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Effect of Dissolved Iron and Oxygen on Stability of HPAM Polymers

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Abstract

This paper describes an experimental study of the stability of an HPAM polymer and an HPAM-ATBS terpolymer in the presence of varying initial levels of dissolved oxygen (0 to 8000 parts per billion, ppb), Fe^{2+} (0 to 220 parts per million, 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°C and 90°C. For Fe^{2+} concentrations between 0 and 30 ppm, viscosity losses were insignificant after one week so long as 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 one week at 90°C with only 10-ppb initial dissolved oxygen, contact with steel caused HPAM-AMPS solution viscosity losses greater than 30%. In contrast at 23°C, contact with steel caused no significant degradation so long as the dissolved O_2 concentration was 1000 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) over chemical means.

Addition of Fe^{3+} to polymer solutions caused immediate crosslinking. Since 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 HPAM solutions, redox couples or cycles can substantially degrade polymers (Pye 1967, Shupe 1981, Grollmann and Schnabel 1981, 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 can also 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.* 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 (3-8 parts per million, 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 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 parts per billion, 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). A number of 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-ATBS terpolymer in the presence of varying initial levels of dissolved oxygen (0 to 8000 ppb), Fe^{2+} (0 to 220 parts per million, 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°C and 90°C. Our hope was that insights from this study would help resolve which of the four approaches mentioned in the previous paragraph is most appropriate.

Experimental

Two polymers were used in this work, called HPAM and HPAM-ATBS. The HPAM polymer was SNF Flopaam 3630S™. This acrylamide-acrylate polymer had an average molecular weight of 18 million g/mol and 30% anionicity. 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 (2-acrylamido-tertbutylsulfonic acid), and had a total anionicity of 25%.

Two brines were used. **Table 1** lists their compositions. They will be called “11%-TDS brine” 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 make-up 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 de-oxygenation and polymer addition.

Table 1—Brine compositions (ppm).

Salt	11%-TDS brine	2.85%-TDS brine
Na_2SO_4	31	0
NaHCO_3	234	138
KCl	4974	0
$\text{MgCl}_2 - 6 \text{H}_2\text{O}$	6264	1949
$\text{CaCl}_2 - 2 \text{H}_2\text{O}$	10208	638
$\text{SrCl}_2 - 6 \text{H}_2\text{O}$	1737	0
$\text{BaCl}_2 - 2 \text{H}_2\text{O}$	196	0
NaCl	92829	26988
TDS	109908	28520

A vortex was formed using a magnetic stirrer, and powder-form polymer was added and then mixed overnight at low speed. The prepared polymer solutions contained 2000-ppm polymer in either 11%-TDS brine or 2.85%-TDS brine. For each polymer, one set of 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 (10–15% hydrogen and 85–90% 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 can be 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, while 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 (CHEMmet™) with a limit of oxygen detection of 1 ppb in aqueous solution. We believe that the above 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 occurs during flame sealing. The erratic nature of viscosity versus 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. Based on mass balance, this solution was added and mixed with anaerobic polymer solution to achieve lots with the desired final dissolved oxygen content, including 10 ppb, 20 ppb, 50 ppb, 200 ppb, 500 ppb, and 2000 ppb. Dissolved oxygen concentrations were confirmed using both our Mettler Toledo probe and the CHEMmet method (Ultra Low Range CHEMmet R-7511). Next, the solutions were distributed into glass bottles—with 40 grams of solution into each 60 cm^3 bottle. Then, using 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 8000-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-gram 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.

