

**IRON SULFIDE SCALE INHIBITION
IN WATER INJECTION WELLS**

BY

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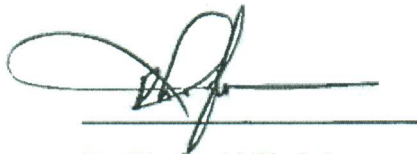
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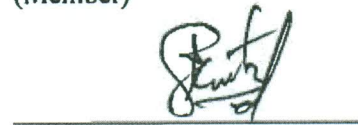
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I dedicate this work to my beloved parents, and sister.

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LIST OF ABBREVIATIONS

HCl	Hydrochloric Acid
SRB	Sulfate Reducing Bacteria
H₂S	Hydrogen Sulfide
EDTA	Ethylenediaminetetraacetic Acid
DTPA	Diethylenetriaminepentaacetic Acid
GLDA	L-glutamic acid-N, N-diacetic Acid
THPS	Tetrakis(hydroxymethyl)phosphonium Sulfate
APCA	Aminocarboxylic Acids
SI	Saturation Index
IAP	Ion Activation Product
K_{sp}	Solubility Product
MIC	Minimum Inhibitor Concentration
ICP-OES	Inductively Coupled Plasma - Optical Emission Spectrometry
MDS	Molecular Dynamic Simulation
XRD	X-Ray Diffraction
IL	Indiana Limestone
PV	Pore Volume
IPV	Injected Pore Volume

ABSTRACT

Full Name : [Nijat Gasimli]

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An important oilfield issue is the formation of a wide range of scales during oil and gas production. Oilfield scales hinder assessing an optimum hydrocarbon production as their precipitation on formation, various surface, and downhole equipment leads to many problems, including pressure decrement, formation damage, and operational failure of subsurface equipment. However, complete and effective removal of some scales cannot be achieved for decades. This is especially true when it comes to iron sulfide scales. This scale can be found in different forms (soft and hard forms), and iron sulfide scale samples taken from sour oil and gas wells are not usually homogenous in terms of mineralogy.

The deposition of iron sulfide is a common problem in sour wells and normally originating from the extracted aqueous phase. Generation of hydrogen sulfide (H_2S) gas from the liquid phase because of pressure diminution within the production period causes pH to increase, which leads to the creation of pH-sensitive scales, including iron sulfides. Based on studies in the Khuff reservoir, iron sulfide scales are likely to deposit on production tubing as well as in the formation rock. Because of the mineral heterogeneity and temperature/pressure changes in the production system, it is challenging to completely dissolve this scale using different chemicals. Although hydrochloric acid (HCl) can eliminate most types of iron sulfide minerals, on the other hand, its utilization is limited by

the temperature since HCl can cause severe corrosion problems at high temperatures. Moreover, the formation of iron sulfide scale in water injection wells is also an expected phenomenon. Therefore, it becomes essential to entirely or partially restrain the occurrence of iron sulfide scale using environmentally friendly chemicals in production tubing, water injection wells and near-wellbore formation. Various scale control chemicals and experimental approaches have been suggested for iron sulfide scale inhibition. Polymeric, phosphonate, and sulfonated co-polymeric inhibitors were used in the literature. However, the subgroup of chelating agents - aminocarboxylic acids were used in this thesis.

Prevention of iron sulfide scale deposition in limestone formation in water injection wells is the primary focus of the thesis. Iron sulfide scale inhibition was studied through a set of dynamic inhibition adsorption experiments. In contrast to conventional experiments, for scale inhibition (static bottle, dynamic filter tube tests) and simulation studies, a novel experimental set-up (coreflooding experiments) proposed for iron sulfide scale formation and inhibition to understand the fundamental dynamics of adsorption of high-pH aminocarboxylic acids with the concentrations of 10 wt%, 15 wt%, and 20 wt% on carbonate rock formations. Alongside dynamic adsorption experiments, in order to understand the depositional behavior of scale crystals (ferric and ferrous ions in this case) in different pH values (1-13) in carbonate rock, ζ -potential measurements were employed.

الرسالة ملخص

الاسم الكامل: نجات قاسملي

عنوان الرسالة: تثبيط مقياس كبريتيد الحديد في آبار حقن المياه

التخصص: الهندسة البترولية

تاريخ الدرجة العلمية: ديسمبر 2021

من القضايا المهمة في حقل النفط تكوين مجموعة واسعة من المقاييس أثناء إنتاج النفط والغاز. تعيق مقاييس حقول النفط تقييم الإنتاج الأمتل للهيدروكربونات حيث يؤدي هطول الأمطار على معدات التكوين والسطح المتنوع وأسفل البئر إلى العديد من المشكلات ، بما في ذلك انخفاض الضغط وتلف التكوين والفشل التشغيلي للمعدات تحت السطحية. ومع ذلك ، لا يمكن تحقيق الإزالة الكاملة والفعالة لبعض المقاييس لعقود. هذا صحيح بشكل خاص عندما يتعلق الأمر بمقاييس كبريتيد الحديد. يمكن العثور على هذا المقياس في أشكال مختلفة (الأشكال اللينة والصلبة) ، وعينات مقياس كبريتيد الحديد المأخوذة من آبار النفط والغاز الحامض لا تكون عادةً متجانسة من حيث علم المعادن.

يعتبر ترسب كبريتيد الحديد مشكلة شائعة في الآبار الحامضة وعادة ما تنشأ من المرحلة المائية المستخرجة. يؤدي توليد غاز كبريتيد الهيدروجين H_2S من المرحلة السائلة بسبب انخفاض الضغط خلال فترة الإنتاج إلى زيادة الرقم الهيدروجيني ، مما يؤدي إلى إنشاء موازين حساسة للأس الهيدروجيني ، بما في ذلك كبريتيدات الحديد. بناءً على الدراسات في خزان الخف ، من المحتمل أن تترسب قشور كبريتيد الحديد على أنابيب الإنتاج وكذلك في صخور التكوين. بسبب عدم تجانس المعادن وتغيرات درجة الحرارة / الضغط في نظام الإنتاج ، من الصعب حل هذا المقياس تمامًا باستخدام مواد كيميائية مختلفة. على الرغم من أن حمض الهيدروكلوريك (HCl) يمكن أن يقضي على معظم أنواع معادن كبريتيد الحديد ، من ناحية أخرى ، فإن استخدامه محدود بسبب درجة الحرارة لأن حمض الهيدروكلوريك يمكن أن يسبب مشاكل تآكل شديدة في درجات الحرارة المرتفعة. علاوة على ذلك ، يعتبر تكوين مقياس كبريتيد الحديد في آبار حقن المياه ظاهرة متوقعة أيضًا. لذلك ، يصبح من الضروري تقييم حدوث مقياس كبريتيد الحديد كليًا أو جزئيًا باستخدام مواد كيميائية صديقة للبيئة في أنابيب الإنتاج وآبار حقن المياه والتكوين بالقرب من حفرة البئر. تم اقتراح مواد كيميائية مختلفة للتحكم في المقياس وأساليب تجريبية لتثبيط مقياس كبريتيد الحديد. تم استخدام مثبطات البوليمر ، الفوسفونات ، البوليمر المشترك المسلفنة في الأدبيات. ومع ذلك ، تم استخدام المجموعة الفرعية من العوامل المخليبية - الأحماض الأمينية الكربوكسيلية في هذه الأطروحة.

التركيز الأساسي للأطروحة هو منع ترسب مقياس كبريتيد الحديد في تكوين الحجر الجيري في آبار حقن المياه. تمت دراسة تثبيط مقياس كبريتيد الحديد من خلال مجموعة من تجارب التثبيط الديناميكي. على عكس التجارب التقليدية ، لتثبيط النقش (الزجاجة الثابتة ، واختبارات أنبوب الفلتر الديناميكي) ودراسات المحاكاة ، اقترح إعداد تجريبي جديد (تجارب غمر الماء) لتشكيل مقياس كبريتيد الحديد والتثبيط لفهم الديناميات الأساسية لامتصاص عالية أحماض أمينو

كربوكسيلية الأس الهيدروجيني بتركيزات 10% بالوزن و 15% بالوزن و 20% بالوزن على التكوينات الصخرية الكربونية. إلى جانب تجارب الامتصاص الديناميكي ، من أجل فهم السلوك الترسبي لبلورات الحجم (الأيونات الحديدية والأيونات الحديدية في هذه الحالة) بقيم مختلفة من الأس الهيدروجيني (1-13) في صخور الكربونات ، تم استخدام قياسات. المحتملة.

CHAPTER 1

INTRODUCTION

1.1 Background

A critical industrial problem that occurs most frequently is mineral scaling. The formation of inorganic scales can create significant economic problems for oil and gas companies. According to [1], scaling problems cost an estimated \$1.4 billion annually in the United States. The most widespread types of inorganic scales encountered in the oil and gas industry are sulfates, carbonates, and sulfides [2], [3]. The formation of these scales on production string and near-wellbore formation causes critical production loss. Taking the following as an example, [4] reported that the formation of barium sulfate scales results in the loss of four million barrels of oil annually. Therefore, in order to recover oil and gas wells at their full potential, it is imperative to remove and prevent formation of inorganic scales. In oilfield applications, scale controlling is achieved by either scale removal, scale formation prevention (scale inhibition) and desulfation of injected seawater [4].

Scale removal can be done through mechanical ways or chemical dissolution [5]. Myriad of chemical dissolvers, such as hydrochloric acid (HCl), organic acids, acrolein, Tetrakis(hydroxymethyl)phosphonium salts, and chelating agents are used for dissolution of different types of scales, more specifically sulfide scales (zinc sulfide (ZnS), lead sulfide (PbS) and iron sulfide (FeS)).

Scale inhibition has been widely investigated to prevent or delay scale formation using chemical inhibitors. Chemical inhibitors, such as, polyphosphates, polycarboxylates, polyphosphonates, phosphino polymers, polyphosphinates and chelating agents are applied in attempt to inhibit formation of different types of oilfield scales [6].

Iron sulfide scale formation occurs mainly in sour oil and gas wells. Its removal and inhibition are considered as the most challenging tasks. Most of the time, the removal process of iron sulfides incorporates both chemical dissolution and mechanical milling [7]. However, in addition to production wells, the formation of iron sulfide scales is an expected phenomenon in water injection wells [8]–[10]. Sea water that contains high concentrations of sulfate ions is usually used as injection fluid and Sulfate Reducing Bacteria (SRB) converts sulfate ions into hydrogen sulfide (H_2S). Therefore, formed H_2S interacts with any iron source causing iron sulfide to form.

To completely remove this type of scales is challenging using different chemicals. Although hydrochloric acid (HCl) can eliminate most types of iron sulfide minerals, on other hand, its utilization is limited with the temperature since HCl can cause severe corrosion problems at high temperatures. Many recent studies have been published using environmentally friendly dissolvers (specially, different types of chelating agents) for iron sulfide scale removal [11]–[17]. However, to achieve to the maximum dissolution of iron sulfide scale having mineral heterogeneity is still challenging goal. Coming to the effective prevention of iron sulfide scales, wide variety of chemical inhibitors and inhibitors mixed with H_2S scavengers and corrosion inhibitors have been used [18]–[22]. Some of the polymeric inhibitors showed promising results to inhibit formation of iron sulfide scale.

1.2 Motivation

There are various experimental methods and inhibitors for studying formation and inhibition of iron sulfide scale. However, the most employed systems are either static bottle tests or dynamic filter block test while most of the studies use polymeric and phosphonic to inhibit iron sulfide scale formation. Unlike all previous studies, sub-group of chelating agents – aminocarboxylic acids were used in this study.

The aforementioned laboratory techniques have some drawbacks to study the inhibition efficiency of the inhibitors. In the case of static bottle tests, the system cannot represent real dynamics of inhibitor adsorption and such experiments cannot be performed at elevated pressure conditions while dynamic filter block tests can be operated at elevated temperature and pressure conditions. However, the problematic aspect of the equipment is that its usage is limited in filter size meaning filter size is very small in length which means the time of adsorption is very low and there is not enough time for chelators to counteract with rock surface. Additionally, filters usually have completely different criteria in terms of pore size and pore throat size distribution. Therefore, such kind of experimental setups do not mimic the actual porous media to analyze scale formation and inhibition.

Therefore, taking the mentioned disadvantages associated with the most-used techniques into the consideration, it becomes important to study iron sulfide scale formation and inhibition using novel methodology proposed in the thesis. The utilization of coreflooding system is essential to understand dynamic nature of adsorption of chelating agents and to evaluate formation damage due to scale precipitation (initial and final rock permeability alteration).

Alongside dynamic adsorption experiments, in order to understand the depositional behavior of scale crystals (ferric and ferrous ions in our case) in different pH values in carbonate rock, ζ -potential measurements were employed.

1.3 Research objectives

This research was focusing on investigating the formation and inhibition of iron sulfide scale in carbonate rock (Indiana limestone) in water injection wells. The set of coreflooding experiments were conducted to study iron sulfide scale formation and inhibition under various temperature conditions using aminocarboxylic acids (ethylenediaminetetraacetic acid (EDTA) and diethylenetriaminepentaacetic acid (DTPA)). Moreover, electrostatic adsorption (precipitation) of scale crystals (Fe^{3+}) on calcite rock surface investigated through performing series of ζ -potential measurements. The primary objectives of this research are:

- Evaluate inhibition efficiency of different concentrations of EDTA and DTPA against scale crystal (Fe^{3+}) on Indiana limestone rock samples through dynamic adsorption tests employing coreflooding setup and Inductively Coupled Plasma - Optical Emission Spectrometry (ICP-OES) under certain temperature conditions;
- Investigate iron precipitation at the wide range of pH environments and analyze solid/solid interaction with carbonate rocks;
- Analyze the effectiveness of the best formulation obtained from dynamic adsorption experiments on carbonate rock samples to study formation damage due to iron sulfide scale precipitation.

1.4 Thesis organization

Chapter 2 of the thesis presents detailed literature review on scale formation, removal, and inhibition in general. The use of various type of scale inhibitors and dissolver using different laboratory techniques were discussed.

Chapter 3 of the thesis provides a description of the methodology and the materials used are explained in detail. A detailed discussion has been provided in the chapter on the equipment and chemicals used in the experiment.

Chapter 4 of the thesis provides the results of the experiments conducted and discussions. An overview of the results of dynamic inhibitor adsorption tests is presented in the first section of the chapter. A discussion of the results of electrostatic adsorption of iron (solid/solid interaction) on calcite mineral was presented in the second section of the chapter. The last section of the chapter provides results and discussions regarding iron sulfide scale formation and inhibition.

Chapter 5 of the thesis presents a summary of all the conclusions and outcomes of this research. Based on this research, further recommendations are outlined within the scope of the chapter.

CHAPTER 2

LITERATURE REVIEW

2.1 Scale challenge during oil and gas production

The deposition of miscellaneous solids through the way of fluid flow (reservoir section, perforations, production string, valves) restrains continuous oil and gas production. It profoundly impacts hydrocarbon recovery [23]. Due to the massive economic loss as a consequence of scale formation, inhibition and effective removal of scales have been extensively inspected in previous studies [13], [24]–[30].

Common inorganic scales in the oilfield applications incorporate carbonate (calcium carbonate), sulfate (barium sulfate, calcium sulfate, strontium sulfate), and sulfide (iron sulfide, zinc sulfide, lead sulfide) scales [2]. **Figure 1** illustrates some of these scales that formed on production tubing and significantly decreased the inner diameter of the tubing. Directions associated with scale control are generally divided into three categories, including scale formation, scale inhibition (prevention), and scale removal. Distinct chemical reactions entail the generation of several different kinds of scale formation. Scale depositions are usually removed by chemical (various solvents) or mechanical (milling) means [31]. In the occasions when challenging scaling occurred in tubing, the only way to remove the deposits is milling or jet blasting [5].



Figure 1 – Precipitation of different inorganic oilfield scales in the production tubing

A wide range of chemicals has been used as a scale dissolver and inhibitors. The scale removal is usually performed using various inorganic, organic acids and chelating agents. Hydrochloric (HCl) acid commonly uses inorganic acid in scale dissolution applications due to its high removal efficiency. However, HCl demonstrates a critical corrosion rate in high temperatures and can cause a sludging issue [32]. Therefore, the utilization of environmentally friendly and non-corrosive chemicals, such as chelating agents in descaling and scale prevention, becomes indispensable.

The appropriate identification of scale mitigation strategy and implementation of removal requires careful evaluation of the source of the scale formation mechanism [33]. Therefore, different removal and inhibition strategies have to be developed according to

the location of scale deposits that are forming either in near-wellbore formation or surface and subsurface production facilities and temperature/pressure conditions.

The composition of brine from different zones of the formation may differ considerably and cause precipitation when mixed in pipes. In addition, wastewater from other industries is often used as fracturing fluid to fracture rock containing oil and gas. Shale gas is exploited using acid mine draining wastewater, for example [34]. The rapid precipitation of barite could occur when ultra-high SO_4^{2-} containing wastewater mixes with downhole brine. Scaling can also occur due to pressure and temperature changes in the transport process; it is possible for a large amount of scale to accumulate on the inside of the pipe. The solubility of CaCO_3 for example dropped drastically with increasing temperature [23]. The often-observed types of the mineral scales are listed in **Table 1**.

Table 1 – Common mineral scale types

Mineral name	Chemical formula
Calcite	CaCO_3
Anhydrite	CaSO_4
Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
Barite	BaSO_4
Celestite	SrSO_4
Mackinawite	FeS
Pyrite	FeS_2
Halite	NaCl
Fluorite	CaF_2
Siderite	FeCO_3

2.2 Mineral scale formation in oil and gas industry

The deposition of scales varies considerably from well to well within the same oil and gas field. Another critical factor is the depth where scale formation occurs. For example, iron sulfide scales can form as different minerals depending on the depth [12], [13]. The primary origin of every type of scale formation is water since water is produced together with oil and gas.

The process of mineral scaling incorporates as a crystallization phase in which inorganic salts having low solubility passing through nucleate and start to grow in either different surfaces or supersaturated solutions (**Figure 2**) [35].

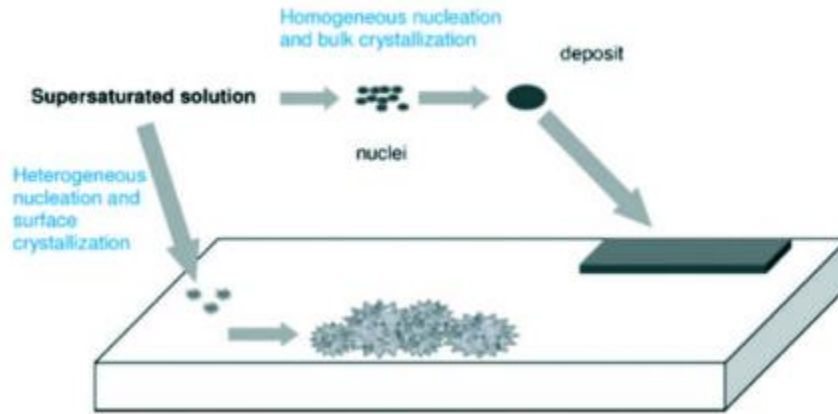


Figure 2 – Mineral scaling schematic [104]

The nucleation and deposition of distinct scales occurs due to different formation mechanisms. Scale deposition mainly forms as a result of supersaturation of excessive quantities cations (Fe^{2+} , Ba^{2+} , Ca^{2+}) mixing with anions (CO_3^{2-} , SO_4^{2-}). The precipitation process starts once the solubility product of a particular material is going to be higher than its K_{sp} value under specific circumstances. The scale precipitation is mostly induced by three following principal mechanism [2], [36].

1. **Incompatible mixing:** interaction between two incompatible water (seawater and formation water) induces scale formation (formation of calcium sulfate, barium sulfate, strontium sulfate).
2. **Autoscaling:** pressure and temperature alteration results in scale formation (formation of carbonate and sulfide scales).

- 3. Evaporation-caused scaling:** pressure decrement causes gas expansion which results in evaporation of brine (formation of Halite (NaCl)).

Alongside the operational problems in production wells caused by scale formation, scales also negatively impact the injection wells (**Figure 3**), and precipitates might diminish the full injection potential of injection wells [37].

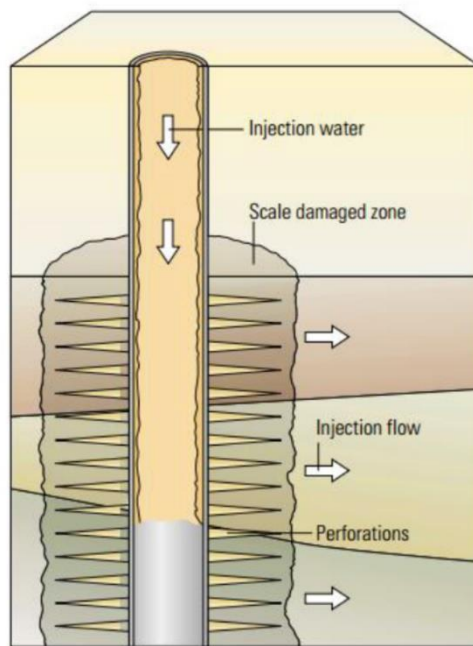


Figure 3 – Damaged injection well by scale deposition [1]

Moreover, scale deposits can precipitate near-wellbore formation pores [23], [38].

Figure 4 shows the schematic of matrix damage due to scale precipitation.

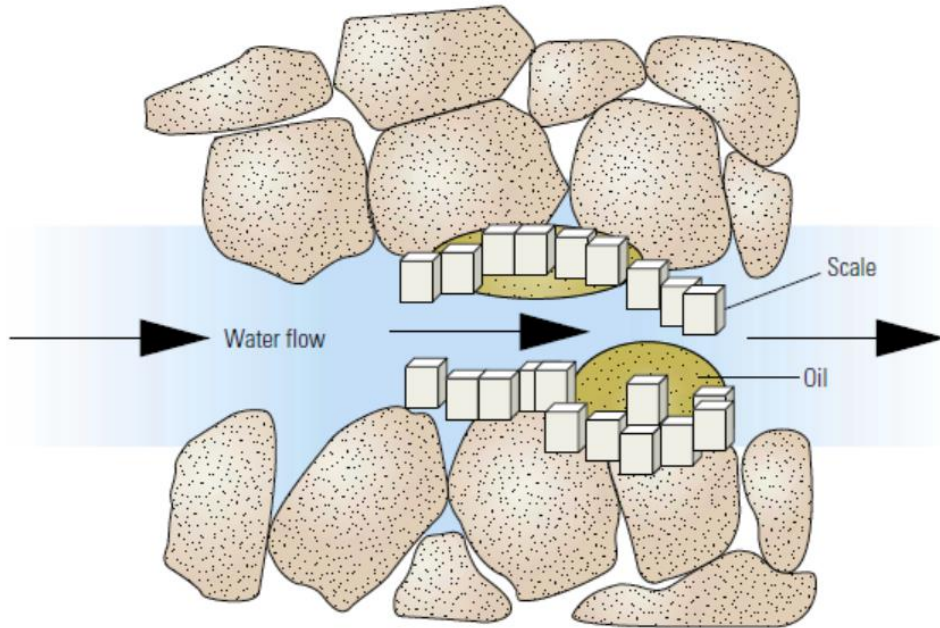


Figure 4 – Formation damage due to scaling [1]

A broad range of reasons causing mineral scaling can be divided into chemical and physical. Various chemical and physical factors triggering scale formation are shown in **Figure 5**.

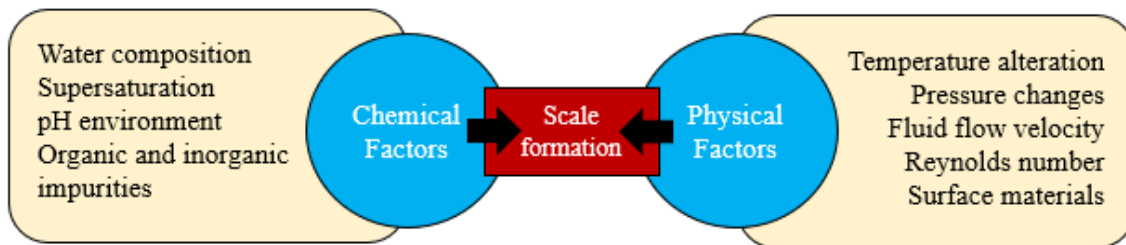


Figure 5 – Physical and chemical factors affecting mineral scaling

Scale formation is governed by the chemistry of the solution (water composition), supersaturation and pH. A combination of inorganic and organic impurities can also profoundly influence the crystallization of undesirable mineral scales and their composition [39]. It is common to inject water into reservoirs and mix this water with formation waters in order to maintain reservoir pressure and optimize oil recovery [40]. A problem arises when sea water with high anion concentrations (especially SO_4^{2-} , CO_3^{2-}) is mixed with formation water that consists of Ca^{2+} , Ba^{2+} , and Sr^{2+} . This is due to the fact that high ion concentrations on mixing may lead to supersaturated conditions and precipitation of scales such as CaCO_3 , CaSO_4 , SrSO_4 and BaSO_4 [23]. A mineral scale can also be classified into pH independent (e.g., barium, strontium, and calcium sulfates) and pH sensitive minerals (e.g., carbonates, sulfides) [41]. The scales can form because alteration of temperature, pressure as well as the partial pressure of CO_2 and H_2S [42], [43].

