

INVESTIGATION OF CHELATING AGENT AS
ACID FRACTURING FLUIDS

BY

RIDHA ABDRABALRASOOL ALABDRABALNABI

A Thesis Presented to the

DEANSHIP OF GRADUATE STUDIES

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN, SAUDI ARABIA

In Partial Fulfillment of the
Requirements for the Degree of

MASTER OF SCIENCE

In

PETROLEUM ENGINEERING

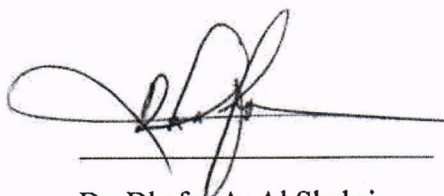
MAY 2023

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

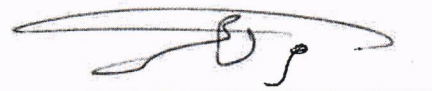
DHAHRAN- 31261, SAUDI ARABIA

DEANSHIP OF GRADUATE STUDIES

This thesis, written by **RIDHA ABDREBALRASOOL ALABDRABALNABI** under the direction of his thesis advisor and approved by his thesis committee, has been presented and accepted by the Dean of Graduate Studies, in partial fulfillment of the requirements for the degree of **MASTER OF SCIENCE IN PETROLEUM ENGINEERING** .



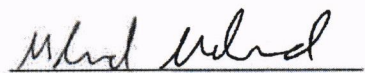
Dr. Dhafer A. Al Shehri
Department Chairman



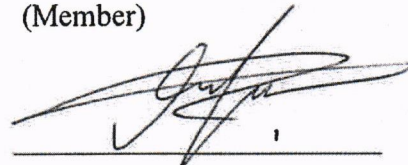
Dr. Murtada Al-Jawad
(Advisor)



Dr. Suliman Al-Homidan
Dean of Graduate Studies



Dr. Mohamed Mahmoud
(Member)



Dr. Mustafa Al-Ramadan
(Member)

Date



© Ridha Al Abdrabalnabi

2023

“To my parents, who gave me their endless love, support, and encouragement during my whole educational life”

ACKNOWLEDGEMENTS

I would like to express my appreciation to everybody who was part of this study, especially my committee members Murtada Al-Jawad, Mustafa Al-Ramadan, and Professor Mohammed Mahmoud.

Thanks to the dean of our college, Abdulaziz Al-Kaabi, my direct manager, Professor Zhengwei Pan, and my mentor at work, Mr. Xianmin Zhou, for their continuous support and motivation before and during my study.

Thanks to every colleague at the college who facilitated every laboratory and piece of equipment to perform the measurements that have been done in this thesis, especially Eassa Abdrabalnabi, Habib Alabbas, Eyad Safi, and the former employees Mubarak Baatiyah and Ahmed Bin Ghanim. And thanks to other colleagues at CPG for their support and motivation.

Thanks to the deanship of research at KFUPM for funding this project.

Finally, special thanks to my parents, wife, daughter, and all family and my close friends Minhal, Ali Jassim and Muntadher Aldar for their support during my study. Without them, I would not be able to complete this achievement.

TABLE OF CONTENTS

ACKNOWLEDGEMENTS	iii
TABLE OF CONTENTS	iv
LIST OF TABLES	vi
LIST OF FIGURES	vii
LIST OF ABBREVIATIONS	ix
ABSTRACT	x
ملخص الرسالة	xii
CHAPTER 1	1
INTRODUCTION.....	1
1.1 Acid Stimulation Methods	1
1.2 Problem Description	4
1.3 Research Objective.....	4
CHAPTER 2	5
2.1 Acid Fracture Conductivity.....	5
2.1.1 Formation Type.....	6
2.2 Acid Fracturing Fluid Systems	8
2.2.1 Organic acids	9
2.2.2 Retarded HCl-based acids.....	9
2.2.3 Gelled HCl acid based on a polymer.	10
2.2.4 Emulsified HCl acid.....	10
2.2.5 Viscoelastic surfactant (VES) HCl acid based.....	11
2.3 Chelating agent fluids	11
2.3.1 L-Glutamic acid N, N-diacetic acid (GLDA).....	13
2.3.2 Ethylenediaminetetraacetic acid (EDTA).....	14
2.3.3 Diethylenetriaminepentaacetic acid (DTPA).....	14
2.3.4 The dissolution mechanism of chelating agents	15
2.3.5 Chelating agent as acid fracturing fluids.....	16
CHAPTER 3	17

3.1	Sample Preparation.....	17
3.2	Fracture Surface Roughness Measurement	19
3.3	Hardness Measurements.....	20
3.4	Fluids Preparation.....	21
3.5	Sample Saturation	22
3.6	Fracture Conductivity Measurements	23
3.7	Acid Treatment.....	24
3.8	Inductively Coupled Plasma (ICP) Measurements.....	25
CHAPTER 4		26
4.1	Layered Carbonate Reservoirs	26
4.1.1	Coreflooding Results.....	26
4.1.2	Fracture Conductivity Results.....	29
4.1.3	Roughness, Hardness, and Imaging Analysis.....	31
4.1.4	ICP Analysis and Dissolution.....	34
4.2	Mixed Minerals of Carbonate Reservoirs	36
4.2.1	Coreflooding Results.....	36
4.2.2	Fracture Conductivity Results.....	40
4.2.3	Hardness, Roughness, and Imaging Analysis.....	41
4.2.4	ICP Analysis	45
CHAPTER 5.....		47
5.1	Conclusions.....	47
5.2	Recommendations	48
REFERENCES.....		49
VITAE.....		52

LIST OF TABLES

Table 1. The details of the experiments	21
Table 2. Pre- and post- stimulation mass data of the samples	36

LIST OF FIGURES

Figure 1. Diagram illustrates the stimulation methods	3
Figure 2. Acid fracturing fluid behavior in the fracture (Williams, Gidley, and Schechter 1979).....	3
Figure 3. Impact of different acid systems on softening of limestone and dolomite carbonate rocks. (Hisham A. Nasr-El-Din et al. 2008)	8
Figure 4. Fracture conductivity measurements for various carbonate minerals under closure stress. (Melendez et al. 2007)	8
Figure 5. Chelating agent rings containing cation (M) (Almubarak, Ng, and Nasr-El-Din 2017).....	12
Figure 6. Acidizing experiments done by chelating agents (Fredd and Fogler 1998a).....	13
Figure 7. Chemical structure of GLDA	14
Figure 8. Chemical structure of EDTA.....	14
Figure 9. Chemical structure of DTPA	15
Figure 10. Conductivity comparison before and after stimulation with different stimulants	16
Figure 11. The casted block and cross section diagram of layered sample.	18
Figure 12. XRD measurements of reservoir samples showing different percentages of carbonate minerals.....	18
Figure 13. Top view of the fracture surface of the layered sample	19
Figure 14. The sample after covering by epoxy	19
Figure 15. Laser profilometer scanner (THORLABS MB1530F/M).....	20
Figure 16. AutoScan scanner	21
Figure 17. Automated saturator by Vinci-technologies.....	22
Figure 18. Schematic of coreflooding system (Tariq, Hassan, et al. 2021)	24
Figure 19. ICP equipment (Optima 8000 ICP-OES by PerkinElmer).....	25
Figure 20. Pressure drop profile of HCl acid fracturing fluid treatment including before and after for conductivity measurement of layered sample.....	27
Figure 21. Pressure drop profile of GLDA fracturing fluid stimulation including pre- and post- conductivity measurement	28
Figure 22. Pressure drop profile of EDTA fracturing fluid treatment including before and after for conductivity measurement.....	29
Figure 23. Fracture conductivity values pre and post acid stimulation	30
Figure 24. Fracture conductivity evolution across the closure stress.	30
Figure 25. The evolutions of fracture surface roughness between pre-and post-treatment in the three: HCl, GLDA and EDTA	32
Figure 26. Fracture surface profile of the samples after the acid treatment by HCl (left), GLDA (middle) and EDTA (right).....	33
Figure 27. Hardness results of the three examined samples after the stimulation	34

Figure 28. ICP analysis of collected samples of calcium (Ca) concentration during HCl, GLDA and EDTA treatment process.....	35
Figure 29. ICP analysis of collected samples of magnesium (Mg) concentration during HCl, GLDA and EDTA stimulation process.	35
Figure 30. Pressure drop profile before, during, and after HCl acid fracturing treatment in a heterogeneous sample.....	37
Figure 31. Pressure drop profile of GLDA acid fracturing fluid treatment including before and after for conductivity measurement of heterogeneous sample.....	38
Figure 32. Pressure drop profile of DTPA acid fracturing fluid treatment including before and after for conductivity measurement of heterogeneous sample.....	39
Figure 33. Fracture conductivity values pre and post acid stimulation in heterogeneous carbonate samples.....	40
Figure 34. Strength measurements evolutions of the three treated samples pre and post stimulation	41
Figure 35. Roughness evolutions in percentage of the three examined samples.....	42
Figure 36. Image illustration of examined sample by HCl between pre and post treatment.....	43
Figure 37. Image illustration of examined sample by GLDA between pre and post treatment.....	44
Figure 38. Image illustration of examined sample by DTPA between pre and post treatment.	44
Figure 39. ICP analysis of collected samples of calcium (Ca) concentration during HCl, GLDA and DTPA treatment process.	46
Figure 40. ICP analysis of collected samples of calcium (Mg) concentration during HCl, DTPA and EDTA treatment process.....	46

LIST OF ABBREVIATIONS

HCl	: Hydrochloric acid
GLDA	: L-Glutamic acid N, N-diacetic acid
EDTA	: Etheylenediaminetetraacetic acid
DTPA	: Diethylenetriamine pentaacetate acid
VES	: Viscoelastic surfactants
XRD	: X-Ray Diffraction
ICP	: Inductively Coupled Plasma
Ca	: Calcium
Mg	: Magnisum
k_{wf}	: Fracture conductivity

ABSTRACT

Full Name : RIDHA ABDRABALRASOOL ALABDRABALNABI
Thesis Title : [INVESTIGATION OF CHELATING AGENT AS ACID
FRACTURING FLUIDS IN LAYERED AND HETEROGENOUS
CARBONATE RESERVOIRS]
Major Field : PETROLEUM ENGINEERING
Date of Degree : May 2023

One of the methods for improving carbonate formation productivity is acid fracturing. The acid injection creates dissolution along the fracture that generates conductivity, defined as the fracture permeability multiplied by its width. Several parameters affect the success of the process of acid fracturing, including acid type, acid concentration, formation type, and contact time. Many fluids have been studied for generating conductivity, starting with strong acids such as hydrochloric acid (HCl) and weak acids such as organic acids. The key issues with HCl are its fast reaction and corroded wellbore tubular. Hydrochloric acid can be retarded by adding gelling agents, emulsifiers, cross-linkers, and viscoelastic surfactants (VES). Such additives can reduce the issues associated with HCl but are costly. This study has investigated and examined chelating agents such as GLDA, EDTA, and DTPA on acid fracturing treatments to sustain the conductivity of layered and mixed minerals in carbonate formations. Chelating agents are less reactive than HCl and do not require loads of corrosion inhibitors, especially in high-temperature environments. The roughness and strength of the fracture surface pre- and post-stimulation were examined utilizing a laser profilometer and an impulse hammer, respectively. The fracture conductivity was evaluated before and after acid etching using a core-flooding device for different flow rates under four closure stresses. Inductively coupled plasma (ICP) analysis was conducted to estimate the change of calcium and magnesium ions due to dissolution. Promising results have been obtained for fracture

conductivity improvement by chelating agents for different pH levels. Different behaviors of surface dissolution were generated after the acid injection, indicating that the pattern is an impact factor for fracture conductivity sustainability. This investigation showed the feasibility of employing chelating agents as acid fracturing fluids in carbonate reservoirs for the first time.

ملخص الرسالة

الاسم الكامل: رضا عبدرب الرسول عبد الله ال عبدرب النبي

عنوان الرسالة:

التخصص: هندسة البترول

تاريخ الدرجة العلمية: مايو 2023

التكسير الحمضي هو إحدى طرق تحسين إنتاجية مكامن الصخور الكربونية. يعمل الحقن الحمضي ذوباناً على طول الكسر الهيدروليكي الذي يولد الموصلية، والتي تُعرّف على أنها نفاذية الكسر مضروبة في عرضها. تؤثر العديد من المعاملات على نجاح عملية تكسير الحمض، بما في ذلك نوع الحمض وتركيز الحمض ونوع صخور المكمن ووقت التلامس. تمت دراسة العديد من السوائل للحفاظ على الموصلية، بدءاً من الأحماض القوية مثل حمض الهيدروكلوريك والأحماض الضعيفة مثل الأحماض العضوية. تتمثل المشكلات الرئيسية مع حمض الهيدروكلوريك في سرعة وقوة التفاعل، كما أنه يؤدي إلى تآكل أنبوب البئر. يمكن إعاقة حمض الهيدروكلوريك عن طريق إضافة عوامل التبلور، والمستحلبات، والرابطات المتقاطعة، والمواد الخافضة للتوتر السطحي اللزجة. يمكن أن تقلل هذه المواد المضافة من المشكلات المرتبطة بـ حمض الهيدروكلوريك، لكنها مكلفة. قامت هذه الدراسة بفحص وفحص سوائل عضوية تحتوي على الكربون مثل GLDA و EDTA و DTPA في معالجات التكسير الحمضي للحفاظ على الموصلية للمعادن ذات الطبقات والمختلطة في مكامن الكربونات. تعتبر هذه السوائل أقل تفاعلاً من حمض الهيدروكلوريك ولا تحتاج إلى كميات كبيرة من مثبطات التآكل، خاصة في البيئات ذات درجات الحرارة العالية. تم فحص خشونة وقوة سطح الكسر قبل التحفيز وبعده باستخدام مقياس بروفيلومتر ليزر ومطرقة نبضية على التوالي. تم تقييم موصلية الكسر قبل وبعد النقش الحمضي باستخدام جهاز غمر اللب لمعدلات تدفق مختلفة تحت أربعة ضغوط إغلاق مختلفة. تم إجراء تحليل البلازما المقترنة حثياً (ICP) لتقدير تغير أيونات الكالسيوم والمغنيسيوم بسبب الذوبان. تم الحصول على نتائج واعدة لتحسين موصلية الكسر بواسطة السوائل المجربة لمستويات مختلفة من الأس الهيدروجيني مقارنة بنتائج حمض الهيدروكلوريك. تم إنشاء سلوكيات مختلفة لذوبان السطح بعد الحقن الحمضي، مما يشير إلى أن النمط هو عامل تأثير لاستدامة موصلية الكسر. أظهر هذا التحقيق ولأول مرة جدوى استخدام عوامل مخلبية كسوائل تكسير حمضي في خزانات الكربونات

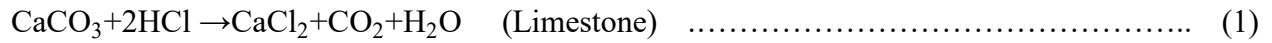
CHAPTER 1

INTRODUCTION

1.1 Acid Stimulation Methods

The stimulation technique employs a variety of methods to increase well productivity in tight reservoirs, including matrix acidizing and hydraulic fracturing (**Figure 1**). Hydraulic fracturing can be divided into two methods: injecting proppant-containing fluid to fill up the propagated fracture or injecting acid to generate irregular fracture faces. Several drawbacks to the hydraulic fracture job with proppant have been reported, including screen out and proppant migration issues during the acid fluid injection. In the acid fracturing process, unique steps must be considered in the design to achieve the job successfully. Initially, a pad fluid is injected into the formation above the breakdown pressure to generate the desired fracture. Then the acid fracturing fluid is injected into the fracture to etch the walls of the fracture, which results in conductive pathways. The reaction between the fracture walls and the injected acid is instantaneous and fast, especially in high temperatures. If the design considers the minimal fluid loss with viscous acid to generate wide fracture, then the spent acid at the layer boundary leads to reduce the rate of live acid when in contact with the feature walls. However, as the fracture flow becomes more turbulent and less laminar, the live acid will more easily contact the fracture walls. The acid will not penetrate very far into the fracture before becoming spent (**Figure 2**). The main advantages of acid fracturing job are screen-out free, easy to pump through the fracture, and the capability of building network in

natural fractured formations. The chemical reactions between the carbonate minerals and the acid fluid are depicted in equations (1) and (2) in which the hydrochloric acid (HCl) reacts in the fracture area to generate dissolution in the fracture walls, hence enhancing the fracturing conductivity.