After the glass bottles were filled with solution, a rubber septum was inserted into the opening and sealed with an aluminum cap. One set of solutions were 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 one 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} using a Brookfield viscometer with a UL adapter. In this paper, we generally only report results at 7.3 s^{-1} . We chose a one-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 one-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 ~17 after the 40- cm^3 liquid equilibrated with the 20- cm^3 gas cap. Consequently, another set of experiments was performed where solutions were stored with a very small (~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. 1-4**. Figs. 1 and 2 apply to 2000-ppm HPAM stored at 23°C and 90°C, respectively. Figs. 3 and 4 apply to 2000 ppm HPAM-ATBS stored at 23°C and 90°C, respectively. Examination of these figures first reveals that for any Fe^{2+} concentration (between 0 and 30 ppm), viscosity losses (for both polymers) were insignificant after one week (at either 23°C or 90°C) so long as the initial dissolved oxygen concentration was 500 ppb or below. 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. 1-4 show expected O_2 concentrations after correction for equilibration with the 20- cm^3 gas cap.) Viscosity losses (at 7.3 s^{-1}) after one week with initial 2000-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 8000-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 once the available dissolved oxygen is depleted, no further oxidative degradation of polymer occurs. For all cases that started with 2000-ppb dissolved oxygen or less, the final dissolved oxygen content after one week was undetectable. Thus, the dissolved oxygen was depleted during storage with the polymer (primarily due to equilibration with the gas cap, as mentioned above). Our findings contradict a myth that has been circulated by some workers in enhanced oil recovery, who suggested that a small number of free-radical or oxygen molecules could theoretically degrade much (or in the extreme limit, all) polymer in a reservoir. Those who advocate this belief typically point to the work of Wellington (1983).

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—e.g., 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 2000-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 2000-ppm HPAM, a 30% loss of viscosity translates to a 19% loss of polymer concentration or a loss of 380 ppm of polymer.

For the cases with initial dissolved oxygen of 8000 ppb, the final dissolved oxygen (after 1 week of storage at either temperature) averaged around 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 one week, all solutions maintained some viscosity, so the residual dissolved oxygen did not completely react with polymer. The dependence of polymer degradation on Fe^{2+} content was much greater with 8000-ppb initial dissolved oxygen than with 2000-ppb or less initial dissolved oxygen. For 8000-ppb initial oxygen, calculated polymer losses ranged from 111 to 1240 ppm—primarily depending on Fe^{2+} content.

Effect of Fe^{2+} . For initial dissolved oxygen levels up to 2000 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 8000 ppb, degradation depended on Fe^{2+} concentration. With no Fe^{2+} present but 8000-ppb initial oxygen, no viscosity losses were noted after one week of storage at 23°C for either polymer (see the open squares in Figs. 1 and 3). At

23°C with 8000-ppb initial oxygen, viscosity losses after one 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).

With no Fe^{2+} present but 8000-ppb initial oxygen, viscosities after one week at 90°C were notably lower than with no initial dissolved oxygen (right-most open squares in Figs. 2 and 4)—being 15% lower for HPAM-ATBS and 32% lower for HPAM. At 90°C with 8000-ppb initial oxygen, viscosity losses after one 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 2000 ppb and 8000 ppb) 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.

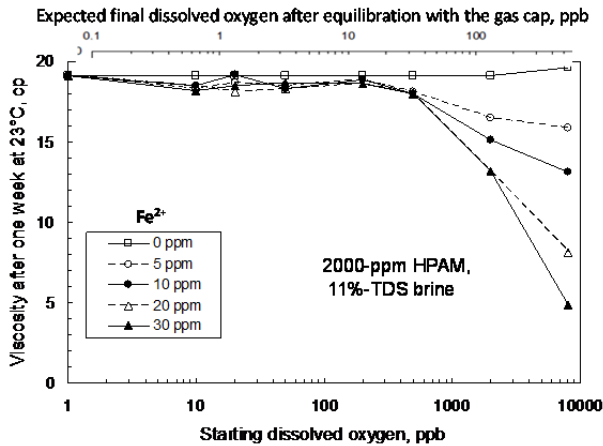


Fig. 1—Effect of dissolved oxygen and Fe^{2+} on HPAM stability at 23°C.

