

Laboratory Evaluation of Peroxides for Degrading Polyacrylamide as Used in Fracturing Suspensions and Solids-Free Systems

Edward Derkach, M-I SWACO; Shauna Hayden, Kim Tresco, Leslie Escobar, and Mark Luyster, TBC-Brinadd, LLC

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Abstract

Synthetic polymer conditioners, such as those formed by the polymerization of either acrylamide monomers or N,N'-methylenebisacrylamide, are considered very effective for generating viscosity and reducing friction when supplied in a water-in-oil emulsion, suspension, dispersion, even as a dry additive for fracturing operations. Thus, these acrylamide-based polymers are commonly utilized in the oilfield to create "slickwater" as their linear structure reduces friction, especially in fresh and non-fresh waters.

Of concern is the potential for these slickwater polymers to create damage. It is critical that their removal and/or degradation upon clean-up and subsequent initial production, especially at lower temperatures, does not interfere with intended conductivity in the proppant/fracture or rapid decline rates. Coupled with these concerns are their tendency for adsorption onto formation surfaces and their relatively strong pyrolytic property, which resists decomposition, thus further contributing to damage.

Oxidizers are commonly used to degrade polymer-based fluids in numerous oilfield drilling, such as solids-free systems, and completion fluids. This paper explores the uses of oxidizers, specifically peroxides, to enhance degradation of slickwater fluids whereby ammonium persulfate is used as a reference. Furthermore, the ability to effectively degrade residual acrylamide after placement in a fracture is assessed using slickwater fluids. This study used selected peroxides and catalysts incorporated into slickwater to assess viscosity degradation versus time and pressure at temperatures ranging from 125°F to 225°F, a practical range for slickwater fracturing. The objective was to determine if an efficient and effective peroxide concentration would degrade viscosity at these relatively low temperatures, i.e. 175°F and less.

Introduction

The continued development of horizontal drilling coupled with hydraulic fracturing technology has increased production from unconventional resources in North America and served as a reliable source of hydrocarbons ([Ayers et al. 2012](#); [Palisch et al. 2008](#)) as well as propelled the US to becoming a sometimes net exporter of crude. Reaching economic rates of hydrocarbon production from shale formations is only possible when micro-fractures are created and connected through effective

stimulation treatments, for example, horizontal fracturing in multiple stages ([Loveless et al. 2011](#)). As a concise preface, creation of fractures in low-permeability rocks involves pumping fluids into the wellbore at elevated rates and pressures. This process may use water, slickwater, and/or crosslinked fluids that include variations of borate and guar, hybrid versions, and combinations thereof. Most recently, the preference has been slickwater.

Slickwater can incorporate numerous variations of biopolymers or polysaccharides such as, but not limited to, any one of the variations of guar: carboxymethyl guar, hydroxymethyl guar, hydroxypropylethyl guar, or O-carboxymethyl-O-hydroxypropyl guar (CMHPG), hydroxyethylcellulose (HEC), and even relatively low concentrations of xanthan. Polyacrylamide (PAM) produced in various forms – such as only acrylamide monomers, with sodium acrylate, 2-acrylamido-2-methylpropane sulfonate (AMPS), or acryloxyethyltrimethyl ammonium chloride (AETAC) – are copolymerized at various percentages to form partially hydrolyzed PAM (PHPAM) ([Paktinat et al. 2011](#); [Ke et al. 2019](#)). Co-monomers of the cationic form of PHPAM can include dimethyldiallylammonium, ethanaminium, and 1,2-dimethyl-5-vinylpyridinium. However the partially hydrolyzed form of PHPAM is typically anionic and widely used in the oil and gas development as well as soil conditioning ([Paktinat et al. 2011](#); [Rodvelt et al. 2015](#); [Swiecinski et al. 2016](#)).

The molecular weight (MW) of commercial PHPAM typically ranges from 3 to greater than 25 million Da. A range of 3 to 12 million Da may be considered relatively HMW, while ranging up to 25 million Da could be considered extremely HMW, whereby "high" and "extremely high" are relative terms. Thus, PHPAM with MW greater than 3 million Da is suited for a wider range of applications versus lower weight PAM due to its higher viscosity, superior friction reduction, and water retention characteristics ([Xiong et al. 2018](#)).

[Xiong et al. \(2018\)](#) reviewed 750 fractured wells across six states and 98% of the wells utilized PHPAM-based friction reducers with the majority using the anionic form. Furthermore, it was estimated that fracturing jobs consume 0.2 to 6.0 tons of PHPAM per well which corresponds to 75,000 tons of PHPAM per year in the US ([FracFocus 2018](#)).

When PHPAM is incorporated into a fracturing fluid, the resulting viscosity impacts fracture initiation as well as the final

size of the fracture ([Habibpour and Clark 2017](#); [Kalganekar and Patil 2012](#)). The primary components of these low-viscosity fracturing fluids are water and relatively low concentration(s) of the aforementioned polymers ranging from typically 0.25 to 10.0 lb per thousand gallons (ppt) ([Jeffery et al. 2013](#); [Palisch et al. 2008](#)), albeit proppant and sand.

The technology of friction pressure reduction was introduced to the oil industry more than six decades ago and, circa 2003, increased usage with greater volumes was driven by horizontal wells and subsequently high-injection-rate slickwater operations also increased ([Ke et al. 2019](#)). However in the previous decade, a shift from traditional guar-based fracturing fluids toward slickwater has transpired ([Poppel 2020](#)).

The relatively lower viscosity of slickwater reduces the capability to suspend and transport proppants versus the previous generation of viscosified fluids. However, this is overcome using higher pumping rates, which in turn leads to significant energy loss due to friction and turbulence ([Palisch et al. 2008](#); [Kaufman et al. 2008](#)). In order to lower the surface pumping pressures and compensate for the energy losses during pumping, a relatively small amount of PHPAM is dissolved in the fluid to enhance friction reduction. In slickwater treatments, a friction reducer is a significant component of the fluid and the relatively long, flexible chain of the selected PHPAM creates the needed reduction in friction ([Kim et al. 1998](#)).

The relatively low viscosity of slickwater is assumed to mitigate damage during post cleanup utilizing water, brine, and/or low-viscosity fluids and sweeps before turning the well over to production. An alternative explanation is that slickwater improves proppant pack conductivity by avoiding gel damage and enables higher injection rates ([McClure et al. 2020](#); [Fredd et al. 2001](#)).

Contrary to the aforementioned benefits, recent published production data and literature suggests that even these low viscosity slickwater fluids cause damage ([Kot et al. 2012](#); [Sun et al. 2010a](#)). Upon start-up, the increased production level and subsequent precipitous decline has been scrutinized. The rapid decline and low estimated ultimate recovery (EUR) are attributed to potential formation damage from adsorption of relatively HMW PHPAM, which plugs the natural and propped fractures, and increases pressure and energy loss of liquids flowing through polluted zones ([Jin et al. 2019](#)). Recent damage studies suggest there is potential formation damage with HMW PHPAM, especially as proppant size decreases ([Hlidek and Duenckel 2020](#)).

Today's wells are designed using longer laterals, thus requiring more water and proppant. Even as the pump rate, dosage, and proppant concentration and type vary from stage to stage, the end result is an increase in volume, e.g., millions of gallons of water and thousands of pounds of PHPAM. Therefore, the risk of impairment due to PHPAM is greater. Even with the application of chemical or enzymatic hydrolysis, the backbone of the PHPAM may not cleave or degrade in its entirety due to a variety of reasons such as insufficient breaker concentration ([Sun et al. 2010b](#)). Couple the increased volume with higher loading of PHPAM and this poses an increasing

challenge to overcoming potential damage to the formation as well as the proppant pack ([Sun et al. 2013](#)).

Due to the PHPAM increased molecular weight and the relatively long chain, this high volume and usage poses the potential for formation damage ([Kaufman et al. 2008](#)). Adsorption of PHPAM onto formation surfaces can plug pores resulting in impeded production ([Ke et al. 2019](#); [Carman and Cawiezel 2007](#)). The PHPAM molecule sustains relatively good thermal stability, in fact, the backbone does not decompose below 300°C (572°F), e.g., pyrolytic, which poses a risk for residual damage simply due to its thermal stability ([Chung et al. 2014](#)). In addition, these relatively strong bonds also resist breaker chemistry ([Kot et al. 2012](#)).

[Ke et al. \(2019\)](#) states that fracturing emulsions contain particle diameters between 0.07 and 1.64 µm. Particle size analyses of dry PHPAM before grinding, shows that their particle size ranges from approximately 600 to 800 µm. While grinding can reduce the particle size, the predominant particle size is not reduced to less than the pore size of a typical shale. Shale matrix ranges from 0.005 to 0.1 µm with a typical range from 0.006 to 0.07 µm. Thus PHPAM polymers are too large to penetrate a shale matrix. As such, partially to fully hydrated PHPAM is likely deposited as a filtercake. Based on the aforementioned, it is likely that the retention of polymer molecules in fractures, even unpropped fractures, will increase the likelihood of damage, thus impeding productivity.

All the aforementioned issues can result in incomplete removal of the PHPAM along the entire length of the production zone or at one or more of the fracturing stages.

In addition, wells drilled worldwide as conventional openhole completions in unconsolidated sands utilizing viscous drilling/completion systems can suffer the same consequences, in part, as the aforementioned polymeric damage in unconventional. Achieving the desired production in these unconsolidated, non-perforated wellbores is dependent upon how effectively the residual filtercake is removed from the surface of the borehole. Filtercake removal is affected by a variety of fluid and wellbore conditions including, but not limited to:

- Polysaccharide concentration and size
- Insoluble solids concentration and size
- Temperature
- Hole angle
- Type of completion fluid
- Method of displacement
- Cleanup technique
- Completion method
- Mitigation of formation solids (e.g., reactive clays)

Drilling production payzones with these specialty systems minimizes formation damage and mitigates liquid and solids invasion into the target formations depositing filtercakes that bridge and seal formations, even fractures. This filtercake must be comprised of material that is removable with post breakers and/or using the initial production to mechanically clean-up (e.g. produce) the filtercake, in some completions. These desirable characteristics are generated by the combination of

properly graded, soluble particles and high-grade polysaccharide polymers. The viscosifying and filtrate-reducing polymers are concentrated in the filtercake with these soluble particles. The polymers provide cohesiveness and can encapsulate the bridging solids. Consequently, the polymers in the filtercake can retard dissolution of the bridging particles and therefore, must be decomposed or degraded to promote a complete and even dissolution of the soluble solids. In wells where coiled-tubing (CT) is employed, this may require degradation of the leak-off only as these systems are typically solids-free due to the hydraulic restrictions.

In summary, breakers, or chemistry specific to degrading PHPAM as well as polysaccharides, can be incorporated in conventional and unconventional fluids to mitigate the risk of formation damage.

Design optimization for breakers for unconventional fluids should incorporate the following criteria:

- Degradation of residual PHPAM, especially at temperatures less than 200°F and preferably less than 150°F
- Potential to improve rapid decline rates and low EUR
- Intended conductivity in the proppant residing in the fracture
- Tolerance for high loading of PHPAM to overcome friction
- Mitigate adsorption of PHPAM onto formation surfaces
- Degradability of the relatively long polymer chains (i.e., HMW)
- Overcome their relatively strong pyrolytic property which resists decomposition
- Residual PHPAM that does not penetrate the shale matrix

Oxidizers

Oxidative breakers are used in the oil and gas industry to destroy and degrade residual filtercakes, viscous fluids, and residual muds (Brady et al. 2000). Typically, this is accomplished whereby a selected oxidizer (e.g., persulfate, peroxide, or hypochlorite) is incorporated into a fluid as used in unconventional completions or as a component of fluid that is used as a breaker for conventional completions. Thus the selected oxidizer is pre-formulated into a system whereby the reaction is delayed for a period of time until such time where this system degrades. Alternatively, an oxidizer is incorporated into a fluid and subsequently pumped to degrade an existing fluid/filtercake.

