

**DEGRADATION OF FRACTURING FLUID POLYMERS**

**Final Report  
Project OE1B**

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## DEGRADATION OF FRACTURING FLUID POLYMERS

BY Bonnie Gall<sup>1</sup>

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### ABSTRACT

Polymer degradation has been studied for a variety of degradation conditions using size exclusion chromatography (SEC) to monitor the progress of the degradation reactions. SEC measures the molecular size of polymer degradation products. Changes in polymer degradation conditions result in changes in the size of polymer degradation products. Size is then related to molecular weight using suitable polymer standards. In this research, the study of hydroxypropyl guar (HPG) degradation has been emphasized since this polymer is most commonly used in fracturing fluids. The SEC studies have been used to help understand the mechanisms of polymer degradation and to suggest ways to design better breaker systems.

Degradation studies include investigations of the effects of breaker type and concentration and of reaction temperature. Three types of breakers have been studied; an oxidant breaker (ammonium persulfate), acids, and enzymes.

Several limitations have been observed when using the oxidant breaker to initiate polymer degradation. Used in low concentration, ammonium persulfate fails to significantly reduce polymer average molecular weight. This may potentially lead to polymer buildup in the fracture and hinder fluid return after a fracture treatment. If breaker concentration is increased, solution

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viscosity will decline too rapidly. The solution will no longer be a useful fracturing fluid for proppant transport. Furthermore, the rate of polymer degradation does not depend on oxidant breaker concentration. The extent of polymer degradation, however, is proportional to the square root of the breaker concentration.

Improved breaker systems which include oxidant breakers require some type of time-delay mechanism to avoid loss of solution viscosity during the fracture stimulation and still reduce polymer molecular size to minimize damage to the fracture. The combination of an oxidant breaker and methanol (often used to stabilize polymer solutions at temperatures above 200° F) was studied but did not produce a suitable time-delayed breaker system. Instead, this combination had the same effect on polymer degradation as that from using a lower concentration of breaker with no methanol present. No "delay" occurred.

A second method of polymer degradation which has been studied is acid-catalyzed hydrolysis. Molecular weight studies have shown that acids do not cause well controlled polymer degradation and often cause increased amounts of precipitates to form. Only with HPG degradation in the presence of appropriate amounts of citric acid do results appear to be encouraging. In this case, polymer average molecular weight reduction proceeds gradually to a non-damaging level.

For polymer degradation using enzyme breakers, results show that polymer molecular weight reduction can be changed by using a different type of enzyme.

Presently, no system which has been examined possesses ideal degradation characteristics. Progress has been made, however, in understanding the nature of fracturing fluid polymer degradation and the effect various degradation conditions have on polymer average molecular weight reduction.

## INTRODUCTION

Water-soluble polymers are commonly used in fracturing treatments to increase the fluid viscosity of hydraulic fracturing fluids for improved proppant placement and fluid loss control. Hydroxypropyl guar (HPG), a chemically modified derivative of a naturally occurring polysaccharide (guar gum) is used most frequently in fracturing fluids. After completion of the fracturing treatment, fluid viscosity should decrease to allow proppant placement and rapid fluid return through the fracture. Ideally, the degraded polymer should produce little residue to restrict the flow of fluids (gas, liquid, or oil) through the fracture. The polymer may cause significant flow restriction in the fracture depending on the degree of degradation (molecular size reduction) and insoluble residues produced during degradation. If fracture conductivity remains low relative to that in the formation (invaded by fracturing fluid), slow fracture cleanup and a non-productive fracture treatment will result. (1)<sup>2</sup>

Studies have been conducted for several years at NIPER (previously the Bartlesville Energy Technology Center) to evaluate the effects of a number of variables on polymer degradation. The objectives of this work are to understand mechanisms of polymer degradation and to identify degradation conditions which minimize damage to the fracture caused by incomplete or inefficient polymer degradation. This increased understanding will allow the development of improved fracturing fluid systems.

Fluid viscosity reduction is not a good measure of possible polymer damage to the proppant pack. (2,3) Instead, polymer degradation has been studied by measuring the molecular size of polymer degradation products. Size

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<sup>2</sup>Underlined numbers in parentheses refer to the list of references at the end of this report.

exclusion chromatography (SEC) is used to determine changes in polymer molecular size. Size is then related to polymer molecular weight using available water-soluble polymer standards (high-molecular-weight-dextrans). The SEC system and methods have previously been described. (4)

Previous studies have also related molecular weight reduction to restricted flow through small pore size filters. These filters are capable of retaining partially degraded polymer molecules. (3,5) The polymer buildup restricts liquid flow through the filtering medium. This method was used to relate the degree of polymer degradation to possible fracture damage. The report (3) on this work is included in its entirety in appendix A.

Flow restriction also depends on the amount of insoluble or "visible" residues produced during polymer degradation. These precipitates alter the pore size characteristics of the filtering medium. Polymers which produce insoluble residues require greater molecular weight reduction to prevent polymer buildup in the filtering medium. Polymers which do not produce insoluble residues cause flow restriction only when the polymer molecular size and the filter medium pore size are comparable. These studies also show that excessive break conditions (high breaker concentration, high temperature, etc.), however, usually cause rapid solution viscosity reduction. These gels no longer give adequate fracturing fluid performance.

This report will summarize a number of different break conditions and their effect on polymer degradation. Many parameters affect polymer degradation. They include polymer/breaker type and concentration, reaction time, temperature, and additives to the fluid composition (salts, crosslinkers, stabilizers, acids, etc.). In this study, some work has been done to investigate a number of these variables; but not every possible variation has been explored in depth. Considerable information has been obtained on the

effect of concentration and reaction time, however, for oxidant breaker initiated degradation in the temperature range of 70° to 90° C. For the oxidant breaker, polymer degradation proceeds through a series of free radical reactions. Kinetic studies, which will be described, support this view of the reaction mechanism.

Since a number of reaction mechanisms can result in polysaccharide polymer degradation, a brief summary of the most important modes of polymer molecular size reduction include:

1. Enzymatic cleavage of terminal sugar groups on the polysaccharide molecule cause progressive molecular size reduction. Since enzymes are sensitive to temperature, enzyme breakers are usually limited to reservoir temperatures lower than 60° C (140° F).
2. Side chain removal may be caused by oxidizing agent attack or by shearing forces. Side chain removal can change solution viscosity or create water-insoluble reaction products.
3. Polymer backbone cleavage may be initiated by hydrolysis or by free radical attack (initiated by oxidizing agents). The hydrolysis rate increases with increasing acid concentration. Polymers with chemically modified or complex side chains are less susceptible to degradation.
4. High temperatures cause polymer dehydration. The polymer structure collapses under extreme conditions. Degraded polymer solutions have a burnt or carmel color and odor. A brown, insoluble residue is formed. Formation temperatures greater than 115° C (240° F) are sufficient to degrade most polysaccharide polymer structures completely without the addition of other breakers. Greater efforts are required to stabilize rather than degrade the polymer in hot reservoirs.

## EXPERIMENTAL PROCEDURES

### Molecular Weight Studies

Polymer characterization and degradation studies were performed using a commercial size exclusion chromatographic system. The SEC system, columns, and procedures have been described. (4)

Although SEC separates molecules according to size, results are typically reported as molecular weight distributions (MWD). Standards of known molecular weight are used to calibrate the column elution times. For aqueous polymer solutions, high-molecular-weight dextran standards are used. Figure 1 shows a composite chromatogram of the dextran MWD curves. Most changes in MWD of polymer solutions studied will be reported as changes in average molecular weight ( $\bar{M}_w$ ). To calculate  $\bar{M}_w$ , the chromatographic curve is divided into sections (N); the height (or volume) is measured for each section ( $h_i$ ); and the molecular weight of each section ( $M_i$ ) is determined from the calibration standards. The average molecular weight is calculated using the following equation:

$$\bar{M}_w = \frac{\sum_{i=1}^N (h_i M_i)}{\sum_{i=1}^N h_i} \quad (1)$$

Figure 2 shows the calibration curve constructed from dextran SEC curves which are used as standards. One basic problem with this calibration method is the lack of suitable water-soluble polymer standards with molecular weights above 2 million daltons (d.). Even this high molecular weight standard (T-2000 dextran) had a very broad molecular weight distribution. Therefore, molecular weights reported in this study are relative and not absolute values. They should be used mainly for comparative studies. Progress of

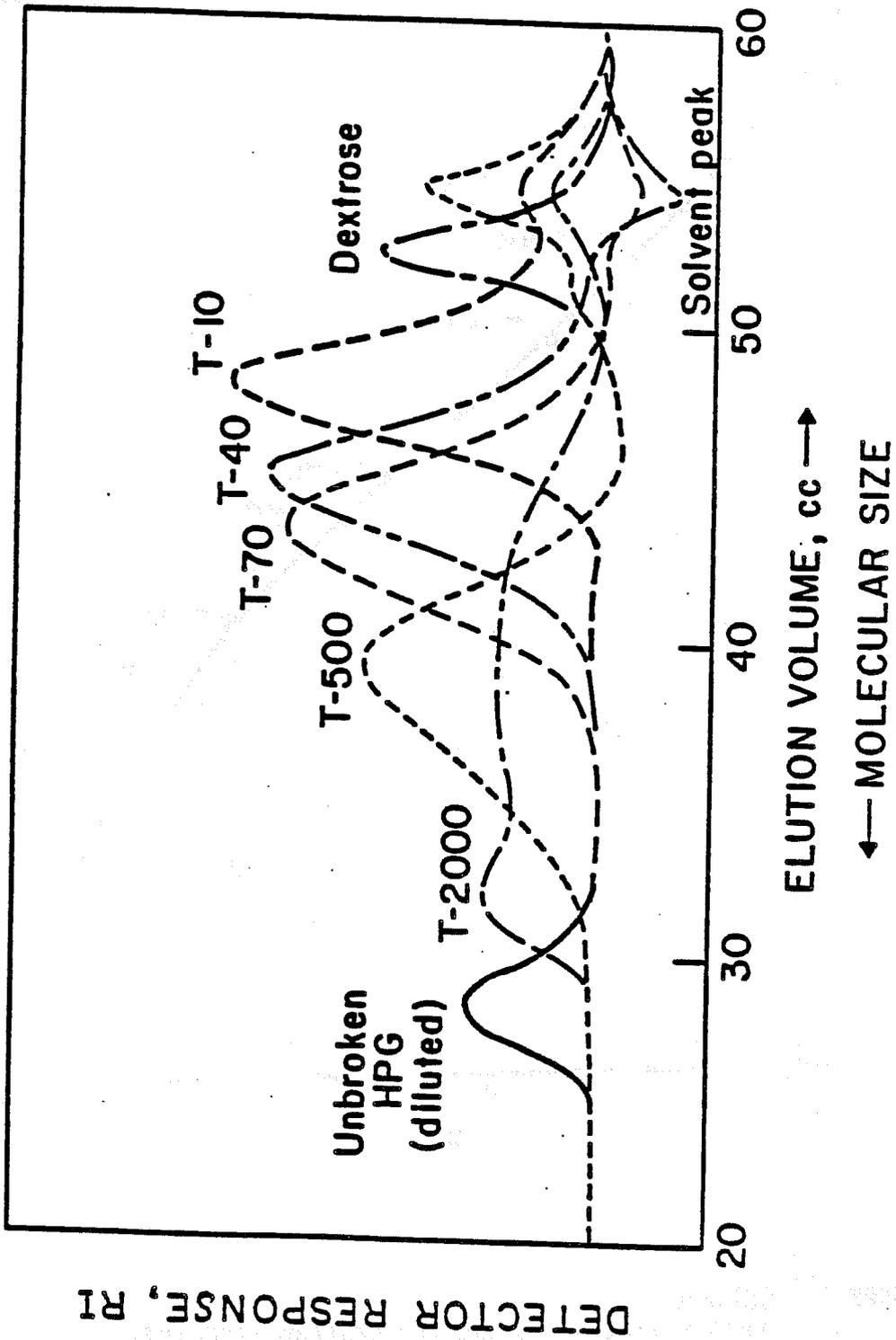


FIGURE 1. Composite chromatogram of dextran standards and unbroken HPG gel.

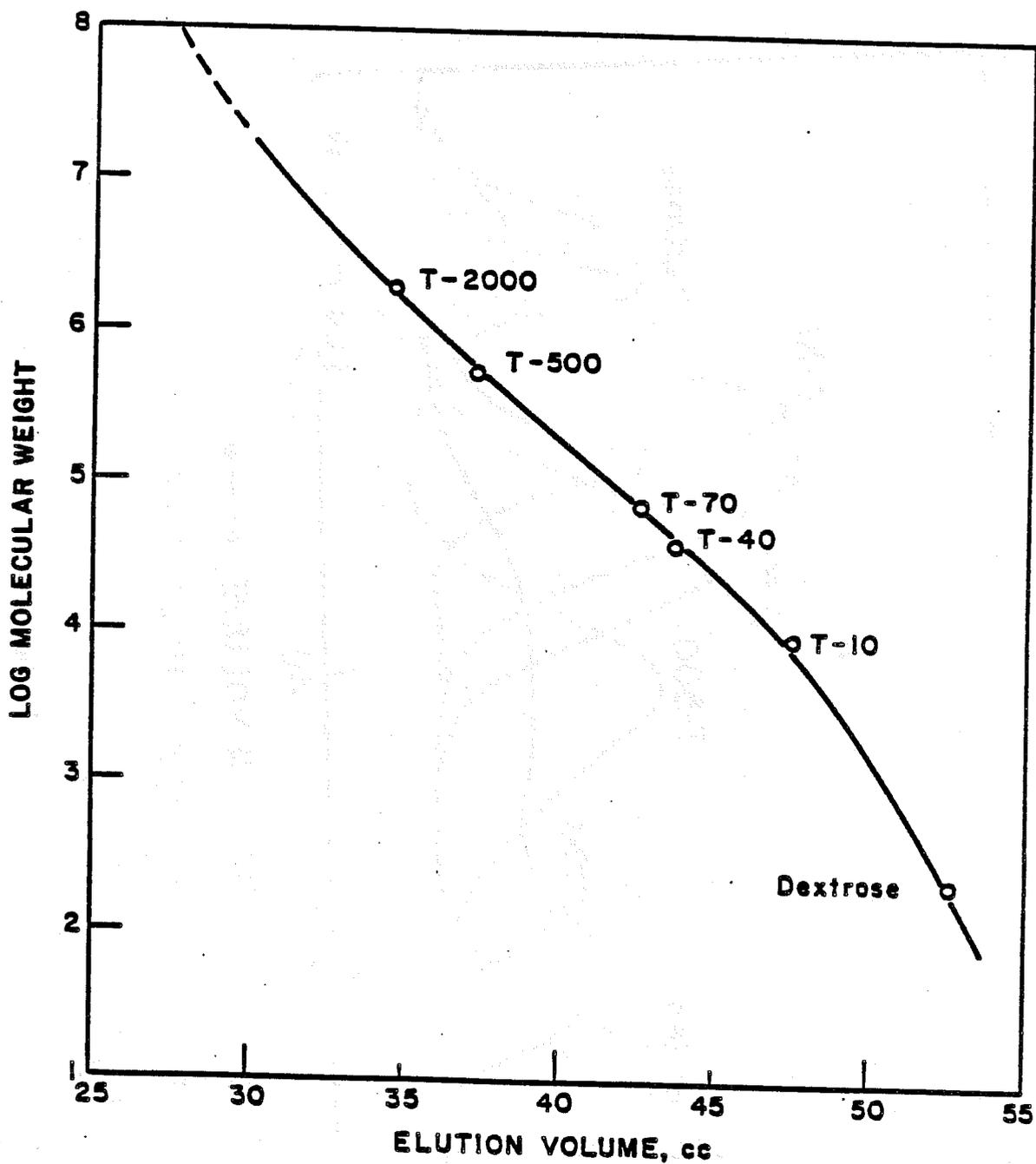


FIGURE 2. Calibration curve of log average molecular weight versus elution volume for dextran standards.

polymer degradation was monitored by determining  $\bar{M}_w$  changes for various reaction conditions. For oxidant breaker figure 1 initiated degradation, the shape of the MWD curve remained the same as  $\bar{M}_w$  decreased. Other breaker types may attack the polymer more selectively and change the size distribution of the polymer degradation products. Kinetic studies described in this report apply only to oxidant breaker initiated reactions.

### Polymer Solution Preparation

Polymer solutions were prepared using a constant torque mixer/stirrer to aid in polymer dispersion and to provide reproducible mixing conditions. In most cases, the dry polymer was sprinkled into a stirring buffer solution (0.12 percent  $\text{KH}_2\text{PO}_4$ ). Solution pH was raised to 10 with 10 percent KOH and then reduced to pH 6 with 10 percent  $\text{H}_3\text{PO}_4$  to aid polymer hydration and dispersion. Other additives such as additional salts, crosslinkers, gel stabilizers, or breakers could also be added as required.

Commercially available fracturing fluid systems were prepared according to instructions provided by the supplier. Mixing instructions were similar, but composition of the fluid (additives, etc.) varied.

The breaker was usually dissolved in a small amount of water just before addition to the polymer solution to aid in uniform mixing with the polymer. Breaker solutions could not be prepared in advance, however. The breakers could decompose in water and change their reactivity.

Concentrations of solution component were calculated on the basis of 100 percent activity and reported as weight percent (per weight of solution). For comparison with common oilfield units, a breaker concentration of 1 lb/1,000 gal is equivalent to 0.012 percent by weight. A polymer concentration of 40 lb/1,000 gal is equivalent to 0.48 percent by weight.

