

Stability of Partially Hydrolyzed Polyacrylamides at Elevated Temperatures in the Absence of Divalent Cations

Abstract

At elevated temperatures in aqueous solution, partially hydrolyzed polyacrylamides (HPAM) experience hydrolysis of amide side groups. However, in the absence of dissolved oxygen and divalent cations, the polymer backbone can remain stable so that HPAM solutions were projected to maintain at least half their original viscosity for over 8 years at 100°C and about 2 years at 120°C. Within our experimental error, HPAM stability was the same with/without oil (decane). An acrylamide-AMPS copolymer (with 25% AMPS) showed similar stability to that for HPAM. Stability results were similar in brines with 0.3% NaCl, 3% NaCl, or 0.2% NaCl + 0.1% NaHCO₃. At temperatures of 160°C and above, the polymers were more stable in brine with 2% NaCl + 1% NaHCO₃ than in the other brines. Even though no chemical oxygen scavengers or antioxidants were used in our study, we observed the highest level of thermal stability reported to date for these polymers. Our results provide considerable hope for the use of HPAM polymers in enhanced oil recovery at temperatures up to 120°C if contact with dissolved oxygen and divalent cations can be minimized.

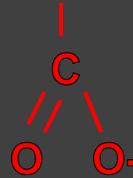
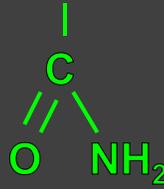
Calculations performed considering oxygen reaction with oil and pyrite revealed that dissolved oxygen will be removed quickly from injected waters and will not propagate very far into porous reservoir rock. These findings have two positive implications with respect to polymer floods in high-temperature reservoirs. First, dissolved oxygen that entered the reservoir prior to polymer injection will have been consumed and will not aggravate polymer degradation. Second, if an oxygen leak (in the surface facilities or piping) develops during the course of polymer injection, that oxygen will not compromise the stability of the polymer that was injected before the leak developed or the polymer that is injected after the leak is fixed. Of course, the polymer that is injected while the leak is active will be susceptible to oxidative degradation. Maintaining dissolved oxygen at undetectable levels is necessary to maximize polymer stability. This can readily be accomplished without the use of chemical oxygen scavengers or antioxidants.

Introduction

In chemical flooding applications for enhanced oil recovery, polymers are needed to provide effective sweep efficiency and mobility control. Depending on injection rates, formation permeability, and well spacing, the polymers must be stable for many years at reservoir conditions. Two chemical species are known to critically impact stability for partially hydrolyzed polyacrylamides (HPAM): divalent cations and oxygen.

Effect of Divalent Cations. HPAM polymers are known to be unstable at elevated temperatures if divalent cations are present (Davison and Mentzer 1982, Zaitoun and Potie 1983, Moradi-Araghi and Doe 1987, Ryles 1988). For temperatures above 60°C, acrylamide groups within the HPAM polymer experience hydrolysis to form acrylate groups. If significant concentrations of divalent cations (especially Ca²⁺) are present, HPAM polymers can precipitate if the fraction of acrylate groups (i.e., the degree of hydrolysis) in the polymer becomes too high. These facts limit the utility of HPAM polymers for many potential EOR applications in warmer reservoirs. Moradi-Araghi and Doe (1987) indicated hardness limits in brines for various temperatures: 2,000 mg/L for 75°C, 500 mg/L for 88°C, and 270 mg/L for 96°C. For brines containing less than 20 mg/L divalent cations, they suggest that polymer hydrolysis and precipitation will not be a problem for temperatures of 204°C or greater. A few reservoirs exist that have low-cation resident formation brines that still allow the use of HPAM polymers, even though the reservoir temperature is relatively high (Tielong et al. 1998, Santoso et al. 2003).

What is the upper temperature limit for HPAM use in chemical EOR?



- Above 60°C, acrylamide groups hydrolyze to form acrylate groups.
- If the degree of hydrolysis is too high and too much Ca²⁺ or Mg²⁺ is present, HPAM polymers precipitate.

Temperature, °C:	75	88	96	204
Max Ca ²⁺ + Mg ²⁺ , mg/L:	2000	500	270	20

(from Moradi-Araghi and Doe, 1987)

This precipitation problem can be overcome by copolymerizing acrylamide with monomer groups (such as AMPS or vinylpyrrolidone) that resist hydrolysis (Doe et al. 1987, Moradi-Araghi et al. 1987). These polymers have significantly improved resistance to precipitation; however, they are noticeably more expensive and less efficient viscosifiers than HPAM.

Maitin (1992) and Sohn et al. (1990) proposed a concept that could considerably widen the applicability of HPAM polymers. They described polymer floods in the German Oerrel and Hankensbuettel fields that had resident brine salinities around 17% total dissolved solids (TDS). Because HPAM is not an efficient viscosifier in saline brines, polymer solutions were prepared and injected in fresh water. Conventional wisdom at the time argued that this process would not be effective because the saline formation water would mix with the low-salinity polymer solution, substantially decrease its viscosity, and compromise sweep. However, Maitin demonstrated that if the mobility of the injected polymer formulation was low enough, the fresh water polymer bank could maintain its integrity during displacement of oil in a reservoir with saline brine.

In concept, this idea could be extended to application of HPAM solutions in hot reservoirs with saline, high-hardness brines. If the mobility of a low-hardness HPAM solution is sufficiently low, the polymer bank will displace oil and brine ahead of it with minimum mixing. Even though the HPAM in the polymer bank may experience hydrolysis with time, it will remain an effective viscosifier because there are insufficient divalent cations present to precipitate the polymer.

Depending on circumstances, ion exchange from clays could allow dissolution of significant concentrations of divalent cations (Pope et al. 1978, Lake 1989). To avoid HPAM precipitation, the release of divalent cations from clays must be understood and controlled. Understanding divalent cation release requires characterization of the type, quantity, and current divalent-cation loading of clays present and the influence of polymer adsorption on the clays. Controlling the release of divalent cations may be accomplished by maintaining a fixed ratio of monovalent to divalent cations in the injection water (Lake 1989), which would require injection of low salinity water to keep the divalent cation concentration low (e.g., below 20 ppm). Other concepts that have been considered include (1) preconditioning the clays using a preflush and (2) polymer adsorption onto clays to slow cation release.

Approaches to mitigating HPAM precipitation:

1. A few hot reservoirs exist with low hardness waters.
2. Hydrolysis-resistant monomers (AMPS, NVP) can be incorporated into PAM polymers (Moradi-Araghi, Doe 1987). They tend to be expensive and less effective as viscosifiers.
3. Fresh water HPAM solutions can provide efficient sweep with minimum mixing with saline brines if polymer mobility is sufficiently low (Maitin 1992). Requires that cation exchange be understood and controlled.

Effect of Dissolved Oxygen. The presence of dissolved oxygen by itself may not be detrimental to the stability of HPAM polymers (Knight 1973, Muller 1981). However, HPAM polymers can experience severe degradation by free radical attack if oxygen combines with metals (especially ferrous iron), residual initiators (remaining from polymerization), or other free radical generating chemicals (Knight 1973, Shupe 1981, Muller 1981, Yang and Treiber 1985). Fortunately, most reservoirs have a reducing environment, and produced waters typically contain no detectable dissolved oxygen. With good management of surface facilities (inert gas blanketing, minimizing leaks, and gas stripping where necessary), recycled produced water can be used to prepare EOR solutions that are oxygen free. If necessary, chemical oxygen scavengers and antioxidants can be used (Shupe 1981, Wellington 1983, Yang and Treiber 1985, Levitt and Pope 2008). However, use of these chemicals (1) are generally less cost-effective than gas stripping for oxygen removal, (2) can accelerate polymer degradation if oxygen is reintroduced after addition of the oxygen scavenger, and (3) can accentuate problems with microbial growth.

Past studies have examined HPAM stability in “oxygen free” solutions to 105°C. Shupe (1981) reported a 13% loss of viscosity at 105°C (from 38 to 33 cp) over ~250 days for 2,000 mg/L HPAM (Dow Pusher 500™) in brine with 3,841 mg/L TDS salinity, including 10 mg/L divalent cations. Ryles (1988) reported a 12% loss of viscosity at 90°C (from 11.7 to 10.3 cp) over ~580 days for 1,000 mg/L HPAM in brine with 1% NaCl and 0.4% sodium orthosilicate.

If divalent cations are not a problem, what is the upper temperature limit for HPAM use in EOR?

- Maximizing polymer stability requires minimizing oxygen contact.
- Most reservoirs produce water with no detectable dissolved oxygen.
- Oxygen-free EOR solutions can readily be prepared **in the field** by (1) preventing leaks, (2) gas blanketing tanks and mixing facilities, (3) gas stripping if necessary, (4) adding chemical oxygen scavengers if necessary.