Variations in temperature or pressure can change the supersaturation state, causing scale mineral precipitation. Calcium bicarbonate-containing subsurface waters release CO_2 when they reach the surface, causing the pH to rise and precipitation of calcium carbonate. Further, hydrodynamic conditions like fluid flow velocity [44], pipe diameter [45], Reynolds number [46] and surface roughness [47] as well as types of surface materials can influence scale mineral formation.

In most carbonate and sandstone formations, iron sulfide and calcium carbonate scales predominate. Based on percentages, the most common scale types in carbonate and sandstone reservoirs are summarized in **Figure 6**.

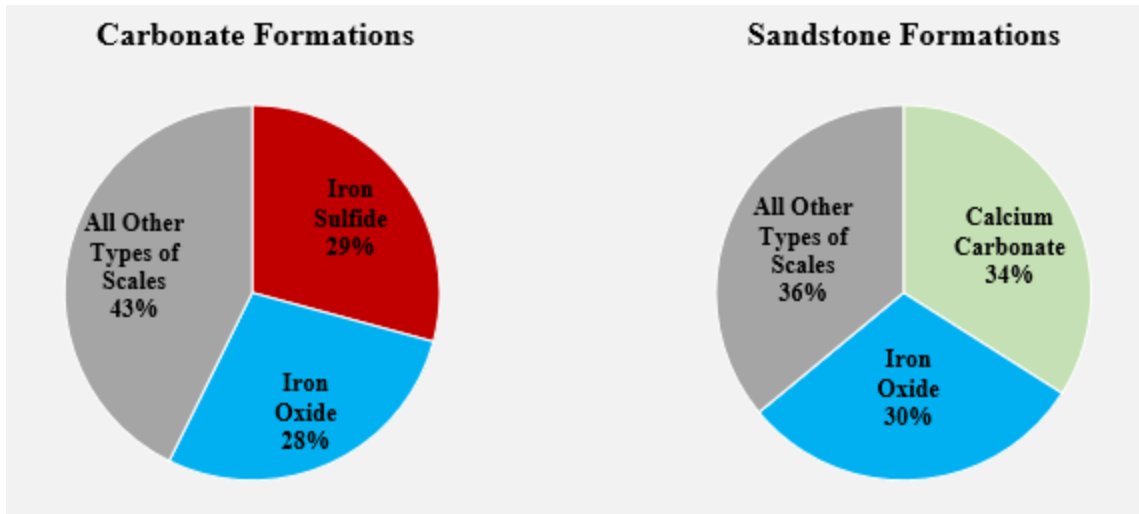


Figure 6 – Proportion of the most common scales according to formation types [10]

Nucleation and crystal growth are two mechanisms responsible for mineral crystallization.

2.2.1 Mechanism of nucleation

In general terms, nucleation process can be divided into two stages which can be categorized as follows:

- Primary nucleation
- Secondary nucleation

A nucleation structure that does not contain pre-formed crystals is referred to as primary nucleation. However, secondary nucleation refers to the nucleation systems in which nuclei creation happens in a supersaturated mixture that already has a pre-formed crystal.

There are two possible ways that primary nucleation can occur:

- Homogeneous nucleation
- Heterogeneous nucleation

Homogenous nucleation is based on collisions between molecules. However, heterogeneous nucleation happens when there is an interaction with external particles – this interaction results in the heterogeneous formation of crystals.

Crystal nucleation is the series of molecular collisions, and once the nuclei become in a critical size, they can resist redissolving. As a result, nuclei will start to grow, which will lead to the precipitation of crystals in our case scale deposits. **Figure 7** shows the representation of heterogeneous and homogeneous nucleation.

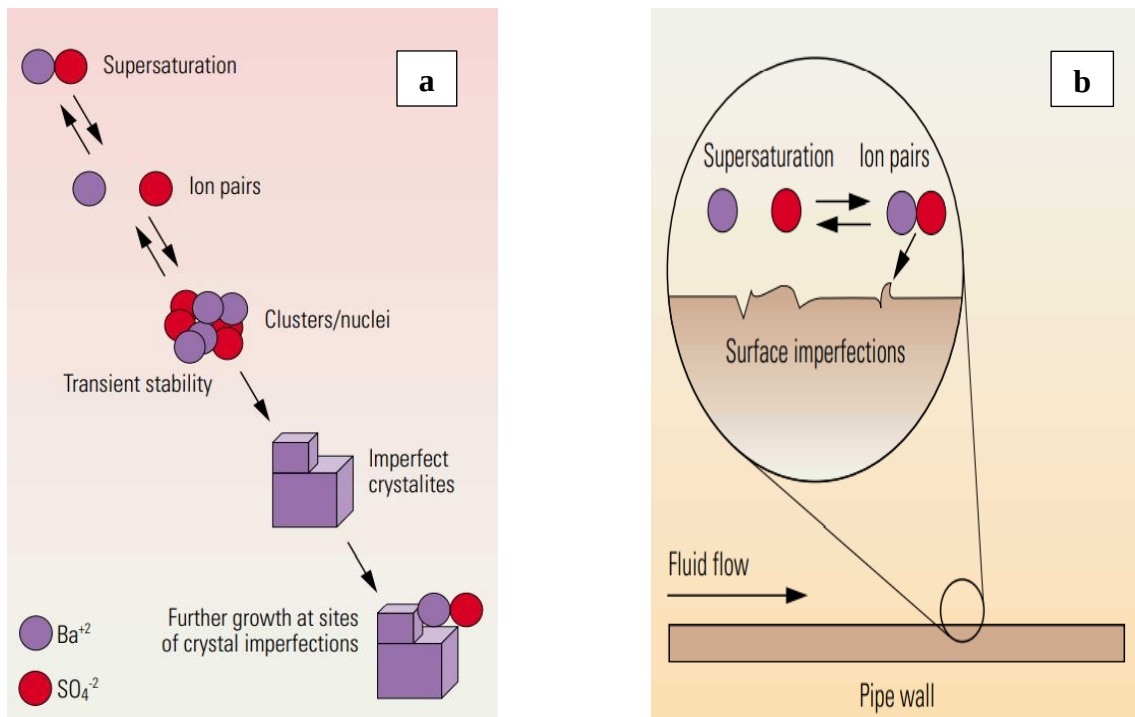


Figure 7 – Nucleation mechanisms: a) Homogeneous b) Heterogeneous [1]

2.2.2 Ostwald step rule

As a general rule, solids with the highest solubility precipitate first since their interfacial tension is lowest between the solid and solution. This means that the least stable form will precipitate first. Ostwald states that "an unstable system does not necessarily

become the most stable state directly, but rather into one most like its own.". It implies the reaction might not necessarily proceed to the most stable thermodynamic state, but the fastest kinetic one. As solid solutions are almost always metastable, it is difficult to reach thermodynamic equilibrium [48].

2.2.3 Crystal growth

Crystal growth is a process of adsorption of atoms and molecules on the surface of mineral crystals. This process continues with the formation of the crystal lattices. Such evolution of adsorption of atoms and molecules results in the formation of more complex and stable mineral crystals [4]. The surface form of crystals proposed not to be precisely smooth but indicated as composed of kinks and steps as depicted in **Figure 8** which fastening rate of the crystal growth [49].

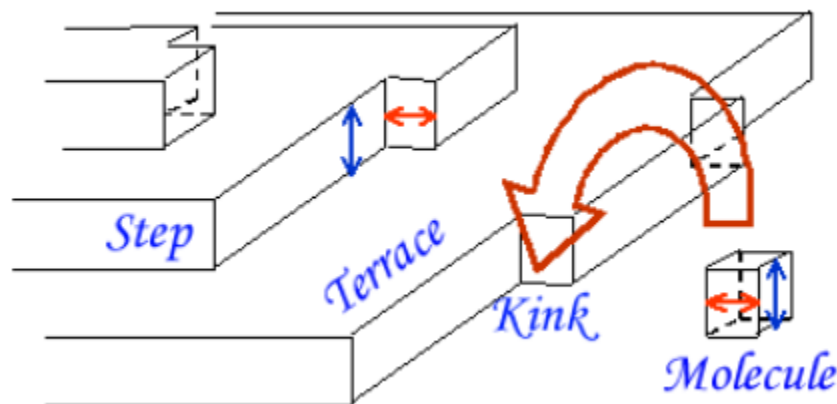


Figure 8 – The form of crystal surfaces [32]

Based on **Figure 8**, the simple steps toward the growth of crystals can incorporate several stages as follows:

1. Atoms and molecules transportation in the solution
2. Atoms attaching to the surface

3. Atoms movement on the surface
4. Assemblage of atoms on edges or kinks

2.2.4 Saturation Index

The necessary theories that worth to mention while discussing the scale formation are Saturation Index (SI) and solubility product (K_{sp}). In a solution, salt and minerals undergo a dissolution reaction and it is represented by **Eq. 2.1**.



As a result of the law of mass action at equilibrium, the dissolution reaction yields the following equation **Eq. 2.2**:

$$K_{sp} = \frac{[A]^x \times [B]^y}{[A_x B_y]} \quad (2.2)$$

where the terms indicated in parenthesis accounts for the concentration of each specific component that contains the system. It is accepted that if the K_{sp} of the system is higher than 1, the given mineral is the soluble. Contrarily, if K_{sp} value is less than or equal to 1, it implies insolubility of the given mineral. In the cases when equilibrium of the system is not achieved, the term, Ion Activation Product (IAP) in the solution is proposed and defined as in **Eq. 2.3**.

$$IAP = [A]_{actual}^x \times [B]_{actual}^y \quad (2.3)$$

When non-equilibrium conditions exist, the salt/mineral solution can be undersaturated, saturated, or supersaturated. In non-equilibrium conditions, the SI of a

solution determines whether it is undersaturated, saturated, or supersaturated. The saturation state of the solution is determined using **Eq.2.4**.

$$SI = \log_{10} \left(\frac{IAP}{K_{sp}} \right) \quad (2.4)$$

The solution is considered as saturated if $SI = 0$, undersaturated if $SI < 0$ and supersaturated if $SI > 0$.

2.2.5 Induction time

The supersaturation and the appearance of crystals are usually separated by a period of time. This period of time is called the induction time. As shown in **Figure 9**, the induction time could consist of several different parts [48] which are relaxation time (time for molecular clusters achieving quasi-steady-state distribution), stable nucleus formation time, and further nucleus growth time. There are a variety of factors that influence induction time, including temperature, agitation speed, and seed content. Measurements of induction time typically involve visual methods, laser light scattering, or electric zone sensing [30].

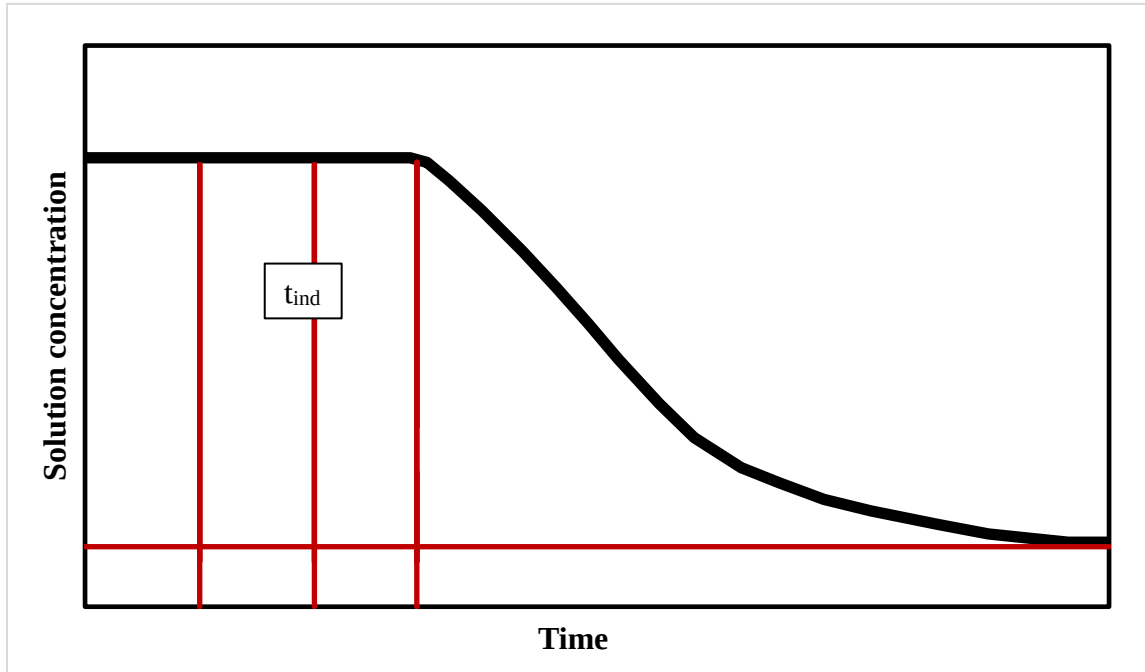


Figure 9 – Desupersaturation curve [30]

2.3 Scale control strategies

Scale control covers prevention and removal techniques that are applicable to remove the already formed scale precipitates or to inhibit the formation of oilfield scales. Myriad chemical inhibitors and techniques have been used aiming to prevent scale formation and dissolve the scale deposits, and they will be discussed in this section.

2.3.1 Scale removal

The removal of scale must be quick, damage-free, and effective in preventing precipitation from after it has already been formed on the wellbore, tubing, or formation. The most important aspect of removing scale is to know the type and quantity of scale, as well as its composition and texture. The strength of scales varies from delicate whiskers to brittle crystals with high microscopy to rock-like layers with low permeability. Scale deposits can also contain impurities that can affect their resistance to removal.

In oil and gas industry, two types of removal strategies are utilized when scales are already formed.

- Mechanical removal
- Chemical dissolution

In oilfield applications, mechanical milling might be a removal option if scale precipitation occurred in the wellbore and in an easily accessible location. However, mechanical removal operation is an expensive and complicated task because of the difficulties that arise during drilling processes. Mechanical methods cannot be applied to deposits that are formed in the near-wellbore formation. Because of the limitations of milling operations, chemical removal is preferable [2].

A one-stage chemical treatment that is applicable for removing and preventing the scale deposition through one-stage treatment could not be achieved yet [50]. Chemical dissolution and mechanical removal are utilized when scales are already formed. The well-known chemicals used for scale removal are HCl, organic acids (maleic, formic, citric, and acetic acids) and chelating agents.

2.3.2 Scale inhibition

The term "scale inhibition" describes the procedure of applying chemical inhibitors in order to prevent the formation of different kinds of scales or to delay the formation of scale as much as possible. Scale inhibitors are water-soluble chemicals that can inhibit the crystallization of minerals by interfering with the water-soluble molecules involved [51].

During the inhibition process, either thermodynamically stable regions are created by the introduction of substances that react with scale generating substances or crystal

growth can be quenched by incorporation of inhibitors that quench the formation of crystals.

Scale inhibitors have not made much progress in recent years; the advances have generally been in biodegradable products [4]. As a matter of fact, there are a number of scale inhibitor application methods to deliver scale inhibitors in the field; however, a few of the most common are listed below [4][52]:

- Downhole squeeze treatment
- Continuous inhibitor injection
- Slowly-releasing scale solid inhibitor compositions

The effectiveness of scale inhibition process is evaluated by the concentration of scale inhibitor in the produced water and flowback water after the treatment to determine if the treatment was successful.

a. Downhole squeeze treatment

Scale inhibitor squeeze treatments are aimed at preventing the formation from being damaged by scale deposition. There is no doubt that the scale inhibitor will continue to operate above the wellhead to protect the pipes from scaling, but a further dose of a similar inhibitor may have to be used at the topside.

By applying a squeeze treatment, a scale inhibitor solution is introduced into a well above the pressure of the formation, allowing the scale inhibitor to get into the deep into near wellbore formation [53], [54]. The inhibitor injection stage is followed by the shut-in period (usually for a couple of hours) of the well. The basic purpose of the shut-in period is allowing the inhibitor to be retained the rock pores. As the well starts producing, scale inhibitors retained in the pores starts dissolving in produced water. Therefore, the produced water should contain enough scale inhibitor to hinder the scale deposition [4], [55]. **Figure 10** illustrates the squeeze treatment procedures.

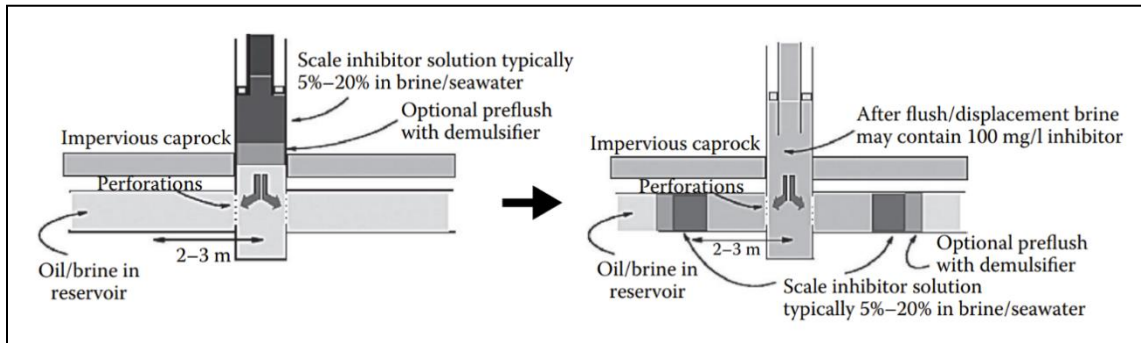


Figure 10 – Scale inhibitor squeeze treatment [40]

It is worth to mentioning the concept of minimum inhibitor concentration (MIC) within downhole squeeze treatment. MIC is defined as the minimum required inhibitor concentration (threshold scale inhibitor concentration) according to the given brine that is able to prevent scale formation. When the inhibitor concentration in produced water becomes lower than MIC, it results in scale precipitation [54], [55]. In such cases, the second stage squeezing should be performed to maintain high inhibitor concentration. **Figure 11** shows that concentration of the used scale inhibitor falls below MIC (2ppm) after 92 days of production.

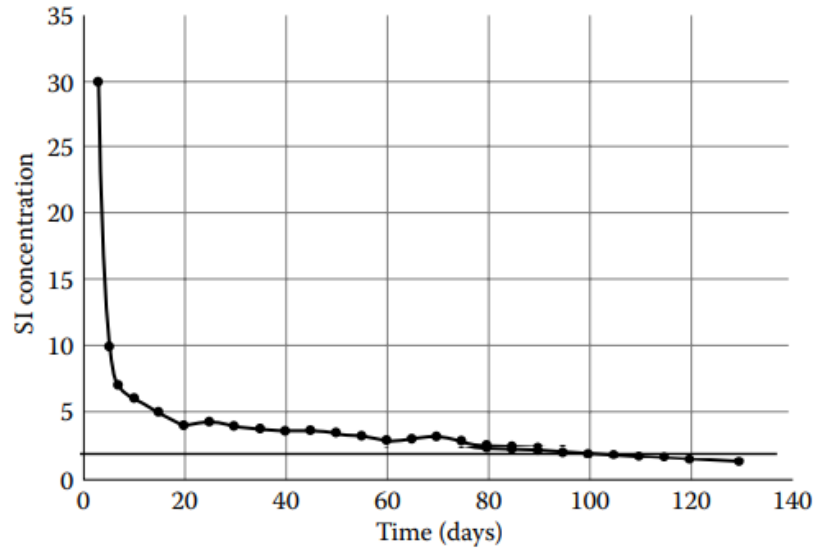


Figure 11 – Inhibitor concentration (ppm) after squeeze treatment

Squeeze treatment usually includes the following three stages following with shut-in and production (**Figure 12**)[54], [55]:

1. Preflush – is for cooling the formation around the near-wellbore in order to pave the way for transportation of the inhibitors far away from the near-wellbore region.
2. Main Slug - scale inhibitor volume is injected, which typically contains inhibitor chemical in the concentration range of 2.5% to 20%.
3. Overflush – brine overflush is implemented to push the injected inhibitor slug to the region that away is away from the near wellbore region in order to allow the inhibitor to occupy a larger volume of rock.

injection of inhibitors in injector wells also prevents scaling problems in the producing wells [6]. Usually, the continuous injection into produced water is done through the wellhead, where other chemicals are injected, such as corrosion inhibitors. However, in reality a lot of scale inhibitors are not compatible with all type of corrosion inhibitors. Instead of using injection wells, in order to inject scale inhibitors either a capillary string or gas lift system can be used [56], [57].

c. Slowly-releasing scale solid inhibitor compositions

Utilizing very fine, coated particles that contain scale inhibitors can help to prevent the use of water during squeeze treatments. Upon restarting production, the suspended scale inhibitor particles in a liquid hydrocarbon can be pushed into the pores of a formation, slowly releasing inhibitors into the produced water [6]. Sulfate scaling has been successfully controlled with this technology [58].

A variety of means are available for producing particles containing scale inhibitors, such as 100% solid products, encapsulated products, and highly porous materials that are capable of capturing the inhibitors. An improved method to generate particles containing scale inhibitor is by using inverse emulsions or suspensions containing suitable monomers in a thermally-initiated polymerization reaction [6].

Generally, according to [59], the following parameters should be satisfied in order to achieve a perfect scale inhibitor:

- Effective scale control at a low inhibitor concentration
- Compatibility with sea and formation water

- Balanced adsorption-desorption properties allowing the chemicals to be slowly and homogeneously released into the production water
- High thermal stability
- Low toxicity and high biodegradability
- Low cost

One type of chemicals those are used as inhibitors in oil and gas industry to prevent formation of different types of scales are chelating agents. The following section is discussing various types of chelating agents and discusses applications and chemistry of aminocarboxylic acids.

2.4 Chelating agents

2.4.1 An overview of chelating agents

Aminocarboxylic acids (APCA) types of chelating agents with different concentrations was proposed to use for iron sulfide scale inhibition and for the purpose of squeeze treatment procedure in the field application. Chelating agents have a widespread application in numerous industries, including agriculture, textile, water purification, as well as in the oil and gas industry [60].

APCA and tetrakis(hydroxymethyl)phosphonium sulfate THPS have been widely used for iron sulfide scale dissolution and showed promising results [32], [43], [61], [62]. In comparison with HCl, these types of acids results in formation of a more stable complex and reducing the chance of reprecipitation. Chelating agents are accepted more thermally stable than HCl [63].

2.4.2 Aminocarboxylic acids

Organic composites that have two or more groups (ligands) that are able to donate electrons to capture or adsorb the positively charged ions (metal ions) are named as chelating agents. In other words, the main purpose of chelating agents is to react with metal ions to form a water-soluble and more stable complex. The formation of one or more than one heterocyclic ring is associated with the formation of several coordinate bonds (**Figure 12**). Chelating agents contain various functional groups, such as carboxyl, hydroxyl, nitro, and so on.

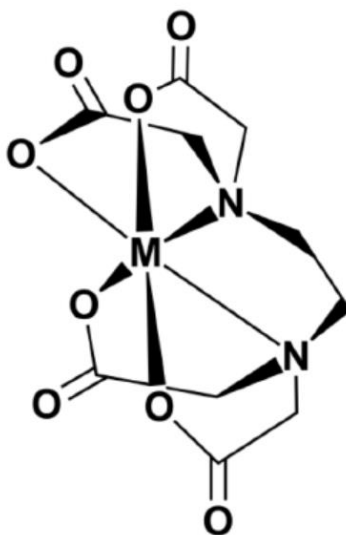


Figure 13 – Chelated rings with M cation

The stability constant of the chelating agent determines its affinity towards the metal ion. Such complexes are found to be high in stability and are affected by factors such as pH, metal ion type, concentration, pressure, and temperature [60].

The application of chelators in the petroleum industry primarily covers dissolution, removal of different types of scales, and iron control. In addition to their use in descaling processes, chelating agents have been used for carbonate and sandstone acidizing as stimulation agents [64].

The metal ion forms a complex with the ligand when the ligand donates electrons to it. Nitrogen and oxygen atoms are usually the electron donors in these compounds. Oxygen atoms in carboxylic acids have unsaturated electron configurations, while nitrogen atoms have lone pair electron configurations. Metal atoms can form complexes with APCA. Six ligands are used to capture metal ions using EDTA, a hexadentate chelating agent. In a similar way, DTPA is an octadentate chelating agent, which has eight sites where electrons can be donated to the metal ion.

