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

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Summary

At elevated temperatures in aqueous solution, partially hydrolyzed polyacrylamides (HPAMs) 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 more than 8 years at 100°C and for approximately 2 years at 120°C. Within our experimental error, HPAM stability was the same with and without oil (decane). An acrylamide-AMPS copolymer [with 25% 2-acrylamido-2-methylpropane sulphonic acid (AMPS)] showed similar stability to that for HPAM. Stability results were similar in brines with 0.3% NaCl, 3% NaCl, or 0.2% NaCl plus 0.1% $NaHCO_3$. At temperatures of 160°C and greater, the polymers were more stable in brine with 2% NaCl plus 1% $NaHCO_3$ 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 (EOR) 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 before 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 be accomplished readily without the use of chemical oxygen scavengers or antioxidants.

Introduction

In chemical-flooding applications for EOR, 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 affect stability critically 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 greater than 60°C, acrylamide groups within the HPAM polymer experience hydrolysis to form acrylate groups. If significant concentrations of divalent cations (especially Ca^{2+}) 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: 2000 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).

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 widen the applicability of HPAM polymers considerably. They described polymer floods in the German Oerrel and Hankensbuettel fields that had resident brine salinities of approximately 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 (1992) demonstrated that, if the mobility of the injected polymer formulation were low enough, the freshwater 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.

Effect of Dissolved Oxygen. The presence of dissolved oxygen by itself may not be detrimental to the stability of HPAM polymers

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(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) is 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) during approximately 250 days for 2000 mg/L HPAM (Dow Pusher 500™) in brine with 3841 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) during approximately 580 days for 1000 mg/L HPAM in brine with 1% NaCl and 0.4% sodium orthosilicate.

Paper Objectives. In this paper, 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 have. We also compare stability results for HPAM with those for a copolymer of acrylamide and 2-acrylamido-2-methylpropane sulfonic 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 O_2 4700i(X) Traces™ modules and two InPro 6950™ O_2 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 method (CHEMET™) with a limit of oxygen detection between 1 and 5 ppb in aqueous solution (Yang and Treiber 1985; Seright and Henrici 1990).

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

Four brines were used, containing (1) 0.3% NaCl, (2) 3% NaCl, (3) 0.2% NaCl plus 0.1% $NaHCO_3$, and (4) 2% NaCl plus 1% $NaHCO_3$. 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 cm^3 of polymer solution was placed in a 150-cm^3 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 and 180°C), 30 cm^3 of decane was 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 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 be made readily on these samples. A disadvantage is that, if the seal is compromised for our sample cylinders, the entire sample is lost. Fortunately, we have refined the technique so that no samples were lost over the course of the past two years.

Results

Viscosity values vs. 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(specific viscosity) vs. 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).

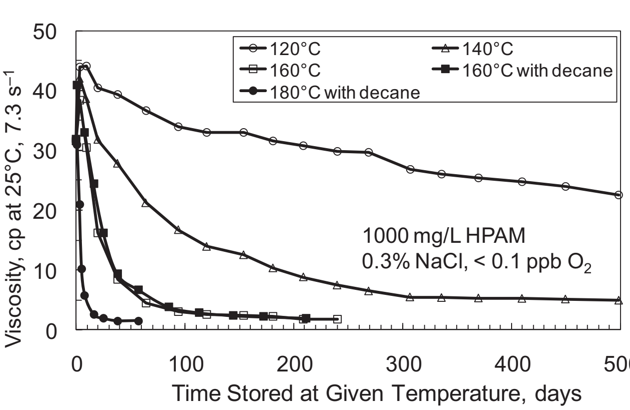

Fig. 1—Stability for HPAM in 0.3% NaCl. Viscosity vs. time.

