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Is Polymer Retention Different Under Anaerobic vs. Aerobic Conditions?

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Abstract

This paper examines whether retention of partially hydrolyzed polyacrylamide (HPAM) is different under anaerobic versus aerobic conditions. Both static (mixing with loose sand) and dynamic methods (core floods) were used to determine HPAM retention. There are both advantages and disadvantages associated with determining polymer retention using static tests versus dynamic tests and using aerobic versus 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 45-75 μ g/g with 1% of either pyrite or siderite to 137-174 μ g/g for 10% pyrite or siderite to 1161-1249 μ g/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. Theses results may be tied to iron solubility. When polymer solutions were mixed with 100% pyrite over the course of 12 hours, 360–480-ppm iron dissolved into polymer solutions under both aerobic and anaerobic conditions, whereas with 100% siderite, only 0-0.6-ppm 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 μ g/g at 6 ft/d versus 43.2 μ g/g at 30 ft/d. In contrast, retention values were fairly consistent (40.6 – 47.8 μ g/g) between 6 ft/d and 33 ft/d under anaerobic conditions.

Introduction

In polymer flooding, polymer retention is defined to include the combined effects of polymer adorption 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 μ g/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 μ g/g for the Tambaredjo polymer flood in Suriname. In our laboratories using clean sands (Zhang and Seright 2014, 2015), some very low retention values (< 10 μ g/g) have been measured. On the other hand, we have also occasionally witnessed polymer retention values up to 1,000 μ g/g in multi-darcy 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 processes take place with ambient oxygen present. Wang (1993) found that surfactant retention values were significantly lower in reservoir anaerobic conditions than 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 μ g/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 hydrolyzed polyacrylamide (HPAM) undergo degradation by redox cycles when both Fe²⁺ 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), Fe²⁺ (0 – 220-ppm) and Fe³⁺ (0 – 172-ppm). For 2000-ppm HPAM at 23°C and 90 °C, no significant viscosity loss was observed after one week when less than 200 ppb dissolved oxygen was present. Above that level, significant viscosity losses were seen and increased with Fe²⁺ concentration. At 23°C with 8000 ppb initial oxygen, a 75% loss occurred for HPAM with 30-ppm Fe²⁺. 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 presense 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). Once 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 *et al.* (1993) showed that surfactant retention on natural kaolin clays can be reduced (from 990 to 400~650 μ g/g) by using dithionite-containing brine prewash to remove iron. 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 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), while 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 using a colorimetric method (CHEMetTM). The oxygen levels in aqueous solutions were less than 5 parts per billion (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- μ m filters after preparation. The polymers used in our tests were SNF FlopaamTM 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 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 in between 106 and 180 μ m. 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 μ m. This sand was used as received. We also mixed Ottawa sand with pyrite (FeS₂) and siderite (FeCO₃) mineral powders to the desired mineral concentration to study the effect of iron and oxygen on polymer retention. Surface area (from BET measurements) of each composition is listed in Table 1. For comparison, the surface area of Berea sandstone measured by Wang *et al.* (1993) was 0.3 to 0.6 m²/g.

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	Compositions
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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, two liters of brine were flushed through the packs to condition the sand.

Static Equilibrium Adsorption

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

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

Dynamic Retention Experiments

Three sets of polymer-retention experiments were conducted with sandpacks to test the effect of redox state on polymer retention: (1) one set under aerobic conditions, (2) a second by extensive flushing with oxygen-free brine (where oxygen was removed by bubbling anaerobic gas through the brine), and (3) 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%, 15% siderite and 1%, 10%, 20% pyrite.

During the restoration process, about 60 pore volumes (PV) of oxygen-free synthetic brine (with or without sodium dithionite) were injected before retention measurements. Those injected brines were de-oxygenated 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 around -580 mV (meter reading. -370 mV after adjustment to standard conditions). A special coreflood arrangement was prepared which 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 ppm 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 was 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 the 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 calculated as shown in Eq.2.

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



Figure 1—Effluent Concentration Curve of Polymer and Tracer for Computation of Polymer Retention and IAPV

Similarly, inaccessible pore volume (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.

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

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 discernable 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 polymer retention is concentration-dependent in the semi dilute region.