Where symbols in the equation can be defined as CaCO_3 is calcium carbonate, HCl is hydraulic acid, CaCl_2 is calcium chloride, CO_2 is carbon dioxide, H_2O is water, $\text{CaMg}(\text{CO}_3)_2$ is magnesium carbonate, and MgCl_2 is magnesium chloride.

The term "fracture conductivity" can be defined as the fracture width times the fracture permeability. Essentially, the fracture conductivity is affected by the closure stress when the generated fracture starts closing, which will reduce the formation productivity. Furthermore, sufficient dissolution of minerals and non-uniform etching patterns across the fracture surface are requirements for a successful acid fracturing job. To perform a successful acid fracturing job, several factors must be considered, such as type and concentration of acid, type of formation, injection rate, and time. A successful non-uniform pattern of the fracture surface is crucial to retaining conductive pathways between the fracture and the production well; hence, the increase in closure stress has less impact on the fracture conductivity. (Nierode and Kruk 1973) introduced an empirical correlation demonstrates the relation between the fracture conductivity to strength of the rock, dissolved volume, and the closure stress of the formation (equation 3).

$$w k_f = C_1 \exp(-C_2 \sigma_c) \quad \dots\dots\dots (3)$$

Where the wk_f is the fracture conductivity, and C_1 is a function of initial conductivity, and C_2 is a function of rock embedment strength.

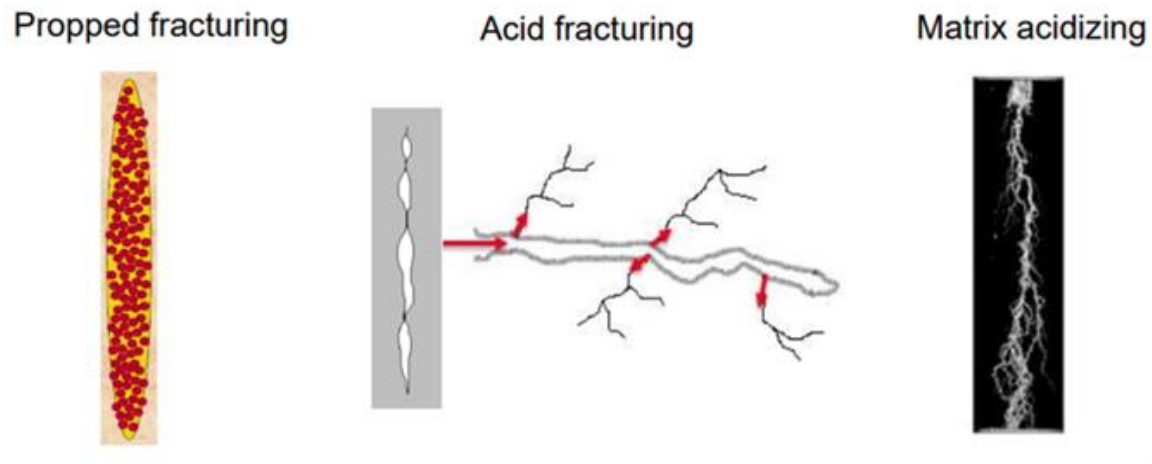


Figure 1. Diagram illustrates the stimulation methods

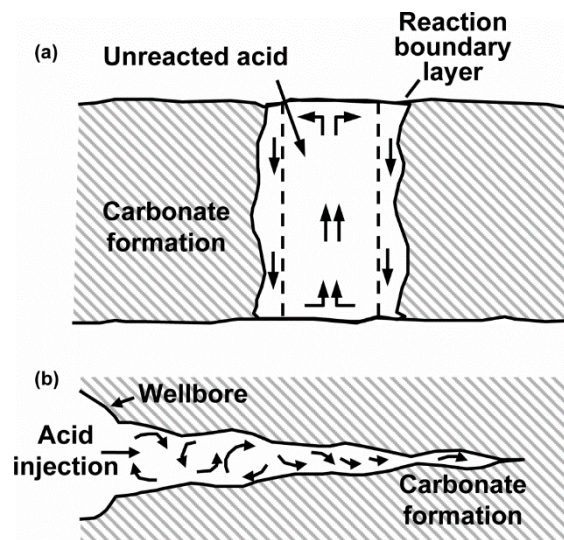


Figure 2. Acid fracturing fluid behavior in the fracture (Williams, Gidley, and Schechter 1979)

1.2 Problem Description

Acid fracturing processes are applied to enhance the productivity of carbonate reservoirs by creating rough fracture surfaces that remain conductive to formation fluids after the fracture closure. Over the course of history, different acid types have been investigated for acid fracturing, including strong and weak acids. The drawbacks of organic acids are their low dissolving power and low resultant fracture conductivity. For the strong acid (HCl), it's corrosive and requires numerous additives. An alternative fracture fluid with high performance and fewer disadvantages should be introduced to replace the conventional acids.

1.3 Research Objective

Examine the effectiveness of environmentally friendly chelating agents as acid fracturing fluids in a carbonate formation containing layered or mixed minerals (i.e., calcite and dolomite). Chelating agents could serve as a better alternative for hydrochloric acid at high temperatures (HCl). The study tests the hypothesis that chelating agents can generate sufficient fracture conductivity without damaging the fracture face or weakening the formation's mechanical properties. In summary, the following items will be investigated:

1. The potential of chelating agents to produce adequate fracture conductivity in layered and mixed carbonates.
2. On the fracture face, test the permeability impairment or enhancement.
3. Evaluating the impact of the tested fluids on the mechanical properties of the rock and surface roughness.
4. Performance comparison with the conventional HCl acid.

CHAPTER 2

LITERATURE REVIEW

2.1 Acid Fracture Conductivity

A measure of the flow capacity through an acidized fracture is called acid fracture conductivity. The main goal of acid fracturing is to permanently convert the acidized fracture into a conductive flow route that can withstand the pressure of the overburden and successfully link the reservoir to the wellbore. It is difficult to predict acid fracture conductivity since it is a stochastic process and is affected by a variety of factors. Therefore, testing and studying acid fracture conductivity via an experimental approach is a common procedure. The first laboratory study on acid fracture conductivity was performed by (Broadbent, Knox, and Fredrickson 1968). They concluded that temperature, formation type, acid type, acid concentration, and acid-rock contact time impacts acid fracture conductivity. Since the study's conclusion, the remarked aspects have been extensively discussed in the literature. Several experimental studies showed that the relationship between acid fracture conductivity and these properties can be explained by the etched pattern that the acid generated on the fracture faces and the strength of the rock that survived after the acid injection (Gomaa and Nasr-El-Din 2009; Melendez et al. 2007; Beg et al. 1998). In order to optimize treatment parameters, (Anderson and Fredrickson 1989) developed a laboratory approach to assess the conductivity of cores throughout acid fracturing. They verified that treatment parameters such as acid type and concentration, reaction time, temperature, and flow regime affect fracture conductivity, which is influenced by the amount of rock dissolved. A longer contact time did not always result in a higher fracture conductivity, according to several other researchers (Van Domelen, Gdansk, and Finley 1994; Van Domelen 1992; Camilo Malagon, Pournik, and Hill

2008) who investigated the relationship between contact time and acid fracture conductivity. They concluded that the ideal contact time should be identified to achieve the highest conductivity for a specific formation and acid type.

2.1.1 Formation Type

One of the main factors that directly influencing the acid fracturing job performance is the type of formation. Every lithology has its chemical and mechanical characteristics; hence the productivity enhancement will be different from type to another. Tight carbonate formations are being investigated to improve the well productivity using acid fracturing, therefore the researchers have been studied different carbonate minerals as it is impacting directly to the fracture conductivity improvement. Basically, several main physical mechanical and chemical parameters related to the formation type should be considered which are the roughness, hardness, reactivity of the formation, and minerals solubility. The rock surface roughness can be quantified by how much the deviation occurred in scale of irregularity on the surface. While the rock hardness is expressed as the relative resistance of rock to being scratched. Several studies investigated the effect of rock strength on acid fracture conductivity. (Nierode and Kruk 1973) provided the industry with a correlation of rock embedment strength and fracture closure stress to provide final reservoir conductivity following an acid fracture stimulation treatment. (Beg et al. 1998) investigated the effects of acids on Indiana limestone and Clerkfork dolomite, emphasizing the role of surface roughness and rock embedment strength on fracture conductivity. (Gong, Lacote, and Hill 1999) obtained similar results. (Hisham A. Nasr-El-Din et al. 2008) conducted laboratory experiments on limestone and dolomite samples using various acid types to investigate the effect of rock softening on fracture response. They revealed that the acid system used made a difference in the

degree of rock softening, which was found to be greater on limestone than on dolomite (**Figure 3**). (Melendez et al. 2007) concluded that the chalk is weakest compared to dolomite and limestone as closure stress increases, hence higher reduction in fracture conductivity due to that. Thus, the rock strength is crucial if the dissolved channel is not presented (**Figure 4**).

The first investigations of surface profile were done by (Gong, Lacote, and Hill 1999; Ruffet, Féry, and Onaisi 1998), they found that the etching roughness is caused by the alteration of the mechanical, geometrical, and mineralogy nature. In the last three decades, extensive studies have been investigated the fracture surface characterization utilizing smooth and rough surface at laboratory scale (Pournik et al. 2007; C Malagon, Pournik, and Hill 2008; Lu et al. 2017).

Another crucial parameter is the formation reactivity with acids in which it is considered as the reaction kinetics. Several studies have been done on pure calcite to pure dolomite measuring the reaction kinetics using the rotating disk apparatus (RDA). They have done the investigations for various acid concentration under different rotation speed and they found that the chemical composition of the rock type and temperature are crucial in the reaction speed (Ivanishin and Nasr-el-din 2021; Mccune et al. 1973; Taylor, n.d.).

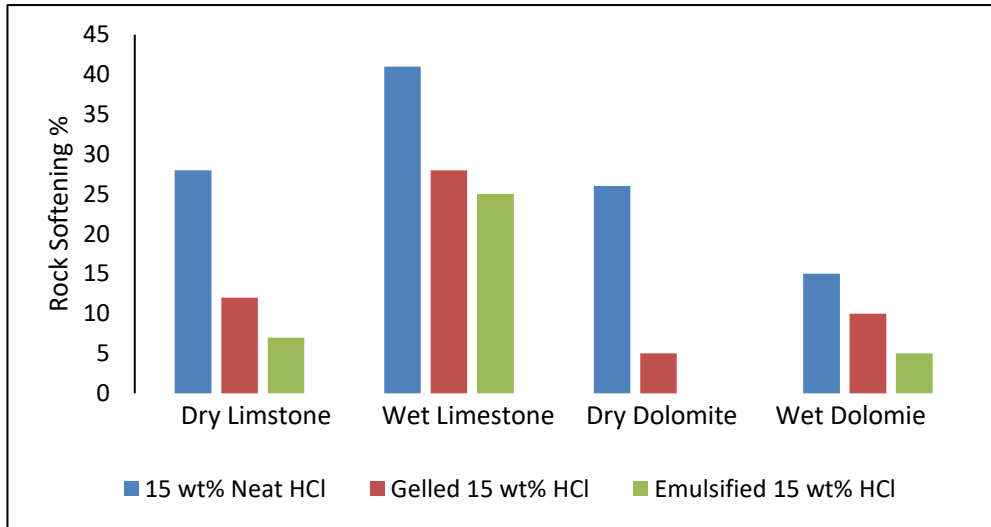


Figure 3. Impact of different acid systems on softening of limestone and dolomite carbonate rocks. (Hisham A. Nasr-El-Din et al. 2008)

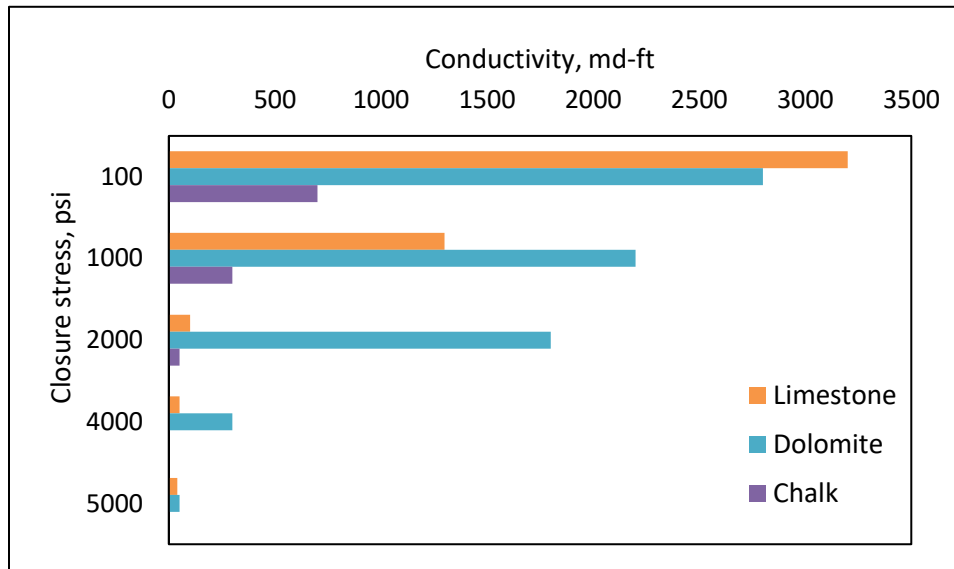


Figure 4. Fracture conductivity measurements for various carbonate minerals under closure stress. (Melendez et al. 2007)

2.2 Acid Fracturing Fluid Systems

The type and concentration of the acid used are very important when it comes to acid fracturing. Researchers have looked into different acidic fluids to see which ones work best for increasing

productivity. Hydrochloric acid (HCl) is the most used fluid due to its strong dissolving abilities. However, less common organic acid fracture fluids are preferred in situations with high temperatures.

2.2.1 Organic acids

To avoid the rapid reactions generated by HCl acid, the field frequently employs formic and acetic acids. In high-temperature situations, these fluids are less corrosive and require fewer inhibitors than HCl. Their low dissolving power, however, limits their use in acid fracturing. Although formic acid is stronger than acetic acid, it is uncommon to use either acid alone. In high-temperature conditions, they are frequently combined with HCl (Kalfayan 2008). Weak acids, both liquid and solid, can be injected. For example, a solid precursor of lactic acid has been utilized in the field to mitigate corrosion (Nasr-El-Din et al., 2007). A borate gel with a high pH was used to transport solid beads in the study. The well was shut down 24 hours after the job was executed to enable the reaction to finish before beginning the flow back operation. Despite the fact that the solid beads were effectively inserted in the fracture, the acid employed in the fracture job did not greatly increase the production rate due to its delayed reactivity and limited dissolving power.

2.2.2 Retarded HCl-based acids.

There is a basic method available that utilizes pure HCl acid with no complex additions. HCl acid, on the other hand, interacts aggressively with carbonate rocks, especially at high temperatures, resulting in uneven acid dissolution along the crack. Even when different additives are used to address these concerns, pure HCl produces considerable corrosion at high temperatures. To address this issue, new acid systems and additives were designed to decrease corrosion and enhance acid penetration lengths. These additives can help slow down the process and limit fluid loss, resulting in greater acid penetration duration. However, in calcite formations, plain HCl acid

should not be used alone, especially in low permeability formations that require a long acid penetration distance (Nierode and Kruk 1973).

2.2.3 Gelled HCl acid based on a polymer.

Linear and cross-linked gelled acids are extensively employed as acid fracturing fluids. Guar is a polymer that is commonly used in gelled pad fluid and is generally cross-linked with borate. The above-mentioned mechanism, on the other hand, is incompatible with acid because it hinders crosslinking; borate demands a high pH environment. CMHPG (carboxymethyl hydroxypropyl guar) is a polymer that is often employed in HCl acid gelling and is typically cross-linked with zirconium chelate. Other guar derivatives that are commonly used include hydroxypropyl guar (HPG) and hydroxyethyl cellulose (HEC). Because of their high viscosity, such fluids are more retarded than ordinary HCl, allowing them to minimize the fluid loss rate (Barati and Liang 2014).

