

Feasibility of Using Produced Water for Crosslinked Gel-Based Hydraulic Fracturing

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ABSTRACT

A vast quantity of produced water (3.8 million barrels in 2002) is generated during gas production in the San Juan Basin, New Mexico. Most of the saline produced water is re-injected into disposal wells at an average cost of \$1-\$4 per barrel. Due to the persistent drought condition in New Mexico, beneficial use of the produced water is receiving increasingly more attention in the gas production industry. Based upon the Resource Management Plan (2003) proposed by the Bureau of Land Management, about 10,000 new wells will be approved on federal land in the San Juan Basin for the next 20 years. Given the volume of fresh water required for hydraulic fracturing during well development, reclaiming produced water as the base fluid for fracturing not only may alleviate the impact of fresh water shortage, it also may lower the cost of well stimulation treatment.

Produced water from a gas-producing well near Aztec, New Mexico is used as the base fluid for this study. Thirty-pound gels are formulated with CMHPG, a zirconium-based crosslinker, persulfate breakers, and other ingredients. The apparent viscosity of the gels is measured using Fann Model 35A viscometers and the bottom-hole temperature simulated in the experiments is about 128 °F. The rheological effects of several parameters, including pH, hydration time, ionic strength, and presence of sulfate, are evaluated.

The experimental results demonstrate the feasibility of using produced water from Aztec, NM as a base fluid for crosslinked gel-based hydraulic fracturing. Hydration time and pH are shown to influence the maximum achievable viscosity significantly. An excellent positive correlation is observed between the maximum achievable viscosity and the hydration time. For the solution pH, gellation at pH 5.5 exhibits the best rheological performance. By adjusting the hydration time, the gel loading, and the amount of breakers applied, it is conceivable that crosslinked gels with optimal rheological characteristics can be formulated with produced water as the base fluid for well stimulations.

INTRODUCTION

New Mexico ranks 2nd in natural gas production and 2nd in proven gas reserves of all producing states and the Gulf Coast region. Currently, there are about 23,600 active gas-producing wells in New Mexico with a large portion in the San Juan Basin of northwest New Mexico [1]. Based upon the Resource Management Plan (2003) proposed by the Bureau of Land Management, about 10,000 new production wells on federal land will be approved in the San Juan Basin region for the next 20 years [2]. A significant amount of produced water (TDS > several thousand mg/L, low organic content) can be generated during gas production. In 2002, around 3.8 million barrels of produced water were generated during gas production in the San Juan Basin [3]. Over 90% of the produced water was re-injected into class II wells for disposal at an average cost of \$1-\$4 per barrel [4]. Although the use of produced water for oil and gas drilling and slick-water-based fracturing have been explored in the San Juan Basin, little research was conducted to use produced water in crosslinked gel-based hydraulic fracturing [5]. Slick-water-based fracturing uses the inertial force to minimize the settling of proppants and therefore is not suitable for deep-zone fracturing due to the excessive applied pressure required at the surface. Crosslinked gel, on the other hand, with its high apparent viscosity can carry a wide range of sand loading for deep-zone fracturing at moderate applied pressures. Reclaiming produced water for crosslinked gel-based hydraulic fracturing not only can expand the beneficial use of produced water in the oil and gas industry but may also alleviate the impact of fresh water shortage due to the drought conditions in New Mexico.

Depending upon the hydraulic fracturing method used, several hundred to several thousand barrels of fresh water are utilized for each fracturing and each well during development may require several fracturing jobs at different depths. This amounts to a significant consumption of fresh water. Presently, fresh water from San Juan River and Animas River is used as the base fluid for natural gas well development in the San Juan Basin. Little information is available in the literature regarding substituting fresh water with produced water as the base fluid for crosslinked gel-based hydraulic fracturing. In offshore drilling, due to the location limitation, some studies were conducted to examine the applicability of using seawater (TDS ~ 35,000 mg/L, sulfate ~ 3,000 mg/L) as the base fluid [6]. Poor viscosity was observed possibly due to the reduction of the effective crosslinker concentration resulting from pH shift and chelation. Proper rheological characteristic of the fracturing fluid is crucial to the success of the stimulation treatment. Loss of fluid viscosity can lead to ineffective proppant transport, distribution, and placement as well as reduced fracture geometry resulting in loss of revenue [7].

Since produced water is different from fresh water primarily in the ionic composition, the rheological effects of parameters pertinent to ionic species, including hydration time, pH, ionic strength, and the presence of sulfate, were studied and presented in this paper.