With respect to the use of oxidizers in a breaker solution, almost every practical product/chemistry has been utilized in the oilfield within the realm of judicious health, safety, and environmental (HSE) practices. For example, hypochlorite is more commonly used versus hydrogen peroxide where the latter is a very effective oxidizer however increasingly dangerous when handling at concentrations greater than 20%, even 15% by weight. Ozone is one of the strongest oxidizers with respect to its measured oxidation potential as is chlorine and chlorine dioxide. However subsequent reactions, especially with organic material, yields a very fast and violent reaction. In contrast, when aqueous solutions such as surface water supply the air (or oxygenation) and the concentration of oxidizing and reducing materials is so low, most oxidation–

reduction (redox) reactions are extremely slow and consumed in their entirety. Contrasting slow reactions with nearly instantaneous reactions, such as lime and carbon dioxide, dictates a preference for a relatively strong reductant and weak oxidizer, albeit non-combustible, where a reaction is preferably controlled and delayed. As a desired reaction transpires in an aqueous environment relatively slowly whereby a catalyst is sometimes utilized even required.

The relative voltage potential for selected oxidizing and reducing agents, are shown in Fig. 1 whereby the strongest reductants are the weakest oxidants. It is important to recognize that although an environment may be strongly oxidizing or reducing, the voltage potential for the half-cell reaction does not influence the rate (Nalco 1988). Compare the $E^\circ(\text{V})$ values for half-cell reactions and note that Mg^{2+} , Ca^{2+} , and Li^+ are relatively strong reducers as they readily donate electrons. The former are typically inorganic peroxides with the latter a hypochlorite and all commercially available. However, the commercial forms of Mg^{2+} and Ca^{2+} are attractive with respect to cost, relatively strong reducers, the potential to accelerate thus control their reaction, as well as impart relatively safer handling and logistics.

Half-reaction				
Element	Oxidant	Reductant		$E^\circ(\text{V})$
Li	$\text{Li}^+ + \text{e}^-$	$\text{Li}(\text{s})$		-3.0401
K	$\text{K}^+ + \text{e}^-$	$\text{K}(\text{s})$		-2.931
Ca	$\text{Ca}^{2+} + 2\text{e}^-$	$\text{Ca}(\text{s})$		-2.868
Na	$\text{Na}^+ + \text{e}^-$	$\text{Na}(\text{s})$		-2.71
Mg	$\text{Mg}^{2+} + 2\text{e}^-$	$\text{Mg}(\text{s})$		-2.70
Mg	$\text{Mg}(\text{OH})_2 + 2\text{e}^-$	$\text{Mg} + 2\text{OH}^-$		-2.690
Mg	$\text{Mg}^{2+} + 2\text{e}^-$	$\text{Mg}(\text{s})$		-2.372
Al	$\text{H}_2\text{AlO}_3^- + \text{H}_2\text{O} + 3\text{e}^-$	$\text{Al} + 4\text{OH}^-$		-2.33
Al	$\text{Al}(\text{OH})_3 + 3\text{e}^-$	$\text{Al}(\text{s}) + 3\text{OH}^-$		-2.31
H	$\text{H}_2 + 2\text{e}^-$	2H^+		-2.23
Al	$\text{Al}^{3+} + 3\text{e}^-$	$\text{Al}(\text{s})$		-1.662
Zn	$\text{Zn}(\text{OH})_4^{2-} + 2\text{e}^-$	$\text{Zn}(\text{s}) + 4\text{OH}^-$		-1.199
Mn	$\text{Mn}^{2+} + 2\text{e}^-$	$\text{Mn}(\text{s})$		-1.185
Fe	$\text{Fe}(\text{OH})_2 + 2\text{e}^-$	$\text{Fe}(\text{s}) + 2\text{OH}^-$		-0.89
Fe	$\text{Fe}_2\text{O}_3(\text{s}) + 3\text{H}_2\text{O} + 2\text{e}^-$	$2\text{Fe}(\text{OH})_2(\text{s}) + 2\text{OH}^-$		-0.86
Ti	$\text{TiO}^{2+} + 2\text{H}^+ + 4\text{e}^-$	$\text{Ti}(\text{s}) + \text{H}_2\text{O}$		-0.86
Zn	$\text{Zn}^{2+} + 2\text{e}^-$	$\text{Zn}(\text{s})$		-0.7618
Cr	$\text{Cr}^{3+} + 3\text{e}^-$	$\text{Cr}(\text{s})$		-0.74
Ag	$\text{Ag}_2\text{S}(\text{s}) + 2\text{e}^-$	$2\text{Ag}(\text{s}) + \text{S}^{2-}(\text{aq})$		-0.69
Pb	$\text{PbO}(\text{s}) + \text{H}_2\text{O} + 2\text{e}^-$	$\text{Pb}(\text{s}) + 2\text{OH}^-$		-0.58
Fe	$\text{Fe}^{3+} + \text{e}^-$	$\text{Fe}(\text{s})$		-0.44
Cr	$\text{Cr}^{3+} + \text{e}^-$	Cr^{2+}		-0.42
Cu	$\text{Cu}_2\text{O}(\text{s}) + \text{H}_2\text{O} + 2\text{e}^-$	$2\text{Cu}(\text{s}) + 2\text{OH}^-$		-0.360
Pb	$\text{PbSO}_4(\text{s}) + 2\text{e}^-$	$\text{Pb}(\text{s}) + \text{SO}_4^{2-}$		-0.3588
Pb	$\text{PbSO}_4(\text{s}) + 2\text{e}^-$	$\text{Pb}(\text{Hg}) + \text{SO}_4^{2-}$		-0.3505
Co	$\text{Co}^{2+} + 2\text{e}^-$	$\text{Co}(\text{s})$		-0.28
Ni	$\text{Ni}^{2+} + 2\text{e}^-$	$\text{Ni}(\text{s})$		-0.25
Ag	$\text{AgI}(\text{s}) + \text{e}^-$	$\text{Ag}(\text{s}) + \text{I}^-$		-0.15224
O	$\text{O}_2(\text{g}) + \text{H}^+ + \text{e}^-$	$\text{HO}_2^-(\text{aq})$		-0.13
Pb	$\text{Pb}^{2+} + 2\text{e}^-$	$\text{Pb}(\text{s})$		-0.126
Fe	$\text{Fe}^{3+} + \text{e}^-$	$\text{Fe}(\text{s})$		-0.04
Fe	$3\text{Fe}_2\text{O}_3(\text{s}) + 2\text{H}^+ + 2\text{e}^-$	$2\text{Fe}_3\text{O}_4(\text{s}) + \text{H}_2\text{O}$		0.22
O	$\text{O}_2(\text{g}) + 2\text{H}_2\text{O} + 4\text{e}^-$	$4\text{OH}^-(\text{aq})$		0.401
Au	$[\text{AuI}_2]^- + 3\text{e}^-$	$\text{Au}(\text{s}) + 4\text{I}^-$		0.56
Au	$[\text{AuI}_2]^- + \text{e}^-$	$\text{Au}(\text{s}) + 2\text{I}^-$		0.58
O	$\text{O}_2(\text{g}) + 2\text{H}^+ + 2\text{e}^-$	$\text{H}_2\text{O}_2(\text{aq})$		0.7
Ag	$\text{Ag}^+ + \text{e}^-$	$\text{Ag}(\text{s})$		0.7996
Fe	$2\text{FeO}_4^{2-} + 5\text{H}_2\text{O} + 6\text{e}^-$	$\text{Fe}_2\text{O}_3(\text{s}) + 10\text{OH}^-$		0.81
Species	Oxidant	Reductant		$E^\circ(\text{V})$
NH4	$\text{S}_2\text{O}_8^{2-} + 2\text{H}^+ + 2\text{e}^-$	2HSO_4^-		2.12

Figure 1 – Selected redox potentials for electron transfer at 77.0°F (25.0°C) and 1 mol/L for aqueous species at 1 atm. Note: ammonium persulfate is listed in the last row.

Peroxide Chemistry

In one realm an oxidizing agent is a chemical species that undergoes a chemical reaction that takes one or more electrons from another atom. In the second realm, an oxidizing agent is

a chemical species that transfers electronegative atoms, usually oxygen, to a substrate. Molecular O₂ and the formation of hydroxyl and peroxide radicals serves as an efficient biopolymer breaker (Dobson et al. 1993). The use of oxidizers can be expanded to degrade polyelectrolytes, specifically synthetic organic polyelectrolytes such as polyacrylamide.

Xiong et al. (2018) shows that free radicals attack the polymer backbone via “hydrocarbon abstraction at both the secondary and tertiary carbons, as well as the primary amine, generating polymer radicals.”

As an example, Figure 2 shows how oxidizers can attack the backbone of polymers using peroxides, whereby peroxides generate free radicals. Moderate strength acid, as an external catalyst, hydrolyzes the acetal linkage resulting in two smaller fragments. Cleavage exposes aldehyde or ketone groups whereby, oxidation of the first aldehyde group exposes the next site on the glucose ring. The process repeats until the glucose backbone is destroyed.

Mechanism for an Acid Peroxide Combined Attack on Polymer Structures

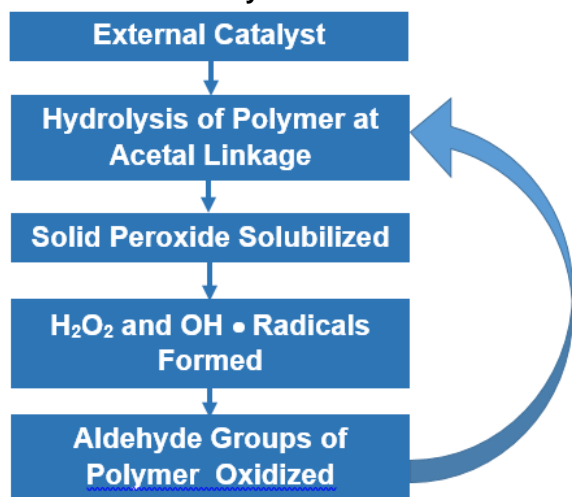


Figure 2 – Polymer decomposition repeating flow loop utilizing solid peroxide.

As a preface for hypochlorite oxidizers, the geometry of a biopolymer (e.g., xanthan) exists in a slightly ordered conformation in an alkaline solution, but not to the same degree as in a solution with low pH values (Fig. 3). Since the glycosidic linkage is shielded in these conditions, hypochlorites will attack the hydroxyl sites. Alkaline ring separation is slower than the acid attack on the glycosidic position, but once the ring has been cleaved, oxidative degradation of the aldehyde, or ketone groups, provides efficient biopolymer decomposition (Hsia Chen and Sheppard 1979). While this chemistry is effective, two counter effects should be noted: 1) dissipation of the oxidizer on surface dilutes the desired concentration, and 2) the interaction of the oxidizer with iron oxide, for example, a non-pickled workstring or tubing, that introduces an inordinate amount of “rust” which reacts and subsequently precipitates.