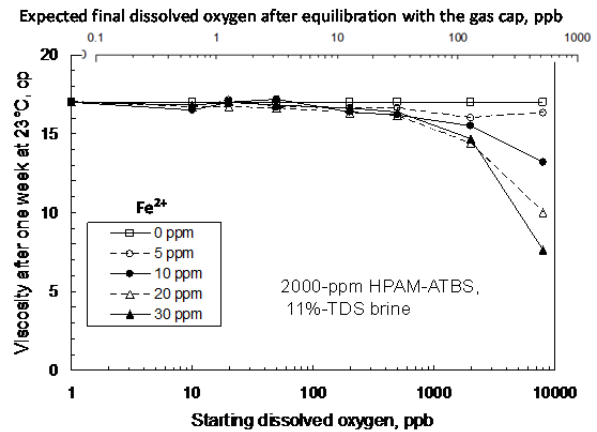


Fig. 3—Effect of dissolved oxygen and Fe^{2+} on HPAM-ATBS stability at 23°C.

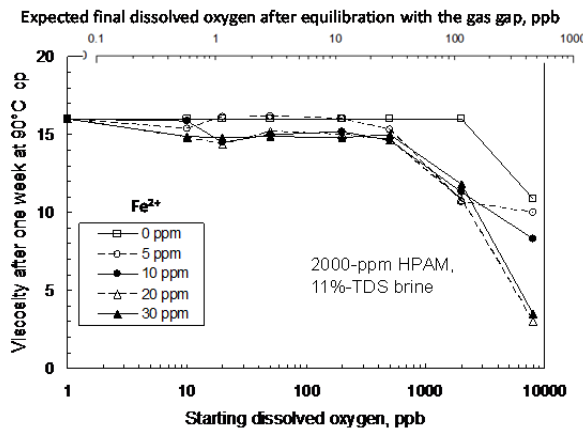


Fig. 2—Effect of dissolved oxygen and Fe^{2+} on HPAM stability at 90°C.

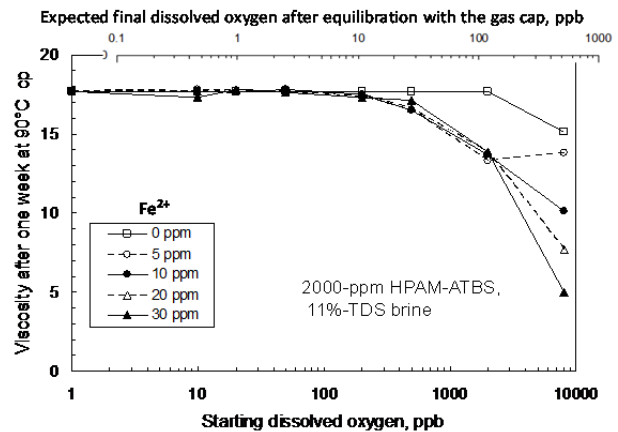


Fig. 4—Effect of dissolved oxygen and Fe^{2+} on HPAM-ATBS stability at 90°C.

Effect of Salinity. A separate study was performed using the two brines (2.85% TDS and 11% TDS). In this case, we focused on 2000-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 above experiments. Fig. 5 shows the results. In 11%-TDS brine, polymer solution viscosity was independent of Fe^{2+} concentration after storage for one week at either 23°C or 90°C. The same was true at 23°C with HPAM-ATBS in 2.85%-TDS brine. After one week at 90°C in 2.85%-TDS brine, the viscosity with low-to-moderate iron concentrations was about 20% higher than after one 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 one week decreased with increased iron content—presumably because of a mild degradation (open circles in Fig. 5).

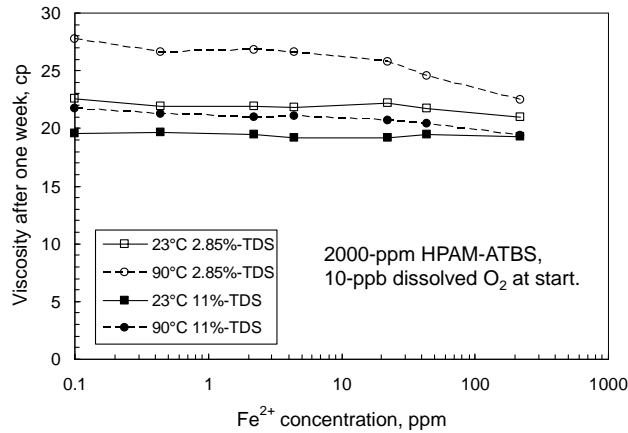


Fig. 5—Effect of Fe²⁺, temperature, and salinity on HPAM-ATBS stability.