### Degradation Conditions

Prepared polymer solutions were placed in a constant temperature bath. Solution samples were withdrawn periodically for SEC analysis. Additional measurements such as viscosity and fluid leakoff tests could also be performed. Molecular weight studies using oxidant breakers were performed at 70°, 80°, and 90° C. Acid breaker studies were performed at 70° C.

### Viscosity Measurements

A Contraves Low-Shear 30 viscometer was used to measure viscosities of partially degraded or degraded polymer solutions. Viscosity measurements were made at ambient temperatures and do not represent viscosities under reservoir conditions. Partially degraded polymer solutions could have a relatively low solution viscosity and still have a number of polymer molecules with a high polymer molecular weight. A correlation between viscosity and  $\bar{M}_w$  of partially degraded polymer solutions is given in appendix A.

### Fluid Loss Measurements

Fluid loss measurements were made using a pressurized fluid loss cell and small pore size filters. Filter size was usually 0.05 micrometers. This was small enough to retain partially degraded polymer molecules with molecular weight greater than approximately  $3 \times 10^5$  d. Gas pressure of 100 psig was used to force the solution through the filter.

The amount of fluid passing through the filter was measured as a function of time. For wall building fluids, fluid loss is a function of the square root of time (6). A fluid loss coefficient can be calculated from the slope of accumulated fluid volume versus the square root of time:

$$C = 0.0164 M/A \quad (\text{ft}/\text{min.}^{\frac{1}{2}}) \quad (2)$$

where M is the slope of the curve and A is the area of the filter in  $\text{cm}^2$ .

## OXIDANT BREAKER INITIATED DEGRADATION OF HPG

### Degradation Mechanism

Formation temperature determines the type of breaker used in a fracturing stimulation treatment. For intermediate temperatures (60° to 115° C or 140° to 240° F), oxidant breakers such as ammonium persulfate,  $\text{NH}_4\text{S}_2\text{O}_8$ , are used in most fracturing fluids. The persulfate ion reacts with water to form hydroxyl radicals which in turn attack the ether linkages in the polysaccharide molecules (Z). The persulfate ions can also react directly with the polymer molecules (P). A chain reaction is initiated since the reaction products are also free radicals.



The polymer radicals may undergo decomposition or continue free radical reactions. They may also react with oxygen or other impurities in the fluids. Reaction with oxygen can form a peroxide which is unstable at higher temperatures but may be relatively stable at ambient temperatures.



The symbol  $R^\bullet$  represents a number of possible free radicals such as  $HO^\bullet$  and  $P^\bullet$ .

Termination of the chain reaction occurs when the free radicals combine.



The initial fast reduction in polymer molecular weight can be attributed to these chain reactions. Higher breaker concentration initiates more reaction chains and results in an increased number of polymer fragments of lower molecular weight. Slower, thermal degradation also occurs. The proportion of polymer degradation caused by thermal degradation mechanisms increases as temperature increases. In actuality, no oxidant breaker is added to fracturing fluids used in reservoirs with temperatures above 115° C and is often not used in reservoirs with temperatures above 90° C.

### Kinetics of Chain Reactions

A general treatment of the kinetics of chain reactions shows that the rate of formation of a product of the chain reaction is proportional to the

rates of the various steps,

$$\text{initiation} \propto r_i \quad (\text{equation 1})$$

$$\text{propagation} \propto r_p \quad (\text{equations 4, 5, and 6})$$

$$\text{breaking} \propto r_b \quad (\text{equation 9})$$

by the equation

$$\text{rate} \propto r_p (r_i/r_b)^{1/w} \quad (10)$$

where  $w$  is the order of the chain-breaking reaction with respect to the chain carrier. (7) If one free radical is involved in the chain breaking step,  $w$  equals 1. If two free radicals are involved,  $w$  equals 2.

Normally, reaction kinetics are studied by monitoring changes in reactant concentrations during the reaction. In this study, changes in polymer average molecular weight were observed. Changes in  $\bar{M}_w$  may not always be a useful parameter to study degradation. Some depolymerization reactions can produce reaction products with increased molecular weight through crosslinking of reaction products. (8) In these studies, however, the MWD curve for HPG appears to retain the same relative shape and  $\bar{M}_w$  appears to decrease uniformly as the reactions progress. Changes in this parameter were examined using kinetic analysis techniques to learn more about mechanism of degradation.

Many free radical chain reactions exhibit first-order reaction kinetics. When a reaction is first-order, a plot of  $\log \bar{M}_w$  versus time should be a straight line. If the reaction is second-order, a plot of  $1/\bar{M}_w$  versus time should be a straight line. Degradation rates may also be the sum of rates from several degradation mechanisms. Both breaker initiated reactions and thermal degradation reactions contribute to polymer  $\bar{M}_w$  reduction. Techniques are available to separate two first-order concurrent reactions, for example. Since polymer degradation is complex, the results of kinetic analysis may only confirm or contradict the general mechanism of degradation.

### Results and Discussion

Degradation experiments were performed to determine the effects of breaker concentration and temperature on polymer molecular weight reduction.

Figure 3 shows HPG  $\bar{M}_w$  reduction at 70° C for different initial concentrations of ammonium persulfate breaker. Molecular weight decrease is

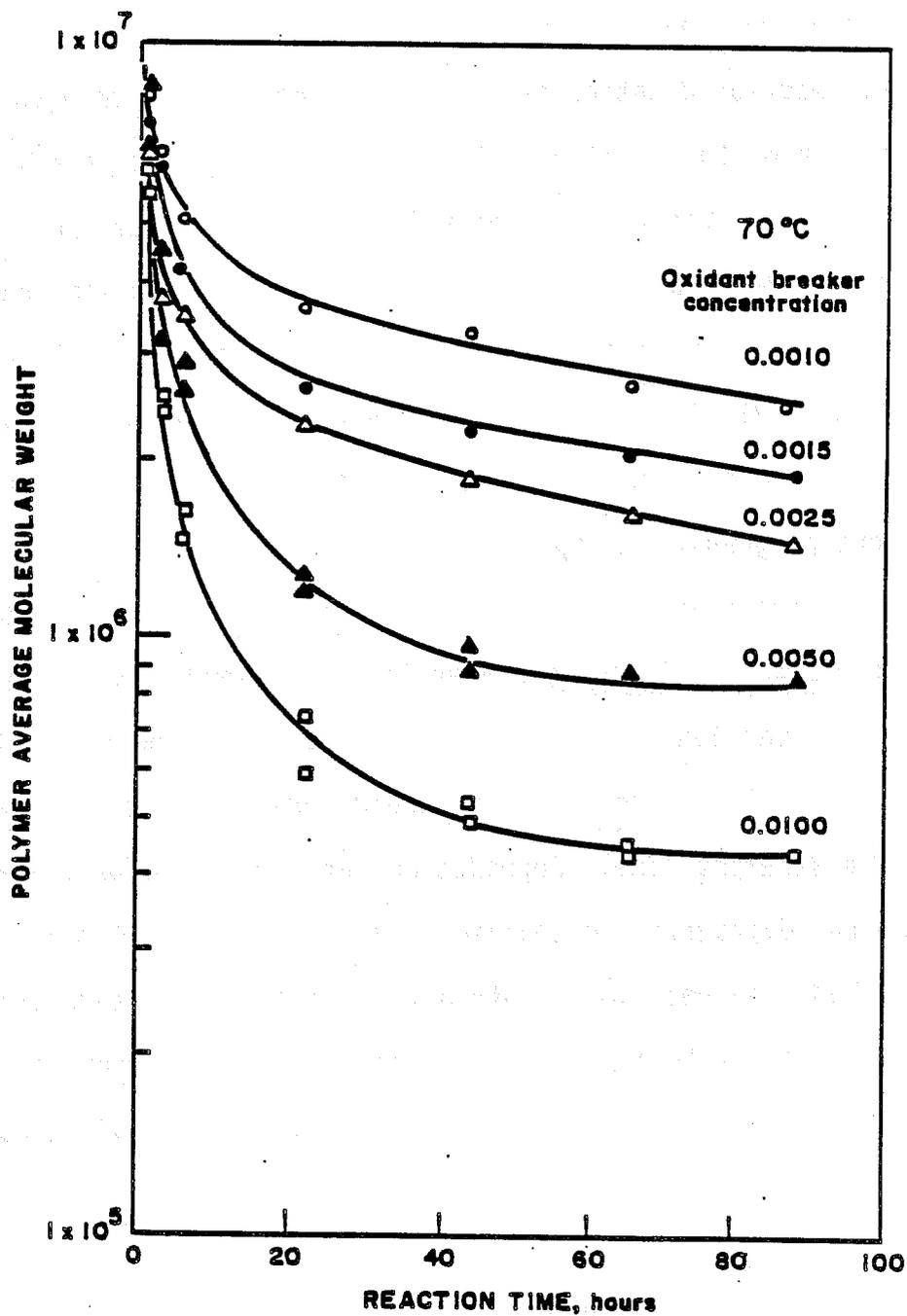


FIGURE 3. Decrease in HPG average molecular weight as a function of time for different initial ammonium persulfate breaker concentrations (in weight percent). Reaction temperature was 70° C.

most rapid within the first 10 hours of reaction time and levels off after about 24 to 48 hours. As breaker concentration increases, lower values of  $\bar{M}_w$  are reached as degradation terminates.

Figures 4 and 5 show the results of similar experiments performed at 80° and 90° C, respectively. Qualitatively, the results are similar to those at 70° C with a rapid drop in polymer  $\bar{M}_w$  within the first 3 to 10 hours and a general leveling off of  $\bar{M}_w$  after 24 to 48 hours. The extent of degradation increases, however, as temperature increases.

Figure 6 compares  $\bar{M}_w$  decrease at the three temperatures for the same initial breaker concentration. For the higher breaker concentration (0.005 percent),  $\bar{M}_w$  decreases by a factor of 2 for each 10-degree rise in temperature. The effect is not as great for the lower breaker concentration (0.001 percent) where each 10-degree rise in temperature reduces polymer average molecular weight only by a factor of 1.3.

Many reactions that proceed by free radical mechanisms show reaction rate increases of factors of 2 to 3 for each 10-degree rise in temperature. (9) The rate of oxidant breaker decomposition (reaction 3) is known to increase with increasing temperature. (10) In addition temperature may affect the number of chain steps before termination reactions become important. Lower breaker concentrations result in the initiation of fewer chain reactions. Other reactions such as reactions with oxygen or other impurities may become important enough to affect the number of free radical reactions which occur before termination. These reactions may also account for the difference in temperature dependence at low breaker concentration.

The  $\bar{M}_w$  decrease appears to have a fast component (breaker initiated) and a slow component (thermal, impurities, etc.). If an extrapolation of the slow component is made to zero time, the molecular weight decrease caused only by

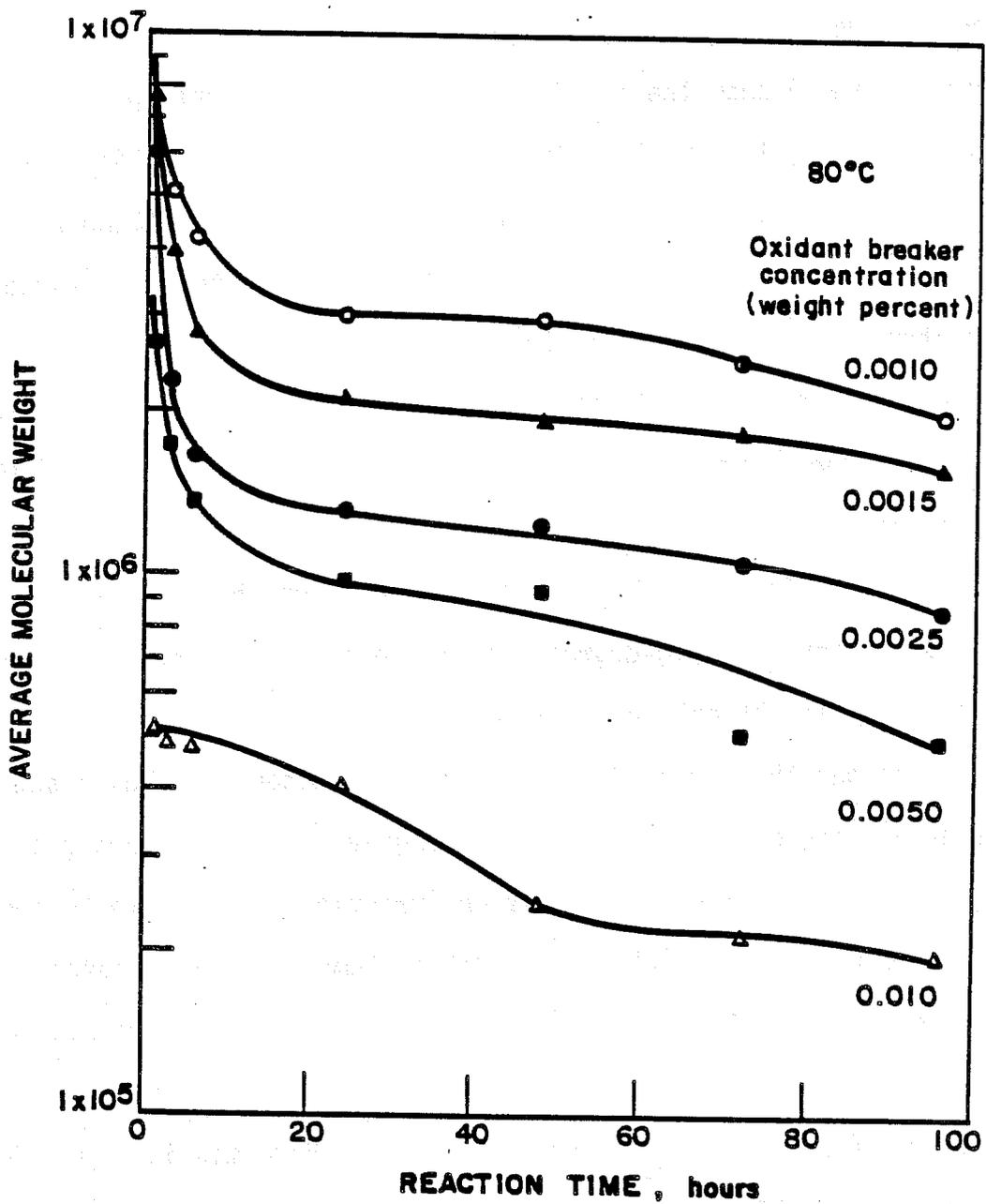


FIGURE 4. Decrease in HPG average molecular weight as a function of time for different initial ammonium persulfate breaker concentrations (in weight percent). Reaction temperature was 80°C.

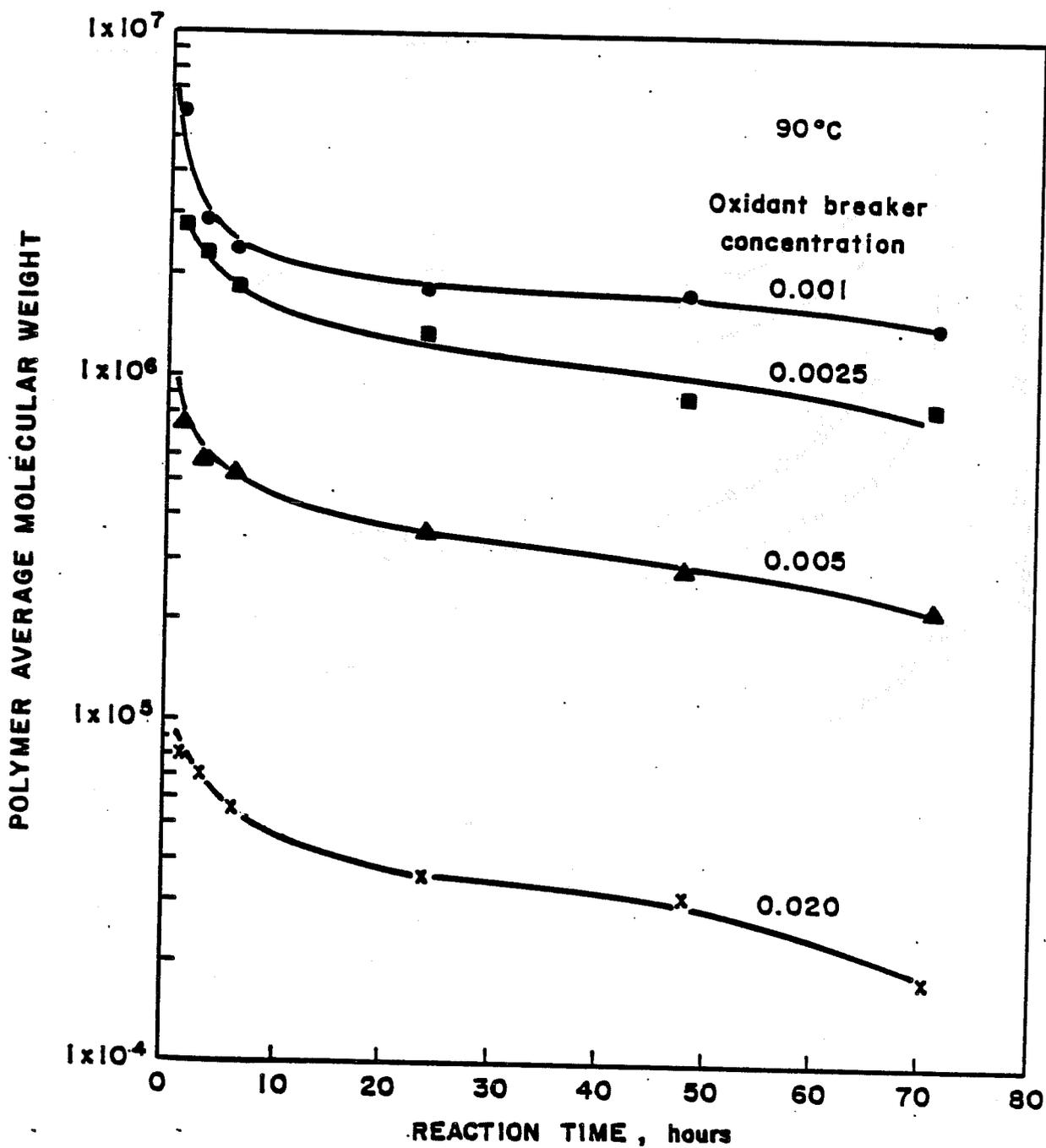


FIGURE 5. Decrease in HPG average molecular weight as a function of time for different initial ammonium persulfate breaker concentrations (in weight percent). Reaction temperature was 90° C.