Lab record to date: Shupe (1981) reported a 13% viscosity loss after 250 days at 105°C when a chemical oxygen scavenger was used.

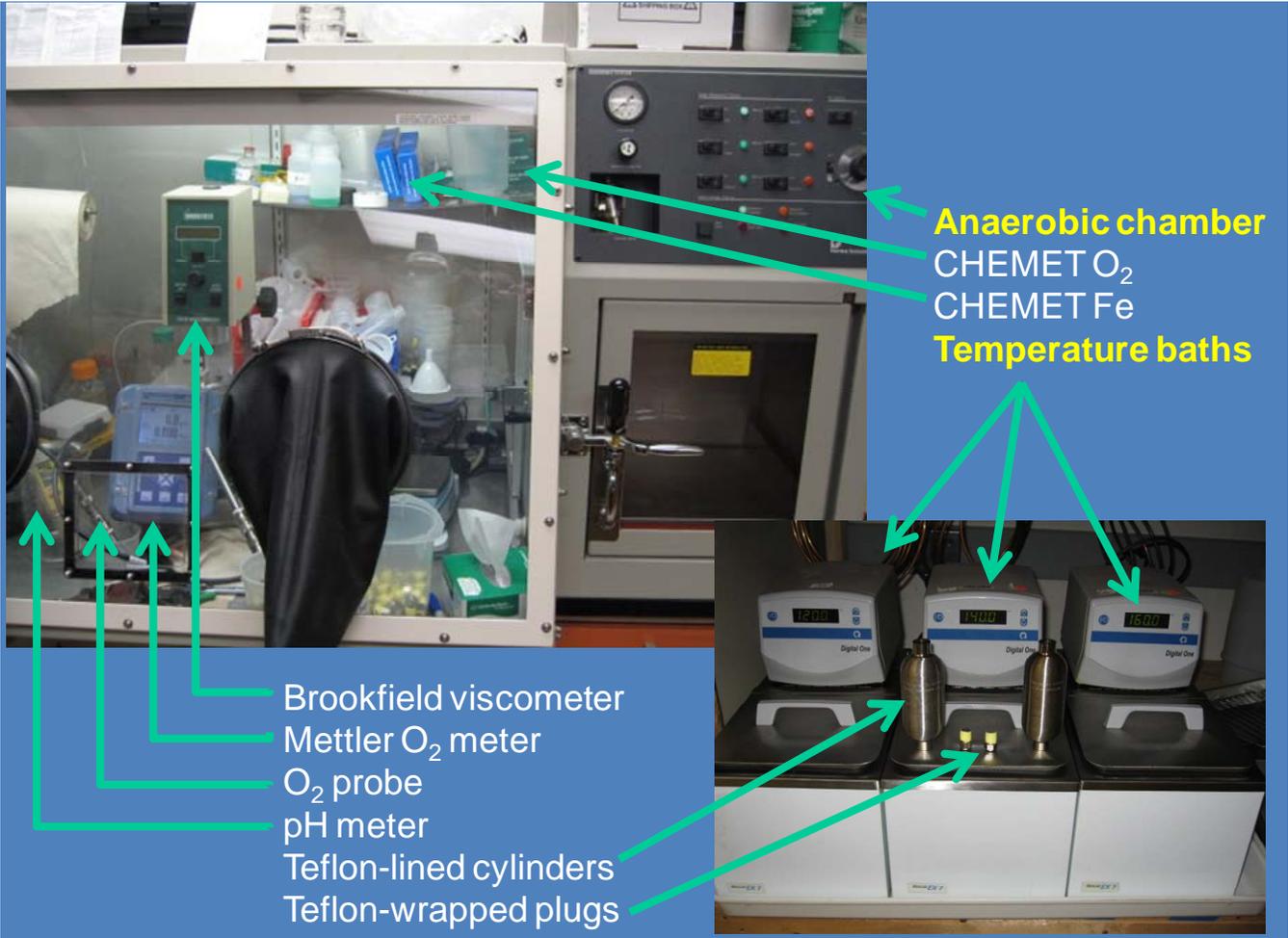
Report Objectives. In this report, we explore the temperature limits of stability to 180°C for HPAM polymer solutions if divalent cations and dissolved oxygen are not present. In general, we examine stability for HPAM solutions at higher temperatures than previous investigators. We also compare stability results for HPAM with those for a copolymer of acrylamide and 2-acrylamido-2-methylpropane sulphonic acid (PAM-AMPS). We are particularly interested in determining polymer stability without using chemical oxygen scavengers and antioxidants. We first describe an effective method to prepare, store, and study polymer solutions that contain less than 0.1 parts per billion (ppb or µg/L) dissolved oxygen. Next, we report stability results for solutions of HPAM and PAM-AMPS and in four brines using various temperatures. We also consider the extent of oxygen transport through a reservoir if the injected water contains dissolved oxygen.

Experimental Method

Polymer samples were prepared and viscosities, pH values, and dissolved oxygen levels were measured inside an anaerobic chamber (Forma Scientific Model 1025™). This unit 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. Oxygen measurements were made with a Mettler Toledo Model M700X™ meter that was equipped with two O₂ 4700i(X) Traces™ modules and two InPro 6950™ O₂ sensors. This meter was sensitive to 0.1 ppb oxygen in 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 that were prepared in the anaerobic chamber typically contained 0.0 ppb dissolved oxygen (i.e., less than 100 parts per trillion). Our oxygen measurements were significantly more accurate than those reported by previous researchers, who used a colorimetric metric method (CHEMET™) with a limit of oxygen detection between 1 and 5 ppb in aqueous solution (Yang and Treiber 1985, Seright and Henrici 1990).

Preparing, Storing, and Studying O₂-Free Polymer Solutions in the Laboratory. Our Method:

- Prepare solutions in an anaerobic chamber with 10% H₂ + 90% N₂ circulated through Pd catalyst.
- O₂ levels measured to <0.001% in the chamber atmosphere and to <0.1 ppb in solution.
- Brine reduced to <0.1 ppb O₂ by bubbling chamber gas into the brine (requires ~ 1 hour).
- Polymer stored and mixed in the chamber.
- Solutions sealed in 150 ml teflon-lined cylinders.
- Solutions stored in 120°C-180°C baths outside the anaerobic chamber.
- Viscosity at 7.3 s⁻¹, O₂, and pH measured inside the anaerobic chamber (at 25°C).



New Features of Our Method:

- Uses a new oxygen meter that measures to 0.1 parts per billion (ppb) in solution.
- Confirmed that our solutions were prepared with <0.1 ppb O_2 and maintained at this level throughout the study.
- No need for chemical oxygen scavengers.

Advantage of our method over previous methods:

- Measure viscosity, dissolved O_2 , and pH on the SAME sample throughout the study.

Disadvantage:

- If the storage cylinder leaks, the sample is lost.

Our work focused on two polymers. The first was SNF Flopaam 3830S™, Lot R 2279. The manufacturer estimated the polymer molecular weight was 18-20 million daltons and the degree of hydrolysis was about 40%. The second polymer was SNF AN125 VHM™, Lot UB 5069. This acrylamide-AMPS copolymer had a molecular weight of 6-8 million daltons and contained 25% AMPS.

Four brines were used, containing: (1) 0.3% NaCl, (2) 3% NaCl, (3) 0.2% NaCl + 0.1% NaHCO₃, and (4) 2% NaCl + 1% NaHCO₃. Brines were mixed and filtered through 0.45 μm Millipore filters outside the anaerobic chamber. Then the brine was moved into the chamber, and a pump was used to bubble anaerobic gas through the brine. Less than 1 hour was required to drive the dissolved oxygen content below 0.1 ppb. A vortex was formed using a magnetic stirrer and powder-form polymer was added in the traditional manner and then mixed overnight at low speed. (Powder-form polymers were stored inside the anaerobic chamber.) Polymer solution viscosities were measured inside the anaerobic chamber at 7.3 s⁻¹ and room temperature using a Brookfield Model DV-E™ viscometer equipped with a UL adapter. After preparation, 70 cm³ of polymer solution were placed in a 150-cm³ Teflon-coated stainless steel cylinder and sealed shut with stainless steel plugs with blemish-free threads that were wrapped with yellow 3.5 mil gas-line Teflon tape. (Normal white Teflon tape was inadequate.) In some cases (with HPAM to be stored at 160°C and 180°C), 30 cm³ of decane were added to the sample. Then the cylinders were removed from the anaerobic chamber and placed in silicone oil baths (Thermo Neslab EX7™) for various times at different temperatures ranging from 120°C to 180°C. When a viscosity measurement was to be made, the cylinder was removed from the silicone bath, cooled rapidly in an ice bath, and then brought into the anaerobic chamber for viscosity, oxygen, and pH measurements at room temperature. After the measurements, the sample was returned to the same cylinder, resealed, removed from the anaerobic chamber, and returned to the appropriate silicone bath. An advantage of this method over previous flame-sealed glass-ampoule methods is that all measurements over time were made on the same polymer solution sample. Also, pH and dissolved oxygen measurements could readily be made on these samples. A disadvantage is that if the seal is compromised for our sample cylinders, the entire sample is lost. Fortunately, we have perfected the technique so that no samples were lost over the course of the past year.