Dissociation of chelating agents to engender ionized forms is described below in the series of following deprotonation reactions of H_4X (where X stands for ligand).

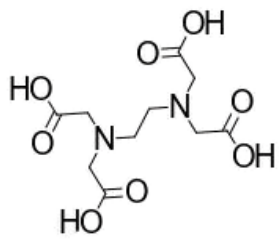
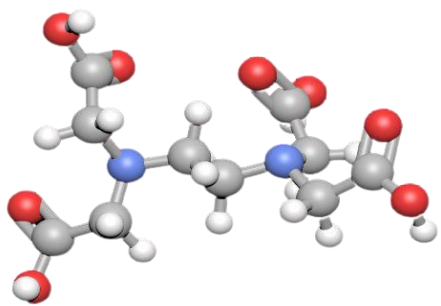
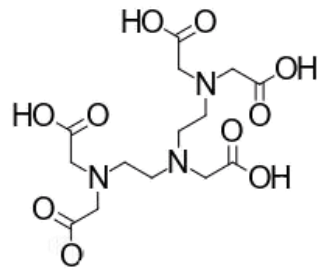
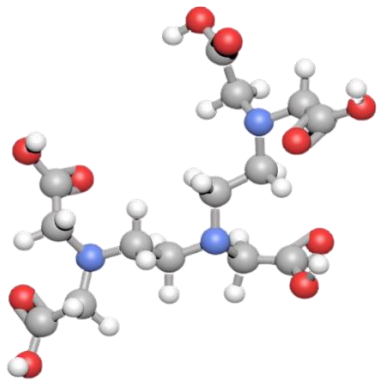
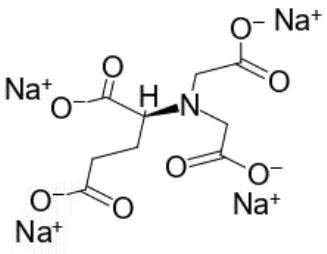
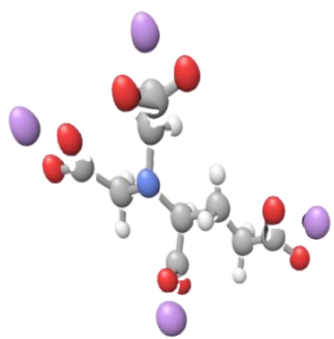


Table 2 and **Table 3** illustrate the chemical formula, 2-D, and 3-D structures of the three widely used APCA in the petroleum industry.

Table 2 – Aminocarboxylic acids

Chelating agents	Abbreviation	Chemical Formula
Ethylenediaminetetraacetic acid	EDTA	$C_{10}H_{16}N_2O_8$
Diethylenetriaminepentaacetic acid	DTPA	$C_{14}H_{23}N_3O_{10}$
L-glutamic acid-N, N-diacetic acid	GLDA	$C_9H_9NO_8H_4$

Table 3 – 2-D and 3-D structures of aminocarboxylic acids

Chelating agents	2-D Structure	3-D Structure
EDTA		
DTPA		
GLDA		

The distribution of ionic species of EDTA and DTPA as a function of pH is shown in **Figure 14**. For instance, EDTA is in the form of H_2Y^{2-} at pH 4.4. However, DTPA exists as HX^{3-} at pH 6.4. The trend claims that each type of chelating agents behaves uniquely to complex metal ions depending on pH environment.

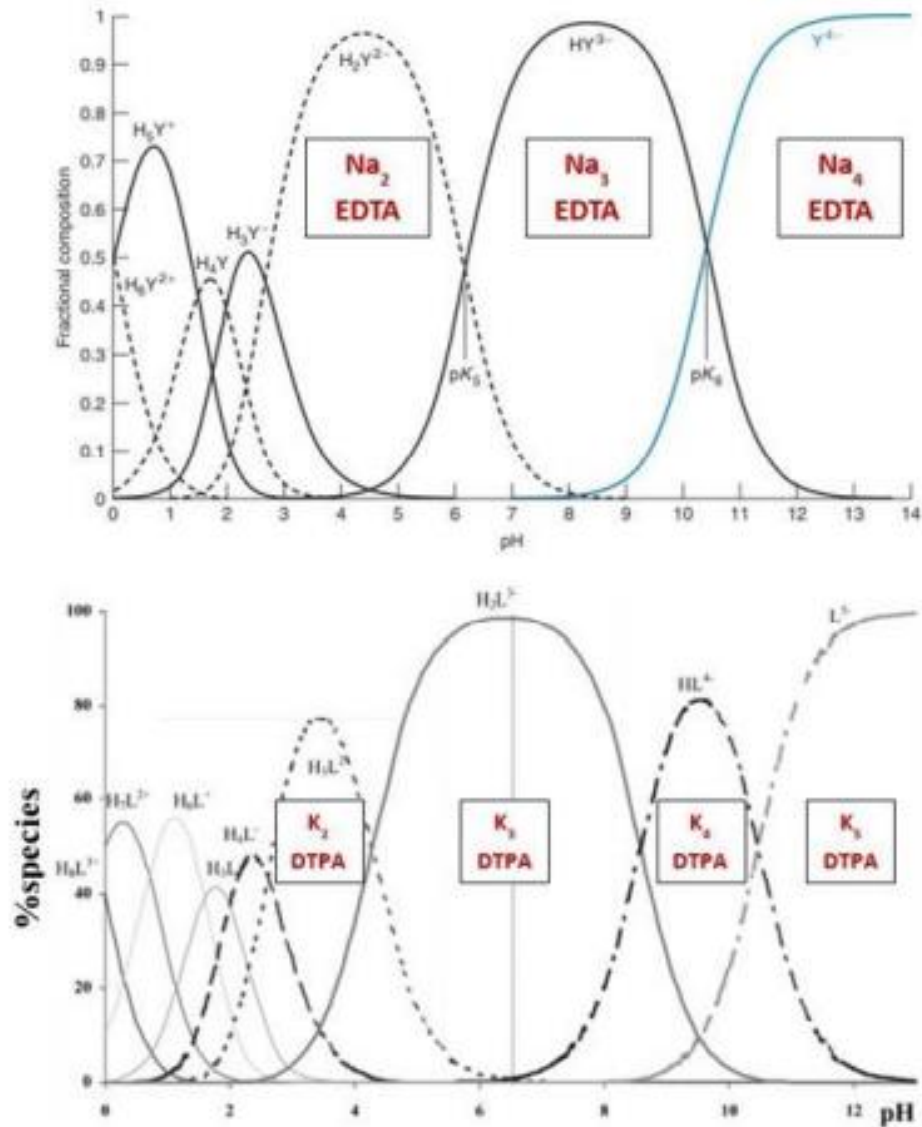


Figure 14 – Speciation diagrams (EDTA and DTPA)

[65] studied the reaction mechanisms between simple organic acids, chelating agents with calcite. The main conclusion was that reaction rates are extensively dependent on proton attack during the reaction between chelating agents and calcite at low pH values, and proton attack controls the reaction rate. However, at high pH, ligand attack hinders the reaction rate between calcite and chelating agents.

The effectiveness of chelating agents is a strong function of pH. Generally, the chelators that show higher stability constant for iron, their ability to catch and hold the iron in solution for an extensive range of pH is high [32]. Stability constants of EDTA, DTPA, and GLDA at 77°F against Iron (II) and Iron (III) are shown in **Table 4**.

[32] showed the optimum pH range for aminocarboxylic acids for Iron (III) at 77°F. EDTA is more effective at pH values between 1 and 10. However, the optimum pH range for DTPA is considered from 2 to 11. Compared to DTPA and EDTA, the ideal pH range for GLDA varies between 2 and 8.

Table 4 – Stability constants at 77°F [32]

Ion	EDTA	DTPA	GLDA
Iron (II)	14.3	16.5	8.7
Iron (III)	25.7	28	15.2

2.5 Iron sulfide scale

The common type of scale, which causes inaccurate well integrity determination and operational problems, is the iron sulfide scale [66]. Scale formed in the downhole and near-surface side of the production tubing in sour gas wells is illustrated in **Figure 15**.

Approximately 43% of the scales in the Ghawar field in Saudi Arabia is considered as iron sulfide scale [67]. The most crucial detail for the removal and inhibition process of the iron sulfide scale is to know the origin of the iron and to understand the creation mechanism of the iron sulfide precipitates.

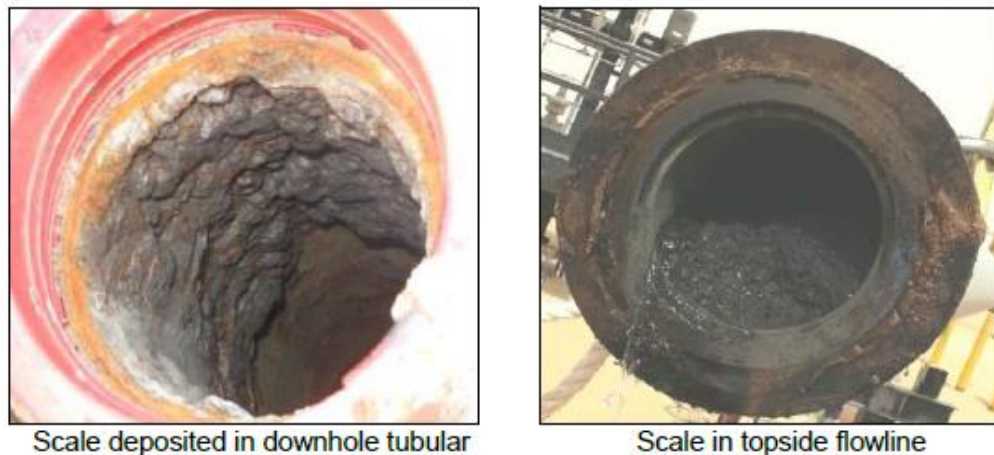


Figure 15 – Iron sulfide scale deposition in sour gas wells tubing

The formation of iron sulfide scales highly depends on the source of iron and H_2S . Most of the time the iron originates from iron-rich minerals, produced water, and corrosion products while H_2S comes from acid well treatments, SRB, seawater injection and the hydrolysis of metal sulfides [68]. Since the focus of the thesis is iron sulfide scale formation and inhibition in water injection wells, it is worth to mentioning the iron sulfide formation mechanism in sea-water injection wells.

The injected sea-water usually contains the concentration of the sulfate ions. On the other hand, the formation could have SRB. The SRB usually transform the sulfate ions and causes H_2S generation. Hence, the reaction between H_2S and any source of iron will be the reason for forming iron sulfide scale and its deposition. **Figure 16** shows microbial corrosion and the mechanism of iron sulfide formation by SRB. It is evident from the figure that SRB triggers sulfate ions to form H_2S . The ferrous ions (which is indicated as anode) readily react with generated H_2S and precipitate as iron sulfide (indicated as FeS).

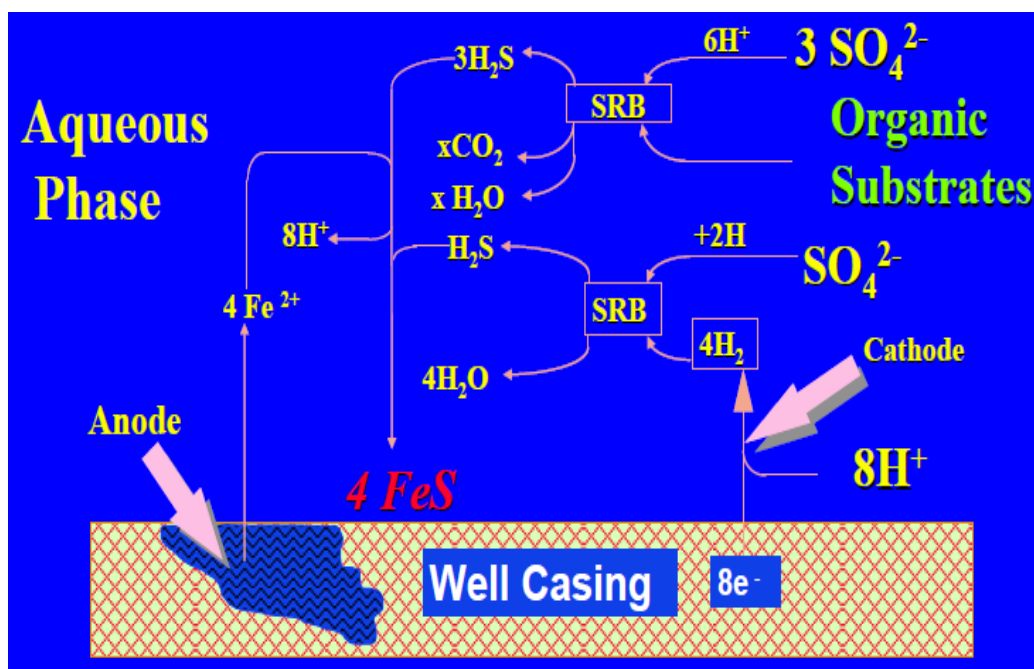


Figure 16 – Microbial corrosion by SRB and FeS formation

Therefore, iron precipitation in formation plays a vital role in the formation of the iron sulfide scale. Thus, it is intended to be introduced the literature survey on formation damage due to iron deposition in the following section.

2.5.1 Source of iron and formation damage due to iron precipitation

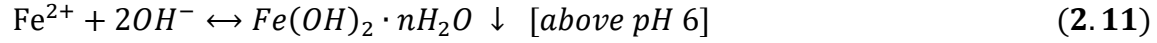
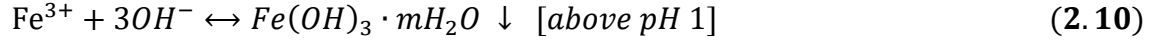
In the scenarios where acid injection is applied, acid solution might be contaminated with iron. The primary reason for this tendency is a reaction of the acid solution with the iron-containing products and equipment, including storage tanks, coiled tubing, fittings, casing, and tubing [69]. As mentioned earlier in the chapter, formation itself can contain hematite, magnetite, pyrite, siderite and chlorite can play the role of iron source [70]. Among these minerals, siderite mineral has the source of Fe(II) while hematite has Fe (III) [71].

The oxidation state of iron usually is either +2 or +3 and iron oxidation or reducing characteristic highly depends on the solvent system and associated anion. In the system in which oxygen participates, ferric is considered as more stable one. However, in an oxygen-free system ferrous is the more stable one. Scale formation and rust initiated by oxygen corrosion more likely produces ferric ions and this is the main trend in water injection wells. Therefore, injection triggers more serious ferric precipitation. Production wells, however, is mainly face challenges related to ferrous precipitation [71].

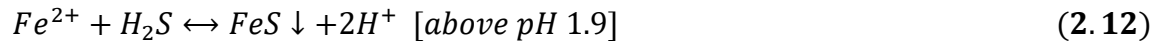
The vital scenario during acidizing that helps to minimize the precipitation of Fe (OH)₃ is the reduction reaction of ferric through metallic iron (**Eq.2.9**).



Based on the many previous research, it can be said that Fe (OH)₃ is the most damaging iron precipitate as a result of acidizing [72]. When the pH of the environment becomes 1 (**Eq.2.10**), iron (III) hydroxide readily precipitates. However, iron (II) hydroxide starts to deposit at pH of 6 (**Eq.2.11**) [73].



The presence of H_2S in sour oil and gas wells, triggers precipitation of iron (II) sulfide as pH value of the system becomes higher than 1.9 (**Eq.2.12**) as reported in [69], [73]. Moreover, presence of H_2S causes reducing Fe^{3+} into Fe^{2+} and results in precipitation of elemental sulfur (**Eq.2.13**) [71].



The pore throat of the formation rock can be blocked by the precipitation of iron sulfide minerals, such as pyrite, mackinawite, and pyrrhotite as well. Therefore, mean pore throat diameter of Indiana limestone rocks and mean particle size of iron sulfide minerals is vital to mention.

Table 5 – Properties of Indiana limestone and iron sulfide scale mineral

Rock/minerals	Indiana limestone	Indiana limestone	Iron sulfide	Iron sulfide
Brine permeability, mD	70	20	-	-
Mean pore throat diameter, μm	44	19	-	-
Mean particle size, μm	-	-	75-150	296
References	[74]	[74]	[15]	[66]

Table 5 shows the pore throat size of the Indiana limestone rock for the corresponding brine permeability of the rock and the iron sulfide mineral mean particle size. The information mentioned in the table proves that the formation of iron sulfide scale can definitely cause pore throat blockage.

To sum up, it is evident that different type of iron compounds and iron sulfide minerals can precipitate and potentially causing plugging of pore spaces and pore throats and will lead to permeability reduction associated with formation damage.

2.5.2 Iron sulfide scale formation

Sour gas wells often encounter problems related to iron sulfide deposition, which results in a severe loss of gas production and blockage of downhole tubular [75]. Iron could be formed through the process of acid injection as a result of severe corrosion of injection tubing.

The formation of the iron sulfide scale highly depends on the following factors [2], [76]:

- Mineralogy of the formation
- pH environment
- Pressure and temperature

Based on laboratory researches, it is revealed that iron sulfide can experience crystalline transformations from sulfur-insufficient to sulfur-abundant in different conditions [77], [78]. Depending on the parameters mentioned above, several forms of iron

sulfide scales can form. These scales differ from each other following the iron-sulfur ratio. Typical forms of iron sulfides are listed in **Table 6**.

Table 6 – Typical forms of iron sulfide minerals

Scale Name	Chemical Formula
Pyrite	FeS_2
Marcasite	FeS_2
Pyrrhotite	Fe_7S_8 or Fe_{1-x}S
Troilite	FeS
Greigite	Fe_3S_4
Mackinawite	$(\text{Fe, Ni})_9\text{S}_8$ or $(\text{Fe, Ni})_{1+x}\text{S}$

Each type of scale has specific chemical and physical properties, which are quite salient to consider while developing new formulations for chemical dissolution of scale precipitation and inhibition process. The reaction between the hydrogen sulfide and iron causes the generation of iron sulfide scale.

H_2S gas is one of the common gases in the oil and gas industry and is well known for its damaging and venomous character. Biotic and abiotic processes are the principal origin of reservoir souring [30], [79], [80]. [81] reported that the followings (**Table 7**) are considered the vital souring mechanisms associated with both processes.

Table 7 – Sources of reservoir souring

Biotic	• H_2S produced in injectors utilize water with high sulfate content • Due to SRB (Sulfate Reducing Bacteria)
Abiotic	• Thermochemical sulfur reduction • Hydrolysis of metal sulfides • Thermal hydrolysis of organic sulfur compounds

Several authors have extensively examined the reaction between cation (Fe^{2+}) and sulfide ions [30], [82]. Throughout the production phase of the oil and gas, pressure depletion causes the evolution of the gases like carbon dioxide (CO_2) and H_2S . As a result of an increase in pH, pH-caused scale formation becomes inevitable [83]. The following reactions are for illustrating the formation mechanism.



Along with the pH and specifications of the aqueous phase, crystalline transformation depends on the oxidation stage on the surface of primarily formed iron sulfides. Iron monosulfides might alter into the form of pyrite [84]. The scale layer can incorporate separate layers of deposits with different chemical and physical properties. Based on the studies on Khuff gas wells where two-layered scale deposition was observed, it revealed that iron sulfide scale in well tubular formed because of pre-formed siderite and ferric compounds. The outer layer was composed of siderite and ferric mixture, and the inner layer included pyrite. The formation of the iron sulfide was a consequence of the following reactions:



Ferrous iron can form in reservoir conditions. Ferrous iron is not considered a problematic issue unless there is no sulfide in the system. However, ferric iron can deposit

in the form of iron hydroxide at pH values higher than one (**Eq.2.19**). Ferric iron can transform into the ferrous form if sulfide presents in the system.



2.5.3 Iron sulfide scale removal and inhibition

The traditional way of scale dissolution incorporates the use of hydrochloric acid (HCl). HCl is able to remove most of the mineral deposits. However, HCl demonstrates a critical corrosion rate in specifically high temperatures and can cause a sludging issue. Therefore, it sometimes becomes expensive to utilize HCl since it requires supplementary chemicals in order to manage the reaction rate [41].

According to [70], HCl acid is sufficient to iron sulfide deposits with low sulfur contents, such as mackinawite, pyrrhotite, and troilite. The types of iron sulfide minerals can be distinguished with iron-sulfur rations since the iron to sulfur ratio is an essential factor for the chemical removal process of scales. The acid solubility of different iron sulfide minerals is shown in **Table 8**.

Table 8 – Acid solubility of iron sulfide minerals [30], [85]

Scale Name	Chemical Formula	Acid Solubility
Pyrite	FeS ₂	Slow and Difficult
Marcasite	FeS ₂	Slow and Difficult
Pyrrhotite	Fe ₇ S ₈ or Fe _{1-x} S	Moderate
Troilite	FeS	Rapid and Easy
Greigite	Fe ₃ S ₄	Fast
Mackinawite	(Fe, Ni) ₉ S ₈ or (Fe, Ni) _{1+x} S	Fast

Iron could form through acid injection due to severe corrosion of injection tubing [86]. [86] presented study for iron sulfide formation and precipitation in sour gas wells during acid injecting. They used different concentrations of HCl mixed with corrosion inhibitors.

The main challenges with iron sulfide scales are:

- This form of scales is hard to study under an anaerobic condition in a laboratory environment;
- Having different iron-to-sulfur ratios within the crystalline structures makes the study more complicated.

During the period of acid stimulation, iron generation and iron sulfide deposition were studied throughout four different stages. The stages include iron formation due to reaction between injected acid and tubing; dissolving carbonate reservoir rock while injecting acid; scale creation during sour gases saturated acid, and sour gases saturated formation water injection. 26 wt% HCl acid mixed with corrosion inhibitors injected, and concentration was decreased to 18 wt% HCl because of corrosion of tubing. Corrosion inhibitors are often used in the industry to avoid the corrosion of carbon steel. However, their use at temperatures above 100°C is not successful [87]. As a consequence, while matrix acidizing acid in carbonate reservoirs, there is a high possibility of having formation damage in the near-wellbore region due to the generation of iron sulfide and iron carbonate scale, and the main source of the iron is tubular corrosion in an acidic environment. It is concluded that in carbonate reservoirs, iron sulfide generation occurs during the injection

of acid saturated with sour gas and formation water saturated with sour gases mixed with acid.

One of the significant properties is thermal stability which is high for pyrite, and it is challenging to remove pyrite-containing scale using acids. As the iron to sulfur ratio becomes 1:1 or very close, one thermal stability of the minerals is going to be less, and they are relatively easy to be removed by acids [13]. Because scale samples are not homogenous in terms of mineralogy, field scale samples can be contained a mixture of several minerals. The mineral heterogeneity causes complexity in the removal process. Another problematic aspect of the iron-sulfide scale is wettability. Naturally, iron sulfide scales are oil-wet, and this organic coverage (coating) on inorganic scales hinders the removal process using unsophisticated acids and chelating agents [75].

Temperature variation is a very sophisticated factor for iron sulfide solubility. Unlike other sulfide scales, as temperature increases, the solubility ability of iron sulfide scales decreases [82]. Equilibrium constants (K_{eq}) of iron sulfide scales are so low, as shown in **Table 9**.

Table 9 – Equilibrium constants of iron sulfide scales [83]

Scale Name	Equilibrium constants (K_{eq})
Pyrite	8.51×10^{-26}
Mackinawite	2.88×10^{-18}
Pyrrhotite	2.7×10^{-19}

Chemical dissolvers can be considered as effective and ideal if the well productivity increases, the loss of wellbore integrity does not happen, and no safety problems occur. Myriad solvents have been proposed to remove iron sulfide scales effectively.

Descaling process of the iron sulfide scale using chemical treatment hugely depends on temperature and pressure conditions. As mentioned before, HCl is a mostly-used chemical agent for sulfide scales. However, its effectiveness on the iron sulfide scale removal process is limited with temperature [43]. Acid dissolution to solute the iron sulfate scale is hazardous due generation of extremely toxic and corrosive H₂S gas [88]



[88] reported principal aspects for chemicals, which can be taken into account as optimal iron sulfide scale solvers:

- Comparable dissolving capacity as concentrated HCl acid
- Low corrosivity to mild steel completion
- The metal loss should be < 0.05 lbs/ft² during descaling treatment
- No free H₂S gas released after dissolving the iron sulfide scales
- Non-acid formulations preferred. The neat product should have a pH value higher than the onset pH for iron sulfide re-precipitation (pH > 2.0).
- Stable at downhole temperature (up to 315 °F).

Overall, the removal process of iron sulfide scale using chemical dissolution is risky, and many chemical agents have been introduced.

The two of the main problems with hydrogen-sulfide gas production during descaling processes has been identified [89]. One of them is burning hydrogen-sulfide gas, which is very harmful due to its toxic composition. Burning hydrogen-sulfide gas leads to the formation of sulfur dioxide and sulfur trioxide, which are vital contaminants. Another problematic point is considered operational issues due to hydrogen sulfide in the oil and gas industry.

