

**Optimizing Non-Freshwater Fracturing Fluid Rheology
Utilizing Chelating Agents**

BY

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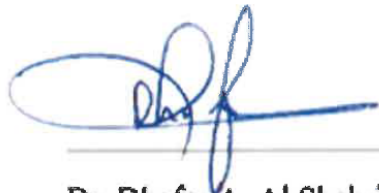
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LIST OF ABBREVIATIONS

A	:	Core cross-section area
c	:	Ostwald constant at specific temperature
CMHPG	:	Carboxymethyl hydroxypropyl gua
DI	:	Deionized Water
DW	:	Deionized Water
DSC	:	Differential scanning calorimetry
DSL	:	Differential scale loop
DSL	:	Differential scale loop
DSL	:	Differential scale loop
DTPA	:	Diethylenetriamine pentaacetate acid
EDTA	:	Ethylenediaminetetraacetic acid
EPTA	:	Ethanollic phosphotungstic acid
FW	:	Formation Water
GLDA	:	L-glutamic acid-N, N-diacetic acid
HCl	:	Hydrochloric acid
HEDTA	:	Hydroxyethylethylenediaminetriacetic acid
HHP	:	Hydraulic horsepower

HMDTMP :	Hexamethylene-diamine-tetramethylene-phosphonic
HPG :	Hydroxypropyl guar
HPHT :	High pressure high temperature
ICP_OES:	Inductively Coupled Plasma Optical Emission Spectroscopy
K :	Permeability
LNG :	liquified natural gas
MGDA :	Methylglycine N.N-diacetic acid
PW :	Produced Water
SW :	Seawater
TDS :	Total Dissolved Solid
Q :	Flow rate inside core
μ :	Apparent viscosity
Δx :	Length (core length),
ΔP :	Pressure difference.
ρ :	Fluid density
ν :	Kinematic viscosity

|

ABSTRACT

Full Name : [Amro Abdelrahman Ahmed Othman]

Thesis Title : [Optimizing Non-Freshwater Fracturing Fluid Rheology Utilizing Chelating Agents]

Major Field : [Petroleum Engineering]

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This research developed a new hydraulic fracturing fluid system that optimizes the non-freshwater Fracturing fluid rheology utilizing chelating agents. A minimal set of additives, including polymer, crosslinker, and chelating agents, were employed in this study. The reason for using crosslinkers is to raise the viscosity and elasticity while the cheating agents are employed to mitigate the impact of saline water. The research initially involved testing polymer compatibility with seawater under standard and harsh conditions. Subsequently, chelating agents were introduced into the system. The addition of crosslinkers posed compatibility challenges due to the high salinity and pH of chelating agents, prompting an in-depth investigation into individual ions in the selected seawater. The effect of each ion on the system was reported, and the conclusions were used to develop a better system. A complex study was performed on the CMHPG polymer, different chelating agents, and different crosslinkers to determine the best system that works under different conditions. A fracturing fluid system with high viscosity and minimum scale caused was identified. The system's performance was assessed through core flooding experiments conducted on Berea sandstone and Scioto core samples, measuring gelation and breaking with Differential Scanning Calorimetry (DSC) to determine suitable treatment times and temperatures, considering both instant and delayed crosslinkers. The efficiency of chelating agents in capturing cations was evaluated using Differential Scale Loop (DSL)

and Inductive Coupled Plasma (ICP) techniques, leading to the identification of the most effective chelating agent. The study is a field application of using SW instead of freshwater in hydraulic fracturing treatments to save freshwater water and reduce costs and efforts. This research successfully developed an optimal fracturing fluid system compatible with SW and can be utilized under different conditions. This system overcomes high salinity issues, including scale, component compatibility, and stability issues.

ملخص الرسالة

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عنوان الرسالة: تحسين لزوجة المياه عالية الملوحة المستخدمة في سوائل النفط الصخري باستخدام عوامل الخلب

التخصص: هندسة البترول

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هذا البحث طور مزيج جديد وحسن ريلوجيا سائل التكسير الهيدروليكي من اساس مياه مالحة باستخدام عوامل الخلب. بأقل عدد من الاضافات تشمل المبلمر أو البوليمر، عوامل التشبيك وعوامل الخلب تم اجراء الدراسة. الغرض من استخدام عوامل التشبيك للربط بين البوليمرات لرفع لزوجة ولدونة السائل اما عوامل الخلب فاستخدمت لتخفيف اثناء ملوحة الماء. ابتدا البحث بالعمل على التوافق بين المبلمر والماء المالح في الحالة القياسية (25 درجة مئوية، 1 بار) وفي الحالة القياسية (120 درجة مئوية، 34.5 بار) لاحقا تم اضافة عوامل الخلب للمنظومة. في المرحلة الثانية تمت اضافة عوامل التشبيك التي سببت حالة من عدم التوافق في المنظومة بسبب الملوحة العالية وارتفاع الاس الهيدروجيني الحادث بسبب عوامل الخلب. عدم التوافق هذا قاد لدراسة اولية اساسية لايونات المكونة للمياه المالحة المستخدمة في الدراسة تم ايراد اثر كل ايون في لزوجة المياه ومن ثم استخدمت خلاصات هذه الدراسة لتطوير ريلوجيا السائل الهيدروليكي. تم دراسة السائل بصورة موسعة باضافة عدد من عوامل الخلب وعدد من عوامل التشبيك بصورة منظمة لايجاد المزيج الافضل المتوافق مع مظم ظروف المكامن. تم تحديد المزيج المناسب ذو اللزوجة العالية المتوافق مع معظم الظروف. ومن ثم تم تقييم هذا المزيج عن طريق حقن العينات، حلقة القشرة الملحية التفاضلية، المسح التفاضلي للسرعات الحرارية و جهاز البلازما المقترنة حثياً وهذا ساهم في معرفة عوامل الخلب الاكثر فاعلية. هذه الدراسة هي تطبيق لاستخدام المياه المالحة بدلا عن المياه العذبة في التكسير الهيدروليكي للحفاظ على المياه العذبة وتقليل التكاليف والمجهود. هذا البحث نجح في تطوير سائل تكسير هيدروليكي متوافق مع درجات الملوحة العالية وظروف المكامن القاسية ويتخطى مشاكل التوافق بين مضافات سائل التكسير الهيدروليكي.

CHAPTER 1

Introduction

1.1 Fracturing Fluids

1.1.1 Water-based Fracturing Fluid

Hydraulic fracturing is applied to enhance hydrocarbon recovery of low permeability formations. Many factors need to be considered in the fracture design such as formation type, reservoir conditions, and the availability of freshwater which is affected by the allowed budget. The hydraulic fracture design includes selection of the fluid type, proppant type, injection rate, and treatment volume. In hydraulic fracturing operations, the fluid slurry is injected to propagate the fracture and keep it open. Hydraulic fracturing can be used either to control and reduce sand production or to improve well productivity. The productivity is increased by placing a conductive fracture to bypass the near wellbore damage, extending the fracture to a significant depth, and alter the reservoir fluid flow (Economides & Nolte, 2000).

The earliest attempt to stimulate the flow of hydrocarbon from a well was in the 1860s, using explosive charges in the borehole (Shooters, 2014). The first successful job was performed in Kansas in 1947. In that time, the performed jobs consisted of 750 gallons of gelled crude oil or kerosine and 400 lbs of sand, with 10-15 hydraulic horsepower (HHP). After that, water is used in hydraulic fracturing, and surfactants and clay stabilizers were added for the first time. In the 1960s, large-scale hydraulic fracturing operations began. In the 1970s, crosslinking agents were developed and used widely, while in the 1980s, horizontal drilling was invented. Modern fracturing operation utilizes more than 1,500 HHP and pump rates larger than 100 bbls/ min. In 2012, 2.5 million hydraulic fracturing operations have been performed worldwide, over 1

million of them were in the US (Gandossi & Von EStroff, 2015; Hoffman et al2014). The following summarizes the common water-based fracturing fluids: a) **Conventional fluid** which includes gelling agents (linear gel, crosslinked), guar, and its derivatives are used as viscosifiers to get the required fluid viscosity to frack the formation and transport proppant. Guar is a long-chain polymer with high molecular weight. The guar derivative powders are prepared by exposing the guar to high pH water for a certain time. Hydration of the guar form the linear gel which is used as a lead of the fracturing fluid (Prepad). Adding crosslinkers to the gelled fluid increases the viscosity and reduces the needed concentration of polymer, which raises the fracturing fluids carrying capacity. Several types of crosslinkers are used and breakers are needed to allow the flow back (Barati & Liang, 2014).

b) **Slickwater**, in this type more than 90% of the frack fluid volume is water, the guar or its derivatives (i.e. CMHPG) are added in small amounts to raise the viscosity and distribute the proppant into the required locations of the fracture. This type needs a high pumping rate and excessive usage of freshwater. These water-based fluids are used for several reservoir types and at wide ranges of temperatures. However, they can form an emulsion and cause water blockage, and scale precipitation near-wellbore (Barati & Liang, 2014; Gaurina-Međimurec et al., 2021; Liang et al., 2016; Singh, 2014). c) **Viscoelastic surfactants**, this type of fluid was developed to prevent the damage caused by the residue left after an incomplete break of polymers. The added surfactants form micelles that increase the water viscosity without using the crosslinkers. The formed rod-shaped structured chains break into small micelles when exposed to oil or gas and subsequently the viscosity breaks (K.B. Naceur; Michael J. Economides, 1989). d) **Alcohol and emulsion fluids**. e) **Hybrid fracks** using slickwater followed by cross-linked fluid to achieve the good properties in both types mentioned (Barati & Liang, 2014b ; Fink, 2021).

1.1.1.1 Freshwater less fracturing fluid

The fracturing fluid can be classified into a) water-based fracturing fluids and b) water-less fracturing fluids. The second type includes liquid CO₂, liquid N₂, liquified natural gas (LNG), and heavy oil. The fluids in the second type are used to avoid water blockage in sensitive formations. Recently a freshwater-less fracturing fluid terminology has been introduced to cover all water-less fluid mentioned and the seawater and produced water, excluding the freshwater from the definition. In this section seawater-based as part of freshwater-less fracturing fluids and its additives are reviewed. Also, the ions exist in seawater and the scales they form, beside the proposed additives in the formulation proposed in this research which is, the polymers, chelating agents, and crosslinkers.

Seawater fracturing fluids and associated ions

The oil and gas industry recently showed a great interest in utilizing seawater (SW) instead of freshwater in hydraulic fracturing operations. This is due to the high cost and scarcity of freshwater and challenges in transportation to offshore platforms (Harris & van Batenburg, 1999). Seawater becomes under research focus to replace the scarce freshwater. Using seawater can provide a cut in water transport costs in offshores. However, using seawater causes formation damage and reduces the viscosity. To solve this issue a lot of additives are used to capture the ions, prevent the damage, and improve the rheology. The ions associated with seawater cause instability issues for the fluid at high temperatures and may form scales. It experiences a delay in the hydration of the gelling agent and crosslinking mechanism changes. Therefore, crosslinker has more effect on the seawater more than on the freshwater (Alohaly et al., 2016). The SW-based fracturing fluids are categorized into three groups based on the thickener used: a) synthetic polymer, b)

viscoelastic surfactant, and c) plant gum or its modified products (Gao et al., 2015). The main concern with SW is the ions (e.g, Sulfate) that could damage the formation and impact the fracturing fluid rheology. In fracturing fluid preparation, many factors are considered to reduce the formation damage and improve the viscosity. Both divalent (Ca^{2+} , Mg^{2+}) and monovalent (Na^+ , K^+) ions are present in the SW, which affects its rheology. The divalent ions were found to be the source of precipitation and viscosity reduction. Monovalent ions only reduced the viscosity when the divalent ions are absent (Elsarawy et al., 2017). Table 1 shows typical values of the ions found in two different types of seawater found in the literature, these regions are the Gulf region and the South China Sea region.

Table 1 Examples for two different formulations of seawater

Gulf region (Derkani et al., 2019)		South China Sea region (Zhuang et al., 2017)	
Compound	g/L	Compound	g/L
NaCl	40.3	NaCl	24.53
MgCl ₂	8.46	MgCl ₂	5.2
CaCl ₂	1.79	CaCl ₂	1.16
NaHCO ₃	0.16	NaHCO ₃	0.21
Na ₂ SO ₄	6.58	Na ₂ SO ₄	4.09
		KCl	0.695
TDS	57.29	TDS	35.885

Scale Inhibitors

The Scale is one of the serious problems in the oil and gas industry, it may cause failure, increase cost and decrease production (Olajire, 2015). The most common type of scale when using the seawater is the formation scale because the connate water in the formation contains calcium and barium ions. Many types of scales can occur with the use of SW-based fracturing fluids either due to ions or due to change in physical conditions. Several types of scale can be noticed in this situation: a) calcium carbonates (CaCO_3) which increase with temperature, pH, and decrease of TDS, b) calcium sulfates CaSO_4 (Gypsum), c) barium Sulfate BaSO_4 (Barite), and d) iron scales (i.e. Ferrous Carbonate FeCO_3) (FQE-Chemicals, 2018). Ca^{2+} and Mg^{2+} ions precipitation may happen at high pH (greater than 10). Therefore, it is necessary to control the pH level as well as using scale inhibitors. The thermal stability of SW must be carefully observed (Prakash et al., 2016).

One of the solutions is to prevent or reduce precipitation and deposition of scale formation during fracturing using scale inhibitors. When fracturing with seawater the type of ions associated with seawater determines the scale that may occur in the fracturing system. The scale inhibitors prevent the precipitation of carbonates and sulfates (calcium carbonate, calcium sulfate, and barium sulfate) which may plug off the formation (Binmerdhah, 2007). Many kinds of scale inhibitors are discussed in the literature including, acrylic acid polymers, maleic acid polymers, phosphates, ammonium chloride NH_4Cl , ethylene glycol, polyacrylate, and phosphonates (Hexamethylene-diamine-tetramethylene-phosphonic (HMDTMP) and Diethylene -triamine-pentamethylene-phosphonic). HMDTMP proved that it can prevent calcium sulfate scale with scale index < 1 (Amjad & Koutsoukos, 2014; Kan et al., 2009; Mazumder, 2020). A gelled polymeric phosphonate-seawater based can prevent calcium scale at high temperatures. The pH adjusting agents can be used to prevent the magnesium scale.

Since scale inhibitors interact with metallic crosslinkers, the viscosity of seawater is affected (Almubarak et al., 2019).

pH/buffer Controllers

Usually called buffers, they are added to either increase or decrease the pH of the fluid system. They are used in gelled and crosslinked treatments to maintain their effectiveness. The pH distresses the initial gelation rate, stability and breaking properties. The right pH of the fluid must be gotten before adding a crosslinker. Examples of buffers that increase the pH are sodium hydroxide and potassium hydroxide (Harris, 1988).

Bactericide/ Biocides

The presence of bacteria reduces the holding capacity of the fracturing fluid, and the organisms release the hydrogen sulfates gas from seawater. These two issues need to be prevented using bactericides and biocides. Glutaraldehyde, $\text{CH}_2(\text{CH}_2\text{CHO})_2$, the commercial name is glutaral is the biocide used in fracturing operations. It is used with seawater fracturing fluid to prevent microbial growth which leads to erosion and corrosion of pipes during fracturing operations. Amides and aldehydes are often used as biocides with the seawater-based fracturing fluid. It inhibits micro-organisms that could produce gases e.g. hydrogen sulfides (Xue & Voordouw, 2015).

Breakers

The breakers reduce the viscosity of fracturing fluid after the established fracture closes. This can be done by breaking long-chain molecules into a smaller molecule, which leads to the gel breakdown, and releases the proppants into the fracture, then allows fracturing fluid to flow back. The breakers work as crosslinker absorbers leaving no crosslinkers or little amounts of

crosslinkers within the fluid. While it improves fracture conductivity, it risks the proppant placing and may cause premature screen out. The viscoelastic surfactant fluids prepared from seawater-based fluid experience stability in terms of viscosity, adding the normal nanoparticles to this fluid breaks it slowly. This behavior is good in terms of placing the proppant efficiently and fluid cleanup, but this too stable viscosity drop causes slow cleanup which may affect the fracture conductivity. To avoid this a controlled time breaker is desired. Surface modified nanoparticles are examples of a time-controlled breaker (Almubarak et al., 2019; Patil et al., 2013; Sangaru et al., 2017).

The breakers increase the fluid elasticity which allows relaxed hydration to ease the flow to the fracture through the wellbore. Bromate breakers are the most common breakers, besides the peroxydisulfates such as ammonium persulfate $(\text{NH}_4)_2\text{S}_2\text{O}_8$. Two common types of breakers are used, the first is the internal breakers which are directly added with the fluid during surface mixing. They and breaks the viscoelastic fluids without the need for contacting the reservoir fluid. At this type, no much pressure or time is required to break the fluid, ease the cleanup of viscoelastic fluids and prevent viscous emulsions. The second is the external breakers which added to the flow back (Almubarak et al., 2019; Crews & Huang, 2007; Patel & Raju, 2020).

Achieving the required viscosity with a specific fluid such as crosslinked fluids in the lab rheometers is not enough to be applied in fracturing. Because recent studies revealed that the pressure in the reservoir reduces the viscosity measured in laboratories by 80%. (Fuller, 2017) proposed mechanism utilizes the pressure effect and shift the crosslink/temperature stability of borate-crosslinked gels. Subsequently, this leads to irreversibly breaking the viscosity (Armstrong et al., 2010).

Fracturing fluid additives have been questioned by many environmental organizations, this pushed the research toward producing environmentally friendly additives. Breakers were no exception to this concern, for this reason, enzymes have been used as an alternative for oxidative chemical breakers because of many purposes. They are naturally regenerating catalytic breakers, polymer specific, eco-friendly, miscible, easily operated, cause no harm to the equipment.

Clay Stabilizers

The fine migration into the well is one of the main problems faces the production operations. In fine migrations clay particles move and cause extra drag force. The clay stabilizers create brine carrier fluids, which prevent swelling and migration of formation clays or fine sands that could block pore spaces and reduce formation permeability. As active clay minerals are in the formation, it is necessary to use clay stabilizers. Tetra-methyl ammonium chlorite $(\text{CH}_3)_4\text{N}^+\text{Cl}^-$, potassium chloride, polyamine, and calcium chloride are the common clay stabilizers (Gaurina-Medimurec et al., 2021; Patel & Raju, 2020).

Surfactants

After fracturing and placing proppants in tight and nano permeability formations (<0.01 md) the remaining fluid blocks the formation and limits the production to fracture surface. To solve this issue the surfactants need to be effective by changing the wettability of the rock, reduce the interfacial tension between solids and fluids, and forming stable emulsions between oil and water. The surfactants help in reducing seawater fracturing fluid surface tension aiding fluid recovery by working as demulsifiers or support other additives. Some surfactants can react with the formation, and some of them can be retrieved with produced water. Methanol, isopropanol alcohols are typical examples of surfactants (Reynolds, 2020).

Acids

This is usually 5 - 15% and sometimes to 28% of Hydrochloric acid (HCl) or Muriatic acid. The acid serves different purposes including, cleaning the cement and drilling mud prior to fracturing fluid injection and provide an accessible path to the formation, helps to dissolve minerals, and initiate fissure (cracks) before pumping the fracturing fluid.

Friction Reducers

Sodium acrylate acrylamide polymer ($C_3H_3NaO_2$)_n, another type is Polyacrylamide (C_3H_5NO)_n (Baker et al., 2001). It slicks the water and allows the injection of fluid at optimum rate and pressure by minimizing friction between fluid and pipe.

Chelating Agents

Chelating agents were originally used to remove formation damage by the filter cake, and scale around the perforation. Recently, chelating agents are used as a replacement for breakers, iron controls, viscosifiers, such as surfactants, polymers, and cross-linkers (Hassan et al., 2020). Several types of chelating agents are used in the industry such as Ethylenediaminetetraacetic acid (EDTA), Ethanolic phosphotungstic acid (EPTA), and L-glutamic acid-N, N-diacetic acid (GLDA). Figure 1 shows the chemical structure of different chelating agents used in the industry.

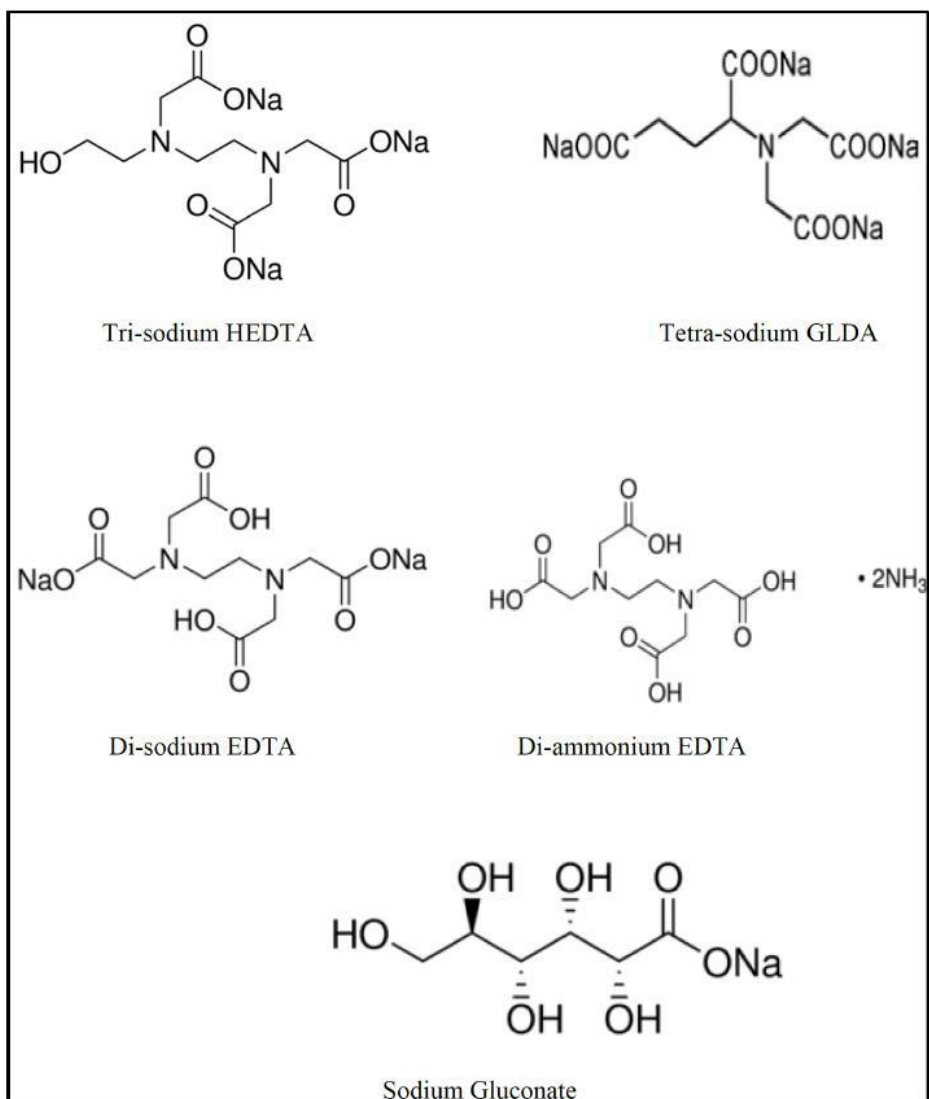


Figure 1 Chemical structure of different chelating agents (Elsarawy et al., 2016)

Chelating agents are ultimately used in seawater-based fracturing fluids to remove the impact of seawater by removing its hardness. This hardness impact polymers' performance and damages the formation. Chelating agents can also be used in improving the thickening effect besides the polymers and crosslinkers. The excess chelating agent can impact the breaker and crosslinker, it is also required to use the minimum concentration to remove this hardness. This study focused on GLDA application to SW. GLDA as a chelating agent proved to work as a replacement for crosslinkers, breakers, biocide, clay stabilizers, and HCl. It reduces the interfacial tension of fracturing fluid. It is compatible with SW and

shows stability in high-temperature formations up to 300 oF, and can be used to control the reaction rate (Kamal et al., 2018; LePage et al., 2011). It has a different reaction to minerals at different pH levels (Hassan et al., 2020).

Proppants

Solid materials typically sand, treated sand, or manmade ceramic materials, designed to keep an induced hydraulic fracture open during and following the fracturing treatment. It should be carefully selected when seawater is used to have the following properties: it should resist corrosion and crushing and has a low density to reduce the settling velocity (Gaurina-Medimurec et al., 2021). The proppants are selected based on several criteria, which are represented by a) proppant strength, proppant grain size, and grain distribution, b) amounts of sizes and impurities, c) Proppant density, and d) Roundness and sphericity (Liang et al., 2016). There are several types of proppants used with different types of fracturing fluid and different reservoirs, these types have different properties and costs. These proppants are mined natural sand proppants, ceramic proppants, resin-coated proppants, and light-weighted proppants (Liang et al., 2016).

1.1.2 Energized Fracturing Fluids (Foams)

The energized forms are used to serve several purposes, limiting the amount of water invasion into the formation which reduces the blockage caused by water. It also minimizes the water contact to sensitive clays, improves the recovery due to the free gas filling near the fracture area. Many foam systems are used in the industry, CO₂ and N₂ with HPG and foaming agents (energized) are used to reduce formation damage. They can be used with small volumes of slickwater but foam stability issues are faced. They can also be used with and crosslinkers as well as viscoelastic surfactants (Barati & Liang, 2014; Fink, 2021).

1.1.3 Oil-based Fracturing Fluids

The Oil-based, benefits are low water usage and better fluid handling but riskier and has a high cost which achieves the slowest proppant settlement and highest fracture conductivity (Fink, 2021; Gaurina-Medimurec et al., 2021). Many fracturing fluid types are used in the industry since there are different formations, lithologies, and mineral components, as well as different formation fluids, different objectives, pumping configurations, and technologies (Gupta, 2010).

1.2 Problem statement

Due to the scarcity and high cost of freshwater, especially in the Gulf region, the utilization of seawater as a fracturing fluid gained noticeable interest. Seawater usage instead of freshwater can address some of these problems and cut costs. However, what differentiates the seawater from freshwater that it contains high total dissolved solids (TDS) (Harris & van Batenburg, 1999). This TDS may damage the formation and degrade the performance of the fracturing fluids. To reduce the damaging effect and improve the rheology of the seawater many additives are added, some of them are expensive, while the others are toxic additives. Many studies were performed on saline waters and their applications on hydraulic fracturing, however the claim of ability to use it in hydraulic fracturing is questioned. This study explores the use of saline waters including seawater and produced water in hydraulic fracturing fluid.

Few studies explored the use of chelating agents on fracturing fluids to overcome the issue of the ions associated with saline waters. This study utilizes different chelating agents to neutralize the effect of ions associated with saline waters and make that water behave as freshwater. The rheology and proppant settlement, the scale inhibition, effluent tests, and

core flooding experiments were used to evaluate the resulting fluid. From this work it was found that it is possible to use different chelating agents at different conditions for different purposes on fracturing fluids. The findings of this work opened the door for further investigation to apply them in different aspects of petroleum industry, such as EOR and drilling fluids.

1.2.1 Research Objectives

This research aims to formulate a cheap effective fracturing fluid with the minimum number of additives then describes some preliminary results achieved from that fluid. It also shows a plan to apply these formulated fluids with proppant on carbonate formations. Then, it suggests the better formulation which achieves the slowest proppant settlement and highest fracture conductivity.

Due to the high cost and shortage of freshwater, seawater-based fracturing fluid can be utilized. The seawater has monovalent and divalent ions that affect both the formation and rheology of fracturing fluid. Many additives are used to eliminate the impact of these ions. However, these additives could be costly, toxic, and could harm the environment.

The goal of this research is to formulate seawater-based fracturing fluid with the minimum number of additives. Chelating agent, namely GLDA, will be used to capture the unwanted ions and provide thickening effect. The formulation will be tested with proppant to measure the settling velocity and will be applied in the API conductivity cell. The research also has theoretical parts which include measuring the compatibility of the additive with several analytical techniques as nuclear magnetic resonance NMR and Fourier transform infrared FTIR and specify the dominating fluid behavior is it thickening or crosslinking. These data can be applied to kinetic modeling. The planned tasks include:

- a. Optimizing fluid system by performing viscosity tests at different conditions such as concentration, temperature, pH, water salinity, and shear rates. The flow sweep and frequency sweep experiments will be performed in Anton Paar rheometer (MCR 302).
- b. Testing the compatibility of the additives using various analytical techniques.
- c. Test proppant settlement using static measurement.
- d. Test the formation damage and fluid performance on core flooding system.

1.3 Methodology

This section specifies the equipment used through this research. The main evaluation tests used for this research were the rheology tests, where different standard rheometers including MCR-302 rheometer were used. Also, the conductivity, and pH measurements, the differential scale loop (DSL), VINCI core flooding system, Inductive coupled plasma ICP-OES, and differential scanning calorimetry (DSC).

1.3.1 Rheometers

Anton parr MCR-302, and Chandler 555 viscometer are used to assess the rheological properties of various fluids including viscosity. with time and shear. Different conditions including temperature, pressure, and shear rate are applied to the fluid variations.

1.3.2 Differential scale loop (DSL)

Is an equipment used to examine the for scale formation, and scale inhibitors, in aqueous solutions. Different chelating agents with different conditions were tested with this device at high temperatures and pressures, and the results were used to enhance the fluid prepared.

1.3.3 VINCI core flooding system

Is a simple and industry competent core flooding system used for single and multiphase flow at different conditions. It was used to measure the permeability and to view the impact of salinity through different scenarios and after each stage of the pumping. Some cores were cracked to mimic the fluid flow through a fracture, and to compare the cracked to solid core sample.

1.3.4 Inductively coupled plasma ICP-OES

Inductively Coupled Plasma Optical Emission spectroscopy (ICP-OES) is used to analysis the salinity of the fluids, to find how much of certain ions are in a sample. In this study, this equipment was used to study the chelating agents types and concentration effect on the saline waters. It was used also for the effluent study to measure the scales formed in cores, during core flooding.

1.3.5 Differential scanning calorimetry (DSC)

The Differential scanning calorimetry equipment is used to study the fluids gelation kinetics. In this study it was used to subject heat to the developed fracturing fluid samples to measure the gelation behavior and time with heat added.

1.4 Thesis Organization

This work is presented in nine chapters. The aim is to show the research in a step by step details and to present the main results from each step. The findings of the chapters are solving the issues faced at the research phase. The following listing shows a brief for each chapter.

Chapter 1: This chapter shows a brief for the subject of research, the reason for the research. Also, the study objectives and the equipment utilized.

Chapters 2: This chapter is a literature review on chelating agents types, usage with saline waters, and its compatibility with other fracturing fluid components at different conditions. This review specifies the gaps and the current saline water-based hydraulic fracturing fluid current status to fulfill the objectives of the study.

Chapter 3: This chapter explores the preparation methods, test the performance of polymer and chelating agents at saline and freshwaters. Study of pH effect at standard condition. Different pH chelating agents, and different concentration of high pH GLDA were used. The study of high pH fluid at high pressure high temperature.

Chapter 4: The study in this chapter identifies salt ion significantly influences the viscosity of the CMHPG polymer. It shows the result of addition chelating agents to hydrated polymer on individual saline ions solutions compared to saline water and deionized water (freshwater). The impact of varied ions (Na^+ , Ca^{2+} , Mg^{2+} , and SO_4^{-2}) concentrations on the rheology of CMHPG polymer was studied. The high pH GLDA impact was tested with various salt ions at 1 M concentration. The study was conducted at fixed temperature of 70 °C.

Chapter 5: This chapter is a continuation of chapter 4 study and divided to 3 parts: the first part handles the crosslinker concentration effect. The second optimizes the chelating agent at a selected crosslinker concentration. The first and second parts were performed at a fixed temperature of 70 °C. The third part reports the temperature effect for the optimized concentrations of the crosslinker and chelating agent for each individual ion at 120 °C. The SW and DI experiments were performed as the baseline for all three experiment sets.

Chapter 6: This chapter suggest the best polymer at high temperatures 120 °C for both freshwater and saline water. It also shows the results of complex fluid polymer, a crosslinker, and different concentrations of high pH GLDA chelating agent at saline water under at high

temperature of 120 °C compared to freshwater. The study also compared similar fluids at ramped temperature from 25 °C to 120 °C.

Chapter 7: The study in chapter 6, showed that the high pH chelating agent is not compatible with zirconium crosslinkers at high salinity and high temperature. In this chapter different chelating agents including (low pH GLDA, high pH GLDA, low pH DTPA and high pH EDTA) were tested at 70 °C. Conductivity measurements, ICP and DSL measurements were conducted on different combinations and the better formulation was suggested.

Chapter 8: The selected formulation found in chapter 7 was applied to thermal measurements utilizing DSC to find the gelation time and explain the behavior at different conditions. This fluid was also tested on VINCI core flooding system utilizing standard methods and the permeability for different cases was measured.

Chapters 9: This chapter finalizes the results and outcomes of the study as one body. It also suggests the continuation in the area in order to complete the aspects of utilizing chelating agents in fracturing fluids as well as the other applications of oil industry.

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CHAPTER 2

Chelating Agents As a Solution of Saline Water Fracturing Fluids Associated Issues: A Review

2.1 Introduction: Fracturing Fluids

Hydraulic fracturing is employed to improve the recovery of hydrocarbons from formations with low permeability. The fractured design is affected by the formation type, reservoir conditions, availability of freshwater, and budget constraints. This design encompasses the selection of fluid and proppant types, injection rate, and treatment volume. The process involves injecting a fluid slurry to create and maintain fractures. Hydraulic fracturing serves several purposes: improved well injectivity, storage and environmental remediation, controlling sand production, and enhancing well productivity. Productivity is boosted by creating a conductive fracture to bypass near-wellbore damage, extending the fracture to a significant depth, and modifying the flow of reservoir fluids (Economides & Nolte, 2000). In the 1860s, the initial effort to stimulate the reservoir involved the utilization of explosive charges within the borehole. (Shooters, 2014). In Kansas, in 1947, the first successful hydraulic fracturing job was performed. During this period, the operations involved 750 gallons of gelled crude oil or kerosene, 400 lbs of sand, and 10-15 hydraulic horsepower (HHP). Subsequently, water became the primary fluid for hydraulic fracturing and surfactants, along with clay stabilizers. Large-scale hydraulic fracturing operations commenced in the 1960s. By the 1970s, crosslinking agents were developed and widely employed. In the 1980s, horizontal drilling was invented. Modern fracturing operations now utilize over 1,500 HHP and pump rates exceeding 100 bbls/min. As of 2012, more than 2.5 million hydraulic fracturing operations have been conducted globally, with over 1 million of them taking place in the United States. (Gandossi & Von EStroff, 2015; Hoffman

et al2014). Various types of fracturing fluids find application in the industry due to the diverse nature of formations, lithologies, mineral components, formation fluids, objectives, pumping configurations, and technologies (Gupta, 2010). The fracturing fluid is either water-based or water-less fracturing fluid, which is classified as oil-based or energized fracturing fluids.

2.1.1 Water-based Fracturing Fluid

The water-based fracturing fluids are mainly of 5 types: a) **Conventional fluid**, which employs gelling agents such as linear gel and crosslinked gel, utilizing guar and its derivatives to enhance fluid viscosity for fracturing the formation and transporting proppant. Guar, a high molecular weight long-chain polymer, is exposed to high pH water to produce guar derivative powders. The hydration of guar forms the linear gel, utilized as the lead for the fracturing fluid (Prepad). The addition of crosslinkers to the gelled fluid enhances viscosity and elasticity and reduces the required polymer concentration, thereby increasing the carrying capacity of the fracturing fluid. Various types of crosslinkers are employed, and breakers are necessary to facilitate flow back. (Barati & Liang, 2014). b) **Slick-water**, in this category, over 90% of the hydraulic fracturing fluid volume comprises water, with guar or its derivatives (such as CMHPG) added in minimal quantities to elevate viscosity and effectively distribute proppant throughout the desired areas of the fracture. This approach necessitates a high pumping rate and the extensive use of freshwater. These two types find application in various reservoir types and across a broad temperature spectrum; they have the potential to create emulsions, leading to water blockage and scale precipitation near the wellbore (Barati & Liang, 2014; li et al., 2021; Liang et al., 2016; Singh, 2014). c) **Viscoelastic surfactants**: this fluid was formulated to mitigate the harm

arising from the remnants left behind following an incomplete breakdown of polymers. The incorporated surfactants create micelles, elevating water viscosity without relying on crosslinkers. The structured chains formed in a rod-shaped manner break into smaller micelles upon exposure to oil or gas, leading to subsequent viscosity reduction (Naceur & Economides, 1989). **d) Alcohol and emulsion fluids.** **e) Hybrid fracks:** One of the examples of hybrid fracturing fluids is utilizing slick water and subsequently employing crosslinked fluid to attain favorable characteristics from both mentioned types. (Barati & Liang, 2014b; Fink, 2021).

2.1.2 Oil-based Fracturing Fluids

The advantages of the oil-based option include reduced water usage and improved fluid handling, but they come with higher risks and costs. This approach results in slower proppant settlement and provides the highest fracture conductivity. In this type, the fluids used are liquified natural gas (LNG) and heavy oil. (Fink, 2021; Gaurina-Međimurec et al., 2021).

2.1.3 Energized Fracturing Fluids (Foams)

Energized variations fulfill various purposes, including limiting water intrusion into the formation to decrease blockage from water. They also decrease water interaction with sensitive clays and improve recovery by facilitating the presence of free gas near the fracture area. The industry utilizes various foam systems, such as CO₂ and N₂ with HPG and energized foaming agents, to lessen formation damage. Although they can be applied with small slick water volumes, challenges related to foam stability may emerge.

Furthermore, these energized forms can be used in conjunction with crosslinkers and viscoelastic surfactants. (Barati & Liang, 2014; Fink, 2021).

As the human population increased, the demand for additional energy rose, making hydraulic fracturing treatments the most reliable method for oil and gas production. Consequently, there has been an evolution in the scale and frequency of hydraulic fracturing treatments, accompanied by advancements in the quantity, variety, and size of additives used. Since the early fifties, the challenges associated with hydraulic fracturing have evolved. Recently, freshwater-less fracturing fluid terminology has been introduced in the research to cover all water-less fluids mentioned, including seawater and produced water, excluding freshwater from the definition, given its cost and scarcity. The primary emphasis of this paper is on the utilization of chelating agents as additives in saline water-based fracturing fluids. It begins by introducing saline water fracturing fluids and examining the challenges linked to their use. Subsequently, it delves into the definitions and benefits of frequently used fracturing fluid additives, followed by a review of the theory and application of chelating agents in saline water fracturing fluids.

2.2 Saline Water Fracturing Fluids

The oil and gas industry has recently demonstrated significant interest in employing saline waters (SW) instead of fresh water for hydraulic fracturing operations. This interest is from the elevated costs and limited availability of freshwater, coupled with cost and challenges in its transportation to offshore platforms. Also, utilizing water produced from oil production and post-fracturing treatment flow-back solves the disposal issues (Harris & van Batenburg, 1999). There is a growing research focus on substituting freshwater with

saline water. Nevertheless, the utilization of seawater may damage the formation, impair the permeability of the fracture face, damage the proppant pack, and reduce the viscosity (Hassan et al., 2020). The issues arise from the interaction of associated ions, with salts reacting and causing the formation of scales. Various additives are utilized to capture these ions, prevent formation damage, and enhance rheological properties. The SW-based fracturing fluids are categorized into three groups based on the thickener used: a) synthetic polymer, b) viscoelastic surfactant, and c) plant gum or its modified products (Gao et al., 2015). Research on saline water fracturing fluids includes experimental investigations into hydration and formulation of fracturing fluids and fundamental studies on the associated salts. It also includes the field studies that apply the findings from experimental research. Al-Muntasheri, (2014) conducted a comprehensive review of hydraulic fracturing fluids at the beginning of the new millennium. The review encompassed advancements in the design of water-based fracturing fluids, incorporating both freshwater and produced water. In a specific study, freshwater was employed to produce a high-viscosity fracturing fluid using CMHPG polymer, surfactant, buffer, gel stabilizer, pH stabilizer, and zirconium crosslinker. The resulting fluid demonstrated the ability to sustain a viscosity above 200 cP for 90 minutes under varying shear rates and high temperatures (Kalgaonkar & Patil, 2012).

By the year 2005, the number of horizontal wells in the Barnett Shale had surpassed that of vertical wells, utilizing water ranging from 2,900 to 20,700 m³ per well by 2010. The freshwater usage for hydraulic fracturing in the Barnett Shale had reached 145 Mm³ by June 2011, supporting the stimulation of approximately 15,000 wells. Another instance of substantial water consumption occurred in the Haynesville shale-gas play, where there were 1,820 wells by mid-2011. The total water usage in this case amounted to 36 Mm³,

with a median of 21,500 m³ per well for horizontal wells in 2010. This extensive water consumption is anticipated to rise in response to the growing demand for natural gas (Nicot & Scanlon, 2012). This water needs to be replaced with a sustainable source of seawater or produced water. Given the substantial demand for water, the limited availability of freshwater, the necessity to manage produced water disposal, and the abundance of seawater, the latter has been suggested as a viable alternative. Within the formation, oil is naturally coupled with high-salinity water. When these formations encounter other sources of high-salinity water, various types of scales can be generated (BinGhanim et al., 2017).