Results

Viscosity values versus time and temperature are plotted in **Fig. 1** for one of the data sets. (Values for other experiments can be found in Seright et al. 2009.) From regressions of $\ln(\text{specific viscosity})$ versus time (**Fig. 2**), we determined viscosity decay constants (main values listed in **Table 1**) and correlation coefficients (values in parentheses in **Table 1**). Specific viscosity is (polymer solution viscosity minus solvent viscosity) divided by solvent viscosity. Viscosity decay constant is the time (as estimated by the regression) for the specific viscosity to fall to $1/e$ (i.e., 0.368) times the zero-time specific viscosity

(which also is estimated by the regression). (The zero-time specific viscosity was usually greater than the original specific viscosity because amide hydrolysis occurred during the first 1-3 days of exposure to high temperature.)

TABLE 1—VISCOSITY DECAY CONSTANTS (CORRELATION COEFFICIENTS) FOR POLYMER SOLUTIONS, DAYS						
Polymer	Brine	120°C	140°C	160°C	160°C with oil	180°C with oil
HPAM	0.3% NaCl	783 (-0.880)	149 (-0.989)	61(-0.938)	41 (-0.976)	13 (-0.887)
	0.2% NaCl, 0.1% NaHCO ₃	869 (-0.862)	205 (-0.988)	73 (-0.969)	76 (-0.974)	35 (-0.873)
	3% NaCl	749 (-0.884)	377 (-0.943)	127 (-0.966)	46 (-0.965)	15 (-0.865)
	2% NaCl, 1% NaHCO ₃	472 (-0.915)	445 (-0.930)	155 (-0.982)	193 (-0.995)	71 (-0.946)
PAM-AMPS	0.3% NaCl	1590 (-0.693)	327 (-0.977)	71 (-0.973)		
	0.2% NaCl, 0.1% NaHCO ₃	1090 (-0.765)	662 (-0.935)	147 (-0.992)		
	3% NaCl	504 (-0.784)	388 (-0.891)	77 (-0.958)		
	2% NaCl, 1% NaHCO ₃	613 (-0.937)	473 (-0.856)	165 (-0.976)		

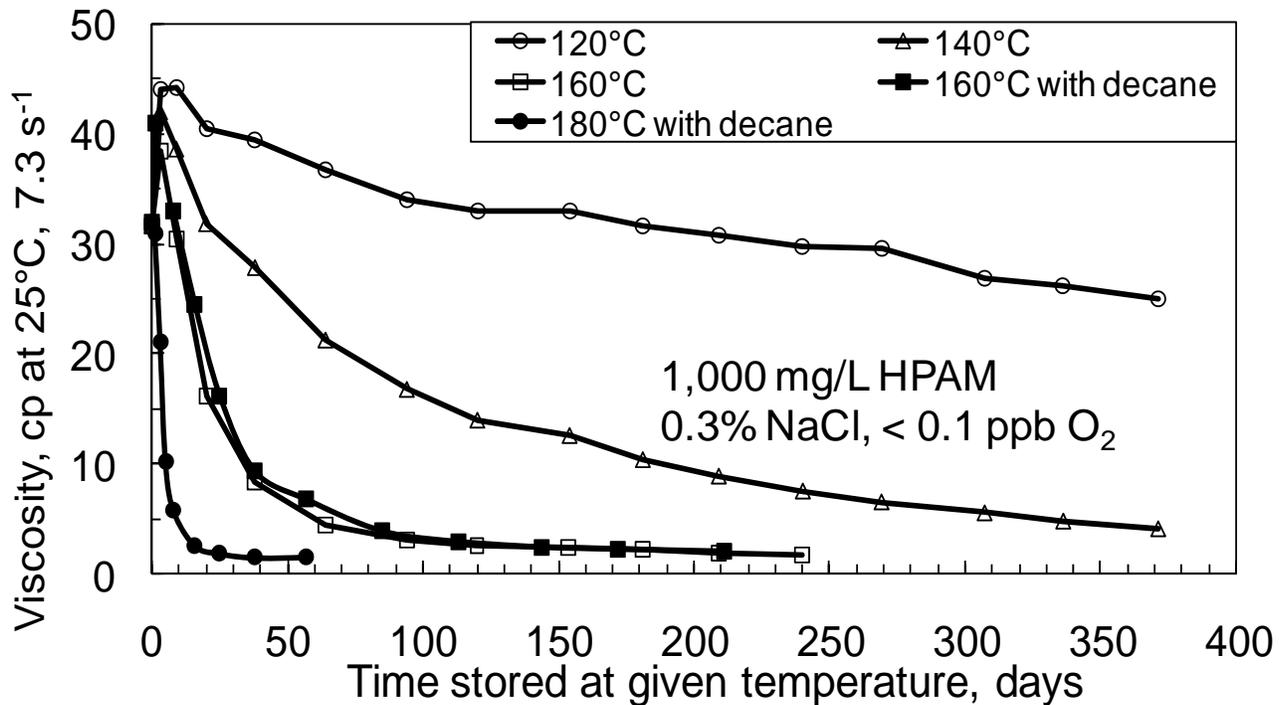
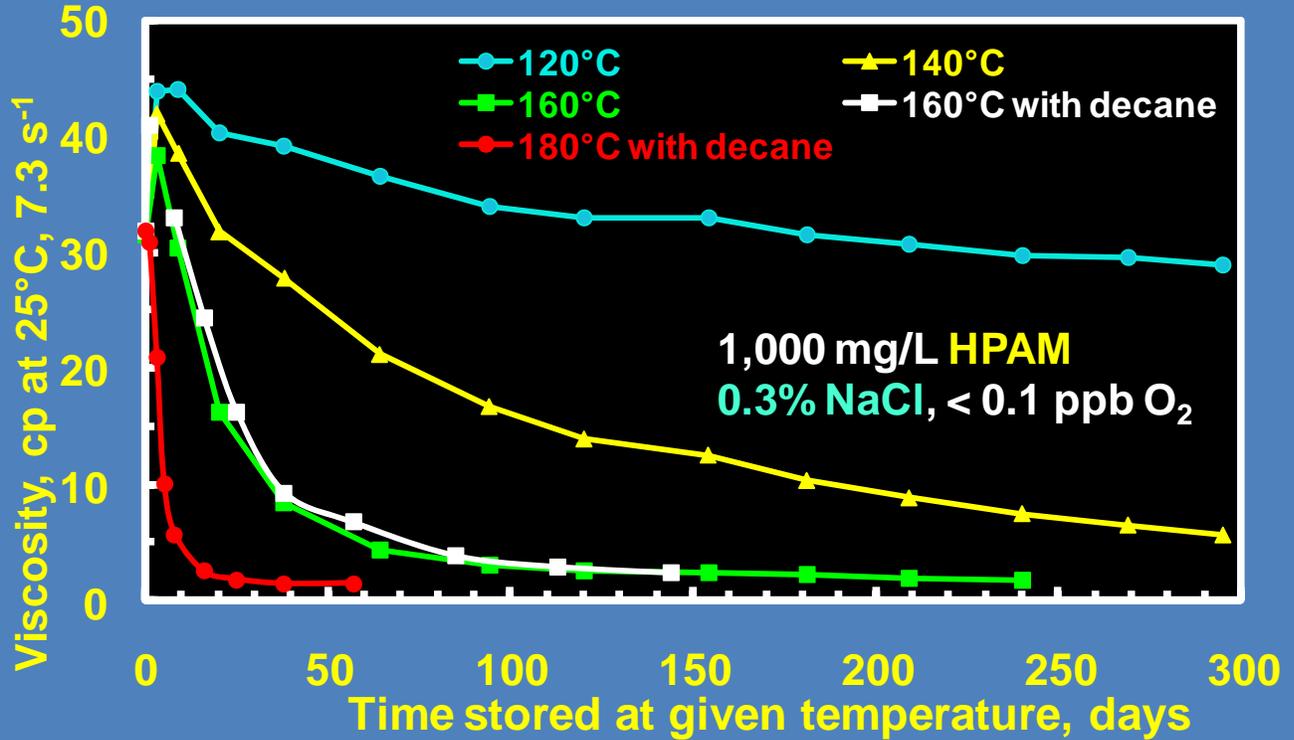


Fig. 1—Stability for HPAM in 0.3% NaCl. Viscosity versus time.

Time/Temperature Behavior of Polymer Stability

- Stability must be studied **EITHER** at reservoir temperature for **MANY** years **OR** at **several** temperatures and use an Arrhenius analysis.



