

**STUDYING THE BREAKING MECHANISM OF POLYMER-BASED IN SITU
GELLED ACIDS USING SOLID BREAKER**

A Thesis

by

ZHIDA TIAN

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

August 2012

Major Subject: Petroleum Engineering

Studying the Breaking Mechanism of Polymer-Based in situ Gelled Acids Using Solid
Breaker

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ABSTRACT

Studying the Breaking Mechanism of Polymer-Based in situ Gelled Acids Using Solid Breaker. (August 2012)

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Chair of Advisory Committee: Dr. Hisham A. Nasr-El-Din

In situ gelled acids that are based on polymers have been used in the field for several years as an acid diversion agent. These acids should not cause permanent formation damage, and should clean-up rapidly and completely when the well is put back on production. However, recent lab studies indicated that a significant amount of gel was retained inside the core even when the recommended breaker concentration was used. This gel significantly reduced the core permeability. Therefore, the objective of this study is to examine the working mechanisms of the solid breaker and the factors that affect the breaking time. The flowback of the spent acid and the core damage induced by it will also be assessed in detail.

Viscosity and rheological experimental studies were conducted using polymer-based in situ gelled acids that used Zr as a crosslinker agent. To form the gel, this acid was neutralized using Pink Desert limestone to pH 3.5-4. The rheological properties of the gel were measured under different breaking conditions for 2 hr using HPHT rotational and oscillatory rheometers. Temperature (150 to 250°F), shear rate (0.1 to 1000 s⁻¹), and breaker concentrations (0 to 32 lb/Mgal) were the main parameters that

were investigated in this study. Experimental results showed that there is no need to add more than 16-ppg breaker concentration at 150°F, while 4-ppg breaker concentration is enough at temperatures higher than 200°F. A full breaking of these acids was obtained when the values of elastic modulus (G') were equalized with the viscose modules (G'').

An HPHT filter press was used to simulate the flowback of the spent acid. Viscosity measurements of filtered fluids were used to determine the degree of gel degradation. Carbonate cores that had a 2.5 in. diameter and 0.25 in. thickness were used. Temperature (75 to 250°F) and breaker concentrations (0 to 16 lb/Mgal) were the main parameters that were investigated in this study. Experimental results showed that there was always a gel left inside the rock, and such caused permeability reduction. Time needed to flowback the solution decreased by 50% when the temperature was increased from 150 to 200°F, while it decreased by only 30% when the breaker concentration was doubled. At 150°F, 16-ppg breaker concentration was recommended for breaking the gel. At higher temperatures ($>150^\circ\text{F}$), 8-ppg breaker concentration was enough to help degrade the gel.

DEDICATION

This thesis is dedicated to my parents who have supported me all the way since the beginning of my studies.

Also, this thesis is dedicated to my advisor who has been a great source of motivation and inspiration.

Finally, this thesis is dedicated to all those who believe in the richness of learning.

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Thanks also go to my friends and colleagues and the department faculty and staff for making my time at Texas A&M University a great experience. I also want to extend my gratitude to all the Texas elementary teachers and students who were willing to participate in the study.

Finally, thanks to my mother and father for their encouragement and to my girlfriend's for her patience and love.

NOMENCLATURE

P	Pressure, psi
T	Time, minutes
Q	Flow rate, cm ³ /s
A	Cross-sectional area to flow, cm ²
K	Permeability, darcy
μ	Fluid viscosity, mPa. S
ΔP	Applied pressure difference, atm/cm
ΔL	Thickness of the medium, cm
K_I	Power-law constant, mPa.s ⁿ ;
γ	Shear rate, s ⁻¹
n	Power-law index, dimensionless.

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CHAPTER I

INTRODUCTION AND LITERATURE REVIEW

The success of matrix acidizing does not depend only on the amount of acid injected, but also on the placement of acid into the right area. Live acids, which are expected to react with a low permeability zone, always flow into the high permeability zone. Flowing of acids into high permeability zones will leave the low permeability zone untreated, thus leading to the failure of matrix acidizing. Accurate acid placement is a key factor in increasing permeability around the wellbore. In addition, the hydrofluoric acid reacts very quickly with carbonate reservoir rock, especially at high temperatures. Jin et al. (2007) indicated that the length of wormholes, which is important in matrix acidizing, is associated with reaction rate. The rapid reaction rate limits acid penetration into the formation, which can lead to surface washout in matrix acidizing. This means that as more acid is pumped down to the treated zone, much of them will be spent at the rock surface; this does not help wormhole penetration. Mechanical methods and chemical methods have both been applied to improve acid diversion. Mechanical methods include ball sealers, solid particles, coiled tubing, packers and bullhead techniques. However, most of these mechanical methods have some drawbacks. Thomas and Milne (1995) showed that conventional bullhead techniques didn't provide successful acid diversion.

This thesis follows the style of *SPE Journal*.

Fujian et al. (2009) presented that seal ball diverting can't be used in the screen well and open hole. Ball sealers can only be applicable to cased and perforated wells; In addition to this, a sufficient pressure must be applied to keep the seal balls inside the perforations. The roundness and smoothness of the perforation holes also impact the effectiveness of seal balls. Solid particle diverting does not suit deep acid treatment because they will cause serious damage to the formation. Frank et al. (2007) presented that setting packers often requires multiple stages of operations; this will cause much more time and money. In addition, placing isolation packers in open hole completions is a hard task to finish and may not be effective. Although the use of coiled tubing is a popular mechanical method in acid placement, it is more expensive and time consuming than chemical methods (Chang et al. 2007). Another drawback of the coiled tubing is that the tubing diameter is much smaller than that of the drill pipe or production tubing. It can limit the injection rate and pressure. Bhalla (1995) also presented that when treating long horizontal wells, extending coil tubing may be stuck at the toe of the well, so usually it requires tractors or vibrators. So compared to mechanical methods, usually chemical methods are more effective inside the formation. Chemical methods include gelling, foaming, emulsifying the acid, or crosslinking suitable acid gelling agents.

Nasr-El-Din et al. (2008) found that a polymer concentration increase in hydrochloric acid can lead to a significant enhancement in apparent viscosity and an obvious decrease in the dissolution rate with calcite. Polymer-based acid can be used to retard reaction rate, hence increasing the length of the wormhole. Hansford and Litt (1968) indicated that the addition of the polymer to the acid can decrease the diffusivity

rate of H^+ . So when the polymer is added to the acid system during matrix acidizing, the diffusion rate of H^+ from the acid system to rock surface is reduced. The polymer can also adhere on the surface rock forming a barrier. This barrier can also reduce the reaction rate between acid and calcium carbonate. The transfer rate of reaction products away from the surface would also be reduced by the addition of polymer to the acid system. De Rozieres et al. (1994) showed that a high viscosity will reduce the diffusion coefficient of the hydrogen ion (H^+) and, as a result, the rate of mass transfer of the acid into the rock surface will decrease.

Even when polymer is added to the acid system, for un-crosslinked acid, acid placement cannot be achieved. Crosslinked acid which uses a crosslinker to combine large polymer molecules has a much higher viscosity than un-crosslinked acid. Nasr-El-Din et al (2003) indicated that the crosslinked acid can be divided into two groups. For the first type of crosslinked acids, the acids are crosslinked at the surface before they are injected down to the wellbore. For the second type of crosslinked acids, they are uncrosslinked after they are injected into formation, but as the reaction between hydrofluoric acid and calcium carbonate starts, the crosslink of polymers will then initiate. This means that the crosslinking reaction occurs in the formation. The second type of crosslinked acid is called in situ gelled acid. Conway et al. (1999) mentioned that the in situ gelled acid was very viscous, especially in the pH range of 2-4. Aluminium ions, zirconium ions and ferric ions are always used as a crosslinker for in situ gelled acids. It is well known that the ferric ions in the system can precipitate; therefore ferric ions can cause formation damage. Taylor et al. (1999) showed that the

presence of hydrogen sulfide in the wellbore can affect the precipitation of iron compounds. In sweet wells (no hydrogen sulfide), ferric ions will precipitate in the pH range of 1-2. Crowe (1985) and Brezinski (1999) showed that in sour wells, ferric ions and hydrogen sulfide will form precipitation at a pH value around 2. So when using ferric ions as a crosslinker, the precipitation problem associated with it would always occur. Abdel Fatah et al. (2008) found that in situ gelled acids with an aluminum crosslinker form a gel at a pH value higher than zirconium or ferric ions. So compared to the other two crosslinkers, the zirconium crosslinker is more suitable.

In situ gelled acid combines acid diversion and matrix acidizing at the same time; therefore it reduces the complexity of operation (Chang et al. 2001). Moorhouse et al. (1998) showed that zirconium-crosslinked and ferric-crosslinked polymers have been used to control the acid placement. The initial live acid, which contains a polymer, crosslinker, buffer and breaker, is prepared at the surface. When the initial live acid is pumped down to the formation, the acid would react with calcium carbonate and after some acid is spent, the pH value would rise. Hill et al. (2005) indicated that at a pH value of nearly 2, the crosslinking of the carboxyl groups in the polymer would initiate. So the viscosity of the in situ gelled acid increases to plug the high permeability treated zone, and forces the next acid stages to the lower permeability zones. As the reaction continues, when the pH value reaches around 3-4, the viscosity would reduce. In order to make sure that there is a complete reversal of the crosslinking process, breaker is always added to the acid system. Nasr-el-din et al. (2002) mentioned that the mechanism of the breaker is reducing the valence of the multi-valent cation or forming

a more stable compound with the cross-linker. For a ferric crosslinker, as the pH rises, the reducing agent converts the ferric ions to ferrous ions. The polymer is not crosslinked by ferrous ions so the viscosity of the in situ gelled acid will collapse. For a zirconium crosslinker, the fluoride ions can form more stable compounds with zirconium crosslinker, so carboxyl groups will be separated from the crosslinker, thus reducing the viscosity. Therefore, a gel breaker is necessary when in situ gelled acid is used. Kalfayan and Martin (2009) found that the viscosity of in situ gelled acid decreased when fluoride breaker was added in the system. If the viscosity is reduced, gel residue after acid treatment is easy to flow back. Taylor and Nasr-El-Din (2001) indicated that temperature will also affect the behavior of the gelled acid.

Because most wells are located at several thousand feet depth, it usually takes some time to pump in situ gelled acid to the pay zone. During this period of time, dispersed gel breakers inside the mixed fluid may react quickly and cause the fluid to degrade before it reaches the target zone. Therefore, adding the breaker after pumping in situ gelled acid was one technique used in the field. However, the high viscosity of the gel does not allow the breaker to fully disperse, which causes the in situ gelled acid not to be degraded. Boles et al. (1996) shows that retarded gel breakers can be added to in situ gelled acid before pumping it into the target zone. This kind of breaker reacts very slowly, and reduces viscosity gradually. Boles et al. 1996 recommended coating the breaker with a wooden resin material. It is important to highlight that this is the same breaker that is used in this work.

After finishing acid diversion, there is always gel left inside formation, and such causes formation damage. This is a disadvantage of in situ gelled acid. Taylor and Nasr-el-din (2002) mentioned that formation damage is either caused by polymer entrapment or the precipitation of a crosslinker. Roberts et al. (2000) have shown that the adsorption of polymer molecules to the formation grains can cause local buildup of polymer concentration at pore throats, which results in a permeability reduction. Bazin et al. (1999) also mentioned that formation damage due to gel entrapment was one of the main problems caused by acid viscosity increases. Mohamed et al. (1999) examined acidizing treatments of a large number of seawater injectors with in situ gelled acid. Field data indicated that the in situ gelled acid system can cause formation damage in some cases. Recent studies have indicated that gel residue inside the formation is still hard to remove completely, even when the suitable breaker was used. Sometimes, the permeability reduction caused by gel residue is bigger than the permeability increase created by acid treatment (Flippen et al. 1997). Lynn and Nasr-El-Din (2001) studied the removal of the remaining gel in the lab and they found that even at a flowback rate up to 30 cm³/min, complete removal of the residual gel in wormholes cannot be reached.

Some previous work has been conducted to measure rheological properties such as viscous modulus and elastic modulus. Jin Liu al. (2001) has indicated that rheological measurements were used to characterize gelants and gels. Gomaa and Nasr-El-Din (2010) have shown that the viscoelastic properties can have big effects on diversion, where increasing the G' increased the acid diversion ability. Marshall and

Metzner (1966) stated that polymer-based fluids, which have partly viscous modulus and partly elastic modulus, can have the best results.

The fluid used a zirconium-crosslinker and novel coated breaker as additives in the research. Nasr-El-Din et al. (2002) have shown that zirconium compounds will not precipitate in the presence of hydrogen sulfide. Novel coated breaker can reverse this procedure and then reduce polymer residue in the wormholes to prevent formation damage. However, different compositions of additives into acid results in different properties of acid (Romero-Zeron et al. 2004). Abdel Fatah et al. (2008) showed that gelation pH depends on crosslinker type, and corrosion inhibitor has opposite effects on Zr-based acid. Therefore, the first objective of this study is to examine the working mechanisms of the solid breaker and the factors that affect the breaking time. Rheological and viscosity measurements were provided in this work. Temperature (150 to 250°F), shear rate (0.1 to 1000s⁻¹), and breaker concentrations (0 to 32 lb/Mgal) were the main parameters that were investigated in this study.

Another objective of this study is to investigate factors that affect the flowback rate of neutralized acid. An HP/HT filter press was used to simulate the flowback of the spent acid. Viscosity measurements were used to determine the degree of gel degradation. Carbonate cores that had a 2.5 in. diameter and 0.25 in. thickness were used. Temperature (75 to 250°F) and breaker concentration (0 to 16 lb/Mgal) were the main parameters that were investigated in this study.

CHAPTER II

BACKGROUND OF COATED SOLID BREAKER

Acid solutions are always used to increase permeability of the formation around the wellbore. Because the reaction rate of hydrofluoric acid with carbonate is so fast, polymer gels are combined with this acid to reduce the reaction rate. Another benefit of adding polymer is it helps to finish acid diversion. Uniform distribution of the acid on the reacted zone is a key factor in matrix acidizing. Usually the polymers are crosslinked with zirconium, titanium or other high valent cationic ions. Sometimes after acid treatment, there are gels left inside the wormholes, which may cause formation damage. In order to prevent formation damage caused by in situ gelled acids, gel breaker is used in acid treatment.

Gel breakers used in these fluids are formed from materials which have the ability to complex with the organometallic crosslinkers. Fluoride, phosphate, sulfate anions and multi-carboxylated compounds are commonly known materials capable of complexing with the titanium and zirconium crosslinkers. Fluorspar, cryolite, fluorosilicates, fluoroborates and fluorophosphates are applicable materials which can release fluoride ions. Among these choices, because fluorspar is readily available in nature so it is commonly used. The main composition of fluorspar is calcium fluoride. The fluoride ions released from fluorspar can form a more stable compound with zirconium ions, which can break the linkage of the crosslinked polymer fluid.

Retarded gel breakers are developed to allow in situ gelled acid to finish the acid treatment first and gradually reduce the viscosity of the fluid after finishing acid diversion. Retarded gel breakers are fluorspar coated, or encapsulated with a water insoluble wood resin to reduce the release rate of complexing materials. This can allow the viscosity of an in situ gelled acid to reduce gradually. It is important to highlight that the fluorspar coated with wood resin is what I used in my research. **Fig. 1** shows the amount of fluoride released as a function of time for uncoated breaker, product between 10-16 mesh and product between 10-40 mesh. The wood resin is mainly composed of high molecular weight phenolic compounds and resin acid. It also contains some neutral materials. The resin is insoluble in both aliphatic hydrocarbons and water. It is always extracted from resinous pine wood with a coal tar hydrocarbon. The hydrocarbon is then removed by evaporation. After removing hydrocarbon, a mixture of wood resin and the water insoluble resin are left. A suitable petroleum hydrocarbon can dissolve the wood resin but the resin is insoluble in it. In this way, the resin can be separated from the wood resin.