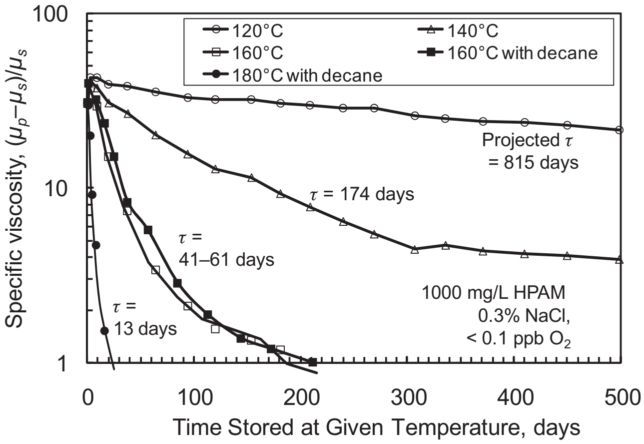

Fig. 2—Stability for HPAM in 0.3% NaCl. Specific viscosity vs. time.

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.)

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 3 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 3 days at 120°C in 3% NaCl, HPAM-solution viscosity increased only from 39.3 to 39.4 cp. After 3 days at 120°C or greater, 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 approximately 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). Considering our correlation coefficients (first column of parentheses data in Table 1), we cannot conclude that the stability at 120°C depends on salinity (between 0.3 and 3% NaCl) or $NaHCO_3$ 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 approximately 2 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) or $NaHCO_3$ content (0, 0.1, or 1%), or whether the polymer is HPAM or PAM-AMPS. The viscosity-decay constants at 140°C averaged approximately 1 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% $NaHCO_3$was present. The overall salinity (from 0.3 to 3% TDS), the presence of oil (decane), or the type of polymer (HPAM vs. PAM-AMPS) did not affect stability definitively. The viscosity-decay constants at 160°C were 1.5 to 4 months without carbonate and 5 to 7 months with 1% $NaHCO_3$.

At 180°C in the presence of decane (last column of Table 1), the HPAM viscosity-decay constants were approximately 2 weeks without carbonate, 5 weeks with 0.1% $NaHCO_3$, and 10 weeks with 1% $NaHCO_3$.

Our polymer solutions were maintained in a reducing environment for the duration of the study. Specifically, the oxidation-reduction potential for freshly prepared solutions was approximately −500 mV, and, after 500 days of storage at various temperatures, the oxidation-reduction potential was still approximately −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

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	815 (–0.907)	174 (–0.963)	61 (–0.938)	41 (–0.976)	13 (–0.887)
HPAM	0.2% NaCl, 0.1% $NaHCO_3$	869 (–0.862)	205 (–0.988)	73 (–0.969)	76 (–0.974)	35 (–0.873)
HPAM	3% NaCl	749 (–0.884)	377 (–0.943)	127 (–0.966)	46 (–0.965)	15 (–0.865)
HPAM	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	1,590 (–0.750)	327 (–0.984)	71 (–0.973)	—	—
PAM-AMPS	0.2% NaCl, 0.1% $NaHCO_3$	1,090 (–0.779)	662 (–0.935)	147 (–0.992)	—	—
PAM-AMPS	3% NaCl	504 (–0.784)	388 (–0.891)	77 (–0.958)	—	—
PAM-AMPS	2% NaCl, 1% $NaHCO_3$	613 (–0.937)	473 (–0.856)	165 (–0.976)	—	—

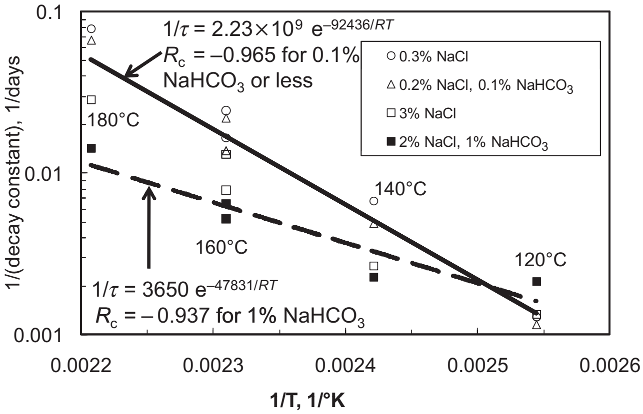

Fig. 3—HPAM Arrhenius plots, < 0.1 ppb dissolved O_2, no divalent cations.