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 re-measured their viscosities (Figs. 6 and 7). Greater Fe²⁺ concentrations generally led to greater polymer degradation. However, the greatest viscosity loss was noted between 0- and 10-ppm Fe²⁺. 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 Fe³⁺).

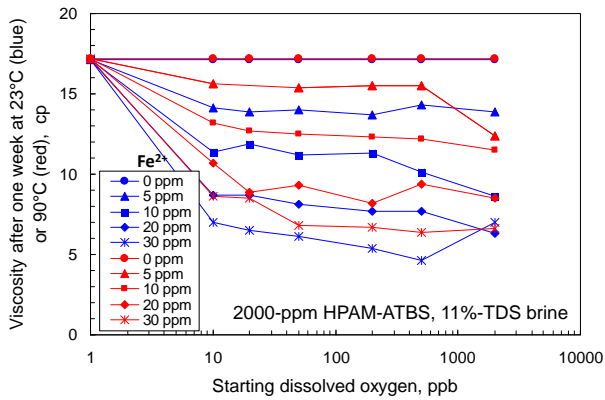


Fig. 6—HPAM solution viscosity losses after re-exposure to the atmosphere (at 23°C).

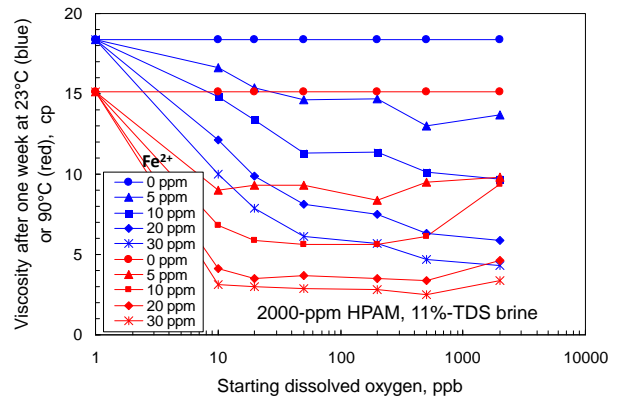


Fig. 7—HPAM-AMPS solution viscosity losses after re-exposure to the atmosphere (at 23°C).

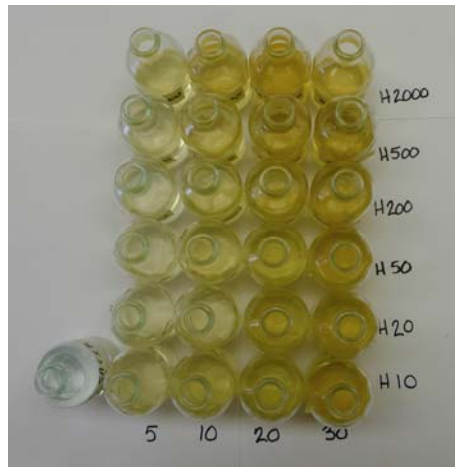


Fig. 8—HPAM-AMPS samples after exposure to air (11%-TDS brine).

Bottom numbers show iron content (in ppm) while 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.

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 1981, 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 above experiments), using 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 both at 23°C 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 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% (1000-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.



Fig. 9—2000-ppm HPAM-ATBS in 2.85%-TDS water with various FeCl_3 levels (1-500 ppm), 10-ppb initial O_2 . Day 0.



Fig. 10—2000-ppm HPAM-ATBS in 11%-TDS brine with various FeCl_3 levels (1-500 ppm), 10-ppb initial O_2 . Day 0.