The process of producing resin coated gel breaker is complicated, but the basic theory is that mixing the resin with acetone or methanol, the solvents which can dissolve the resin. The fluorspar is then added to the solution of resin. After mixing a while, the gel breaker material is thoroughly coated with resin solids. The solids of the coated gel breakers are then allowed to dry. Finally, the acetone or methanol evaporate and leave the resin coated breaker formed . This allows the particles to be easily poured and

dispersed within the polymer gel. The weight percentage of resin in this product is between 10 to 80%, with 10 to 20% preferred.

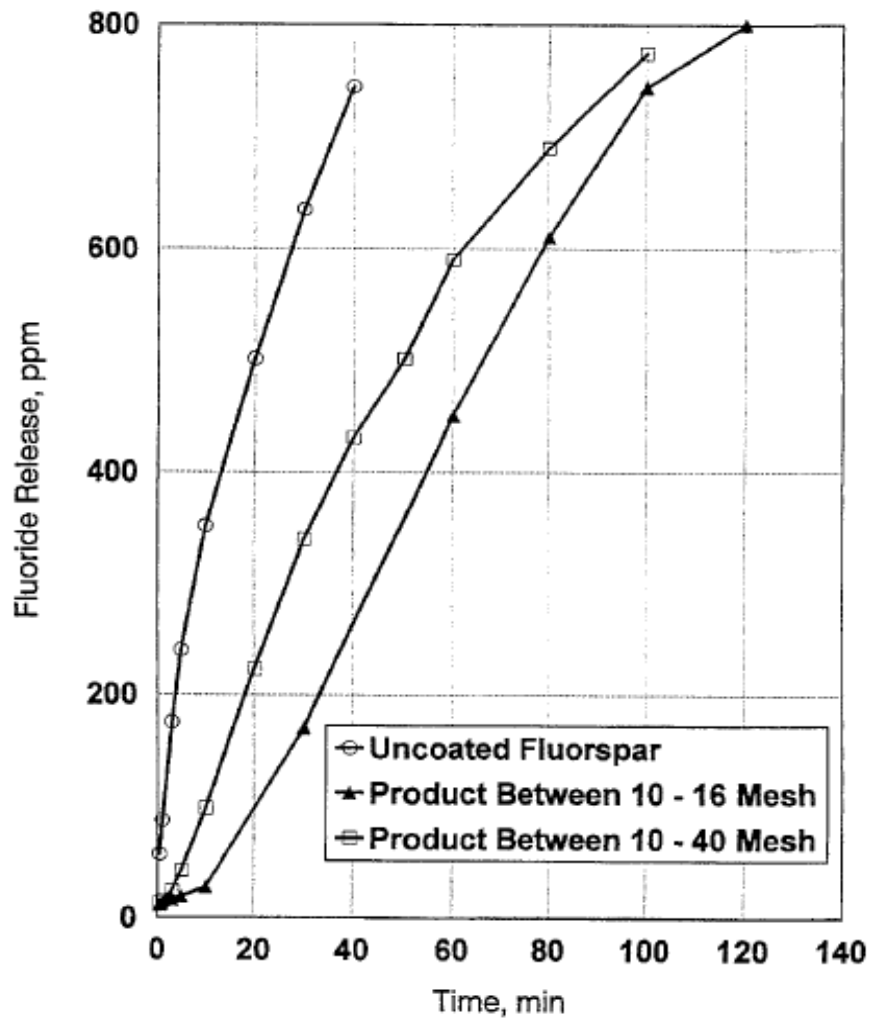


Fig. 1—The amount of fluoride released as a function of time for uncoated fluorspar, product between 10-16 mesh and product between 10-40 mesh. (Boles et al., 1996)

CHAPTER III

RHEOLOGICAL PROPERTIES MEASUREMENT EXPERIMENT

Materials

Hydrochloric acid (ACS reagent grade) was titrated using a 1N sodium hydroxide solution to determine its concentration, and was found to be 36.8 wt%. All acid solutions were prepared using deionized water with a resistivity of 18.2 MΩ.cm at room temperature. Polymer and other additives were all oilfield chemicals, and were used without further purification.

Measurements

Rheology and viscosity measurements of live and partially spent acids were made using a HTHP viscometer at temperature range of 75-250°F and 300 psi. To resist corrosion by acids, both the rotor (R1) and the bob (B1) of the viscometer were made of Hastelloy C. The viscosity was measured as a function of shear rate (from 0.1 to 1020 s⁻¹). Measurements were conducted at atmospheric pressure and temperature. pH values were measured using 950 ROSS FASTQC.

Procedures

Table 1 lists the formulae of the in situ gelled acid system examined in the present work. In situ gelled acids contained acid, a polymer, a cross-linker, a breaker, and a corrosion inhibitor. The study also included two types of experiment setups: The first one is to investigate how the viscosity of the gel was reduced as a function of time

for 120 min. In this set of experiments, the effect of temperature (150-250°F) and breaker concentration (0-32 lb/Mgal) on the breaking of partially neutralized in situ gelled acid (pH 3.5-4) will be researched. The following procedures were used:

1. The acid solution was prepared by adding polymer, crosslinker, buffer to water, based on the concentration shown in Table 1. A magnetic stirrer was used to mix the acid solution.
2. The pre-determined volume of HCl was neutralized calcium carbonate powder to pH of 3.
3. The partially neutralized HCl was added to the mixing solution shown in the first step and leave to mix for 10 minutes. The final pH values was around 3.5 - 4.
4. Apparent viscosity, elastic modulus, and viscous modulus were measured for 120 min. to show how the partial neutralized in situ gelled acid (formed gel) break with time.

The second set of the experiments investigated the effect of the breaker concentration (0-4 lb/Mgal) on the apparent viscosity of in situ gelled acid at pH range from 0 to 5 at 200°F. The following procedures were used:

1. The sequence of adding chemicals was: water, corrosion inhibitor, HCl, polymer, crosslinker and buffer. The acids with additives were mixed for 20 minutes using a magnetic stirrer.
2. Breaker was added just before acid neutralization.
3. pH value was monitored during neutralization.

4. Apparent viscosity measurement was done at different pH values.

Table 1—Formula of the in situ gelled acid examined in the present study.

Component	Concentration
Hydrochloric acid	5 wt% HCl
Acid gelling agent: a mixture of acrylic polymers (30-60 wt%), hydrotreated middle petroleum distillates (10-30%), nonylphenoethoxylate (1-5 wt%)	20 gal/Mgal
Corrosion inhibitor: a mixture of Methanol (1-5%), isopropanol (1-5wt %), formic acid (30-60 wt%), organic sulfur compound (1-5%), quaternary ammonium compound (1-5wt%), haloalkylheteropolycycle salt (10-30wt%), aromatic aldehyde (10-30%), oxyalkylated fatty acid (10-30 wt%), benzyl chloride (10-30 wt%)	4 gal/Mgal
Cross-linker (Mixture of aluminum and zirconium salts in water)	4.5 gal/Mgal
Breaker (Resin coated inorganic salt breaker for crosslinked acid)	0-16 lb/Mgal
Buffer: poly (oxy-1,2-ethanediyl)	2 gal/Mgal

Results and Discussion

Viscosity Measurements—Constant Shear Environment

Fig. 2 shows the effect of breaker concentration on the viscosity of in situ gelled acid during 2 hrs breaking time at 150°F and a shear rate value of 100 s⁻¹.

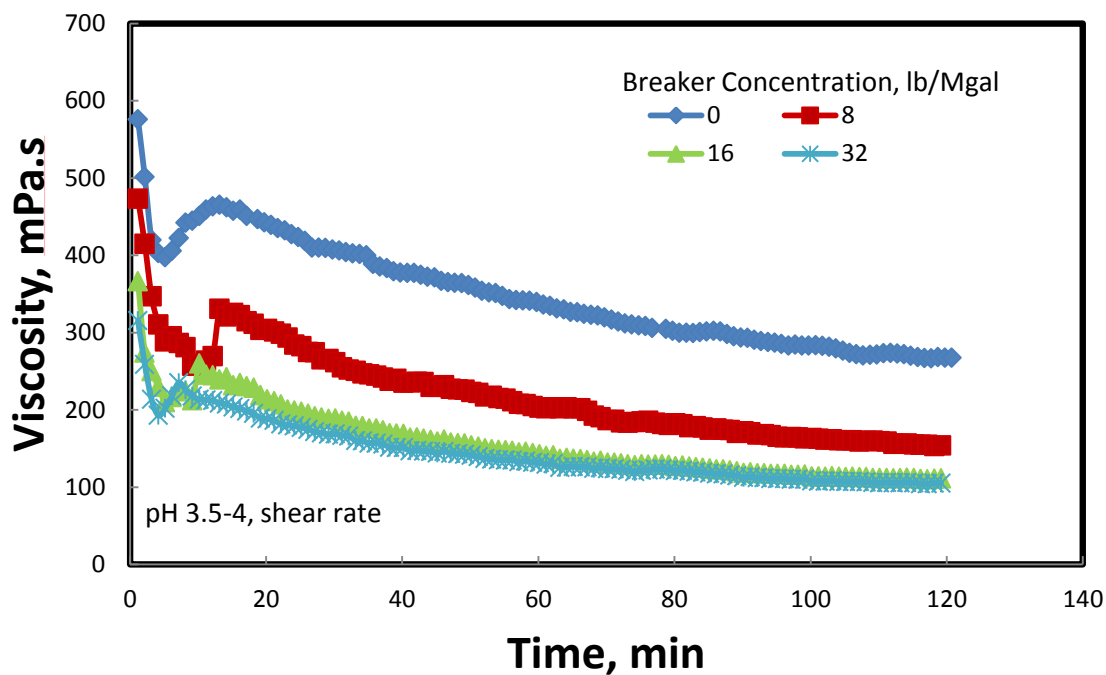


Fig. 2—The effect of breaker concentration on the viscosity reduction of partially neutralized in situ gelled acid as a function of time, 150°F, pH 3.5- 4, 100 s⁻¹ shear rate.

The highest viscosity was achieved when no breaker was added to the acid where viscosity dropped from nearly 500 to 300 mPa.s after 2hrs. This drop in the viscosity was because of shearing the polymer. Most of the polymers used in oil industry degrade by shear rate. However, viscosity reduction with time was increased by increasing the breaker concentration, Fig. 2. Increasing the breaker concentrations from 8 to 16 lb/Mgal reduced the viscosity of in situ gelled acid by almost 50 mPa.s during the first hour. However, during the second hour, the viscosity difference became almost 30 mPa.s. When the breaker concentration was doubled from 16 lb/Mgal to 32 lb/Mgal, the viscosity behavior of the gel did not change much during two hours. This means that 16 lb/Mgal had released enough fluoride ions to react with crosslinker, there is no need to

add more than that. Based on these results, the optimum breaker concentration exists between 8 lb/Mgal and 16 lb/Mgal and there is no need to add more than 16-ppg breaker concentration.

Fig. 3 shows the effect of breaker concentration on the viscosity of in situ gelled acid at 200°F.

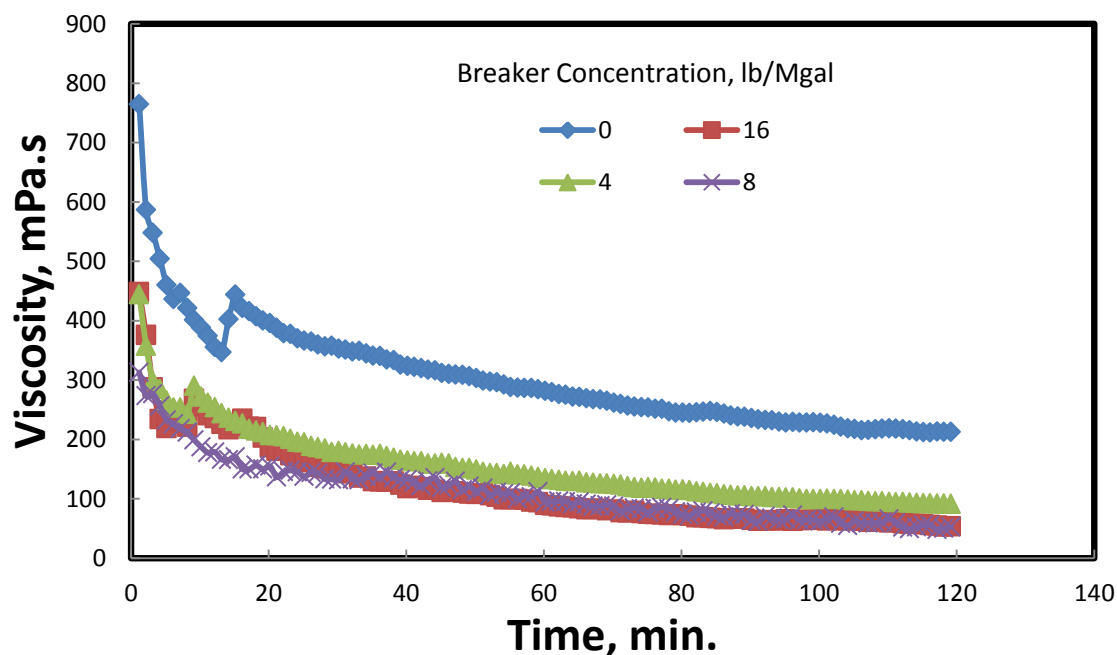


Fig. 3—The effect of breaker concentration on the viscosity reduction of partially neutralized in situ gelled acid as a function of time, 200°F, pH 3.5- 4, 100 s^{-1} shear rate.

It was clear that viscosity decreases with time even when no breaker was added because of the shear environment in the viscometer. As the breaker concentration increased, the viscosity of in situ gelled acid decreased. At any concentration greater than 4, the viscosity drop with time was nearly the same. Therefore, at this condition

there was no need to add more than 4 lb/Mgal of breakers. Compared to Fig. 2, at 200°F, the viscosity difference between adding breaker and without adding breaker is larger than the difference at 150°F. This indicated that the breaking efficiency is higher when increasing temperature.

At 250°F, in situ gelled acid without and with 4 lb/Mgal breaker were both totally broken, **Fig. 4**.

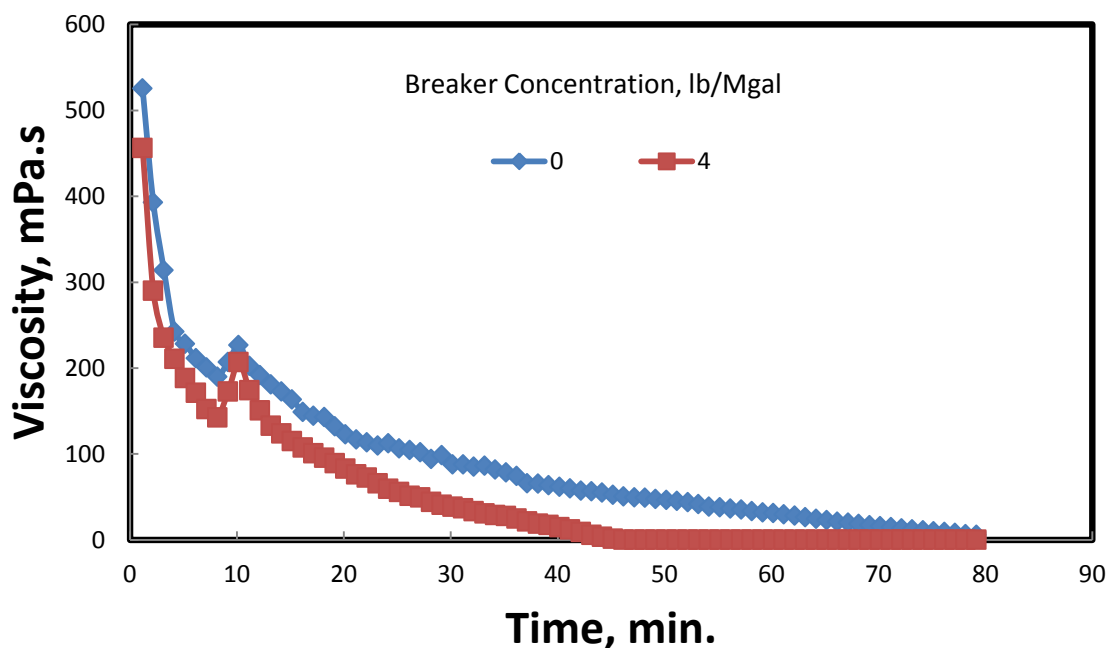


Fig. 4—The effect of breaker concentration on the viscosity reduction of partially neutralized in situ gelled acid as a function of time, 250°F, pH 3.5- 4, 100 s⁻¹ shear rate.