Moreover, hydrogen sulfide can cause corrosion complications. The acid attack and ferric ion are underlined as the primary source of corrosion. A minor amount of corrosion inhibitors, such as aldehydes and aldehyde condensation products (amine), is enough to prevent corrosion.

1. The new formulation has the ability to dissolve acid-soluble sulfide-containing scale without the production of hydrogen sulfide gas.
2. Using HCl or H₂SO₄ are beneficial acids, but there is a need for corrosion inhibitors.

As a conclusion, it is concluded that using HCl with enough corrosion inhibitors is the most effective way not to produce hydrogen sulfide gas.

Further, in the studies, new robust non-corrosive and environmentally friendly chemicals - chelating agents have been suggested.

[43] introduced a novel approach to remove iron sulfide scales by lowering the issues related to chemical dissolution. The scale was composed of different types of minerals. Three samples and five solvers were used in the experiments. The iron sulfide scales mainly consisted of pyrrhotite (>64 wt%), pyrite, and marcasite. The description of the five dissolvers is as shown in the below table.

Table 10 – Iron sulfide scale dissolvers

Generic Description	Composition Details
Fluid A	20% HEDTA, pH = 2.5
Fluid B	DTPA solution (pH = 11)
Fluid C	5% HCl + 10% DTPA
Fluid D	EDTA Derivative, pH = 6
Fluid F	THPS + NH ₄ (aqueous solution)

The ratio of the dissolvers volume to scale volume varied between 4 to 20 and 12 showed the best performance in terms of solubility at 95°C for 24 hours. Fluid D was a robust dissolver among the above-mentioned solvents. The mild pH value was favorable because of the risks associated with high corrosion rate and high re-precipitation of scale. This solvent had the capability to dissolve mixed field scale samples.

[90] used a polymer-based chemical system at different pH values and temperatures for iron sulfide scale (pyrite, pyrrhotite, marcasite) removal. The proposed dissolver showed excellent performance at low and mild pH. The main advantages of the solution were reduced H₂S generation, which leads to achieving a low corrosion rate in comparison with HCl and the ability to dissolve pyrite and marcasite minerals.

[91] suggested various chemicals for the elimination of iron sulfide scales (pyrite (FeS₂), marcasite (FeS₂), pyrrhotite (Fe₇S₈), and mackinawite (Fe₉S₈)) with various compositions. THPS chelating agent was used with the concentration differing from 15

wt% to 75 wt%. The use of 50 wt% of THPS is recommended since it had the highest dissolution efficiency.

[92] introduced a new formulation for the dissolution of the iron sulfide scale in the basis of carboxylate copolymer. 10:1 ratio was used (chemical to scale ratio) and tested on marcasite, pyrite, pyrrhotite, troilite, and five different field scale samples. THPS and 25% acetic acid showed better results to dissolve the iron sulfide scale. The new solvent outperformed 7.5% HCl.

[12], [93] introduced a new chemical solvent that is mainly suitable to dissolve pyrite iron sulfide scale. DTPA was used as a chelating agent keeping a high pH value, and potassium carbonate was used as a catalyst that can be mixed with DTPA at concentrations of more than 3 wt% in order to improve dissolution efficiency. 85% of removal of pyrite iron sulfide scale achieved at 70 °C within 48 hours.

[94] proposed polymer and THPS based scale dissolvers using synthetic iron sulfide that mimic the equal concentration of different minerals from field scale sample. Three dissolvers were used in the experiments, including:

1. Polymer-based dissolver
2. THPS-based dissolver
3. Mixed dissolver (polymer + THPS)

The scale was composed of 26 wt% pyrite and the first and second type of chemical mixtures showed low dissolution capacity while mixed dissolver improved removal efficiency and particle size distribution.

[95] used various organic acids (maleic, glutamic, succinic, and gluconic acids), chelating agents (EDTA and DTPA), and proposed a new formulation which is the mixture of these chemicals. Results showed that introduction of a new dissolver to the field scale sample (55 % pyrrhotite, 21 % calcite, 8 % pyrite, and 6 % troilite) at 125°C with mixing ratio 2 g scale: 20 g dissolver. The new formulation, which was the mixture of acid and chelating agents and organic acids, showed 80% dissolution.

[14], [96] introduced a new acid system called NEFAS, which is an acid solution of catalytic reagent added to HCl to achieve the solution that can be an alternative to HCl. The iron sulfide scale sample was composed of 55% pyrrhotite, 8% pyrite, 6% troilite. NEFAS and the solid material ratio were equal to 10:1, and the solubility test was performed at 125°C at 2, 6, 12, 24 hours. They found that NEFAS dissolved 83g/lit of the iron sulfide scale within 6 hours with a 0.04lb/ft² corrosion rate, which was quite low compared with HCl. However, dissolution efficiency was approximately the same with HCl with 75 wt% NEFAS.

[97] investigated ZnS inhibitor's efficiency with the use of the stress test method, and they used three types of scale inhibitors, and these three inhibitors showed different results according to the zinc to sulfur ratio.

However, [98] used polymer-based inhibitors using the static and dynamic conditions for mild and severe conditions. They also tested the effects of the brine salinity on the efficiency of the scale inhibitors.

[99] discussed kinetics and inhibition of ferric sulfide. They used the most famous scale inhibitors, namely Phosphino-poly(carboxylic acid) (PPCA) and Poly(vinyl sulfonate

(PVS), alongside five chelating agents. The used chelating agent EDTA showed better results.

[7] investigated iron sulfide inhibitor, which was a high molecular weight sulfonated copolymer under the alternative anaerobic experimental configurations. They concluded that to achieve a high-quality dispersive iron sulfide inhibition process, scale particle size, sulfide, and iron initial concentrations should be well defined and defined one sequence of significance. This yields the following sequence: brine chemistry > sulfide concentration > iron concentration > pH > time > temperature. This sequence simply shows which parameter is more important to consider during inhibition processes.

[25], [26] worked on the development of novel inhibitors to effectively reduce the formation of iron sulfide scale in an anoxic environment. In addition to the newly proposed chemical, they examined the efficiency of well-known inhibitors, including phosphonates, carboxylic acid polymers. The study proposed a new chemical that can control the scale deposition at limited values, and the chemical has the ability to increase the water wetness of the scale.

Chemicals used during the experiments are NaCl, $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, SrCl_2 , MgCl_2 , Na_2SO_4 , $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ and biological reagent - PIPES (Piperazine-1, 4-Bis (2-ethane sulfonic acid) sesquisodium salt (enzyme grade)). Solutions were prepared at anaerobic conditions, as discussed in [25].

Specific brine composition was used, which has 10 mg/L Fe^{2+} and 50 mg/L S^{2-} concentration of ions. Static bottle tests were performed at 70°C temperatures, using a 6.7 pH solution. Different concentrations of polymeric and novel polymeric inhibitors were

tested. Only the latter chemical showed promising results since the use of the new chemical higher concentration than 100 mg/L in the solution dispersed for some period. 50 mg/L of the inhibitor was considered as adequate to disperse the solution, which is admixed with 30 mg/L Fe^{2+} and 20 mg/L S^{2-} . The ability of the solution to disperse iron ions further tested in the conditions 50°C and 70°C. Dynamic scale loop experiments using each solution with different concentration (0, 50, 100, 150 mg/L) under 70°C and 300 psi conditions utilized. The results of the oil-water partitioning test showed that with the use of appropriate concentrations of the chemical could handle to keep the oil quality. Novel inhibitor demonstrated perfect results for nucleation of particles and effectively reduced the iron sulfide deposition in the flowline.

CHAPTER 3

METHODOLOGY & MATERIALS

3.1 An overview of the research methodology

The scope of this chapter includes details of the experimental methodology and the materials used during this study. The section provides the information regarding chemicals, rock types, rock and chemical preparation and equipment used within the framework of this research. Furthermore, the detailed methodology to fulfill the objectives of the research is discussed. Additionally, brief overview on conventional laboratory testing methods and simulation technique to study scale formation prediction and inhibition are discussed.

The conventional laboratory methods to study iron sulfide scale formation, inhibition and inhibitor efficiency include the following [6]:

- Static bottle tests
- Dynamic tube-blocking test
- Static adsorption tests
- Compatibility tests

In addition to mentioned laboratory techniques, Molecular Dynamic Simulation (MDS) has also been used to assess the adsorption phenomenon of the inhibitors. There are several disadvantages of the mentioned techniques to study iron sulfide inhibition. Firstly, the dynamic filter block test is limited with the filter size, which does not represent actual

formation. Secondly, a static experimental test is limited with low-temperature conditions, and natural dynamics of the inhibition process cannot be investigated. Finally, through MDS, it is not easy to catch the nature of dynamic adsorption. Therefore, this study presents series of investigations, including adsorption, mineralogy, solid/solid interaction, and cation tracking experiments that were utilized throughout the period of the research. **Table 11** provides information about the equipment that is used for the above-mentioned experiments.

Table 11 – Equipment used during experiments

Experiments	Equipment
Mineralogy	X-Ray Diffraction (XRD)
Particle size	Particle size analyzer
Dynamic adsorption	Coreflooding setup
Cation tracking	Inductively Coupled Plasma (ICP)-OES
Solid/solid interaction (Surface charge investigation)	ζ-potential (Zeta potential)

The research incorporates three main stages, and these stages are illustrated in **Figure 17**. A study on the adsorption of aminocarboxylic acids (EDTA, DTPA) in carbonate rock samples (Indiana Limestone) in **Phase 1** was conducted. A dynamic adsorption experiment of chelating agents was carried out on Indiana limestone core samples using a coreflooding setup, and ICP-OES was used to monitor iron concentration during the experiment. Further in the experiments, solid/solid (iron/calcite in our case)

interaction and iron (ferric (Fe^{3+}) and ferrous (Fe^{2+})) precipitation on calcite rock surface in pH environments varying from 1 to 13 were studied in **Phase 2**. This stage of the project also examined the effect of different types of salts and EDTA on iron precipitation. Final phase of the research – **Phase 3**, involves experiments to study formation and inhibition (using the optimum chelating agent concentration determined in the Phase 1) of iron sulfide scale by employing coreflooding setups.

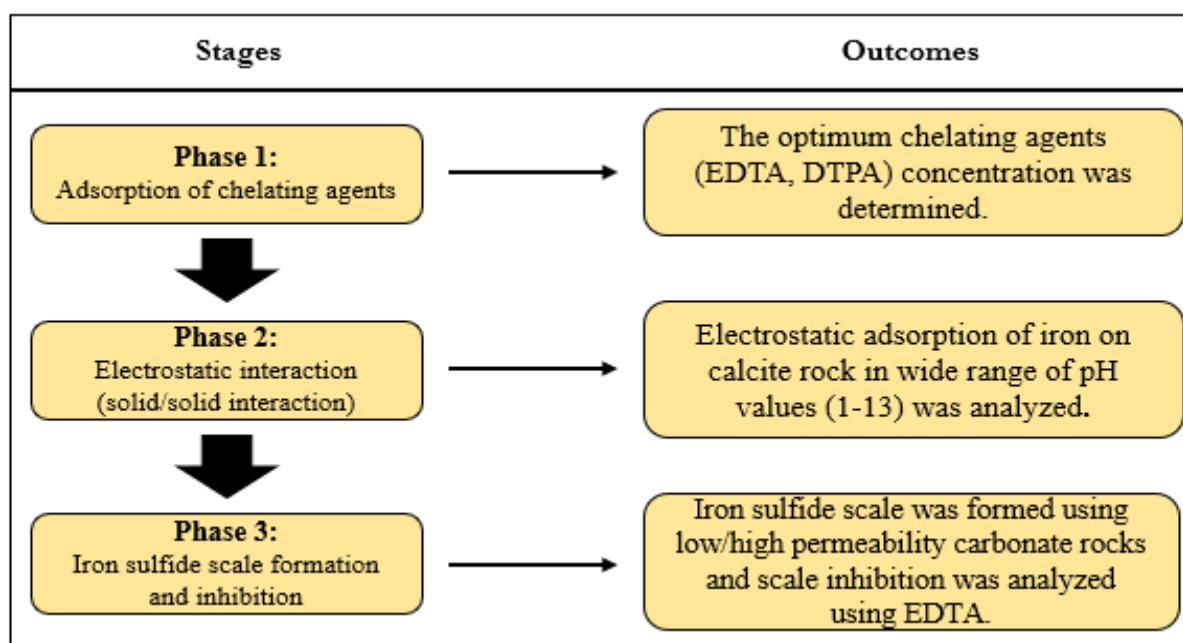


Figure 17 – Phases of the conducted research

In the following sections of the chapter 3, a detailed explanation of materials and methods used in the research is provided.

3.2 Materials and equipment

This section provides detailed description of the materials and equipment used in each of three phases.

3.2.1 Adsorption of chelating agents on carbonate rock samples (Phase 1)

As mentioned briefly earlier in the chapter, in order to determine optimum chelating agent concentration dynamic adsorption approach was used and to conduct these experiments the coreflooding setups were performed. 19 Indiana limestone core samples (**Figure 18**) with the length of 6 inches (15.24 cm) and 1.5 inches (3.81 cm) of diameter were used during adsorption experiments.



Figure 18 – Indiana limestone rock sample with its dimensions

Prior to coreflooding experiments, core preparation (core cleaning, core cutting), core sample weighting, fluid preparation, saturating core samples, pore volume (PV), porosity determination were conducted.

The rock core samples were first cleaned with ethanol using a Soxhlet extractor. They were then dried in oven at 70°C. The dry weight of rock samples (M_{dry}) was determined using digital scale. Furthermore, core samples exposed into a vacuum pressure for 3-4 hours and then were saturated with brine solution (3wt% KCl) at the pressure of 1500 psi. Brine saturation was performed for 24 hours, and the wet weight of the samples (M_{wet}) was measured. The brine density (density of 3 wt% KCl = 1.0175 g/cm³) and

viscosity were then identified at room temperature. Pore volume (V_{pore}) of the rock core samples was calculated with **Eq. 3.1**.

$$V_{pore} = \frac{M_{wet} - M_{dry}}{\rho_{brine}} \quad (3.1)$$

The porosity of the samples, however, was calculated using **Eq. 3.2**.

$$\phi = \frac{V_{pore}}{V_{bulk}} \quad (3.2)$$

The core preparation and porosity calculation procedures were listed in the **Figure 19**.

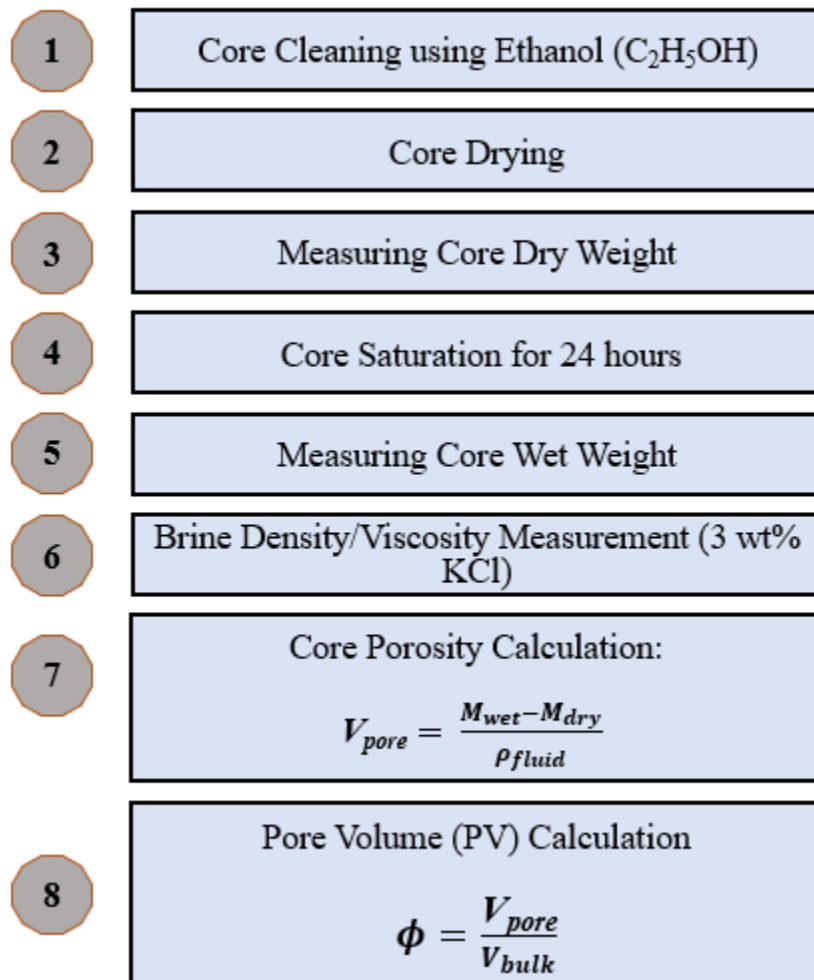


Figure 19 – Rock sample preparation prior to coreflooding experiments

a. Coreflooding equipment

After the core preparation, linear coreflooding setup for dynamic adsorption experiments was made prepared and the Core Lab Minimum Miscibility Pressure system (MMP) shown in **Figure 20** was used. Before the adsorption experiments, following aqueous solutions and chemicals with the concentrations and pH values shown in **Table 12** were prepared. 10 wt%, 15 wt%, and 20 wt% EDTA (purchased from BASF) were prepared and using sodium hydroxide (NaOH) the pH of solutions increased to nearly 11 for each concentration of the EDTA. In addition to EDTA, 2 EDTA solutions with 10 wt% mixed with 5000 ppm MgCl_2 and CaCl_2 with pH = 11 were prepared. These 2 solutions were used to study the impact of the Mg^{2+} and Ca^{2+} cations on adsorption of the chelating agents. Moreover, 20 wt% DTPA with pH = 11 and 10000ppm (~ 2800 ppm Fe^{3+}) FeCl_3 .

Table 12 – Chemicals used in adsorption experiments with their pH and concentrations

Chemicals	Concentrations	pH
Potassium Chloride (KCl)	3 wt%	-
Ethylenediaminetetraacetic Acid (EDTA)	10 wt%, 15 wt%, 20 wt%	10.8 – 11.2
Diethylenetriaminepentaacetic Acid (DTPA)	20 wt%	11.2
Ferric Chloride (FeCl_3)	~ 10000 ppm	-
EDTA mixed with Calcium Chloride (CaCl_2)	10 wt% EDTA + 5000 ppm CaCl_2	11
EDTA mixed with Magnesium Chloride (MgCl_2)	10 wt% EDTA + 5000 ppm MgCl_2	11



Figure 20 – Coreflooding apparatus (CoreLab)

A brief description of the used coreflooding system is described below:

1. The core holder is used to apply the required temperature and pressure to the core sample. The core holder has one inlet and one outlet.
2. The fluids are inserted into the core holder using High Pressure (HP) pumps at the desired flow rate (very low flow rate in our case), as shown in Figure 13. The maximum available flow rate that can be injected using these pumps is $90 \text{ cm}^3/\text{min}$. The injection rate used during this research is $0.5 \text{ cm}^3/\text{min}$.
3. The core holder is heated using the oven and temperature controller.
4. High confining pressure inside the core holder is created using the syringe pump. High pressure is formed utilizing water, and this pump can create up to 7500 psi pressure.

5. Pressure transducers are connected at the inlet and outlet sections in order to continuously monitor pressure changes during the core flooding and to determine pressure drop.
6. Backpressure should be kept 400-500 psi less than the overburden pressure. 1000 psi back pressure and 1500 psi overburden pressure are applied in our study.

Coreflooding setup for the adsorption experiments is illustrated in **Figure 21**. 3 fluid accumulators (3,4,5 shown in **Figure 21**) were used and they filled up with 3 solutions (3 wt% KCl, chelating agents, and ~10000 ppm FeCl₃). The experiments were performed at 3 different temperatures (77 °F, 120°F, 200°F) and 3 of the experiments contained 3 wt% KCl preflush and injecting 10000 ppm FeCl₃ solution at mentioned temperatures. An entire number of the adsorption experiments with corresponding temperature conditions are described in **Table 13**.

The stabilized pressure drop values for three constant flow rates were used to calculate initial rock permeability using Darcy equation (**Eq. 3.3**)

$$k = \frac{122.812 q \mu L_{core}}{\Delta P d_{core}^2} \quad (3.3)$$

Where:

k – core permeability in mD

q – flow rate in cm³/min

μ – fluid viscosity in cP (μ of 3 wt% KCl = 1)

L_{core} – length of the core in inches

ΔP – pressure drop across the core in psi

d_{core} – diameter of the core in inches

The experiments start with preflush (injecting 3 wt% KCl) to measure the initial permeability of the rock samples using three various flow rates and stabilized pressure differential were identified.

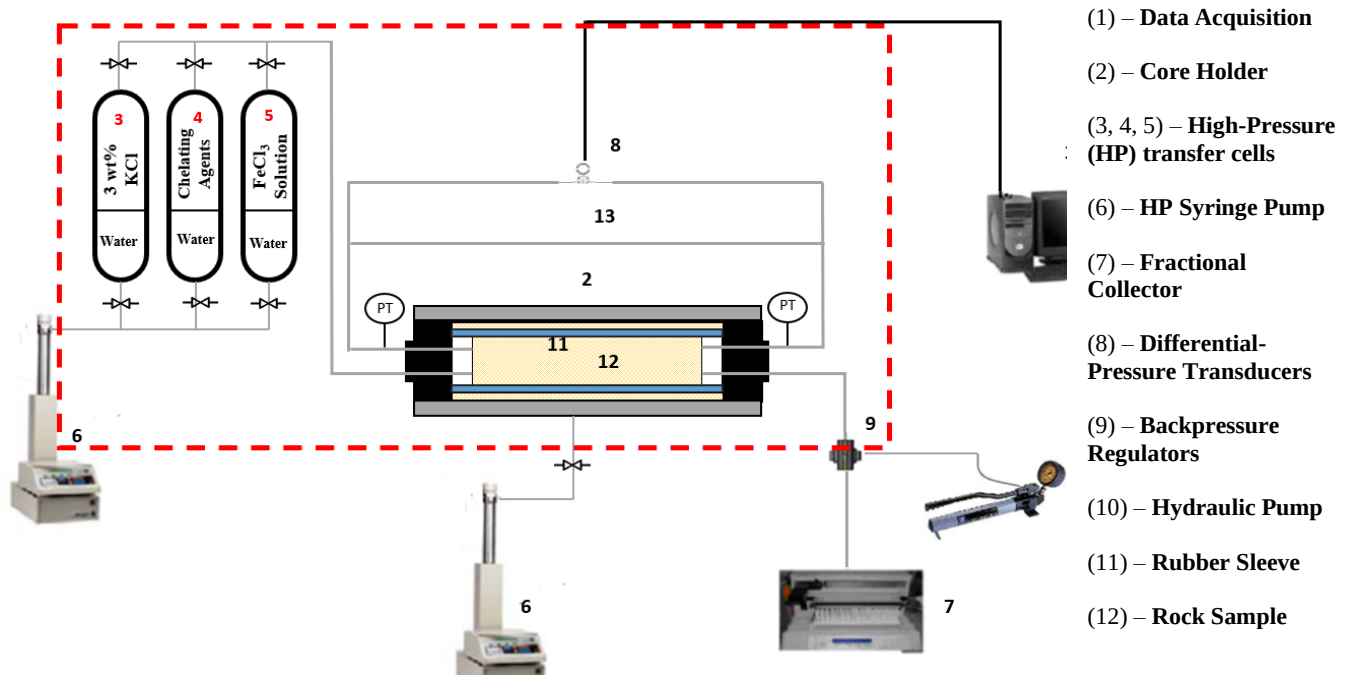


Figure 21 – Coreflooding setup for dynamic adsorption experiments

Table 13 – Number of experiments and their descriptions

Experiments	Number of experiments	Temperature
KCl preflush and FeCl ₃ injection	3	77 °F, 120°F, 200°F
KCl preflush, EDTA and FeCl ₃ injection	9	77 °F, 120°F, 200°F
KCl preflush, EDTA (with soaking time) and FeCl ₃ injection	3	77 °F
KCl preflush, EDTA (mixed with MgCl ₂ , CaCl ₂) and FeCl ₃ injection	2	77 °F
KCl preflush, DPTA and FeCl ₃ injection	2	77 °F, 120°F

The conditions of the coreflooding experiments, injection sequence of the solutions and injected pore volume of each fluid are represented in **Table 14** and **Table 15** respectively. **Table 16** represents the properties of the Indiana limestone core rock samples used in coreflooding experiments.

