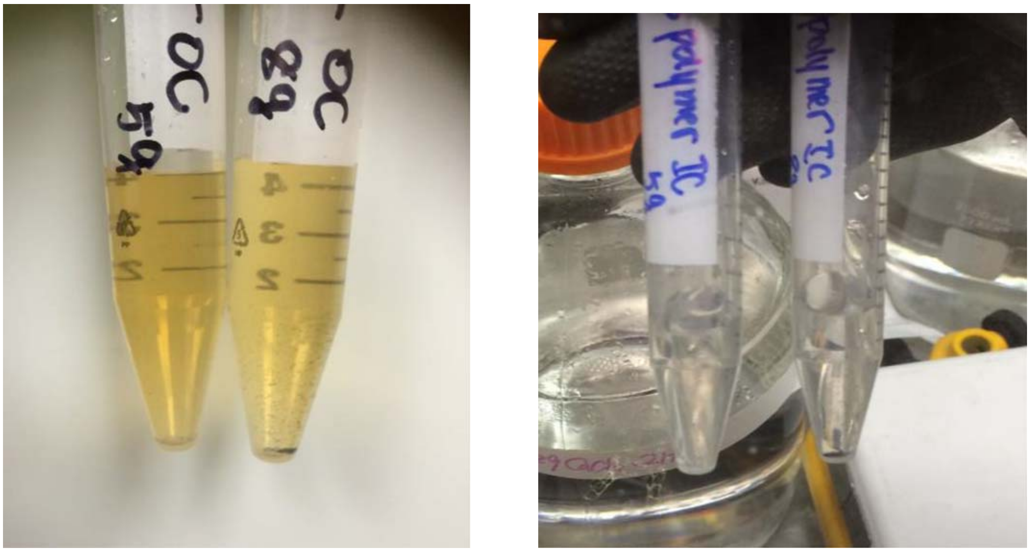
These observations provide an additional reason to maintain oxygen-free conditions when injecting polymer during polymer floods in reservoirs with high pyrite content (e.g., the Tambaredjo field in Suriname). Oxygen injected into the reservoir may react with pyrite to form Fe^{3+}, which complexes with HPAM, and that complex is stripped from the solution as it attempts to propagate through the reservoir. Recall that field polymer-retention values for the Tambaredjo field were reported to be high (Manichand and Seright 2014). In contrast, for reservoirs that contain much more siderite than pyrite (e.g., Seright et al. 2010), this problem may be less severe.

Sandpack Experiments. Dynamic-retention experiments with sandpacks with different mineral concentrations are summarized in **Table 5.** Hydrodynamic retention is negligible because of high permeability of sandpacks (>1 darcy under most circumstances). In agreement with static-retention results, dynamic-polymer (3230S HPAM) retention for pure silica did not depend on whether the conditions were aerobic or anaerobic. Also, polymer-retention values were essentially the same for the static and dynamic experiments (29–38 µg/g).

Interestingly, retention values in the presence of pyrite were lower for the dynamic experiments than for the static experiments. When injecting 1,500 ppm of 3230S into sand with 1 to 20% pyrite, the retention values were essentially the same (36.5–47.0 µg/g), regardless of pyrite content or whether the system was aerobic or anaerobic (middle part of Table 5). In contrast, static-retention values on 10% pyrite were 174 µg/g when anaerobic and 291 µg/g

Sand	Aerobic pH	 E_h (mV)	 Iron Content (ppm)	Anaerobic pH	 E_h (mV)	 Iron Content (ppm)
Pure Pyrite	2.8	206	480	3.6	–172	360
Pure Siderite	5.2	221	0	5.2	–160	0.6

Table 4—The pH, E_H, and iron content of contacted solutions.



(a) Pyrite supernatant under aerobic conditions.

(b) Pyrite supernatant under anaerobic conditions.

Fig. 3—The 1500-ppm HPAM 3230S decanted after mixing with pyrite-content samples: (a) pyrite supernatant under aerobic conditions and (b) pyrite supernatant under anaerobic conditions.

		Aerobic			Anaerobic		
		Retention (R, μg/g)	Permeablity (k, darcies)	Rock (M_{rock}, g)	Retention (R, μg/g)	Permeablity (k, darcies)	Rock (M_{rock}, g)
1500-ppm 3230S μ = 5.9 cp at 23°C	Pure Quartz	35.0	9.1	37.5	35.0	11.2	37.0
		27.6	10.9	37.3	31.9	12.0	37.3
		34.7	11.4	37.5			
	1% Siderite	46.1	9.4	37.4	37.6	9.7	37.6
		40.8	9.8	37.2			
	10% Siderite	95.6	1.9	36.4	50.8	2.0	37.6
	1% Pyrite	37.0	10.1	37.0	36.5	11.3	36.8
		39.2	11.3	37.7			
	10% Pyrite	43.2	10.5	38.9	40.6	10.4	38.2
					41.5	11.1	39.0
		**211.2	10.2	39.9	**47.8	9.7	40.1
	20% Pyrite	47.0	9.6	40.1	46.4	9.4	40.8
1500-ppm 3630S μ = 16.1 cp at 23°C	15% Siderite	193.6	0.52	39.4	65.9	0.56	39.7
2500-ppm 3630S μ = 29.5 cp at 23°C	10% Siderite	130.3	1.7	38.6			
	20% Siderite	261.0	0.34	40.9			
	20% Pyrite	92.0	9.2	40.7	53.1	9.1	40.9
					48.7	8.8	40.1
					*31.7	9.1	41.0