The viscosity of acid with 4 lb/Mgal breaker reached zero after 40 minutes and viscosity of acid without breaker reached zero after 80 minutes. This indicates that adding 4lb/Mgal of breaker reduced the breaking time by nearly 50% at a high

temperature. Based on the results shown in Figs. 2-4, breaker concentration of 16 lb/Mgal was recommended at temperature equal to 150°F, where 4 lb/Mgal of breaker concentration is enough at a temperature higher than 200°F.

Viscosity Measurements—Shear Ramp Environment

In the previous set of experiments (Figs. 2-4), the shear rate environment during the viscosity measurements were constant at 100 s^{-1} . However in the next set of experiments, shear ramps from 0.1 to 1000 s^{-1} were designed at 20, 80 and 140 min during the viscosity measurements, while shear rate was kept at 100 s^{-1} during all other experiments. In situ gelled acid will not flow inside the porous medium at constant shear rate, as there is a difference in diameter between pores and pore throats. Therefore, it was recommended to highlight the effect of shearing the gel during breaking time.

Fig. 5 shows the viscosity reduction of in situ gelled acid with time when no breaker was added to the gel at 150°F. After the first shear ramp at 20 min., the viscosity of the gel was reduced from 340 to 75 mPa.s, while it reduced to 40 mPa.s after the second shear ramp at 80 min. Shearing the gel significantly reduced the viscosity.

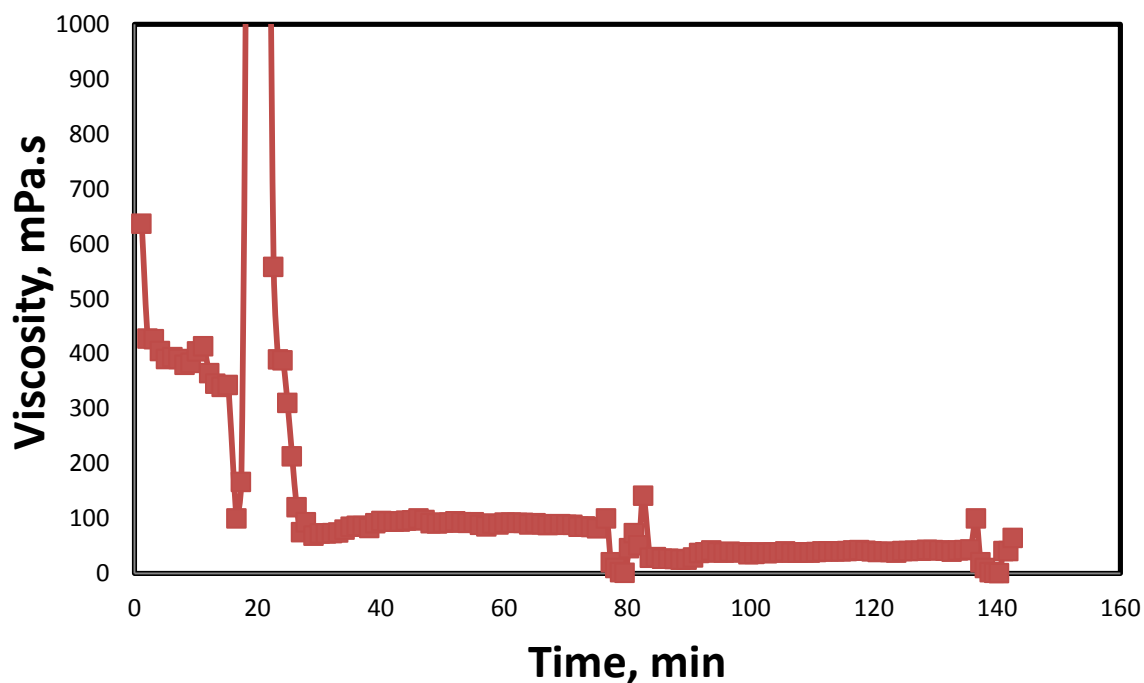


Fig. 5—Viscosity reduction with time and shear ramp of partially neutralized in situ gelled acid at 0 lb/Mgal breaker, 150°F, pH 3.5- 4, 100^{-1} s shear rate.

Fig. 6 shows the viscosity reduction of in situ gelled acid with time when 4 lb/Mgal was added to the gel at 150°F. The viscosity of gel was reduced from 243 to 12 mPa.s after the first shear ramp, while it reduced to zero after 50 min, before the second shear ramp, Fig. 5. By shearing only the gel without adding breaker, the viscosity was reduced by 40% after 2 hrs. The same viscosity reduction was obtained after adding 4 lb/Mgal of solid breaker without shearing, Fig. 2. However, shearing and adding 4 lb/Mgal breaker can completely break the gel after 50 min.

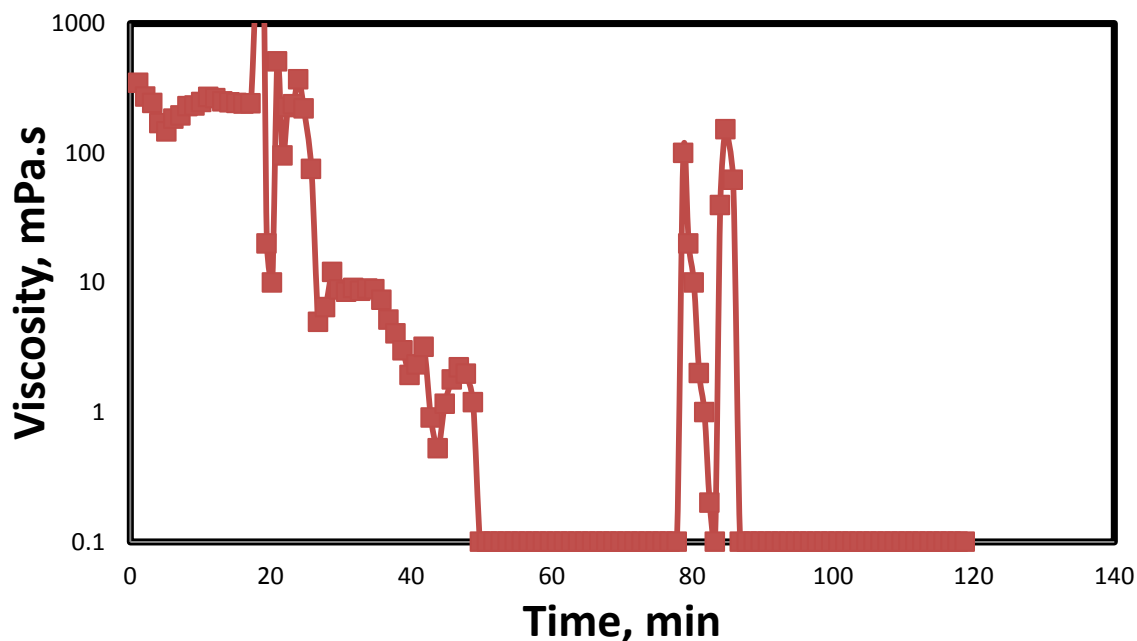


Fig. 6—Viscosity reduction with time and shear ramp of partially neutralized in situ gelled acid at 4 lb/Mgal breaker, 150°F, pH 3.5-4, 100^{-1} s shear rate.

Rheology Measurements

Figs. 7 - 9 plot the elastic and viscous modulus versus time for partially spent acids (pH 3.5) at 150°F and at breaker concentrations of 0, 4, and 8 lb/Mgal, respectively. **Fig. 7** shows that the elastic modulus was dominant over the viscous modulus during the whole experiment. The viscous modulus was mainly 2 Pa while the elastic modulus dropped from 13 to 9 Pa after 120 min. Gomaa and Nasr-El-Din 2010 highlighted that a semisolid elastic behavior was observed when an elastic modulus was dominant. This behavior forced the formed gel to remain inside the formation, causing plugging to the treated area. Therefore a full break was achieved when viscous modulus

will be dominant or the difference between elastic modulus and viscous modulus is negligible.

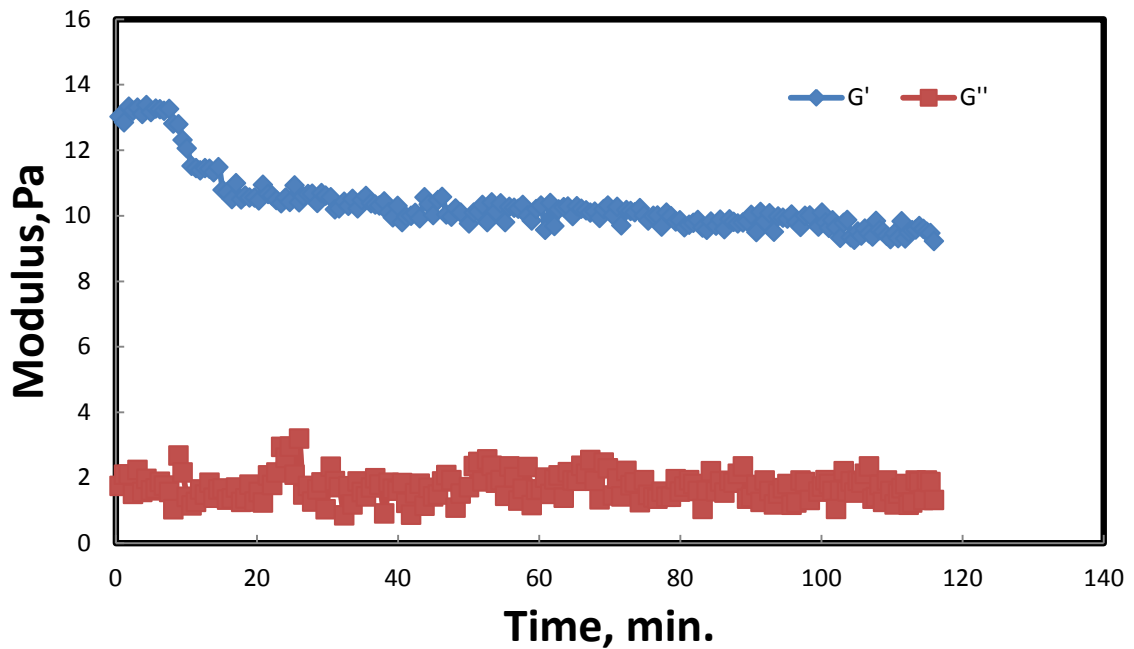


Fig. 7—Elastic and viscous moduli as function of time 0 lb/Mgal breaker, 150°F, pH 3.5-4, 1 HZ frequency.

Fig. 8 shows the elastic and viscous moduli of gel acid at 150°F when 4 lb/Mgal breaker were added to the system. The elastic modulus decreased slightly at first hour and then almost kept constant at the end of the experiments. No breaking was observed when 4 lb/Mgal was used at 150°F.

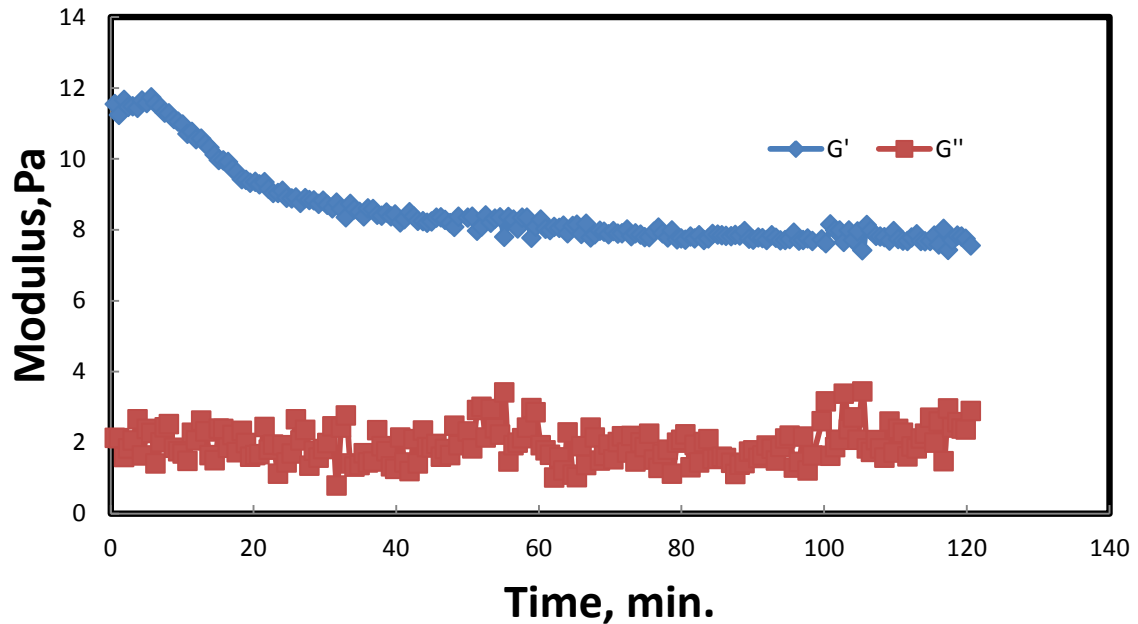


Fig. 8—Elastic and viscous moduli as function of time 4 lb/Mgal breaker, 150°F, pH 3.5-4, 1 HZ frequency.

Fig. 9 shows the elastic and viscous moduli as a function of time when 8 lb/Mgal breaker concentration was applied to the system at 150°F. Viscous modulus increased and elastic modulus decreased during the first 20 min, almost kept constant during the remaining time. Compared with Fig. 7 and 8, the difference between the viscous modulus and the elastic modulus when 8 lb/Mgal was used was much smaller than when 0 and 4 lb/Mgal breaker concentration was used. So the liquid-like property of acid gel is more obvious. This indicated that solid breaker became more effective by increasing the breaker concentration.

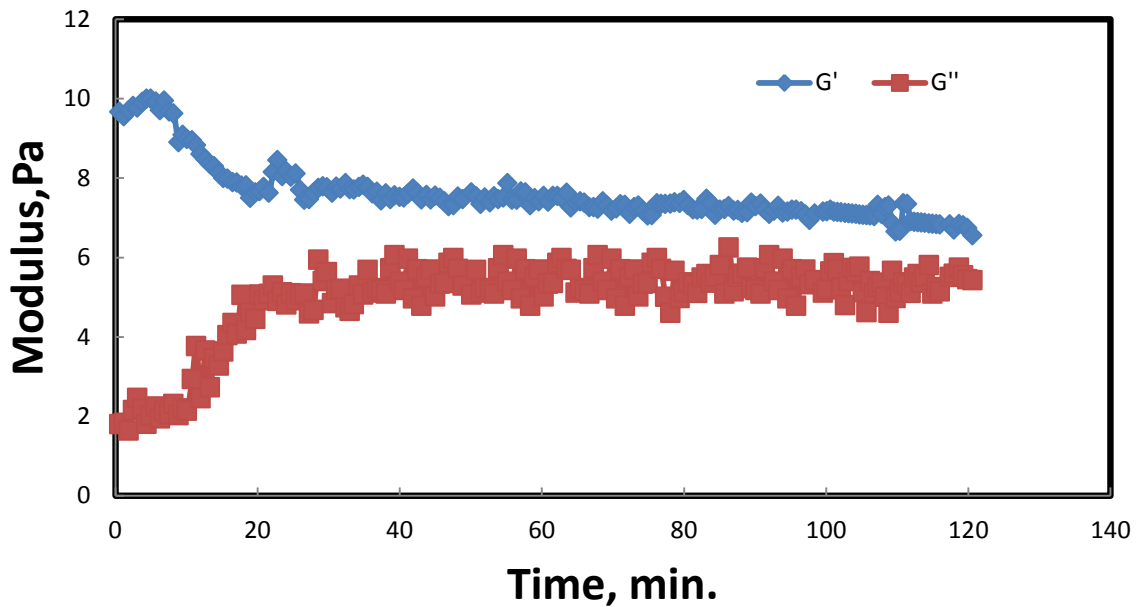


Fig. 9—Elastic and viscous moduli as function of time 8 lb/Mgal breaker, 150°F, pH 3.5-4, 1 HZ frequency.