There were several attempts to treat the produced water; however, treating the produced water in hydraulic fracturing operations results in suboptimal quality fracturing fluids, typically characterized by elevated hardness and salinity levels. This claim is particularly applicable to flowback fluid, which often contains a high polymer loading (Haghshenas & Nasr-El-Din, 2014). Using the water-based fracturing fluid has some limitations, such as the high cost, huge water consumption, formation damages, and costly disposal challenges (Anandan et al., 2017; Faroughi et al., 2018; Yekeen et al., 2018). A study focused on the design and operation of a membrane to treat the saline waters from bacteria, selected ions, and hardness (Basu et al., 2015). These kinds of studies are expensive and not sustainable for the huge consumption in the fields.

2.2.1 Hydration Studies

The study of the hydration of various polymers by (Das et al., 2014) examined the impact of varying concentrations of KCl on the hydration and viscosity of diverse polymers, including CMC, HPG, and CMHPG. The polymer hydration was sustained for 60 minutes,

revealing a significant decrease in viscosity. It is worth noting that the study utilized only a 7% concentration of KCl as a salt, which does not accurately replicate saline water conditions. The HPG and CMHPG polymers were hydrated at different sources of seawater with the availability of crosslinkers and other additives. The tests were performed at high temperatures to measure viscosity at a shear rate of 40 1/s, and the results were compared to those of individual ions. The study identified that concentrations exceeding 4 g/l of sulfate, 0.6 g/l of calcium, and 1.7 g/l of magnesium led to a delay in hydration, modified the crosslinking mechanism, and resulted in the formation of BaSO₄ scales (Alohaly et al., 2016). Similarly, (Yamak et al., 2018) studied the hydration of the polymers in saline waters. The study emphasized that saline water, when combined with a delayed crosslinker and a phosphonate-based scale inhibitor, could uphold a stable fluid viscosity of 500 cP under conditions of 250°F and a shear rate of 40 1/s. This stability persisted for two hours before experiencing a breakdown, in contrast to freshwater, which exhibited prolonged stability.

Huang et al., (2005) assessed the hydration of a 30pptg CMHPG in untreated produced water with a total dissolved solids (TDS) of 23,000 when a 70Q CO₂ foamed 30-lb crosslinker was introduced. Various pH values and appropriate hydration times were examined. Notably, a pH of 5.7 at a hydration time of 40 minutes resulted in a viscosity of 2500 cP, with viscosity increasing as hydration time extended. Subsequently, the crosslinked fluid was utilized to stimulate a well in San Juan County, New Mexico, USA, specifically targeting deep zones in hydraulic fracturing formations. The treatment led to a doubling in gas production. Li et al., (2015) achieved the maintenance of a viscosity of 100 cP for produced water with a total dissolved solids (TDS) concentration of 330,000 mg/L

at 275 °F. This viscosity was accomplished through the incorporation of diverted alcohol, an organometallic crosslinker, and various additional additives.

2.2.2 Associated ions

The ions associated with seawater lead to instability issues for the fluid at high temperatures and may form scales. It may cause a gelling agent hydration delay and may change crosslinking mechanisms. Consequently, the crosslinkers have more impact on the seawater than on the freshwater (Alohaly et al., 2016). The main concern with SW is the ions (e.g., sulfate) that could damage the formation and impact the fracturing fluid rheology. Saline water contains both divalent ions (Ca^{2+} , Mg^{2+}) and monovalent ions (Na^+ , K^+), influencing its rheological properties. Divalent ions were identified as causing precipitation and reducing viscosity. In the absence of divalent ions, monovalent ions only lead to viscosity reduction. (Elsarawy et al., 2017). Table 2 shows the typical values of the ions found in two different types of seawater in the literature: the Gulf region and the South China Sea region.

Table 2 Examples of two different formulations of seawater

Gulf region (Derkani et al., 2019)		South China Sea region (Zhuang et al., 2017)	
Compound	g/L	Compound	g/L
NaCl	40.3	NaCl	24.53
MgCl ₂	8.46	MgCl ₂	5.2

CaCl ₂	1.79	CaCl ₂	1.16
NaHCO ₃	0.16	NaHCO ₃	0.21
Na ₂ SO ₄	6.58	Na ₂ SO ₄	4.09
		KCl	0.695
TDS	57.29	TDS	35.885

2.3 Fracturing Fluid Additives

The optimum fracturing fluid needs to have the ability to initiate and propagate fractures, carrying proppants to the intended location in the fracture at a low settlement velocity. Following the treatment, the fluid should undergo a controlled break, transforming into a low-viscosity fluid for post-treatment cleanup. Additionally, the fluid must be compatible with both the formation rock and fluid to minimize damage. It should effectively reduce friction pressure losses and employ environmentally friendly chemicals that adhere to local regulations. Furthermore, the fluid should prove to be cost-effective. To effectively control these properties, a wise selection of additives is essential. The subsequent sections will review the primary additives, their properties, and their respective uses (Das & Rahim, 2014; Samuel et al., 2000)

2.3.1 Polymers

The crucial additive in fracturing fluids for enhancing water viscosity is the gelling agent. The increased viscosity contributes to more effective hydraulic fracturing, higher proppant transport ability, wider fractures, and lower fluid leak to the formation. Higher viscosity can be achieved by increasing gel loading, represented by the volume of gel added (in gallons) per thousand gallons of water (gpt). Commonly employed concentrations for added polymers used in the industry are 50-200 pounds per 1000 gallons of water. Polymers utilized in fracturing are water-soluble and may originate from natural sources like guar. Chemical processes are applied to natural polymers to attain the desired physical properties. Examples of modified guar derivatives include carboxymethyl hydroxypropyl guar (CMHPG) or carboxymethyl hydroxyethyl cellulose guar (HEC). These polymers are desired and widely used due to their cost-effectiveness and easy hydration. The low gel load of these polymers has the potential to result in high viscosity and efficient proppant transportation (Fink, 2021; Gaurina-Medimurec et al., 2021; Harris, 1988; Montgomery, 2013). In comparison to synthetic systems, natural guar polymers exhibit superior shear stability and more effective cleanup (Al-Muntasheri, 2014). Recent developments in the polymerization process have been reviewed with a focus on polymer interactions, polymerization mechanisms, and industry-utilized techniques. (Bahri-Laleh et al., 2018). CMHPG is produced by diluting native guar in a particular solution to achieve a more robust chain. This guar derivative is favored in the industry due to its enhanced hydration, prolonged degradation, and resilience in low-pH environments. (Abdul Majid et al., 2017; Alohalay et al., 2016; Szopinski et al., 2015; Wilson, 2017).

2.3.2 Crosslinkers

Crosslinkers are introduced to enhance fluid viscosity at lower molecular weights. These substances connect the long chains of the polymer, elevating not only the viscosity but also the fluid's elasticity. In CMHPG, different guar networks can be formed using either hydroxyl groups with borate or carboxyl groups with metals, such as zirconium. Borate enables reversible crosslinking in CMHPG, facilitating prolonged suspension of proppants at high shear rates. Conversely, zirconium irreversibly crosslinks with CMHPG, demonstrating minimal proppant settling at low shear rates. (Hu et al., 2015). Crosslinking guar derivatives can be achieved through two methods: reversible and irreversible crosslinking, depending on the shear rate of the operation. Specific catalysts can be employed to generate various polymer types with the desired properties. One of these catalysts is introduced by (Hanifpour et al., 2020). These catalysts allow for alterations in the constitutional structure of reversible polymers. Upon removal, the stability characteristic of irreversible polymers can be maintained. The stability of irreversible polymers is attributed to a bond energy stronger than that of reversible polymers (Nishimura et al., 2017; Zhang et al., 2018).

2.3.3 Breakers

Breakers reduce fracturing fluid viscosity after the fracture closes, breaking down long-chain molecules and releasing proppants. This breaking enhances fluid flow back, but breakers absorb crosslinkers, risking proppant placement and premature screen-out. Seawater-based viscoelastic surfactant fluids with normal nanoparticles experience stable viscosity, aiding proppant placement and cleanup. However, a viscosity drop that is too

stable can result in slow cleanup, impacting fracture conductivity. To address this, a time-controlled breaker, like surface-modified nanoparticles, is desired. (Almubarak et al., 2019; Patil et al., 2013; Sangaru et al., 2017). Breakers enhance fluid elasticity, easing hydration flow to the fracture through the wellbore. Bromate breakers, along with peroxydisulfates like ammonium persulfate $(\text{NH}_4)_2\text{S}_2\text{O}_8$. Two types are employed: internal breakers added during surface mixing break viscoelastic fluids without contacting reservoir fluid, requiring minimal pressure or time, facilitating fluid cleanup, and preventing viscous emulsions. External breakers are added to the flow back (Almubarak et al., 2019; Crews & Huang, 2007; Patel & Raju, 2020). Lab rheometers alone cannot predict applicability in fracturing as reservoir pressure reduces measured viscosity by 80% (Fuller, 2017). A suggested mechanism utilizes pressure to alter crosslink/temperature stability in borate-crosslinked gels, irreversibly breaking viscosity. (Armstrong et al., 2010).

2.3.4 Acids

Acids are employed in the primary stages of standard hydraulic fracturing treatments (pad fluid stage), typically at concentrations ranging from 5% to 30% hydrochloric acid (HCl). The acid serves different purposes in hydraulic fracturing, including cleaning the cement and drilling mud prior to fracturing fluid injection and providing an accessible path to the formation. It helps in dissolving minerals and initiates fissures (cracks) before pumping the fracturing fluid. The acid is also used in acid fracturing, which serves as an alternative to propped fractures in formations like dolomites and limestones, where the acid dissolves the rock to create conductivity without using proppants to prevent fracture closure (Economides & Nolte, 2000).

2.3.5 pH/buffer Controllers

Commonly referred to as buffers, these substances are introduced to adjust the pH of the fluid system, either increasing or decreasing it. The pH buffers are employed in gelled and crosslinked treatments and play a crucial role in preserving their efficacy. The pH significantly influences the initial gelation rate, stability, and breaking properties. It is imperative to achieve the appropriate pH before introducing a crosslinker. Sodium hydroxide and potassium hydroxide are examples of buffers that raise the pH (Othman et al., 2021; Othman et al., 2023; Harris, 1988). The pH-adjusting agents can be used to prevent the magnesium scale (Almubarak et al., 2019).

2.3.6 Bactericide/ Biocides

Bacterial presence diminishes the fracturing fluid's holding capacity, and these organisms release hydrogen sulfide gas from seawater. Bactericides and biocides are employed to prevent the issues introduced by bacterial presence. Utilized in fracturing operations, glutaraldehyde, $\text{CH}_2(\text{CH}_2\text{CHO})_2$, serves as a biocide. When employed with seawater fracturing fluid, it prevents microbial growth that could cause erosion and corrosion of pipes during fracturing operations. Amides and aldehydes are commonly paired with seawater-based fracturing fluid as biocides. Their function is to inhibit microorganisms that may produce gases, such as hydrogen sulfide. (Xue & Voordouw, 2015).

2.3.7 Clay Stabilizers

Fine migration into the well poses a significant challenge in production operations. In this process, clay particles move, resulting in additional drag force. Clay stabilizers are

employed to generate brine carrier fluids, preventing the swelling and migration of formation clays or fine sands. This prevention is crucial as it avoids blockage of pore spaces and helps maintain formation permeability, especially when active clay minerals are present in the formation. Clay swelling is more pronounced in freshwater compared to saline water, requiring the use of clay stabilizers. Saline water, up to 8 wt. % clay, does not necessitate the application of clay stabilizers. Common clay stabilizers include tetra-methyl ammonium chloride $(\text{CH}_3)_4\text{N}^+\text{Cl}^-$, potassium chloride KCl, polyamines (i.e. Agmatine $\text{C}_5\text{H}_{14}\text{N}_4$), and calcium chloride CaCl_2 (Gaurina-Međimurec et al., 2021; Mahmoud & Nasr-El-Din, 2011; Patel & Raju, 2020).

2.3.8 Friction Reducers

Primarily employed with slickwaters requiring lower viscosities, this fluid type is suitable for very tight formations to generate extended and intricate fractures. Sodium acrylate acrylamide polymer $(\text{C}_3\text{H}_3\text{NaO}_2)_n$, another type is Polyacrylamide $(\text{C}_3\text{H}_5\text{NO})_n$ (Baker et al., 2001). It slicks the water and allows the injection of fluid at optimum rate and pressure by minimizing friction between fluid and pipe. The following paragraphs are for the additives added to improve the performance of the saline waters.

2.3.9 Surfactants

Following fracturing and proppant placement in tight and nano-permeability formations (<0.01 md), the residual fluid blocks the formation and limits the production to the fracture surface. Addressing the blockage requires an effective surfactant that can change the wettability of the rock, reduce the interfacial tension between solids and fluids, and form stable emulsions between oil and water. These surfactants assist in lowering seawater

fracturing fluid surface tension, facilitating fluid recovery by acting as demulsifiers or supporting other additives. Some surfactants can react with the formation, and some of them can be recovered with produced water. Examples include methanol and isopropanol alcohols (Reynolds, 2020). The improved gelling performance of viscoelastic surfactants (VES) when exposed to saline water-associated ions makes them a feasible choice for increasing seawater viscosity. They can be a viable substitute for polymers and crosslinkers (Barati & Liang, 2014). Although VES possess shear-thinning viscoelastic properties, they leave no residue during flowback and can be customized with internal and external breakers. In research conducted by (Sun et al., 2019), they developed a seawater-based fracturing fluid system by integrating anionic and non-ionic viscoelastic components. This advancement not only lowers offshore fracturing preparation expenses but also provides valuable insights into formulating fracturing fluids utilizing produced water. A different research (Othman, Alsulaimani, et al., 2022) examined the influence of anionic, cationic, and neutral polymers on VES rheology in saline water. The synthetic seawater, originating from the sea, had a total dissolved solids (TDS) of 32,500 mg/L and a sodium ion concentration of 1,320 mmol/L. This fluid system exhibits excellent high-shear rate performance while causing minimal formation damage. Zhang et al., (2019) highlighted the excellent salt tolerance of viscoelastic surfactants, making them well-suited for application in saline water as fracturing fluids. Crews (2005) introduced an internal breaking system; he utilized aqueous breakers to control viscosity decrease between 80-225 °F for VES saline water fluids.

2.3.10 Scale Inhibitors

Scale is one of the serious problems in the oil and gas industry, and it may cause failure, increase costs, and decrease production (Olajire, 2015). Various scales may develop when using SW-based fracturing fluids, either due to ions or alterations in physical conditions. The principal and most problematic scales in reservoirs are calcium sulfate and barium sulfate, as they are present in the connate water of the formation. The initial strategy for employing saline water in hydraulic fracturing involves eliminating these ions to prevent scale formation through specific treatments, as the associated ions determine the type of scale. Different scale types can be observed in this scenario: a) calcium carbonates (CaCO_3), which increase with temperature, pH, and decrease of TDS; b) calcium sulfates CaSO_4 (Gypsum); c) barium Sulfate BaSO_4 (Barite), and d) iron scales (i.e. Ferrous Carbonate FeCO_3) (FQE-Chemicals, 2018). Scale inhibitors can be used to prevent these types of scales (Binmerdhah, 2007). At the $\text{pH} > 10$, Ca^{2+} and Mg^{2+} ions are expected to precipitate. Therefore, it is necessary to control the pH level and use scale inhibitors at these pH levels. At these values, the thermal stability of SW must be carefully observed (Prakash et al., 2016). Numerous types of scale inhibitors are explored in the literature, including acrylic acid polymers $(\text{C}_3\text{H}_4\text{O}_2)_n$, maleic acid polymers $(\text{C}_4\text{H}_4\text{O}_4)$, phosphates PO_4^{3-} , ammonium chloride NH_4Cl , ethylene glycol $(\text{C}_2\text{H}_6\text{O}_2)$, polyacrylate $(\text{C}_3\text{H}_3\text{O}_2)_n$, and phosphonates (Hexamethylene-diamine-tetramethylene-phosphonic (HMDTMP) and Diethylene -triamine-pentamethylene-phosphonic). HMDTMP proved that it can prevent calcium sulfate scale with a scale index < 1 (Amjad & Koutsoukos, 2014; Kan et al., 2009; Mazumder, 2020). At high temperatures, the gelled polymeric phosphonate-seawater-based solution can prevent calcium scale formation (Almubarak et al., 2019).

In a study by (Hou et al., 2023), seawater underwent treatment with barium to induce barium sulfate precipitation. Barium chloride dihydrate was utilized to extract sulfate from the seawater, leading to additional benefits through the removal of barium sulfate. In a separate investigation, fracturing fluids were developed using diverse seawater sources. The composition included CMHPG polymer, surfactant, biocides, acetic acid, breakers, metallic and dual crosslinkers, and scale inhibitors at elevated temperatures. The research indicated calcium sulfate precipitation around 300 °F, highlighting the advantages of seawater use and diminishing the requirement for clay stabilizers unless surpassing 8 wt. % clay. (Almubarak et al., 2019). The study inadequately addressed compatibility issues, lacked coverage across a broad temperature range, and failed to attain high viscosities. In the case of high-pressure, high-temperature (HPHT) conditions, scale inhibitors adversely affected the viscosity of seawater (Almubarak et al., 2016). Managing the aging scale in high-pressure, high-temperature (HPHT) wells is challenging because scale inhibitors become less effective under these conditions. The molecular instability in HPHT environments often results in a reduction of inhibitor efficacy, requiring higher concentrations of inhibitors (BinGhanim et al., 2017).

2.3.11 Chelating Agents

Chelating agents are organic molecules with a negative charge that can form coordination bonds with metal ions. The chelation process, leads to the creation of stable ring-like structures surrounding the metal ions, and effectively preventing their interaction with other ions in the solution. The stability of the complex formed between the metal and ligand is influenced by the characteristics of both the metal ion and the chelating agent. Aminopolycarboxylic acids represent a select group of chelating agents with the ability to

create stable complexes with alkaline-earth metals like calcium and magnesium. The equilibrium constants ($\text{Log } K_{MY}$) of CDTA, DTPA, and EDTA for different complex formed between the metal and ligand are 12.3, 10.34, and 10.59 for calcium and 11.34, 8.92 and 8.69 for magnesium, respectively. This value indicates that these chelating agents form stable complexes with calcium and magnesium as $\text{Log } K_{MY}$ is greater than 8. Aminopolycarboxylic acids experience a gradual release of protons to attain complete ionization. In the case of chelating agents like EDTA or CDTA, each possessing four carboxylic acid groups, the dissociation reactions are as follows (Fredd & Fogler, 1998):



Chelating agents were initially employed to remove formation damage caused by filter cake and scale around perforations. They have recently been claimed to be used as substitutes for breakers, iron controls, and various viscosifiers like surfactants, polymers, and crosslinkers. (Hassan et al., 2020). The industry utilizes various chelating agents, including Ethylenediaminetetraacetic acid (EDTA), N-hydroxyethyl ethylenediamine NN', N'-triacetic acid (HEDTA) Ethanolic phosphotungstic acid (EPTA), and L-glutamic acid-N, N-diacetic acid (GLDA). Figure 1 describes the chemical structures of different chelating agents employed in the industry. Chelating agents play a crucial role in seawater-based fracturing fluids by mitigating the impact of seawater through the removal of its hardness. The hardness of seawater negatively affects polymer performance and harms the

formation. Additionally, chelating agents contribute to enhancing the thickening effect, complementing the roles of polymers and crosslinkers. It is essential to use the minimum concentration of chelating agents to avoid adverse effects on breakers and crosslinkers. As an example, GLDA serves as a versatile chelating agent, replacing crosslinkers, breakers, biocides, clay stabilizers, and hydrochloric acid (HCl). It effectively reduces the interfacial tension of the fracturing fluid, exhibits compatibility with seawater, demonstrates stability in high-temperature formations (up to 300 °F), and can be employed to control the reaction rate. (Kamal et al., 2018; LePage et al., 2011). The GLDA has a different reaction to minerals at different pH levels (Hassan et al., 2020).

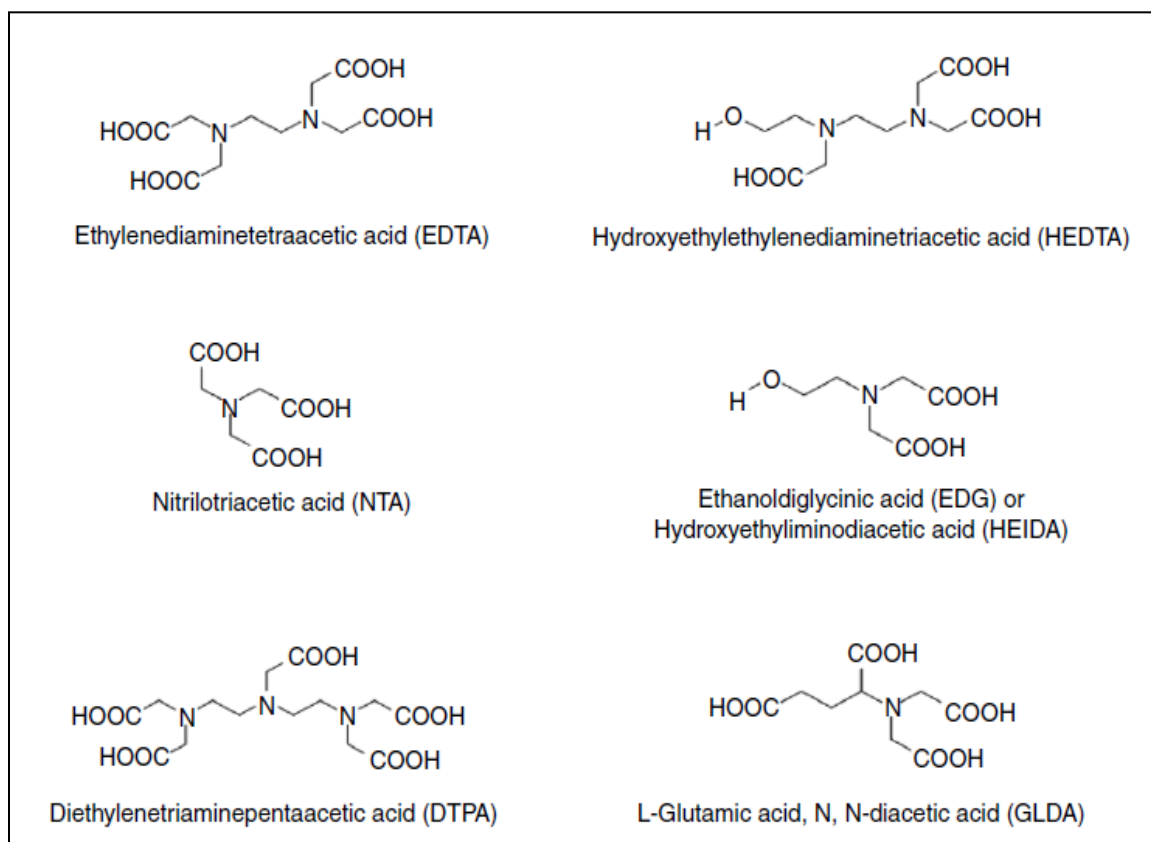


Figure 2 Chemical structure of different chelating agents (Mahmoud et al., 2016).

2.3.10.1 Chelating Agents in Acid Stimulation

Nasr-El-Din, et al., (2014) introduced the use of N,N-diacetic acid (GLDA), methylglycine N,N-diacetic acid (MGDA), and N-hydroxyethyl ethylenediamine NN', N'-triacetic acid (HEDTA) in acid fracturing for carbonate formations. Effective treatment can be attained within a pH range of 3 to 6 and at temperatures up to 300 °F. The fluid exhibits compatibility with various fracturing fluid additives, and for temperatures exceeding 200 °F, chelation and preferential precipitation methods have been implemented. (Barati & Liang, 2014). All chelating agents enhance fracture conductivity and induce controlled acid etching on the fracture surface, surpassing the performance of HCl-based fluids. Chelating agents exhibit minimal corrosion rates at elevated temperatures and can operate up to 200 °C without the corrosion issues faced by HCl-based fluids. The use of HCl acids can lead to clay decomposition, fluosilicate precipitation, calcium fluoride precipitation in the presence of carbonates, silica-gel filming, and colloidal silica-gel precipitation. To address these challenges, 15 wt. % and 20 wt. % GLDA chelating agents were employed. The reaction rate of chelating agents can be regulated by pH, with higher pH values recommended at elevated temperatures to achieve optimal acid fracture patterns (Aljawad et al., 2019; Mahmoud et al., 2016; Mahmoud & Nasr-El-Din, 2011).

In another work focusing on sandstone formations, the efficacy of HCl acidizing was compared to two different types of chelating agents alongside a foaming agent, and the subsequent well flow back fluid was analyzed. The chelating agents exhibited notable dissolving power, excellent ion control, and low tendencies for sludging (Ameur et al., 2015). Wang et al., (2019) investigated the conductivity of fractures following acid stimulation with chelating agents. Their findings indicated that, in deep sandstone, the

conductivity of chelating acid fracturing exceeded that of conventional acid by 10%. Upon long-term examination, the conductivity experienced only a 20% decrease compared to the 50% decline observed with conventional acid.

2.3.10.2 Chelating agents as Breakers

When employed as a breaker for crosslinked gel, EDTA operates by capturing the crosslinking metal ions through ligands that undergo hydrolysis, leading to the hydrolyzation of the polymer. In comparison to conventional enzyme and oxidizer breakers, EDTA proved to be more effective in reducing viscosity. The breaking time demonstrated a decrease with an increase in concentration, as indicated in the study by (Smith & Weaver, 1993). Only EDTA, zirconium, and the type of water used in fracturing are considered. Other chelating agents and crosslinkers were not part of the study. Ion III EDTA and Copper II EDTA chelating agents were employed as delayed breakers, gradually released during fracturing to disrupt a fluid crosslinked with a zirconium metal crosslinker. These chelating agents functioned as delayed breakers, slowly released over time to outcompete the polymer for the metal crosslinker, as detailed by (Dawson et al., 2004). To facilitate controlled release once the fluids reached the formation, the chelating agents underwent modification by coating with pellets. These pellets, permeable to water formation, would rupture under the pressure of fracturing and formation (Dawson et al., 2004).

2.3.10.3 Chelating Agents with Crosslinked Fluid

There has been a lack of extensive investigation into the application of chelating agents in crosslinked fracturing fluids for capturing ions associated with saline waters. The use of

seawater in hydraulic fracturing poses a risk to the proppant pack and the permeability of the fracture face. This risk arises from the presence of sulfate ions in seawater, which can potentially react with divalent ions in the formation, like calcium, resulting in the creation of calcium sulfate. Calcium sulfate is known for its tendency to block the pore throats, consequently reducing permeability (Hassan et al., 2020). Since the 1980s, chelating agents have been employed in delayed crosslinking, first introduced by (Almond, 1984). Almond utilized a zirconium crosslinker in conjunction with aluminum chelating agents and CO₂ to lower the pH to less than 5.5. A novel chelating agent was later introduced to extend the crosslinking mechanism (Putzig & St.Clair, n.d.). Le & Wood, (1992) were pioneers in introducing chelating agents as water softeners to enhance the stability of water fracturing fluids with high salinity.

Case studies were conducted on high-pressure, high-temperature (HPHT) scenarios treated with chelating agents, with comparisons made to scale inhibitors. The theory and application of chelating agents in different productivity aspects were reviewed (Almubarak et al., 2017). Kamal et al., (2018) Introduced is a versatile system for fracturing fluid suitable for both proppant fracturing (high pH) and acid fracturing (low pH) operations in sandstone formations. This fluid system integrates the use of the biodegradable GLDA, capable of replacing multiple additives like crosslinker, breaker, biocide, and clay stabilizer. The linear fluid underwent testing at a high shear rate of 511 1/s, focusing on GLDA as the chelating agent. Being a surface-active fluid, GLDA reduces interfacial tension, addressing the water-blockage effect. The investigation solely considered high temperatures without using a crosslinker to assess compatibility challenges. The research also investigated the compatibility between produced water and various fracturing fluid

systems, encompassing chelating agents and borate crosslinkers. (Elsarawy et al., 2018). The study explored the individual and combined impacts of divalent and monovalent ions. The divalent cations present in produced water resulted in a reduction of fluid viscosity by 100 cP.

2.3.10.4 Fundamental Study on Chelating Agents

Barri et al., (2022) formulated equations for determining the density and viscosity of a specified chelating agent at various temperature and concentration values, demonstrating very acceptable error levels. Their study aimed to ascertain the solubilities and fluid properties of the chelating agent at different temperatures, calcium ion concentrations, and chelating agent concentrations. Sodium-based chelating agents, namely EDTA, DTPA, and HEDTA, were utilized and prepared using both seawater and deionized water. Notably, Na₅DTPA and Na₃HEDTA chelating agents exhibited solubility in the pH range of 2 to approximately 13 for all concentrations investigated, up to 40 wt%, without any precipitation. Na₃HEDTA, in particular, is highly recommended for its environmental friendliness. On the other hand, the Na₂EDTA chelating agent presents solubility limitations influenced by solution pH. For EDTA solutions, a pH higher than 7.5 is recommended to prevent solid precipitation. Interestingly, the solution pH has a negligible impact on the chelate's viscosity and density at low temperatures.

2.4 Conclusions

Chelating agents are versatile fluids with a range of functions. They serve as substitutes for acids in acid stimulation. They can also be utilized as breakers, as well as ion-sequestering agents, effectively replacing scale inhibitors. Additionally, they facilitate scale and metal

removal. By manipulating the pH of chelating agents, one can govern the behavior of the fluid, enhancing the thermal stability of saline waters and regulating the environmental pH. Moreover, chelating agents contribute to enhancing the viscosity of fracturing fluids.

2.5 Future Study

Investigating the compatibility of chelating agents with different crosslinkers and additives, particularly in elevated temperature environments, may yield valuable insights into their extensive applicability and potential synergistic effects. Examining the prolonged impact of utilizing saline water fracturing fluid on formation damage through either field or laboratory studies can provide essential information for practical applications. Conducting a fundamental study on the specific ions linked to saline water (SW) will contribute to a deeper understanding of their individual effects and interactions in hydraulic fracturing processes.

CHAPTER 3

Chelating Agents Usage in Optimization of Fracturing Fluid Rheology Prepared from Seawater¹

3.1 Abstract

Hydraulic fracturing consumes massive volumes of freshwater that is usually scarce and costly. Such operation is not sustainable, and hence seawater could be used as an alternative. Nevertheless, seawater has high total dissolved solids (TDS), affecting the fracturing fluid rheology and providing a damage potential to the subterranean hydrocarbon reservoirs. Resolving these issues requires fracturing fluid systems with many additives, which results in an expensive and non-eco-friendly system. This study proposes eco-friendly and biodegradable chelating agents that could replace many additives such as scale inhibitors and crosslinkers.

The study aims to optimize the rheology of seawater fracturing fluids using a chelating agent and polymer. By optimizing N,N-Dicarboxymethyl glutamic acid (GLDA) conditions, high viscosity was achieved using a standard industry rheometer. The GLDA was mixed with carboxymethyl hydroxypropyl guar (CMHPG) polymer and tested in both deionized water (DW) and seawater (SW). The polymer was examined first, where the rheology did not show a time-dependent behavior. The polymer in SW showed a slightly higher viscosity than in DW. The GLDA and CMHPG were tested at different temperatures, pH, and concentrations.

¹ This chapter is copied from the manuscript: **Othman, A.**, Aljawad, M. S., Mahmoud, M., Kamal, M. S., Patil, S., & Bataweel, M. (2021). Chelating agents usage in optimization of fracturing fluid rheology prepared from seawater. *Polymers*, 13(13), 2111.

These sets showed a time-dependent viscosity behavior, which can be utilized in various fracturing steps. Results showed that the solution pH and GLDA concentration significantly impacted the fluid viscosity magnitude and behavior. The developed formulation is shear thinning, where the viscosity declines as the shear rate increases. The temperature negatively impacted the viscosity and caused the formulation to break. The study provided an understanding of how to optimize the rheology of SW fracturing fluid based on GLDA chelating and CMHPG polymer.

3.2 Introduction

Hydraulic fracturing processes involve pumping slurry to create fractures in the formation and keep them open under closure stresses. Hydraulic fracturing is implemented to increase well productivity and control sand production. This could be achieved through bypassing the near wellbore damage, extending the fracture to a significant depth within the formation, and alter the flow pattern (Economides & Nolte, 2000). The stimulation attempts started in the 1860s with explosive charges (Wickard et al., 2016). These attempts continued until 1947, where the first successful hydraulic fracturing job was performed in Kansas, USA. Only 2.84 m³ (750 gallons) of crude oil or kerosene, 18.14 kg (40 lbs) of sand, and 7.46–11.2 kW (10–15 hydraulic horsepower—HHP) were used in the fracturing operation. After that, water-based fracturing fluids are used instead of oil-based. Surfactants and stabilizers were used for the first time. Crosslinkers were developed and used broadly with a target to improve the fluid viscosity. In the 1980s the horizontal drilling revolutionized the fracturing industry and led to massive fracturing operations with more than 1119 kW (1500 HHP) and 950 m³/h (100 bbls/min) pumping rates. In 2012, more

than 2.5 million fracturing jobs were performed worldwide; more than 40% of those jobs were in the US (Hoffman et al., 2014; Gandossi & Von ESTroff, 2015).

In hydraulic fracturing design, the fluid viscosity needs to be optimized. The fracturing fluids should be able to carry the proppant with low settlement velocity and create long fractures. It should have the minimum pressure losses when transported in the tubing and fractures, low fluid loss, and ready to flow back after proppant placement (ready to break). It should also be compatible with formation fluids (Das & Rahim, 2014; Samuel et al., 2000). Based on the formation type, government and environment regulations, budget, and water availability, different types of hydraulic fracturing fluid can be used. These fracturing fluids are based on water, oil, alcohol, and foams. The water-based fracturing fluid includes crosslinked fluid, slickwater fluid, and viscoelastic surfactant, while the oil-based can be crosslinked and emulsified (Montgomery, 2013). The crosslinked gel has high proppant transport capacity and distribution efficiency. The disadvantages of the gel are the need for high pumping pressures and its damaging impact. Slick water needs lower power to pump the fluid, is cheaper than the crosslinked fluid, and it provides lower damaging impact. However, it has lower transport capacity and poor distribution of the proppant. The foam fluids can carry the proppant better than slickwater; it consumes less water and reduces formation damage. On the other hand, it has poor suspension and distribution for the proppant when high reservoir temperatures are experienced (Isah et al., 2021).

The gelling agents are hydrated—mixed with water—to prepare the linear gel fluid, which is used as a pre-pad (lead fluid) to condition the formation and initiate the fractures. The guar derivative powders are prepared by exposing the guar to a high pH water for a certain time. Different polymers provide different leak-off properties to the formation. Guar is a

long-chain polymer with a high molecular weight (Fink, 2021). A crosslinker is added to the linear gel to help increase the viscosity and propagate the fracture. This crosslinked fluid is also used to transport the proppant into the fracture (Barati & Liang, 2014). Adding crosslinkers to the gelled fluid increases the viscosity and reduces the needed concentration of polymer, which raises the fracturing fluids carrying capacity. Several types of crosslinkers are used based on the needs. After proppant placement, the flow back is necessary; hence, breakers must also break these crosslinked fluids (Fink, 2021). One of the robust methods to investigate the properties of the required fluids is through numerical simulations (Hemmati-Sarapardeh et al., 2018; Zare et al., 2019). In this approach, the needed fracturing fluids can be screened based on the reservoir conditions and required properties.

Optimizing hydraulic fracturing operations to use less freshwater and toxic additives became a necessity. Using water-based fracturing fluid has some limitations such as high cost, huge water consumption, formation damage, and costly disposal (Anandan et al., 2017; Faroughi et al., 2018; Yekeen et al., 2018). Freshwater is mostly used in fracturing operations; nevertheless, it is an expensive and unsustainable option. Seawater is another alternative that is cheap and sustainable. The high salinity of seawater could result in formation damage and viscosity degradation. Several additives could be used to reduce the impact of different ions exist in seawater. In freshwater or seawater, fracturing fluids might contain gelling agents, crosslinkers, breakers, surfactants, scale inhibitors, corrosion inhibitors, clay stabilizers, biocide/bactericide, fluid loss inhibitors, chelating agents, pH modifiers, and acids (Harris, 1988).

Several types of chelating agents are used in the industry, such as ethylenediaminetetraacetic acid (EDTA), Diethylenetriamine pentaacetate acid (DTPA), Ethanolamine phosphotungstic acid (EPTA), and L-glutamic acid-N,N-diacetic acid (GLDA), Hydroxyethylethylenediaminetriacetic acid (HEDTA). Figure 3 (Mahmoud & Abdelgawad, 2015) shows the chemical structure of different chelating agents used in the industry.

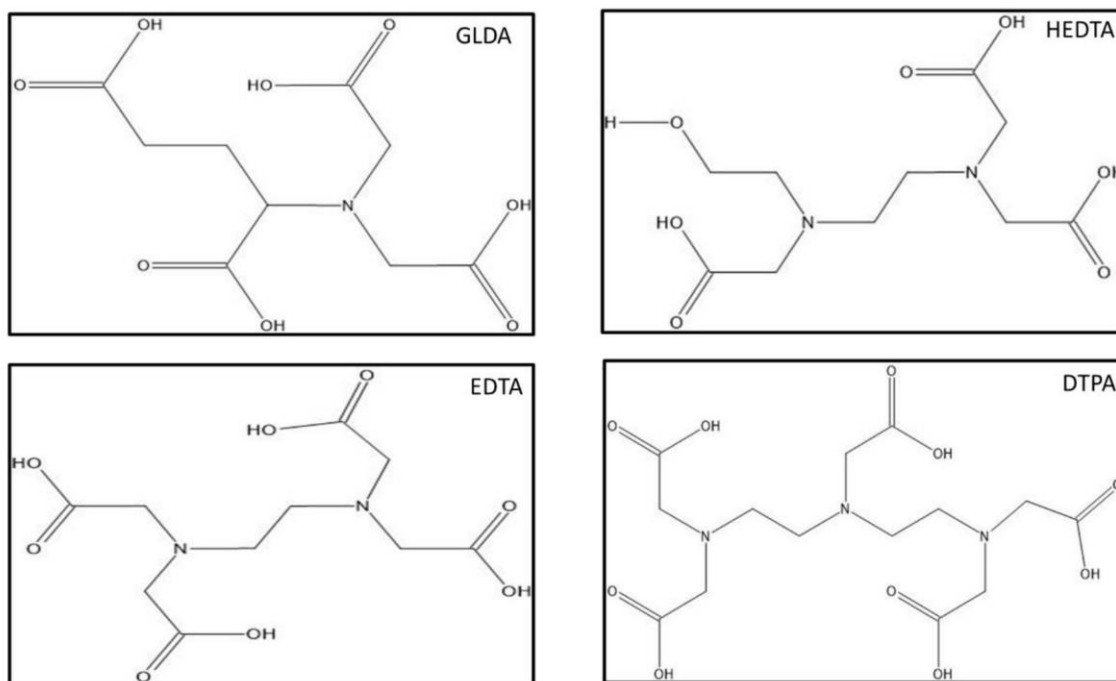


Figure 3 Chemical structure of different chelating agents.

Chelating agents are used to replace many additives such as crosslinkers, breakers, and biocides. Different chelating agents have been tested with several polymers (i.e., HPG, Xanthan, Thermoviscofying polymer) to inspect the rheology and the fluid stability in HPHT conditions. A study showed that the high pH GLDA, DTPA, and EDTA chelating agents act as crosslinker. However, only the GLDA breaks at high temperatures (Mohammed et al., 2017).

The two main additives utilized in this study to improve the seawater (SW) rheology are polymer and chelating agents. The gelling agent is the most important additive in fracturing fluids used to increase the water viscosity. High viscosity leads to efficient hydraulic fracturing, high proppant carrying capacity, wider fractures, and reduced fluid loss to the formation. Higher viscosity can be obtained by increasing gel loading, which is the volume of the gel used (in gallons) per thousand gallons of water (gpt). Polymers for fracturing purposes are water-soluble and could come from natural sources such as guar. Chemical modification is applied to natural polymers to achieve the desired physical properties. Carboxymethyl hydroxypropyl guar (CMHPG) or carboxymethyl hydroxyethyl cellulose guar (HEC) are examples of modified guar derivatives. They are desired and widely used because of their low cost and ease of hydration. The low gel load of these polymers could achieve high viscosity and proppant transport (Fink, 2021; Gaurina-Međimurec et al., 2021; Harris, 1988; Montgomery, 2013). Natural guar polymers have high shear stability and better clean-up compared to other systems (Al-Muntasheri, 2014). Recent advances in the polymerization process have been reviewed in terms of polymer interactions, polymerization mechanisms, and techniques used in the industry (Bahri-Laleh et al., 2018). CMHPG is created by dilution of native guar in a specific solution to get a more rigid chain. CMHPG guar derivative is preferred in the industry for its better hydration, slower degradation, and tolerance to a low pH environments. Figure 4 shows the generic structure of CMHPG (Abdul Majid et al., 2017; Alohalay et al., 2016; Szopinski et al., 2015; Wilson, 2017).

