

# Rheological Study of Seawater-Based Fracturing Fluid Containing Polymer, Crosslinker, and Chelating Agent

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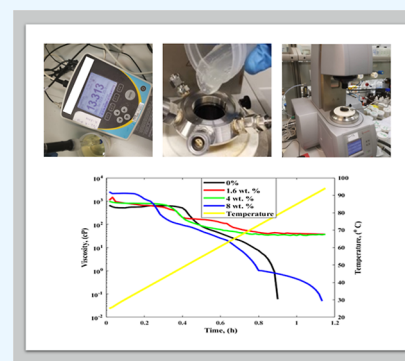
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**ABSTRACT:** Freshwater is usually used in hydraulic fracturing as it is less damaging to the formation and is compatible with the chemical additives. In recent years, seawater has been the subject of extensive research to reduce freshwater consumption. The study aims to optimize the rheology of seawater-based fracturing fluid with chemical additives that reduce the formation damage. The studied formulation consists of a polymer, a crosslinker, and a chelating agent to reduce seawater hardness. We used a standard industry rheometer to perform the rheology tests. By comparing five distinct grades [hydroxypropyl guar (HPG) and carboxymethyl hydroxypropyl guar (CMHPG)], we selected the guar derivative with the best rheological performance in seawater. Five different polymers (0.6 wt %) were hydrated with seawater and freshwater to select the suitable one. Then, the best performing polymer was chosen to be tested with (1.6, 4, and 8 wt %) *N,N*-dicarboxymethyl glutamic acid GLDA chelating agent and 1 wt % zirconium crosslinker. In the first part, the testing parameters were 120 °C temperature, 500 psi pressure, and 100 1/s shear rate. Then, the same formulations were tested at a ramped temperature between 25 and 120 °C. We observed that higher and more stable viscosity levels can be achieved by adding the GLDA after polymer hydration. In seawater, an instantaneous crosslinking occurs once the crosslinker is added even at room temperature, while in freshwater, the crosslinker is activated by ramping the temperature. We noted that, in the presence of a crosslinker, small changes in the chelating agent concentration have a considerable impact on the fluid rheology, as demonstrated in ramped temperature results. It is observed that the viscosities are higher and more persistent at lower concentrations of GLDA than at higher concentrations. The study shows the rheological response when different chemical additives are mixed in saline water for hydraulic fracturing applications.



## 1. INTRODUCTION

Hydraulic fracturing is applied to enhance the hydrocarbon recovery of low permeability formations. The recovery can be increased by placing a conductive fracture to bypass the near wellbore damage or extending the fracture to a significant depth to alter the reservoir fluid flow. The type of formation and freshwater availability are two of the most important considerations for fracture design. The design considers optimizing the fluid system, proppant type, injection rates, and volumes.<sup>1</sup> High viscosity and elasticity values are needed to transport the proppant, reduce settling velocity, and prevent proppant screen out. However, the fluid viscosity should be reduced after proppant placement to ease the flow back. It should also have low fluid loss properties and be compatible with formation fluids.<sup>2,3</sup> The fracturing fluid could be oil-based, water-based, or energized fracturing fluid. The water-based fracturing fluid has several drawbacks, including its high cost, large water consumption, formation damage, and expensive disposal issues.<sup>4–6</sup>

In 1953, the first-time water was used in hydraulic fracturing, also a variety of gelling agents were introduced.<sup>7</sup> Guar

derivatives are water-soluble and come from natural sources; they are commonly used to viscosify the fracturing fluids.<sup>8</sup> Guar is a long-chain polymer with a high molecular weight and extensive intermolecular association. Guar is chemically modified to achieve desired physical properties.<sup>9</sup> Usually, guar derivative powders are prepared by exposing the guar to high pH water for a certain time. Guar gums contain as much as 10–14% insoluble residue depending on the gum purity and method of isolation. These residues damage the proppant pack and the formation, making hydraulic fracturing jobs inefficient. However, guar is chemically modified to reduce the percentage of insoluble residue. The guar is treated with oxide, propylene oxide, and chloroacetic acid in an alkaline medium to produce hydroxyethyl guar (HEG), hydroxypropyl guar (HPG), and

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carboxymethyl guar (CMG). Another valuable grade of the guar is carboxymethyl hydroxypropyl guar (CMHPG) polymer. It can be prepared by adding guar to isopropyl alcohol and then sodium hydroxide pellets. Next, monochloro sodium acetate, chilled propylene oxide, and sodium borohydride should be added, respectively, with continuous mixing and heating. With several cycles of cooling and filtration, the CMHPG is synthesized.<sup>10–14</sup>

Crosslinkers are employed to enhance the fracturing fluid elasticity and viscosity without increasing the polymer concentration. This added elasticity changes the fluid behavior from viscous to viscoelastic. The crosslinked polymer has better viscosity and proppant carrying capacity than linear gel, but it is more damaging to the formation.<sup>7,14,15</sup> Crosslinking agents, which are a mixture of phosphate esters with metals, enable the fluid to transport more proppant into the fractures. Aluminum, antimony, borate, zirconium, titanium, potassium hydroxide (KOH), and isopropanol ( $\text{CH}_3$ )<sub>2</sub>CHOH are crosslinkers that are usually employed in the industry. Borate salts are instant crosslinkers that are used to keep the viscosity stable at high temperatures. They can be combined with the gelling agent to produce borate-crosslinked guar derivatives. In field operations, the delayed crosslinkers are more often used to transport proppant within the wellbore with lower frictional losses. Zirconium is an example of a delayed crosslinker. The Zr-crosslinked agent can be prepared by combining zirconium oxychloride, acetic acid, and triethanolamine. This crosslinker can increase the viscosity and breaking time at high temperatures.<sup>12,14,16–21</sup>