Fig. 10 and **Fig. 11** show the effect of the breaker concentration on the elastic and viscous moduli, respectively. As the breaker concentration increased, the elastic modulus decreased while the viscous modulus was increased. This confirms the breaking efficiency of the gel was increased by increasing the breaker concentration.

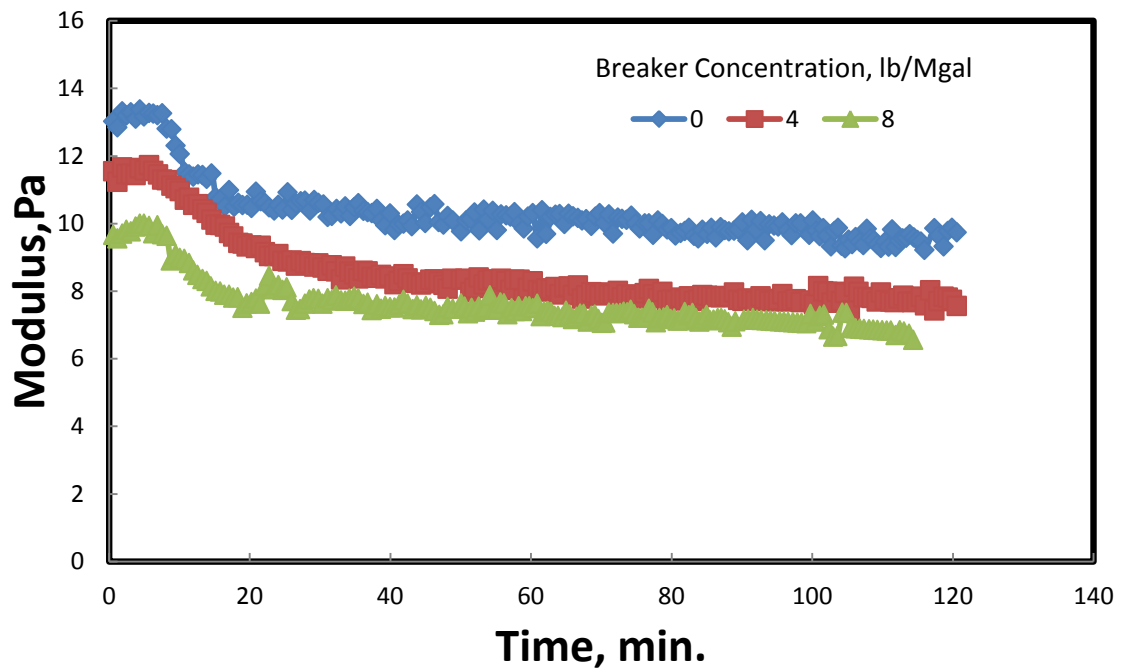


Fig. 10—Elastic modulus as function of time for 0, 4, and 8 lb/Mgal breaker, 150°F, pH 3.5-4, 1 HZ frequency.

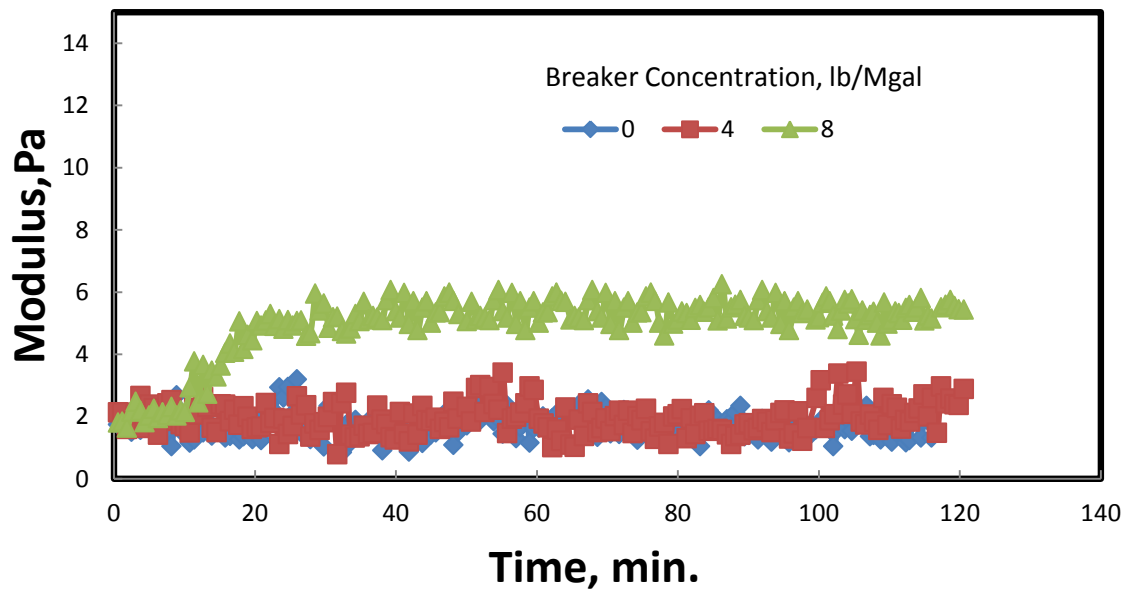


Fig. 11—Viscous modulus as function of time for 0, 4, and 8 lb/Mgal breaker, 150°F, pH 3.5-4, 1 HZ frequency.

Fig. 12 shows the behavior of viscous and elastic moduli without breaker at 200°F. Both the elastic modulus and viscous modulus decreased during the first 20 min. The elastic modulus decreased from 11 to 8 Pa, while the viscous modulus decreased from 2 to 1 Pa in this period of time. For the remaining time, both elastic modulus and viscous modulus almost kept constant with a 7 pa difference.

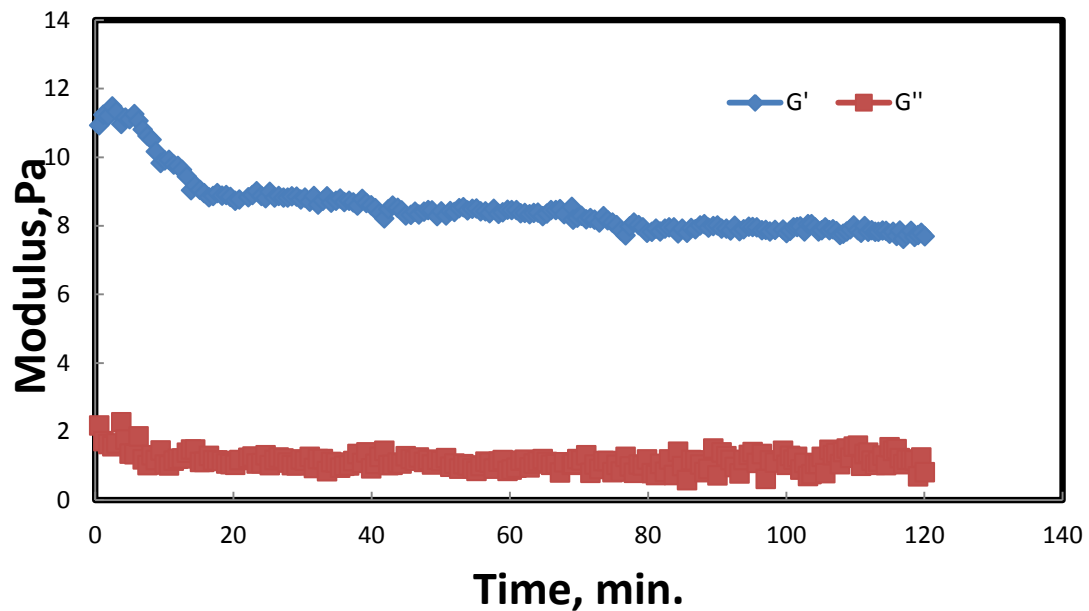


Fig. 12—Elastic and viscous moduli as function of time 0 lb/Mgal breaker, 200°F, pH 3.5-4, 1 HZ frequency.

Fig. 13 shows the modulus behavior with 4 lb/Mgal breaker at 200°F. During 120 min., the elastic modulus decreased from 10 to 6 Pa, while the viscous modulus was almost constant at 2 Pa. Compared to Fig. 12, the difference between the elastic modulus and the viscous modulus becomes less by 3 Pa when 4 lb/Mgal were used.

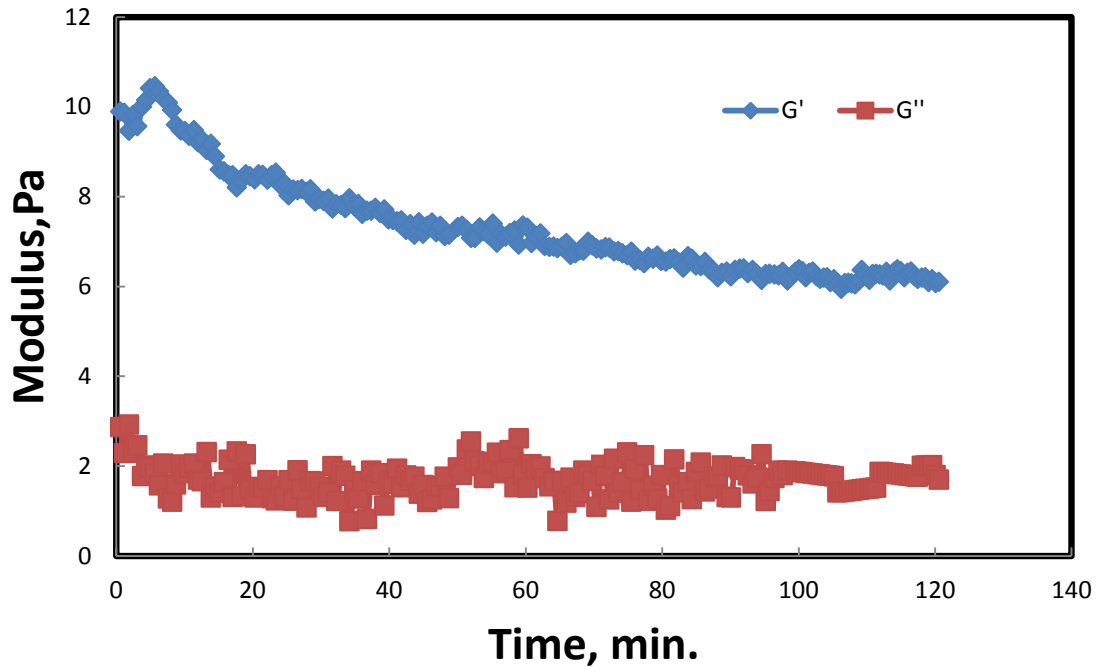


Fig. 13—Elastic and viscous moduli as function of time 4 lb/Mgal breaker, 200°F, pH 3.5-4, 1 HZ frequency.

Fig. 14 shows the elastic and viscous moduli when 8 lb/Mgal breaker were applied at 200°F. The elastic modulus almost kept around 6 Pa while the viscous modulus kept around 5 Pa. Increasing the breaker concentration allowed the gel to break more. Based on the rheological properties measurements, it is recommended to use 8 lb/Mgal at 200°F not 4 lb/Mgal as it was shown by viscosity measurements.

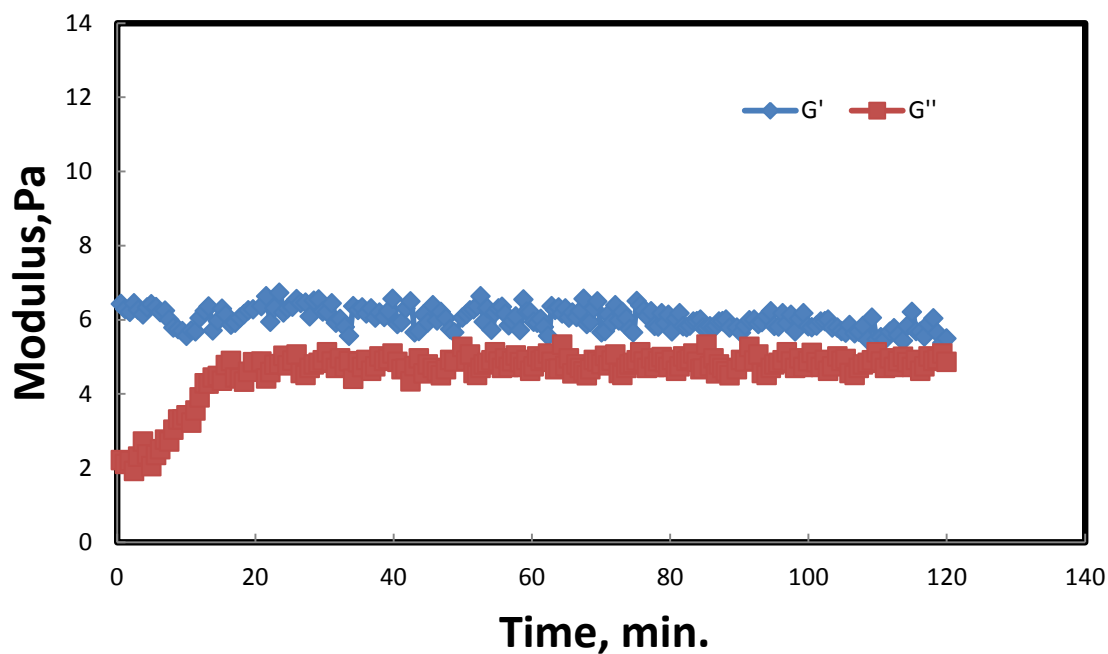


Fig. 14—Elastic and viscous moduli as function of time 8 lb/Mgal breaker, 200°F, pH 3.5-4, 1 HZ frequency.

Fig. 15 shows the elastic modulus of partially neutralized in situ gelled acid as function of time for 0, 4, and 8 lb/Mgal breaker at 200°F. At the first 20 minutes, the elastic modulus of the acids with 0 ppg and 4 ppg had the same trend and they were almost the same. For the acid with 8 ppg, the elastic modulus did not change with time and it stayed around 6 Pa. After 20 minutes, the elastic modulus of the acid without breaker stopped decreasing, but acid with 4 ppg, the elastic modulus still decreased slightly. At the end of two hours, it decreased to 6 Pa and had the same modulus with the acid with 8 ppg. During the whole time, the acid with 8-ppg breaker concentration stayed the same around 6 ppg and did not change much.

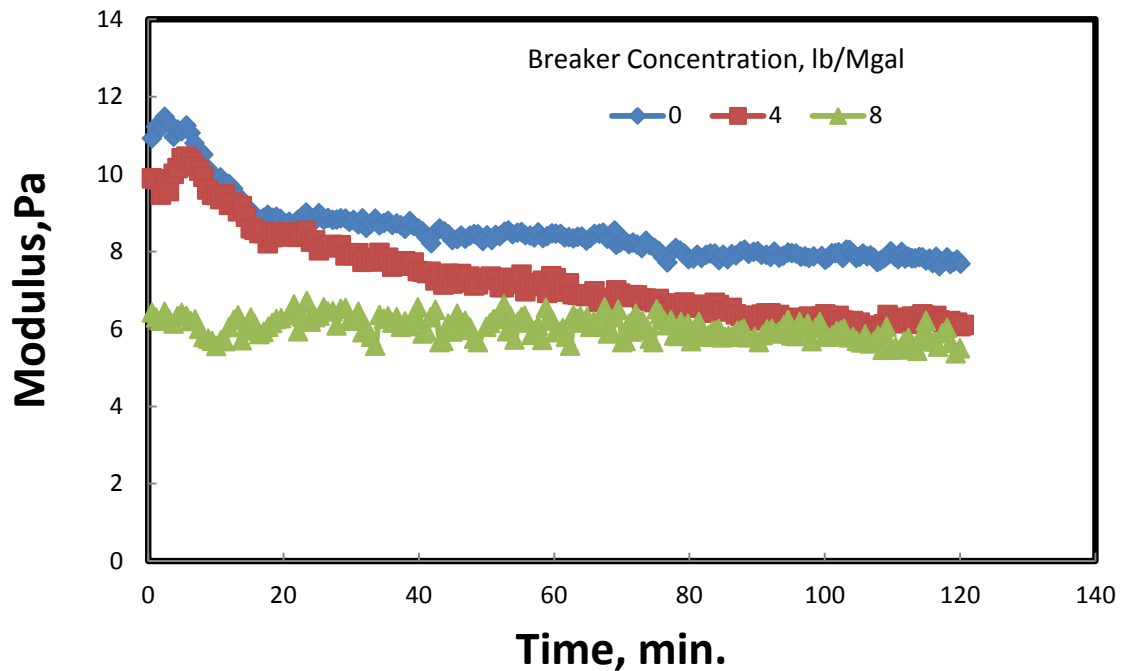


Fig. 15—Elastic modulus as function of time for 0, 4, and 8 lb/Mgal breaker, 200°F, pH 3.5-4, 1 HZ frequency.

