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The Optimal Use of Enhanced Oil Recovery Polymers Under Hostile Conditions

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The Optimal Use of Enhanced Oil Recovery Polymers Under Hostile Conditions

by

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Dedication

To Sam.
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The Optimal Use of Enhanced Oil Recovery Polymers Under Hostile Conditions

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The purpose of this work is to frame the main issues one must face in the design of a mobility control process using polyacrylamide and related acrylic polymers under hostile conditions. Proper preliminary lab evaluation techniques, chemical degradation and related calcium tolerance issues, thermal degradation, and economic optimization based upon injectivity are discussed. Emphasis is placed on stability under alkaline conditions, the use of sodium dithionite to prevent thermal degradation, and the beneficial use of in-situ hydrolysis to increase injectivity.

Filtration properties are a focus of screening experiments, and though it often takes several days to achieve acceptable filter ratios in the lab, experience from two field observations indicate that even high molecular weight polymers have filtration ratios on the order of 1.2 or less before they are injected, so preparation procedures that do not result in this may not yield results that scale to the field.

Chemical stability issues with acrylamide polymers are addressed in two parts, the first describing the kinetics of hydrolysis under neutral and alkaline conditions and the
second estimating the calcium tolerance of aged polymers using industrial and lab produced analogues. Under alkaline conditions, hydrolysis is very rapid, even at low temperatures. Though aged copolymers of acrylamide (AM) and 2-acrylamide 2-methyl propane sulfonate (AMPS) exhibit similar calcium tolerances to similarly aged polyacrylamide (PAM), viscosity loss is much higher for the latter as this limit is approached.

Thermal, or “oxidative” degradation, is examined using Pourbaix diagrams for iron to understand the commonly reported relationships between pH, Eh, and stability. The beneficial effects of sodium carbonate and sodium dithionite on polymer solutions as well as some inconsistencies in the literature point towards a catalytic role played by ppb level amounts of iron in oxidative degradation mechanisms. It is put forward that addition of sodium dithionite is a conservative approach to all acrylic-backboned polymer floods, and practical issues related to this are discussed.

A simple analytical model is developed to take a brief look at economic optimization of polymer viscosity, and this is used to demonstrate the benefits of in-situ hydrolysis in alkaline or high-temperature floods.
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Chapter I: Introduction

BACKGROUND

Soon after the advent and widespread acceptance of waterflooding in the 1950’s it became apparent that the displacement of oil by water was often detrimentally affected by heterogeneity and poor mobility ratio. By the early 1960’s, adding water-soluble polymers to the injection water was identified as a way to economically lower the mobility ratio, improving areal sweep and fractional flow. The use of surfactant to mobilize trapped oil, with a concomitant increase of as much as an order of magnitude in water relative permeability, necessitated the use of polymer for this process as well.

In the 1970’s and 1980’s, researchers such as Zaitoun and Potie (1983) and Moradi and Doe (1987) identified limiting conditions for the use of polyacrylamide, the most commonly used polymer for enhanced oil recovery. Sorbie (1991) provides a comprehensive review of literature pertaining to polymers for enhanced oil recovery through the 1980’s, including the period of highest activity in this area. Recently, the identification of high performance surfactants for high temperature and high salinity applications has placed increased necessity on the development of polymers capable of withstanding these conditions.

The use of polymers for enhanced oil recovery (EOR) now extends back 50 years (Pye, 1964), with the vast majority of research and field application involving partially hydrolyzed polyacrylamide (HPAM). Polyacrylamide (PAM) is a homopolymer of acrylamide, and “hydrolyzed” refers to the labile amine, which is susceptible to a reaction involving water at high temperature and/or high or low pH, resulting in an anionically...
charged acrylate moiety at the site of hydrolysis. A small amount of hydrolysis has a beneficial effect, increasing solution viscosity, and so typically it is the partially hydrolyzed form, HPAM, which is used for EOR. The structure of HPAM is presented in Figure 1.

![Structure of partially hydrolyzed polyacrylamide (HPAM)](image)

Figure 1-1: Structure of partially hydrolyzed polyacrylamide (HPAM). Typically, $\tau = 0.2$ – 0.3. Polyacrylamide (PAM) corresponds to $\tau = 0$.

The key limitations identified for HPAM include:

- Chemical stability; precipitation if hydrolysis continues in-situ and a substantial amount of divalent cations, such as Ca$^{++}$ or Mg$^{++}$ are present
- Thermal Degradation; loss of viscosity due to radical degradation of the acrylic backbone, particularly at high temperatures and/or in the presence of iron.
- Reduced injectivity compared to water due to higher viscosity.

Chemical stability warrants the most attention, but can be managed at conditions harsher than previously thought through new methods, and even profited from if well understood. Thermal degradation must - and can quite easily – be avoided with simple additives. Injectivity reduction is an economic tradeoff, and must be weighed against increased recovery efficiency.
DESCRIPTION OF CHAPTERS

In the research presented herein, currently available conventional PAM and HPAM polymers as well as variants of PAM polymers including monomers with improved properties such as 2-acrylamido 2- methyl propane sulfonate (AMPS) are examined for use with a focus on high temperature and high salinity conditions.

Chapter II: Preliminary Screening of Polymers, discusses basic properties of the polymers investigated, including filtration properties, surfactant compatibility, and solution viscosity.

Chapter III: Chemical Stability and Calcium Tolerance, is divided into two coupled parts. The first part examines the chemical stability of the acrylamide and AMPS moieties as a function of temperature and pH. Because large samples are required to perform calcium tolerance and viscosity experiments, the second part of this chapter uses industrial and lab-prepared analogues of the chemically altered polymers to investigate the calcium and salinity tolerance that can be expected after extended aging in the reservoir. Of particular interest is the stability of the AMPS moiety as well as the net improvement in calcium tolerance gained after aging when a small amount of AMPS is copolymerized with acrylamide, compared to that of conventional HPAM. Additionally, the use of sodium metaborate is investigated as a sequestering agent for calcium.

Chapter IV: Thermal Stability, investigates methods for preventing the radical-induced breakdown of the acrylic backbone. It has been shown that radicals can be generated from (i) the auto oxidation of iron, (ii) the combination of oxygen with residual initiators from polymerization at high temperature, and (iii) the reaction of oxygen with the sulfur dioxide radical when sodium dithionite is used. These processes were investigated using PAM and HPAM. In some cases, such as at high temperature or pH when hydrolysis would complicate viscometric interpretation, the ammonium salt of poly(acrylic acid) (PAA), the equivalent of fully hydrolyzed polyacrylamide, is used as a
surrogate. The proper use of sodium dithionite to prevent radical degradation and the beneficial stabilizing effects of sodium carbonate were investigated in detail.

Chapter V: Injectivity and Economic Optimization, presents a framework for determining optimum viscosity of injected fluid as trade off between injectivity, oil recovery efficiency, and polymer cost. For simplicity, Newtonian fluid properties are assumed. The concept of in-situ hydrolysis is evaluated using this analytical model, as has been recently reproposed (Levitt et al., 2008).

Chapter VI: Summary, Conclusions, and Recommendations, summarizes my view of the limiting conditions under which the studied acrylic polymers can be economically applied for EOR and gives broad recommendations which can guide selection in various environments. Recommendations for future work are also presented.
Chapter II: Polymer Preparation and Preliminary Screening

INTRODUCTION

In recent years, several new types of acrylic polymers have become commercially available and are under consideration for use in enhanced oil recovery (EOR) applications, with two major changes including an increase in molecular weights available and the inclusion in some cases of moieties that increase viscosity through inter- or intramolecular interactions. There are several important characteristics that must be tested before it is prudent to inject a new polymer into a formation. These include:

- Low cost
- Good filtration properties
- Suitable viscosity
- Surfactant compatibility
- Salinity and calcium tolerance
- Thermal stability
- Mechanical stability
- Good injectivity
- Good transport in reservoir rocks
- Low retention

Some of these characteristics, such as viscosity, are easily measured, whereas others, such as transport properties, require more time consuming experiments. A screening program for novel polymers should strike a balance between expediency and early identification of likely problems that may occur later in the entire program. What follows is a brief introduction to the proper hydration procedure for acrylic polymers as well as filter ratio, viscosity, and screen factor testing.
Polymer preparation

Foshee et al. (1976) showed that proper hydration of powdered polymer in the laboratory requires polymer powder to be completely separated and slowly sprinkled into the shoulder of the vortex of the stirring brine solution. The solution should be allowed to hydrate overnight, although once the polymer particles are visibly dissolved after 2-3 hours, stirring is not necessary except solutions should be stirred prior to use. One criticism of this slow and gentle hydration procedure is that it does not seem representative of field hydration conditions, under which polymer is typically well separated, but mixed under higher shear conditions and injected after only at most a few hours of hydration. While it is true that higher shear conditions may result in a reduction of molecular weight, the goal of laboratory screening is typically not to prepare and test the solution as it will be injected, but to study the solution as it will occur in the formation. From this perspective, the long mixing time is appropriate. If, on the other hand, the goal is to study injectivity and plugging behavior, more rapid hydration may be appropriate, however it is also likely that higher shear as well as some prefiltration is appropriate as well in this case if the result is to have relevance to field conditions.

Filter ratio

Filtration was identified very early on as an efficient method to remove microgels (Foshee et al., 1976) and filtration tests have long been used (Chauveteau and Kohler, 1984, Sorbie, 1991, Burcik and Thakur, 1972) to identify possible plugging behavior. The filtration test typically consists of the timed filtration of a polymer solution under constant pressure, with the filtration ratio (F.R.) being the ratio of the time of elution for a certain volume increment towards the end of the filtration over the same volume towards the beginning. A higher filtration ratio implies that more microgels or insoluble particles are being filtered out. The benefit of using cellulose filters over discs of reservoir or
surrogate rock include ease of use and repeatability, while the disadvantage primarily concerns the applicability of the filter to the particular formation under investigation. As demonstrated by Wreath (1989), filtration ratio increases with decreasing pressure or filter pore size. Whereas with a 1.2 μm filter the effect of differences in experimental conditions – for instance, doubling pressure – are reflected in the filtration ratio, with a larger, 5 μm filter both solutions pass with close to unit filtration ratio, and hence the test is of little utility. For a 2000 ppm polyacrylamide solution in 10% NaI brine, Wreath obtained a filtration ratio of 1.26 using a 1.2 μm filter, 10 psi pressure drop, and defining filtration ratio as:

\[ F.R. = \frac{t_{200mL} - t_{180mL}}{t_{80mL} - t_{60mL}} \]

Trieber and Yang (1986) suggest using a method that scales more directly to the reservoir, and they present results with several types of polymers for which solution quality is reported in throughput (ft³/ft²) of polymer before onset of plugging behavior. Although several cores were arranged in series with increasing diameter in order to replicate the flow regime at various distances from the wellbore, their data indicates that the vast majority of plugging behavior occurs within the first few tenths of an inch. More recently, Seright et al. (2008) demonstrated that, using 10 micron filters, the amount of throughput prior to the onset of plugging was comparable to that seen in Berea sandstone, however their results with HPAM may be poor due to their choice of an HPAM with degree of hydrolysis of around 0.4 for use in a hard brine. Several easily performed chemical well treatments have been reported to effectively remove polymer induced plugging near the wellbore (Dalrymple et al., 1990, Brandon and Pin, 1995, Nasr El-Din et al., 2005), so the onset of plugging after large volumes of polymer have been injected is perhaps not as serious problem as it once was.
The primary concern from a polymer screening perspective is not so much welfare of the wellbore as the ability of the polymer to pass through this exceedingly rigorous filtration process. It is difficult to imagine that transport through several feet of even a high permeability reservoir does not effectively filter out all polymer microgels. From this standpoint, good filtration performance through a small filter relative to the polymer hydrodynamic radius should be a prerequisite prior to the investment of a large amount of time in researching a novel polymer.

While filtration is always strongly recommended prior to testing in a core, it is not strictly required for bulk measurements such as viscosity, as microgels affect these properties little. However for novel polymers that make use of inter or intramolecular mechanisms to enhance viscosity, this must be verified.

**Viscosity**

The acrylic polymers under investigation are shear thinning, and thus the shear rate at which viscosity measurements are made requires consideration. Typical shear rates expected in a typical reservoir except close to the wells are on the order of 1-10 s\(^{-1}\) (assuming the shear rate correction coefficient C is on the order of 1). For many polymers and conditions this corresponds to a Newtonian region, however for some, particularly higher molecular weight, polymers the shear thinning region begins as low as 0.1 s\(^{-1}\). In these cases, measurements at lower shear rates are necessary if low shear viscosity is desired, for instance to determine intrinsic viscosity.

The relationship between polymer concentration and viscosity is well established in the literature. Also established in the literature but somewhat less well known is the relationship between salinity and viscosity, particularly at very high salinity. While HPAM viscosity drops quickly as salinity approaches 1-3% total dissolved solids (TDS), very little decrease is seen after that point as salinity continues to increase. While
intrinsic viscosity measurements can be used to correlate viscosity to molecular weight using the Mark-Houwink equation, this relies on parameters may not be well established and depend on degree of hydrolysis, making it difficult to use in practice. At high salinity, the shielding of anionic moieties causes the effect of the degree of hydrolysis to diminish. This suggests the measurement of intrinsic viscosity at high salinity if polymers of differing degree of hydrolysis are to be compared, however it is not clear what if any salinity corresponds to constant viscosity as a function of degree of hydrolysis. Alternatively, scanning salinity with a constant polymer concentration affords a qualitative appreciation of both relative molecular dimension and the effect of intramolecular repulsion.

**Screen factor**

Jennings et al. (1971) describe the use of a screen viscometer to obtain an approximate measure of resistance factor that reflects both the viscosity and the viscoelasticity of a solution. A typical device consists of a glass tube with two timing marks and a series of five 100 mesh screens of \( rac{1}{4} \) inch diameter at the bottom. The screen factor reported is the ratio of the flow time for the polymer solution to the flow time for the appropriate solvent. Whereas a low amount of polymer degradation is difficult to detect viscometrically, viscoelasticity drops much more rapidly, and this is reflected by a drop in resistance factor in porous media as well as a drop in screen factor. Thus the screen viscometer is a useful tool to measure loss of viscoelasticity in the field and detect the onset of degradation.
Hydrophobically modified polymers

Taylor and El-Din (1995) reviewed recent literature, mostly patents, concerning hydrophobically modified associative polymers. These are typically terpolymers similar in composition to HPAM with 0.1-3.0 mol% N-alkyl substituted hydrophobic monomers C₈-C₁₂ in length. Above a critical polymer concentration, intermolecular association of these molecules increases solution viscosity. In addition, other monomers with improved thermal stability, such as AMPS or NVP may be copolymerized with these molecules.

There are several references in the patent literature to successful flow of associative polymers through porous media, however most data that is reported corresponds to very high pressure gradients. Bock et al. (1987a, 1987b) use approximately 500 md Berea sandstone disks to test the mechanical stability of synthesized polymers, and report resistance factor data as well. Resistance factors of around 360 and 1000 are reported at frontal velocities of 1 ft/day. Both types of experimental polymers retain at least 50% of original viscosity after being subjected to flow rates of 1000 ft/day. As a side note, Beck reports that too much hydrophobic content may lead to high adsorption and plugging, however no data is presented on this. Evani (1989) reports resistance factors of 6-31 at a frontal velocity of 111 ft/day in 1 inch Berea cores ranging from 150-300 md.

EXPERIMENTAL PROCEDURES

Polymer hydration

Polymers were hydrated in a manner similar to that described by Foshee with the following exceptions. Whereas Foshee et al. (1976) recommend adding polymer powder over the course of 60 seconds such that all polymer is added before the solution develops
too much viscosity to allow adequate dispersal, it was found that extending the time of addition to 3-4 minutes, as is necessary for higher concentration stocks, did not prevent this. Additionally solutions were blanketed with argon, covered with Parafilm™ and stirred continuously at 100-200 rpm overnight or longer in some cases. In some cases where solution viscosity prevented the use of a stirbar an overhead mixer was used instead.

In the field hydration case, polymer was dispersed in an air current and sprayed with brine as it was dropped into a hydration tank. The hydration tank was used in a batch mode, such that viscosity and filter ratio could be monitored and polymer could be hydrated until an acceptable value was reached.

**Filter ratio**

Filter ratio was measured using a stainless steel Fann filter press bell filled with at least 220 mL of polymer. The bell was pressurized to 15 psi using argon. A 90 mm diameter 1.2 micron Millipore cellulose filter was used. Effluent was collected in a graduated cylinder and the time for 60, 80, 180, and 200 mL to be filtered was recorded. The filter ratio is then calculated as

\[
F \ R \ _R \ = \ \frac{t_{200\ mL} - t_{180\ mL}}{t_{180\ mL} - t_{60\ mL}} ;
\]

unless otherwise noted. A photo of the filtration assembly is presented in Figure 2-1.

**Viscosity**

Viscosity was measured using a Contraves LS-30 rheometer over the range of 0.0174-128.5 s⁻¹. In most cases viscosity was measured as a function of salinity since the focus of this study was high temperature and salinity applications. As the shear thinning nature of polyacrylamide polymers is well established and a relatively narrow range of
shear rates are of interest in the reservoir, only the viscosity at 11 s\(^{-1}\) is reported unless otherwise noted. It was originally intended that a TA Instruments ARES LS-1 rheometer would be used to measure the complex viscosity of the polymers studied and that this would be correlated to screen factor measurements performed on samples during the chemical and thermal stability tests described in subsequent chapters. However due to the reactivity of solutions containing sodium dithionite as well as the large sample sizes required and difficulty excluding oxygen in these tests they were not performed. Magbagbeola (2008) presents the rheological flow properties of some of the polymers described here in greater detail.

**Screen factor**

A screen viscometer was designed similar to the one described by Jennings et al. (1971) and discussed above. Five 100-mesh screens with diameter ¼ inch are used, however the device was modified so that only 15 mL of solution is required. Additionally, a curve was generated with mineral oils of different viscosities so that the time for an inelastic viscous solution of a given viscosity could be calculated. This curve is presented in Figure 2-2. The use of this time rather than the time for the solvent to pass as the denominator allows the calculation of a screen factor that reflects only the elasticity of the solution. Both this value, which will be referred to as the viscosity-normalized screen factor (S.F\(_{\text{Normalized}}\)) and the traditional screen factor developed by Jennings (S.F\(_{\text{Jennings}}\)) are reported.

**Degree of hydrolysis**

Degree of hydrolysis was measured using \(^{13}\)C NMR, as recommended by Taylor and Nasr-el-Din (1994). NMR work was performed by UT Analytical Services Laboratory in the Department of Chemistry and Biochemistry using a Varian Inova 500.
A delay time of 2 s was determined to be necessary from preliminary experiments, and approximately 900 cycles were acquired (1 hour acquisition time). Peaks were assigned to the carbonyl carbon of acrylamide (180 ppm), acrylate (183 ppm), and AMPS (176 ppm) moieties (Parker and Lezzi, 1993). The concentration in mol % of each moiety was calculated as the fraction of the integration of the peak corresponding to the carbonyl carbon of that moiety divided by the sum of the integration of all carbonyl peaks.

It was determined that 3-4 wt% polymer was required to obtain a sufficiently low signal to noise ratio in one hour. In order to lower the viscosity such that high molecular weight polymers of this concentration could be hydrated, much less transferred into a 5 mm NMR tube, salinity of at least 3% was used. In addition, 10% D$_2$O (Fisher Scientific) was added to all samples.

**EXPERIMENTAL RESULTS**

A summary of polymers that were screened for use is presented in Table 2-1. Flopaam™ 3330S (SNF Floerger) is a commonly used HPAM similar in molecular weight and degree of hydrolysis to the oft-referenced Pusher™ 700 (Dow) commonly used in the 70’s and 80’s. This and other commercially available polymers produced by SNF Floerger contain a small amount of a thiol-containing antioxidant. While the molecular weight of this polymer, reported by the manufacturer as 8 million, is quite high, much higher molecular weight polymers are now available. Flopaam™ 3630S (SNF Floerger), Hengfloc 62020 (Hengju), Hengfloc 63020 (Hengju), and Hengfloc 63026 (Hengju) are higher molecular weight HPAM polymers. The first two are similar, though prepared by different methods. Hengfloc 63020 has a higher degree of hydrolysis and Hengfloc 63026 has both a higher molecular weight and a higher degree of hydrolysis, so these last two polymers may not be suited for use in hard brines.
Flopaam™ 3230S and Flopaam™ 2330S (SNF Floerger) are low molecular weight polymers suitable for very low permeability formations. For instance, Flopaam™ 3230S has been passed through cores with permeabilities below 5 mD without plugging (Slaughter, 2010).

AN-125 is a copolymer of acrylamide (AM) and 2-acrylamido 2 methylpropane sulfonate (AMPS), or poly(AM-co-AMPS) copolymer, containing around 25% AMPS and having a molecular weight similar to Flopaam™ 3330S. SuperPusher SAV301 (SNF Floerger) is a polymer that contains n-vinyl pyrrolidone (NVP), but whose precise structure is kept confidential at the request of the manufacturers. This polymer was only available in low molecular weights, similar to that of Flopaam™ 3230S, at the time that experiments were commenced.

SuperPusher™ B192, SuperPusher™ S255, and SuperPusher™ D118 (SNF Floerger) and Kypam 5 (Hengju) are low molecular weight HPAM polymers which have been modified by the manufacturers in order to impart a higher solution viscosity than conventional HPAM polymers of similar molecular weight and degree of hydrolysis. SuperPusher™ B192, S255, and D118 are hydrophobically modified, whereas Kypam 5 is described as having a “comb-like” structure that provides a steric hindrance to the collapsing of the hydrodynamic volume.

FA920SH is an unhydrolyzed polyacrylamide (PAM) of similar molecular weight to Flopaam™ 3330S.

**Polymer hydration and filtration**

Results of hydration and filtration experiments conducted with Flopaam 3330S are presented in Table 2-2. While two days of hydration were required under laboratory mixing conditions to obtain a filtration ratio of around 1.2, the same results were obtained under field mixing conditions in one hour. This could be due to either better dispersal of
the polymer powder, higher shear mixing conditions, or a combination of the two. The slightly lower viscosity in the field suggests that some degradation occurred, likely due to either high shear conditions or the presence of around 0.5 ppm of iron in the field brine. Unfortunately no screen factor data was taken during the field observation.

Flopaam 3630S, a higher molecular weight polymer, proved slightly more challenging to obtain a suitable filtration ratio of around 1.2. Table 2-3 presents filtration experiments performed with Flopaam 3630S. Three methods were identified by which suitable filtration ratios could be achieved. First, the polymer could be mixed with a stirbar at low rate, as described above, for 4-5 days. Alternatively, an overhead mixer could be used such that higher shear could be applied. In this case low filtration ratios could be obtained after overnight mixing, however some viscosity loss results from this procedure, as indicated in Figure 2-3. Finally, rapid hydration could be achieved by initial dispersion of the polymer and a few hours mixing at low speed followed by a few seconds to minutes of very high shearing, for instance in a Waring blender.