2.2.4 Emulsified HCl acid.

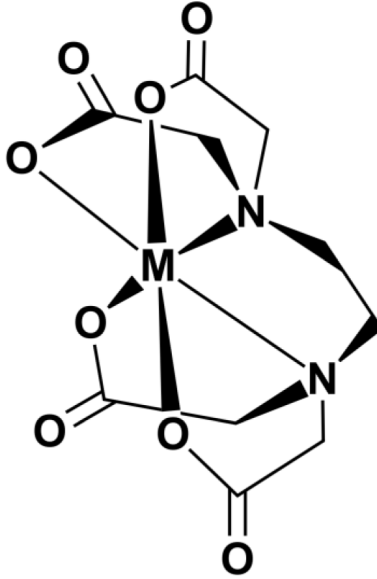
Emulsified acid is a viable solution for improving high-temperature carbonate reservoirs. It helps prevent fluid loss and enables deep acid penetration. However, it has some limitations, including limited acid stability. When using emulsified acid for high-temperature applications, it's important to add additional corrosion inhibitor loadings to prevent coiled tubing corrosion. Unfortunately, corrosion inhibitors can destabilize the emulsifier, reducing the stability of the emulsified acid. If there are ferric ions present in the system, the emulsion's stability may also decrease due to corrosion. Additionally, if the oil reservoir of the fracture contains high levels of asphaltene, scale precipitation can occur at the fracture face, which is another potential issue with using emulsified acid. (Mahmoud 2017).

2.2.5 Viscoelastic surfactant (VES) HCl acid based.

One option for fluids that cause less fracture damage is a viscoelastic surfactant (VES). Typically, VES is used as a diverter in acid fracturing operations, and the system's pH controls its viscosity. This increased viscosity allows for fluids to be redirected to less permeable zones. However, VES can be expensive, and its viscosity is reduced at high temperatures, which are its main drawbacks. (Barati and Liang 2014). It is important to note that the presence of ferric ions can greatly affect VES acid systems. These ions can interact with the VES, decreasing viscosity and potential damage to the fracture face. Additionally, the retention of carbonate reservoirs is a significant issue when using VES acid systems. To address these problems, internal and external breakers are necessary to reduce VES viscosity, especially in gas reservoirs (Mahmoud 2017).

2.3 Chelating agent fluids

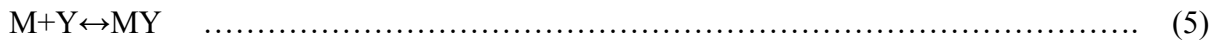
Standard acids like HCl can cause significant corrosion, poor penetration, and sludge buildup when exposed to high temperatures. To tackle these problems, researchers have suggested the use of organic acids. However, these acids can also present issues with solubility and compatibility. To combat these challenges, chelating agents have been proposed because of their ability to dissolve materials effectively, low levels of corrosion and sludge buildup, strong iron control, and environmentally friendly and highly degradable properties (Almubarak, Ng, and Nasr-El-Din 2017). Chelating agents are molecules with two or more groups capable of donating electrons to coordinate bonds with a central metal atom as a result of multiple coordinate bonds being formed by a single molecule, one or more heterocyclic rings are produced (Morgan and Drew 1920). Figure 5 shows the chelated rings.



3

Figure 5. Chelating agent rings containing cation (M) (Almubarak, Ng, and Nasr-El-Din 2017)

The stability constant of a chelating agent defines its affinity to a metal ion, the higher the stability constant, the more stable the chelated product. Equations (5) and (6) can be used to compute the stability constant (Shulman and Dwyer 1964).



$$\text{Stability Constant} = \log \left(\frac{[MY]}{[M][Y]} \right) \quad \dots\dots\dots (6)$$

In the oil and gas industry, chelating agents fluids refer to a subgroup known as aminopolycarboxylic acids such as glutamic acid (GLDA) , ethylenediaminetetraacetic acid (EDTA), diethylenetriaminepentaacetic acid (DTPA), hydroxyethylethylenediaminetriacetic acid (HEDTA) which are commonly used. The first trial for using the chelating agents as acidizing fluids was done by (Fredd and Fogler 1998b) and they have observed that wormholes similar to those generated by HCl but thinner and have better mechanical integrity (**Figure 6**).

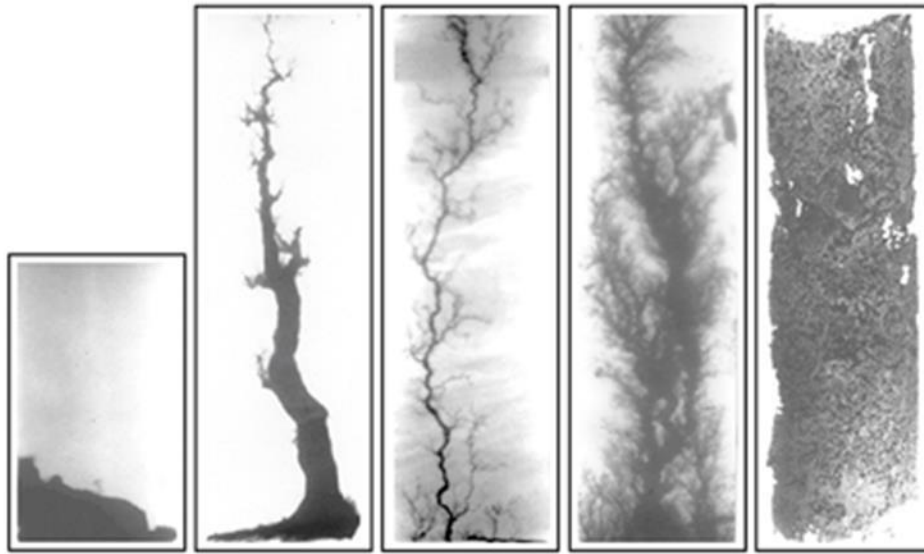


Figure 6. Acidizing experiments done by chelating agents (Fredd and Fogler 1998a)

2.3.1 L-Glutamic acid N, N-diacetic acid (GLDA)

GLDA (Figure 7) is used for iron management and reservoir acidification. In both water and highly concentrated acid solutions, GLDA is exceedingly soluble. Because it has larger groups attached to the imminodiacetic acid part, GLDA is less likely to crystallize. It is readily biodegradable since it is manufactured from L-glutamic acid or MSG. GLDA has also been demonstrated to be less corrosive than other chelating agents. In terms of stability constants, GLDA was discovered to be less stable than EDTA and HEDTA (Heus, Lammers, and Volmer 2013; LePage et al. 2011).

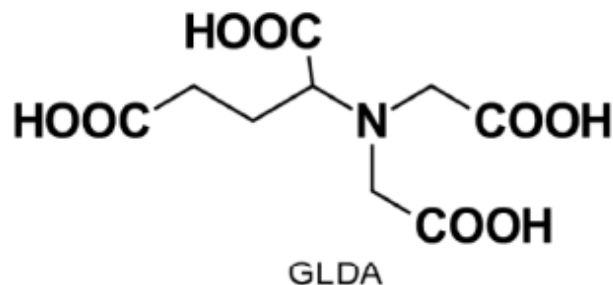


Figure 7. Chemical structure of GLDA

2.3.2 Ethylenediaminetetraacetic acid (EDTA)

In the oil and gas industry, EDTA is often used for scale removal, iron management, and stimulation fluid duties. It does, however, have significant drawbacks. One of these is that it is not easily biodegradable, which makes it illegal in several nations. Furthermore, because of its ampholytic nature, it is insoluble in water and less soluble in acid solutions. Because of these disadvantages, researchers are currently looking for alternatives to EDTA (**Figure 8**).

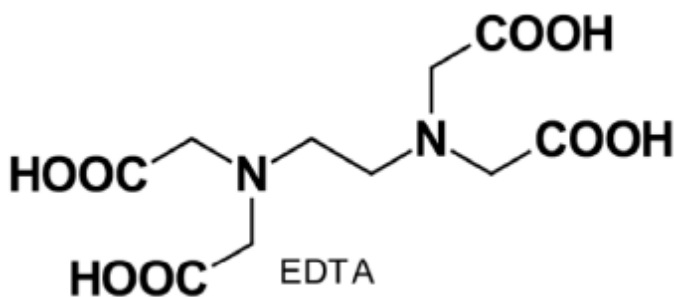


Figure 8. Chemical structure of EDTA

2.3.3 Diethylenetriaminepentaacetic acid (DTPA)

Figure 9 shows that DTPA has the highest stability constants compared to other chelating agents used in the petroleum industry. As a result, it is commonly used for scale removal as a basic

solution without causing any tube corrosion or toxic gas formation. However, it is important to note that this fluid is not biodegradable and may face solubility issues in acidic solutions and water.

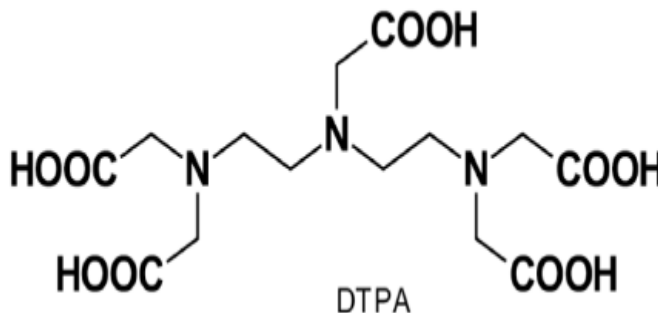


Figure 9. Chemical structure of DTPA

2.3.4 The dissolution mechanism of chelating agents

Chelating agents use a process called chelating agent-assisted dissolution to target mineral surfaces, like calcite or dolomite. This process involves two mechanisms: a solution coordination mechanism at high pH and a surface complexation mechanism at low pH.(Chang and Matijević 1983). There are two mechanisms involved in chelating agent adsorption on the surface. One of them is the surface complexation mechanism, which involves chelating agents binding to the surface. The other mechanism involves five steps (Carbonaro et al. 2008):

1. The chelating agent moves from the bulk solution to the surface.
2. The initial complex is adsorbed.
3. The adsorbed complex is converted into a form that can detach from the surface.
4. The complex is removed from the lattice.
5. The surface complex diffuses back into the bulk solution.

2.3.5 Chelating agent as acid fracturing fluids

Recent studies (Tariq, Aljawad, et al. 2021; Tariq, Hassan, et al. 2021) used acid fracturing fluids to investigate the impact of chelating agents on pure types of carbonate rocks (Austin chalk, Indiana limestone, and Silurian dolomite). The experiments were carried out with GLDA and EDTA and compared to plain 15% HCl. Under different closure stresses, viable conductivity results were obtained after treatment with chelating agents, as shown in **Figure 10**.

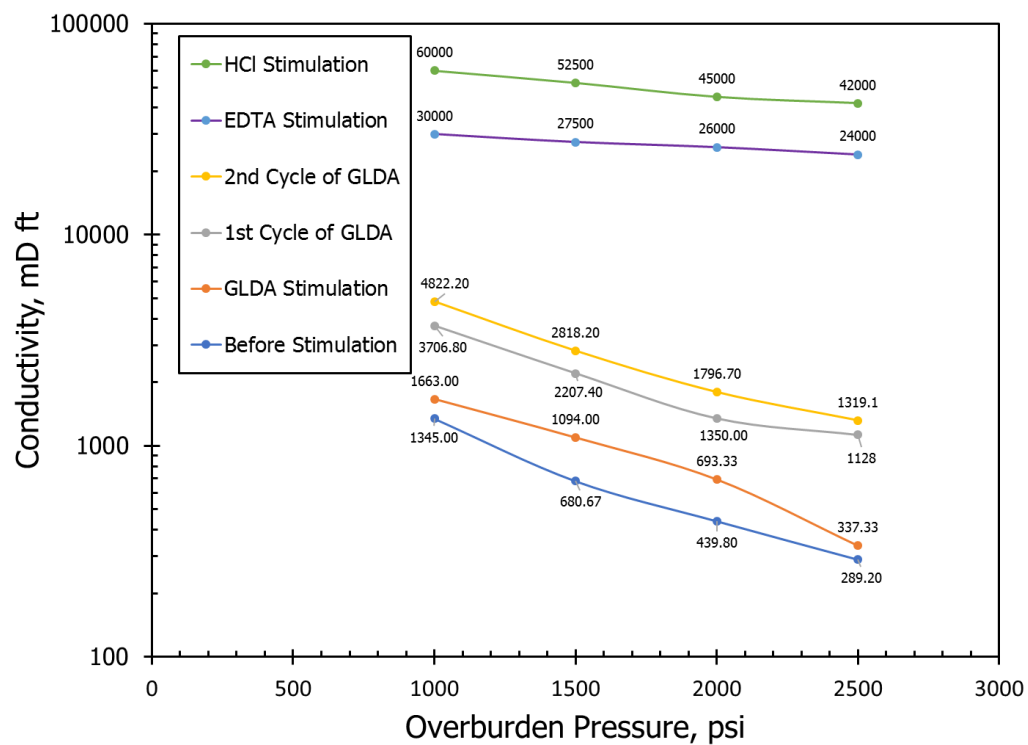


Figure 10. Conductivity comparison before and after stimulation with different stimulants

CHAPTER 3

METHODOLOGY

In this study, the experimental work was divided into two phases depending on the type of formation. According to the design of the study, there were layered and mixed carbonate samples that include minerals from Indiana limestone and Silurian dolomite formations. The first phase investigated the chelating agents on the layered mineral samples, while the second phase examined the mixed mineral samples which both exist in nature such as Khuff formation. The following procedure was applied in two phases to achieve the objective of the study to the referred formation.

3.1 Sample Preparation

Since layered carbonate samples were not available, samples were casted from carbonate rocks and cementitious materials for the first phase. Outcrop samples of Indiana limestone and Silurian dolomite will be crushed using a crushing machine to make powder samples. Each layer is composed of 60% cementitious materials of sand and cement in a 1:1 ratio, with the remaining 40% being carbonate mineral. A cubic block sample with dimensions of six inches on each side was casted as shown in the picture (**Figure 11**).

In the second phase, real reservoir mixed carbonate plug samples of dimensions 2 inches length and 1.5 inches diameter have been brought from the ARAB-D formation in Saudi Arabia and are a composite of dolomite and limestone with different percentages as determined by XRD measurements using an instrument from (company name and model) shown in **Figure 12**.



Figure 11. The casted block and cross section diagram of layered sample.

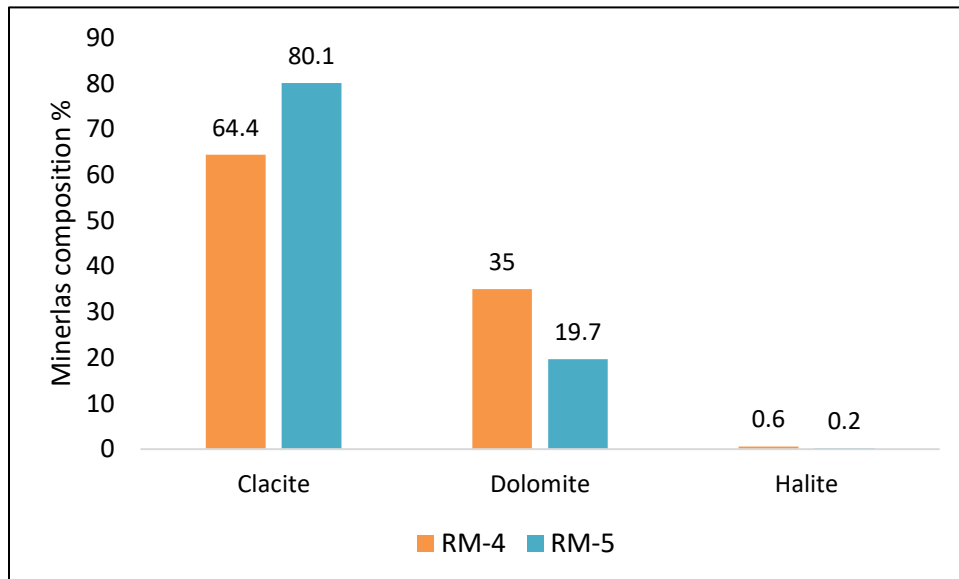


Figure 12. XRD measurements of reservoir samples showing different percentages of carbonate minerals

Then plug samples have been extracted utilizing a plugging machine from the casted block of dimensions 6 inches in length and 1.5 inches in diameter. A smooth fracture has been created on all samples by cutting the sample into two halves along the sample length horizontally, as shown in Figure 13, which shows the top view of the fracture surface of the layered samples. To prevent fluid from flowing out of the sample during the experiment, epoxy material has been applied over the sample, covering the inlet and outlet sides except the fracture surface (**Figure 14**). However,

the epoxy material does not react with acidic fluids, so acid invasion around the sample is not expected.