EXPERIMENTAL METHODS

Produced water from a gas-producing well near Aztec, NM is used as the source water. The produced water was collected after the API separator in the field and glutaraldehyde was added immediately into the produced water as a bactericide. Table 1 shows the average composition of the produced water. The fluid system employed in this study is the Purgel III LT CO₂ used by XTO Energy (Farmington, New Mexico) in hydraulic fracturing of the Dakota formation (~ 6000 ft). It consists of carboxymethyl hydroxypropyl guar gum (CMHPG), zirconium-based crosslinker, persulfate breaker,

breaker catalyst, non-foaming surfactant, foaming agent, and delayed release persulfate breaker. The bottom-hole temperature simulated in the experiments is about 128 °F. The CMHPG employed has a backbone of $\beta(1\rightarrow4)$ D-mannose units with $\alpha(1\rightarrow6)$ galactosyl side chains. The substitution sites for carboxymethyl and hydroxypropyl groups are on the mannose and galactose units.

Ingredients of the hydraulic fracturing fluid are obtained from Halliburton (Farmington, New Mexico) and mixed using a Waring™ commercial blender. Thirty-pound gels are used in the experiments unless otherwise noted. A 30-lb gel is equivalent to 30 lbs of dry CMHPG gelling agent in 1,000 gallons of base fluid. In order to facilitate the addition of CMHPG, liquid gel concentrate consisting of CMHPG and a hydrocarbon carrier is formulated (four pounds of polymer to one gallon of hydrocarbon carrier). The produced water is first adjusted to the desired pH with glacial acetic acid and a proper amount of liquid gel concentrate is then added into the solution for hydration. After hydration, the crosslinker is added into the solution followed by the breakers and other ingredients. The same amount of crosslinker is used for all the experiments presented in this paper. After mixing, the fluid is placed in a heat cup at 128 °F and the viscosity is measured using a Fann Model 35A viscometer. Since the gel is a non-Newtonian fluid with apparent viscosity as a function of the shear rate, viscosity is measured at a shear rate of 37.7 s^{-1} for high viscosity and 511 s^{-1} as the fluid is breaking below several hundred cp. The rheological effects of several parameters, including pH, hydration time, ionic strength, and presence of sulfate, are evaluated. Several benchmarks of the crosslinked gel are used as the qualifiers of proper rheological characteristics for hydraulic fracturing. They are:

- Maximum achievable apparent viscosity ($> 1,500\text{ cp}$ at 37.7 s^{-1})
- Sustainable sand carrying viscosity ($> 500\text{ cp}$ for over 1.5 hours)
- Final fluid viscosity after breaking ($< 10\text{ cp}$)

RESULTS AND DISCUSSION

The maximum achievable apparent viscosity of the cross-linked gel at a shear rate of 37.7 s^{-1} is evaluated first without the addition of the persulfate breakers. Solution pH and hydration time are the variables of the study. Once their proper settings are identified, breakers are then introduced to examine the overall rheological performance. The objective is to demonstrate the feasibility of using the produced water from Aztec, NM as the base fluid for hydraulic fracturing.

Effect of pH

Since carbon dioxide is employed with this particular fracturing fluid, a zirconium-based crosslinker, which has a better CO_2 compatibility, is used instead of borate-based crosslinkers. Thirty-pound CMHPG gels are hydrated for 40 minutes at pH 4.6, 5.7, and 7.2, respectively followed by crosslinking. Figure 1 shows the apparent viscosity of these fluids with time lapsed after crosslinking. The 30-lb gel hydrated at pH of 5.7 performs the best with a maximum apparent viscosity of about 2,500 cp.

This result is consistent with the findings from Rose et al. [8]. Although it is well known that in aqueous solutions zirconium hydrolysis and polymerization increase with the increase of pH in the absence of strong ligands, little is known about Zr speciation in polymer gels [9]. Recently, however, Rose and his co-workers were able to show that in polymer microgels, Zr-dimers prevail at pH 6 while cyclic tetramers are predominant at pH 7 [8]. With the dominance of tetramers and other large aggregates

formed by it, a significant portion of the crosslinking Zr may be rendered incapable of performing the crosslinking function leading to a lower viscosity [10]. Using molecular modeling Chandrasekaran et al. were able to propose the coordination of carboxylate groups on a pair of CMHPG chains with cations during crosslinking [11]. At more acidic pHs (e.g., pH 4.6), fewer carboxylate groups on the CMHPG chains are de-protonated, which may adversely affect the process of crosslinking.

Effect of Hydration Time

Produced water with its high ionic concentration is lesser a good solvent for CMHPG and therefore proper hydration of the guar derivative may be crucial in achieving the desirable rheological characteristics. The apparent viscosity of 30-lb gels with 10, 40, 70, and 100 minutes of hydration prior to crosslinking (at pH ~ 5.5) is monitored with respect to the time lapsed after crosslinking. A higher value of maximum viscosity is observed with a longer hydration time as shown in Figure 2. The viscosity values averaged between 60 and 120 minutes exhibit an excellent positive correlation with hydration time as depicted in Figure 3. Gradual conformation change of the CMHPG molecules during hydration or dispersion of polymer aggregates over time is speculated as the main process contributing to the observed phenomenon.