Examples of commercially available alkaline earth (i.e. inorganic) and metal peroxides include, but are not limited to:

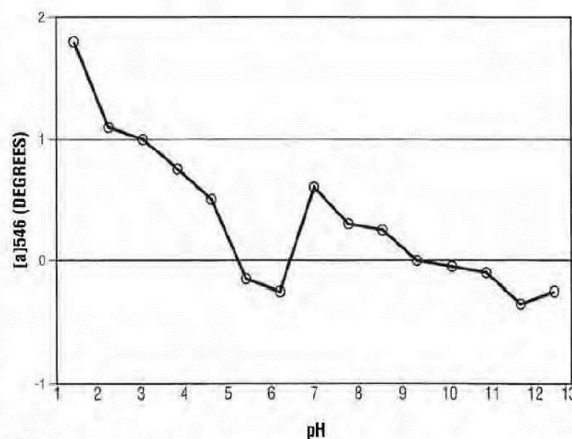
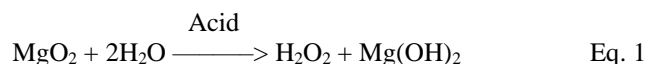


Figure 3 – Effect of pH on the optical rotation of xanthan in water at 86°F (Hsia Chen and Sheppard 1979).

calcium peroxide (CaO₂), magnesium peroxide (MgO₂), and zinc peroxide (ZnO₂). Due to the extremely low solubility of this class of peroxides, they remain stable for extended periods of time while in an alkaline environment, such as leak-off into a formation and/or as a component of a filtercake. Upon contact with a low-pH fluid, the solid peroxide will decompose to form hydrogen peroxide according to the generalized reaction in Eq. 1:



The hydrogen peroxide (H₂O₂) produced in the above reaction is much less stable than the magnesium peroxide from which it was formed, and as such will begin to decompose rapidly while the residual magnesium hydroxide is digested by the low-pH fluid. The generation of oxygen from peroxide decomposition is expressed as Eq. 2:



Autoxidation, or rapid decomposition of susceptible molecules of biopolymers and starch, occurs as the polymer is exposed to the oxygen (Eq. 3):



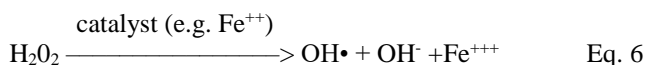
The polymer, P•, is now considered a free radical as is the peroxide. Initiation of a radical species may be slow because of the high activation energy required. However, in the presence of an activator such as a transition metal, the reaction is relatively faster. Thus once a radical species has formed, it will react extremely fast with oxygen, producing a hydroperoxide radical (Eq. 4):



Which in turn propagates the chain reaction shown in Eq. 5:



Hydroperoxide (POOH) decomposition may then follow several different reaction paths depending on the composition of the solution and the physical conditions. One of the products of H_2O_2 decomposition is hydroxyl radicals ($\text{OH}\cdot$). The formation of these radicals from hydrogen peroxide is enhanced in the presence of transition metal catalysts (Fig. 4). Examples of these catalysts include iron (Fe), manganese (Mn), and copper (Cu). Per [Schumb et al. 1955](#), the metal catalyzed decomposition of hydrogen peroxide proceeds according to [Eq. 6](#):



These highly reactive $\text{OH}\cdot$ species initiate chain reactions with various functional groups on the polymer structures. The strong oxidizing power of the $\text{OH}\cdot$ radicals allows them to attack points on the polymer which are resistant to acid alone.

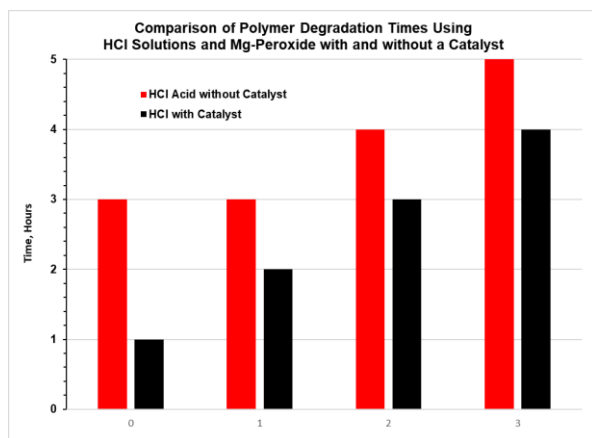


Figure 4 – Approximate polymer degradation times using residual filtercakes comprised of biopolymer, starch, and sized salt in a solution of magnesium peroxide with and without a catalyst were static aged at 125°F.

Benefits of Peroxide-Type Breakers

Alkaline earth metal peroxides are effective for degradation of many natural polysaccharides such as cellulose, guar, starch, xanthan, and their derivatives, which have been synthesized to produce a myriad of products (e.g., CMHPG) for various even unique oilfield applications. These magnesium and calcium-type peroxides provide several benefits which include:

- Delayed reaction when applied in water-based fracturing fluids due to their elevated pH environment (i.e., preferably greater than 9.0 pH thus alkaline)
- Activation by temperature or contact by a relatively low-pH fluid (e.g., less than 6.5 pH thus acidic).
- Commercially available in solid form
- Formulated as a suspension
- Ability to encapsulate
- Variation of potential reactivity (e.g., O_2)
- Mg^{2+} and Ca^{2+} reduced assay are classified as “non-oxidizer” when transporting
- Work effectively for applications up to almost 200°F ([Guerin et al. 2015](#))

The available oxygen typically ranges from approximately 6% to 17%, and this species, initiates degradation as shown in [Eq. 2](#), [Eq. 3](#) and [Eq. 4](#). The purity for the magnesium variation ranges from 30% to 37% while the purity for the calcium variation typically exceeds 60%.

For discharge offshore US, drilling fluids need to meet both a daily minimum and a monthly average minimum 96-hour LC_{50} of at least 30,000 ppm in a 9:1 seawater to drilling fluid suspended particulate phase (SPP) volumetric ratio using *Mysidopsis bahia* ([US EPA 2017](#)). The bioassay data for peroxide shows that the 96-hr LC_{50} ranges from 236,000 to greater than 1,000,000 ppm thus classified as “acceptable” for offshore use.

As an example, magnesium peroxide remains inactive when added to a water-based buffered fluid system as this chemistry is from a class of peroxides that will remain stable for extended periods of time in an alkaline fluid environment. Thus the peroxide persists as an inert component of the fluid system, its leak-off, and as deposited into a filtercake. When the now residual magnesium peroxide is exposed to a low-pH fluid, it begins to release hydrogen peroxide as shown in [Eq. 1](#). As the reactions proceed rapidly, the peroxide will locally degrade residual polysaccharides and polymers. This promotes degradation of these polymers, lower fluid viscosity, and even dispersion of residual polymers and filtercakes. It follows that the initial clean-up of a well would realize improved removal efficiency due to a reduction in polymer size, reduction in viscosity, and/or the dispersion of the residual filtercake.

The next sections explore the utilization of these peroxides for degradation of PHPAM and fluids viscosified with these synthetic molecules as well as degradation of biopolymers as utilized in a coiled tubing system.

Laboratory Method and Results

Slickwater Fluids – Unconventional Application

To assess the effectiveness of the aforementioned peroxides, numerous simulations were performed at temperatures of 125, 150, 175, and 200°F. However, a few simulations were performed at 225°F to affirm if the incorporation of a peroxide is necessary. Degradation of PHPAM proceeds faster as viscosity decreases more rapidly at elevated temperature and salinity ([Wu et al. 2012](#), [Sun et al. 2010a](#); [2010b](#)) even as conventional oxidizers are effective for temperatures above 200°F ([Guerin et al. 2015](#)). As such, magnesium peroxide, calcium peroxide, calcium peroxide as a reduced assay, combinations thereof (i.e. buffered peroxides), and ammonium persulfate were incorporated at various concentrations. Two forms of ammonium persulfate were used, non-encapsulated (APS) and encapsulated (EAPS). In addition, catalysts were introduced where deemed applicable, using organic catalysts. Thus, selected combinations of these breakers were used to determine an effective concentration to degrade PHPAM slickwater with respect to time and temperature, while generally simulating field operations.

To further, the efficiency of buffered peroxides versus

ammonium persulfate, at selected concentrations and temperatures, was evaluated by measuring viscosity degradation, with and without their addition, in a slickwater base using fresh and 10,000 TDS water/brine. The objective was two-fold: 1) effective viscosity degradation as close to the viscosity of water as practical and 2) identify effective breaker concentration(s) for temperatures less than 200°F. Success in degradation was measured as attaining a significant reduction in viscosity as compared to the baseline after static aging. Any measurement meeting these criteria would warrant further investigation, thus allowing customization.

This assessment utilized a Grace M5600 rheometer ([Grace Instrument 2008](#)) to capture viscosity under pressure and temperature, whereby an arbitrary timeline was utilized to simulate a pumping/fracturing operation. While other evaluation methods such as regained permeability testing and measuring the subsequent molecular weight, e.g., utilizing multi-angle laser light scattering (MALLS) ([Ke et al. 2019](#)) are documented, this assessment focused on viscosity as a means to assess the ability to degrade a PHPAM suspension that is pre-hydrolyzed versus time.

This Grace M5600 rheometer ([Fig. 5](#)) enables the nearly instantaneous measurement of small changes in shear stress by non-mechanically transmitting a zero-friction rotational torque signal from the pressure containment area/cup. The outer cylinder is driven by a stepper motor which generates speeds ranging from 0.0001 to 1,100 rpm. Thus, the relatively low range of speed allows for assessing fluids at relatively low shear rates to more definitively determine if viscosity persists with exposure to a selected peroxide versus time and temperature. In addition, measurements can be captured using pressures up to 1000 psi. It follows that this instrument/model would mitigate experimental artifacts such as manipulation when using manual rheometers as well as spurious viscosity readings due to temperature and the ability to measure under pressure.



Figure 5 – Grace 5600-2 Model Rheometer ([Grace Instruments 2008](#)).

The laboratory method involved the preparation and mixing

of a slickwater fluid such as utilized in fracturing operations, at a dosage as applied in operations where relatively elevated viscosity is required (e.g., the toe of the completion). For these tests, an anionic HMW PHPAM supplied as a 45% w/w oil-based suspension was used for formulating in fresh water and a 10,000 TDS synthetic brine. The PHPAM suspension was previously produced to specification and packaged in 330-gal totes and currently stored. The synthetic brine/base was formulated and mixed prior to a specification of 10,000 TDS with no multivalence whereby the specific gravity approximated 1.005.

[Figures 6a](#) and [6b](#) show results from quality control tests conducted via a flow loop. As this suspension was used to formulate slickwater fluids for assessing potential oxidizers, it was surmised that a consistent and stable suspension would mitigate testing artifacts. The parameters utilized for these tests are shown in [Table 1](#).

Table 1 – Test Parameters Using PHPAM Suspension	
Pump Rate (average)	14.2 gal/min
Test Fluid	10,000 TDS synthetic brine
Tubing OD	0.5 in.
Straight Tube Length	12 ft
Temperature (range)	78 to 81 °F
Test Period	10 min
N _{RE} (range)	145,000 – 152,000

[Fig. 6a](#) shows flow loop results where the aforementioned synthetic brine was dosed at 0.25 gallons per thousand (gpt). The first run used a suspension prepared in the laboratory, the second used a sample collected from the initial production batch, and the third used a retain sample from the same production batch after 30-days of storage. The y-axis is focused on the range of 50 to 90% drag reduction to facilitate differentiating the results. All exhibited very similar drag reduction, approximately 79-80% over the 10-minute test period, as well as time to attain maximum reduction. These results are presented to verify not only, drag reduction, but also the need to mitigate artifacts for ensuing tests whereby peroxides are incorporated into this suspension.