	Table						
	Adsorption	Results (µg/g)	C _o (ppm)	Solid Liquid Ratio	Sand (g)	Polymer (g)	
Sand	Aerobic	Anaerobic					
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

Table 3—Static Adsorption for 1500-ppm 3230S

	Adsorption	Results (µg/g)
Sand	Aerobic	Anaerobic
Pure Quartz (SiO ₂)	29	38
1% Pyrite + 99% Silica	148 135	61 75
10% Pyrite + 90% Silica	291	174
100% Pyrite	2154	1189
1% Siderite + 99% Silica	34 51	45 47
10% Siderite + 90% Silica	128	137
100% Siderite	1185 1211	1249 1161



Figure 2—Effects of Iron Mineral Concentration and Oxygen on HPAM Static Retention at 23°C.

For pure silica sand, due to 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 definatively 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.

Disscussion Table 4 shows pH, E_H and iron concentration of the 1500-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 VACUettesTM kit). Note that pyrite contact resulted in 360 – 480-ppm iron released into polymer solutions under both aerobic and anaerobic conditions, whereas siderite contact induced only 0 – 0.6-ppm 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 mixed with anaerobic pyrite was clear (Fig. 3b).

	100	io i pin, i				liene	
		Α	erobic		Ar	naerobic	
Sand	рН	E _H (mV)	Iron Content (ppm)	рН	$E_H(mV)$	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—pH, E_H and Iron Content of Contacted Solutions

a) Pyrite supernatant under aerobic conditions.

b) Pyrite supernatant under anaerobic conditions.

Figure 3—1500-ppm HPAM 3230S decanted after mixing with pyrite content samples.

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, total organic carbon analysis should detect degraded (low-Mw) HPAM as well as undegraded (high-Mw) HPAM. Consequently, an alternative mechanism or mechanisms must be envisioned for the polymer loss.

Based on 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 both during aerobic and anaerobic conditions (Table 3 and Fig. 2). Second, the presence of ferric iron (Fe³⁺) appears to play a role. We suggest that aerobic pyrite results in generation of ferric iron (Fe³⁺) in the solution (Table 4). As observed by Seright and Skjevrak (2015), this Fe³⁺ complexes with and removes HPAM

from solution. In contrast for anaerobic pyrite, even though a large concentration of ferrous iron (Fe²⁺) dissolves (Table 4), Fe²⁺ 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 Fe³⁺ and no additional polymer losses are attributed to complexation with Fe³⁺. 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.

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., Daqing, Seright *et al.* 2010), this problem may be less severe.

Sand Pack Experiments

Dynamic retention experiments using sandpacks with different mineral concentrations are summarized in Fig. 4 and Table 5. 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 μ g/g).

Figure 4—Effects of Iron Concentration and Oxygen on HPAM Dynamic Retention at 23°C.

		-	Aerobic		Anaerobic			
		Retention (R, μg/g)	Permeablity (k, D)	Rock (M _{rock} , g)	Retention (R, µg/g)	Permeablity (k, D)	Rock (M _{rock} , g)	
		35.0	9.1	37.5	35.0	11.2	37.0	
	Pure Quartz	27.6	10.9	37.3	31.9	12.0	37.3	
		34.7	11.4	37.5				
	1%	46.1	9.4	37.4	37.6	9.7	37.6	
S 2 2	Siderite	40.8	9.8	37.2				
1 323 @ 23	10% Siderite	95.6	1.9	36.4	50.8	2.0	37.6	
ар вр 10 ср	1%	37.0	10.1	37.0	36.5	11.3	36.8	
1500 1 = 5.	Pyrite	39.2	11.3	37.7				
L U		43.2	10.5	38.9	40.6	10.4	38.2	
	10% Pyrite				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 @ 23°C	15% Siderite	193.6	0.52	39.4	65.9	0.56	39.7	
ູດ	10% Siderite	130.3	1.7	38.6				
3630: @ 23 ⁽	20% Siderite	261.0	0.34	40.9				
ppm 5 cp	0001	92.0	9.2	40.7	53. 1	9.1	40.9	
500- = 29	20% Pyrite				48.7	8.8	40.1	
л= 1					*31.7	9.1	41.0	

Table 5—Sand Pack D	ynamic Retention Measurements ((Injection speed at	t around 32 ft/d).

