Effect of Dissolved Iron and Oxygen on Stability of Hydrolyzed Polyacrylamide Polymers

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Summary

This paper describes an experimental study of the stability of a hydrolyzed polyacrylamide (HPAM) polymer and an HPAM-2-acrylamido-tertbutylsulfonic acid (ATBS) terpolymer in the presence of varying initial levels of dissolved oxygen (0 to 8,000 ppb), Fe^{2+} (0 to 220 ppm), and Fe^{3+} (0 to 172 ppm). A special method was developed to attain and confirm dissolved-oxygen levels. Stability studies were performed at 23 and 90°C. For Fe^{2+} concentrations between 0 and 30 ppm, viscosity losses were insignificant after 1 week when the initial dissolved oxygen concentration was 200 ppb or less. Above this level, significant viscosity losses were seen, especially if iron was present.

If the temperature is high, a greater need arises to strive for very low dissolved-oxygen content. For samples stored for 1 week at 90°C with only 10-ppb initial dissolved oxygen, contact with steel caused HPAM-ATBS solution viscosity losses greater than 30%. In contrast at 23°C, contact with steel caused no significant degradation when the dissolved O_2 concentration was 1,000 ppb or less. Several different methods are discussed to control oxidative degradation of polymers during field applications. We advocate physical means of excluding oxygen (e.g., stopping leaks, better design of fluid transfer, gas-blanketing, gas-stripping) rather than chemical means.

Addition of Fe^{3+} to polymer solutions caused immediate crosslinking. Because crosslinked polymers were never observed during our studies with Fe^{2+}, we conclude that free Fe^{3+} was not generated in sufficient quantities to form a visible gel.

Introduction

During polymer, surfactant/polymer, or alkaline/surfactant/polymer floods, the injected polymer solution must maintain viscosity for a substantial portion of the transit through the reservoir. When both Fe^{2+} and oxygen are present in aqueous hydrolyzed polyacrylamide (HPAM) solutions, redox couples or cycles can substantially degrade polymers (Pye 1967; Shupe 1981; Grollmann and Schnabel 1982; Ramsden and McKay 1986; Levitt et al. 2011a). In the absence of dissolved oxygen and oxidizing agents, HPAM can be quite stable in the presence of ferrous iron [Fe^{2+}] (Shupe 1981; Yang and Treiber 1985; Seright et al. 2010). HPAM also can be reasonably stable in the presence of dissolved oxygen in the absence of Fe^{2+} and free-radical-generating impurities, if certain conditions [oxidation-reduction potential (E_h), pH, brine composition, temperature] are met (Knight 1973; Muller 1981; Levitt et al. 2011a,b). Ramsden and McKay (1986) and Levitt et al. (2011a) observed that pH and E_h are key factors in HPAM/PAM stability in the presence of Fe^{2+}. Polymer degradation is highest at acidic pH values and can be negligible under alkaline conditions. Levitt et al. (2011a,b) point out that the pH dependence of polymer stability is closely tied to the pH dependence of iron solubility. Iron solubility can be especially low at higher pH values if carbonate/bicarbonate is present—leading to enhanced polymer stability.

Seright et al. (2010) noted that even if ambient levels of dissolved oxygen are present (3 to 8 ppm), the highly reducing conditions and iron minerals (e.g., pyrite, siderite) in an oil reservoir will usually consume that oxygen within hours or days, even at a low temperature. In field applications of some low- to moderate-temperature chemical floods, no attempt was made to exclude oxygen. In other cases, oxygen removal or exclusion was attempted, but atmospheric leakage occurred so that low levels of dissolved oxygen were present (e.g., <50 ppb). Large differences of opinion exist on how to treat these situations, including (1) removing all iron (Levitt et al. 2011a), (2) removing all dissolved oxygen (Seright et al. 2010), (3) addition of free-radical scavengers or adjustment of E_h and/or pH (Wellington 1983; Gaillard et al. 2010), and (4) no action (Wang et al. 2008). Several studies characterized HPAM degradation in solutions with both Fe^{2+} and ambient levels of dissolved oxygen (Grollmann and Schnabel 1982; Ramsden and McKay 1986). Numerous investigations have examined HPAM stability with Fe^{2+} present but without dissolved oxygen (Shupe 1981; Yang and Treiber 1985; Ryles 1988; Seright et al. 2010; Levitt et al. 2011a).

Gaillard et al. (2010) examined polymer stability in the presence of 50-ppb and 500-ppb initial dissolved oxygen. Otherwise, we are not aware of any studies of HPAM stability in the presence of measured, low levels of dissolved oxygen with Fe^{2+} present. Consequently, this paper describes an experimental study of the stability of an HPAM polymer and an HPAM-2-acrylamido-tertbutylsulfonic acid terpolymer in the presence of varying initial levels of dissolved oxygen (0 to 8,000 ppb), Fe^{2+} (0 to 220 ppm), and Fe^{3+} (0 to 172 ppm). A special method was developed to attain and confirm dissolved-oxygen levels. Stability studies were performed at 23 and 90°C. Our hope was that insights from this study would help resolve which of the four approaches mentioned in the preceding paragraph is most appropriate.

Experimental

Two polymers were used in this work, called hydrolyzed polyacrylamide (HPAM) and HPAM-2-acrylamido-tertbutylsulfonic acid (ATBS). The HPAM polymer was SNF Flopaam 3630S. This acrylamide-acrylate copolymer had an average molecular weight of 18 million g/mol and 30% anionicity. (HPAM is an abbreviation that is commonly used for both hydrolyzed polyacrylamides and acrylamide-acrylate copolymers.) The HPAM-ATBS polymer was SNF Flopaam 5115SH. This acrylamide-acrylate-ATBS terpolymer had an average molecular weight of 15 million g/mol, 15% ATBS, and had a total anionicity of 25%.

Two brines were used. **Table 1** lists their compositions. They will be called "11%-TDS brine" (with TDS standing for total dissolved solids throughout this paper) and "2.85%-TDS brine." The 11%-TDS brine describes the formation water associated with a particular polymer-flooding field candidate. This brine was used in most experiments. The 2.85%-TDS brine describes alternative polymer makeup water for the target field polymer flood and was used in a few experiments. Brine was filtered through a 0.45-μm Millipore filter before deoxygenation and polymer addition.

A vortex was formed with a magnetic stirrer, and powder-form polymer was added and then mixed overnight at low speed. The prepared polymer solutions contained 2,000-ppm polymer in either 11%-TDS brine or 2.85%-TDS brine. For each polymer, one set of

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Ion	11%-TDS Brine	2.85%-TDS Brine
Na^+	36,600	10,660
K^+	2,609	0
Mg^{2+}	749	233
Ca^{2+}	2,780	174
Sr^{2+}	570	0
Ba^{2+}	110	0
Cl^-	66,300	17,353
HCO_3^-	170	100
SO_4^{2-}	21	0
TDS	109,908	28,520

Table 1—Brine compositions (ppm).

solutions was mixed outside our anaerobic chamber to contain ambient levels (3,300 ppb) of dissolved oxygen. A second set of polymer solutions was mixed inside the anaerobic chamber. This unit (Forma Scientific Model 1025) continuously circulated an anaerobic gas (10 to 15% hydrogen and 85 to 90% nitrogen) through a palladium catalyst and a desiccant. Any free oxygen was reacted with hydrogen to form water, which was removed by the desiccant. More details about the anaerobic chamber and our methodology are found in Seright and Henrici (1990) and Seright et al. (2010).