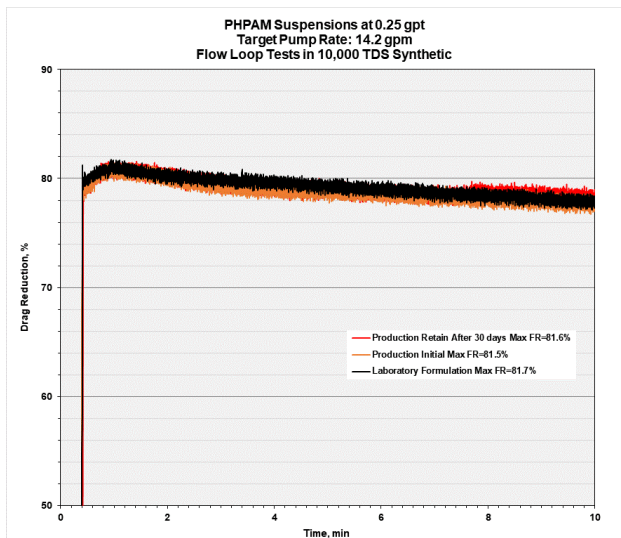


Figure 6a – Comparison of anionic PHPAM suspensions of a laboratory sample (black line), initial production batch (yellow line) and post 30-day retained sample (red line). The y-axis is focused on the range of 50 to 90% drag reduction to facilitate differentiating the data.

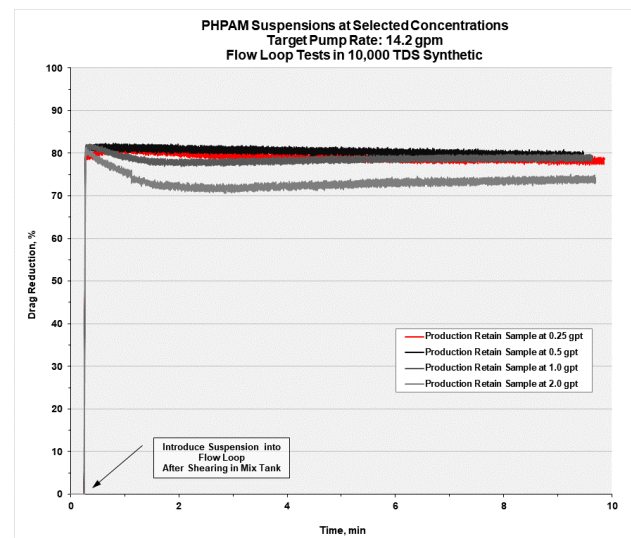


Figure 6b – Flow loop runs at 0.5, 1.0, and 2.0 gpt for comparison to the post 30-day retain at 0.25 gpt as shown in Fig. 6a. The drag reduction decreases as expected with increasing concentration, for 1.0 and 2.0 gpt, where their viscosity increases. However at these concentrations, the drag reduction increases after approximately 3 to 4 minutes of pumping.

Fig. 6b shows the flow loop results where the dose rate was increased from the previous 0.25 gpt to 0.5, 1.0, and 2.0 gpt. As expected, drag reduction decreased with increasing concentration of PHPAM for suspensions at 1.0 and 2.0 gpt. For these concentrations, the drag reduction decreased initially, approximately 3 to 7%, as the dose rate increased. The decreasing drag reduction corresponds with increased viscosity, however nominally, as shown in Fig. 6c. Nevertheless, elevated viscosity is more advantageous when assessing the potential to degrade a residual slickwater fluid that includes breakers thus the necessity to utilize a more viscous suspension than is typically applied in slickwater operations (Carman and Cawiezel 2007).

The preparation of these slickwater fluids included fresh water or synthetic brine plus the aforementioned suspension and selected peroxides, whereby each combination was sheared at 1,000 rpm for 30 seconds to produce slickwater. An additional 10 seconds of mixing was used for the addition of a catalyst. Next, the pre-mixed slickwater was introduced into the rheometer's pressure containment cup and approximately 400 psi was applied. The total timeline for each test was approximately 105 minutes. The sequence and time for each step is shown below. The rationale was to condense time to expedite and maximize the number of tests while generally simulating field operations:

- **5 minutes:** establish initial viscosity at temperature and pressure to compare to the final viscosity at a shear-rate of 511 sec^{-1} (e.g., simulated pumping)
- **30 minutes:** decrease shear rate to 40 sec^{-1} to simulate velocity in a fracture

- **60 minutes:** Allow slickwater to static age at temperature and pressure (e.g., shut-in)
- **10 minutes:** Increase shear rate to 511 sec^{-1} and measure subsequent/final viscosity for comparison

The use of 40 sec^{-1} to simulate velocity in a fracture during the 30-minute period was arbitrary, however Montgomery (2013) states that service company literature reports different shear rates, usually 170 or 511 sec^{-1} with rates as low as 30 sec^{-1} .

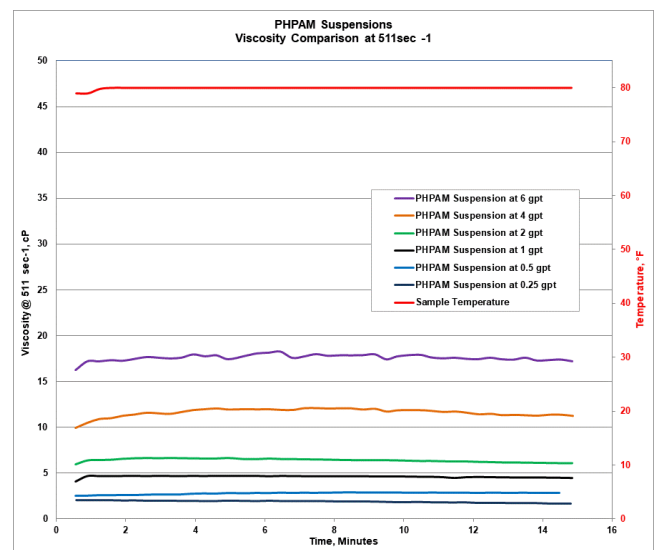


Figure 6c – Comparison of viscosity at 511 sec^{-1} for a given dose rate for PHPAM suspensions in 10K TDS brine. Note that viscosity increases nominally as the dose rate increases from 0.25 to 6.0 gpt.

Slickwater Results at 225°F

This test series at 225°F included a slickwater baseline using a concentration of 6 gpt (Fig 7). The initial viscosity of the 6-gpt baseline averaged 19 cP at 511 sec⁻¹ during the 5-min interval. At 40 sec⁻¹ the viscosity increased as expected and ranged from 91 to 53 cP. After static aging, the viscosity was compared to the initial, and averaged 12 cP. This viscosity reduction, within this timeframe, was most likely due to thermal degradation.

As a comparison, APS and EAPS were incorporated into the 6-gpt slickwater system at 2 ppt. After static aging, the viscosity for the former averaged 12 cP and the latter averaged 7 cP. As a further comparison, a slickwater system with Buffered I at 2 ppt exhibited viscosity after static aging that averaged 4 cP. Again, this viscosity is less than 6 gpt baseline.

At this temperature, thermal degradation is most likely the mechanism for viscosity reduction. These slickwater systems with breakers exhibit a spike followed with precipitous degradation over the 30-min period with the exception of the slickwater system with APS, which increased. This initial viscosity spike is typical when incorporating oxidizers as they initially elevate pH thus temporarily buffer a fluid/system.

The incorporation of Breaker L and Buffered K in the PHPAM suspension yielded inefficient viscosity at 40 sec⁻¹. However, the incorporation of Buffered I and J provided significantly more viscosity at the same shear rate. After static aging the suspension with Buffered J, the viscosity measured approximately 2 to 3 cP versus Buffered I, which exhibited 4 to 5 cP. Note that Buffered J required only a concentration of 0.45 ppt.

In summary, all of these slickwater systems exhibited viscosity spikes. The APS breaker aided in viscosity degradation at this temperature, which resulted in viscosity less than the baseline. In addition, two of the buffered peroxides remained stable at 40 sec⁻¹, Buffered I and Buffered J. After static aging, Buffered J showed substantially reduced viscosity compared to the baseline and only required 0.45 ppt.

Slickwater Results at 200°F

This test series at 200°F includes a PHPAM slickwater as a baseline using a concentration of 6 gpt (Fig 8). The initial viscosity of this baseline averaged 20 cP at 511 sec⁻¹ during the 5-min interval. At 40 sec⁻¹, the viscosity decreased and ranged from 93 to 30 cP. After static aging, the viscosity averaged 9 cP. The viscosity reduction within this test period was most likely due to thermal degradation. As a comparison, APS and EAPS were incorporated into the slickwater system at 2 ppt. After static aging, the viscosity averaged approximately 12 to 13 cP for both breaker systems. Note that the viscosity with the incorporation of these breakers is greater than the baseline.

As a further comparison to reduce viscosity, four slickwater systems incorporating different combinations of buffered peroxides were tested and ranged from 0.45 to 2.15 ppt. These are designated A thru D. Again, all these slickwater systems exhibited a spike followed with precipitous

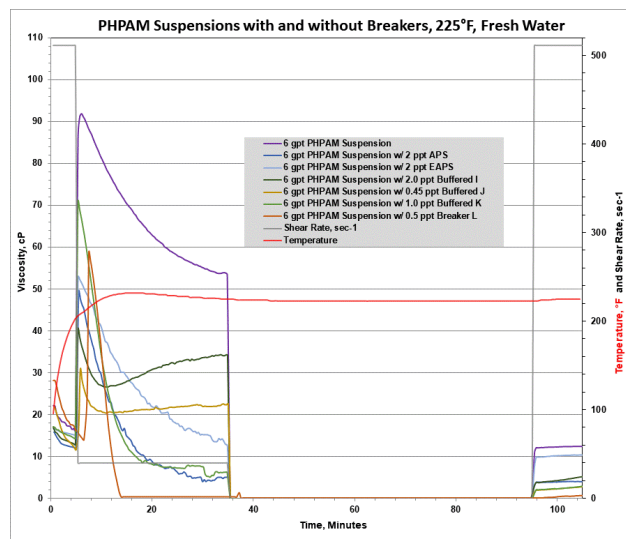


Figure 7 – Comparison of slickwater systems with selected persulfate and buffered breakers. Slickwater baseline, 6 gpt, is shown as a purple line.

degradation over the 30-min period with the exception of the slickwater systems with Buffered B and D, which stabilized at approximately 20 cP. Note that the viscosity degraded prematurely to less than 10 cP at 40 sec⁻¹ for the slickwater systems with Buffered A and C. The concentration of Buffered B at 0.45 ppt exhibited less than 5 cP after static aging, while maintaining viscosity that ranged from 18 to 20 cP at 40 sec⁻¹.

Again at 200°F, like 225°F, all systems exhibited a spike. Though they provided sufficient viscosity at 40 sec⁻¹, EAP and APS were substantially greater than the baseline after aging. Once again, the buffered peroxides retained relative stability at 40 sec⁻¹, and after aging achieved significantly reduced viscosity below the baseline.

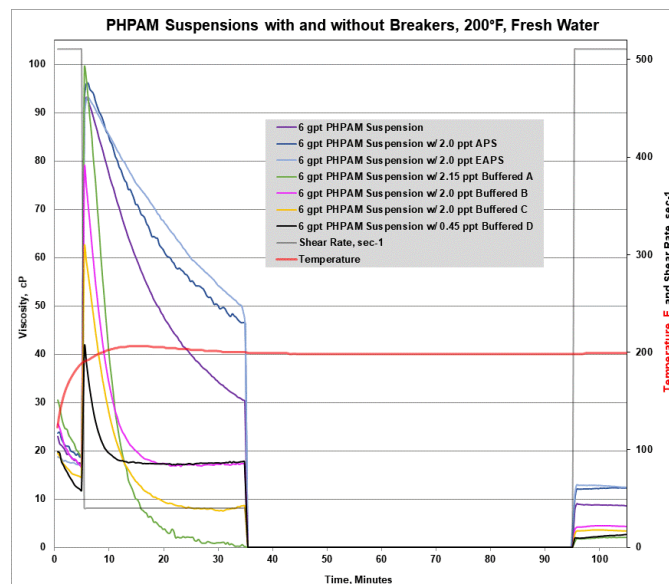


Figure 8 – Comparison of slickwater systems with selected persulfate and buffered breakers 200°F.