In most cases after seven 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 FeCl_3 (17-to-172-ppm Fe^{3+}). After seven days storage at either 23°C 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 FeCl_3 completely gelled, so no viscosity could be measured. Also, for the 2.85%-TDS samples that were stored at 23°C, samples with 50-500-ppm 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.

Results with Solid Iron Contact. We also tested cases where steel nails (>98% iron) were stored with the polymer solutions. The nails weighed 1.74 g and were 4.80-cm long and 0.25 cm in diameter. The nail head was 0.60 cm in diameter and 0.10 cm thick. For these samples, no FeCl_2 or FeCl_3 was added, but they all initially contained 10-ppb 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 seven days of 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.

Table 2—Effect of contact with steel. HPAM-ATBS (2000 ppm) viscosities after 7 days. 10-ppb initial O₂.

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

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 2000-ppm HPAM-ATBS in 11%-TDS brine at 23°C with a gas cap of ~0.2 cm³ and 60 cm³ of solution in each glass bottle. With this ratio of gas to liquid, only ~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, 1000, and 3300 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), and **Fig. 14** plots final pH. E_h was measured using a Eutech Instruments Model Oakton ORPTestr 10™ E_h meter, while pH was measured using a Eutech Instruments Model Oakton pHTestr 30™ pH meter.

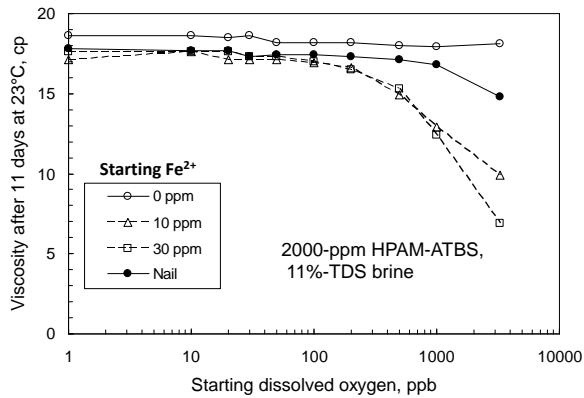


Fig. 11—Final viscosity with minimum gas cap.

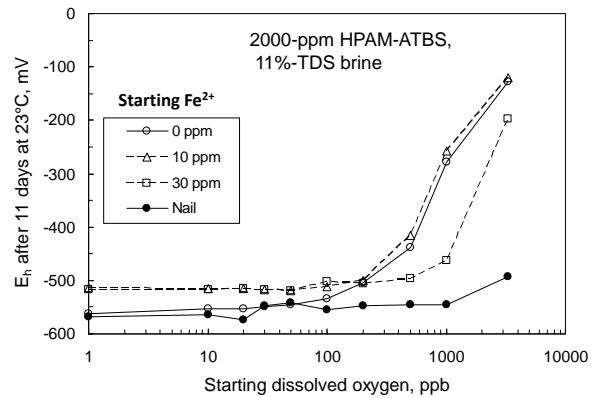


Fig. 13—Final E_h with minimum gas cap.

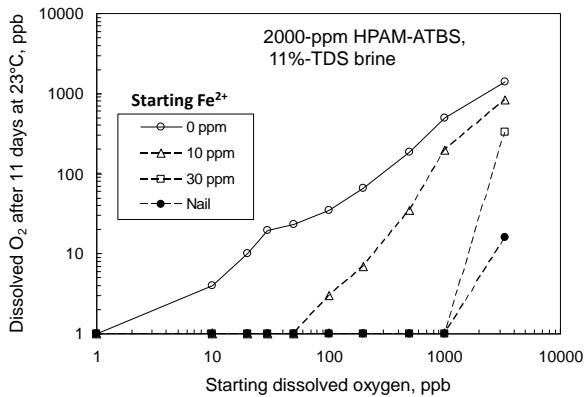


Fig. 12—Final dissolved O₂ with minimum gas cap.