Table 14 – Conditions used in adsorption experiments

Coreflooding conditions	Values
Back pressure, psi	1000
Confining pressure, psi	1500
Flow rate (during experiment), cm ³ /min	0.5
Flow rates (preflush, initial permeability determination), cm ³ /min	0.25, 0.5, 0.75
Temperature conditions, °F	77, 120, 200

Table 15 – Fluid injection sequences and pore volumes (adsorption experiments)

Injection sequence	Injected fluids	Injected pore volume
1	3 wt% KCl (Preflush)	2 - 3 PV
2	Inhibitor injection	2 PV
3	3 wt% KCl flush	2 PV
4	FeCl ₃ injection	2 PV
5	3 wt% KCl overflush	2 PV

Table 16 – Rock properties (inhibitor adsorption)

Core type	Core #	Core Length (cm)	Dry Weight (g)	Wet Weight (g)	Core Porosity (%)
IL	N1	15.24	396.376	420.314	13.54
IL	N2	15.24	397.575	421.745	13.67
IL	N3	15.23	395.750	420.370	13.93
IL	N5	15.20	398.888	421.750	12.93
IL	N6	15.20	375.649	405.726	17.01
IL	N7	15.19	393.656	420.654	15.27
IL	N8	15.20	393.681	420.790	15.33
IL	N9	15.18	396.044	421.750	14.54
IL	N10	15.25	387.202	412.300	14.20
IL	N11	15.22	390.471	417.377	15.22
IL	N12	15.20	387.822	411.858	13.60
IL	N13	15.20	388.951	413.050	13.63
IL	N14	15.21	388.951	413.098	13.66
IL	N15	15.22	385.700	419.570	19.16
IL	N16	15.23	385.750	419.620	19.20
IL	N17	15.20	395.667	419.677	14.90
IL	N18	15.21	389.950	414.051	13.80

IL	N19	15.24	389.551	413.841	13.73
IL	N20	15.24	393.699	420.700	15.02

With the help of the proposed method, it was able to understand the adsorption capacity of the rocks with and without different concentration and type of chelating agents at varying temperature conditions. In order to evaluate the degree of the adsorption effluent samples during the adsorption experiments were collected. Initial and final concentrations (using effluent samples) of the ferric in the aqueous solutions was analyzed and determined using ICP-OES.

b. ICP-OES equipment

ICP – OES is a widely-used and powerful technique to analyze and capturing chemical elements. The system gives quantitative amount of trace elements within the solid or liquid samples. The purpose of using Optima 8000 ICP-OES (manufactured by PerkinElmer, **Figure 22**) is to determine the variation of heavy metal concentration (Fe^{3+} ions in our case) in inlet sample (ferric solution that will be injected through the core) and effluent samples (collected during the coreflooding experiment). In this way, the adsorption efficiency and ability of capturing the ferric ions from aqueous solution of the chelating agents can be scrutinize. This will help to identify concentration and type of chelators in which maximum adsorption can be obtained.

The method is based on analyzing the photons emitted by excited atoms after they have lost their energy and returned to their original state. Peristaltic pumps are used to introduce the diluted effluent solution into the system. A system nebulizer converts the

solution into a fine aerosol. The different atomic species within the aerosol are then excited by a plasma source. Argon gas ionized with a high concentration of electrons carries the plasma heat current at over 6000 K. ICP software determines what type of elements are present in the sample based on the standard emission intensity and the corresponding concentration.



Figure 22 – ICP – OES (PerkinElmer)

The inhibition efficiency of the inhibitors therefore calculated knowing the ferric concentration in injected solution and effluent samples using **Eq. 3.4**.

$$\text{Inhibition Efficiency} = \frac{\text{Inlet } Fe^{3+} \text{ concentration} - \text{Maximum outlet } Fe^{3+} \text{ concentration}}{\text{Inlet } Fe^{3+} \text{ concentration}} \quad (3.4)$$

The flow chart shown in **Figure 23**, represents key stages for inhibitor adsorption experiments to evaluate inhibition efficacy.

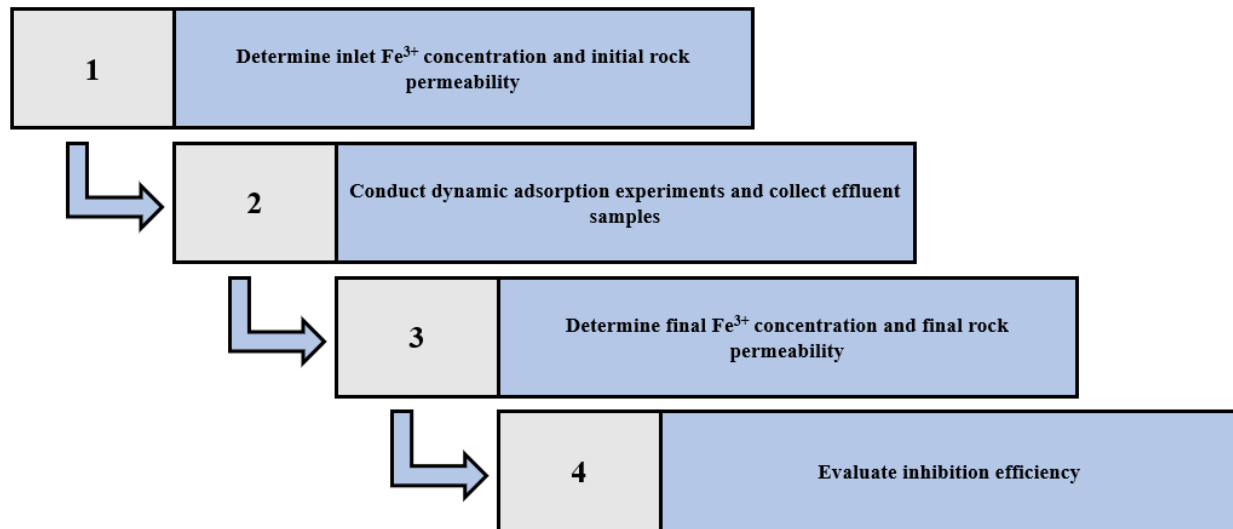


Figure 23 – Flow chart detailing the stages of the inhibitor adsorption experiments

3.2.2 Electrostatic adsorption of iron on carbonate rock (Phase 2)

Solid/liquid and solid/solid interactions can be determined through the set of ζ -potential measurements. Through the production life of the wells, various operations cause alteration of reservoir environment (pH), which influences the surface charge of the rocks. This pH variability results in changing the surface chemistry of minerals, which provokes the generation of problems such as wettability alteration and solid particles precipitation. The necessity of ζ -potential measurements in this study is to understand the adsorption and precipitation of ferric ions on calcite minerals in a wide range of pH values (1-13) through the surface charge measurements. In addition, the impact of the several types of salts (MgCl_2 , CaCl_2 , and NaCl) on ferric precipitation has been studied.

The basic working theory of the ζ -potential is based on measuring the magnitude of the charge or electrostatic repulsion and attraction among particles. Surface charge

measurements give detailed information about dispersion, aggregation, solid adsorption, and particle precipitation.

a. Mineralogy experiment

XRD has extensive use in various industries as well as the petroleum industry. XRD works based on produced X-Rays and according to intensity and scattering angle of the leaving X-Rays from the mineral. The mineral composition of the rock samples and field-scale samples can be identified through XRD experiments. In our work, this machine is essential to determine the precise mineralogy of the samples that are used in the ζ -potential measurement.

An intelligent diffractometer with a Cu-source by Malvern Panalytical (**Figure 24**) is employed to analyze the mineralogical composition of the rock sample. 6 grams of Indiana rock sample powder is enough to determine the mineralogy of the rock sample using this specific equipment. Indiana limestone rock sample were crushed in order to obtain the powder form of the rock sample.



Figure 24 – XRD machine (Malvern Panalytical)

The mineral constituents of the rock powder were calcite (99.7%) and quartz (0.3%). XRD patterns showing the relation between intensity and the degree (**Figure 25**).

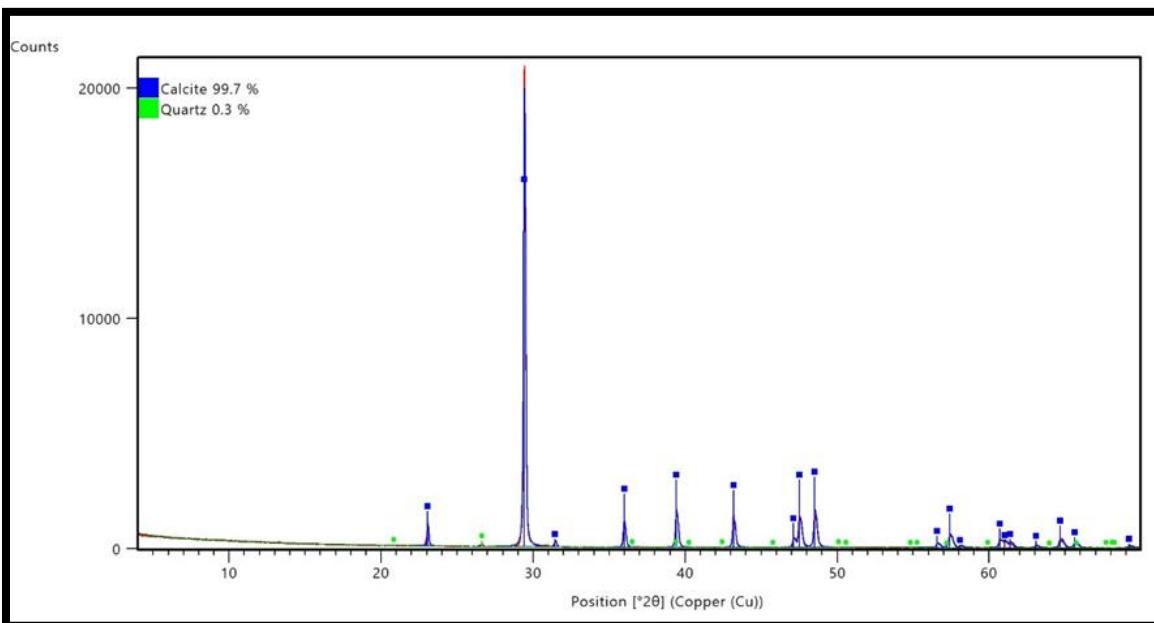


Figure 25 – XRD patterns for calcite mineral

b. Particle size measurement

The equipment used for zeta potential has a threshold value for the mean size of particles since the equipment is sensitive to particle size, and the precision of the surface charge experiments highly depends on particle size. It is usually recommended that before conducting a zeta potential test, particle size analysis should be performed to ensure that the mean particle size of crushed minerals is within the operational limits of the specific machine.

A laser diffraction particle size analyzer (PSA) HELOS by Sympatec (**Figure 26**) is utilized for analyzing the particle size of the rock sample powder that will be used during zeta potential experiments. Using PSA, the mean particle size of the powder is determined. The mean particle size of particles should be within the range for the zeta potential measurements. However, particle sizes were not reduced to nanoscale to maintain the mineral surface structure and crystallographic orientations.



Figure 26 – PSA analyzer (HELOS Sympatec)

The particle size distribution of calcite mineral used in the zeta potential measurements is shown in **Figure 27**. The mean particle size of calcite mineral was equal to 4.42 μm .

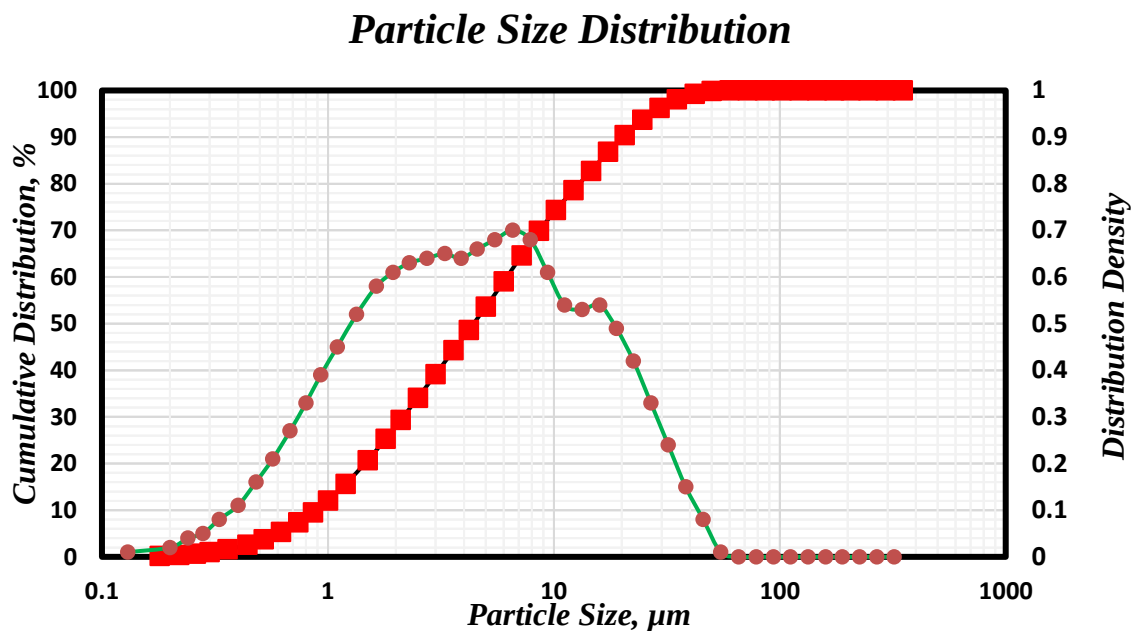


Figure 27 – Particle size distribution of calcite mineral

c. Zeta potential measurements

A fine powder of calcite mineral was used during the zeta potential measurements. The surface charge measurements were performed using ζ -potential. To analyze the iron precipitation at pH environment ranging from 1 to 13, a buffer solution was prepared, and pH control was achieved using 0.1 M of nitric acid and sodium hydroxide. As an iron source, different concentrations of FeCl_3 that contains 100 ppm, 500ppm, 1500 ppm, 5000 ppm and 10000 ppm of Fe^{3+} ions and FeCl_2 that contains 100 ppm, 500ppm, 1500 ppm, 3000 ppm, 5000 ppm and 10000 ppm of Fe^{2+} ions.

Powdered calcite mineral was washed with deionized water (HPLC grade from Sigma-Aldrich), the suspension agitated using an orbital shaker for a period of 24 h after which insoluble particles were filtered and dried overnight at 176 °F in a vacuum oven. The salt solutions with the concentrations of 0.1 M and 1 M and 5 different concentrations of ferric solutions were freshly prepared in the days of experiments.

10 mg of mineral powder was conditioned in a 30 mL of buffer solution of changing pH (1-13) for 24 h before the measurements. The procedures were continued with the preparation of samples to study ferric precipitation of on calcite mineral mixing 1 mL of conditioned samples (pH 1- 13) and 1 mL of iron solutions with varying $\text{Fe}^{3+}/\text{Fe}^{2+}$ constituent. The mixtures were vibrated and allowed to maintain equilibrium before performing the measurements. Another set of sample preparation were done to study the effect of 0.1 M and 1 M concentrations of salts (NaCl , CaCl_2 , MgCl_2) on Fe^{3+} adsorption on calcite particle surface using the same procedures.

Further in the experiments, the effect of 10 and 20 wt% of EDTA on surface charge of calcite mineral in wide range of pH environment. This will be helpful for the identification of the electrostatically stable environments where EDTA is able to hinder iron precipitation.

The Malvern Zetasizer Nano Z (**Figure 28**) was utilized to conduct zeta potential measurements on samples in electrolytic solution. A laser doppler electrophoresis method was used to measure zeta potentials of colloidal suspensions, and the application of a voltage across a cell determined particle mobility, which was used to calculate particle zeta potential using the Henry equation (**Eq.3.5**).

$$U_E = \frac{3E\zeta f(kR)}{3\eta} \quad (3.5)$$

Where:

U_E – electrophoretic mobility

E – dielectric constant

ζ – zeta potential

$f(kR)$ – Henry's function (1.5 according to Smoluchowski)

η – viscosity

All measurements were conducted at 77 °F and ambient pressure using disposable capillary cells (**Figure 28**). The equipment and cells were calibrated before every set of measurements.



Figure 28 – Zeta potential tool and capillary cell

Solid particle precipitation is defined by zero potential charge (ZPC). In the cases where zeta potential is determined as near zero surface charge, this is the reason of not very stable aqueous system. Zeta potential of the system with 0 to ± 5 indicates low level of stability and/or precipitation. **Figure 29** represents the stability behavior of a system depending on zeta potential.

Zeta potential, mV		Excellent stability
	60	
		Good stability
	30	
		Stable
	10	
		Instable
	5	
		Agglomeration/Precipitation
	0	
		Agglomeration/Precipitation
	-5	
		Instable
	-10	
		Stable
	-30	
		Good stability
	-60	
		Excellent stability

Figure 29 – Stability behavior of a system

To prepare the solutions with mentioned concentrations certain amount of ferric chloride (60% of purity), sodium chloride, calcium chloride dihydrate ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$), magnesium chloride, ferrous chloride (99% of purity), and EDTA was used. The solutions were prepared using deionized water. **Table 17** represents the details of the preparation of different concentrations of 1 L solutions.

Table 17 – Prepared solutions (1 L)

Solutions	Chemicals (purity%)	Concentrations	Amount used
FeCl ₃	Ferric chloride (60%)	100 ppm [Fe ³⁺]	0.8 grams
		500 ppm [Fe ³⁺]	2.4 grams
		1,500 ppm [Fe ³⁺]	7.3 grams
		5,000 ppm [Fe ³⁺]	24.25 grams
		10,000 ppm [Fe ³⁺]	48.5 grams
FeCl ₂	Ferrous chloride (99%)	100 ppm [Fe ³⁺]	0.23 grams
		500 ppm [Fe ³⁺]	1.15 grams
		1,500 ppm [Fe ³⁺]	3.45 grams
		3,000 ppm [Fe ³⁺]	6.9 grams
		5,000 ppm [Fe ³⁺]	11.5 grams
		10,000 ppm [Fe ³⁺]	23 grams
NaCl	Sodium chloride (98%)	0.1 M	5.8 grams
		1 M	58 grams
CaCl ₂	Calcium chloride dihydrate (99%)	0.1 M	11.1 grams
		1 M	111 grams
MgCl ₂	Magnesium chloride	0.1 M	9.52 grams
		1 M	95.2 grams

The flow chart shown in **Figure 30** illustrating every step and the objectives (outcomes) of the zeta potential measurements corresponding to the stages. To sum up, through series of zeta potential tests iron precipitation on calcite surface as a result of solid/solid interactions in 13 pH environment was analyzed. Furthermore, impact of salts which is naturally contain in formation rock and 2 concentrations of EDTA on iron deposition was studied.

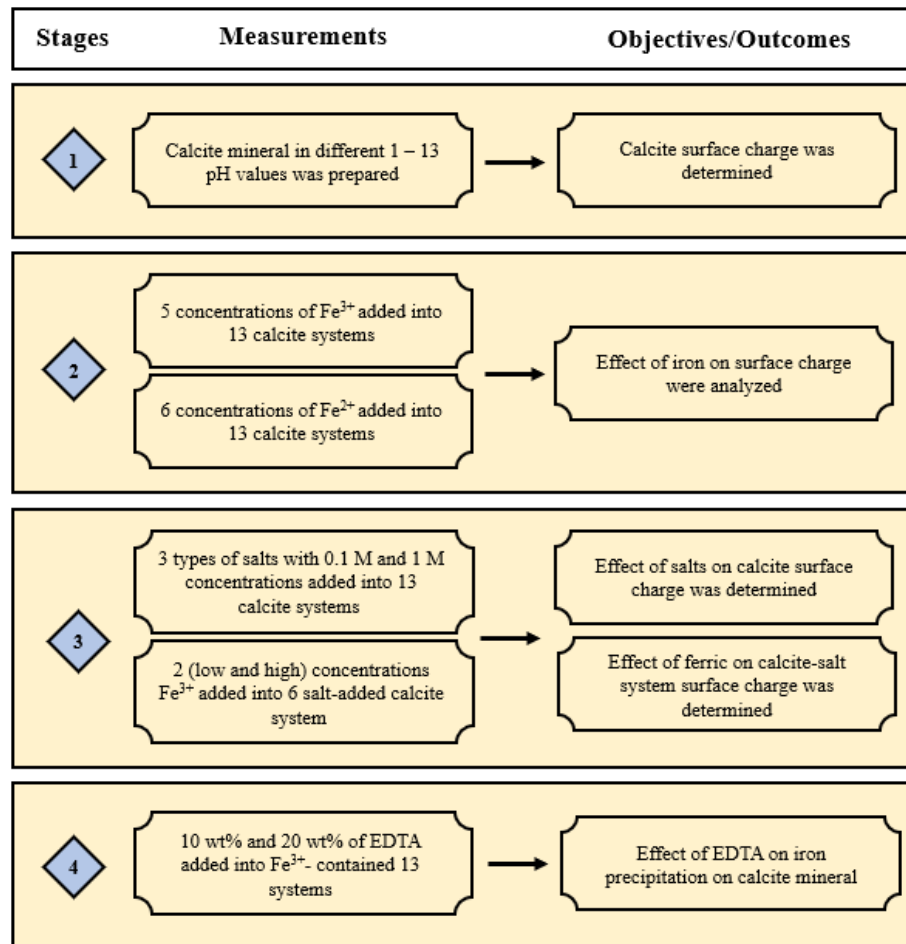


Figure 30 – Flow chart detailing the zeta potential measurements and their objectives

3.2.3 Iron sulfide scale formation and inhibition (Phase 3)

The third phase of this experimental research incorporates the formation and inhibition of iron sulfide scale in carbonate rock samples utilizing coreflooding setup. Iron sulfide scale formation was achieved by simultaneous injection of sodium sulfide and iron chloride into Indiana limestone core samples. The best- performing chelating agents' concentration that obtained from dynamic inhibitor adsorption experiments discussed earlier in Chapter 3 was used to inhibit the formation of the iron sulfide scale formation. The experiments were performed with and without the inhibitor and final rock permeabilities were determined. The rock and fluid preparation prior to coreflooding experiments were the same as discussed in adsorption experiments within Chapter 3. **Table 18** shows initial rock properties determined before flooding experiments.

Table 18 – Rock properties (scale formation and inhibition)

Core #	Experiments	Core Length (cm)	Dry Weight (g)	Wet Weight (g)	Core Porosity (%)
NF-1	Scale	15.20	377.87	406.094	16
	Formation (without inhibitor)				
NI-1	Scale	15.22	379.04	407.922	16.3
	inhibition (with inhibitor)				

It is worth mentioning that formation damage due to scale precipitation can be occurred through 2 mechanisms:

1. Plugging of pore throats
2. Solid particle precipitation (scale crystals) due to interactions

To consider formation damage happened due to interactions zeta potential was employed and discussed earlier in this chapter. However, formation of scales results in permeability reduction as well. This tendency occurs because of blockage of pore throats of formation rock. The low and high permeability Indiana limestone core samples were used throughout scale formation and inhibition experiments in order to take into account the influence of pore throat size (plugging phenomenon) in scale formation. **Figure 31** shows plugged pore throats as a result of scale precipitation [54].



Figure 31 – Formation damage due to scale deposition

The following sections introduce the details and coreflooding setups prepared for iron sulfide scale formation and prevention.

a. Iron sulfide scale formation

During scale formation experiments coreflooding setup was used. Iron sulfide scale was formed injecting sodium sulfide (Na_2S) and ferric chloride (FeCl_3) simultaneously. The experiments were performed at 176 °F. Figure 32 illustrates the setup used for scale formation. 3 accumulators were filled with 3 wt% KCl, 3 wt% Na_2S , and 2.5 wt% FeCl_3 .

Table 19 depicts the amount of prepared chemicals. However, **Table 20** represents the conditions at which scale formation experiments were conducted in coreflooding.