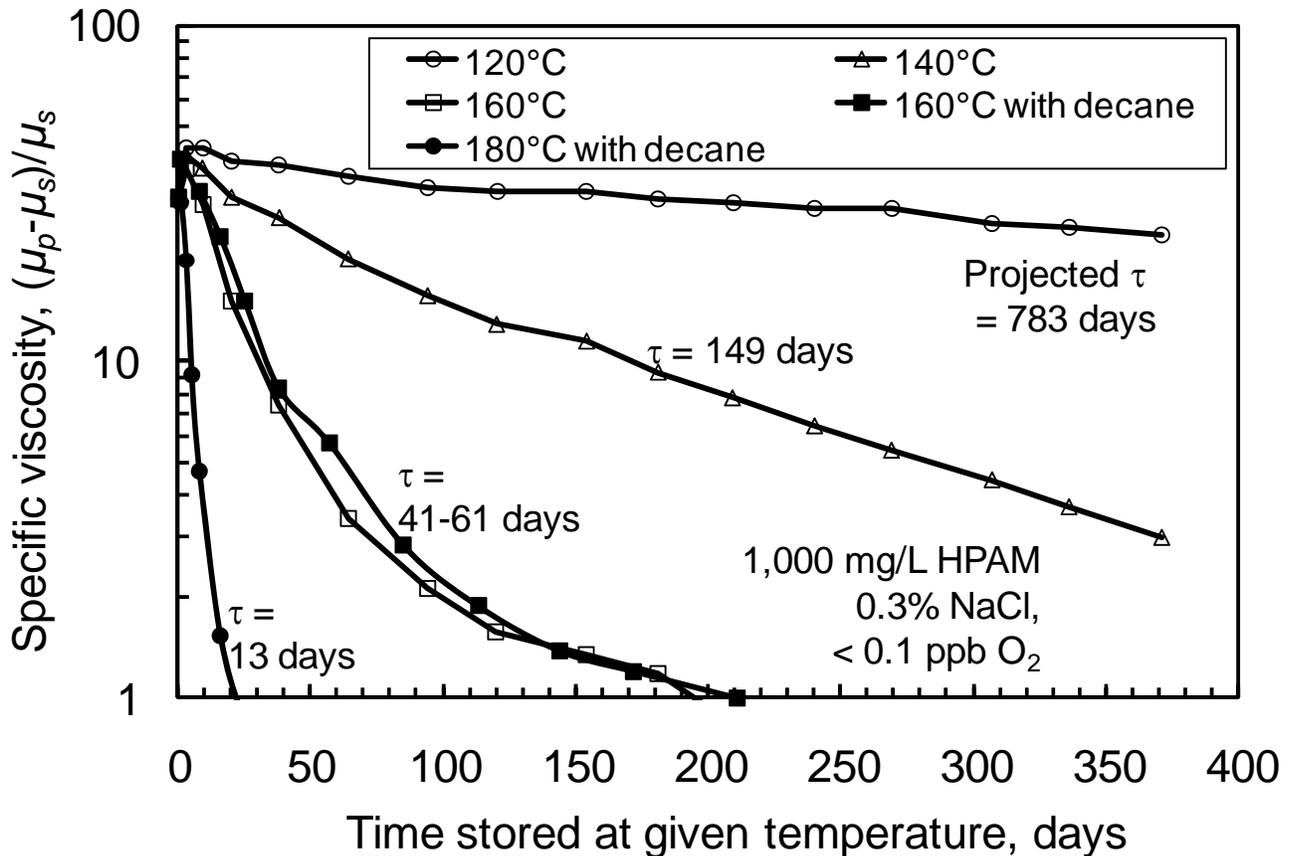


Fig. 2—Stability for HPAM in 0.3% NaCl. \ln (specific viscosity) versus time.

Hydrolysis

Evidence of amide hydrolysis can be seen in most of our data sets. When neutral amide groups hydrolyzed to become negatively charged acrylate groups, the increased charge density along the HPAM backbone extended the polymer coil somewhat and increased solution viscosity. This effect was most evident in low salinity brines. For example, after three days at 120°C in 0.3% NaCl, HPAM solution viscosity increased from 31.6 to 44 cp, and PAM-AMPS solution viscosity increased from 25.7 to 33.7 cp. In more saline solutions, the viscosity increase was often less dramatic because charges on the polymer were screened by the salts. For example, after three days at 120°C in 3% NaCl, HPAM solution viscosity only increased from 39.3 to 39.4 cp. After three days at 120°C or hotter, the viscosities either held steady or began to decrease, suggesting that the hydrolysis reaction was nearly complete. This behavior is consistent with previous literature reports (Davison and Mentzer 1982, Moradi-Araghi and Doe 1987, Ryles 1988).

Although a small amount of ammonium was generated during the hydrolysis reaction, pH changes were minor during the course of our studies. The initial pH ranged from 6.9 to 7.3 for the polymer solutions prepared in brines with 0.3% NaCl or 3% NaCl. Within 10 days of storage at elevated temperatures, most of these solutions experienced a pH increase to about 7.6. Subsequent pH values remained stable. For the polymer solutions prepared in brines with NaHCO_3 , the initial pH ranged from 8.3 to 8.6. These solutions experienced no significant pH changes as a result of storage at elevated temperatures.

Stability Observations with < 0.1 ppb Dissolved Oxygen

Depending on salinity, our projected decay constants at 120°C ranged from 472 to 869 days for HPAM and from 504 to 1,590 days for PAM-AMPS (first data column of Table 1). We note that our correlation coefficients (first column of parentheses data in Table 1) were not as high as we would like—because the degradation process was not far along after 371 days at 120°C. At present, we can't conclude that the stability at 120°C depends on salinity (between 0.3% and 3% NaCl), NaHCO_3 content (0%, 0.1%, or 1%), or whether the polymer is HPAM or PAM/AMPS. Considering the uncertainty in the regressions, our current best guess is that the viscosity decay constant is around two years at 120°C.

Our regressions had stronger correlations for the higher temperatures. At 140°C, all correlation coefficients for the HPAM solutions were better than -0.93 and for the PAM-AMPS solutions were between -0.85 and -0.98 (second data column of Table 1). Just as at 120°C, the data to date at 140°C do not definitively allow us to conclude that stability depends on salinity (between 0.3% and 3% NaCl), NaHCO_3 content (0%, 0.1%, or 1%), or whether the polymer is HPAM or PAM/AMPS. The viscosity decay constants at 140°C averaged about one year.

At 160°C, all correlation coefficients for the HPAM solutions were better than -0.93 (third and fourth data columns of

Table 1). Table 1 indicates significantly improved HPAM stability when 1% NaHCO₃ was present. The overall salinity (from 0.3% to 3% TDS), the presence of oil (decane), or the type of polymer (HPAM versus PAM-AMPS) did not definitively affect stability. The viscosity decay constants at 160°C were 1.5 to 4 months without carbonate and 5 to 7 months with 1% NaHCO₃.

At 180°C in the presence of decane (last column of Table 1), the HPAM viscosity decay constants were about 2 weeks without carbonate, 5 weeks with 0.1% NaHCO₃, and 10 weeks with 1% NaHCO₃.

Our polymer solutions were maintained in a reducing environment for the duration of our study. Specifically, the oxidation reduction potential for freshly prepared solutions was about -500 mV, and after 336 days of storage at various temperatures, the oxidation reduction potential was still around -500 mV for all solutions, regardless of the level of degradation experienced by the polymer. This fact may ultimately be of use in judging the mechanism of degradation for HPAM solutions in an oxygen-free environment.

Arrhenius Analysis

As expected, polymer stability decreased with increased temperature (*T*). This information can be used to perform an Arrhenius analysis and estimate activation energies (*E_a*) that allow prediction of polymer stabilities at other temperatures. Eq. 1 shows a form of the Arrhenius equation.

$$E_a = R d[\ln (1/\tau)]/d(1/T) \dots \dots \dots (1)$$

Fig. 3 provides Arrhenius plots for our HPAM viscosity decay constants (τ) from Table 1 (reciprocal decay constant versus reciprocal of absolute temperature). A regression on the data with 1% NaHCO₃ (solid squares in Fig. 3) yielded an activation energy (*E_a*) of 48.8 kJ/mol, with a correlation coefficient (*R_c*) of -0.940. A regression on the remaining data (open symbols, with 0.1% or less NaHCO₃) in Fig. 3 yielded an activation energy of 91.8 kJ/mol, with a correlation coefficient of -0.963.

Fig. 4 provides Arrhenius plots for our PAM-AMPS viscosity decay constants from Table 1. A regression on the data with 1% NaHCO₃ (solid squares in Fig. 4) yielded an activation energy of 45.9 kJ/mol, with a correlation coefficient of -0.935. A regression on the remaining data (open symbols, with 0.1% or less NaHCO₃) in Fig. 4 yielded an activation energy of 81.9 kJ/mol, with a correlation coefficient of -0.911.

