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Rheological Interactions Between Divalent Barium and Sulfate Ions in Hydroxypropyl Guar Polymer Fracturing Fluids

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ABSTRACT - The use of produced water as a primary component in formulating polymer-based fracturing fluids is becoming a viable option due to the limited availability of fresh water in the field. Nevertheless, the practical use of production water faces several challenges due to its complex composition, which includes monovalent and divalent ions that considerably affect the fluid's viscosity. Recent studies have shown that calcium ions substantially influence the viscosity of linear fracturing fluids, whereas magnesium ions, do not have a notable effect. However, the effects of other divalent ions commonly found in production water, such as barium and sulfate, remain underreported. In this study, the influence of barium and sulfate ions on linear fracturing fluids will be examined. The viscosity of linear gel fracturing fluids, prepared using hydroxypropyl guar (HPG) polymer with varying concentrations of barium and sulfate ions, will be investigated under different shear rates and temperatures. The results indicate that produced water contains barium and sulfate ions, which affect the rheology of the linear fracturing fluid. A concentration of 150 ppm of $BaCl_2$ can increase the viscosity by 30%, whereas 150 ppm of Na_2SO_4 increases the HPG viscosity by 7% at ambient temperature (25 °C). At 70 °C, the effect of barium and sulfate ions on the increase in viscosity of the HPG linear fracturing fluid are observed to be less significant.

Keywords: polymer, hydroxypropyl guar, fracturing fluid, barium ion, sulfate ion, rheology.

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INTRODUCTION

Water-based fracturing fluid is the pioneer and remains the most widely used fluid in fracturing operations for both conventional and unconventional oil and gas reservoirs (Al-Hajri et al., 2022). The primary objective of fracturing is to enhance permeability around the wellbore (Setyo Rahayu et al., 2025; Usman et al., 2022), enabling formation fluids to flow more freely into the wellbore and thereby increasing well productivity. Water-based fracturing fluids are primarily composed of water, a polymer as a thickening agent, and a proppant (Almubarak et al., 2022; Kamal et al., 2018; X. Li et al., 2020; Muqtadir et al., 2018).

Linear gel, a type of water-based fracturing fluid, is commonly used in unconventional fracturing operations (Hu et al., 2018. Its advantages include high pumping rates exceeding 60 bbl/min (1 bbl = 158.9 L) (Korlepara, 2019, low cost, minimal formation damage, and excellent drag reduction performance (Barati & Liang 2014; Cheng, 2012; M. Zhao et al., 2024; M.-W. Zhao et al., 2024). However, in field applications, linear gel has limitations in its ability to transport large amounts of proppant (J. Wang et al., 2020). Linear gel fracturing fluid primarily consists of water with a very low concentration of linear polymer, which acts as a friction reducer to minimize friction losses along the flow line during transport downhole. Linear fluids are composed of uncross linked polymer solutions, such as guar, guar derivatives, cellulose, cellulose derivatives, other polysaccharides like xanthan or diutan, and synthetic polymers (L. Li et al., 2016). Depending on the polymer concentration, the viscosity of a linear fluid can be several orders of magnitude higher than that of slickwater, resulting in considerably enhanced proppant suspension and transport capabilities. While linear gels effectively control fluid loss, formations with higher permeability may still experience excessive fluid loss (T. Li & Wan 2017; Murthy & Chavali 2020). In lower-permeability formations, linear gels typically form thick filter cakes on the formation surface (Roman, 2012. Most water-based fracturing fluids are prepared using guar and its derivatives (Weaver et al., 2002).

Guar gum, the most commonly used polymer in fracturing fluids, is derived from the seeds of *Cyamopsis tetragonoloba* (Hasan & Abdel-Raouf 2018a; Montgomery 2013). However, its application faces several limitations (Barati & Liang 2014; Trivedi et al., 2005), including reduced viscosity due to uncontrolled hydration rates (Alohaly et al., 2016; Sun et al., 2015; Zhang et al., 2024), pH-dependent solubility (Coulter et al., 1983; Mudgil et al., 2014; Venugopal, 2010), turbidity in aqueous dispersions (Theocharidou et al., 2022), high susceptibility to microbial attacks that limit long-term stability (Pasha & Ngn 2008; Paudel et al., 2022; Wilson et al., 2024), and residual buildup (Almond & Bland 1984; Alohaly et al., 2016; Roman, 2012). To enhance its solubility and overall performance, chemical modifications are made to the guar gum structure. The most common derivatives of guar gum u cscarboxymethyl guar (CMG) (Dodi et al., n.d.; Gong et al., 2012), and carboxymethyl hydroxypropyl guar (CMHPG) (Shi & Zhang 2007; Szopinski et al., 2015).

Hydroxypropyl guar gum (HPG), a modified form of guar gum, is one of the polymers used as a thickener in water-based fracturing fluids (Weaver et al., 2002). HPG is nonionic and has the chemical structure CH_2-$CH(OH)CH_3$ (Hasan & Abdel-Raouf 2018b). However, during its use, HPG becomes a primary source of contaminants in fracturing flowback fluids and a major contributor to environmental harm, due to its high content of non-degradable residues (8–12%) and water-insoluble materials (20–25%) (Wang et al., 2023). Despite these drawbacks, HPG exhibits good temperature resistance (Zhang et al., 2023).