Almubarak et al. designed different formulations of SW-based fluid using CMHPG and other additives; they could achieve 200 cP viscosity at 148.8 °C and 100 s<sup>-1</sup>. They also analyzed the fluid performance using different tools such as a coreflood and zeta potential under different reservoir conditions. The designed fluids were used in conventional and unconventional wells in Saudi Arabia, and the fluid prevented forming scales and proppant impairment.<sup>22</sup> In another study, the zirconium crosslinker was added to nonfiltered SW in the Ghawar field in Saudi Arabia; the designed formulation reduced the impact of calcium, magnesium, and sulfate. The fluid showed stability at high temperatures up to 148.8 °C and resulted in low precipitation and good suspension properties.<sup>23</sup> Also, other studies were performed in different countries, such as the study on the South China Sea, where the researchers designed a continuously mixed SW-based fracturing fluid using the HPG polymer. They recommend using the proposed formulation and continuously mixing equipment on large scales.<sup>24</sup> CMHPG and metal crosslinkers formulations were also used with SW in the North Sea in Ensign tight gas fields. At adjusted pH, 87.8 °C, and 100 s<sup>-1</sup>, the researchers achieved over 600 cP viscosity.<sup>17</sup>

Seawater (SW) has lately become a popular alternative to freshwater in hydraulic fracturing operations. The reasons for this are the cost and scarcity of freshwater and the logistical difficulties in transporting it to offshore sites.<sup>15</sup> SW abundance solves the cost, transport, and scarcity issues, but it may generate other challenges such as formation damage, unstable fluid system, and low viscosities. To solve the SW issues, many additives are used to capture the damaging ions and improve the rheology. At high temperatures, the ions in SW may induce instability in the fluid and even form scales. It takes longer for the gelling agent to hydrate in SW, and the crosslinking

mechanisms differ. Consequently, the crosslinker has a greater impact on SW than on freshwater.<sup>25</sup> The key concern with SW is the presence of ions (e.g., sulfate) that might harm the formation and affect the fracturing fluid rheology. The SW rheology is affected due to the abundance of divalent (Ca, Mg) and monovalent (Na, K) ions, resulting in reduced viscosity. The major cause of precipitation and viscosity decrease is the divalent ions; nevertheless, monovalent ions reduce the viscosity in the absence of divalent ions.<sup>26</sup> The lower the salinity of the SW, the better the rheology of the formulated fluid. The SW composition and salinity varies from region to region; however, the experiments results can be applied to different SW formulations with slight changes.

One of the recent methods to solve the SW problem is to use the chelating agent to capture the ions and reduce the SW hardness.<sup>1,27,28</sup> In the low permeability offshore reservoir in south China, a successful proppant placement job was performed using instant dissolving SW has been prepared by adding HPG polymer, chelating agent, weak alkaline pH buffer, and instant and delayed crosslinker.<sup>29</sup> Initially, chelating chemicals were utilized to eliminate formation damage caused by the filter cake and scale deposition around the wellbore. In recent years, chelating agents have also been utilized as breakers, iron controls, and viscosifiers.<sup>30</sup> The industry uses various types of chelating chemicals, including ethylenediaminetetraacetic acid (EDTA), ethanolic phosphotungstic acid (EPTA), and L-glutamic acid-N, N-diacetic acid (GLDA). Chelating agents are generally employed in SW-based fracturing fluids to minimize the effects of SW by capturing the ions that impact the rheology and harm the formation. Chelating agents may also be utilized to enhance the thickening effect. The excess chelating agent may impact the crosslinker; thus, the chelating agent must be used in precise concentrations to reduce water hardness. Chelating agents such as GLDA are effective in the substitution of crosslinkers, breakers, biocide, clay stabilizers, and HCl. It decreases fracturing fluid's interfacial tension and is compatible with SW and stable at elevated temperatures up to 300 °F.<sup>27,28</sup> It has different reaction mechanisms with minerals at different pH levels.<sup>30</sup> The lower the salinity of the SW, the better the rheology of the formulated fluid. The SW composition varies from one region to another; however, the results of our research can be applied to different SW formulations with slight changes.

In this research, we intended to utilize saline water to replace freshwater in fracturing fluids. We wanted to design an efficient fracturing fluid with fewer additives. In this work, we tested a polymer, a crosslinker, and a chelating agent under different conditions. The first part of the study aims to understand the interaction of CMHPG polymer with a delayed crosslinker (Zr) and GLDA chelating at a saline environment representing seawater. The rheology response is compared to that of freshwater. Also, the impact of seawater in each individual chemical was thoroughly investigated. Gao et al. had studied the SW when the GLDA chelating agent was added to the hydrated CMHPG polymer under different conditions.<sup>24</sup> In this research, we want to optimize the SW-based fluid when the GLDA chelating agent and zirconium delayed crosslinker are added to the hydrated CMHPG polymer.