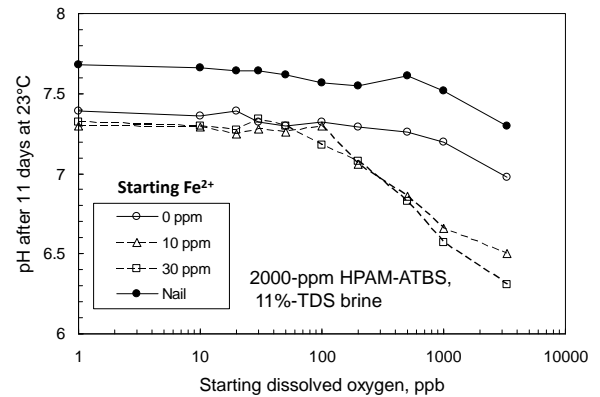


Fig. 14—Final pH with minimum gas cap.

Fig. 11 suggests that the onset of significant polymer degradation at 23°C begins at ~200-ppb dissolved oxygen. This value is much closer to the 500-ppb initial O₂ value associated with the bottom x-axis scale in Fig. 3 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-cm³ gas cap reduced the dissolved O₂ to ~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. 1-4, the onset of polymer degradation was insensitive to dissolved iron concentration. Again, the

onset of polymer degradation was noted at ~200-ppb dissolved oxygen in Fig. 11. Also in agreement with Figs. 1-4, in the presence of high dissolved O₂ levels, polymer degradation increased with increased dissolved iron concentration. With 30-ppm Fe²⁺ and 3300-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 O₂ concentrations up to 1000 ppb. For 3300-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 O₂ 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 O₂) correlated well with the onset of increases in oxidation-reduction potential (E_h), as shown in Fig. 13. However, the severity of polymer degradation did not correlate well with E_h. With 3300-ppb initial dissolved O₂, the final E_h values were virtually identical (~120 mV) for 0-ppm Fe²⁺ and 10-ppm Fe²⁺ (Fig. 13). A 42% viscosity loss was seen with 10-ppm Fe²⁺, but no degradation occurred with 0-ppm Fe²⁺ (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-ppm or 30-ppm Fe²⁺ was present (Fig. 14). In contrast, the stoichiometry associated with the reaction between Fe²⁺ and oxygen generally indicates acid consumption (Ramsden and McKay 1986). Presumably, our observed pH reductions were associated with oxidation of the polymer. This point deserves future investigation.

For the 0-ppm Fe²⁺ 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 about 10% of the original value. Since there was no iron and no polymer degradation associated with these cases, we expected no losses of oxygen due to 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 Fe²⁺ cases in Fig. 12 (i.e., the open triangles), all samples with 50-ppb or less of initial O₂ were completely depleted of dissolved oxygen. Since polymer degradation was insignificant for these cases, we assume that the oxygen losses were due to reaction with Fe²⁺. For samples with more than 50-ppb initial O₂, dissolved oxygen was detected after 11 days of storage. Similarly for the 30-ppm Fe²⁺ cases in Fig. 12 (i.e., the open squares), dissolved oxygen was detected after 11 days in samples with more than 1000-ppb initial O₂. The equilibrium constant for Fe²⁺ reacting with O₂ suggests that no more than one of the species should be present in solution after equilibrium is attained. Consequently, one would expect cases where dissolved oxygen remains in Fig. 12 to be depleted of Fe²⁺. However, if oxygen is stoichiometrically reacted with Fe²⁺ to form Fe₂O₃, 50 ppb of oxygen should only deplete 1% of the original 10-ppm of Fe²⁺. Similarly, 1000 ppb of oxygen should only deplete 8% of the original 30-ppm of Fe²⁺. We wonder if the polymer has an ability to chelate some of the Fe²⁺ and prevent it from reacting with O₂.

