THE DEGRADATION OF HYDROXYPROPYL GUAR FRACTURING FLUIDS BY ENZYME, OXIDATIVE, AND CATALYZED OXIDATIVE BREAKERS

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ABSTRACT

The effects of pH, temperature, and hydroxypropyl guar (HPG) concentration on HPG solution and gel degradation by enzyme, oxidative, and catalyzed oxidative breakers were examined in a series of static break tests. HPG solution and gel degradation were inferred from reductions in viscosity over a 24 hour time period. Steady shear viscosity measurements were also made with the GRI/TAMU Rheology Flow Loop to determine the short-term (< 3 hours) effects of conventional oxidative breakers on the viscous properties of neutral pH titanate crosslinked HPG gels. The results of the static break testing and the steady shear viscosity measurements demonstrate the difficulties in pumping sufficient breaker concentrations to prevent proppant pack permeability damage without jeopardizing the success of the fracturing treatment.

INTRODUCTION

Since 1983, the Gas Research Institute (GRI), a not-for-profit membership organization, has funded extensive hydraulic fracturing research to improve the understanding, implementation, and computer modeling of the hydraulic fracturing process. As part of GRI's research program, Crockett, Willis, and Cleary[1] developed a three-dimensional (3D) fracture propagation model for real-time analysis of hydraulic fracture growth. Results of numerous 3D computer model analyses of fracturing treatments have demonstrated that accurate predictions of fracture geometry are not possible when reservoir parameters and fracturing fluid viscous properties are uncertain.

To improve the knowledge of the viscous properties of fracturing fluids, GRI funded the development and testing of the GRI Rheology Unit.[2] The GRI Rheology Unit consists of a van containing two Fann Model 50 viscometers and a complete wet chemistry lab. In field operations, the GRI Rheology Unit is used to check fracturing fluids and chemical additives for contaminants and to measure the viscous properties of the actual fracturing fluids being pumped during the treatment. Today, the GRI Rheology Unit represents the state-of-the-art in fracturing fluid quality control.

The chemical complexity of modern fracturing fluids demands rigorous fluid quality control before and during a fracture treatment to ensure that fracturing fluid physical properties are within design specifications. For example, a typical crosslinked HPG gel system is created from a base fluid that is generally water and HPG polymer. A vast array of chemicals are available that can be added to alter the physical and chemical properties of the base fluid. Some examples of typical additives would be biocides, breakers, crosslinkers, and gel stabilizers. Since the rheological properties of fracturing fluids are the result of the chemical composition, each additive will have some effect on the rheological properties of the fluid.

Service companies provide the rheological properties for their own fluids, as well as recommendations for the types and amounts of additives. Typically, the service company recommendations are based on extensive laboratory testing of the fluids. Research with the GRI Rheology Unit has found that laboratory measured properties are often not reproduced under field conditions.[2-3] Several reasons can explain discrepancies between laboratory and field fluid properties, such as, water constituents, contamination of chemical additives, and the age of the field chemical additives. With extensive field fracturing fluid quality control measurements, however, fracturing fluid problems can be diagnosed or fracturing fluid properties can be optimized on location before the treatment begins.

Quality control of field fracturing fluids with the GRI Rheology Unit has led to the identification of several field fluid problems. One of the problems identified was the scheduling and addition of chemical breakers used to degrade the fracturing fluid after the treatment. The Well Stimulation Laboratory at Texas A&M University (TAMU) and the GRI/TAMU Rheology Flow Loop have subsequently been used for a comprehensive examination of the degradation of HPG fracturing fluids by enzyme, oxidative, and catalyzed oxidative breakers.

PROBLEM IDENTIFICATION

One of the properties of an ideal fracturing fluid is that the fluid should be easily removed from the fracture and formation after the treatment has ended. Removing the fracturing fluid after the treatment is necessary to prevent plugging the proppant pack with high molecular weight polymers. Chemical breakers can be used to degrade fracturing fluids so that the fluids can be removed from the fracture.

Ideally, the breakers should not affect the rheological properties of the fluid during a treatment, but after the fracture closes, the breakers should degrade the fluid rapidly. Realistically, the breakers that have been developed do not "controllably" degrade the fracturing fluid. Degradation begins immediately when the chemicals are added to the fluid in the surface pumping equipment.

Cooke[4] has demonstrated that the polymer concentration remaining in the fracture after the treatment is several times higher than the concentration mixed at the surface because of fluid leakoff. The fluid leakoff is principally water because flow of the polymer through the small pore throats in the formation is restricted by the size of the polymer molecules.[5] As a result, the polymer concentration remaining in the fracture can be several times the concentration originally mixed and pumped at the surface. Breaker concentrations should, ideally, be sufficient to degrade the polymer concentration remaining in the propped fracture.

Traditionally, only very low breaker concentrations have been added to degrade the fracturing fluids, but during the past year, new fracture treatment techniques have been proposed that include "aggressive" or very high breaker concentrations.[6] Two problems, however, occur when using high concentrations of conventional (granular persulfate) breakers. First, conventional breakers are water soluble, and the breaker leaks off with the water into the reservoir. Thus, the breaker concentration remaining in the propped fracture can be insufficient to degrade the polymer concentration remaining in the propped fracture. Second, and more importantly, conventional breakers react rapidly with the polymer and can degrade the fluid within minutes at reservoir temperatures.

A paradox thus exists with the use of conventional breakers. On one hand, the breaker concentration must be sufficient to degrade the polymer remaining in the fracture after closure, but on the other hand, adding the required breaker concentration degrades the fluid so rapidly that proppant transport properties can be lost and the success of the treatment jeopardized.

Research with the GRI Rheology Unit has shown that many fracturing fluid problems in the field are caused by chemical breakers.[3] Typical problems associated with the breakers were either (1) the wrong type breaker was being used or (2) the wrong amount of breaker was added for the given conditions. Problems with breaker type or concentrations can result in the fracturing fluid either not degrading at all or degrading too quickly. When a fracturing fluid degrades too quickly, it cannot effectively transport the proppant down the fracture. If the wrong breaker type or a low concentration of breaker is used, the propped fracture can be plugged with high molecular weight polymers long after the treatment.

Based on the repetitive field fluid problems caused by breakers, a research program was designed to accomplish the following objectives.

1. Examine the effects of pH, temperature, and polymer concentration on HPG solution and gel degradation by enzyme, oxidative, and catalyzed oxidative breakers.
2. Identify the appropriate breaker system for HPG solutions and gels in the temperature range 120°F to 140°F.
3. Demonstrate the effects of conventional breakers on the viscous properties of neutral pH titanate crosslinked HPG gels at 125°F, 150°F, and 200°F using steady shear viscosity measurements.

REVIEW OF LITERATURE

Hydraulic fracturing fluid (polymer) degradation can be investigated using two different approaches. The first approach is to perform polymer degradation studies. These studies are principally concerned with the loss of solution viscosity resulting from a reduction in polymer molecular weight. A second approach is to measure proppant pack permeability damage caused by the fracturing fluid polymers. Both approaches will allow one to determine the applicable breaker types; however, the two approaches can result in different concentrations of breakers necessary to degrade fracturing fluids. In general, the results from polymer degradation studies indicate that low breaker concentrations are required, while the results from proppant pack permeability damage studies indicate that very high concentrations of breaker are required.