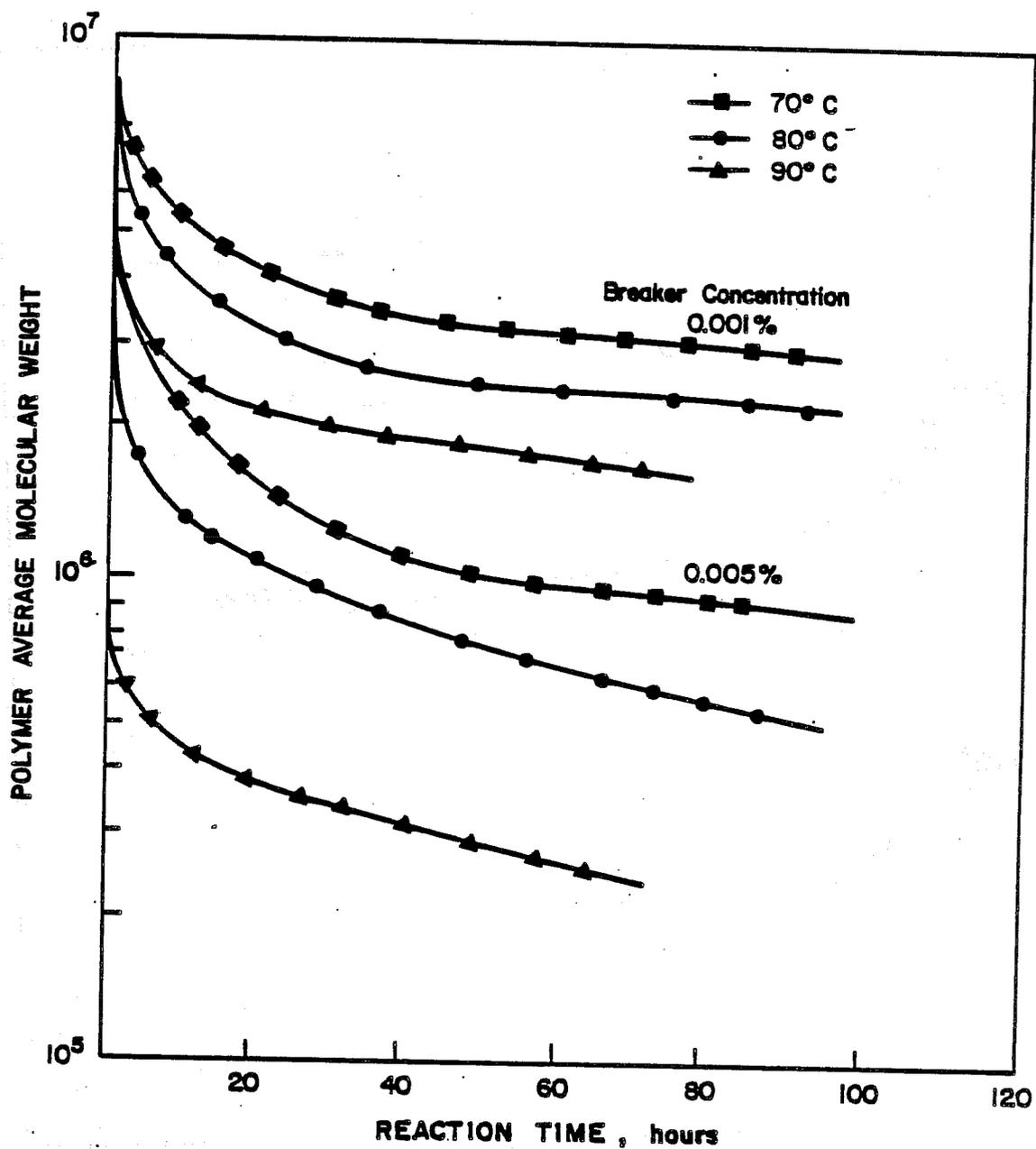


FIGURE 6. Comparison of HPG average molecular reduction for two different initial ammonium persulfate breaker concentrations at three temperatures.

the breaker can be estimated. These values depend on the square root of the breaker concentration, as shown in figure 7. This relationship is found at all three reaction temperatures. The dependence on the square root of the breaker concentration is analogous to polymerization reactions (i.e., increase in molecular weight) where the overall reaction rate is proportional to the square root of the initiator concentration. (11)

If the molecular weight degradation rates are examined to determine possible reaction kinetics, the analysis shows that the data best fit a composite of two first-order rate curves. These two first-order rates correspond to the faster, breaker initiated degradation, and the slower, thermal degradation. To separate the breaker initiated degradation, molecular-weight values are determined by subtracting the extrapolated slow degradation portion of the curve ( $\bar{M}_w^*$ ) from the actual measured molecular-weight values, ( $\bar{M}_w$ ). If the reactions are first-order, a plot of  $\log (\bar{M}_w - \bar{M}_w^*)$  versus time should be a straight line.

Figure 8 shows this relationship for the first 7 hours of reaction time at 70° C. These data are a composite of at least three experiments using the same breaker concentration (0.005 percent). The straight line fit has a slope of  $-0.11 \text{ hours}^{-1}$  with a correlation coefficient of 0.98.

A similar analysis for different initial breaker concentrations shows no difference in the rate of molecular weight decrease. The rate of degradation does not depend on breaker concentration. Scarcely any molecular weight data were obtained for the first few hours of reaction time for the other initial breaker concentration. Further studies are needed to verify this observation.

A similar analysis has been made for HPG degradation at 80° C using 0.005 percent breaker to initiate degradation. The plot of  $\log (\bar{M}_w - \bar{M}_w^*)$  as a function of time is also shown in figure 8. The slope of this curve is twice

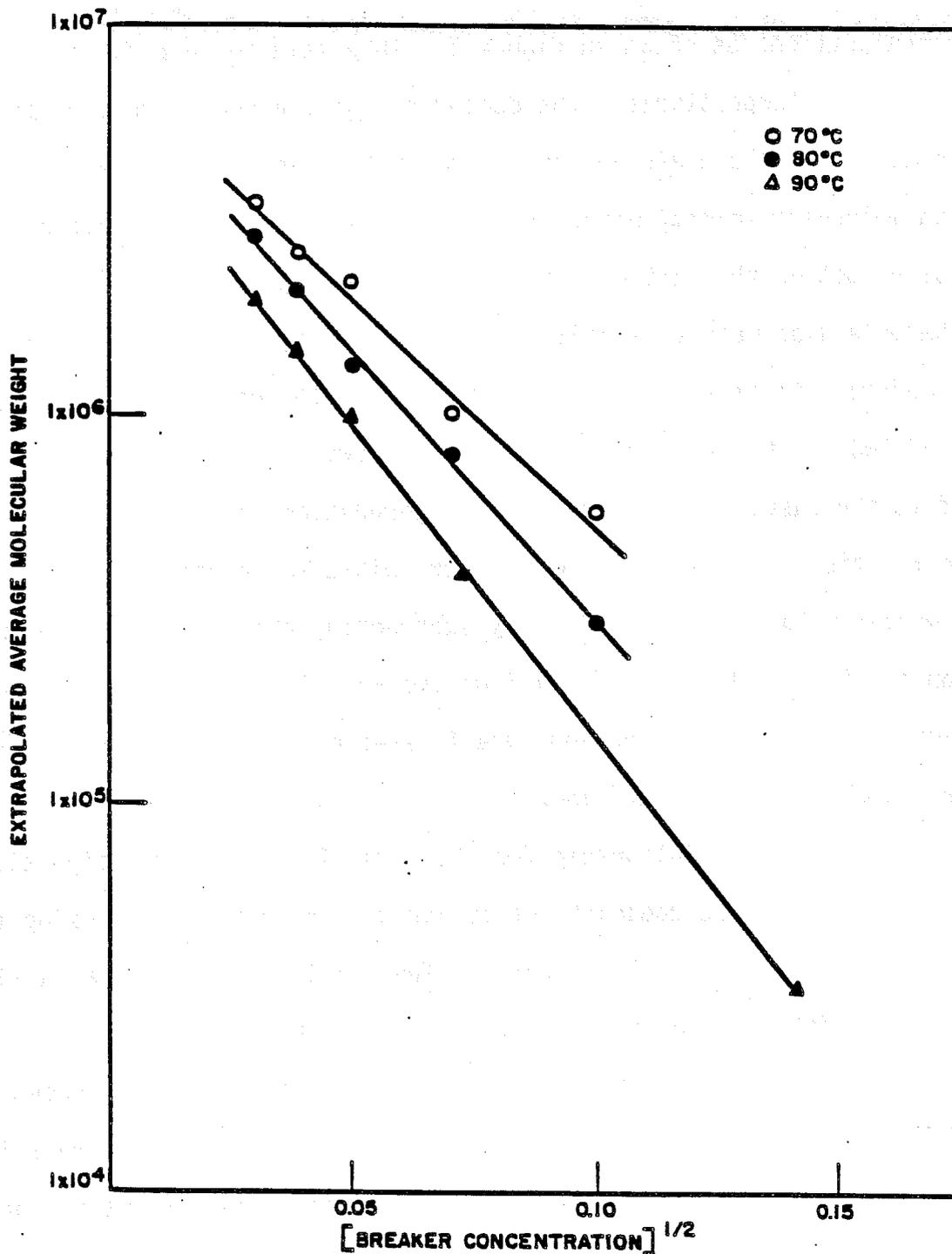


FIGURE 7. Maximum decrease in HPG average molecular weight caused only by oxidant breaker initiated degradation reactions as a function of the square root of the breaker concentration.

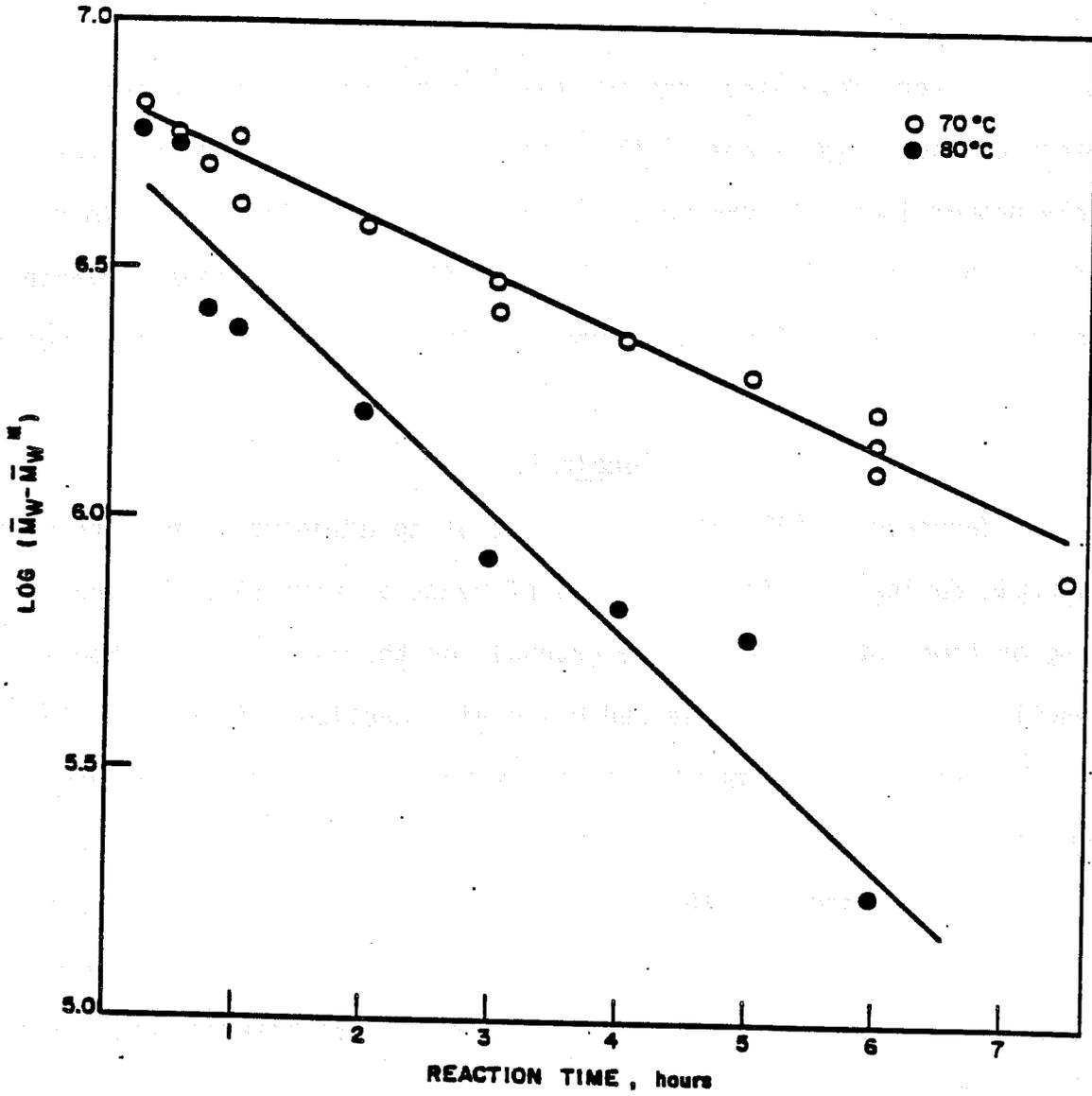


FIGURE 8. Kinetic analysis of HPG average molecular weight decrease caused only by oxidant breaker initiated reactions. Initial breaker concentration was 0.005 percent. Reaction temperatures were 70 and 80° C.

as great as the slope of the curve for the 70° C data. (The correlation coefficient is 0.94.) The slopes are -0.23 and 0.11 hours<sup>-1</sup>, respectively. The rate of the reaction has increased a factor of 2 for the 10-degree temperature rise, as shown previously with the extrapolated molecular weight data.

Many reactions involving free radical chains show a first order dependence on time. The slope of this type of plot is proportional (or inversely proportional) to the rate constants of the various steps in the mechanism. There may also be a dependence on the concentrations of various components such as the solvent or polymer. Studies of the types have not yet been performed.

### Conclusions

o The decrease in HPG molecular weight using ammonium persulfate breaker is most rapid during the first few hours of reaction time (3 to 10 hours depending on temperature), then more gradual for the next 24 to 48 hours. The fast reaction is caused by a free radical chain reaction initiated by the breaker. The slow reaction may be caused by thermal degradation or other reactions not identified.

o Temperature increases the rate of HPG molecular weight degradation caused by the breaker. The rate increases by a factor of 2 for an increase in temperature of 10 degrees (70° to 80° C) for an initial breaker concentration of 0.005 percent.

o The rate of HPG molecular weight reduction does not appear to depend on the initial amount of breaker in solution. Adjusting breaker concentration to control the rate of molecular weight degradation should be ineffective.

o The extent of molecular weight decrease caused by the breaker depends on the square root of the breaker concentration. The total molecular weight

decrease caused by both the fast and slow degradation mechanisms depends on temperature as well as breaker concentration. The dependence on polymer concentration was not considered in this study.

### DESIGN OF BETTER BREAKER SYSTEMS

The oxidant breaker reduces polymer molecular weight (and solution viscosity) very quickly. Adjusting the breaker concentration does not change the rate of reduction but only changes the degree or extent of degradation. Some other method must be found to control the action of the breaker to allow the retention of high solution viscosity during the fracture stimulation. This should then be followed by rapid polymer degradation for efficient fluid return to minimize damage to the propped fracture.

Changes in breaker reactivity could be done mechanically by encapsulating the breaker in a material that would dissolve or break after fracture closure. (12) This could also be done chemically by including an inhibitor with the breaker. The breaker should react with the inhibitor more rapidly than with the polymer. After depletion of the inhibitor, the remaining breaker can then cause polymer degradation. A third method to vary breaker reactivity would be to use different chemicals which initially are less reactive than ammonium persulfate.

One fracturing fluid system available commercially does include both a breaker and a stabilizer in the fluid formulation. The rate of polymer molecular weight decline was much slower for this system. Figure 9 shows the percent of the initial polymer molecular weight which was retained by solution of 40 lb/1,000 gal gel (HPG) with stabilizer alone, breaker alone, and with a combination of both stabilizer and breaker as a function of time. The rate of degradation was reduced considerably by the addition of this stabilizer.