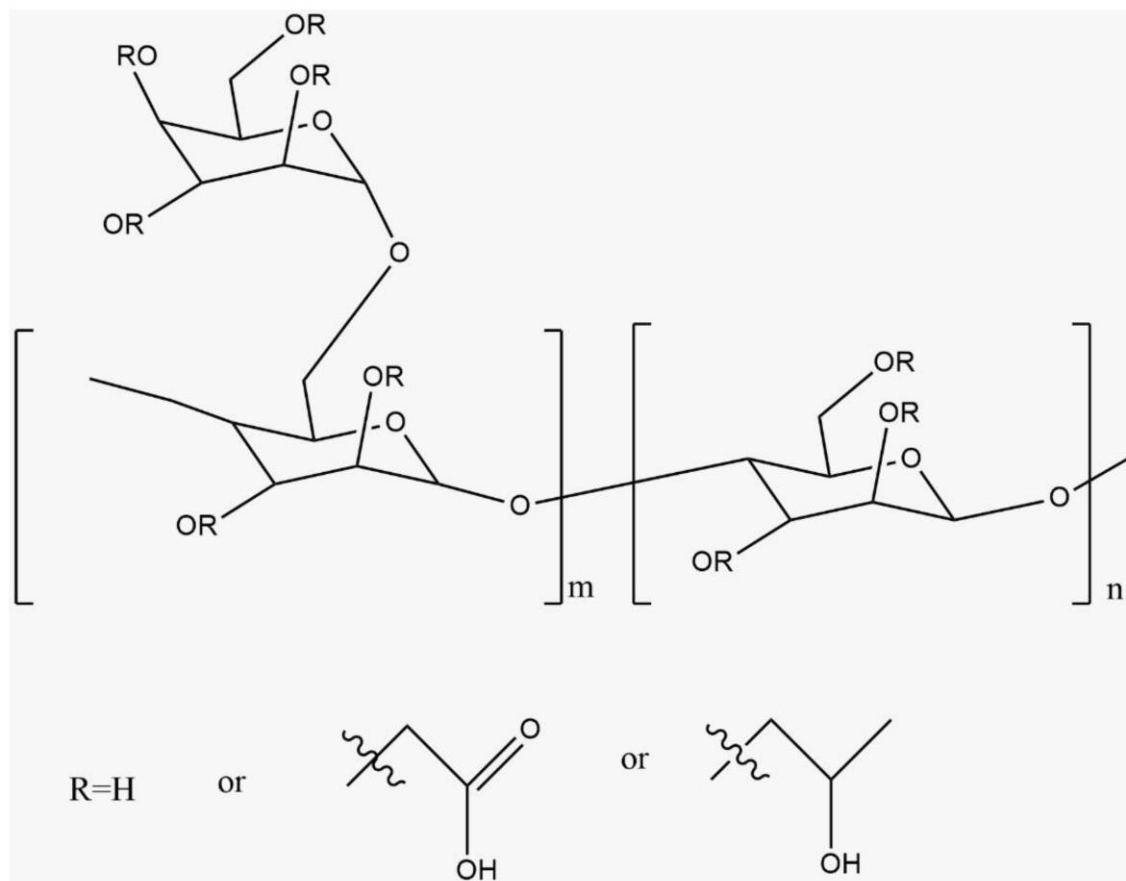


Figure 4 CMHPG generic structure (Szopinski et al., 2015).

Different guar networks can be generated in CMHPG either using hydroxyl group with borate or carboxyl group with metal, i.e., zirconium. CMHPG is reversibly crosslinked by borate, which allows the proppant to be suspended for longer times at high shear rates. While zirconium irreversibly crosslinked with CMHPG where the minimal proppant settling is noticed at low shear rates (Hu et al., 2015).

There are two methods to crosslink guar derivative, reversible and irreversible crosslinking, depending on the expected shear rate of the operation. Under specific catalysts, several polymer types can be produced with the desired properties; one of these catalysts is introduced by (Hanifpour et al., 2020). The constitutional structure of the reversible

polymers can be changed using these catalysts; once it is removed, the stability as irreversible polymers can be retained. The irreversible polymer's stability comes from the stronger bond energy than the reversible polymer (Nishimura et al., 2017; Zhang et al., 2018).

The second additive is the GLDA chelating agents (L-glutamic acid-N,N-diacetic acid). Chelating agents were initially used to reduce formation damage caused by filter cakes and scales around the perforation. Recently, chelating agents were used as a replacement for breakers, iron controls, and viscosifiers such as surfactants, polymers, and cross-linkers [30]. Chelating agents are used with seawater-based fracturing fluids to remove the impact of seawater by removing its hardness. The water hardness impact polymers' performance and damages the formation. Chelating agents can also be used in improving the thickening effect besides polymers and crosslinkers. The excess concentration of chelating agents can impact the breaker and crosslinker; it is also required to use the minimum possible to remove seawater hardness.

This study focused on GLDA application to SW. GLDA as a chelating agent proved to work as a replacement of crosslinkers, breakers, biocide, clay stabilizers, and HCl. It reduces the interfacial tension of fracturing fluid, compatible with SW, and shows stability at high-temperature environments up to 150 °C (Economides & Nolte, 2000; Kamal et al., 2018; LePage et al., 2011). It has different reaction mechanisms with minerals at different pH levels (Hassan et al., 2020). It is also biodegradable, which makes it environmentally superior to the other chelating agents.

To prepare GLDA chelating agent, the speciation chart is used. Speciation determines the equilibrium distribution of chemical species in aqueous solutions. Chemical equilibrium

methods are used to determine this distribution (i.e., finding the degree of dissociation constant). In the speciation curves, the percentage of the ions within the compounds are plotted against the pH level. Each curve has a specific number of hydrogen ions. At a specific pH, the GLDA will be formed of several species with different hydrogen atoms. Figure 5 shows the speciation curves for GLDA in NaCl (aqueous solution) for several ionic strengths.

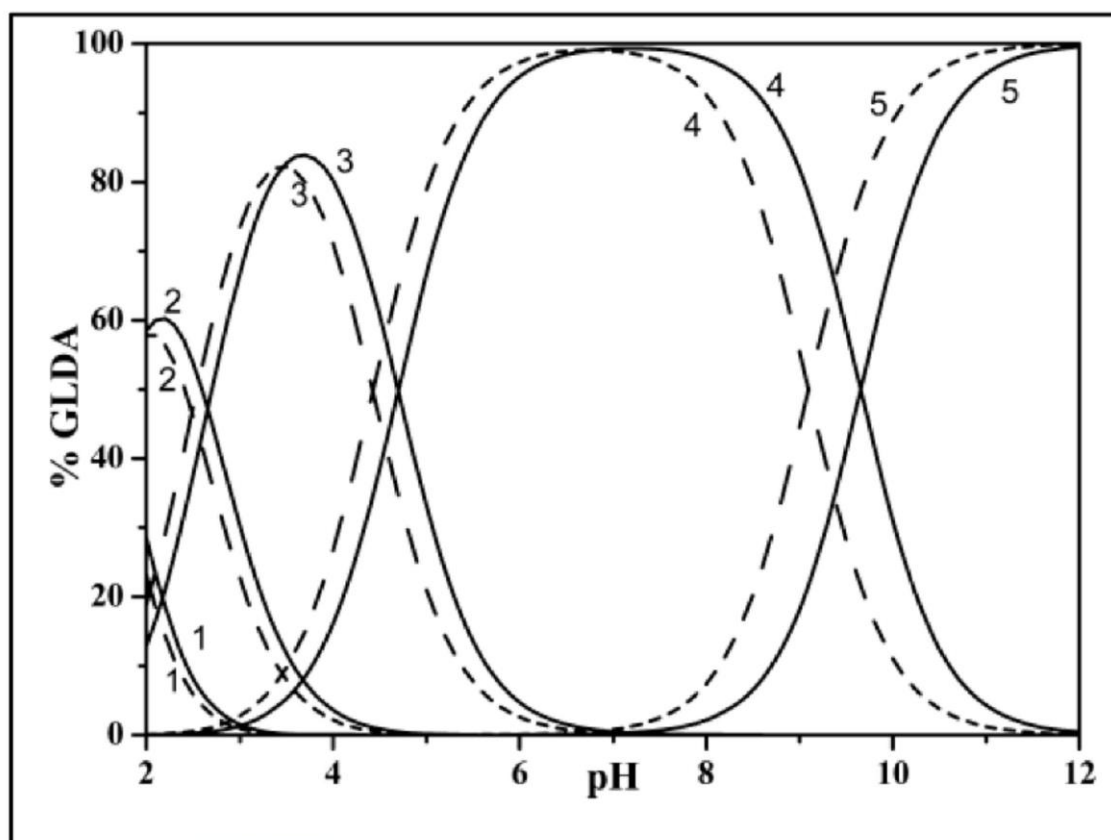


Figure 5 Speciation diagram for GLDA (L) in NaCl(aq) at $I = 0.1 \text{ mol.kg}^{-1}$ (solid line) and 0.5 mol.kg^{-1} (segment line); $c_L = 0.01 \text{ mol.dm}^{-3}$ 1 = H_4L ; 2 = H_3L ; 3 = H_2L ; 4 = HL ; 5 = L_{free} Reprinted with permission from (Bretti et al., 2016) copyright (2021) American

Many challenges face freshwater usage in hydraulic fracturing due to the high cost, scarcity of freshwater, and transportation difficulties to offshore platforms. Hence, the oil and gas industry showed a great interest in utilizing seawater (SW) instead of freshwater in hydraulic fracturing operations. Two types of ions are abundant in SW: divalent (Ca^{+} , Mg^{+})

and monovalent (Na^+ , K^+) ions; these ions affect the fracturing fluid rheology and could damage the formation. The monovalent ions only affect the rheology when divalent ions are absent (Elsarawy et al., 2018). At a pH greater than 10, we can expect the precipitation of (Ca^+ , Mg^+) ions, forming different scales. Therefore, scale inhibitors should be used, and pH should be controlled to avoid scale precipitation. SW thermal stability should also be monitored carefully (Prakash et al., 2016).

In this research, gelling chelating, polymer, and pH adjusting agents were tested with SW. The solution rheology was tested at different conditions (i.e., concentrations, pH, temperature, pressure, shear rate), aiming to identify the optimum. This study shows the impact of GLDA chelating on the rheology of seawater. Noting that the standard GLDA used in this study (high and low pH) is 40% active concentration of the used GLDA solution. It also illustrates how the pH level could be adjusted to obtain the desired viscosity behavior.

3.3 Materials and Methods

The focus of the study is to optimize chelating agents' concentration and pH to accomplish high viscosity utilizing the competent industry rheometer (Anton Paar-MCR 302), provided by Anton Paar company, Graz, Australia. SW-based fracturing fluid was formulated by adding CMHPG polymer and GLDA chelating agents to SW. Different pH levels (adjusted with sodium hydroxide (NaOH)), polymer concentrations, and chelating agent concentrations were tested at standard conditions and at high pressure and high temperature (HTHP) (i.e., 75–100 C and 3.45 MPa). All experiments were performed at a constant shear rate of 511 1/s to assess the viscosity behavior versus time. At 10 wt. % GLDA and 8.85 pH, different shear rates (100 1/s, 171 1/s, 511 1/s, and 1022 1/s) were

tested to evaluate the shear impact on the viscosity magnitude. Anton Paar rheometer was used for most of the tests using a concentric cylinder for experiments at ambient conditions, and the pressure cell was used for higher temperatures. The concentric cylinder volume was 20 mL, while the pressure cell volume was 14 mL. First, to provide a benchmark for the experiments, the CMHPG polymer was tested as a standalone additive with 0.5 wt% and 1 wt% concentration in seawater (SW) and deionized water (DW). This test was performed at ambient conditions and then at HPHT. The composition of SW used in this research is shown in the following Table 3.

Table 3 SW formulation used in the experiments.

Compound (Anhydrite)	g/L
NaHCO ₃	0.165
Na ₂ SO ₄	6.339
NaCl	41.172
CaCl ₂ .2H ₂ O	2.387
MgCl ₂ .6H ₂ O	17.644
Total dissolved solids (TDS)	67.707

Following the baseline tests, the GLDA was tested at both ambient and high temperatures. Two types of GLDA provided by the Nouryon company, Dammam Saudi Arabia (both were 40% active of the provided liquid solution) were used:

1. A low pH GLDA (pH = 4) where NaOH was added to raise the pH gradually from 4 to 10.
2. A high pH GLDA as received from the manufacturer, the pH measured was 13.7, without NaOH addition.

The pH was recorded using two methods, OAKLON pH2700 pH meter, and litmus papers. Next, employing only the high pH GLDA, different concentrations were used to prepare the samples: 1 vol%, 3 vol%, 5 vol%, and 10 vol% and test its rheology at standard conditions.

3.3.1 Concentric Cylinder Experiments (Standard Conditions)

The base GLDA pH was 13.7, but the prepared solution with SW and CMHPG polymer with different GLDA concentrations altered the solution pH level. 1 vol% concentration of GLDA resulted in 10.2 pH, 3 vol% resulted in 10.7 pH, 5 vol% GLDA concentration resulted in pH = 11, and 10 vol% resulted in 11.8 pH. The experiments in this research can be divided as follows: A baseline testing of the polymer potential without GLDA, 0.5 wt%, and 1 wt. % CMHPG polymer was conducted with DW and SW at standard conditions for 8 h. The following experiments were performed for 48 h with SW to test the hydration for 0.5 wt. % of CMHPG and 10 vol% of GLDA at 5 different pH levels between (4–10). First, the specific pH GLDA was added to SW, where CMHPG polymer was added gradually and mixed for 10 min. The mixture was left for another 10 min inside the concentric cylinder as a procedure to equilibrate the temperature. The viscosity of all five samples was measured for 48 h at a 511 1/s shear rate. Similar series of experiments were performed with high pH GLDA (10–13) where NaOH was added. Polymer and GLDA concentration of 0.5 vol% and 10 vol% were used, respectively. Similar preparation procedure, waiting

time, and shear rate were applied. To reach equilibrium in viscosity values, the experiments were performed for 72 h. This set of experiments showed the impact of polymer concentration, chelating pH, and water type on the formulation rheology. The shear rate impact on rheology was also tested.

3.3.2 Pressure Cell Experiments (HPHT)

The second set of experiments was performed at HPHT with 0.5 wt% CMHPG polymer and high pH GLDA, where no NaOH was added. 1 vol%, 3 vol%, 5 vol%, and 10 vol% of high pH GLDA (13.7) were used to prepare the SW-based solution, then 0.5 wt. % CMHPG was added at 100 C and 3.45 MPa. At different temperature (25 °C, 75 °C, and 100 °C), a 3 vol% GLDA was added to 0.5 wt% CMHPG. The same standard preparation method, equilibrium time, and shear rate were used in all the experiments. This set of experiments showed the impact of temperature and GLAD concentration on the formulation rheology. More than 40 experiments were performed in this research, excluding the repeated ones. Table 4 shows a summary of performed experiments in both ambient conditions and HPHT. It shows a summary of the comparison between ambient and HPHT conditions.

Table 4 Rheology experiments performed at standard and HPHT conditions.

Ambient Conditions	HPHT	Comparison
DW with 0.5 wt% and 1 wt% CMHPG (Baseline test)	SW with 0.5 wt% and 1 wt% CMHPG (100 °C) (Baseline test)	DW vs. SW
SW with 0.5 wt% and 1 wt% CMHPG (Baseline test)		Temperature impact on rheology
pH tests	Temperature tests	

10 vol% GLDA (4–13.7 pH) and 0.5 wt% CMHPG	3 vol% GLDA (13.7 pH) and 0.5 wt% polymer (25 °C, 75 °C, 100 °C)	GLDA impact at ambient conditions
1 vol%–10 vol% GLDA (13.7 pH) and 0.5 wt% CMHPG		GLDA impact at different temperatures

3.4 Results and Discussions

This section shows the impact of CMHPG polymer with and without GLDA at different conditions on the formulation rheology. The impact of GLDA pH and concentration at different temperatures were examined.

3.4.1 pH control

Two GLDA types were obtained from the manufacturer: one is low pH (4) and the other is high pH (13.7). As mentioned before, the low pH GLDA solution was raised from pH of 4 to higher values using NaOH. Figure 6 shows a relation between the added mass of NaOH and GLDA pH level. The figure shows that as the mass of NaOH increases, the pH level increases. An exponential function was used to predict the pH level from the added mass of NaOH. The figure also shows the bound of the 95% confidence interval. This positive correlation can be employed to find the required NaOH mass to get the desired pH level. NaOH and KOH were used to raise the pH level of GLDA from 4 to 9. This is to investigate if the type of salt used to increase the pH has any impact on the rheology. Both showed a similar effect on the rheology of the SW at similar pH, as the viscosity values and trend were similar (Figure 7). The black backgrounds in Figure 7 and the subsequent ones are the error bars. Since the data points of each curve are more than 1000, the bars form this black background. These bars show the variability of the plotted data; for this reason, we

see the black background of curves thicker than other parts in some parts of the curves, similar method was used in (Longo et al., 2013).

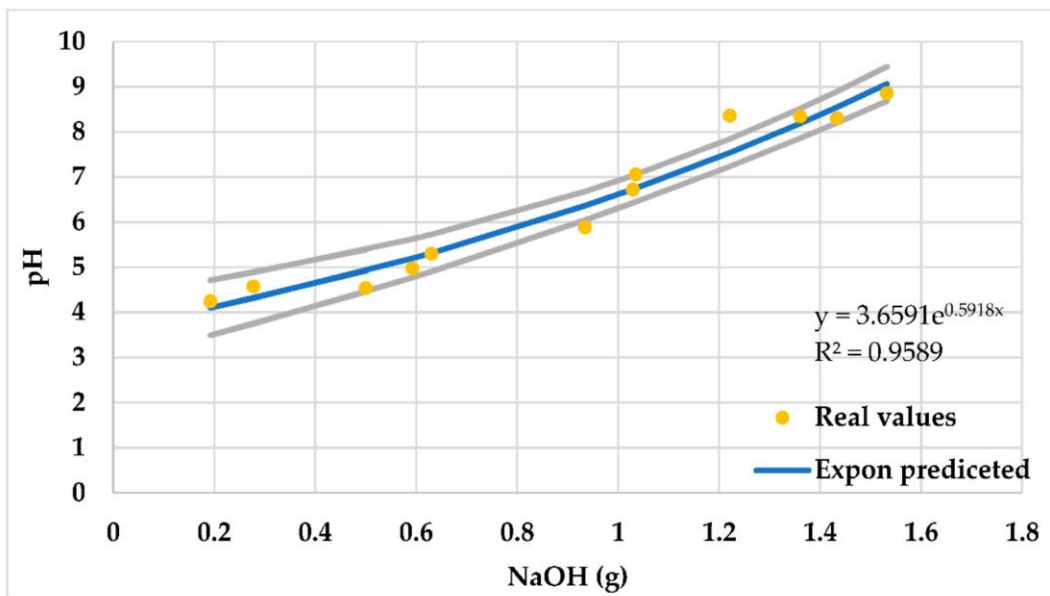


Figure 6 Effect of adding NaOH on chelating agent pH level when 10 vol% added to SW.

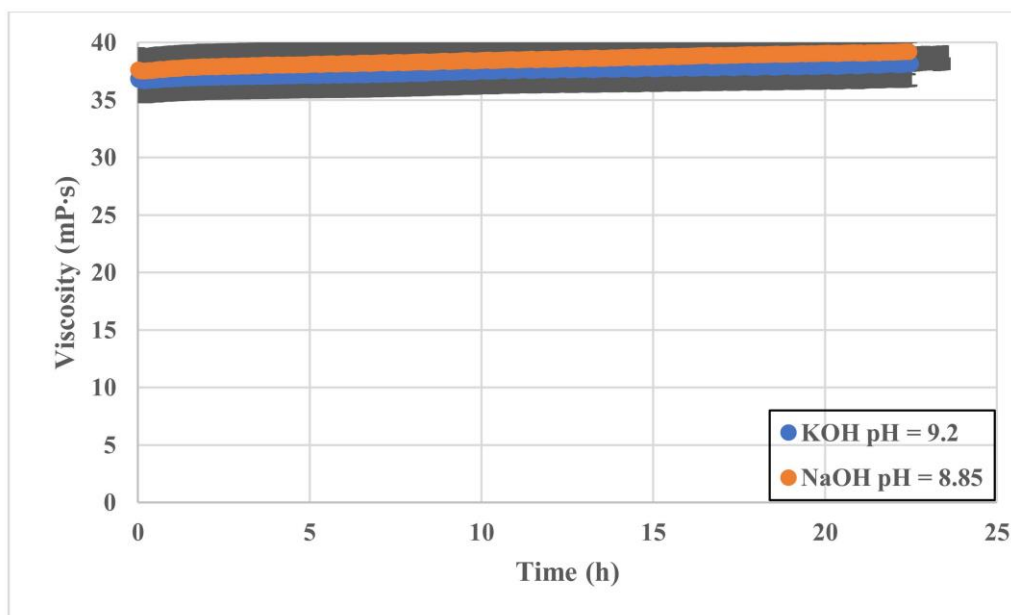


Figure 7 Rheology comparison for different pH controllers added to GLDA.

3.4.2 GLDA pH Impact on Viscosity

GLDA solutions at different pH levels were added to SW and mixed with 0.5 wt% CMHPG polymer. The viscosity of the solution was tested at standard conditions. Figure 8 shows how the GLDA pH affects the viscosity of the solution at 1 min, 2 h, 24 h, and 48 h of shearing, respectively. The values of the first 2 h of shearing (blue and red circles) show the big difference in viscosity between the high and low pH samples. We can notice from the figure that as the pH exceeds 10, the viscosity of the solution drops sharply. While after shearing for a long time (i.e., 48 h), the viscosity of the high pH samples increases sharply. On the other hand, the samples' viscosity when the pH is lower than 10 stayed almost constant even after shearing for 48 h.

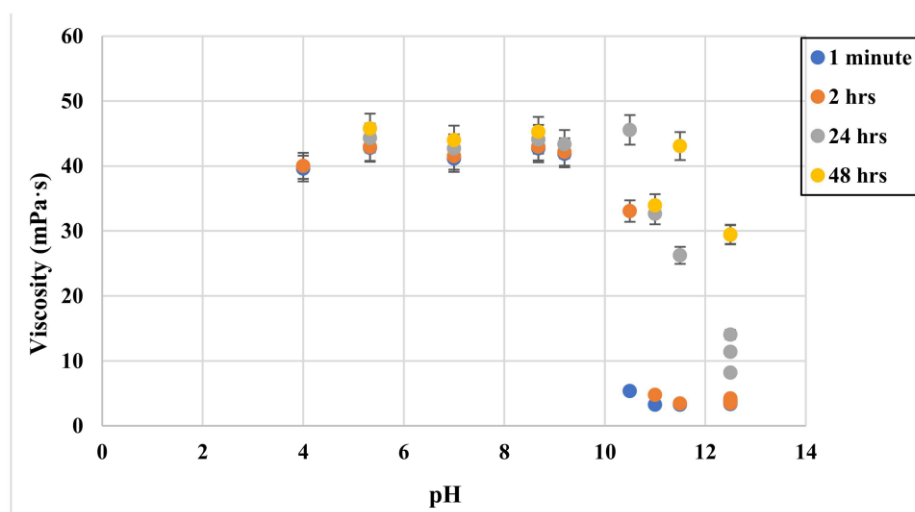


Figure 8 Viscosity versus GLDA pH at 1 min (blue circle), 2 h (red circle), 24 h (black triangle), and 48 h (yellow square).

3.4.3 Prolong Viscosity Tests

3.4.3.1 Standard Conditions

At standard conditions, the viscosity along shearing time was acquired from the rheometer, which was performed at a shear rate of 511 1/s. First, DW and SW were tested as a base case with only CMHPG polymer (i.e., in the absence of GLDA). The results indicated that

the DW-based fluid has a slightly higher viscosity as compared to SW. In general, the water type did not impact the viscosity magnitude within 8 h of shearing.

Different pH solutions $4 < \text{pH} < 10$ were obtained by adding NaOH to low pH GLDA. These solutions were used to prepare different SW-based samples and tested at ambient conditions. The selected concentration of CMHPG polymer and GLDA were 0.5 vol% and 10 vol%, respectively. The tested viscosities for these samples are shown in Figure 9. It clearly shows that increasing the pH from 4 to 10 of the low pH GLDA by adding NaOH did not impact the viscosity magnitude or trend.

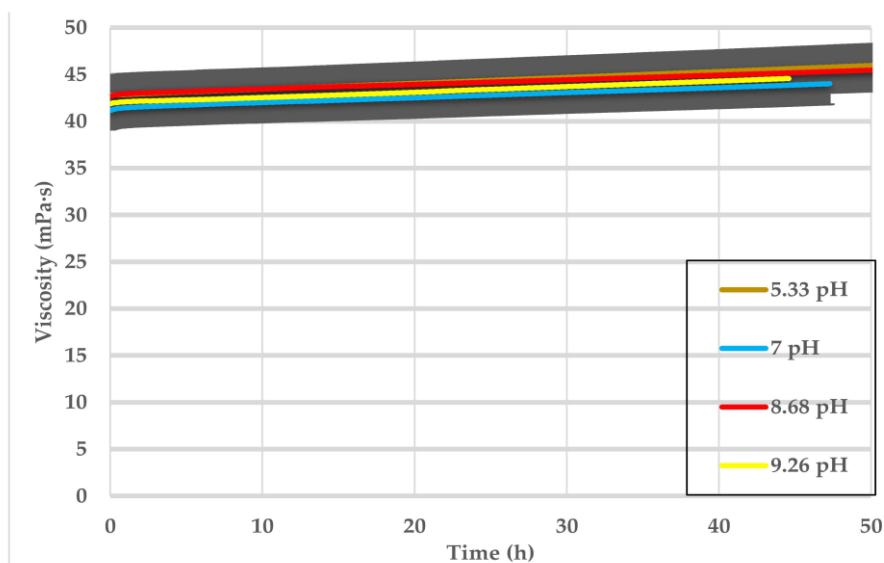


Figure 9 SW based viscosity versus time, 0.5 wt% CMHPG polymer mixed with low pH values of GLDA < 10 .

The GLDA solutions with pH higher than 10 were prepared using NaOH from the low pH GLDA. In all cases, SW is mixed with 10 vol% of GLDA and 0.5 wt% CMHPG polymer at standard conditions. The results showed that the viscosity starts at very low values (3 mPa.s to 5 mPa.s) and reaches high values after shearing for a couple of hours. At late shearing times, the high pH GLDA viscosity increases gradually, showing similar behavior to those in Figure 9. As the pH of the GLDA increases, the increase in viscosity takes longer durations to appear, as illustrated by the curves turning points shown in Figure 10.

The GLDA pH level might impact the speed of polymer hydration, and hence the time-dependent behavior appeared.

The high pH GLDA provided by the company was tested to find the most practical concentration. It is desirable to use the lowest GLDA concentration that will still reduce SW hardness. GLDA of 1 vol%, 3 vol%, 5 vol%, and 10 vol% concentrations were added to SW and mixed with 0.5 wt% CMHPG polymer. The viscosity versus time of the tested solutions is shown in Figure 11. The figure indicates that the higher the GLDA concentration, the longer time it takes to achieve high viscosity. This is similar to the pH behavior shown in Figure 10, which could be attributed to delayed hydration of polymer. It can also be noticed from this set of experiment, that the 1 vol% concentration of high pH GLDA (13.7) has similar behavior to the lower pH (10.5) 10 vol% GLDA (see Figures 10 and 11). This shows that the higher pH GLDA with lower concentration could give the same viscosity trend and value to the higher concentration lower pH GLDA. High GLDA concentration or pH might be desirable if a delayed viscosity increase is needed.

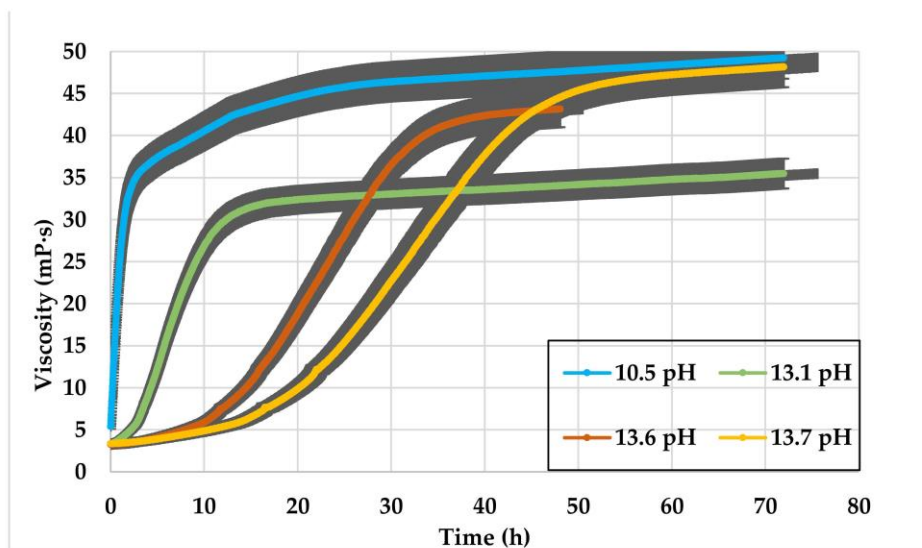


Figure 10 SW based viscosity versus time, 0.5 wt% CMHPG polymer mixed with 10 vol% high pH GLDA > 10.

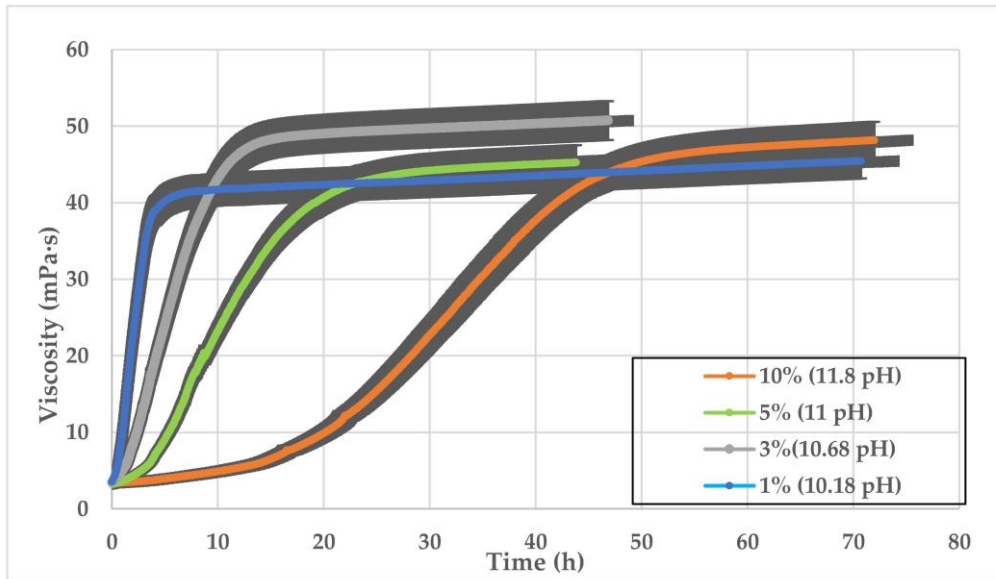


Figure 11 SW based viscosity versus time, 0.5 wt% CMHPG polymer at high pH values of GLDA (13.7) with different GLDA concentrations.

To test the shear rate impact, 10 vol% GLDA with pH = 8.85 was added to SW and 0.5 wt% polymers at standard conditions. The tested shear rates were 100 1/s, 171 1/s, 511 1/s, and 1022 1/s which are industry standard. Figure 12 shows that as the shear rate increases, the viscosity values decrease, showing a shear-thinning behavior.

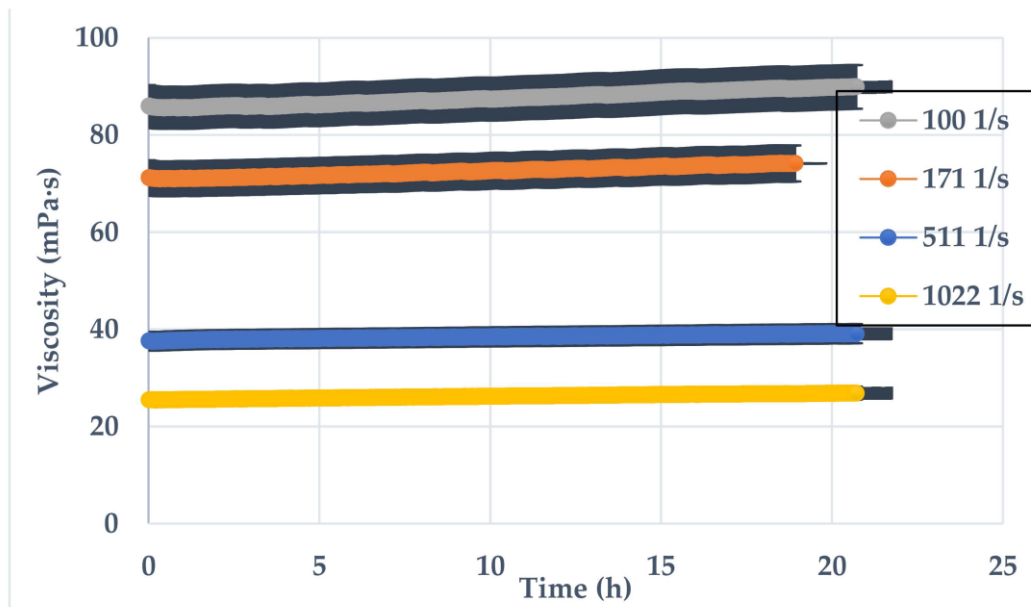


Figure 12 SW-based viscosity versus time, 0.5 wt% CMHPG polymer 10 vol% of GLDA with (pH = 8.85) at standard conditions and different shear rates.

3.4.3.2 HPHT Conditions

In this set of experiments, a 3 vol% of the standard high pH GLDA (13.7) was mixed with SW and 0.5 wt% CMHPG. Three samples were prepared and tested at 25 °C, 75 °C, and 100 °C. All experiments were performed at pressure cells of 3.45 MPa and a shear rate of 511 1/s. The viscosities of samples at the different temperatures are compared in Figure 13. It is noticed that the higher the temperature, the lower the viscosity magnitude. The thickening effect breaks at less than 15 h when the temperature is 100 °C.

Figure 14 shows the impact of GLDA on formulation rheology at different temperatures. At 25 °C, the 3 vol% GLDA and no GLDA samples (all are SW-based mixed with polymer) were tested and compared. The tests were at 100 °C, as shown in Figure 14 The viscosity starts at higher points when no GLDA is added to the solution in both low and high temperatures. The figure indicates that after shearing, the GLDA samples provided higher viscosity at high and low temperatures. It clearly shows the thickening effect of GLDA when added to CMHPG polymer

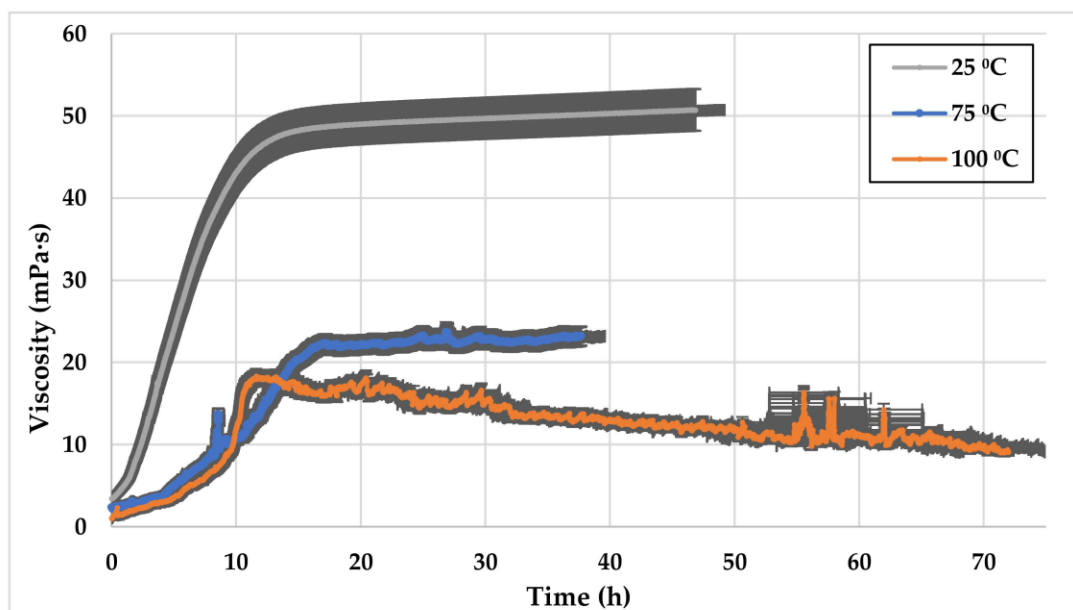


Figure 13 SW-based viscosity versus time, 0.5 wt% CMHPG polymer 3 vol% high pH GLDA (13.7) at different temperatures.

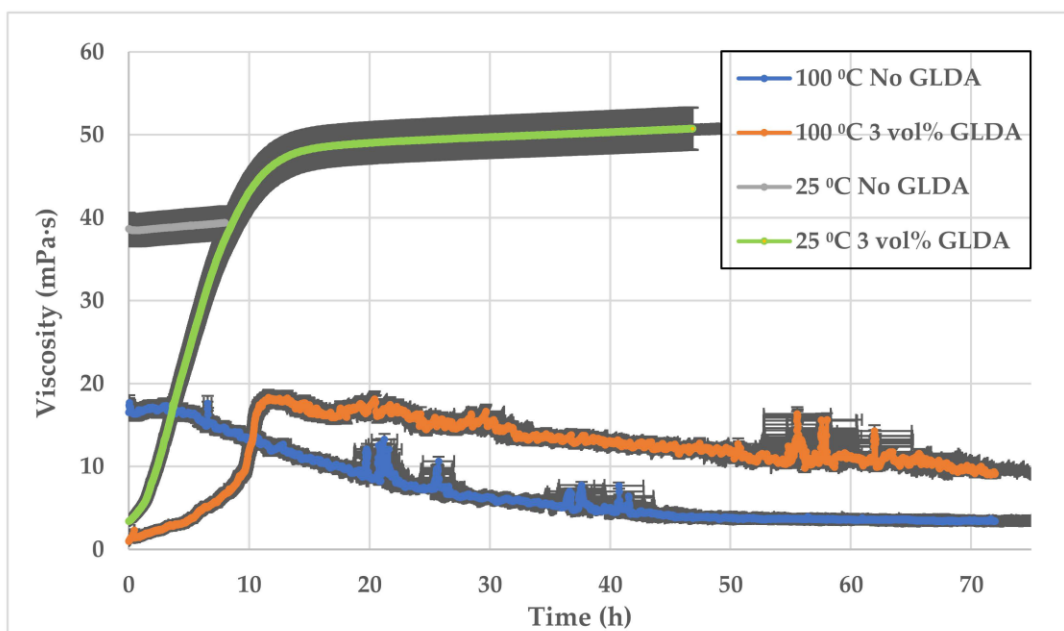


Figure 14 SW-based viscosity versus time, 0.5 wt% CMHPG polymer with and without 3 vol% high pH GLDA (13.7) at two temperatures 25 °C, and 100 °C.

3.5 Conclusions

This paper discusses the rheology of SW-based fracturing fluid when the CMHPG polymer and GLDA chelating agent are the only additives. The water type (SW vs. DW) did not impact the rheology of CMHPG polymer even after 8 h of constant shearing. The formulation suggested in this research can replace freshwater, cut transportation cost in offshore operations, and reduce operating costs. We observed that the formulation viscosity and the hydration time could be designed by either varying the GLDA concentration or pH value. The higher the concentration and pH value, the longer it takes for the polymer to hydrate and the viscosity to increase. This control can be used to reduce the pumping power necessary to transport fracturing fluid into the formation. GLDA chelating agent improved the performance because it captures the SW ions and reduces its hardness, which reduces the formation damage due to SW usage. The combination of CMHPG polymer and GLDA

chelating provide a thickening effect which is reduced at 100 °C. The suggested formulation is considered eco-friendly and biodegradable.

CHAPTER 4

Effect of Seawater Ions on Polymer Hydration in the Presence of a Chelating Agent: Application to Hydraulic Fracturing¹

4.1 Abstract

Seawater (SW) and produced water (PW) could replace freshwater in hydraulic fracturing operations, but their high salinity impacts the fluid stability and results in formation damage. Few researchers investigated SW and PW individual ions' impact on polymer hydration and rheology. This research examines the rheology of carboxy methyl hydroxy propyl guar (CMHPG) polymer hydrated in salt ions in the presence of a chelating agent. The effect of various molar concentrations of SW and PW salt ions on the rheology of CMHPG polymer solution was examined. The tested salt ions included calcium chloride, magnesium chloride, sodium chloride, and sodium sulfate, which were compared to SW and deionized water (DI) solutions. The solutions were tested at 70 °C temperature, 500 psi pressure, and 100 1/s shear rate. A GLDA chelating agent was utilized at different concentrations to examine their impact on stabilizing the solution viscosity. We found that adding the GLDA to magnesium and calcium chloride solutions increased the viscosity. Results showed that sulfate ions control the rheology of seawater due to their similar rheological response to the addition of GLDA. The results help to understand how the SW and PW ions impact the rheology of fracturing fluids.