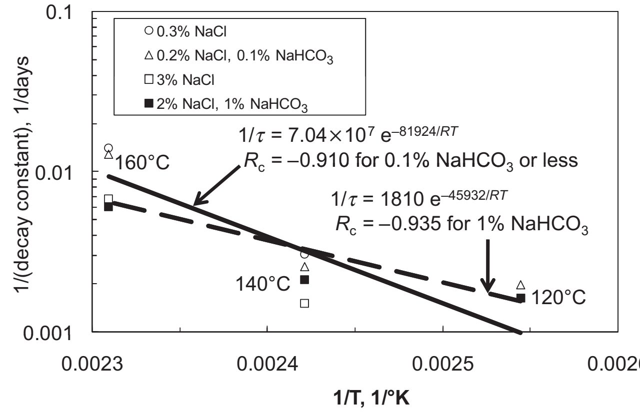

Fig. 4—PAM-AMPS Arrhenius plots, < 0.1 ppb dissolved O_2, no divalent cations.

of polymer stabilities at other temperatures. Eq. 1 shows a form of the Arrhenius equation:

$$E_a = R\ \mathrm{d}\big[\ln(1/\tau)\big]/\mathrm{d}(1/T). \quad (1)$$

Fig. 3 provides Arrhenius plots for our HPAM viscosity-decay constants (τ) from Table 1 (reciprocal decay constant vs. reciprocal of absolute temperature). A regression on the data with 1% $NaHCO_3$ (solid squares in Fig. 3) yielded an activation energy (E_a) of 47.8 kJ/mol, with a correlation coefficient (R_c) of –0.937. A regression on the remaining data (open symbols, with 0.1% or less $NaHCO_3$) in Fig. 3 yielded an activation energy of 9.24 kJ/mol, with a correlation coefficient of –0.965.

Fig. 4 provides Arrhenius plots for our PAM-AMPS viscosity-decay constants from Table 1. A regression on the data with 1% $NaHCO_3$ (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 $NaHCO_3$) in Fig. 4 yielded activation energy of 81.9 kJ/mol, with a correlation coefficient of –0.910.

Low-Carbonate Brines. For three of the brines (0.3% NaCl, 3% NaCl, and 0.2% NaCl plus 0.1% $NaHCO_3$), the temperature and viscosity-decay behavior for HPAM was statistically no different from that of 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% $NaHCO_3$ brine. The correlation coefficient was –0.947. 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.

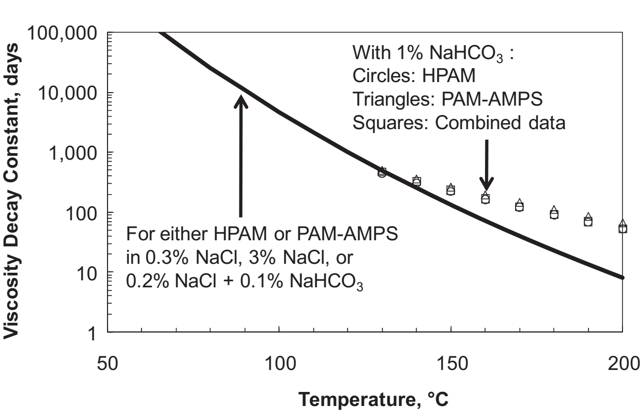

Fig. 5—Projected stabilities, < 0.1 ppb dissolved O_2, no divalent cations.

$$1/\tau = 2.64\times10^{9}\ e^{-93{,}538/RT}. \quad (2)$$

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 $NaHCO_3$, based on Eq. 2.

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.

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

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 approximately 3,240 days (8.9 years) at 100°C and approximately 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 is 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 approximately 250 days for 2000 mg/L HPAM in brine with 3841 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 approximately 580 days for 1000 mg/L HPAM. Our results predict an 8% loss of HPAM viscosity after 580 days at 90°C.