Additional studies which will be described, have investigated other

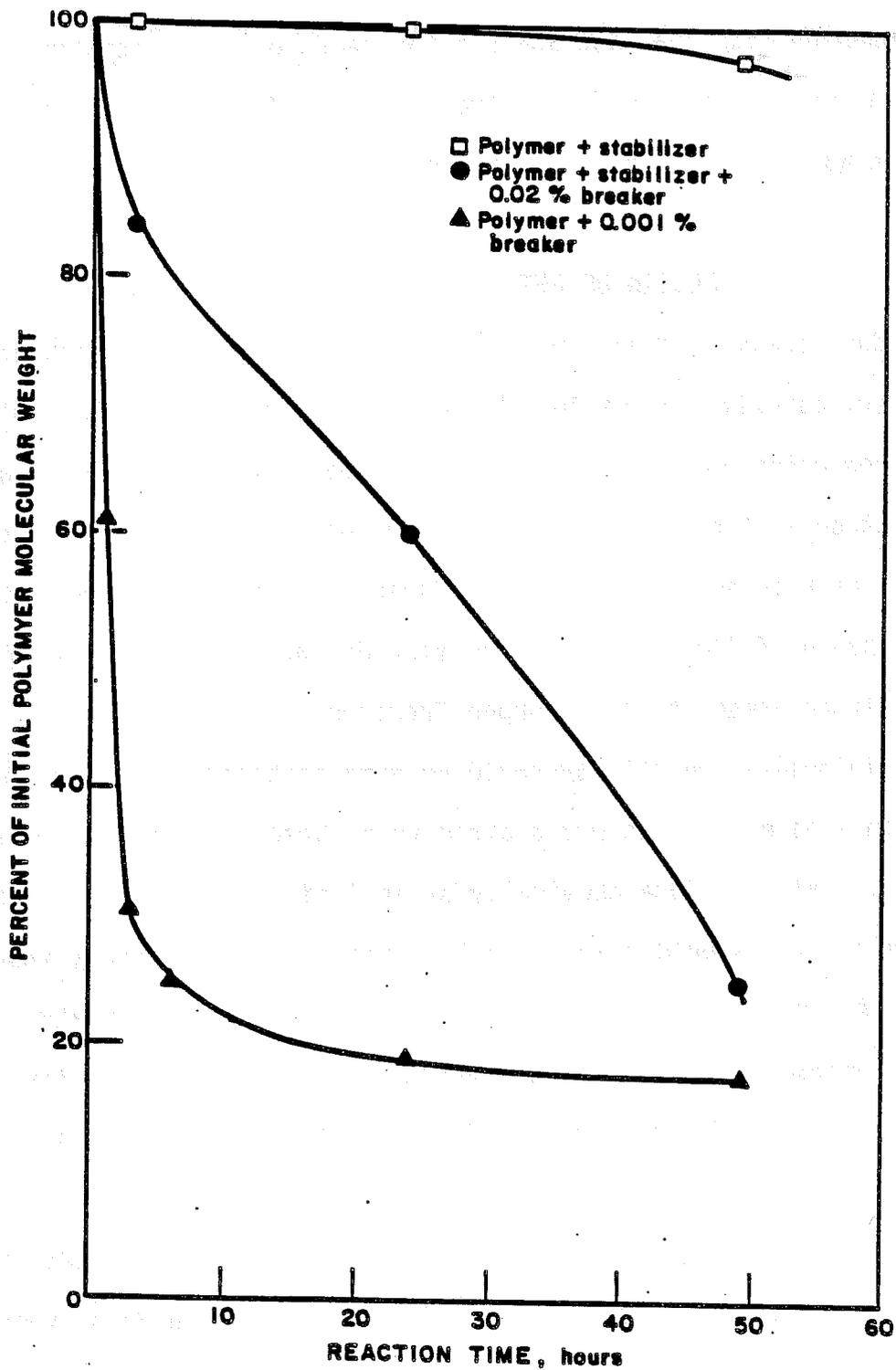


FIGURE 9. Comparison of HPG molecular reduction using an oxidant breaker and using an oxidant breaker with a gel stabilizer.

degradation mechanisms such as acid-catalyzed hydrolysis and enzyme initiated degradation. Breakers used in these studies have shown a variation in reactivity. One attempt has also been made to study an oxidant breaker with a polymer stabilizer in solution as described in the next section.

## INFLUENCE OF METHANOL ON HPG DEGRADATION

### Background Information

The effect of methanol on HPG molecular weight degradation has been examined for two reasons. First, as part of our research efforts, NIPER provides laboratory research capabilities in support of the fracture stimulations of the Multi-Well Experiment (MWX) conducted by the Department of Energy in western Colorado. Methanol was used as a prepad to the stimulation of the Paludal Zone performed in June 1984. The methanol was found in the returned fluids after the fracture stimulation. The polymer Mw remained above 1 million for almost 1 month after the stimulation. (Results are summarized in appendix A.) Difficulties were encountered in cleaning up the well. Therefore, it was useful to determine whether the presence of methanol contributed to slow polymer degradation which in turn contributed to slow fluid return. Second, methanol is a fracturing fluid additive which is used to stabilize polymer solution viscosity in high temperature reservoirs. As a polymer stabilizer, it should affect polymer degradation initiated by a breaker. HPG molecular weight reduction was examined for solutions containing both breaker and methanol and compared to results with no methanol in solution.

### Results

Methanol competes with the polymer for the free radicals produced by the breaker. Figure 10 shows the results of molecular weight studies at 70°C with 1 percent methanol and 0.005 percent breaker (ammonium persulfate) in solution with the polymer. Also included on the figure are results from the

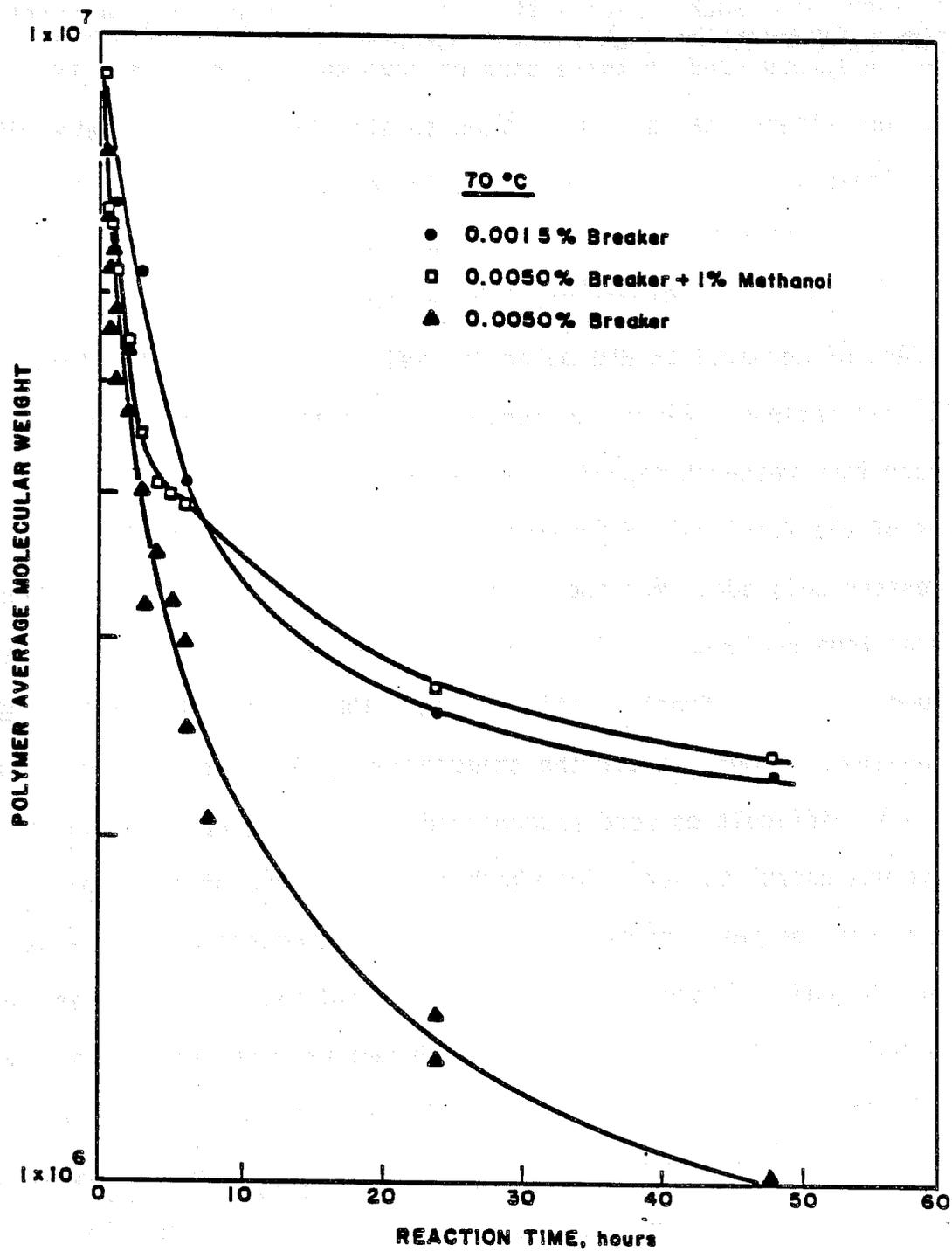


FIGURE 10. Comparison of HPG average molecular weight reduction for solutions with and without methanol. Degradation initiated by ammonium persulfate breaker at 70° C.

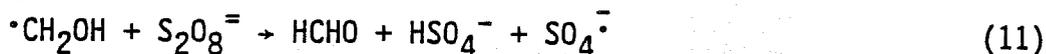
degradation studies without methanol for 0.005 and 0.0015 percent breaker. Initially (first 3 hours), degradation is unaffected by the methanol in solution. After that time, however, the rate of degradation is greatly affected. The final extent of molecular weight decrease compares with that obtained using a breaker concentration 3.3 times lower with no methanol in solution.

An identical experiment performed at 80° C has similar results, as shown in figure 11. The final level of  $\bar{M}_w$  reduction is comparable for solutions containing 0.005 percent breaker and 1 percent methanol and those containing 0.0015 percent breaker and no methanol. Increasing the methanol concentration to 5 percent decreases the effectiveness of the breaker by a factor of 5. A solution containing 0.005 percent breaker and 5 percent methanol attains the same final  $\bar{M}_w$  as one broken with 0.001 percent breaker.

Therefore, the practical effect of the addition of methanol is to reduce the breaker concentration. The methanol does not appear to change the initial rate of degradation.

### Discussion

Methanol competes with the polymer for reaction with the free radicals generated by the breaker. The reaction of methanol with persulfate has been studied previously (10). The degradation mechanism is complex and not completely understood. Reactions similar to those of breaker with the polymer also occur.



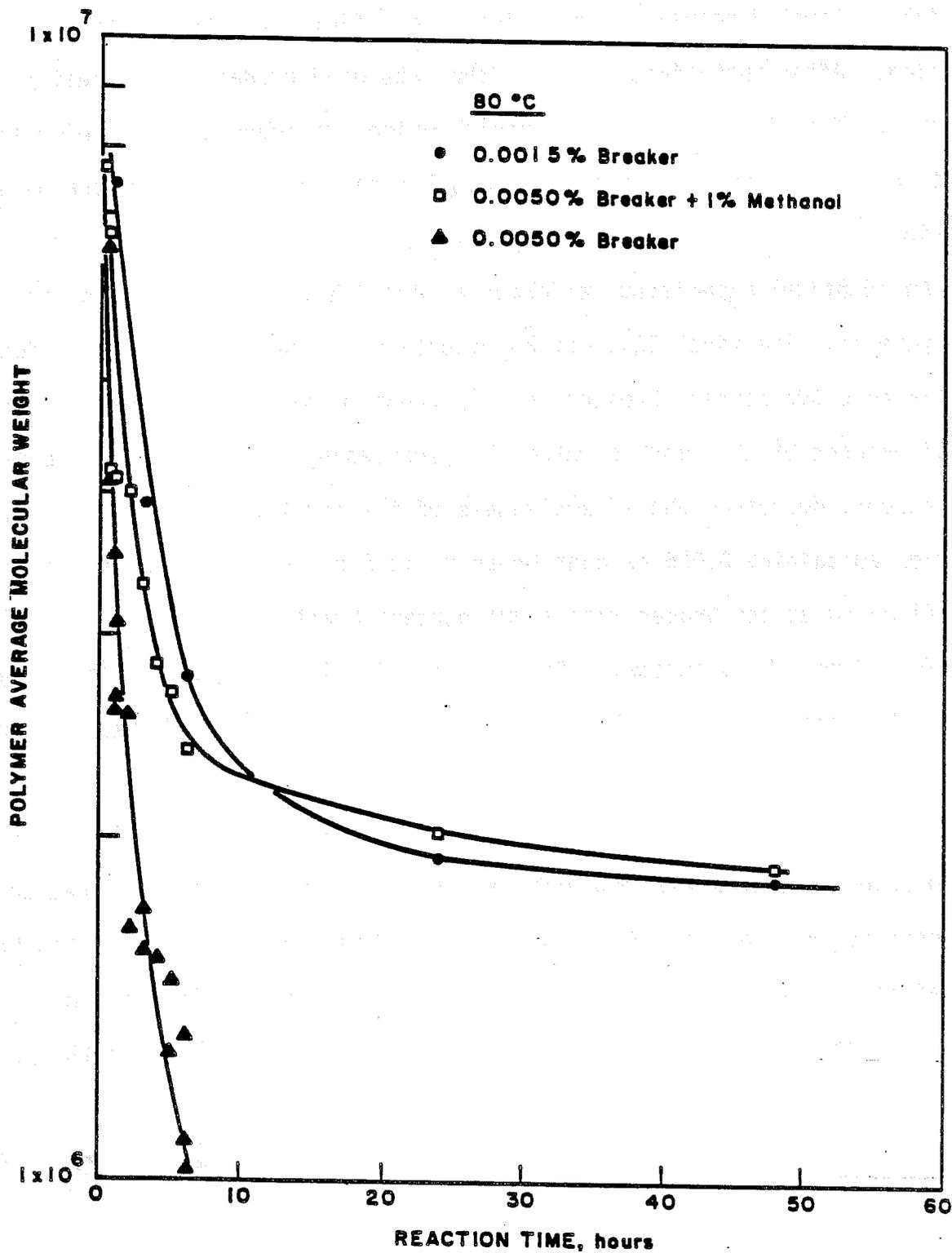


FIGURE 11. Comparison of HPG average molecular weight reduction for solutions with and without methanol. Degradation initiated by ammonium persulfate at 80° C.

These reactions produce a different radical,  $\cdot\text{CH}_2\text{OH}$ , which can react with the polymer.

Changes in the reactions with the polymer depend on the reactivity of the radical,  $\cdot\text{CH}_2\text{OH}$ , compared to the other chain carriers. In addition, other termination steps such as



can change the extent of the reactions with the polymer. These reactions should cause faster depletion of the breaker and less overall polymer degradation.

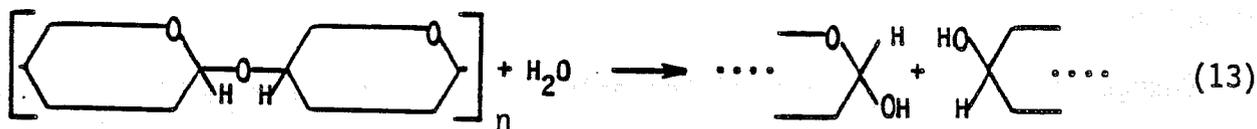
### Conclusions

- o Methanol is not a good candidate to improve the characteristics of oxidant breaker initiated polymer  $\bar{M}_w$  degradation. Methanol reacts with the breaker and with the free radicals produced by the breaker.
- o Initial rate of polymer  $\bar{M}_w$  decrease is not visibly affected by methanol in solution. The extent of molecular weight degradation is greatly affected as the methanol terminates the chain reactions causing polymer degradation.
- o Addition of 1 percent methanol is equivalent to reducing the breaker concentration by a factor of 3.3. Addition of 5 percent methanol is equivalent to reducing the breaker concentration by a factor of 5.

## POLYMER DEGRADATION USING ACID BREAKERS

### Background Information

Polysaccharides such as HPG and HEC are known to undergo degradation by hydrolysis. A generalized reaction can be written:



The presence of acids in solution increases the rate of this type of reaction. HPG and HEC are not suitable viscosifiers for acid fracturing fluids because of the rapid loss of viscosity and instability in hot concentrated acids (13). A more controlled polymer degradation reaction may be obtained, however, using low concentrations of strong acid (HCl) or weak acids (acetic and citric acids) to adjust acid concentrations. Molecular weight degradation of these polymers was monitored as a function of reaction time at 70° C in order to evaluate this type of breaker for conventional fracturing fluid systems. Comparisons were made with degradation rates using other breakers such as oxidizers.

### Results and Discussion

All measurements were made using 40 lb/1,000 gal polymer gel. Molecular weight measurements were obtained from the SEC curves after various reaction times at 70° C. Three acids were used in the degradation study: a strong acid, hydrochloric; and two weak acids, acetic and citric.

#### HPG Acid Hydrolysis

Molecular weight reductions for HPG solutions containing the three different acids are listed in table 1 for reaction times of 3 and 48 hours at 70° C.

TABLE 1. Degradation of 40 lb/1,000 gal HPG Using Different Acids at 70°C

Acid Type	Acid Conc. (percent)	pH	Time (hours)	$\bar{M}_w \times 10^{-6}$ (daltons)
HCl	0.044	2	3	7.6
			48	0.18
	0.35	1.9	3	0.64
			24	0.23
Citric	0.5	3.5	3	7.5
			48	1.4
	2.0	2.5	3	4.2
			48	0.35
Acetic	0.84	3.6-3.2	3	9.4
			48	2.7
	1.05	3.4	3	9.9
			48	4.1
	2.1	5.0	3	9.6
			48	10.0
5.25	3.1	3	-	
		48	1.7	

### Hydrochloric Acid

Degradation of HPG was too rapid using an acid concentration of 0.35 percent by volume (10 gal concentrated HCl/1,000 gal). Polymer  $\bar{M}_w$  was already less than 1 million d. within 1 hour of reaction time. When the acid concentration was reduced to 0.044 percent (1.1 gal/1,000 gal), the rate of polymer molecular weight reduction was much slower. After 3 hours, the polymer  $\bar{M}_w$  was about 7 million. d. After 48 hours, however,  $\bar{M}_w$  was reduced to  $1.8 \times 10^5$  d. This gel should cause little flow restriction through a proppant pack.