Viscosities and dissolved-oxygen levels were measured inside the anaerobic chamber. Two methods were used to make oxygen measurements. One method was a Mettler Toledo Model M700X meter that was equipped with two O_2 4700i(X) Traces modules and two InPro 6950 O_2 sensors. This meter was sensitive to 0.1 ppb oxygen in the liquid phase and 0.001% in the gas phase. One sensor continuously monitored oxygen in the chamber's atmosphere, whereas the other was used to measure dissolved oxygen in our aqueous solutions. Under most circumstances, the meter indicated 0.000% oxygen in our chamber gas. As an exception, the chamber gas could rise to 0.035% oxygen immediately after moving items into the anaerobic chamber from the transfer chamber. (When anything was brought in from outside the main chamber, the transfer chamber was purged twice with pure nitrogen gas and once with our anaerobic gas, interspersed with evacuations to 65-kPa vacuum.) Within 45 minutes of making a transfer, the oxygen content in the main chamber returned to 0.000%. Polymer solutions prepared in the anaerobic chamber contained 0.0 ppb dissolved oxygen (i.e., less than 100 parts per trillion). The second oxygen-detection method used a colorimetric method (CHEMet) with a limit of oxygen detection of 1 ppb in aqueous solution. We believe that the aforementioned method (preparing and sealing samples inside an anaerobic chamber) is greatly superior to methods that store samples in flame-sealed glass ampoules (Wellington 1983; Yang and Treiber 1985; Wu et al. 2009). Oxygen can leak into the ampoules when the glass neck collapses unless extreme care and luck occur during flame sealing. The erratic nature of viscosity vs. time that was reported for flame-sealed samples supports our suggestion—because variable amounts of oxygen leak in from sample to sample. In contrast, viscosity trends from our method appear much smoother (see Seright et al. 2010).

Stock solutions were prepared of 1% $FeCl_2$ in 11%-TDS brine and in 2.85%-TDS brine. These stock solutions were prepared oxygen-free inside the anaerobic chamber. In most cases, to achieve a given dissolved-oxygen level, we brought air-saturated polymer solutions into the anaerobic chamber that contained 3,300-ppb dissolved oxygen. On the basis of mass balance, this solution was added and mixed with anaerobic polymer solution to achieve lots with the desired final dissolved oxygen content, including 10, 20, 50, 200, 500, and 2,000 ppb. Dissolved-oxygen concentrations were confirmed with both our Mettler Toledo probe and the CHEMet method (Ultra Low Range CHEMet R-7511). Next, the solutions were distributed into Wheaton glass serum bottles—with 40 g of solution into each 60-cm^3 bottle. Then, with Eppendorf digital pipets, a small amount of stock Fe^{2+} chloride solution was added to achieve the desired concentration: 5, 10, 20, or 30 ppm of Fe^{2+}.

To achieve 8,000-ppb dissolved oxygen, we bubbled pure oxygen through the polymer solutions (outside the anaerobic chamber) until the desired level was reached (while monitoring with a Mettler Toledo probe). Next, the two stock polymer solutions (one HPAM and one HPAM-ATBS) were put into the anaerobic chamber. Inside the chamber, 40-g aliquots were placed in 60-cm^3 bottles. Then, small aliquots of anaerobic 1% $FeCl_2$ stock solution were pipetted into the bottles to achieve the desired Fe^{2+} concentration.

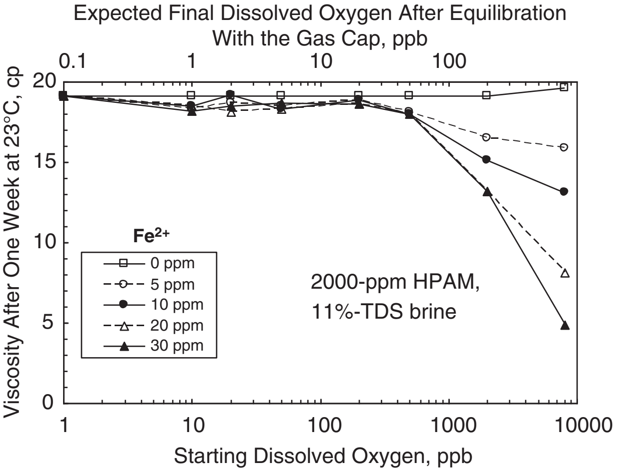

Fig. 1—Effect of dissolved oxygen and Fe^{2+} on HPAM stability at 23°C.

After the glass bottles were filled with solution, a rubber septum was inserted into the opening and capped with an aluminum cap. The glass bottles have a special lip at the opening that facilitates sealing with the rubber septum. A Wheaton crimper was used to crimp the aluminum cap around the bottle lip—thereby preventing pressure inside the bottle from expelling the rubber septum. Examples of this lip and the unsealed bottles are shown later in this paper. Examples of the sealed bottles are also shown later. One set of solutions was removed from the anaerobic chamber and immersed in a silicon oil bath at 90°C for a week. The second set remained in the anaerobic chamber at a nominal temperature of 23°C. After 1 week, viscosities were measured inside the anaerobic chamber (at 23°C) at shear rates of 3.65, 7.3, 14.6, and 36.5 s^{-1} with a Brookfield viscometer with a UL adapter. In this paper, we generally only report results at 7.3 s^{-1}. We chose a 1-week storage period because of evidence that dissolved oxygen would be consumed after a few hours' or days' contact with pyrite or siderite in reservoir rock (Seright et al. 2010). A second reason for the choice was the phenomenon of hydrolysis of amide groups on the polymers, followed by precipitation with divalent cations (Moradi-Araghi and Doe 1987; Ryles 1988; Levitt et al. 2011b). A 1-week storage period was short enough to avoid this precipitation phenomenon, allowing us to focus on oxidative degradation of the polymers. (Of course, we are aware of the literature and important implications of the hydrolysis/precipitation problem, but that topic is outside the scope of this paper.)

The presence of a 20-cm^3 gas cap above our 40 cm^3 of stored liquid was probably a major factor in diminishing the dissolved-oxygen level during our first experiments. Specifically, Henry's law predicts that the initial dissolved oxygen should eventually be reduced by a factor of approximately 17 after the 40-cm^3 liquid equilibrated with the 20-cm^3 gas cap. Consequently, another set of experiments was performed in which solutions were stored with a very small (approximately 0.2 cm^3) gas cap.

Results

Effect of Dissolved Oxygen. The effects of dissolved oxygen and Fe^{2+} on polymer stability in 11%-TDS brine are demonstrated in **Figs. 1 through 4.** Figs. 1 and 2 apply to 2,000 ppm hydrolyzed polyacrylamide (HPAM) stored at 23 and 90°C, respectively. Figs. 3 and 4 apply to 2,000 ppm of HPAM-2-acrylamido-tertbutylsulfonic acid (ATBS) stored at 23 and 90°C, respectively. Examination of these figures first reveals that for any Fe^{2+} concentration (between 0 and 30 ppm), viscosity losses (for

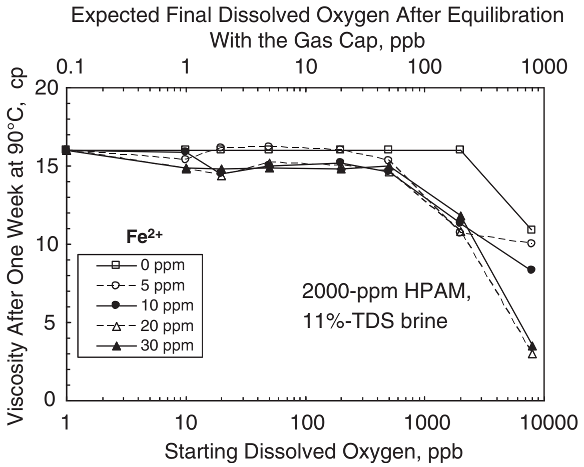

Fig. 2—Effect of dissolved oxygen and Fe^{2+} on HPAM stability at 90°C.