Discussion

No Action If Water Contains No Fe²⁺. Recall our original issue at the beginning of this paper: What approach should be taken to minimize oxidative degradation of HPAM polymers in field applications? In this section, we discuss how our results impact 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, Wang *et al.* 2011, Zhu *et al.* 2013, DeLaplace *et al.* 2013), 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. Based on 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 Fe²⁺ 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 of 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 5000 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 1000-ppm Daqing HPAM solution (25.8 cp) that initially contained 3300-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 one day at 45°C, while 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 where polymer was injected with high-dissolved oxygen levels, it seems likely that the injected polymer solutions contained little or no Fe²⁺—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 Fe²⁺ 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 1–2 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 one hour for an HPAM solution that was produced from a well and 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); 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 where 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-ATBS) were insignificant after one week (at either 23°C or 90°C) so long as dissolved oxygen concentration was 200 ppb or below. 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 where 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 once the free oxygen is consumed. The contrary view of Wellington (1983) should be mentioned. Wellington and other 1970-1980s 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 anti-oxidant formulation to neutralize free-radicals and promote polymer stability. This approach has been 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 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, Ryles 1983, Yang and Treiber 1985). 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). Since addition of the stabilizing chemicals adds significantly to costs in a chemical flood, our observation raises the question whether gas-blanketing of tanks and mixing facilities and prevention of oxygen leaks is more cost-effective than use of these chemical stabilizers.

Chemical oxygen scavengers, such as sodium dithionite, have been used to remove oxygen from EOR solutions. If oxygen is reintroduced after application of the sodium dithionite, significant polymer degradation has been observed (Knight 1973, Shupe 1981, Yang and Treiber 1985, Levitt *et al.* 2011a). Levitt *et al.* noted that the presence of bicarbonate can mitigate this degradation. Although 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 ongoing use of chemicals. 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 (Han 2013) 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.* chose to remove the dissolved and particulate iron through precipitation by mixing with air and bleach. Extensive processing of the water through tanks and filtration was required, in addition to the expense of 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), 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.* 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 HPAM or HPAM-ATBS solutions in 2.85%-TDS or 11%-TDS brines:

1. For Fe^{2+} concentrations between 0 and 30 ppm, viscosity losses were insignificant after one week (at either 23°C or 90°C) so long as the initial dissolved oxygen concentration was 200 ppb or below. Above 200-ppb initial dissolved oxygen, significant viscosity losses were seen, especially for storage at 90°C.
2. 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.
3. During our first studies with a 20-cm³ gas cap over 40 cm³ 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 8000-ppb initial dissolved oxygen, the final dissolved oxygen was about 300 ppb after one week of storage at either 23°C or 90°C.
4. 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 1000 ppb or less.
5. For initial oxygen concentrations of 8000 ppb, polymer degradation depended on Fe^{2+} concentration. With no Fe^{2+} present but 8000-ppb initial oxygen, no viscosity losses were noted after one week of storage at 23°C for either polymer. At 23°C with 8000-ppb initial oxygen, viscosity losses after one 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 8000-ppb initial oxygen, viscosities after one 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 8000-ppb initial oxygen, viscosity losses after one week increased with increased iron content—reaching an additional 67% loss for either polymer with 30-ppm Fe^{2+} .
6. When anaerobic or low-oxygen solutions were exposed to atmospheric oxygen, polymer degradation increased substantially with increased Fe^{2+} concentration.
7. 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 both in 2.85%-TDS brine 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.
8. Since 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.
9. 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 so long as the dissolved O_2 concentration was 1000 ppb or less.

Significance of Findings

Consistent with the approach taken during some large-scale polymer floods, 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, our work indicates that short-term (i.e., one week) polymer degradation is minor so long as dissolved oxygen concentration is 200 ppb or below. 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 addition of certain chemicals (e.g., alcohols, thiourea, formaldehyde, sodium borohydride) appear to stabilize polymer solutions in the presence of dissolved iron and oxygen. 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. Since 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 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

- ATBS = 2-acrylamido-tertbutylsulfonic acid
 E_h = oxidation-reduction potential, mV
ppb = parts per billion
ppm = parts per million

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SI Metric Conversion Factors

cp x 1.0* E-03 = Pa·s

ft x 3.048* E-01 = m