These gels did not contain sufficient buffer to maintain the original gel pH of 6. However, final solution pH of the two solutions was not significantly different even though HCl concentration changed by an order of

magnitude. The rate of hydrolysis must be a more complicated function of hydrogen ion concentration than reflected by the pH value of the solution alone.

In conclusion, hydrochloric acid caused too rapid HPG degradation except when present in very low concentrations. Further investigations are needed to determine whether a low concentration of HCl is a useful fracturing fluid breaker.

### Citric Acid

Degradation rate of HPG in the presence of citric acid was slower than in the presence of HCl. Higher citric acid concentration was required to affect polymer degradation characteristics. Solution pH was higher than after addition of HCl. At this pH, however, all three acid groups on the citric acid molecule should be ionized.

Two concentrations of citric acid were used, 0.5 and 2 percent by weight (40 and 160 lb/1,000 gal). The lower concentration did not reduce polymer  $\bar{M}_w$  below 1 million d. even after 48 hours reaction time at 70° C. Two percent citric acid did maintain high polymer molecular weight for the first few hours but resulted in a  $\bar{M}_w$  less than  $4 \times 10^5$  d. after 48 hours at 70° C.

HPG broken with 2 percent citric acid also showed rapid fluid flow through small pore size filters (0.05 $\mu$ m) indicating good fluid return characteristics. The calculated fluid loss coefficient was 0.011 ft/min<sup>1/2</sup>. This compares favorably with results for polymer degraded to the same molecular weight using oxidant breaker (3).

To reach this molecular weight, the oxidant breaker caused a much faster molecular weight decrease, as shown in figure 12. The citric acid may cause more favorable degradation conditions than the oxidant breaker. However, further evaluations including pH and viscosity measurements must be made

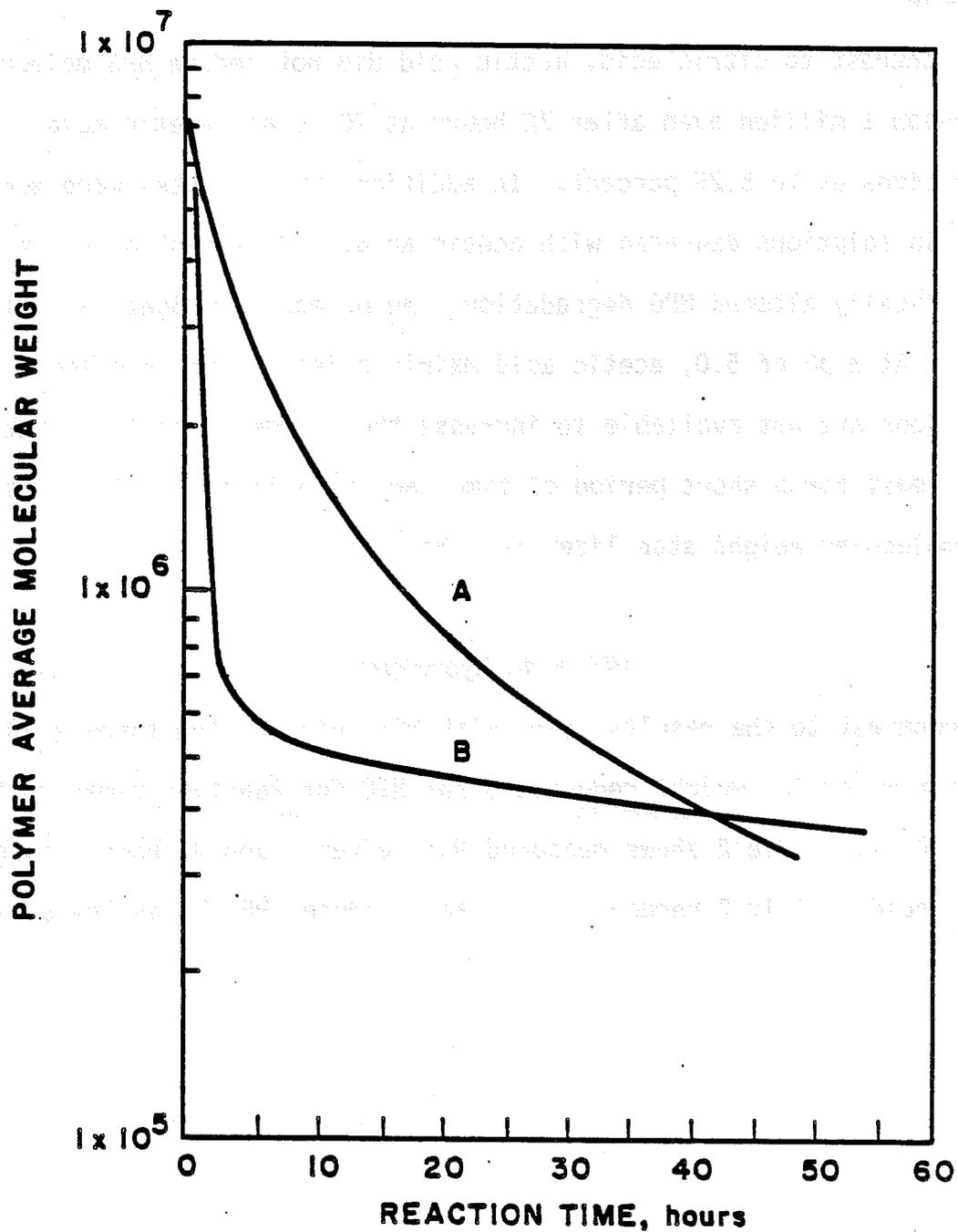


FIGURE 12. Comparison of HPG average molecular weight decrease with time at 70° C for A) acid-catalyzed hydrolysis using 2 percent citric acid and B) oxidant initiated degradation using 0.1 percent ammonium persulfate.

before citric acid can be recommended for use in fracturing fluids.

### Acetic Acid

In contrast to citric acid, acetic acid did not reduce HPG molecular weight below 1 million even after 72 hours at 70° C and acetic acid concentrations up to 5.25 percent. In addition, precipitates were more apparent in solutions degraded with acetic acid. Adjustment of solution pH to 5.0 dramatically altered HPG degradation. No molecular weight reduction was observed. At a pH of 5.0, acetic acid mainly exists in the non-ionic form. Hydrogen ions are not available to increase the polymer hydrolysis rate. In fact, at least for a short period of time, acetic acid at pH of 5.0 is a good polymer molecular weight stabilizer (as shown in Table 1).

### HEC Acid Hydrolysis

In contrast to the results found with HPG, none of the three acids caused significant molecular weight reductions for HEC for reaction times up to 48 hours at 70° C. Table 2 shows measured  $\bar{M}_w$ 's after 3 and 48 hours using the different acids. Only 2 percent citric acid reduced HEC  $\bar{M}_w$  as low as 1 million daltons.

TABLE 2: Degradation of 40 lb/1000 gal HEC Using Different Acids at 70°C.

Acid Type	Acid Conc. (percent)	pH	Time (hours)	$\bar{M} \times 10^{-6}$ (daltons)
HCl	0.044	2.4	3	7.5
			48	5.2
Citric	0.50	3.25	3	7.0
			48	3.2
	2.0	2.6	3	5.8
			48	1.0
Acetic	0.84	3.4	3	6.1
			48	3.7
	1.05	3.9	3	7.2
			48	5.5
	2.1	5.0	3	7.2
			48	7.0

Hydrochloric acid at this concentration did not cause significant polymer molecular weight reduction. This is in contrast to the  $\bar{M}_w$  reduction of HPG using HCl.

The extent of degradation in the presence of acetic acid was a function of solution pH rather than the acetic acid concentration. The acetic acid must be ionized (hydrogen ions released into solution) before HEC  $\bar{M}_w$  reduction occurs. This compares with the degradation results for HPG in the presence of acetic acid where pH plays a significant role in the availability of hydrogen ions to catalyze the hydrolysis rate.

Finally, citric acid caused greater molecular weight reduction than acetic acid. This compares with HPG degradation in the presence of these two acids. The magnitude of molecular weight reduction was not as great for HEC, however.

Besides poor molecular weight reduction, acid catalyzed HEC degradation had a second detrimental feature. Considerable amounts of insoluble residue were produced during hydrolysis particularly in the presence of citric acid. This suggests that acid catalyzed HEC degradation favors removal of side chains from the polymer cellulose backbone. These side chains are initially added to cellulose to render it water soluble. Their removal, therefore, results in precipitation of the insoluble cellulose polymer. In addition, a previous study of acid hydrolysis (14) showed that precipitates can be formed by the recombination of degradation products in the presence of acids.

A fluid loss test was performed on the HEC gel degraded to a  $\bar{M}_w$  of 1 million d. in the presence of citric acid. The calculated fluid loss coefficient of  $0.0014 \text{ ft/min}^{\frac{1}{2}}$  was even lower than results reported previously for non-degraded and partially degraded HEC and HPG gels (3). HPG gel degraded under the same conditions ( $\bar{M}_w = 3 \times 10^5 \text{ d.}$ ) passed easily through the filter, and the calculated fluid loss coefficient was more than 6 times greater than for the HEC solution.

### Summary and Conclusions

A brief summary of the results of acid-catalyzed hydrolysis of HPG and HEC includes:

- o HPG and HEC gel degradation is accelerated in the presence of ionized weak acids such as acetic and citric acids as well as strong acids such as hydrochloric acid. SEC can be used to monitor polymer degradation through polymer average molecular weight changes.
- o For HPG, a strong acid can be present only in very low concentration to prevent too rapid polymer molecular weight degradation.
- o HPG degradation in the presence of acetic acid gave poor results. Acetic acid concentrations up to 5 percent failed to reduce polymer

molecular weight below 1 million. Solutions also appeared to produce more insoluble residues with acetic acid in solution. If solution pH was maintained above 5, however, hardly any molecular weight reduction was observed.

- o The use of citric acid appeared to result in "improved" polymer molecular weight reduction. When average molecular weight reductions of HPG were compared for degradation using citric acid and oxidant breaker, citric acid caused a more gradual  $\bar{M}_w$  reduction initially while reducing  $\bar{M}_w$  after 48 hours to well below 1 million daltons.
- o None of the three acids provided adequate molecular weight reduction of HEC gels. In addition, increased amounts of precipitates were observed in HEC solutions degraded by acid catalyzed hydrolysis reactions.

In most cases, acids used as fracturing fluid breakers do not cause improved polymer average molecular weight reduction characteristics either because reaction rates are not well controlled or because increased precipitates are produced which can cause additional proppant pack damage. Only with HPG degradation in the presence of appropriate amounts of citric acid do the results appear to be encouraging. Additional studies including viscosity measurements, pH adjustment, and concentration variations are needed before the use of citric acid in fracturing fluids can be evaluated.

## POLYMER DEGRADATION USING ENZYME BREAKERS

### Background Information

For reservoirs with temperatures lower than 60° C (140° F), enzymes can be used to degrade fracturing fluid polymers. At higher temperatures, the enzymes will be denatured and lose their activity. In this study, two enzyme

breakers were evaluated: A commercial enzyme mixture, GBW-3, supplied by Halliburton, Inc. and an enzyme which shows a high degree of specificity for galactomannas, a class of polysaccharides which includes guar gum and HPG. This enzyme, Hemicellulase-B 1500, was supplied by Miles Laboratory.

In addition to temperature, enzyme reactivity with polymers such as HPG and HEC depends on pH, breaker concentration, and breaker activity.

### Results and Discussion

Breaker effectiveness for the two enzyme breakers was compared by measuring the average molecular weights of the broken polymer solutions as a function of reaction time, breaker concentration, and pH. The results for HPG are shown in Table 3. The results for HEC are given in table 4.

TABLE 3: -- Comparison of HPG degradation using two enzyme breakers at 50°C

Breaker	Concentration (percent)	Time (hours)	pH	$\bar{M}_w \times 10^{-6}$ (daltons)
GBW-3	0.001	3	3.5	8.0
		48		4.5
Hemicellulase-B	0.001	3	3.5	7.5
		48		1.0
GBW-3	0.001	3	7.0	8.0
		48		6
Hemicellulase-B	0.001	3	7.0	7.5
		48		2.3
Hemicellulase-B	0.005	3	3.5	2.2
		48		0.64
		3	7.0	2.0
		48		0.97

The results for HEC are given in table 4.

TABLE 4: Comparison of HEC degradation using two enzyme breakers at 50° C.

Breaker	Concentration (percent)	Time (hours)	pH	$\bar{M}_w \times 10^{-6}$ (daltons)
GBW-3	0.001	3	3.5	3.1
		48		0.26
Hemicellulase-B	0.001	3	3.5	3.1
		48		0.36
GBW-3	0.001	3	7.0	5
		48		0.44
Hemicellulase-B	0.001	3	7.0	2.6
		48		0.32
GBW-3	0.005	3	3.5	1.0
		48		0.095
Hemicellulase-B	0.005	3	3.5	0.60
		48		0.096
GBW-3	0.005	3	7.0	0.50
		48		0.089
Hemicellulase-B	0.005	3	7.0	0.35
		48		0.091

Hemicellulase-B is a more effective enzyme breaker for HPG than the enzyme mixture, GBW-3. The differences are not significant for brief reaction times (3 hours). After 48 hours, however, HPG average molecular weight is 3 to 4 times lower using Hemicellulase-B rather than GBW-3 at both pH 3.5 and 7.0. Since GBW-3 is a mixture of enzymes, possibly only a fraction of the breaker is effectively attacking the HPG molecule.

The activity of both breakers is reduced by approximately a factor of 2 as pH is increased from 3.5 to 7.0. This is in agreement with the information provided by the supplier based on viscosity measurements of the degraded polymer solutions. A 5-fold increase in breaker concentration does not produce a corresponding 5-fold decrease in polymer  $\bar{M}_w$ . The reduction is

closer to a factor of 2 at both pH 3.5 and 7.0.

No consideration is given to degradation by other mechanisms such as acid catalyzed hydrolysis. This mechanism is more important at the lower pH, as discussed in the previous section on acid breakers. In this case, the temperature for the enzyme reactions is lower than the temperature of the hydrolysis reaction discussed previously. The exact magnitude of the importance of hydrolysis at 50° C has not been investigated.

Both enzyme breakers effectively degraded HEC and reduced HEC  $\bar{M}_w$  more effectively than they reduced HPG  $\bar{M}_w$ . Solution pH did not greatly affect  $\bar{M}_w$  reductions, particularly after 48 hours of reaction time. Neither breaker, therefore, has an advantage over the other as a degradant for HEC.

### Conclusions

Two enzyme breakers show different reactivity with HPG when used at 50°C to degrade the polymer. Reactivity also depends on breaker concentration and pH. A few hours of reaction time is not sufficient, however, to significantly reduce polymer molecular weight. Instead, 48 hours is required to reduce  $\bar{M}_w$  when using the more effective breaker, Hemicellulase-B.

For field application, the reactivity of enzyme breakers should be evaluated to ensure that they are effective with HPG. In addition, shut-in time before flowback should be longer than the typical 3 to 6 hours to allow sufficient time for the breaker to react since solutions with low polymer molecular weight flow more easily through the propped fracture and require less time to clean up.

In contrast, no difference in reactivity is observed for the two enzyme breakers when they are used to degrade HEC solutions. Nor does pH have a significant effect on HEC  $\bar{M}_w$  reduction. Therefore, generalizations should not

be made concerning enzyme reactivity. Each enzyme and polymer combination can show different degrees of interaction.

### SUMMARY AND CONCLUSIONS

- o Size exclusion chromatography is a useful method for studying degradation of polymers used in hydraulic fracturing fluids. The effects of changes in reaction parameters can be studied by observing changes in the molecular weight distribution of the polymer degradation products. A better understanding of these effects can lead to improvements in the design of breaker systems which allow solution viscosity to remain high during fracture treatment and then effectively degrade the polymer to minimize flow resistance during fluid cleanup and production.
- o Oxidant breakers initiate free radicals which attack the polymer. Degradation occurs through a series of chain reactions which result in polymer fragments of smaller and smaller size. Oxidant breakers cause the most rapid molecular weight decrease within the first 3 to 10 hours. These results depend upon temperature but are independent of initial breaker concentration. A more gradual molecular weight decrease occurs within the next 24 to 48 hours. Additional degradation mechanisms such as thermal degradation, hydrolysis, and reactions with other components in the system also contribute to molecular weight decrease.
- o An increase in oxidant breaker concentration results in an increase in the extent of molecular weight reduction. The extent in the molecular weight reduction is proportional to the square root of the breaker concentration.
- o The initial rate of HPG molecular weight reduction is not dependent on the initial oxidant breaker (ammonium persulfate) concentration. Adjusting breaker concentration is not an effective way to retard the initial

degradation of the polymer.