In practice, the polymer is dissolved in water to create a water-based fracturing fluid. Initially, fresh water was used. However, due to concerns about availability, cost, and environmental impact, several studies have explored the use of produced water. The application of produced water in fracturing fluids has been widely investigated developed in various studies. Its advantages include its abundant and easy of availability in the field, reduced costs associated with surface facilities, and the utilization of otherwise unused produced water, making it a more economical option (Oetjen et al., 2018; Ruyle & Fragachan, 2015). However, the use of produced water presents challenges regarding its characteristics, which can affect rheology and formation damage when compared to the use of fresh water (Elsarawy et al., 2016a).

Total dissolved solids (TDS), pH, salinity, and ion content all influence the viscosity of water-based fracturing fluids. Research on the effects of salinity and TDS on water's fracturingfluid viscosity has considered not only produced water but also seawater, which has very high salinity levels. The use of seawater results in the greatest reduction in viscosity compared to freshwater (Othman et al., 2022, 2023. Salinity and TDS values particularly affect the viscosity stability of fracturing fluids at elevated temperatures (Othman et al., 2022).

Previous studies indicated that both monovalent (Elsarawy et al., 2016a; Esmaeilirad et al., 2016; Haghshenas & Nasr-El-Din 2014) and divalent ions (Haghshenas & Nasr-El-Din 2014), including K^+, Na^+, Ca^{2+}, and Mg^{2+}, affect the viscosity of linear fracturing fluids (Elsarawy et al., 2016a, 2016b. The viscosity of fracturing fluids is highly influenced by the concentration of divalent cations, regardless of the concentration of monovalent cations. Monovalent cations reduce the viscosity of fracturing fluids only in the absence of divalent cations and have no considerable effect when Ca^{2+} and Mg^{2+} ions are present (Esmaeilirad et al., 2016; Haghshenas & Nasr-El-Din 2014).

However, the salts present in produced water are highly complex, and their solubility is influenced by changes in pressure and temperature. The solubility of these salts can lead to additional formation damage issues, such as mineral deposition or scale formation. Scale develops through two crystallization processes: surface crystallization and bulk crystallization, with scaling being a combination of both (Antony et al., 2011; Hasson et al., 2011; Lee & Lee 2005). Different nucleation mechanisms drive crystallization on a material's surface and in its bulk. Nucleation occurs through two mechanisms: homogeneous and heterogeneous (Olajire 2015). Scaling incorporates aspects of both processes (Al-Roomi & Hussain 2016). Surface crystallization arises from various types of heterogeneous nucleation, whereas bulk crystallization primarily results from homogeneous nucleation.

One type of scale that is particularly difficult to manage and incurs high treatment costs is barium sulfate scale (Makmur 2022; Kelland 2011; Valadbeygian et al., 2023; Vetter 1975). The presence of divalent barium ions also contributes to the TDS content of produced water. Additionally, interactions between polymers and produced water containing certain ions can trigger the deposition of both organic and inorganic minerals, which can be analyzed using flowback water samples (Xu et al., 2024). Experimental data on the specific impact of the divalent cation Ba^{2+} and anion SO_4^{2-} on HPG is limited. It is widely recognized that divalent cations such as Ca^{2+} and Mg^{2+} can influence the behavior of linear and crosslinked gels based on guar and its derivatives. However, research on the effects of divalent ions, including barium and sulfate, on linear gels has been limited. Therefore, further investigation is needed to understand the influence of barium (Ba^{2+}) and sulfate (SO_4^{2-}) ions on the viscosity of water-based fracturing fluids. The aim of this study was to examine the effect of barium and sulfate ions on the viscosity of linear gels at both room and reservoir temperatures. In field applications, the results of this study are expected to offer new insights into the use of produced water containing barium and sulfate ions as a component in linear gel fracturing fluids.

Materials and methods

Materials and sample preparations

To investigate the impact of barium and sulfate ions on fracturing fluids, synthetic single-salt solutions were prepared by dissolving reagent-grade $BaCl_2$ and Na_2SO_4 (Merck Chemical, Indonesia) in demineralized water (Brataco, Indonesia; electrical conductivity < 1.3 μS/cm) at concentrations of 0, 50, 100, and 150 ppm. These concentrations were selected to represent the actual levels of barium and sulfate ions found in the produced water from the TNJ oil field in Indonesia (Table 1). The synthetic solutions were then mixed with HPG (Fig. 1), supplied by DEoRC Chemical (China), and stirred at 600 rpm for 30–50 min.

Table 1. Composition of produced water in the TNJ Oil Field, Indonesia

Ion Type	Concentration, ppm (1 ppm = 1 mg/L)
Na^+	1225
Ba^{2+}	75.1
Cl^-	1115
SO_4^{2-}	1.29
TDS	3010
pH	6.81

HPG is a naturally derived thickener based on guar gum, a natural polysaccharide extracted from the seeds of guar beans. Guar gum is a galactomannan composed of an α-(1, 4)-linked β-D -mannopyranose backbone with branch points at the 6-position linked to α-D-galactose (i.e., 1,6-linked α-D-galactopyranose) (Fig. 1) (Hasan & Abdel-Raouf, 2018b. This bonding structure facilitates the polymer's rapid dissolution in water. The rapid hydration of hydroxypropyl guar shortens the manufacturing cycle and is easy to formulate while maintaining an eco-friendly profile, thereby optimizing gel production.