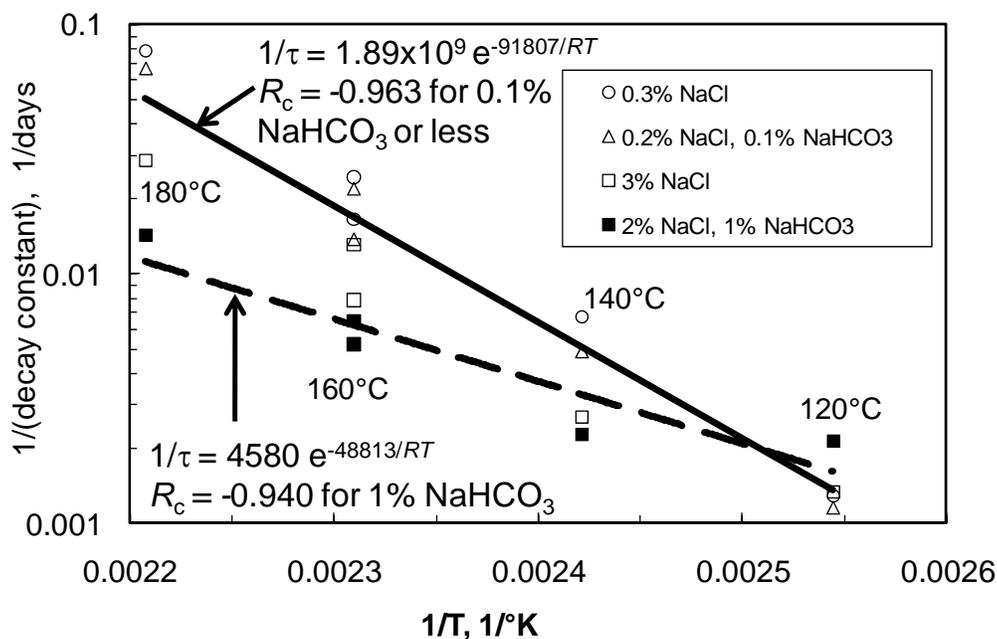


Fig. 3—HPAM Arrhenius plots, < 0.1 ppb dissolved oxygen, no divalent cations.

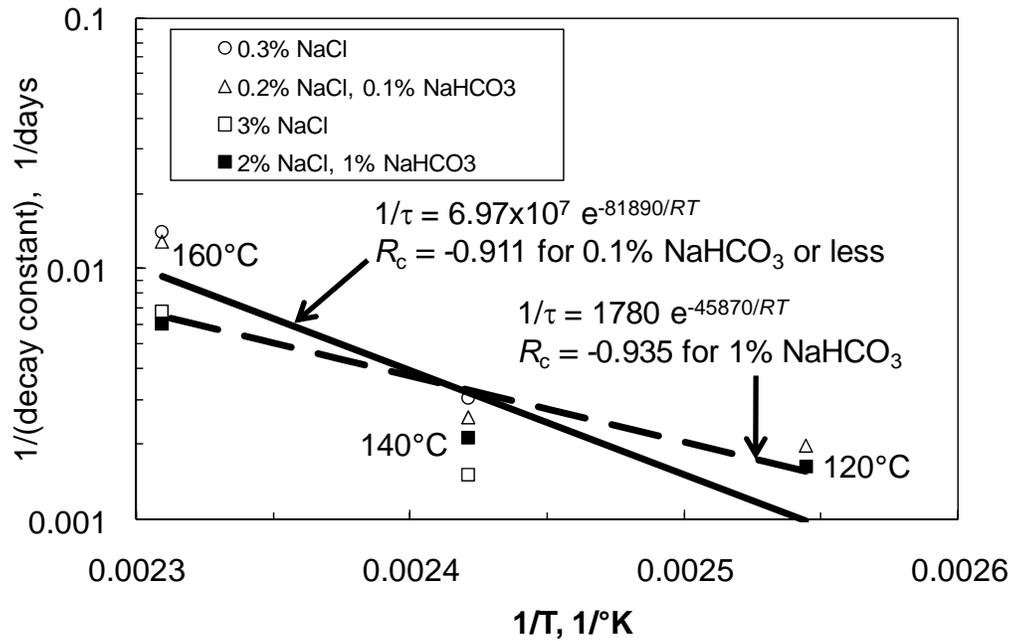


Fig. 4—PAM-AMPS Arrhenius plots, < 0.1 ppb dissolved oxygen, no divalent cations.

Low Carbonate Brines. For three of the brines (0.3% NaCl, 3% NaCl, and 0.2% NaCl + 0.1% NaHCO₃), the temperature and viscosity decay behavior for HPAM was statistically no different than for PAM-AMPS. Eq. 2 shows the regression equation where all viscosity decay constants for both polymers were included in the regression (Data Rows 1-3 and 5-7 in Table 1), except those for the 1% NaHCO₃ brine. The correlation coefficient was -0.945. The parameters and correlation coefficients for regressions associated with the solid-line relations in Figs. 3 and 4 and the combined data (Eq. 2) were sufficiently similar that use of Eq. 2 is justified.

$$1/\tau = 2.47 \times 10^9 e^{-93300/RT} \dots\dots\dots(2)$$

The Arrhenius analysis can be used to estimate polymer solution viscosity and stability as a function of temperature and time. **Fig. 5** (the solid curve) projects viscosity decay constants for oxygen-free HPAM and PAM-AMPS solutions with 0.1% or less NaHCO₃, based on Eq. 2.

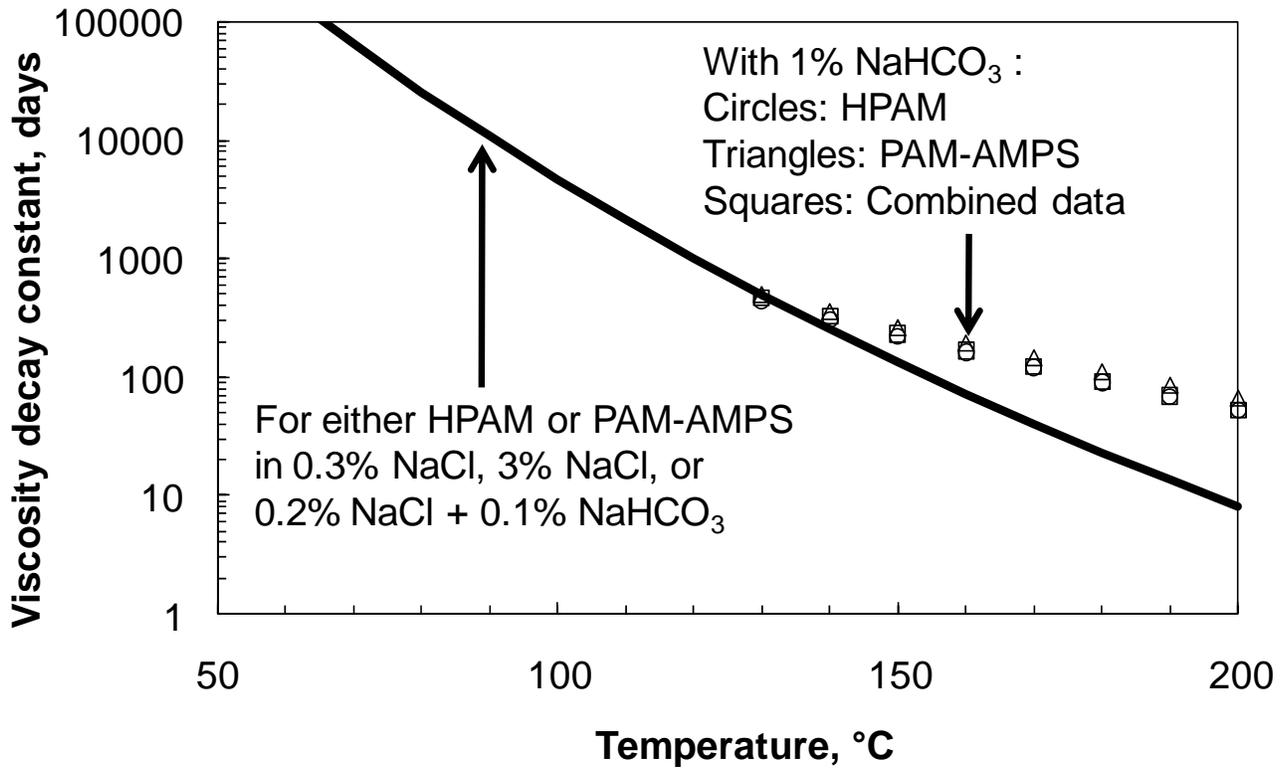


Fig. 5—Projected stabilities, < 0.1 ppb dissolved oxygen, no divalent cations.