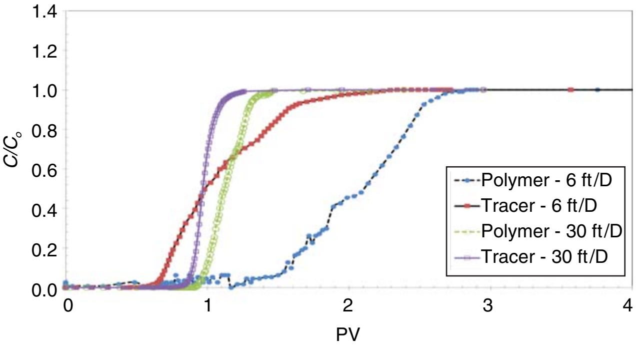
* Pretreated with oxygen-free brine containing 1% sodium dithionite.
** Injected at 6 ft/D.

Table 5—Sandpack dynamic-retention measurements (injection speed at approximately 32 ft/D).

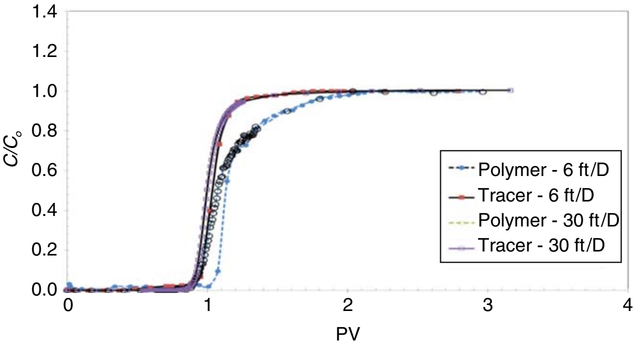
when aerobic. Considering our injection rates (25–50 ft/D) during the dynamic experiments, the time for polymer to transit the core was one hour or less. For comparison, polymer was exposed to the sand for approximately 12 hours for the static experiments. Possibly, the polymer was not exposed to the sand for sufficient time during the dynamic experiments.

To determine whether flow rate affected retention in sand with pyrite, one comparable test was conducted with the injection rate lowered to approximately 6 ft/D for sand with 10% pyrite. Results are shown in Table 5. Comparisons of breakout curves at different flow rates are shown in **Fig. 4.** Under aerobic conditions, polymer retention was 211.2 D at 6 ft/D vs. 43.2 μg/g at 30 ft/D. Polymer broke out later at lower rate (1.8 PV at 6 ft/D vs. 1 PV at 30 ft/D), which led to a higher retention. However, under anaerobic conditions, polymer retention was 47.8 μg/g at 6 ft/D vs. 40.6–40.5 μg/g at 33 ft/D. And the breakout curves between those two injection speeds showed much less difference compared with aerobic conditions. The effluent contained 2 ppm of iron during the oxygen-free brine flush, and no iron was detected in polymer effluents under both aerobic and anaerobic conditions. This rate-dependent retention for sand with pyrite under aerobic conditions could indicate that a ferric coating on pyrite surfaces may complex with and deplete more polymer at slower rates. In contrast, under anaerobic conditions, ferrous iron had less effect on retention. Another possible reason may be that Fe^{3+} can complex with the polymer to form gel particles that are removed by filtration when moving through porous media. Flow rate cannot be reduced to 1 ft/D because of the concern about minor pressure change, which increases cumulative errors and affects retention results. However, this rate is highly suggested by using low-permeability cores to further investigate relationship between retention and flow rate with the presence of iron minerals. It is assumed that retention will reach a maximum value after polymer and sand have contacted sufficiently.

When 10% siderite was present, dynamic retention of 3230S HPAM was noticeably less than during static-retention tests (50.8–95.6 μg/g vs. 128–137 μg/g). Also, dynamic retention appeared higher under aerobic conditions vs. anaerobic conditions (95.6 vs. 50.8 μg/g), in contrast to the results from the static adsorption experiments. Several explanations for the differences are conceivable. First, Mungan (1969) and Zhang and Seright (2014) also noted that adsorption from static measurements was higher than retention from dynamic measurements. In this previous literature, this observation was attributed to larger contact area between the polymer solution and the rock surface in loose sand, whereas in a compacted sandpack, a lower fraction of the siderite area may be accessible to the polymer. A second explanation is that the dynamic-retention experiments were performed too fast to allow adequate dissolution and reaction with iron—as mentioned for the pyrite experiments earlier. If the dynamic experiments had been performed at lower rates, retention values