Polymer Degradation Studies

It has been established that the apparent viscosity of polymer solutions is a function of the molecular weight or the degree of polymerization.[7] Early investigators used the reduction in solution viscosity as a measure of polymer degradation. The early investigators assumed that a "broken" fluid would have a solution viscosity less than 10 cp, but subsequent investigators argued that the solution viscosity of a broken fluid should be 2-3 cp.[8]

More recent investigations of polymer degradation have used size exclusion chromatography (SEC) to measure the apparent average molecular weight of the polymer solution.[8-10] Gall and Raible[8] have reported that a reduction in solution viscosity does not eliminate the possibility of proppant pack damage, and typical breaker schedules are normally insufficient for complete polymer degradation.

Proppant Pack Permeability Reduction Studies

Several researchers have examined fracturing fluid degradation by analyzing the "flow impairment characteristics" of typical fracturing fluids through proppant packs.[4-5,11-14] Results have shown that proppant concentration, porosity of the proppant pack, polymer residue, breaker type, breaker concentration, and break temperature are the variables that determine proppant pack permeability reduction. In general, a breaker concentration above the concentration required to reduce solution viscosity is necessary to reduce proppant pack permeability damage.

Recently, Brannon and Pulsinelli[13-14] presented the results of proppant pack permeability reduction studies conducted to determine the concentration of breaker necessary to reduce proppant pack damage to a desired level. The results of this research demonstrated that a breaker concentration several times the amount traditionally used may be required to significantly reduce proppant pack permeability damage.

Table 1 has been prepared from results contained in the literature as a guide to polymer degradation mechanisms. The most common polymers used in fracture treatments are guar and the guar derivative HPG. Depending on the pH and the bottomhole temperature, a number of breakers can be used to degrade these polymers. The information in Table 2 presents the consensus in the literature of what types of breakers can be used and under what conditions the breakers should work.[4-6,8-14]

EXPERIMENTAL METHOD

To examine the influence of pH, polymer concentration, temperature, breaker type, and breaker concentration on HPG degradation, long term (24 hour) static break tests were conducted with fluid degradation inferred from reductions in apparent viscosity over time. Table 3 outlines the scope of the testing of HPG solutions (linear gels). Additionally, static break tests were conducted for borate and titanate crosslinked HPG gels. Table 4 outlines the scope of the static break tests for HPG gels.

Dynamic break tests were used to examine the changes in the viscous properties of a neutral pH titanate crosslinked HPG gel over time with oxidative breakers included. Dynamic break tests are short term (3 hour) tests conducted with the GRI/TAMU Rheology Flow Loop. Table 5 outlines the breaker concentrations tested with the GRI/TAMU Rheology Flow Loop. In conjunction with the dynamic break tests, special tests combining steady shear viscosity measurements and static break testing techniques were conducted for the titanate crosslinked gels with the oxidative breaker concentrations shown in Table 6.

Break Criteria

The static break tests for this research use a common break criteria that was established based on the results obtained by Gall and Raible.[8] Gall and Raible reported the average apparent molecular weights of HPG polymer solutions that were degraded under the conditions imposed by Cooke[4] and Almond and Bland[12] in proppant pack permeability reduction studies. Gall and Raible found that degraded polymer average apparent molecular weights less than 1 X 10^6 resulted in 10 to 30% proppant pack damage. Base on their experimentally determined relationship between average apparent molecular weight and apparent viscosity, an average apparent molecular weight of 1 X 10^6 for a degraded 40-lbm/1,000-gal HPG gel corresponds to a solution viscosity of approximately 3 cp.

For our research, we considered an HPG solution or gel to be "broken" when the viscosity was less than or equal to 3 cp after 24 hours at the test temperature and cooling to below 80°F.

Static Break Tests

For static break tests of HPG solutions at temperatures less than 200°F, 250-ml samples were mixed in glass bottles and placed in a preheated constant temperature water bath. After one hour in the bath, each sample was removed, and the apparent viscosity was measured with a Fann Model 35 viscometer at a shear rate of 511 sec^{-1}. After measuring the apparent viscosity, the sample was immediately replaced in the constant temperature bath. Apparent viscosity measurements were repeated at 3, 6, and 24 hours.

After the apparent viscosity measurement at 24 hours, the samples were removed from the bath and allowed to cool for four hours to a temperature of less than 80°F. A final apparent viscosity measurement was made at a shear rate of 511 sec^{-1} with a Fann-35 viscometer.

For static break tests of HPG solutions at temperatures greater than 200°F, HPG solutions were placed in 90-ml stainless steel sample cylinders. The sealed cylinders were immersed in an oil bath for 24 hours, and then removed and allowed to cool to less than 80°F in four hours. After cooling, the apparent viscosity was measured with a Fann-35 viscometer at a shear rate of 511 sec^{-1}.

The static break test procedure for titanate and borate crosslinked gels differed slightly from the procedure for HPG solutions. At temperatures less than 200°F, crosslinked samples were mixed in 250-ml glass bottles and placed in a constant temperature bath. After 1, 3, 6, and 24 hours, the samples were inspected for degradation by attempting to pour a small sample from the bottle. When a portion of the sample could be poured from the bottle, the apparent viscosity was measured with a Fann-35 viscometer at a shear rate of 511 sec^{-1}. At temperatures greater than 200°F, crosslinked gel samples were poured into 90-ml stainless steel sample cylinders and placed in an oil bath. Only an initial and final viscosity measurement were made at temperatures above 200°F.

After 24 hours, the crosslinked samples were removed from the constant temperature bath and allowed to cool for four hours to below 80°F. If the samples had degraded, the apparent viscosity was measured with a Fann-35 viscometer at a shear rate of 511 sec^{-1}.

Chemicals for the breaker testing were supplied by service companies, and the service company directions for mixing the fluids were followed exactly. In general, base solutions containing Bryan/College Station tap water and HPG polymer were mixed daily for each of the polymer concentrations being tested, and the base solutions were allowed to sit overnight to ensure complete hydration. After sitting overnight, the samples were stirred for approximately 10 minutes before splitting the base solutions into 250-ml samples. Crosslinkers and breakers were then added to the individual samples as necessary before immersing the samples in the constant temperature baths. The oxidative breaker used in this research was ammonium persulfate (AP), and the catalyzed oxidative breaker was ammonium persulfate with triethanolamine (CAP).

Dynamic Break Tests

The GRI/TAMU Rheology Flow Loop was designed to measure the viscous properties of hydraulic fracturing fluids at representative temperatures and shear rates encountered in the creation of hydraulic fractures. The flow loop is also a circulating system that allows the changes in viscous properties to be measured with respect to time.

State-of-the-art techniques including dynamic crosslinker injection, continuous shear during gelation, controlled temperature history, and controlled shear history are used to obtain reproducible measurements of the viscous properties of hydraulic fracturing fluids using both a pipe viscometer and a Brookfield TT100 process viscometer.[15]

The experimental method for steady shear viscosity measurements was developed to examine the changes in the viscous properties of neutral pH titanate crosslinked 40-lbm/1,000-gal HPG gels over time with oxidative breakers included. At temperatures of 125°F, 150°F, and 200°F, a base case was run consisting of a neutral pH titanate crosslinked 40-lbm/1,000-gal HPG gel without breaker. At each temperature, two additional cases were run with the breaker concentrations indicated in Table 5. Each case was repeated three times to evaluate the reproducibility of the measurements.