- o Temperature increases the rate of molecular weight decrease. A 10-degree rise in reaction temperature increases the rate by a factor of 2.
- o The initial rate of HPG molecular weight decrease is not affected by the addition of methanol to the solution. Methanol competes with the polymer and changes the extent of polymer molecular weight reduction. Addition of methanol to HPG gels has almost the same effect as reducing the initial oxidant breaker concentration.
- o Acid-catalyzed hydrolysis causes different amounts of polymer molecular weight reduction depending on the type of polymer and type of acid used. Very low concentrations of HCl cause significant HPG molecular weight reductions within 48 hours but do not affect HEC molecular weight values. Acetic acid does not efficiently reduce HPG or HEC molecular weight. Results are dependent on pH. Citric acid was more effective at reducing the molecular weight of HPG than of HEC.
- o As a degradant for HPG gels, citric acid is a candidate for further study. Using citric acid, polymer molecular weight remains high for several hours and then declines to a low level within the next 24 hours. Citric acid is not suitable for use with HEC because of the significant amounts of precipitates produced during reaction. These precipitates will decrease the conductivity of the proppant pack.
- o Enzyme breakers exhibit different reactivities depending on solution pH, temperature, and type of polymer. All these factors must be considered when designing enzyme breaker systems which reduce polymer molecular weight in low temperature reservoirs.
- o An improved breaker system should show the following degradation characteristics: delayed polymer molecular weight reduction and little

production of undesirable products such as precipitates. These characteristics should result in a fracturing fluid with high proppant carrying capacity during fracture stimulation and little resistance to fluid flow through the fracture for rapid fluid cleanup.

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## NOMENCLATURE

C	--	Fluid loss coefficient (ft/min <sup>1/2</sup> )
d.	--	Dalton, unit of molecular weight
HEC	--	Hydroxyethyl cellulose
HPG	--	Hydroxypropyl guar
$\bar{M}_w$	--	Average molecular weight of polymer
$\bar{M}_w^*$	--	Extrapolated average molecular weight
MWD	--	Molecular weight distribution
MWX	--	Multiwell Experiment (Department of Energy)
P	--	Symbol for polymer molecule
R	--	Symbol for free radical molecule
$r_b$	--	Rate of chain breaking reaction
$r_i$	--	Rate of chain initiation reaction
$r_p$	--	Rate of chain propagation reaction
SEC	--	Size exclusion chromatography

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## Appendix A

SPE paper 13566 - "Molecular Size Studies of Degraded Fracturing Fluid  
Polymers".



SPE 13566

## Molecular Size Studies of Degraded Fracturing Fluid Polymers

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### ABSTRACT

Effective degradation of fracturing fluid polymers is necessary to minimize fracture and formation damage to allow rapid fluid return and economic production of gas (and/or oil). In this study, size exclusion chromatography (SEC) was used to investigate degradation of water-soluble polymers, such as modified guar and cellulose polymers.

SEC was used to monitor the decrease in molecular size of the polymer degradation products using oxidant breakers in the temperature range 343 K to 370 K (158°F to 205°F). SEC, however, was capable of monitoring the effects of polymer type and concentration, breaker type and concentration, break time and temperature. The SEC results were then correlated with solution fluid loss characteristics and residue production to define the molecular size reduction needed to minimize damage to a propped fracture. Results were compared to sandpack damage studies reported in the literature. Greater insoluble residue production required greater molecular weight reduction to minimize damage. SEC results were also correlated with solution viscosity. Measured viscosities depended on polymer concentration and degree of polymer degradation. Low solution viscosity did not guarantee reduction of polymer molecules to a non-damaging size.

SEC analysis should also be useful for evaluating new or improved breaker and polymer systems. Presently available breaker systems (in the temperature range of this study) did not provide both high initial solution viscosity and efficient molecular size reduction to minimize damage.

### INTRODUCTION

Water-soluble polymers have many applications in the petroleum industry. As an additive to hydraulic fracturing fluids, they increase fluid viscosity to

provide proppant carrying ability and fluid loss control. After completion of the fracturing treatment, fluid viscosity should decrease to allow proppant placement and rapid fluid return from the fracture. Efficient polymer degradation is required to minimize restriction of fluid and gas flow through the fracture. If fracture conductivity remains low relative to the formation area invaded by fracturing fluid, the result will be slow fracture clean-up and a non-productive fracture treatment. (1)<sup>1</sup>

Polymer degradation under reservoir conditions can be complex. (2,3) Loss of solution viscosity has often been used as a measure of polymer degradation. Solution viscosity, however, is a complex physical parameter which can depend on polymer interactions in solution as well as polymer size (molecular weight) and concentration. Loss of viscosity may be caused by a decrease in polymer intermolecular attractions as well as a decrease in molecular size of the polymer. Low viscosity fluids that are considered "broken" (less than 10 cP) may contain molecules with molecular weights greater than 5 million. Even solutions with viscosities less than 3 cP can have as much as 20 percent of the polymeric material with molecular weights greater than 2 million. (4) This material can retard fluid flow through formation and fracture flow channels.

Commonly used fracturing fluid polymers can also produce insoluble residues which reduce fracture conductivity. Previous investigators have studied fracturing fluid polymer degradation to determine the effect of insoluble residues on fracture damage. Cooke (5) correlated the increase in polymer residue volume with a reduction of fracture conductivity. In general, the amount of damage increased with the amount of residue in the following order: polyacrylamide < modified cellulose < modified guar gum < guar gum. Further investigations by Almond, (6) however, showed that the order of increasing polymer residue and damage could be altered by varying polymer

References and illustrations at the end of the paper.

<sup>1</sup>Underlined numbers in parentheses refer to references listed at the end of the paper.

degradation conditions. Modified cellulose for certain break conditions left an "invisible" residue in a sand pack which severely restricted fluid flow. This "invisible" residue corresponded to incompletely broken polymer. Solution viscosity, on the other hand, was low for these break conditions. Loss of viscosity could not be used as a measure of low fluid flow damage associated with "residue free" behavior.

Almond and Bland (7) also studied polymer degradation with high breaker concentration and long break time to eliminate the effects of the "invisible" residue on formation damage. Sandpack permeability damage correlated with polymer residue volume, as shown by investigations of Cooke. Polymer gels degraded at high temperature conditions (greater than 405 K or 270°F) produced the least amount of fracture damage. More damage resulted with gels degraded with enzymes at low temperatures (lower than 333 K or 140°F), and the greatest damage was found in the intermediate temperature range using oxidizing breakers. Typical breaker schedules designed to reduce solution viscosity do not necessarily eliminate the contribution of incompletely broken polymer to fracture damage. Investigations using residue volume may not be sensitive enough to investigate the effects of both types of residue on fracture damage.

Many factors affect the degree of polymer degradation and the amount of residue remaining after degradation. Polymer degradation depends on polymer/breaker type and concentration, reaction time, temperature, and the presence of fluid constituents (salts, crosslinkers, acids, etc.). Insoluble residues may be produced by degradation reactions or may be present as impurities in the polymer. Impurities are often removed by processing or chemical alteration of the polymer.

Tyssee and Vetter (2) discussed the need for development and application of analytical methods of polymer analysis in order to understand polymer chemistry under field conditions. They analyzed the returned fracturing fluids for total organic carbon and total carbohydrate content. These measurements gave information on the gross changes during polymer degradation. To obtain more detailed information, Tyssee and Vetter recommended using high pressure liquid chromatography techniques for the analysis of polymers and their degradation products. Size exclusion chromatography (SEC), which separates molecules by size, is a useful tool to examine the progress of polymer breakdown for different reaction conditions. At the time of their report, however, they had only limited success using this technique.

This report describes the use of SEC as a technique to study fracturing fluid polymer degradation. Filtration studies were used to relate fluid loss characteristics and residue weight of degraded polymers to molecular weight reduction. Small pore size filters were used to retain not only insoluble residues but also polymer molecules with average molecular weights greater than  $3 \times 10^5$ . Increased fluid loss characteristics with filters would imply greater ease of fluid flow through the fracture and therefore better fracture cleanup. Residue remaining on the filter would be a combination of both types of residue until break conditions reduced molecular weights well below this average. Additional comparisons of fracture damage were made with the sandpack studies reported in the

literature. The results of laboratory degradation studies and analysis of returned fluids from a fracture treatment are described.

#### EXPERIMENTAL PROCEDURES Fracturing Fluid Polymers

Most fracturing fluid polymers are polysaccharides or high molecular weight polymer chains made up of sugar molecules. The most commonly used fracturing fluid polymer is hydroxypropyl guar (HPG). HPG is produced by chemical alteration of a naturally occurring polysaccharide, guar gum.

In this study, HPG, guar gum, and a third group of polysaccharides (chemically modified cellulose) were selected for study because each type produced different quantities of insoluble residue when degraded. Modified celluloses such as hydroxyethyl cellulose (HEC) and carboxymethyl hydroxyethyl cellulose (CMHEC) produce no insoluble residue for most degradation conditions. Insoluble residues for HPG have been reported as 1 to 2 percent. (7,8) Different treatment and source of polymer may affect the amount of residue, however. (9) Guar gum produces considerably more insoluble residue. Values of 8 to 10 percent by weight (7,8) and 10 to 14 percent (10) have been reported.

The fracturing fluid polymers were prepared with buffers ( $\text{KH}_2\text{PO}_4$ ) and salts ( $\text{KNO}_3$  or  $\text{KCl}$ ). The polymer gels were mixed with an oxidant breaker (usually ammonium persulfate) and then placed in a constant temperature bath. Samples were collected for analysis at various time periods. These samples were analyzed for polymer molecular weight, residue weight, filtration properties, and solution viscosity.

#### Size Exclusion Chromatography

SEC is a high pressure liquid chromatographic technique that separates molecules according to size. An extensive discussion of the technique is found in a text by Yau, Kirkland, and Bly. (11) A summary of the technique is given by Abbott. (12) Specific details of the chromatographic system used in this study were reported previously. (13)

Degraded polymers solutions were analyzed on SEC columns (type PW (polyacrylamide) gels on a support of hydroxylated polyether based material labelled TSK columns). This type column has been used to study high molecular weight dextrans, polyacrylamides, and several other water-soluble polymers. (14) Their use with typical fracturing fluid polymers such as guar and guar derivatives has not been reported previously.

High molecular weight dextrans were used to relate elution volume (which depended on molecular size) with molecular weight. These standards have relatively broad molecular weight distributions (MWD) and were compatible with the aqueous solvent systems used in this study. Progress of polymer degradation could be monitored by simple comparison of the MWD curves. Fig. 1 shows the change in MWD with time for a 40 lb/1000 gal HPG gel broken with oxidant breaker. Usually, however, average molecular weights,  $M_w$ , of the sample were calculated by digitizing the chromatographic curve and using the following equation:

$$\bar{M}_w = \frac{\sum_{i=1}^N (h_i M_i)}{\sum_{i=1}^N h_i} \dots\dots\dots(1)$$

Where  $h_i$  was the height at the elution volume of section  $i$ ; and  $M_i$  was the molecular weight of section  $i$  as determined from a calibration curve. The calibration curve based on the average molecular weights of the dextrans as supplied by the manufacture is shown in Fig. 2. The line is a third order fit of  $\log \bar{M}_w$  versus elution volume and calculates  $\bar{M}_w$ 's of the standards within 5 percent.

A composite chromatogram of dextran standards measured with these SEC columns is shown in Fig. 3. The lack of suitable standards with molecular weights greater than  $2 \times 10^6$  (dextran T-2000) prevented calibration of larger molecular sized polymers. Therefore, accuracy was limited to extrapolated values for polymers with molecular weights greater than  $2 \times 10^6$ . Fig. 4 gives an estimate for the size/molecular weight relationship for the dextrans calculated from the pore size distribution of a second column set where the upper limit on pore size is known. Once again, extrapolation to higher molecular weights is an estimate of molecular size.

A further limitation for absolute molecular weight measurement was due to differences in molecular shape of the dextran standards and fracturing fluid polymers. Dextrans are more linear molecules than the more highly branched fracturing fluid polymers. (15) The more compact fracturing fluid polymer molecule has a higher molecular weight than comparable dextran molecules of the same size. The absolute calibration using SEC for these aqueous polymers is not precise. However, SEC was useful for measuring molecular size distribution and changes of polymers as degradation conditions were varied. In the remaining discussion, references to gel molecular weights are only for comparison.

All solutions were filtered through a 5  $\mu$ m filter to remove large residues that could damage the columns. Solutions were also diluted to at least 0.15 percent polymer concentration to avoid chromatographic viscosity effects. Greater dilution was required for non-degraded polymer solutions.

#### RESIDUE WEIGHT AND FLUID LOSS MEASUREMENTS

These studies were conducted using a gas pressurized filter apparatus. The polymer solutions were filtered through specific pore size filters (mixed ester cellulose) using gas pressures up to 200 psig. Although filters ranging in size from 0.05 to 5  $\mu$ m were used, most filtration studies were made with 0.05  $\mu$ m filters and 100 psig gas pressure. Polymer solutions were also measured by SEC for molecular weight distributions. In addition to insoluble residues, the 0.05  $\mu$ m filter retained polymer degradation products with molecular weights greater than  $3.5 \times 10^5$ . Larger filter sizes were used to retain degraded polymer with higher molecular weight and to examine the effect of the insoluble residues on filtration characteristics.

These polymer solutions showed wall building characteristics so that fluid flow through the filter was a linear function of the square root of time. (16) Fluid loss coefficients were determined from the

slopes of the square root of time plots. Fig. 2 shows the change in fluid loss rate for degraded polymer solutions as molecular weight decreased. In oil field units, the fluid loss coefficients ( $C_{III}$ ) are calculated using the following equation:

$$C_{III} = 0.0164 M/A \text{ (ft/min)}^{1/2} \dots\dots\dots(2)$$

where:  $M$  = slope  
 $A$  = filter area

After filtration, the residue on the filter was dried and weighed. After correction for the weight of salts, the remaining residue consisted of insoluble residues and polymer degradation products.

#### RESULTS

##### Molecular Weight - Fluid Loss Correlations

The three polymer types chosen for study showed different molecular weight - residue weight characteristics which could be attributed to the different amounts of insoluble residue produced during degradation. HEC gels showed a steady decline in residue weight as molecular weight decreased, as shown in Fig. 6. Residue weight approached zero as most of the polymer was reduced to a size that passed through the 0.05  $\mu$ m filter. The average molecular weight when most of the polymer passed through the filter was approximately  $2.5$  to  $3.0 \times 10^5$ . Fluid loss characteristics, however, did not increase until the residue collected on the filter was less than 10 percent of the original amount of polymer in solution, as shown in Fig. 7.

Residue weight did not decline as smoothly for HPG degradation (see Fig. 8). Residue weight remained high as HPG degraded until  $\bar{M}_w$  approached  $2.5$  to  $3.0 \times 10^5$ . Below this value, residue weight remained constant at 6 percent. This value was higher than the 1 to 2 percent insoluble residue reported previously. The use of the 0.05  $\mu$ m filter, however, could account for the increased amount of residue. Fluid loss coefficients for the HPG solutions did not increase until the molecular weight of the degraded polymer had decreased well below the size that passed through the filter, as shown in Fig. 9.

The residues found in guar gum had an even greater effect on the molecular weight - residue weight relationship, as shown in Fig. 10. A constant minimum residue weight of 9 percent was reached when degradation conditions reduced the polymer molecular weight well below the level required for HPG and HEC. This minimum residue weight compared with previously reported residue weights for guar gum. This residue changed the pore size characteristics of the filter and retained smaller polymer molecules than observed with the other polymer types.

Guar gum also had slightly higher fluid loss characteristics than HPG and HEC for all polymer molecular weight ranges. The fluid loss coefficient did not increase significantly, however, until residue weight was reduced to less than 20 percent of the original amount of polymer in solution, as shown in Fig. 11.

Fig. 12 is a composite graph showing the effect of the polymer average molecular weight on the fluid loss coefficients for the three polymer types. The differences in the three polymer types can clearly be

seen. An increase in insoluble residue production required a corresponding decrease in average molecular weight to attain the same increase in fluid loss (or ease in fluid flow through a filtering medium). For example, to increase fluid flow by a factor of five, HEC  $\bar{M}_w$  must be reduced to  $2.5 \times 10^5$ ; HPG must be reduced to  $\bar{M}_w = 1 \times 10^5$ ; and guar gum must be reduced to  $\bar{M}_w = 2.5 \times 10^4$ .

Only a small amount of degraded polymer larger than the pore size of the filter was needed to control fluid loss through the filter. HPG and guar gum residues changed the pore size characteristics of the filter and retained degraded polymer of lower molecular weight than occurred with HEC degradation.

#### Changing Filter Pore Size

Using larger pore size filters had a greater effect on HEC fluid loss characteristics than on HPG fluid loss. HEC passed through a  $0.22 \mu\text{m}$  filter without restriction after very mild molecular weight degradation. HPG required much greater molecular weight reduction than HEC. HPG filtration is summarized in Table 1. Fluid loss did not increase significantly for the solution with lower breaker concentration for either filter size. For the higher breaker concentration, the fluid loss coefficient had increased for the  $0.22 \mu\text{m}$  by a factor of 4.4 when was reduced to  $4.7 \times 10^5$ . The fluid loss coefficient had also increased for the  $0.05 \mu\text{m}$  filter but not to such a large extent. The residues produced by HPG degradation changed the filtration properties of the larger filter as well. Without these residues, HEC solutions were not restricted in the same manner and required less molecular weight reduction than the HPG gel. Similar results were seen using 0.8 and  $5.0 \mu\text{m}$  filters.

#### Sandpack Damage Studies

A wide variety of pore sizes can be found in sandpicks (or a propped fracture in the reservoir). HPG and guar gum degradation residues affect the pore sizes in this filtration medium just as they do for the filter studies. Proppant pack damage studies reported in the literature (5-7) show that higher polymer concentrations resulted in more residue in the fracture and greater flow restriction through the sandpack. In addition, break conditions could be varied to reduce fluid flow through the sandpack even with polymers that produced no insoluble residues. (7)

Experiments were conducted to determine the molecular weights of degraded polymers under break conditions described in these sandpack damage studies. In general, these break conditions resulted in apparent solution viscosities lower than 3 cP which compared with viscosities reported by the sandpack damage studies.