Brine With 1% $NaHCO_3$. For the brine with 1% $NaHCO_3$, regression of viscosity-decay constants associated with both polymers (fourth and eighth rows in Table 1) yield Eq. 4, with a correlation coefficient of –0.940.

$$1/\tau = 4{,}580\ e^{-48{,}800/RT}. \quad (4)$$

In 1% $NaHCO_3$, the regressions for HPAM data only, PAM-AMPS data only, and the combined data predicted noticeably different results for temperatures below 140°C. However, for temperatures greater than 140°C, the predictions from the regressions were quite similar (symbols in Fig. 5). Consequently, the use of Eq. 4 should be confined to temperatures of 140°C and greater when 1% $NaHCO_3$ 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 and divalent cations are 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 Fe^{2+} (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. Fe^{3+} may crosslink HPAM to form a gel, but it does not induce polymer degradation unless a redox couple is formed (Ramsden and McKay 1986).

Anticipated Oxygen 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 five 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:

$$1/\left[1+R_pS_{or}/\left(1-S_{or}\right)\right]. \quad (5)$$

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 and 232°C. Rates of oxygen consumption (dm_{O_2}/dt, in lbm/sec) predicted on the basis of these parameters have a significant variation. However, Eq. 6 provides the median prediction:

$$-dm_{O_2}/dt = m_o\left(p_{O_2}\right)^{0.6} 1{,}200\ e^{-8{,}504/T}. \quad (6)$$

In this equation, m_o is the mass of oil per unit of bulk reservoir volume, p_{O_2} is the partial pressure of oxygen in atm, and T is temperature in K. On the basis of 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 foot of net pay, $S_{or} = 0.3$, and porosity (ϕ) of 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 some time between several hours and many weeks.

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), and 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, because 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 being isolated in grain interiors.

In some circumstances, pyrite, siderite, and organic matter can lower levels of dissolved oxygen in aquifers and petroleum reservoirs dramatically. 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 μmol O_2/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 either can reprecipitate as an iron oxide/hydroxide or go into solution as Fe^{2+}. Whether the iron goes into solution is largely dependent on the Eh and pH of the pore

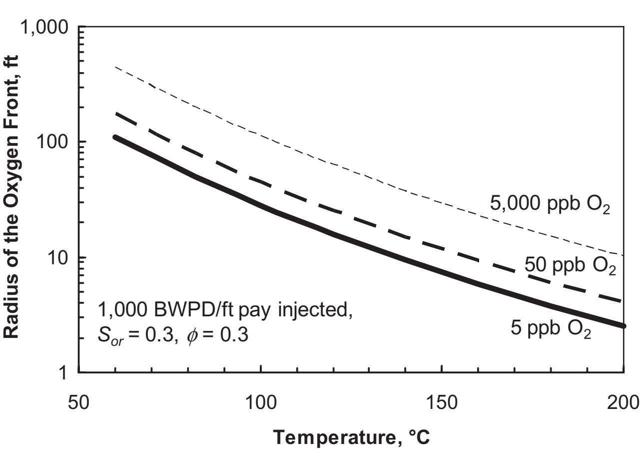

Fig. 6—Predicted radius at which dissolved O_2 will be totally consumed by reaction with oil.

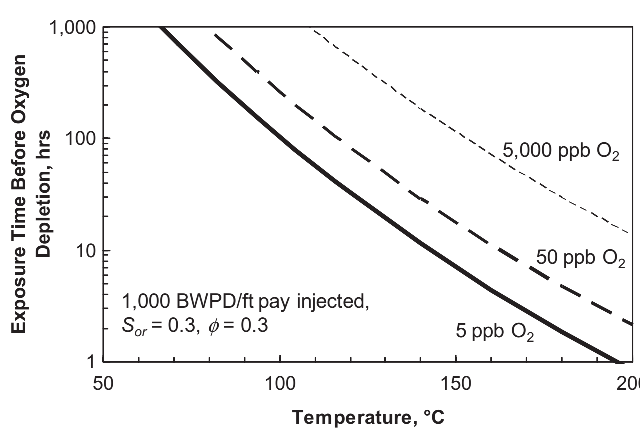

Fig. 7—Predicted time at which dissolved O_2 will be totally consumed by reaction with oil.