Eq. 2 can be coupled with Eq. 3 to allow projection of individual viscosity levels (μ/μ_o) as a function of time (t) and temperature.

$$\mu/\mu_o = e^{-t/\tau} \dots\dots\dots(3)$$

For example, these equations predict that for an HPAM solution in 0.3% NaCl brine, the time to reach a viscosity level 50% of the starting value would be about 3,240 days (8.9 years) at 100°C and about 2 years at 120°C. These results provide hope that HPAM solutions could have sufficient stability for applications in many high-temperature chemical floods if dissolved oxygen is eliminated and contact with divalent cations are avoided.

In the most positive HPAM stability results to date, Shupe (1981) reported a 13% loss of viscosity at 105°C (from 38 to 33 cp) over ~250 days for 2,000 mg/L HPAM in brine with 3,841 mg/L TDS salinity (after using a chemical oxygen scavenger to remove dissolved oxygen). For comparison, our results (Eqs. 2 and 3) predict an 11% loss of HPAM viscosity after 250 days at 105°C, without the use of any oxygen scavenger or antioxidant package. In another example, Ryles (1988) reported a 12% loss of viscosity at 90°C (from 11.7 to 10.3 cp) over ~580 days for 1,000 mg/L HPAM. Our results predict an 8% loss of HPAM viscosity after 580 days at 90°C.

Brine with 1%NaHCO₃. For the brine with 1% NaHCO₃, regression of viscosity decay constants associated with both polymers (last rows in Table 1) yield Eq. 4, with a correlation coefficient of -0.940.

$$1/\tau = 4580 e^{-48800/RT} \dots\dots\dots(4)$$

In 1% NaHCO₃, the regressions for HPAM data only, PAM-AMPS data only, and the combined data predicted noticeably different results for temperatures below 140°C. However, above 140°C, the predictions from the regressions were quite similar (symbols in Fig. 5). Consequently, use of Eq. 4 should be confined to temperatures of 140°C and above when 1% NaHCO₃ is present.

Effect of Dissolved Oxygen, Metals, and Free-Radical Generators.

Our work indicates that HPAM polymer solutions can maintain high viscosities for considerable periods at elevated temperatures if dissolved oxygen is excluded. Results from Shupe (1981), Muller (1981), and Yang and Treiber (1985) support this view even if iron, other metals, or free-radical generators are present. In contrast, in the presence of dissolved oxygen and certain chemicals, HPAM degradation can be rapid and severe. Shupe (1981) reported viscosity losses from 60% to 80% in 20 minutes at 86°C for an HPAM solution with 500 mg/L of sodium hydrosulfite or potassium persulfate. Shupe

also found that in the presence of oxygen, only 60 mg/L of any of five free radical scavengers led to rapid HPAM degradation at 80-86°C, because these materials promoted hydroperoxide free radicals upon reaction with oxygen. Further, he reported a 55% viscosity loss within 1-2 minutes after adding 10 mg/L Fe²⁺ (ferrous iron, pH 8) at room temperature, after exposure to atmospheric oxygen. Yang and Treiber (1985) demonstrated that once the free oxygen is consumed, oxidative degradation of HPAM stops. Fe³⁺ may crosslink HPAM to form a gel, but it does not induce polymer degradation unless a redox couple is formed (Ramsen and McKay 1986).

Anticipated O₂ Transport through a Reservoir

Will significant HPAM degradation occur if some oxygen is introduced, e.g., from leakage before injection? How long will it take for the reducing environment of the reservoir to scavenge that oxygen? Will the polymer degrade before the oxygen is removed? As a solution propagates through a reservoir, compositional changes can occur through convective mixing, partitioning, retention or reaction, mineral dissolution, and ion exchange.

Partitioning. The solubility of oxygen in oil is roughly 5 times greater than that in water (Kubie 1927). If an aqueous solution that contains some oxygen is injected into a reservoir, oxygen will partition from the water phase into the oil phase. This process will substantially retard the movement of the oxygen front by the factor in Eq. 5, where R_p is the oil/water partition coefficient (5 in this case), and S_{or} is the residual oil saturation.

$$1 / [1 + R_p S_{or} / (1 - S_{or})] \dots \dots \dots (5)$$

For example, assume that the residual oil saturation is 30%. For R_p=5, partitioning will reduce the rate of oxygen propagation by a factor of 0.318.

Reaction with Oil. Of course, oxygen can react with oil. Prats (1982) summarized kinetic parameters for oxidation of crudes from a dozen sets of measurements at temperatures between 60°C and 232°C. Rates of oxygen consumption (dm_{O2}/dt, in lbm per second) predicted based on these parameters have a significant variation. However, Eq. 6 provides the median prediction.

$$- dm_{O_2}/dt = m_o (p_{O_2})^{0.6} 1200 e^{-8504/T} \dots \dots \dots (6)$$

In this equation, m_o is the mass of oil per unit of bulk reservoir volume, p_{O2} is the partial pressure of oxygen in atm, and T is temperature in °K. Based on Eq. 6 (and assuming isothermal conditions), Fig. 6 plots the predicted radius at which dissolved oxygen will be totally consumed by reaction with oil [for the specific case of injecting water at 1,000 BWPD per ft of net pay, S_{or}=0.3, and porosity (φ) is 0.3]. Three initial levels of dissolved oxygen in the injection water are considered, ranging from 5 to 5,000 ppb. For the same conditions, Fig. 7 plots the time required for oxygen to be consumed by the oil. Depending on temperature and initial oxygen content, Figs. 6 and 7 suggest that dissolved oxygen may exist in the reservoir for sometime between several hours and many weeks.

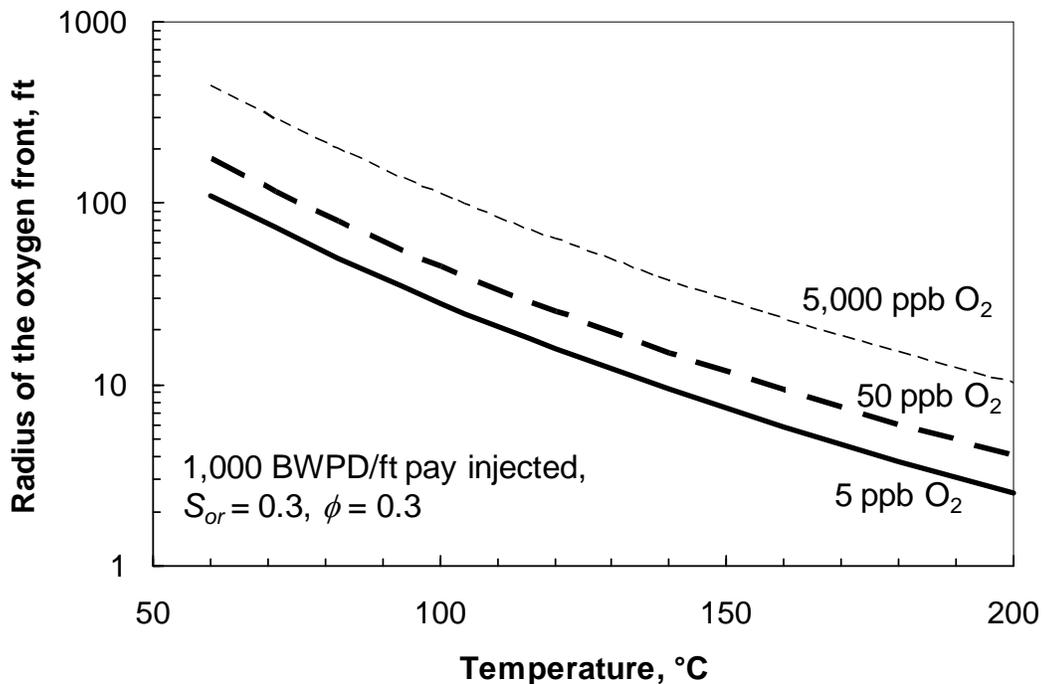


Fig. 6—Predicted radius at which dissolved oxygen will be totally consumed by reaction with oil.