Fig.16 shows the viscous modulus of partially neutralized in situ gelled acid as function of time for 0, 4, and 8 lb/Mgal breaker at 200°F. During the whole time, although there was small decreasing trend at the first 10 minutes, the viscous modulus of the acid with 0 ppg was around 1 Pa and the viscous modulus of the acid with 4 ppg was around 2 Pa. For the acid with 8-ppg breaker concentration, the elastic modulus stayed around 2 Pa during the first 10 minutes, then it increased from 2 Pa to 4 Pa during 10 minutes to 20 minutes. After 20 minutes, the viscous modulus stayed around 4 Pa. This means that 8-ppg breaker concentration made the fluid property of in situ gelled acid more obvious.

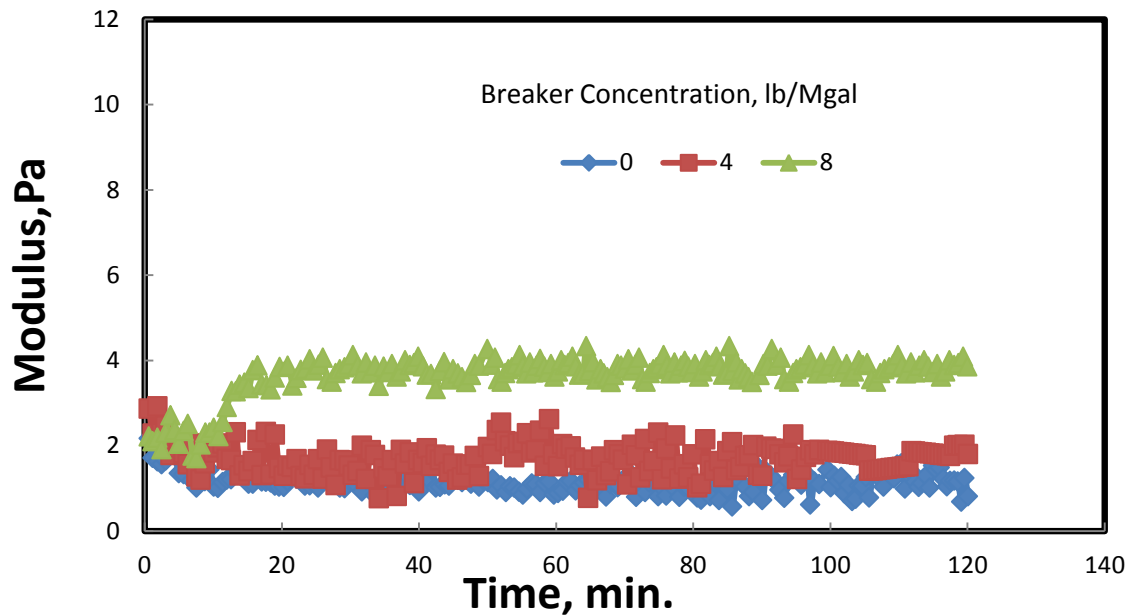


Fig. 16—Viscous modulus as function of time for 0, 4, and 8 lb/Mgal breaker, 200°F, pH 3.5-4, 1 HZ frequency.

Fig. 17 shows the viscous and elastic moduli during the breaking of gel at 250°F without breaker. The elastic modulus decreases for the first 25 min to 4.5 Pa and the viscous modulus stays around 1 Pa. The difference between elastic and viscous moduli is 3.5 Pa. There is no indication that the gel was broken.

Fig. 18 shows the modulus behavior after adding 4 lb/Mgal breaker. The elastic modulus is dominant at first 10 min only, then it decreased to nearly zero, while the viscous modulus goes up to 5 Pa. Gel changes from a solid-like material to liquid-like material. This means that 4 lb/Mgal at 250°F was enough to fully break the gel. This agrees with what was shown with the viscosity measurements.

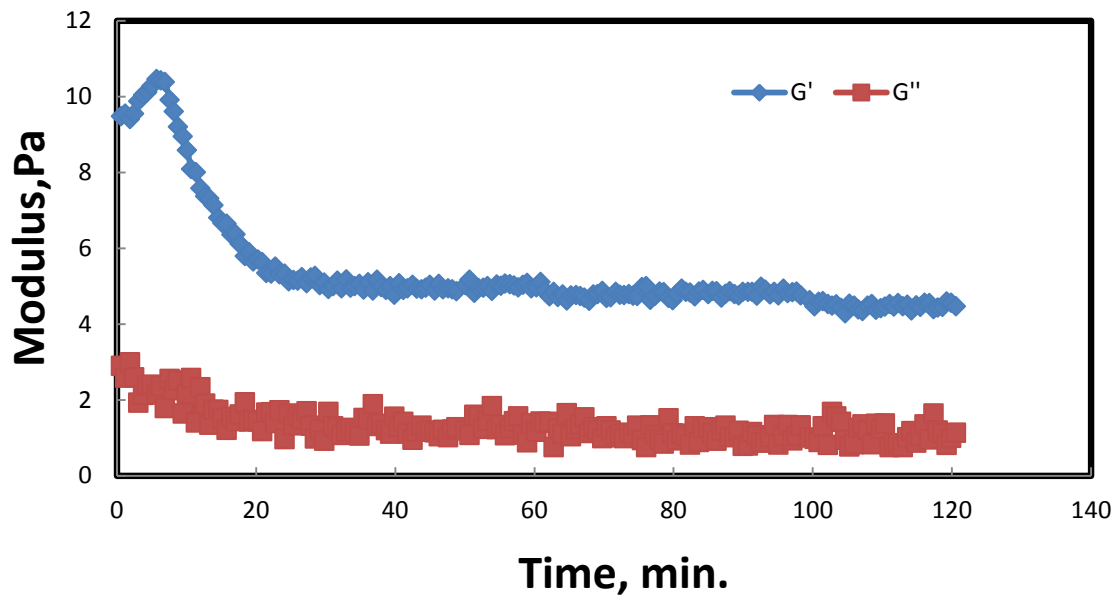


Fig. 17—Elastic and viscous moduli as function of time 0 lb/Mgal breaker, 250°F, pH 3.5-4, 1 HZ frequency.

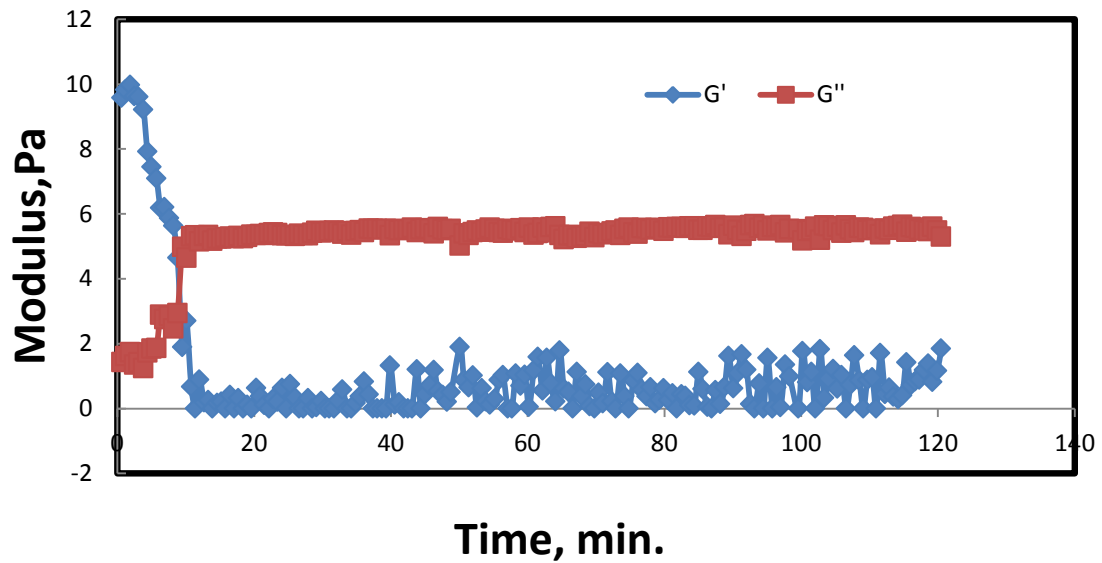


Fig. 18—Elastic and viscous moduli as function of time 4 lb/Mgal breaker, 250°F, pH 3.5-4, 1 HZ frequency.

Fig. 19 shows the elastic modulus of partially neutralized in situ gelled acid as function of time for 0, 4, and 8 lb/Mgal breaker at 250°F. The elastic modulus of in situ gelled acid decreased from 10 Pa to 5 Pa during the first 30 minutes and then it stayed around 5 Pa from 30 minutes to 120 minutes. For the acid with 4-ppg breaker concentration, the elastic modulus decreased from 10 Pa to 0 Pa at the first 10 minutes and then kept around 0 Pa from 10 minutes to 120 minutes. This means that after 10 minutes, there was not a solid-like property for the in situ gelled acid with 4-ppg breaker concentration. This means that 4-ppg breaker concentration could eliminate the in situ gelled acid's solid-like property.

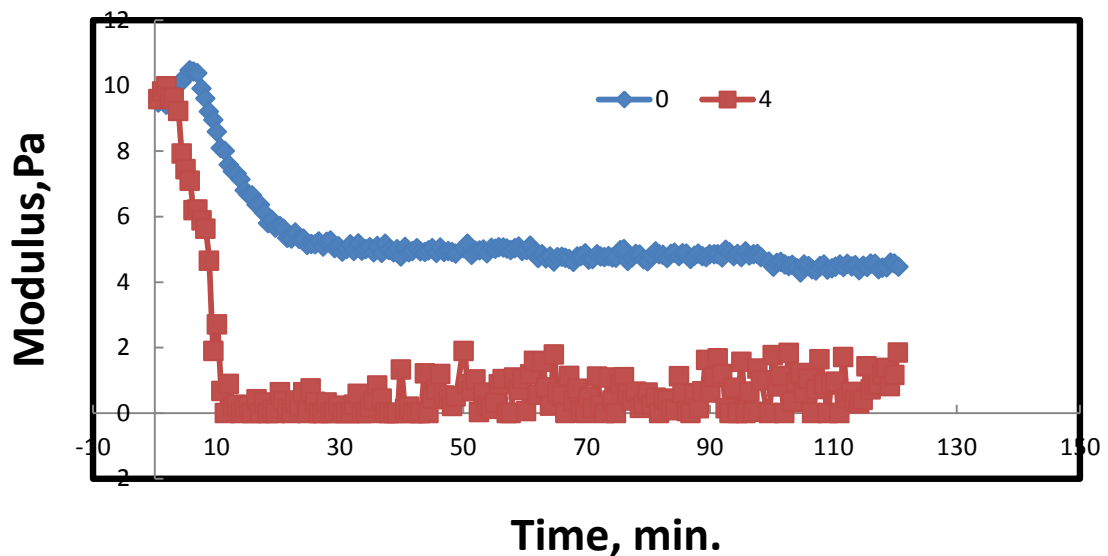


Fig. 19—Elastic modulus as function of time for 0, 4, and 8 lb/Mgal breaker, 250°F, pH 3.5-4, 1 HZ frequency.

Fig. 20 shows viscous modulus of partially neutralized in situ gelled acid as function of time for 0, 4 and 8 lb/Mgal breaker at 250°F. For the acid without breaker, the viscous modulus decreased from 3 Pa to 1Pa during the first 20 minutes and then it almost stayed the same. For the acid with 4-ppg breaker, the viscous modulus increased from 1.5 Pa to 5.5 Pa at the first 10 minutes and then stayed around that value until the end of experiment. There was almost 4 Pa viscous modulus difference for the acid with 4-ppg and 0-ppg breaker concentrations. 4-ppg breaker could make the in situ gelled acid became more fluid like at 250°F.

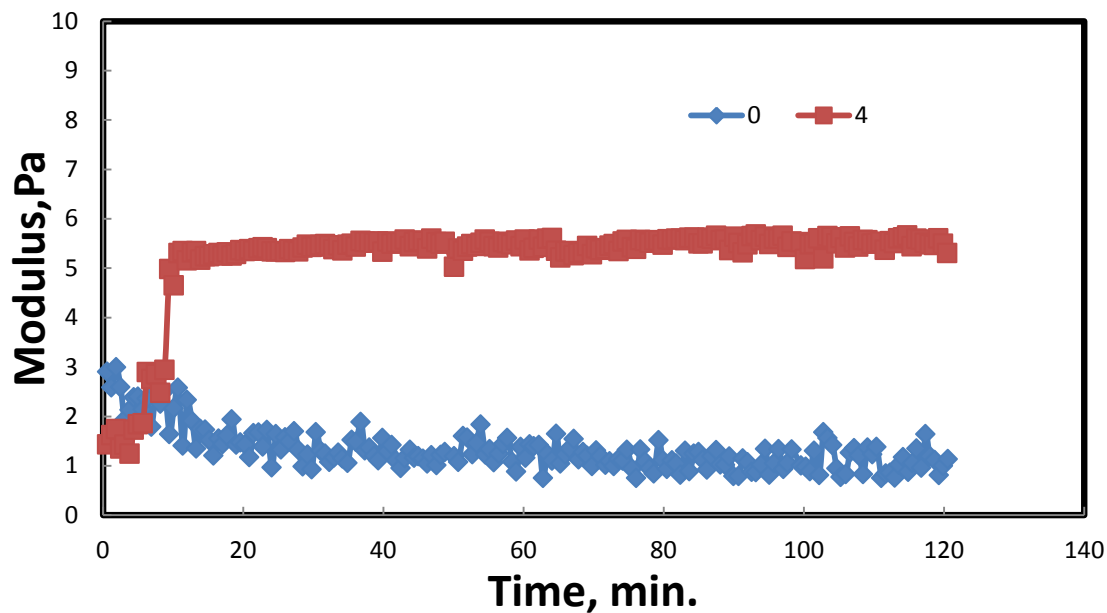


Fig. 20—Viscous modulus as function of time for 0, 4, and 8 lb/Mgal breaker, 250°F, pH 3.5-4, 1 HZ frequency.

Viscosity Test With Different pH Values

Fig. 21 shows the viscosity measurement at different pH values without and with 4 lb/Mgal breaker. The temperature was set at 200°F. At pH values less than 2, there was not much difference in viscosity between the acid systems which were made with and without the breaker. However, at pH greater than 2, viscosity was less by 90 mPa.s for the system that has 4 lb/Mg breaker. This means that breaker began to break the crosslinked gelled acid at pH greater than 2. This can significantly affect the diversion ability of the acid. As there will be less viscosity at the diversion pH period (pH from 2 to 4).