## 2. METHODOLOGY

**2.1. Materials.** The experiments were conducted on different grades of HPG and CMHPG polymers to select the

suitable polymer for further inspection. Anton Paar-MCR 302 is the utilized rheometer to achieve these goals. This section shows the composition of the utilized SW and the names, types, and chemical structure of the polymers. Also, basic details about the GLDA chelating agent and zirconium crosslinker are illustrated. Table 1 shows the main components that we find in general SW with details of individual salts and the total dissolved solids in grams/liter.

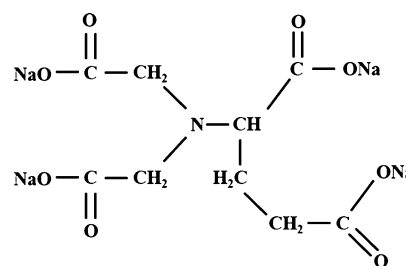
**Table 1. SW Used in Fracturing Fluid Preparation**

| component                            | g/l    |
|--------------------------------------|--------|
| NaHCO <sub>3</sub>                   | 0.165  |
| Na <sub>2</sub> SO <sub>4</sub>      | 6.339  |
| NaCl                                 | 41.172 |
| CaCl <sub>2</sub> ·2H <sub>2</sub> O | 2.387  |
| MgCl <sub>2</sub> ·6H <sub>2</sub> O | 17.644 |
| total dissolved solids (TDS)         | 67.707 |

The structure and the link position of the polymer chain (where it crosslinks with the other polymers) affect the properties of the solution. Consequently, this is the reason why there are many derivatives of the, that is, guar, which achieves the different properties. HPG is the most common polymer; however, the CMHPG guar derivative is preferred in the industry because of its better hydration, slower degradation, and compatibility with high and low pH environments.<sup>23,25,31</sup> The details of HPG and CMHPG grades are shown in Table 2.

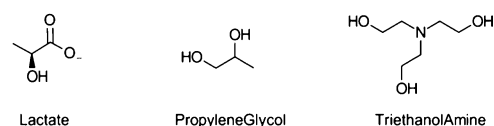
In this study, we used Dissolvine StimWell DGH GLDA, a high pH GLDA chelating agent. It has a pH of 13.9, but when 1 w/v % is used, the pH is in the range of 11–11.8. The fluid has 47% active content, and its chemical structure is abbreviated by GLDA-Na<sub>4</sub> and the detail is given in Figure 1. The chelating agent is more effective on a specific ion (i.e., high pH GLDA chelate calcium ions first), and the pH of the chelating agent affects chelating efficiency. Once this ion is dominant on SW, the more the chelating agent, the better the rheology and vice versa. This study can be expanded to the individual ions associated with SW. The functional groups (i.e., carboxyl group) associated with chelating agents can capture the ions from the SW and form stable compounds. The chelating agent loses the hydrogen from the carboxylic group and lets the ionized form of the chelating agent chelate the ions.<sup>29,32</sup>

Zirconium (Zr) has four electrons in the outer valence and exists in an ionic state (Zr<sup>4+</sup>). They are stabilized by ligands which are chemicals that attach to help stabilize nanoparticles in solution. They are employed to prevent Zr oxides from precipitating and to restrict the development of Zr nano-



**Figure 1.** Dissolvine StimWell DGH GLDA structure.

particles beyond what is required. Different ligands can create different zirconium crosslinkers with different performances, and they are shown in Figure 2.<sup>33</sup> In the experiments, we used ready liquid with assumed 14% active content. The liquid Zr-crosslinker is added after the addition of GLDA.



**Figure 2.** Ligands structure used with Zr crosslinker.

**2.2. Procedures.** All tests were conducted in Anton Paar's high-pressure, high-temperature (HTHP) at a constant pressure of 500 psi, shear rate of 100 1/s, and different temperature levels. Polymers were hydrated in seawater (SW) or de-ionized (DI) water for at least 40 min in all experiments. In the inspection of the crosslinker and chelating agent, we added the chelating agent to the hydrated polymer and mixed it for 5 min, and then, we added the crosslinker and mixed it for the same duration. When the fluid was ready, we loaded it in the HPHT cell and raised the temperature to 120 °C and the pressure to 500 psi. In all fixed temperature tests, we added 10 min of waiting time to equilibrate the fluid. Then, we began shearing and monitoring the viscosity. In ramped temperature experiments (from 25 to 120 °C at a rate of 1 °C/minute), we used the same preparation process. Then, we loaded the fluid to the HPHT cell, applied the required pressure, and then began ramping the temperature and shearing simultaneously.

**2.3. Experimental Design.** We did 32 experiments in this study, which are detailed in Table 3. First, we evaluated five grades of HPG and CMHPG in DI and SW to determine the best polymer for our needs. The selected polymer was utilized for all subsequent experiments. We next hydrated the selected polymer (XLFC-3B CMHPG) in DI and SW and added only the zirconium crosslinker without any other additives. The purpose was to understand the interaction of the crosslinker

**Table 2. HPG and CMHPG Polymers; Names, Types, and Chemical Structures**

| Name         | Type  | Chemical Structure   |
|--------------|-------|--|
| LH 212       | HPG   | $\text{Guar} - (\text{ONa})_n + n\text{H}_2\text{C} - \text{CHCH}_3 \rightarrow \text{Guar} - (\text{OCH}_2\text{CHCH}_3)_n^-$   |
| LH 202       | CMHPG | $\text{Guar} - (\text{ONa})_n + \text{ClCH}_2\text{COONa} \rightarrow \text{Guar} - (\text{OCH}_2\text{COONa})_n + n\text{NaCl}$ |
| XLFC-3B (ST) | CMHPG | (Gupta and Carman., 2009)  |
| S 285        | CMHPG | Not available  |
| S 284        | CMHPG | Not available  |