For a standard test in the GRI/TAMU Rheology Flow Loop, the system was first preheated to the test temperature. Once at temperature, the mixing of the test fluids began. For every test, the time of mixing, fluid transfer, and heat transfer was carefully controlled. The breaker was added to the base solution 3 minutes prior to crosslinker injection. After crosslinker injection, the fluid was circulated through a high shear loop at a shear rate of 675 sec^{-1} for 2.5 minutes for test temperatures below 200°F or 1350 sec^{-1} for 3.5 minutes for test temperatures at 200°F. The fluid was then diverted to the low shear loop to measure the viscous properties of the fluid.

In the low shear loop, the fluid was circulated for three hours at a shear rate of 100 sec^{-1}. Every 20 minutes, the shear rate was stepped down to 75 sec^{-1} for 2 minutes and 50 sec^{-1} for 2 minutes while the shear stress response was recorded. The shear rate was then stepped up to 75 sec^{-1} for two minutes and then back to 100 sec^{-1}. The power model parameters, K and n', were determined from the shear stress response measured as the shear rates were decreased from 100 sec^{-1} to 50 sec^{-1}. The apparent viscosity at a shear rate of 100 sec^{-1} was then calculated from the power model parameters.

Special Tests

After the dynamic tests had been terminated, three samples of the gel were placed in preheated glass jars. The glass jars were then sealed and placed in a preheated water bath. Twenty-four hours after the samples had been originally crosslinked, the samples were removed from the water bath and allowed to cool to below 80°F. A single measurement of the apparent viscosity at a shear rate of 511 sec^{-1} was then made with a Fann-35 viscometer. These special tests were performed to determine how each breaker concentration worked after 24 hours.

DISCUSSION OF RESULTS

Static Break Tests

Figs. 1 through 16 contain results from the static break tests. Each figure is a graph of solution (apparent) viscosity at a shear rate of 511 sec^{-1} versus breaker concentration. The viscosity data in these graphs were measured after the samples had been at the test temperature for 24 hours and cooled to below 80°F. Unless noted, the data are for 40-lbm/1,000-gal HPG solutions and gels.

pH Effect

Table 2 indicates that enzyme breakers are most effective in a low pH range ($pH << 7$). Fig. 1 shows the effect of pH on enzyme breaker performance from tests at 140°F. Fig. 1 demonstrates that the enzyme breaker degrades HPG solutions adequately in the low pH range, but as the pH increases, the enzyme breaker becomes less effective. The same trends shown in Fig. 1 were seen in all enzyme breaker tests in the temperature range 80°F of 140°F. These data verify that enzyme breakers are only effective in a low pH range.

The exact opposite effect is seen in Fig. 2. Fig. 2 contains the results from tests of HPG solution degradation by catalyzed oxidative breakers at 80°F. Fig. 2 shows that in the high and neutral pH ranges, the catalyzed breaker system worked adequately, but in the low pH range, virtually no degradation occurred with the breaker concentrations tested. As the test temperature was increased to 120°F, however, the effects of pH on catalyzed oxidative breaker performance were less dramatic. Static break test results of HPG solutions with catalyzed oxidative breakers indicate that catalyzed oxidative breaker systems should be used in neutral and high pH ($pH > 7.5$) HPG fluids.

The effect of pH on oxidative breaker (AP) performance can be seen in Figs. 3 and 4. Fig. 3 presents the results of tests of HPG solutions conducted at 140°F. Note that for identical breaker concentrations, the breaker works best in the high pH range. At 180°F, however, Fig. 4 shows that pH is less of a factor on AP breaker performance in HPG solutions. Fig. 4 shows very little difference in the results from the three pH ranges at 180°F.

HPG Concentration

As expected, different HPG concentrations require different amounts of breaker to degrade the solution. Fig. 5 contains the results from low pH HPG solutions containing AP breaker that were tested at 140°F. In Fig. 5 it is shown that for higher polymer concentrations, a higher AP concentration must be used to degrade the solution. The same trend was also observed for enzyme and catalyzed oxidative breaker systems at all temperatures tested. Recognizing that increasing the HPG concentration requires higher breaker concentrations is very important. Fluid loss from the fracture during a treatment will concentrate the polymer in the proppant pack after closure. Therefore, the polymer concentration remaining in the fracture can be several times the concentration mixed at the surface. Ideally, the breaker concentration should be sufficient to degrade the polymer concentration remaining in the propped fracture.

Temperature Effects

The effects of temperature on oxidative breaker performance in high pH HPG solutions is shown in Fig. 6. Note that as the temperature increases, the amount of oxidative breaker required to reduce the solution viscosity to 3 cp decreased. The same trend was observed for enzyme and catalyzed oxidative breakers from 80°F to 120°F. Also shown in Fig. 6 is that as the temperature was increased to 280°F, a breaker was still required to reduce the solution viscosity of HPG solutions to be below 3 cp.

Figs. 7 and 8 show the effects of temperature on oxidative breaker performance in neutral pH titanate crosslinked HPG gels. Fig. 7 contains the results from tests conducted at 120°F to 180°F, and Fig. 8 contains the results from tests conducted at 220°F to 280°F. As demonstrated in Fig. 6 for HPG solutions, as the temperature increased, the concentration of AP required to reduce solution viscosity decreased. Fig. 8 shows that for a titanate crosslinked gel, breakers were required at the highest temperature tested (280°F) to reduce the solution viscosity. Complete results from static break tests for both HPG solutions and gels indicate that breakers are required at temperatures up to 280°F to degrade neutral and high HPG fluids in a 24 hour period. For low pH HPG solutions and gels, breakers were required at temperatures up to 200°F. Since static breaker tests were not conducted above 280°F, it is possible that breakers are needed at temperatures exceeding 280°F.

Fig. 9 shows the effects of temperature on oxidative breaker performance in a high pH borate crosslinked gel. Borate crosslinked gels were tested with ammonium persulfate breakers at temperatures ranging from 120°F to 180°F. Fig. 9 shows for borate crosslinked HPG gels that as the temperature increases, the concentration of AP needed to degrade the fluid decreases.

One of the objectives of the static break tests was to determine the appropriate breaker system in the temperature range 120°F to 140°F. The problem in this temperature range is that all three of the breaker systems tested work to some degree. Based on the effects of pH, however, it can be concluded that enzyme breakers are the appropriate choice with low pH HPG fluids. In the neutral and high pH ranges, both catalyzed ammonium persulfate and ammonium persulfate alone will degrade the HPG fluids.

Fig. 10 contains a comparison of the results from tests of neutral pH HPG solutions at 120°F with AP and CAP breakers. While some difference exists, the results are roughly equivalent in the neutral pH range. With high pH HPG solutions tested at 120°F, however, more pronounced differences are seen between the two breaker systems as shown in Fig. 11. Fig. 11 shows that with a high pH HPG solution at 120°F, AP alone reduced the solution viscosity to a lower level than an equivalent AP concentration with a catalyst.

Fig. 12 compares the results from tests of neutral and high pH HPG solutions containing AP and CAP which were tested at 130°F. Fig. 12 shows that at 130°F for both neutral and high pH HPG solutions, AP without a catalyst is the appropriate breaker system. Similar results were found at 140°F, as shown in Fig. 13. Figs. 12 and 13 indicate that as the temperature increases above 120°F, the addition of the catalyst can be detrimental to the degradation of the HPG solution. Thus, at temperatures above 120°F with neutral and high pH HPG solutions, AP without a catalyst is the appropriate breaker system.

For borate crosslinked HPG gels, Fig. 14 shows a comparison of the static break test results for gels containing AP and AP with a catalyst tested at 130°F. As was shown with HPG solutions, the addition of a catalyst was detrimental to the reduction in solution viscosity at equivalent breaker loadings. Therefore, at temperatures above 120°F with borate crosslinked gels, AP without a catalyst is the best breaker system.