Using molecular mechanics and Monte Carlo methods, Petkowicz et al. showed that the galactosyl substitution significantly lowers the spatial extension of the polymer chain when compared with that of a pure mannan chain [12]. This conformation of galactomannan may be due to the intramolecular hydrogen bonding between the galactosyl side groups and the mannosyl residues. In another study by Kirschner et al., water was shown to disrupt intramolecular hydrogen bond networks by forming intermolecular hydrogen bonds with polysaccharides [13]. It is speculated that due to this process, radius of gyration (R_G) of the CMHPG polymer may increase with hydration time exposing more coordination sites for Zr and consequently the process of crosslinking is enhanced leading to a higher viscosity. Another possibility of the hydration effect is the slow dispersion of the CMHPG aggregates over time during hydration. Clumping of CMHPG during the initial hydration stage is often observed when preparing the gel. If the dispersion process is slow, increasing the hydration time should give rise to a higher solvated CMHPG concentration in the solution and therefore a higher gel viscosity after crosslinking. Further research of the polymer in produced water using light scattering techniques is currently underway to understand the hydration process.

Overall Rheological Performance with Produced Water

With the effects of pH and hydration time identified, persulfate breaker and delayed persulfate breaker are then incorporated into the experiments to examine the overall rheological performance. Thirty-pound and twenty five-pound gels are hydrated at pH 5.5 for 40 minutes before the addition of breakers and the crosslinker. Figure 4 shows the rheological performance of these fluids. Although the 30-lb gel is not able to break within 120 minutes, by adjusting the amount of CMHPG to 25 lbs per 1000 gallons and having the same amount of breakers, the gel is able to meet the minimal requirements for the breaking pattern.

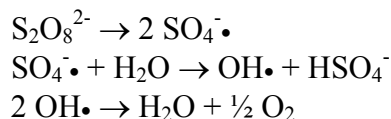
Effect of Ionic Strength

Since the ionic composition of produced water can vary significantly from well to well, it is of interest to examine the impact of ionic strength on the rheological performance of the crosslinked gels. Appropriate amounts of salts are added into Milli-Q water to simulate different ionic compositions of produced water as shown in Table 2. The water is then adjusted to pH 5.5, added CMHPG for a 30-lb

gel, hydrated for 40 minutes, and then crosslinked. No breakers are added for the experiments. Figure 5 shows the relationship of the viscosity values averaged between 60 and 120 minutes after crosslinking and ionic strengths. The synthetic water with an ionic strength of 0.32 is almost identical to the produced water from Aztec, NM in ionic composition. The resulted gel exhibits a maximum achievable viscosity comparable to that of Aztec produced water with 40-minute hydration time. A similar agreement is also observed for the synthetic water with an ionic strength of 0.31, which has a reduced sulfate concentration and an increased chloride concentration compared to that of Aztec produced water. Nevertheless, no discernable correlation is observed between the maximum achievable viscosity and ionic strength. The concentration of sulfate also appears to have minimal effect on the maximum achievable viscosity.

Effect of Sulfate

When fresh water is used as the base fluid for hydraulic fracturing in the field, potassium chloride (KCl) is typically added in the water to a concentration of 2% in an attempt to minimize the coagulation of clay particles. With the addition of KCl in fresh water, the high concentration of sulfate in produced water stands out as a major chemical difference between fresh water and produced water. There are concerns as how sulfate would affect the breaking of fracturing fluids since sulfate and/or bisulfate is frequently the product of persulfate oxidation. It has been shown that persulfate in aqueous solutions of pH between 3 and 13 will undergo thermal decomposition via the reactions illustrated below. The rate of decomposition at this pH range is independent of ionic strength [14].



In the presence of crosslinked CMHPG, persulfate is assumed to undergo induced decomposition through the oxidation of the polymer as well as self-decomposition to form HSO_4^- and O_2 [15]. With the high sulfate concentration in produced water, persulfate self-decomposition may be inhibited rendering more sulfate free radicals for polymer breaking and consequently causing pre-mature breaking of the gel. In order to evaluate the magnitude of self-decomposition during gellation, the percent of persulfate disintegrating within two hours is calculated. The decomposition reaction follows a 1st order reaction with a rate constant of $6 \times 10^{-5} \text{ (min}^{-1}\text{)}$ at an ionic strength of 0.4 and 122 °F, which are similar to the gellation conditions (ionic strength: 3.2, 128 °F) for produced water [14]. There is only a 0.7 % reduction in the persulfate concentration via self-decomposition within two hours. This result suggests that the gel breaking process by persulfate should have minimal influence from the sulfate concentration.