Slickwater Results at 175°F

This test series at 175°F included slickwater baselines using concentrations of 6 gpt and 4 gpt, in fresh water and 10,000 TDS synthetic brine respectively (Fig 9). The initial viscosity of the freshwater baseline for 6 gpt, averaged 17 cP at 511 sec⁻¹. At 40 sec⁻¹, the viscosity decreased and ranged from 85 to 72 cP. After static aging, the viscosity averaged 12 cP. The viscosity reduction, within this test period, was relatively unchanged.

As a comparison, APS and EAPS breakers were evaluated and both individually incorporated into the above slickwater systems at 2 ppt. The suspension with the APS exhibited viscosity from 85 to 72 cP at 40 sec⁻¹ and the EAPS ranged from 88 to 43 cP. After static aging, the viscosity averaged 12 cP and 8 cP, respectively for the APS and EAPS. This is indicative of only nominal degradation of viscosity at 511 sec⁻¹. Note that the viscosity was elevated where it is critical, however only nominal degradation was seen after static aging.

The initial viscosity of the freshwater baseline for 4 gpt slickwater suspension, averaged 8 to 9 cP at 511 sec⁻¹. At 40 sec⁻¹, the viscosity increased and ranged from 30 to 22 cP. After static aging, the viscosity averaged 7 to 8 cP. This viscosity reduction at 511 sec⁻¹, within this test period was relatively unchanged.

As a comparison, APS and EAPS breakers were evaluated, both individually incorporated into the above slickwater system at 2 ppt. The suspension viscosity at 40 sec⁻¹ with the APS ranged from 30 to 22 cP and the EAPS ranged from 28 to 12 cP. After static aging, the viscosity averaged 7 to 6 cP, for both the EAPS and APS. Again, the viscosity is elevated where it is critical, however only nominal degradation was seen after static aging.

As a further comparison, these slickwater systems incorporated different combinations of buffered peroxides, designated E thru H. None of these slickwater systems

exhibited stable viscosity during the 30-min period at 40 sec⁻¹ as the viscosity spiked and then decreased. However, Buffered E maintained viscosity greater than 20 cP. After static aging the viscosity of the slickwater systems that incorporated Buffered E, F, and H all averaged 7 to 5 cP, thus less than their respective baselines.

At this temperature, thermal degradation of the slickwater baseline was again apparent. However, the incorporation of 2 ppt APS exhibited elevated viscosity at 40 sec⁻¹ with nominal viscosity degradation after static aging. The use of Buffered E provided relatively less viscosity at 40 sec⁻¹, however the viscosity was reduced to approximately 5 cP after static aging.

To further the testing, all breakers were evaluated in a 4-gpt slickwater suspension formulated in a 10,000 TDS brine. The viscosity for this baseline is less than the 6-gpt baseline at all shear rates as expected due to less concentration and increased TDS. Note that the viscosity for the slickwater system with EAPS was elevated at 40 sec⁻¹, while the slickwater system with the APS exhibited decreasing viscosity. After static aging, the viscosity of the APS averaged 7 cP, same as the baseline, while the EAPS exhibited a nominal increase, approximately 9 cP. Four buffered peroxides, designated M thru P, were also evaluated. All exhibited decreasing viscosity at 40 sec⁻¹ and after static aging, compared to the baseline. Buffered P exhibited the most effective viscosity degradation, at the lowest concentration.

At 175°F in freshwater, nearly all the systems exhibited a spike in viscosity. Though they provided sufficient viscosity at 40 sec⁻¹, the buffered peroxides showed a greater reduction in viscosity as compared to the EAP, APS and baseline.

In 10,000 TDS brine, no viscosity spikes were apparent. At 40 sec⁻¹, all viscosity was virtually stable. After aging, the buffered peroxides were reduced approximately 50% below the baseline.

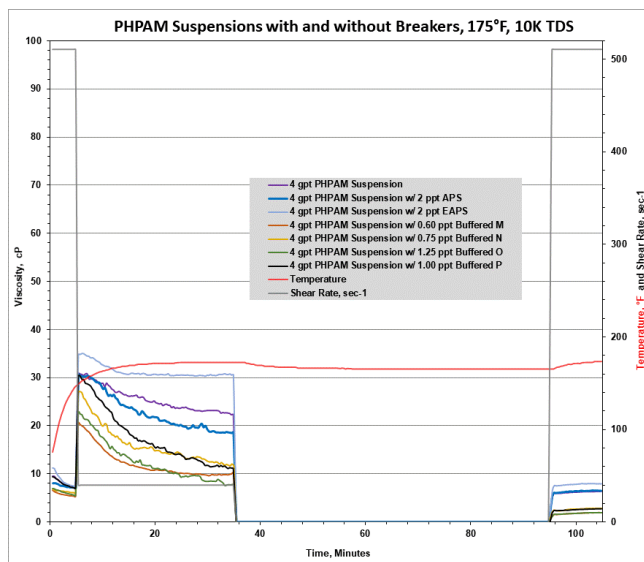
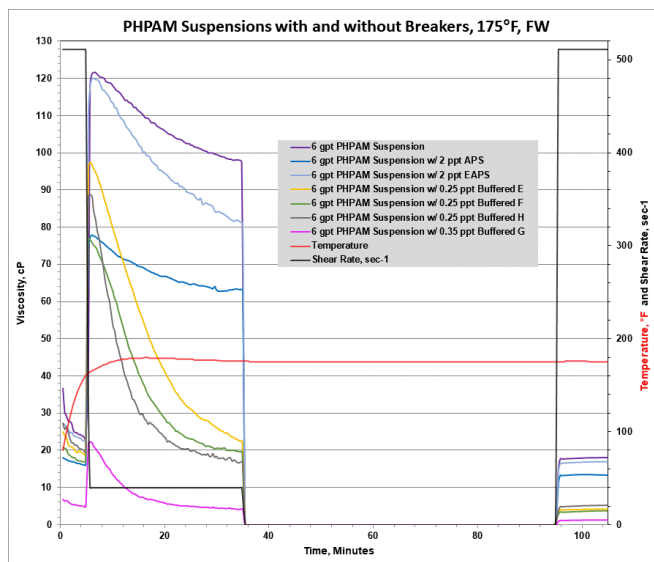


Figure 9 – Comparison of a 10,000 TDS slickwater baselines at 6 (left) and 4 (right) gpt, respectively, with selected persulfate and buffered breakers.

Slickwater Results at 150°F

This test series at 150°F included a slickwater baseline using only a concentration of 6 gpt in fresh water and a 10,000 TDS synthetic brine (Figures 10a and 10b). The initial viscosity in fresh water ranged from 33 to 24 cP at 511 sec⁻¹. At 40 sec⁻¹, the viscosity increased and ranged from 125 to 142 cP. The initial viscosity in 10,000 TDS ranged from 11 to 10 cP at 511 sec⁻¹. At 40 sec⁻¹, the viscosity decreased nominally and ranged from 41 to 36 cP. After static aging, the baseline viscosity was nearly identical at 511 sec⁻¹ before and after static aging.

The use of APS and EAPS decreased the viscosity in the fresh water and 10,000 TDS slickwater systems at 40 sec⁻¹, with the exception of EAPS in only the 10,000 TDS brine. Furthermore, the use of 2-ppt APS in the fresh water decreased, and stabilized the viscosity to approximately 100 cP. The use of 2-ppt EAPS decreased the viscosity, which ranged from 100 to 88 cP (Fig. 10a). In the 10,000 TDS slickwater system (Fig 10b) the viscosity decreased nominally from 40 to 30 cP with 2-ppt APS while the use of 2-ppt EAPS elevated the viscosity to approximately 40 cP. After static aging, the viscosity for both slickwater systems in fresh water decreased nominally. In the 10,000 TDS brine, no significant change in viscosity was apparent.

To further, a Buffered Q and Breaker T systems were incorporated at 2.0 ppt in fresh water. The use of Buffered Q in the fresh water decreased the viscosity at 40 sec⁻¹, ranging from approximately 86 to 28 cP. After static aging the viscosity decreases to approximately 7 cP, more than one third of the baseline viscosity (Fig 10a). In the 10,000 TDS slickwater system (Fig 10b) the viscosity at 40 sec⁻¹ decreased and ranged from 26 to 10 cP with 1.0 ppt of Breaker T. After static aging, the viscosity decreased to approximately 3 cP.

In summary, the use of Buffered Q in fresh water degraded the viscosity at 40 sec⁻¹ however, the viscosity remains sufficiently elevated and after static aging degrades to

approximately 7 cP. The use of APS and EAPS in freshwater only nominally degraded the viscosity after static aging. In 10,000 TDS brine, the EAPS and APS maintained consistent viscosity at 40 sec⁻¹ and Breaker T providing lower viscosity at the same shear rate. After static aging, EAPS and APS were essentially equal to the baseline, where Breaker T exhibited 60% less viscosity.

Slickwater Results at 125°F

This test series included slickwater baselines using concentrations of 6 and 4 gpt in freshwater and a 10,000 TDS synthetic brine (Figures 11a, 11b, 11c, 11d). The initial viscosity of the freshwater baseline started at 40 cP and stabilized at 25 cP at 511 sec⁻¹. At 40 sec⁻¹, the viscosity increased and ranged from 132 to 120 cP. After static aging, the viscosity was nearly identical to the baseline viscosity of 25 cP, thus within the test period, the viscosity is relatively unchanged. In contrast, the initial viscosity of the 10,000 TDS baseline (at 4 gpt) started at approximately 8 cP. At 40 sec⁻¹, the viscosity increased and ranged from 23 to 15 cP. After static aging, the viscosity was nearly identical to the baseline viscosity of 7 cP, thus within the test period, the viscosity is relatively unchanged.

Next APS and EAPS were incorporated into slickwater systems at various concentrations in freshwater. These systems stabilized at relatively less viscosity than the baseline reading at 40 sec⁻¹. However, minimal degradation of viscosity was apparent after aging (Fig. 11a).

Next, three breakers with catalysts were incorporated into the slickwater system as 3.0-ppt Breaker ZA, 3.5-ppt Buffered ZB, and 3.0-ppt Buffered ZC. At 40 sec⁻¹ ZA and ZC exhibited similar viscosity, approximately 80 to 60 cP; Breaker ZB reduced the viscosity from 60 to 40 cP. However, after static aging these slickwater systems exhibited relatively similar viscosities of approximately 12 to 14 cP (Fig. 11b).

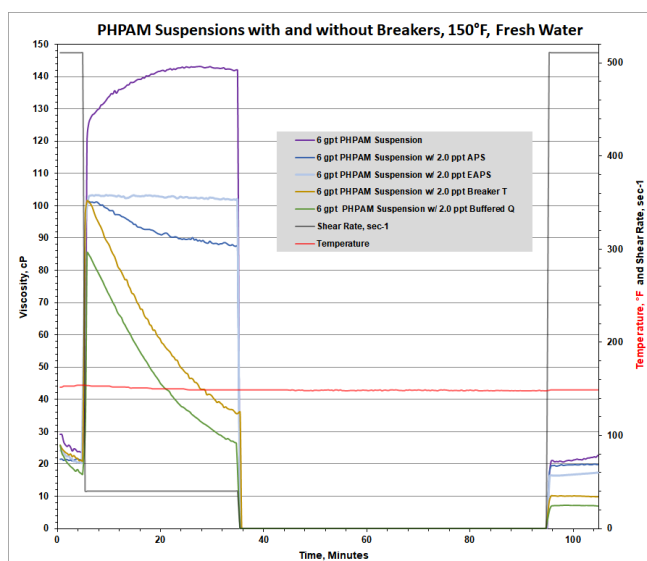


Figure 10a – Slickwater system in fresh water with selected persulfate and buffered breakers.