Effects of Crosslinker

Fig. 15 shows the effect of titanate crosslinker addition on the performance of ammonium persulfate breaker at 200°F. Fig. 15 shows that the addition of the crosslinker required a higher breaker concentration to reduce the solution viscosity to 3 cp. For the HPG solution, 0.45-lbm/1,000-gal AP was required, while for the HPG titanate crosslinked gel, 2.0-lbm/1,000-gal AP was required.

Fig. 16 shows the effect of borate crosslinker addition on the performance of AP breaker at 140°F. As opposed to the result seen for the titanate crosslinker, the addition of the borate crosslinker did not appear to have a significant effect on the reduction in solution viscosity at equivalent breaker loadings. Proppant pack permeability damage studies, however, have shown that the addition of borate crosslinker increases the concentration of breaker required to reduce proppant pack damage.[13-14]

Dynamic Break Tests

Results from dynamic break tests of neutral pH titanate crosslinked 40-lbm/1,000-gal HPG gels are shown in Figs. 17 through 19. Figs. 17 through 19 are graphs of apparent viscosity at a shear rate of 100 sec^{-1} versus time. Each curve is labeled with the AP breaker concentration in lbm/1,000-gal.

Fig. 17 presents the results obtained at 125°F. Results from the static break tests indicated a breaker concentration of 3.0-lbm/1,000-gal AP was required at 125°F to reduce the solution viscosity to below 3 cp after 24 hours at temperature, then cooling to less than 80°F. At 125°F, three cases were tested. The first case was for the gel without breaker (labeled 0.0 in Fig. 17), the second case was with 1/3 of the required breaker loading (1.0-lbm/1,000-gal AP), and the third case was with the required breaker loading. As seen in Fig. 17, the addition of the breaker has a dramatic effect on the viscous properties of the gel. Even at the fractional loading of the required breaker concentration, the gel never attains the apparent viscosity of the fluid without breaker, and the viscous properties of the gel rapidly decrease with time. At the required breaker loading, within 1-1/2 hours, the gel degraded to below the minimum viscosity that could be measured in the flow loop.

The results from the special tests showed that the 1.0-lbm/1,000-gal AP concentration reduced the solution viscosity to 11 cp at a shear rate of 511 sec^{-1} after 24 hours at temperature and cooling to below 80°F (including flow through the loop for 3 hours). The 3.0-lbm/1,000-gal AP breaker loading broke the gel as expected. Results from the dynamic break tests and the special tests show that the breaker concentrations required for degrading HPG gels drastically reduce the viscous properties of the gels in a relatively short time, but the required breaker loadings must be used to degrade the solutions to within the break criteria.

Fig. 18 contains the results for neutral pH titanate crosslinked gels at 150°F. Results from the static break tests indicated 2.2-lbm/1,000-gal AP breaker was required to degrade the gel; therefore, tests were run with the required breaker loading and approximately 1/3 of the required breaker concentration. Again the results were very dramatic. With 0.75-lbm/1,000-gal ammonium persulfate breaker, the fluid degraded to below the minimum viscosity that could be measured in the flow loop within 1-1/2 hours. With the required breaker loading, the fluid degraded to below the minimum viscosity within 1 hour. Special tests confirmed that 2.2-lbm/1,000-gal AP breaker were required to degrade the gel to within the break criteria.

Fig. 19 contains the results for neutral pH titanate crosslinked gels at 200°F. The required breaker concentration from the static tests was 2.0-lbm/1,000-gal AP. Tests were run on the GRI/TAMU Rheology Flow Loop with 0.0-, 0.2-, and 2.0-lbm/1,000-gal AP breaker concentrations. Fig. 19 contains the results for the gel without breaker and with the 0.2-lbm/1,000-gal AP breaker concentration. As seen in Fig. 19, 0.2-lbm/1,000-gal AP breaker reduced the apparent viscosity to below the minimum viscosity that could be accurately measured in about 1 hour, and 0.2-lbm/1,000-gal AP represents only 1/10 of the amount of breaker required as indicated by the results of the static break tests. The gels with the required breaker concentration could not be presented in Fig. 19 because they crosslinked and degraded before the fluid sample reached 200°F (approximately 18 minutes).

CONCLUSIONS

This research was conducted to improve the understanding of the variables affecting HPG solution and gel degradation by oxidative, enzyme, and catalyzed oxidative breakers. A comprehensive examination of the variables affecting HPG solution degradation was made using static break tests with polymer degradation inferred from reductions in apparent viscosity over time. Additionally, the effects of oxidative breakers on titanate crosslinked HPG gel viscous properties were examined with the GRI/TAMU Rheology Flow Loop. The results from this research justify the following conclusions.

1. Enzyme breakers can be used to degrade low pH ($3 < pH < 4$) HPG fracturing fluids at temperatures less than or equal to 140°F (60.0°C), but enzyme breakers are not effective when the pH is greater than 7.5.

2. Catalyzed ammonium persulfate can be used to degrade HPG fracturing fluids at temperatures below 120°F (48.9°C) when the pH is greater than 7.5.

3. Ammonium persulfate can be used to degrade HPG fracturing fluids at temperatures greater than or equal to 120°F (48.9°C).

4. In the temperature range 120°F (48.9°C) to 140°F (60.0°C), enzyme breakers are the most effective for low pH ($3 < pH < 4$) HPG fracturing fluids, and ammonium persulfate breaker without a catalyst is the most effective if the pH is greater than 7.5. At temperatures greater than 120°F, the catalyst triethanolamine should not be used with ammonium persulfate breaker.

5. For high temperature applications, low pH ($3 < pH < 4$) HPG solutions will degrade without breakers at temperatures greater than 200°F. With a pH greater than 7.5, however, ammonimum persulfate breaker was required to break HPG solutions and neutral pH ($7.5 < pH < 8.5$) titanate crosslinked HPG gels at the highest temperature tested [280°F (137.8°C)].

6. Conventional ammonium persulfate breaker drastically alters the viscous properties of neutral pH titanate crosslinked HPG gels. Ammonium persulfate breaker concentrations that are a fraction of the amount required to reduce proppant pack permeability damage will rapidly degrade the gel viscous properties. As a result of rapid degradation, proppant transport properties may be lost , and the success of the fracturing treatment jeopardized.

Table 7 has been prepared to summarize the properties of enzyme, oxidative, and catalyzed oxidative breakers. Table 7 represents (A) contributions from the literature (see Table 2), plus, (B) the results of the static break tests conducted as part of this research.

RECOMMENDATIONS

The results from this research should aid in the selection of an appropriate breaker type for hydraulic fracturing applications; however, under field conditions, the concentrations of breakers required can be different from the concentrations suggested by the results of the static break tests.

In the field, a fracturing fluid is exposed to contaminants in the water used to mix the fluids and contaminants in the frac tanks and surface pumping equipment. Additionally, the fluid can react with the reservoir fluids and reservoir rock. As a result, the degradation of the polymer under field conditions can be different from the degradation measured in laboratory experiments.

In field fracturing operations, the service company should be consulted to determine the breaker type and concentration. Generally, the service company will have experience gained from previous fracture treatments in the same formation. Based on experience gained from fracturing the same formation, the service company should be able to make sound breaker type and concentration recommendations.