Observation of field mixing of Flopaam 3630S using a Fabtek™ venturi-style hydration unit allowed the comparison between lab and field hydration procedures. Rapid viscosity loss was observed during measurements, greatly complicating results. Filtration ratios under unity and viscosity loss of a standard left out during filtration suggested degradation of the polymer during the test, possibly due to the 0.3-0.4 ppm of iron in the solution. Nonetheless filtration results indicate polymer was suitably hydrated by field equipment in only 45 minutes. By comparison, several days of mixing in the lab with a magnetic stir bar are required to obtain comparable filtration ratios. A lab prepared solution was subsequently sheared in a Waring blender for 5 seconds at a time on low, after which viscosity, screen factor, and filter ratio were measured again. Shearing for 5 seconds resulted in a similar filter ratio, viscosity and screen factor to that
obtained under field mixing conditions. However, it seems likely from the transient nature of the properties measured in the field that oxidative, more than mechanical, degradation was the cause of the loss of viscosity in the field. Therefore these results should not be viewed as general.

AN-125, a copolymer of acrylamide (AM) and 2-acrylamido 2-methyl propane sulfonate (AMPS) having 20-30% AMPS, was slightly more difficult to obtain suitable filtration performance with. Filtration results with AN-125 are presented in Table 2-4. Suitable filtration ratios were also obtained using high shear or 4-5 days of mixing.

Suitable filtration performance was not achieved with SuperPusher™ B192, S255, and D118, hydrophobically-modified HPAM polymers. Using the standard hydration procedure described above, the polymer solutions would not pass through a 1.2 \( \mu \)m filter and the effluent had a viscosity similar to water. Next, the polymer solution was sheared using a Waring blender at different speeds for 3 minutes. As shear increased, solution viscosity dropped but effluent viscosity was higher, indicating that more polymer was passing through the filter. Even when viscosity had dropped an order of magnitude due to shearing, effluent viscosity was still lowered again by half and filtration ratio was 2.5, as illustrated in Figure 2-4. Surfactant was next added in an attempt to shield some of the polymer hydrophobes and decrease intermolecular associations. This was very effective; adding just 0.5-1% \( \text{C}_{20-24} \) internal olefin sulfonate (IOS) was sufficient to allow solutions of SuperPusher B192 and S255 to obtain filtration ratios below 1.2. However, a significant drop in viscosity accompanied this improvement in filtration. For example, a 1500 ppm solution of SuperPusher™ S255 had a viscosity of only 6 cP once surfactant was added, compared to several hundred cP prior to the addition of surfactant. It seems that the both the enhanced viscosity and filtration issues are the result of intermolecular associations between the hydrophobes. Thus it seems that
these associative polymers are not suitable for use in polymer or surfactant-polymer floods as a mobility control agent as envisioned here.

Cursory screening by filtration testing was performed with several other high molecular weight polymers, and these are summarized in Table 2-1. The unfortunately-named SuperPusher™ SAV301 is not a hydrophobically-modified HPAM like others of this trademark, but a low molecular weight modified polyacrylamid polymer that includes NVP, and easily passed the filtration test. Kypam 5 is described by the manufacturer as a “comb” polymer that is similar to HPAM but includes moieties that cause the molecule to be sterically hindered from collapsing into an unperturbed configuration. The filtration ratio of this polymer was still 1.5 after 4-5 days mixing, which is slightly higher than the desirable range, however much better than the ratios above 2 seen with associative polymers. While it is possible these polymers will be appropriate for higher permeability reservoirs further testing should focus on the polymer’s transport properties. Hengfloc™ 62020, 63020, and 63026 are high molecular weight HPAMs and were able to be filtered suitably after extended mixing.

**Viscosity**

Viscosity-concentration and viscosity-salinity relationships for three relatively low molecular weight polymers are presented in Figures 2-5 and 2-6. Note that these measurements were made at 70 s⁻¹ for the purposes of a specific coreflood. This is well in to the shear-thinning region, and hence the values reported here are lower than elsewhere. As discussed above, a near-plateau in viscosity occurs above 1% T.D.S.

Viscosity-salinity relationships for 1500 ppm Flopaam 3330S, Flopaam 3630S, Hengfloc 63020, Hengfloc 63026, and Kypam 5 are presented in Figure 2-7. It is apparent that the polymers described as high molecular weight by their manufacturers indeed have much higher viscosity at all salinities. From the viscosity values at high
salinity, it appears that Flopaam 3630S and Hengfloc 63020 are of comparable molecular weight and have more than double the viscosity of Flopaam 3330S under the same conditions. While the high salinity values are comparable for these two polymers, the viscosity of Hengfloc 63020 is higher at low salinity and decreases more rapidly, consistent with the higher degree of hydrolysis that was measured. Results with Kypam 5 are notable in that solution viscosity continues to decrease with increasing salinity up to at least 100,000 ppm NaCl. This could be explained by the presence of intramolecular steric hindrance, as claimed by the manufacturer, though no attempt was made to verify this mechanism.

Viscosity-salinity relationships of three acrylamide-based polymers under investigation for possible use at high temperature are presented in Figure 2-8, as well as Flopaam 3330S for comparative purposes. These polymers are an unhydrolyzed polyacrylamide (FA920SH), a poly(AM-co-AMPS) copolymer (AN-125), and a polymer incorporating n-vinyl pyrrolidone (NVP). It appears from viscosity values at high salinity that Flopaam 3330S, AN-125, and FA920SH are of approximately the same molecular weight, however there are significant differences at low salinity due to differences in ionic character, with the unhydrolyzed polymer having much lower viscosity and the sulfonated polymer having higher viscosity than conventional HPAM. These differences highlight the difficulty in making molecular weight comparisons between polymers with differing ionic character.

Approximate molecular weights were calculated for some polymers by measuring the intrinsic viscosity, as demonstrated in Figure 2-9, and using Mark-Houwink parameters of K = 0.00719 and a = 0.77 reported by Klein and Conrad (1980) for PAM in 0.5 M NaCl. However, in order to decrease intramolecular anionic repulsion further, 1 M
NaCl brine was used as a solvent. Results of these calculations are presented in Table 2-1.

The effect of brine hardness on viscosity decline with increasing salinity is demonstrated in Figure 2-10 for a polymer with low (< 0.33) degree of hydrolysis (\( \tau \)). Although viscosity decreases to values lower than those observed from increasing monovalent cation concentration alone, viscosity remains high even in the presence of over 10,000 ppm Ca\(^{2+} \). Thus if degree of hydrolysis remains low, calcium tolerance is no more an issue than salinity tolerance, that is to say viscosity decline is experienced but the effect is not tremendous. As we shall see in the following chapter, once \( \tau \) increases past around 0.35, calcium tolerance becomes a much bigger issue.

As illustrated in Figure 2-11, polymer viscosity was observed to increase over time in alkaline solutions. An increase in viscosity with pH is well known and can be attributed to the increased deprotonization of carboxyl moieties. However an increase in viscosity over time while pH remains constant implies the hydrolysis of additional amide moieties. This suggested an investigation of the effect of pH on hydrolysis kinetics, and further discussion of this will be presented in the following chapter.

DISCUSSION

Filtration testing using 1.2 \( \mu \)m filters provides valuable information. Low filtration ratios are achievable even for very high molecular weight polymers. However, sometimes long hydration times or higher shear are required. Field data indicates that greater shear is applied during field hydration, and thus the use of more shear in the lab is probably warranted. Results with hydrophobically modified polymers indicate that transport in low to moderate permeability reservoir rocks may be poor, and the effect of surfactant on viscosity filtration properties are consistent with claims that intermolecular association between hydrophobes effect the behavior of the macromolecules. A sterically
hindered polymer exhibited much better filtration properties but further investigation into transport properties may be warranted.

The use of salinity scans for the purpose of inferring approximate molecular dimensions as well as the ionic character of polymers has been demonstrated.

Further field testing is necessary to determine the appropriate shear conditions for the laboratory. A screen viscometer is useful for rapid measurements in the field. The effects of chemical and thermal stability will be addressed in later chapters.
Table 2-1: Screened polymers

<table>
<thead>
<tr>
<th>MFG</th>
<th>Polymer</th>
<th>Description</th>
<th>Intrinsic Viscosity (1 M NaCl)</th>
<th>Approximate MW (M Daltons)</th>
<th>τ</th>
<th>σ</th>
<th>Filtration Ratio</th>
<th>Mixing time (days)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SNF</td>
<td>Flopaam 2330S</td>
<td>HPAM</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SNF</td>
<td>Flopaam 3230S</td>
<td>HPAM</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SNF</td>
<td>Flopaam 3330S</td>
<td>HPAM</td>
<td></td>
<td></td>
<td>0.27</td>
<td>-</td>
<td>1.2</td>
<td>2(lab), 90 min(field)</td>
</tr>
<tr>
<td>SNF</td>
<td>Flopaam 3630S</td>
<td>HPAM</td>
<td>2100 +/- 420</td>
<td>13-17</td>
<td>0.3</td>
<td>-</td>
<td>1.2-1.4</td>
<td>4-5</td>
</tr>
<tr>
<td>SNF</td>
<td>Flopaam 3830S</td>
<td>HPAM</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SNF</td>
<td>Flopaam 1630S</td>
<td>HPAM</td>
<td></td>
<td></td>
<td>0.12</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hengju</td>
<td>Hengfloc 63020</td>
<td>HPAM</td>
<td>1830 +/- 800</td>
<td>10-14</td>
<td>0.36</td>
<td>-</td>
<td>1.3</td>
<td>5</td>
</tr>
<tr>
<td>Hengju</td>
<td>Hengfloc 63026</td>
<td>HPAM</td>
<td>3350 +/- 140</td>
<td>23-34</td>
<td>0.46</td>
<td>-</td>
<td>1.3</td>
<td>11</td>
</tr>
<tr>
<td>Hengju</td>
<td>Hengfloc 62020</td>
<td>HPAM</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SNF</td>
<td>FA920SH</td>
<td>PAM</td>
<td>700 +/- 350</td>
<td></td>
<td>0</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SNF</td>
<td>AN-125</td>
<td>Poly(AM-co-AMPS)</td>
<td></td>
<td></td>
<td>0</td>
<td>0.2-0.3</td>
<td>1.2-1.4</td>
<td>4-5</td>
</tr>
<tr>
<td>SNF</td>
<td>SuperPusher SAV301</td>
<td>NVP containing polymer</td>
<td></td>
<td></td>
<td></td>
<td>1.2</td>
<td></td>
<td>2</td>
</tr>
<tr>
<td>SNF</td>
<td>SuperPusher B192, S255, D118</td>
<td>Hydrophobically modified HPAM</td>
<td></td>
<td></td>
<td>0.27</td>
<td>-</td>
<td>failed</td>
<td>N/A</td>
</tr>
<tr>
<td>Hengju</td>
<td>Kypam 5</td>
<td>Sterically modified PAM</td>
<td></td>
<td></td>
<td>0.36</td>
<td></td>
<td>1.5</td>
<td>4-5</td>
</tr>
</tbody>
</table>

Table 2-2: Mixing results with Flopaam 3330S

<table>
<thead>
<tr>
<th>Polymer conc.</th>
<th>Batch</th>
<th>NaCl conc.</th>
<th>Mixing type</th>
<th>Mixing time</th>
<th>F.R.</th>
<th>Viscosity (cp)</th>
<th>Screen time (s)</th>
<th>S.F. Normalized</th>
<th>S.F. Jennings</th>
<th>F.R. Vol Increments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1500 ppm</td>
<td>MF1</td>
<td>2.80%</td>
<td>Overhead @ 400rpm</td>
<td>43 hrs</td>
<td>1.18</td>
<td>8.7</td>
<td>100</td>
<td>4.69</td>
<td>20</td>
<td>66-99/33-66</td>
</tr>
<tr>
<td>1500 ppm</td>
<td>MF1</td>
<td>4.50%</td>
<td>Field Venturi-style</td>
<td>1 hr</td>
<td>1.23</td>
<td>8.4</td>
<td></td>
<td></td>
<td></td>
<td>66-99/33-66</td>
</tr>
<tr>
<td>5000 ppm</td>
<td></td>
<td>0.1%</td>
<td></td>
<td>1 hr</td>
<td>1.24</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>125-175/50-100</td>
</tr>
<tr>
<td>7000 ppm</td>
<td></td>
<td>1%</td>
<td></td>
<td>1 hr</td>
<td>1.47</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>125-175/50-100</td>
</tr>
</tbody>
</table>
Table 2-3: Mixing results with Flopaam 3630S

<table>
<thead>
<tr>
<th>Polymer conc.</th>
<th>Batch</th>
<th>NaCl conc.</th>
<th>Other ions</th>
<th>Mixing type</th>
<th>Mixing time</th>
<th>F.R.</th>
<th>Viscosity (cP)</th>
<th>Screen time (s)</th>
<th>S.F. Normalized</th>
<th>S.F. Jennings</th>
</tr>
</thead>
<tbody>
<tr>
<td>1500ppm</td>
<td>CB2088</td>
<td>3.00%</td>
<td>-</td>
<td>Stirbar</td>
<td>6 hrs</td>
<td>2.06</td>
<td></td>
<td>305</td>
<td></td>
<td>61</td>
</tr>
<tr>
<td>1400 ppm</td>
<td>UE4553</td>
<td>0.50%</td>
<td>0.002% Ca++</td>
<td>Stirbar</td>
<td>3 days</td>
<td>1.9</td>
<td></td>
<td>47</td>
<td>370</td>
<td>3.54</td>
</tr>
<tr>
<td>1400 ppm</td>
<td>UE4553</td>
<td>0.50%</td>
<td>0.002% Ca++</td>
<td>Stirbar/Blender</td>
<td>3 days/5 sec</td>
<td>1</td>
<td></td>
<td>16</td>
<td>125</td>
<td>3.37</td>
</tr>
<tr>
<td>1400 ppm</td>
<td>UE4553</td>
<td>0.50%</td>
<td>0.002% Ca++</td>
<td>Stirbar/Blender</td>
<td>3 days/10 sec</td>
<td>1.1</td>
<td></td>
<td>3</td>
<td>56</td>
<td>6.26</td>
</tr>
<tr>
<td>1400 ppm</td>
<td>Field batch</td>
<td>0.50%</td>
<td>0.3 ppm Fe+++</td>
<td>Fablet</td>
<td>45 minutes</td>
<td>0.9</td>
<td></td>
<td>17</td>
<td>126</td>
<td>3.21</td>
</tr>
<tr>
<td>1500ppm</td>
<td>CB2088</td>
<td>3.00%</td>
<td>-</td>
<td>Stirbar</td>
<td>5 days</td>
<td>1.2-1.4</td>
<td></td>
<td>20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1500ppm</td>
<td>CB2088</td>
<td>3.00%</td>
<td>-</td>
<td>Overhead @ 400rpm</td>
<td>6 hrs</td>
<td>1.48</td>
<td></td>
<td>19.24</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1500ppm</td>
<td>CB2088</td>
<td>3.00%</td>
<td>-</td>
<td>Overhead @ 600rpm</td>
<td>21.5 hrs</td>
<td>1.29</td>
<td></td>
<td>16.6</td>
<td>118</td>
<td>3.07</td>
</tr>
<tr>
<td>1500ppm</td>
<td>CB2088</td>
<td>3.00%</td>
<td>0.1% NaHCO3</td>
<td>Overhead @ 400rpm</td>
<td>~ 24 hours</td>
<td>1.72</td>
<td></td>
<td>18.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1500ppm</td>
<td>CB2089</td>
<td>3.00%</td>
<td>0.1% NaHCO3</td>
<td>Overhead @ 400rpm</td>
<td>~ 24 hours</td>
<td>1.52</td>
<td></td>
<td>18.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1500ppm</td>
<td>CB2088</td>
<td>3.00%</td>
<td>-</td>
<td>Overhead @ 800rpm</td>
<td>16.5 hrs</td>
<td>1.26</td>
<td></td>
<td>14.149</td>
<td></td>
<td></td>
</tr>
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Table 2-4: Mixing results with AN-125

<table>
<thead>
<tr>
<th>Polymer conc.</th>
<th>Batch</th>
<th>NaCl conc.</th>
<th>NaHCO3 conc.</th>
<th>Mixing type</th>
<th>Mixing time</th>
<th>F.R.</th>
<th>Viscosity (cP)</th>
<th>Screen time (s)</th>
<th>S.F. Normalized</th>
<th>S.F. Jennings</th>
<th>F.R. Vol Increments</th>
</tr>
</thead>
<tbody>
<tr>
<td>500 ppm</td>
<td>4558A</td>
<td>3.00%</td>
<td>0.10%</td>
<td>Stirbar</td>
<td>4 days</td>
<td>1.14</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>140-160/40/60</td>
</tr>
<tr>
<td>1000 ppm</td>
<td>4558A</td>
<td>0.10%</td>
<td></td>
<td>Stirbar</td>
<td>4 days</td>
<td>1.36</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>140-160/40/60</td>
</tr>
<tr>
<td>1500 ppm</td>
<td>4558A</td>
<td>3.00%</td>
<td>0.10%</td>
<td>Overhead @ 500rpm</td>
<td>26 hrs</td>
<td>2</td>
<td>7.3</td>
<td>75</td>
<td>4.11</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>1500 ppm</td>
<td>4558A</td>
<td>3.00%</td>
<td>0.10%</td>
<td>Overhead @ 800rpm</td>
<td>43 hrs</td>
<td>1.37</td>
<td></td>
<td>6</td>
<td></td>
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</tr>
</tbody>
</table>
Figure 2-1: Filtration Test Apparatus
Figure 2-2: Screen time for oils through low-volume screen factor device

\[ t = 2.1685\mu + 2.4323 \]

\[ R^2 = 0.9977 \]
Figure 2-3: Effect of mixing speed on resulting solution viscosity and filter ratio. 1500 ppm Flopaam 3630S in 3% NaCl, 17 – 22 hours mixing except as noted.

Figure 2-4: Viscosity loss from filtration of associative polymer
Figure 2-5: Viscosity of low molecular weight polymers in high salinity brine at high shear rate, 38 °C.
Figure 2-6: Viscosity-salinity relationship for low molecular weight polymers
Figure 2-7: Viscosity profile of several commercially available high molecular weight HPAMs as well as Kypam 5, a modified HPAM. 1500 ppm polymer, 23 C.
Figure 2-8: 1500 ppm polymer (unless noted) with 1000 ppm NaHCO$_3$, pH 8-8.5

Figure 2-9: Calculation of intrinsic viscosity for Flopaam 3630S in 1 M NaCl
Figure 2-10: Effect of hardness on viscosity at low degree of hydrolysis. 1500 ppm Flopaam 3630S, 23 C
Figure 2-11: Evolution of viscosity at 38°C with sodium metaborate
Chapter III: Chemical Stability and Calcium Tolerance

LITERATURE REVIEW

Early Work Concerning Chemical Instability of Polyacrylamide

The hydrolysis of polyacrylamide (PAM) and partially hydrolyzed polyacrylamide (HPAM) polymers at elevated temperatures was noted by Muller et al. (1980, 1981a, 1981b) and Shupe (1981) due to the increase of viscosity, change in pH, and evolution of ammonia observed in PAM solutions aged at elevated temperature, as well as precipitation with divalent cations. Muller et al. performed an early and particularly in-depth analysis of the change in viscosity and conformational properties of HPAM with degree of hydrolysis ($\tau$) ranging from 0 to 0.49 in the presence of various amounts of NaCl, MgCl$_2$, and CaCl$_2$. They found that precipitation can occur when $\tau$ exceeded about 0.3, but that this depended on the charge density ($\alpha\tau$), which is the product of $\tau$ and the degree of ionization ($\alpha$), which relates to the pH.

Davidson and Metzner (1982) noted the precipitation of HPAM when aged at 90°C in the presence of calcium and magnesium and determined that this was due to further hydrolysis of the polymer followed by the precipitation of an insoluble salt. After further investigation it was determined that 70°C was the temperature at which precipitation became an issue in seawater for a time period of 200 days.

Zaitoun and Potie (1983) performed a detailed investigation of the precipitation phenomena between HPAM and calcium. They determined that precipitation can occur when the degree of hydrolysis ($\tau$) exceeds 0.35 at 30°C or 0.33 at 80°C. In the limiting conditions of $\tau = 1$, (i.e. complete hydrolysis, or poly(acrylic acid) (PAA)) precipitation occurs at the stoichiometric equivalence point, where 1 mol of Ca$^{++}$ is present for every two moles of acrylate moiety. As degree of hydrolysis decreases, an increasing excess of
calcium over stoichiometric equivalence is required before precipitation occurs, but this excess does not depend on polymer concentration. In this region, the precipitation is described in the terminology of Ikegami and Imai (1962) as a site fixation phenomenon. At lower \( \tau \), below about \( \tau = 0.6 \), the precipitation phenomenon is theta type, resulting from poor solvation. In this region, the critical degree of hydrolysis is independent of polymer concentration and redissolution is observed at very high calcium concentrations.

Zaitoun and Potie also noted that precipitation occurred at higher calcium concentrations when NaCl was added, and that it was difficult to cause precipitation when more NaCl than CaCl\(_2\) was present. In addition it was noted that Ba\(^{++}\) had an effect similar to Ca\(^{++}\), but Mg\(^{++}\) had a lesser effect on precipitation behavior. Finally, it was noted that solution clarity correlated with filterability through 3 \( \mu \)m filters.

**Kinetics of Hydrolysis**

The kinetics of hydrolysis are a strong function of pH, and can be understood as a combination of acid and basic hydrolysis mechanisms and neighbor effects, as well as the buffering effect of evolved ammonium, as explained by Kheradmand (1987). In small molecules, amide hydrolysis proceeds through an acid or basic mechanism. The rate is lowest at neutral pH and increases linearly as pH rises or falls. In a macromolecule, the neighboring units can catalyze or retard hydrolysis. At low pH, protonated neighboring acrylate moieties catalyze further hydrolysis, while at high pH ionized acrylate moieties repel hydroxide molecules resulting in autoretard kinetics, which makes it difficult to achieve \( \tau > 2/3 \) (Kulicke and Horl, 1985) in the lab. Due to the evolution of ammonium ion (pK\(_a\) = 9.7) the pH tends toward around 8.2 as hydrolysis proceeds, complicating the interpretation of results in unbuffered solutions.