* Pretreated with oxygen-free brine containing 1% sodium dithionite.

** Injected at 6 ft/d.

Interestingly, retention values in the presence of pyrite were lower for the dynamic experiments than for the static experiments. When injecting 1500-ppm 3230S into sand with 1% to 20% pyrite, the retention values were essentially the same (36.5-47.0 μ g/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 μ g/g when anaerobic and 291 μ g/g 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 about 12 hours for the static experiments.

To determine whether flow rate affected retention in sand with pyrite, one comparable test was conducted with the injection rate lowered to around 6 ft/d for sand with 10% pyrite. Results are shown in Table 5. Comparisons of breakout curves at different flow rate are shown in Fig. 5. Under aerobic conditions, polymer retention was 211.2 μ g/g at 6 ft/d versus 43.2 μ g/g at 30 ft/d. Polymer broke out later at lower rate (1.8 PV at 6 ft/d versus 1 PV at 30 ft/d), which led to a higher retention. However, under anaerobic conditions, polymer retention was 47.8 μ g/g at 6 ft/d versus 40.6 - 40.5 μ g/g at 33 ft/d. And the break out curves between those two injection speeds showed much less difference compared to aerobic

conditions. The effluent contained 2-ppm 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.

Figure 5-Effluent Concentration of Tracer and Polymer at Different Flow Rate (1500 ppm 3230S, 10% pyrite).

When 10% siderite was present, dynamic retention of 3230S HPAM was noticeably less than during static retention tests (50.8-95.6 μ g/g versus 128-137 μ g/g). Also dynamic retention appeared higher under aerobic conditions versus anaerobic conditions (95.6 versus 50.8 μ g/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 measurents 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 may have been more consistent with the static results. This argument suggests that the static retention results are more applicable to a field application. A third factor helps to explain why retention on siderite was sensitive to the presence of oxygen for the dynamic experiments (Fig. 4) 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, this argument also favors acceptance of the static retention results over the dynamic results.

Several exploratory experiments were performed using 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 qualtitatively consistent with that using the lower-Mw 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 ppm to 8 ppm over 60 PV of brine injection. The last three (anaerobic) rows of Table 5 reveal that this dithonite flush reduced HPAM retention modestly (from ~50 μ g/g to 31.7 μ g/g)— possibly because the dithonite treatment removed signicant 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).

Fig. 4 shows HPAM retention increased with increased iron content during the dynamic experiments.

Conclusions

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

- 1. 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.
- 2. For both aerobic and anaerobic conditions, HPAM retention increased significantly with increased pyrite or siderite content. Static retention under anaerobic conditions ranged from 45-75 μ g/g with 1% of either pyrite or siderite to 137-174 μ g/g for 10% pyrite or siderite to 1161-1249 μ g/g for 100% pyrite or siderite.
- 3. 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.
- 4. 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).
- 5. 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. Theses results may be tied to iron solubility. When polymer solutions were mixed with 100% pyrite over the course of 12 hours, 360-480-ppm iron dissolved into polymer solutions under both aerobic and anaerobic conditions, whereas with 100% siderite, only 0-0.6-ppm iron dissolved.

6. 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 μ g/g at 6 ft/d versus 43.2 μ g/g at 30 ft/d. In contrast, retention values were fairly consistent (40.6 – 47.8 μ g/g) between 6 ft/d and 33 ft/d under anaerobic conditions.

Nomenclature

E _h	= oxidation-reduction potential, mV.
C _{polyo}	= Initial polymer concentration, ppm.
C _{polv}	= Equilibrium or produced-polymer concentration, ppm.
C _{trac}	= Produced-tracer concentraton minus zero-baseline tracer concentration, mg/L.
C _{traco}	= Stablilized produced-tracer concentration minus zero-baseline tracer concentration, mg/L.
IAPV	= Inaccessible pore volume.
M _{polv}	= Mass of polymer solution, g.
M _{sand}	= Mass of sand, g.
R	= Retention of polymers, $\mu g/g$.
$ ho_{ m p}$	= Density of polymer solution, g/cm^3 .
μ	= Solution viscosity, mPa-s.

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