The results of these comparative studies showed that regardless of polymer type, polymer solutions with high molecular weight degradation products ( $\bar{M}_w > 8 \times 10^6$ ) caused extensive damage to fluid flow in the sandpicks. Intermediate range degradation products ( $\bar{M}_w = 1$  to  $6 \times 10^6$ ) caused significant amounts of damage, generally 40 to 60 percent. HPG caused more damage than HEC. For average molecular weights less than 1 million, damage to fluid flow ranged from 10 to 35 percent with HPG again causing more damage than HEC. These damage figures were

reported for 40 to 50 lb/1000 gal polymer concentrations. Higher polymer concentrations caused more damage for the polymers that produced more residue.

Type of breaker (enzyme, oxidizer, thermal) also affected the degree of molecular weight reduction and the amount of reported damage. High temperatures which promote thermal breaking reduced polymer molecular weight to less than  $1 \times 10^4$ . A dark brown precipitate similar to that observed by previous researchers (2,7) was formed. Without additional fluid flow reduction from incompletely broken polymer, this residue was the least damaging in the sandpack damage studies.

For the oxidant breaker conditions described in the sandpack damage studies,  $\bar{M}_w$  were not reduced below  $5 \times 10^5$ , however. This was the molecular weight at which fluid loss coefficients began to increase significantly with the  $0.22 \mu\text{m}$  filter. Further studies would be necessary to determine whether additional molecular weight reduction of HPG would reduce damage in a proppant pack.

#### Submicron Particle Size Analysis

Samples of degraded HPG solutions were sent to an independent laboratory for submicron particle size analysis. Degradation products from  $0.01$  to  $10 \mu\text{m}$  in particle size could be observed using a low-angle, light-scattering technique. Figs. 13 and 14 show the particle size analysis for 40 lb/1000 gal HPG solutions broken with two different concentrations of oxidant breaker. These analyses showed polymer molecules in the submicron range as well as larger residues that were not observed by SEC analysis. (Concentration of particles was not proportional to peak intensity.) Break conditions which reduced polymer size also reduced the size of the larger residues. SEC may indirectly monitor the benefits of reduction in the size of these larger residues. Additional evaluation of this technique could help explain the effects of different breaker systems on the residues up to the micrometer size.

#### Molecular Weight - Viscosity Correlation

Viscosities were routinely measured with a Contraves Low-shear-30 Viscometer at ambient temperature. Low viscosity measurements did not guarantee low molecular weight degradation products. Solution viscosities depended on both polymer concentration and polymer average molecular weight. The degraded polymer solutions also showed little non-Newtonian viscosity behavior (apparent viscosities were relatively independent of shear rate).

A linear relationship between the  $\log \bar{M}_w$  and the inverse of the viscosity ( $\mu^{-1}$ ) was found for degraded polymer solutions that eluted within separation range of the SEC columns (for calculations). For the linear relationship to be valid, solution viscosities should not be too high (non-Newtonian) or too low (approaching solvent viscosity) for the linear relationship to hold. This relationship is shown in Fig. 15 for HPG gels with different initial HPG concentrations. For clarity, data points are shown for only one concentration for clarity. All the data can be normalized to compare to the 40 lb/1000 gal concentrations by using the following equation:

$$\log \bar{M}_w - \log (40/C_i)^2 = a - b/\mu \dots \dots \dots (3)$$

where  $\bar{M}_w$  = average molecular weight  
 $C_i$  = polymer concentration in lb/1000 gal  
 $\mu$  = viscosity in cP  
 a and b = constants

Correlations are shown for HPG (Fig. 16) and HEC and CMHEC (Fig. 17). Slight differences in the HPG and modified cellulose polymers do not exceed limits of experimental error and scatter in the data.

## DISCUSSION

SEC analysis to monitor polymer degradation can be used in the following areas: evaluation of existing fracturing fluid formulations for specific reservoir applications; and testing of new products (breakers, polymers, additives, etc.) to determine improvements in degradation and cleanup characteristics.

### Tests of Field and Laboratory Samples

SEC analysis of field and laboratory samples of degraded polymer solutions was performed in support of the Department of Energy sponsored research program to stimulate gas production from low-permeability lenticular sandstones in the Western United States. A stimulation treatment was conducted May 4, 1984, at the Multi-Well Experiment (MWX) site, Rulison Field, Garfield County, Colorado, S34, T6S, R94W. The stimulation was conducted at depths of 2155 to 2179 m (7070 to 7150 ft) using a transition metal crosslinked HPG gel fracturing fluid and 87543 kg (193,000 lb) of sand. Within the first 2 days after the stimulation, 42 percent of the stimulation fluids was recovered, and 60 percent was recovered after 19 days of cleanup. Problems encountered during cleanup included sand production into the wellbore and low gas production.

SEC analysis of the returned fluids indicated that polymer molecular weights were very high even though solution viscosity was low. Results are tabulated in Table 2.

Polymer concentrations were estimated using two methods. The area under the SEC curve was calibrated with polymer solutions of known concentration. Peak areas were used to obtain the concentration values in Table 2. Concentrations were also estimated using the molecular weight - viscosity correlation described in Equation 3. These values differed from the values in Table 2 by less than 20 percent.

From the molecular weight - fluid flow studies, flow through the propped fracture could be greatly reduced. Formation gas pressures, however, may have been sufficiently high to push the solution including some of the sand toward the wellbore.

At least two factors contributed to the retention of high HPG molecular weight in the fracture. Formation temperature of 390K (205°F) was considered high enough to break the polymer so that only a small amount of oxidant breaker was added at the end of the fracturing treatment. In actuality, this temperature can reduce solution viscosity with only a gradual reduction in polymer molecular weight. Secondly, methanol was used as a prepard to the fracturing fluid stimulation and returned with the polymer in the

returned fluids. Methanol had a stabilizing effect on polymer degradation by scavenging free radicals and terminating the chain reactions initiated by the breakers. (3)

Degradation of the same fracturing fluid polymer system was studied in the laboratory to determine the effects of reservoir temperature and methanol on molecular weight reduction. Table 3 shows polymer viscosity and average molecular weight for times up to 7 days in the high temperature bath.

It required 30 days in the fracture before polymer molecular weight reached the same level as it did in the laboratory in 7 days. Table 4 shows the stabilizing effects of methanol on polymer solutions with and without breaker present. Molecular weights for all these solutions would be greater than 5 million.

In summary, the design of the fracturing fluid overestimated the effect of thermal degradation and ignored the stabilizing properties of methanol. As a result, fluid return from the formation was very slow, and gas production was delayed for several months.

### Breaker Evaluation

In an attempt to reduce polymer molecular weight as much as possible, certain limitations of existing oxidizer breakers became apparent. If low breaker concentrations were used, solution viscosity was reduced without significantly reducing polymer molecular weight. If breaker concentration was increased, however, solution viscosity was reduced within the first hour. This limited the polymer solution's usefulness as a fracturing fluid. Table 5 shows viscosities after 1 hour at 343 K (180°F) and average molecular weights after 72 hours at the same temperature for 40 lb/1000 gal HPG solutions. Further reduction in oxidant breaker concentration improved early viscosity retention but did not improve molecular weight reduction even at higher reaction temperatures as shown in Table 3. Results suggest that improved breaker systems should be developed to retain solution viscosity for a desired length of time yet reduce the size polymer degradation products to minimize fracture damage.

### CONCLUSIONS

- o Size Exclusion Chromatography can be used to study conditions which affect fracturing fluid polymer degradation. The degradation of guar gum, HPG, and modified cellulose polymers was studied using this analytical method.
- o SEC analysis and fluid loss filtration studies showed the extent of polymer degradation required to ensure rapid fluid return after hydraulic fracture stimulation using aqueous-based hydraulic fracturing fluids.
- o Retention of partially degraded polymer by a filtration medium (filter or sandpack) greatly reduced fluid flow through the medium. Insoluble residues produced during degradation affected the pore size characteristics of the filtration medium. Therefore polymers that produced insoluble residues (HPG, guar gum) required greater

molecular weight reduction to minimize damage than those that were residue free (HEC, CMHEC).

- o To increase fluid loss coefficients by a factor of 5 (using a 0.05  $\mu\text{m}$  filter), reductions to the following average molecular weights were required: HEC,  $\bar{M}_w = 2.5 \times 10^5$ ; HPG,  $\bar{M}_w = 1.0 \times 10^5$ ; and guar gum,  $\bar{M}_w = 2.5 \times 10^4$ .
- o Low viscosity did not ensure rapid fluid return because low viscosity fluids contained sufficient partially degraded polymer and residues to damage and restrict the fracture.
- o Viscosities of degraded polymer solutions were functions of polymer concentration and molecular weight. A correlation between the log of the polymer average molecular weight and the inverse of solution viscosity was the same for HPG and HEC within experimental limitations.
- o Returned fluids from the MWX-1 stimulation indicated high molecular weight polymer in the fracture many days after the treatment.
- o For the MWX stimulation, polymer degradation was inhibited by the presence of methanol. Insufficient breaker was added to bulk of the polymer solution. Formation temperature was not high enough to ensure thermal breaking.
- o Laboratory degradation studies showed methanol inhibited polymer degradation even with breaker in the solution.

#### NOMENCLATURE

- A = Filter area ( $\text{cm}^2$ )
- $C_i$  = Polymer concentration (lb/1000 gal)
- $C_{III}$  = Fluid loss coefficient ( $\text{ft}/\text{min}^{1/2}$ )
- CMHEC = Carboxymethyl cellulose
- $h_i$  = Height of a section of the molecular weight distribution curve
- HEC = Hydroxyethyl cellulose
- HPG = Hydroxypropyl guar
- $M_i$  = Molecular weight at  $h_i$
- $\bar{M}_w$  = Weight average molecular weight
- MWD = Molecular weight distribution
- SEC = Size exclusion chromatography
- $\mu$  = Viscosity (cP)

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TABLE 1. - Fluid loss coefficients for 40 lb/1000 gal HPG solutions of different average molecular weight

$\bar{M}_w$	Reaction time at 343°K (158°F) (hours)	Breaker conc. (lb/1000 gal)	Fluid loss coefficient (ft/min <sup>2</sup> ) for filters	0.22 μm	0.05 μm
3x10 <sup>6</sup>	0	-	1.4x10 <sup>-3</sup>	1.4x10 <sup>-3</sup>	1.4x10 <sup>-3</sup>
4x10 <sup>6</sup>	2	0.8	1.8x10 <sup>-3</sup>	1.8x10 <sup>-3</sup>	1.5x10 <sup>-3</sup>
6x10 <sup>6</sup>	2	1.6	2.0x10 <sup>-3</sup>	2.0x10 <sup>-3</sup>	1.8x10 <sup>-3</sup>
9x10 <sup>6</sup>	16	0.8	1.8x10 <sup>-3</sup>	1.8x10 <sup>-3</sup>	1.5x10 <sup>-3</sup>
7x10 <sup>6</sup>	16	1.6	6.2x10 <sup>-3</sup>	6.2x10 <sup>-3</sup>	3.2x10 <sup>-3</sup>

TABLE 3. - Average molecular weight and viscosity of crosslinked 40 lb/1000 gal HPG versus degradation time at 370°K. Viscosities measured at 298°K and 27 sec<sup>-1</sup>

Time (hours)	$\bar{M}_w$	No breaker $\bar{M}_w$	Viscosity (cP)	0.005% w/w breaker $\bar{M}_w$	Viscosity (cP)
7	very high	very high	82	2.5 x 10 <sup>6</sup>	3.2
24	very high	very high	51	1.3 x 10 <sup>6</sup>	3.0
48	7.7 x 10 <sup>6</sup>	7.7 x 10 <sup>6</sup>	6.3	1.0 x 10 <sup>6</sup>	2.4
72	2.8 x 10 <sup>6</sup>	2.8 x 10 <sup>6</sup>	3.8	0.8 x 10 <sup>6</sup>	2.0
144	0.9 x 10 <sup>6</sup>	0.9 x 10 <sup>6</sup>	2.9	0.4 x 10 <sup>6</sup>	1.8

TABLE 2. - Molecular weights and viscosities of MXH returned fluids

Date	Fluid returned %	$\bar{M}_w$	Viscosity (cP at 298 K)	Estimated concentration (lb/1000 gal)
3-84	24	8x10 <sup>6</sup>	1.4	8
9-84	57	7x10 <sup>6</sup>	2.0	8
21-84	60	2x10 <sup>6</sup>	1.8	17
6-84	77	0.7x10 <sup>6</sup>	1.1	9

TABLE 4. - Viscosity (298 K and 27.7 sec<sup>-1</sup>) of crosslinked HPG reacted at 363 K

Time (hours)	No methanol or breaker (cP)	5% methanol (cP)	5% methanol and 0.006% w/w breaker (cP)
6	107.7	153	29.1
24	32.2	79.9	15.2
48	22.5	62.6	13.1
168	7.6	21.4	7.0

TABLE 5. - HPG broken at 343 K using ammonium persulfate oxidant breaker

Breaker concentration (percent)	Viscosity at 1 hour (cP)	Molecular weight at 72 hours
0.025	6.5	3x10 <sup>6</sup>
0.05	5.8	2x10 <sup>6</sup>
0.10	1.7-2.5	2-4x10 <sup>5</sup>

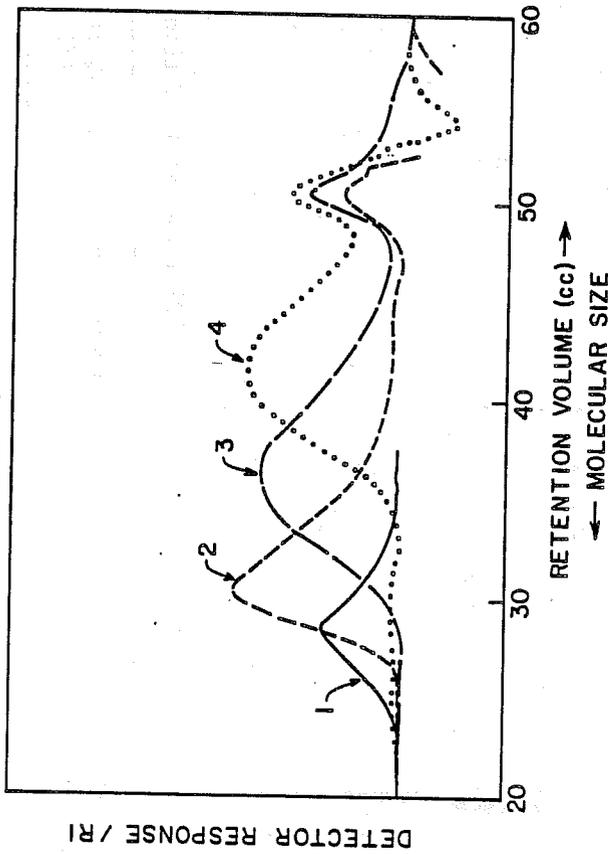


Fig. 1—Composite size exclusion chromatogram of degraded 40-lb HPG gel. Curve 1, gel contained no breaker; Curves 2, 3, and 4 were analyzed after 1, 2, and 24 hours of reaction time.

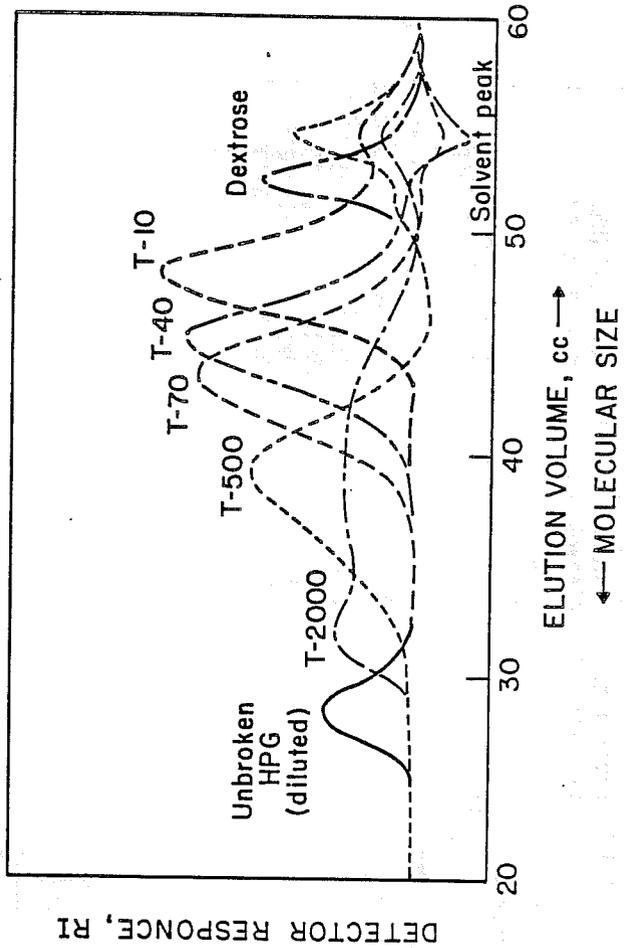


Fig. 3—Composite chromatogram of dextran standards and unbroken HPG gel.