It must be noted that there is some disagreement (or rather, hidden variables) in the discussion of the effect of pH on the initial kinetics of PAM hydrolysis in the literature. Muller (1981) reports that hydrolysis of a post hydrolyzed HPAM with initial \( \tau = 0.3 \) is much more rapid at neutral pH than at pH 10 at 90 C, and only slightly more
rapid at neutral pH than at pH 10 at 60°C. Kheradmand (1987), working with a copolymer with initial $\tau = 0.17$, reports initial hydrolysis reaction constants monotonically increasing with pH in the range of 6.3 to 12 at 80°C. Kheradmand astutely observes the contradiction between his results and those of Muller, and attributes this effect to the cotacticity of his sample. As copolymers of acrylamide and sodium acrylate have a less random (i.e. more block like) distribution than post hydrolyzed samples, one would expect fewer amide moieties with 1 or 2 neighboring acrylate moieties, and hence electrostatic interactions between attacking OH$^-$ ions and neighboring acrylate moieties should provide less of a retarding effect in copolymers. Kheradmand goes on to demonstrate this. However there are two other factors that help explain the differences between his experiments and Muller’s experiments. First, the initial degree of hydrolysis was only about half that of Muller’s polymer, which of course lowers the neighboring effects. Somewhat less obvious is the effect that temperature plays, which is apparent from examining Muller’s data, which shows much less of a difference between hydrolysis kinetics at 60°C than at 90°C. If one considers the hydrolysis achievable at room temperature under basic – but not neutral – conditions demonstrated herein and long known to those who have produced HPAM by this method, it is clear that there is a temperature below which hydrolysis is faster under basic conditions for polymers with a low initial degree of hydrolysis.

Moradi-Araghi and Doe (1987) performed a thorough investigation into hydrolysis and precipitation of PAM. Although the pH is not reported, no buffer was used (Moradi-Araghi, 2006) so the pH was likely close to neutral. They found that, at near neutral pH, hydrolysis proceeds slowly but will result in complete hydrolysis of amide moieties after several months at temperatures of 100°C and higher. From experiments at various temperatures, a set of guidelines for the use of PAM and HPAM was developed such that, depending on the amount of calcium present, the expected hydrolysis and the measured cloud point data, the upper temperature limit to avoid
precipitation can be estimated. Thus for very hard brines, a limit of 75°C was identified, whereas for brines with less than 20 ppm of total hardness, there is essentially no temperature limit as far as chemical stability is concerned since completely hydrolyzed PAM (that is, poly(acrylic acid), or PAA) can withstand this much calcium. One criticism of this approach is that, although polymers may not precipitate below these limits, the viscosity may decrease substantially, as indicated in the present work, and this may effectively preclude the use of these polymers under some conditions. Thus the experimental basis for the temperature guidelines commonly used for HPAM may be insufficiently conservative.

Methods for Improving Stability or Calcium Tolerance

Several researchers (Moradi-Araghi et al. (1987); Doe et al. (1987); Taylor and El Din (1985); Martin et al. (1983)) have examined the effects of including co-monomers to improve chemical stability or viscosity in the presence of salt. This may be achieved either by reducing the extent of hydrolysis or by finding other ways to increase the viscosity to negate the reduction of hydrodynamic radius due to shielding by cations. These include:

- Substituting some of the acrylamide moieties within the molecule with other nonionic monomers more resistant to chemical alteration, and whose presence may also stabilize neighboring acrylamide moieties. Examples are N-vinyl pyrrolidone (NVP) and diacetone acrylamide (DAAM).
- Substituting some of the acrylate moieties with another anionic monomer more resistant to cation shielding and/or precipitation itself, and which may also stabilize neighboring acrylamide moieties. An example is sodium 2-acrylamido-2-methylpropane sulfonate (AMPS).
• Sterically hindering the polymer chain so that the hydrodynamic radius does not fully collapse to a random coil configuration at high salinity. These have been called "comb" polymers.

• Adding a small amount of hydrophobe so that intermolecular associations increase solution viscosity, but still allow for flow through porous media.

These mechanisms are not mutually exclusive.

The difficulty in using some of these improved polymers is that their flow properties and long term chemical stability have not been tested to nearly the extent of HPAM. Available data on copolymers of PAM including AMPS and NVP indicate that both moieties are more chemically stable than acrylamide. Also a lower ultimate degree of hydrolysis may result after extended aging when AMPS or NVP is substituted for some of the AM moieties in HPAM (e.g. poly(AM-co-AMPS)), indicating neighbor effects are significant. For the case of AMPS, it has yet to be determined what properties the aged polymer will have, particularly in terms of calcium tolerance. As poly(AM-co-AMPS) ages at high temperature, some of the AM moieties will hydrolyze, leaving AA. Although sulfonate groups are typically regarded as more resistant to precipitation, it is unclear how the resulting terpolymer of AMPS, AA, and AM will behave in the presence of divalent cations. Additionally, Parker and Lezzi (1993) report that the AMPS moiety itself is susceptible to hydrolysis at temperatures above roughly 100 °C. They report a sudden and rapid hydrolysis of AMPS moieties after 50 days at 120 °C and after only 4 days at 150 °C. Using the rule of thumb that rate constants double every 10 °C, it could be expected that at 100 °C hydrolysis of AMPS moieties may occur after approximately 200 days. Hydrolysis of AMPS was not reported by Moradi-Araghi et al. (1987), though it would likely not be detected by titration as the pKa of sulfonates is so low. The symbol σ is used to represent the mol fraction of AMPS moieties on a polymer, analogous to the use of τ to represent mol fraction of AA moiety.
Sodium metaborate ($\text{Na}_2\text{B}_2\text{O}_4 \cdot 8\text{H}_2\text{O}$), is an alkali that has been used in the detergent industry for its ability to sequester calcium. The metaborate ion has an apparent pK$_a$ around 10 (Nguyen et al., 2010). Calcium metaborate has an apparent solubility (Nikolaev and Chelischeva, 1940) around 0.25%.

**EXPERIMENTAL PROCEDURES AND EQUIPMENT**

The experimental approach taken in this paper is as follows: First, PAM, HPAM, poly(AM-co-AMPS) polymers, and other polymers have been aged at temperatures between 25°C and 126°C and pH between 7 and 10.5. These samples contain roughly 0.5M $\text{Na}^+$ with the anions consisting of $\text{Cl}^-$ or a buffer, and contain no calcium. Viscosity, pH, redox potential, and degree of hydrolysis were measured at roughly logarithmically spaced time intervals. From this data, some kinetic data as well as the ultimate degree of hydrolysis after around 1 year was determined.

Analogous laboratory and industrial prepared samples with similar degree of hydrolysis were then prepared or obtained from vendors and tested to determine calcium tolerance as well as salinity tolerance. The onset of turbidity with increasing calcium is defined as calcium tolerance, which has been shown to correspond with the onset of plugging, whereas the decrease in viscosity with the addition of monovalent and/or divalent salts is defined as salinity tolerance. One of the key findings of this research is that the viscosity decline experienced when calcium is added may be a limiting factor prior to the onset of turbidity.

**Chemical stability experiments**

Two rounds of chemical stability experiments were performed. As procedures were still being refined during the first round, more data is available from the second. Of particular note, few NMR data on the degree of hydrolysis were obtained from the first set of experiments, and more ampoules were lost due to the use of inferior ampoules and
sealing techniques. Before discussing the details of the procedure employed for each round of experiments, it is worth explaining some of the experimental issues confronted.

**Notes on the use of sodium dithionite**

Chapter IV discusses thermal stability issues, however a brief mention is necessary here. Several methods have been previously employed to prevent the radical degradation of the acrylic backbone during aging at high temperature. The most common are purification of the polymer solution to remove residual impurities from polymerization (Kheradmand, 1987), removal of oxygen (Yang and Treiber, 1983), or the addition of a stabilizing package (Wellington, 1983). Additional precautions may be required in the presence of iron.

Sodium dithionite is a strong reducing agent, which forms \( \cdot \text{SO}_2 \) radicals in solution that are capable of reducing iron as well as oxygen. While this makes it effective at preventing Fenton-type reactions, it also means that it is very reactive. While \( \cdot \text{SO}_2 \) radicals will not react with the polymer backbone itself, they may react with oxygen to form peroxyl radicals, and this will result in hydrogen abstraction from the polymer backbone, backbone cleavage, and a loss of solution viscosity. Additionally, iron, once brought into the reduced state, can cause degradation upon autoxidation. Whichever of these mechanisms is responsible for the degradation often observed when sodium dithionite-containing polymer solutions are allowed to contact air, it is clear that the mixture of sodium dithionite with oxygen in the presence of polymer should be avoided to the greatest extent possible.

The most important thing to avoid is the introduction of more oxygen once sodium dithionite has been added to the polymer solution. Additional benefit can be obtained by minimizing the amount of oxygen in solution when sodium dithionite is added, or by adding it prior to hydrating polymer. Because polymer hydration takes a day or more under laboratory conditions and it is difficult to exclude oxygen during this whole time as well as during subsequent mixing, the former approach was taken.
Polymer solutions were kept under an argon blanket as much as possible starting after the addition of polymer to the brine solution, and sodium dithionite was added to the final solution immediately prior to putting polymer into ampoules and sealing. Experiments indicated that hydrating the polymer under an argon blanket for several days lowers dissolved oxygen to around 1 ppm. Under those conditions, the viscosity loss when sodium dithionite was added was minimal. After the addition of sodium dithionite, oxygen was rigorously excluded with an argon blanket. When viscosity measurements were made after aging, oxygen was similarly excluded by the use of a wind guard with positive argon pressure fitted to the Contraves LS-30 viscometer.

\textit{Sealing ampoules under vacuum}

In order to prevent the mixture of additional oxygen into polymer solutions containing sodium dithionite, polymer samples were aged in sealed glass ampoules. This method has been reported with success in the literature (Moradi-Araghi et al., 1987). For the first round of experiments, commercially available pre-scored 15 mL Whatman™ ampoules, Fisherbrand™ 5 mL pipettes, and Fisherbrand™ 15mL pipettes were used. A tube was inserted into the bottom of the vessel and argon was used to displace the air inside. Polymer was then injected into the bottom of the vessel with a syringe and the vessel was blanketed with argon and then quickly attached to a flexible hose connected to a vacuum pump. The vessel was then flame sealed under vacuum. After several attempts, it was discovered that the sealing under vacuum of these thin glass ampoules caused a fracture to form at the base of the seal where the curvature was highest, and that this led to air leakage, and in some cases rupture once the samples were placed at temperature. Very few of these samples survived at 100 C. Some samples were potted in epoxy, however many of these leaked as well. The most successful method for sealing in the first round of experiments was achieved by sealing the vessels under atmosphere rather than under vacuum, although this raised concerns about air intrusion during sealing.
Thicker, custom made borosilicate glass ampoules and a manifold for purging with argon and sealing ampoules under vacuum were commissioned from the Department of Chemistry glass shop for the second round of experiments. An oxygen scrubber was made for the inlet gas stream from a tube of copper windings inside a heater. These ampoules have had a much lower incidence of failure.

**Dissolution of silica at high temperature and pH**

Several authors have noted the dissolution of glass or siliceous sand at high temperature and pH, which is of interest not only when glass ampoules are used, but in sandstone reservoirs as well, and as such warrants some discussion here.

Bunge and Radke (1982) claimed alkaline flooding is impossible due to dissolution of quartz, which would greatly retard the propagation of an alkali front. Southwick (1985) found that quartz dissolution only buffers the alkalinity at a slightly lower pH but does not significantly reduce useful alkalinity, defined as that which buffers pH above 9.5. Useful alkalinity is however reduced by the combination of dissolved silica and kaolinite clay in particular to form more silica rich and basic clays (e.g., zeolites). This was not a problem in terms of consumption with sodium carbonate at 80 C, but could be a problem in terms of plugging with zeolites, as indicated by Okoye et al. (1990), however it is important to note that these experiments were done with NaOH at a pH above 13. Most coreflooding data showing permeability loss has been performed with NaOH at a pH of 13 or above, so it is unclear how these results will apply to a pH around 11, resulting from the use of Na$_2$CO$_3$, which is now the most common alkali for EOR.

In steam flooding, bicarbonate in the source water decomposes into CO$_2$ and OH$^-$ at elevated temperatures. CO$_2$ tends to stay in the gas phase whereas OH$^-$ concentration can become elevated at the condensation front, and permeability damage has been reported in these situations as well (Okoye et al., 1990). While lab work must be conducted to determine the temperature limit for use of sodium carbonate, it seems from the lack of permeability reduction at 90 C and minimal reduction at 120 C with 15 wt%
KOH shown by Bertaux and Lemanczyk (1987) that the use of sodium carbonate may in fact be feasible up to 120 C or higher.

An additional challenge that may be anticipated in high temperature alkali applications, and which has particularly challenging experimental implications, is the formation of colloidal silica phases when samples of alkali solutions that have equilibrated at high temperature in the presence of silica are subsequently cooled. While in the field this is a potential production problem, which may be mitigated by the delay in breakthrough of the alkali front, in the lab it leads to difficulty in interpreting viscosity data. Silica solubility increases dramatically at high pH and temperature, and this causes some of the silica to dissolve from the inside of the glass ampoule. When temperature is subsequently lowered, solubility drops and some of the silica in solution precipitates as a colloid, and some silica likely remains in solution as well. Colloidal silica chemistry is complex, and is further complicated by the presence of a polymer that can flocculate it. This is out of the scope of this work, however it is important to recognize its possible involvement as a complicating factor.

Experimentally, the questions of relevance are (i) does the dissolution of silica affect the pH or redox potential of the polymer solution and thus have an effect on the chemical or thermal stability, and (ii) does the dissolved silica itself or condensed or colloidal phases formed affect the solution viscosity. The answers to these questions at this time appear to be (i) no, not in the pH range investigated, and (ii) yes, at least once cooled. The silica in solution may not affect solution viscosity appreciably, although even this may warrant testing, however once cooled the solution is supersaturated and a dense colloidal silica phase forms.

Colloidal silica appeared to be present after cooling samples heated under alkaline conditions, as illustrated in Figure 3-1. While the colloidal phase was not analyzed, similar phases were present after heating ampoules with only Na₂CO₃ and sodium dithionite, but no polymer present. Viscosity measurements made from samples of the
supernatant appear to follow a higher trend than those made on lower temperature or pH samples with a similar degree of hydrolysis, as illustrated in Figure 3-2, indicating that the presence of silica or colloidal silica may have increased solution viscosity in some cases. By comparison, samples heated at lower pH follow a more consistent trend, as will be presented below. Silica does not readily participate in redox reactions, and molecular weight degradation was not observed viscometrically in high pH experiments. Thus while it appears the degree of hydrolysis data from these experiments are valid, the viscosity data should be viewed as likely affected by the presence of dissolved or colloidal silica, and this will be noted in experiments where it is relevant.

First-round chemical stability experiments

The first round of experiments were commenced in the Fall of 2007.

500 g of polymer solution was prepared by slowly adding 0.75 g of polymer powder to the shoulder of the vortex of 499.25 g of a brine solution consisting of 3% NaCl and 0.1% NaHCO$_3$. The resulting solution had a nominal polymer concentration of 1500 ppm, however the moisture content of the polymer powder was typically around 10%, and so the precise concentration was closer to 1350 ppm. This is accurate for all experiments described, and nominal concentrations are reported unless otherwise noted. For TS-6, a 2000 ppm polymer stock was used due to the lower molecular weight of SuperPusher SAV301.

The polymer solution was allowed to hydrate for 2-3 days while mixing slowly under Parafilm® and an argon blanket. After hydration, viscosity was measured using the Contraves LS-30. 2-3 drops of a 2000 ppm solution of resazurin was then added, such that the concentration in the solution was approximately 0.5 ppm. Resazurin is a redox indicator and initially gives a blue color to the solution. Once reduced it is clear, after which it turns pink gradually and reversibly as $E_{Ag+/AgCl}$ increases from about -100 mV to 0 mV. After the resazurin was added, a rigorous argon blanket was established
and sodium dithionite was added from a 8\% stock solution prepared immediately before use and kept under an argon blanket as well. Additionally the pipette used to transfer the sodium dithionite was first flushed with argon.

The dithionite was allowed to mix into the solution under gentle stirring. The solution quickly lost color indicating a highly reduced condition. It was observed that if the solution was stirred rapidly, a pinkish hue returned to the vortex, and so this was avoided. About 5 minutes after the addition of the dithionite, viscosity of the stock solution was carefully measured under an argon blanket to ensure excessive degradation had not occurred from the addition of sodium dithionite. Meanwhile, a syringe and the first vessel were flushed with argon and the filling and sealing of the pipettes was begun.

Pre-scored 15 mL Whitman ampoules, Fisher 5 mL pipettes, and Fisher 15mL pipettes were all used as vessels for polymer samples. As vessels were filled with polymer, the 1/8” tube used to flush the vessel was withdrawn. When the vessel was either 4/5ths full (pipettes) or filled to just below the neck (prescored ampoules) the syringe was removed and then the thumb was used to seal the opening as the tube emitting argon was withdrawn. The vessel was then quickly attached to the tube transmitting vacuum and immediately sealed. As previously mentioned, these vessels were not of sufficient thickness and glass quality to be sealed under vacuum, and many ruptured, either after sealing or when placed in the oven. After sealing about 40 vessels, the viscosity of the stock solution was again carefully measured under an argon blanket to ensure degradation had not occurred during the experiment, and pH and $E_{\text{Ag}/\text{AgCl}}$ were usually measured as well.

The samples were left at room temperature and then examined the next morning. Some samples had turned pink, indicating air leakage. These samples were opened, viscosity was measured, and they were discarded. The remaining samples were placed in the oven, half at 85 C and half at 100 C. For experiments TS-4 and TS-5, it was noticed
that the vacuum sealed pipettes had a fracture at the seal, and so these pipettes were potted in epoxy.

Samples were removed from the oven at roughly exponentially spaced time intervals and viscosity was carefully measured under an argon blanket. Samples that turned pink typically had much lower viscosities and these were assumed to have been contaminated with air and disregarded. After about 200 days, remaining samples were removed and analyzed. At this point a procedure for degree of hydrolysis measurement by NMR had been developed, and so the remaining samples were analyzed for this as well, as described below.

**Second-round chemical stability experiments**

The second round of chemical stability experiments was begun in Spring 2008. In the interim, several improvements were made to the procedure, (i) thicker, borosilicate glass ampoules and a manifold for purging and vacuuming the ampoules were commissioned from the University of Texas Department of Chemistry and Biochemistry glass shop (Figure 3-3); (ii) a stirring vessel capable of mixing under argon atmosphere was commissioned from the glass shop as well, which allowed for better exclusion of air and easier filling of ampoules; (iii) the NMR procedure for measuring degree of hydrolysis was refined, and polymer concentration was increased to 2500 ppm in order to make NMR quantification easier. Additionally, handling procedures had been improved such that the addition of resazurin indicator was no longer deemed necessary; $E_{\text{Ag}/\text{AgCl}}$ would be measured directly and cross-referenced with viscosity to determine if molecular weight degradation had occurred. Because Kheradmand (1987) has shown that concomitant molecular weight degradation only slightly speeds hydrolysis, NMR measurements were sometimes made on samples despite evidence of minor molecular weight degradation, though thoroughly degraded samples were discarded.

Other than the changes noted above, the procedures were similar to those used in the first round of experiments, except for the operation of the manifold for purging and
sealing of ampoules (Figure 3-3). Both vacuum and argon are supplied to the manifold, with the argon run through an oxygen stripping unit made from a stainless steel column packed with copper turnings and placed inside a heater. The manifold is equipped with a 3-way valve at the inlet such that the manifold can be put under vacuum or positive argon pressure with the turn of a switch. Additionally each ampoule slot is fitted with a valve such that individual ampoules can be isolated from the manifold. Prior to filling the ampoules, the manifold was placed under vacuum with each individual ampoule slot valve closed. After being filled with polymer and blanketed with argon, samples were rapidly transferred to the manifold, and as each ampoule was attached to the manifold the corresponding manifold slot valve was opened for 2 seconds and then closed so that the headspace was evacuated. Once all ampoule slots had been filled each individual ampoule slot valve was again opened. When the vacuum/pressure gauge reached a steady value (typically about -24 inches Hg), the manifold 3-way valve was switched to argon. When the vacuum/pressure gauge reached 15 psi, the manifold 3-way valve was switched back to vacuum and the cycle was repeated. After three cycles, with the manifold under argon pressure, the individual ampoule valves were each closed and then the manifold 3-way valve was switched back to vacuum. Each ampoule valve was then opened while the corresponding ampoule was flame sealed, and then closed again.

For the second round of experiments, samples were placed at 35 C, 55 C, 70 C, 85 C, 100 C, and 126 C, however an oven malfunction caused the loss of most 55 C samples. The polymers used in the second round of experiments were primarily FA920SH, an unhydrolyzed polyacrylamide, and AN-125, a poly(AM-co-AMPS) copolymer of a similar molecular weight. Experiments were buffered with sodium carbonate (pH ~11) and monosodium phosphate/bisodium phosphate (pH ~6.7), though in mixing pH seems to have dropped slightly. Each experiment was designed with the total amount of sodium to be similar to that in the first experiments, i.e. around 0.5 M
including the buffer when applicable. Table 3-1 presents the conditions for chemical stability experiments undertaken during rounds 1 and 2.

**In-NMR tube chemical stability experiments**

Some polymer samples were sealed in NMR tubes and heated as such. This method presents both advantages and disadvantages compared to the method described above. The primary advantage is its simplicity. Only one sample must be made, and measurements are made on the same sample each time. Additionally there is less time delay between removing the sample from the oven and starting the NMR run, allowing short time scale kinetics to be more easily observed. The primary disadvantage is the necessity for high (2-4 wt%) polymer concentration in order to get NMR response in a reasonably short time, as explained below. This causes two complications: first, there is the possibility that the order of magnitude increase in polymer concentration over that used in the field causes the rate of hydrolysis to increase, though there is nothing in the literature to this effect; and second the buffering capacity required to prevent the large amount of ammonia that is released in the event of full hydrolysis (about 0.5 M) may exceed the solubility limits of the buffers. The second concern can be mitigated at pH 8.2, as this is the pH to which the solution is driven as by the evolution of ammonia. In addition, if a large amount (0.5 M or so) of buffer can be solubilized, the pH may remain almost constant until hydrolysis exceeds around 50%, so early kinetics may be observed. One final difficulty with these experiments is the inability to make viscosity or wet chemistry measurements until the end of the experiment.

It should be noted that in these experiments, as with the other chemical stability experiments, times reported correspond to heating times, even though sometimes samples waited in queue for long times prior to NMR measurements. When heating times and/or temperatures were low compared to wait times, samples were discarded, as it was no longer plausible that hydrolysis was solely representative of that obtained during heating.
Low-Temperature Hydrolysis

Samples of PAM, HPAM, and poly(AM-co-AMPS) polymers were hydrolyzed at room temperature under alkaline conditions and low temperature for use in calcium and salinity tolerance experiments. A number of approaches were taken in order to maximize the degree of hydrolysis and concentration of the stock generated while at the same time minimizing the salinity after neutralization as well as the time required for extensive hydrolysis. In the first attempts, a 5000 ppm polymer stock was hydrated in 1 M NaOH for several days under an argon blanket at room temperature, such that extensive hydrolysis occurred during hydration. After several days, the stock was neutralized by addition of HCl. A sample of the stock was analyzed by NMR for degree of hydrolysis, as described below. The remainder of the stock was divided between ultrafiltration cells and concentrated, then diluted with deionized water in order to lower the salinity. While extensive hydrolysis was readily achieved, lowering the salinity proved challenging as effluent from the ultrafiltration cells consistently had lower salinity than expected, indicating an association with the polymer.