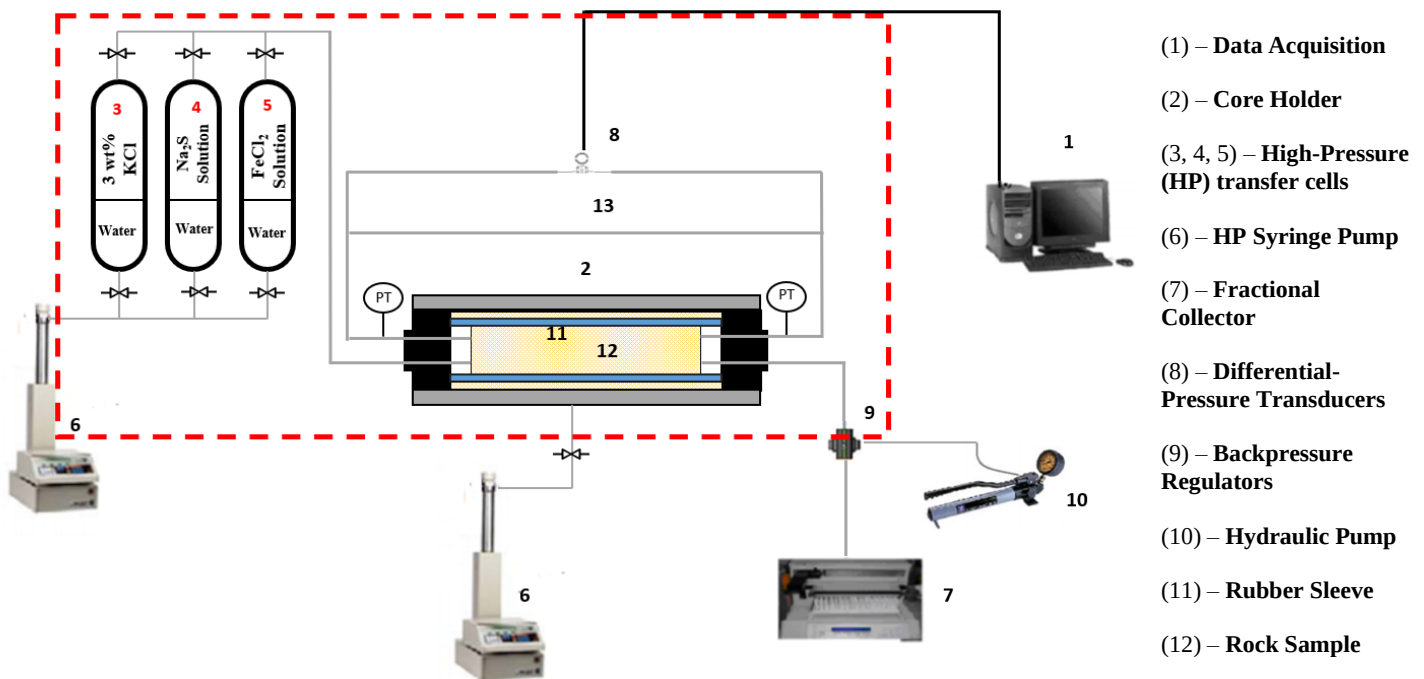


Figure 32 – Coreflooding setup for iron sulfide formation

Table 19 – Chemical concentrations used in scale formation experiments

Chemical used	Weight used, grams
Sodium sulfide	15
Ferric chloride	12

Table 20 – Scale formation and inhibition coreflooding tests conditions

Coreflooding conditions	Values
Back pressure, psi	1000
Confining pressure, psi	1500
Flow rate (during experiment), cm ³ /min	0.5
Flow rates (preflush, initial permeability determination), cm ³ /min	0.25, 0.5, 0.75
Temperature conditions, °F	176

Finally, the fluid injection sequence of the solutions and injected pore volume of each fluid in scale formation experiments are represented in **Table 21**Table 21. The Indiana limestone rock samples with low and high permeability were used to analyze iron sulfide formation.

Table 21 – Fluid injection sequences and pore volumes (scale formation experiments)

Injection sequence	Injection fluids	Injected pore volume
1	3 wt% KCl (Preflush)	2 - 3 PV
2	Na ₂ S and FeCl ₃ injection	1.5 PV
3	3 wt% KCl overflush	2-3 PV

The last section of the Chapter 3 discusses the details of iron sulfide scale inhibition experiments performed in the study.

b. Iron sulfide scale inhibition

Iron sulfide scale inhibition experiments were done using coreflooding setup. The coreflooding conditions during inhibition experiments were the same as in the formation section. However, inhibition setup incorporates 4 accumulators instead of 3. **Figure 33** shows the setup with 4 accumulators that was employed in scale prevention stage of this study. 1 additional accumulator compared with formation experiments was filled with the best-adsorbing chelating agent obtained from dynamic inhibitor experiments conducted in Phase 1.

The fluid injection sequence of the solutions and injected pore volume of each fluid in inhibition experiments are represented in **Table 22** . The Indiana limestone rock samples with low and high permeability were used to analyze iron sulfide scale inhibition.

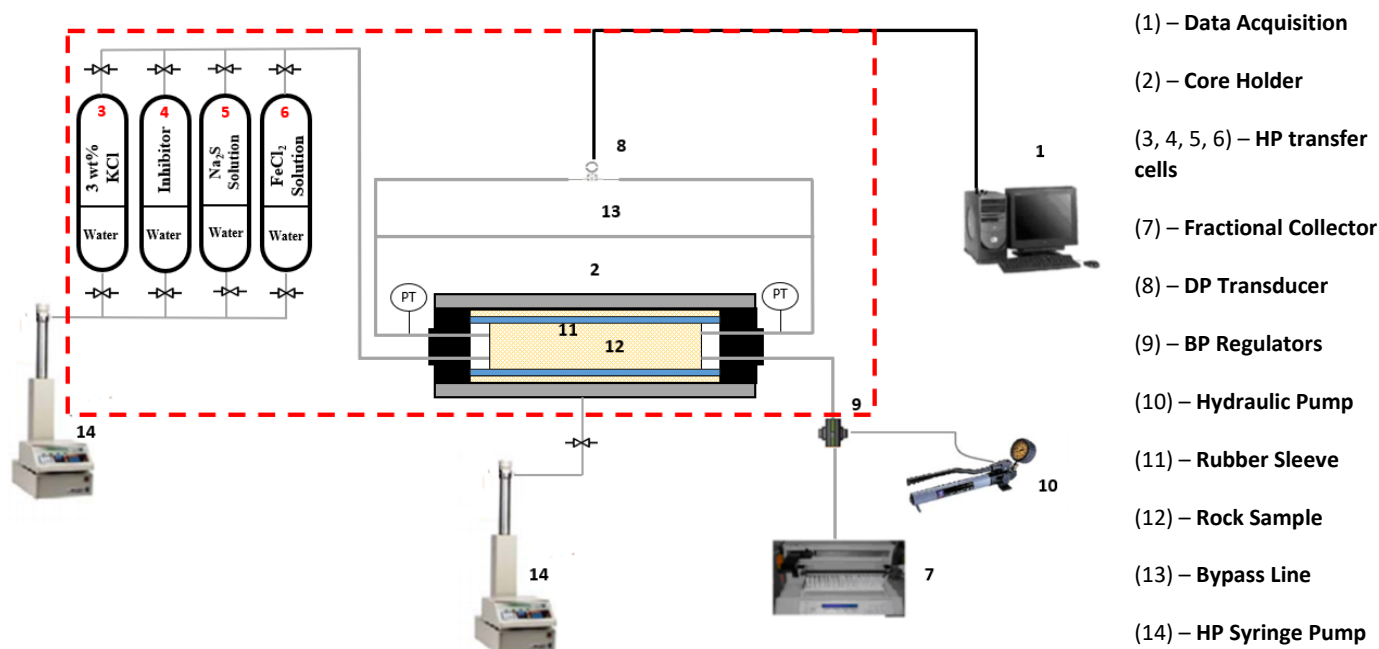


Figure 33 – Coreflooding setup for iron sulfide inhibition

Table 22 – Fluid injection sequences and pore volumes (scale inhibition experiments)

Injection sequence	Injection fluids	Injected pore volume
1	3 wt% KCl (Preflush)	2 - 3 PV
2	Chelating agent	2 PV
3	3 wt% KCl flush	2 PV
4	Na ₂ S and FeCl ₃ injection	1.5 PV
5	3 wt% KCl flush	2-3 PV

The next chapter of the thesis will discuss the results obtained from Phase 1, Phase 2, and Phase 3.

CHAPTER 4

RESULTS & DISCUSSION

4.1 Dynamic inhibitor adsorption experiments

The dynamic adsorption test was conducted using coreflooding setup. During the first stage of the experiments, precipitation of ferric ions on Indiana limestone core samples and their iron adsorption efficacy were investigated at temperature conditions of 77 °F, 120°F, 200°F. After this set of experiments, EDTA (10 wt%, 15 wt%, 20 wt %) and DTPA (20 wt %) were used to study the best-performing inhibitor for ferric ions to complex iron in carbonate rock samples. As mentioned in Chapter 3 some experiments were also conducted to analyze the effect of soaking time and addition of CaCl_2 and MgCl_2 on the inhibitor adsorption in rocks. The effluent samples were collected during the experiments and then analyzed through ICP-OES to determine ferric concentration at the time of coreflooding experiments.

4.1.1 Iron (III) adsorption experiments (without inhibitors)

The FeCl_3 solution was injected through the core samples without inhibitors in the first three experiments at 77 °F, 120°F, 200°F. The initial rock permeability was determined with the 3 wt% KCl injection and is shown in **Table 23** alongside an initial ferric concentration in the injected ferric solution. Flooding experiment was performed at ambient temperature using N3, at 120°F using N12, and at 200°F using N7 core samples. **Figure 34** illustrates coreflooding results for experiments conducted at 77 °F. It can be

seen from the figure that after FeCl_3 injection pressure differential between inlet and outlet section increased almost ten times because of iron starts blocking pore throats.

Table 23 – Initial rock permeability and initial iron (III) concentration

Core #	Initial rock permeability, mD	Initial Fe^{3+} concentration, ppm
N3	19.9	2800
N12	9.9	2800
N7	24.9	2800

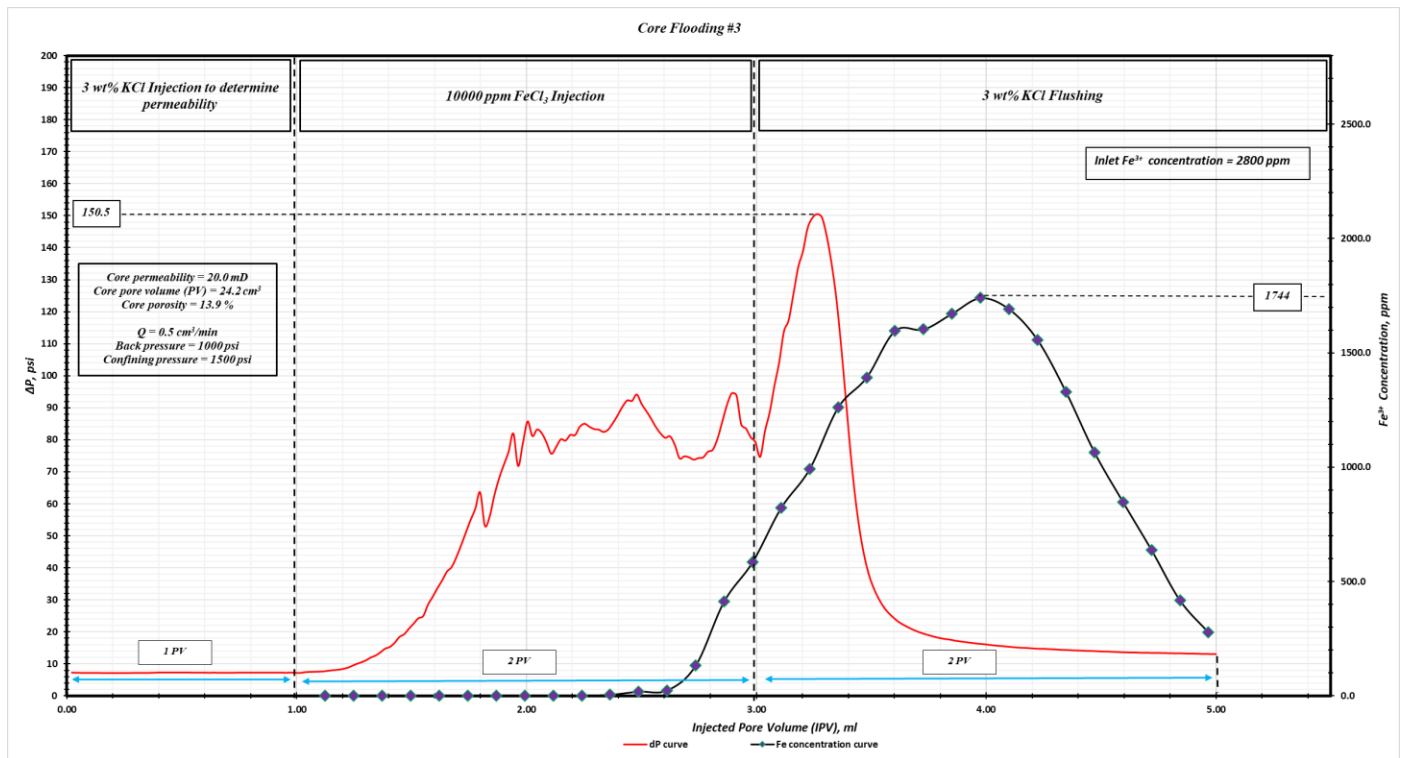


Figure 34 – Pressure drops and iron (III) concentration at 77 °F

Initial Fe^{3+} concentration and initial rock permeability in this experiment were determined as 2800 ppm and 19.9 mD respectively. The maximum determined Fe^{3+} concentration during experiment was 1744 ppm and the change of Fe^{3+} concentration in the experiment is shown in **Figure 35**. For the second [N12 core] and the third [N7 core] experiment, which conducted at 120 °F and 200 °F, Fe^{3+} concentration during the experiment is represented in **Figure 36** and **Figure 37** respectively.

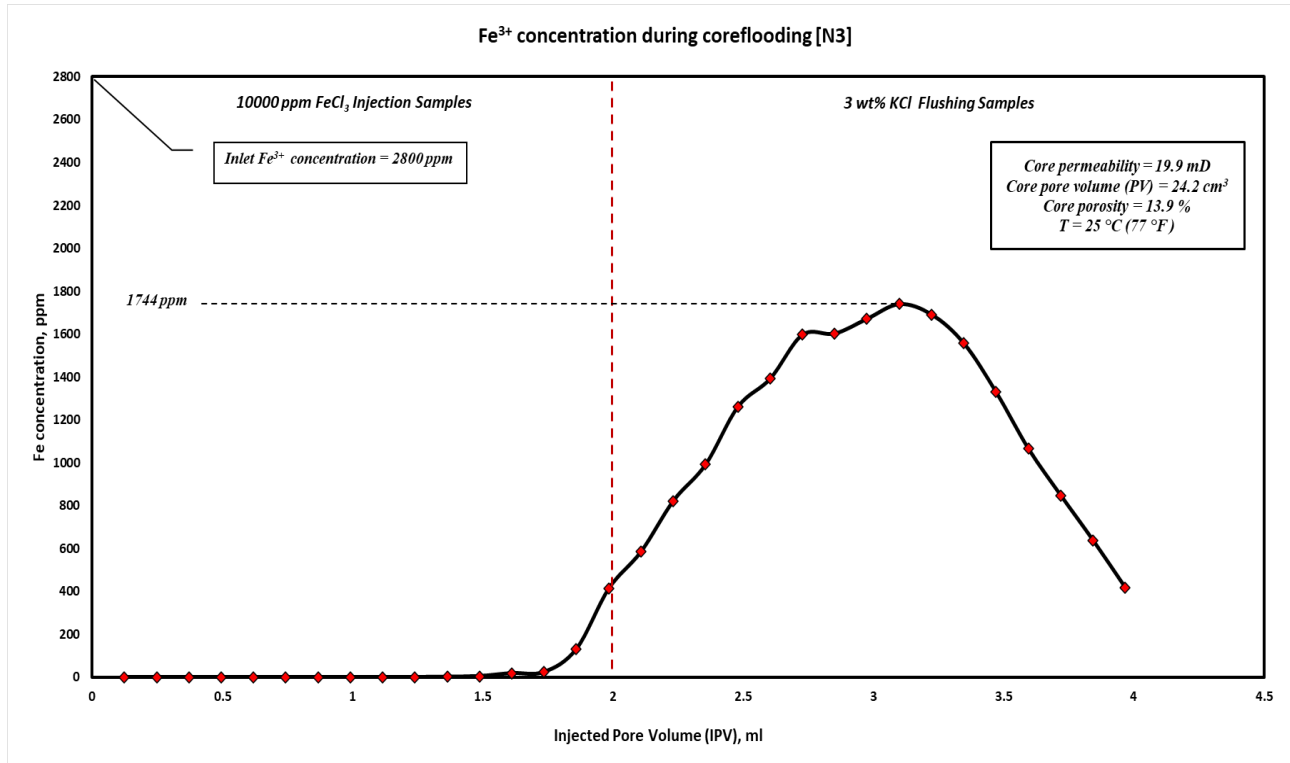


Figure 35 – Fe^{3+} concentration at 77°F (without inhibitor)

During the second and third coreflooding experiments inlet Fe^{3+} concentration in injected solutions was 2800 ppm. The intrinsic rock permeability was 9.9 and 24.9 mD in N12 and N7 cores respectively. The low concentration of Fe^{3+} ions in the very first injected 1.5 PV of FeCl_3 is because of injected KCl to determine initial rock permeability was still

in the system. Thus, effluent samples did not contain any significant concentration of ferric ions.

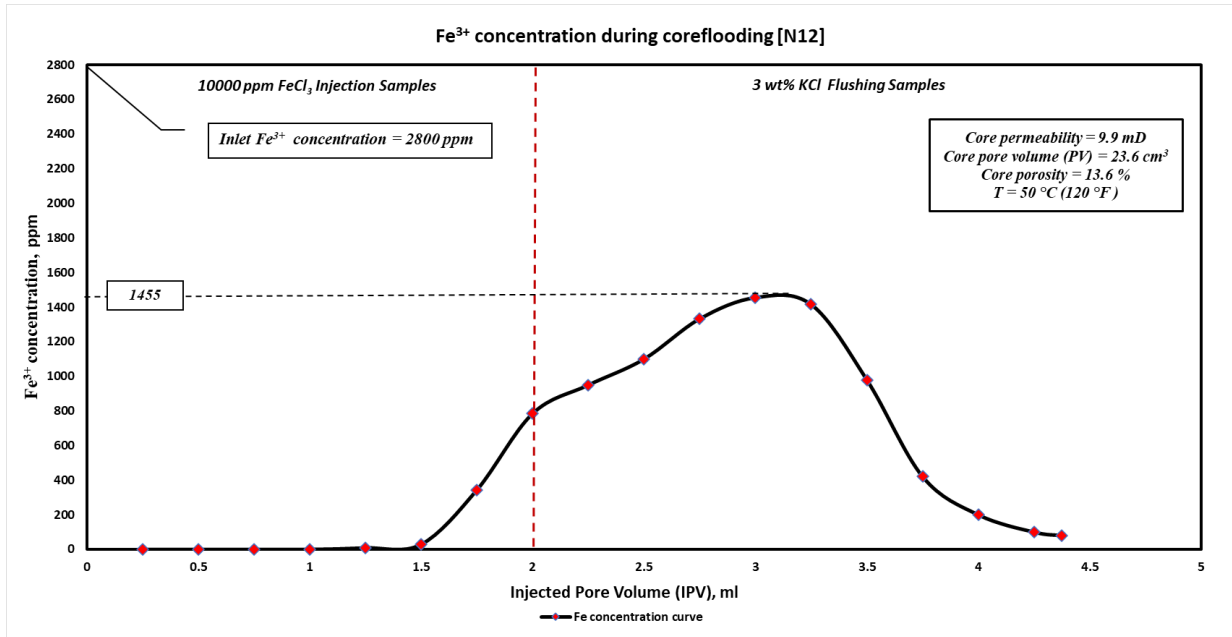


Figure 36 – Fe³⁺ concentration at 120°F (without inhibitor)

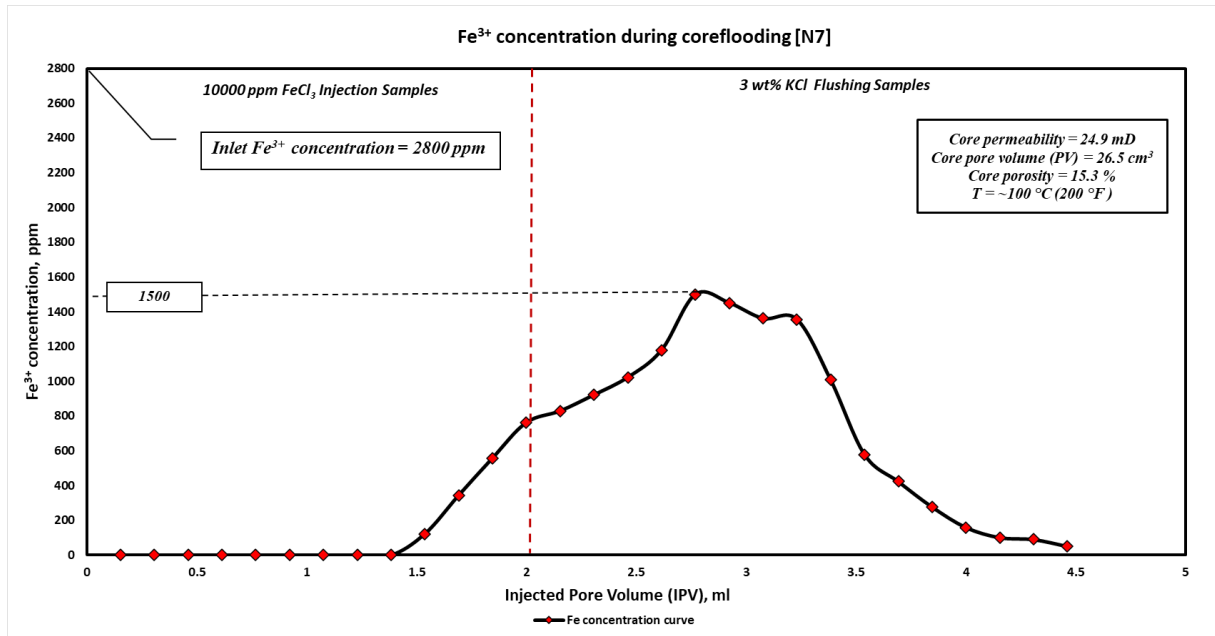


Figure 37 – Fe³⁺ concentration at 200°F (without inhibitor)

The maximum iron concentration in effluent samples at 120°F was 1455 ppm while it was 1500 ppm at temperature of 200°F. Hence, the obtained natural adsorption capacities of Indiana limestone core samples were calculated and are shown in **Figure 38**.

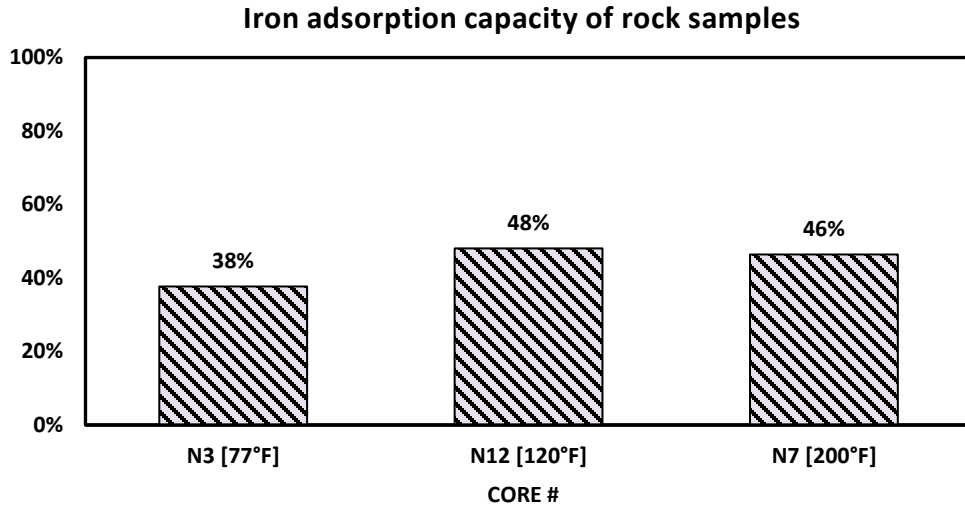


Figure 38 – Iron adsorption capacity of IL core samples

It can be seen from **Figure 38**, ferric adsorption capacity of the IL rocks is 38%, 48%, and 46% at 77 °F, 120°F, and 200°F respectively. Therefore, permeability alteration at these three temperature conditions were determined and $K_{final}/K_{initial}$ is reported for all three cases in **Figure 39**. It is evident from the figure that at ambient temperature iron (III) precipitation causes 50% of permeability reduction while it is determined as 33% and 42% permeability abatement at 120°F, and 200°F accordingly. The $K_{final}/K_{initial}$ ratio is important to define formation damage in terms of percentage.