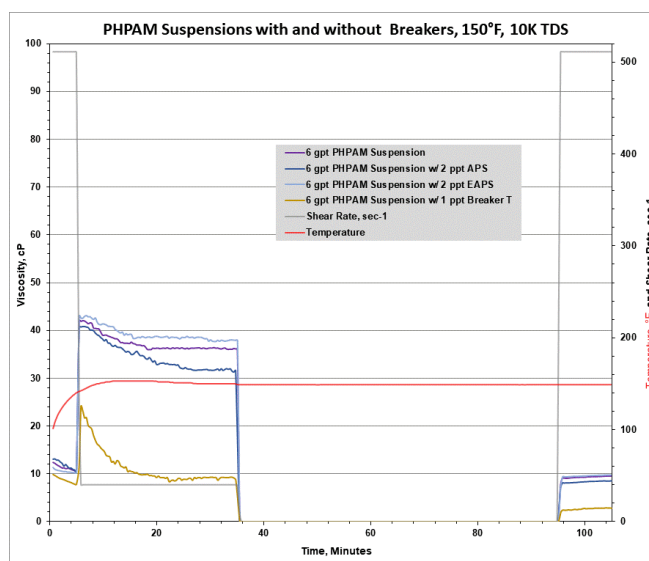
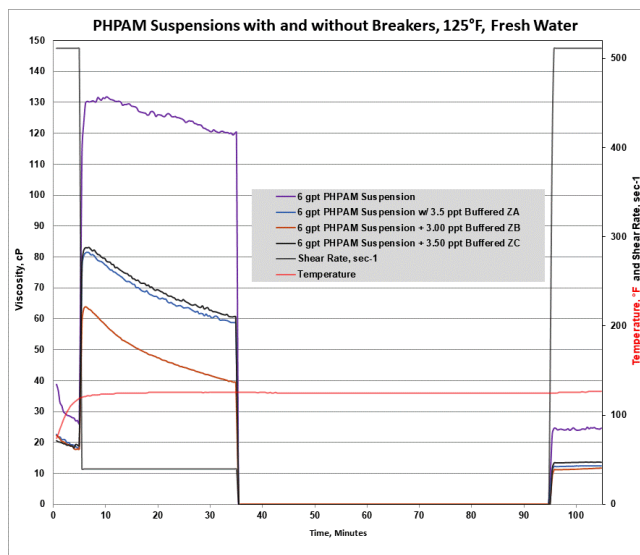
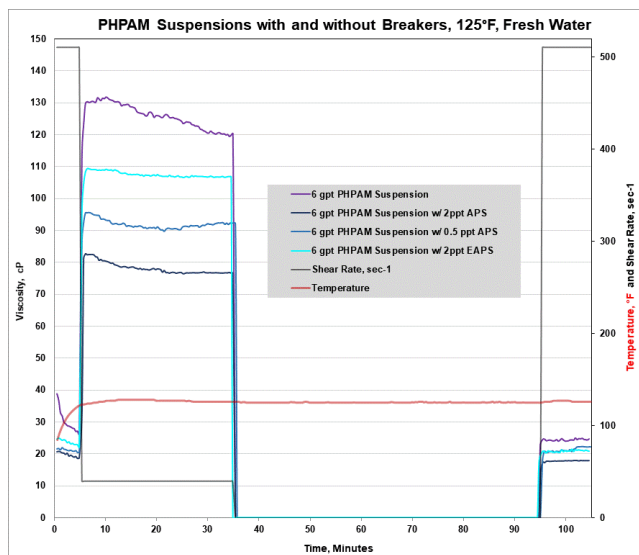


Figure 10b – Slickwater system in 10,000 TDS brine with selected persulfate and buffered breakers.

To further assess the viscosity degradation, two buffered peroxides X and Y (without catalysts) were incorporated into slickwater systems (Fig. 11c). At 40 sec^{-1} , the viscosity decreased from 27 to 5 cP for Buffered X and from 45 to 25 cP for Buffered Y. After static aging, both exhibited low viscosity (6 to 7 cP). However, Buffered Y exhibited elevated viscosity at 40 sec^{-1} , which is approximately 75% less than the baseline viscosity.

To confirm the efficiency of Buffered X peroxide, a 4-gpt slickwater system in 10,000 TDS brine was evaluated and compared with persulfate breakers (Fig. 11d). At 40 sec^{-1} and after static aging, the EAPS and APS elevated the viscosity above the baseline. However, at 40 sec^{-1} the viscosity for Buffered X decreased from 24 to 8 cP. After static aging, Buffered X averaged 4 cP.

The persulfates in fresh water maintained a reduced, but consistent, viscosity at 40 sec^{-1} and after aging showed minimal viscosity degradation. When evaluating the buffered peroxides with catalysts under the same conditions, the viscosity at 40 sec^{-1} was nominally reduced, as compared to the use of persulfates. However after static aging, nominal benefits were realized (Fig. 11b). The buffered peroxides, X and Y exhibited a significant reduction in viscosity at 40 sec^{-1} , in both 4 and 6 gpt systems that were incorporated in fresh water and 10,000 TDS brine (Fig. 11c, Fig. 11d). After static aging, Buffered and X and Y achieve nearly the same viscosity reduction, 60 to 70%, however Buffered X did not maintain the same level of viscosity at 40 sec^{-1} . In contrast, Buffered X as incorporated into 10,000 TDS brine, while decreasing viscosity at 40 sec^{-1}



Figures 11a and 11b – Comparison of a slickwater system at 6 gpt in fresh water with persulfate breakers (left) and same slickwater system with buffered breakers and catalysts (right).

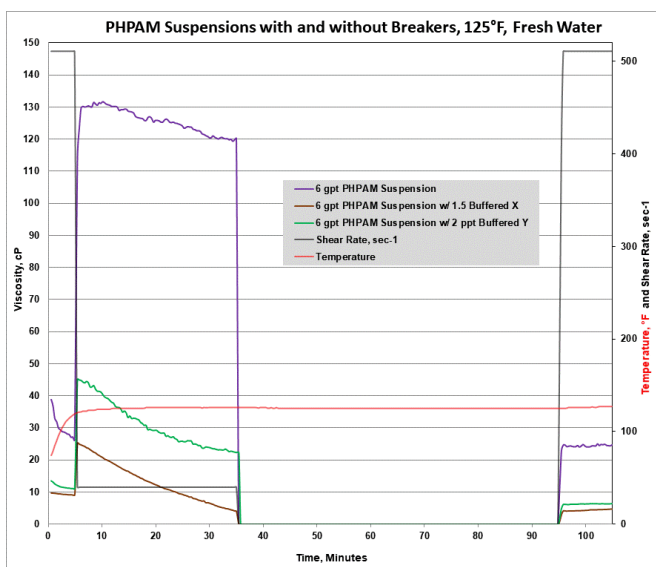


Figure 11c - Comparison of slickwater systems at 6 gpt in fresh water with buffered peroxides and no catalysts.

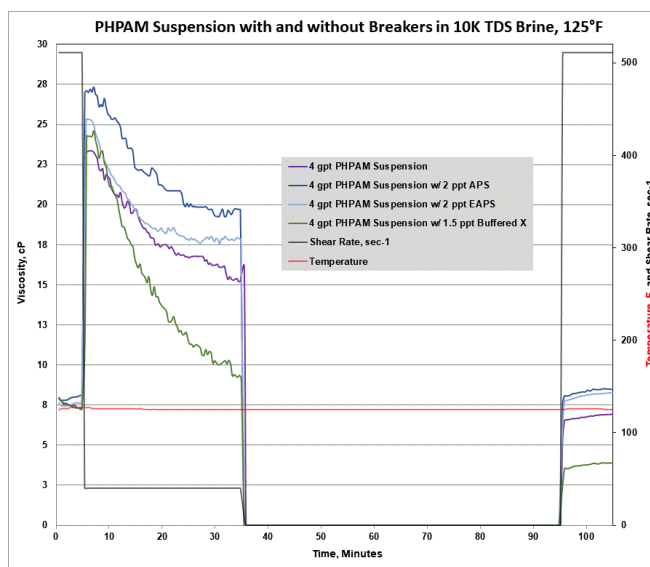


Figure 11d – Comparison of a slickwater system at 4 gpt in 10,000 TDS with persulfate and buffered breakers.

from approximately 25 to 10 cps, realized a 50% reduction in viscosity after static aging.

Coiled Tubing Fluid – Conventional Application

A polymer-based, solids-free system used for drilling laterals via coiled tubing (CT), was assessed with respect to the potential to remediate reported damage. Operations suspected excessive viscous leak-off during drilling of the horizontal intervals as the cause of damage as recent production did not achieve programmed rates. Specifically, the concern was invasion of a solids-free CT system into the producing formation either as whole fluid, filtrate, and/or filtercake, where the filtercake likely formed close to the toe. As these systems are typically disposed of during or after drilling the programmed interval, due to the accumulation of formation solids (e.g., finer clay and silt-sized particles), coupled with the fact that these systems are designed as solids-free, whole fluid invasion into the sandstone matrix was suspected as the more likely damage mechanism.

It was postulated that the incorporation of a breaker during drilling would subsequently degrade the viscosity of any residual whole fluid thus improving initial clean-up of the well and alleviating this perceived damage. Thus objectives dictated that the essential drilling parameters, e.g, viscosity, lubricity, and hydraulic friction reduction must not degrade while drilling to the programmed total depth. Thus, the design was to incorporate a breaker which would remain nearly inert until drilling reached total depth. The required period to delay viscosity reduction for this solids-free system was established using previous horizontals including a safety factor and determined to be 40 hours.

To assess the validity of incorporating an internal breaker, laboratory simulations were performed by dynamically aging representative CT systems and incorporating five different peroxides to evaluate relative stability versus time. The products for the CT system are shown in [Table 2](#). The CT systems were assessed for a period of 40 hours at 165°F, which represents the approximate bottomhole static temperature (BHST) in the field.

The first phase assessed these different peroxides as incorporated into the CT system which included all the typical components as required for CT conventional drilling. The second phase assessed only those peroxides that demonstrated degradation of the low-ends in Phase I, however the lubricant was removed in Phase II. In addition a buffer was incorporated as peroxides elevate the pH of water-based drilling systems ([Dobson and Kayga 1993](#)). The third phase incorporated selected lubricants as the original was deemed incompatible, in addition to selected peroxides from Phase II to maintain compatibility, time-delay break, and measure the coefficient of friction (COF) of the system.

Table 2 – Products and Base Formulation for 8.7-lb/gal Coiled Tubing Drilling System and Selected Breakers

Product/Function	Conc.	Units
6% KCl for inhibition and density	0.965 to 0.953	bbl/bbl
Xanthan+Diutan blend	1.1	lb/bbl
Shale inhibitor	8.0	lb/bbl
Corrosion inhibitor	1.0	lb/bbl
Oxygen scavenger	0.2	lb/bbl
Hydraulic friction reducer	1.1	lb/bbl
Mechanical friction reducer	3.4	lb/bbl
Biocide	0.4	lb/bbl
Oxidizers		
Mg Peroxide	2.0	lb/bbl
Ca Peroxide	2.0	lb/bbl
Ca Peroxide ¹	2.0	lb/bbl
Ca Peroxide suspension	2.4	% v/v
Ca Peroxide suspension ¹	2.4	% v/v

1. Reduced assay

For each phase, rheological properties were recorded initially (at ambient temperature), after 24 hours, and after 40 hours of dynamic aging at 165°F. FANN 35A and Brookfield LVDV+II viscometers were used to measure the corresponding viscosity.

Coiled Tubing – Phase I Results

[Figure 12](#) and [Figure 13](#) show the CT systems and dry oxidizers yielded the formation of predominant grease. Note that the formation of grease is visible after 24 hours thus its development most likely occurred in less than 24 hours and in the absence of formation solids. To determine if the grease was dispersible, 0.25 lb/bbl of citric acid was added and each jar dynamically aged for an additional three (3) hours however the grease persisted ([Fig. 13](#)). The combination of pH, lubricant, and peroxide in these CT systems most likely promoted the formation of a potassium-calcium soap/grease.