Table 3. Summary of the Performed Experiments

| water type | polymer (wt %)              | crosslinker (wt %) | chelating agent (wt %) | chelating agent type | sequence of blend            | temperature (°C)                 | number of experiments |
|------------|-----------------------------|--------------------|------------------------|----------------------|------------------------------|----------------------------------|-----------------------|
| DI, SW     | 0.6 of 5 different polymers | –                  | –                      | –                    | –                            | 120 °C                           | 10 (Figures 3 and 4)  |
| DI, SW     | 0.6                         | 1                  | –                      | –                    | with and without crosslinker | 120 °C                           | 4 (Figures 6 and 7)   |
| DI, SW     | 0.6                         | 1                  | 1.6, 4, 8              | high pH GLDA (13.7)  | GLDA then polymer hydration  | 120 °C                           | 6 (Figures 8 and 9)   |
| DI, SW     | 0.6                         | 1                  | 1.6, 4, 8              | high pH GLDA (13.7)  | Polymer hydration then GLDA  | 120 °C                           | 6 (Figure 10)         |
| DI         | 0.6                         | 1                  | 1.6, 4, 8              | high pH GLDA (13.7)  | Polymer hydration then GLDA  | Temperature ramp 25 °C to 120 °C | 4 (Figure 11)         |
| SW         | 0.6                         | 1                  | 1.6, 4, 8              | high pH GLDA (13.7)  | Polymer hydration then GLDA  | Temperature ramp 25 °C to 120 °C | 4 (Figure 12)         |

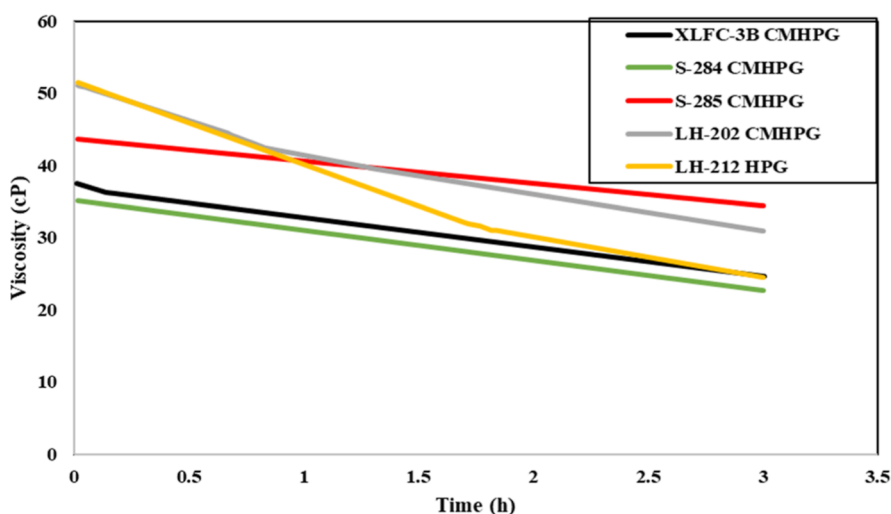


Figure 3. Viscosity of 0.6 wt % polymers hydrated in DI water tested at 120 °C, 100 1/s, and 500 psi.

and polymer in different water environments. Then, in two different sets of experiments, GLDA was added before and after polymer hydration to select the suitable procedure and verify the polymer hydration order (before or after GLDA addition). In both sets, the crosslinker was added as the last step, and the temperature was fixed at 120 °C. The impact of GLDA concentration was examined lastly with fixed polymer and zirconium concentrations in both DI and SW at ramped temperature experiments (from 25 to 120 °C at a rate of 1 °C/minute).

### 3. RESULTS AND DISCUSSION

This section discusses the viscosity of different HPG and CMHPG guar derivatives hydrated in DI and SW without any additional additives. Figure 3 shows the viscosity of different polymers in DI water after we hydrated all the polymers for 45 min and then the viscosity recorded for 3 h at 100 1/s shearing rate, 120 °C, and 500 psi pressure. The figure reports the viscosity of XLFC-3B, S284, S285, L202 CMHPG, and L212 HPG. All the polymers exhibited steady viscosity behavior; however, LH-212 showed drastic decrease in viscosity. We also noticed that the CMHPG is more stable than the HPG, that is, S-284, XLFC-3B, and S-285 sustained a minimal and gradual reduction in viscosity after 3 h. S-285 exhibited the highest viscosity with freshwater at the end of the test.