METHODOLOGY

Viscosity measurement

The viscosities of the HPG fracturing fluid solutions were measured using a Brookfield DV-1LV rheometer (Figure 2; supplied by AMETEK Brookfield, USA). The instrument is equipped with a water bath, enabling experiments to be conducted at elevated temperatures. According to the equipment manual, 16 mL of sample is required for each experiment. Before evaluating the impact of barium and sulfate ions on the viscosity of the HPG fracturing fluid, the effect of hydration time was first investigated by varying the mixing times of the HPG solutions from 10 to 50 min. HPG solutions with a concentration of 3.6 g/L (3600 ppm) were prepared to achieve a standard viscosity of approximately 25–55 cP (1 cP = 1 mPa·s) at a shear rate of 170 s^{-1} at ambient temperature, following the recommended guidelines provided by the supplier. The solutions were mixed using a Thermo Scientific (USA) magnetic stirrer at 600 rpm. Subsequently, the viscosities of the HPG solutions were measured at three different shear rates: 7, 170, and 322.2 s^{-1}. Each measurement was repeated at least twice to ensure consistency of the results.

The second set of experiments investigated the effects of temperature, barium, and sulfate ions on the viscosity of the HPG solution. Experiments were conducted at two temperatures: 25°C (ambient temperature) and 70°C (reservoir temperature), under varying shear rates. The test solutions were prepared by dissolving 3.6 g/L of HPG in 100 mL of demineralized water. The solution was stirred using a magnetic stirrer at 600 rpm for 30 min, after which 16 mL of the solution was transferred into a sample holder for viscosity testing. The addition of salts ($BaCl_2$ and Na_2SO_4) to the demineralized water was carried out prior to the

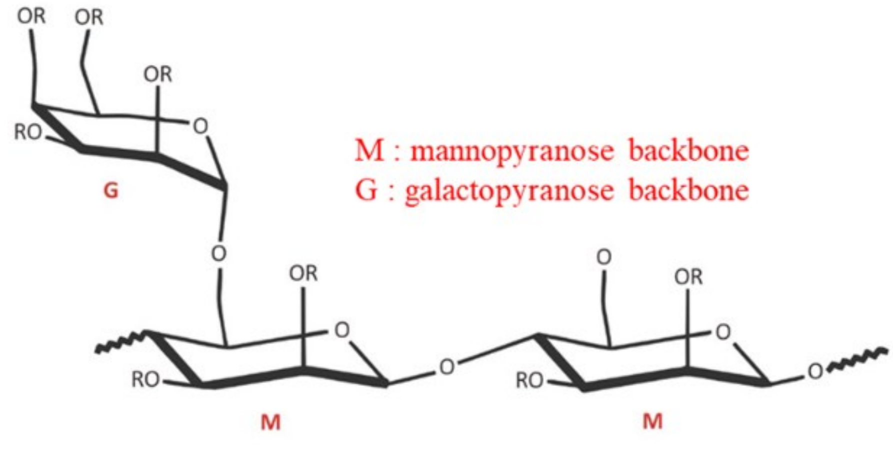

Figure 1. Molecular structure of hydroxypropyl guar (Adapted from Ospennikov et al., 2023, published under a Creative Common CC BY license.

addition of HPG. Salt concentrations of 50, 100, and 150 ppm were used. As in the first set of experiments, each measurement was repeated at least twice to assess experimental uncertainty.

Residue measurement

In this study, the experimental procedures were based on previous studies by Almubarak, Carrascal –Delgado, and Hai (Almubarak et al., 2020; Delgado et al., 2014; Hai et al., 2018), with slight modifications to the temperature settings and the gel breaker used in the water bath. The water bath temperature was set to 70°C, and ammonium persulfate was used as the gel breaker at a concentration of 2% by volume. The viscosity solution was prepared by adding ammonium persulfate at the end of the mixing process. After preparing 100 mL of the linear gel solution, 2% by volume of ammonium persulfate was added and mixed for 5 min until a homogeneous solution was obtained. Before residue testing, 100 mL of the solution was first tested for viscosity at ambient temperature and then transferred into a measuring cup and heated in a water bath preset to the desired temperature. The solution was observed every 10 min until breakage occurred. Breakage was identified by the appearance of sediment or clots. After breakage, the sample was filtered using Whatman filter paper (150-mm diameter) and dried. The residue was calculated based on the weight of the dried filtered solids (m) relative to the volume (V) of the sample solution used, as shown in Equation 1.

$$\eta = \frac{m}{V}, mg/L \qquad (1)$$

RESULT AND DISCUSSION

Effect of hydration time

Hydration is the process in which polymer chains absorb water and transform from a compact helical structure to a more extended and flexible configuration. Hydration was assessed based on viscosity, with stable viscosity indicating a fully hydrated state. Hydration time is influenced by factors such as the type of solvent, polymer type, and polymer concentration (Alohaly et al., 2016). Figure 3a shows the effect of hydration time on HPG viscosity at three different shear rates: 7, 170, and 322.2 s^{-1}. As shown in Figure 3a, the optimum hydration time for the HPG solution was achieved at 30 min, with stable viscosity values at shear rates of 7, 170, and 322.2 s^{-1}. At 10 and 20 min, the solution was considered not yet homogeneous, as indicated by inconsistent viscosity values across both high and low shear rates. This inconsistency is attributed to incomplete interactions between the polymer chains and the ions present in the water used as the solvent. The measurement at a shear rate of 170 s^{-1} follows the recommended practice from the chemical supplier, while the shear rate of 322.2 s^{-1} was selected to compare the measured viscosity of the HPG solution with that obtained using the Fann VG rheometer at 300 rpm. The viscosity of the HPG solution with a concentration of 3.6 g/L is within the standard viscosity range provided by the chemical supplier (see Figure 3b), confirming that the procedure reported in this study produces consistent viscosity results comparable to the supplier's data.