(a) Aerobic Condition



(b) Anaerobic Condition

Fig. 4—Effluent concentration of tracer and polymer at different flow rate (1,500-ppm 3230S, 10% pyrite): (a) aerobic condition and (b) anaerobic condition.

may have been more consistent with the static results. This argument suggests that flow rates should be representative of the field application when performing dynamic-retention tests. A third factor helps to explain why retention on siderite was sensitive to the presence of oxygen for the dynamic experiments (Table 5) but not sensitive to oxygen for the static experiments (Fig. 2). Oxidative degradation during the aerobic experiments resulted in viscosity losses. During the dynamic experiments with siderite, these viscosity losses were interpreted as high retention (because a capillary viscometer was used for polymer detection). In contrast, these viscosity losses did not affect the retention calculations during the static experiments because TOC was used for polymer detection. For our circumstances, it is suggested in future study to perform dynamic-retention tests with the TOC detection method and compare results to those of the viscosity method to quantify the effect of polymer degradation.

Several exploratory experiments were performed with an HPAM with higher molecular weight (i.e., Flopaam 3630S). The bottom rows of Table 5 show these results. With 15% siderite, 3630S HPAM dynamic retention was three times higher under aerobic conditions than under anaerobic conditions. This result was qualitatively consistent with that using the lower-molecular-weight HPAM. As expected, 3630S retention increased with increased siderite content.

One dynamic-retention experiment was performed after flushing the core (i.e., a 20% pyrite sandpack) with brine containing 1% sodium dithionite. During this flush, the iron concentration in the effluent slowly decreased from 10 to 8 ppm over 60 PV of brine injection. The last three (anaerobic) rows of Table 5 reveal that this dithionite flush reduced HPAM retention modestly (from ≈50 μg/g to 31.7 μg/g)—possibly because the dithionite treatment removed significant iron from the core. In contrast, injecting brine without sodium dithionite resulted in no iron concentration in the effluent. This last fact suggests that the dynamic-retention experiments occurred too rapidly to allow much iron to dissolve—in contrast to our static experiments (see Table 4).

Conclusions

From this work, we recognize that there are both advantages and disadvantages associated with determining polymer retention with static tests vs. dynamic tests and with aerobic vs. anaerobic conditions. The primary lessons learned from this work were

- From static-retention measurements, polymer adsorption values on pure silica sand or Berea sandstone were small, and they showed little difference between experiments conducted aerobically or anaerobically.
- From static-retention measurements under both aerobic and anaerobic conditions, HPAM retention increased significantly with increased pyrite or siderite content. Static retention under anaerobic conditions ranged from 45 to 75 μg/g with 1% of either pyrite or siderite to 137–174 μg/g for 10% pyrite or siderite to 1161–1249 μg/g for 100% pyrite or siderite.
- If iron minerals are present, the most-representative polymer-retention results are obtained (for both static and dynamic tests) if conditions are anaerobic. Retention values (from static measurements) under aerobic conditions were commonly twice those determined under anaerobic conditions.
- If iron minerals are present and retention tests are performed under aerobic conditions, TOC or some similar method should be used for polymer detection. Viscosity detection of polymer may provide retention values that are too high (because oxidative degradation can be misinterpreted as polymer retention).
- For a broad range of siderite content, retention from static tests did not depend on whether dissolved oxygen was present. However, for a broad range of pyrite content, HPAM retention was significantly lower in the absence of dissolved oxygen than under aerobic conditions. These results may be tied to iron solubility. When polymer solutions were mixed with 100% pyrite over the course of 12 hours, 360–480 ppm of iron dissolved into polymer solutions under both aerobic and anaerobic conditions, whereas with 100% siderite, only 0.0–0.6 ppm of iron dissolved.
- If dynamic methods (i.e., corefloods) are used to determine polymer retention under aerobic conditions, flow rates should be representative of the field application. Rates that are too high lead to underestimation of polymer retention. With 10% pyrite, dynamic retention was 211 μg/g at 6 ft/D vs. 43.2 μg/g at 30 ft/D. In contrast, retention values were fairly consistent (40.6–47.8 μg/g) between 6 and 33 ft/D under anaerobic conditions.

Nomenclature

C_{polyo} = initial polymer concentration, ppm
C_{poly} = equilibrium or produced-polymer concentration, ppm
C_{trac} = produced-tracer concentration minus zero-baseline tracer concentration, mg/L
C_{traco} = stabilized produced-tracer concentration minus zero-baseline tracer concentration, mg/L
E_h = oxidation-reduction potential, mV
$IAPV$ = inaccessible PV
M_{poly} = mass of polymer solution, g
M_{sand} = mass of sand, g
R = retention of polymers, μg/g
ρ_p = density of polymer solution, g/cm^3
μ = solution viscosity, mPa·s

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