A comparative study of 25-lb gels is performed with produced water and produced water doped with sodium sulfate to increase the sulfate concentration from 6,700 mg/L to 10,000 mg/L. Same amounts of persulfate breaker and delayed persulfate breaker were added in the fracturing fluids. No enhancement of breaking is observed with the increase of the sulfate concentration as demonstrated in Figure 6.

CONCLUSIONS

This study demonstrates the feasibility of using produced water from Aztec, NM as a base fluid for crosslinked gel-based hydraulic fracturing. Hydration time and pH are shown to influence the maximum achievable viscosity significantly. An excellent positive correlation is observed between the

maximum achievable viscosity and the hydration time. For the solution pH, gellation at pH 5.5 exhibits the best rheological performance. By adjusting the hydration time, the gel poundage, and the amount of breakers applied, it is conceivable that crosslinked gels with optimal rheological characteristics can be formulated with produced water for well stimulations.

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Table 1. Produced water composition

Specific gravity	1.0083
pH	8.03
HCO ₃ ⁻ (mg/L)	1,290
Cl ⁻ (mg/L)	2,990
SO ₄ ²⁻ (mg/L)	6,730
Na ⁺ (mg/L)	5,380
K ⁺ (mg/L)	68
Mg ²⁺ (mg/L)	16
Ca ²⁺ (mg/L)	145
Iron (mg/L)	0.58
TDS (mg/L)	16,230

Table 2. Composition and ionic strength of simulated produced water

	Case I	Case II	Case III	Case IV	Case V
Ionic Species	mg/L	mg/L	mg/L	mg/L	mg/L
Na ⁺	5305	2875	3685	6925	6044
K ⁺	68	68	68	68	68
Mg ²⁺	18	18	18	18	18
Ca ²⁺	144	144	144	144	144
SO ₄ ²⁻	6761	1690	3380	10141	3380
Cl ⁻	2797	2797	2797	2797	6438
HCO ₃ ⁻	1307	1307	1307	1307	1307
TDS	16400	8900	11400	21400	17400
IS	0.32	0.16	0.21	0.42	0.31