Figure 4 shows the behavior of these polymers in SW when hydrated for 45 min and then sheared for 3 h at 100 1/s shearing rate, 120 °C, and 500 psi pressure. We observe that

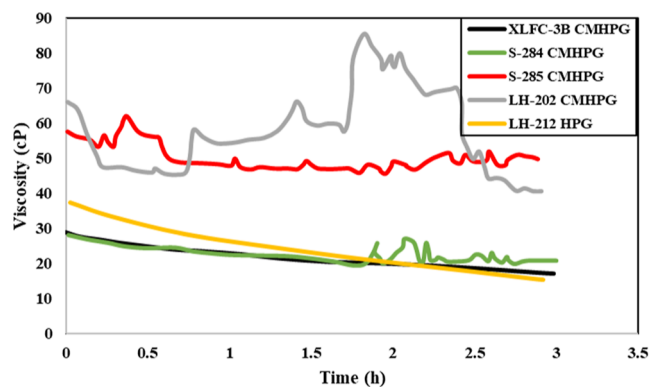
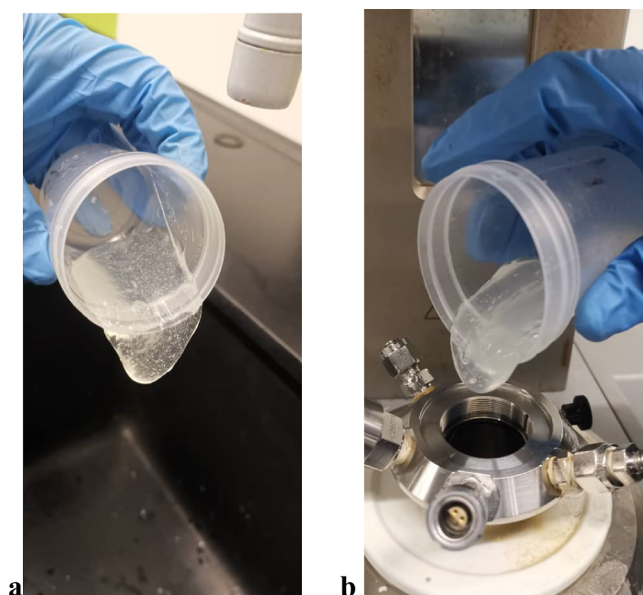


Figure 4. Viscosity of 0.6 wt % polymers hydrated in SW water tested at 120 °C, 100 1/s, and 500 psi.

LH-202 and S285 have the higher viscosities that exceed 60 cP but they were not stable, while the S-284 exhibited a fluctuation after 2 h. When hydrated on SW, most of the guar derivatives are not stable at high temperatures. Besides identifying the better guar derivative at high temperatures, we used some additives to obtain higher viscosities and stabilize the prepared fluids in the harsh reservoir conditions. From the figure, we noted that XLFC-3B and LH-212 are the most stable polymers; however, the viscosity of LH-212 decreased dramatically with time. We noticed that the hydration of the polymers did not complete at the decided 45 min, except for the XLFC-3B CMHPG and LH-212-HPG. We believe that

most of these polymers are originally designed from guar to withstand harsh conditions when hydrated in fresh water. In this study, we decided to use polymers with saline water. Therefore, most of these polymers were stable in freshwater but not in the SW. Because of the stable behavior of XLFC-3B, we decided to test the polymer with the crosslinker and chelating agent and subject it for further investigation. Comparing the viscosity of these polymers in SW to DI water, we noted that in the SW, the temperature affects the stability of most of the polymers at gelation regions.

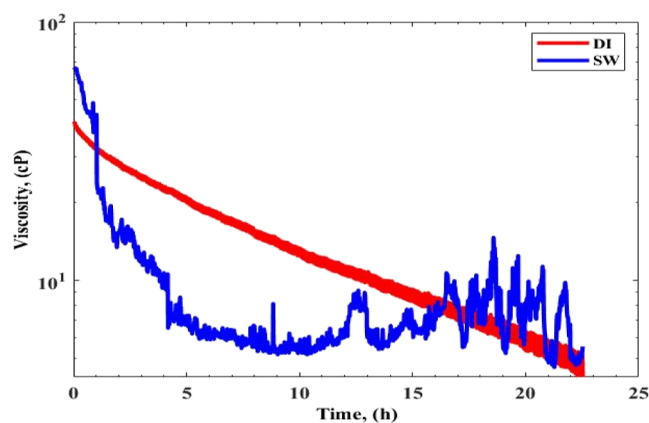
**3.1. Water Salinity Impact.** This section addresses the physical appearance when 1 wt % Zr crosslinker added to 0.6 wt % XLFC-3B CMHPG polymer hydrated in DI and SW. Here, we compare the mixtures at two different conditions (25 °C and 120 °C). In DI-based fluid, we noticed that the mixture crosslinked as we increased the temperature from 25 to 120 °C. The fluid looked viscous before doing the rheology test and even after the fluid was cooled to 25 °C. The physical appearance of the fluid is shown in Figure 5a. When the



**Figure 5.** (a) DI-based crosslinked gel after heating to 120 °C, (b) SW-based crosslinked gel before heating.

crosslinker is added to the hydrated polymer in SW, it instantly crosslinked before heating at 25 °C, as shown in Figure 5b. When the temperature reached 120 °C, the SW-based fluid lost its integrity, and the viscosity decreased. The zirconium is a delayed crosslinker and works after heating which is the expected outcome in DI. However, we observed that the salt ions in SW act as catalyst agents to the Zr crosslinking, which makes it possible to crosslink at low temperatures.