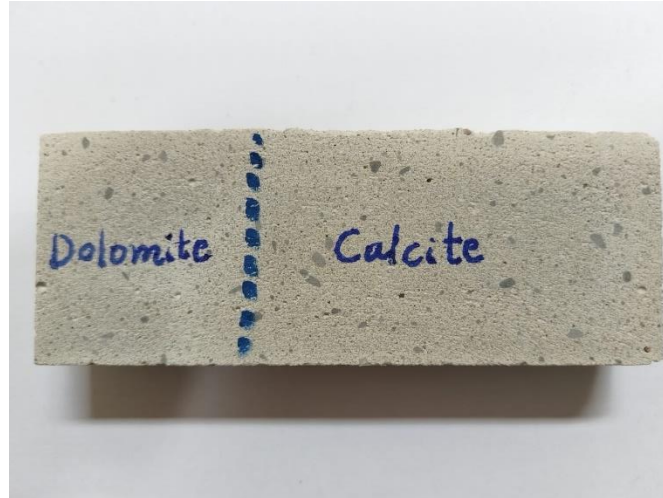


Figure 13. Top view of the fracture surface of the layered sample



Figure 14. The sample after covering by epoxy

3.2 Fracture Surface Roughness Measurement

The laser scanning profilometer (Kruss surface roughness analyzer—SRA) system was used to evaluate the fracture surface roughness (**Figure 15**), including 3D descriptions of the fracture surface pre and post acid treatment to visualize the fracture face etching at different scales. Typical confocal microscopes use a rotating pinhole disk to generate an image at each specified height to

scan an area of the sample. Rather than just holes, the disk inside the SRA has micro lenses, which increase light yield and allow for the analysis of low-reflectivity or even transparent surfaces. This device employs a laser displacement sensor to determine the variation in surface topography in the vertical direction (z coordinate) as a function of surface position (x and y coordinates). Measurements are taken as the sample is moved along its length (in the x direction) on a moving table. The sample is then moved 0.05 inch along its width (in the y direction), and measurements are taken along its length.



Figure 15. Laser profilometer scanner (THORLABS MB1530F/M)

3.3 Hardness Measurements

To evaluate the changes in rock hardness, the impulse hammer is utilizing the device developed by NER (Figure 16). The device is capable of characterizing the mechanical strength and elastic stiffness. In addition to that, the technique is non-destructive, even for soft materials, and provides point measurements that can be utilized to map evolutions in the mechanical properties. Pre-

treatment measurements of the fracture surface will be generated to evaluate the performance of the acid after the treatment, so another measurement must be done post-stimulation. The reduction in the generated data led to a result of rock softening.



Figure 16. AutoScan scanner

3.4 Fluids Preparation

In this study, five fluids were prepared to measure fracture conductivity and acid injection. Brine is to measure the fracture conductivity before and after the acid treatment. Four acids are used to treat the samples, as shown in **Table 1**.

Table 1. The details of the experiments

Sample Tag	Acid Name	pH	Sample type	Initial rock strength (GPa)
RM-1	15 wt% HCl	1.8	Layered	23.20
RM-2	20 wt% GLDA	4.0	Layered	25.90

RM-3	20 wt% EDTA	10.0	Layered	23.90
RM-4	15 wt% HCl	1.8	Heterogeneous	8.0
RM-5	20 wt% GLDA	4.0	Heterogeneous	8.30
RM-6	20 wt% DTPA	10.0	Heterogeneous	7.45

3.5 Sample Saturation

To saturate all samples with 3% KCl brine fluid, a Vinci-technologies automate saturator (Figure 17) is used. The vacuum is applied at the beginning to remove all air from pore spaces, and then brine is introduced to fill it up at atmospheric pressure. An injection pump connected with the saturator built in will pressurize the cell up to 2,000 psi to make sure that the samples are fully saturated with brine. The same brine is used to measure fracture conductivity pre- and post-acid treatment and to flush the sample to remove acidic precipitations.



Figure 17. Automated saturator by Vinci-technologies

3.6 Fracture Conductivity Measurements

A coreflooding setup is used to measure the fracture conductivity before and after the treatment to evaluate the acid performance of generating sustained conductive pathways. The coreflooding system (**Figure 18**) is composed of an injection pump, two accumulators to retain the brine and the acidic fluid, a core holder, a back pressure regulator (BPR), a fraction collector to collect effluent samples, and a differential pressure device to record the pressure across the sample during the fluid flow. Four injection rates—2.5, 5.0, 7.5, and 10. cm³/minute are used for each confining pressure out of four: 1000, 1500, 2000, and 2500 psi. Equation (7) is used to calculate the fracture conductivity for each closure stress.

$$kw_f = 8.023 \frac{q\mu\Delta p}{dL} \dots\dots\dots (7)$$

where the fracture conductivity (md-ft) is permeability (k) times fracture width (w_f), q is the injection rate in cm³/ minute, μ is the brine viscosity in centipoise, Δp is the differential pressure in psi, d is the sample diameter in cm, and L is the sample length.

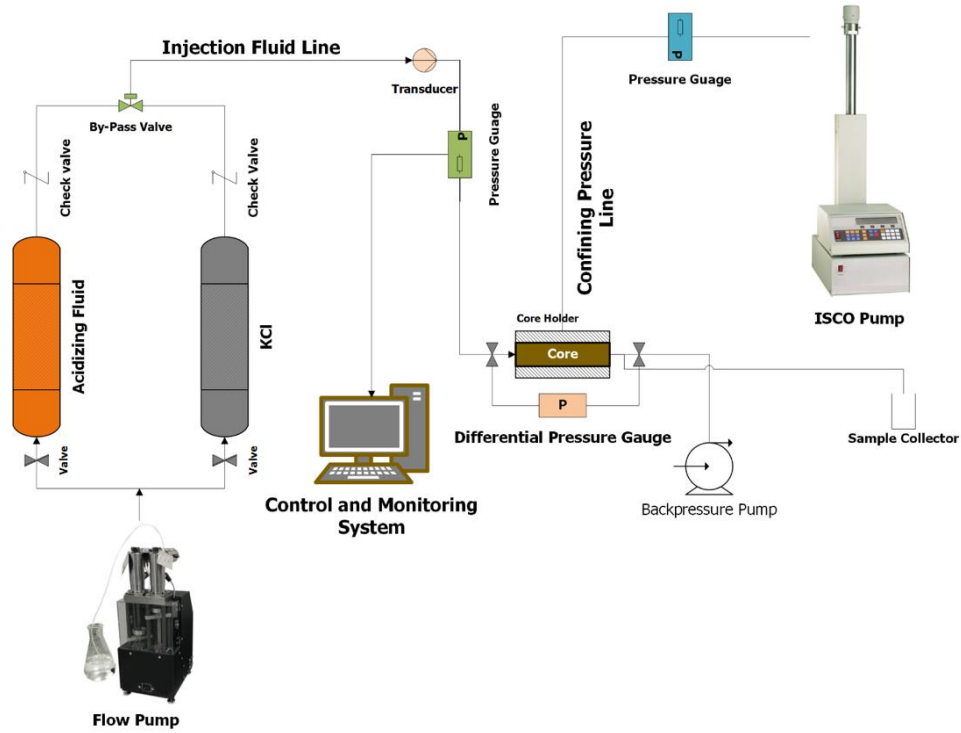


Figure 18. Schematic of coreflooding system (Tariq, Hassan, et al. 2021)

3.7 Acid Treatment

Several parameters play key roles in the process of acid treatment. Treatment time, flow rates, and temperature are crucial to having sufficient improvement in fracture conductivity. Since there is a difference in sample dimensions, a consistent procedure has been set for each phase. All treatment experiments have been set to a constant temperature of 100°C. For the layered samples, the dimensions are 15.24 cm in length and 3.750 cm in diameter. The mixed mineral samples measure 5.50 cm in length and 3.750 cm in diameter. 3 mL/minute injection for a duration of 30 minutes is designed for the layered samples, and in the mixed samples, the injection rate was 5 ml/minute for a duration of 20 minutes. The reason to increase the flow rates of the shorter ones is to avoid any dissolution at the fracture inlet, which could damage the sample.

3.8 Inductively Coupled Plasma (ICP) Measurements

During the stimulation, effluent samples will be collected at regular time intervals to evaluate the change in calcium and magnesium ions due to dissolution. Inductively coupled plasma optical emission spectrometry (Optima 8000 ICP-OES by PerkinElmer) will be utilized to analyze the collected samples (**Figure 19**).



Figure 19. ICP equipment (Optima 8000 ICP-OES by PerkinElmer)

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Layered Carbonate Reservoirs

The first phase of the study investigated layered synthesis samples composed of cementitious material, dolomite, and limestone. Roughness and hardness measurements have been done before and after the core flooding experiments. Sample saturating has been done to ensure there is no gas prior to the fracture conductivity evaluation. The results of fracture conductivity and acid stimulation are categorized as acid fracturing fluid based.

4.1.1 Coreflooding Results

a. Hydrochloric (HCl) Acid

Because HCl has a high dissolution power, it can etch larger volumes of fracture surfaces faster than any other fluid. After measuring conductivity, 30 minutes of acid injection were performed at an elevated temperature of 100 °C using a core flooding system (**Figure 18**); the total acid injected volume was 90 cm³. Figure 20 depicts the pressure profile before stimulation during conductivity measurements at designed rates and confining pressures (see the left part of the figure). The pressure profile increased during HCl injection due to the reaction at the fracture's inlet, then fluctuated during dissolution, resulting in a nearly zero pressure drop (see the middle of the figure). The effect of stimulation can be seen during post-stimulation conductivity measurements (as shown on the right side of the figure); there was a significant pressure drop, indicating improved fracture conductivity under the same closure stress.

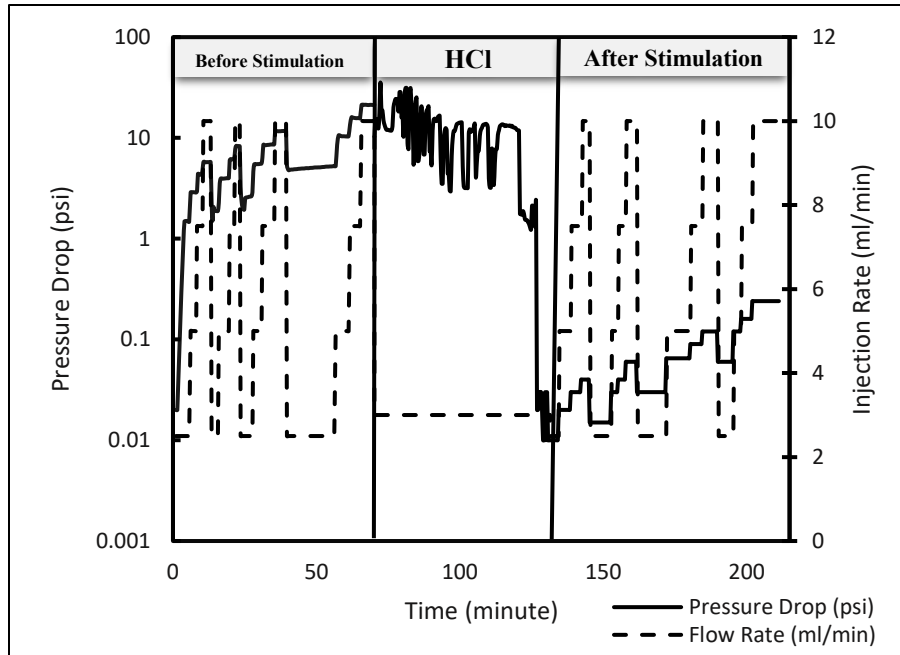


Figure 20. Pressure drop profile of HCl acid fracturing fluid treatment including before and after for conductivity measurement of layered sample

b. Glutamic Diacetic (GLDA) Acid

Figure 21 demonstrates the pressure drop along the length of the core before, during, and after GLDA stimulation. Before the treatment, fracture conductivity was measured at the specified flow rates and confining pressures. During GLDA stimulation, the pressure increased while the acid was flowing over the fracture surface. The pressure drop then nearly reached zero, indicating the presence of a conductive channel within the fracture face. The pressure drop after stimulation was lower than the pressure profile before stimulation. At the highest injected rate of 10.0 cm³/minute and a closure pressure of 1,500 psi, the differential pressure dropped from 8.5 psi to 2.8 psi.

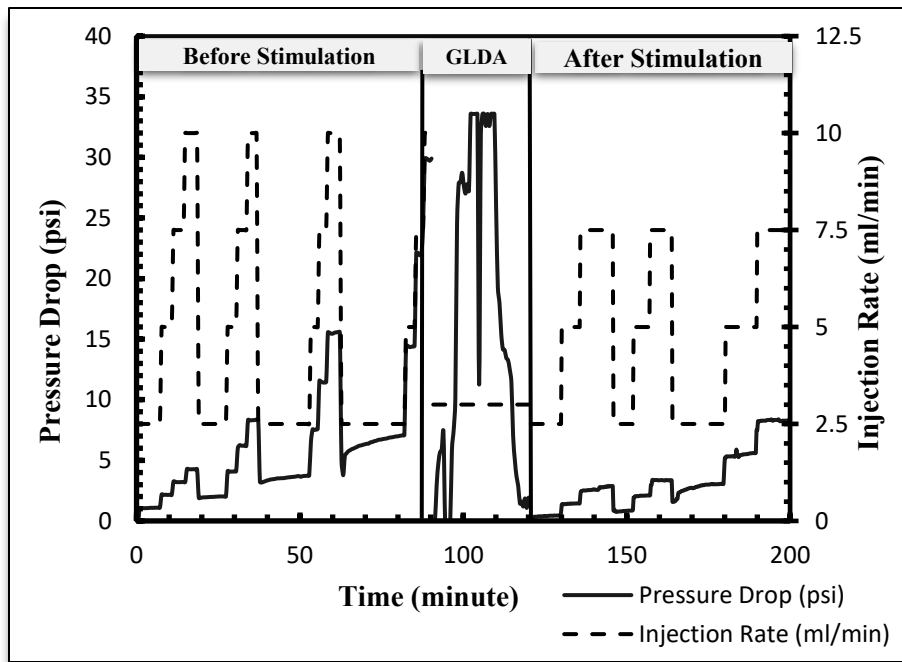


Figure 21. Pressure drop profile of GLDA fracturing fluid stimulation including pre- and post- conductivity measurement

c. Ethylene Diamine Triacetic (EDTA) Acid

Aminopolycarboxylic acid is a good replacement for stimulation, iron control, and scale removal (Almubarak, Ng, and Nasr-El-Din 2017). The same procedure was used with EDTA. Because EDTA is effective at high pH, the concentration used was 20% with a pH of 10. Figure 22 illustrates the effect of EDTA on the layered sample. The experiment was carried out with a core flooding system at four different injection rates to measure conductivity before and after acid injection. The EDTA treatment injection rate was 3.0 cm³/minute. Several samples of effluent were collected for geochemical analysis. The graph represents similar behavior to previous treatments, with the pressure dropping at the end of the treatment. Even though the pressure data were lower after treatment, indicating improved fracture conductivity, the improvements were minor when compared to the two acidic fluids.