Effect of divalent barium ions and temperature on the viscosity of HPG

Figure 4 presents the results of varying barium ion concentrations and temperatures on the viscosity of HPG solutions. As shown in Figure 4, the viscosity of the HPG solution at both ambient (25°C) and reservoir (70°C) temperatures increased with higher barium concentrations. A more significant increase in viscosity was observed at 25°C compared to 70°C. These findings are consistent with previous studies on the effects of divalent ions, particularly calcium (Ca^{2+}) and magnesium (Mg^{2+}), on linear and crosslinked gel-type polymers (Fig. 5). In crosslinked gels, the presence of calcium ions at elevated temperatures, such as reservoir conditions, reduces viscosity, whereas the effect of Mg^{2+} ions is minimal and can be neglected (Elsarawy et al., 2016b; Esmaeilirad et al., 2016; Haghshenas & Nasr-El-Din, 2014). In contrast, for linear gels, Ca^{2+} ions increase the viscosity, although the increase is not as significant as that caused by Ba^{2+} ions. Calcium ions at concentrations up to 30,000 ppm only enhance the viscosity by 16% (Sun et al., 2015, while 150 ppm of $BaCl_2$ can increase the viscosity by 30% (Fig. 4).

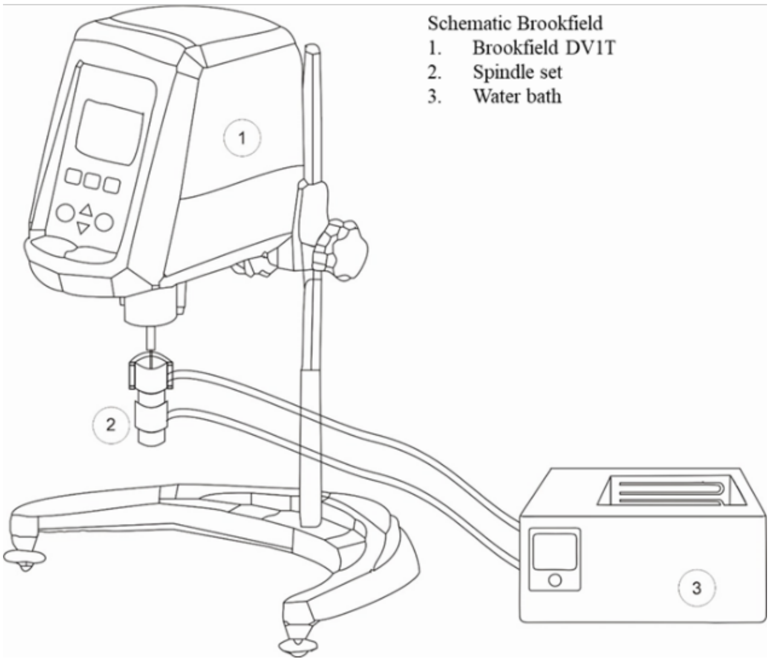

Figure 2. Schematic of the Brookfield DV-1LV rheometer

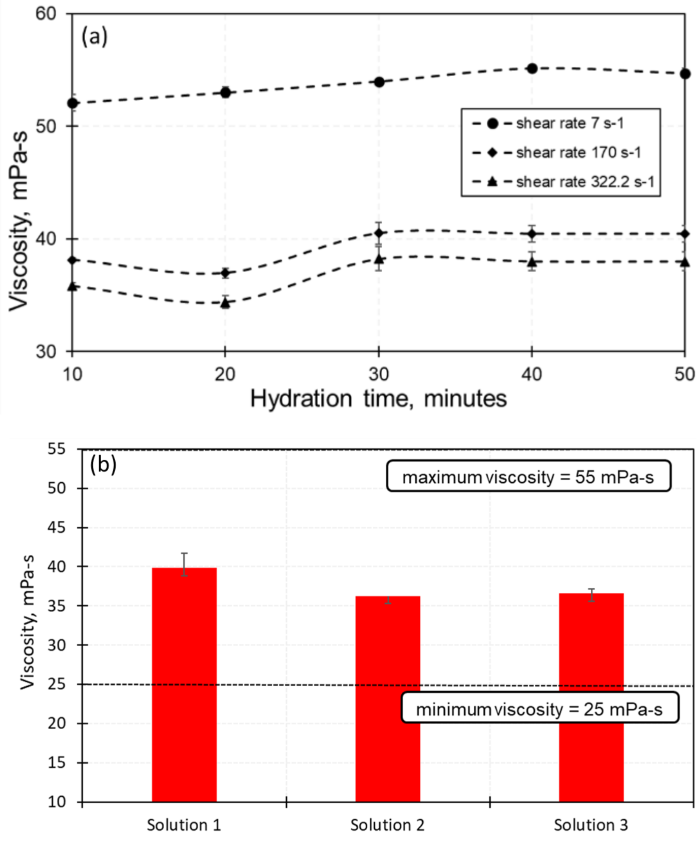

Figure 3. Effect of hydration time at shear rates of 170 and 322 s^{-1} (a) and the viscosity range (b) of HPG at room temperature at a shear rate of 170 s^{-1}