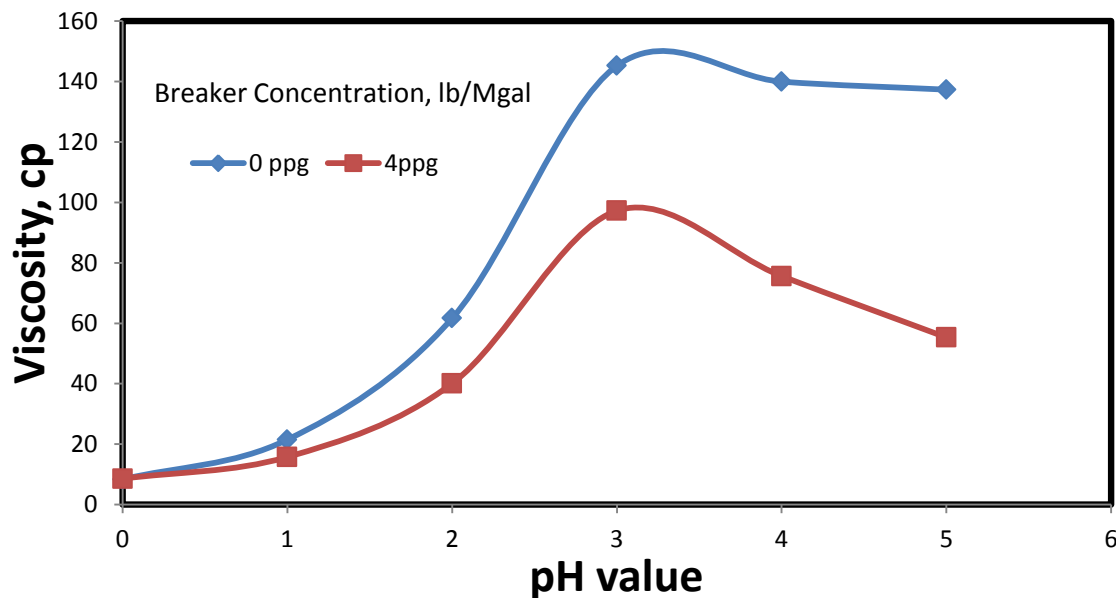


Fig. 21—Viscosity as a function of equilibrium pH value for in situ gelled acid at 0 and 4 lb/ Mgal, 200°F, 100 s⁻¹.

CHAPTER IV

FILTRATION EXPERIMENT

In situ gelled acids that are based on polymers have been used in the field for several years as an acid diversion agent. Recent studies have indicated that there was always gel left inside the formation during the flowback of spent acid. This will reduce permeability and cause formation damage. The objective of this study is to assess in detail the flowback of the spent acid and the core damage induced by it. At the same time, the breaking mechanism of solid breaker would also be researched.

Experimental studies were conducted using polymer-based in situ gelled acids that use Zr as a crosslinker agent. A novel coated solid breaker was examined in this experiment. An HPHT filter press was used to simulate the flowback of the spent acid. Viscosity measurements were used to determine the degree of gel degradation. Carbonate cores that had a 2.5 in. diameter and 0.25 in. thickness were used. Temperature (75 to 250°F) and breaker concentrations (0 to 16 lb/Mgal) were the main parameters that were investigated in this study.

Experimental results showed that there was always a gel left inside the rock. This gel can cause permeability reduction. Time needed to flowback the solution decreased by 50% when the temperature was increased from 150 to 200°F, while it decreased by only 30% when the breaker concentration was doubled. At 150°F, 16-ppg breaker concentration was recommended for breaking the gel. At higher temperature (>150°F), 8-ppg breaker concentration was enough to help with degrading the gel. This

paper will discuss the results obtained in the lab, and recommend at what conditions polymer-based in situ gelled acid can be used in the field with minimum damage.

Materials

Hydrochloric acid (ACS reagent grade) titrated using a 1N sodium hydroxide solution to determine its concentration, and was found to be 36.8 wt%. All acid solutions were prepared using deionized water with a resistivity of 18.2 M Ω .cm at room temperature. Polymer and other additives were all oilfield chemicals, and were used without further purification.

Indiana limestone (2.25 inch in diameter and 0.25 inch in thickness) was used to simulate the formation at different temperatures and pressures.

Measurements

1. Filtration measurements of partially spent acids were made using an HTHP filtration cell at temperature range of 75-250°F and 100psi.
2. Viscosity measurements of filtrated acids were made using HTHP viscometer at room temperature and 300 psi. To resist corrosion by acids, both the rotor (R1) and the bob (B1) of the viscometer were made of Hastelloy C. The viscosity was measured as a function of shear rate (from 0.1 to 1000 s⁻¹). pH values were measured using 950 ROSS FASTQC.

Procedures

Table 1 lists the formulae of the in situ gelled acid system examined in the present work. In situ gelled acids contained acid, a polymer, a cross-linker, a breaker, and a corrosion inhibitor. The study included three types of experiment setups: The first one is to investigate the filtration volume of spent acid as a function of time and find its damage to the core. In this set of experiments, the effect of temperature (75-250°F) and breaker concentration (0-16 lb/Mgal) were used on the breaking of partially neutralized in situ gelled acid (pH 3.5-4). The following procedures were used:

1. The acid solution was prepared by adding polymer, crosslinker, buffer to water based on the concentration shown in Table 1. A magnetic stirrer was used to mix the acid solution.
2. The pre-determined volume of HCl was neutralized calcium carbonate powder to pH 0-1.
3. The partially neutralized HCl was added to the mixing solution shown in the first step and mix them together for 10 minutes. The final pH values was around 3.5-4.
4. The initial permeability of the core was measured by using water at 60 psi and room temperature, the diameter of the core 2.25 inch and the thickness of the core is 0.25 inch.
5. A filtration test was made by adding prepared spent acid into cell and then set the temperature (75°F-250°F) and pressure (100 psi). Leave it for one hour and then record the filtration volume and

filtrated acid would be collected.

6. Filtration test with internal gel was made by using water at last at 60 psi.

The second set of the experiments investigated the apparent viscosity of filtrated in situ gelled acid. The following procedures were used:

1. Leave the filtrated gel acid to room temperature and then dump it into the cell of viscometer.
2. The pressure is set at 300 psi and temperature is 75°F.
3. The shear rate is set at 0.1, 0.3, 0.5, 0.7, 1, 3, 5, 7, 10, 30, 50, 70, 100, 300, 500, 700, 1000 s⁻¹.

Results and Discussion

Darcy's Law for Filtration Test

Darcy law equation is applied in calculating initial permeability of the core K1, overall permeability with external gel K2 and permeability with internal gel K3.

$$Q = \frac{-KA \Delta P}{\mu \Delta L} \dots\dots\dots (1)$$

Q = flow rate, cm³/s

A = cross-sectional area to flow, cm²

K = permeability, darcy

μ = fluid viscosity, mPa.S

ΔP = Applied pressure difference, atm/cm

ΔL = thickness of the medium, cm

In this experiment, 60 psi is applied when measuring the permeability of the Indiana limestone (2.25 inch×0.25 inch) using DI water at room temperature.

$$\text{So } A = \pi \times \left(\frac{2.25 \text{ inch} \times 2.54 \text{ cm / inch}}{2} \right) \times 2 = 25.65 \text{ cm}^2$$

$$\mu = 0.89 \text{ cp}$$

$$\Delta L = 0.635 \text{ cm}$$

Permeability Test

Table 2 shows the initial permeability of Indiana limestone and permeability after removing surface gel. The initial permeability of selected limestone are almost the same. Permeability for all limestone is around 40 md.

Permeability for limestone after removing surface gel was tested with distilled water. At 150°F, when the concentration of solid breaker increased from 4 ppg to 16 ppg, permeability increased from 6.25 md to 19.35 md. The permeability increased 300% after adding more solid breaker. This means that there were less amount of gel left inside limestone, more in situ gelled acid had already been broken by solid breaker. At 200°F, when the concentration of solid breaker increased from 4 ppg to 16 ppg, permeability increased from 24.39 to 28.32. The effect of solid breaker at 200°F was not as obvious as it was at 150°F. This was because viscosity of in situ gelled acid decreased obviously at higher temperature even without breaker. At 250°F, when the concentration of solid breaker increased from 4 ppg to 16 ppg, permeability increased from 30.6 md to 32.4 md. So permeability after using different breaker concentrations are almost the same at 250°F. At 150°F, breaker concentration increase from 4 ppg to 16 ppg resulted on 300%

permeability increase. At higher temperature (200°F and 250°F), temperature increase had more positive effects on reducing internal damage than breaker concentration increase.

Table 2—Initial permeability test for limestone and permeability test after removing surface gel.

room temperature	Initial Permeability k1(darcy)	Permeability after removing gel k3(Darcy)
150F,4ppg	0.040675404	0.006250518
150F,8ppg	0.038844049	0.016684242
150F,16ppg	0.038539465	0.019350698
200F,4ppg	0.042371821	0.024397533
200F,8ppg	0.038863326	0.025531046
200F,16ppg	0.040752516	0.028327047
250F,4ppg	0.040428655	0.030604869
250F,8ppg	0.039807921	0.030928731
250F,16ppg	0.040212747	0.032456275

Table 3 shows the internal damage percent caused by gel left inside limestone.

Damage percent= $1 - \text{permeability after removing gel} / \text{initial permeability of Indiana limestone}$

At 150°F, when the concentration of breaker increased from 4 ppg to 16 ppg, damage percent decreased from 84.6% to 49.7%, more amount of in situ gelled acid had been degraded. At 200°F, it decreased from 42.4% to 30.5% and at 250°F it decreased from 24.3% to 19.4%. So at 200°F and 250°F, damage percent reduction with breaker concentration increase was not obvious as it was at 150°F. Damage percent reduced by 50% when temperature was increased from 150°F to 200°F and 43% reduction when

temperature was increased from 200°F to 250°F. Temperature effect was more obvious than breaker concentration effect at higher temperature.

Table 3—Damage percent caused by internal gel

	Damage percent caused by gel
150F, 4ppg	0.846331748
150F, 8ppg	0.57048139
150F, 16ppg	0.49789916
200F, 4ppg	0.424203822
200F, 8ppg	0.343055556
200F, 16ppg	0.304900662
250F, 4ppg	0.242990654
250F, 8ppg	0.223050847
250F, 16ppg	0.192885906

Filtration Experiment—Effect of Breaker Concentration and Temperature

Fig. 22 compares filtration rates of partially neutralized in situ gelled acid at 150°F with 4-ppg breaker concentration and without breaker concentration. It showed that at the beginning of filtration period until 1.7 minutes, the flow rates of gelled acids without breaker and with 4-ppg breaker are almost the same. But after that, as more fluids were filtrated through the rock, the flow rate of acid with 4-ppg breaker decreased because a layer of gel was formed at the surface of the rock. This layer of gel would reduce permeability of rock so the filtration rate was affected. But this change was not obvious compared with gelled acid without breaker. The filtration rate of acid without breaker became slower after 1.7 minutes and it almost stopped at 2.2 minutes. The leak

rate was small and finally there were only 65 cm³ filtration fluid out of 130 cm³. This was because that high viscosity acid could form a thicker layer of gel at the surface of rock and there was gel residue inside Indiana limestone. This would block the rock and such cause serious damage.

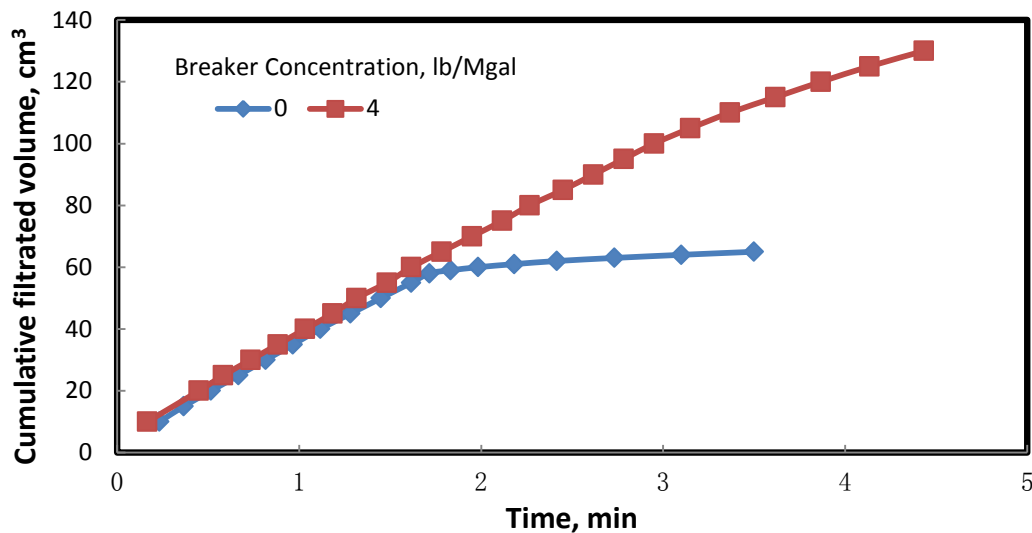


Fig. 22—The effect of 4 ppg and 0 ppg breaker concentration on the filtration rate of partially neutralized in situ gelled acid, 150°F, pH 3.5-4.

Fig. 23 shows the effect of breaker concentration on the filtration rate of partially neutralized in situ gelled acid at 150°F. When the breaker concentration was increased from 4 ppg to 8 ppg, the filtration time decreased from 4 minutes to 2.7 minutes and when the breaker concentration was increased from 8 ppg to 16 ppg, the filtration time

decreased from 2.7 minutes to 2.06 minutes. Although the filtration time change with breaker concentration increase was not linear, filtration rate increase was obvious.

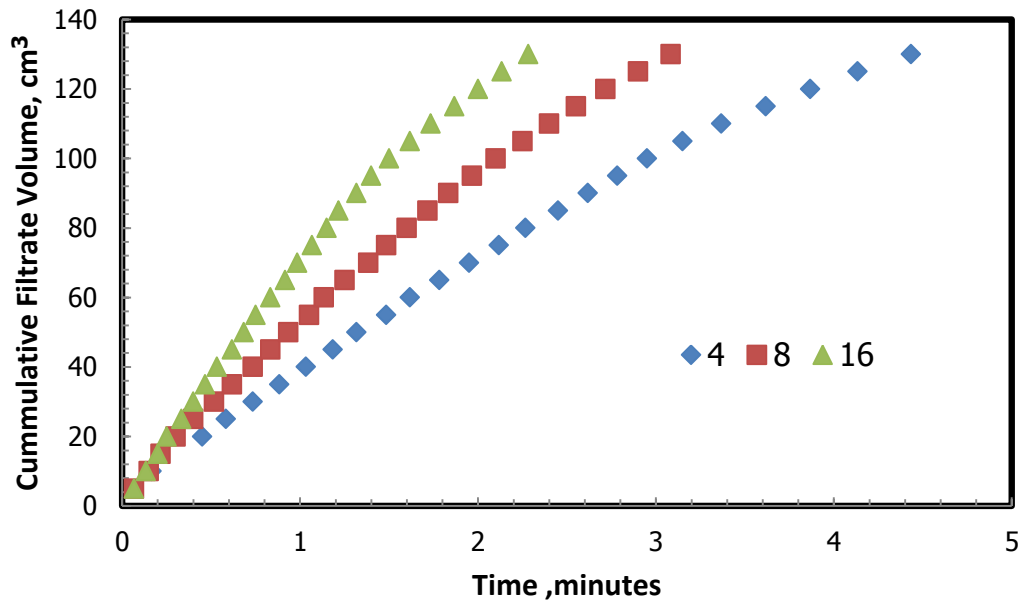


Fig. 23—The effect of breaker concentration on the filtration rate of partially neutralized in situ gelled acid, 150°F, pH 3.5- 4.

Fig. 24 shows the effect of breaker concentration on the filtration rate of partially neutralized in situ gelled acid at 200°F. Compared with figure.23, the time for in situ gelled acid to flow through Indiana limestone became much shorter. This means that high temperature helps degrading in situ gelled acid. At 200°F, the time reduction was within one minute when breaker concentration was doubled. For breaker concentration of 8 ppg and 16 ppg, they almost had the same time of filtration. This indicated that at

200°F, when certain amount of breaker was added (8ppg), the gel had already been fully degraded and there was no need to add more breaker.