waters, with precipitation as oxide/hydroxide favored by higher Eh and pH conditions (e.g., Garrels and Christ 1965). Because 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 influenced in part 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) and 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 performed 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/cm^2·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 cm^2/g was calculated using the method described by Hodson et al. (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 depleted rapidly in the reservoir in several days or less, depending on the amount of oxygen 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 oxygen is reduced below 1 ppb in slightly less than 4 days. For lower concentrations, the oxygen 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 oxygen decreases more rapidly. At 125°C, 5,000 ppb oxygen is reduced below 1 ppb in only 0.04 days (approximately an hour). With 5,000 ppb oxygen and 30% porosity, approximately 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 because of the decreasing reactive surface area.

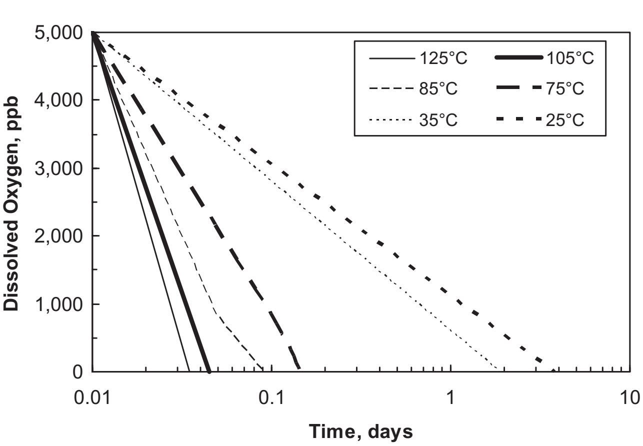

Fig. 8—Depletion of dissolved O_2 during reaction with pyrite-containing sand.

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 approximately 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 because of 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.

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 before 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 plus 0.1% $NaHCO_3$) that contained 1,800 ppb of dissolved oxygen with 30 g of 20/40-mesh frac sand with 1 wt% pyrite added. During 24 hours of storage at 120°C, the solution viscosity dropped from 38 to 20.4 cp and the dissolved-oxygen concentration decreased from 1,800 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 was 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 in which 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 was purged using an hydrogen/nitrogen gas mixture. A solution was prepared that contained 0.1% Daqing HPAM in brine with 0.2% NaCl and 0.1% $NaHCO_3$ (similar to Daqing injection water). After preparation, this solution contained 3,300 ppb of dissolved oxygen. Equal weights of this oxygenated polymer solution were mixed with deoxygenated Daqing sand in the anaerobic chamber and then were stored at 45°C inside the anaerobic chamber. After 1 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 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 has 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

- We developed a method to prepare, store, and test the stability of polymer solutions that contain less than 0.1 ppb of dissolved oxygen.
- In the absence of dissolved oxygen and divalent cations, HPAM solutions were projected to maintain at least half their original viscosity for more than 8 years at 100°C and for approximately 2 years at 120°C.
- Within our experimental error, HPAM stability was the same with and without oil (decane).
- An acrylamide-AMPS copolymer (with 25% AMPS) showed stability similar to that for HPAM. Stability results were similar in brines with 0.3% NaCl, 3% NaCl, or 0.2% NaCl plus 0.1% $NaHCO_3$.
- At temperatures of 160°C and greater, the polymers were more stable in brine with 2% NaCl plus 1% $NaHCO_3$ 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 EOR 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 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 before 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 that of 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 be accomplished readily without the use of chemical oxygen scavengers or antioxidants.