However, the concentration of these ions in produced water in Indonesia is relatively low. Shear rate influences viscosity measurements at 25°C. At a shear rate of 7 s^{-1}, the change in viscosity is approximately 15%, while at shear rates of 170 and 322 s^{-1}, the increase reaches approximately 30%. Specifically, at 170 s^{-1}, viscosity increases by 30% (Fig. 4a). However, at 70°C, changes in shear rate have no significant effect, with the increase in viscosity at this temperature being only approximately 16% (Figure 4b). HPG is a nonionic polymer that is sensitive to high salt concentrations, which can lead to precipitation. However, at low salt concentrations, particularly with low cation content, the effectiveness of crosslinking increases, thereby enhancing viscosity (Whistler, 1993. This phenomenon is attributed to the electrostatic repulsion of anionic groups, which reduces polymer chain connections and decreases the polymer's dynamic radii or hydration (Domelen & Haggstrom, 2011. Based on the conducted experiments, it can be concluded that the interaction of Mg^{2+} with the hydroxyl groups in the polymer solution does not considerably affect the dynamic radii of polymer coils. In contrast, interactions with Ca^{2+} and Ba^{2+} ions influence the dynamic radii of the polymer coil. The change in the polymer coil radii is influenced by the molecular size of the interacting ions. Since the molecular size of Ba^{2+} is larger than that of Ca^{2+} and Mg^{2+}, the viscosity of the linear fracturing fluid solution containing Ba^{2+} is higher compared to solutions containing Ca^{2+} or Mg^{2+} ions.

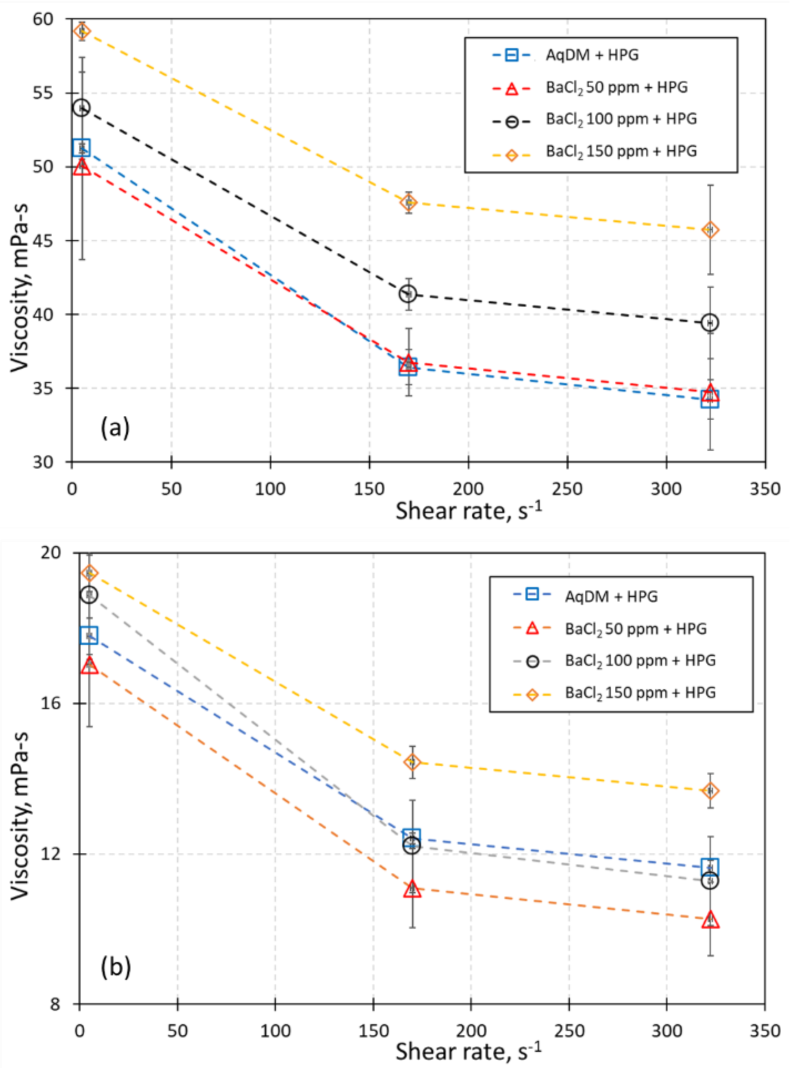

Figure 4. Viscosity of the HPG solution in various concentrations of barium salt at (a) 25 and (b) 70°C.

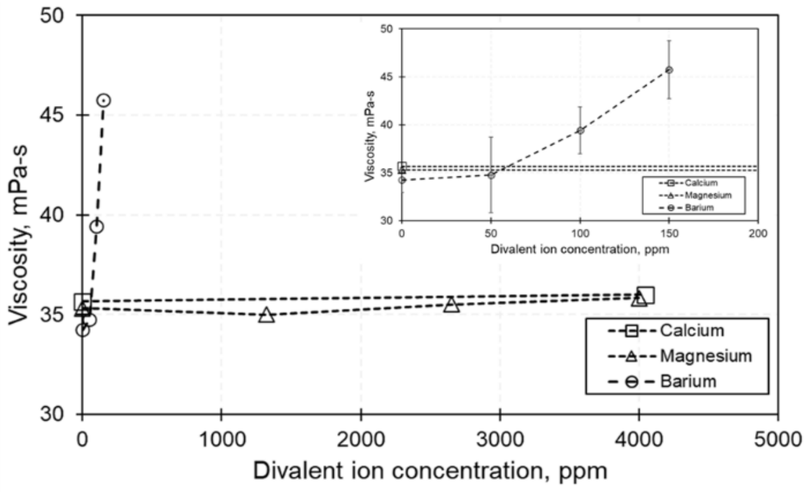

Figure 5. Viscosity of the HPG solution with different divalent ion concentrations at 25°C at a shear rate of 300 s^{-1},

The conclusion of this experiment confirms that guar-based fluids are more sensitive to TDS, salinity, and certain divalent cations (Esmaeilirad et al., 2016. Further research is needed on other types of polymers. Another study has indicated that cellulose-based fracturing fluids exhibit a certain degree of salt resistance (Hua et al., 2016).