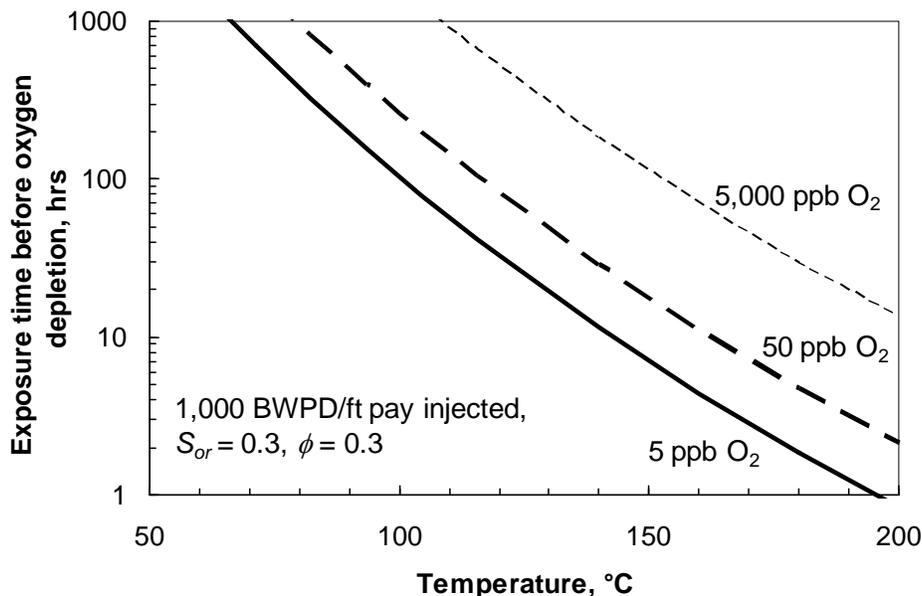


Fig. 7—Predicted time at which dissolved oxygen will be totally consumed by reaction with oil.

Oxygen Removal by Reaction with Minerals. Sedimentary rocks contain a variety of redox sensitive materials that can influence levels of dissolved oxygen and potentially release cations upon dissolution. The most important materials in the present case (i.e., overall reducing conditions into which oxygenated waters are introduced) are pyrite (FeS_2), siderite (FeCO_3), and sedimentary organic matter (e.g., Xu et al. 2000, Hartog et al. 2002, Prommer and Stuyfzand 2005). These materials are commonly present in at least minor amounts in clastic and carbonate reservoir rocks (Johnson-Ibach 1982, Antonio et al. 2000), with the pyrite and siderite largely the result of post-depositional (diagenetic) precipitation (Bathurst 1975, Pettijohn et al. 1987), and the organic matter deposited along with the sediments in the depositional environment. Pyrite and siderite require reducing conditions to form, as the iron is present as Fe^{2+} , and frequently occur together along with relatively high levels of organic matter. Because pyrite and siderite precipitate from solution, they are most commonly present along grain boundaries, and thus are in direct contact with pore fluids rather than isolated in grain interiors.

Pyrite, siderite, and organic matter can in some circumstances dramatically lower levels of dissolved oxygen in aquifers and petroleum reservoirs. Hartog et al. (2002) examined sediments from an aquifer currently under reducing conditions and measured the reactivity of oxygen reducing components in the sediment. They conducted sediment incubations lasting 54 days and observed simultaneous oxidation of pyrite, siderite, and organic matter and measured reduction capacities ranging from 8 to 84 $\mu\text{mol O}_2/\text{g}$. Reactive-transport modeling and on-site measurements further demonstrate the ability of pyrite to rapidly lower (i.e., in a matter of days) dissolved oxygen levels in sediment into which oxygenated water has been introduced (Xu et al., 2000; Prommer and Stuyfzand, 2005; Fernández et al., 2007).

In addition to removing oxygen, oxidation of pyrite and siderite can potentially release Fe^{2+} to the pore waters. Upon dissolution, the iron in the mineral phase can either re-precipitate as an iron oxide/hydroxide, or go into solution as Fe^{2+} . Whether the iron goes into solution or not is largely dependent on the Eh and pH of the pore waters, with precipitation as oxide/hydroxide favored by higher Eh and pH conditions (e.g., Garrels and Christ 1965). As pyrite oxidation itself causes acidification, significant mobilization of Fe^{2+} is possible (Xu et al. 2000). However, in the presence of carbonate minerals, which are often abundant in reservoir rocks, acidification should be limited by carbonate dissolution. Finally, the amount, if any, of Fe^{2+} released to the pore waters is in part influenced by the amount of siderite and pyrite present. Typically these minerals are minor phases in sedimentary rocks (i.e., a few vol% or less), however, they are sometimes present in much larger amounts (e.g., Melvin and Knight 1981, Gaynor and Scheihing 1988).

Geochemical Modeling. In order to quantify the nature of the geochemical alterations that would occur with injection, particularly the amount of time required for the reactions to occur, a geochemical model was employed to simulate injection into a pyrite-bearing reservoir. We focus on pyrite because it is more common than siderite, and its dissolution kinetics have been characterized in detail. The modeling was done using the React program in Geochemist's Work Bench (Bethke 2002).

Assumptions for the model were as follows: The initial fluid contained 0.2 wt % NaCl and 0.1 wt% NaHCO_3 along with trace amounts of Fe^{2+} , Ca^{2+} , Mg^{2+} and SO_4^{2-} . The initial pH was set to 8. The amount of dissolved oxygen varied between 5 and 5,000 ppb, and the temperature varied from 25 to 125°C. Pyrite was assumed to be present at 1 vol. % of the solid phase of the rock, as was calcite. The oxidation of pyrite was treated kinetically whereas other species were considered to be at equilibrium. The kinetic rate constant used for pyrite oxidation at 25°C was 2×10^{-14} moles/ $\text{cm}^2\text{-sec.}$, a value taken from Xu et al. (2000) in a modeling study of pyrite oxidation in sedimentary rocks. For runs at higher temperatures, the kinetic rate constant was estimated assuming that the reaction rate doubled for each 10°C increase in temperature (a common assumption

in geochemical studies, e.g., Langmuir 1997). A reactive surface area for the pyrite of $125 \text{ cm}^2/\text{g}$ was calculated using the method described by Hodson (1998; based upon work by Sverdrup et al., 1990, and Sverdrup, 1996), assuming 1 vol% pyrite (of the solid phase) which consists of 50% fine sand and 50% silt sized crystals.

The results of the simulations demonstrate that dissolved oxygen levels will be rapidly depleted in the reservoir in several days or less, depending on the amount of O_2 in the injection water and the temperature of the reservoir. **Fig. 8** plots dissolved oxygen as a function of time. At 25°C , an original 5,000 ppb of O_2 is reduced below 1 ppb in slightly less than 4 days. For lower concentrations, the O_2 is depleted in shorter time periods: 50 and 5 ppb are reacted away in 0.1 and 0.075 days, respectively. As temperature increases, the rate of the oxidation reaction increases and the O_2 decreases more rapidly. At 125°C , 5,000 ppb oxygen is reduced below 1 ppb in only 0.04 days (about an hour). With 5,000 ppb O_2 and 30% porosity, about 3×10^6 pore volumes of water are needed to oxidize all the pyrite. Of course, as the percentage of pyrite decreases, the reaction rate will also decrease due to the decreasing reactive surface area.

As pyrite oxidation progresses, dissolved iron levels are initially kept low by precipitation of iron oxides. At 25°C , the Fe concentrations in solution are initially controlled by hematite solubility at values near 1 ppb. However, as oxygen levels decrease to values less than ~ 25 ppb, hematite becomes unstable and Fe^{2+} is controlled by siderite solubility, with values near 35 ppb. (Iron in solution is mainly present as Fe^{2+} , with negligible Fe^{3+} concentrations.) At higher temperatures Fe^{2+} levels are kept even lower due to changing Fe-mineral stability. At 125°C , Fe^{2+} concentration is controlled by magnetite solubility and does not rise above 0.3 ppb. The presence/absence of dissolved oxygen does not significantly affect the concentrations of Ca^{2+} or Mg^{2+} in solution.