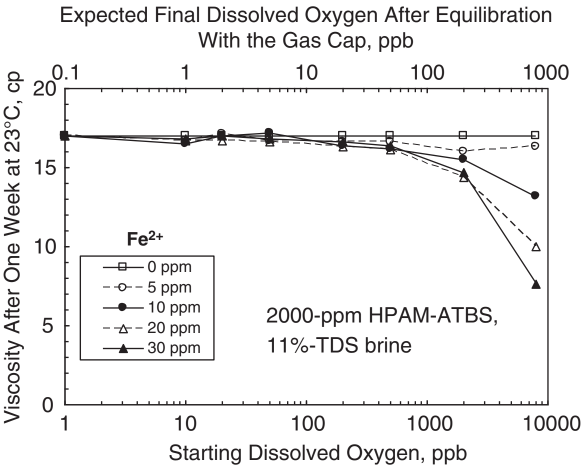

Fig. 3—Effect of dissolved oxygen and Fe^{2+} on HPAM-ATBS stability at 23°C.

both polymers) were insignificant after 1 week (at either 23 or 90°C) when the initial dissolved-oxygen concentration was 500 ppb or less. More conservatively, after accounting for oxygen loss to the gas cap, we lower the 500-ppb initial dissolved-oxygen level to 30-ppb dissolved oxygen. (The top *x*-axis in Figs. 1 through 4 shows expected O_2 concentrations after correction for equilibration with the 20-cm^3 gas cap.) Viscosity losses (at 7.3 s^{-1}) after 1 week with initial 2,000-ppb dissolved oxygen (120 ppb after conservative correction from Henry's law) averaged only 11% for HPAM-ATBS stored at 23°C; 23% for HPAM-ATBS stored at 90°C; 24% for HPAM stored at 23°C; and 30% for HPAM stored at 90°C. Viscosity losses with 8,000-ppb initial dissolved oxygen (480-ppb after equilibration) varied considerably with Fe^{2+} content.

These findings support those of Yang and Treiber (1985) and Seright et al. (2010), who suggested that after the available dissolved oxygen is depleted, no further oxidative degradation of polymer occurs. For all cases that started with 2,000-ppb dissolved oxygen or less, the final dissolved oxygen content after 1 week was undetectable. Thus, the dissolved oxygen was depleted during storage with the polymer (primarily caused by equilibration with the gas cap, as mentioned previously). Our findings contradict the concept that a small number of free-radical or oxygen molecules could degrade much (or in the extreme limit, all) polymer in a reservoir.

Unquestionably, if solutions that contain both polymer and Fe^{2+} are exposed to an infinite source of oxygen (e.g., atmospheric oxygen), polymer degradation will be severe (Shupe 1981; Yang and Treiber 1985; Ramsden and McKay 1986). However, if the oxygen supply is limited—for example, to the amount dissolved in ambient aqueous solutions that are not in contact with air—polymer degradation will be limited. Our results allow a rough estimate of the polymer degraded by dissolved oxygen. For 2,000-ppm HPAM-ATBS, a 23% loss of viscosity translates to a 14% loss of polymer concentration or a loss of 280 ppm of polymer. Similarly, for 2,000-ppm HPAM, a 30% loss of viscosity translates to a 19% loss of polymer concentration or a loss of 380 ppm of polymer.

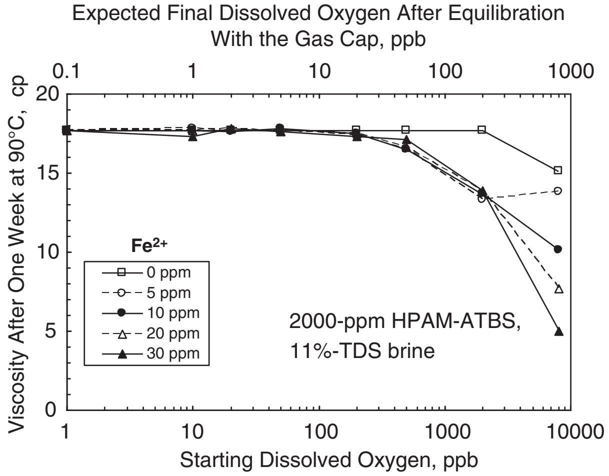

Fig. 4—Effect of dissolved oxygen and Fe^{2+} on HPAM-ATBS stability at 90°C.

For the cases with initial dissolved oxygen of 8,000 ppb, the final dissolved oxygen (after 1 week of storage at either temperature) averaged approximately 300 ppb. This value was in the vicinity of that calculated from Henry's law to account for oxygen migration to/equilibration with the 20-cm^3 gas cap. After 1 week, all solutions maintained some viscosity; thus, the residual dissolved oxygen did not completely react with polymer. The dependence of polymer degradation on Fe^{2+} content was much greater with 8,000-ppb initial dissolved oxygen than with 2,000-ppb or less initial dissolved oxygen. For 8,000-ppb initial oxygen, calculated polymer losses ranged from 111 to 1,240 ppm—primarily depending on Fe^{2+} content.

Effect of Fe^{2+}. For initial dissolved-oxygen levels up to 2,000 ppb (120 ppb after Henry's law correction), there was no significant difference in polymer degradation for Fe^{2+} concentrations between 5 and 30 ppm. For initial oxygen concentrations of 8,000 ppb, degradation depended on Fe^{2+} concentration. With no Fe^{2+} present but 8,000-ppb initial oxygen, no viscosity losses were noted after 1 week of storage at 23°C for either polymer (see the open squares in Figs. 1 and 3). At 23°C with 8,000-ppb initial oxygen, viscosity losses after 1 week increased with increased iron content—reaching a 48% loss for HPAM-ATBS and a 75% loss for HPAM with 30-ppm Fe^{2+} (see the right-most data points in Figs. 1 and 3). (Incidentally, for the case of no iron with 8,000-ppb initial oxygen, the final viscosity increased slightly compared with the other oxygen levels for the open squares in Fig. 1. This small increase is within the experimental error of the viscosity measurements.)

With no Fe^{2+} present but 8,000-ppb initial oxygen, viscosities after 1 week at 90°C were notably lower than with no initial dissolved oxygen (right-most open squares in Figs. 2 and 4)—15% lower for HPAM-ATBS and 32% lower for HPAM. At 90°C with 8,000-ppb initial oxygen, viscosity losses after 1 week increased with increased iron content—reaching an additional 67% loss for either polymer with 30-ppm Fe^{2+} (right-most data points in Figs. 2 and 4).