Determining the breaker concentration required under field fracturing conditions also requires considering the effects of the breakers on the short term viscous properties of the fluids. The primary goal of massive hydraulic fracturing is to create a long propped fracture. The fracture conductivity , while important, is secondary. The results from the dynamic break tests show how fracturing fluids can be affected by breakers. A breaker concentration should be selected that allows the proppant to be placed in the oil or gas zone. If the breaker concentration causes the fluid to degrade rapidly, the proppant transport properties can be lost and the proppant will settle out of zone. Breaker concentrations less than is necessary to reduce proppant pack permeability damage significantly may be required. Quality control checks of the actual fluids being pumped in the field and consultation with the service company representatives should be used to determine the optimal breaker concentration for the formation being treated.

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ACKNOWLEDGEMENTS

The authors would like to thank the Gas Research Institute for funding this research project; Dowell Schlumberger and Halliburton Services for supplying the chemicals; John Ely for outlining the original scope of the project; and the S.A. Holditch and Associates for supplying the facilities, equipment, and personnel required for part of the project.

Table 1

Polymer Degradation Mechanisms

Mechanism	Cause and Effect
Thermal	High temperature causes water to be lost from the polymer chain, which results in polymer dehydration. At temperatures greater than 240°F, thermal degradation is sufficient to degrade the polymer without chemical breakers.
Mechanical	Shear degradation results from shear forces during flow of the polymer. Shear forces can result in (1) polymer side chain removal (2) altered gel network structure.
Biological	Guar and guar derivative polymer solutions and gels are highly susceptible to enzymatic attack by aerobic bacteria. Enzymatic attack reduces polymer molecular weight and solution viscosity. The growth of bacteria can be inhibited by appropriate biocides.
Chemical	Acid catalyzed hydrolysis and oxidative/reductive depolymerization result in cleavage of the polymer chain and a loss in solution viscosity. Typical breakers for temperatures less than 240°F are oxidative, such as potassium or ammonium persulfate.

Table based on the literature.[4-6,8-14]

Table 2

Guar and Guar Derivative Breakers

Enzyme	Oxidative
Typical enzyme breaker is a hemicellulase.	Persulfates (potassium and ammonium) are typical oxidative breakers.
Most effective in a low pH range (pH << 7).	Applicable over a broad pH range (3 < pH < 14).
Ineffective above 140°F.	Requires a catalyst (triethanoloamine) at temperatures less than 130°F.
Effectiveness is altered by crosslinker type.	Reaction rate is rapid in the first 3-10 hours, slowly decreases over the next 24 hours.
Magnitude of polymer degradation is dependent on enzyme concentration.	Magnitude of polymer degradation is dependent on oxidizer concentration.
	Reaction rate increases dramatically at high temperatures (> 160°F).
	Can be encapsulated to create a delayed breaker system.

Table based on the literature.[4-6,8-14]

Table 3
Scope of Static Breaker Testing of HPG Solutions

VARIABLE	RANGE
Temperature (°F)	80, 100, 120, 130, 140, 160, 180, 200, 220, 240, 260, and 280
HPG Polymer Concentration (lbm/1,000-gal)	30, 40, and 50
pH	Low (pH 3 - 4) Neutral (pH 7.5 - 8.5) High (pH 9 - 10)
Breaker Types	Enzyme (80°F-140°F) Catalyzed Oxidative (80°F-140°F) Oxidative (120°F-280°F)
Breaker Concentration	Minimum of three concentrations.

Table 4
Scope of Static Breaker Testing of HPG Gels

VARIABLE	RANGE
Temperature (°F)	120, 130, 140, 160, 180, 200, 220, 240, 260, and 280
HPG Polymer Concentration (lbm/1,000-gal)	40
pH	Neutral (pH 7.5 - 8.5)
Breaker Types	Catalyzed Oxidative (120°F-140°F) Oxidative (120°F-280°F)
Breaker Concentration	Minimum of three concentrations.
Crosslinker Type	Borate (80°F - 180°F) Delayed Titanate (120°F - 280°F)

Table 5
Breaker Concentrations Tested in the GRI/TAMU Rheology Loop

Temp (°F)	Breaker Concentrations Tested (lbm/1,000-gal)		
125	0.00	1.00	3.00
150	0.00	0.75	2.20
200	0.00	0.20	0.50

Table 6
Special Tests

Temp (°F)	Breaker Concentrations Tested (lbm/1,000-gal)	
125	1.00	3.00
150	0.75	2.20
200		0.50

Table 7
Guar and Guar Derivative Breakers

Enzyme	Oxidative	Catalyzed Oxidative
Typical enzyme breaker is a hemicellulase.	Persulfates (potassium and ammonium) are typical oxidative breakers.	Typically are oxidative breakers with triethanolamine.
Most effective in a low pH range (pH << 7).	Applicable over a broad pH range (3 < pH < 14).	Most effective with pH > 7.
Ineffective above 140°F.	Requires a catalyst (triethanoloamine) at temperatures less than 120°F.	Effective at temperatures up to 120°F.
Effectiveness is altered by crosslinker type.	Reaction rate is rapid in the first 3-10 hours, slowly decreases over the next 24 hours.	Reaction rate is rapid in the first 3-10 hours, slowly decreases over the next 24 hours.
Magnitude of polymer degradation is dependent on enzyme concentration.	Magnitude of polymer degradation is dependent on oxidizer concentration.	Magnitude of polymer degradation is dependent on oxidizer concentration.
	Reaction rate increases dramatically at high temperatures (> 160°F).	Relatively insensitive to triethanolamine concentration.
	Can be encapsulated to create a delayed breaker system.	

Table based on the results of research and the literature.[4-6,8-14]

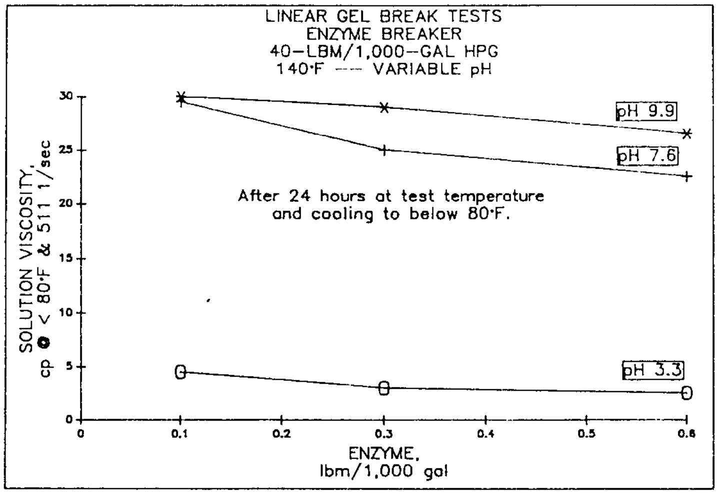

Figure 1 - Effect of pH on enzyme breaker performance in HPG solutions at 140°F

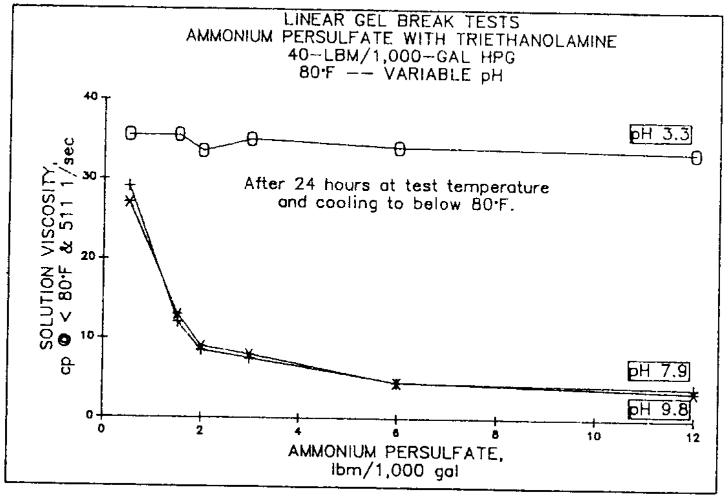

Figure 2 - Effect of pH on catalyzed oxidative breaker performance in HPG solutions at 80°F