In later experiments, polymer concentration was raised to 10,000 ppm and NaOH concentration was lowered to either 0.5 M or 0.1 M so that an acceptably low salinity could be achieved after neutralization solely through dilution. Table 3-2 presents the conditions and hydrolysis achieved in samples prepared by low-temperature hydrolysis.

Degree of Hydrolysis Measurement by NMR

NMR work was performed by UT Analytical Services Laboratory in the Department of Chemistry and Biochemistry using a Varian Inova 500. A delay time of 2 s was determined to be necessary from preliminary experiments, and approximately 900 cycles were acquired (1 hour acquisition time). In some cases where insufficient amounts of polymer were recovered, acquisition time was increased to 16 or 64 hours. Peaks were assigned to the carbonyl carbon of acrylamide (180 ppm), acrylate (183 ppm), and AMPS
moieties (Parker and Lezzi, 1993). The concentration in mol % of each moiety was calculated as the fraction of the integration of the peak corresponding to the carbonyl carbon of that moiety divided by the sum of the integration of all carbonyl peaks.

It was determined that 3-4 wt% polymer was required to obtain a sufficiently low signal to noise ratio in one hour. In order to lower the viscosity such that high molecular weight polymers of this concentration could be hydrated, much less transferred into a 5 mm NMR tube, salinity of at least 3% was used in all experiments. In addition, 10% D₂O (Fisher Scientific) was added to all samples.

Initial degree of hydrolysis was determined by dissolving 4 wt% polymer in 10 wt% D₂O with 3% NaCl. This was performed with all polymers used.

In order to measure degree of hydrolysis during chemical stability experiments, 2-3 ampoules were analyzed for viscosity, pH, and E_{Ag⁺/AgCl}, and if results were comparable for each sample they were combined into an ultrafiltration cell. D₂O was added such that it made up approximately 10% of the volume in the cell and then the contents were concentrated in the cell under 50 psi argon pressure over a 100,000 molecular weight ultrafiltration membrane. Once sample size had been reduced to 1-2 mL, the sample is transferred to the NMR tube. In some cases, volume is reduced to less than 1 mL or to a thin film on the membrane, and had to be reconstituted by addition of D₂O. After transferring the concentrated polymer solution into the NMR tube, the tube was centrifuged to remove air bubbles from solution.

**Salinity Tolerance**

Salinity tolerance experiments were performed with several PAM, HPAM, and poly(AM-co-AMPS) polymers. A 5000 ppm polymer stock was prepared as described in the preceding chapter. 10 mL samples of 1500 ppm polymer with incrementally increasing salinity were prepared in 20 mL vials, then mixed using a vortex mixer. Typically only NaCl was added, but in some cases CaCl₂ was used with a fixed NaCl
background, or hard brines containing both NaCl and CaCl₂ were used. The somewhat arbitrary distinction used between salinity tolerance and calcium tolerance is that in salinity tolerance we are looking at viscosity loss where precipitation is not an issue, such as at low degree of hydrolysis or low hardness, whereas in calcium tolerance experiments we are examining the onset of precipitation phenomena. Salinity tolerance experimental conditions are presented in Table 3-3.

Calcium Tolerance

Calcium tolerance experiments were performed with extensively hydrolyzed PAM, HPAM, and poly(AM-co-AMPS) polymer samples prepared by low-temperature hydrolysis, as described above. In these experiments, 10 mL samples of 1500 ppm polymer were prepared with a constant Na⁺ background and incrementally greater amounts of calcium. Viscosity and/or the onset of turbidity was observed. Typically this would be performed with several different Na⁺ backgrounds, as calcium concentration is a strong function of Na⁺ concentration. Sodium was added either as NaCl, sodium metaborate (Na₂B₂O₄•8H₂O), or a combination of the two. In neutral-pH experiments, tris buffer was sometimes used in order to keep the pH constant. Experiments indicated that this did not affect the viscosity of polymer solutions substantially. Calcium tolerance experimental conditions are presented in Table 3-4.

Chemical Stability Experimental results

Figures 3-4 through 3-8 present viscosity data for the first round of chemical stability experiments, as well as degree of hydrolysis for final samples after 220 days for some of the experiments. Although many of the individual ampoules leaked, enough survived to draw a few important conclusions. In particular, many of the early samples in experiment TS-5 at 100 C seem to have experienced leaks and thus had low viscosities. After the first few days, leaky samples tend to fail or show signs of evaporation through a
fissure, but as ORP and dissolved oxygen were not measured in these early experiments, leakage could not be verified and so the viscosity measurements are reported.

The first point that should be noted is that none of these samples experienced a decline in viscosity, indicating that the backbone is thermally stable for long periods of time under these conditions, which include the presence of 200 – 400 ppm sodium dithionite. This will be discussed further in Chapter IV. In TS-7 (Figure 3-8) at 100 C, which was shown by NMR to be fully hydrolyzed at the end, there is an increase in viscosity followed by a decrease back to the original viscosity, which is the evolution of viscosity to be expected as full hydrolysis occurs.

Figure 3-9 presents degree of hydrolysis data for the few samples for which measurements were successfully made, as well as similar data from Moradi-Araghi and Doe (1987) and Moradi-Araghi et al. (1987). The PAM/HPAM data falls on a similar trend, whereas the poly(AM-co-AMPS) data does not, which is not surprising, as the copolymers in our respective studies contained different amounts of AMPS.

Plotting the sum of acrylate (AA) moieties and AMPS moieties, as shown in Figure 3-10, reveals that the relationship between total anionicity and temperature is close not just for poly(AM-co-AMPS) polymers with different amounts of AMPS, but also between these polymers and conventional HPAMs.

Between the first and second rounds of chemical stability experiments, a series of in-NMR tube chemical stability experiments were undertaken, as presented in Figures 3-11 through 3-15. These experiments demonstrated the complete hydrolysis of AMPS moieties at 100 C, as well as a number of interesting differences between the kinetics of acrylamide hydrolysis under neutral and alkaline conditions. Figure 3-11 demonstrates the hydrolysis of all AMPS moieties to carboxylate moieties between 16 and 380 days at 100 C and pH around 8, as predicted. While hydrolysis is relatively slow even at 100 C at pH 8.2 (Figures 3-12 and 3-13), under alkaline conditions rapid and extensive hydrolysis occurs after only 6 hours of heating at temperatures as low as 55 C, and even
at 23 C significant hydrolysis had occurred by the time the first measurement could be taken (Figure 3-14). After the first sample at 55 C and above under alkaline conditions, experiments were terminated since ammonia liberated by hydrolysis was nearing the buffer capacity of the solutions, and constant pH could no longer be assumed. It must be noted that this relationship between pH and kinetics is similar to that obtained by Kheradmand (1987) (his attempt to explain them away notwithstanding) and opposite those obtained by Muller (1981). The data obtained by Muller under neutral conditions and at 90 C agree fairly well with those obtained in the present study at pH 8.2 and 100 C, with both increasing from $\tau = 0.3$ to about $\tau = 0.5$ in two weeks. The major disagreement occurs between Muller’s data at pH 10 and 90 C and that of the present study at pH 11 and temperatures between 85 C and 100 C presented in Figure 3-14. Despite starting with an originally unhydrolyzed polymer, about 50% hydrolysis has occurred after only 6 hours in the present study, compared with an increase from only $\tau = 0.3$ to $\tau = 0.38$ in two weeks reported by Muller. Since at some point during the 6 hours of heating the polymer in the present study must have been similar to that in Muller’s experiment, it is hard to understand the vastly different results, although the high polymer concentration could play a role in driving the reaction towards the products. In either case, more data is necessary before this long-standing discrepancy can be resolved.

The results for the second round of long-term chemical stability experiments are presented in Figures 3-16 through 3-28. The focus of these experiments was alkaline conditions, particularly a pH of around 10-11, that coincides with the use of sodium carbonate, for example in an ASP injection. The first thing to note is that the kinetics of hydrolysis in these alkaline experiments agree well with those obtained in the high-concentration, in-NMR tube experiments just described, making the idea that rapid kinetics were merely an artifact of the high concentration less plausible.

Another interesting result from this experiment is that, despite the initial rapid kinetics observed at all temperatures under alkaline conditions, at all temperatures
hydrolysis almost completely ceases, reaching a plateau between 65% and 80%, though full hydrolysis of the HPAM copolymer occurred by 288 days, as presented in Figure 3-23. Thus despite the occurrence of a much higher degree of hydrolysis at low temperatures than that occurring under neutral conditions, the autoretarded kinetics resulting from the dissociated carboxylate groups result in a lower ultimate degree of hydrolysis at 100 C. While at very high temperatures (above about 85 C) a lower ultimate degree of hydrolysis occurs under alkaline conditions, at lower temperatures the opposite relationship exists, as illustrated in Figure 3-29.

Results for experiment TS-105 indicate nearly complete hydrolysis of a PAM at 85 C in about 170 days, as illustrated in Figure 3-21. This is higher than the value of around 0.7 expected from earlier experiments as well as from interpolation of the data of Moradi and Doe (1987). One possible explanation of this is the pH, which was around 6.4 in this and other experiments performed using a combination of phosphate buffers. As pH tends towards more acidic conditions, acidic hydrolysis, which is autocatalytic rather than autoretarding, plays a more important role. Additionally, the 85 C oven had much poorer temperature control than the other ovens used, and it is plausible that during some periods the temperature may have exceeded 90 C. The results of TS-106, in which an HPAM (τ = 0.3) was aged with Na₂CO₃ in the same oven, are interesting for comparative purposes. After 290 days, degree of hydrolysis reaches only 0.85, despite the initial degree of hydrolysis. This unequivocally demonstrates a benefit in terms of retarded hydrolysis at high pH. While this effect may seem minor as the difference in resulting degree of hydrolysis at temperatures of 85 C and above may be only 0.15-0.20, this is not the case. As demonstrated by Kulicke and Horl (1985) at slightly lower salinity (0.1M Na₂SO₄), the intrinsic viscosity drops off dramatically as a function of degree of hydrolysis after peaking around τ = 0.7, such that by τ=1 it has returned to a value close to that at τ = 0.
Viscosities are presented for experiments TS-102, TS-103, and TS-106 in Figures 3-17, 3-20, and 3-24 respectively despite the probable confounding presence of colloidal silica. Also, molecular weight degradation is more difficult to identify by a rise in $E_h$ early in an experiment, so the conservative approach is to present all data despite the noise, which is likely due to the presence of small leaks in some ampoules.

The biggest disappointment from the first round of long-term chemical stability experiments was the failure to obtain degree of hydrolysis results for aged poly(AM-co-AMPS) copolymers, in order to extend the results of Parker and Lezzie (1993). Figures 3-25 and 3-26 demonstrate the full hydrolysis of AMPS moieties at 100°C and pH 6.4 between 12 and 133 days, slightly earlier than predicted above. This data and the data from experiment TS-30 are presented together in Figure 3-27. This earlier than expected AMPS hydrolysis may be a result of the pH, which was slightly lower than intended. Parker and Lezzie report that hydrolysis at pH 6 is about 5 times faster than at pH 8 with a similar polymer. Interestingly as of 330 days, the amount of AMPS moiety has remained the same in samples aged at 100°C under alkaline conditions (Figure 3-19). This demonstrates that Parker and Lezzie’s theory of sudden, complete hydrolysis of AMPS once acrylamide is reduced below 25 mol% due to intermolecular catalysis does not apply at high pH, where it seems that the same autoretard kinetics that prevent full hydrolysis of PAM limit the hydrolysis of the AMPS moiety. A summary of data presented here and by Parker and Lezzie concerning stability of poly(AM-co-AMPS) polymer containing approximately 25mol% AMPS is presented in Figure 3-30. According to the Arrhenius model, which seems to fit the data for 100°C, 120°C, and 150°C reasonably, at 85°C hydrolysis of AMPS moieties should occur after around 500 days. These data only apply to pH near neutral, as hydrolysis is retarded under alkaline conditions.
CALCIUM AND SALINITY TOLERANCE EXPERIMENTAL RESULTS

Preliminary calcium and salinity tolerance experiments were performed with a series of HPAM copolymers ranging from $\tau = 0$ (polyacrylamide) to $\tau = 1$ (poly(acrylic acid)) of roughly the same molecular weight. Before presenting the results obtained with these, the limitations of this method should be plainly presented. Because of the difficulty of viscometrically comparing molecular weight between polymers of different degrees of hydrolysis, as well as the slightly differing reactivities of the two monomers, it is challenging to determine whether the molecular weights of each of the set of polymers supplied are the same or not. This makes the exact determination of the relationship between viscosity, salinity, and degree of hydrolysis difficult. Nevertheless, the general relationships can be determined to the extent that molecular weights are comparable, as presented in Figures 3-31 and 3-32.

A more subtle yet equally important limitation to the use of copolymers is the effect of tacticity on calcium tolerance. While some basic relationships between calcium tolerance, degree of hydrolysis, and background salinity, as well as the beneficial use of sodium metaborate, were determined with these copolymers, it was soon realized that at high degrees of hydrolysis the calcium tolerance of copolymerized polymers was much lower than that of post-hydrolyzed polymers. Because these polymers were used as surrogates for aged polymers that would be expected to hydrolyze in a random manner, the low calcium tolerance of copolymers, which is thought to result from the block-like nature of the distribution of moieties, is unnecessarily pessimistic. In some cases, such as the comparison to aged AMPS copolymers, this seems to dominate the results.

Nevertheless, some preliminary observations made using copolymers are valid and useful. Figure 3-33 presents the calcium tolerance of a copolymer with high degree of hydrolysis ($\tau = 0.66$). As discussed above, this amount of hydrolysis is relevant for polymers undergoing extended aging at around 85 C as well as at almost any temperature.
under alkaline conditions, and so many experiments will focus on this and similar polymers. In this and following figures, lines connect points corresponding to the interpolation between the clear sample with the highest and the cloudy sample with the lowest amount of calcium, as is clearly seen in Figure 3-33. In following figures the points corresponding to each sample have been removed for simplicity, however in each case the onset of cloudiness was refined until it was determined within 100 ppm. Additionally all subsequent experiments are performed with 1500 ppm polymer and at 23 C, unless otherwise stated. Figure 3-34 shows the decrease in calcium tolerance with increasing temperature. Figure 3-35 shows the general relationship where calcium tolerance increases with increasing monovalent cation concentration and decreasing degree of hydrolysis.

The effect of degree of hydrolysis on calcium tolerance for copolymers is shown in terms of both the onset of turbidity (Figure 3-36), which draws a hard limit in the amount that can be tolerated, as well as viscosity loss (Figure 3-37), which may render polymer effectively useless prior to the onset of turbidity in some cases.

As demonstrated in Figures 3-38 through 3-40, sodium metaborate may improve both of these aspects of calcium tolerance. However, the benefit is not seen with PAA (Figure 3-41). With less hydrolyzed polymers, one interesting phenomenon is the increase in calcium tolerance exhibited over a relatively narrow sodium metaborate concentration of around 0.5%. This agrees closely with the apparent solubility (Nikolaev and Chelischeva, 1940) of calcium metaborate of 0.25%. Additionally, when a much greater amount of sodium metaborate is added, viscosity remains essentially constant with the addition of calcium, despite the onset of turbidity at the same calcium concentration as without sodium metaborate. Unfortunately these two phenomena do not seem to occur simultaneously, as illustrated in Figure 3-42.

Figure 3-43 shows the calcium tolerance of a post-hydrolyzed polymer with high degree of hydrolysis with and without sodium metaborate. Even without metaborate, the
calcium tolerance of this polymer is much higher, and the increasing tolerance with added sodium is much more significant. Adding sodium metaborate as much as doubles the calcium tolerance.

One complication with the use of any alkali is the possibility of mineral precipitation, often with calcium. While metaborate does not explicitly precipitate with calcium, as pH is increased precipitation may occur, particularly if any bicarbonate, which will be dissociated into carbonate as the pH increases past around 9, is present (Figures 3-44 and 3-45).

Copolymers including AMPS have the potential to increase calcium tolerance as well compared to conventional HPAM. Figure 3-46 demonstrates that, despite early evidence to the contrary obtained with a copolymer, presence of AMPS moieties in a highly chemically degraded polymer does not seem to raise the onset of turbidity. However, viscosity is substantially higher as the tolerance limit is approached, as shown in Figure 3-47. Figure 3-48 demonstrates how both AMPS and sodium metaborate can be used together to improve calcium tolerance. As illustrated in Figure 3-49, calcium tolerance increases greatly with sodium background. With 10% NaCl background, an extensively hydrolyzed poly(AM-co-AMPS) copolymer tolerated over 5000 ppm of calcium without exhibiting turbidity or viscosity loss. A similarly hydrolyzed NVP-containing polymer exhibited no viscosity loss up to 10,000 ppm of calcium, though slight turbidity appeared at this point. These results are so much better than those at lower salinities that further attention was warranted. As dissolution of silica had been such a complicating issue in high-temperature experiments, this round of accelerated aging was performed in plastic containers. It was hypothesized that supersaturation with silica may have led to lower viscosities and earlier precipitation in earlier experiments performed in glassware, however lower salinity background points from earlier experiments were repeated with similar results. Additionally, 20 mM tris buffer was used in this final round of experiments, but investigations determined that this did not
appreciably affect calcium tolerance. Because these results are so different than those obtained with the industrially prepared post-hydrolyzed sample with high degree of hydrolysis, it is suggested that experiments with post-hydrolyzed PAM be repeated as prepared above.

A final study was undertaken to hydrolyze a series of polymers of identical molecular weight through alkaline hydrolysis of PAM at room temperature in order to better quantify the relationship between viscosity, salinity and degree of hydrolysis described above, and these results are presented in Figures 3-50 and 3-51. Results of these experiments are different than expected. A maximum in viscosity at around $\tau = 0.6 - 0.7$, as has been reported by Kulicke and Horl, only occurred at rather low salinity. For around 1-2% NaCl there was little change in viscosity with degree of hydrolysis above 0, and at higher salinity the maximum viscosity occurred with $\tau = 0.43$. This is not inconsistent with results generated above, for instance in Figure 3-2, and would in fact explain some of the heretofore inexplicable variability in viscosity early in the aging experiments as viscosity passes through a maximum with respect to $\tau$. However, though these solutions were hydrolyzed at room temperature, the use of 0.1-1 M NaOH in glass beakers may have caused some silica dissolution, and this may again have affected the solution viscosity.

**DISCUSSION**

The most significant finding of this work is the rapid hydrolysis of PAM under alkaline conditions to a nearly temperature independent value of 60-80%. This represents a great deal more than would be experienced under neutral conditions at low temperature (below around 85 C) but a slight reduction in what would be experienced at high temperature after an extended period of time. Calcium tolerance experiments indicate this reduction would provide a significant benefit at high temperatures. The implications of these findings at low temperatures are that chemical stability and calcium tolerance
issues must be evaluated for all ASP floods, regardless of temperature. In most cases, increased hydrolysis will increase viscosity, providing a benefit. At the same time, precipitation of calcium with alkali will almost always precede the onset of calcium tolerance issues under alkaline conditions. That is to say, the calcium tolerance of the brine, rather than the polymer, should be the limiting factor in the design of ASP floods. A further benefit of rapid hydrolysis at high pH is the potential for injecting less viscous unhydrolyzed PAM or low-degree of hydrolysis HPAM in order to increase injectivity drastically. Even at low temperature the degree of hydrolysis and viscosity will increase to a maximum over the course of a few days. This concept will be explored further in a later chapter.

Another significant finding is the lability of AMPS moieties at 100 C and pH 6.4 – 8, though not at pH 10 – 11 in the timescale of interest. This suggests that there is little benefit to using a poly(AM-co-AMPS) polymer rather than conventional HPAM at 100 C.

Calcium tolerance was examined not only in terms of the onset of turbidity, as has been done in previous papers and the results of which have been used to set current safe limits for the use of HPAM, but also in terms of the viscosity loss experienced as precipitation is approached. The latter property will make the use of polymer uneconomical in some cases far before the onset of turbidity, and so in some cases these old guidelines may not be sufficiently conservative.

Both incorporation of AMPS and/or NVP moieties and the use of sodium metaborate have been seen to increase calcium tolerance significantly under certain conditions. While the inclusion of AMPS moieties did not appear to significantly delay the onset of turbidity under the conditions studied (using lab produced analogues comparable to the molecules produced during aging tests), viscosity remains much higher as the point where precipitation occurs is approached. The conditions studied are representative of extended aging at 85 C or under alkaline conditions at any temperature.
Using similar analogues, sodium metaborate increases calcium tolerance almost two-fold when 0.6 wt% is added, but the effect diminishes if more is used. This amount corresponds with literature values for the apparent solubility of calcium metaborate. At higher concentrations, the decrease in viscosity as precipitation approaches is forestalled. This property is not seen at the lower concentration where calcium tolerance is increased, so one must choose between these two possible beneficial properties. It should be noted that preliminary tests with PAA did not find a benefit in terms of calcium tolerance when sodium metaborate was used, however, as noted above, complete hydrolysis under alkaline conditions does not seem to occur readily. When both AMPS containing polymers and sodium metaborate are used, a greater benefit is observed than when either is used alone.

One concern about the use of sodium metaborate, which will hold with any agent that raises pH to 10 or more, is the conversion of bicarbonate ions in solution to carbonate, which will precipitate with calcium at very low levels. This reemphasizes the point made above, that despite the extensive hydrolysis observed under alkaline conditions, geochemical calcium tolerance and not polymer calcium tolerance will usually be the more relevant design constraint.