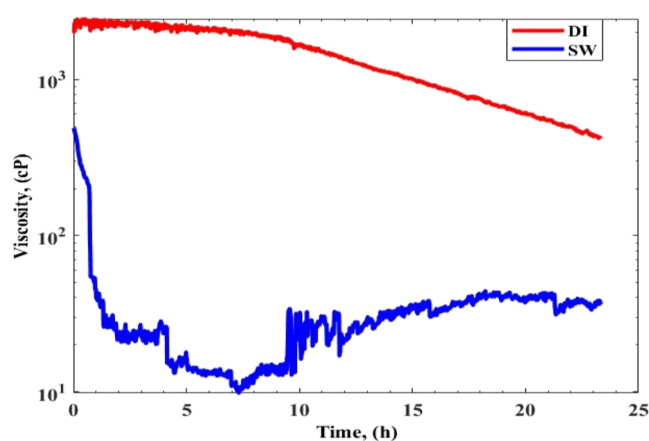
**3.2. Crosslinker Impact.** After the hydration of 0.6 wt % ST CMHPG in DI and SW, we compared the viscosity values at 120 °C, 100 1/s shear rate, and 500 psi pressure. The viscosities of the system in DI and SW are shown in Figure 6. As the red curve illustrates, the viscosity of the DI-based fluid decreases from 40 cP to less than 2 cP in 22 h. The blue line shows the viscosity of the SW-based fluid, which rapidly decreases from 68 to 2 cP in 6 h. However, at late shearing times after 11 h, the viscosity values fluctuated with a bandwidth of 10 cP.



**Figure 6.** Rheology of 0.6 wt % XLFC-3B polymer hydrated in DI and SW at 120 °C, 100 1/s, and 500 psi.

Figure 6 compares the viscosity of crosslinked ST CMHPG in DI and SW as 0.6 wt % CMHPG was hydrated in SW and DI for 40 min before adding 1 wt % zirconium crosslinker. Then, the DI- and SW-based were sheared for 22 h at 120 °C, 100 1/s shear rate, and 500 psi pressure. As we can see from the red curve in the figure, the DI-based fluid's viscosity was over 2000 cP for the first 4 h; after that, it steadily decreased until it reached 400 cP after 22 h. The blue curve shows the viscosity of the crosslinked SW-based fluid. In less than 2 h, the fluid viscosity decreased sharply from more than 500 to 20 cP. Once again, viscosity values fluctuated around 40 cP after 11 h of shearing. Exposing the SW-based fluid to high temperatures for long periods affects the polymer stability significantly, even when using the XLFC-3B polymer, which is proven to withstand high temperatures. However, the impact is more pronounced when adding the crosslinker, which indicates that the salt ions interfere with the crosslinking process resulting in weak links between the polymers.

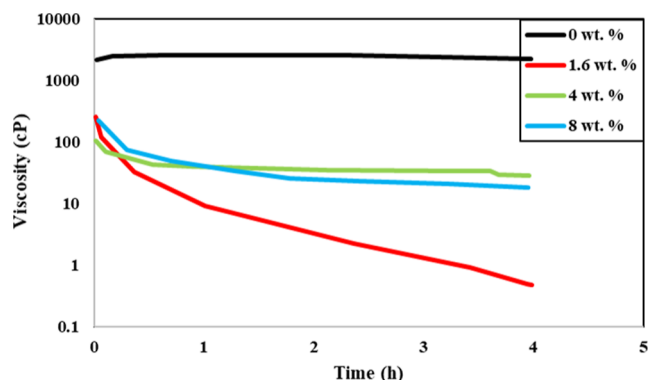
The viscosity of DI- and SW-based polymer increased sharply by adding the crosslinker. We can notice that the crosslinker had a major effect on the behavior of the DI-based fluid than the SW. One might observe that the decline in viscosity without the crosslinker was shaper (see Figures 6 and 7). Except for viscosity magnitude, the SW-based fluid behaved identically with and without the crosslinker. The crosslinker



**Figure 7.** Rheology of 0.6 wt % XLFC-3B polymer hydrated then crosslinked in DI and SW at 120 °C, 100 1/s, and 500 psi.

influenced the viscosity values of the SW, but not on the shape of the curve, as was the case with DI water.

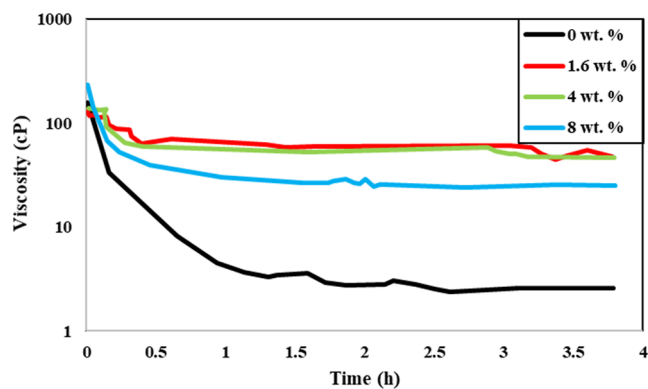
**3.3. Chelating Concentration and Hydration Order Impact.** This section investigated the order of adding polymer and chelating on the fluid system rheology. Also, the impact of GLDA concentration in both DI and SW was investigated. We prepared six fluids systems containing 0.6 wt % CMHPG polymer; three were hydrated in DI, and the other was hydrated in SW. These fluids were mixed with 1.6, 4, and 8 wt % GLDA chelating agent and then 1 wt % zirconium crosslinker was added. All experiments were performed at 120 °C temperature, 100 1/s shear rate, and 500 psi pressure. The high temperature is the main reason we used the high pH chelating agent, as it increases the stability of the CMHPG with SW under those conditions. Figure 8 shows the viscosity