Nomenclature

E_a = activation energy, J/mol
m_{O_2} = mass of oxygen, lbm [kg]
m_o = mass of oil per unit of bulk reservoir volume, lbm/ft^3 [kg/m^3]
p_{O_2} = partial pressure of oxygen, atm [Pa]
R = gas constant, 8.3143 J/mol·K
R_c = correlation coefficient
R_p = oil/water partition coefficient
S_{or} = residual-oil saturation
T = temperature, °C [K]
t = time, days
μ = viscosity, cp [mPa·s]
μ_o = original viscosity, cp [mPa·s]
τ = viscosity-decay constant, days

References

Antonio, M.R., Karet, G.B., and Guzowski, J.P. Jr. 2000. Iron chemistry in petroleum production. *Fuel* **79** (1): 37–45. doi: 10.1016/S0016-2361(99)00132-5.

Bathurst, R.G.C. 1975. *Carbonate Sediments and their Diagenesis*, second edition, No. 12, 658. Amsterdam, The Netherlands: Developments in Sedimentology, Elsevier Science B.V.

Bethke, C.M. 2002. *The Geochemist's Workbench—A User's Guide to Rxn, Act2, Tact, React and Gtplot*, Release 4.0.3, 224. Ubana, Illinois: University of Illinois.

Burger, J.G. 1976. Spontaneous Ignition in an Oil Reservoir. *SPE J.* **16** (2): 73–81. SPE-5455-PA. doi: 10.2118/5455-PA.

Davison, P. and Mentzer, E. 1982. Polymer Flooding in North Sea Reservoirs. *SPE J.* **22** (3): 353–362. SPE-9300-PA. doi: 10.2118/9300-PA.

Doe, P.H., Moradi-Araghi, A., Shaw, J.E., and Stahl, G.A. 1987. Development and Evaluation of EOR Polymers Suitable for Hostile Environments Part 1: Copolymers of Vinylpyrrolidone and Acrylamide. *SPE Res Eng* **2** (4): 461–467. SPE-14233-PA. doi: 10.2118/14233-PA.

Fernández, A.M., Turrero, M.J., Sánchez, D.M., Yllera, A., Melón, A.M., Sánchez, M., Peña, J. et al. 2007. *On site* measurements of the redox and carbonate system parameters in the low-permeability Opalinus Clay formation at the Mont Terri Rock Laboratory. *Physics and Chemistry of the Earth, Parts A/B/C* **32** (1–7): 181–195. doi: 10.1016/j.pce.2006.02.057.

Garrels, R.M. and Christ, C.L. 1965. *Solutions, Minerals and Equilibria*, 450. New York: Harper & Row.

Gaynor, G.C. and Scheihing, M.H. 1988. Shelf Depositional Environments and Reservoir Characteristics of the Kuparuk River Formation (Lower Cretaceous), Kuparuk Field, North Slope, Alaska. In *Giant Oil and Gas Fields: A Core Workshop*, Vol. 1–2, ed. A.J. Lomando and P.M. Hams, 333–389. Tulsa, Oklahoma: Core Workshop Notes, SEPM (Society for Sedimentary Geology).

Hartog, N., Griffioen, J., and van der Weijden, C.H. 2002. Distribution and Reactivity of O_2-Reducing Components in Sediments from a Layered Aquifer. *Environ. Sci. Technol.* **36** (11): 2338–2344. doi: 10.1021/es015681s.

Hodson, M.E., Langan, S.J., and Meriau, S. 1998. Determination of mineral surface area in relation to the calculation of weathering rates. *Geoderma* **83** (1–2): 35–54. doi: 10.1016/S0016-7061(97)00136-5.

Johnson-Ibach, L.E. 1982. Relationship Between Sedimentation Rate and Total Organic Carbon Content in Ancient Marine Sediments. *AAPG Bulletin* **66** (2): 170–188.

Knight, B.L. 1973. Reservoir Stability of Polymer Solutions. *J. Pet Tech* **25** (5): 618–626; *Trans.,* AIME, **255**. SPE-4167-PA. doi: 10.2118/4167-PA.