An interesting complication that was encountered, which greatly obfuscated interpretation of viscosity measurements that were made on polymer samples that had been aged under alkaline conditions, was the dissolution of silica from the glassware used to age them, particularly when the samples were aged at high temperature. Although the results were most noticeable in high temperature samples that exhibited colloidal silica precipitates when cooled, the presence of varying amounts of dissolved silica may explain the discrepancy between the viscosity-degree of hydrolysis relationships of samples aged at high and low temperature under alkaline conditions. While the presence of dissolved silica is treated here as an experimental complication, it may prove to have some relevance in the field, as silica will likely dissolve from silicate formations in
similar quantities. While the viscosity in the reservoir may not be affected by the
colloidal precipitates seen in samples cooled after heating, these too may be relevant
during production.
Table 3-1: Chemical Stability Experiments

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<tr>
<th>Experiment</th>
<th>Start date</th>
<th>Polymer conc</th>
<th>Polymer</th>
<th>Buffer</th>
<th>pH</th>
<th>NaCl</th>
<th>Na$_2$S$_2$O$_4$</th>
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<td>1500 ppm</td>
<td>Flopaam 3330S</td>
<td>1000 ppm NaHCO$_3$</td>
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<td>100 ppm</td>
<td>1 ppm resazurin, small ampoules potted in epoxy</td>
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<td>AN-125 lot 4558A</td>
<td>1000 ppm NaHCO$_3$</td>
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<td>200 ppm</td>
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<td>Flopaam 3630S</td>
<td>1000 ppm NaHCO$_3$</td>
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<td>1 ppm resazurin, 5 and 20 mL pipettes potted in epoxy</td>
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<td>Flopaam 3630S</td>
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<td>2%</td>
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<td>2%</td>
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<td>2%</td>
<td>400 ppm</td>
<td>Improved ampoules and manifold *126 C in 12/18/08</td>
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<td>7.2</td>
<td>2%</td>
<td>400 ppm</td>
<td>Improved ampoules and manifold</td>
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</table>
Table 3-2: Low-Temperature Hydrolysis Experiments

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Polymer</th>
<th>NaOH</th>
<th>°C</th>
<th>Time</th>
<th>τ</th>
<th>σ</th>
<th>Lab ware</th>
</tr>
</thead>
<tbody>
<tr>
<td>HAMPS 1</td>
<td>AN-125</td>
<td>1 M</td>
<td>23</td>
<td>5 days</td>
<td>0.4</td>
<td>0.27</td>
<td>glass beaker</td>
</tr>
<tr>
<td>HAMPS 3</td>
<td>AN-125</td>
<td>1 M</td>
<td>23</td>
<td>5 days</td>
<td>0.38</td>
<td>0.23</td>
<td>glass beaker</td>
</tr>
<tr>
<td>HAMPS 4</td>
<td>AN-125</td>
<td>1 M</td>
<td>23</td>
<td>5 days</td>
<td>0.38</td>
<td>0.26</td>
<td>plastic beaker</td>
</tr>
<tr>
<td>HSAV301</td>
<td>SAV301</td>
<td>1 M</td>
<td>23</td>
<td>5 days</td>
<td>0.18</td>
<td>-</td>
<td>plastic beaker</td>
</tr>
<tr>
<td>JW1</td>
<td>FA920SH</td>
<td>0.1M</td>
<td>23</td>
<td>8 days</td>
<td>0.43</td>
<td>-</td>
<td>glass beaker</td>
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<tr>
<td>JW2</td>
<td>FA920SH</td>
<td>1 M</td>
<td>23</td>
<td>8 days</td>
<td>0.62</td>
<td>-</td>
<td>glass beaker</td>
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<tr>
<td>JW3</td>
<td>FA920SH</td>
<td>0.1M</td>
<td>23</td>
<td>2 days</td>
<td>0.3</td>
<td>-</td>
<td>glass beaker</td>
</tr>
<tr>
<td>GC1</td>
<td>FA920SH</td>
<td>1 M</td>
<td>23</td>
<td>10 days</td>
<td>0.59</td>
<td>-</td>
<td>plastic beaker</td>
</tr>
</tbody>
</table>

Table 3-3: Salinity Tolerance Experiments

<table>
<thead>
<tr>
<th>Polymer Conc.</th>
<th>Polymer</th>
<th>τ</th>
<th>Buffer</th>
<th>Notes</th>
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<tr>
<td>1500 ppm</td>
<td>JW3</td>
<td>0.3</td>
<td>Tris</td>
<td>Post-hydrolyzed lab samples</td>
</tr>
<tr>
<td>1500 ppm</td>
<td>JW2</td>
<td>0.6</td>
<td>Tris</td>
<td>Post-hydrolyzed lab samples</td>
</tr>
<tr>
<td>1500 ppm</td>
<td>JW1</td>
<td>0.4</td>
<td>Tris</td>
<td>Post-hydrolyzed lab samples</td>
</tr>
<tr>
<td>1500 ppm</td>
<td>ALP-99</td>
<td>1</td>
<td>Tris</td>
<td></td>
</tr>
<tr>
<td>1500 ppm</td>
<td>FA920SH</td>
<td>0</td>
<td>Tris</td>
<td></td>
</tr>
<tr>
<td>1500 ppm</td>
<td>Hengfloc 63020</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1500 ppm</td>
<td>Hengfloc 63026</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1500 ppm</td>
<td>Kypam 5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1500 ppm</td>
<td>ALP-99</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1500 ppm</td>
<td>FA920SH</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1500 ppm</td>
<td>Flopaam 3330S</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1500 ppm</td>
<td>AN977SH</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>1500 ppm</td>
<td>Flopaam 3630S</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1500 ppm</td>
<td>Flopaam 3630S</td>
<td></td>
<td></td>
<td>9:1 (NaCl/CaCl2) scan</td>
</tr>
<tr>
<td>1500 ppm</td>
<td>AN-125</td>
<td></td>
<td></td>
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<tr>
<td>2000 ppm</td>
<td>SuperPusher SAV301</td>
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<tr>
<td>Date (approx.)</td>
<td>Polymer Conc.</td>
<td>Polymer</td>
<td>τ</td>
<td>σ</td>
</tr>
<tr>
<td>---------------</td>
<td>---------------</td>
<td>----------</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>Fall 2007</td>
<td>1500</td>
<td>AN-977</td>
<td>0.66</td>
<td>Scan</td>
</tr>
<tr>
<td>Fall 2007</td>
<td>Differing</td>
<td>AN-977</td>
<td>0.66</td>
<td>2500</td>
</tr>
<tr>
<td>Fall 2007</td>
<td>1500</td>
<td>AN-977</td>
<td>0.66</td>
<td>No</td>
</tr>
<tr>
<td>Fall 2007</td>
<td>1500</td>
<td>FP 3330</td>
<td>0.27</td>
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</tr>
<tr>
<td>Fall 2007</td>
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<td>AN 956 MPM</td>
<td>0.5</td>
<td>Scan</td>
</tr>
<tr>
<td>Spring 2008</td>
<td>1500</td>
<td>ALP-99</td>
<td>1</td>
<td>Scan</td>
</tr>
<tr>
<td>Spring 2008</td>
<td>Differing</td>
<td>ALP-99</td>
<td>1</td>
<td>2500</td>
</tr>
<tr>
<td>Spring 2008</td>
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<td>Hengfloc 63020</td>
<td>0.39</td>
<td>No</td>
</tr>
<tr>
<td>Spring 2008</td>
<td>1500</td>
<td>ALP-99</td>
<td>1</td>
<td>2500</td>
</tr>
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<td>Spring 2008</td>
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<td>HAMPS1</td>
<td>1</td>
<td>2500</td>
</tr>
<tr>
<td>Spring 2008</td>
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<td>AN-977</td>
<td>0.66</td>
<td>2500</td>
</tr>
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<td>HAMPS1</td>
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<td>Spring 2008</td>
<td>750</td>
<td>HAMPS1</td>
<td>25</td>
<td>2,500</td>
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<td>AN 945 MPM</td>
<td>0.38</td>
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</tr>
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<td>Spring 2008</td>
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<td>0.5</td>
<td>20,000</td>
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<td>0.3</td>
<td>20,000</td>
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<tr>
<td>Summer 2008</td>
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<td>No</td>
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<td>Summer 2008</td>
<td>1500</td>
<td>HF 63214</td>
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<tr>
<td>Summer 2008</td>
<td>1500</td>
<td>HF 64814</td>
<td>0.59</td>
<td>12,500</td>
</tr>
<tr>
<td>Summer 2008</td>
<td>1500</td>
<td>HAMPS3</td>
<td>25</td>
<td>Scan</td>
</tr>
<tr>
<td>Summer 2008</td>
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<td>HAMPS4</td>
<td>0.38</td>
<td>0.26</td>
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<td>Spring 2009</td>
<td>1500</td>
<td>HSAV301</td>
<td>0.18</td>
<td>100,000</td>
</tr>
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<td>Spring 2009</td>
<td>1500</td>
<td>GCI</td>
<td>0.59</td>
<td>100,000</td>
</tr>
</tbody>
</table>
Figure 3-1: Colloidal silica present in ampoules after heating under alkaline conditions followed by cooling
Figure 3-2: Alkaline samples aged at high temperature in glass have a higher viscosity than those with the same degree of hydrolysis that were aged at lower temperatures.

Colloidal silica visible in ampoules

Figure 3-3: Manifold for purging and sealing ampoules with one ampoule in place.
Figure 3-4: TS-2 - 1500 ppm Flopaam 3330S, 3% NaCl, 0.1% NaHCO₃, 100 ppm sodium dithionite, 1ppm resazurin, 85 C or 100 C

* Some of these ampoules may have leaked due to poor sealing system.
Figure 3-5: TS-4 - 1500 ppm AN-125, 3% NaCl, 0.1% NaHCO₃, 200 ppm sodium dithionite, 1ppm resazurin, 85 C or 100 C

* Some of these ampoules may have leaked due to poor sealing system.

$\tau = 0.38$
Figure 3-6: TS-5: 1500 ppm Flopaam 3630, 3% NaCl, 0.1% NaHCO₃, 200 ppm sodium dithionite, 38ppm CaCl₂, 1ppm resazurin, 85 C or 100 C

* Many of these ampoules may have leaked due to poor sealing system.
Figure 3-7: TS-6: 1500 ppm SAV301, 3% NaCl, 400 ppm sodium dithionite, 1ppm resazurin, 100°C

\[ \tau = 0.4 \]
Figure 3-8: TS-7: 1500 ppm Flopaam 3630, 3% NaCl, 0.1% NaHCO₃, 400 ppm sodium dithionite, 1ppm resazurin, 85 C or 100 C
Figure 3-9: Hydrolysis of PAM and poly(AM-co-AMPS) after extended aging (100 days for Moradi-Araghi et al., Moradi–Araghi and Doe, 220 days for authors)
Figure 3-10: Total anionicity (i.e., sum of AA and AMPS) of PAM and poly(AM-co-AMPS) after extended aging (100 days for Moradi-Araghi et al, Moradi-Araghi and Doe, 220 days for authors)
Figure 3-11: (TS-30) Hydrolysis kinetics of 4% poly(AM-co-AMPS), 20 mM NaHCO₃ (pH 7.6-8.3) at 100°C.
Figure 3-12: (TS-31) Hydrolysis kinetics of 4% HPAM, 20 mM NaHCO₃ (pH around 8) at 100 C
Figure 3-13: (TS-32) Hydrolysis kinetics of 4% PAM, 20 mM NaHCO$_3$ (pH around 8) at 100 C
Figure 3-14: (TS-34) Hydrolysis kinetics of 4% PAM, 0.5 M Na₂CO₃ (pH 10.5-11)
Figure 3-15: (TS-36) Hydrolysis kinetics of 4% PAM, 0.25 M Na$_2$HPO$_4$, 0.25 M NaH$_2$PO$_4$ (pH around 12.4)
Figure 3-16: (TS-102) 2500 ppm FA920SH, 1% Na₂CO₃, 2% NaCl, 400 ppm sodium dithionite
Figure 3-17: (TS-102) 2500 ppm FA920SH, 1% Na$_2$CO$_3$, 2% NaCl, 400 ppm sodium dithionite
Figure 3-18: (TS-103/4) 2500 ppm AN-125, 1% Na₂CO₃, 2% NaCl, 400 ppm sodium dithionite
Figure 3-19: (TS-103/4) 2500 ppm AN-125, 1% Na$_2$CO$_3$, 2% NaCl, 400 ppm sodium dithionite
Figure 3-20: (TS-103/4) 2500 ppm AN-125, 1% Na₂CO₃, 2% NaCl, 400 ppm sodium dithionite
Figure 3-21: (TS-105) 2500 ppm FA920SH, 100 mM monobasic sodium phosphate, 100 mM dibasic sodium phosphate, 2% NaCl, 400 ppm sodium dithionite
Figure 3-22: (TS-105) 2500 ppm FA920SH, 100 mM monobasic sodium phosphate, 100 mM dibasic sodium phosphate, 2% NaCl, 400 ppm sodium dithionite
Figure 3-23: (TS-106) 2500 ppm Flopaam 3630S, 1% Na$_2$CO$_3$, 2% NaCl, 400 ppm sodium dithionite
Figure 3-24: (TS-106) 2500 ppm Flopaam 3630S, 1% Na₂CO₃, 2% NaCl, 400 ppm sodium dithionite
Figure 3-25 (TS-107) 2500 ppm AN-125, 100 mM monobasic sodium phosphate, 100 mM dibasic sodium phosphate, 2% NaCl, 400 ppm sodium dithionite
Figure 3-26: (TS-107) 2500 ppm AN-125, 100 mM monobasic sodium phosphate, 100 mM dibasic sodium phosphate, 2% NaCl, 400 ppm sodium dithionite
Figure 3-27: Hydrolysis kinetics of poly(AM-co-AMPS) at 100 °C found in experiment TS-30 (pH 7.6-8, 4% polymer) and TS-107 (pH 6.4, 0.25% polymer, 400 ppm sodium dithionite)
Figure 3-28 (TS 107) 2500 ppm AN-125, 100 mM monobasic sodium phosphate, 100 mM dibasic sodium phosphate, 2% NaCl, 400 ppm sodium dithionite
Figure 3-29: Hydrolysis of PAM and after 100 days under alkaline or neutral conditions
Figure 3-30: Arrhenius plot of complete AMPS hydrolysis at near-neutral pH

\[ y = -10904x + 24.223 \]

\[ R^2 = 0.9632 \]
Figure 3-31: Relationship between viscosity, salinity, and degree of hydrolysis for 1500 ppm solutions of a series of copolymers of approximately the same molecular weight.
Figure 3-32: Relationship between viscosity, salinity, and degree of hydrolysis for 1500 ppm solutions of a series of copolymers of approximately the same molecular weight.
Figure 3-33: 1500 ppm HPAM copolymer ($\tau = 0.66$), 23 C
Figure 3-34: 1500 ppm HPAM copolymer ($\tau = 0.66$), 55 C

Figure 3-35: Calcium tolerance for HPAM copolymers

1500 ppm polymer, 23 C

Figure 3-35: Calcium tolerance for HPAM copolymers
Figure 3-36: Effect of NaCl background concentration on viscosity loss as calcium is added to an HPAM copolymer ($\tau = 0.66$)
Figure 3-37: Effect of degree of hydrolysis on viscosity loss as calcium is added to HPAM copolymers with 2% NaCl background
Figure 3-38: Effect of sodium metaborate on cloud point with an HPAM copolymer ($\tau = 0.66$)
Figure 3-39: Effect of metaborate upon viscosity loss upon addition of calcium to an HPAM copolymer ($\tau = 0.7$)
Figure 3-40: Effect of sodium metaborate on cloud point with an HPAM copolymer (τ = 0.5)
Figure 3-41: Calcium tolerance of poly(acrylic acid) with sodium metaborate
Figure 3-42: The viscosity elevating benefits of sodium metaborate with an HPAM copolymer ($\tau = 0.66$) are not present at the same concentration as the cloud point elevating benefits.
Figure 3-43: Calcium tolerance of post-hydrolyzed HPAM ($\tau = 0.59$, industrial source)
Figure 3-44: Variation of pH with addition of sodium metaborate to deionized water
Figure 3-45: Mineral formation limits of calcium and magnesium tolerance with and without bicarbonate and/or sulfate in approximate amounts present in seawater.
Figure 3-46: Polymer tacticity may dominate the presence of AMPS moieties as far as calcium tolerance is concerned.
Figure 3-47: Despite similar calcium tolerance, the viscosity of aged poly(AM-co-AMPS) polymer is higher as that limit is approached.
Figure 3-48: AMPS and sodium metaborate can be used simultaneously with beneficial effects.
Figure 3-49: Viscosity loss with addition of tolerance of aged polymers in high salinity brine
Figure 3-50: 1500 ppm of PAM, 3 post-hydrolyzed HPAMs hydrolyzed at 23 C from the same PAM, and PAA of approximately the same molecular weight.
Figure 3-51: Change in viscosity with degree of hydrolysis at various salinities
CHAPTER IV: THERMAL STABILITY

LITERATURE REVIEW

Degradation mechanisms

The degradation experienced by organic compounds present when ferrous iron (Fe++) is oxidized to ferric iron (Fe+++), as first described by Fenton (1894), and can be generalized by the following:

\[
X^n + H_2O_2 \rightarrow X^{n+1} + OH^- + \cdot OH
\]

Where \( X^n \) is a transition metal in an oxidizable state, such as Fe++, Co++, or Cu+. The above reaction, leading to the formation of the very strongly oxidizing hydroxyl radical (\( \cdot OH \)), is still commonly used in industrial applications where the rapid destruction of organic molecules is required, for instance in the treatment of wastewater. In the absence of further ferrous iron this reaction would cease, however if a mild reducing agent is added, which is capable of reducing some of the iron without directly reacting with the peroxide, a redox cycle is set up, whereby a small amount of iron can be used to slowly churn out radicals. This is the general manner, for instance, in which free-radical polymerizations are performed.

Later researchers have noted the formation of peroxides in a multi-step process during the autoxidation of iron, obviating the need for \( H_2O_2 \) in the above reaction, as below:

\[
\begin{align*}
Fe^{2+} + O_2 & \rightarrow Fe^{3+} + \cdot O_2^- \\
\cdot O_2^- + H^+ & \rightarrow \cdot HO_2 \\
Fe^{2+} + \cdot HO_2 & \rightarrow Fe^{3+} + HO_2^- \\
HO_2^- + H^+ & \rightarrow H_2O_2
\end{align*}
\]

after Ramsden and McKay (1986 – II)
Hence a peroxide need not be explicitly added for radicals to form. Thus it is clear that iron, when allowed to oxidize, can lead to the formation of very strongly oxidizing hydroxyl radicals (•OH).

Pye (1967) first noted the loss in viscosity of partially hydrolyzed polyacrylamide (HPAM) solutions in the presence of iron in his patent for the application of sodium dithionite to prevent iron scale, and explicitly notes the compatibility of sodium dithionite with polymers. Early research that focused on finding suitable methods to stabilize polymer solutions performed by Schurz (1972), Knight (1973) and Chauveteau and Kohler (1974) focused on the use of either sodium dithionite or formaldehyde. Schurz reported that sodium dithionite is strongly preferred because of its ability to prevent radical degradation in the presence of iron, which formaldehyde cannot. Chauveteau and Kohler reported the stability of polymer solutions containing sodium dithionite for several days as long as air was excluded. Knight presented an extensive discussion of both chemicals and performed long-term stability experiments under a variety of conditions, but in the end recommended formaldehyde over sodium dithionite due to the handling difficulties of the latter, though it must be noted that iron was conspicuously absent from his experiments. Furthermore, Burcik and Thakur (1972) quickly pointed out that formaldehyde, though not an effective oxygen scavenger, caused solutions of Dow Pusher™ 700 HPAM to crosslink. Though unnoticed in Knight’s screen factor tests, this mixture plugged a 5 µm fritted disc immediately.

Muller (1981b) appears to be the first to correctly identify residual impurities remaining in the polymer from polymerization as a key contributor to the radical degradation of polyacrylamide. Muller demonstrated with purified polyacrylamide samples that no molecular weight reduction occurs at 100 C in the presence of oxygen.

Shupe (1981) analyzed Dow Pusher™ 500 and identified 6.5 ppm of a primarily iron substance in the solid powder, which resulted in about 6.5 ppb of iron in the polymer solution. Shupe uses several antioxidants to attempt to slow degradation in the presence
of oxygen, but all speed degradation, leading to the conclusion that the stabilized radicals react with oxygen to form hydroperoxide radicals. Severe degradation was also noted when solutions containing sodium dithionite were heated in the presence of air, however very little degradation was observed when at room temperature when sodium dithionite was added to polymer solutions containing oxygen or when these solutions were allowed to encounter further oxygen, contrary to earlier findings (Knight, 1973). In the presence of oxygen, degradation was more rapid at pH 12 than at pH 8.

Wellington (1983) performed an extensive review of literature on radical degradation mechanisms and screened xanthan gum at 97°C with several different oxygen scavengers, radical transfer agents, and sacrificial easily oxidizable compounds, but used brines that did not contain iron (although copper was used in some experiments). Wellington finds that, unlike HPAM, xanthan gum degrades in the presence of dithionite. He finds that a combination of a sacrificial alcohol, an oxygen scavenger, a radical transfer agent, and sufficient sodium concentration slow degradation to an acceptable rate. While several possible degradation mechanisms are outlined, no effort is made to determine which, if any, of these mechanisms is at play or how specifically this “shotgun approach” manages to prevent them.

A study by Grollman and Schnabel (1982) and a series of studies by Ramsden and colleagues (Ramsden and McKay, 1986 – I, 1986 – II, and Ramsden et al., 1987) brought to light the possible degradation mechanisms of polyacrylamide following the introduction of radical species. Grollman and Schnabel illustrated the mechanism by which the oxidation of iron results in the cleavage of polymer backbone, a key step being the abstraction of hydrogen from the polymer backbone. The relative reactivities of each hydrogen are determined, and the backbone hydrogen are found to be much more frequently abstracted than the amine hydrogen. Nevertheless, only about 1% of attacking hydroxyl radicals are found to result in main chain scission. Ramsden and McKay found that purified polymer solutions are stable in the presence of both iron and oxygen, so long
as the pH is 8 or greater, despite visual evidence of rapid oxidation. This illustrates the importance of both residual impurities and pH in oxidative degradation of PAM. They go on to show that the reason for this stability is the apparent lack of formation of hydroxyl radicals in the autoxidation of iron at high pH, rather than a lack of reactivity of hydroxyl radicals with PAM under these conditions. A non-radical path for the oxidation of iron at high pH has also been shown by Beylerian and Asaturyan (2004).

Several themes can be identified from the literature, although as of yet there is no consensus on the best method for the stabilization of polymer in the reservoir. Previous research as well as our current work suggests that molecular weight reduction can occur in the lab when any two of the three of oxygen, iron, and/or residual initiators from polymerization are present unless antioxidants or sacrificial easily oxidizable species are present, however there are notable exceptions to this:

• When iron is not present, the degradation is slow except at elevated temperatures, and even then can be prevented if oxygen is removed or if the polymer is purified.
• Rapid degradation is observed when iron is added to commercially produced polymer solutions
• At high pH (8 and above) and in the presence of iron, if residual initiators are removed through purification, degradation is not observed even in the presence of oxygen, despite the visual evidence of rapid conversion of Fe(II) to Fe(III).
• If sodium dithionite is present, no degradation is observed even in the presence of both iron and residual impurities
• Degradation may occur at room temperature when dithionite is added and oxygen is present, however there are conflicting reports in the literature of whether this occurs or not, so even this may be related to the particular
polymerization conditions or impurities. In any case, if only the 8ppm or so of oxygen in solution is allowed to react the degradation is limited.