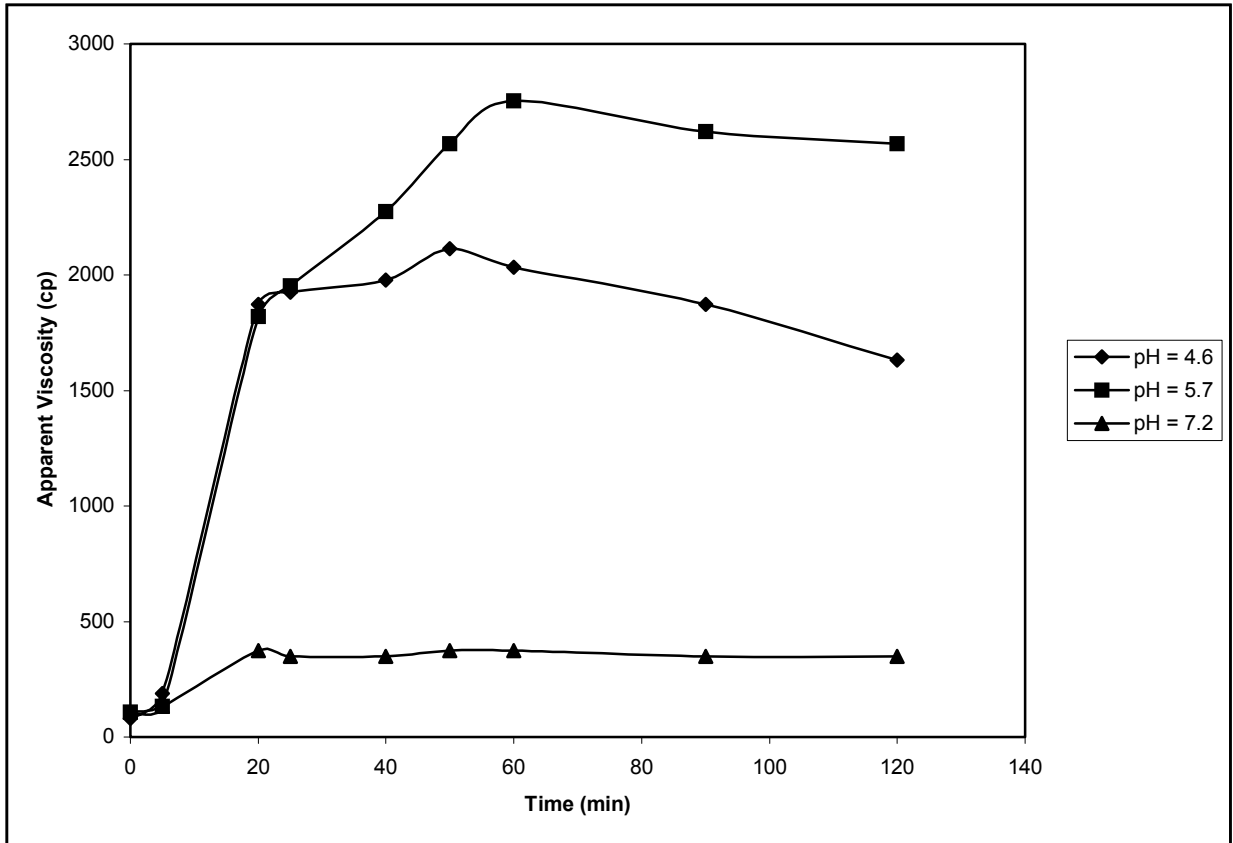


Figure 1. The Effect of pH on Apparent Viscosity

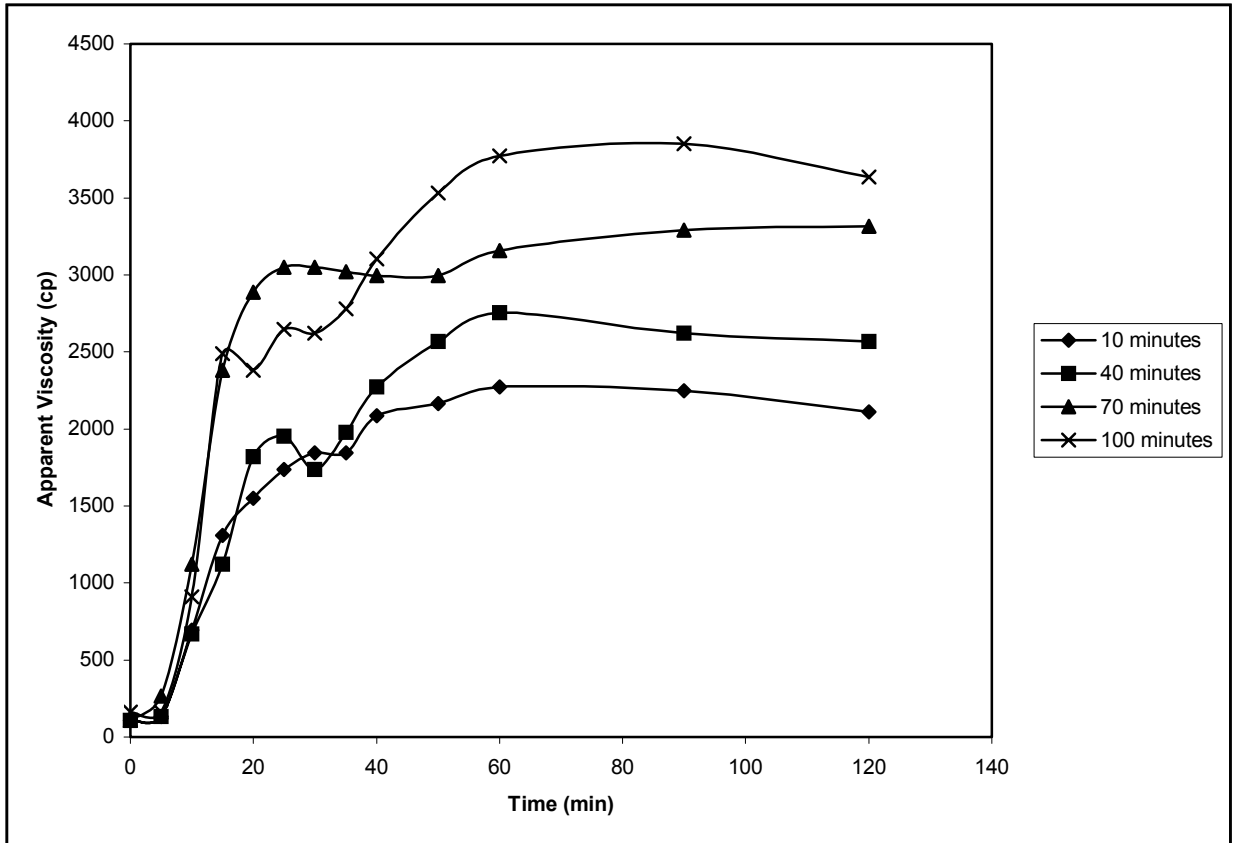


Figure 2. The Effect of