Effect of sulfate concentration and temperature on the viscosity of HPG

Figure 6 shows the effect of three different sulfate concentrations (50, 100, and 150 ppm) at two different temperatures (25 and 70°C) on the viscosity of the HPG solution. The results show that the addition of sulfate had no considerable effect on the viscosity of the HPG solution at either temperature, consistent with the findings of (Alohaly et al., 2016). Across various shear rates and temperatures, SO_4^{2-} ions were found to have minimal impact on HPG viscosity (Figure 6). This observation aligns with previous studies on crosslinked gels, where sulfate ions were reported to have little effect on viscosity (Elsarawy et al., 2016a). However, high sulfate concentrations in produced water can lead to premature gel breaking (Huang et al., 2005. Furthermore, to better understand the effect of sulfate concentration, future experimental studies should be planned at concentrations above 150 ppm. High sulfate levels are characteristic of seawater with high salinity, and when mixed with formation water rich in barium ions, they are likely to form barium scale, which is difficult to manage (Budiman & Alajmei 2023).

The presence of sulfate anions had no considerable effect on the viscosity of the linear gel. This is because the hydroxyl groups (OH^-) in the polymer structure primarily interact with cations in the solution, reducing the dynamic radius of the polymer coils, increasing the molecular weight, and thereby enhancing the viscosity of the linear gel. Based on this mechanism, the addition of Na_2SO_4 to the linear gel solution leads to interactions between Na^+ ions and the polymer's OH^- groups. Since the molecular weight of Na^+ (23 g/mol) is smaller than that of Ba^{2+} (56 g/mol), the viscosity of the linear gel in the presence of Ba^{2+} ions is higher than with Na^+ ions. As shown in Fig. 7a, the presence of sulfate anions at 25°C increases the viscosity by only 8%. In Fig. 7b, no significant change in viscosity is shown with varying sulfate concentrations at 70°C. The viscosity of linear HPG gels is highly dependent on the interaction between hydroxypropyl (or polyhydroxypropyl) groups and polysaccharides. Cations interact with the hydroxyl (OH^-) groups of the polymer, reducing the dynamic radius of the polymer structure (Sun et al., 2015.

Effect of barium and sulfate on the residue

In addition to the rheological properties of the fracturing fluid, its breakdown and chemical cleaning characteristics are critical for maintaining high fracture conductivity (Almubarak et al., 2020; Yao et al., 2021. Materials that assist in breaking down the gelling fluid are known as gel breakers. These materials can break polymer bonds into smaller fragments or eliminate the crosslinking

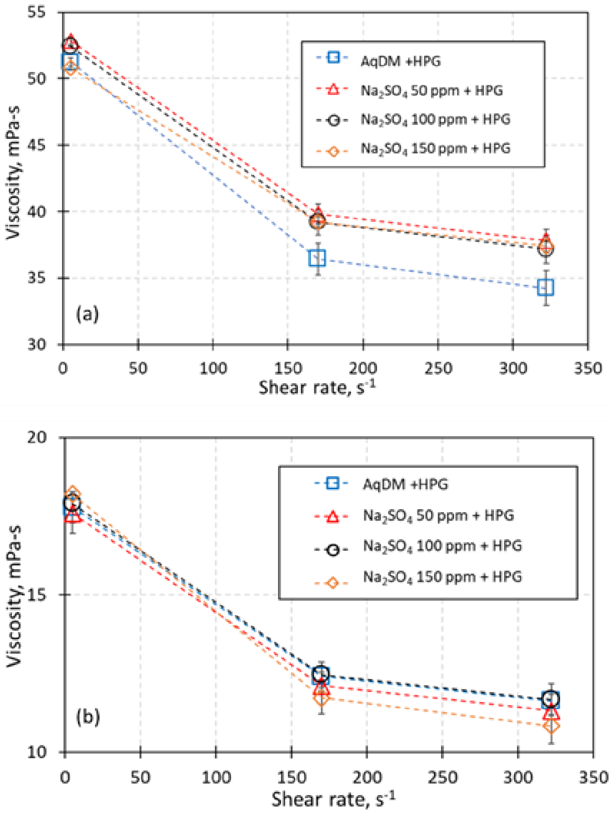

Figure 6. Viscosity of the HPG solution in various concentrations of natrium sulfate at 25 and 70°C