Iron-Oxidation Products. Solutions with iron and high initial dissolved-oxygen concentrations (especially 2,000 and 8,000 ppb)

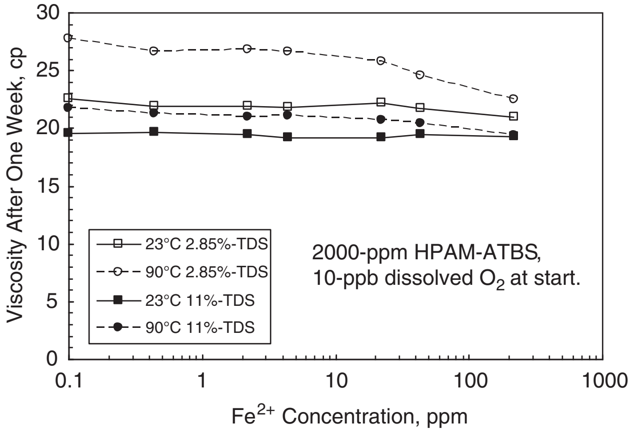

Fig. 5—Effect of Fe^{2+}, temperature, and salinity on HPAM-ATBS stability.

acquired a yellow-orange tint with time—especially at 90°C. In no case did we see signs of gelation, which occurs when Fe^{3+} crosslinks the polymer. The implication is that Fe^{3+} was not present or available to the polymer during this portion of our experiments.

Effect of Salinity. A separate study was performed with the two brines (2.85% TDS and 11% TDS). In this case, we focused on 2,000-ppm HPAM-ATBS with 10-ppb initial dissolved oxygen at the start of the experiment. We also examined a broader range of Fe^{2+} concentrations, including 0.44, 2.2, 4.4, 22.2, 44.4, and 220 ppm. All other aspects of the experimental technique were the same as for the previous experiments. **Fig. 5** shows the results. In 11%-TDS brine, polymer solution viscosity was independent of Fe^{2+} concentration after storage for 1 week at either 23°C or 90°C. The same was true at 23°C with HPAM-ATBS in 2.85%-TDS brine. After 1 week at 90°C in 2.85%-TDS brine, the viscosity with low-to-moderate iron concentrations was approximately 20% higher than after 1 week at 23°C. Presumably, hydrolysis of the amide groups at 90°C enhanced the viscosity in the 2.85%-TDS brine (Moradi-Araghi and Doe 1987). We assume that this effect was not seen at 90°C for the 11%-TDS brine because the higher salinity screened the charge-repulsions on the anionic polymer. For the case with 90°C and 2.85%-TDS brine, we also note that viscosity after 1 week decreased with increased iron content—presumably because of a mild degradation (open circles in Fig. 5).

Subsequent Re-exposure to Oxygen. After our measurements in the anaerobic chamber, we removed the samples from the chamber and exposed them to air. We then remeasured their viscosities **(Figs. 6 and 7).** Greater Fe^{2+} concentrations generally led to greater polymer degradation. However, the greatest viscosity loss was noted between 0- and 10-ppm Fe^{2+}. All iron-containing samples turned yellow, and samples with the highest iron concentrations acquired the most color **(Fig. 8).** No sign of gelation was seen (implying no formation of soluble Fe^{3+}). Bottom numbers show iron content (in ppm), whereas right numbers show original oxygen content (in ppb). H means it was stored at 90°C. The vial at the lower left contained the original polymer solution with no iron.

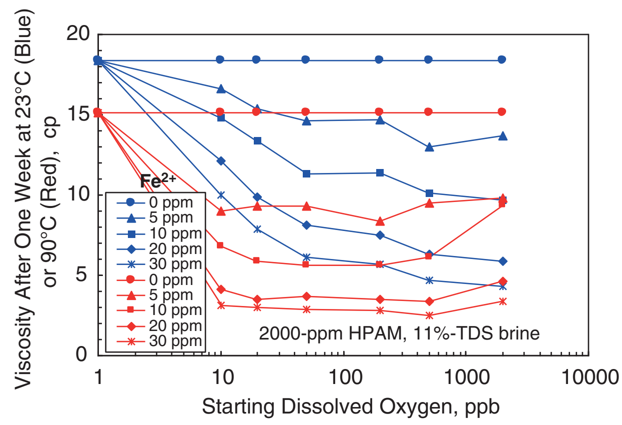

Fig. 7—HPAM-ATBS-solution viscosity losses after re-exposure to the atmosphere (at 23°C).

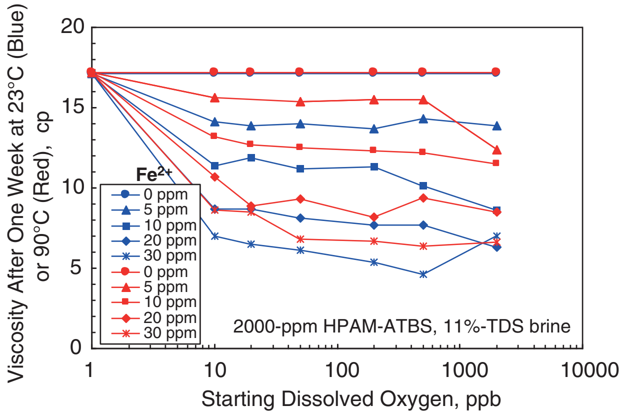

Fig. 6—HPAM-solution viscosity losses after re-exposure to the atmosphere (at 23°C).

Effect of Fe^{3+}. Argument exists about the mechanistic steps in oxidation of Fe^{2+} to Fe^{3+} and its relation to polymer degradation (Grollmann and Schnabel 1982; Wellington 1983; Ramsden and McKay 1986; Levitt et al. 2011a). If oxidation was allowed to proceed all the way to form Fe^{3+}, we wondered how the polymer would react to exposure to Fe^{3+}. Consequently, a series of tests were performed (similar to the previous experiments), with FeCl$_3$ instead of FeCl$_2$. Tests were performed with FeCl$_3$ concentrations of 0, 1, 5, 10, 50, 100, and 500 ppm, equating to Fe^{3+} concentrations of 0, 0.344, 1.72, 3.44, 17.2, 34.4, and 172 ppm, respectively. Experiments were performed as both 23 and 90°C and with 2.85%-TDS brine and 11%-TDS brine.

When adding FeCl$_3$ stock solutions to the polymer solution (with 10-ppb initial O$_2$), a yellow-orange material quickly formed. This happened with polymer both in the 2.85%-TDS **(Fig. 9)** and 11%-TDS brines **(Fig. 10).** Presumably, this gel formed from the crosslinking of the polymer by Fe^{3+}. This also happened when

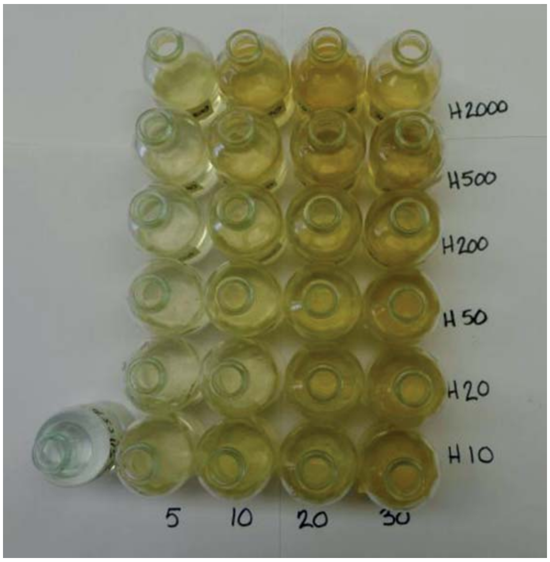

Fig. 8—HPAM-ATBS samples after exposure to air (11%-TDS brine).