Hydration Time before Crosslinking

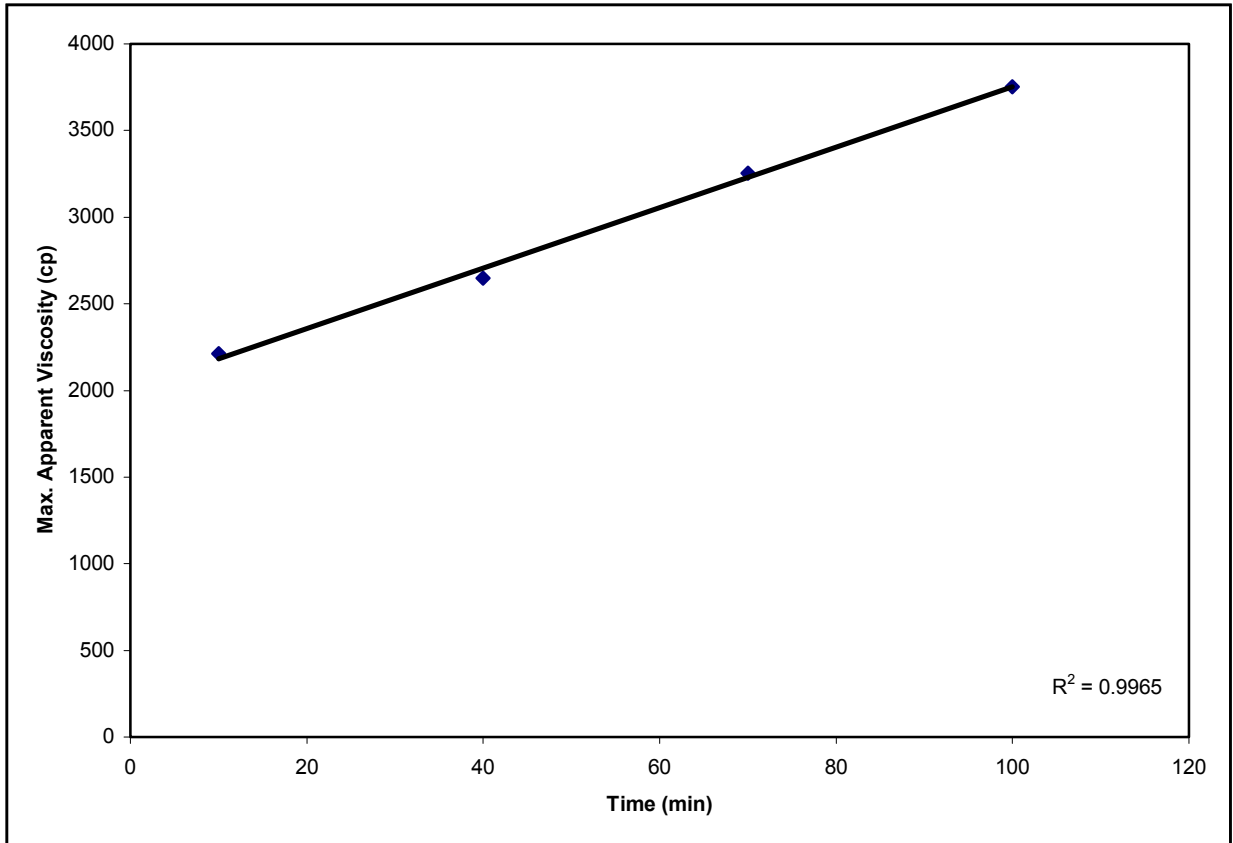


Figure 3. Correlation between the Maximum Achievable Viscosity and the Hydration Time