¹ This chapter is copied from the manuscript: **Othman, A.**, Murtaza, M., Aljawad, M. S., Kamal, M. S., Mahmoud, M., & Kalgaonkar, R. A. (2022). Effect of Seawater Ions on Polymer Hydration in the Presence of a Chelating Agent: Application to Hydraulic Fracturing. ACS omega, 8(1), 969-975.

4.2 Introduction

The exploration of unconventional reservoirs has extensively increased with the increase in global energy demand. Productivity demands hydraulic fracturing in unconventional reservoirs. Hydraulic fracturing is used to stimulate a well by inducing fractures within the formation that boost reservoir productivity. This is accomplished by introducing fracturing fluid at a higher pressure than the formation fracture pressure. Proppant is utilized to keep the induced fractures open and prevent their closure after the hydraulic-surface pressure has been removed. The design of the fracturing fluid and its viscosity play a crucial role in determining the success or failure of hydraulic fracturing operations. Additionally, fracturing-fluid viscosity is essential for establishing the required width for proppant entrance into the fracture, allowing for proppant transport from the wellbore to the fracture tip, controlling fluid loss into the formation, and controlling pressure to ensure appropriate fracture height and growth (Das & Rahim, 2014; Fink, 2021; Samuel et al., 2000).

Water-based fluids are the most utilized type of fluids in hydraulic fracturing. Hydraulic fracturing of unconventional shale wells requires millions of gallons of fresh water. However, the availability of fresh water is one of the difficulties that face this operation, especially in water-deprived regions (Almubarak et al., 2019). Also, transporting fresh water to offshore locations is costly, which adds to the difficulty of storing water storage on-site. The scarcity of freshwater resources and the transportation and maintenance costs are both significant drawbacks. On the contrary, produced water from oil and gas operations and seawater are readily available. They could potentially replace fresh water in hydraulic fracturing if the associated challenges are addressed. Therefore, seawater and produced water can play a significant role in reducing fracturing operation costs (Harris &

van Batenburg, 1999). The major challenges associated are the high total dissolved solids (TDS), pipes corrosion, scaling potential, and polymer hydration (Gupta et al., 2018).

A typical fracturing fluid contains water, viscosifiers, proppants, friction reducers, biocides, and other additives. Polymer-based viscosity-modifying agents such as poly(acrylic acid), poly(vinyl alcohol), guar gum and its derivatives, cellulose, and poly(acrylamide) are widely utilized. The number of functional groups, their location, and polymer molecular weight determine the characteristics of the polymer (Othman, Alsulaimani, et al., 2022). Among the guar gum derivatives, hydroxypropyl guar (HPG) and carboxymethyl hydroxypropyl guar (CMHPG) are extensively used in hydraulic fracturing due to the ease of hydration and minimum residue content (Harris, 1988). The guar derivatives can be crosslinked to generate very high viscosity at a low concentration. A crosslinker is utilized to achieve high viscosity values that can range from hundreds to thousands of centipoises. The most popular metals for crosslinking guar-based fracturing fluids are boron, zirconium, and titanium (Gaurina-Međimurec et al., 2021).

The challenge with utilizing produced water (PW) and seawater (SW) is the high concentration of ions such as Ca^{2+} and Mg^{2+} , which influence the thermal stability and the fracturing fluid viscosity. The presence of these ions could delay or prevent polymer hydration. Moreover, they may induce corrosion, cause scale, and reduce gel stability. Both monovalent (Na^+ and K^+) and divalent (Ca^{2+} and Mg^{2+}) ions affect the viscosity and stability of fracturing fluids. The divalent ions are the source of viscosity reduction and precipitation, which is stronger with the presence of calcium ions. Monovalent ions reduced the viscosity only when no divalent ions existed in the prepared fluid (Elsarawy et

al., 2016). In sandstone formations, the positive ions tend to be attracted to negatively charged rock. The anions such as SO_4^{2-} tend to disrupt the equilibrium of the fluid system, release the negatively charged oil compounds, and form compounds with the cations. The low salinity water can attract the cations in the formation brine, release the oil compounds, and improve productivity (Tahir et al., 2020). These ions may damage the formation or reduce the retained fracture conductivity. The precipitation of divalent ions (Ca^{2+} and Mg^{2+}) may occur at a pH higher than 10, and different scales can be formed. Therefore, the pH should be increased or scale inhibitors should be used if low pH is needed. High pH environments are needed to maintain stability at high temperatures (Li et al., 2016; Prakash et al., 2016). The pH control improves the crosslinker durability with shearing, while the chelating agents capture the ions and reduce the PW and SW hardness.

Chelating agents are compatible with PW and SW and can improve thermal stability, reduce surface tension, adjust the pH, and as acids, breakers, biocides, and clay stabilizers. Different chelating agents used in the oil industry include ethylenediaminetetraacetic acid (EDTA), ethanolic phosphotungstic acid (EPTA), and L-glutamic acid-N,N-diacetic acid (GLDA). The chelating agents are used to reduce the interfacial tension; the high pH chelating agents increase the negative value of zeta potential and change the rock toward water wet and enhance the productivity (Mahmoud & Abdelgawad, 2015). Chelating agents such as GLDA are stable at elevated temperatures up to 300 °F. It reacts differently with ions at different pH ranges (Alohaly et al., 2016; Economides & Nolte, 2000; Hassan et al., 2020; Kamal et al., 2018; LePage et al., 2011). The ions reduce the crosslinking capabilities of the guar due to their precipitation (Alohaly et al., 2016). EDTA is used in

the industry to capture anions such as sulfate and carbonate, while the GLDA is used to capture the cations such as calcium and magnesium (Hassan et al., 2020).

The literature showed that salt ions have an impact on the fracture fluid rheology and stability. However, little research has been done on the impact of each monovalent and divalent cation in the PW or SW on the viscosity, crosslinking, and breaking of fracturing fluids. In this study, we evaluated the impact of varied ions (Na^+ , Ca^{2+} , Mg^{2+} , and SO_4^{2-}) concentrations on the rheology of CMHPG polymer. We also investigated the effectiveness of GLDA as a chelating agent in various salt ions at 1 M concentration. Experiments on fresh water and seawater solutions were carried out as a standard to determine which salt ion significantly influences the viscosity of the CMHPG polymer.

4.3 Methodology

4.3.1 Materials

In this study, we examined the hydration of the CMHPG polymer in DI, SW, and various concentrations of calcium chloride ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$), magnesium chloride ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$), sodium chloride (NaCl), and sodium sulfate (Na_2SO_4). We also looked at how well the polymer performed when SW, DI, and the other ions were combined with various concentrations of high pH GLDA. To attain rheological properties, we utilized an Anton Paar-MCR 302 rheometer. Table 5 shows the details of SW-associated salts in gram/liter.

Table 5 Ions Associated With 1 Liter of SW

Ions	Weight (g/L)	Molar concentration (mol/L)
Mg^{2+}	2.1098	0.0104

Ca^{2+}	0.6496	0.0044
Na^{+}	18.3017	0.313
Cl^{-}	32.3278	0.2199
SO_4^{-2}	4.2864	0.0302
HCO_3^{-1}	0.1198	0.0014

These ions affect the hydration of the polymer; however, in this work, we used the CMHPG polymer. The CMHPG is preferred by the industry because it has unique properties; it does not degrade as fast as the other polymers, it works fine at low pH, and it hydrates better than other polymers. Hydration is the process by which polymer chains absorb water to change their configuration from the compact state of coils into a more extended and relaxed state. The stable viscosity is recognized as the maximum hydrate state (Abdul Majid et al., 2017; Alohalay et al., 2016; Wilson, 2017).

To capture and remove the effect of the ions on the polymer, high pH GLDA chelating agent (N,N-dicarboxymethyl glutamic acid) was used. We received and used the GLDA product as it is having pH around 13.7. The GLDA raises the pH of solutions from 6 to more than 10, depending on the concentration of the GLDA. The fluid has 40% active content, and its chemical structure is detailed in Figure 15.

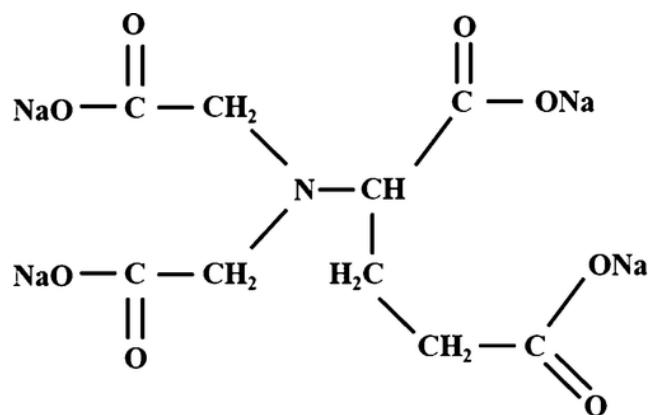


Figure 15 Dissolvine StimWell DGH GLDA structureGLDA-Na4.22 Reprinted with permission from ref (Othman, Aljawad, et al., 2022) Copyright 2022, American Chemical Society.

4.3.2 Procedures

The hydration period in each test was set at 45 min, and the GLDA was mixed for 5 min after hydration. All experiments were conducted under uniform conditions: 70 °C temperature, 500 psi pressure, and 100 1/s shear rate utilizing Anton Paar MCR-302 high-pressure cell geometry. We investigated SW, DI, $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, NaCl, and Na_2SO_4 solutions in the first phase of the tests. Three different concentrations of each salt solution (1, 0.5, and 0.1 M) were examined. To explore the impact of GLDA concentrations at various salt ions, while comparing to SW and DI, a high pH (13.7) GLDA solution was used in the second phase. GLDA was used in three different concentrations (4, 10, and 20 wt %).

4.3.3 Experimental Design

The first phase's purpose was to assess the performance of CMHPG in various salts used at different concentrations. The CMHPG polymer was hydrated for 45 min in solutions of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, NaCl, and Na_2SO_4 at concentrations of 0.1, 0.5, and 1 M. The second phase's goal was to restore the polymer's viscosity by using GLDA, a chelating agent. There were three different concentrations of the GLDA utilized (4, 10, and 20 wt

%). The polymer was hydrated for 45 min in DI, SW, and 1 M of above-mentioned salts separately followed by GLDA which was mixed for 5 min. Table 6 summarizes the concentrations and testing conditions applied in the study.

Table 6 Summary of the Performed Exp 1

Water type	polymer (wt %)	Ion concentration (M)	chelating agent (wt %)	chelating agent type	Temperature (°C)	Number of experiments
DI, SW	0.6				70 °C	2
CaCl ₂ ·2H ₂ O, MgCl ₂ ·6H ₂ O, NaCl, Na ₂ SO ₄	0.6	1, 0.5, 0.1			70 °C	12
DI, SW	0.6		4, 10, 20	High pH GLDA (13.7)	70 °C	6
CaCl ₂ ·2H ₂ O, MgCl ₂ ·6H ₂ O, NaCl, Na ₂ SO ₄	0.6	1	4, 10, 20	High pH GLDA (13.7)	70 °C	12

4.4 Results and Discussions

4.4.1 Effect of Ions Concentration on the Viscosity

The baseline experiment of DI was repeated at 70 °C in 0.6 wt % CMHPG polymer hydrated in DI for 45 min to assess the deviation of the measured viscosity from the true values. The average percentage error was calculated, and the error bars were added to Figure 16; the same was applied to the subsequent figures. The average percentage error in

the DI experiment was 1.6%, which is within the acceptable range. For the rest of the figures, we illustrated the standard deviation from the average value for each data set.

The impact of several individual ions on the rheology of the polymer was examined in the first phase of the study. The various ions were investigated at three different concentrations (0.1, 0.5, and 1 M). Figure 17 depicts the effects of NaCl at three different concentrations, including 1 M NaCl, 0.5 M NaCl, and 0.1 M NaCl, on the viscosity of the polymer under investigation. The results showed that NaCl had an impact on CMHPG's viscosity. The viscosity decreased from 80 cP in DI water to 75 cP after the addition of 0.1 M NaCl. Furthermore, as the concentration of NaCl increased, the viscosity dropped from 75 to 69 cP.

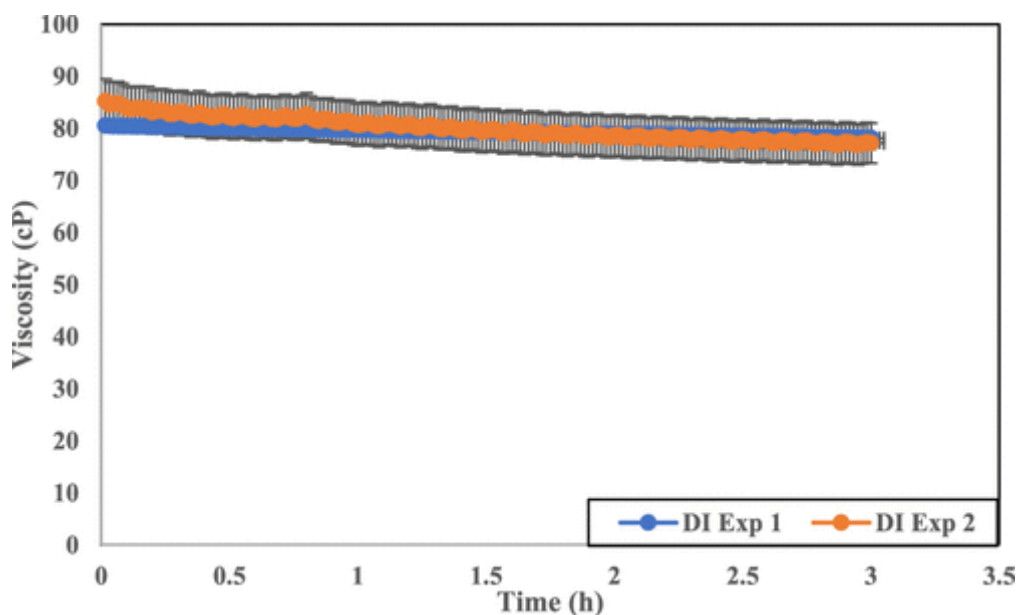


Figure 16 Average percentage error of two DI-based solution experiments.

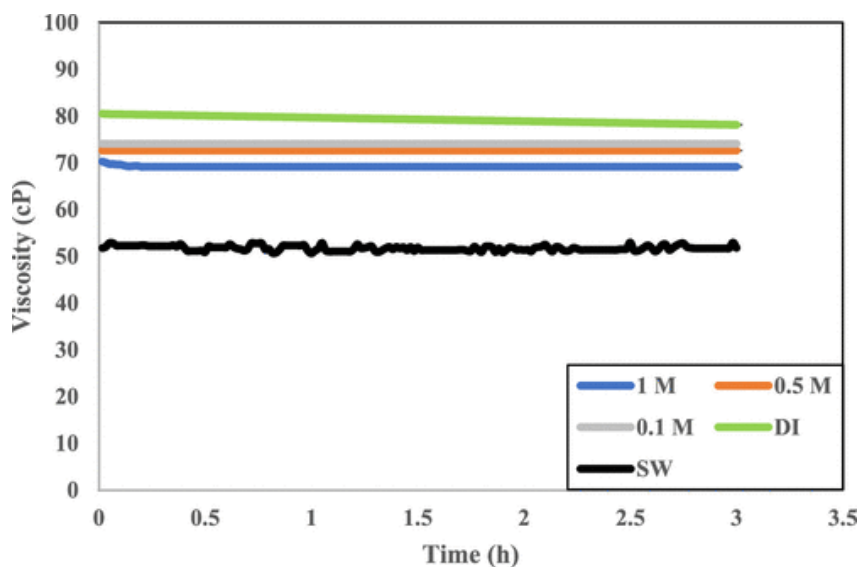


Figure 17 0.6 wt % CMHPG in different concentrations of NaCl at 70 °C, 100 1/s, and 500 psi.

water to 75 cP after the addition of 0.1 M NaCl. Furthermore, as the concentration of NaCl increased, the viscosity dropped from 75 to 69 cP. This decrease in viscosity indicates that the addition of Na^+ ions slightly hindered the polymer's hydration. This decrease is caused by the reduction of mutual repulsion between charges in the polymer backbone. The excess positive ions in the solution formed a shield that prevented repulsion (Guo et al., 1998). Table 7 specifies the standard deviation (STDEV) in viscosity for each concentration of sodium chloride.

Table 7 Viscosity Average and STDEV for Sodium Chloride Solution

Solution	Average viscosity	STDEV
1 M	68.826	0.246
0.5 M	71.781	0.449
0.1 M	72.559	0.381
SW	51.717	0.526

The viscosity profile of a CMHPG polymer that has been hydrated in MgCl_2 at concentrations of 1, 0.5, and 0.1 M is shown in Figure 18. It should be emphasized that MgCl_2 at any concentration has a negligible impact on the viscosity of the polymer. Additionally, all concentrations have a rather narrow range of viscosity values, between 72 and 75 cP. As the MgCl_2 concentration increased, the viscosity profile varied, dropping from 75 to 72 cP. Among all the salt ions, MgCl_2 was the most stable solution at 70 °C when the ion concentration changed. Table 8 specifies the viscosity STDEV for each concentration of magnesium chloride.

In CaCl_2 solutions, the performance of the CMHPG polymer was evaluated at three different concentrations: 1, 0.5, and 0.1 M. Figure 19 presents the viscosity profiles for all three concentrations. CaCl_2 was found to have no effect on the polymer's stability. However, compared to sodium and magnesium ions, it resulted in a wider range of viscosity values.

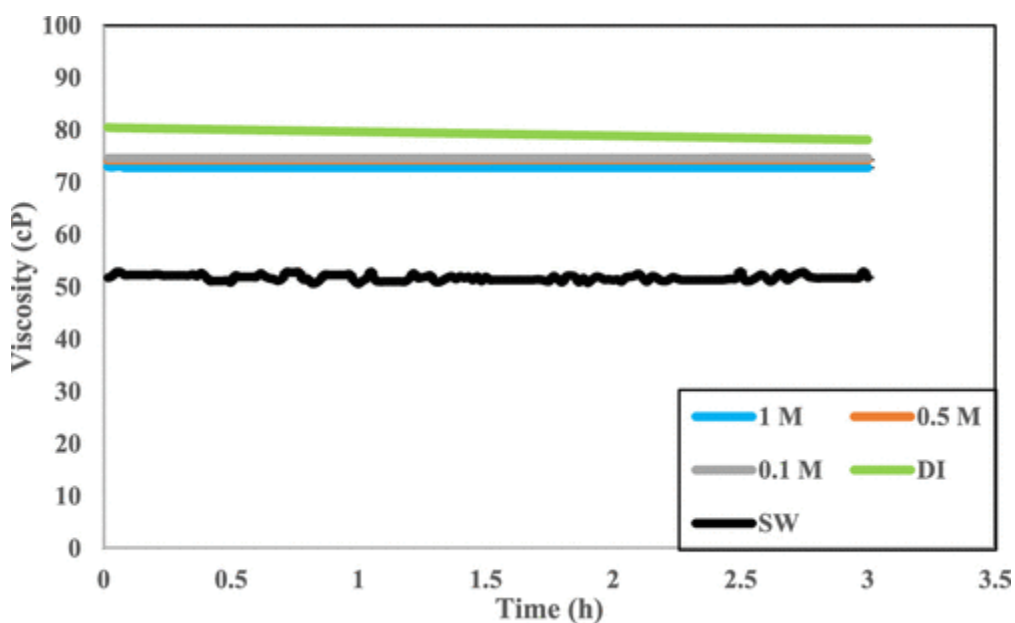


Figure 18 0.6 wt % CMHPG in different concentrations of MgCl_2 at 70 °C, 100 1/s, and 500 psi.

Table 8 Viscosity Average and STDEV for Magnesium Chloride Solution

Solution	Average viscosity	STDEV
1 M	70.273	0.219
0.5 M	73.426	0.324
0.1 M	72.343	0.358

For instance, the viscosities of CaCl_2 solutions were 71, 73, and 81 cP for 1, 0.5, and 0.1 M, respectively. Furthermore, a small decrease in viscosity at the beginning of the test was observed in all three tested concentrations. A similar behavior was observed in the 1 M MgCl_2 solution. Table 9 specifies the viscosity STDEV for each concentration of calcium chloride. Finally, the CMHPG polymer was tested in Na_2SO_4 solution to examine the effect of sulfate on the polymer performance. A 0.6 wt % of the polymer was hydrated for 45 min in 1, 0.5, and 0.1 M of the salt. Then the rheology tests were performed for the three solutions at 70 °C and 500 psi.

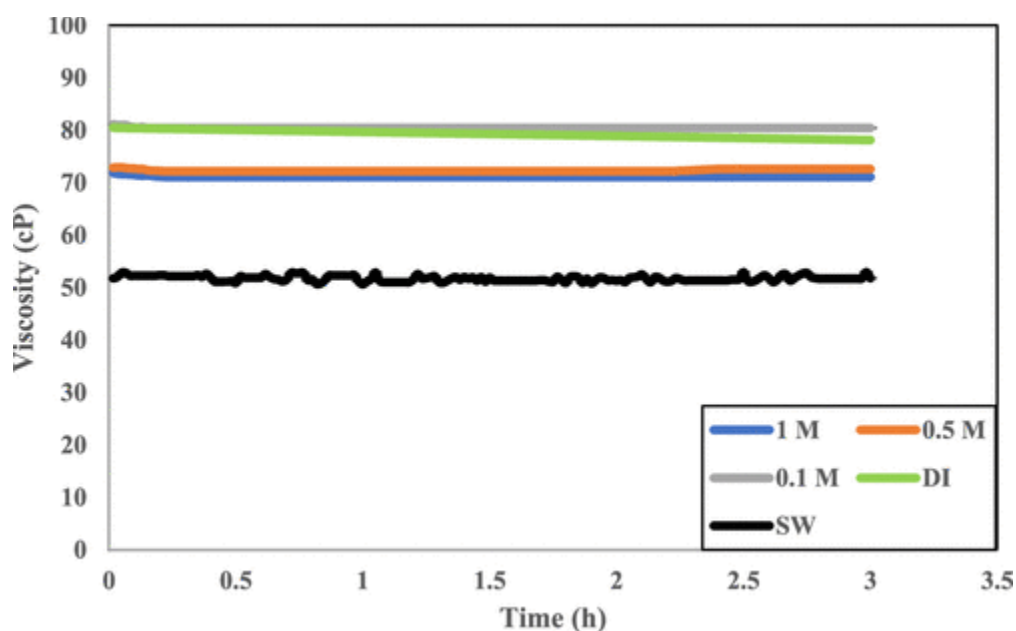
**Figure 19 0.6 wt % CMHPG in different concentrations of CaCl_2 at 70 °C, 100 1/s, and 500 psi.**

Table 9 Viscosity Average and STDEV for Calcium Chloride Solution

Solution	Average viscosity	STDEV
1 M	70.607	0.285
0.5 M	72.268	1.262
0.1 M	79.554	0.483

Figure 20 shows the results of these experiments. It can be noted that all concentrations of Na_2SO_4 affected the polymer hydration. The increase in the concentration had an important impact on viscosity. For the 1 M, the viscosity started low at 42 cP, and in less than 15 min, it reached 50 cP. However, it took 2 h and 45 min to nearly reach 60 cP. When the concentration was decreased to 0.5 M, a similar behavior was noted but in a narrower window between 70 and 77 cP. When the concentration decreased to 0.1 M better stability and higher viscosity were achieved reaching 87 cP. We noted that the sodium sulfate affects the system's stability and hence the fluctuations in the viscosity results. Table 10 specifies the viscosity STDEV for each concentration of sodium sulfate.

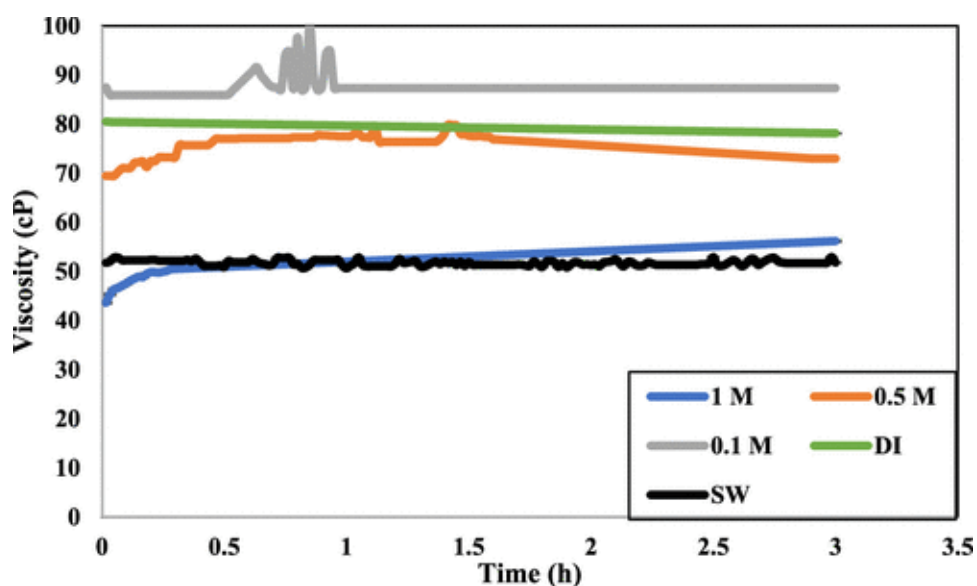


Figure 20 0.6 wt % CMHPG in different concentrations of Na_2SO_4 at 70 °C, 100 1/s, and 500 psi.

Table 10 Viscosity Average and STDEV for Sodium Sulfate Solution

Solution	Average viscosity	STDEV
1 M	52.831	2.185
0.5 M	74.823	2.519
0.1 M	87.436	2.165

4.4.2 Effect of Chelating Agent

From the experiment, it can be concluded that when the CMHPG polymer is dissolved in $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, and NaCl solutions, the change in concentration has a small impact on the rheology. It was found that the concentration has a significant impact when the polymer is dissolved in Na_2SO_4 ; however, in all tested ions, decreasing the concentration increased the viscosity. This is because more positive ions of sulfur besides sodium are shielding the polymer ions and preventing the ion repulsion (Guo et al., 1998). As the water is a good solvent for the sodium sulfate, the sodium sulfate prevents the interaction between the gel and the water, it interacts strongly with water. As a result, the water easily can be released from the gel network, which ruins the polymer hydration and the gelation process (T. Singh et al., 2009).

In the second part of the study, we tested the effect of the high pH GLDA chelating agent on the CMHPG polymer hydrated in $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, NaCl, and Na_2SO_4 and compared it with GLDA in SW and DI. Figure 21 displays the viscosity of 0.6 wt % of polymer hydrated for 45 min in 1 M of CaCl_2 , MgCl_2 , NaCl, and Na_2SO_4 ions individually. The figure also shows the viscosity of the same polymer concentration hydrated in SW and

DI water. From Figure 21, the viscosity of DI is the highest and most stable solution among the solutions.

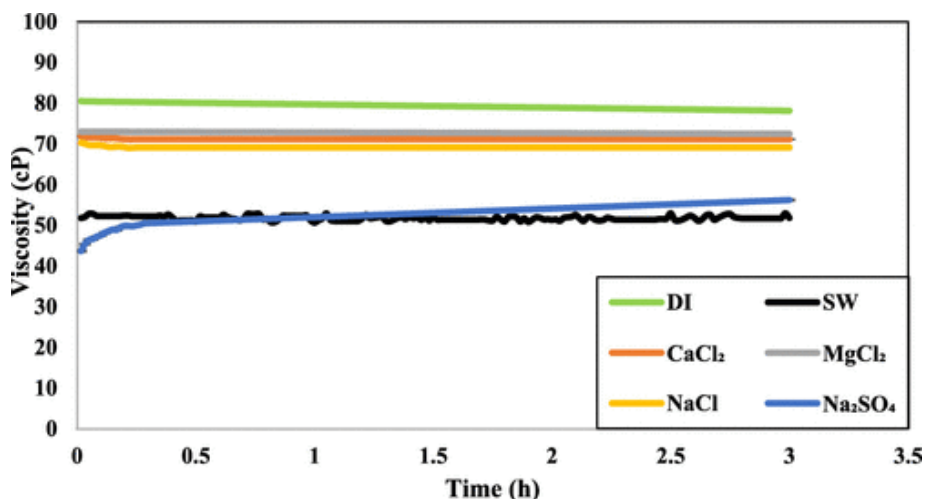


Figure 21 0.6 wt % CMHPG in 1 M of individual ions compared to SW and DI at 70 °C, 100 1/s, and 500 psi.

The viscosity in DI exceeded 80 cP, while in MgCl₂, CaCl₂, and NaCl solutions, it showed very stable and similar viscosity values (72, 70, and 69 cP). SW and Na₂SO₄ were not stable and had much lower viscosity compared to the other solutions. Similar results of DI and SW were achieved in a similar study (Othman, Aljawad, et al., 2022). From the figure, it can be concluded that Na₂SO₄ is the source of viscosity reduction of the SW. Using the high pH increases the stability; however, the FTIR test performed by (Kamal et al., 2018) showed that at higher pH, a reaction happens between the GLDA and the base. This results in partial loss of a proton from the COOH group attached to the GLDA, which results in the presence of COO⁻. This causes the viscosity to break which we noticed with the higher GLDA concentrations.

The effect of the chelating agent was investigated by adding 4% of high pH (13.7) GLDA. First, 0.6 wt % of the polymer was hydrated for 45 min in the desired salt solution. Figure 22 shows that adding 4% of high pH GLDA raised the viscosities to that of DI water

without a chelating agent. However, it did not significantly affect the DI. On the contrary, Na_2SO_4 was negatively affected by the high pH GLDA, and the viscosity was less than 10 cP in all added GLDA concentrations.

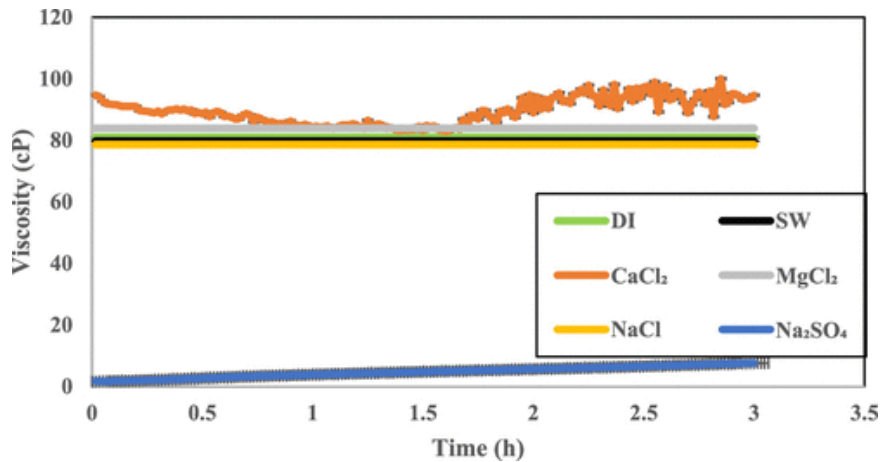


Figure 22 0.6 wt % CMHPG in individual ions with 4% added GLDA compared to SW and DI at 70 °C, 100 1/s, and 500 psi.

Similar conclusions and results were achieved in (Elsarawy et al., 2016) The figure also indicates that the GLDA positively impacted the Ca^{2+} solution as the viscosity reached 100 cP after 3 h. Although the SW contained Na_2SO_4 , the GLDA could enhance its viscosity noticeably. The chelating agent did not only capture the ions, which make the solution behave like freshwater, but also increases the viscosity (Kamal et al., 2018). Table 11 specifies the viscosity STDEV for each solution when 4% GLDA was added.

Table 11 Viscosity Average and STDEV for SW, DI and Individual Ions Solutions When 4% GLDA was Added

Solution	Average viscosity	STDEV
1 M	52.831	2.185
0.5 M	74.823	2.519
0.1 M	87.436	2.165

Figure 23 shows the viscosity results when adding 10% of high pH GLDA to the polymer solution hydrated in DI, SW, and 1 M of each of the ions individually. We can note that the viscosity of DI, SW, MgCl_2 , and CaCl_2 slightly improved.

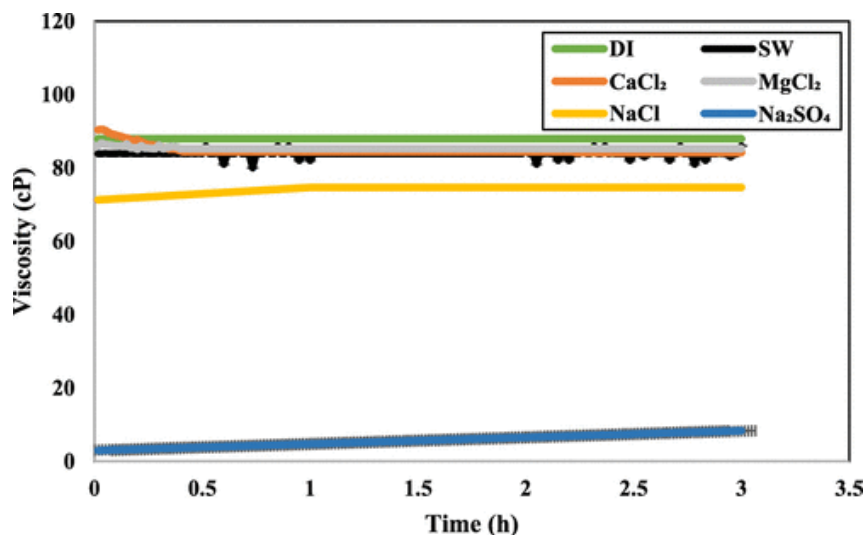


Figure 23 0.6 wt % CMHPG in individual ions with 10% added GLDA compared to SW and DI at 70 °C, 100 1/s, and 500 psi.

Also, near the end of the test, the viscosity of CaCl_2 started increasing. Even with the 10 wt % GLDA, the Na_2SO_4 viscosity did not improve. The stability of SW was affected by the increase of GLDA, probably because of the negative behavior noted with sulfate ions. NaCl solution showed different behavior as the viscosity started at a lower value and increased with hydration. Although the behavior is not clear, similar behavior was noted with the lower GLDA volumes. Table 12 specifies viscosity STDEV of the solutions when 10% GLDA was used.

Table 12 Viscosity Average and STDEV for SW, DI and Individual Ions Solutions When 10% GLDA was Added

Solution	Average viscosity	STDEV
NaCl	73.751	1.136
CaCl_2	83.355	2.460

MgCl ₂	86.148	0.671
Na ₂ SO ₄	15.365	1.263
DI	86.067	0.427
SW	85.661	3.996

The addition of high pH GLDA in higher concentrations delays the polymer hydration (Othman, Aljawad, Kamal, et al., 2021; Othman, Aljawad, Mahmoud, et al., 2021). In Figure 24, it can be noted that the addition of 20 wt % affected the solution behavior. It delayed the polymer hydration, but in different degrees, as was noted in all solutions except Na₂SO₄. CaCl₂ was the most affected as the hydration was delayed more; however, more viscosity gained after 1.5 h. All concentrations of GLDA could not raise the values of sodium sulfate viscosity as the chelating agent's mission is to chelate the cations. From our results and what has been highlighted in the literature (Tahir et al., 2020), the sulfate presence is good for after fracturing processes; however, while fracturing, it decreases the viscosity and disturbs the fluid system equilibrium. Table 13 specifies each solution's STDEV when 20% GLDA is used.

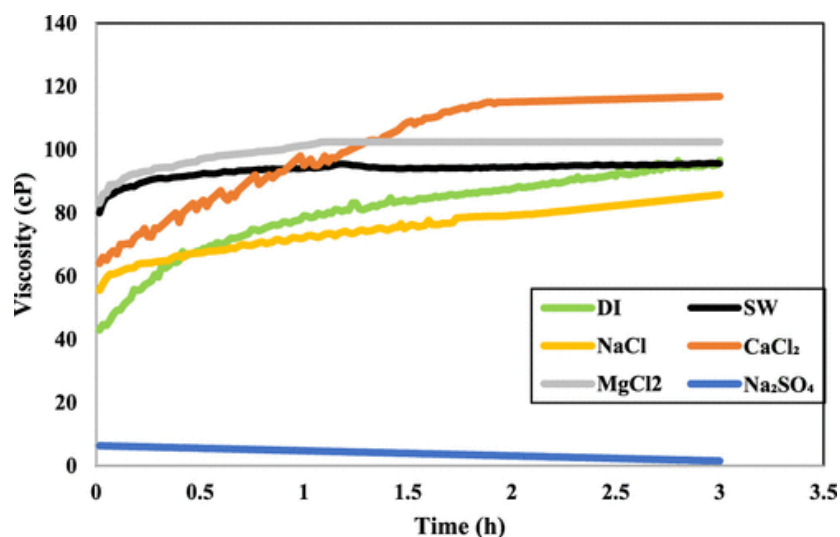


Figure 24 0.6 wt % CMHPG in individual ions with 20% added GLDA compared to SW and DI at 70 °C, 100 1/s, and 500 psi.

Table 13 Viscosity Average and STDEV for SW, DI and Individual Ions Solutions When 20% GLDA Added

Solution	Average viscosity	STDEV
NaCl	74.866	6.924
CaCl ₂	30.275	4.62
MgCl ₂	99.825	4.178
Na ₂ SO ₄	3.0260	1.678
DI	80.488	12.64
SW	93.573	2.406

Figure 25 shows a bar chart comparing the GLDA concentrations after 3 h of shearing. The light color represents the 0% GLDA, the dark colors represent the 20% GLDA, and the middle bars show the 4 and 10% GLDA.

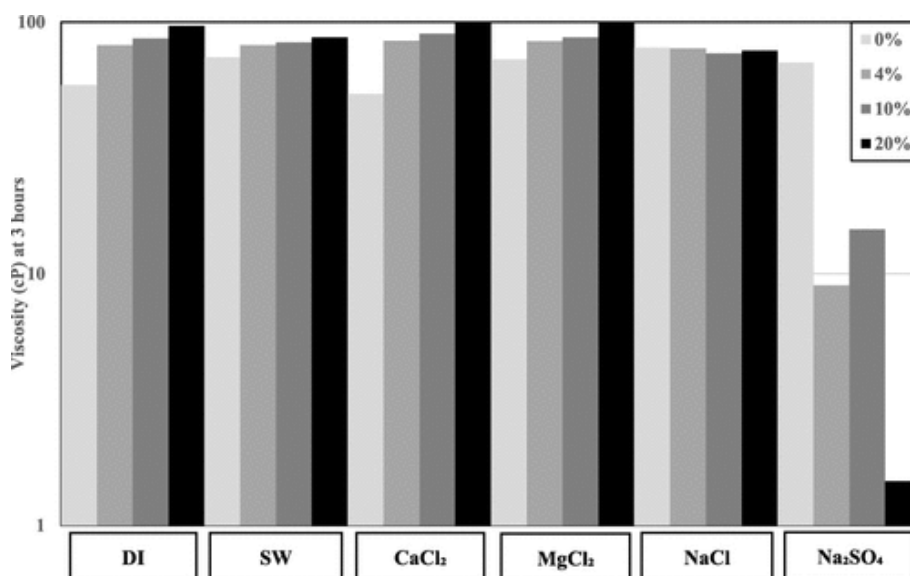


Figure 25 GLDA concentration effect on rheology, the columns shows 0, 4, 10, and 20% starting from the left.

Table 14 Remarkable Results of Individual Ions Study

system without chelating agent	system with chelating agent
the concentration of NaCl, CaCl ₂ , and MgCl ₂ did not affect the viscosity	high pH GLDA favors cations, it captures calcium first, and it has negative effect on sulfate
the concentration of Na ₂ SO ₄ has a major impact on viscosity	GLDA at low concentration gave higher viscosities

It can be noted that small volumes of GLDA can perform as well as big volumes. The differences in viscosity values between 4 and 20% are not great in the DI, CaCl₂, and MgCl₂. The increase in GLDA concentration did not improve individual ions' performance. However, in the cases of Na₂SO₄, the higher the GLDA, the lower the viscosity. A similar but small effect was also noted on NaCl; these ions reflected their impact on the SW behavior. Table 14 is a summary for all remarkable results of the individual ion study on a hydrated polymer in the presence of a high pH GLDA chelating agent.

4.5 Conclusions

The study evaluated the effect of SW and PW salt ions on the rheology of the CMHPG polymer. The research showed that the rheology of a system reacts differently to various ions, with divalent ions having the most significant effect. In addition, it was noticed that sulfate has an important impact on rheology. Nevertheless, GLDA improved the rheology and minimized the impact of salt ions in SW and PW-based fracturing fluid rheology.