Kubie, L.S. 1927. The Solubility of O_2, CO_2, and N_2 in Mineral Oil and the Transfer of Carbon Dioxide from Oil to Air. *Journal of Biological Chemistry* **72** (2): 545–548.

Lake, L.W. 1989. *Enhanced Oil Recovery*, 396–400. Englewood Cliffs, New Jersey: Prentice Hall.

Langmuir, D. 1997. *Aqueous Environmental Geochemistry*, 600. Upper Saddle River, New Jersey: Prentice Hall.

Levitt, D.B. and Pope, G.A. 2008. Selection and Screening of Polymers for Enhanced-Oil Recovery. Paper SPE 113845 presented at the SPE/DOE Symposium on Improved Oil Recovery, Tulsa, 19–23 April. doi: 10.2118/113845-MS.

Maitin, B.K. 1992. Performance Analysis of Several Polyacrylamide Floods in North German Oil Fields. Paper SPE 24118 presented at the SPE/DOE Enhanced Recovery Oil Symposium, Tulsa, 22–24 April. doi: 10.2118/24118-MS.

Melvin J. and Knight A.S. 1981. Lithofacies, Diagenesis and Porosity of the Ivishak Formation, Prudhoe Bay Area, Alaska. In *AAPG Memoir 37: Clastic Diagenesis*, ed. D.A. McDonald and R.C. Surdam, 347–365. Tulsa, Oklahoma: AAPG.

Moradi-Araghi, A. and Doe, P.H. 1987. Hydrolysis and Precipitation of Polyacrylamide in Hard Brines at Elevated Temperatures. *SPE Res Eng* **2** (2): 189–198. [paper in journal, not in OnePetro – only conf. paper has doi]

Moradi-Araghi, A., Cleveland, D.H., Jones, W.W., and Westerman, I.J. 1987. Development and Evaluation of EOR Polymers Suitable for Hostile Environments: II—Copolymers of Acrylamide and Sodium AMPS. Paper SPE 16273 presented at the SPE International Symposium on Oilfield Chemistry, San Antonio, Texas, USA, 4–6 February. doi: 10.2118/16273-MS.

Muller, G. 1981. Thermal stability of polyacrylamide solutions: effect of residual impurities in the molecular-weight-degradation process upon heating. *Polymer Bulletin* **5** (1): 39–45. doi: 10.1007/BF00255085.

Pettijohn, F.J., Potter, P.E., and Siever, R. 1987. *Sand and Sandstone*, second edition, 553. New York: Springer-Verlag.

Pope, G.A., Lake, L.W., and Helfferich, F.G. 1978. Cation Exchange in Chemical Flooding: Part 1—Basic Theory Without Dispersion. *SPE J.* **18** (6): 418–434. SPE-6771-PA. doi: 10.2118/6771-PA.

Prats, M. 1982. *Thermal Recovery*. Monograph Series, SPE, Richardson, Texas **7:** 94.

Prommer, H. and Stuyfzand, P.J. 2005. Identification of Temperature-Dependant Water Quality Changes during a Deep Well Injection Experiment in a Pyritic Aquifer. *Environ. Sci. Technol.* **39** (7): 2200–2209. doi: 10.1021/es0486768.

Ramsden, D.K. and McKay, K. 1986. The degradation of polyacrylamide in aqueous solution induced by chemically generated hydroxyl radicals: Part II—Autoxidation of Fe^{2+}. *Polymer Degradation and Stability* **15** (1): 15–31. doi: 10.1016/0141-3910(86)90003-0.

Ryles, R.G. 1988. Chemical Stability Limits of Water-Soluble Polymers Used in Oil Recovery Processes. *SPE Res Eng* **3** (1): 23–34. SPE-13585-PA. doi: 10.2118/13585-PA.

Santoso, E.A., Fanadi, A., Nasoetion, S. Moersidik, S.S., and Hamzah, U.S. 2003. Zero Discharge Strategy on Water Quality, A Case Study in Minas OU. Paper SPE 80562 presented at the SPE Asia Pacific Oil and Gas Conference and Exhibition, Jakarta, 15–17 April. doi: 10.2118/80562-MS.