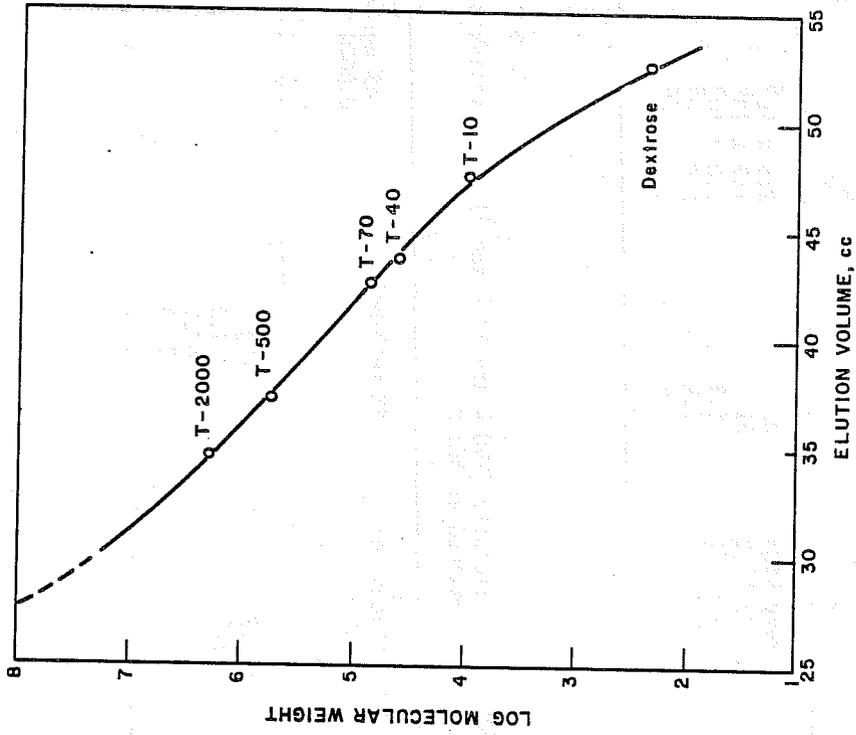


Fig. 2—Calibration curve of log molecular weight vs. elution volume for dextran standards.

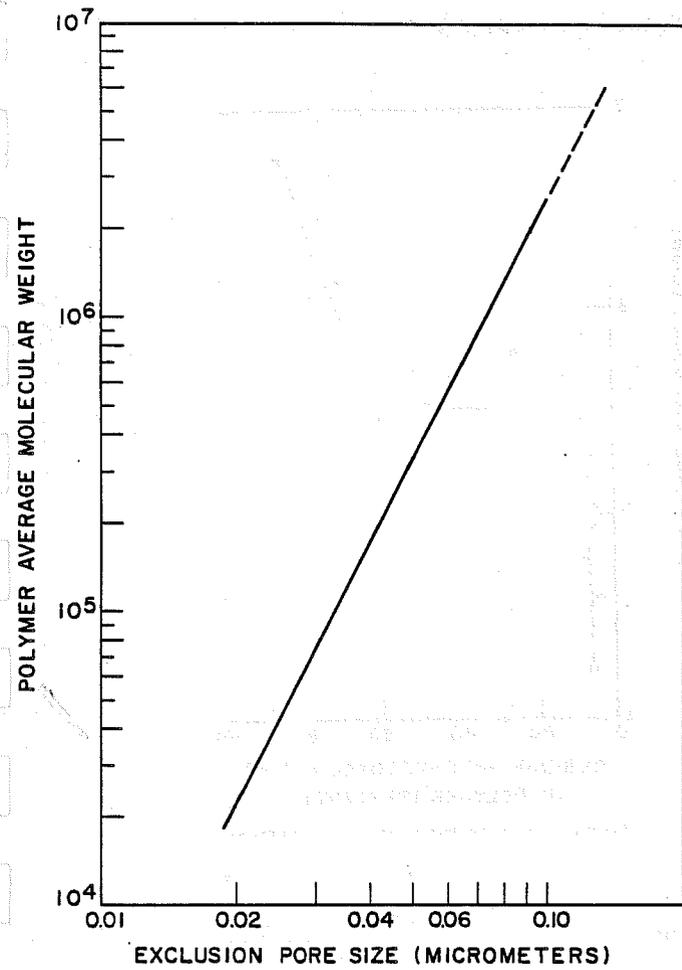


Fig. 4—Estimated polymer average molecular weight and molecular size relationship.

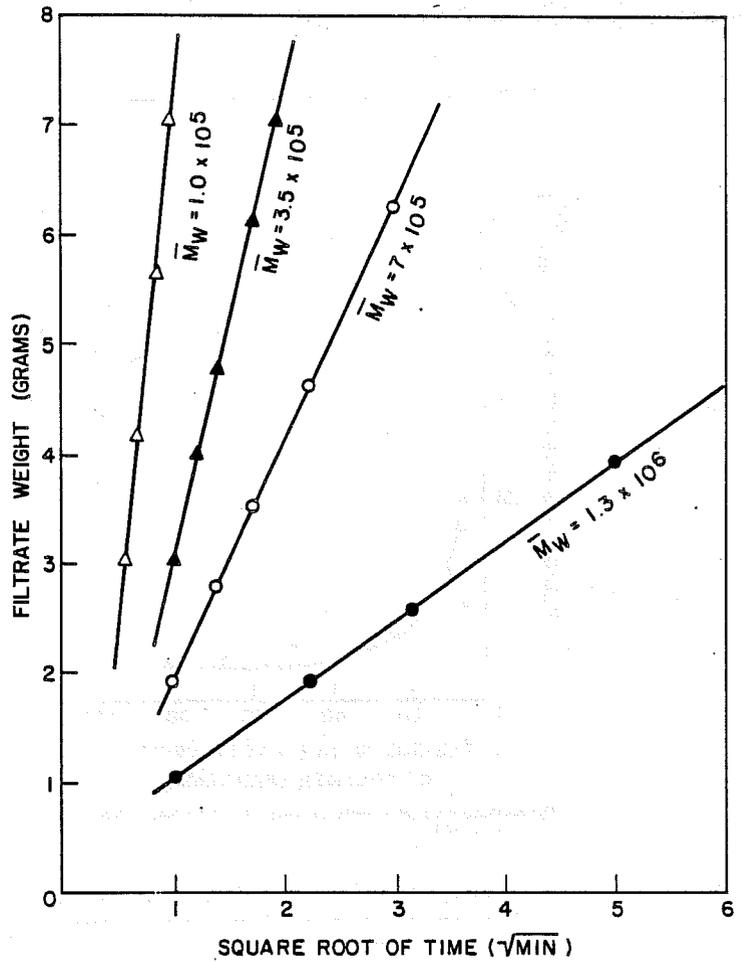


Fig. 5—Static fluid-loss curves: filtrate passing through a 0.05  $\mu\text{m}$  filter as a function of the square root of time for different HEC molecular weights.

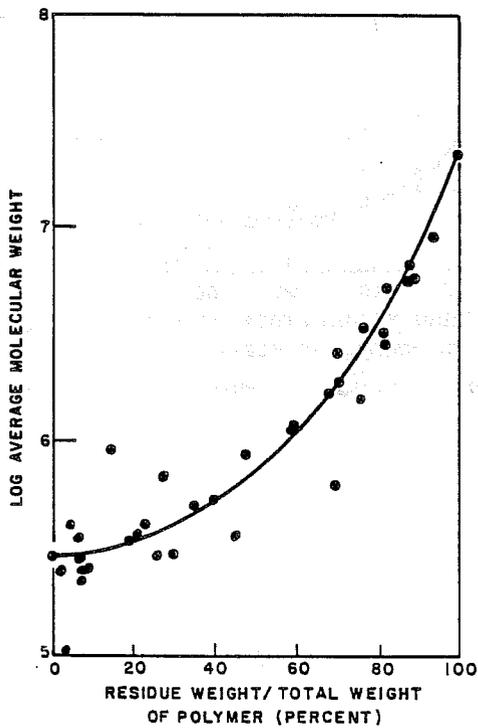


Fig. 6—Residue weight vs. molecular weight for 40-lb HEC gel. Filters were 0.05  $\mu\text{m}$ .

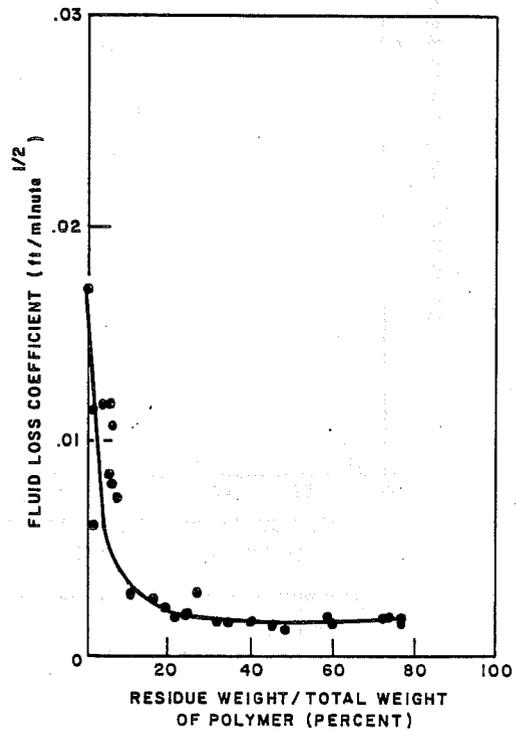


Fig. 7—Residue weight vs. fluid-loss coefficient for 40-lb HEC gel.



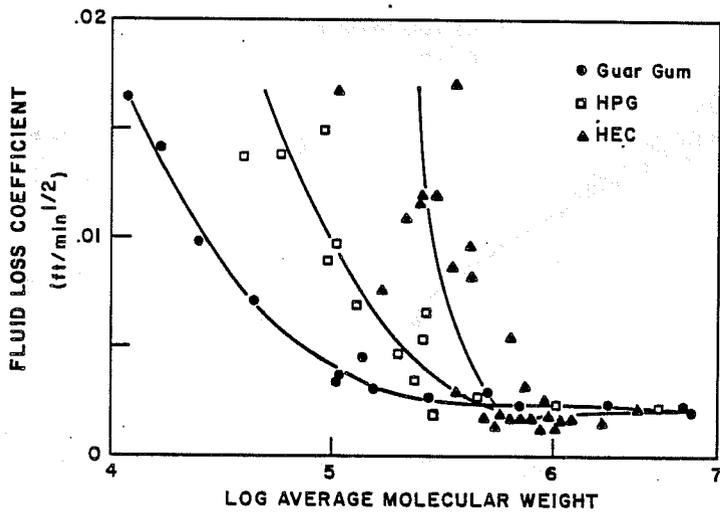


Fig. 12—Fluid-loss coefficient as a function of degraded polymer molecular weight.

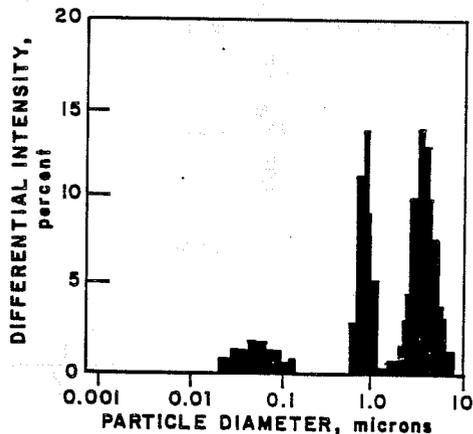


Fig. 13—Particle-size analysis of 40-lb HPG gel degraded with 0.006% oxidant breaker.

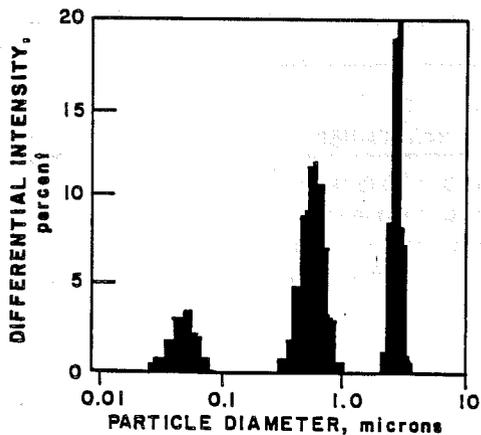


Fig. 14—Particle-size analysis of 40-lb HPG gel degraded with 0.012% oxidant breaker.

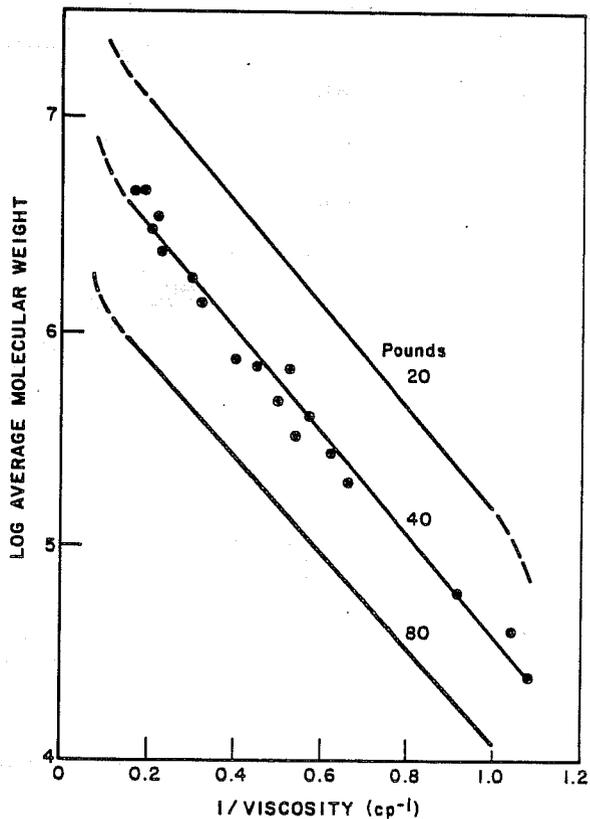


Fig. 15—Molecular weight-viscosity correlation for degraded HPG gels as a function of initial polymer concentration.

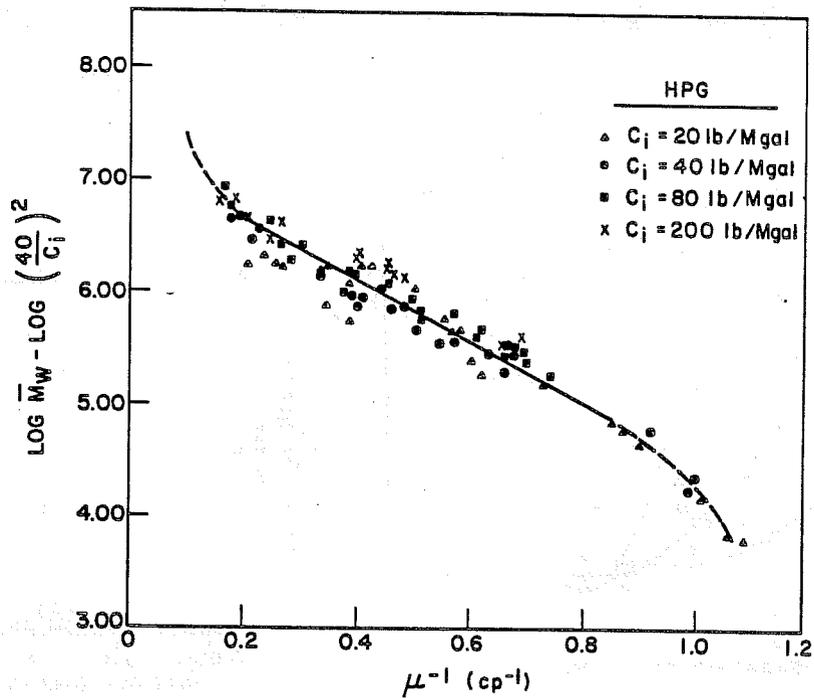


Fig. 16—Molecular weight-viscosity correlation for degraded HPG gels.

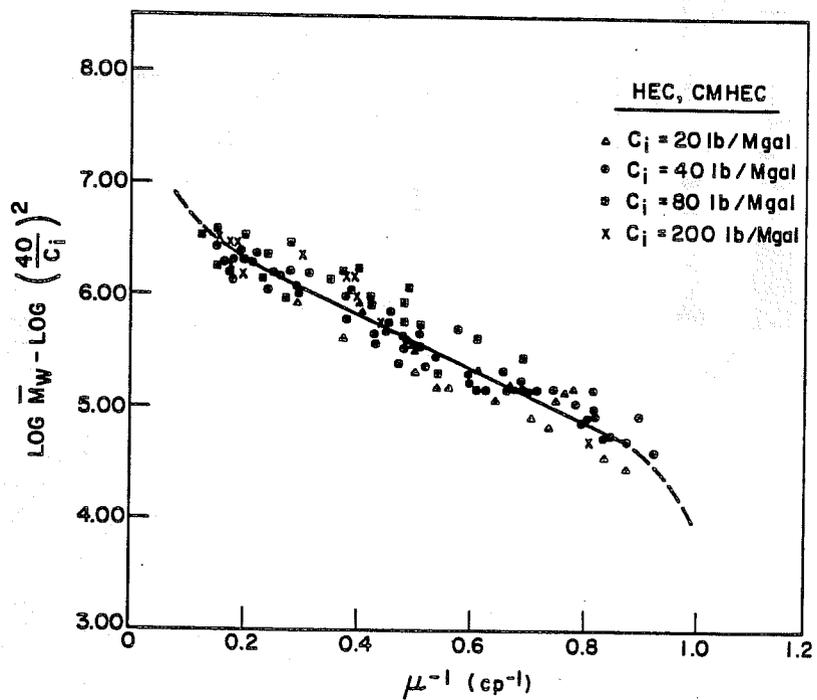


Fig. 17—Molecular weight-viscosity correlation for degraded HEC and CMHEC gels.