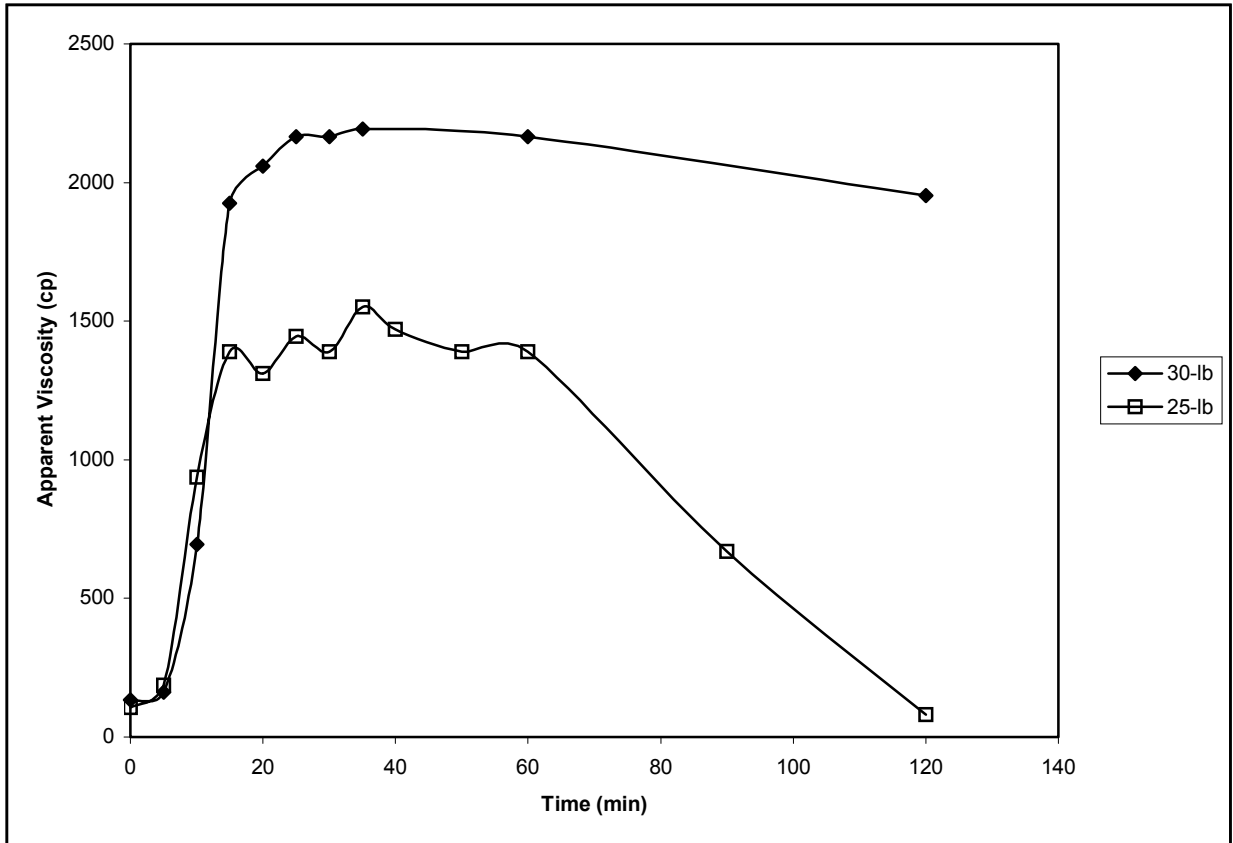


Figure 4. The Overall Rheological Performance of 25-lb and 30-lb gels

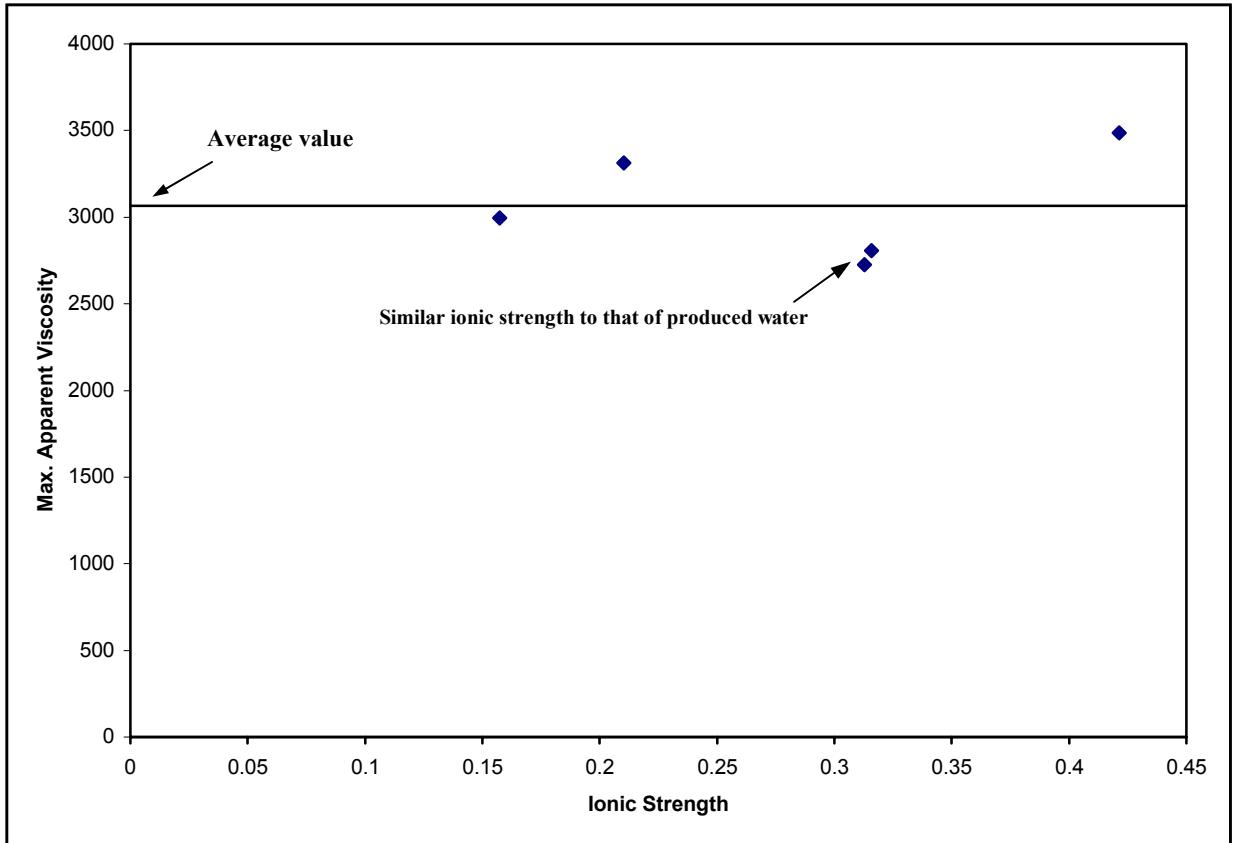


Figure 5. Correlation between