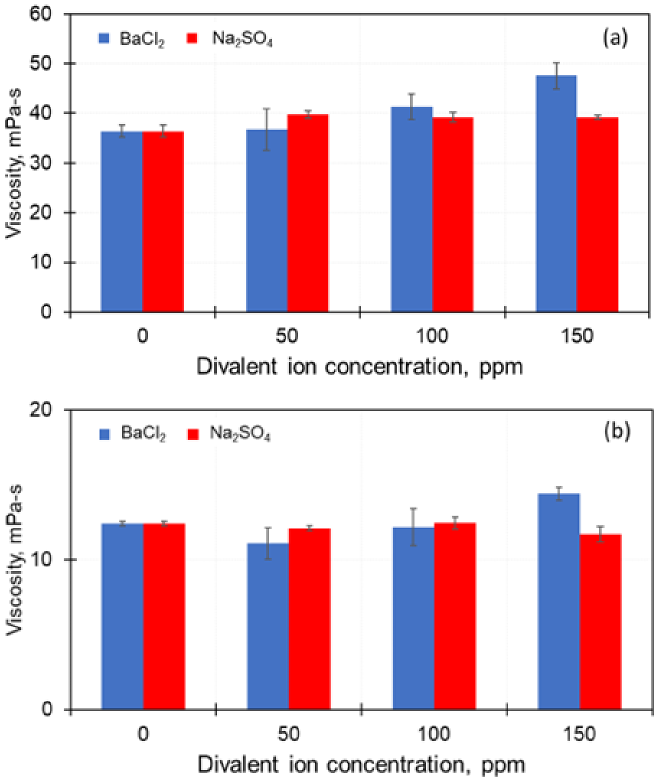

Figure 7. Viscosity of the HPG solution in natrium sulfate and barium chloride at (a) 25 and (b) 70°C using shear rate of

Table 2. Residue test

No	Polymer concentration, g/L	Cross-link, % v	Breaker, % v	T, °C	Residue, mg/L
1	4	-	0.2	70	210
2	4.5	0.55	0.05	90	634
3	4.5	0.55	0.08	90	278
4	4.5	0.55	0.05	120	326
5	4.5	0.55	0.05	150	197

effect in the gelling fluid (Al-Muntasheri et al., 2018; Reddy, 2014. Common types of gel breakers include oxidative agents, acids, and enzymes (J. Wang et al., 2020.

Generally, the typical residue value for fracturing fluids is approximately 550 mg/L (Yao et al., 2021. Residue levels depend on the crosslinker concentration, breaker concentration, and temperature (Asmorowati et al., n.d.; Yao et al., 2021. Higher breaker concentrations and elevated temperatures tend to reduce residue formation (Table 2). In this study, ammonium persulfate was used as a breaker at a concentration of 2% by volume. The results showed that the presence of barium and sulfate in the water increased residue levels by 5–25 percent, as shown in Fig. 8. At the highest tested concentration, $BaCl_2$ produced a residue of 460 mg/L, and Na_2SO_4 produced 502 mg/L. Both values remain below the international standard.

Degradation is often caused by changes in the chemical and/or physical structure of the polymer chain, leading to a reduction in the polymer's molecular weight. The structural characteristics of a polymer largely determine its susceptibility to degradation (Speight, 2020. Moreover, polymer degradation typically results from the scission of macromolecular main chains or side chains. Natural causes of polymer degradation include thermal activation, hydrolysis, biological activity (e.g., enzymes), oxidation, photolysis, and radiolysis (Madhavan et al., 2010; Müller 2002).

The increase in residue could be attributed not only to incomplete polymer breakage but also to the solubility and interaction between barium and the polymer. Further research is needed to identify the specific residual minerals produced.

HPG viscosity correlation due to barium concentration and temperature changes

The viscosity of polymer solutions exhibiting shear thinning behavior can be modeled using a power-law Equation 2 (Delshad et al., 2008. Shear thinning behavior, also known as pseudoplasticity, is a property of fluids in which viscosity decreases as the shear rate (the rate at which layers of fluid slide past each other) increases. This means that the fluid flows more easily under higher shear stress.

$$\mu = K\gamma^{n-1} \tag{2}$$

where μ is viscosity (mPa-s), K is the flow consistency index (mPa.sn), n is the flow behavior index (unitless), and γ is the shear rate (1/second). The values of K and n are influenced by the polymer concentration (Hashmet et al., 2014. Based on the results of testing the effect of barium

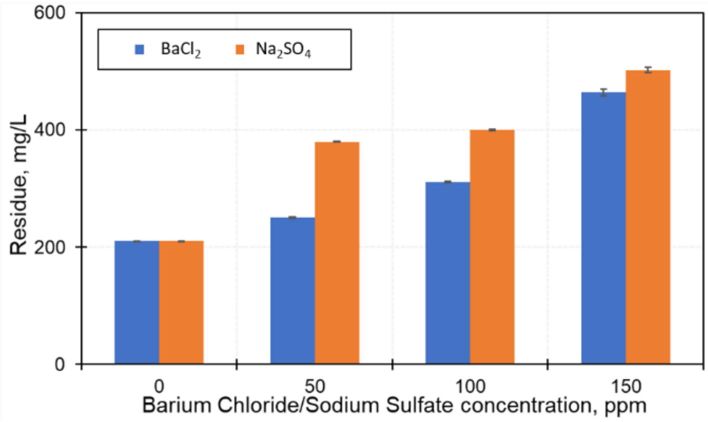

Figure 8. Effects of barium chloride and sodium sulfate concentrations on the residue polymer.

ions on HPG viscosity, the values of K and n are also influenced by the concentration of barium ions in the water sample. The correlation between the value of K and the concentration of barium ions is linear (Equation 3), while the correlation between barium concentration and the value of n is quadratic or polynomial (Equation 4).

$$K = a_1 C_D + a_2 \tag{3}$$

$$n = -b_1 C_D^2 + b_2 C_D + b_3 \tag{4}$$

C_D is dimensionless for the concentration parameter (Equation 5) that measures vertical and horizontal shifts due to changes in barium ion concentration in HPG solution. Next, eq. 3 and 4 are substituted into Equation 2, resulting in a correlation for viscosity against barium ion concentration (Equation 6).

$$C_D = \frac{(C_{test} - C_{ref})}{C_{ref}} \tag{5}$$

$$\mu = (a_1 C_D + a_2)\gamma^{\left((-b_1 C_D^2 + b_2 C_D + b_3) - 1\right)} \tag{6}$$