Fig. 9—The 2,000-ppm HPAM-ATBS in 2.85%-TDS water with various $FeCl_3$ levels (0 to 500 ppm), 10-ppb initial O_2. Day 0.

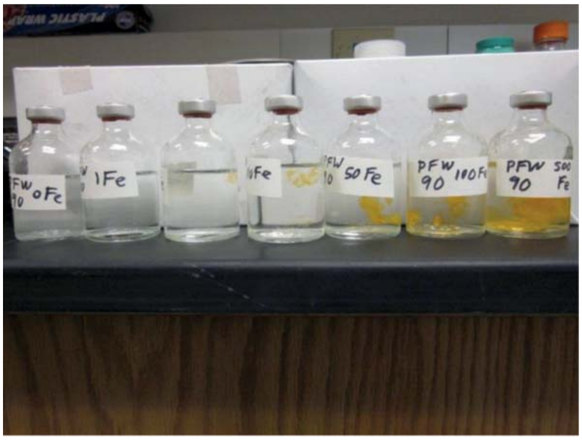

Fig. 10—The 2,000-ppm HPAM-ATBS in 11%-TDS brine with various $FeCl_3$ levels (0 to 500 ppm), 10-ppb initial O_2. Day 0.

the dissolved-oxygen concentration was 0.0 ppb. In both brines, the yellow-orange gel/precipitate formed even when the target $FeCl_3$ concentration was 1-ppm and when the stock solution contained 0.1% (1,000-ppm) $FeCl_3$. As can be seen in Figs. 9 and 10, greater amounts of yellow-orange gel/precipitate formed with higher target $FeCl_3$ concentrations. This yellow-orange gel/precipitate would not homogenize with vigorous stirring or shaking. Nevertheless, we proceeded with the experiment by storing the samples at room temperature and 90°C.

In most cases, after 7 days of storage, the sample appearance was similar to that at Day 0. However, those samples that were stored at 90°C took on an orange color for solutions that contained 50 to 500 ppm of $FeCl_3$ (17 to 172 ppm of Fe^{3+}). After 7 days' storage at either 23 or 90°C, we measured viscosities of those parts of the sample that had not gelled. For both temperatures and both brines, samples with 500 ppm of $FeCl_3$ completely gelled; thus, no viscosity could be measured. Also, for the 2.85%-TDS samples that were stored at 23°C, samples with 50 to 500 ppm of $FeCl_3$ gelled completely. For those samples (or parts of the sample) that did not gel, viscosity losses were negligible for $FeCl_3$ concentrations of 10 ppm or less and were generally modest for $FeCl_3$ concentrations of 50 ppm or more. These findings are in agreement with Ramsden and McKay (1986). Because crosslinked polymers were never observed during our studies with Fe^{2+}, we conclude that free Fe^{3+} was not generated in sufficient quantities to form a visible gel during the Fe^{2+} experiments. We recognize the possibility that very small Fe^{3+} particles may exist that we could not detect visibly.

Results With Solid-Iron Contact. We also tested cases in which steel nails (>98% iron) were stored with the polymer solutions. The nails weighed 1.74 g and were 4.80 cm in length and 0.25 cm in diameter. The nail head was 0.60 cm in diameter and 0.10 cm in thickness. For these samples, no $FeCl_2$ or $FeCl_3$ was added, but they all initially contained 10 ppb of dissolved oxygen. The samples with the nails became colored, compared with the samples containing no nail. This coloring was assumed to be associated with iron entering the solution from the nail.

Table 2 lists viscosities for these samples after 7 days' storage. For samples stored at 23°C, contact with nails caused viscosity losses (at 7.3 s^{-1}) of only 3.0% in 2.85%-TDS water and 12.2% in 11%-TDS brine. In contrast for samples stored at 90°C, contact with nails caused viscosity losses (at 7.3 s^{-1}) of 34.4% in 2.85%-TDS water and 31.5% in 11%-TDS brine. These results suggest that if temperature is high, a greater need arises to strive for very low dissolved-oxygen content.

Results With Minimum Gas Cap During Storage. After realizing that significant oxygen partitioned into the gas cap during the previous experiments, we performed four sets of experiments with 2,000-ppm HPAM-ATBS in 11%-TDS brine at 23°C with a gas cap of approximately 0.2 cm^3 and 60 cm^3 of solution in each glass bottle. With this ratio of gas to liquid, only approximately 10% of the original dissolved oxygen should partition into the gas cap. We examined cases with initial dissolved-oxygen concentrations of 0, 10, 20, 30, 50, 100, 200, 500, 1,000, and 3,300 ppb. After 11 days' storage at 23°C, **Fig. 11** plots viscosity (at 7.3 s^{-1}, 23°C), **Fig. 12** plots final dissolved-oxygen concentration, **Fig. 13** plots final E_h (oxidation-reduction potential, in mV), and **Fig. 14** plots final pH. E_h was measured with a Eutech Instruments Model Oakton ORPTestr 10 E_h meter, whereas pH was measured with a Eutech Instruments Model Oakton pHTestr 30 pH meter. (To correct to standard conditions, instrument E_h values required addition of 0.21 V to correct the readings from the Oakton ORP Ag/AgCl reference electrode.)

Fig. 11 suggests that the onset of significant polymer degradation at 23°C begins at approximately 200-ppb dissolved oxygen. This value is much closer to the 500-ppb initial O_2 value associated with the bottom *x*-axis scale in Fig. 3 rather than to the 30-ppb conservative estimate from Henry's law, associated with the top *x*-axis scale in Fig. 3. As a possible explanation, in the earlier experiments, oxygen in the gas cap probably continually replenished dissolved oxygen that was depleted by reaction with either iron or polymer. For example, for the case of 500-ppb initial dissolved oxygen, partitioning into the 20-cm^3 gas cap reduced the dissolved O_2 to approximately 30 ppb—leaving 94% of the initial oxygen in the gas cap. As the dissolved oxygen was consumed by reaction with iron or the polymer, oxygen from the gas cap migrated back into solution (maintaining the Henry's-law equilibrium constant).

In agreement with Figs. 1 through 4, the onset of polymer degradation was insensitive to dissolved-iron concentration. Again,

Storage Temperature:		23°C				90°C			
	Shear Rate (s^{-1}):	36.5	14.6	7.3	3.65	36.5	14.6	7.3	3.65
Brine	Nail?	cp at 23°C				cp at 23°C			
2.85%-TDS	No	14.54	19.05	23.2	27.2	16.28	22.2	27.6	32.4
2.85%-TDS	Yes	14.2	18.6	22.5	26.6	12.84	15.9	18.1	20.0
11%-TDS	No	12.72	16.1	18.8	21.2	13.5	17.3	20.3	23.0
11%-TDS	Yes	11.9	14.7	16.7	18.2	10.72	12.65	13.9	14.8

Table 2—Effect of contact with steel. HPAM-ATBS (2,000 ppm) viscosities after 7 days. 10-ppb initial O_2.

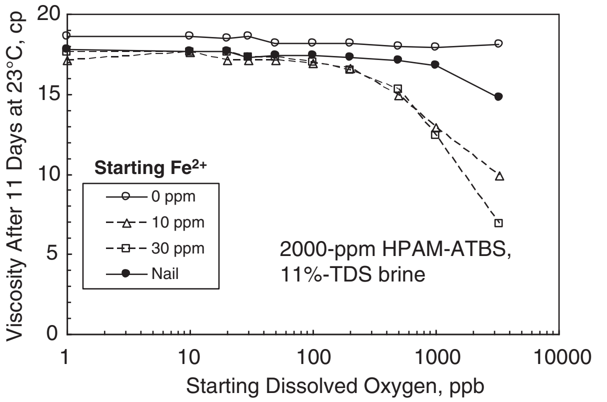

Fig. 11—Final viscosity with minimum gas cap.