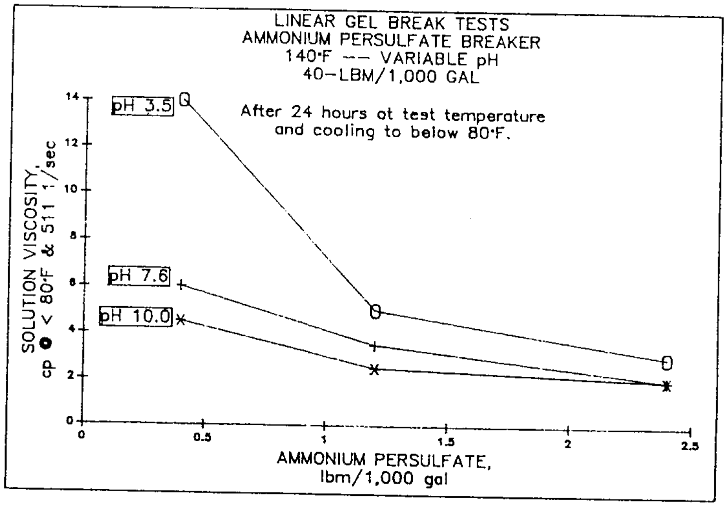

Figure 3 - Effect of pH on oxidative breaker performance in HPG solutions at 140°F

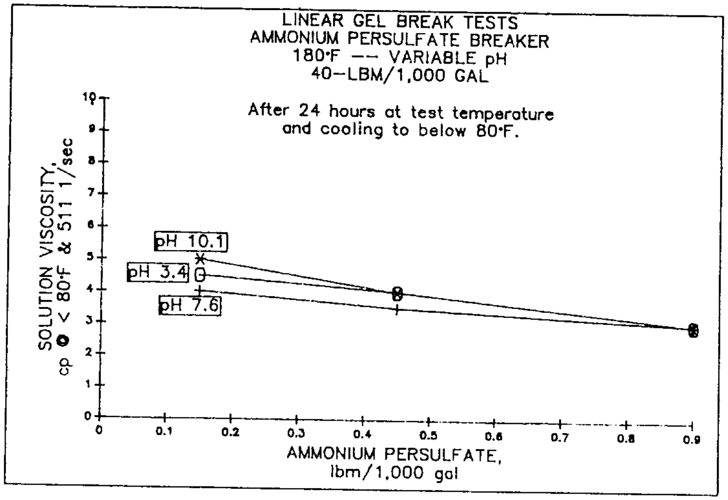

Figure 4 - Effect of pH on oxidative breaker performance in HPG solutions at 180°F

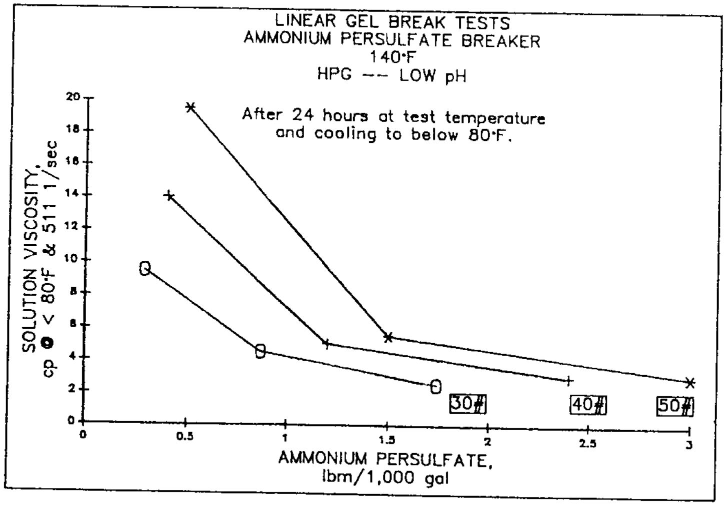

Figure 5 - Effect of HPG concentration on oxidative breaker performance in low pH HPG solutions at 140°F

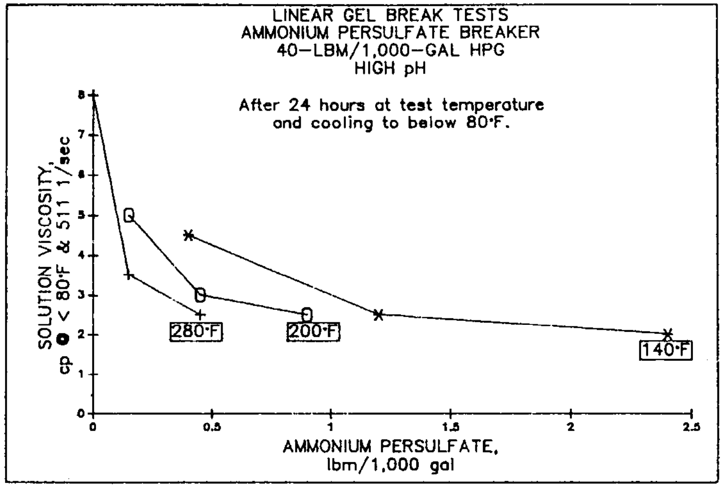

Figure 6 - Effect of temperature on oxidative breaker performance in high pH HPG solutions

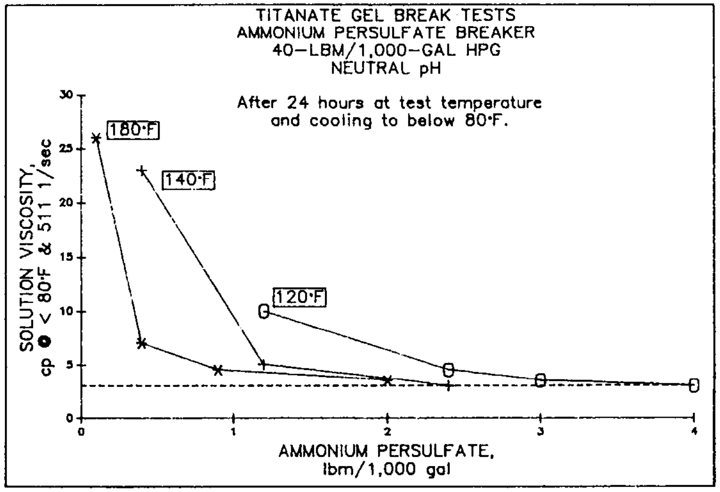

Figure 7 - Effect of temperature on oxidative breaker performance in titanate crosslinked gels (120 - 180°F)