1. The concentration of the salt has no significant effect on CMHPG rheology, except in the case of Na_2SO_4 .
2. Na_2SO_4 is the source of viscosity reduction when the polymer is dissolved in seawater. Therefore, treated water with lower contents of sulfate can improve the rheological properties of seawater-based or produced water-based fracturing fluids.
3. High pH GLDA increases the viscosity of DI, SW, and individual salt solutions such as NaCl , CaCl_2 , and MgCl_2 .
4. The higher the concentration of Na_2SO_4 solution, the lower the repulsion in the polymer backbone, which reduces the viscosity.
5. If a limited high pH GLDA is added to SW or PW solutions, it will chelate Ca^{2+} ion first.
6. The high pH chelating agent has an adverse impact on Na_2SO_4 ; it breaks the viscosity of the solution.
7. Increasing the GLDA concentration up to 20% changes the behavior of the ions, DI and SW. In these solutions,

CHAPTER 5

Individual Seawater Ions' Impact on the Rheology of Crosslinked Polymers in the Presence of a Chelating Agent¹

5.1 Abstract

Seawater (SW) has the potential to replace freshwater in hydraulic fracturing operations, which promotes sustainability. In this study, we investigated the influence of SW ions individually on a crosslinked polymer solution containing a chelating agent. The tested salts include calcium chloride, magnesium chloride, sodium chloride, and sodium sulfate. First, the concentrations of the delayed zirconium crosslinker, which is used to crosslink the carboxymethyl hydroxypropyl (CMHPG) polymer, and high-pH GLDA were optimized. The testing parameters for the crosslinker and chelating agent optimization experiments were a 70 °C temperature, a 500 psi pressure, and a 100 1/s shear rate. However, the temperature was raised to 120 °C representing harsh reservoir conditions. Results showed that sulfate had a significant effect on the rheology of the crosslinked CMHPG polymer. Unlike DI water, the viscosity of SW and individual ions increased when the crosslinker concentration was increased. In addition, the solution stability of magnesium chloride and DI water was improved.

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Adding a chelating agent at a low concentration improved the solution stability of magnesium chloride and DI water. These findings are critical for comprehending the rheology of produced water and SW-based fracturing fluid.

5.2 Introduction

Hydraulic fracturing is applied to remove damage near the wellbore, to propagate the fracture deeper into the formation, or to change the flow regime. It is applied to recover extra oil from low-permeability formations or stop sand production from unconsolidated formations. The fracturing process can be accomplished by creating a fracture that can withstand the closure pressure using proppants. The formation type and the accessibility of freshwater are two factors that should be considered when planning a fracturing job. The chosen additives, proppant, and injection rate will reflect this (Economides & Nolte, 2000).¹ In fracturing fluid design, the optimal viscosity will be the one that allows for the deepest possible cracks to form while yet being feasible to use. It ought to be elastic and viscous enough to keep the proppant suspended with the lowest possible settling rate. This fluid should break and flow back out of the formation once the proppant has been placed (Das & Rahim, 2014; Das & Rahim, 2014). Fracturing fluids are based on water, oil, alcohol, and foams. The choice of fracturing fluid is determined by factors such as formation type, governmental laws, environmental laws, cost, and water availability. The waterbased type includes viscoelastic surfactants, slick water, and crosslinked fluid (Das & Rahim, 2014). Vast volumes of water are consumed in heavy hydraulic fracturing treatments; in conventional formations, it reaches 3 million bbl, while it exceeds 13 million bbl in unconventional formations (Almubarak et al., 2019).

The best fracturing fluid will help achieve these goals when designing a fracture. Fracture design aims to find the optimum dimensionless fracture conductivity by optimizing other parameters such as the fracture half-length, width, and permeabilities of the fracture and reservoir. These parameters require that the fluid be capable of transporting the proppant with minimal velocity settling, fluid loss, and formation damage (Barati & Liang, 2014). The fracturing fluid contains many additives to achieve these properties, and the essential additives are the gelling agents. Guar is the most preferred gelling agent, a polymer with a high molecular weight, long chain, and intermolecular hydrogen bonds. The purity of the gum and separation process govern the solid residue in the guar gum, with the insoluble residue ranging between 10 and 14%. As a result of obstructing the flow inside the cracks, these residues limit fracturing efficiency. Hydroxypropyl guar (HPG) is the most popular guar derivative in the oil industry. In contrast, carboxymethyl hydroxypropyl (CMHPG) guar is the most preferred owing to its efficient hydration and low residual content (Harris, 1988; Cheng et al., 2002). Once the polymer is hydrated in water, it forms the pad, a linear fluid in unconventional formation or crosslinked in conventional formation. The pad initiates the fracture and affords enough leak-off as the slurry (crosslinked fluid + proppant) is pumped to the formation; lesser fluid will be lost (Cheng et al., 2002). Figure 26 shows the CMHPG structure (Fink, 2021).

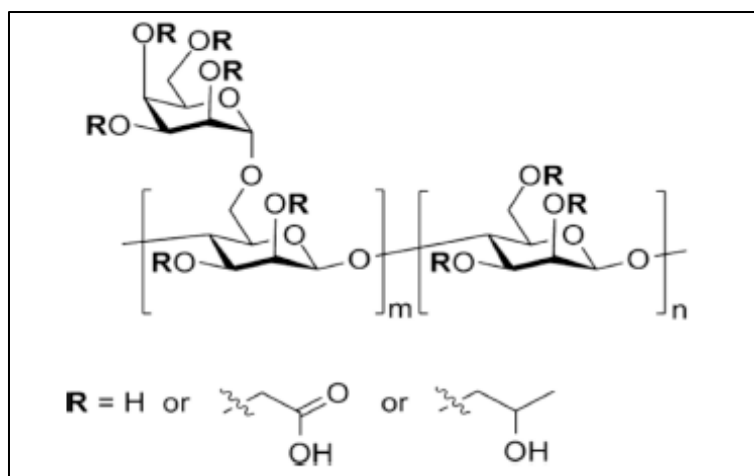


Figure 26 Generic structure of CMHPG. Adapted with permission from ref (Szopinski et al., 2015). Copyright 2015 Elsevier.

A fluid with a greater viscosity is required for a fracture to propagate since the viscous fluid exerts more pressure. This high viscosity may be attained by adding a crosslinker.⁶ At lower concentrations of guar derivatives, the crosslinker may increase the viscosity to hundreds of centipoise, yet the excessively viscous fluid destroys the formation. Additionally, the crosslinker enhances the fluid's elasticity, transforming its viscous behavior into viscoelastic behavior. Crosslinkers are a combination of phosphate esters, potassium hydroxide (KOH), isopropyl alcohol (CH₃)₂CHOH, and metals such as aluminum, antimony, and titanium, with borate and zirconium being the most prevalent. Borates are immediate crosslinkers used to maintain viscosity stability at elevated temperatures; they generate borate-crosslinked guar derivative salt. Fracturing tasks employ delayed zirconium crosslinkers to transport proppants with little energy (Almubarak et al., 2020; Fink, 2021; Gaurina-Medimurec et al., 2021; Harris, 1988; Harris & van Batenburg, 1999).

Saline water has a solid crosslinking mechanism and low hydration levels compared to freshwater. The water hardness caused by the divalent ions associated with saline water

induces hydration deficiency and formation damage. The instability of produced water (PW)- and SW-based fluids at high temperatures is another issue. The chelating agents are used in the oil industry as acids, breakers, and biocides; they are compatible with PW and SW. They are robust enough to be utilized as a clay stabilizer, pH regulator, ion regulator, surface tension reducer, and thermal stabilizer. Chelating compounds are used in fracturing procedures to entrap ions and lessen PW and SW hardness. A variety of chelating compounds, such as ethylenediaminetetraacetic acid (EDTA), ethanolic phosphotungstic acid, and L-glutamic acid-N,N-diacetic acid (L-glutamic acid- N,N-diacetic acid) (GLDA), are employed in the oil business. EDTA binds anions like sulfates and carbonates, whereas GLDA binds cations like calcium and magnesium. GLDA can withstand temperatures up to 149 °C without degrading. As GLDA's pH changes, its reaction to ions changes. The crosslinking process may be compromised by using chelating agents at excessive concentrations; thus, the chelating agent concentrations must be managed (Kamal et al., 2018; LePage et al., 2011; Hassan et al., 2020; Mahmoud & Abdelgawad, 2015).

Companies, academic institutions, and government centers all pushed for examining the feasibility of using PW and seawater (SW) in hydraulic fracturing operations as alternatives to fresh water. Several factors pushed the research toward these alternatives, including freshwater scarcity, transport and reserve logistics in offshore locations, and the added expense of chemicals like clay stabilizers (Li et al., 2016). The expense of PW disposal and treatment and the abundance of SW in offshore sites are further justifications for using saline water. PW and SW may have comparable salinities and the same ions, except that the PW may have associated hydrocarbon. The exact ion solutions can be used in both, disregarding the dispersed hydrocarbon. PW is either made up of water trapped during the

formation of the rocks or low-quality water like flow-back water or lake or river surface water. PW may come from water flooding or the flowback after hydraulic fracturing (Harris & van Batenburg, 1999). The main issue to be concerned about when using SW and PW is the presence of ions, like calcium, carbonates, and sulfates, which can cause scale and corrosion and harm the formation or reduce the fracture conductivity. The ions also delay polymer hydration, which lowers the viscosity of the fracturing fluid and the gelhydrocarbon stability of the fracturing fluid (Gupta et al., 2018).

The total dissolved solids (TDSs) in the PW can reach 400,000 ppm, but the average values are between 100,000 and 300,000 globally. Even within the same reservoir, the TDS of the PW can change depending on the season (summer or winter), field, location, and basin (Li et al., 2016). While the TDS for SW in the gulf region can reach 67,700 ppm with an average of 45,000 with a hardness that ranges between 6648 and 8648 ppm (Othman, Aljawad, Mahmoud, et al., 2021; Saeed et al., 2019). The salts synthesizing the SW and PW are sodium chloride, calcium chloride, magnesium chlorides, and sodium sulfates. In addition to these salts, the PW contains water-soluble organic materials. Infeasible treatment methods are used to treat PW, including sulfate removal or a substantial number of divalent ions. Total hardness, influenced by related divalent, is another measure used to assess PW or SW quality. Therefore, a solution containing exclusively monovalent ions, such as potassium chloride solutions, might have a near-zero hardness despite a high total ionic concentration. Generally, the hardness increases with TDS because PW and SW often include monovalent and divalent cations. The calcium (Ca^{2+}) and magnesium (Mg^{2+}) concentrations in the SW can be used to get the equivalent calcium carbonate (CaCO_3) which is translated to SW total hardness (Li et al., 2016)

$$\text{Total hardness (ppm as CaCO}_3\text{)} = 2.5[\text{Ca}^{2+}] + 4.1 [\text{Mg}^{2+}] \quad 5.1$$

The viscosity and stability of saline water-based fracturing fluids are affected by monovalent (Na^+ and K^+) and divalent (Ca^{2+} and Mg^{2+}) ions. The monovalent ions lower the fluid's viscosity if the saline water system does not have divalent ions (Elsarawy et al., 2017). Because Ca^{2+} and Mg^{2+} ions reduce the polymer hydration, they reduce the viscosity of PW and SW. Many additives, such as gel breakers and pH control agents, might be rendered ineffective by these ions (Gupta et al., 2018). Besides the viscosity reduction, Ca^{2+} and Mg^{2+} can precipitate at a pH higher than 10; they reduce the crosslinking, and different scales can be formed. Therefore, the pH should be controlled, or scale inhibitors should be used if a high pH is needed. The thermal stability of the PW- or SW-based fluid should be carefully monitored. High-pH environments are needed to maintain stability at high temperatures (Alohaly et al., 2016; Li et al., 2016; Prakash et al., 2016).

This study investigates the crosslinker effect on the individual ions associated with the SW and PW, which are Ca^{2+} , Mg^{2+} , Na^+ , and SO_4^{2-} . The other ions associated with SW and PW are not tested in this study because they have little effect on the saline water behavior. The study was performed at a 1M concentration of each ion. Other research studied different ion concentrations and the chelating agent's effect (Othman, Murtaza, et al., 2022). This work is divided into three parts; the first part handles the crosslinker concentration effect. The following part optimizes the chelating agent at a selected crosslinker concentration. The first and second parts were performed at a fixed temperature. The third part reports the temperature effect for the optimized concentrations of the crosslinker and chelating agent. The SW and DI experiments were performed as the baseline for all three experiment sets.

5.3 Methodology

5.3.1 Materials

In this work, we investigated the effects of various crosslinker concentrations in DI, SW, and 1 M calcium chloride ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$), 1 M magnesium chloride ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$), 1 M sodium chloride (NaCl), and 1 M sodium sulfate (Na_2SO_4). We utilized the zirconium delayed crosslinker, XLFC-3B CMHPG polymer, and GLDA with a high pH of 13.7. The viscosity values were obtained using a high-pressure high-temperature Anton Paar-MCR 302 rheometer. Table 15 contains SW-associated salt concentrations in grams/liter. Each salt is diluted in DI water to form 1 M of the ion.

Table 15 SW Formulation Used in Experiments

Compound (anhydrite)	g/L
NaHCO_3	0.165
Na_2SO_4	6.339
NaCl	41.172
$\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$	2.387
$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	17.644
Total dissolved solids (TDS)	67.707

The CMHPG cationic polymer employed in these tests as a gelling agent has previously shown positive results when hydrated in DI and SW (Othman, Aljawad, et al., 2022). When the chain of CMHPG polymers absorbs water, it transforms from a compacted state to an

extended-relaxed state named hydration. Since CMHPG hydrates quicker, is more stable at low pH, and degrades more slowly than competing polymers, it has widespread usage in fracturing fluids (Alohaly et al., 2016; Abdul Majid et al., 2017; Wilson, 2017).

The metallic crosslinkers polymerize into oxide nanoparticles, which subsequently bond with the polymer through hydrogen bonds, resulting in a fluid with the desired viscosity. However, given that these bonds cannot be repaired if broken, it is important to control the release of metallic crosslinkers using appropriate ligands. Typically, the zirconium crosslinker will have three ligands, lactate ligand, propylene glycol, and triethanolamine, which is clarified in Figure 27 (Othman et al., 2022). In this work, we utilized a liquid zirconium crosslinker collected from the chemical company; we assumed that the active content was 14% to ease the calculations.

We used a high-pH GLDA- Na_4 chelating agent (N,N-dicarboxymethyl glutamic acid) to prevent scaling when SW comes into contact with the formation water. The GLDA used had a 40% active content. We measured the pH of the received GLDA batch; the pH was around 13.7. As mentioned in the MSDS, this GLDA was specially intended to dissolve the CaSO_4 scale. GLDA is eco-friendly and biodegradable in freshwater; it takes time to degrade in saline water. Our pH measurements showed that adding GLDA adjusted the solution's pH from 7 to 10.5 in the case of 4 wt % GLDA and more than 11 in the case of 10 wt %.

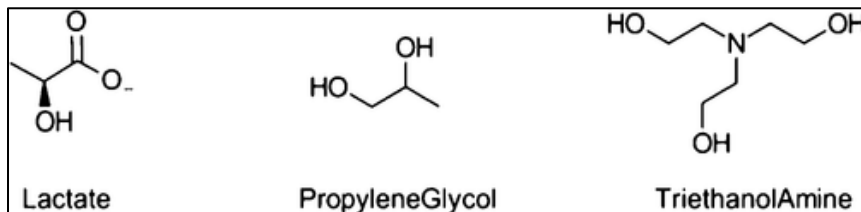


Figure 27 Metal crosslinker crosslinking a guar derivative. Adapted with permission from ref (Othman et al., 2022), copyright 2022 American Chemical Society.

5.3.2 Procedures

In the first section, we investigated the effect of crosslinker concentration following polymer hydration in individual ions, DI, and SW. Therefore, the first section helps to comprehend the effect of varying concentrations of crosslinked polymer in individual ions, DI and SW. At this point, the optimal crosslinker concentration is determined. The second section examines the impact of varying concentrations of GLDA on the crosslinked polymer. The research was done by selecting just two concentrations (4 and 10 wt %) since the very high concentration had a detrimental effect based on our previous study (Othman et al., 2022). Finally, the optimized GLDA concentration was tested with the crosslinked polymer at different temperatures. In all experiments, the testing parameters were a 70 °C temperature (or 120 °C in temperature effect assessment), a 500 psi pressure, and a 100 1/s shear rate.

5.3.3 Experimental Design

In the preparation, we hydrated the polymer at 500 rpm for 45 min, and then the chelating agent was added and mixed for 5 min, after which we added the crosslinker and stirred it for 5 min. The volume of the prepared fluid was 21 mL for all tested solutions. The polymer concentration was fixed at 0.6 wt % CMHPG in all experiments. In the first set, we added the Zr-crosslinker at a different concentration of 0.3, 0.6 wt %, or 1 wt %. The experiments were performed at 70 °C. In the second set, we added 1 wt % Zrcrosslinker to optimize the chelating agent, and two GLDA concentrations were used, 4 and 10 wt %. Then, the 1 wt % Zrcrosslinker and 4 wt% GLDA concentrations were selected to be tested at 120 °C. Table 16 shows the experiments' concentrations, solutions, and conditions.

Table 16 Summary of Experiments' Solutions, Concentrations, and Conditions

Solution type	polymer (wt %)	Crosslinker concentration (wt %)	chelating agent (wt %)	Temperature (°C)	number of experiments
DI, SW	0.6	0.3, 0.6, 1		70	6
CaCl ₂ ·2H ₂ O, MgCl ₂ ·6H ₂ O, NaCl, Na ₂ SO ₄	0.6	0.3, 0.6, 1		70	12
DI, SW	0.6	1	4, 10	70	4
CaCl ₂ ·2H ₂ O, MgCl ₂ ·6H ₂ O, NaCl, Na ₂ SO ₄	0.6	1	4, 10	70	8
DI, SW	0.6	1	4	120	6
CaCl ₂ ·2H ₂ O, MgCl ₂ ·6H ₂ O, NaCl, Na ₂ SO ₄	0.6	1	4	120	12

5.4 Results and Discussions

To ensure the quality of the experiments, we repeated one of the baseline experiments and calculated the error. The deviation of the measured viscosity from the real values was evaluated by repeating the DI baseline experiment at 70 °C in the 0.6 wt % CMHPG polymer that was hydrated in DI for 45 min. Figure 28 shows error bars based on a computed average percentage error, and succeeding experiments were assumed to have similar errors. The DI experiment had an average error of 1.6%, which is within the standard error margin. Other experiments in the study were repeated, and the error was found to be less than 5%.

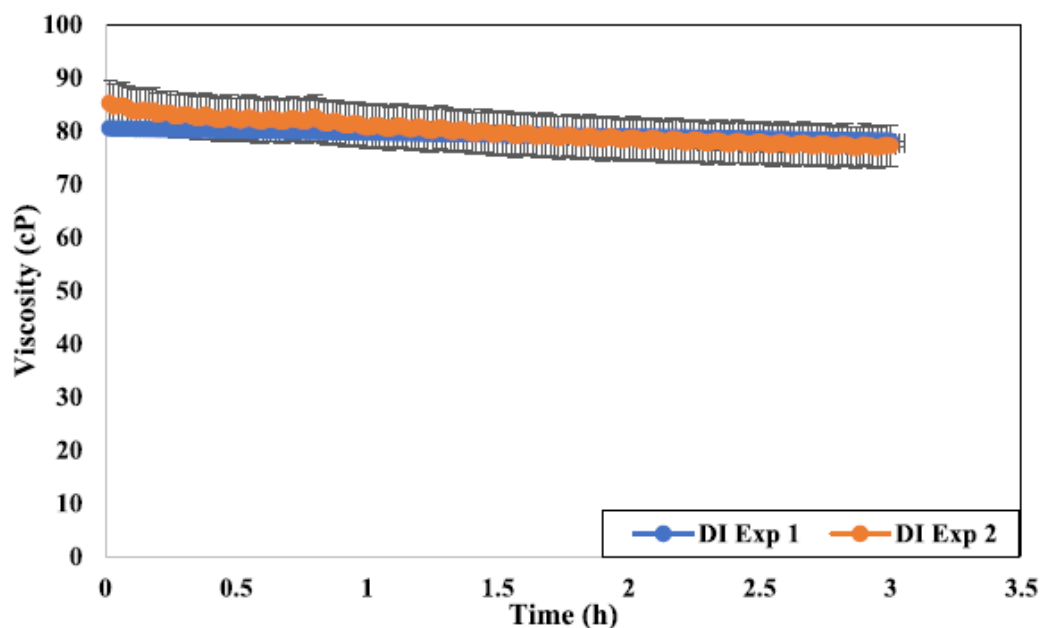


Figure 28 Error bars for 0.6 wt % CMHPG in DI water-based fluid, at 70 °C, 100 1/s, and 500 psi.

5.4.1 Crosslinker Impact on Viscosity

The viscosities of DI water, SW, and individual ion solutions of crosslinked CMHPG are presented. The zirconium crosslinker concentrations of 0.3, 0.6, and 1 wt % were tested in the mentioned solutions. 0.6 wt % CMHPG was hydrated, and then the crosslinker was added. All experiments were run at 70 °C, 100 1/s, and 500 psi. Figures 29-31 show how the crosslinker changes the individual ions' rheology. Magnesium chloride had the highest viscosity among the individual ion salts across all Zrcrosslinker concentrations. Nonetheless, its behavior was different from that of the calcium chloride solution. On the other hand, the sodium chloride solution had lower viscosity values than calcium chloride across all Zr-crosslinker concentrations while maintaining a similar behavior.

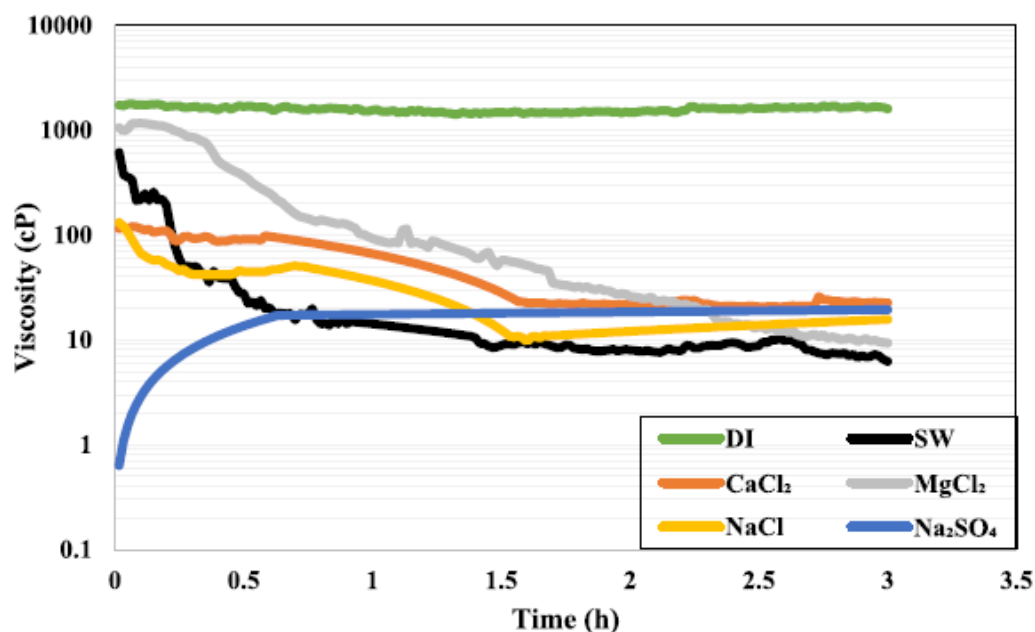


Figure 29 0.3% Zr and 0.6 wt % CMHPG hydrated in DI water, SW, and individual ions at 70 °C, 100 1/s, and 500 psi.

Adding the 0.3 wt % Zr-crosslinker to DI water increased the solution viscosity, as seen in Figure 29. After 3 h, DI water's viscosity remained unchanged between 1800 and 1500 cP. All solutions showed a decline in viscosity except the sodium sulfate solution, which had unstable reverse behavior. The viscosity of all individual ion salts dropped below 100 cP in 30 min and declined quickly due to insufficient zirconium crosslinking. If there is not enough zirconium to crosslink the polymer, mutual repulsion between charges in the polymer backbone will decrease and cause this fast viscosity reduction. In the sodium sulfate case, the solution's high concentration of positive ions acted as a barrier, preventing any repulsive forces from being exerted (Guo et al., 1998).

Figure 30 shows the 0.6 wt % Zr concentration results with DI, SW, and the individual ions. We noticed that the viscosity of the DI-based solution dropped significantly from 1613 to 650 cP. On the other hand, the individual ions and SW showed similar behavior but different values. The sodium chloride and calcium chlorides had similar viscosity

trends. The SW and magnesium chloride showed identical behaviors and values, which indicates that the SW viscosity is controlled in this case by magnesium chloride. However, the viscosity might be insufficient for the field requirements to transport the proppant.

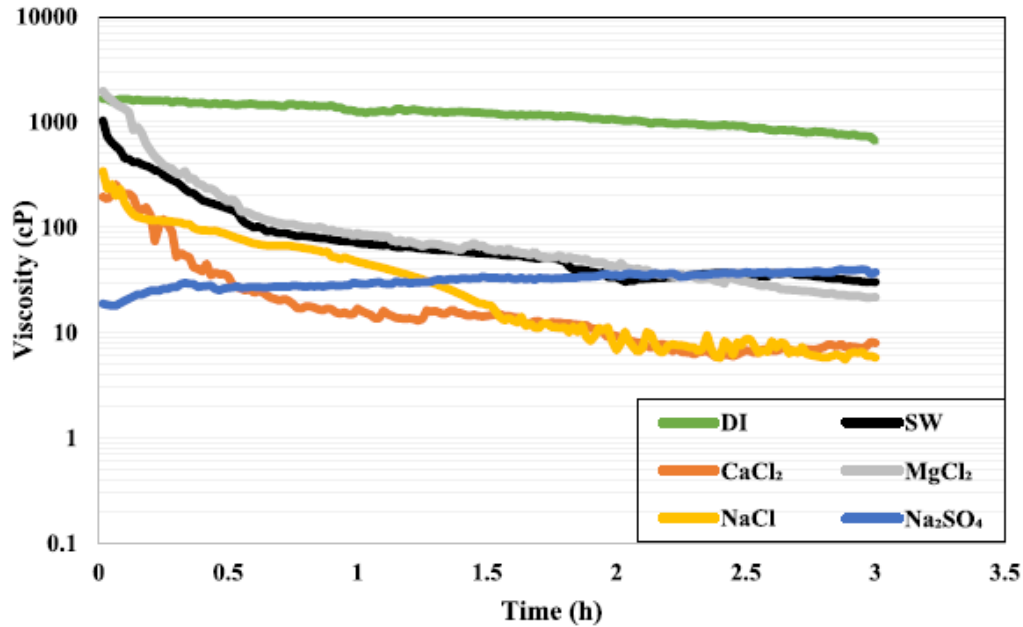


Figure 30 0.6% Zr and 0.6 wt % CMHPG hydrated in DI water, SW, and individual ions at 70 °C, 100 1/s, and 500 psi.

Lastly, we tested the 1 wt % zirconium crosslinker and plotted the values in Figure 31. The first hour saw a rapid decrease in the viscosity of the solutions. Both SW and magnesium chloride, at this concentration, had high viscosities of 150 cP even after 1 h, which was not the case with DI. Sodium sulfate performed better at higher crosslinker concentrations but was unstable. Since metallic crosslinkers like zirconium generate tiny oxides that make hydrogen bonds with the polymer, the bonds cannot reheal after they are broken because of the shear rate, which is reflected in the dropped viscosity of DI (Almubarak et al., 2020).

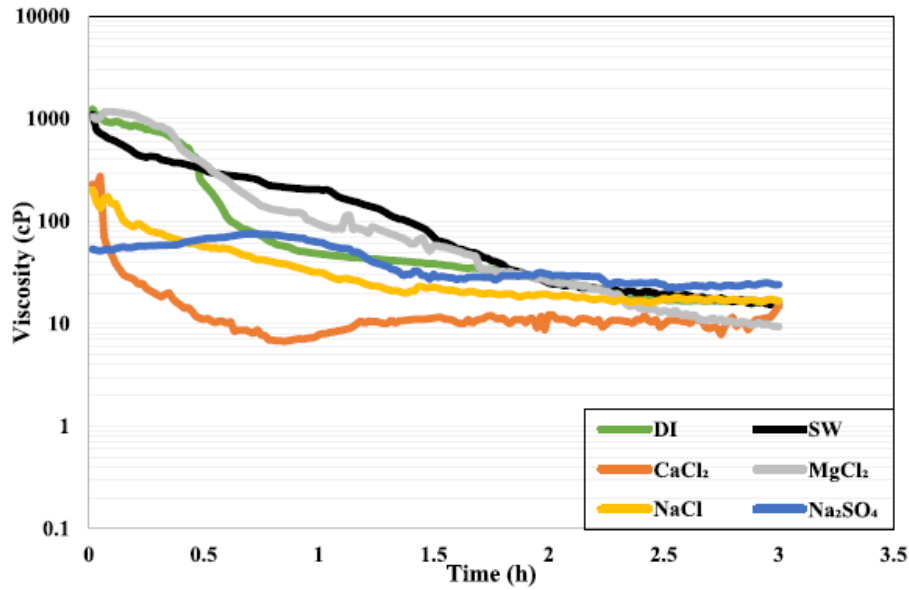


Figure 31 1 wt % Zr and 0.6 wt % CMHPG hydrated in DI water, SW, and individual ions at 70 °C, 100 1/s, and 500 psi.

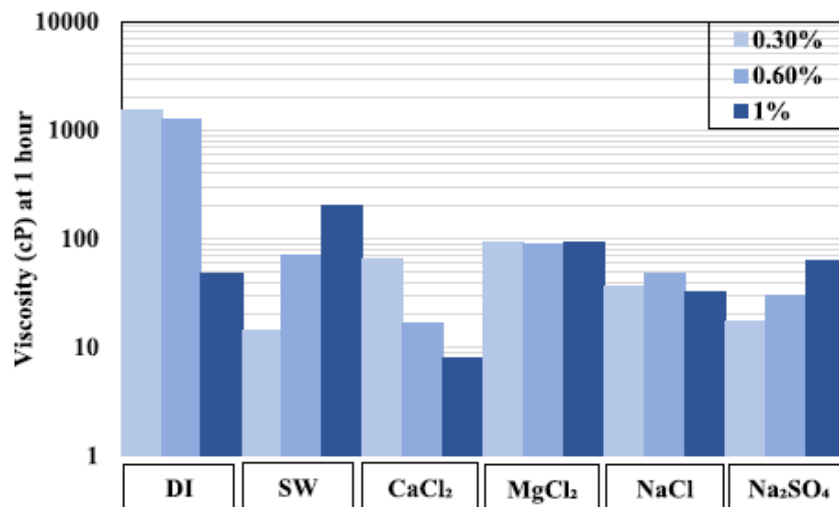


Figure 32 Zr-crosslinker concentration effect on viscosity at 1 h; the columns show 0.3, 0.6, and 1 wt % from the left.

Figure 32 shows a bar chart for DI water, SW, and individual ion salts at 1 h for different crosslinker concentrations. We made this comparison only at 1 h because most solutions reached the same low viscosity level after 3 h. Bear in mind that it could take an hour to complete the fracture process and get the proppant to the formation. The crosslinker concentration significantly affected both DI and SW fluids after 1 h. Increasing the crosslinker concentration impacted the SW solution positively but negatively impacted the

DI water solution. Concentration change had little impact on MgCl_2 and NaCl at 1 h, while adding a crosslinker caused a decrease in the viscosity of calcium chloride.

5.4.2 Chelating Agent Impact on Viscosity

In this part, we investigated the effect of GLDA concentration on the 1 wt % zirconium crosslinked solution at 70 °C. We displayed the outcomes for the 4% GLDA in Figure 33 and the 10% GLDA in Figure 34. The pH of the solutions rose from 7 to 10.5 after adding 4 wt % GLDA and over 11 after adding 10 wt % GLDA. Our prior research showed that an increase in pH slows the progress of viscosity rise (Othman et al., 2021). After 3 h, calcium chloride and magnesium chloride reached 80+ cP after adding 4 wt % GLDA concentration (Figure 33). The SW was similar in behavior to calcium chloride but had a slightly lower viscosity. The behavior of sodium chloride was quite similar to that of calcium chloride, although its viscosity was far lower. Sodium sulfate becomes unstable and loses its viscosity dramatically. Instead of the ions in DI, GLDA chelated the crosslinker, which decreased the viscosity.

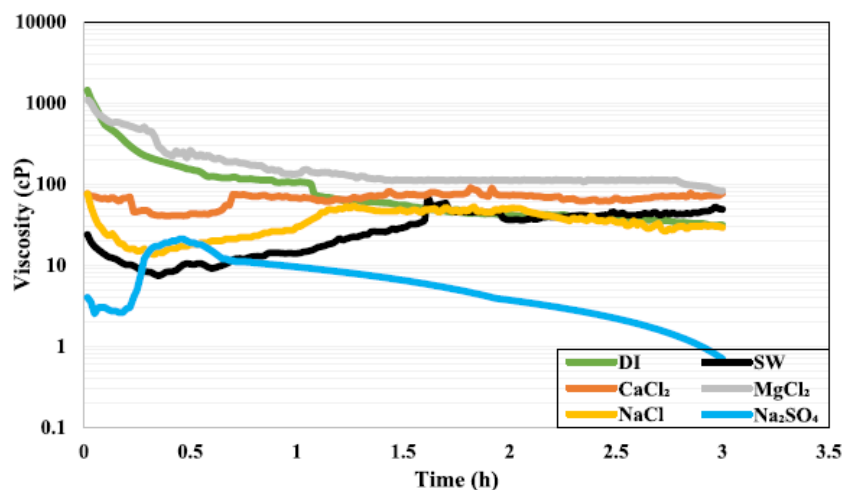


Figure 33 4 wt % GLDA, 1 wt % Zr, and 0.6 wt % CMHPG hydrated in SW and individual ions, 70 °C, 100 1/s, and 500 psi.

For the DI-based crosslinked fluid, when adding 10 wt % GLDA (Figure 34), the initial viscosity was only 100 cP instead of 1700, but it was stable. The results were similar to what one would expect from polymer hydrated in DI water without a crosslinker. This result confirms that the chelating agent attacked the crosslinker instead of the ions; however, the viscosity value was still not low (Othman et al., 2022). Similarly, the delayed crosslinking behavior was also seen in divalent ions. In contrast, divalent ions like sodium chloride and sodium sulfate had very low and unstable viscosity behavior. Both divalent and monovalent ions affected the SW's behavior, and the SW exhibited low steady viscosity values. Note that the 10 wt % GLDA positively impacted the divalent positive ion solution (i.e., Ca^{2+} and Mg^{2+}) but had negative impacts on the others. It is possible that the affinity of GLDA to the divalent ions prevented the negative interaction with the crosslinker. 4 wt % GLDA provided superior results for all ions and delivered improved stability during the first hour, as required by industry standards. For this reason, this concentration will be the focus of the subsequent research phase.

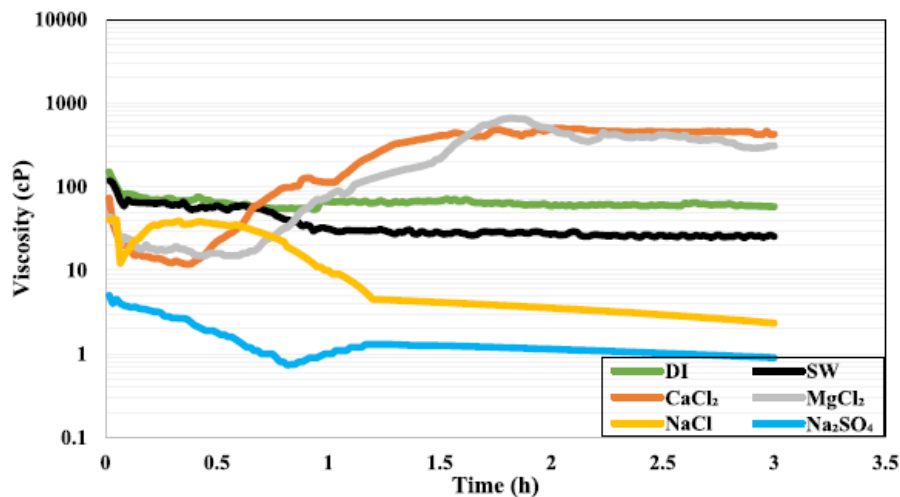


Figure 34 10 wt % GLDA, 1 wt % Zr, and 0.6 wt % CMHPG hydrated in DI, SW, and individual ions, 70 °C, 100 1/s, and 500 psi.

From Figures 33 and 34, we note that the viscosity values are quite similar after 1 h for both GLDA concentrations. Figure 35 is intended to compare the viscosity in bar chart representation at 3 h as the viscosity variation is huge. Viscosity values after 3 h, when 4 and 10 wt % chelating agents were applied to the crosslinked polymer, are shown in the bar chart (Figure 35). Significant variations in viscosity were observed, notably for the divalent ions. GLDA's delay feature was functional in these ions, as was with the DI. When we added more GLDA, the solution became more viscous after 3 h. The SW had viscosity values between the divalent and monovalent ions; however, the inclusion of GLDA lowered its viscosity value.

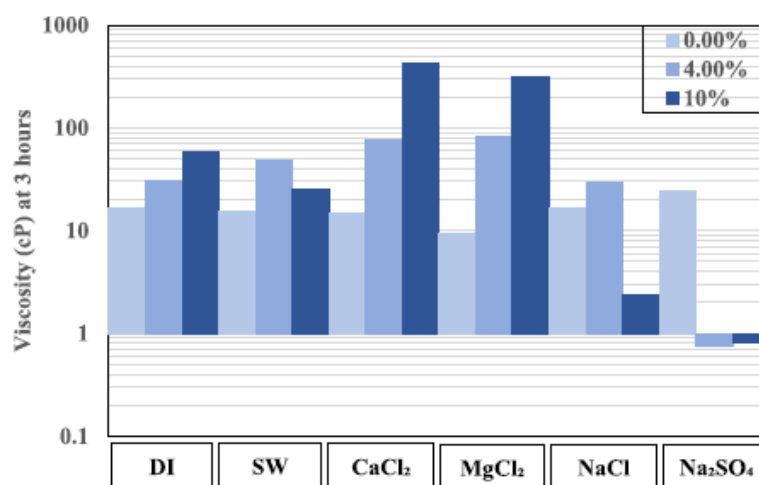


Figure 35 Chelating agent impact on the crosslinked fluid at 3 h; the columns show 0, 4, and 10 wt % from the left.

5.4.3 Temperature Effect

In this part of the study, 70 and 120 °C temperatures were investigated for a 1 M concentration of the individual ion. After the crosslinker and chelating agent optimization, the viscosity measurements were performed using 1 wt % Zr-crosslinker, 4 wt % GLDA, and 0.6 wt % CMHPG as we targeted a 1 h duration. The results were compared to the DI solution in Figure 36. The concepts gained from Figures 37-40 were applied to understand

SW behavior in Figure 41. When we raised the temperature to 120 °C, DI behavior followed the same trend as viscosity behavior at 70 °C (Figure 12), while the value decreased by 1 order of magnitude. Once the fluid was tested at a high temperature, the viscosity dropped from 1100 to 200 cP even before shearing, yet it broke very fast to less than 100 cP in 7 min.

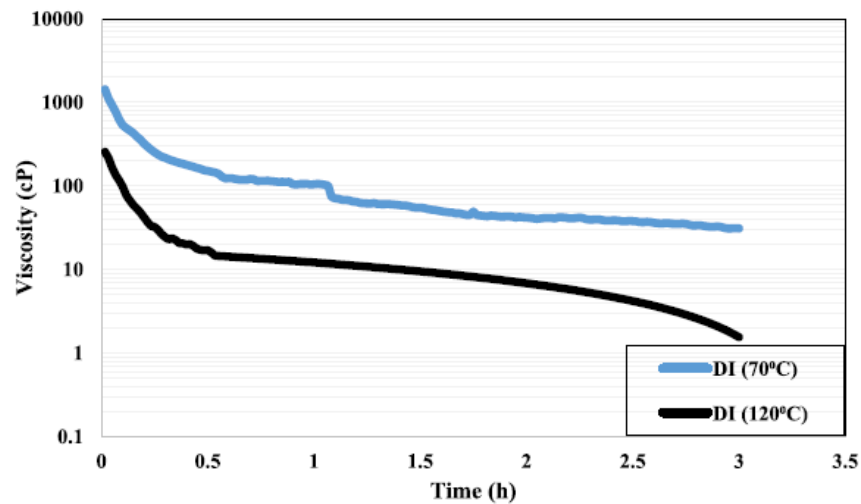


Figure 36 Temperature effect, 1 wt % Zr, 4 wt % GLDA, and 0.6 wt % CMHPG hydrated in DI, 70 °C vs 120 °C, 100 1/s, and 500 psi.

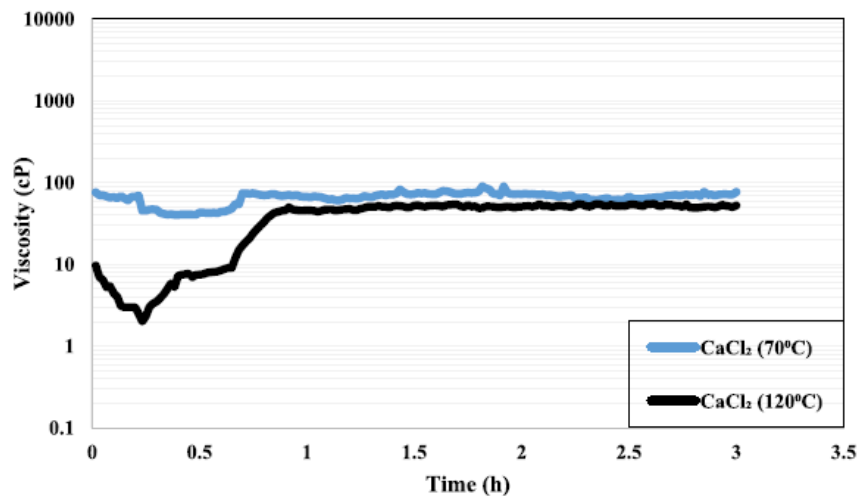


Figure 37 Temperature effect, 1 wt % Zr, 4 wt % GLDA, and 0.6 wt % CMHPG hydrated in CaCl₂, 70 °C vs 120 °C, 100 1/s, and 500 psi.