[Figure 14](#) shows rheology measurements versus time, specifically the low-end (i.e., 6-rpm, 3-rpm, and 0.3-rpm) rheology. All CT systems included a peroxide plus citric acid at concentrations of 2.0 lb/bbl and 0.25 lb/bbl, respectively. These shear rates were selected as viscosified (e.g., biopolymers) brine-based systems will typically manifest degradation of their corresponding low-end (6-rpm, 3-rpm, and 0.3-rpm) readings more readily than the high-end (600-rpm) readings.

Note the CT system that incorporated the calcium peroxide suspension exhibited a more apparent decrease in viscosity. Furthermore, the CT systems that incorporated dry calcium peroxide and magnesium peroxide exhibited a relatively slight decrease of their 0.3-rpm readings however, the 6-rpm and 3-rpm readings exhibited only a marginal change over 40 hours. CT systems that incorporated the calcium peroxide suspension exhibited the greatest degradation in viscosity. Based on these results, the calcium peroxides were selected for further assessment in Phase II.



Figure 12 – Post 40 hours: Left to right: Control, calcium peroxide suspension, and dry peroxide in suspension with 0.25-lb/bbl citric acid. Note formation of grease.



Figure 13 – Post +3 hours: Left to right, magnesium peroxide, calcium peroxide, and reduced peroxide after dynamic aging with 0.25 lb/bbl of citric acid. Grease remains.

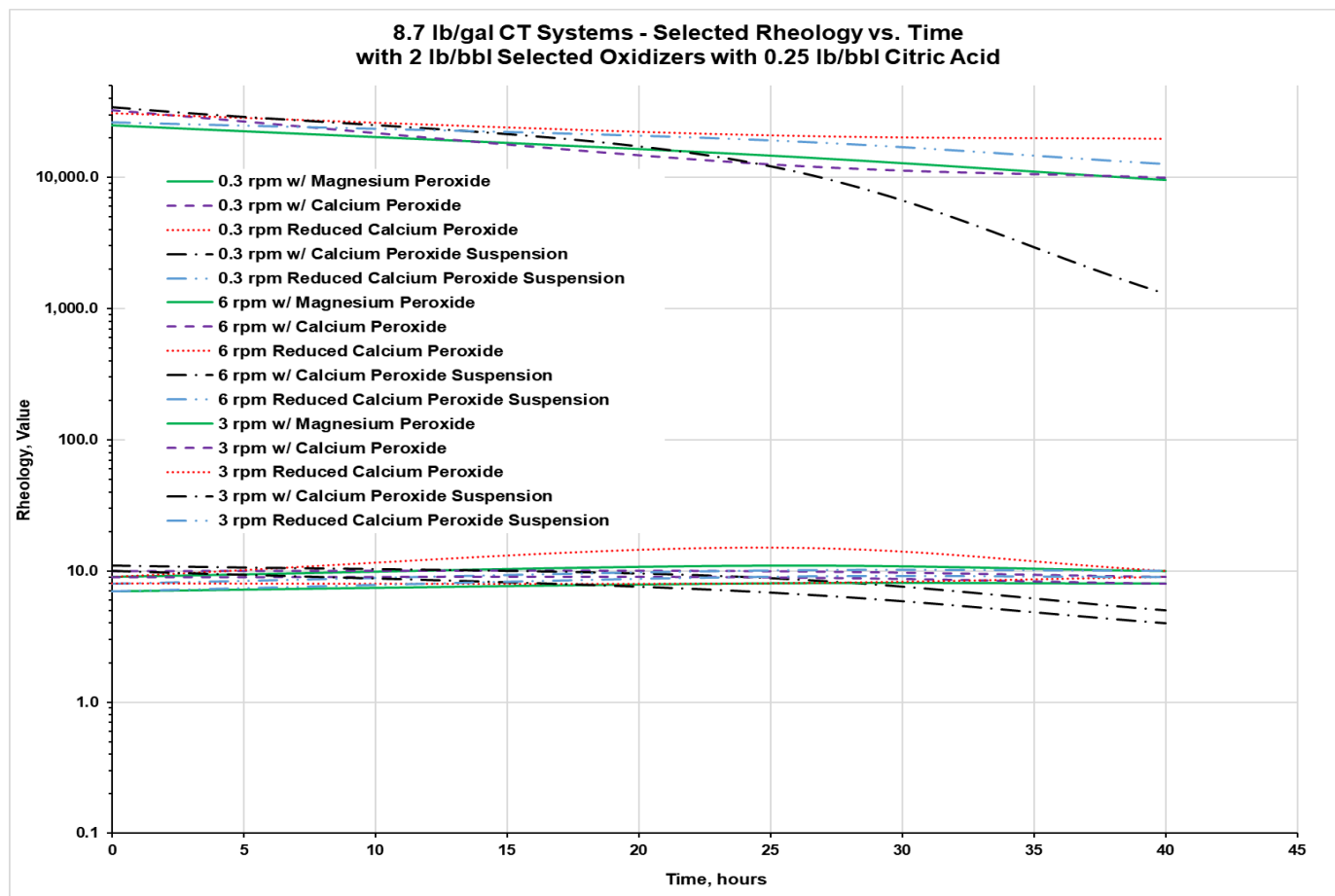


Figure 14 – Rheology of CT systems with oxidizers plus 0.25 lb/bbl of citric acid. Note that the CT system with the calcium peroxide suspension (purple dashed line shown as –) exhibited a viscosity decrease as measured at 0.3-rpm, 3-rpm, and 6-rpm readings vs the other CT systems with selected peroxides.

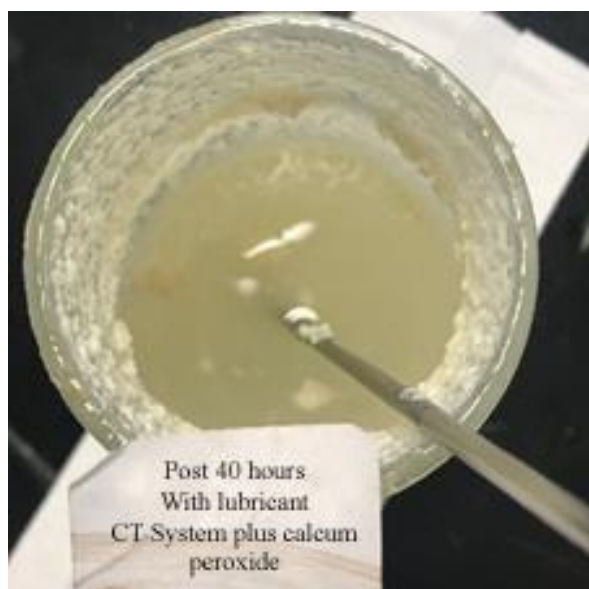


Figure 15 – Phase II, Post 40 hours. Figure 15A (left) shows the CT system plus lubricant and Ca-peroxide. Greasing is ubiquitous as adheres to the side of the jar. Figure 15B (right) shows the CT System with calcium peroxide suspension however no lubricant was incorporated.

CT – Phase II Results

Using the dry and liquid calcium peroxide additives from Phase I that demonstrated degradation of the low-end rheology, CT systems were statically aged without a lubricant to determine if the grease/cheese issue was mitigated. [Figure 15](#) shows a CT system incorporated with the calcium peroxide suspension (with no lubricant) after 40 hours of static aging. Note the absence of visible grease and cheese. It is likely that the removal of this lubricant mitigates the formation of grease and cheese. However, the desired mechanical friction reduction would need to be confirmed. It is plausible that a lubricant that is comprised of nil to minimal refined oil plus surfactants and/or alcohol, thus no vegetable or tallow sourced, would promote friction reduction with little to no greasing and cheesing in the presence of a peroxide ([Sharma et al. 2006](#)).

[Figure 16](#) shows rheology measurements versus time for both high-end (600-rpm reading) and low-end (6-rpm, 3-rpm, and 0.3-rpm readings), respectively, for two controls versus selected CT systems. Two CT systems were built, with one incorporating dry calcium and magnesium peroxide and the other incorporating calcium peroxide suspension with no lubricant. This data showed the presence of the dry peroxides exhibited negligible decrease of their low-ends and nil decrease of the 600 rpm over 40 hours. The CT system that incorporated calcium peroxide suspension exhibited the most relative decrease of the three low-end readings as well as the high-end when compared to the controls and to the other CT systems. When compared to the rheology of the base, 6% KCl (purple lines), the low-end readings for this CT system, after 40 hours are nearly equivalent.

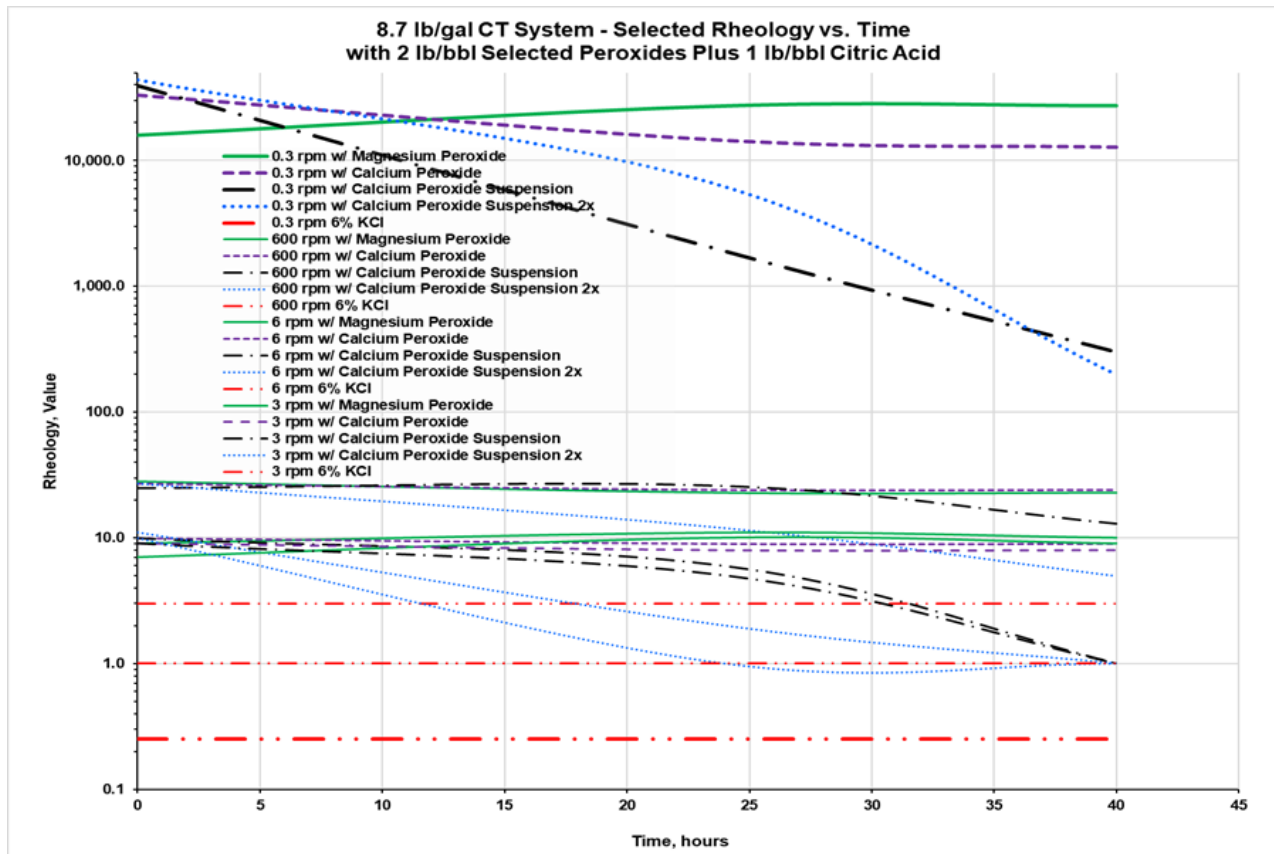


Figure 16 – Rheology of CT systems with oxidizers plus 1.0 lb/bbl of citric acid. Note that the CT system with the calcium peroxide suspension (purple dash line shown as –.) exhibited a viscosity decrease as measured at 0.3-rpm, 3-rpm, 6-rpm and 600-rpm readings vs the other CT systems with selected peroxides and the base fluid (6% KCl).