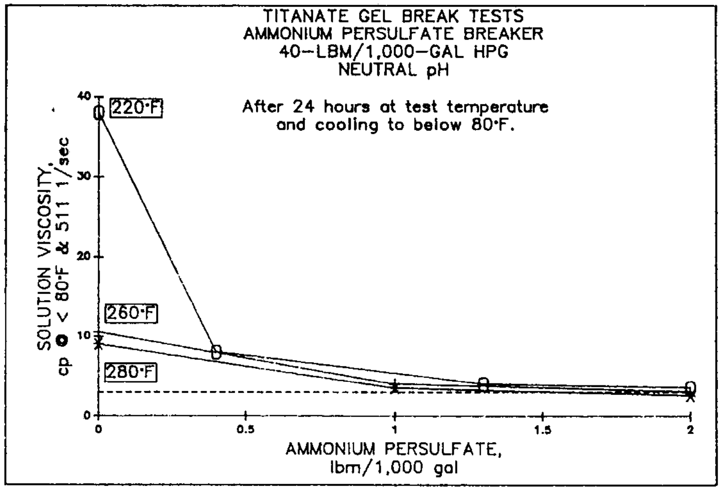

Figure 8 - Effect of temperature on oxidative breaker performance in titanate crosslinked gels (220 - 280°F)

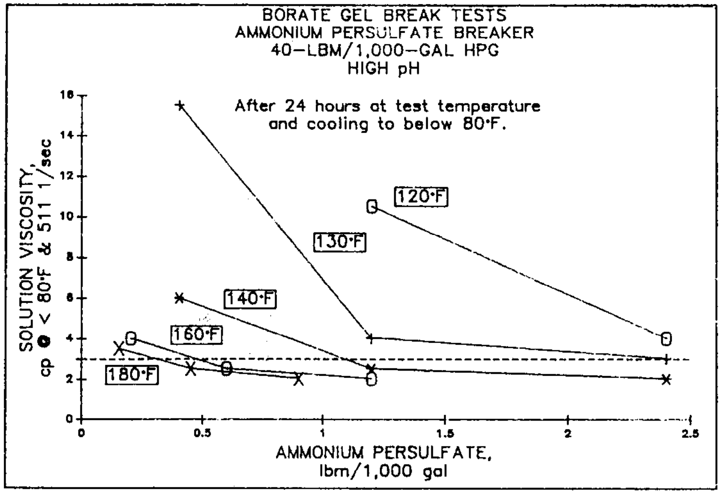

Figure 9 - Effect of temperature on oxidative breaker performance in borate crosslinked gels (120 - 180°F)

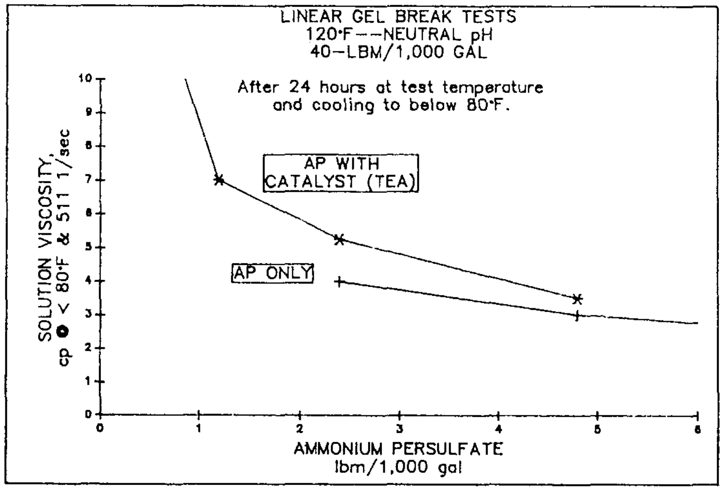

Figure 10 - Comparison of oxidative and catalyzed oxidative breakers in neutral pH HPG solutions at 120°F

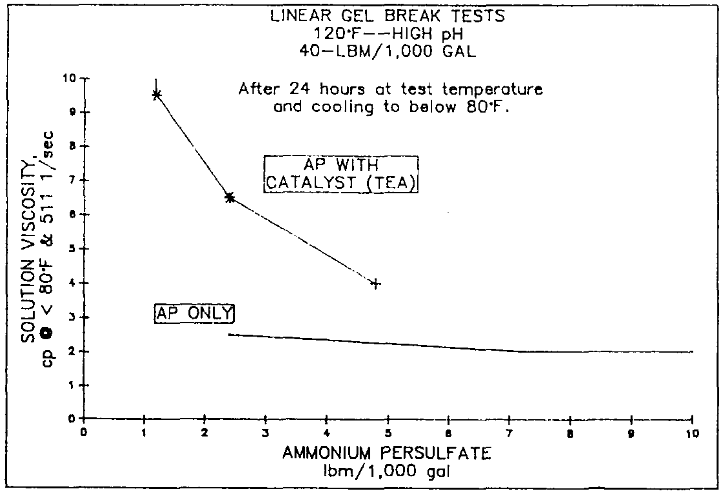

Figure 11 - Comparison of oxidative and catalyzed oxidative breakers in high pH HPG solutions at 120°F

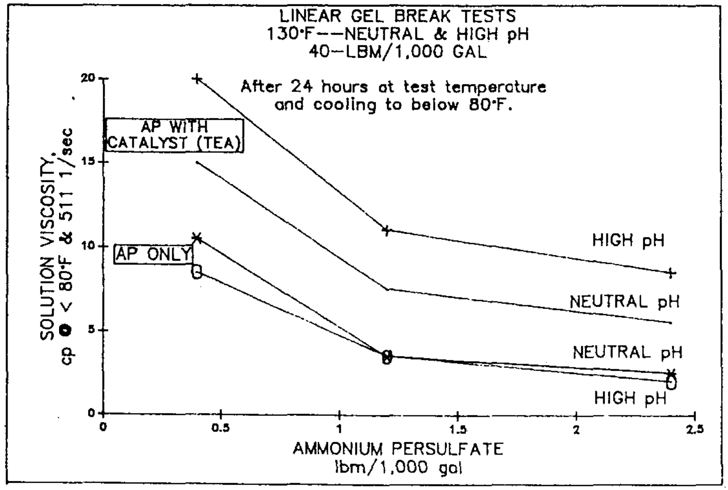

Figure 12 - Comparison of oxidative and catalyzed oxidative breakers in HPG solutions at 130°F

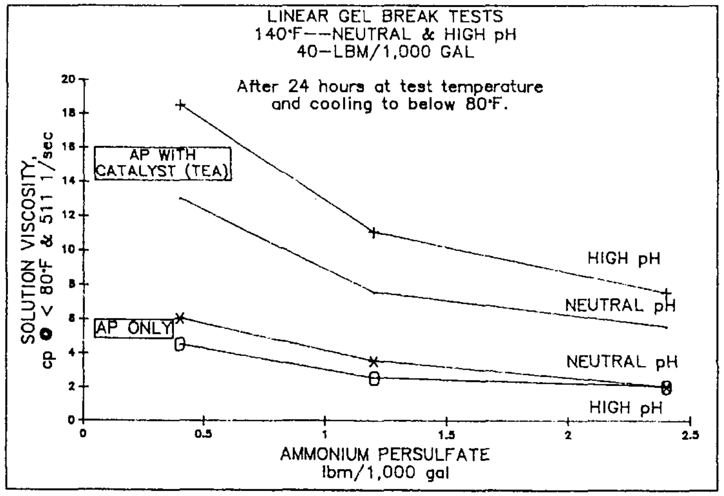

Figure 13 - Comparison of oxidative and catalyzed oxidative breakers in HPG solutions at 140°F