Because of the chelating agent, the viscosity did not exceed 100 cP in all temperatures for calcium chloride. The higher temperatures decreased its viscosity in the first hour and

delayed the crosslinking; a spoon-like trend can be seen at 120 °C in Figure 37. After 3 h, the viscosity values reach similar figures (more than 50 cP) at both temperatures. The high-pH GLDA decreased the viscosity at the beginning but increased it at the end of the test.

The viscosity of magnesium chloride (shown in Figure 38) started at 1 order of magnitude lower for the high temperature. Then, it induced the spoon-like behavior and increased again to slightly higher than 20 cP. The high temperature affected the viscosity of the crosslinked magnesium chloride throughout the test. Even with the high-pH chelating agent, the viscosity did not improve. After 1 h, the solution behavior at a high temperature and the low temperature was similar but with a significantly lower value.

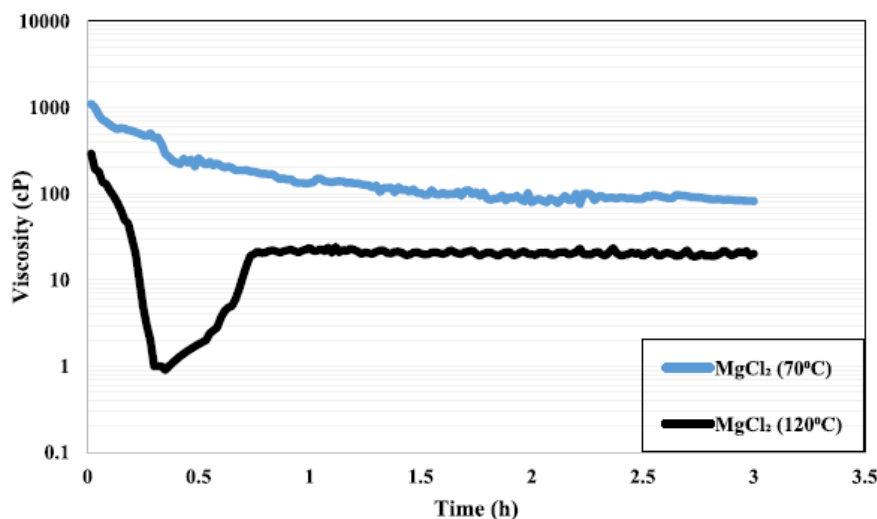


Figure 38 Temperature effect, 1 wt % Zr, 4 wt % GLDA, and 0.6 wt. % CMHPG hydrated in MgCl₂, 70 °C vs 120 °C, 100 1/s, and 500 psi

The results of the temperature inspection of sodium chloride and sodium sulfate are shown in Figures 39 and 40, respectively. In both fluids, the higher temperature resulted in higher viscosity than the lower temperature. For the two solutions, low temperature (70 °C) did not show any better stability behavior, and they were unstable. At 120 °C, sodium chloride and sodium sulfate showed a rise in viscosity in the first hour and then became stable. This

behavior was the unlike the behavior of the divalent ion exhibited in Figures 36 and 37. All the viscosity values of sodium chloride and sodium sulfate reported in the figures are very low compared to the DI water, divalent ions, and even the SW. These results were confirmed by what was reported in ref (Othman et al., 2022); the sulfate disturbs the fracturing fluid's stability and decreases the fluid's viscosity. The sodium sulfate prevents the hydrogen bonds between the polymer and the water. The polymer network then releases the water, and the viscosity breaks (Othman, et al., 2022).

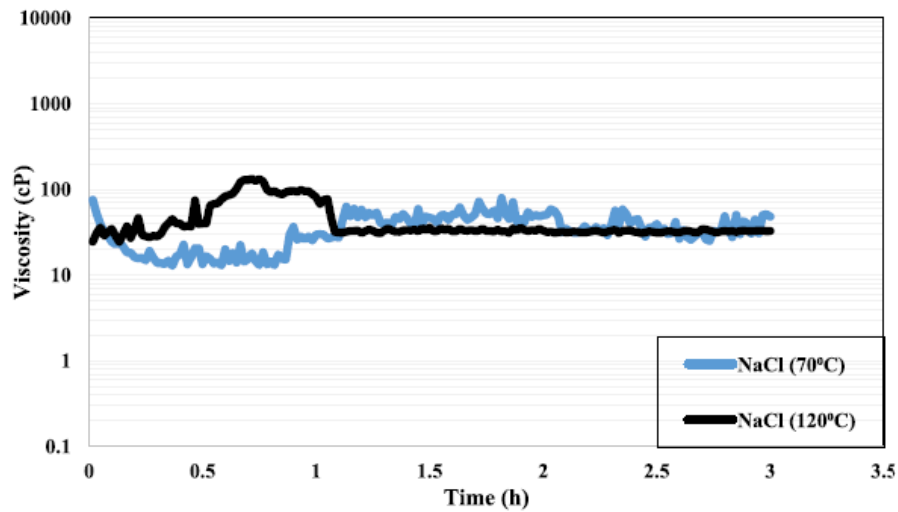


Figure 39 Temperature effect, 1 wt % Zr, 4 wt % GLDA, and 0.6 wt % CMHPG hydrated in NaCl, 70 °C vs 120 °C, 100 1/s, and 500 psi.

The SW (Figure 41) has more stability at higher temperatures than the individual ions, which indicates that the ions interact with each other and affect the overall viscosity. Yet, at the lower temperature, we noted the spoon-like effect in the divalent ions, which indicates their dominance on the SW behavior. The highpH GLDA worked fine with the SW and formed a stable crosslinked fluid.

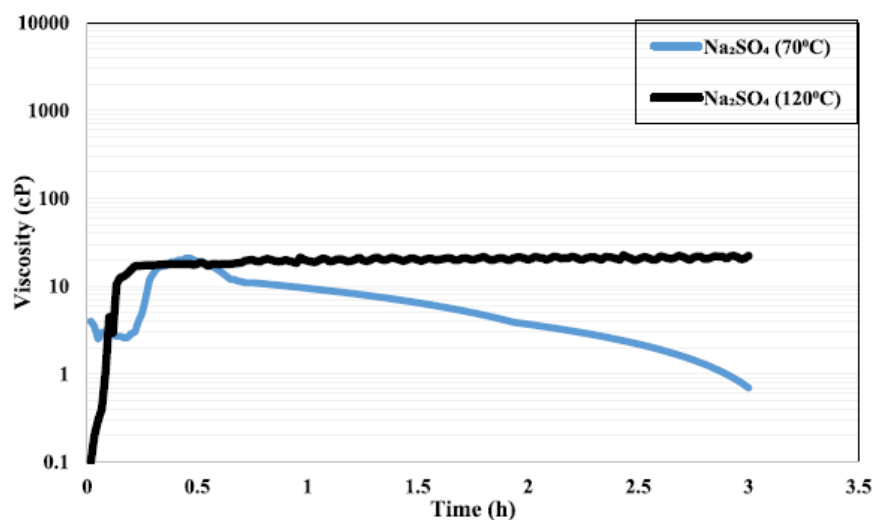


Figure 40 Temperature effect, 1 wt % Zr, 4 wt % GLDA, and 0.6 wt % CMHPG hydrated in Na₂SO₄, 70 °C vs 120 °C, 100 1/s, and 500 psi.

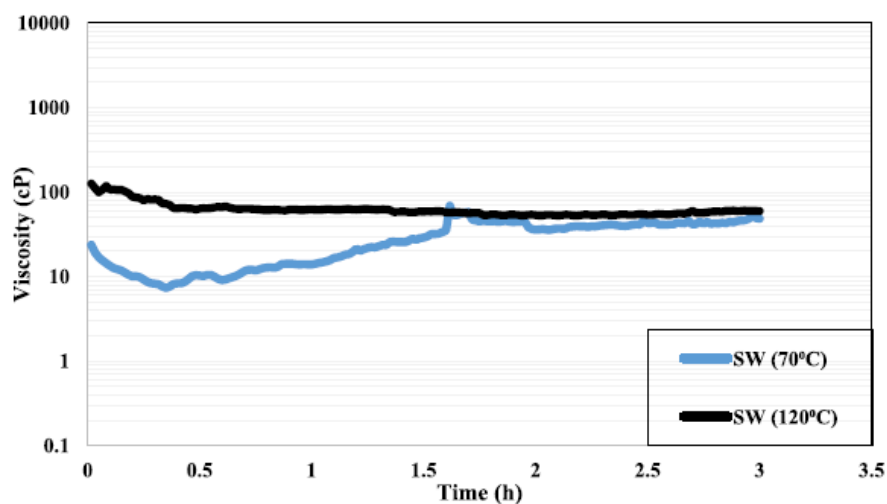


Figure 41 Temperature effect, 1 wt % Zr, 4 wt % GLDA, and 0.6 wt % CMHPG hydrated in SW, 70 °C vs 120 °C, 100 1/s, and 500 psi.

Figures 42 and 43 show the temperature influence on the solution's viscosity after 1 h and 3 h, respectively. Higher temperatures decrease the viscosity at 1 h, except for the sodium solutions and SW. The instability we noted in sodium chloride and sodium sulfate (Figures 39 and 40) negatively affected the SW viscosity more than the other ions. The temperature did not significantly impact the calcium chloride viscosity at this time. After 3 h (Figure

43), the temperature impact appeared clearly on DI and sodium sulfate solutions. The rest of the ions showed similar behaviors.

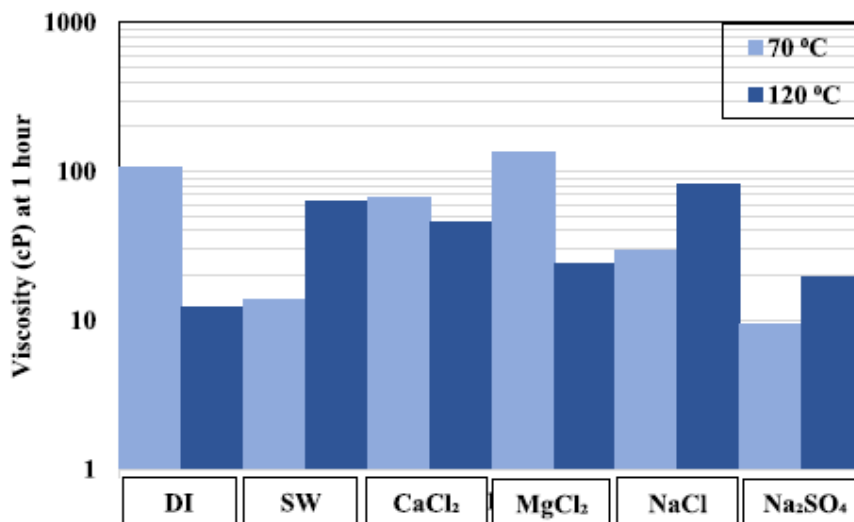


Figure 42 Zr-crosslinker concentration effect on viscosity at 1 h; the columns show 70 °C vs 120 °C, from the left, 100 1/s, and 500 psi

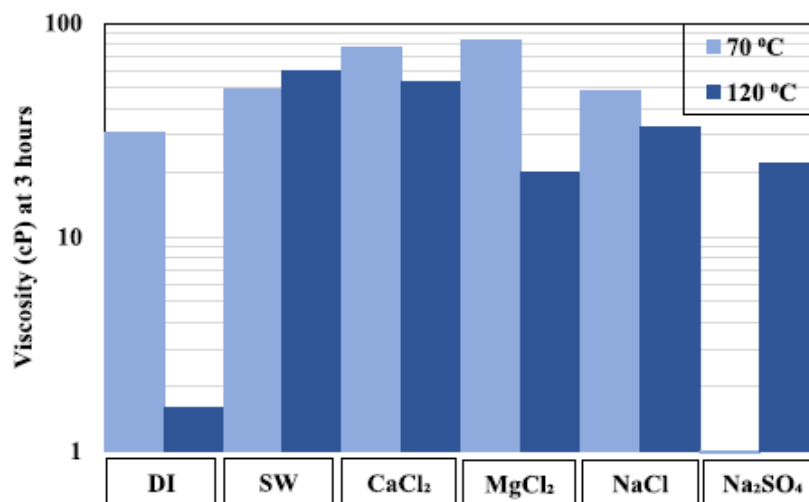


Figure 43 Zr-crosslinker concentration effect on viscosity at 3 h; the columns show 70 °C vs 120 °C, from the left, 100 1/s, and 500 psi.

5.5 Conclusions

This research evaluates the rheology of the CMHPG polymer crosslinker, and chelating agent at varying temperatures and concentrations of individual ions. We compared the

performance of the crosslinker in ions to its performance in DI and SW solutions and assessed the stabilities of the ions at different pH and temperatures. The suggested optimum chelating agent and crosslinker concentrations outperformed the other concentration variants for different ions. Understanding the effect of each ion helps in the evaluation of other saline water types.

1. The crosslinker influences fluid behavior in addition to viscosity.
2. In the case of a solution with only the crosslinker and polymer: (a) the zirconium crosslinker preferred magnesium chloride over calcium chloride, resulting in enhanced viscosity. No amount of crosslinker seemed sufficient to change this preference. It was found that (b) the viscosity values and behaviors of calcium chloride and sodium chloride were similar.
3. In the SW and the individual ions, the viscosity value increases as the zirconium crosslinker concentration rises. However, low zirconium concentrations in DI water are sufficient to crosslink the solution.
4. Adding more crosslinker concentration raised the viscosity of all ions initially and increased the SW viscosity after an hour.
5. SW behavior is controlled by more than one ion, which changes with the concentration of GLDA, the crosslinker, and the environment temperature.
6. The viscosity of divalent ions decreases as temperature rises.
7. Among the saline water-associated ions, Na_2SO_4 has the lowest viscosity and stability. Therefore, it proved to be the source of viscosity reduction and instability in saline water.

8. For all individual ions at 70 °C, and in the first hour, the lower the GLDA concentration, the better the viscosity.
9. High-pH GLDA delays the viscosity of divalent ions at high temperatures and the viscosity of monovalent ions and the SW at low temperatures.
10. The overall performance of the SW at high temperatures is better than all of the individual ions separately.

CHAPTER 6

Rheological Study of Seawater-Based Fracturing Fluid Containing Polymer, Crosslinker, and Chelating Agent¹

6.1 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.

¹ This chapter is copied from the manuscript: **Othman, A.**, Aljawad, M. S., Kamal, M. S., Mahmoud, M., Patil, S., & Alkhowaildi, M. (2022). Rheological Study of Seawater-Based Fracturing Fluid Containing Polymer, Crosslinker, and Chelating Agent. ACS omega, 7(35), 31318-31326.

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.

6.2 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 (Economides & Nolte, 2000). 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 (Das & Rahim, 2014; Samuel et al., 2000). It should also have low fluid loss properties and be compatible with formation fluids. 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 (Anandan et al., 2017; Faroughi et al., 2018; Faroughi et al., 2018).

In 1953, the first-time water was used in hydraulic fracturing, also a variety of gelling agents were introduced (Gandossi & Von EStroff, 2015). Guar derivatives are water-soluble and come from natural sources; they are commonly used to viscosify the fracturing fluids (Barati & Liang, 2014). Guar is a long-chain polymer with a high molecular weight and extensive intermolecular association. Guar is chemically modified to achieve desired physical properties (Cheng et al., 2002). 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 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 (Fink, 2021; Gaurina-Međimurec et al., 2021; Harris, 1988; Montgomery, 2013; Pasha & Swamy, 2008).

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 (Gandossi & Von ESTroff, 2015; Harris, 1988; Harris & van Batenburg, 1999). 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 (CH₃)₂CHOH 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 (Almubarak et al., 2021; Langford et al., 2013; Fink, 2021; Harris, 1988; Powell et al., 1998; Stringfellow et al., 2014; Tran et al., 2015; Zhou et al., 2021)

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⁻¹. They also analyzed the fluid performance using different tools such as a core flood 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 (Almubarak et al., 2016). 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 (Abdul Majid et al., 2017). 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.²⁴ 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⁻¹, the researchers achieved over 600 cP viscosity (Langford et al., 2013).

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 (Harris & van Batenburg, 1999). 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 (Alohaly et al., 2016). 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 (Ca²⁺, Mg²⁺) 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 (Elsarawy et al., 2018). 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 (Economides & Nolte, 2000; Kamal et al., 2018; LePage et al., 2009). 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 (Hassan et al., 2020). 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 (Othman, Aljawad, Mahmoud, et al., 2021). 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 (Hassan et al., 2020; LePage et al., 2009). It has different reaction mechanisms with minerals at different pH levels (Othman, Aljawad, Mahmoud, et al., 2021). 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 (Gao et al., 2015). 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.

6.3 Methodology

6.3.1 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 17 shows the main

components that we find in general SW with details of individual salts and the total dissolved solids in grams/liter.

Table 17 SW Used in Fracturing Fluid Preparation

Compound	g/L
NaHCO ₃	0.165
Na ₂ SO ₄	6.339
NaCl	41.172
CaCl ₂ .2H ₂ O	2.387
MgCl ₂ .6H ₂ 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 (Abdul Majid et al., 2017; Alohalay et al., 2016; Wilson, 2017). The details of HPG and CMHP grades are shown in Table 18.

Table 18 HPG and CMHPG Polymers; Names, Types, and Chemical Structures

Name	Type	Chemical Structure
LH 212	HPG	$\text{Guar} - (\text{ONa})_n + n\text{H}_2\text{C} \begin{array}{c} \text{---} \text{CHCH}_3 \\ \diagdown \quad \diagup \\ \text{O} \end{array} \rightarrow \text{Guar} - (\text{OCH}_2\text{CHCH}_3)_n$ ONa
LH202	CMHPG	$\text{Guar} - (\text{ONa})_n + n\text{ClCH}_2\text{COONa} \rightarrow \text{Guar} - (\text{OCH}_2\text{COONa})_n + n\text{NaCl}$
XLF-3b (ST)	CMHPG	(Gupta and Carmen., 2009)
S 285	CMHPG	Not available
S 284	CMHPG	Not available

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-Na4 and the detail is given in Figure 44. 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 (Hassan et al., 2020; Nouryon, 2020).

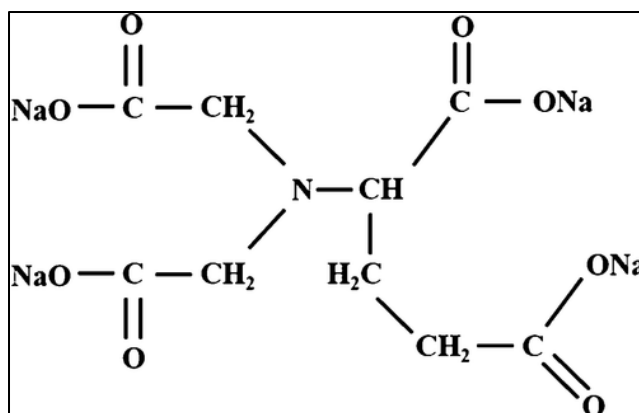


Figure 44 Dissolvine StimWell DGH GLDA structure.

Zirconium (Zr) has four electrons in the outer valence and exists in an ionic state (Zr^{4+}). 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 nanoparticles beyond what is required. Different ligands can create different zirconium crosslinkers with different performances, and they are shown in Figure 45. In the experiments, we used ready liquid with assumed 14% active content. The liquid Zrcrosslinker is added after the addition of GLDA.

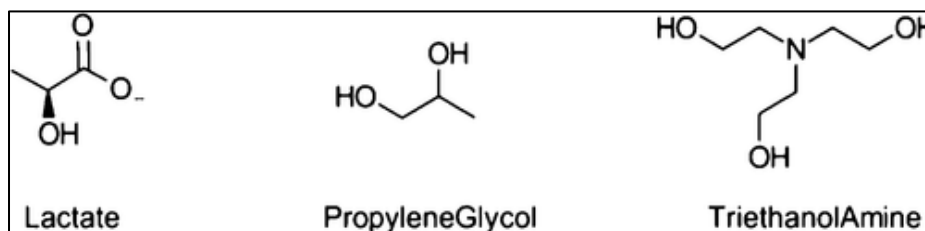


Figure 45 Ligands structure used with Zr crosslinker.

6.3.2 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.

6.3.3 Experimental Design

We did 32 experiments in this study, which are detailed in Table 19. 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 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).

Table 19 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 45 and 46)
DI, SW	0.6	1	-	-	With & without crosslinker	120 °C	4 (Figures 48 and 49)
DI, SW	0.6	1	1.6, 4, 8	High pH GLDA (13.7)	GLDA then polymer hydration	120 °C	6 (Figures 50 and 51)
DI, SW	0.6	1	1.6, 4, 8	High pH GLDA (13.7)	Polymer hydration then GLDA	120 °C	6 (Figure 52)
DI	0.6	1	1.6, 4, 8	High pH GLDA (13.7)	Polymer hydration then GLDA	Temperature ramp from 25 °C to 120 °C	4 (Figure 53)
SW	0.6	1	1.6, 4, 8	High pH GLDA (13.7)	Polymer hydration then GLDA	Temperature ramp from 25 °C to 120 °C	4 (Figure 54)

6.4 Results and Discussions

This section discusses the viscosity of different HPG and CMHPG guar derivatives hydrated in DI and SW without any additional additives. Figure 46 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.

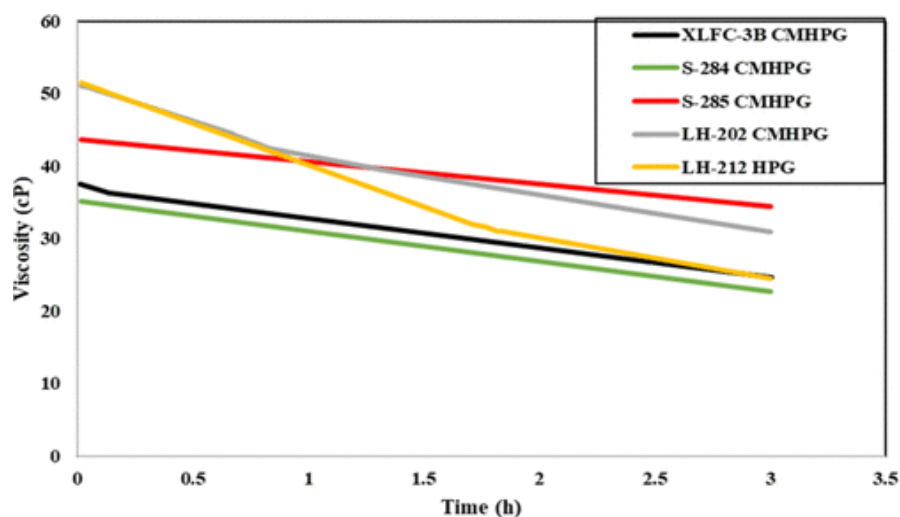


Figure 46 Viscosity of 0.6 wt % polymers hydrated in DI water tested at 120 °C, 100 1/s, and 500 psi.

Figure 47 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 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.

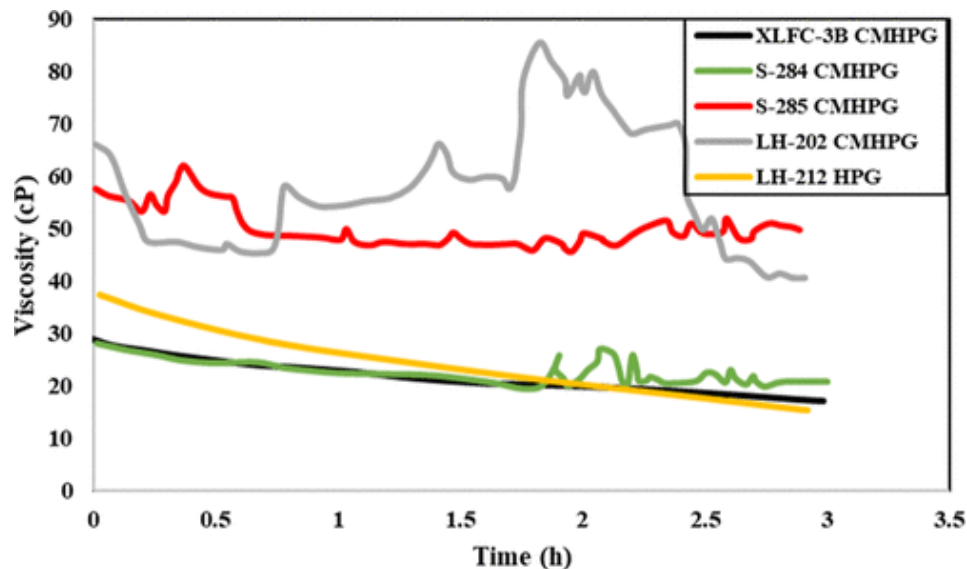


Figure 47 Viscosity of 0.6 wt % polymers hydrated in SW water tested at 120 °C, 100 1/s, and 500 psi.

6.4.1 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 48a. When the crosslinker is added to

the hydrated polymer in SW, it instantly crosslinked before heating at 25 °C, as shown in Figure 48b. 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.

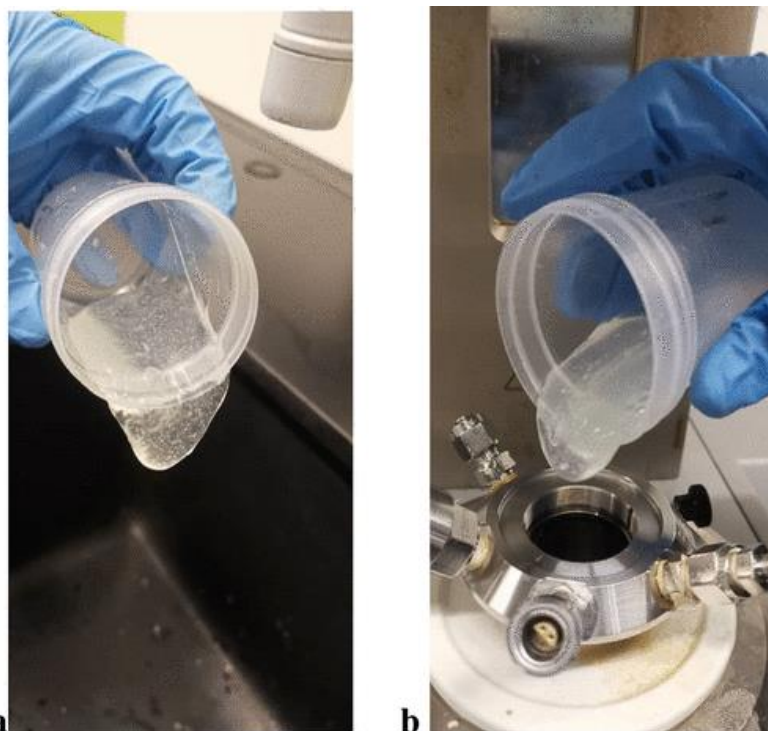


Figure 48 (a) DI-based crosslinked gel after heating to 120 °C, (b) SW-based crosslinked gel before heating.

6.4.2 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 49. 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.

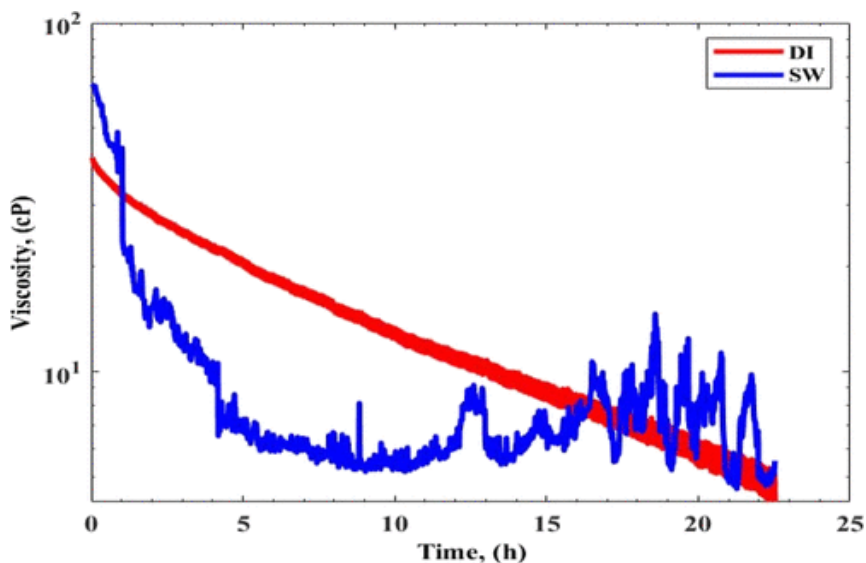


Figure 49 Rheology of 0.6 wt % XLFC-3B polymer hydrated in DI and SW at 120 °C, 100 1/s, and 500 psi.

Figure 48 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 49 and 50). Except for viscosity magnitude, the SW-based fluid behaved identically with and without the crosslinker. The crosslinker influenced the viscosity values of the SW, but not on the shape of the curve, as was the case with DI water.

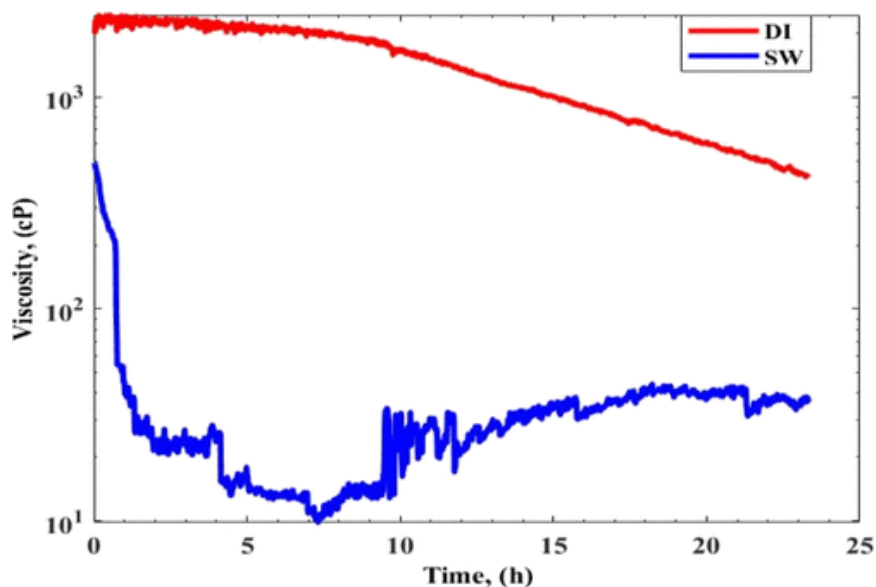


Figure 50 Rheology of 0.6 wt % XLFC-3B polymer hydrated then crosslinked in DI and SW at 120 °C, 100 1/s, and 500 psi.

6.4.3 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 50 shows the viscosity 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.

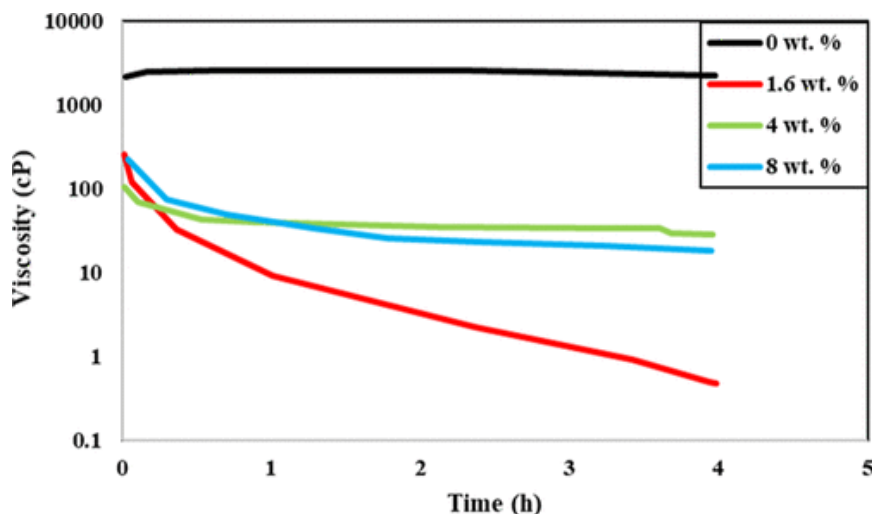


Figure 51 Rheology of 0.6 wt % XLFC-3B polymer, 1 wt % Zr in DIbased fluid, GLDA concentrations added after hydration at 120 °C, 100 1/s, and 500 psi.

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 Ca^{2+} , 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.

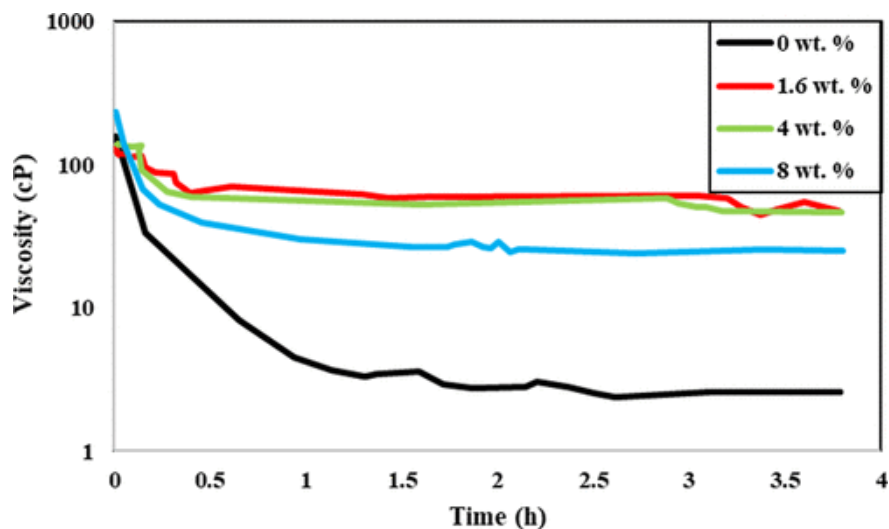


Figure 52 Rheology of 0.6 wt % XLFC-3B polymer, 1 wt % Zr in SW-based fluid, and GLDA added after hydration at 120 °C, 100 1/s, and 500 psi.

Figure 52 shows the viscosity of the three SW-based fluids compared with crosslinked polymer in SW without a chelating agent. Figure 53 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 51. 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 % GLDA. The GLDA did not interfere with the crosslinking process as it chelates the divalent cations in SW such as Ca^{++} . Because of that, adding chelating proved to be a viable option in SW as compared to DI-based fracturing fluid.

Figure 53 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 53. 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.

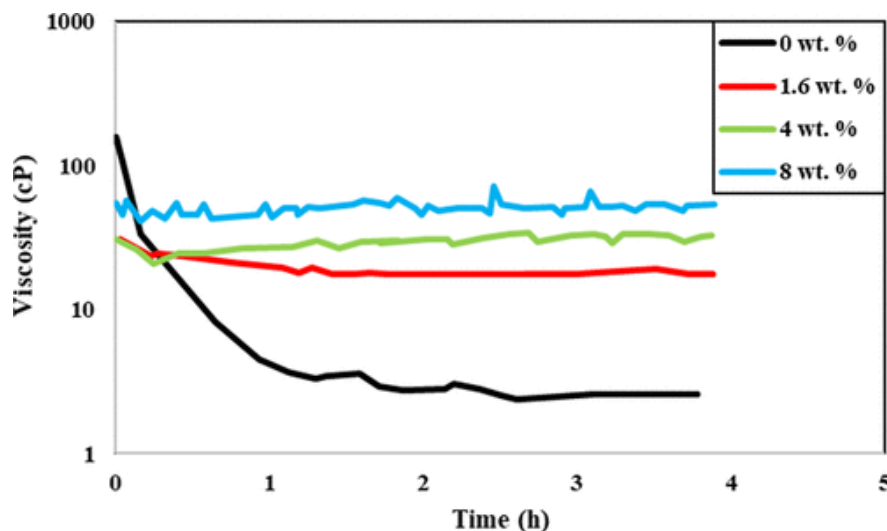


Figure 53 Rheology of 0.6 wt % XLFC-3B polymer, 1 wt % Zr in SW-based fluid, and GLDA added before hydration at 120 °C, 100 1/ s, and 500 psi.

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 52. 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 52 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.

6.4.4 Ramped Temperature Impact

The fluid system composition is similar in this set of experiments compared to 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 54 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 51 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 55 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 48.

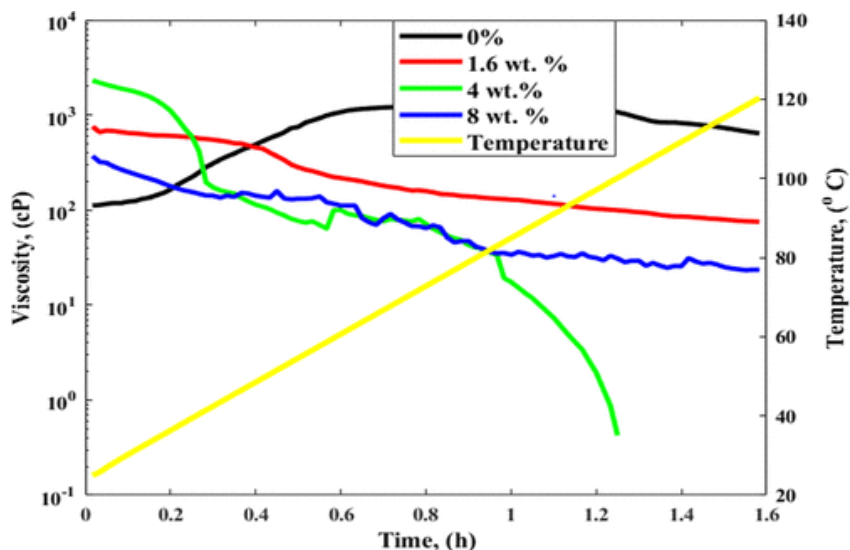


Figure 54 Rheology of 0.6 wt % XLFC-3B, 1 wt % Zr in DI-based fluid, and GLDA concentrations at ramped temperature (25–120 °C), 100 1/s, and 500 psi.

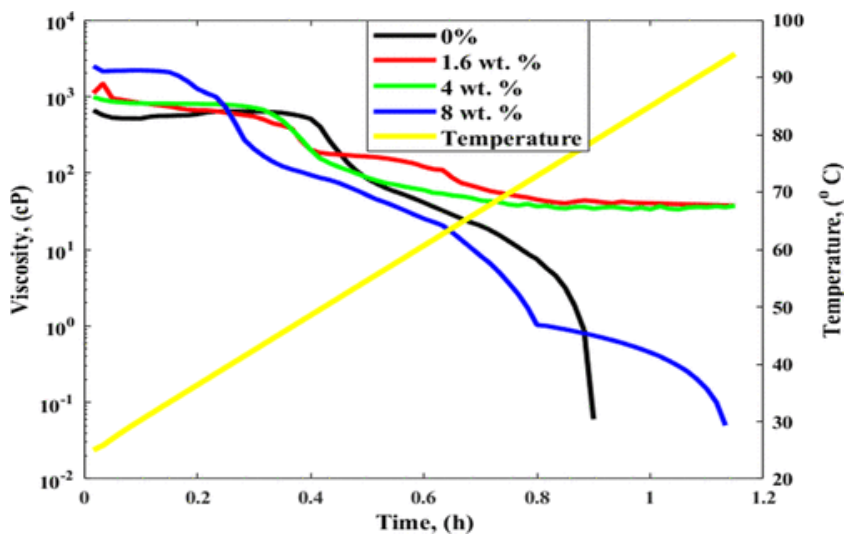


Figure 55 Rheology of 0.6 wt % XLFC-3B, 1 wt % Zr in SW-based fluid, and GLDA concentrations at ramped temperature (25–90 °C), 100 1/s, and 500 psi.

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.

6.5 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 SWbased 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.

CHAPTER 7

A Study of Crosslinked Gel and Chelating Agent Compatibility in High Salinity Environments¹

7.1 Abstract

The utilization of high-salinity water in hydraulic fracturing is recommended to promote a sustainable process. However, the high concentration of total dissolved solids (TDS) in seawater and produced water results in scales within the formation and affects the fracturing fluid viscosity. Chelating agents prevent scaling, due to the interaction between the formation water and the saline fracturing fluids. This research tests the scaling tendency when saline water and formation water are mixed in a high-salinity environment. It also highlights the incompatibility issues appears between some crosslinked-gels and chelating agents, and offers a solution to these issues. Five crosslinked-gels prepared with crosslinkers obtained from different companies were examined: three zirconium-based crosslinked-gels, one zirconium-borate, and one borate crosslinker. Four types of low pH GLDA and DTPA, and high-pH GLDA and DTPA chelating agents were tested in this study. We utilized the differential scale loop (DSL 4025) to evaluate the effect of these chelating agents with 67,000 ppm TDS-produced water and 241,000 ppm TDS-formation water. Employing Anton Paar-MCR 302 rheometer, simple rheology tests were used to quantify the impact of chelating agents in the crosslinked gel viscosity.