While these observations are hardly enough evidence to diagnose all potential degradation mechanisms, the effect on stability of raising solution pH or using sodium dithionite, a strong reducing agent, demonstrate that pH and $E_n$ (i.e. oxidation-reduction potential) are important factors, suggesting the use of Pourbaix diagrams to understand the role of iron, as well as perhaps some other factors, on polymer stability. Figure 4-1 presents a Pourbaix diagram for iron in aqueous solution, as presented by Hem (1961). As pH increases, iron becomes less soluble, hence less is in solution and able to participate in redox reactions. As $E_n$ decreases, on the other hand, solubility increases, however the distance from the area where redox cycling of iron can occur (corresponding to the non-vertical dashed lines in the figure) becomes greater. It is the author’s belief that either or both of these approaches can be used to successfully prevent the oxidative degradation of polymer through Fenton-type reactions.

Aside from Fenton-type reactions involving iron or other transition metals, a few other degradation mechanisms seem plausible given the observations above, and these can be understood by examining the types of radicals that cause them. Three types of radicals that may be present in dilute polymer solutions in the lab and the reservoir include carbon-centered (e.g., from residual initiators), sulfur-centered (e.g., from sodium dithionite), or oxygen centered (e.g., from decomposition of peroxide initiators or autoxidation of iron, as discussed above). While only oxygen-centered radicals are believed to be efficient hydrogen abstractors, both carbon-centered and sulfur-centered radicals react with oxygen rapidly (near diffusion controlled limits), in some cases producing oxygen-centered radicals. Autoxidation of polymers and/or the presence of alkyl peroxide groups on the polymers as theorized by some early researchers (Wellington, 1983) is unlikely given the stability of purified commercial polymers with oxygen at elevated temperatures found by Muller (1981b) and others.
Radical-induced oxidation is often attributed to oxygen-centered radicals, particularly the powerful hydroxyl radical (Grollman and Schnabel, 1982). Hydroxyl radicals can form by the reduction of a peroxide by iron as first observed by Fenton, and as discussed at length above. Peroxides may be present as residual initiators (Kheradmand, 1987) or formed by the autoxidation of iron (Ramsden and McKay, 1986-II). Hydroxyl radicals are very strong oxidizers, and will abstract hydrogen almost indiscriminately from the nearest molecule. As such, true antioxidants are typically not very effective, though easily oxidized compounds such as alcohols or glycols may be used as sacrificial substrate (Anbar et al., 1966). However, peroxide-decomposing antioxidants may be effective at preventing the formation of hydroxyl radicals. Peroxyl and superoxide radicals are also oxygen centered but are slightly weaker than the hydroxyl radical, as discussed below.

Carbon-centered radicals can be formed by the decomposition of residual initiators, such as azo compounds, at high temperatures, or as byproducts of alkyl peroxy initiators. These radicals are relatively weak, and only able to abstract allyl hydrogen, hence their efficiency for radical polymerization of vinyl polymers. Though unable to abstract hydrogen from a saturated carbon backbone, they can react with oxygen to form alkyl peroxyl radicals. These types of radicals are described by different authors as "slightly reactive (Fossey et al., 1995)" and capable of abstracting hydrogen from a polymer backbone (Moad and Solomon, 2006), at least at high temperatures (Alfassi, 1997). In this case the depolymerization reaction proceeds until the oxygen is consumed. This is consistent with the degradation seen in unpurified polymers at high temperatures when oxygen is present. Some carbon-centered radicals as well as peroxyl radicals may be trapped with antioxidants, such as phosphite or hindered phenols.

The dithionite ion rapidly decomposes to bisulfite and thiosulfate (Carvalho and Schwedt, 2001). The sulfur dioxide radical is a transient reaction product. Commercial samples of sodium dithionite frequently contain greater amounts of these radicals and
these reduce to a steady state amount of around 0.01 mole % in aqueous solution (Rinker et al., 1959). The sulfur dioxide radicals are strong reductants and will not abstract hydrogen directly, however they will rapidly react with oxygen, if present, to form sulfur dioxide and superoxide radicals, which are not typically regarded as strongly oxidizing but may be capable of abstracting hydrogen (Afanas’ev, 1989). In the absence of further oxygen, this depolymerization reaction also ceases.

The question, then, is how these results should be interpreted as relates to the reservoir environment. It turns out that identifying just what conditions prevail in the reservoir is a complicated task. It has been shown that reservoirs are typically in at least a slightly reduced condition (Shafer and Pirson, 1969) with $E_h$ between -400mV and +100mV, but generally below -100 mV, where they can be considered anaerobic, and pH between 7 and 8. However, these values only express the intensity of oxidation-reduction potential and acidity/basicity, respectively. Buffering capacity is used to describe the ability of an acid/base couple to buffer against a change in conditions, and poising represents analogous the analogous concept for redox couples. The amount of poise present in reservoir redox couples is both variable and scantily reported. While the decomposition of organic material is generally correlated with generating highly reducing conditions (i.e. low $E_h$), iron is thought to play an important role in the poising of many geological systems. Zobell (1946) reports poise for marine sediments between about 10 and 60 milliequivalents of FeCl₃ per gram of mud, but notes that preliminary measurements in petroleum reservoirs show more strongly reducing conditions (lower $E_h$) but less poise. This is consistent with the fact that, as $E_h$ decreases, less and less iron is in the oxidized state, as illustrated in Figure 4-1, so little poising is possible with the dominant Fe³⁺/Fe²⁺ system, much as a buffer far from its pKₐ offers little buffering capacity. So, the reservoir may be thought of as an anaerobic and highly reduced, though not necessarily highly reducing environment. A further complication may be present in the case where partially oxygenated water has been injected into a reservoir for decades.
The next and more challenging question is the limiting conditions under which the relevant oxidation-reduction reactions can occur. While Pourbaix diagrams for iron present a frame in which the potential for redox cycling, with concomitant degradation, can be viewed, they are at a certain level simplified, and in natural systems can not practicably capture all of the potential oxidation-reduction couples (Stumm, 1961). This can be appreciated by observing the change to the Pourbaix diagram for iron when 10 ppm sulfate and 100 ppm bicarbonate is added (Figure 4-2). Thus while Pourbaix diagrams are instructive in a general sense, it is necessary to expose polymer solutions with candidate stabilizing packages to the types of radicals present in field conditions, and work towards performing experiments with commercial polymer samples and field brines. Ultimately, these results need to be verified under field conditions.

**Potential stabilization methods**

**Reducing agents**

Sodium dithionite and sodium sulfite or bisulfite are commonly referenced reducing agents in the polymer stability literature. Sodium dithionite is a powerful reducing agent and exists in equilibrium with the SO₂ radical, as mentioned above. Each dithionite ion is capable of forming two radicals, which can each reduce Fe(III) to Fe(II). Dithionite is capable of reducing water and is thus quite unstable in solution (Carvalho and Schwedt, 2001) particularly at high temperature (Rinker et al., 1965), however the SO₂ radical appears to persist sufficiently to propagate low Eₜ fronts in situ (Amonette et al., 1994, Istok et al., 1999). With transition metals such as iron kept in the reduced state, it appears that Fenton-type reactions are prevented.

Sodium sulfite is another reducing agent that can be used to scavenge oxygen, but is not powerful enough to reduce iron. Sodium bisulfate and ammonium bisulfate are closely related compounds, which are often preferred in the field due to their higher solubility and lower molecular weight. The pKₐ of the disassociation of bisulfite to
sulfite is 6.4 and it has been shown that sulfite is the species that reacts with oxygen, hence the rate of oxygen scavenging increases with pH, at least up to pH 10 (Miron, 1981). The difficulty in using sulfite or bisulfate is that the scavenging of oxygen can be quite slow unless catalyzed by a transition metal, which may itself cause degradation. There are reports that the use of sulfite may cause greater degradation to polymer than dithionite in the field (Dunlop, 1973), and this is likely due to the use of transition metals as a catalyst.

Hydrogen gas is also a powerful chemical reducing agent that can reduce iron, though this has not always been recognized by those using it (Seright et al., 2009).

**Alkali**

Sodium hydroxide and sodium carbonate are commonly used alkali in ASP flooding, and sodium metaborate has recently become attractive for reasons mentioned in the previous chapter. There are at least three possible mechanisms by which alkali may improve polymer stability: Increasing pH to a range where radicals are apparently not formed during the oxidation of iron, lowering the solubility of transition metals such as iron, and direct antioxidant effects of the anions.

Beneficial effects of raising pH above 8 have been demonstrated by Ramsden and McKay (1986-II) and this can be achieved with any of these alkali. Their results may be explained by the existence of a non-radical path for oxidation at high pH (Beylerian and Asaturyan, 2004), or alternatively by the increased distance from the region where iron redox transitions occur on the Pourbaix diagram.

The solubility of divalent cations such as iron are limited at high pH, particularly in the presence of carbonate, as illustrated in Figure 4-3. Note that this is a further simplification of the Pourbaix diagram, in that all iron is assumed to be in the reduced state. The solubility of ferrous iron is lowered from thousands of ppm at near neutral pH to the ppb level at pH 10, or to hundredths of ppb if much carbonate is present. The
precipitation of iron to very low levels may effectively prevent it from participating in adverse redox reactions.

Rice and Wilkes (1994) reported a ten-fold increase in hydroxyl radical scavenging rate by bicarbonate as pH increased from 7 to 10, disassociating the ions into carbonate. While no data has been found specifically concerning the metaborate anion, the complex relationship between the presence of other anions and the ability for the oxidation of organics to occur, as described below, suggest at least the possibility of this sort of mechanism with other anions as well.

**Antioxidants**

Antioxidants have historically been divided into two classes. Primary antioxidants, also referred to as chain breaking donors or acceptors, are those that can participate in a chain terminating reaction with peroxyl radicals. Sterically hindered phenols or amines are the most common types. Hindered phenols can act as either proton donors or acceptors and stabilize the resulting radical using mesomeric forms. Secondary antioxidants, also referred to as peroxide decomposers, are able to prevent the formation of radicals by decomposing their precursors. These are typically organophosphorus or organosulfur compounds, such as phosphates, thioesters, mercaptans. It is now common to use the combination of a primary and secondary antioxidant in non-EOR polymer stabilization applications, however these are typically not in aqueous solution. Additionally it should be noted that the terms “primary” and “secondary” may be oversimplistic, since many antioxidants can function in both ways.

Inorganic molecules can also act as antioxidants. Wellington observed that his polymer stability package for xanthan gum, first designed for use in a high salinity brine, was ineffective in an unbuffered, low salinity brine. Wellington determined that, under his experimental conditions, a brine concentration of at least 1.2% TDS was required for long-term stability. Liao et al. (2001) reported an effect of inorganic anions on the scavenging of hydroxyl radicals. Hydroxyl radical concentration resulting from a
combination of hydrogen peroxide and UV decreased with increasing chloride concentration, up to 1250 mM, or 7.3% as NaCl. Scavenging behavior of bicarbonate was more complex, with significant scavenging only when a background of 250 mM chloride was present. Thus it is clear that inorganic ions can play an important, if complex, antioxidant role.

_Sacrificial, oxidizable compounds_

Alcohols and other low molecular weight substrates with easily abstractable hydrogen can play a sacrificial role and prevent oxidation of the polymer backbone, as previously noted by Shupe (1981), Wellington (1983), Ryles (1983), and Yang and Treiber (1985). Primary alcohols are most easily oxidized. Anbar et al. (1966) showed that the apparent rate constant for oxidation of various solvents by the hydroxyl radical increases with carbon length and decreases with additional OH groups. Shupe (1981) reported that primary alcohols were more effective at preventing degradation than secondary alcohols, with isobutanol and n-butanol among the most effective, in agreement with the difference in rate constants found by Anbar and Neta. Glycols and surfactants, particularly those of higher molecular weight, should also act as sacrificial agents that may be oxidized in lieu of the polymer backbone, as observed by Shupe. It should be noted that rate constants for reactions between the hydroxyl radical and most of these compounds are near diffusion controlled limits, so the differences in rate may be less important than the ratio of substrate to polymer.

**EXPERIMENTAL PROCEDURES**

**Viscosity measurement**

Viscosity measurements were made using a Contraves LS-30 viscometer at 23 C. While measurements were typically made at several shear rates, viscosities are reported
at 11 s$^{-1}$ unless otherwise stated, as this is considered representative of the far from wellbore region. When dithionite was used, viscosity measurements were made under an argon blanket, which was achieved by providing slight positive pressure to the wind guard on the LS-30.

**Use of ALP-99 (poly(acrylic acid)) as a surrogate**

Stability of the acrylic backbone to radical degradation, as discussed above, can be observed viscometrically. At room temperature and neutral pH, any change in viscosity can be attributed to change in molecular weight distribution of the polymer. At elevated temperature, hydrolysis may also cause a change in solution viscosity and so observation of degradation is more complicated. Performing experiments in 3% NaCl or above limits the change in viscosity due to hydrolysis. Some experiments were also performed using poly(ammonium acrylate) (PAA), a salt of poly(acrylic acid) which is similar to what is obtained if polyacrylamide is totally hydrolyzed. Because no further hydrolysis can occur, viscometric interpretations of molecular weight degradation are more readily made. It should be noted that PAA is more susceptible to oxidative degradation than PAM because it contains a couple less hydrogens that can be abstracted. Therefore a higher proportion of attacking radicals should lead to chain scission, which should make it a more sensitive indicator of degradation.

**Oxygen determination**

Oxygen determination was made first using Chemets™ colorimetric ampoules, then later using a Mettler Toledo InPro® 6900 O$_2$ sensor.

**Oxidation reduction potential (ORP) measurement**

ORP was measured using an Accumet platinum pin Ag/AgCl combination electrode with 4 M KCl filling solution, giving the electrode a potential of +200 mV in reference to a saturated hydrogen electrode. Thus E$_a$ is obtained by adding 200 mV to the
reported EAg/AgCl values. ORP probes were calibrated using quinhydrone in pH 7 buffer, which should have a potential of 93 mV at 23 C with an Ag/AgCl probe.

Degradation with the addition of iron

In some cases iron was added as FeCl₂, or FeCl₃. When FeCl₂ was used the solution was first bubbled with hydrogen gas to ensure iron was in the reduced state.

Polymer purification

Some samples of polymer were purified by soaking the dry powder in methanol, washing with methanol three times and then drying prior to hydration, after Kheradmand (1987).

EXPERIMENTAL RESULTS

Experiments concerning degradation with sodium dithionite or sulfite

A preliminary experiment aimed at resolving the discrepancy in the literature concerning the presence or absence of degradation when sodium dithionite is added to an HPAM solution and allowed further contact with oxygen determined that viscosity of Flopaam 3630S was reduced by more than half after an hour of slow mixing in the presence of air, as illustrated in Figure 4-4. Interestingly, the relative viscosity decline at the highest shear rates was much less (around 20%), however this does not explain the discrepancy, since Shupe measured viscosities at a shear rate of 14.7 s⁻¹.

Subsequent experiments were conducted to determine the extent of degradation and conditions where degradation occurs. Viscosity loss was minimal when either 400 ppm sodium dithionite or 1000 ppm sodium sulfite (uncatalyzed) were added to a 2000 ppm solution of FA920SH containing dissolved oxygen and no further air was allowed to mix with the solution, as illustrated in Figure 4-5. When dissolved oxygen was lowered to 1 ppm by stirring under an argon blanket, degradation was negligible. Long-term aging experiments (Chapter III) with sodium dithionite added to blanketed polymer
solutions and sealed in glass ampoules demonstrate that polymer solutions are stable for long periods of time with dithionite present if oxygen is excluded.

A sample of FA920SH was purified as described above in order to determine whether the residual impurities in the polymer contribute to the degradation experienced when oxygen mixes with polymer solutions containing sodium dithionite, and to test the hypothesis that differences between these impurities are to blame for the inconsistent nature of this phenomenon in the literature. It should be noted that the method of purification employed—methanol extraction—has been shown by Kheradmand to remove organic impurities, however it cannot be expected to remove inorganic impurities such as iron. Fortunately, Shupe analyzed the Pusher 500 sample he worked with and reported the presence of 6.5 ppm of iron in the dried polymer powder, which he did not remove. 400 ppm sodium dithionite was added to both purified and unpurified FA920SH in 3% NaCl. The solution was then pipetted into ampoules and sealed with no attempt to exclude oxygen. The geometry of the ampoules are such that they contain approximately 15 mL of polymer and 5 mL of headspace when sealed. Both polymers degraded completely over the course of a week at either 100 C or 126 C, as illustrated in Tables 4-1 and 4-2.

The experiments were repeated, this time with 1% Na$_2$CO$_3$ and 2% NaCl, rather than only NaCl. In this case, the difference between the stability of the purified and unpurified polymer was striking, as illustrated in Tables 4-3 and 4-4. While the unpurified polymer with sodium carbonate degraded slower than either the purified or unpurified solutions containing NaCl only, the purified polymer showed no loss upon heating at either 100 C or 126 C for 1 month. These results show that residual organic impurities play a significant—but not singularly important—role in the oxidative degradation of PAM from sodium dithionite and oxygen.

What, then, can explain the difference in observed degradation between Shupe and others in the literature? Shupe reports 6.5 ppb of iron is present in his diluted
polymer solution. Others (Kheradmand, 1987) have identified that Pusher™ 700, a similar HPAM produced by Dow, contained 10% Na₂CO₃ in the solid powder. From Shupe’s report of the carbonate and bicarbonate concentrations in his experimental brine, we can calculate a pH of 9.2 using the Henderson-Hasselbalch equation, and from the solubility product of FeCO₃ a corresponding solubility of ferrous iron around 1.3 ppb, much less than the 6.5 ppb present. If, however, an additional 100 ppm of Na₂CO₃ was added from the polymer powder, we can calculate a pH of 9.5 and a corresponding solubility of ferrous iron around 0.6 ppb.

Hence one plausible explanation for the difference in observed degradation in the presence of sodium dithionite and oxygen is a combination of the presence or absence of residual organic impurities from polymerization and the ppb-level solubility of iron, also a residue from polymerization. Shupe reports very little degradation at room temperature and severe degradation at 86 C with unpurified polymer in a brine with somewhat high pH and alkalinity, resulting in low iron solubility. This is consistent with the hypothesis that the solubility of iron at ppb-levels is a controlling factor in the low temperature degradation from oxygen and sodium dithionite. At high temperature, it seems that residual organic impurities play an important role as well. Further experiments could be conducted to determine the precise amount of iron required to cause low-temperature degradation of HPAM in the presence of sodium dithionite and oxygen, and it follows from this hypothesis that the amount would be in the range of 1 ppb, an amount which is likely present as a contaminant or as residue from polymerization, and as such need not be added explicitly, but can be controlled by limiting solubility. An alternative hypothesis is that the presence of carbonate and bicarbonate ions, which have reported antioxidant properties as discussed above, or the concomitant change in pH, limited the degradation observed by Shupe, however the small magnitude of both of these factors suggest they play only a minor role.
In order to verify that solutions containing significant quantities of iron would be effectively stabilized by the use of sodium dithionite, 20 ppm of Fe(III) as FeCl₃ was added to polymer solutions after sodium dithionite and in some cases Na₂CO₃ or Na₂SO₃, and the solutions were then heated at 100 C. In these experiments, PAA was used as described above so that only changes in molecular weight would be observed viscometrically. Table 4-5 and Figure 4-6 present the results of these experiments. Addition of uncatalyzed Na₂SO₃ prior to sodium dithionite did not result in lower degradation from the reaction of the scavenger with dissolved oxygen, rather the degradation occurred when the Na₂SO₃ was added instead. Significantly less degradation occurred when Na₂CO₃, was present. The aging experiments indicated that sodium dithionite adequately protects unpurified polymer from degradation in the presence of large amounts of iron at 100 C so long as additional oxygen is excluded. The final, one month sample for the experiment with only sodium dithionite and NaCl seems to have leaked, as indicated by the detection of 1.5 ppm of dissolved oxygen and Eₘ of +206 mV, as opposed to -420mV observed immediately after mixing and -91 mV to +23 mV observed in ampoules heated for less time and without observed leaks or degradation.

**Experiments concerning the beneficial effects of alkali**

From the preceding experiments, it is clear that specific alkali, pH, and/or solubility of iron play an important role in the stability of the acrylic backbone of HPAM to oxidative degradation resulting from at least one source of radicals. A series of experiments was therefore conducted to determine the effect of alkali on other sources of radicals.

20 ppm Fe³⁺ or Fe²⁺ was added as a chloride salt to PAA solutions in either 1% NaCl or Na₂CO₃ and then heated at 100 C in sealed, purged ampoules. Because of reports that ferrous iron causes more severe degradation than ferric iron, the experiment was performed with both. Results of these experiments are presented in Figure 4-7.
Although the immediate degradation experienced upon the addition of iron was greater when ferrous iron was added, in both cases degradation was severe when NaCl was present prior even to heating the samples. In the presence of Na₂CO₃, on the other hand, degradation was greatly retarded.

Next, the above experiment was repeated with various other alkali at 23 C. While PAA solutions with NaCl or NaHCO₃ present lost all viscosity upon addition of ferrous iron, the solution containing sodium metaborate (Na₂B₂O₄•8H₂O) lost only around 40% immediately, and still had a third of its original viscosity after 52 days. The solution containing Na₂CO₃ experienced a similar viscosity loss to that observed at 100 C. An interesting observation was made that the solutions containing Na₂CO₃ and Na₂B₂O₄•8H₂O, which both kept at least some of their viscosity, each presented an orange precipitate, which can be assumed to be ferric iron carbonate or hydroxide. While iron precipitates at very low levels as iron carbonate, it likely does not precipitate directly with metaborate, which is known to sequester divalent cations. However by raising the pH to around 10 or 11, metaborate causes the formation of iron hydroxide, lowering the solubility of iron(II) to the ppb level. Thus the relative stability of polymer solutions in this experiment is proportional to the relative solubility of iron.

An experiment was conducted to determine how degradation varies with the amount of iron(III) added. Results are presented in Figure 4-8. No difference was observed in the range of 0.2-20 ppm iron(III) when samples were heated at 100 C, however an additional sample with 20 ppm iron(III) and pH adjusted to 10 with NaOH experienced significantly less viscosity loss. This experiment is difficult to interpret because both high temperature and iron are known to cause degradation when polymer is not purified and oxygen is not completely removed, as was the case here.

Next an experiment was conducted to determine the stability of PAA at high temperature in the presence of various alkali without iron explicitly added but with about 6 ppm dissolved oxygen. Results are presented in Figure 4-9. The first thing that should
be noted is that the pH in each case is a little lower than should be expected. For instance, the pKₐ of the bicarbonate/carbonate couple is 10.25, so when a substantial amount of carbonate is added to a solution containing essentially no bicarbonate, the pH is typically around 11, but drops upon extended mixing as CO₂ from the air mixes with the solution. Additionally the low pH of the solution containing no buffer suggests that some of the alkali is consumed deprotonating protonated carboxyl groups of the polymer. The solution containing sodium carbonate exhibited the greatest long-term stability, and the solution containing metaborate degraded a little slower than the NaCl and NaOH controls. Unfortunately the pH of the NaOH control dropped to 9.1 so the effect of the metaborate ion could not be ascertained. While its inability to directly precipitate iron explains the poorer stability compared to Na₂CO₃, one might also expect either an antioxidant effect, as is reported with other alkali, or conversely an accelerating effect if iron was sequestered in a manner that allowed it to participate in redox cycling.