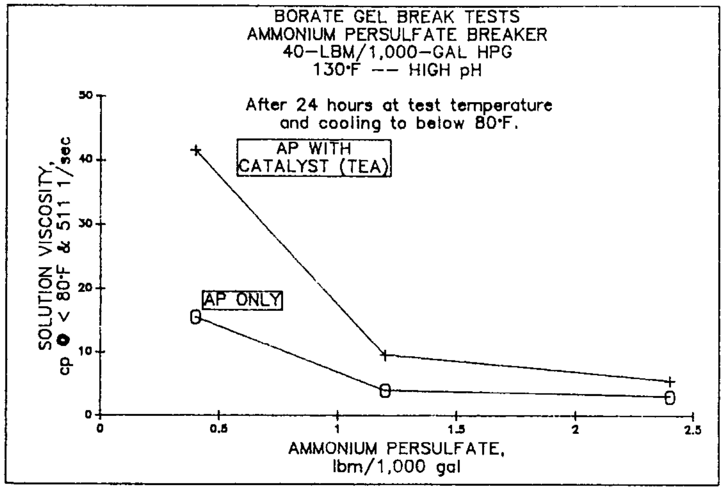

Figure 14 - Comparison of oxidative and catalyzed oxidative breakers in borate crosslinked HPG gels at 130°F

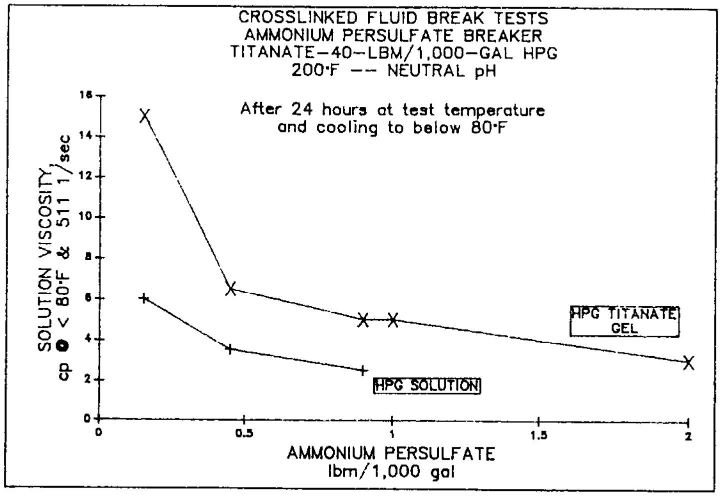

Figure 15 - Comparison of oxidative breaker performance in HPG solutions and titanate crosslinked gels at 200°F

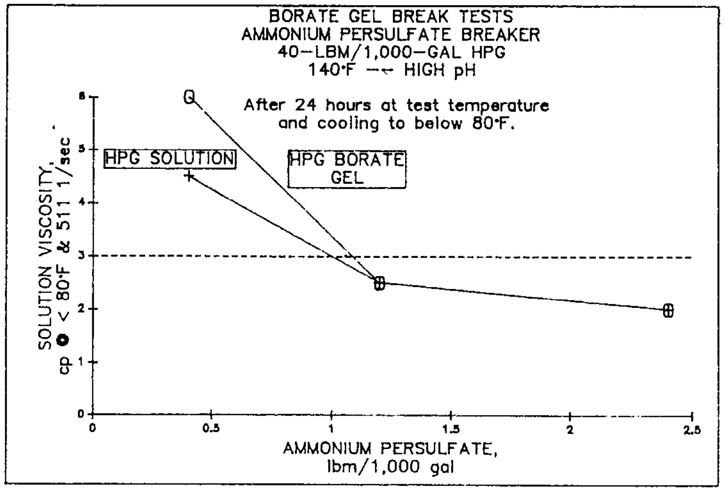

Figure 16 - Comparison of oxidative breaker performance in HPG solutions and borate crosslinked gels at 140°F

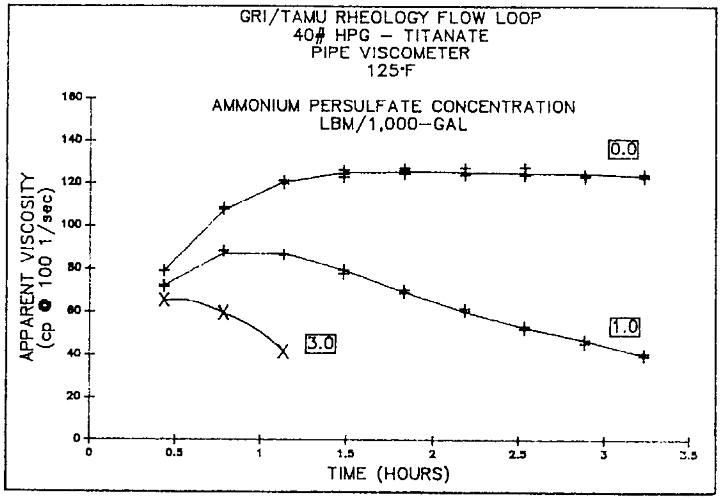

Figure 17 - Effects of oxidative breakers on the viscous properties of titanate crosslinked gels at 125°F

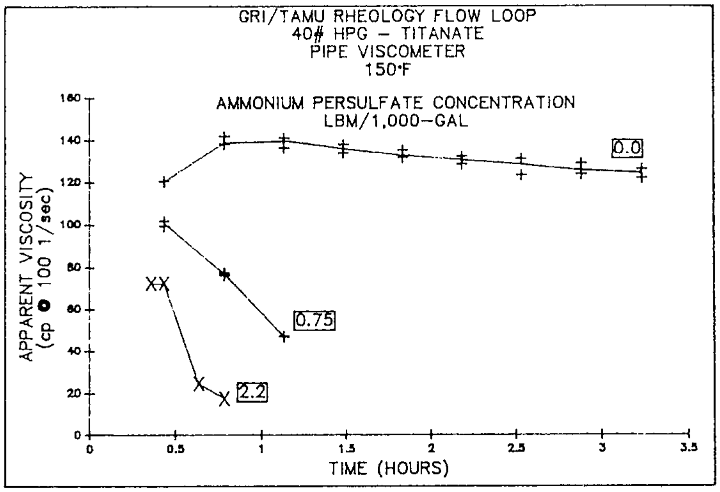

Figure 18 - Effects of oxidative breakers on the viscous properties of titanate crosslinked gels at 150°F

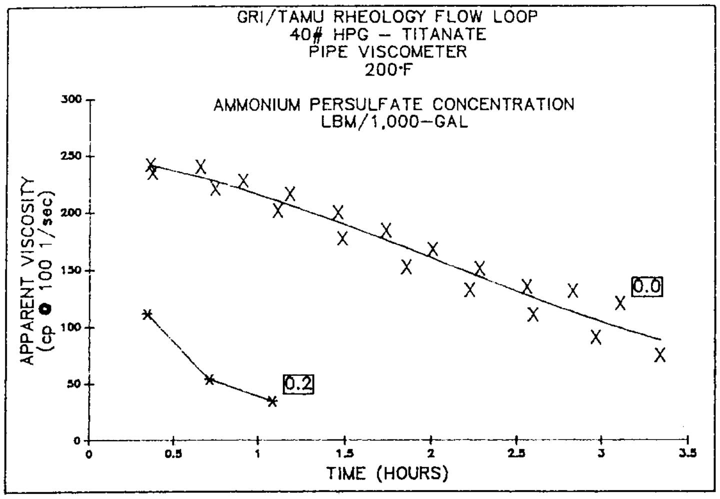

Figure 19 - Effects of oxidative breakers on the viscous properties of titanate crosslinked gels at 200°F