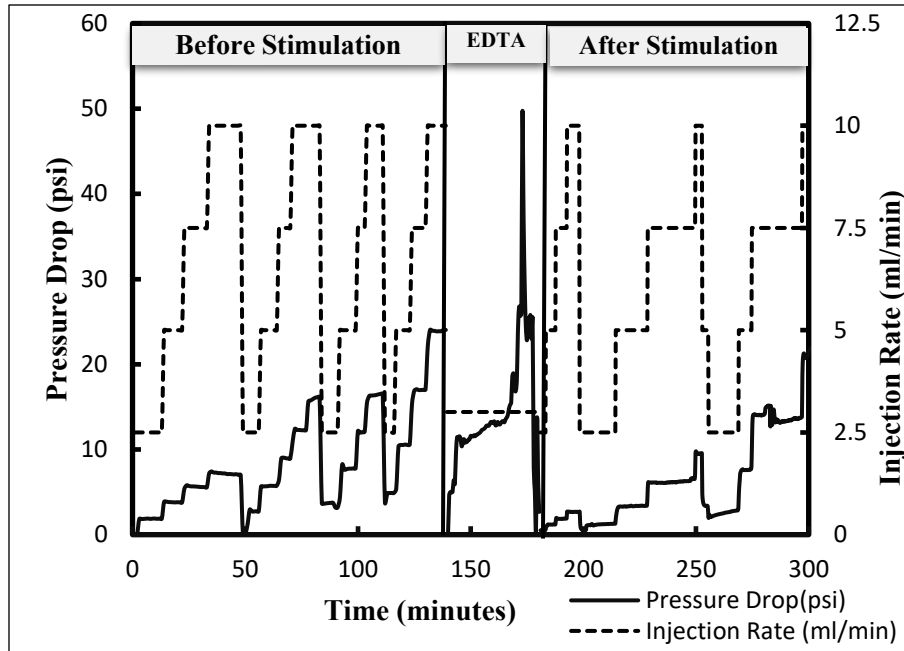


Figure 22. Pressure drop profile of EDTA fracturing fluid treatment including before and after for conductivity measurement

4.1.2 Fracture Conductivity Results

The fracture conductivity of all samples was measured before and after acid etching experiments. The conductivity was examined at four different closure stress values: 1,000, 1,500, 2,000, and 2,500 psi. The pressure drop for each closure stress was measured using four injection rates (2.5, 5.0, 7.5, and 10.0 cm³/minute). **Figure 23** depicts the trend of the three samples' average values prior to stimulation. Because of the strength of HCl dissolution, the improvement in fracture conductivity by HCl acid fluid is noticeable and expected. The measured fracture conductivity after GLDA treatment is approximately 20 times higher than before stimulation. EDTA treatment is less effective than GLDA but still improves fracture conductivity compared to before stimulation as it can be seen in **Figure 24** which shows the fracture conductivity evolutions in percentage.

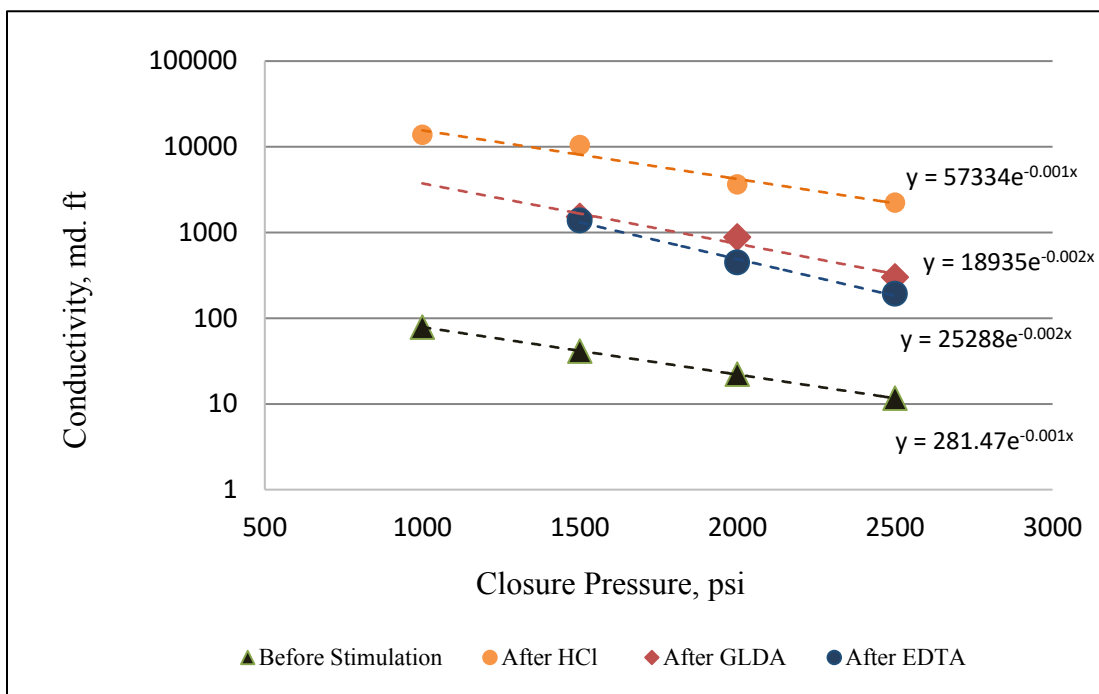


Figure 23. Fracture conductivity values pre and post acid stimulation

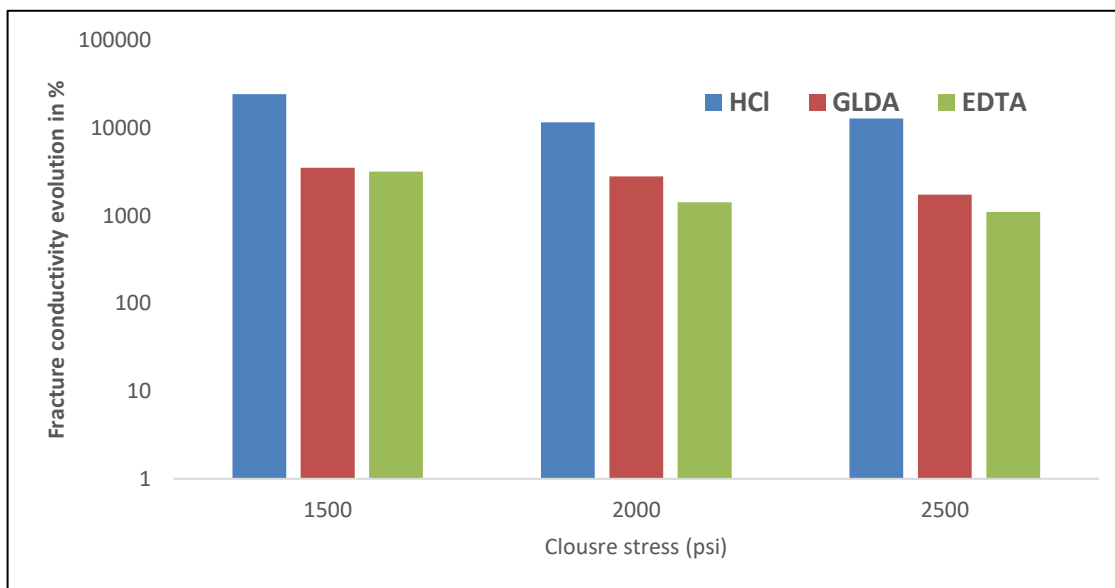


Figure 24. Fracture conductivity evolution across the closure stress.

4.1.3 Roughness, Hardness, and Imaging Analysis

The dissolution power plays an important role in changing the roughness of the fracture surface. The data in **Figure 25** represents the changes in average roughness between pre- and post-stimulation. It demonstrates that the acid fracturing fluid HCl caused the greatest change in surface roughness due to its high dissolving power and fast reaction kinetics when compared to other fluids. The less reactive fluids also caused changes in surface roughness, but GLDA is more reactive than EDTA. Any change in surface roughness, on the other hand, can improve fracture conductivity. It should be noted that the roughness produced by GLDA and EDTA was comparable.

Figure 26 illustrates the performance of each acid fracturing fluid used using images generated by a laser profilometer scan. The injection was made from the dolomite layer side; the images clearly show that the most affected layer is calcite, where a larger area was dissolved, particularly by HCl. Due to its lower reactivity, the rock sampled with EDTA was less impacted during treatment. The strong performance of HCl in creating continuous clear channels from the inlet to the outlet of the treated sample can be seen. GLDA could also generate a channel, but it would be shallower, especially in the dolomite section.

Although HCl acid treatment generated the highest fracture conductivity, it also caused mechanical damage to the rock. This may influence long-term fracture conductivity because harder rocks can keep the channel open for longer periods of time. **Figure 27** shows that HCl reduced the initial average hardness of the sample by 70%, from 26 GPa to 8 GPa. GLAD and EDTA, on the other hand, reduced the rock strength to 13.6 GPa and 20.5 GPa, respectively. As a result of the less damaging impact, it is possible that GLDA stimulation results in greater extended fracture productivity than HCl.

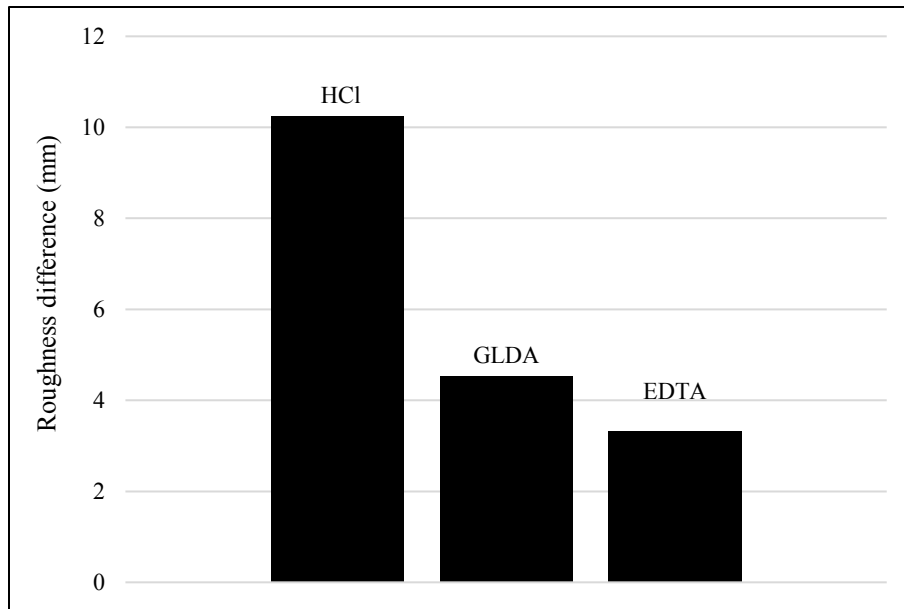


Figure 25. The evolutions of fracture surface roughness between pre-and post-treatment in the three: HCl, GLDA and EDTA

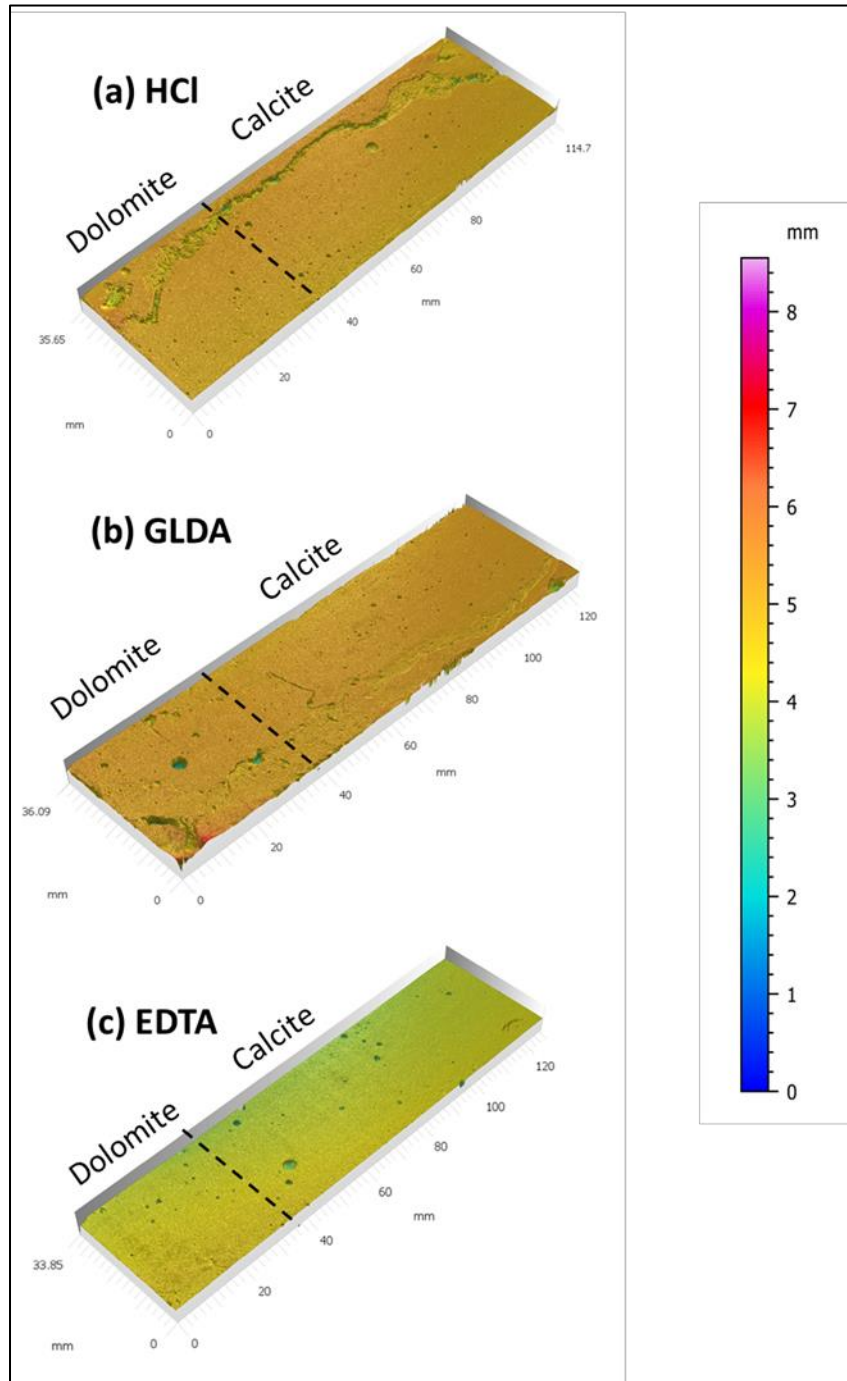


Figure 26. Fracture surface profile of the samples after the acid treatment by HCl (left), GLDA (middle) and EDTA (right)

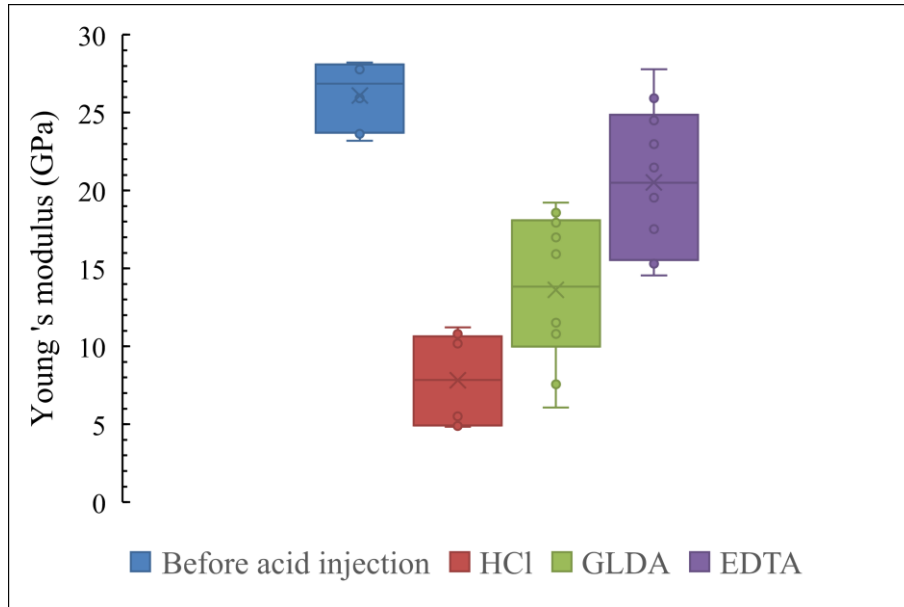


Figure 27. Hardness results of the three examined samples after the stimulation

4.1.4 ICP Analysis and Dissolution

Throughout acid fracturing fluid stimulation, effluent samples were collected at regular intervals to quantify rock dissolution. **Figure 28** shows that the average calcium concentrations for HCl, GLDA, and EDTA were 4,000, 2,500, and 1,500 mg/L, respectively. While the average magnesium concentrations for HCl, GLDA, and EDTA were 1,000, 100, and 50, respectively, as shown in **Figure 29**. In comparison to the other two fluids, HCl injection resulted in the highest dissolved amount of both ions. Chelating agents demonstrated the feasibility of dissolving carbonate minerals in **Figures 28** and **29**. It confirms the previous sections' findings that HCl has the fastest reaction kinetics, followed by GLDA and EDTA. Although GLDA demonstrated superior dissolution in this study, this may not always be the case. Because the pH of the system has a significant impact on dissolution, more testing of different pH ranges is required.