An additional experiment was performed to test the effect of Na₂CO₃ on the degradation caused by heating polymer solutions in the presence of excess oxygen and residual impurities in order to test a hypothesis that iron alone was the impurity that caused degradation with oxygen at high temperature. As illustrated in Figure 4-10, this hypothesis was disproved.

*Experiments with various other stabilizers*

Several other antioxidants or sacrificial, easily oxidizable compounds were tested to determine their ability to retard degradation caused by either the presence of residual impurities and a small amount of dissolved oxygen at high temperature with or without iron. Table 4-7 and Figure 4-11 present results of tests with some stabilizers used in the literature. Thiourea and mercaptobenzothiazole (MBT), both antioxidants, and isopropanol (IPA), an easily oxidizable alcohol, resulted in much less degradation when iron(III) was added to PAA than was observed in earlier experiments presented in Figure
4-7 and Table 4-6. However, none of these sufficed to protect the polymer from degradation when samples were subsequently heated to 100 C. It should be noted that though sodium sulfite caused a large initial drop in viscosity and experienced further loss upon the addition of iron and heating, it seems that further decline was arrested, and viscosity was stable between around 180 and 700 hours. It should also be noted that the viscosity drop due to the addition of sodium sulfite is greater than reported earlier, around 25% instead of only 5% reported in Figure 4-5. This is likely due to the low salinity in this experiment, which results in a more extended molecule that will lose more of its hydrodynamic radius per scission, as well as perhaps the lack of amide hydrogen.

Figure 4-12 presents results when similar experiments were performed with various solvents and a surfactant. While quite significantly none of the solutions lost more than 8% of their viscosity when FeCl₃ was added, all viscosity enhancement was lost within a week when heated at 100 C, with IPA and IBA allowing slower degradation than EGBE, DGBE, or C₂₀₋₂₄ internal olefin sulfonate (C₂₀₋₂₄IOS). Thus while neither sacrificial solvents nor the antioxidants tested above are sufficient alone to stabilize the acrylic backbone of PAA or PAM at 100 C, all impart some resistance to immediate degradation when iron is encountered at low temperature, and thus may find beneficial application in low-temperature applications where iron is present. However, long term testing is first necessary to determine if the initial stability observed persists, or if degradation is merely retarded.

Figures 4-13 through 4-16 present experiments performed in either 3% NaCl or 1% Na₂CO₃, 2% NaCl brine with one or more stabilizers present and no iron added. From Figures 4-13 and 4-14, it is apparent that with NaCl (1) all of the solutions experience at least a 20% decline within the first week at 100 C and lose all enhanced viscosity at 126 C within the same time frame; (2) the retarding benefits of the sacrificial solvents used are IBA > IPA >> DGBE, consistent with the findings of Anbar et al. (1966); (3) for some reason the solutions with MBT have a higher original viscosity.
This last observation demands further investigation. The solution pH is a likely culprit, as these solutions were unbuffered and all except the one containing MBT have lower viscosity than expected. The original pH of all of the samples was 5.4-5.5, except for the sample containing MBT, which was slightly higher at 5.84. This may be due to the reported pKa of 6.9 for MBT (Lia et al., 2007). Although the differences in measured pH are small, these are all very close to the carboxyl pKa, hence a small changes in this region can be expected to have a large impact on the fraction of deprotonated carboxyl moieties and hence on solution viscosity. This also implies a different configuration of the molecule, and thus casts some doubt on the comparison with the other samples, hence the experiment should be repeated at a fixed pH.

Figures 4-15 and 4-16 present results in similar experiments where Na₂CO₃ was used, resulting in a pH around 10. The higher initial viscosity lends credence to the theory that the discrepancy in initial viscosities between samples in the previous experiment is due to differences in pH. The samples at 100 C and 126 C degraded to similar viscosities as those with NaCl presented previously with the exception of the samples at 126 C containing IBA. This is somewhat difficult to interpret, as it would be expected that the corresponding 100 C sample would have remained viscous as well. Since these results hinge on a single data point it would be premature to draw any conclusions. However, as two samples that inexplicably maintained high viscosity contained IBA, further investigation with this solvent may be warranted.

Accelerated degradation experiments were performed using the combination of UV light and hydrogen peroxide, in what is sometimes referred to as the “UV-Fenton” reaction. In these experiments various stabilizers were added to 2000 ppm Flopaam 3330 in a 250 ppm TDS brine containing 140 ppm NaHCO₃. 0.03 g of 5% H₂O₂ was added to 5 g of polymer with 2% solvent and the solutions were then capped with argon and placed under UV light. As shown in Figure 4-17, IBA and IPA again outperformed DGBE, though all solutions degraded slower than those with no solvent.
Additional miscellaneous experiments

A titration of saturated FeCl$_3$ in DI was performed using sodium dithionite, and results are presented in Figure 4-18. 5000 ppm FeCl$_3$6H$_2$O was added to DI and pH was raised to 7.4 with NaOH. 2% sodium dithionite was added drop wise, and after 26 drops (about 0.0052 L) E$_h$ had dropped to -280 mV and pH had risen to 7.9. This corresponds to a drop in solubility of iron(II) from about 1000 ppm (the approximate amount added initially) to only 100 ppm, severely confounding the results. However the calculated stoichiometry from these two limiting cases correspond to a reduction of from 0.74 to 7.4 moles of iron per mol of dithionite, which brackets the literature value of 2. Additionally, under the initial pH and E$_h$ conditions of the experiment, reference to Figure 4-1 indicates that most of the iron should have already been in the ferrous state. Hence, little can be made of this experiment, except to demonstrate quantitatively the ability of sodium dithionite to reduce iron. By comparison, in a 1000 ppm solution of sodium sulfite in pH 7 buffer a redox potential of +170 mV was measured. Figure 4-1 puts this close to a region where redox transitions can occur with iron, consistent with sulfites inability to prevent degradation in the presence of iron.

One final general observation can be made from a number of experiments presented in Chapter 3 that may be of use to experimentalists performing similar stability experiments. It was observed that samples that contained dithionite and which had aberrantly low viscosities after aging typically had higher E$_h$ than those that kept their viscosity, as illustrated in Figure 4-19. It is suspected that this is due to small fractures in the sealed portion of the ampoules that were sometimes visible upon close inspection, and which may have allowed slow intrusion of air. Hence the high E$_h$ values are thought to be symptomatic of a leak rather than the direct cause of the degradation. This once again highlights the usefulness of ORP measurements in studies of oxidative degradation.
DISCUSSION

It is difficult to bring an investigation to a close that has failed to quantitatively explain the phenomena in question. What can be provided is an outline of factors effecting stability and the parameters of importance.

It has been demonstrated that both pH and \( E_h \) are of critical importance to the understanding of oxidation of acrylic polymers, suggesting the use of Pourbaix diagrams as a frame of reference. In particular, Pourbaix diagrams for iron, including carbonate if applicable, can be instructive. In a simplified manner, the solubility of ferrous iron, as presented in Figure 3, can help interpret the effect of alkali on stability.

**Efficacy of sodium dithionite to prevent thermal degradation**

It has been demonstrated that polymer solutions containing around 400 ppm sodium dithionite show no signs of degradation over periods as long as a year and at temperatures up to 126°C. Likewise, no signs of degradation were observed over one month in solutions saturated with iron at temperatures of 100°C. This is the only method that has been shown to protect PAM in the presence of iron.

The weakness of this method of polymer stabilization is the susceptibility of polymer to degradation once dithionite is added. It has been demonstrated that iron likely plays a key role in this degradation. While schemes for a reaction between sulfur dioxide radicals and oxygen have been proposed (Levitt et al., 2008), it now seems equally plausible that the degradation sometimes attributed to a reaction between oxygen and dithionite is in fact due to a reaction between ppb-level amounts of ferrous iron and oxygen. This is consistent with the rapid degradation seen with ferrous – but not ferric – iron in the field, as well as with results with other reducing agents.

Whatever the mechanism or mechanisms at play, there are several viable schemes by which degradation can be avoided. The first and most preferable approach is to add sodium dithionite prior to the addition of polymer, however this requires that oxygen be
excluded from this point forward. This is particularly preferable if some iron is present in
the make up brine. An alternative approach would be to add an antioxidant prior to the
polymer, which would slow oxidative degradation of the polymer from the iron in
solution at ambient temperature and in the presence of air. Once hydrated, sodium
dithionite could be slip-streamed into the solution on its way to the injection well such
that further contact with air would not be an issue, although around a 10% loss of
viscosity should be expected from the reaction of the sodium dithionite with dissolved
oxygen. Experiments indicate that the most preferred “antioxidant” for this purpose
would in fact be Na₂CO₃, although a solvent, surfactant, or antioxidant such as thiourea or
MBT may provide sufficient protection during hydration. There is also some indication
that if Na₂CO₃ is added first, less viscosity loss will occur upon addition of sodium
dithionite.

If no iron is present in the make up brine, then polymer can be hydrated in the
presence of air and then dithionite can be slip streamed in, with only a small loss of
viscosity, as mentioned above. This can be thought of as an alternative to Wellington’s
package of NaCl, Na₂SO₃, IPA, and thiourea, which has been shown to prevent oxidative
degradation at 97°C with a biopolymer in the absence of iron, and with which similar
results could be expected with PAM.

The remaining question, then, is whether sodium dithionite is required at low
temperatures if minimal amounts of iron are present, or whether a less reactive chemical
could be used to stabilize PAM for a sufficiently long time. Further experiments are
needed to determine this, and the parameters that should be respected in reference to the
reservoir brine in question include total iron, total alkalinity, hardness, pH and E₈ at a
minimum. The present study as well as the literature unequivocally recommends the use
of thick, vacuum sealed glass ampoules as the most reliable way to test samples.

It has been reported in the literature that low-E₈ fronts can be propagated using
sodium dithionite in the subsurface. However, retardation of the front can be expected,
and will be proportional to the poising of the rock, analogous to the retardation of an alkaline front due to geochemical reactions. In order to accurately predict the ability to propagate a low \( E_h \) front, measurement of poising in preserved reservoir cores is advised.

**Beneficial effects of sodium carbonate**

Sodium carbonate has been shown to have a dramatic stabilizing effect on PAM and PAA in the presence of several different radical-generating mixtures. These include reactions between sodium dithionite and oxygen at either high or low temperature and reactions between iron, oxygen, and residual impurities at either high or low temperature. The benefit is greater with sodium carbonate than with metaborate at a similar pH, and so it appears that either specific antioxidant properties of carbonate or the lower solubility of iron are the cause of the difference in stability, with the latter being the simpler explanation.

Despite the significant improvement in stability in the presence of sodium carbonate, this alone does not appear sufficient to prevent degradation over long periods of time resulting from residual impurities and dissolved oxygen at 100 C. Thus the use of dithionite is still recommended.

**Efficacy of various solvents as sacrificial substrates**

Anbar et al. (1966) investigated the rates of hydrogen abstraction from various solvents and found that the apparent rate constant for oxidation of various solvents by the hydroxyl radical increases with carbon length and decreases with additional OH groups. Primary alcohols, such as IBA, are more easily oxidized than secondary alcohols, such as IPA, and solvents with additional electron withdrawing groups, such as the glycol ethers studied here, are also difficult to oxidize. This agrees with findings here as well as those of Shupe that IBA performs better than at IPA as a sacrificial agent. This, along with its lower flash point, suggest it should perform better than IPA in Wellington’s protective
package. More surprising was the far worse performance seen with either EGBE or DGBE as sacrificial agents.
Figure 4-1: Pourbaix diagram of for 0.01-100 ppm dissolved iron in aqueous solution (from Hem, 1961)
Figure 4-2: Pourbaix diagram of 0.01 ppm iron, 10 ppm sulfur as sulfate, and 100 ppm bicarbonate in aqueous solution (from Hem, 1961)
Figure 4-3: Solubility of ferrous iron in the presence of various amounts of carbonate or bicarbonate ion as bicarbonate.
Figure 4-4: Addition of sodium dithionite or molar equivalent NaCl blank to 1500 ppm Flopaam 3630S in 3% NaCl with no attempt to exclude oxygen.
Figure 4-5: Viscosity retention upon addition of oxygen scavenger to 2000 ppm solution of FA920SH, 3% NaCl

Table 4-1: 2000 ppm FA920SH, 3%NaCl, 400 ppm sodium dithionite, no attempt to exclude air from ampule headspace

<table>
<thead>
<tr>
<th>SAMPLE #</th>
<th>VISC (cp)</th>
<th>DO (ppm)</th>
<th>pH</th>
<th>$E_{AgCl}$ (mV)</th>
<th>Time Heated (hrs)</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stock</td>
<td>8.64</td>
<td>6</td>
<td>6.03</td>
<td>69.4</td>
<td>0</td>
<td>Initial reading</td>
</tr>
<tr>
<td>Stock</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>5.62</td>
<td>6</td>
<td>7.83</td>
<td>-60</td>
<td>25</td>
<td>After dithionite</td>
</tr>
<tr>
<td>2</td>
<td>2.2</td>
<td>5</td>
<td>7.5</td>
<td>-39</td>
<td>168</td>
<td></td>
</tr>
<tr>
<td>126 C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stock</td>
<td>8.64</td>
<td>6</td>
<td>6.03</td>
<td>69.4</td>
<td>0</td>
<td>Initial reading</td>
</tr>
<tr>
<td>Stock</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>1.42</td>
<td>7</td>
<td>7.9</td>
<td>-27</td>
<td>25</td>
<td>After dithionite</td>
</tr>
<tr>
<td>2</td>
<td>0.9</td>
<td>1.2</td>
<td>7.06</td>
<td>120</td>
<td>168</td>
<td>sample was brown</td>
</tr>
</tbody>
</table>
Table 4-2: 1500 ppm methanol-washed FA920SH, 3%NaCl, 400 ppm sodium dithionite, no attempt to exclude air from ampule headspace

<table>
<thead>
<tr>
<th>SAMPLE #</th>
<th>VISC (cp)</th>
<th>DO (ppm)</th>
<th>pH</th>
<th>$E_{AgCl}$ (mV)</th>
<th>Time Heated (hrs)</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stock</td>
<td>5.5</td>
<td>6</td>
<td>5.65</td>
<td>-18.2</td>
<td>0</td>
<td>initial reading</td>
</tr>
<tr>
<td>Stock</td>
<td>5.03</td>
<td>0</td>
<td>5.34</td>
<td>-475.6</td>
<td>0</td>
<td>after dithionite</td>
</tr>
<tr>
<td>1</td>
<td>2.09</td>
<td>5</td>
<td>7.9</td>
<td>75.5</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>1.42</td>
<td>6</td>
<td>6.58</td>
<td>-11.1</td>
<td>168</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0.8</td>
<td>3.2</td>
<td>7.5</td>
<td>45</td>
<td>712</td>
<td></td>
</tr>
<tr>
<td>126 C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stock</td>
<td>5.5</td>
<td>6</td>
<td>5.65</td>
<td>-18.2</td>
<td>0</td>
<td>initial reading</td>
</tr>
<tr>
<td>Stock</td>
<td>5.03</td>
<td>0</td>
<td>5.34</td>
<td>-475.6</td>
<td>0</td>
<td>after dithionite</td>
</tr>
<tr>
<td>1</td>
<td>1.07</td>
<td>5</td>
<td>8.07</td>
<td>56.3</td>
<td>25</td>
<td>cloudy</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>3.1</td>
<td>4.98</td>
<td>49</td>
<td>168</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0.81</td>
<td>0.23</td>
<td>7.1</td>
<td>23.6</td>
<td>700</td>
<td></td>
</tr>
</tbody>
</table>

Table 4-3: 1500 ppm FA920SH, 2%NaCl, 1% Na$_2$CO$_3$, 400 ppm sodium dithionite, no attempt to exclude air from ampule headspace

<table>
<thead>
<tr>
<th>SAMPLE #</th>
<th>VISC (cp)</th>
<th>DO (ppm)</th>
<th>pH</th>
<th>$E_{AgCl}$ (mV)</th>
<th>Time Heated (hrs)</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stock</td>
<td>13.79</td>
<td>10</td>
<td>10.29</td>
<td>-18</td>
<td>0</td>
<td>initial reading</td>
</tr>
<tr>
<td>Stock</td>
<td>4.83</td>
<td>12</td>
<td>9.93</td>
<td>-160.7</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>126 C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stock</td>
<td>13.79</td>
<td>10</td>
<td>10.29</td>
<td>-18</td>
<td>0</td>
<td>initial reading</td>
</tr>
<tr>
<td>Stock</td>
<td>7.1</td>
<td>12</td>
<td>9.88</td>
<td>-43.2</td>
<td>25</td>
<td></td>
</tr>
</tbody>
</table>

Table 4-4: 1500 ppm methanol-washed FA920SH, 2%NaCl, 1% Na$_2$CO$_3$, 400 ppm sodium dithionite, no attempt to exclude air from ampule headspace

<table>
<thead>
<tr>
<th>SAMPLE #</th>
<th>VISC (cp)</th>
<th>DO (ppm)</th>
<th>pH</th>
<th>$E_{AgCl}$ (mV)</th>
<th>Time Heated (hrs)</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stock</td>
<td>9.53</td>
<td>10.97</td>
<td>-53</td>
<td>0</td>
<td>After dithionite added</td>
<td></td>
</tr>
<tr>
<td>Stock</td>
<td>8.76</td>
<td>10.85</td>
<td>-678</td>
<td>0</td>
<td>After dithionite added</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>13.02</td>
<td>10</td>
<td>10</td>
<td>64.5</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>13</td>
<td>4</td>
<td>9.7</td>
<td>70</td>
<td>712</td>
<td>Cloudy at 23 C</td>
</tr>
<tr>
<td>4</td>
<td>13</td>
<td>4</td>
<td>9.7</td>
<td>70</td>
<td>712</td>
<td>Cloudy at 23 C</td>
</tr>
<tr>
<td>126 C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stock</td>
<td>9.53</td>
<td>10.97</td>
<td>-53.4</td>
<td>0</td>
<td>Initial reading</td>
<td></td>
</tr>
<tr>
<td>Stock</td>
<td>8.76</td>
<td>10.85</td>
<td>-677.7</td>
<td>0</td>
<td>After dithionite</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>11.43</td>
<td>11</td>
<td>9.8</td>
<td>33.8</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>12</td>
<td>4.1</td>
<td>9.6</td>
<td>68</td>
<td>700</td>
<td>Cloudy at 23 C</td>
</tr>
</tbody>
</table>
Table 4-5: Viscosity retained upon addition of 400 ppm sodium dithionite to 1500 ppm ALP-99 in various brines, 23 C

<table>
<thead>
<tr>
<th>Brine</th>
<th>Viscosity Retention (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1% NaCl</td>
<td>85%</td>
</tr>
<tr>
<td>1% Na2CO3</td>
<td>91%</td>
</tr>
<tr>
<td>1% NaCl, 1000 ppm Na2SO3*</td>
<td>82%</td>
</tr>
</tbody>
</table>

*added immediately before sodium dithionite

Figure 4-6: 1500 ppm ALP-99, 1% NaCl or Na2CO3, 400 ppm sodium dithionite, 20 ppm Fe(III) as FeCl₃, aged at 100 C

Legend:
- 1% NaCl, 400 ppm sodium dithionite
- 1% Na2CO3, 400 ppm sodium dithionite
- 1% NaCl, 1000 ppm sodium sulfate, 400 ppm sodium dithionite

Leak detected
Figure 4-7: 1500 ppm ALP-99, 1% NaCl or Na$_2$CO$_3$, 20 ppm Fe$^{3+}$ or Fe$^{2+}$ as chloride salt, 8 ppm oxygen, 100 °C

Table 4-6: 1500 ppm ALP-99, 0.3% NaCl, 0.363M sodium as NaCl, Na$_2$CO$_3$, Na$_2$B$_2$O$_4$•8H$_2$O, or NaHCO$_3$, 20 ppm Fe$^{2+}$ an chloride salt, 8 ppm oxygen, 23 °C

<table>
<thead>
<tr>
<th>Salt</th>
<th>NaCl</th>
<th>Na$_2$CO$_3$</th>
<th>Na$_2$B$_2$O$_4$•8H$_2$O</th>
<th>NaHCO$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Original viscosity</td>
<td>30.8</td>
<td>38.1</td>
<td>38.1</td>
<td>35.4</td>
</tr>
<tr>
<td>20 min after iron added</td>
<td>1.3</td>
<td>29.4</td>
<td>23.5</td>
<td>1.3</td>
</tr>
<tr>
<td>52 days later</td>
<td>-</td>
<td>24.9</td>
<td>12.6</td>
<td>-</td>
</tr>
</tbody>
</table>
Figure 4-8: 750 ppm ALP-99, 3% NaCl, about 6 ppm O₂, and various amounts of Fe(III) added as FeCl₃ prior to heating at 100 C
Figure 4-9: 1500 ppm ALP-99, 0.1M of various buffers, about 6 ppm O₂, 100 C

Figure 4-10: Degradation of 3630S with 1% Na₂CO₃ and 2% NaCl at high temperature with no attempt to exclude oxygen from ampoules
Table 4-7: 1500 ppm ALP-99, 0.1M NaCl, 1000 ppm various stabilizers, 20 ppm Fe(III) as FeCl₃, viscosity during mixing of additives and iron prior to experiment

<table>
<thead>
<tr>
<th>Additive</th>
<th>Before additive</th>
<th>After additive</th>
<th>After Fe(III)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thiourea</td>
<td>31.61</td>
<td>31.14</td>
<td>30.01</td>
</tr>
<tr>
<td>MBT</td>
<td>31.61</td>
<td>29.95</td>
<td>27.11</td>
</tr>
<tr>
<td>Sodium Sulfite</td>
<td>31.61</td>
<td>20.96</td>
<td>17.41</td>
</tr>
<tr>
<td>IPA</td>
<td>32.40</td>
<td>31.80</td>
<td>30.01</td>
</tr>
</tbody>
</table>

Figure 4-11: 1500 ppm ALP-99, 0.1M NaCl, 1000 ppm various stabilizers, 20 ppm Fe(III) as FeCl₃, aged at 100 C
Figure 4-12: 1500 ppm ALP-99, 0.1M NaCl, 1000 ppm various solvents or surfactant, 20 ppm Fe(III) as FeCl₃, aged at 100 C
Figure 4-13: 1500 ppm ALP-99, 3% NaCl, various solvents and/or stabilizers, aged at 100 C
Figure 4-14: 1500 ppm ALP-99, 3% NaCl, various solvents and/or stabilizers, aged at 126°C.
Figure 4-15: 1500 ppm ALP-99, 2% NaCl, 1% Na₂CO₃, various solvents and/or stabilizers, aged at 100 C
Figure 4-16: 1500 ppm ALP-99, 2% NaCl, 1% Na₂CO₃, various solvents and/or stabilizers, aged at 126 C
Figure 4-17: Accelerated degradation experiments using H₂O₂ and UV light

Figure 4-18: Titration of saturated FeCl₃ solution with sodium dithionite
Figure 4-19: Use of ORP as a qualitative indicator of degradation in chemical stability experiments
Chapter V: Economics and In-Situ Hydrolysis

**RECOVERY MODEL**

A simplified recovery model was developed in order to allow a first-order attempt at optimization of polymer concentration. Displacement efficiency is calculated using Buckley-Leverett theory, areal sweep is modeled using the theory of Koval (1963), and net present value (NPV) is then calculated using an injectivity relation. The model neglects:

- Non-Newtonian effects
- Polymer adsorption and permeability reduction
- Gravity and capillary forces
- Capital costs

Areal sweep is calculated using relations developed by Koval, as below

\[
N_{pD} = \frac{2(KV_{pi})^{1/2} - 1}{V_{pi} - 1},
\]

where \(N_{pD}\) is recovery in pore volumes, \(V_{pi}\) is the number of pore volumes injected, and \(K\) is the Koval recovery factor, which is the product of \(E\), a subfactor relating to mobility, and \(H\), a subfactor related to heterogeneity, and are calculated as below:

\[
E = \left(0.78 + 0.22 \left(\frac{\mu_w}{\mu_s}\right)^{1/4}\right)^4
\]

\[
H = \log\left(\frac{V_{D-P}}{(1 - V_{D-P})^{1/5}}\right)
\]

\[
K = EH
\]

The application of Buckley-Leverett theory to water and polymer flooding is well understood (Pope, 1980) and will not be expounded upon here.