Seright, R.S. and Henrici, B.J. 1990. Xanthan Stability at Elevated Temperatures. *SPE Res Eng* **5** (1): 52–60. SPE-14946-PA. doi: 10.2118/14946-PA.

Seright, R.S., Campbell, A.R., and Mozley, P.S. 2009. Stability of Partially Hydrolyzed Polyacrylamides at Elevated Temperatures in the Absence of Divalent Cations. Paper SPE 121460 presented at the SPE International Symposium on Oilfield Chemistry, The Woodlands, Texas, USA, 20–22 April. doi: 10.2118/121460-MS.

Shupe, R.D. 1981. Chemical Stability of Polyacrylamide Polymers. *J. Pet Tech* **33** (8): 1513–1529. SPE-9299-PA. doi: 10.2118/9299-PA.

Snavely, E.S. Jr. 1971. Chemical Removal of Oxygen from Natural Waters. *J. Pet Tech* **23** (4): 443–446. SPE-3262-PA. doi: 10.2118/3262-PA.

Sohn, W.O., Maitin, B.K., and Volz, H. 1990. Preconditioning Concepts in Polymer Flooding in High-Salinity Reservoirs: Laboratory Investigations and Case Histories. *SPE Res Eng* **5** (4): 503–507. SPE-17675-PA. doi: 10.2118/17675-PA.

Sverdrup, H. 1996. Geochemistry, the key to understanding environmental chemistry. *Science of the Total Environment* **183** (1–2): 67–87. doi: 10.1016/0048-9697(95)04978-9.

Sverdrup, H., de Vries, W., and Henriksen, A. 1990. *Mapping Critical Loads*, 124. Geneva: Nordic Council of Ministers.

Tielong, C., Zhengyu, S., Fan, Y., Changzhong, H., Ling, Q., and Jinxing, T. 1998. A Pilot Test of Polymer Flooding in an Elevated- Temperature Reservoir. *SPE Res Eval & Eng* **1** (1): 24–29. SPE-36708-PA. doi: 10.2118/36708-PA.

Wang, D., Han, P., Shao, Z., Hou, W., and Seright, R.S. 2008. Sweep Improvement Options for the Daqing Oil Field. *SPE Res Eval & Eng* **11** (1): 18–26. SPE-99441-PA. doi: 10.2118/99441-PA.

Weeter, R.F. 1965. Desorption of Oxygen From Water Using Natural Gas for Countercurrent Stripping. *J. Pet Tech* **17** (5): 515–520. SPE-933-PA. doi: 10.2118/933-PA.

Wellington, S.L. 1983. Biopolymer Solution Viscosity Stabilization—Polymer Degradation and Antioxidant Use. *SPE J.* **23** (6): 901–912. SPE-9296-PA. doi: 10.2118/9296-PA.

Xu, T, White, S.P., Pruess, K., and Brimhall, G.H. 2000. Modeling of Pyrite Oxidation in Saturated and Unsaturated Subsurface Flow Systems. *Transport in Porous Media* **39** (1): 25–56. doi: 10.1023/A:1006518725360.

Yang, S.H. and Treiber, L.E. 1985. Chemical Stability of Polyacrylamide Under Simulated Field Conditions. Paper SPE 14232 presented at the SPE Annual Technical Conference and Exhibition, Las Vegas, Nevada, USA, 22–26 September. doi: 10.2118/14232-MS.

Zaitoun, A. and Potie, B. 1983. Limiting Conditions for the Use of Hydrolyzed Polyacrylamides in Brines Containing Divalent Ions. Paper SPE 11785 presented at the SPE Oilfield and Geothermal Chemistry Symposium, Denver, 1–3 June. doi: 10.2118/11785-MS.

SI Metric Conversion Factors

cp × 1.0*	E−03 = Pa·s
ppb × 1.0*	E−00 = μg/L

*Conversion is exact.

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