the Maximum Achievable Viscosity and Ionic Strength

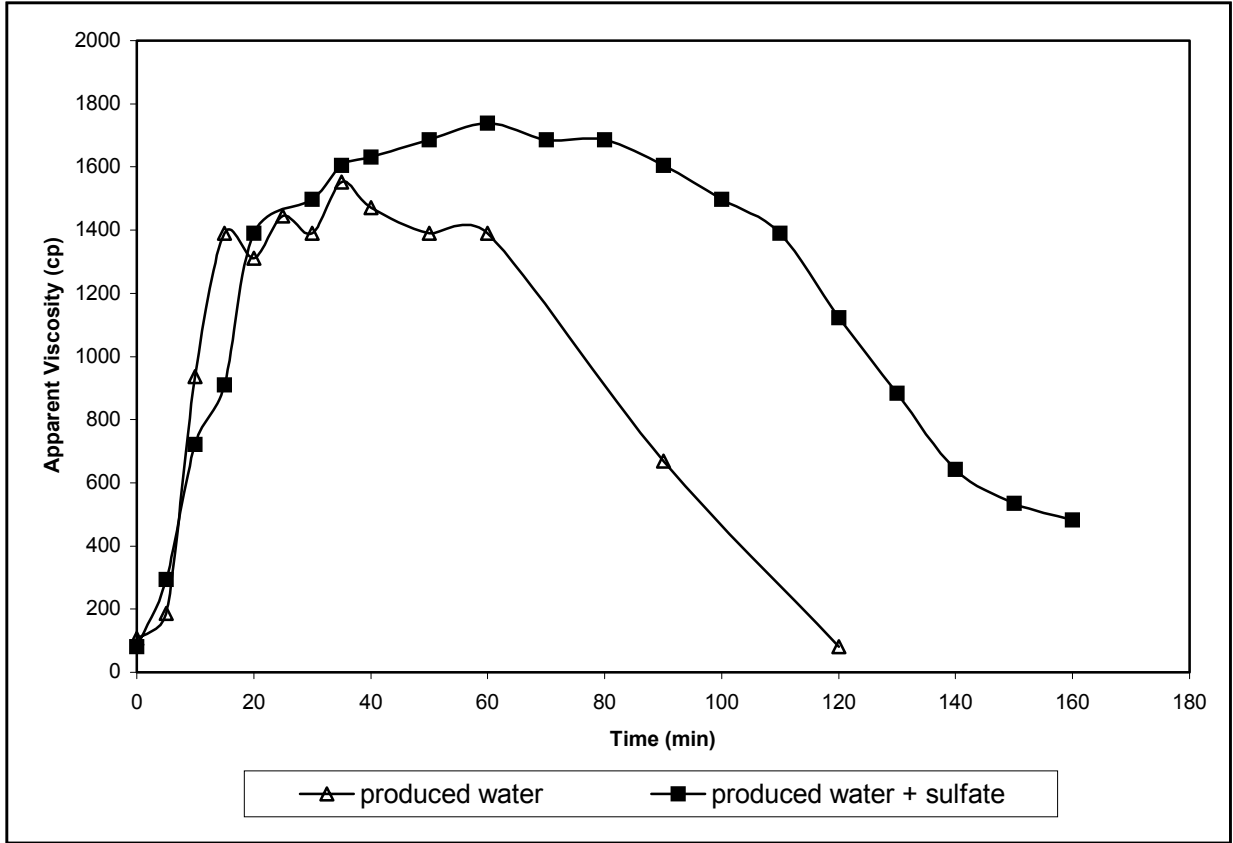


Figure 6. Breaking Patterns of Fracturing Fluids with and without the Addition of Sulfate