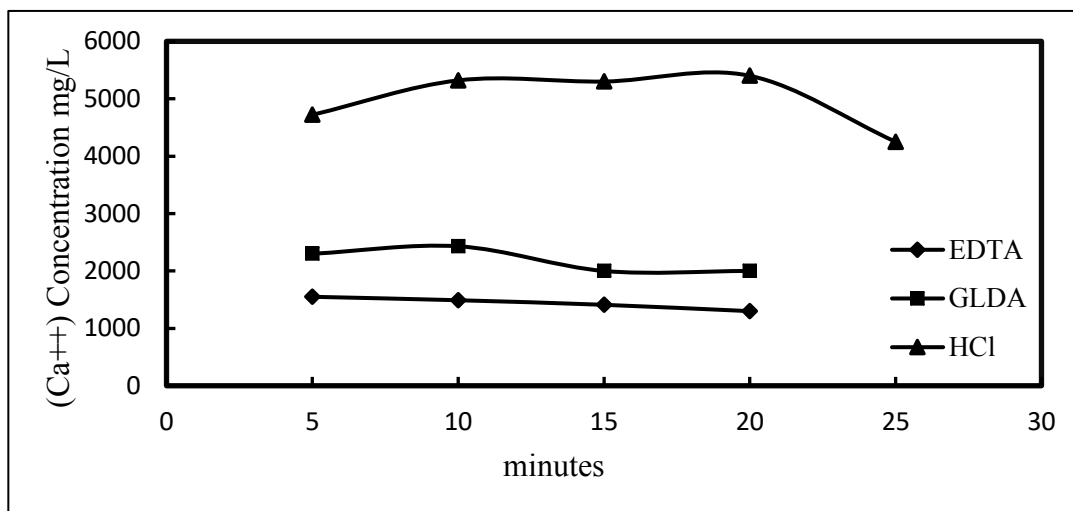


Figure 28. ICP analysis of collected samples of calcium (Ca) concentration during HCl, GLDA and EDTA treatment process.

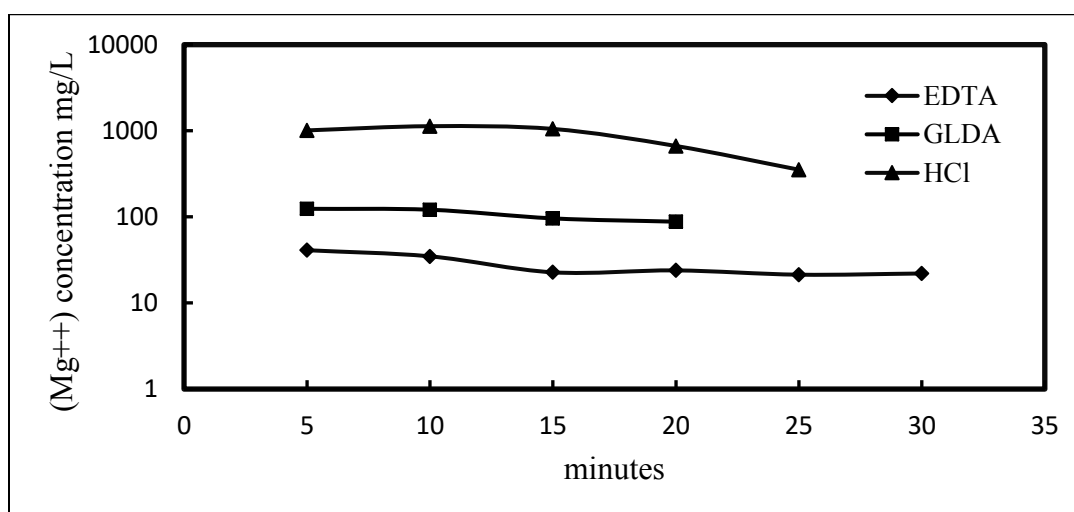


Figure 29. ICP analysis of collected samples of magnesium (Mg) concentration during HCl, GLDA and EDTA stimulation process.

The sample weights before and after the fluid injection were measured to determine the amount of dissolution in terms of mass. In comparison to the chelating agents, the HCl fluid is found to have etched deeper on the fracture surface, resulting in a larger volume being dissolved and thus a larger change in weight being observed. **Table 2** shows the results of stimulated samples.

Table 2. Pre- and post- stimulation mass data of the samples

Sample number	Pre-injection mass (grams)	Post-injection mass (grams)	Stimulation fluid	Dissolution amount (grams)
RM-1	290.283	287.129	HCl	3.154
RM-2	295.7	294.497	GLDA	1.203
RM-3	307.912	306.808	EDTA	1.104

4.2 Mixed Minerals of Carbonate Reservoirs

The presence of carbonate in some reservoirs is in a mixture shape in terms of mineralogy. In Saudi Arabia, the most famous reservoir that has a mineralogy mixture is the Khuff formation, which contains the carbonate minerals in a variety of percentages. The heterogeneous samples were examined, and the same procedure was applied: creating a smooth fracture, epoxy coating, and roughness and hardness measurements. Then, the samples were saturated before fracture conductivity measurements and acid injection treatments. After acid treatment, roughness, hardness, and fracture conductivity were measured to observe the evolution of the fracture surface.

4.2.1 Coreflooding Results

a. Hydrochloric (HCl) Acid

The same procedure has been applied to coreflooding experiments starting with fracture conductivity measurements prior the acid treatment. Before the coreflooding, the sample was saturated with brine of 3% KCl. Four injection rates (2.5, 5, 7.5, and 10) cm³/minute were used

each time to measure the fracture conductivity under four closure stresses (1,000, 1,500, 2,000, and 2,500) psig. For each flow rate, the stabilized differential pressure drop was recorded. HCl was injected into the fracture surfaces to generate etching along the length for 10 minutes at rate 10 ml/minute. The reason behind high injection rate is due to the length of sample to speed up the flow at the fracture face and avoiding the acid accumulation. Figure 30 shows the differential pressure and injection rate before, during, and after stimulation. The middle section of the figure shows the treatment differential pressure which reach zero psi at the end of the treatment.. A clear evidence to the fracture conductivity improvement was illustrated by the post treatment measurements. A significant pressure drop reduction was noticed even at high closure stress and high injection rate.

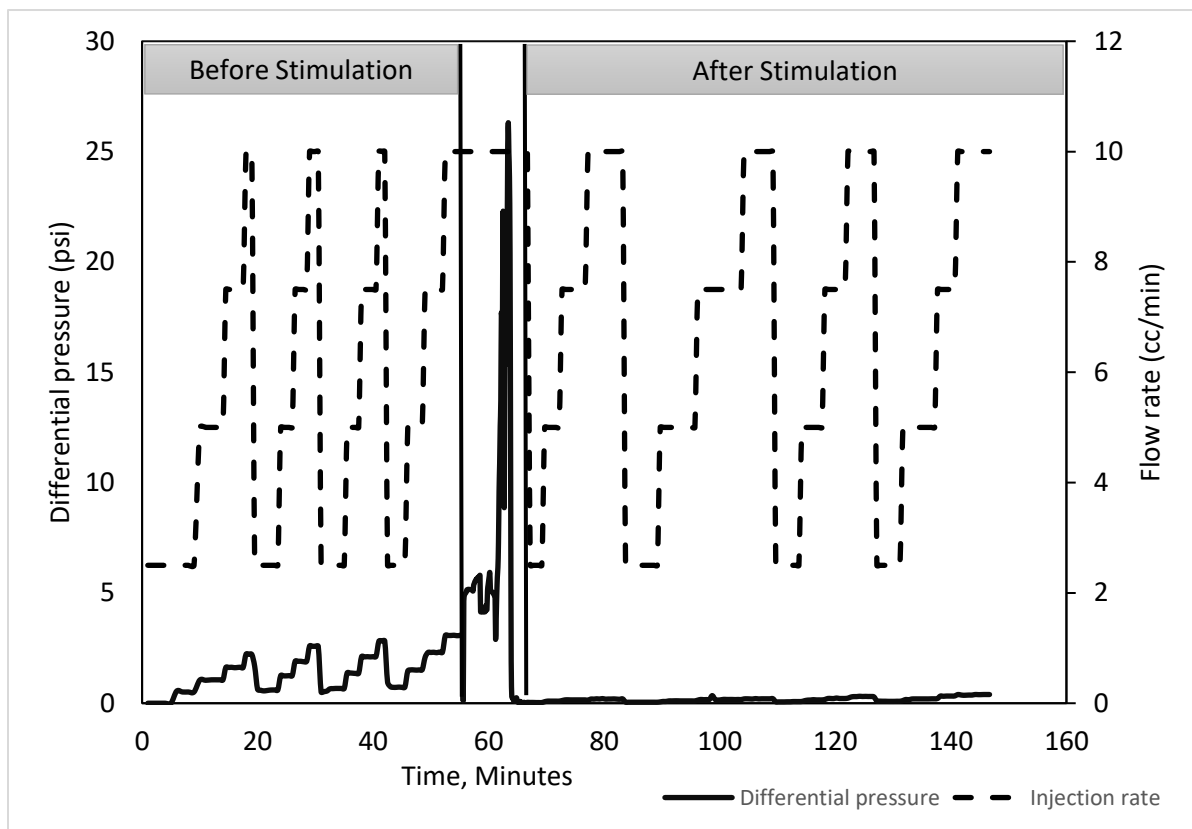


Figure 30. Pressure drop profile before, during, and after HCl acid fracturing treatment in a heterogeneous sample.

b. Glutamic Diacetic (GLDA) Acid

Figure 31 shows the differential pressure drop before, during, and after GLDA injection in the heterogenous carbonate sample. The first part (left) illustrates the pressure drop before acid treatment and compares it with the measurement after treatment utilizing 3% KCl brine. Four different injection rates were used under four different closure stresses. Then in the middle part of the figure, GLDA was injected into the fracture space for 17 minutes at 5 mL/minute to generate etching along the fracture surface. The dissolution power of GLDA is lower than HCl, so lower flow rate is considered as well. The increase in pressure at the beginning of GLDA injection is due to carbonate and GLDA interaction. The sharp reduction indicates that the channel between the sample inlet and outlet was generated. The right part provides prove that GLDA improved the fracture conductivity due to the pressure drop reduction for same flow rates and closure stress. At closure stress of 1,500 psig and 10 mL/ minute flow rate, the pressure decreased from 4.5 to 0.6 psig.

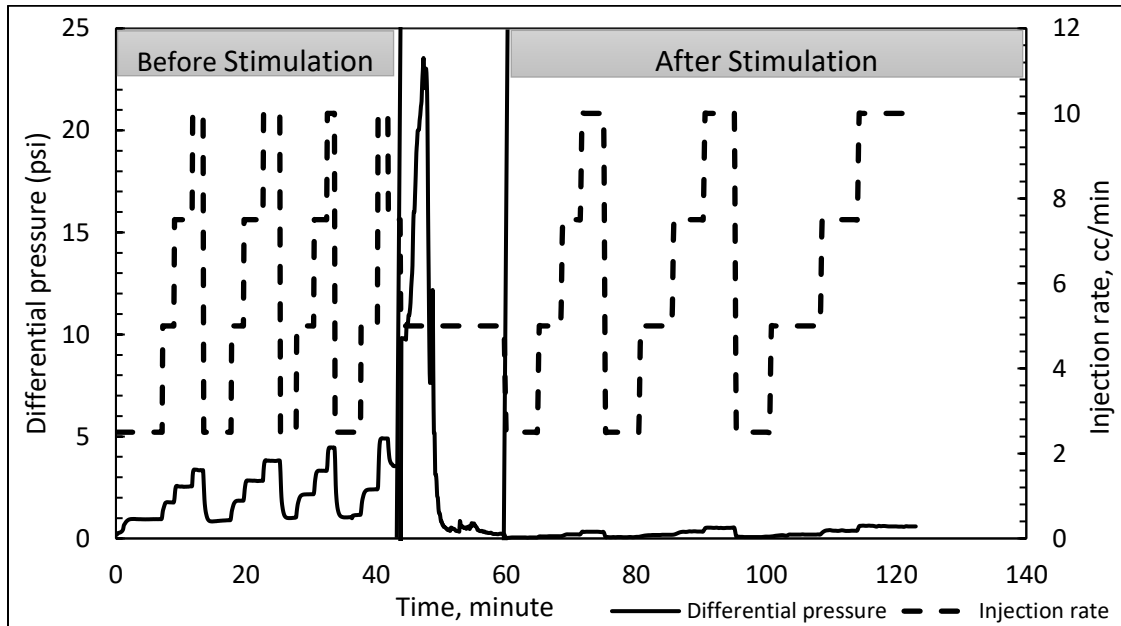


Figure 31. Pressure drop profile of GLDA acid fracturing fluid treatment including before and after for conductivity measurement of heterogeneous sample

c. Diethylene Triamine Pentaacetic (DTPA) Acid

In **Figure 32**, a pressure drop was recorded first during the fracture conductivity measurements prior to the acid treatment. Four different injection rates (2.5, 5.0, 7.5, and 10.0) cm³/minute were utilized in this stage by brine of 3%KCl under four closure stresses. Then, DTPA was injected into fracture for around 20 minutes at 5.0 mL/minute to examine its outcomes compared to the HCl acid. Remarkably, distinct behavior was noticed of this fluid during the stimulation time. Pressure fluctuations reached to around 45 psig led to nearly zero psig at the end of the treatment. Post stimulation (the right part) measurements, same brine was injected to evaluate the performance of the pressure drop after DTPA injection. The measurements showed that minor improvement in the pressure drop.

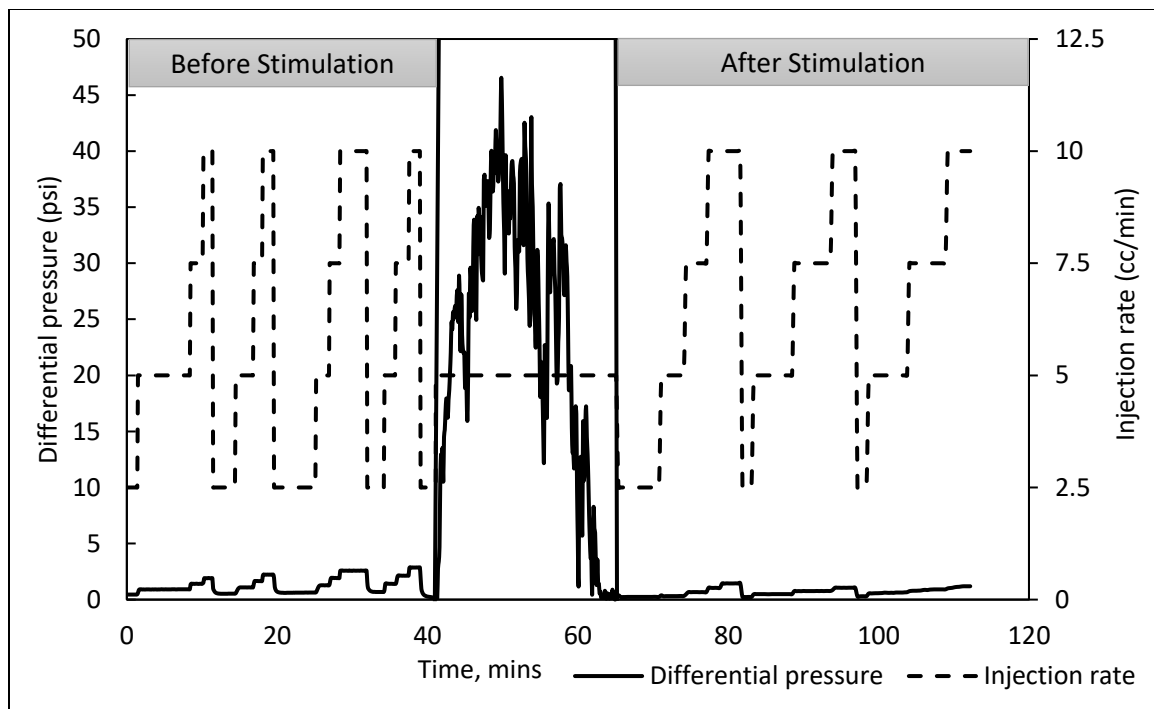


Figure 32. Pressure drop profile of DTPA acid fracturing fluid treatment including before and after for conductivity measurement of heterogeneous sample

4.2.2 Fracture Conductivity Results

Figure 33 summarizes the results of fracture conductivity measurements utilizing equation (3) and recorded differential pressure for each sample pre- and post-acidic treatment. The average fracture conductivity was taken for each closure stress, as represented in the figure. In general, chelating agents proved to sustain fracture conductivity sufficiently compared to HCl. It could be that the high pH level of DTPA caused the relatively lower performance compared to the low pH GLDA. The data in figure 33 could be fitted with an exponential equation, which shows that the fracture conductivity exponentially declines with the increase in closure stress. Usually, the fracture conductivity decreases with time as closure stress increases, and the samples treated by GLDA and DTPA showed no significant changes in the trend, indicating that chelating agents, especially GLDA, could be a good alternative to conventional acid.