¹ This chapter is copied from the manuscript: **Othman, A.**, Aljawad, M. S., Kamal, M. S., Mahmoud, M., Sultan, S. A., & Kalgaonkar, R. A. (2023). A Study of Crosslinked Gel and Chelating Agent Compatibility in High Salinity Environments. Energy & Fuels

Low concentrations of DTPA chelating agent, prevented scale formation, and showed the best performance in capturing ions on ICP measurements. Simultaneously, when the 0.1 wt. % DTPA added to a 1 wt. % zirconium-borate crosslinked fracturing fluid, the viscosity exceeded 2000 cP. The DTPA is compatible with crosslinked-gels in high salinity environments, and exhibits low scale and stable viscosity values. The better combinations and concentrations of the fracturing fluids was suggested following the the comparison of the highest viscosity, lowest conductivity, and the lowest detected scale.

7.2 Introduction

The oil and gas industry employs hydraulic fracturing to extract hydrocarbons from tight rock formations. It involves pumping water, sand, and chemicals into the rock at high pressure, creating hydraulic fractures that help hydrocarbon extraction. The fracturing fluids aim to generate wide and long fractures with minimal fluid loss while carrying proppants at low settling velocity. This operation should create a fracture that remains open under closure stress to help achieve these goals.

Formation type, freshwater availability, selected additives, proppant type, and injection rate influence the fracturing process (Economides & Nolte, 2000). During design, optimizing fracturing fluid viscosity is crucial. Once proppants are placed, the fluid viscosity should decrease to the minimal during flow back (Montgomery, 2013; Samuel et al., 2000). Fracturing fluids are categorized as water-based, oil-based, alcohol-based, or foam-based. The category choice depends on the formation type, government/environment regulations, budget, and freshwater water availability. Water-based fluids, including crosslinked gel, slick-water, and viscoelastic surfactant, are commonly used (Almubarak et al., 2016). Water consumption in heavy hydraulic fracturing can reach 3 million gallons

in conventional formations and over 13 million gallons in unconventional formations (Harris & van Batenburg, 1999).

Governments and organizations are concerned regarding freshwater scarcity, while companies are concerned about the high cost of transporting freshwater to offshore locations or the treatment of produced water. These reasons led the development of freshwaterless fracturing fluid either by utilizing seawater, produced, and sewage water (Gupta et al., 2018). Utilizing saline water (SW) raises concerns due to the detrimental effects of ions (e.g., calcium, carbonate, sulfate) on reservoir permeability, retained fracture conductivity, and the stability of fracturing fluids. Interactions of injected formation water can lead to precipitation, scaling, corrosion, and delay in hydration, resulting in reduced viscosity and stability of the fracturing fluid. These saline waters can be a sustainable alternative to freshwater if some additives are used. For example, the chelating agents were developed to reduce the salinity impact of SW and are supposedly compatible with the fracturing fluid chemicals (Hassan et al., 2020).

The presence of Ca^{2+} and Mg^{2+} ions in SW decreases viscosity by negatively affecting hydration. These ions can also impede the effectiveness of certain additives, such as pH buffers and breakers (Hassan et al., 2020). Besides this reduction, the ions such as Ca^{2+} and Mg^{2+} precipitates and form scales at pH higher than 10 including sulfides such as pyrrhotite, sulfates such as ferrous gypsum, and carbonates such as calcite (Li et al., 2016). The pH can be adjusted by pH buffers and scale can be removed by scale inhibitors. It is crucial to carefully monitor the thermal stability of SW-based fluids as maintaining stability at high temperatures often requires high pH environments (Alohaly et al., 2016; Cheng et al., 2002; Prakash et al., 2016). The presence of divalent cations determines the total hardness of SW.

Solutions containing only monovalent KCl can have low hardness despite high total dissolved solids (TDS). The SW typically contains monovalent and divalent cations, increasing hardness with higher TDS. The total hardness in SW is calculated based on the concentrations of calcium (Ca^{2+}) and magnesium (Mg^{2+}), which are used to quantify the equivalent of calcium carbonate (CaCO_3), as shown in equation (Prakash et al., 2016).

$$\text{Total hardness (ppm as CaCO}_3\text{)} = 2.5[\text{Ca}^{2+}] + 4.1 [\text{Mg}^{2+}] \quad 7.1$$

Using SW to design fracturing fluid can damage the formation and reduce the proppant transport efficiency. The SW-based fracturing fluid's design should consider the proppant's transport with minimal settling velocity while minimizing fluid loss and formation damage in reservoir conditions. Typical fracturing fluids contain various chemicals, including gelling agents, crosslinkers, biocides, chelating agents, buffers, clay stabilizers, and more (Almubarak et al., 2019). Gelling agents are crucial additives for achieving desired outcomes. Guar, a high molecular weight polymer with intermolecular hydrogen bonding, is a widely preferred gelling agent as it raises the viscosity to suspend proppant and improve leak-off properties. Guar gum's purity and isolation method govern the insoluble residue, typically 10-14%. Such residues can impede fracturing efficiency by obstructing flow within fractures. The commonly used guar derivative in the oil industry is HPG (hydroxypropyl). At the same time, the preferred choice is CMHPG (carboxymethyl hydroxypropyl guar) due to the fast hydration and minimal (Abdul Majid et al., 2017; Harris, 1988). CMHPG polymer undergoes a hydration process that transitions from a compacted to an extended-relaxed state upon water absorption. It is preferred in fracturing fluids due to its faster hydration, greater stability at low pH, and longer degradation time than other polymers (Cheng et al., 2002; Fink, 2021; Wilson, 2017).

In operations, linear gels, formed using gelling agents, act as low-viscosity pre-pads to cool down the formation and initiate fractures. The gelling agents can be crosslinked with specific groups and play a role in maintaining open fractures after proppant placement (Barati & Liang, 2014). A higher viscosity fluid is required to exert greater pressure for fracture propagation. Adding a crosslinker enables the attainment of this elevated viscosity. When added to lower concentrations of guar derivatives, the crosslinker increases viscosity by one or more orders of magnitude. However, the highly viscous fluid can cause formation damage. The crosslinker also improves the fluid's elasticity, transforming its behavior from viscous to viscoelastic. This viscoelastic property improves the fluid's ability to carry proppants. Crosslinkers typically consist of potassium hydroxide (KOH), phosphate esters, isopropanol ($(\text{CH}_3)_2\text{CHOH}$), and various metals such as titanium, aluminum, and antimony; the most commonly used crosslinkers are borate and zirconium. Borates act as instant crosslinkers, maintaining stable viscosity at high temperatures and forming borate-crosslinked guar derivative salts. Delayed zirconium crosslinkers are employed in fracturing operations to efficiently transport proppants with minimal power requirements (Abdul Majid et al., 2017; Almubarak et al., 2020; Barati & Liang, 2014; Gupta et al., 2018; Kamal et al., 2018).

Chelating agents find applications in the industry as breakers, acids, and biocides; these chelating agents are compatible with SW. They possess various functions, such as increasing thermal stability, reducing surface tension, controlling ions, regulating pH, and acting as clay stabilizers. Commonly used chelating agents in the oil industry include ethylenediaminetetraacetic acid (EDTA), ethanolic phosphotungstic acid (EPTA), diethylenetriamine pentaacetate (DTPA), and L-glutamic acid-N, N-diacetic acid (GLDA).

GLDA remains stable at elevated temperatures up to 149°C and exhibits different ion reactions with changes in pH; however, it exhibits instability with crosslinked-gels. DTPA is the most stable chelating agent with high salinity fluids. Chelating agents enhance the SW fracturing fluids' performance in fracturing operations by capturing ions and reducing water hardness. It is important to control the concentrations of chelating agents to avoid potential interference with the crosslinking mechanism (Harris & van Batenburg, 1999; LePage et al., 2009; Li et al., 2016; Mahmoud & Abdelgawad, 2015; Othman, Aljawad, et al., 2022).

Chelating agents encompass a variety of distinct functional groups, including carboxyl, amine, ether, nitro, and hydroxyl. These functional groups possess the capability to bind tightly or chelate ions on surfaces, resulting in the formation of robust complexes. Thus, the crosslinkers contain ions can be attacked by the excess chelating agents. Notably, the carboxyl group stands out as the most proficient in creating highly stable compounds. The strength of chelation relies on the distribution of ionic species, primarily influenced by stability constants and solution pH. Augmenting the chelation strength enhances the stability of the complex compounds generated through the sequestration of metal ions by chelating agents. Chelation aptitude is defined by the stability constant, representing the ratio of chelated metal ions in equilibrium with free metal ions and chelating agents in the solution. This stability constant dictates the fluid's stability. When stability constants exceed a value of 8, they are categorized as resilient chelates. DTPA boasts the highest stability constants, followed by EDTA. The pH exerts a significant influence on the reaction rate, with an increase in pH correlating with an acceleration in the reaction rate⁸.

To enhance the polymer's molecular weight, crosslinkers are employed, a process that transforms the polymer backbone into a three-dimensional configuration. This results in a substantial elevation of the initial viscosity of the linear gel, escalating it from below 50 cP to a range in the hundreds or thousands. Moreover, this crosslinking augments the elasticity and the capacity to transport proppants within the fluid. In the case of gels derived from guar and CMHEC, crosslinkers such as Boron, Titanium, and Zirconium are utilized. It's worth noting that Iron, Chromium, and Aluminum can also facilitate crosslinking in guar-based gels, although they are not frequently employed. Each crosslinking agent comes with its distinctive set of prerequisites and behaviors. Borate and various metal ions are employed to establish connections within the linear material, requiring an elevated pH level of 7.5. This process leads to the formation of a dynamic ionic bond, in which the borate ion links cis-diols on the galactose molecule. In contrast, the crosslinking with metal ions takes place over a broader spectrum of pH levels, depending on the specific ion utilized. Gels that undergo crosslinking with zirconate exhibit a higher tolerance for elevated downhole temperatures compared to those crosslinked with borate. When metal crosslinked guar forms a chemical gel, the network of bonds is susceptible to disruption through shearing, and these gels do not undergo complete restoration. Temperature and pH exert an accelerating effect on the crosslinking reaction, whereas the introduction of organic molecules, known as ligands, can introduce delays (Gaurina-Međimurec et al., 2021).

The research highlights the interactions of chelating agents with zirconium and borate crosslinked gel in high-salinity systems. We aim to find the better compatible variation represented by high viscosity and stable performance. The resulting formulation should

work perfectly in different environments with multiple salinities, normal and harsh conditions. Different chelating agents' chelation capability was first measured using the differential scale loop and conductivity measurements. The inductive coupled plasma (ICP) was used to test the chelating agents' capabilities. Then, the viscosity of each fluid combination was measured and the optimum formulation was proposed.

7.3 Methodology

7.3.1 Materials

The materials used in the study are SW with 67,000 TDS, XLFC-3B CMHPG polymer, zirconium crosslinker, borate crosslinker, dual zirconium-borate crosslinker, high and low pH GLDA, high pH EDTA, and low pH DTPA. The equipment used to gain the results was a differential scale loop (DSC 4025), inductive coupled plasma (ICP), pH and conductivity meter, and Anton Paar-MCR 302 rheometer to measure the viscosity of the variations. The better performance gelling agent, CMHPG, was suggested as it has faster hydration and better stability; it was utilized in these experiments because it resulted in higher viscosity when hydrated with DI and SW (U.S. Environmental Protection Agency, 2012). The study uses three types of crosslinkers: the metallic zirconium delayed crosslinker, borate instant crosslinkers, and dual zirconium-borate crosslinkers. The metallic crosslinkers polymerize into oxide nanoparticles and then bond with polymer with hydrogen bonds where viscosity fluid is achieved. However, these bonds cannot re-heal; therefore, the release of metallic crosslinker should be regulated using suitable ligands. The zirconium crosslinker usually consists of three ligands: lactate ligand, Propylene Glycol, and Triethanolamine (Kamal et al., 2018). We used the liquid zirconium crosslinker as

received from the company; the active content was assumed to be 14% for calculation purposes.

A high and low pH GLDA chelating agent (N, N-Dicarboxymethyl glutamic acid) was used in the study. We measured the pH of the high pH GLDA, and it was around 13.7 pH, while the lower one was 4; notice that both have active contents of 40%; as mentioned in the material safety data sheet (MSDS). The high pH GLDA-Na₄ was specially designed for CaSO₄ scale dissolution. Adding GLDA adjusted the solution's pH from 7.5 (of SW and polymer) to 10.5 in the case of 4% GLDA. Both high pH EDTA and low pH DTPA were prepared in the lab by raising the pH of DI using KOH and then slowly adding the powder chemical. The active content of these fluids was only 4%; however, they both have better chelation ability compared to GLDA. Therefore, in rheology tests we decided to compare similar volumes from these liquids of 40% active GLDA, and 4% active (DTPA, &EDTA). In the scale loop, we compared the performance of 0.1 wt.%, 0.4 wt.% and 1 wt. % chelating agents.

7.3.2 Procedures

The scale tests are measurement of differential pressure in the scale loop lines; the higher the value, the higher the formed scale. To measure the performance of the chelating agents, they were added at different concentrations and compared to each other through the recorded differential pressure. The SW and formation water (FW) are mixed at 70 °C and 120-170 psi at a flow rate of 20 cc/min at 10 psi differential pressure limit condition to form the scale. Similar chelating agent concentrations added to SW and the degree of chelation was measured with ICP. Then, a fluid system of SW-based crosslinked polymer and chelating agent combinations was subjected to conductivity measurements. After the

fluid scaling analysis, the rheology of the proposed fracturing fluids was measured. The optimum concentration of the zirconium crosslinker (1 wt. %) was selected in a similar study 23. We selected 4 wt. % GLDA, 0.4 wt. % DTPA and EDTA (similar volumes, different active content) and measured their impact on the viscosity of the SW fracturing fluid. All experiments fixed the testing conditions at 70 °C temperature, 500 psi, and 100 1/s shear rate. Figure 56 is a schematic plot of the scale loop showing the details of the equipment and the process. The first and second pumps are used to pump the PW and FW, and the freshwater in the cleaning step. While the third pump is used to pump the scale inhibitor and the citric acid in the cleaning step.

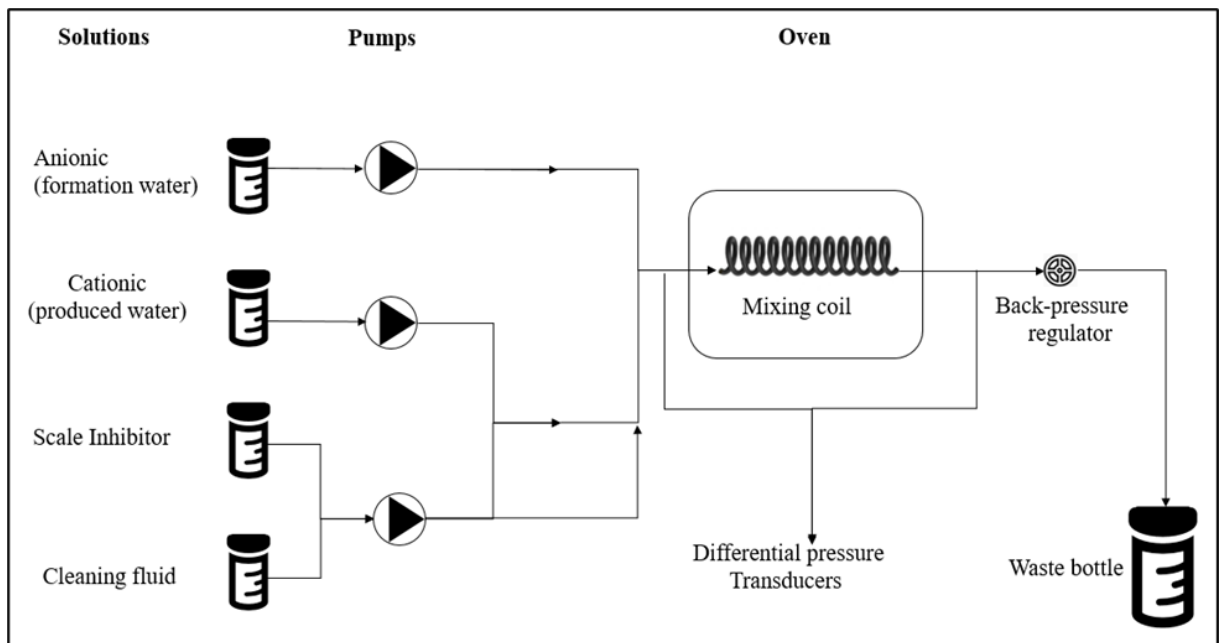


Figure 56 Ligands structure used with Zr crosslinker.

7.3.3 Experimental Design

7.3.3.1 Design of the Scale Loop Experiments

The scale experiments in the DSL were performed in 5 steps as shown in Table 1: waiting transient period before reaching steady state, prescale, cleaning, scale, and cleaning again.

The prescale means the mixture of SW and FW, while the scale represents the mixture of SW, FW, and the scale inhibitor (chelating agent). The control of the volume of the chelating agent pumped with the mixture of SW and FW is possible through the concentration change in the program and the flow rate of each fluid. The results are evaluated through the peak of the differential pressure and the duration before cleaning starts. Once the pressure limit is reached, the cleaning starts. Table 20 is a program summary of the schedule and procedure used in the scale loop experiments, while Table 21 is full cleaning schedule after each experiment.

Table 20 Summary of the Performed Experiments

Step	Fluid	Inhibitor concentration (ppm)	Differential pressure (psi)	Flow (cc/min)	Duration (hh:mm)	P1	P2	P3
Wait to reach targeted T	-	0	0.6	8	00:30	4	4	0
Prescale	PW+FW	0	10	20	00:40	10	10	0
Cleaning	Water	100	10	6	00:45	2	1.9	2.1
Scale	PW+ Inh.+ FW	10000 (1% EDTA)	10	20	00:40	10	5	5
Cleaning	Steps in Table 20	100	10	0	00:45	2	1.9	2.1

Table 21 Cleaning schedule

Solution	Duration (hh:mm)	P1 flow	P2 flow	P3 flow

Citric acid 0.1 m	00:15	0	0	5
Citric acid 0.1 m	00:01	0	0	3
Water	00:20	4	4	0
Citric acid 0.1 m	00:05	0	0	5
Water	00:05	8	0	0

7.3.3.2 Design of the Viscosity Experiments

Fifteen viscosity measurements were performed in the study, in which 0.6 wt. % of CMHPG polymer was stirred in 21 ml solution for 45 minutes at 500 rpm. Then, the 4 wt. % GLDA or 0.4 wt. % of either EDTA or DTPA were stirred for 5 minutes followed by adding 1 wt. % of Zr, or ZrBr crosslinker and mixed for less than 5 minutes. The results are expressed by comparing crosslinked gel comparison results to pure SW. Also, the better variation of zirconium and chelation was compared to two selected crosslinked-gels, either to zirconium or zirconium borate crosslinker. Table 22 shows the testing parameters and experiments performed in the research.

Table 22 Summary of the experiments and their conditions

Solution type	Polymer (wt %)	Crosslinker concentration (wt %)	Chelating agent (wt %)	Chelating agent type	Number of experiments
SW- Zr, Br, & ZrBr crosslinkers	0.6	1	-	-	6

SW- Zr crosslinkers & chelating agents	0.6	1	0.4, 4	High pH GLDA High pH EDTA Low pH GLDA Low pH DTPA	5
SW- ZrBr crosslinkers & chelating agents	0.6	1	4, 10	High pH GLDA Low pH GLDA Low pH DTPA	5

7.4 Results and Discussion

7.4.1 Scale Formation Prevention

7.4.1.1 Differential Scale Loop Measurements

The prescale is named in the scale loop for part of the experiment in which the SW and FW are mixed at certain conditions. In our experiments, a specific pressure limit was set to detect the scale, which was 10 psi. This test was performed alongside the scale test each time. We performed 12 experiments in the scale loop where the prescale and scale readings are shown in each. Figure 57 shows the quality of the results from the scale loop for selected 8 prescales, as this curve is the same (SW+FW) for all experiments at similar conditions of 70 °C and 120-170 psi. It can be noticed that, up to 8 psi, the prescale formation goes fast, then rises until it reaches 10; this behavior was repeated in all experiments. From Figure 57, for all scale experiments one fixed prescale is needed. The average for these 8 experiments is represented in the figure. The scale loop's threshold is 3.5 psi, below which the readings are not considered scale.

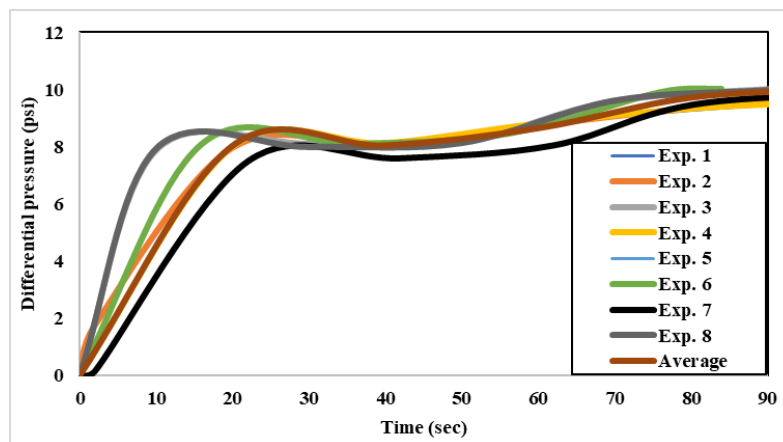


Figure 57 Prescale shows the scale formed from FW and SW at 70 °C and 120-170 psi.

The average prescale (FW+SW) curve was selected and plotted in Figures 58, 59, and 60 to compare it with the chelating agents with concentrations of 0.1 wt. %, 0.4 wt. % and 1 wt. %, respectively. Figure 58 represents 0.1 wt. % chelating agent (GLDA, DTPA, and EDTA) mixed with SW to capture the ion and then with the FW. This procedure mimics the fluid pumped to the formation as the chelating agent is added to SW before being sent to the formation. We are comparing the behavior of the chelating ions at the same time window. The scale formation at 0.1 wt. % chelating agent concentration was less than 4 psi in the case of EDTA, meaning no scale was formed. In the case of GLDA, the scale was formed, and its behavior was not similar to the standard behavior of the pre-scale. The DTPA showed similar behavior to the pre-scale curve, but the scale was slightly less and did not reach the threshold of 10 psi at the designed time.

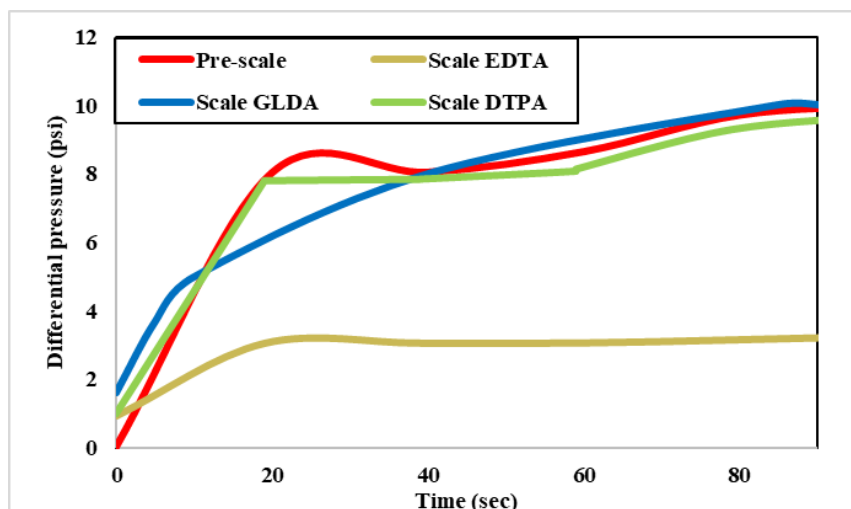


Figure 58 Scale formed from FW and SW + 0.1 wt. % chelating agent at 70 °C, and 120-170 psi.

The same pre-scale test was shown in Figure 59 to show the effect 0.4 wt. % chelating agents' concentration. This concentration of chelating agent had a clearer impact on the scale formation and behavior. The EDTA was confirmed to remove the scales with a minimum concentration, which aligned with the previous results. The DTPA behavior improved at higher concentration; with a scale curve shape similar to the pre-scale as the pressure drop was reduced to less than 5 psi, showing its ability to remove the scale. The GLDA performance at higher concentration (0.4wt%) is better than at low concentration; however, scales presence is obvious from the high pressure drop data.

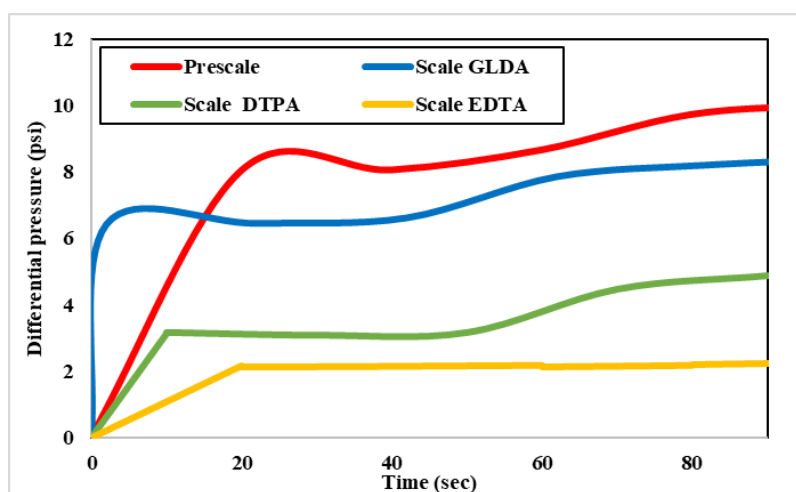


Figure 59 Scale formed from FW and SW + 0.4 wt. % chelating agent at 70 °C, and 140 psi.

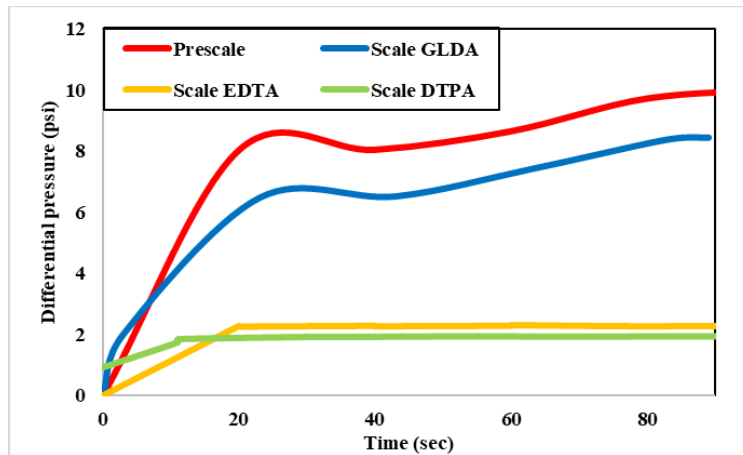


Figure 60 Scale formed from FW and SW+ 1 wt. % chelating agent at 70 °C, and 140 psi.

Figure 60 shows the results of 1 wt. % chelating agents with SW and FW. The DTPA at higher concentrations outperformed the EDTA; however, they both removed the scale efficiently. The GLDA performance improved as it took longer to reach the 6 psi threshold, and could barely reach 8 threshold within the designed time window. We can conclude that at 70 °C and 120-170 psi, the EDTA has the best performance with scale removal, while more GLDA concentration is needed to perform a similar job.

74.1.2 Conductivity measurements

Conductivity is a gauge of how easily the electrical current passes through a substance (water, in our case). Certain dissolved inorganic ions affect conductivity, including chloride, sulfate, phosphate (negatively charged), sodium, magnesium, and calcium (positively charged). Furthermore, temperature plays a role in conductivity, with higher water temperatures corresponding to increased conductivity; therefore, it is measured at the standard conditions (Barnes, 1995). The chelating agents are anticipated to capture the ions but have different performances. Measuring their conductivity is another way to track their performance.

Table 23 pH and conductivity of the individual fluids

Fluid	pH	Conductivity Uc/ms
DI	7	1.7
SW	7.9	72538
Zr2 crosslinkers	9.55	67886
GLDA	13.9	11865

Besides the scale loop experiments, the conductivity measurement is another approach to give a general overview of the ability of chelating agents to chelate cations. The GLDA was selected as it had the worst performance with the scale loop. We wanted to ensure that it could capture the cations in high concentrations. Table 23 shows the conductivity and the pH for the selected crosslinker, GLDA, SW, and deionized water (DI). Figure 61 shows the pH conductivity at different GLDA and zirconium concentrations. From the figure it can be noted that as the GLDA concentration increase the fluid pH increase and the conductivity decrease.

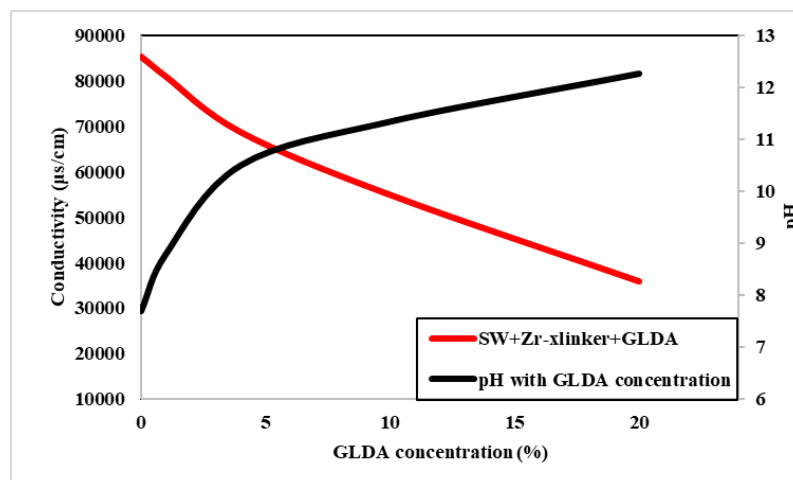


Figure 61 Conductivity and pH measurement with different GLDA concentrations

7.4.1.3 ICP scale detection

The GLDA did not give the results needed on the scale loop and it was a need to confirm the results with different tool. Different concentrations of chelating agents were added to SW and evaluated with ICP at 1000 times dilution. Figure 62 shows the calcium and magnesium concentration in ppm before (SW) and after adding the specific chelating agent. It can be noted that the higher the concentration, the higher the chelation ability. The DTPA outperformed the other chelating agents, showing less TDS of calcium and magnesium than the other chelating agents, even when compared to the higher concentration GLDA.

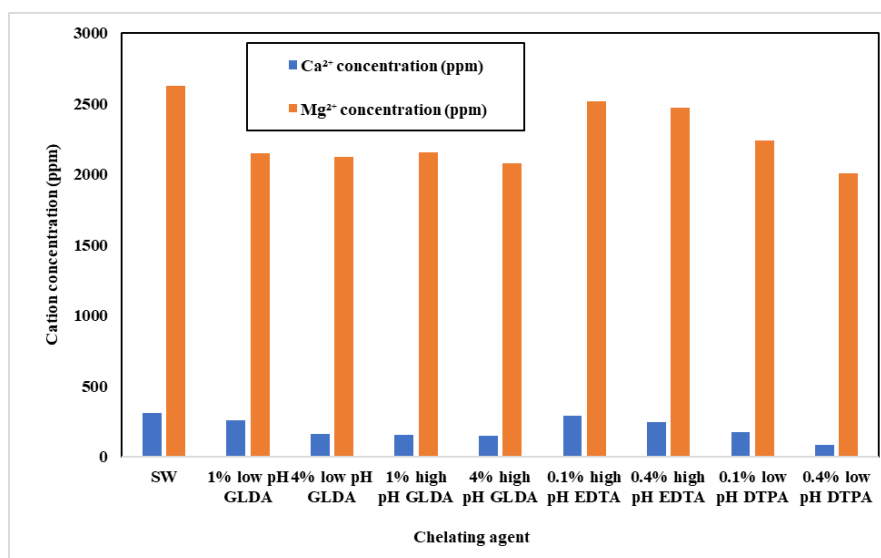


Figure 62 ICP measurement in ppm for different chelating agents

7.4.2 Impacts of crosslinker type on the viscosity

This part of the results discusses different crosslinked-gels compared to the non-crosslinked fracturing fluid. Figure 62 gives the viscosity details of 5 different crosslinked-gels, three of which are zirconium crosslinked-gels (Zr1, Zr2, and Zr3), and the rest are dual crosslinker (ZrBr) and a borate crosslinker (Br). All these fluids are comprised of 0.6 wt. % polymers and 1 wt. % crosslinker in 67,700 TDS saline water. The rheology tests were performed at 70 °C and 500 psi. From Figure 63, we can note that most crosslinked-gels start at very high viscosity values, reaching these viscosities when no chelation is used. The viscosity of most crosslinked-gels remains stable with time. The viscosities rapidly fall in Zr1 crosslinked gel because of the slippage effect²⁵. An example is noted with the crosslinked fluid Zr1. Two crosslinked-fluids (Zr2 and ZrBr) in Figure 64,65 were subjected to different chelating agent types and concentrations for further experiments. Although the trend of the specific fluid was clear, the viscosity curves exhibited fluctuations. This behavior was noted through most of the viscosity experiments. At 70 °C and higher temperatures and with high salinity, the linear CMHPG polymer remains stable, and the borate crosslinkers yield more stable systems when compared to zirconium systems. However, when it comes to the addition of chelating agents to the system, they are not only capturing the cations, but they also attack the zirconium ions, and the behavior becomes considerably intricate. This behavior persists throughout all performed experiments, and in cases where the trend is unclear, data smoothing techniques were applied. In this research, we emphasize the instability issue arising from the interaction of crosslinkers and chelating agents; therefore, the fluctuations appear in the following figures.

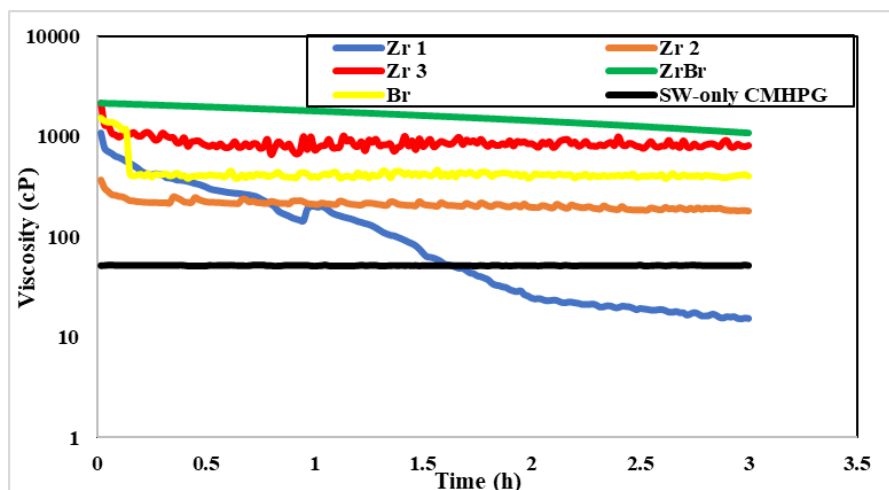


Figure 63 1 wt. % Zr and 0.6 wt % CMHPG hydrated in SW at 70 °C, 100 1/s, and 500 psi.

7.4.3 Impact of chelating agent type on the viscosity

Four chelating agents were used as part of four crosslinked gel system: high pH EDTA, high pH GLDA, low pH GLDA, and low pH DTPA. Similar volumes of different active contents were used. First, these combinations were tested with Zr2 crosslinker, widely used in the industry. Using similar volumes for different active contents results in different concentrations in wt. %. The concentrations used were 4 wt. % for GLDA and 0.4 wt. % for DTPA and EDTA. Figure 64 shows the base line result was the Zr curve, zirconium crosslinker with no chelation, in which the viscosity decreases slowly from 300 to 200 cP. Both 0.4 wt. % high pH EDTA and 4 wt. % high pH GLDA resulted in very low viscosities after 3 hours. Both low pH GLDA and DTPA chelating agents performed better than the high pH. Comparing the viscosity 0.4 wt. % low pH DTPA was better than 4 wt. % low pH GLDA. It was found that the viscosity of the SW-based crosslinked fluid rises with time when low the pH DTPA is added to crosslinked gel system. This behavior can reduce the pumping power, energy consumption, and drag force. The chelating agents exhibit varying effects on the viscosity of saline water-based fluids. In the figure, we note that all types and concentrations of the chelating agents reduce the viscosity when compared to the

crosslinked polymer without chelating agents. When considering the polymer-chelating agent system under standard conditions, the GLDA chelating agent slightly increased the viscosity. However, this was not the case when the system was complicated: higher pH chelating agents, the addition of metal crosslinkers, and elevated temperatures.

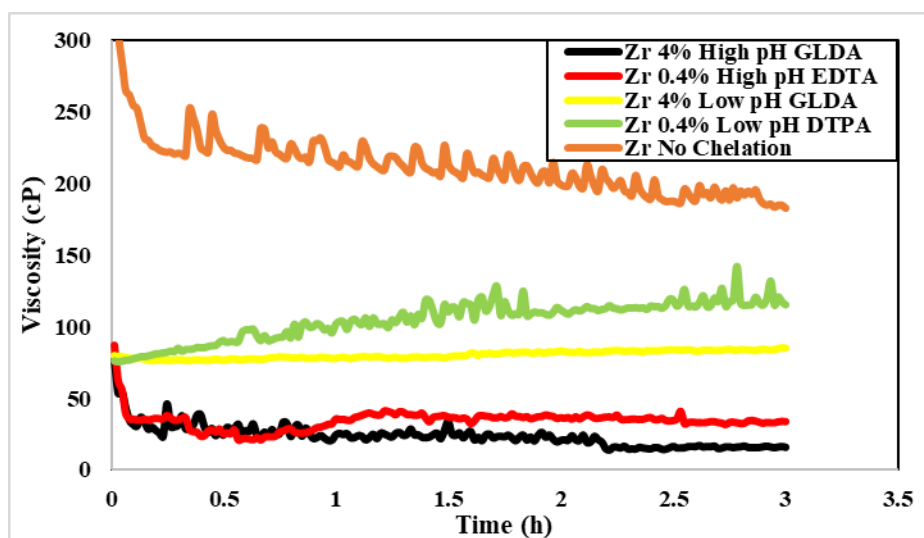


Figure 64 1 wt. % Zr and 0.6 wt % CMHPG hydrated in SW and different chelating agents at 70 °C, 100 1/s, and 500 psi.

However, in high salinity systems with polymer, zirconium crosslinkers, and chelating agents at elevated temperatures, compatibility issues were encountered. It became evident that GLDA not only interacted with the ions in saline water but also affected the metal crosslinkers. Hence, we explored the other chelating agents and borate crosslinkers on these conditions to find the chelating agent with the least effect on the crosslinked system.

Figure 65 discusses the Zirconium borate (ZrBr) along with 0.4, 0.4, and 4 wt. % concentrations of EDTA, DTPA, and GLDA, respectively. The baseline result was the zirconium-borate dual crosslinker with no chelation. Three chelating agents were used: high pH GLDA, low pH GLDA, and low pH DTPA. The chelating agents have affected the dual crosslinker ZrBr more than the zirconium crosslinker. It reduced the viscosity by

one order of magnitude in the case of low pH GLDA and two orders of magnitude in the case of high pH GLDA. However, the 0.4 wt. % low pH DTPA outperformed the GLDA fluids and reduced the viscosity by reasonable values. Figures 63 and 64 shows that adding a chelating agent reduces the viscosity of the fracturing fluid and its capability to transport the proppant. In both crosslinked-gels, the low-pH chelating agents performed better than high-pH chelating agents. The DTPA with lower concentration outperformed the higher concentration of both GLDA types. These findings can be applied to both types of crosslinkers. The reaction rate of the chelating agent with ions is influenced by the pH, and in the case of high pH GLDA, we observe a notably rapid reaction rate, which is evident in the figure where the instability is depicted. The DTPA crosslinked gelled system can provide high viscosity for proppant transport at the same time prevent any scaling, which is a major challenge resolved in this research.