Figure 17a – Post 24 hours: Left to right, glycol blend lubricant and HMW glycol lubricant. No formation of grease is visually apparent.



Figure 17b – Post 40 hours: Left to right, glycol blend lubricant and HMW glycol lubricant. No formation of grease is visually apparent.

Coiled Tubing Phase III Results

This test phase assessed the performance of the calcium peroxide suspension in the presence of alternative lubricants. [Fig17a](#) and [17b](#) show two lubricants, HMW glycol and glycol blend, incorporated into the CT system with the calcium peroxide suspension at 24 and 40 hours, respectively. Note that no grease and/or cheese are apparent after 40 hours.

Initial and post measurements with a pH meter showed the pH of these CT systems ranged from 10.3 to 10.7 initially and 11.5 to 11.7 after 40 hours. The less than 0.3 logarithm change/difference in pH after 40 hours is relatively small, even in a logarithmic scale; however it is indicative that these lubricants in the presence of the internal oxidizer remained nearly constant. Furthermore, their combination in this CT

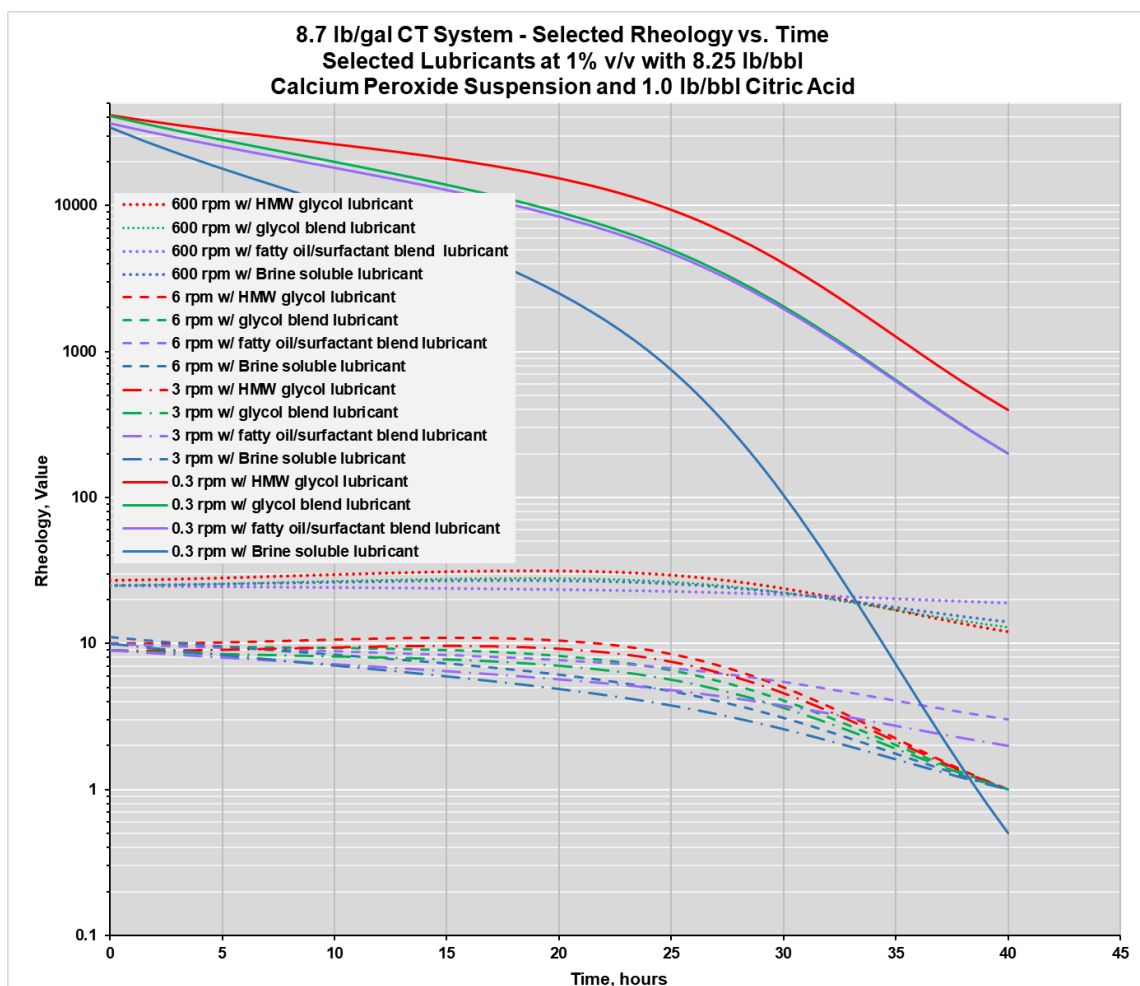


Figure 18 – Rheology versus time for CT systems with HMW glycol, glycol blend, fatty oil/surfactant blend, and brine-soluble lubricant. Note these systems are stable for approximately 25 to 35 hours at high shear rates (e.g., 600 rpm) while their low shear rates begin to degrade. The 0.3 rpm shear rate is the first indicator of viscosity degradation in the presence of these peroxides.

system remains alkaline as all buffered in a similar manner.

Figure 18 shows rheology measurements versus time, high-end (600-rpm rheology) and low-end (6-rpm, 3-rpm, and 0.3-rpm rheology) versus the aforementioned lubricants. All CT systems utilized the calcium peroxide suspension at 2 lb/bbl plus citric acid at 1 lb/bbl. Note these systems were stable for approximately 25 to 35 hours at high shear rates (e.g. 600 rpm). After 25 to 30 hours, their low-shear-rate rheology began to degrade. The 0.3-rpm shear rate is a typical indicator of polymer degradation in the presence of this internal breaker.

Based on these results, the coefficient of friction (COF) was assessed. Figure 19 shows the COF measurements over a period of 36 hours. For this assessment, a series of jars was prepared for each CT system plus lubricant and calcium peroxide suspension. A fresh sample jar was pulled every four hours with the COF being determined. The jar was then discarded to avoid any artifact of the temperature change due to its removal from the oven. Note that the CT system with the glycol blend and calcium peroxide suspension show stability for approximately 15 to 20 hours vs the control.

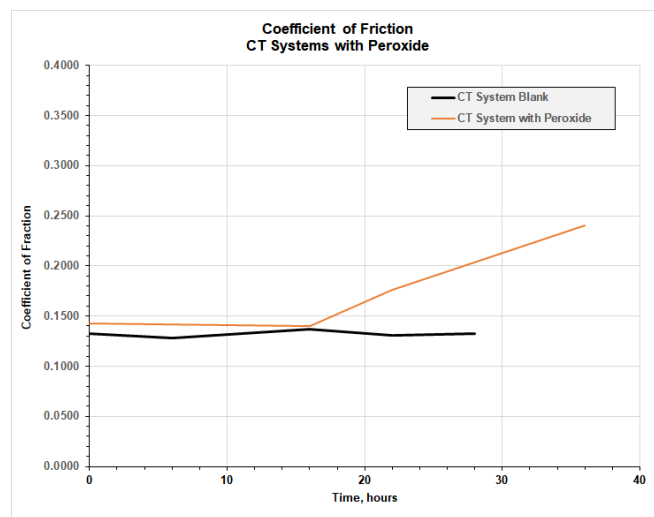


Figure 19 – Comparison of Coefficient of Friction for CT system with and without peroxide.

Conclusions

Peroxides Used in Unconventional Fluids

- In summary, these results show that APS and EAPS increase the slickwater viscosity exponentially at 40 sec^{-1} . These results, specifically the utilization of APS and EAPS at and less than 175°F , contrast, in part, with the utilization of persulfates as reported by [Sun et al. 2010a, 2010b](#).
- Thermal degradation of the slickwater baselines are apparent at temperatures at and above 175°F .
- At 225°F , at a concentration of 0.45 ppt, Buffered J not only provides stable viscosity 40 sec^{-1} , this system also provides 80% viscosity reduction.
- At 200°F , the use of Buffered D, at 0.45 ppt, provided stable viscosity at 40 sec^{-1} , subsequently reduced the viscosity of the suspension after static aging approximately 67%.
- At 175°F in freshwater, buffered peroxides provide sufficient viscosity at 40 sec^{-1} . In 10,000 TDS brine, at 40 sec^{-1} all viscosity was virtually stable. After aging in both environments, the buffered peroxides reduced viscosity 50% or greater as compared to the baseline.
- At 150°F in fresh water, Buffered Q degraded the viscosity at 40 sec^{-1} ; however the viscosity remains sufficiently elevated and after static aging reduces the viscosity approximately 60%. In 10,000 TDS brine, Breaker T exhibited lower viscosity at 40 sec^{-1} and after static aging exhibited 60% less viscosity than the baseline.
- At 125°F , the buffered peroxides in fresh water outperformed the combination of buffered peroxides and catalysts and realized approximately 10% better performance over the systems with catalysts.
- At 125°F in both fresh water and 10,000 TDS brine, Buffered X exhibited similar performance when incorporated into slickwater systems at 4 and 6 gpt. Buffered Y decreased the viscosity approximately 60% in fresh water after aging and maintained nominal viscosity at 40 sec^{-1} , whereas the Buffered X did not. After aging, Buffered Y reduced the viscosity 60 to 70% in fresh water and 50% in 10,000 TDS brine.
- [Table 3](#) summarizes the optimal breakers and concentrations at various temperature and fluid environments as used in unconventional applications.

Table 3 – Optimal Breaker and Concentration

Temp (°F)	Environment	Optimal Breaker	Concentration (ppt)
125	Freshwater	Buffered X	2.0
	10,000 TDS	Buffered Y	1.5
150	Freshwater	Breaker T Buffered Q*	2.0 2.0
	10,000 TDS	Breaker T	1.0
175	Freshwater	Buffered E*	0.25
	10,000 TDS	Buffered P	1.0
200	Freshwater	Buffered D	0.45
225	Freshwater	Buffered J	0.45

*Includes catalyst

Peroxides Used in Coiled Tubing Fluids

- The calcium peroxide suspension generated an effective delay mechanism when incorporated into this brine-based, solids-free system at the temperature tested, i.e. 165°F . Thus it can be considered for use as a delayed breaker at lower temperatures
- The calcium peroxide suspension promoted greater than 90% degradation of the low-end rheology as compared to the initial viscosity measured at ambient conditions.
- Lubricants that utilize vegetable and/or fatty oil are incompatible with these oxidizers as the combination of temperature and pH yield greasing (i.e., clings to the sample jars).

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Nomenclature

<i>BHT</i>	= Bottomhole Temperature
<i>CT</i>	= Coiled tubing
<i>Da</i>	= Dalton unit of mass
<i>GPT</i>	= Gallons per thousand
<i>HMW</i>	= High molecular weight
<i>MW</i>	= Molecular weight
<i>PAM</i>	= Polyacrylamide
<i>PHPAM</i>	= Partially hydrolyzed polyacrylamide
<i>PPT</i>	= Pounds per thousand
<i>TDS</i>	= Total dissolved solids
<i>N_{RE}</i>	= Reynolds number

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