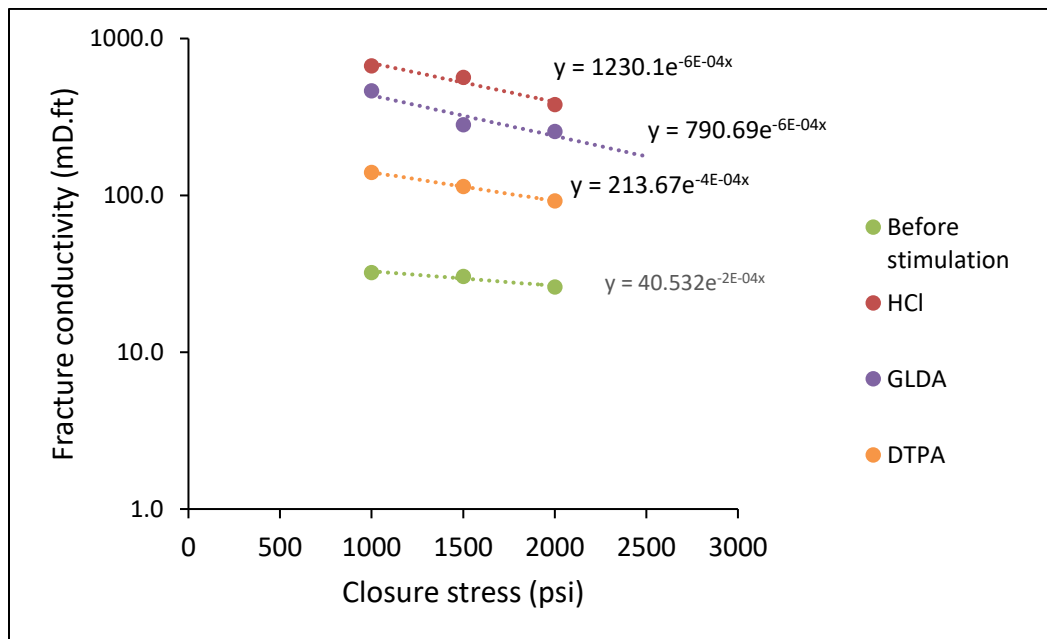


Figure 33. Fracture conductivity values pre and post acid stimulation in heterogeneous carbonate samples

4.2.3 Hardness, Roughness, and Imaging Analysis

Figure 34 depicts the obtained results of hardness changes between the initial measurement and the results after acid treatment. The initial measurement prior to the acid stimulation yielded a range of 7.5-8.2 GPa Young's modulus (YM). The results after the treatment showed that due to the higher dissolution on the fracture surface, DTPA showed more than 50% reduction in YM. Surprisingly, HCl and GLDA showed lower impact than DTPA. Nevertheless, HCl acid reduces the rock strength to a larger extent as compared to GLDA.

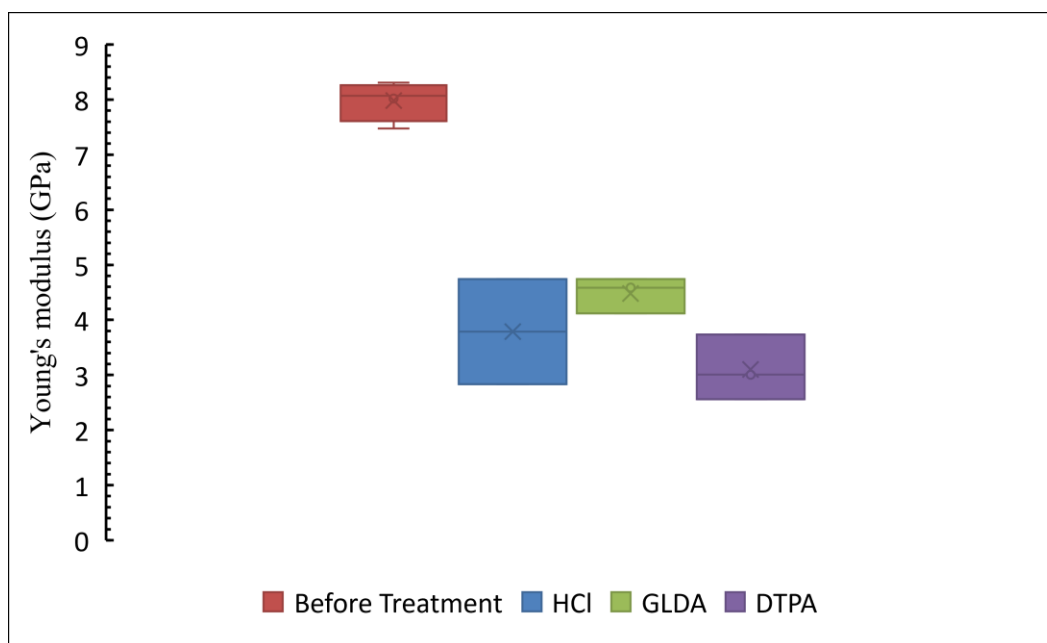


Figure 34. Strength measurements evolutions of the three treated samples pre and post stimulation

Figure 35 represents the roughness change in percentage between pre- and post-acidic treatment. The roughness data was given from the profilometry device in micromillimeter units, but that's not representative in this case since the samples are not homogeneous. Relatively, DTPA is giving high evolution compared to GLDA, although HCl is providing the highest change. The reason is due to the dissolving power of DTPA and the fact that it has five carboxylic groups beside the

three amino atoms, which make it one of the strongest chelating agents. Close results were obtained for HCl and DTPA of 64% and 62%, respectively, while half of that was obtained for GLDA.

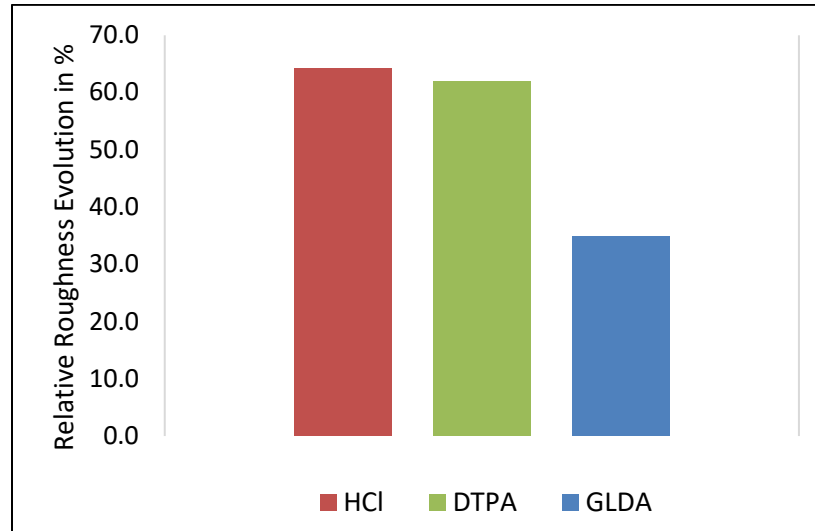


Figure 35. Roughness evolutions in percentage of the three examined samples.

Figure 36 shows the behaviour of HCl etching over the fracture surface through image obtained using the laser profilometer. Clear channeling pattern, however there is a minor penetration into the sample then back to continue the flow. At the fracture outlet side, HCl generated three parallel channels which is providing an evidence that high injection rate the better to improve fracture

conductivity by generating multiple pathways. However, deeper channel is not feasible as well for long term since the closure stress is increasing thus the fracture closed.

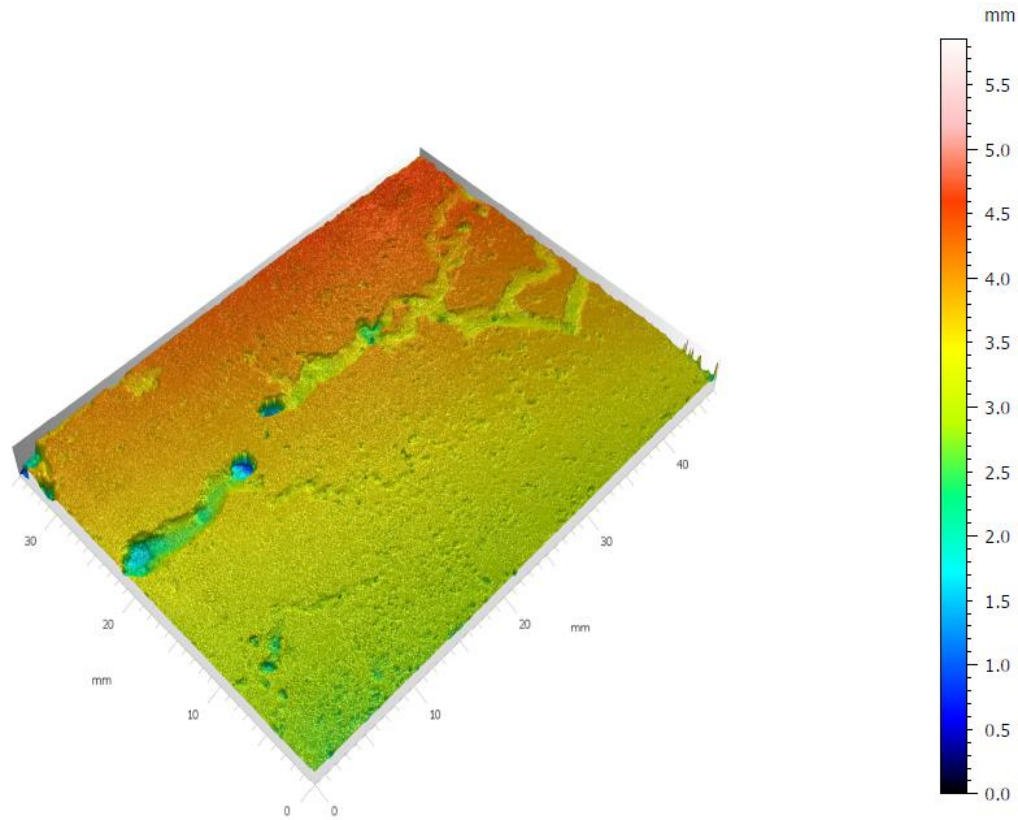


Figure 36. Image illustration of examined sample by HCl between pre and post treatment.

In the GLDA treatment, different etching behavior was observed, as represented in Figure 37. Because GLDA is less reactive than HCl acid, the fluid treated the sample from the edges. As shown in **Figure 33**, the generated channel was sufficient to improve fracture conductivity. Another channel may be created over the fracture surface for long-term treatment at the same or lower injection rate. In this case, a rougher surface in different areas of the surface was required to prevent the fracture from completely closing.

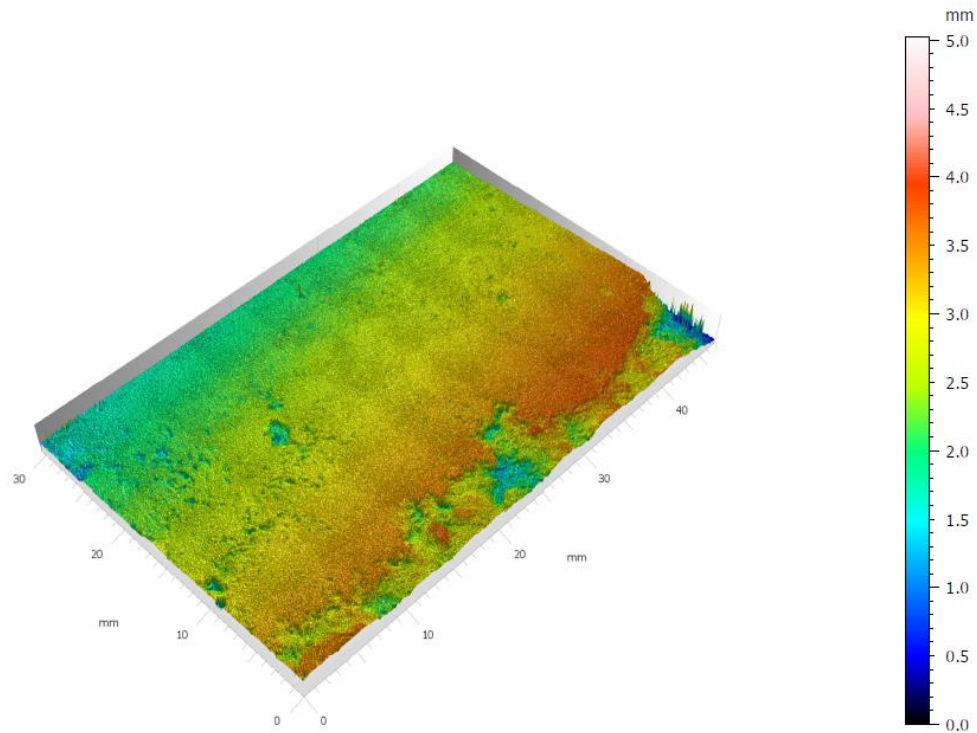


Figure 37. Image illustration of examined sample by GLDA between pre and post treatment.

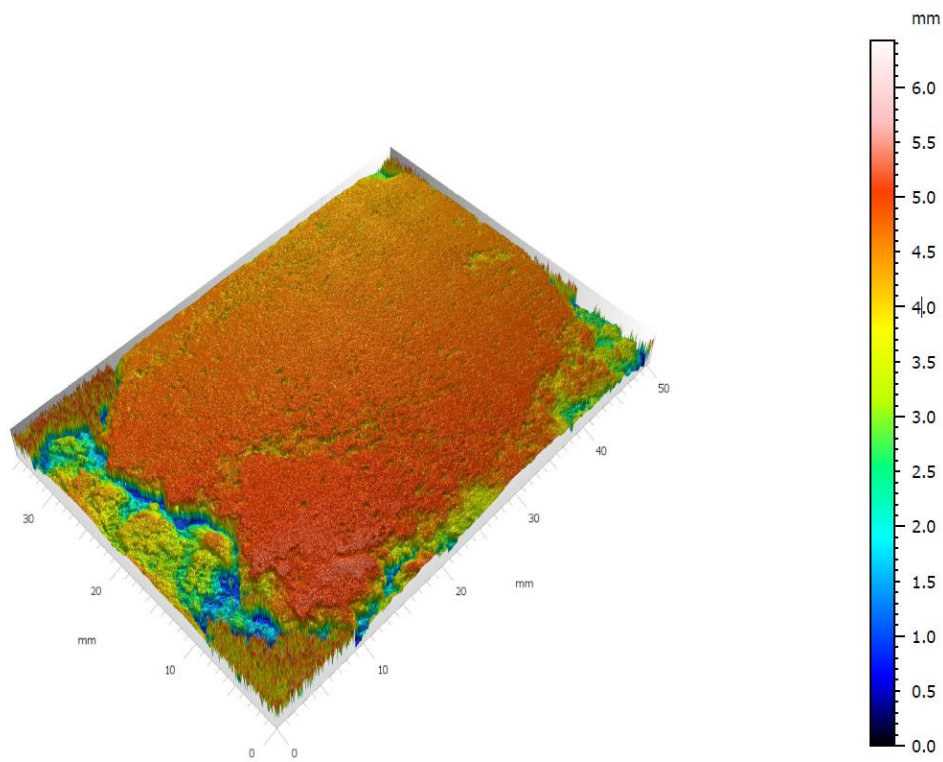


Figure 38. Image illustration of examined sample by DTPA between pre and post treatment.