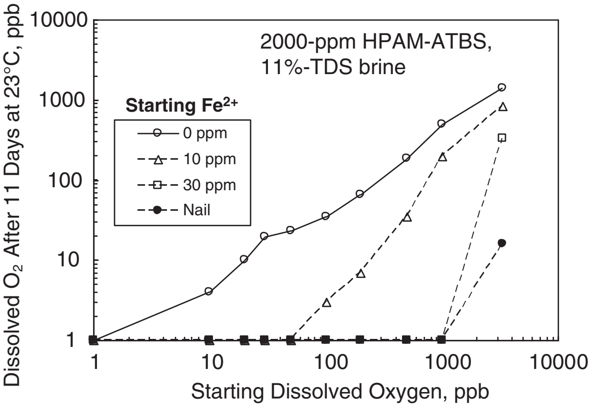

Fig. 12—Final dissolved O_2 with minimum gas cap.

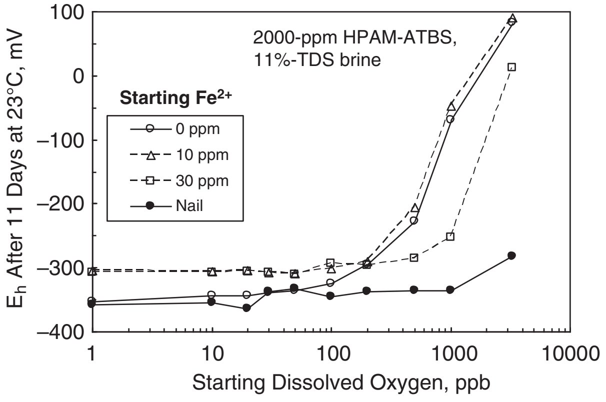

Fig. 13—Final E_h with minimum gas cap.

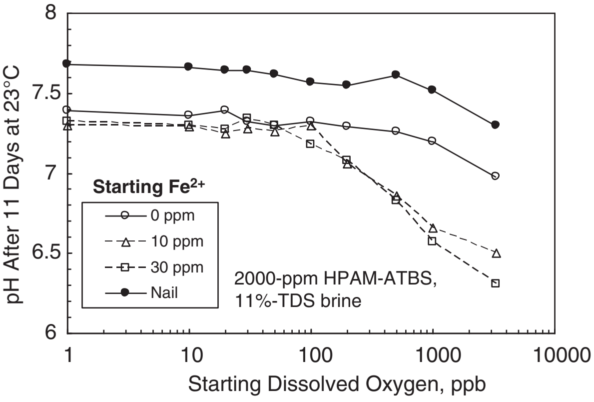

Fig. 14—Final pH with minimum gas cap.

the onset of polymer degradation was noted at approximately 200-ppb dissolved oxygen in Fig. 11. Also in agreement with Figs. 1 through 4, in the presence of high dissolved-O_2 levels, polymer degradation increased with increased dissolved-iron concentration. With 30-ppm Fe^{2+} and 3,300-ppb initial dissolved oxygen, a 61% viscosity loss was noted at 23°C (Fig. 11).

When contacting solid iron (i.e., a nail) at 23°C, less than 6% viscosity loss was seen for dissolved O_2 concentrations up to 1,000 ppb. For 3,300-ppb dissolved oxygen, a 17% viscosity loss was noted after 11 days in contact with a nail. Recall that more-dramatic viscosity losses were seen with only 10-ppb initial O_2 at 90°C in the presence of solid iron (Table 2).

Consistent with the suggestion of Levitt et al. (2011a), the onset of polymer degradation (i.e., at 200-ppb initial O_2) correlated well with the onset of increases in E_h, as shown in Fig. 13. However, the severity of polymer degradation did not correlate well with E_h. With 3,300-ppb initial dissolved O_2, the final E_h values were virtually identical (approximately 90 mV) for 0-ppm Fe^{2+} and 10-ppm Fe^{2+} (Fig. 13). A 42% viscosity loss was seen with 10-ppm Fe^{2+}, but no degradation occurred with 0-ppm Fe^{2+} (Fig. 11). Interestingly, the smallest change in E_h was noted for solutions that contacted solid iron (Fig. 13).

Significant reductions in pH were noted above 100-ppb initial dissolved oxygen when either 10- or 30-ppm Fe^{2+} was present (Fig. 14). The stoichiometry associated with the reaction between Fe^{2+} and oxygen generally indicates acid consumption (Ramsden and McKay 1986). However, subsequent complexation of Fe^{3+} with OH^- results in significant acid generation*, thus explaining the behavior in Fig. 14. As mentioned earlier, the lack of the formation of a visible gel suggests that any Fe^{3+} that is present does not appear to crosslink the polymer. As an alternative explanation, our observed pH reductions might be associated with oxidation of the polymer.

For the 0-ppm Fe^{2+} cases in Fig. 12 (i.e., the open circles), the final dissolved-oxygen concentration was consistently close to half the initial value. From Henry's law, we expected a consistent loss of oxygen to the gas cap—but only approximately 10% of the original value. Because there was no iron and no polymer degradation associated with these cases, we expected no losses of oxygen caused by reaction with iron or polymer. We presume that the additional oxygen losses occurred during opening/measurement at the end of the experiment.

For the 10-ppm Fe^{2+} cases in Fig. 12 (i.e., the open triangles), all samples with 50-ppb or less of initial O_2 were completely depleted of dissolved oxygen. Because polymer degradation was insignificant for these cases, we assume that the oxygen losses were caused by reaction with Fe^{2+}. For samples with more than 50-ppb initial O_2, dissolved oxygen was detected after 11 days of storage. Similarly, for the 30-ppm Fe^{2+} cases in Fig. 12 (i.e., the open squares), dissolved oxygen was detected after 11 days in samples with more than 1,000-ppb initial O_2. The equilibrium constant for Fe^{2+} reacting with O_2 suggests that no more than one of the species should be present in solution after equilibrium is attained. Consequently, one would expect cases in which dissolved oxygen remains in Fig. 12 to be depleted of Fe^{2+}. However, if oxygen is stoichiometrically reacted with Fe^{2+} to form Fe_2O_3, 50 ppb of oxygen should only deplete 1% of the original 10 ppm of Fe^{2+}. Similarly, 1,000 ppb of oxygen should only deplete 8% of the original 30 ppm of Fe^{2+}. We wonder if the polymer has an ability to chelate some of the Fe^{2+} and prevent it from reacting with O_2.

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*Personal communication with D.D. Levitt and S. Jouenne, Total (Pau, France), and N. Gaillard, SNF (Andrezieux, France), 20 May 2014.