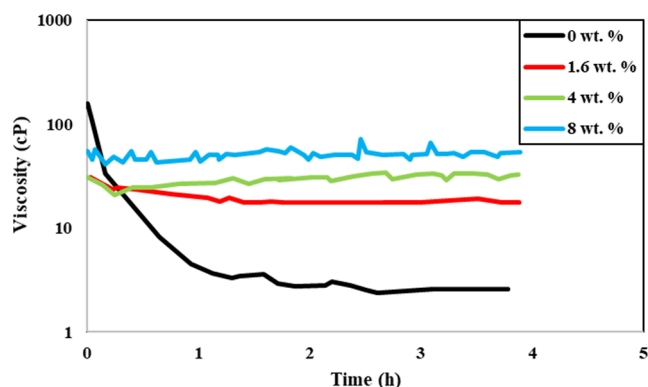
**Figure 8.** Rheology of 0.6 wt % XLFC-3B polymer, 1 wt % Zr in DI-based fluid, GLDA concentrations added after hydration at 120 °C, 100 1/s, and 500 psi.

of the three DI-based fluids compared with the crosslinked polymer in DI without a chelating agent. The crosslinked polymer with no GLDA had the highest and most stable viscosity. The addition of GLDA at any concentration lowered the system viscosity. We could notice that adding 1.6 wt % of GLDA resulted in the least stable system. Due to the absence of cationic ions such as  $\text{Ca}^{++}$ , GLDA chelates the zirconium, which is also cationic, resulting in less efficient crosslinking. Nevertheless, higher concentrations of GLDA resulted also in a thickening effect. Adding a chelating agent in DI-based water did not improve the stability and the viscosity values, but it reduced them. Hence, a crosslinker should not be mixed with a DI-based solution containing a chelating agent. However, when comparing the DI results to SW-based fluid, GLDA chelating at any concentration improved the viscosity as it captured the associated ions and allowed better attachment for the crosslinker to the polymer backbone.

Figure 9 shows the viscosity of the three SW-based fluids compared with crosslinked polymer in SW without a chelating agent. Figure 10 shows the viscosity of the three systems but with a reversed order (chelating was added before polymer hydration). We noticed that the viscosity values increase during all shearing times in the presence of GLDA compared to the crosslinked polymer without the GLDA. This behavior is opposite to the behavior we noted with DI-based fluid in Figure 8. We can see that increasing the chelating agent concentration results in higher initial viscosity values. All GLDA concentrations gave stable viscosity values; however, the 1.6 and 4 wt % gave higher viscosity than the 8 wt %



**Figure 9.** Rheology of 0.6 wt % XLFC-3B polymer, 1 wt % Zr in SW-based fluid, and GLDA added after hydration at 120 °C, 100 1/s, and 500 psi.

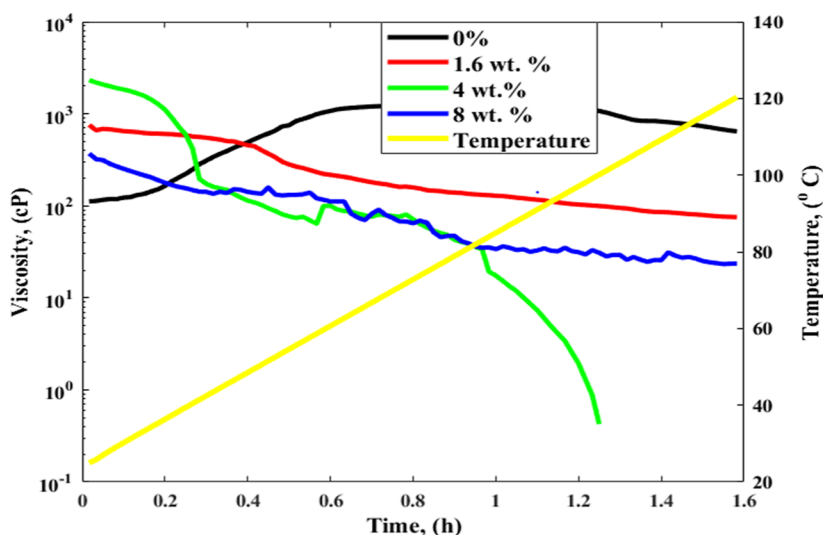


**Figure 10.** Rheology of 0.6 wt % XLFC-3B polymer, 1 wt % Zr in SW-based fluid, and GLDA added before hydration at 120 °C, 100 1/s, and 500 psi.

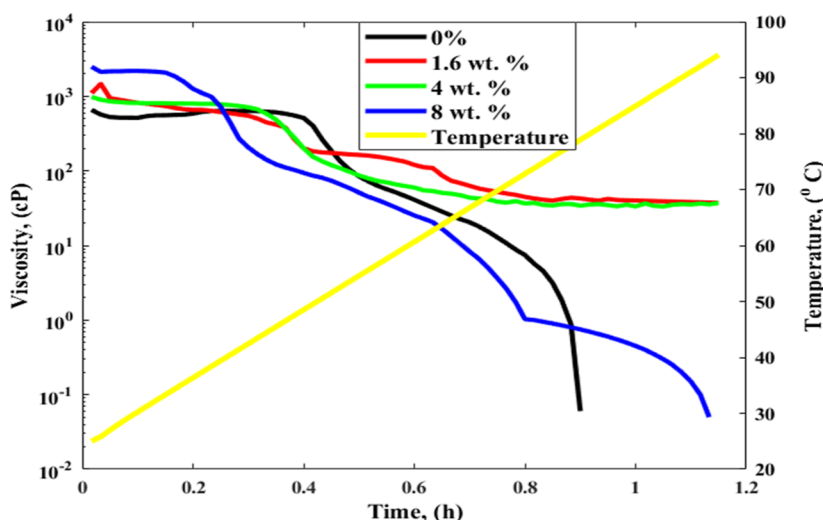
GLDA. The GLDA did not interfere with the crosslinking process as it chelates the divalent cations in SW such as  $\text{Ca}^{++}$ . Because of that, adding chelating proved to be a viable option in SW as compared to DI-based fracturing fluid.