Where C_{test} is the concentration of barium ions in the test (ppm), and C_{ref} is the reference concentration of barium ions (ppm). The determination of the viscosity correlation constant for barium ions was performed using Solver feature in Excel. The optimum constant was obtained with an average error value of 0.06. The complete equation for viscosity of HPG due to barium concentration can be seen in Equation 7.

$$\mu = (-0.147 C_D + 61.526)\gamma^{\left((-0.063 C_D^2 + 0.114 C_D + 0.9487) - 1\right)} \tag{7}$$

Furthermore, the equation for viscosity change with temperature change is obtained in Equation 8 (Goel et al., 2000. Where a_T and b_T are horizontal and vertical shift factors that correlate which correlated with temperature and shear history (Goel et al., 2000; Williams et al., 1955). The horizontal and vertical shift factors related to temperature is obtained through Equation 9 and Equation 10.

$$\mu(T) = \frac{a_T}{b_T}\mu \tag{8}$$

$$\log a_T = \frac{-c_1 (T - T_0)}{(c_2 + T - T_0)} \tag{9}$$

$$\log b_T = \frac{-d_1 (T - T_0)}{(d_2 + T - T_0)} \tag{10}$$

where μ is the viscosity of HPG due to changes in barium ion concentration in eq. 6. The viscosity correlation coefficient with temperature changes was determined using Solver. Table 3 shows the coefficient of the shifting temperature equation with R-square value 98% and average error 5%, the small error percentage is also shown in graph (Fig. 9). In the graph, the solid line indicates the

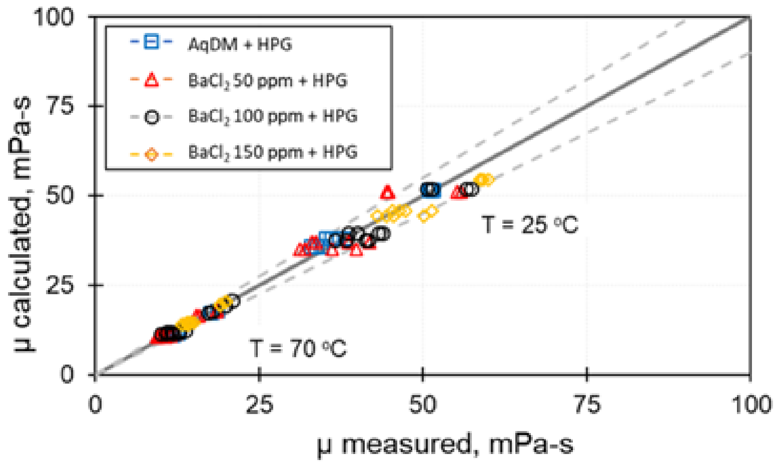

Figure 9. Viscosity ratio between measurement and correlation at 25 and 70 °C

trend line with an R-square of 1, while the dotted line represents the area with a percentage error of 10%. But this correlation has still limitation in concentration HPG used (3.6 g/L).

Table 3. Coefficient of the shifting temperature of HPG viscosity

c_1	0.5983
c_2	2.7020
d_1	-0.0155
d_2	-0.0108
Σ error	5.05
Average error	0.05
R^2	0.98

CONCLUSION

We investigated the effect of adding barium (Ba^{2+}) and sulfate (SO_4^{2-}) ions to linear fracturing fluids at different temperatures, complemented by residue analysis, and the results are summarized as follows. The optimum hydration time for HPG was determined to be 30 minutes, as indicated by the stable viscosity values obtained at shear rates of 7, 170, and 322 s^{-1}. The presence of barium salts increased the viscosity of the HPG linear gel at ambient temperature (25°C) where barium ions from a 150-ppm $BaCl_2$ solution enhanced viscosity by 30%, showing a greater effect compared to other divalent cations such as Ca^{2+} and Mg^{2+}. However, this viscosity enhancement was not significant at 70°C, likely due to the increased solubility of $BaCl_2$ at higher temperatures, which may weaken the interaction between barium ions and the polymer. In contrast, Na_2SO_4 at the same concentration exhibited no substantial effect on the viscosity of HPG linear gels, as the OH^- groups within the polymer structure interact primarily with cations in the water, reducing the dynamic radius of the polymer chains, increasing the molecular weight, and thereby increasing viscosity.

The residue content in the linear fracturing fluid was found to depend on the crosslink concentration, breaker concentration, temperature, and salt concentration, with the linear gel containing Na_2SO_4 producing more residue than the one containing $BaCl_2$. Additionally, the correlation of HPG viscosity, the presence of barium ions, and temperature changes follows a power-law relationship between viscosity and shear rate. These findings are crucial for enhancing the understanding of the physical mechanisms governing the influence of barium and sulfate ions on the rheology of fracturing fluids, which in turn affects the design and effectiveness of fracturing treatments in field applications. Future work will extend this investigation beyond linear gel systems to include crosslinked fracturing fluids.

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GLOSSARY OF TERM

Symbol	Definition	Unit
HPG	Hydroxypropyl guar	
ppm	Parts Per Million	
bbl	Barrel	
L	Liter	
mg/L	mili gram/ liter	
η	residue	mg/L
m	Weight of dried fliter solid	mg
V	Volume of the solution	L
μ	viscosity	mPa-s
K	Flow consistency index	mPa.sn
γ	Shear rate	1/sec
n	Flow behaviour index	
C_D	Dimensionless concentration parameter	

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