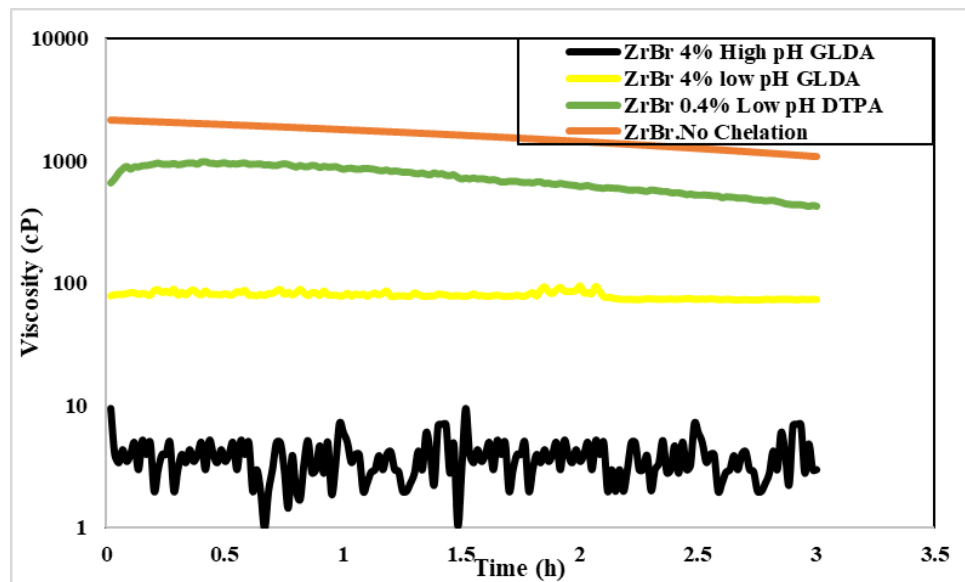


Figure 65 1 wt. % ZrBr and 0.6 wt % CMHPG hydrated in SW and different chelating agents at 70 °C, 100 1/s, and 500 psi.

7.5 Conclusions

The study investigates the challenges arising from the incompatibility observed between zirconium and zirconium borate crosslinked fluids with some chelating agent. The research performed scaling, conductivity, cation capturing, and rheology measurements to evaluate the fracturing fluid combinations. The scale measurements were performed with PW and FW mixtures with specific chelating agent concentrations. The outcomes of the study are summarized in the following points:

1. With scale loop evaluation, the high pH EDTA outperformed the other chelating agent in scale inhibition, then the low pH DTPA, and then the high pH GLDA.
2. As the GLDA concentration increases, the fluid pH increase, and the conductivity decrease.
3. The low pH DTPA performed better than pH EDTA and high pH GLDA.in ion capturing evaluated by ICP.
4. Some crosslinked fluids exhibit a sudden reduction in viscosity when measured with a rheometer, and this behavior has no effect on viscosity and is known as the slippage effect.
5. High pH GLDA reduces the viscosity of the crosslinked fracturing fluid and can be used as a breaker for these types of fluids.
6. The use of low concentrations of pH DTPA with zirconium and zirconium borate resulted in high viscosity crosslinked fluid.
7. The borate crosslinkers are more stable with the chelating agents than the zirconium crosslinkers.
8. The high pH GLDA is not suitable for high salinity environments at high temperatures.

CHAPTER 8

Analytical Techniques

8.1 Thermal Analysis

8.1.1 Introduction

Thermal analytical methods can be used to study solid-state kinetics, measuring the properties of a sample while heating or at constant temperature. These methods are thermogravimetry (TGA), which is used when the sample loses weight; differential scanning calorimetry (DSC), which studies heat consumed or evolved; powder x-ray diffraction (PXRD); and nuclear magnetic resonance (NMR). With the help of this equipment, we should convert the measured parameter into α to use the available thermal models. The solid-state models are used for homogeneous reactions, which deal with solutions and gases where the rate of reaction depends on the reaction order. Heterogeneous is called solid reaction and deals with particle size, interface advance, and geometric shape. One of the heterogeneous models is degradation, which depends on mechanistic assumptions. Mechanistic assumptions are used to categorize the solid-state models. These assumptions are the rate of nuclei formation, interface, diffusion, and geometrical shape.

The other methods to categorize the solid-state models are the shape methods. When it is difficult to follow the reaction steps experimentally, note these reaction forms: nucleation, diffusion, geometrical contraction, and reaction order. Nucleation describes hydration, adsorption, dissolution, crystallization, and decomposition and happens when there are impurities, surfaces, edges, dislocations, and cracks. The diffusion happens when the movement is restricted depending on the concentration. Geometrical contraction assumes that the reaction progresses toward the center of the crystal, which controls the rate of

degradation. At the same time, the reaction order assumes that the reaction rate is proportional to concentration (Khawam & Flanagan, 2006).

The graphical shape interpretation is based on the experiment's results, and the basic equations used for the interpretations are

$$g(\alpha) = Kt \quad 8.1$$

$$K = A e^{-\frac{E_a}{RT}} \quad 8.2$$

Where K : Rate constant, A : Exponential factor, E_a : Activation energy, R : Gas constant, T : Absolute temperature.

Ther model fitting is either isothermally or non-isothermally in which we fit the curves to find K , A , and E_a . There is also a model-free method where we find E_a in which we do not use mechanistic assumptions (Khawam & Flanagan, 2006).

8.1.2 Gelation (Crosslinking)

Previously, gelation kinetics was commonly studied using rheological measurements; however, the thermal methods explain the phenomenon in more detail. Crosslinking behavior, thickening, and thinning phenomena are under inspection in these analytical techniques. Crosslink bonds affect heat conduction because new bonds in polymers are introduced, and these bonds open new channels, which contribute to thermal conductivity. Differential scanning calorimetry DSC analytical technique can indicate crosslinking, and from that, the heat flow can be calculated, and then simple kinetic modeling can be applied (Kikugawa et al., 2013; Walha et al., 2016). The most used equation to model the gelation is the Avrami equation (equation 8.3)

$$\ln\{-\ln(1 - x_t)\} = \ln k_t + m \ln t \quad 8.3$$

Where x_t Is the fractional gelation, m is an exponent related to the order, t is the time during gelation, and k_t Represents the rate constant (Mohamed et al., 2015).

In thermal analysis, we target specific heat capacity. Specific heat capacity is the amount of energy in joules required to change 1 gram of a substance 1 °C. ($C_p = q/m \cdot \Delta T$). The Heat capacity is the property under inspection in the analysis, and it changes with the change in mass of the substance; as we increase the mass, the heat capacity will increase ($CH = q/\Delta T$). While it is more accurate to measure the specific heat capacity because it does not depend on the mass and will be constant for substances no matter what the mass was, we measured the weight of the samples before and after to eliminate this factor (Feidt, 2017). The thermal analyses were performed with high-temperature differential scanning calorimetry (HDSC). Differential scanning calorimetry (DSC) is the most common thermal analysis method due to the wide range of information it provides. A technique in which the difference in energy input into a substance and reference material is measured as a function of temperature, while the substance and reference material are subjected to a controlled temperature program. The LIN-SEIS high-temperature DSC PT1600 (HDSC/DTA) is designed to deliver the highest calorimetric sensitivity, short-time constants, and a condensation-free sample chamber (Linseis, 2020).

8.1.3 Example of Procedures

The tables and figures below show the key guidelines for analyzing the fluid thermally utilizing DSC. Table 24 shows heat versus time and temperature for one sample at 3 different heating rates, which were acquired from the DSC. Plotting these data shows the

behavior gained from these data, which is shown in Figure 66. We can note the behavior of the fluid, and as the heat increases with the increase of temperature, this indicates the gelation point for the fluid. We need to do some analysis of the data to find the model aligns with this fluid.

Table 24 Sample of heat versus time and temperature at 3 different heating rates

5 k/min			10 k/min			15 k/min		
Time	Temperature	Heat Flow	Time	Temperature	Heat Flow	Time	Temperature	Heat Flow
min	°C	W/g	min	°C	W/g	min	°C	W/g
18.82	140	0.1479	55.84	139.96	0.3175	81.17	139.98	0.4809
18.83	139.97	0.1479	55.84	139.91	0.3176	81.18	139.88	0.4811
18.84	139.94	0.148	55.85	139.85	0.3177	81.18	139.8	0.4812
18.84	139.9	0.148	55.85	139.8	0.3178	81.19	139.73	0.4813
18.85	139.88	0.1481	55.86	139.75	0.3179	81.2	139.63	0.4814
18.85	139.85	0.1481	55.87	139.68	0.318	81.2	139.53	0.4815
18.86	139.82	0.1482	55.87	139.61	0.318	81.21	139.46	0.4816
18.86	139.8	0.1482	55.88	139.56	0.3181	81.21	139.38	0.4817
18.87	139.77	0.1483	55.88	139.52	0.3182	81.22	139.28	0.4819
18.88	139.74	0.1483	55.89	139.45	0.3183	81.22	139.21	0.482
18.88	139.71	0.1484	55.89	139.4	0.3183	81.23	139.13	0.482
18.89	139.69	0.1484	55.9	139.35	0.3184	81.24	139.03	0.4821
18.89	139.65	0.1485	55.91	139.28	0.3185	81.24	138.94	0.4823
18.9	139.62	0.1486	55.91	139.23	0.3185	81.25	138.86	0.4824
18.9	139.6	0.1486	55.92	139.18	0.3186	81.25	138.79	0.4825
18.91	139.57	0.1487	55.92	139.12	0.3187	81.26	138.69	0.4826
18.92	139.54	0.1487	55.93	139.05	0.3188	81.26	138.61	0.4827
18.92	139.51	0.1488	55.93	139	0.3189	81.27	138.54	0.4828
18.93	139.49	0.1489	55.94	138.95	0.319	81.28	138.44	0.4829
18.93	139.46	0.1489	55.95	138.88	0.3191	81.28	138.36	0.483
18.94	139.42	0.149	55.95	138.83	0.3191	81.29	138.29	0.4831
18.94	139.4	0.149	55.96	138.79	0.3192	81.29	138.19	0.4832
18.95	139.37	0.149	55.96	138.72	0.3193	81.3	138.09	0.4834
18.96	139.34	0.1491	55.97	138.65	0.3194	81.3	138.02	0.4834

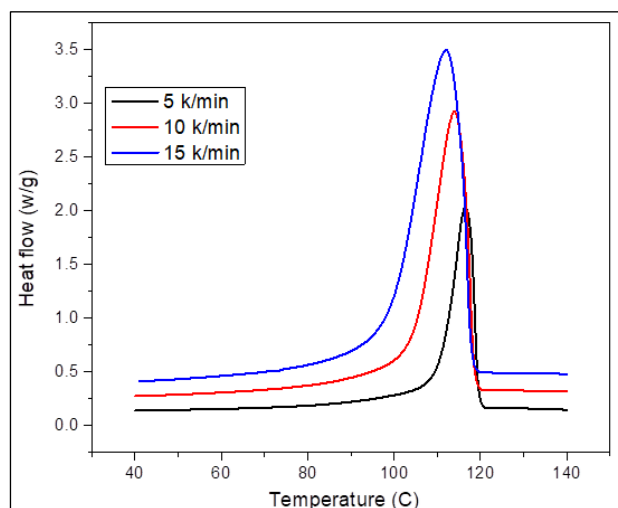


Figure 66 heat flow versus temperature

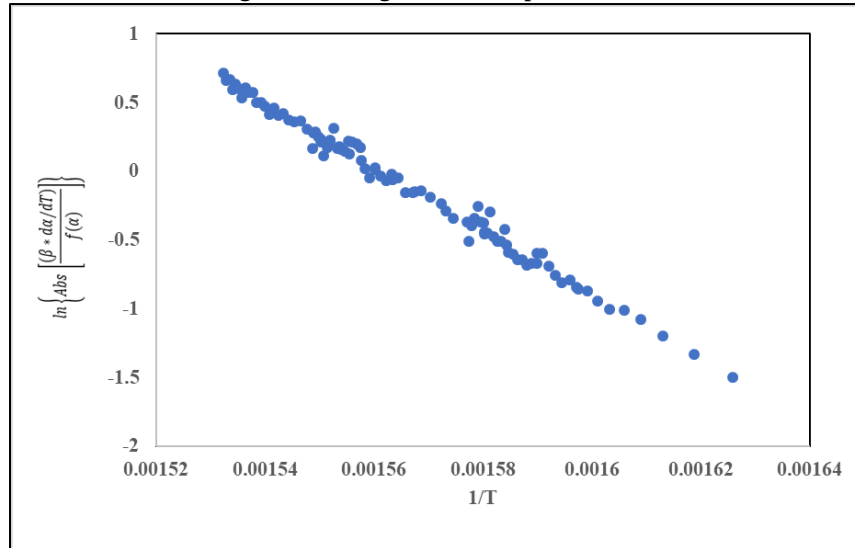
The steps are as follows: we calculate the area under the heat rate curve for each heating rate separately. Area of each rectangle. Then, we calculate the alpha (α) for each heat rate,

which is the summation of cumulative areas of these columns; then, these values are used to calculate the alpha percentages (alpha/total area). Then, the derivative of alpha is calculated with respect to the change in the equivalent value of temperature ($d\alpha/dT$). We find β , which represents the reciprocal of temperature. Then we find the last part of the analysis part: $\ln \beta * d\alpha/dT$ or $d\alpha/dT$; all these steps are specified in Table 25. Then, for specific values of α selected for each heating rate and interpolated, these values were plotted versus β and fitted to a selected model, as we noted in Figure 67.

Table 25 Steps of thermal analysis

							$\left(\beta \frac{d\alpha}{dT}\right)$	$\ln \left\{ Abs \left[\frac{(\beta * d\alpha/dT)}{f(\alpha)} \right] \right\}$
Area of each rectangle	α	α (%)	actual $d\alpha/dT$	$\beta=1/T$	$10^3 \beta$	$f(\alpha)=1-\alpha$		

Figure 67 Fitting results to a specific model



8.2 Applications of the Designed Fluid

8.2.1 Core Flooding System

The fluid system assessed in the core flooding experiments is 0.6 wt. % CMHPG polymer, 1 wt. % zirconium crosslinker, 0.1 wt. % DTPA chelating agent. The core flooding experiments were performed on 4 Berea sandstone samples (high permeability) and one tight core sample of Scioto rock. This tight core was broken vertically to mimic the fracture interface.

8.2.2 Methodology

8.2.2.1 Experimental Setup

A simple set-up of Vinci core flooding was utilized to test the formation damage to two accumulators, one inside the oven at 70 °C holding the FW, and one outside the oven at the room conditions, holding the SW, the chelating agent and the breaker and the fracturing fluid (FF). Figure 68 shows the setup used in the experiments. The figure also shows the pumps used for pushing the fluid into the core samples the backpressure pump, the drain, and the core holder.

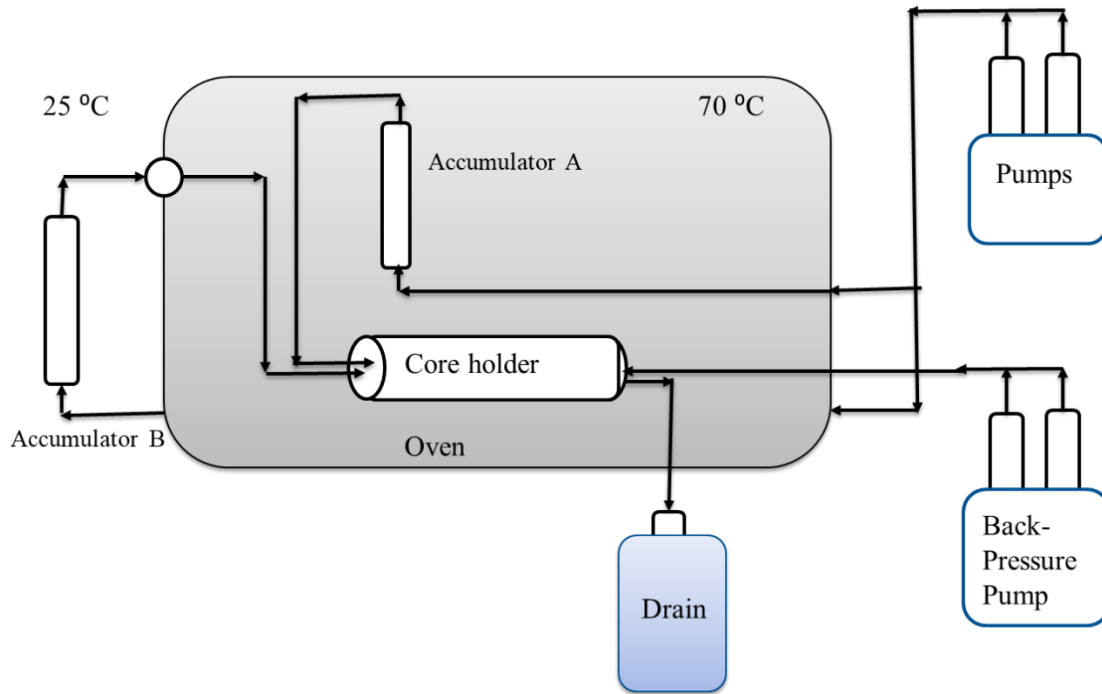


Figure 68 Core flooding experiment setup

8.2.2.1 Procedures

All core samples were 3 inches *1.5 inches and flooded initially with formation water of 242,000 TDS, at the rate of 1 cc/min, at the tests were performed at 70 °C. In the first experiment, the sample was flooded with formation water, and then the permeability was measured. Then, the sample was taken for NMR measurements and flooded with 3-pore volume seawater at a rate of 0.1 cc/min. Effluent measurements were performed at the end of 1 pore volume and 2 pore volumes to inspect the scale formation through ICP. Then, the sample was flooded with formation water at a rate of 1 cc/min for 3 pore volumes, and the permeability was measured again. In the second experiment, the sample was flooded with formation water, and then the permeability was measured. The sample was taken for NMR measurements and then flooded with 0.1 wt. % DTPA in the saline water at the rate of 0.1 cc/min. Then, the sample was flooded with formation water at a rate of 1 cc/min for 3 pore volumes, and the permeability was measured again. The third experiment was repeated

similarly except the fracturing fluid was added, which is (0.6 wt. % polymer+ 1 wt. % crosslinker + 0.1 wt. % DTPA), then 2 ppt pound per thousand-gallon breaker (ppt). In the fourth experiment, a similar procedure. In the fourth experiment, a similar procedure was followed, except the breaker was within the fracturing fluid, and the core sample was flipped for the flow back. In the fifth experiment, a similar procedure to the fourth experiment was performed on the cracked Scioto core sample.

All procedures are summarized in Table 26, in which the steps are sequenced: the FW represents the formation water, K represents the permeability measurement, NMR for NMR measurement, SW for saline water, and ICP for ICP effluent measurement. FF is for fracturing fluid flooding, FF-B represents the fracturing fluid followed by the breaker, and FF+B represents the fracturing fluid that contains the breaker. Flip is for flipping the core sample, and crack is for fracturing the Scioto tight rock sample. The difference between experiments is highlighted in green.

Table 26 Summary of core flooding procedures and steps

1 st Berea	FW-K-NMR-SW-ICP-NMR-FW-K
2 nd Berea	FW-K-NMR-SW+DTPA-NMR-FW-K
3 rd Berea	FW-K-NMR-FF-B-NMR-FW-K
4 th Berea	FW-K-NMR-FF+B-NMR-Flip-FW-K
5 th Scioto	FW-K-NMR-Crack-FW-K-FF+B-NMR-Flip-FW-K

The permeability is calculated using the darcy equation:

$$K = - \frac{Q * \mu * \Delta x}{A * \Delta P} \quad 8.4$$

Where

K is permeability, Q is flow rate, μ is fluid (formation water) viscosity, Δx is length (core length), A is cross-section area, and ΔP is the pressure difference.

Because any viscosity variation affects the permeability calculations, and the viscosity value of the FW is too low, the Oswald method was used to determine the viscosity of the FW. The viscosity is determined from the following equations:

$$v = c * t \quad 8.5$$

$$\mu = v * \rho \quad 8.6$$

Where c is Ostwald constant at a specific temperature and determined from Table 27, we targeted the viscosity at 70 °C (158 °F); interpolation was used to find the constant c at this temperature. t is time measured by stopwatch, ρ is density, v is kinematic viscosity, and μ is apparent viscosity.

Formation water density $\rho = 1.13$; therefore, the apparent viscosity using equation 8.6 is $\mu = 0.825041$ cP

Results

At 158 °F, the average of 3 times repeated measurement $t = 177$ sec. For the tube of size 50 used in the experiment at 158 °F: $c = 14125$. And using equation 8.5, the kinematic viscosity $v = 0.730125$

Table 27 Ostwald constants for 100 °F and 210 °F

SIZE	C AT 100°F cSt/sec	C AT 210°F cSt/sec
025	0.001944	0.001938
025	0.001952	0.001945
050	0.004002	0.003982
050	0.004257	0.004236
050	0.003902	0.003882
075	0.00766	0.00763
075	0.00729	0.00725
075	0.00723	0.00720
075	0.00778	0.00775
100	0.01515	0.01507
100	0.01405	0.01398
100	0.01421	0.01414
100	0.01462	0.01455
150	0.03376	0.03359
150	0.03692	0.03674
150	0.03502	0.03484
150	0.03396	0.03379
150	0.03674	0.03656
150	0.03818	0.03799
200	0.09438	0.09391
300	0.21981	0.21871
300	0.20643	0.20540
350	0.45213	0.44987
400	1.10221	1.09670
400	1.04913	1.04388

The first four experiments were performed with Bera sandstone, while the last one was performed with Scioto tight rock. For each core sample, the permeability was measured twice before and after flooding with fracturing fluid. The permeability is measured after flooding with FW; after FF, it is also flooding with FW, then measuring permeability. Table 28 specifies the results of core flooding experiments. In the first experiment with SW, only the retained permeability was high (92%), and the scale did not affect the permeability. In

the second experiment, the retained permeability increased by 4 % because of the use of 0.1 wt. % DTPA chelating agent. In the third experiment, the fracturing fluid was pumped without filtering, and then the breaker was pumped; the results showed poor retained permeability, as the fluid was not filtered and the sample was not flipped. In the fourth experiment, the breaker was added to the fracturing fluid before pumping and filtering, and after that, for the flow back, the sample was flipped and flowed back. The value of permeability increased to 30.4 compared to the third experiment. In the fifth, for the Scioto tight rock experiment, the sample permeability was measured first. The sample was cracked, and the permeability was measured again, pumped with filtered fluid, and flipped. The core sample and permeability were measured for the third time. The first value was 0.56 md, the second was 81 md, and after FF, it was 0.54, which indicates the fracturing fluid blocked even the created fracture. This study indicated that the performance of the breakers is not good, and the fluid blocks the permeability of the tight rock.

Table 28 Core flooding experiments results

Core Sample No	Core Sample Type	Added Fracturing Fluid (FF)	Direction of flow	K initial with FW	K with FW after FF	Retained permeability (%)
1	Berea	SW		319	294	92.2
2	Berea	SW+ DTPA		533	513	96.3
3	Berea	FF +DTPA+Breaker		93.4	5.9	6.3
4	Berea	FF +DTPA+Breaker		43.4	13.2	30.4
5	Scioto	FF +DTPA+Breaker		0.56	0.54	0.007
K after fracturing the core was 81 mD						

8.2.1.1 NMR Measurements of Core Samples

The rock NMR measurements showed that the porosity decreased in all the cases except in the case of fracturing fluid, in which we did not flip the flow direction. In the first and second cases, the decrease in porosity indicates scale formation. In the third case, the

viscous fracturing fluid blocked the pores; the pressure increased, and this increase forced the fluid to enter more pores, which was indicated by increased porosity. These results are shown in Table 29.

Table 29 NMR results for core samples before and after

Sample No	After FW flooding (%)	After FF flooding (%)
1	22.2	21.1
2	22.5	21.5
3	18	19.9
4	20.3	20.2
5	17.4	17.7
After Breaking Before Fracturing, Fluid porosity was 16.6		

8.2.1.2 Effluent Measurements (ICP)

In the first experiment, we decided to measure the scaling tendency by taking samples at 1 pore volume (PV) and 2 pore volumes; the results are shown in Table 30. The core sample was flooded by formation water at 70 C at 1 cc/minute; then, the SW was pumped from the accumulator outside.

Table 30 Ions captured at 1 and 2 PVs when SW flowed into FW-flooded sample.

Sample	Magnesium	Calcium
SW (Wet)	17644	2387
1 PV	2777	15709
1 PV	2831	15856
1 PV	2813	16553
2 PV	2357	3630

2 PV	2475	3556
2 PV	2474	3570

8.2.3 Proppant Static Settlement

The test is planned to be applied at high-pressure temperatures in the visualization cell to measure settlement velocity. A transparent graduated glass cylinder with 25 times the proppant diameter is used to eliminate the effect of the proppant stuck on the cylinder wall. A ruler can be placed to measure fluid and proppant levels. (Geri et al., 2019).

The following pictures represent the 20/40 frac sand proppant settlement for the designed fluid of 0.6 wt. % CMHPG, 1 wt. % zirconium crosslinker, and 0.1 wt.% DTPA. The proppant is added at concentrations of (0.5 ppg, 1 ppg, and 2 ppg) and images are taken after mixing properly at 0, 2, 4, 6, 8, 10, 20, and 30 minutes for each concentration. Figure 67 represents 0.5 ppg, Figure 70 represents 1 ppg, and Figure 71 represents the 2 ppg proppant concentration. Another type of proppant is also shown in the study, which is 40/70 proppant and clarified in Figure 72.

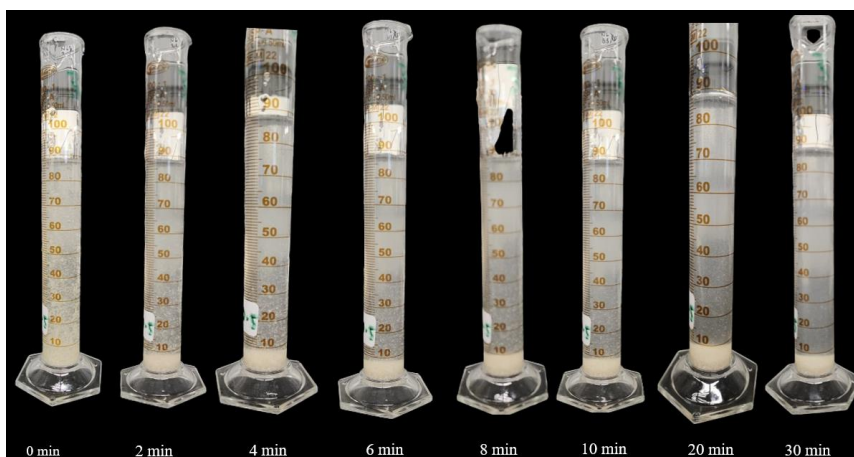


Figure 69 Settlement of 0.5 ppg 20/40 proppant

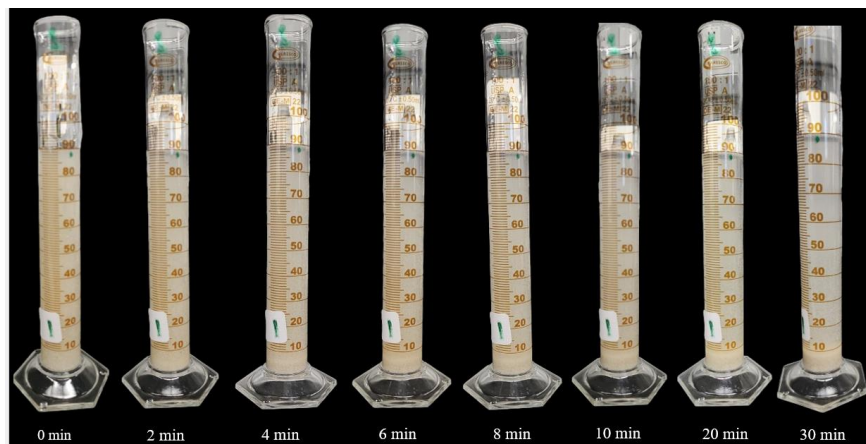


Figure 70 Settlement of 1 ppg 20/40 proppant

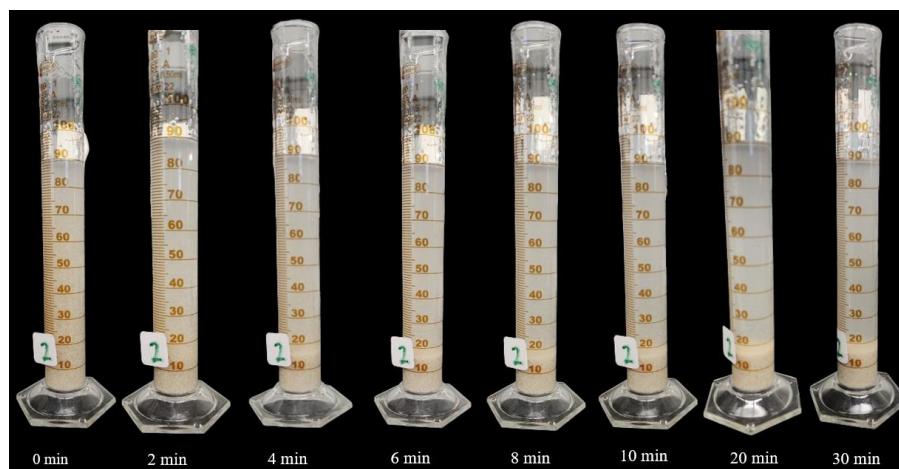


Figure 71 Settlement of 2 ppg 20/40 proppant

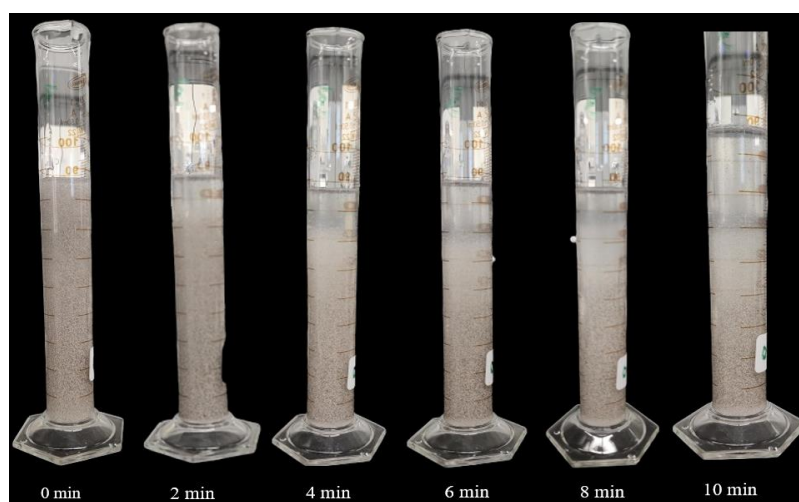


Figure 72 Settlement of 0.5 ppg 40/70 proppant

CHAPTER 9

Discussions and Recommendations

9.1 Introduction

The comprehensive study of the rheology of SW-based fracturing fluids, including the effects of additives and ion concentrations, provides valuable insights for optimizing formulations under diverse conditions. The study's applicability extends to cost-effective and environmentally friendly alternatives for offshore operations. The findings regarding the impact of individual ions, chelating agents incompatibility issues solutions, optimum chelating agents concentration, and temperature effect on rheological behavior contribute to a nuanced understanding of fluid dynamics. Recommendations for further research underscore the importance of expanding the study to encompass a broader range of formulations and environmental conditions. Overall, the study enhances our understanding of fracturing fluid rheology and offers practical insights for improved formulation design.

9.2 Key Findings

In this study, it was revealed that, at low temperatures, increasing both the concentration and pH value of the GLDA chelating agent prolongs the time required for polymer hydration and the subsequent viscosity increase. This mechanism can be employed to minimize the pumping power needed for transporting fracturing fluid into the formation. The enhanced performance attributed to the GLDA chelating agent is a result of its ability to capture seawater (SW) ions and reduce their hardness, thereby mitigating formation

damage associated with SW usage. The investigation into the effects of the polymer and chelating agent on individual ions revealed that, except in the case of Na_2SO_4 , the concentration of salt has an insignificant impact on CMHPG rheology. Na_2SO_4 , in particular, leads to a reduction in viscosity. Additionally, the high pH GLDA elevates the viscosity of distilled water (DI), SW, and individual salt solutions such as NaCl , CaCl_2 , and MgCl_2 while concurrently decreasing the viscosity of Na_2SO_4 . Further exploration involving the polymer, chelating agent, and zirconium crosslinker on individual ions demonstrated that in SW and individual ions, the viscosity increases with rising zirconium crosslinker concentration. However, low concentrations of zirconium in DI water suffice to crosslink the solution. The behavior of SW is influenced by multiple ions, with variations tied to the concentrations of GLDA, the crosslinker, and environmental temperature. Notably, for all individual ions at 70 °C within the first hour, lower concentrations of GLDA correlate with improved viscosity. At high temperatures, the high-pH GLDA induces a delay in the viscosity of divalent ions, while at low temperatures, it delays the viscosity of monovalent ions and SW.

The study also investigated the better polymer performance with SW and the impact of polymer, GLDA, and a crosslinker on seawater rheology. Notably, the study observed disturbances in the rheological behavior of many polymers at elevated temperatures. A more effective preparation method was suggested, involving the addition of a chelating agent and crosslinker after polymer hydration. Additionally, it was observed that in distilled water (DI)-based systems, GLDA chelates the crosslinker in the absence of salt ions, which are not present in DI systems. The study found that temperature ramping activates the Zr crosslinker in DI-based systems, whereas at room temperature, the Zr

crosslinker is activated instantly in SW-based systems. Conductivity measurements performed on GLDA and zirconium crosslinkers revealed that as the GLDA concentration increases, there is an increase in fluid pH and a decrease in conductivity.

The study indicated that the high pH GLDA is incompatible with crosslinkers at high salinity and high temperatures. To address this issue, different chelating agents were introduced to enhance performance and develop a more effective fluid. Various evaluations, including rheology, scaling, and ion detection techniques, were employed to assess different fluid variations. Results from scale loop evaluations demonstrated that, in terms of scale inhibition, high pH EDTA outperformed other chelating agents, followed by low pH DTPA and high pH GLDA. In ion capture tests (ICP), low pH DTPA performed better than pH EDTA and high pH GLDA. Viscosity tests revealed that certain crosslinked fluids experienced a sudden reduction in viscosity, known as the slippage effect, when measured with a rheometer, with no subsequent impact on viscosity. The utilization of low concentrations of pH DTPA with zirconium and zirconium borate resulted in a high-viscosity crosslinked fluid. Notably, the study found that borate crosslinkers exhibit greater stability with chelating agents than zirconium crosslinkers.

9.3 Recommendations

I suggest broadening the scope of the study to encompass a more extensive range of seawater (SW) formulations, incorporating variations in salinity. Additionally, the investigation could be expanded to include produced water with organic compounds, such as oil. Furthermore, a detailed examination of individual associated ions with SW, elucidating their challenges and potential solutions, would enhance the comprehensiveness

of the research. It is also advisable to conduct a more in-depth and fundamental study on alternative chelating agents, such as DTPA and EDTA.

Exploring the multifaceted functions of chelating agents in different aspects of fracturing fluids offers another avenue for investigation. For instance, there is a suggestion to explore the potential use of high-pH GLDA as a breaker for high salinity water when zirconium is used as a crosslinker, as it instantaneously disrupts the fluid. Additionally, the study should delve into the interactions of fluids with various types of formations, considering specific temperature and pressure constraints. Modeling can be employed to incorporate diverse elements of formations, providing a more comprehensive understanding of fluid dynamics in different geological contexts.

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Vitae

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Department, College of engineering University of Khartoum) |

Academic Background

Education

- December 2023
King Fahd University of Petroleum & Minerals, Dharan, Saudi Arabia
Ph.D. in Petroleum Engineering
 - August 2018
King Saud University, Riyadh, Saudi Arabia
M.Sc. in Petroleum Engineering
 - October 2012
University of Khartoum, Khartoum, Sudan
B.Sc. in Petroleum Engineering
- Academic Experience
- 2019, Sep 2023 - Dec
 - Teaching Assistant during Ph.D. program at KFUPM
- Courses: Reservoir Description, Well Logging, Phase Behavior, Geomech & Petrophys,
Numerical Methods in Petroleum Geomechanics, Adv. Fluid Pro. &
Thermodynamics
- Lab Experiments and research work

- 2012 Dec–2013 Dec
- Teaching Assistant at the University of Khartoum

Assisted in production, drilling, and reservoir engineering courses

Software Handled

FRACPRO, Interactive Petrophysics (IP), PROSPER, WELFLO, Ecrin, OFM, Hyses, Abaqus, Jewel suite, Origin, Odeon, and Primavera.

Projects

- Development of Environment-Friendly Fracturing Fluids Based on Produced Water (Aramco-funded project) [Ongoing]
- Optimizing Seawater Fracturing Fluid Rheology Utilizing Chelating Agents- CPG 21106 [Ongoing]
- Research in Hydraulic Fracturing, Data Mining & Modeling Fracture Job [10/2015 – 02/2018]
- Artificial Lift Selection and Design (Computer Program) [2012]
- Nodal Analysis Optimization Project (Case Study with WellFlo Software) [2011]
- Insulation Design for Pipeline (Case Study with HYSES Software) [2010]

Equipment and Lab Work

- Anton-paar and TA rheometers, Chandler viscometer
- Differential scale loop (DSL)
- Differential scanning calorimetry (DSC)
- Inductive Coupled Plasma (ICP)
- Simple NMR measurements
- Vinci core flooding system
- Nondestructive tests (NDT)

Courses and Training

- Project Management Professional Preparatory Course, Milestone Training Center, 2019
- Ministry of Oil (Oil Exploration & Production Administration office and Field, Sudan) [07/2013 – 08/2013]
- Drilling and Workover in Alfoula South Kurdufan

- Field Trip (Khurais Aramco Field CPF, FPF, and Producing Well Visits) [KSU, 2016]
- IWCF Course [KSU, 2015]
- JewelSuite GeoMechanics 1D Model (KFUMP, 2022)

Coursera Platform

- Introduction to Business Analysis Using Spreadsheets: Basics, 2022
- Successful Negotiation: Essential Strategies and Skills, University of Michigan, 2023
- Writing in the Sciences, Stanford University (In progress - 50%)
- Introduction to Programming with MATLAB, Vanderbilt University (In progress - 50%)

Personal Competencies

- Ability to work in a fast-paced environment and meet deadlines, as he is fast learner.
- Forward planner and efficient problem solver
- A history of scholarship achievements
- Enthusiastic self-starter who excels in teamwork and leadership
- Root Cause Analysis, Statistical Process Control (SPC), Documentation and Reporting
- Cross-functional Collaboration, Continuous Improvement
- Fluent English speaker with supporting 6.5 IELTS.

List of Publications

- Othman, A., Aljawad, M. S., Mahmoud, M., Kamal, M. S., Patil, S., & Bataweel, M. (2021). Chelating agents usage in optimization of fracturing fluid rheology prepared from seawater. *Polymers*, 13(13), 2111. <https://doi.org/10.3390/polym13132111>
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- Othman, A., Aljawad, M. S., Kamal, M. S., Mahmoud, M., Patil, S., & Kalgaonkar, R. (2023). Individual Seawater Ions' Impact on the Rheology of Crosslinked Polymers in the Presence of a Chelating Agent. *Energy & Fuels*, 37(10), 7328-7338. <https://doi.org/10.1021/acs.energyfuels.3c00701>
- Othman, A., Tariq, Z., Aljawad, M. S., Yan, B., & Kamal, M. S. (2023). Enhancing Fracturing Fluid Viscosity in High Salinity Water: A Data-Driven Approach for Prediction and Optimization. *Energy & Fuels*. <https://doi.org/10.1021/acs.energyfuels.3c02272>
- Othman, A., Aljawad, M. S., Kamal, M. S., Mahmoud, M., & Patil, S. (2021, December). Optimizing Seawater Based Fracture Fluids Rheology Utilizing Chelating Agents. In *SPE Middle East Oil and Gas Show and Conference* (p. D021S005R003). SPE. <https://doi.org/10.2118/204684-MS>
- Othman, A., Murtaza, M., Aljawad, M., Kamal, M., Mahmoud, M., & Kalgaonkar, R. (2023, March). The Impact of Salt Ions on the Rheology of a Crosslinked Polymer Containing a Chelating Agent. In *Middle East Oil, Gas and Geosciences Show*. OnePetro. <https://doi.org/10.2118/213601-MS>
- Othman, A., AlSulaimani, M., Aljawad, M. S., Sangaru, S. S., Kamal, M. S., & Mahmoud, M. (2022). The synergetic impact of anionic, cationic, and neutral polymers on VES rheology at high-temperature environment. *Polymers*, 14(6), 1145. <https://doi.org/10.3390/polym14061145>
- Othman, A. A., & Amao, A. M. (2019, March). Hydraulic Fracturing Treatments in the Permian Basin: Distillation of Best Practices in the Spraberry and Wolfcamp Formations. In *SPE Middle East Oil and Gas Show and Conference*. OnePetro. <https://doi.org/10.2118/194931-MS>
- Ahmed Othman, A. A., & Amao, A. M. (2018, April). Hydraulic Fracture Treatment Designs: Distillation and Integration of Best Practices in the Spraberry

and Wolfcamp Formations of the Permian Basin. In *SPE Kingdom of Saudi Arabia Annual Technical Symposium and Exhibition* (pp. SPE-192247). SPE. <https://doi.org/10.2118/192247-MS>

- Othman, A., Glatz, G., Aljawad, M. S., Alafnan, S., Alarifi, S. A., & Al Ramadan, M. (2022). Review of Kerogen's Geomechanical Properties: Experiments and Molecular Simulation. *ACS omega*, 7(37), 32829-32839. <https://doi.org/10.1021/acsomega.2c03136>
- Othman, A., Kamal, M. S., Aljawad, M. S., Mahmoud, A., S., Sultan, M., Kalgaonkar, R. (2023) A Study of Crosslinked Gel and Chelating Agent Compatibility in High Salinity Environments. *Energy & Fuels*.