Figure 10 shows the impact of adding GLDA to SW before polymer hydration, given everything else is the same. Reversing the order yielded lower viscosity, as reported in Figure 10. At the first 10 min, all GLDA concentrations gave viscosity lower than the crosslinked polymer without the chelating agent (0 wt %). No matter what the concentration was, the addition of GLDA before hydration lowered the initial viscosity. Because of this, polymer hydration was significantly impacted. After 20 min, the viscosity of crosslinked polymer with no GLDA dropped dramatically, while the GLDA solutions were able to keep the viscosity of the fluid during the test period. The behavior of each GLDA concentration was different from the behavior shown in Figure 9. The viscosity of the 4 and 8 wt % GLDA solution increased, while the viscosity of 1.6 wt % GLDA solution decreased. However, all viscosities reported in Figure 9 were higher. Also, we can get higher viscosities using 1.6 wt % than 8 wt % GLDA when hydrating the polymer first. This order of chelating and polymer mixing allows for better stability and uniform results, as the increase in chelating agent concentration increases the viscosity. However, it produced significantly lower viscosity values, which is not preferred when higher viscosities are out to be achieved.

**3.4. Ramped Temperature Impact.** The fluid system composition is similar in this set of experiments compared to



**Figure 11.** Rheology of 0.6 wt % XLFC-3B, 1 wt % Zr in DI-based fluid, and GLDA concentrations at ramped temperature (25–120 °C), 100 1/s, and 500 psi.



**Figure 12.** Rheology of 0.6 wt % XLFC-3B, 1 wt % Zr in SW-based fluid, and GLDA concentrations at ramped temperature (25–90 °C), 100 1/s, and 500 psi.

the previous ones where it contains CMHPG in SW or DI water, different GLDA concentrations, and Zr crosslinker, respectively. The viscosity was measured during temperature ramping from 25 to 120 °C, at a shear rate of 100 1/s, and pressure 500 psi. Figure 11 shows the viscosity of four DI-based fluid samples displayed with time and temperature. The crosslinked polymer with no GLDA showed an initial low viscosity around 100 cP. However, as the temperature increased, the viscosity increased until it reached 2500 cP at 1 h and 100 °C before it declined. When the polymer is crosslinked in a DI-based solution with no chelating agent added, the crosslinker is temperature-activated. In the 1.6 and 4 wt % GLDA samples, the starting viscosity values were very high (around 1,000 cP), while the 8 wt % GLDA solution started with 500 cP. The sample with the lowest GLDA concentration (1.6 wt %) had more stability and higher viscosity with shearing time. Adding GLDA to DI-based fracturing fluid reduces the stability of the system. Similar behavior to Figure 8 was recorded at temperatures higher than

60 °C. The chelating agent captures the Zr crosslinker in the DI solution, resulting in a decline in viscosity.

We tested the SW-based fluid at a ramped temperature in the following set of experiments. The viscosity was measured during temperature ramping from 25 to 90 °C, at a shear rate of 100 1/s, and pressure 500 psi. Figure 12 shows that all viscosities of SW-based samples started with very high viscosity (1000 cP) and crosslinks instantly either with or without the chelating agent. The no GLDA crosslinked polymer is similar to what we observed in a physical behavior in Figure 5. Also, we noted that lower GLDA concentrations lead to greater stability and viscosity values in SW-based fluid than no GLDA or 8 wt % GLDA samples. Ramping the temperature changed the behavior of the crosslinked SW fluid. It takes a longer time for the chelating agent at lower temperatures to capture the salt ions. Hence it is recommended to use an optimized GLDA concentration depending on the salt concentrations and operating temperatures.

#### 4. CONCLUSIONS AND RECOMMENDATIONS

The study investigated the impact of additives such as polymer, GLDA, and a crosslinker on the rheology of seawater. We selected the better guar derivative and applied a high pH GLDA chelating agent to tackle the salinity issues under harsh conditions. The following can be concluded from this study:

- 1 The behavior of the polymers in SW is highly affected by the elevated temperature; therefore, many polymers exhibit disturbance at high temperatures.
- 2 Adding a chelating agent and crosslinker after polymer hydration is preferable to adding a chelating agent before hydrating the polymer.
- 3 The lower the GLDA concentration, the higher and more stable the viscosity for both DI and SW systems.
- 4 The DI-based system outperformed the SW-based system in terms of stability and viscosity.
- 5 In DI-based systems, the GLDA chelates the crosslinker instead of salt ions which are not available in the DI system.
- 6 In SW-based systems, GLDA increases the stability and viscosity as it captures the ions that negatively impact the rheology.
- 7 Temperature ramping activates the Zr crosslinker in the DI-based system, while at room temperature, the Zr crosslinker was activated instantaneously in the SW-based system.

We recommend extending the study to a wider range of SW formulations, including different salinities. This also can be extended to produce water containing organic compounds (i.e., oil). Also, a detailed study can be performed on individual associated ions with SW, their challenges, and potential solutions.

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#### Notes

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