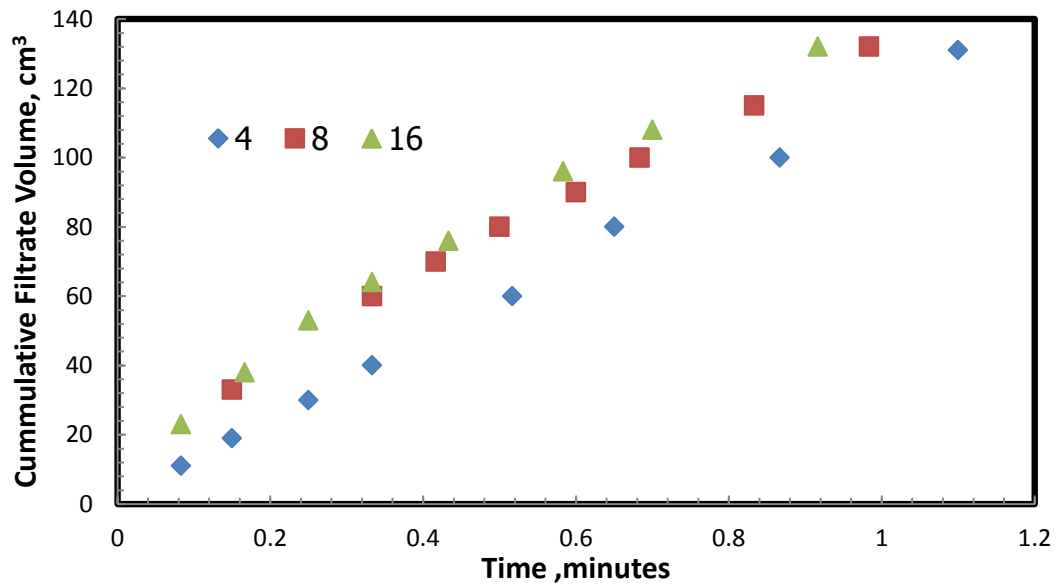


Fig. 24—The effect of breaker concentration on the filtration rate of partially neutralized in situ gelled acid , 200°F, pH 3.5- 4.

Fig. 25 shows the effect of breaker concentration on the filtration rate of partially neutralized in situ gelled acid at 250°F. Although there were slight differences on filtration time between different breaker concentrations, they almost stayed around 40 seconds. Compared with Fig. 23 and Fig. 24, there are obvious time reduction. As the temperature increased, the effect of breaker concentration became less important. Because high temperature can reduce viscosity of in situ gelled acid.

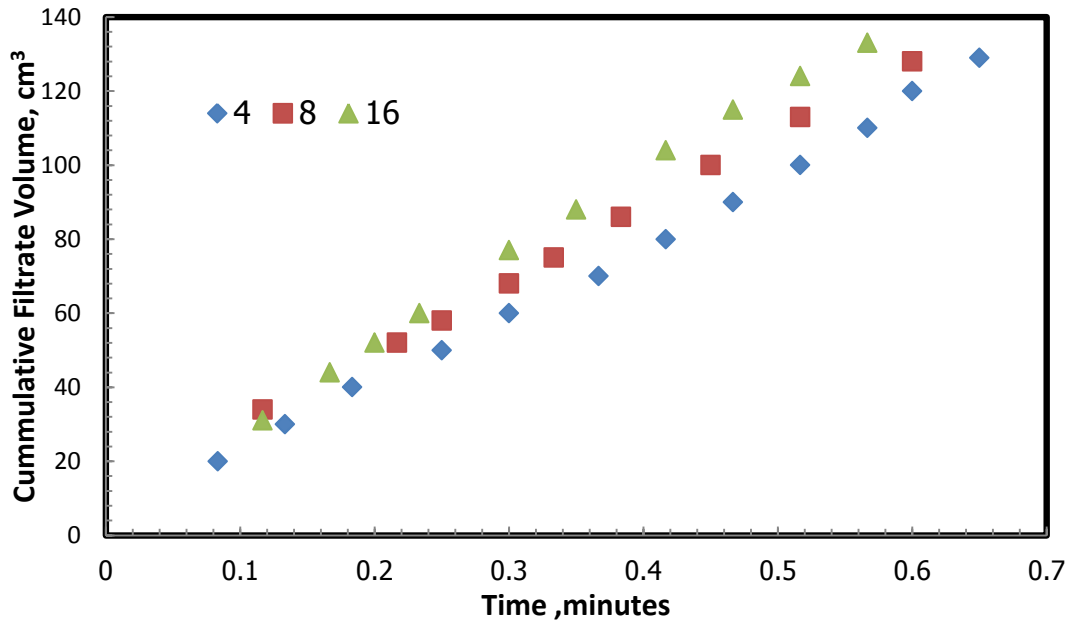


Fig. 25—The effect of breaker concentration on the filtration rate of partially neutralized in situ gelled acid, 250°F, pH 3.5- 4.

Fig. 26 shows the effect of pH values on the filtration rate of in situ gelled acid at 200°F with 4-ppg breaker concentration. The pH values were set at 2, 4, and 5. This figure showed that at pH =4 and pH=5, the filtration rates were almost the same. But at pH=2, the total time for all the in situ gelled acids flowing out of cell reduced from 1.1 minutes to 0.9 minute. At high temperature and high permeability conditions, this reduction could not be neglected. This means that the viscosity of in situ gelled acid at pH value 2 has a lower viscosity that it at pH value 4 or 5. At pH value 2, the viscosity was higher than fresh acid, but it still did not reach the viscosity buildup point.

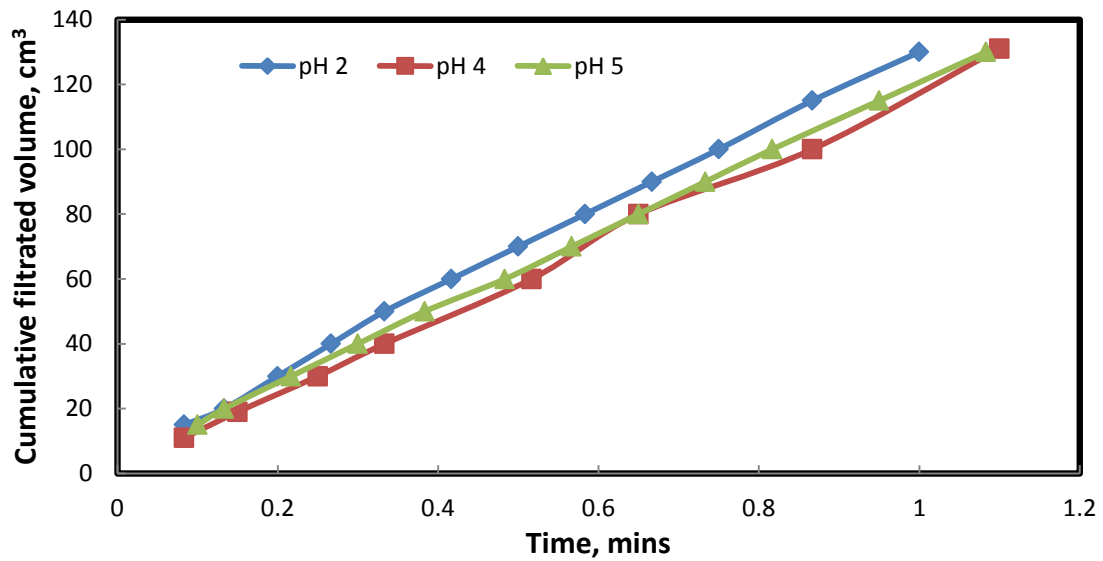


Fig. 26—The effect of pH values on the filtration rate of in situ gelled acid , 200°F, 4ppg.

Viscosity Measurement of Filtrated Fluid—Effect of Breaker Concentration at Different Temperatures

Fig. 27 shows the viscosity measurement of in situ gelled acid at room temperature before and after filtration tests at 150°F without any breaker. Usually, when the acid flew through the rock, because the flow rate was relatively high, there was a shearing force which will cut the high viscosity gel. This would reduce the viscosity of in situ gelled acid. From this figure, although there was a reduction in viscosity after filtration test, the difference was not big. This means that shearing force at this condition would not have big effect on the viscosity of in situ gelled acid.

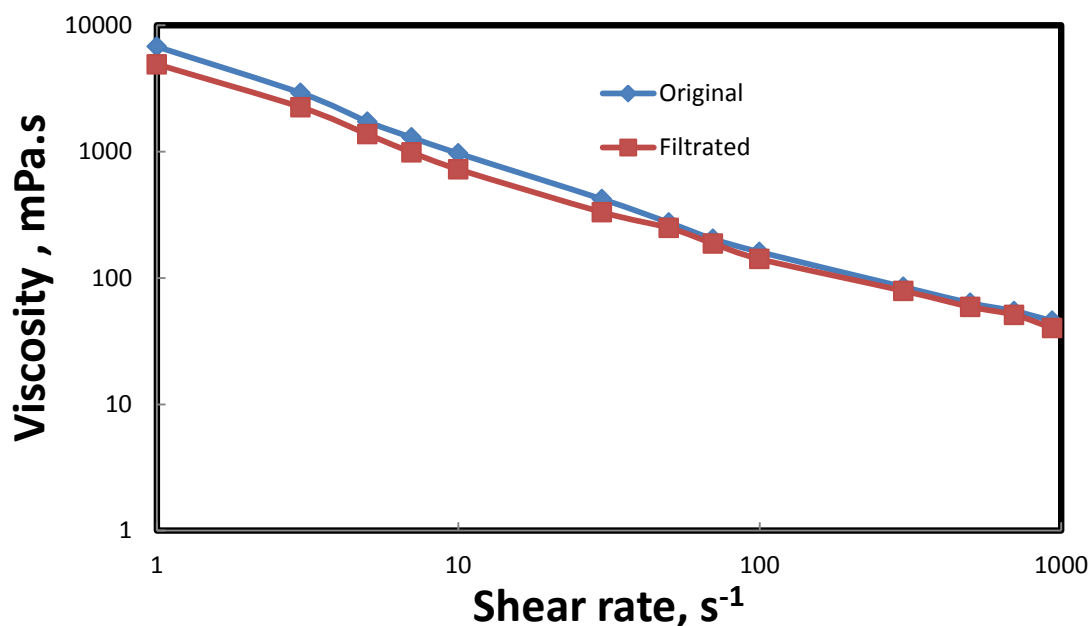


Fig. 27—Viscosity measurement of filtrated in situ gelled acid at room temperature before and after filtration tests at 150°F, 0ppg.

Fig. 28 shows the viscosity measurement of filtrated in situ gelled acid with different breaker concentrations after filtration test at 150°F. They were compared with initial prepared in situ gelled acids with crosslinker and without crosslinker. This figure indicated that viscosity of filtrated in situ gelled acid with 4 ppg, 8ppg and 16ppg breaker concentration all located between viscosity of initial acid with crosslinker and without crosslinker. Most in situ gelled acid had been broke after adding 4-ppg breaker.

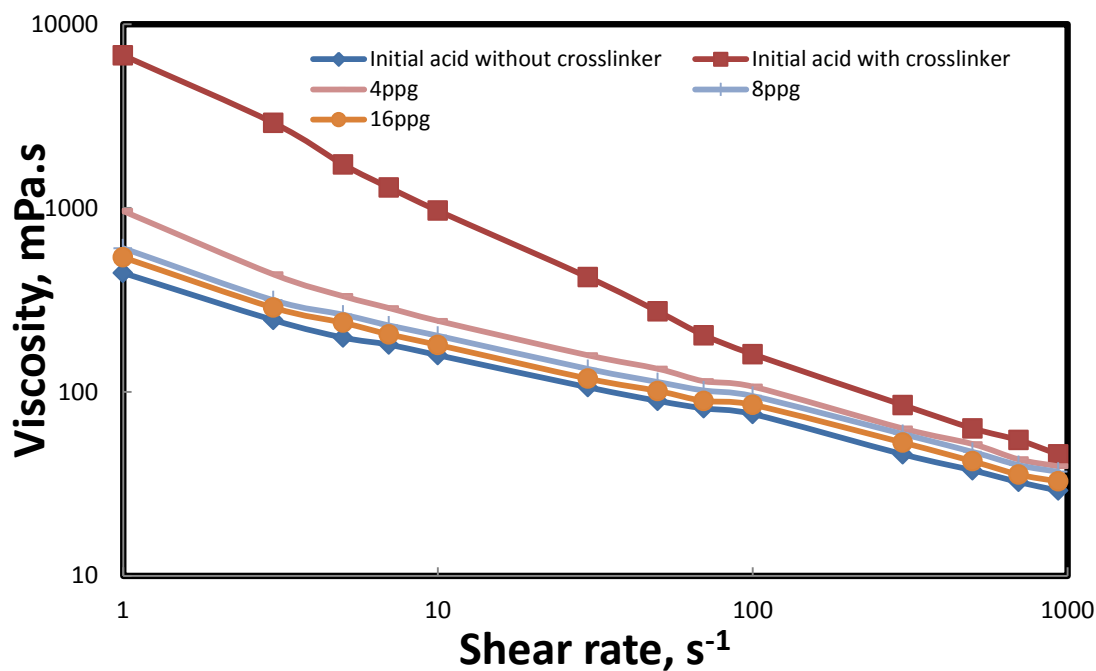


Fig. 28—Viscosity measurement of filtrated in situ gelled acid at room temperature after filtration tests at 150°F different breaker concentrations.

Fig. 29 shows the viscosity measurement of filtrated in situ gelled acid at room temperature after filtration test at 200°F. There was not much difference between Fig. 28 and Fig. 29. This means that when temperature increased from 150°F to 200°F, it did not help solid breaker to become more efficiency in cutting crosslinker. When breaker concentration increased from 8 ppg to 16 ppg, there was only slight difference for viscosity at low shear rates. At higher shear rates, they almost kept the same viscosity with each other. So at 200°F, adding 8-ppg breaker was enough.

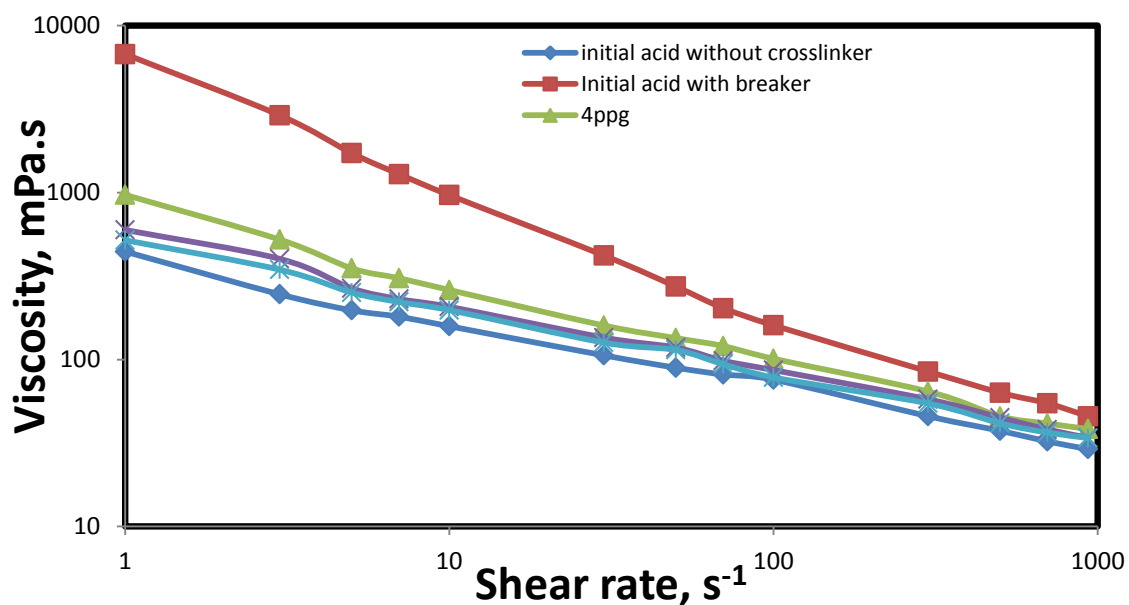


Fig. 29—Viscosity measurement of filtrated in situ gelled acid at room temperature after filtration test at 200°F with different breaker concentrations, 75°F.