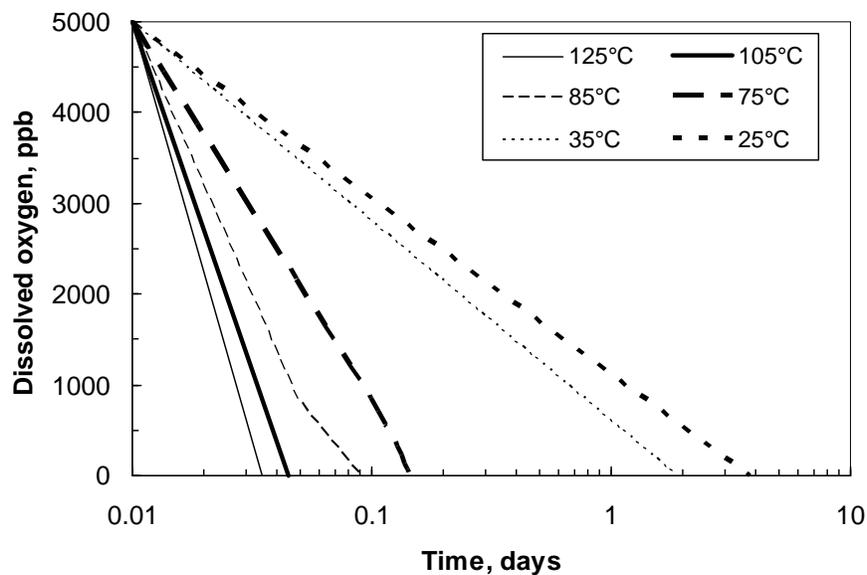
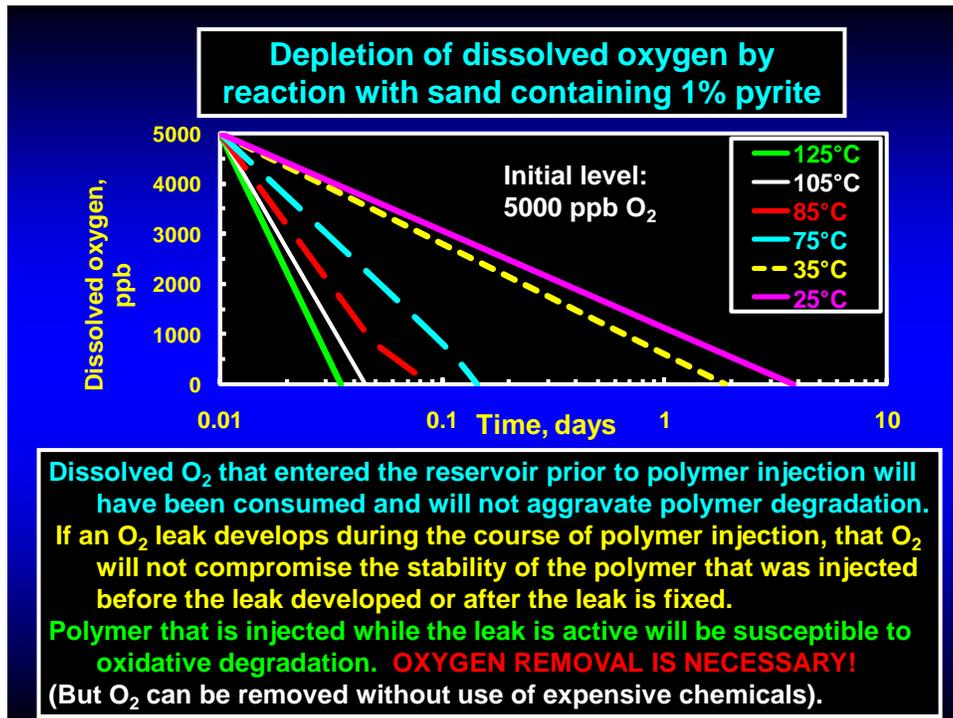


Fig. 8—Depletion of dissolved oxygen during reaction with pyrite containing sand.



Significance for Field Applications. A key message from this analysis is that dissolved oxygen will be removed quickly from injected waters and will not propagate very far into the porous reservoir rock. Also, no significant iron will enter solution until all the dissolved oxygen is consumed. These findings have two positive implications with respect to polymer flooding high-temperature reservoirs. First, dissolved oxygen that entered the reservoir prior to polymer injection will have been consumed, and consequently, will not aggravate polymer degradation. Second, if an oxygen leak (in the surface facilities or piping) develops during the course of polymer injection, that oxygen will not compromise the stability of the polymer that was injected before the leak developed or the polymer that is injected after the leak is fixed. Of course, the polymer that is injected while the leak is active will be susceptible to oxidative degradation.

The analysis does not suggest that oxygen removal is unnecessary for polymer floods. On the contrary, maintaining dissolved oxygen at undetectable levels is necessary to maximize polymer stability. For example during one experiment at 120°C, we stored 70 g of a 0.1% HPAM solution (in brine with 0.2% NaCl + 0.1% NaHCO₃) that contained 1,800 ppb dissolved oxygen with 30 g of 20/40 frac sand with 1 wt% pyrite added. During 24 hours of storage at 120°C, the solution viscosity dropped from 38 cp to 20.4 cp and the dissolved oxygen concentration decreased from 1,800 ppb to 0 ppb. Evidently, polymer degradation can occur more rapidly than the oxygen removal reactions. These findings are consistent with previous literature reports, where the presence of dissolved oxygen was associated with rapid polymer degradation at elevated temperatures (Shupe 1981, Yang and Treiber 1985, Wellington 1983). Therefore to be safe, dissolved oxygen should be maintained at undetectable levels for field applications of polymer floods in high-temperature reservoirs.

In the world's largest polymer flood (in the 45°C Daqing reservoir), oxidative degradation of HPAM was apparently unimportant even though fresh surface water with ambient levels of dissolved oxygen were injected (Wang et al. 2008). At the Daqing polymer flood, a mixture of fresh water (containing 7,000 to 9,000 ppb dissolved oxygen) and produced water (containing 1,000 to 4,000 ppb dissolved oxygen, after exposure to atmospheric conditions) was used to prepare polymer solutions. To test our geochemical modeling results, we performed an experiment where an oxygenated HPAM solution was stored in the presence of deoxygenated Daqing reservoir sand. Analysis revealed that the Daqing reservoir sand contained 0.23% pyrite and 0.51% siderite. This sand was placed in our anaerobic chamber and purged using our H₂-N₂ gas mixture. A solution was prepared that contained 0.1% Daqing HPAM in brine with 0.2% NaCl and 0.1% NaHCO₃ (similar to Daqing injection water). After preparation, this solution contained 3,300 ppb dissolved oxygen. Equal weights of this oxygenated polymer solution were mixed with deoxygenated Daqing sand in the anaerobic chamber and then stored at 45°C inside the anaerobic chamber. After one day, the solution viscosity (at 7.3 s⁻¹) decreased slightly—from 25.8 (original) to 24.1 cp, but the dissolved oxygen level dropped from 3,300 ppb to 0 ppb. These results were consistent with our geochemical modeling effort, which predicted rapid removal of dissolved oxygen by sands containing pyrite and siderite. Although the oxygen that was present did not greatly degrade the HPAM polymer in this case (at 45°C), we strongly advise oxygen removal for polymer floods in hotter reservoirs.

Gas stripping units are commercially available for deoxygenating large volumes of surface waters (e.g., fresh water or seawater that have dissolved oxygen levels greater than 1,000 ppb) to 10 ppb or less. Gas stripping has long been the dominant "mechanical" method to remove oxygen from oilfield waters (Weeter 1965, Snavely 1971).

Conclusions

1. We developed a method to prepare, store, and test the stability of polymer solutions that contain less than 0.1 parts per billion dissolved oxygen.
2. In the absence of dissolved oxygen and divalent cations, HPAM solutions were projected to maintain at least half their original viscosity for over 8 years at 100°C and about 2 years at 120°C.
3. Within our experimental error, HPAM stability was the same with/without oil (decane).
4. An acrylamide-AMPS copolymer (with 25% AMPS) showed similar stability to that for HPAM. Stability results were similar in brines with 0.3% NaCl, 3% NaCl, or 0.2% NaCl + 0.1% NaHCO₃.
5. At temperatures of 160°C and above, the polymers were more stable in brine with 2% NaCl + 1% NaHCO₃ than in the other brines.
6. Even though no chemical oxygen scavengers or antioxidants were used in our study, we observed the highest level of thermal stability reported to date for these polymers. Our results provide considerable hope for the use of HPAM polymers in enhanced oil recovery at temperatures up to 120°C, if contact with dissolved oxygen and divalent cations can be minimized.
7. Calculations performed considering oxygen reaction with oil and pyrite revealed that dissolved oxygen will be removed quickly from injected waters and will not propagate very far into the porous rock of a reservoir. These findings have two positive implications with respect to polymer floods in high-temperature reservoirs. First, any dissolved oxygen that entered the reservoir prior to polymer injection will have been consumed and will not aggravate polymer degradation. Second, if an oxygen leak (in the surface facilities or piping) develops during the course of polymer injection, that oxygen will not compromise the stability of the polymer that was injected before the leak developed or the polymer that is injected after the leak is fixed. Of course, the polymer that is injected while the leak is active will be susceptible to oxidative degradation. Maintaining dissolved oxygen at undetectable levels is necessary to maximize polymer stability. This can readily be accomplished without the use of chemical oxygen scavengers or antioxidants.

Nomenclature

E_a = activation energy, J/mol

m_{O_2} = mass of oxygen, lbs [Kg]

m_o = mass of oil per unit of bulk reservoir volume, lbs/ft³ [Kg/m³]

p_{O_2} = partial pressure of oxygen, atm [Pa]

S_{or} = residual oil saturation

T = temperature, °C[°K]

t = time, days

R = gas constant, 8.3143 J/mol°K

R_c = correlation coefficient

R_p = oil/water partition coefficient

μ = viscosity, cp [mPa-s]

μ_o = original viscosity, cp [mPa-s]

τ = viscosity decay constant, days

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