The representation in **Figure 38** shows how DTPA behaves when it is introduced as an acid fracturing fluid. In the pressure profile (**Figure 32**), there was a fluctuating trend resulting in this kind of pattern. DTPA dissolved the inlet side perpendicular to the flow direction and generated a kind of uniform pattern leading to low fracture conductivity results, then treated the edge of the sample. In addition, the fracture conductivity measurements of the sample stimulated by DTPA showed minor improvement (**Figure 33**).

4.2.4 ICP Analysis

Figures 39 and **40** show the evaluation of dissolved ions of calcium (Ca) and magnesium (Mg) in mg/L for randomly collected samples during the three acid treatment processes. Since the samples do not have the same percentage of carbonate minerals, the variety of concentrations obtained is expected. It can be clearly seen the difference between the three trends in each figure, which give an indication of how capable the fluid is of dissolving calcite and dolomite. The amount of calcium dissolved is higher than magnesium due to the presence of calcium in both calcite and dolomite. DTPA is giving the highest amount in both figures, followed by HCl, and GLDA is the lowest. Although GLDA fluid provided small amounts of dissolved ions, it had better fracture conductivity than DTPA.

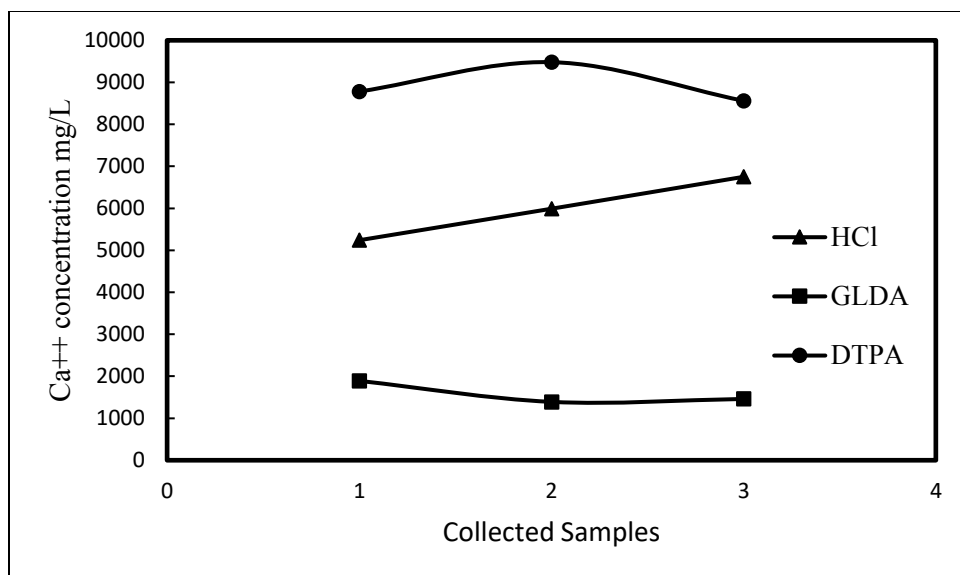


Figure 39. ICP analysis of collected samples of calcium (Ca) concentration during HCl, GLDA and DTPA treatment process.

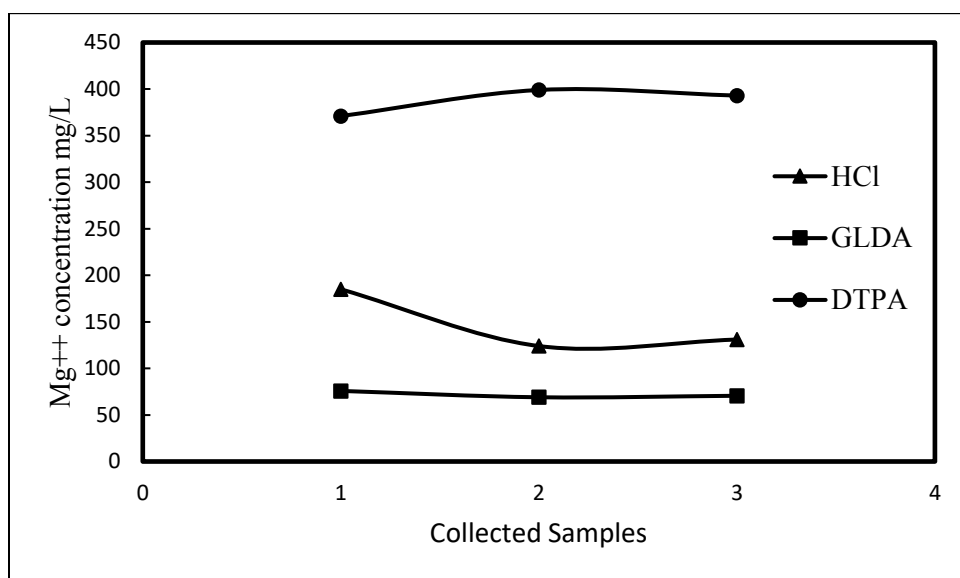


Figure 40. ICP analysis of collected samples of calcium (Mg) concentration during HCl, DTPA and EDTA treatment process

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusions

The study has proposed environmentally friendly fluids as alternatives to the conventional acid fracturing fluid to enhance the fracture conductivity in layered and mixed minerals in carbonate reservoirs. Experimental work has been done by studying the pre-roughness, rock strength, and fracture conductivity before the acid injection across the sample fracture to evaluate the evolutions afterward. In the first phase, chelating agents GLDA and EDTA provided sufficient improvement in fracture conductivity compared to HCl under varying closure stresses, indicating the feasibility of chelating agents to utilize in the layered mineralogy of carbonate reservoirs. The evolution in roughness and rock strength also was obvious, especially in GLDA, as shown in the image, which has generated a channel pattern over the fracture surface while EDTA uniform unclear pattern.

In the second phase of downhole carbonate samples, the fracture conductivity was examined after acid treatment by GLDA and DTPA. The fracture conductivity of both treatments showed improvement; however, the sample treated with GLDA significantly improved. DTPA fluid showed different behavior to the rock strength and roughness. In the imaging, DTPA treated the fracture surface perpendicular to the flow direction in a uniform pattern due to the dissolving power of DTPA. In the last measurement of both phases, ICP analysis showed evidence of the feasibility of chelating agents to dissolve the carbonate samples by quantifying calcium and magnesium ions.

5.2 Recommendations

For more investigation about this research in the future, the optimal acid fracturing fluid-rock contact time could be achieved by performing several experiments at various times, the optimum pH for each fluid of chelating agents, and modeling of the fracture conductivity improvement to consider more parameters. It is also good to perform CT imaging to quantify the dissolution volume generated by the fluid. Molecular dynamic simulation (MDS) between the minerals and chelating agents could also be utilized to understand the fracture surface and fluid interaction better.

REFERENCES

- Almubarak, Tariq, Jun Hong Ng, and Hisham Nasr-El-Din. 2017. "Chelating Agents in Productivity Enhancement: A Review." *Society of Petroleum Engineers - SPE Oklahoma City Oil and Gas Symposium 2017*, no. March: 88–112. <https://doi.org/10.2118/185097-ms>.
- Anderson, M S, and S E Fredrickson. 1989. "Dynamic Etching Tests Aid Fracture-Acidizing Treatment Design." *SPE Production Engineering* 4 (04): 443–49.
- Barati, Reza, and Jenn-Tai Liang. 2014. "A Review of Fracturing Fluid Systems Used for Hydraulic Fracturing of Oil and Gas Wells." *Journal of Applied Polymer Science* 131 (16).
- Beg, M. S., A. O. Kunak, Ming Gong, Ding Zhu, and A. D. Hill. 1998. "A Systematic Experimental Study of Acid Fracture Conductivity." *SPE Production and Facilities* 13 (4): 267–71. <https://doi.org/10.2118/52402-pa>.
- Broadbent, G. C., J. A. Knox, and S. E. Fredrickson. 1968. "Dynamic Etching Tests and Their Use in Planning Acid Treatments." *Society of Petroleum Engineers - SPE Oklahoma Regional Meeting, ORM 1968*. <https://doi.org/10.2523/2362-ms>.
- Carbonaro, Richard F, Benjamin N Gray, Charles F Whitehead, and Alan T Stone. 2008. "Carboxylate-Containing Chelating Agent Interactions with Amorphous Chromium Hydroxide: Adsorption and Dissolution." *Geochimica et Cosmochimica Acta* 72 (13): 3241–57.
- Chang, Han-Chyen, and Egon Matijević. 1983. "Interactions of Metal Hydrous Oxides with Chelating Agents: IV. Dissolution of Hematite." *Journal of Colloid and Interface Science* 92 (2): 479–88.
- Domelen, M S Van. 1992. "Optimizing Fracture Acidizing Treatment Design by Integrating Core Testing, Field Testing, and Computer Simulation." *International Meeting on Petroleum Engineering*. <https://doi.org/10.2118/22393-MS>.
- Domelen, M S Van, R D Gdansk, and D B Finley. 1994. "The Application of Core and Well Testing to Fracture Acidizing Treatment Design: A Case Study." *European Production Operations Conference and Exhibition*. <https://doi.org/10.2118/27621-MS>.
- Fredd, Christopher N, and H Scott Fogler. 1998a. "Influence of Transport and Reaction on Wormhole Formation in Porous Media." *AIChE Journal* 44 (9): 1933–49.
- . 1998b. "The Influence of Chelating Agents on the Kinetics of Calcite Dissolution" 197 (204): 187–97.
- Gomaa, A. M., and H. A. Nasr-El-Din. 2009. "Acid Fracturing: The Effect of Formation Strength on Fracture Conductivity." *Society of Petroleum Engineers - SPE Hydraulic Fracturing Technology Conference 2009*, no. 1994: 644–60. <https://doi.org/10.2118/119623-ms>.

- Gong, Ming, Stephan Lacote, and A D Hill. 1999. "New Model of Acid-Fracture Conductivity Based on Deformation of Surface Asperities." *SPE Journal* 4 (03): 206–14. <https://doi.org/10.2118/57017-PA>.
- Heus, Martin, Hans Lammers, and Arie Volmer. 2013. "Process to Prepare Amino Acid-n, n-Diacetic Acid Compounds." Google Patents.
- Ivanishin, Igor B, and Hisham A Nasr-el-din. 2021. "Journal of Petroleum Science and Engineering Effect of Calcium Content on the Dissolution Rate of Dolomites in HCl Acid" 202 (September 2020).
- Kalfayan, Leonard. 2008. *Production Enhancement with Acid Stimulation*. Pennwell books.
- LePage, James N, C A De Wolf, J H Bemelaar, and Hisham A Nasr-El-Din. 2011. "An Environmentally Friendly Stimulation Fluid for High-Temperature Applications." *SPE Journal* 16 (01): 104–10.
- Lu, Cong, Xiang Bai, Yang Luo, and Jianchun Guo. 2017. "New Study of Etching Patterns of Acid-Fracture Surfaces and Relevant Conductivity." *Journal of Petroleum Science and Engineering* 159: 135–47.
- Mahmoud, Mohamed. 2017. "Determination of the Optimum Wormholing Conditions in Carbonate Acidizing Using NMR." *Journal of Petroleum Science and Engineering* 159: 952–69.
- Malagon, C, Maysam Pournik, and Alfred Daniel Hill. 2008. "The Texture of Acidized Fracture Surfaces: Implications for Acid Fracture Conductivity." *SPE Production & Operations* 23 (03): 343–52.
- Malagon, Camilo, Maysam Pournik, and A. D. Hill. 2008. "The Texture of Acidized Fracture Surfaces: Implications for Acid Fracture Conductivity." *SPE Production and Operations* 23 (3): 343–52. <https://doi.org/10.2118/102167-pa>.
- Mccune, C C, Chevron Oil, La Habra, and Ann Arbor. 1973. "The Dissolution of Dolomite in Hydrochloric Acid" 28: 691–700.
- Melendez, M. G., M. Pournik, D. Zhu, and A. D. Hill. 2007. "The Effects of Acid Contact Time and the Resulting Weakening of the Rock Surfaces on Acid-Fracture Conductivity." *SPE - European Formation Damage Conference, Proceedings, EFDC* 2: 700–710. <https://doi.org/10.2118/107772-ms>.
- Morgan, Gilbert T, and Harry Dugald Keith Drew. 1920. "CLXII.—Researches on Residual Affinity and Co-Ordination. Part II. Acetylacetones of Selenium and Tellurium." *Journal of the Chemical Society, Transactions* 117: 1456–65.
- Nasr-El-Din, H A, A M Al Moajil, and A D Al-Aamri. 2007. "Evaluation of In-Situ Generated Acids for Filter-Cake Cleanup." *European Formation Damage Conference*. <https://doi.org/10.2118/107537-MS>.
- Nasr-El-Din, Hisham A., Saad M. Al-Driweesh, Arthur Steven Metcalf, and John B. Chesson.

2008. “Fracture Acidizing: What Role Does Formation Softening Play in Production Response?” *SPE Production and Operations* 23 (2): 184–91.
<https://doi.org/10.2118/103344-pa>.
- Nierode, D E, and K F Kruk. 1973. “An Evaluation of Acid Fluid Loss Additives Retarded Acids, and Acidized Fracture Conductivity.” In *Fall Meeting of the Society of Petroleum Engineers of AIME*. OnePetro.
- Pournik, M., C. Zou, C. Malagon Nieto, M. G. Melendez, D. Zhu, A. D. Hill, and X. Weng. 2007. “Small-Scale Fracture Conductivity Created by Modern Acid-Fracture Fluids.” *SPE - Hydraulic Fracturing Technology Conference 2007* 2007: 394–415.
<https://doi.org/10.2118/106272-ms>.
- Ruffet, Clotilde S., Jean Jacques Féry, and Atef Onaisi. 1998. “Acid-Fracturing Treatment: A Surface-Topography Analysis of Acid-Etched Fractures to Determine Residual Conductivity.” *SPE Journal* 3 (2): 155–62. <https://doi.org/10.2118/38175-PA>.
- Shulman, A, and F P Dwyer. 1964. “Metal Chelates in Biological Systems.” *Chelating Agents and Metal Chelates*, 383–439.
- Tariq, Zeeshan, Murtada Saleh Aljawad, Amjed Hassan, Mohamed Mahmoud, and Ammar Al-Ramadhan. 2021. “Chelating Agents as Acid-Fracturing Fluids: Experimental and Modeling Studies.” *Energy and Fuels* 35 (3): 2602–18.
<https://doi.org/10.1021/acs.energyfuels.0c04045>.
- Tariq, Zeeshan, Amjed Hassan, Ridha Al-Abdrabalnabi, Murtada Saleh Aljawad, and Mohamed Mahmoud. 2021. “Comparative Study of Fracture Conductivity in Various Carbonate Rocks Treated with GLDA Chelating Agent and HCl Acid.” *Energy and Fuels* 35 (23): 19641–54.
<https://doi.org/10.1021/acs.energyfuels.1c03471>.
- Taylor, K C. n.d. “Measurement of Acid Reaction Rates of a Deep Dolomitic Gas Reservoir,” 49–56.
- Williams, B B, J L Gidley, and R S Schechter. 1979. “Acidizing Fundamentals, 55.” *New York: SPE/AIME*.

VITAE

Name	Ridha Abdrabalrasool Alabdrabalnabi
Nationality	Saudi
Date of Birth	8/28/1991
Email	rnabi29@gmail.com
Address	32617 Qatif, Eastern province, Saudi Arabia
Academic Background	Master of Science in Petroleum Engineering
Publications	1. Ridha Al-Abdrabalnabi, Murtada Saleh Aljawad, Mustafa Al Ramadan, Hasan J. Khan, and Mohamed Mahmoud. Experimental Investigations of Acid Fracturing in Layered Carbonate Rocks Utilizing Chelating Agents. Energy & Fuels. 2. Khan, H. J., Al-Abdrabalnabi, R., & Al-Jawad, M. S. (2023). Fracture Surface Evolution During Acidized Brine Injection in Calcareous Mudrocks. ACS Omega. 3. Hassan, Amjed, Tariq, Zeeshan, Al-Abdrabalnabi, Ridha, Saleh Aljawad, Murtada, and Mohamed Mahmoud. "Evaluating the Impact of Rock Hardness and Roughness on Acid Fracturing Conductivity." Paper presented at the International Petroleum Technology Conference, Riyadh, Saudi Arabia, February 2022.
Educational Background	MSc. Petroleum Engineering – 2023 B.S Petroleum Engineering – 2015 King Fahd University of Petroleum & Minerals, Saudi Arabia.