Fig. 30 shows the viscosity measurement of in situ gelled acid at room temperature after filtration test at 250°F. This figure also did not change much compared with the above two figures. This indicated that temperature did not affect the breaking efficiency of solid breaker.

The last three figures showed the viscosity behavior of filtered fluid at different temperature. All of these viscosity behaviors can be summarized using the power-law equation:

$$\mu = K_1 \gamma^{n-1} \dots\dots\dots (2)$$

Where μ = viscosity, mPa.s; K_1 = power-law constant, mPa.sⁿ; γ = shear rate, s⁻¹; and n = power-law index, dimensionless.

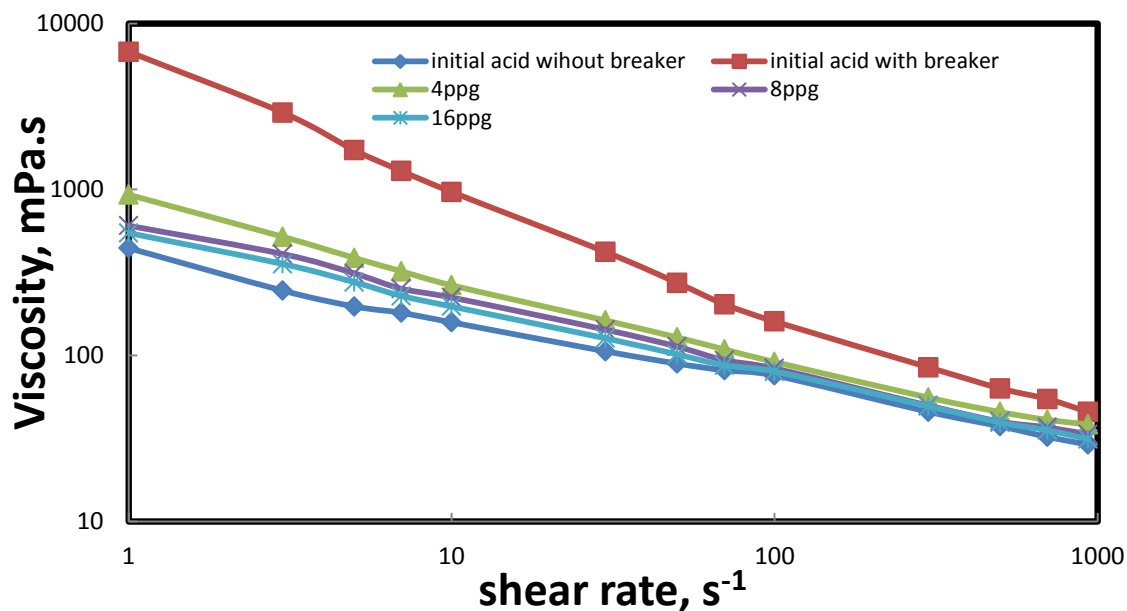


Fig. 30—Viscosity measurement of filtrated in situ gelled acid at room temperature after filtration test with different breaker concentrations at 250°F.

Viscosity Measurement of Filtrated Fluid—Effect of Temperature on Viscosity of Filtrated Fluid

Fig. 31 shows viscosity measurement of filtrated in situ gelled acid at room temperature after filtration test at different temperatures with 4-ppg breaker concentrations. The temperatures were set at 150°F, 200°F and 250°F. In this experiment, after the filtration test at different high temperatures, the filtrated in situ gelled acids cooled down to room temperature and then the viscosities of them were measured at 75°F. From this figure, it indicated that although in situ gelled acids were filtrated at different temperatures with 4-ppg breaker, after cooling down, the viscosities were almost the same. This means that same amount of gel were degraded by 4-ppg

breaker at different temperatures. The filtration rates differences were caused by temperature increase. Because high temperature can decrease the viscosity of in situ gelled acid. But high temperature could not help breaker cutting more gels.

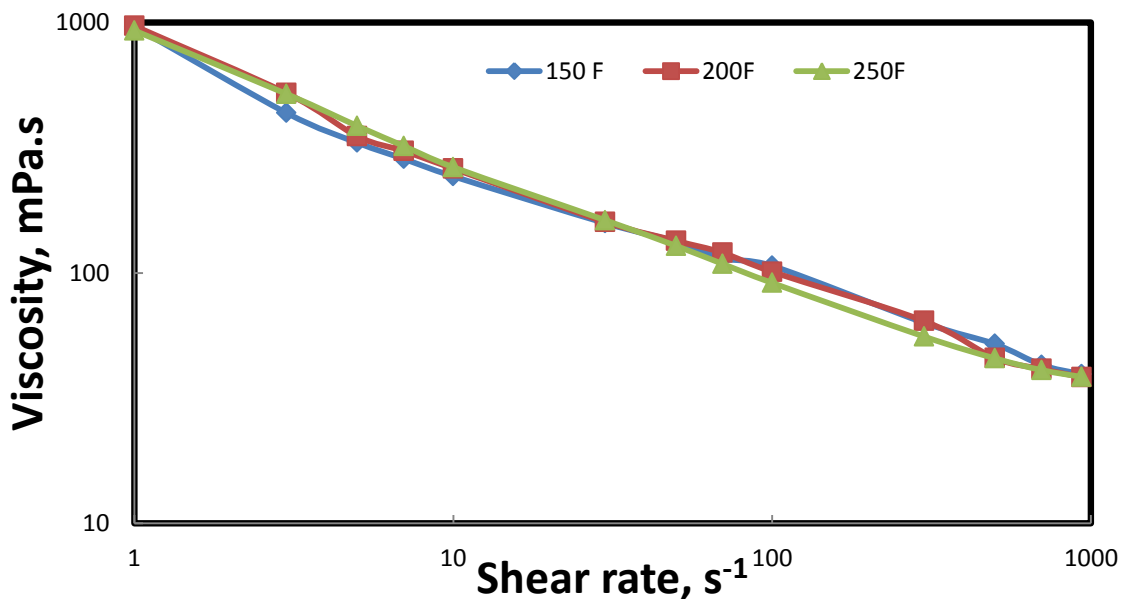


Fig. 31—Viscosity measurement of filtrated in situ gelled acid at room temperature after filtration test at different temperatures with 4-ppg breaker concentrations.

Fig. 32 and Fig. 33 show viscosity measurement of filtrated in situ gelled acid at room temperature after filtration test at different temperatures with 8-ppg and 16-ppg breaker concentrations. From these two figures, although the breaker concentrations were increased, but the viscosity of filtrated in situ gelled acids were still almost the same. So this indicated that temperature increase could not help breaker degrading more amount of in situ gelled acids.

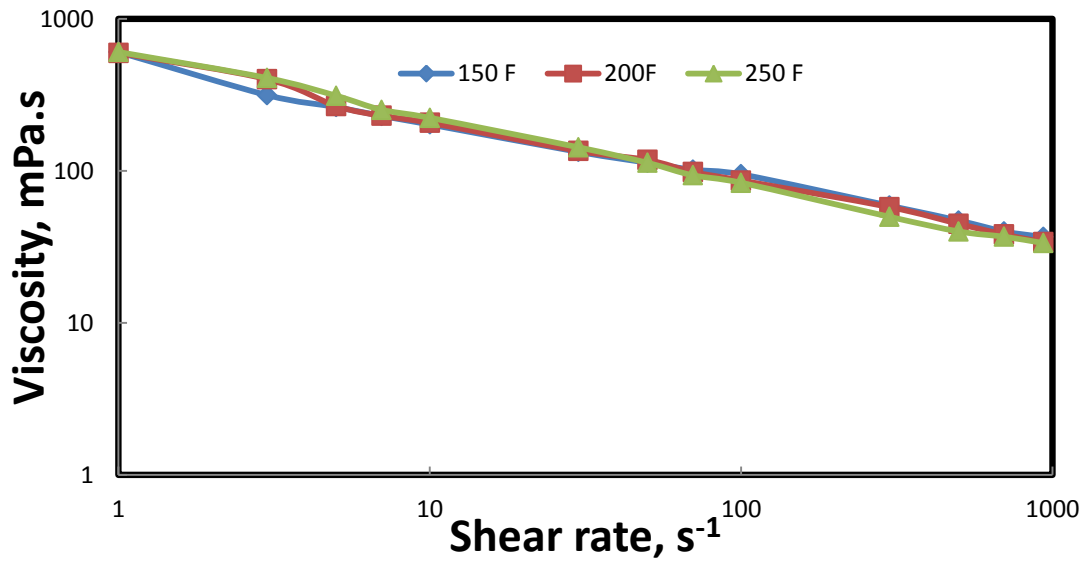


Fig. 32—Viscosity measurement of filtrated in situ gelled acid at room temperature after filtration test at different temperatures with 8-ppg breaker concentrations.

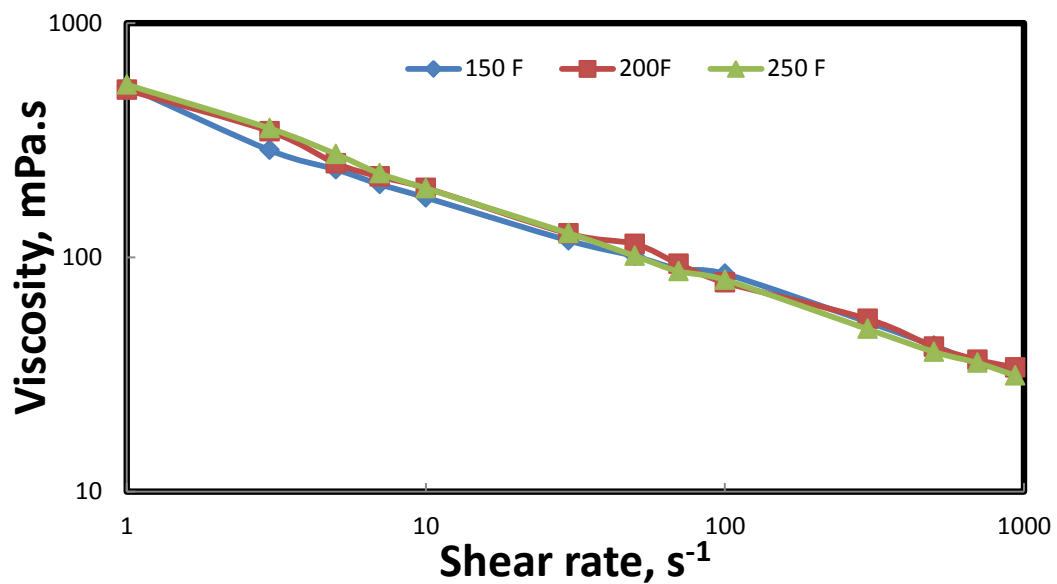


Fig. 33—Viscosity measurement of filtrated in situ gelled acid at room temperature after filtration test at different temperatures with 16-ppg breaker concentrations.

Viscosity Measurement of Filtrated Fluid—Effect of pH Values

Fig. 34 shows the viscosity measurement of filtrated in situ gelled acid with different pH values at room temperature after filtration test with 4-ppg breaker concentrations at 200°F. From this figure, the viscosity at pH value 5 was 100 cp lower than it was at pH value 4 when the shear rate was below 10 s^{-1} . But when the pH value was reduced to 2, the viscosity difference became much larger. So this figure indicated that viscosity at pH 2 was lower than it was at pH value 4 and 5. This explained why the filtration rate at pH value 2 was faster than it was at pH 4 and 5.

Fig. 26 and Fig. 34 showed the effect of pH value on the in situ gelled acid. At pH value 4 and 5, in situ gelled acids almost have the same viscosity so there were no differences on filtration rates. At pH value 2, the viscosity of in situ gelled decreased compared with it at pH value 4 and 5.

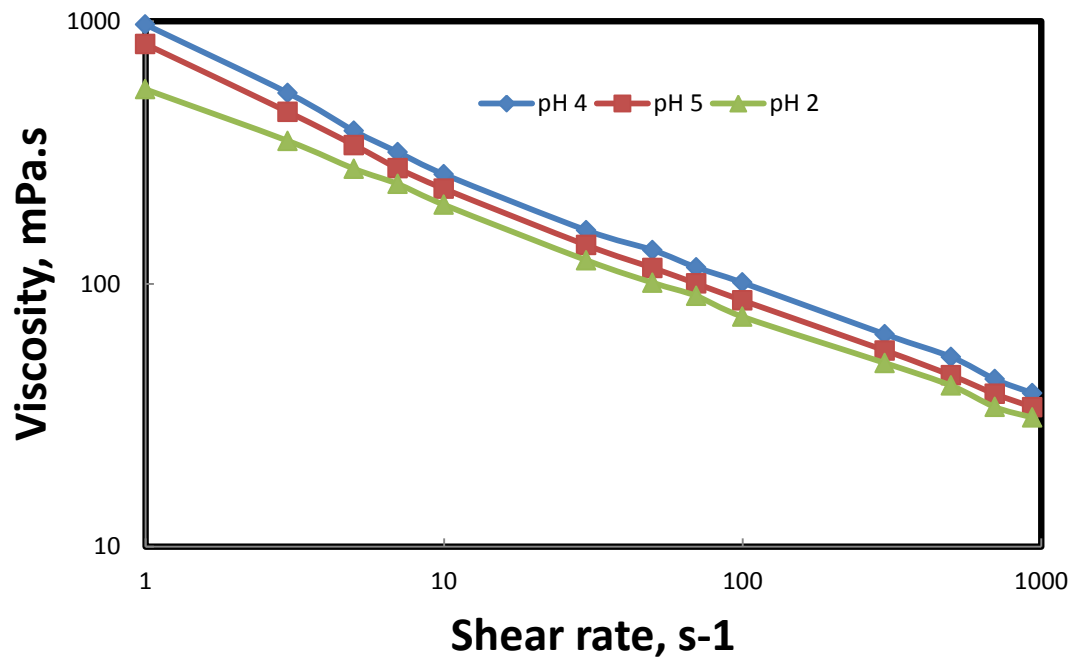


Fig. 34—Viscosity measurement of filtrated in situ gelled acid with different pH values at room temperature after filtration test with 4-ppg breaker concentrations at 200°F.

CHAPTER V

CONCLUSIONS

- 1) Breaker concentration of 16 lb/Mgal was recommended at temperature equal to 150°F, while 8 lb/Mgal of breaker concentration is enough at temperature higher than 200°F.
- 2) A full breaking of these acids was obtained when the values of elastic modulus (G') were equalized with the viscose modules (G'').
- 3) By shearing only the gel, the viscosity was reduced by 40% after 2 hr. The same viscosity reduction was obtained after adding 4 lb/Mgal of solid breaker without shearing. However, shearing and adding 4 lb/Mgal breaker completely broke the gel after 40 min.
- 4) With no shearing, in situ gelled acid was fully broken after 45 min when 4 lb/Mgal breakers used at 250°F. However at lower temperatures, no full break was observed, but a reduction of viscosity and G' were noted. As the breaker concentration increases, the reduction in viscosity increased.
- 5) As the breaker concentration increased, the elastic modulus decreased while the viscous modulus was increased.
- 6) Increase of solid breaker concentration (4 ppg-16 ppg) can decrease the filtration time a lot at 150°F, but at higher temperature (200°F, 250°F), the effect of solid breaker concentration increase was not as obvious as it at 150°F.
- 7) There is always gel left inside the core and reduce permeability. Internal damage

percent decrease by 50% when temperature increase from 150°F to 200°F, it decrease by 30% when the breaker concentration was doubled. At 250°F, breaker concentration increase almost has no effect on damage reduction.

- 8) At 150°F, 16-ppg breaker concentration was recommended for breaking the gel. At higher temperature (>150°F), 8-ppg breaker concentration was enough to help degrading the gel.
- 9) The filtrated fluids have almost the same viscosity as the un-crosslinked polymer solution.
- 10) High temperature does not affect the reaction between solid breaker and corsslinker, but it can reduce the viscosity of gelled acid a lot.

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VITA

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