Discussion

No Action If Water Contains No Fe^{2+}. Recall our original issue at the beginning of this paper: What approach should be taken to minimize oxidative degradation of hydrolyzed polyacrylamide (HPAM) polymers in field applications? In this section, we discuss how our results affect this decision. First, for many of the largest polymer floods (e.g., Daqing, Shengli, Pelican Lake), no effort was made to eliminate dissolved oxygen or control oxidation in the injected polymer solutions. Because these low-temperature polymer floods were quite successful in recovering oil (Wang et al. 2008, 2011; Zhu et al. 2013; Delamaide et al. 2014), it seems likely the HPAM polymers did not suffer severe degradation. Manichand et al. (2013) demonstrated that HPAM solutions propagated more than 300 ft through a reservoir (at 38°C) with no significant degradation even though the injected solutions were saturated with dissolved oxygen. On the basis of the work of Seright et al. (2010), they argued that iron minerals in the reservoir quickly (perhaps a day or two at low temperature; a few hours at elevated temperatures) consumed the dissolved oxygen. From that point on, the solution was in a highly reduced state, and Fe^{2+} dissolved into the polymer solution (Xu et al. 2000), but the polymer did not suffer oxidative degradation. When the polymer was produced, it will degrade rapidly if it mixed with atmospheric oxygen. However, if the polymer solution was collected anaerobically, it suffered little or no viscosity loss (Manichand et al. 2013).

Some have expressed a concern that if oxygenated water is injected into a well for a long time, all the oxygen-consuming minerals will be expended, and an oxygen front will propagate a significant distance into the reservoir. However, calculations reveal that a reservoir with only 1% pyrite can consume all dissolved oxygen (at an ambient level of 5,000 ppb) in 3-million pore volumes of water (Seright et al. 2010). This realization leads to limiting our concern for oxidative degradation to the first week after polymer injection. As further support, Seright et al. (2010) examined a 1,000-ppm Daqing HPAM solution (25.8 cp) that initially contained 3,300-ppb dissolved oxygen. When this solution was mixed with anaerobic Daqing sand (which contained 0.23% pyrite and 0.51% siderite), the dissolved oxygen dropped to zero within 1 day at 45°C, whereas the solution viscosity only dropped to 24.1 cp. Further, we note that most reservoirs are in a highly reduced state and their waters contain no detectable dissolved oxygen (Xu et al. 2000; Hartog et al. 2002; Prommer and Stuyfzand 2005; Fernández et al. 2007).

For the previous floods in which polymer was injected with high dissolved-oxygen levels, it seems likely that the injected polymer solutions contained little or no Fe^{2+}—either because the polymer solutions were made with fresh surface water or because any iron that may have been present was oxidized to a solid (particulate) form. If Fe^{2+} was present (in solution) with an unlimited supply of oxygen (i.e., the atmosphere), severe polymer degradation would occur very quickly. For example, Shupe (1981) observed a 55% viscosity loss within 1 to 2 minutes after adding 10-ppm Fe^{2+} to an HPAM solution at room temperature, after exposure to atmospheric oxygen. Also, Manichand et al. (2013) saw an 80% loss of viscosity within 1 hour for an HPAM solution that was produced from a well and was exposed to air at ambient temperature.

Thus, consistent with the field operations (i.e., polymer floods in reservoirs with temperatures of 50°C or less), the injection of polymer solutions with high dissolved-oxygen saturations should not experience severe oxidative degradation if Fe^{2+} is not present in the injection water. Note that we specify dissolved oxygen—not gaseous, undissolved oxygen. Entrained air would present a much larger oxygen source and polymer-degradation concern than dissolved oxygen.

Oxygen Reduction or Removal If Fe^{2+} Is Present. The Dalia/Camelia polymer flood provides an example of a recent polymer flood in which dissolved oxygen is kept very low (<10 ppb) by design (Morel et al. 2012). How low should the dissolved-oxygen content be in a field application? We found that for Fe^{2+} concentrations between 0 and 30 ppm, viscosity losses [for both HPAM and HPAM-2-acrylamido-tertbutylsulfonic acid (ATBS)] were insignificant after 1 week (at either 23 or 90°C) when dissolved-oxygen concentration was 200 ppb or less. This finding suggests that 200-ppb dissolved oxygen provides an important benchmark to stay below during a polymer flood. For higher dissolved-oxygen concentrations, significant viscosity losses were observed. Because polymer is normally the greatest single expense during a polymer flood, even a 10% loss of viscosity amounts to a substantial financial loss during a field project.

If the dissolved-oxygen level is high, one should ask whether an oxygen leak is present in the flow system. An oxygen leak could provide an unlimited source of oxygen and degradation for the polymer. This point is emphasized by our results when anaerobic polymer solutions were re-exposed to the air—where polymer degradation increased substantially with increased Fe^{2+} concentration. We have witnessed field projects in which less than 10-ppb dissolved oxygen was achieved without resorting to chemical oxygen scavengers.

Use of Chemical Oxygen Scavengers and/or Antioxidants. Our current findings and those of previous researchers (Yang and Treiber 1985; Seright et al. 2010) demonstrated that oxidative degradation of HPAM stops after the free oxygen is consumed. The contrary view of Wellington (1983) should be mentioned. Wellington and other 1970s- to 1980s-era Shell scientists advocated that a small number of free radicals could degrade a significant portion of polymer molecules in a beaker or reservoir (through "auto-oxidation"). We wonder whether Wellington's concept might be based on an assumption of an unlimited oxygen supply. At any rate, Wellington developed an oxygen-scavenger and antioxidant formulation to neutralize free-radicals and promote polymer stability. This approach was applied in some field applications. In particular, the polymer flood at Marmul uses a free-radical scavenger formulation (Koning et al. 1988; Al-Saadi et al. 2012).

Many researchers have noted that the addition of certain chemicals (e.g., alcohols, thiourea, formaldehyde, sodium borohydride) appear to stabilize polymer solutions in the presence of dissolved iron and oxygen (Shupe 1981; Wellington 1983; Yang and Treiber 1985; Ryles 1988). However, we note that the greatest (longest and highest temperature) stability for HPAM reported in the literature involved measured exclusion of dissolved oxygen with no addition of stabilizing additives (Seright et al. 2010). Because the addition of the stabilizing chemicals adds significantly to costs in a chemical flood, our observation raises the question whether the gas-blanketing of tanks and mixing facilities and the prevention of oxygen leaks are more cost-effective than the use of these chemical stabilizers.

Chemical oxygen scavengers, such as sodium dithionite, were used to remove oxygen from enhanced-oil-recovery solutions. If oxygen is reintroduced after the application of the sodium dithionite, significant polymer degradation was observed (Knight 1973; Shupe 1981; Yang and Treiber 1985; Levitt et al. 2011a). Levitt et al. (2011a) noted that the presence of bicarbonate can mitigate this degradation. Although the use of chemical oxygen scavengers may be necessary under some circumstances, we argue that minimizing oxygen by physical means (e.g., stopping leaks, better design of fluid transfer, gas-blanketing, gas-stripping) is more cost-effective than the ongoing use of chemicals. The injection of sulfur compounds may also feed sulfate-reducing bacteria.