Injectivity is calculated as
$$i = \frac{3.541 \Delta P k h}{\frac{\mu_p}{F_t} \left( \ln \left( \frac{d}{R_w} \right) - 0.569 \right)}$$

Where $\mu_p$ is the polymer viscosity used in Koval and Buckley-Leverett calculations and $F_t$ is a modifying factor that accounts for the reduced viscosity during injection when an initially unhydrolyzed polymer is used. This factor will be set to unity until this concept is developed below.

The relation between viscosity and polymer concentration is calculated from as below (UTCHEM 9.0, 2000):

$$\frac{\mu_p}{\mu_w} = \left(1 + \left(A_{p1} C_4 + A_{p2} C_4^2 + A_{p3} C_4^3\right) C_{SEP}^{Sp}\right)$$

Where $C_4$ is polymer concentration, $A_{p1}$, $A_{p2}$ and $A_{p3}$ are constants relating to polymer molecular dimensions commonly used in the chemical simulator UTCHEM, $C_{SEP}$ relates to the ionic environment, and $S_p$ relates to the effect of changes in ionic conditions on the molecule.

Table 5-1 presents economic inputs as well as the values used for the parameters above and Table 5-2 presents reservoir properties used in calculations below except where explicitly stated otherwise.

Figure 5-1 illustrates the recovery calculations using Koval, Buckley-Leverett, and the combined Buckley-Leverett/Koval model for a viscosity ratio of 10. Oil recovery is directly discounted in order to determine a more price-neutral optimum, and then oil and polymer costs are added in order to determine NPV. Maxima of both functions can be easily determined as a function of polymer concentration, expressed in Figure 5-2 as viscosity ratio. The maximum NPV ($14.7$MM) corresponds to a viscosity ratio of 19 and a discounted recovery of 0.19 PV, which is also at a maximum at this viscosity ratio.
IN-SITU HYDROLYSIS

As mentioned in Chapter 3, the injection of unhydrolyzed PAM under alkaline or high temperature conditions that will lead to rapid in-situ hydrolysis has the potential to greatly improve injectivity compared to the injection of a polymer similar to the resulting hydrolyzed polymer, as is currently standard practice. The term $F_i$ has been introduced in the model described above in order to quantify this effect. Figure 5-3 presents the calculated term $F_i$ as calculated from data in Chapter 3 as a function of salinity.

Using the above model and $F_i = 4$ causes the maximum NPV and discounted recovery to increase to $18.1$MM and $0.25$, an increase of 23% in NPV and 32% in discounted recovery. This corresponds to the movement of the maxima from a viscosity ratio of 19, corresponding to a 2.6 cP polymer solution, to a viscosity ratio of 5 and a viscosity of 10 cP. The increased injectivity allows a ten-fold increase in polymer mass while maintaining the same injection rate.

DISCUSSION

Predictive recovery models are notoriously prone to overestimating recovery at poor mobility ratios, and hence underestimate optimum chemical mass. This is part of the reason the optimum the optimal polymer concentrations found above are so low, and so these numbers should be viewed as low estimates. The primary point of the above exercise however is to demonstrate that, particularly in low permeability formations, it is difficult for increased sweep to make up for a loss in injectivity, and so the optimum polymer viscosity will often correspond to the highest viscosity that does not inhibit injectivity, as it has in both cases presented above. An increase in injectivity, such as through taking advantage of hydrolysis kinetics as described herein and/or by injecting above parting pressure, affords as significant improvement to project value.

REFERENCES
Table 5-1: Polymer properties and pricing information

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>AP1</td>
<td>50</td>
</tr>
<tr>
<td>AP2</td>
<td>1</td>
</tr>
<tr>
<td>AP3</td>
<td>10</td>
</tr>
<tr>
<td>Sp</td>
<td>-0.38</td>
</tr>
<tr>
<td>CSEP</td>
<td>0.25</td>
</tr>
<tr>
<td>Rk</td>
<td>1</td>
</tr>
<tr>
<td>discount rate</td>
<td>0.07</td>
</tr>
<tr>
<td>Oil Price</td>
<td>$65/bbl</td>
</tr>
<tr>
<td>Polymer Cost</td>
<td>$1/lb</td>
</tr>
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</table>

Table 5-2: Reservoir and fluid properties

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
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</thead>
<tbody>
<tr>
<td>$\phi$</td>
<td>0.3</td>
</tr>
<tr>
<td>k</td>
<td>0.3 D</td>
</tr>
<tr>
<td>P inj</td>
<td>1800 psi</td>
</tr>
<tr>
<td>qmax</td>
<td>1000 bbl/day</td>
</tr>
<tr>
<td>P res</td>
<td>0 psi</td>
</tr>
<tr>
<td>$\mu$ oil</td>
<td>50 cp</td>
</tr>
<tr>
<td>S or =</td>
<td>0.3</td>
</tr>
<tr>
<td>S wi =</td>
<td>0.2</td>
</tr>
<tr>
<td>$k^o_{ro}$</td>
<td>0.8</td>
</tr>
<tr>
<td>$k^c_{rw}$</td>
<td>0.2</td>
</tr>
<tr>
<td>m =</td>
<td>4.5</td>
</tr>
<tr>
<td>n =</td>
<td>1.9</td>
</tr>
<tr>
<td>R wellbore</td>
<td>0.25 ft</td>
</tr>
<tr>
<td>Thickness</td>
<td>50 ft</td>
</tr>
<tr>
<td>Vdp</td>
<td>0.6</td>
</tr>
<tr>
<td>H (Koval)</td>
<td>5.256233628</td>
</tr>
<tr>
<td>Interwell dist (d)</td>
<td>467 ft</td>
</tr>
<tr>
<td>PV</td>
<td>1.17 MMBBL</td>
</tr>
</tbody>
</table>
Figure 5-1: Separate and combined recovery predictions of using Buckley-Leverett and/or Koval theories with the parameters in Table 2, \( \mu_p = 2.6 \), and \( F_r = 1 \).
Figure 5-2: Maximum NPV and discounted recovery for $F_c = 1$
Figure 5-3: Injectivity enhancement function
Figure 5-4: Maximum NPV and discounted recovery using in-situ hydrolyzing PAM, $F_r = 4$. 
Chapter VI: Summary, Conclusions, and Recommendations

SUMMARY

Several new polymers have been extensively investigated, including HPAMs of more than twice the molecular weights that were available during the last period of high activity in EOR research, as well as commercially available poly(AM-co-AMPS) similar to those Moradi-Araghi et al. (1987) worked with, a polymer containing n-vinyl pyrrolidone (NVP), hydrophobically modified associative polymers, and a sterically hindered “comb” polymer. Filtration testing with 1.2 µm filters proved a useful screening tool and identified that transport issues may occur with associative polymers because the viscosity building mechanism is intermolecular, rather than intramolecular, as seems the case with the sterically hindered polymer. Even the highest molecular weight polymers were successfully filtered if allowed to mix for extended periods of time with a stirbar, or shorter times with higher shear. The results of two field observations of polymer injection indicate that mixing conditions in the field include substantially greater shear, however due to complications resulting from the presence of ferrous iron a quantitative determination of the appropriate amount of shear to use in the lab could not be made. Viscosity-salinity scans were used to qualitatively compare the molecular dimensions and ionic nature of polymers with varied structures and molecular weights.

Chemical stability experiments were performed with PAM, HPAM, and poly(AM-co-AMPS) polymers at temperatures between 25 C and 126 C under both neutral and alkaline conditions. The most significant finding of this study was the rapid hydrolysis kinetics of PAM observed at even low temperatures at the mildly alkaline conditions existing in the presence of sodium carbonate, which implies that extensive hydrolysis will occur during even low-temperature ASP floods. Also of interest was the retardation of hydrolysis at around 70-80% under alkaline conditions, suggesting that
hydrolysis may be incomplete at high pH even at high temperature. Although the
difference between the full hydrolysis experienced under neutral conditions and the
degree of hydrolysis of 0.80-0.85 experienced after extended aging at around 100 C
under alkaline conditions, may seem insignificant, it has been shown (Kulicke and Horl,
1993) that viscosity drops precipitously between \( \tau = 0.7 \) and \( \tau = 1 \). Therefore, above
around 85 C, this retardation may indicate a significant benefit in terms of a higher
polymer viscosity after extended aging under alkaline conditions compared with neutral
conditions. Additionally, results with poly(AM-co-AMPS) copolymers indicate that the
AMPS moiety is labile at 100 C as predicted by Levitt et al. (2008), though this too is
retarded under alkaline conditions. At 85 C and under neutral conditions, a similar total
amount of anionicity resulted from the aging of poly(AM-co-AMPS) and HPAM of a
similar initial degree of anionicity. However the effect of calcium on analogues of the
two aged solutions were markedly different.

Whereas previous studies have examined calcium tolerance primarily in terms of
the onset of turbidity (Zaitoun and Potie, 1983), this study also examined the significant
loss of viscosity as the point of turbidity and subsequent precipitation is approached. This
will limit the feasibility of the use of HPAM to lower calcium concentrations than
previously reported (Moradi-Araghi and Doe, 1987), as viscosity loss is rapid with most
polymers susceptible to precipitation. This result should be verified with lab produced
extensively hydrolyzed polymers that originated as either PAM or typical HPAM
copolymers. Extensively hydrolyzed poly(AM-co-AMPS) polymers, on the other hand,
maintain much higher viscosities as precipitation is approached, though the onset of
turbidity with increasing calcium concentration is almost the same as with similarly
hydrolyzed PAM. The use of sodium metaborate has been shown to either increase
calcium tolerance if around 0.6 wt% is used, or to help maintain higher viscosity as
precipitation is approached if more is used, though these two phenomena do not seem to
happen at the same concentration.
The importance of pH and Eₜ to the stability of the acrylic backbone has been demonstrated, suggesting the use of Pourbaix diagrams – in particular that for iron – to help qualitatively describe this phenomenon. In this context, the use of sodium dithionite to reduce Eₜ to levels where redox cycling of iron cannot occur and the failure of sodium sulfite to do the same can be explained. The stability of the acrylic backbone itself in the presence of sodium dithionite and no other stabilizer has been demonstrated for over one year at 100°C, and samples have maintained their viscosity for over 100 days at 126°C, this despite the presence of dissolved oxygen when dithionite was added. Additionally, sodium carbonate was shown to have a strong stabilizing effect on the acrylic backbone in the presence of several types of attacking radicals. Again, the Pourbaix diagram for iron and carbonate can be instructive. Carbonate causes the precipitation of iron to very low levels, and iron is shown to play a direct or catalytic role in the attack of several types of radicals on the acrylic backbone. However this alone is not enough to protect the acrylic backbone at 100°C and above unless the polymer is purified by methanol washing.

The effectiveness of various solvents and a surfactant were compared as to their relative performance as sacrificial agents to protect the acrylic backbone. The results of Anbar and Neta (1966) regarding the preference of primary alcohols over compounds with additional electron-withdrawing groups is found to hold, though any of these serve to greatly reduce the immediate degradation upon the addition of iron.

The focus by many researchers on oxygen and attempts to stabilize solutions by removing it, while paying no attention to the effect of the method of removal on the Eₜ, has been a tremendous source of confusion in the literature. For instance, in the method of stabilization recently proposed by Seright et al. (2009), hydrogen is used to remove oxygen in preference to sodium dithionite, in a misconceived belief that less degradation will result in the case of an air leak. However, the authors apparently fail to realize that hydrogen is a strong reducing agent, and with iron in the reduced form degradation will
rapidly occur in the event that air is introduced, similar to if sodium dithionite is used. Second, in calculating the length of time that oxygen, if inadvertently injected, will persist in the reservoir, the authors presume stability by invoking rapid consumption of oxygen by the oxidation of ferrous iron present in the reservoir. While technically they are correct that oxygen will be rapidly consumed, the oxidation of ferrous iron has been repeatedly shown to cause rapid degradation.

CONCLUSIONS

The goal of this work in the broadest sense was to determine best practices for the use of acrylic polymers for EOR under harsh conditions, which include high temperature and the presence of iron. A secondary goal was to determine appropriate lab protocol for polymer preparation and testing that scales to the field, and to that end two field observations were particularly instructive. In both cases, the medium and high molecular weight polymer solutions passed 1.2 \( \mu \text{m} \) filtration testing after about an hour of mixing despite the longer mixing time required in the lab, not only illustrating the ability of these field-prepared solutions to pass such a rigorous test, but suggesting that mixing procedures that do not produce solutions with low filtration ratios do not correspond to field conditions. Filtration tests in the lab also allowed the rapid determination that the associative polymers tested will likely not transport in a manner suitable for mobility control applications, though the efficacy of low concentrations of surfactant to shield the intermolecular interactions that prevent transport and build viscosity suggest their use in a water shutoff process.

Field observations were also instructive concerning the proper treatment of source waters containing iron. In the presence of several ppm of iron and/or at high temperature it has been shown that sodium dithionite is necessary to ensure the long term stability of the acrylic backbone. But what about the presence of just a few tenths of a percent of iron and a relatively cool target reservoir, such as was the case in the two fields
observed? The conservative approach, given the remaining uncertainty concerning both the redox conditions of the reservoir and the precise conditions sufficient to allow the progression of each of the multitude of possible radical oxidation mechanisms, seems to be to add a few hundred ppm of sodium dithionite, as was done in one of the fields. Due to the reactivity of sodium dithionite, some care must go into the procedure used for addition. A stock solution of sodium dithionite should be made continuously and immediately before use, and solution $E_h$ should be monitored. The solution should be added downstream of all points where oxygen cannot be rigorously excluded, and this will often mean the hydration of the polymer solution must be completed prior to its addition, despite the presence of small amounts of iron. Degradation over the course of one hour of hydration can be severe in the presence of even a few tenths of a ppm of ferrous iron, as was observed in one of the field observations. One simple way to minimize this, following an age-old practice for well water treatment, is by aerating the source water in order to oxidize and hence lower the solubility of iron as well as $H_2S$ if present, then filter prior to use. In fact, this was done in one of the fields and degradation during hydration was negligible, despite the original presence of 0.5 ppm of iron in the source water, more than in the other field where degradation was observed. In some instances, this may not be feasible, and so a small amount of stabilizer may be added to prevent degradation during hydration. In the case of alkaline-surfactant polymer or surfactant-polymer floods, either sodium carbonate, cosolvent or even surfactant, if added prior to hydration, might suffice as a temporary stabilizer. For polymer floods where aeration of source water or anaerobic hydration is not possible, it is advisable to add a small amount of an antioxidant or sacrificial alcohol, and for the cost and simplicity of handling, isobutanol (IBA) would be a good choice. IBA is among the most preferred solvents in terms of reactivity with hydroxyl radicals, and also has a higher flash point than isopropanol.
As far as chemical stability and calcium tolerance, the method used here of hydration in 0.1M-1M NaOH followed by neutralization can be used to rapidly hydrolyze a polymer in a manner similar to what is expected at high temperature or pH. By varying time before neutralization, one can target a particular degree of hydrolysis, and the microstructure should be similar to that obtained in situ. Turbidity in particular has been seen to be strongly dependant on polymer microstructure, however viscosity loss with the addition of calcium was equally rapid for a post-hydrolyzed HPAM as for a similar copolymer. The practical calcium tolerance limits for extensively hydrolyzed PAM relate to the rapid drop in viscosity as calcium is added, precedes the onset of turbidity. Whereas an extensively hydrolyzed PAM ($\tau=0.59$) lost 70% of its viscosity with the addition of 500 ppm Ca$^{++}$, an extensively hydrolyzed poly(AM-co-AMPS) polymer ($\tau+\sigma=0.61$) lost 50% and the same polymer with 1.2% sodium metaborate lost only 20% of its viscosity. Precipitation has been shown to be a strong function of sodium concentration, and so higher calcium tolerances are obtainable at high salinity. For instance, with 2% NaCl background calcium tolerance of the extensively hydrolyzed PAM and poly(AM-co-AMPS) polymers mentioned above was increased to 2000 ppm Ca$^{++}$, and with a 10% NaCl background calcium tolerance was extended above 5000 ppm with negligible viscosity loss. The dramatic improvement over the results obtained at lower background salinities warrants further investigation.

Conclusions regarding the selection of the most appropriate polymer for given reservoir conditions can be divided according to process, temperature, brine hardness, and formation permeability. These conclusions are made under the assumptions that PAM and HPAM are less expensive than comparable poly(AM-co-AMPS) polymers and/or are available in higher molecular weights than the latter, as currently seems to be the case, and thus are preferable all else being equal. The first conclusion is that the rapid hydrolysis of PAM polymers under alkaline conditions to a nearly temperature-independent level of hydrolysis around 70% recommend the injection of unhydrolyzed
PAM in most alkaline floods where sodium carbonate is not precluded due to calcium precipitation concerns. The rapid onset of hydrolysis implies that the polymer will begin hydrolyzing prior to entering the wellbore, however the low degree of hydrolysis and low viscosity at this point may permit an increase in injectivity by several fold. High temperature (> 70 C) non-alkaline floods may benefit from this as well, but the kinetics are recognized to be particularly favorable under alkaline conditions. Due to the availability of HPAM of higher molecular weight than is currently available for PAM, in very high permeability reservoirs there may be cause to evaluate HPAM as well, but the benefit of increased injectivity may warrant the use of PAM even if the polymer concentration requirement is higher.

In situations where calcium cannot be removed from the source water and/or mixing with divalent cations in the formation is a significant enough concern to warrant the use of sodium metaborate or another sequestering agent, or in high-temperature floods without alkali, the use of polymers containing AMPS or NVP should be considered. For instance, an ASP flood at 85 C is feasible with a relatively hard brine containing an 8:1 Na+/Ca++ ratio using poly(AM-co-AMPS) polymer and sodium metaborate. However, the Ca++ may reduce viscosity as much as 20 – 50% in low salinity water.

Finally, for high permeability, low-temperature polymer and surfactant-polymer floods, a number of suitable high molecular weight polymers are available. These can be chosen with degree of hydrolysis corresponding to the maximum viscosity for a given salinity, though in most cases it will be wise to keep the degree of hydrolysis safely below 35%.

**RECOMMENDATIONS**

Some continuing or related topics that warrant further investigation are presented here.
Modeling of in-situ hydrolysis

In order to feasibly implement the concept of in-situ hydrolysis described herein, the kinetics of hydrolysis and the relationship between viscosity and degree of hydrolysis will need to be added to a modeling program such as UTCHEM. This work has already commenced, and will be described by Lee (2009).

Further evaluation of lab “aged” polymers

It must be emphasized that, while hydrolysis kinetics have been quite extensively studied here and in the literature, the entirety of conclusions drawn regarding the loss of viscosity approaching precipitation rests on about a half dozen experiments. In most of the earlier experiments basic hydrolysis and neutralization were performed in glass beakers, which may have contributed some silica to the experiments. Though initial experiments indicated that this was not a controlling factor, further experiments are warranted, particularly with an “aged” PAM or HPAM, as the only sample studied was industrially prepared and thus may have been hydrolyzed at a higher polymer concentration, where high viscosity caused a greater polydispersivity of hydrolysis degree than would occur in dilute solutions in-situ or prepared in the lab as described above. Further, a similar study should be undertaken with fully hydrolyzed polyacrylamide in order to determine the limits of use at higher temperatures where complete hydrolysis will occur. As full hydrolysis under basic conditions proves difficult, the easy method of doing this would involve the use of poly(acrylic acid) or a salt thereof. However, there may be differences in tacticity between these and fully hydrolyzed PAM samples, so at least some experimentation with the latter should be performed to verify this.

Scale down of field mixing procedures

Degradation due to the presence of iron complicated interpretation of field results, which will be presented in greater detail by Slaughter (2010). A field investigation where
a high molecular weight polymer is hydrated as described above using one or more of the commercially available field hydration units and then characterized by viscosity, filtration ratio, screen factor, and molecular dimensions using light scattering, could then be compared to similar results obtained using different amounts of shear in the laboratory.

**Silica dissolution and precipitation**

As mentioned above, the dissolution of silica at high pH and temperature as well as subsequent precipitation upon cooling complicated some results presented here. Precipitation of colloidal silica could be a serious production concern for high temperature ASP floods. One possible remedy would involve heating the production wells so that precipitation occurs on the surface, rather than in production equipment. Further study is warranted to determine the scope of the problem.

**Propagation of low Eₚ fronts and stability of radicals**

Propagation of low Eₚ fronts in the subsurface has been demonstrated (Istok et al., 1999), however the retardation due to poising of reservoir rocks has not been studied to nearly the degree of similar phenomena such as adsorption. This is of interest, for instance to determine the amount of sodium dithionite is required to propagate a low Eₚ front. Coreflooding experiments as well as geochemical modeling could shed some light on this subject. Electron spin resonance (ESR) experiments with various radicals and sodium dithionite could be used to determine the precise redox conditions necessary to prevent degradation of acrylic polymers.

**Mixing and precipitation of CO₃²⁻ and Ca⁺⁺ in situ**

While calcium can be removed from source waters, little can be done to reduce the hardness of formation brines. Preflooding can take prohibitively long and will not contact all of the formation where the polymer flows. No guidelines exist to determine how much calcium is tolerable in a formation brine when sodium carbonate or another
chemical that can be precipitated by calcium is injected. This problem can be extended as well to the mixing of hydrolyzed polymer with hard brine in-situ.
Bibliography


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