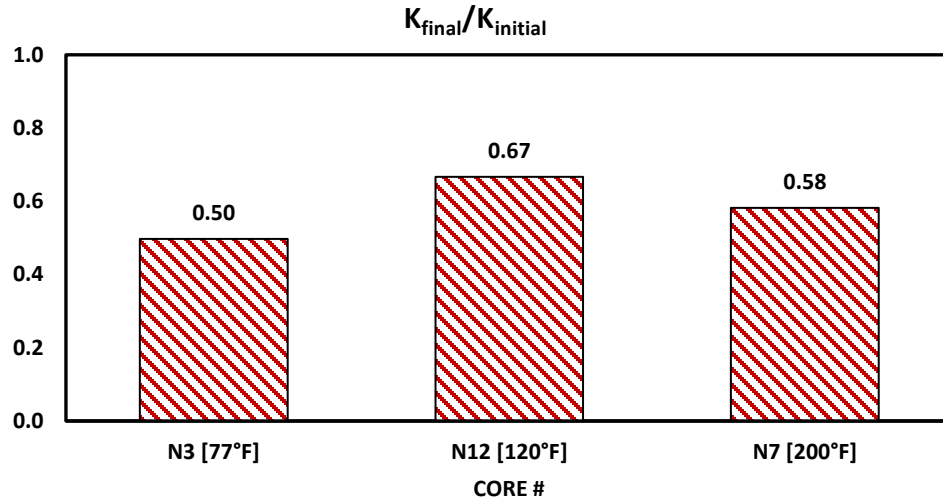


Figure 39 – Permeability change K_f/K_i (without inhibitor)

After determining the natural formation damage as a result of injection of 2800 ppm iron (III)-contained $FeCl_3$ solution, the effect of three different concentrations (10 wt%, 15 wt%, and 20 wt%) of EDTA at 77 °F, 120°F, and 200°F on iron (III) precipitation was analyzed and best-adsorbed EDTA concentration was determined.

4.1.2 Effect of 10 wt% EDTA on inhibition efficiency

The subsequent three experiments covered the injection of 10 wt% EDTA (pH ~11) as an inhibitor before the injection of the ferric solution in the IL rock core samples. These experiments were also performed at the temperature conditions of 77 °F, 120°F, and 200°F. The original brine permeability of the three core samples is reported in **Table 24**. Inhibitor adsorption experiments were performed at ambient temperature using N2, at 120°F using N14, and at 200°F using N8 core samples

Table 24 – Initial rock permeability and initial iron (III) concentration (10 wt% EDTA cases)

Core #	Initial rock permeability, mD	Initial Fe ³⁺ concentration, ppm
N2	22.8	2800
N14	9.9	2800
N8	12.6	2800

Figure 40 depicts coreflooding results for experiments conducted at 77 °F. It can be concluded that injection of 10 wt% EDTA results in significant decrease on pressure drop after FeCl₃ injection compared to the FeCl₃ injection without an inhibitor (**Figure 34**).

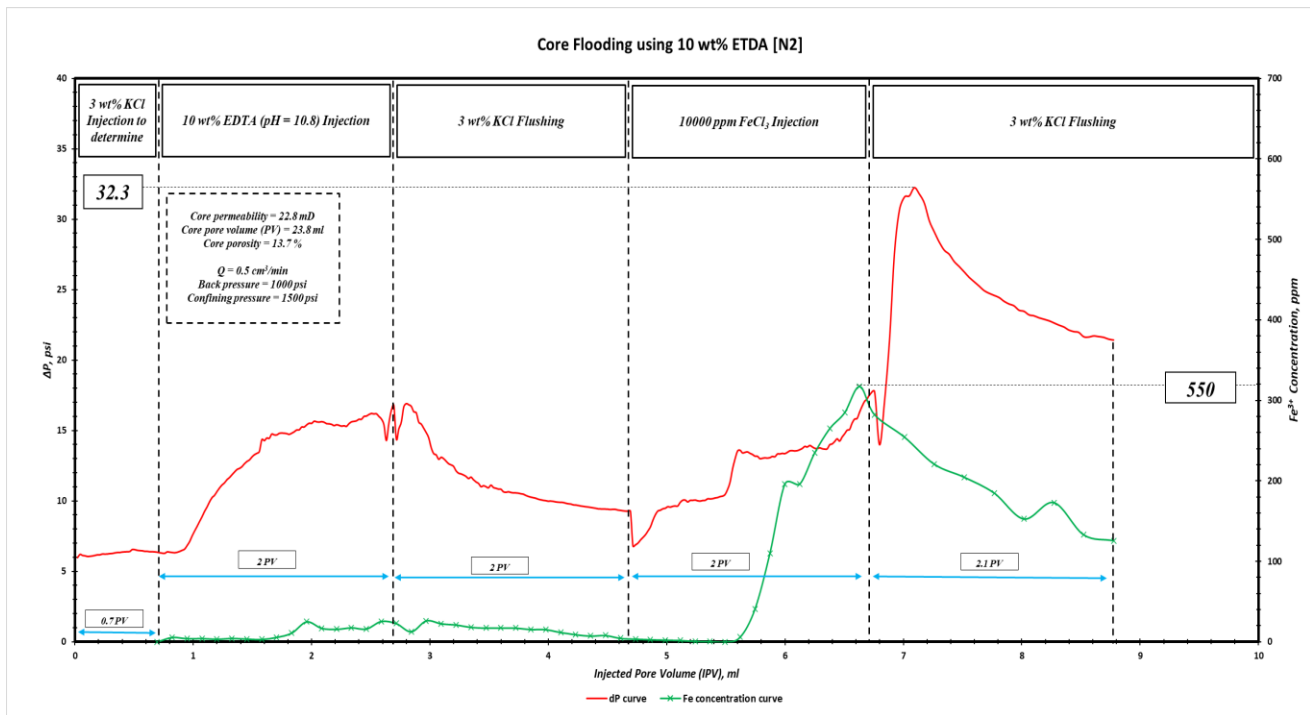


Figure 40 – Coreflooding data and Fe³⁺ concentration during the experiment using 10 wt% EDTA at 77°F

The maximum Fe^{3+} concentration at 77 °F was determined as 550 ppm and the change in Fe^{3+} concentration during flooding experiment is shown in **Figure 41**. Fe^{3+} concentration for the experiments at 120 °F and 200 °F is illustrated in **Figure 42** and **Figure 43** accordingly.

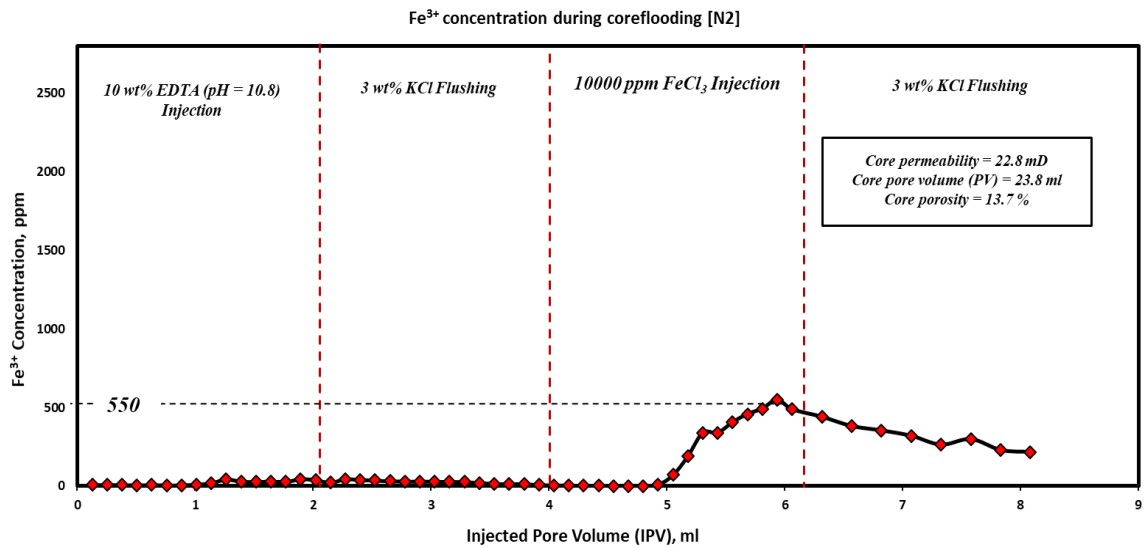


Figure 41 – Fe^{3+} concentration at 77°F using 10 wt% EDTA

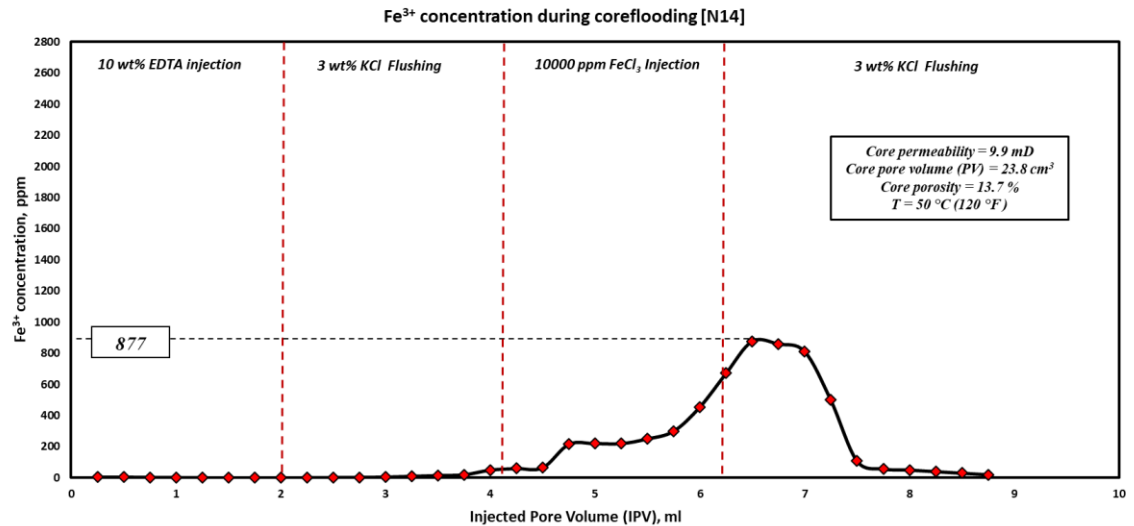


Figure 42 – Fe^{3+} concentration at 120°F using 10 wt% EDTA

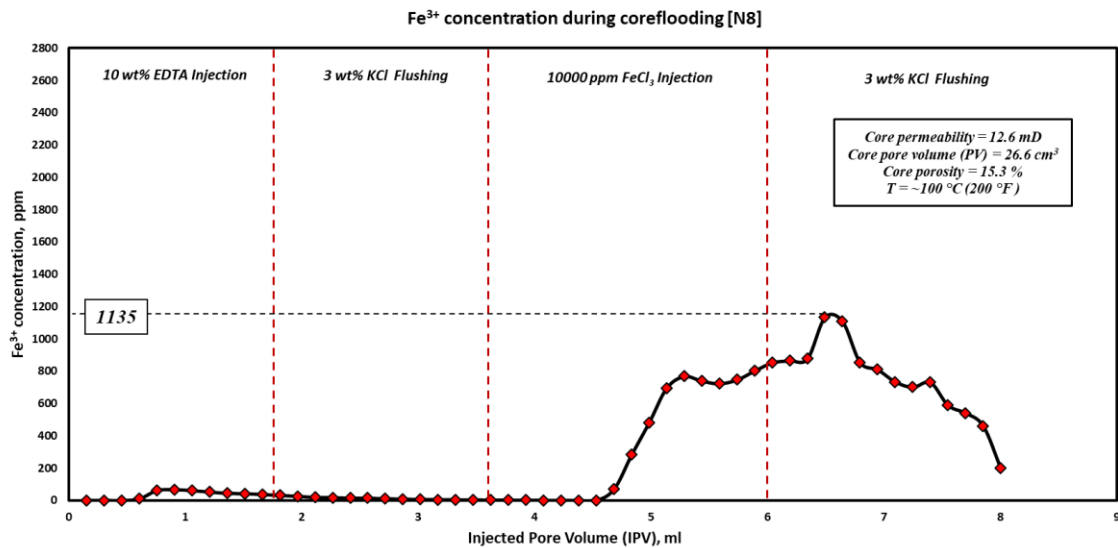


Figure 43 – Fe^{3+} concentration at 200°F using 10 wt% EDTA

The maximum final iron (III) concentration was 877 ppm at 120°F. However, it was determined as 1135 ppm at 200°F. Finally, the inhibition efficiency of 10 wt% EDTA was calculated for all temperature conditions and are depicted in the following figure (Figure 44).

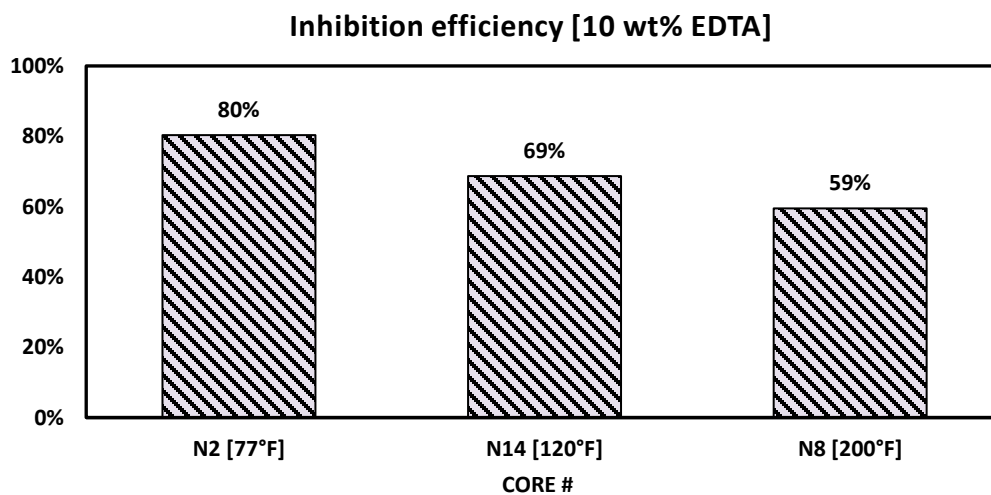


Figure 44 – Inhibition efficiency of 10 wt% EDTA

The results shows that the use of 10 wt% EDTA, can complex 80% of ferric ions from the aqueous solution at ambient temperature. As the temperature increase, the efficacy of 10 wt% EDTA starts to decrease to inhibit ferric precipitation as its inhibition efficiencies were 69% and 59% at 120 °F and 200 °F respectively.

$K_{\text{final}}/K_{\text{initial}}$ ratios are shown for three temperature conditions in **Figure 45**. It is evident from the figure that at ambient temperature iron (III) precipitation causes 23% permeability reduction while it is determined as 28% and 37% permeability abatement at 120°F, and 200°F accordingly.

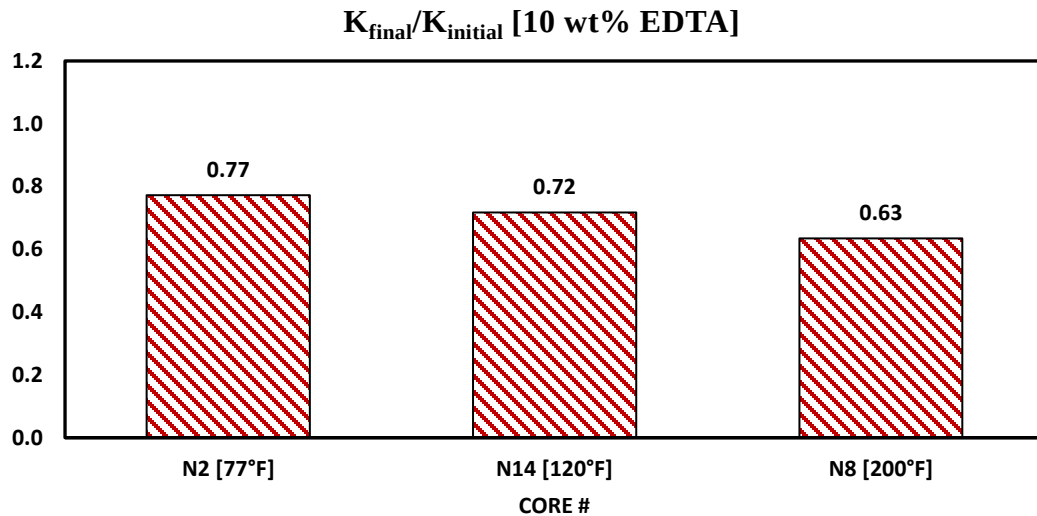


Figure 45 – Permeability change K_f/K_i (with 10 wt% EDTA)

Based on the results from inhibition efficiencies and permeability alteration, it can be concluded that more iron (III) complexed by EDTA, causes less permeability loss, which is shown in **Figure 45**.

4.1.3 Effect of 15 wt% EDTA on inhibition efficiency

Following the 10 wt% EDTA adsorption experiments, the tests with 15 wt% EDTA with pH 11 were performed. The flooding experiments were conducted at ambient temperature using N6, at 120°F using N13, and at 200°F using N20 core samples and their initial rock permeability are shown in **Table 25**.

Table 25 – Initial rock permeability and initial iron (III) concentration (15 wt% EDTA cases)

Core #	Initial rock	Initial Fe ³⁺
	permeability, mD	concentration, ppm
N6	17.5	2800
N13	11.4	2800
N20	12.1	2800

Figure 46 depicts coreflooding results for experiments conducted at 77 °F. In comparison with the experiments performed without EDTA, 15 wt% shows major reduction in pressure drop after injection of ferric solution. As indicated in the figure (**Figure 47**), the maximum final concentration of ferric ions in the solution was equal to 842 ppm at 77 °F which was almost 10% higher than 10 wt% EDTA. Fe³⁺ concentration for the experiments at 120 °F and 200 °F is illustrated in **Figure 48** and **Figure 49** respectively.

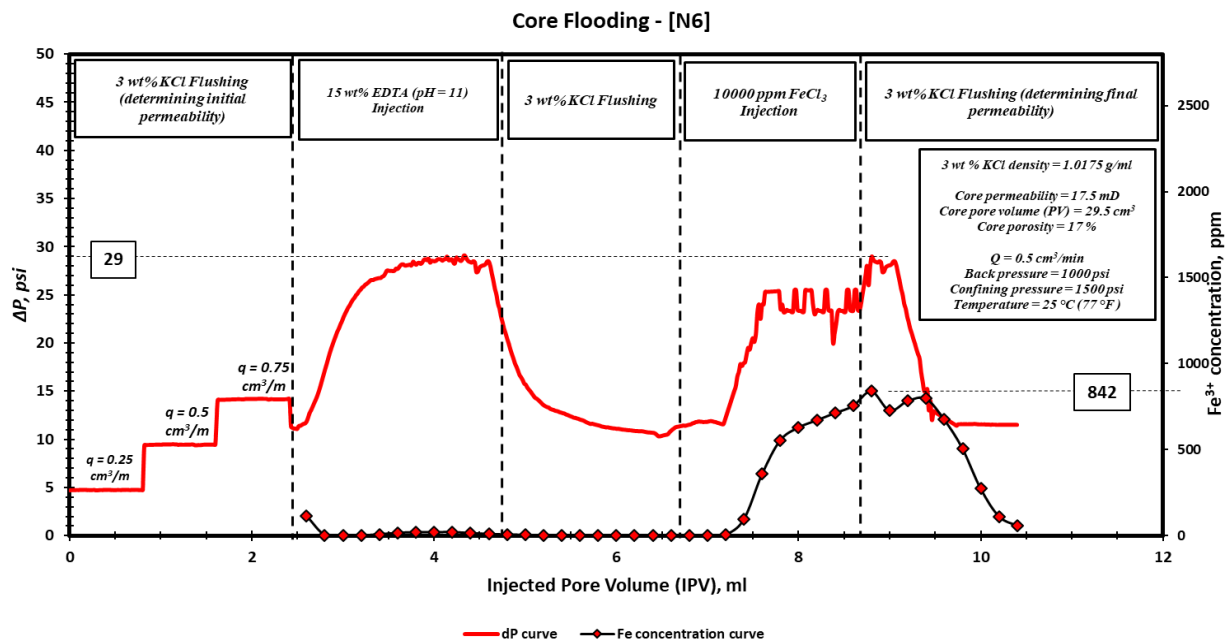


Figure 46 – Coreflooding data and Fe³⁺ concentration during the experiment using 15 wt% EDTA at 77°F

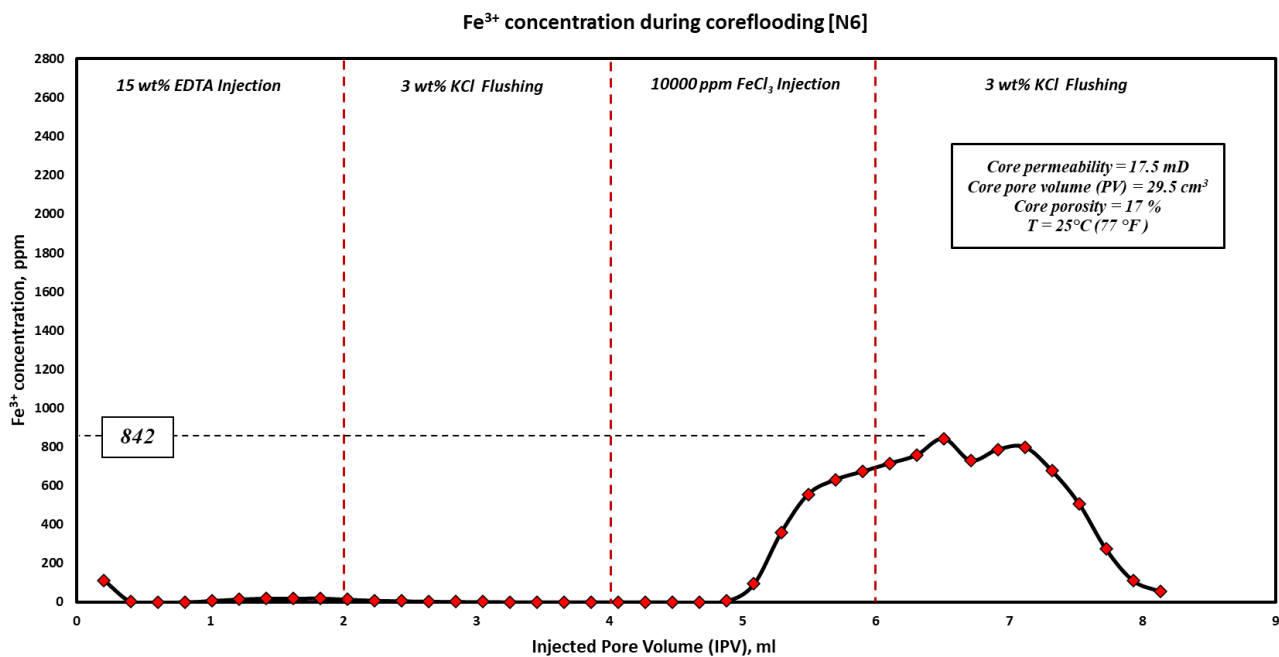


Figure 47 – Fe³⁺ concentration at 77°F using 15 wt% EDTA

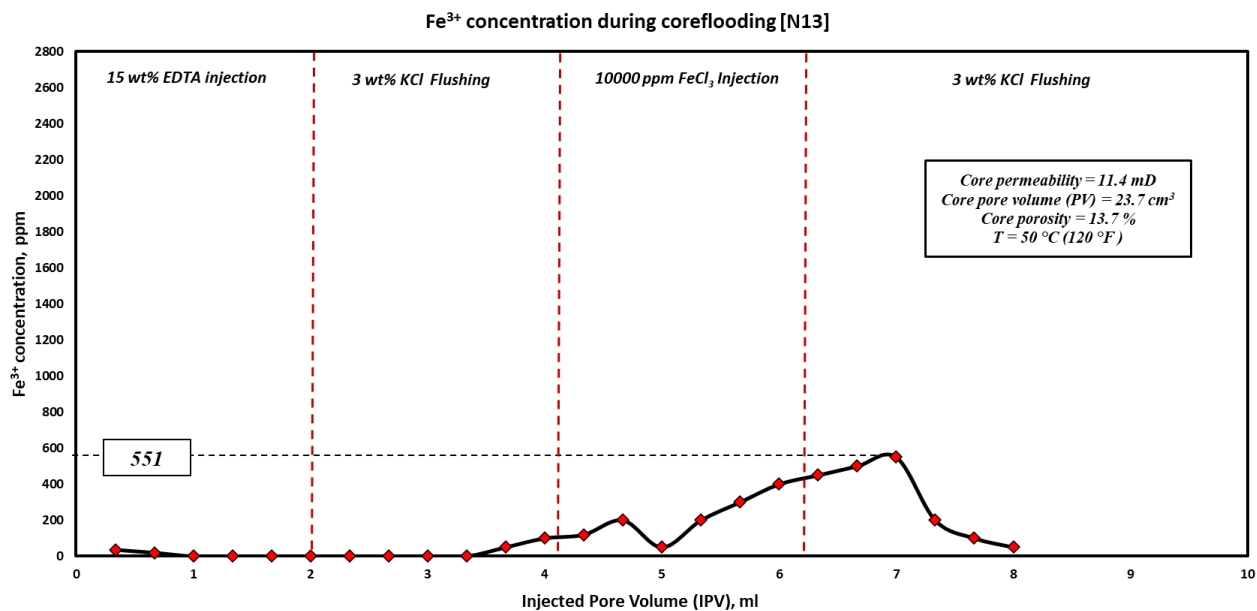


Figure 48 – Fe³⁺ concentration at 120°F using 15 wt% EDTA

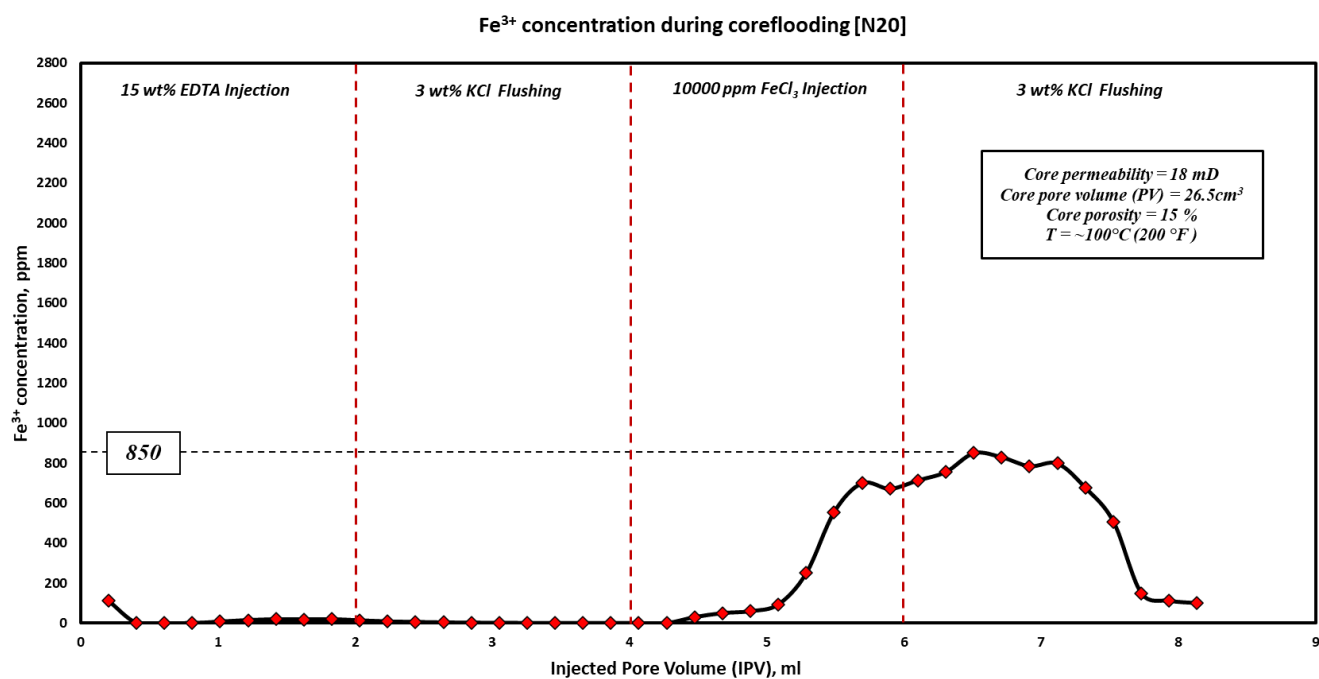


Figure 49 – Fe³⁺ concentration at 200°F using 15 wt% EDTA

The inhibition efficiency of 15 wt% EDTA was calculated for all temperature conditions and are shown in **Figure 50**. It is evident that 15 wt% EDTA showed better results and complexes more iron compared to 10 wt% EDTA at elevated temperatures. However, at ambient temperature condition 15 wt% EDTA was able to complex almost 300 ppm less ferric ions than 10 wt% EDTA.