Removal of Fe^{2+}. Another approach is to precipitate most or all Fe^{2+} from solution by extensive oxygenation of the water before adding polymer in a field application (Levitt et al. 2011a; Irvine et al. 2012). This approach was followed at field projects at the Shengli field in China[**] and the Wainwright B pool in Canada (Irvine et al. 2012). In their polymer flood at Wainwright (which contained 18- to 20-ppm iron), Irvine et al. (2012) chose to remove the dissolved and particulate iron through precipitation by mixing

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[**] Personal communication with P. Han, Daqing Oilfield Company, Daqing, China, 28 December 2013.

with air and bleach. Extensive processing of the water through tanks and filtration was required, in addition to the expense of the disposing of the solid waste. We wonder whether it would have been simpler and more cost-effective to leave the iron in solution—by eliminating any oxygen leakage in the flow stream. Our work reveals that Fe^{2+} in solution has no significant effect on HPAM (other than the electrolyte effect, as for Ca^{2+}) if oxygen is not present. In addition to eliminating oxygen leaks, tankage and mixing facilities should be blanketed by an inert gas. There is a simple, often-overlooked method to reduce oxygen leakage during water introduction into tanks. Typically, water is introduced into the top of the tank—becoming heavily aerated as it drops through air to the liquid surface. Oxygen entrainment and dissolution could be substantially reduced by introducing the water into the tank below the liquid level. In summary, we advocate that efforts should be made to minimize oxygen introduction in the flow stream while leaving the iron in solution. As was demonstrated in this paper and implied by the work of Yang and Treiber (1985), Seright et al. (2010), and Manichand et al. (2013), if temperatures are low, low levels of dissolved oxygen should not cause substantial polymer degradation, even if high levels of dissolved iron are present.

An alternative to precipitating Fe^{2+} by intentional oxygenation is to inject alkaline/polymer solutions, especially with CO_3^{2-} or HCO_3^-. Several researchers reported enhanced HPAM stability under alkaline conditions, including Shupe (1981), Ramsden and McKay (1986), and Levitt et al. (2011b). Levitt et al. (2011b) noted that Fe^{2+} solubility diminishes greatly with increased pH, especially in the presence of carbonate or bicarbonate.

Summary of Findings

The following conclusions were reached during stability studies of 2000-ppm hydrolyzed poly-acrylamide (HPAM) or HPAM-2-acrylamido-tertbutylsulfonic acid (ATBS) solutions in 2.85%- or 11%-TDS brines:

- For Fe^{2+} concentrations between 0 and 30 ppm, viscosity losses were insignificant after 1 week (at either 23 or 90°C) when the initial dissolved-oxygen concentration was 200 ppb or less. Above 200-ppb initial dissolved oxygen, significant viscosity losses were seen, especially for storage at 90°C.
- For initial dissolved-oxygen levels up to 200 ppb, there was no significant difference in polymer degradation for Fe^{2+} concentrations between 5 and 30 ppm.
- During our first studies with a 20-cm^3 gas cap over 40 cm^3 of stored liquid, the liquid was depleted of oxygen by partitioning into the gas cap. In line with expectations from Henry's law, for cases with 8,000-ppb initial dissolved oxygen, the final dissolved oxygen was approximately 300 ppb after 1 week of storage at either 23 or 90°C.
- During further studies with no gas cap, at least half of the dissolved oxygen remained after 11 days if no iron was present. With 10-ppm initial Fe^{2+}, all dissolved O_2 was consumed if the initial dissolved oxygen was 50 ppb or less. With 30-ppm initial Fe^{2+}, all dissolved O_2 was consumed if the initial dissolved oxygen was 1,000 ppb or less.
- For initial oxygen concentrations of 8,000 ppb, polymer degradation depended on Fe^{2+} concentration. With no Fe^{2+} present but 8,000-ppb initial oxygen, no viscosity losses were noted after 1 week of storage at 23°C for either polymer. At 23°C with 8,000-ppb initial oxygen, viscosity losses after 1 week increased with increased iron content—reaching a 48% loss for HPAM-ATBS and a 75% loss for HPAM with 30-ppm Fe^{2+}. With no Fe^{2+} present but 8,000-ppb initial oxygen, viscosities after 1 week at 90°C were notably lower than those with no initial dissolved oxygen—being 15% lower for HPAM-ATBS and 32% lower for HPAM. At 90°C with 8,000-ppb initial oxygen, viscosity losses after 1 week increased with increased iron content—reaching an additional 67% loss for either polymer with 30-ppm Fe^{2+}.
- When anaerobic or low-oxygen solutions were exposed to atmospheric oxygen, polymer degradation increased substantially with increased Fe^{2+} concentration.
- When $FeCl_3$ stock solutions were added to polymer solutions (with 10-ppb initial O_2), a yellow-orange gel/precipitate quickly formed. This happened with polymer in both 2.85%- and 11%-TDS brine. This also happened when the dissolved-oxygen concentration was 0.0 ppb. Greater amounts of yellow-orange gel/precipitate formed with higher target $FeCl_3$ concentrations. For those samples (or parts of the sample) that did not gel, viscosity losses were negligible for $FeCl_3$ concentrations of 10 ppm or less and were modest for $FeCl_3$ concentrations of 50 ppm or more.
- Because crosslinked polymers were never observed during our studies with Fe^{2+}, we conclude that free Fe^{3+} was not generated in sufficient quantities to form a visible gel during the Fe^{2+} experiments.
- For HPAM-ATBS samples stored at 90°C with 10-ppb initial dissolved oxygen, contact with steel caused viscosity losses of 34.4% in 2.85%-TDS brine and 31.5% in 11%-TDS brine. In contrast at 23°C, contact with steel caused no significant degradation when the dissolved-O_2 concentration was 1,000 ppb or less.

Significance of Findings

Consistent with the approach taken during some large-scale polymer floods, the removal of dissolved oxygen from the polymer makeup water is not needed if the water contains no Fe^{2+} and the temperature is low (<50°C). Iron minerals (e.g., pyrite, siderite) in the reservoir quickly consume the dissolved oxygen. From that point on, the solution is in a highly reduced state and Fe^{2+} dissolves into the polymer solution, but the polymer does not suffer oxidative degradation.

If significant Fe^{2+} is present and temperatures are low, our work indicates that short-term (i.e., 1 week) polymer degradation is minor when dissolved-oxygen concentration is 200 ppb or less. Note that we specify dissolved oxygen—not gaseous, undissolved oxygen. Entrained air would present a much larger oxygen source and polymer-degradation concern than dissolved oxygen. If temperature is high (>50°C), a greater need arises to strive for very low dissolved-oxygen content.

Many researchers noted that the addition of certain chemicals (e.g., alcohols, thiourea, formaldehyde, sodium borohydride) appears to stabilize polymer solutions in the presence of dissolved iron and oxygen. However, we note that the greatest (longest and highest temperature) stability for hydrolyzed polyacrylamide reported in the literature involved measured exclusion of dissolved oxygen with no addition of stabilizing additives. Because the addition of the stabilizing chemicals adds significantly to costs in a chemical flood, physical means of excluding oxygen (e.g., stopping leaks, better design of fluid transfer, gas-blanketing, gas-stripping) may be more cost-effective. Injection of sulfur compounds (e.g., sodium dithionite) may also feed sulfate-reducing bacteria.

Another approach is to precipitate most or all Fe^{2+} from solution by the oxygenation of the water before adding polymer in a field application. Extensive processing of the water through tanks and filtration is required, in addition to the expense of disposing of the solid waste. However, it may be simpler and more cost-effective to leave the iron in solution—by eliminating any oxygen leakage in the flow stream. As was demonstrated in this paper, low levels of dissolved oxygen should not cause substantial polymer degradation, even if high levels of dissolved iron are present.

Nomenclature

E_h = oxidation-reduction potential, mV

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SI Metric Conversion Factors

$\text{cp} \times 1.0^*$ $\quad$ $\text{E}-03 = \text{Pa·s}$

$\text{ft} \times 3.048^*$ $\quad$ $\text{E}-01 = \text{m}$

*Conversion factor is exact.

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