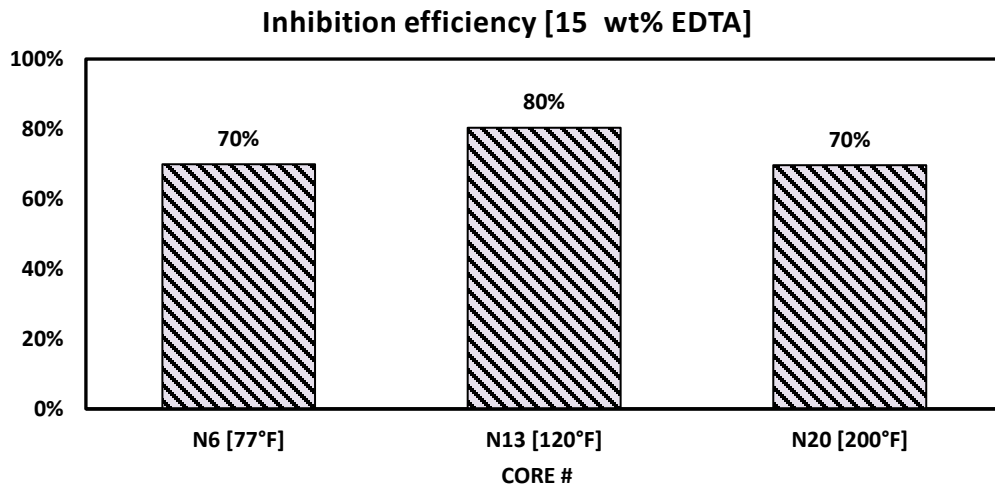


Figure 50 – Inhibition efficiency of 15 wt% EDTA

To evaluate permeability loss due to iron precipitation, final and initial permeability ratios were determined for three temperature conditions.

Figure 51 provides the result of $K_{\text{final}}/K_{\text{initial}}$. The trend was almost as same as in 10 wt% EDTA in which higher concentration of iron complexed yields less permeability decrease. However, at 200 °F, 10 wt% EDTA resulted in 10% of lower inhibition efficiency but in terms of permeability loss the show almost same degree of damage. The core permeability decreased by 26% at ambient temperature condition while at 120 °F it diminished by 19 %. Finally, 15 wt% EDTA worked better than 10 wt% EDTA at 200 °F and caused 24% permeability decrease. Overall, both concentrations of EDTA did not show promising results.

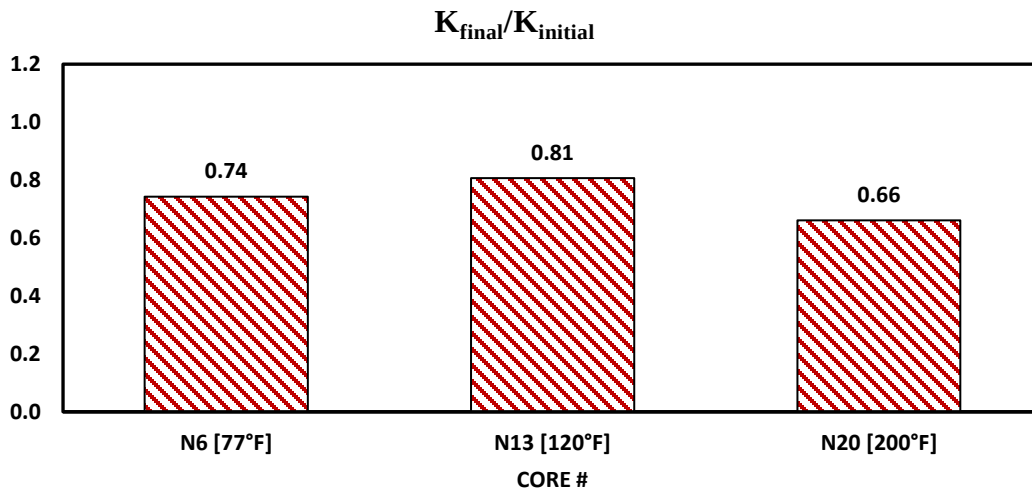


Figure 51 – Permeability change K_f/K_i (with 15 wt% EDTA)

4.1.4 Effect of 20 wt% EDTA on inhibition efficiency

The last EDTA concentration used during adsorption experiments was 20 wt%. The flooding experiments were conducted at ambient temperature using N10, at 120°F using N11, and at 200°F using N9 core samples and their initial rock permeability are detailed in **Table 26**.

Table 26 – Initial rock permeability and initial iron (III) concentration (20 wt% EDTA cases)

Core #	Initial rock permeability, mD	Initial Fe ³⁺ concentration, ppm
N10	12.1	2800
N11	30.2	2800
N9	15.5	2800

During the adsorption experiments using 20 wt% EDTA, the concentration of iron (III) complexed by EDTA at 77°F was equal to 2350 ppm meaning that the maximum ferric concentration in the effluent samples was determined as 450 ppm (**Figure 52**). However, at 120°F, the amount of the complexed iron ions was almost 2400 ppm and final iron (III) concentration was measured at 404 ppm (**Figure 53**).

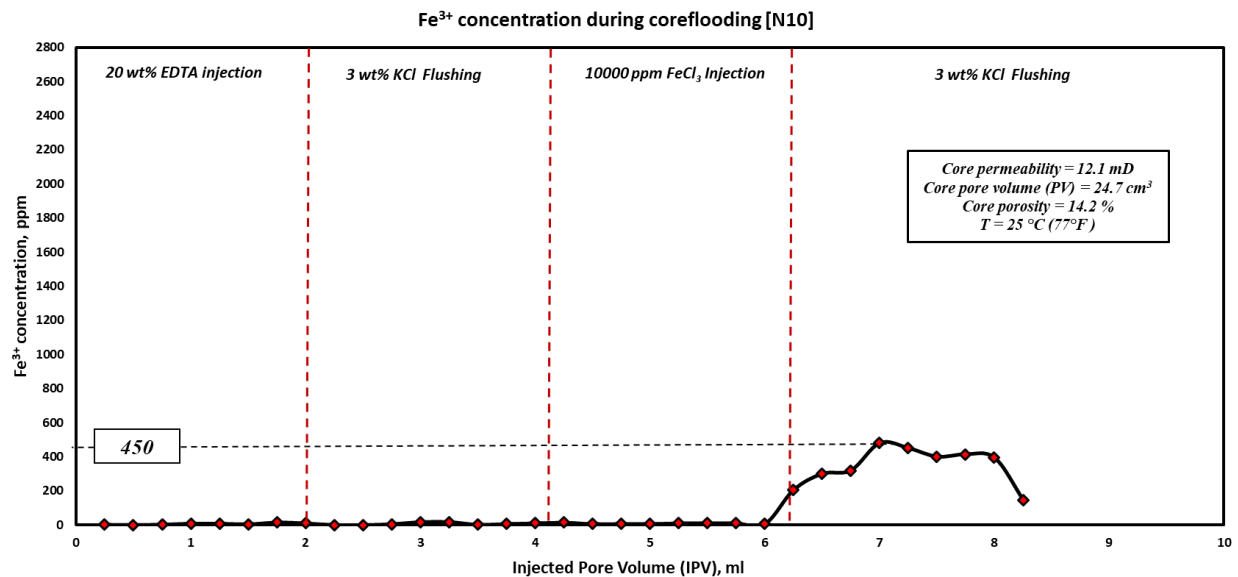


Figure 52 – Fe³⁺ concentration at 77°F using 20 wt% EDTA

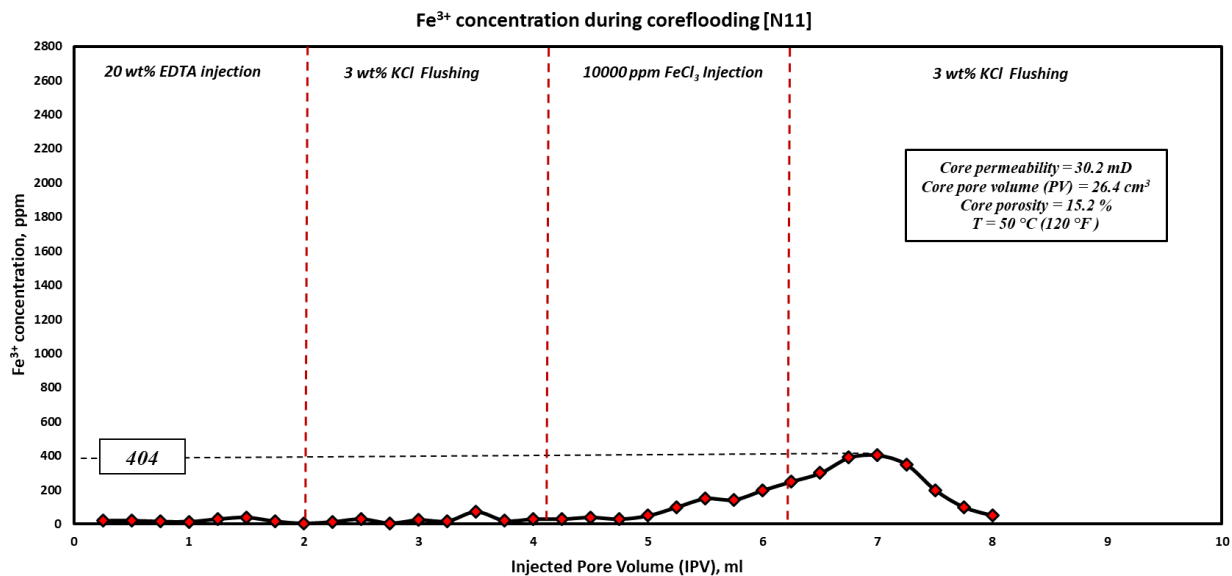


Figure 53 – Fe³⁺ concentration at 120°F using 20 wt% EDTA

The maximum iron (III) concentration recorded in the samples at 200°F was 350 ppm (**Figure 54**) which is the lowest concentration of ferric ions at 200°F in comparison with other EDTA concentrations.

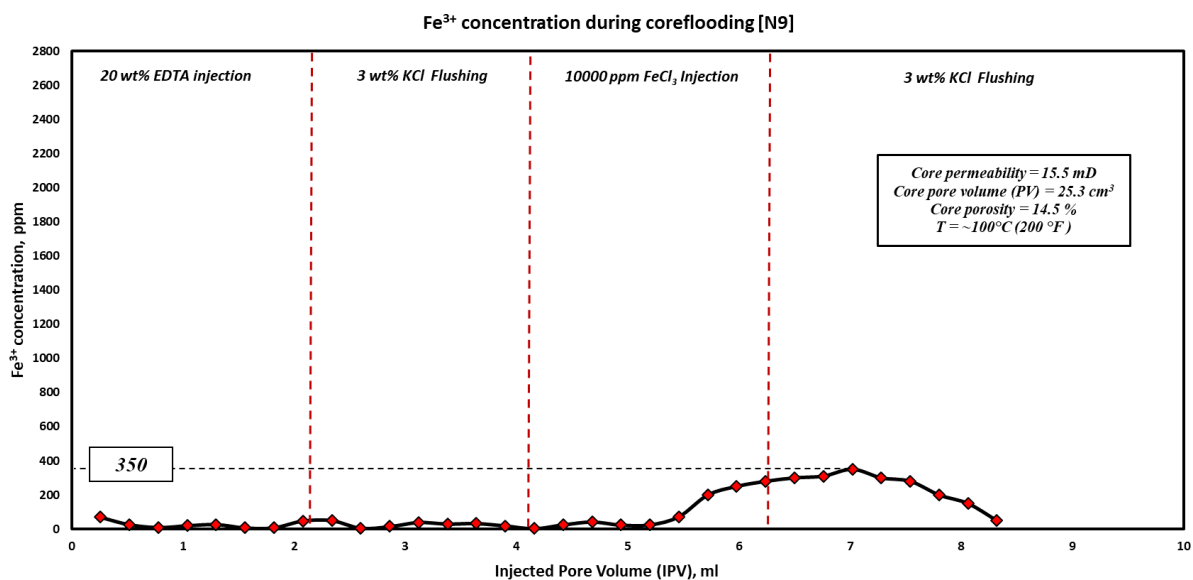


Figure 54 – Fe³⁺ concentration at 200°F using 20 wt% EDTA

After performing ICP analysis of effluent samples, inhibition efficiency of 20 wt% EDTA was calculated and for all temperature conditions and they are shown in **Figure 55**. Based on the results shown in **Figure 55**, 20 wt% EDTA shows the highest inhibition efficiency at ambient temperature with 84%. The inhibition efficiency of 20 wt% EDTA at 120°F calculated as 86% which is higher than both other concentrations of EDTA. Comparably, at 200°F it was 78% which was the highest inhibition efficiency at this temperature conditions.

After determining inhibition efficiencies of 20 wt% EDTA, permeability alteration using $K_{\text{final}}/K_{\text{initial}}$ was also calculated for this concentration of EDTA at three temperature conditions.

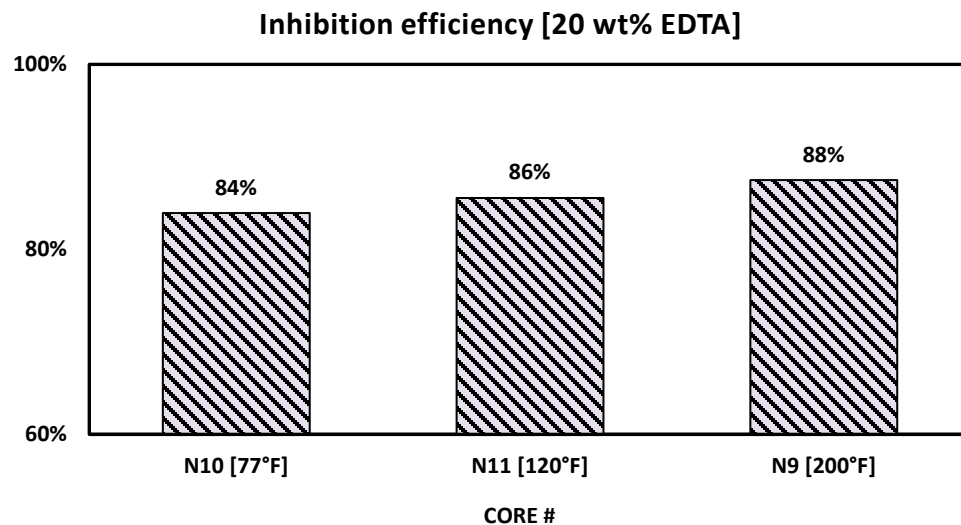


Figure 55 – Inhibition efficiency of 20 wt% EDTA

Figure 56 illustrates the permeability ratios in order to evaluate the damage due to iron (III) precipitation when 20 wt% EDTA was used as an inhibitor. Having a high degree of EDTA adsorption at 200°F reflects to permeability variation at this temperature as permeability increased by 8%. The permeability loss was determined as 8% at 120°F and 26% at 77°F.

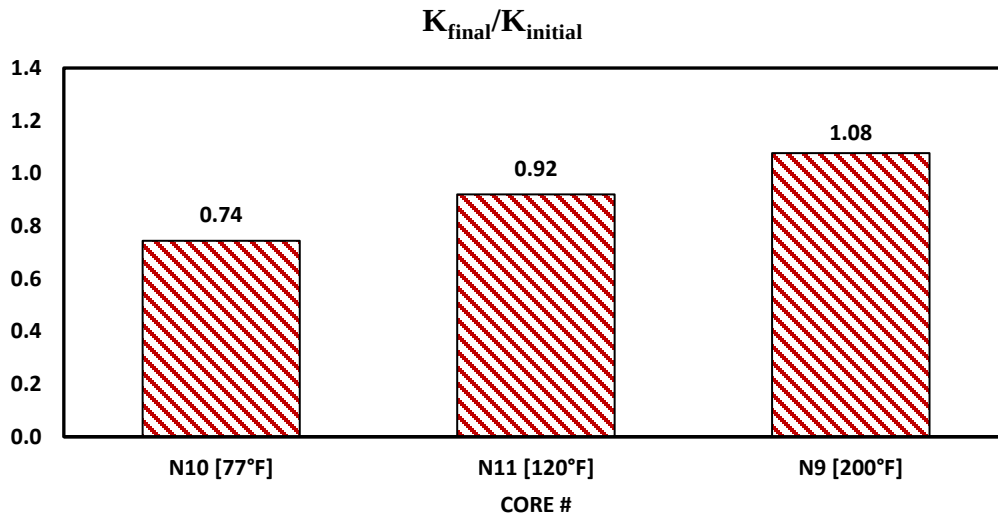


Figure 56 – Permeability change K_f/K_i (with 20 wt% EDTA)

4.1.5 Effect of cations on EDTA adsorption

Alongside using different EDTA concentrations, the effect cations which are constituents of the formation and injected water, on EDTA concentration was investigated. The effect of Mg^{2+} and Ca^{2+} on adsorption of 10 wt% EDTA and inhibition efficiency was determined at ambient temperature using the core samples N19 and N1 respectively.

Table 27 – Initial rock permeability and initial iron (III) concentration (cation effects)

Core #	Initial rock permeability, mD	Initial Fe³⁺ concentration, ppm
N1	17.9	2800
N19	17.8	2800

The effect of mentioned cations on adsorption of 10 wt% EDTA was analyzed and iron (III) concentration in effluent samples and final/initial permeability ratios were determined. N1 core was used to inject CaCl₂ while N19 core sample was used to study the effect Mg²⁺ cation. The pressure drops across the core samples and change in ferric concentration throughout the experiments for Ca²⁺ and Mg²⁺ cases are shown in **Figure 57** and **Figure 58**. The initial rock permeabilities of the core samples were 17.9 and 17.8 mD for N1 and N19 cores accordingly in **Table 27**.

The maximum observed Fe³⁺ concentration in effluent samples was 1222 ppm and 1335 in the case of CaCl₂ and MgCl₂ injected together with 10 wt% EDTA. Therefore, addition of Ca²⁺ cations yield inhibition efficiency of 56% while Mg²⁺ resulted in 52% of efficacy.

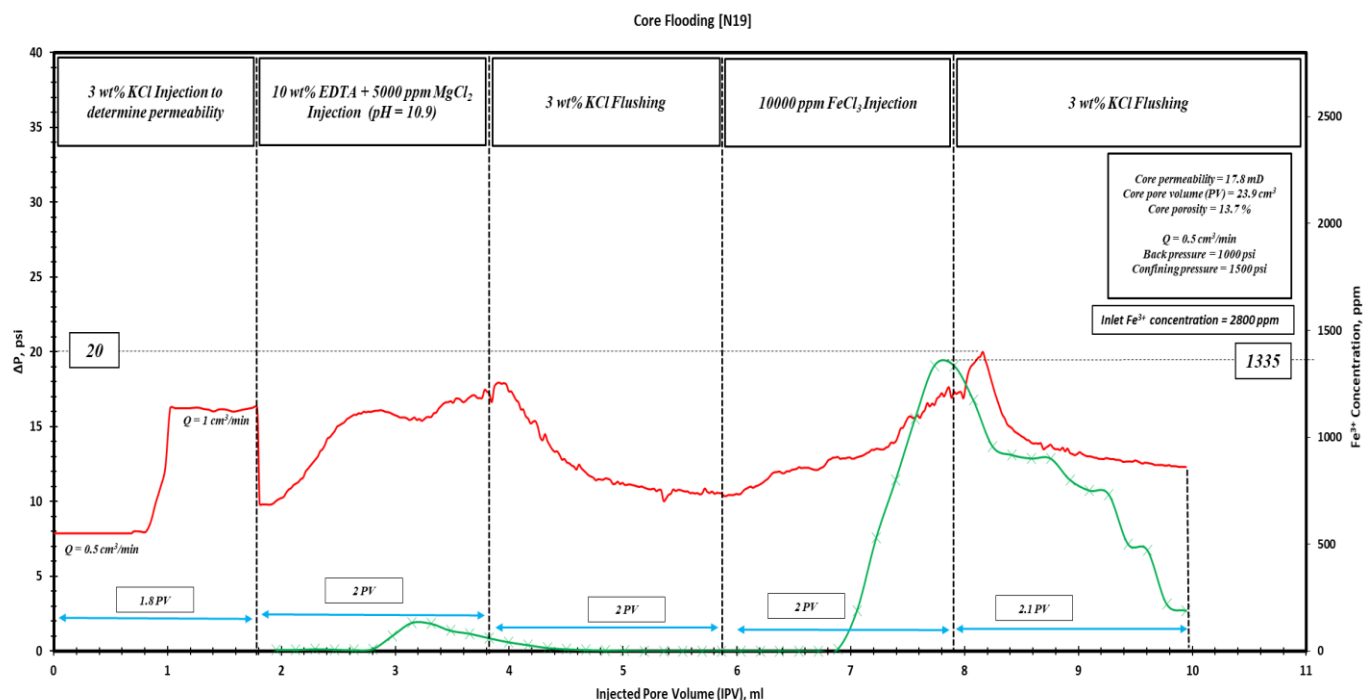


Figure 57 – Coreflooding data and Fe³⁺ concentration during the experiment using 10 wt% EDTA with Ca²⁺ at 77°F

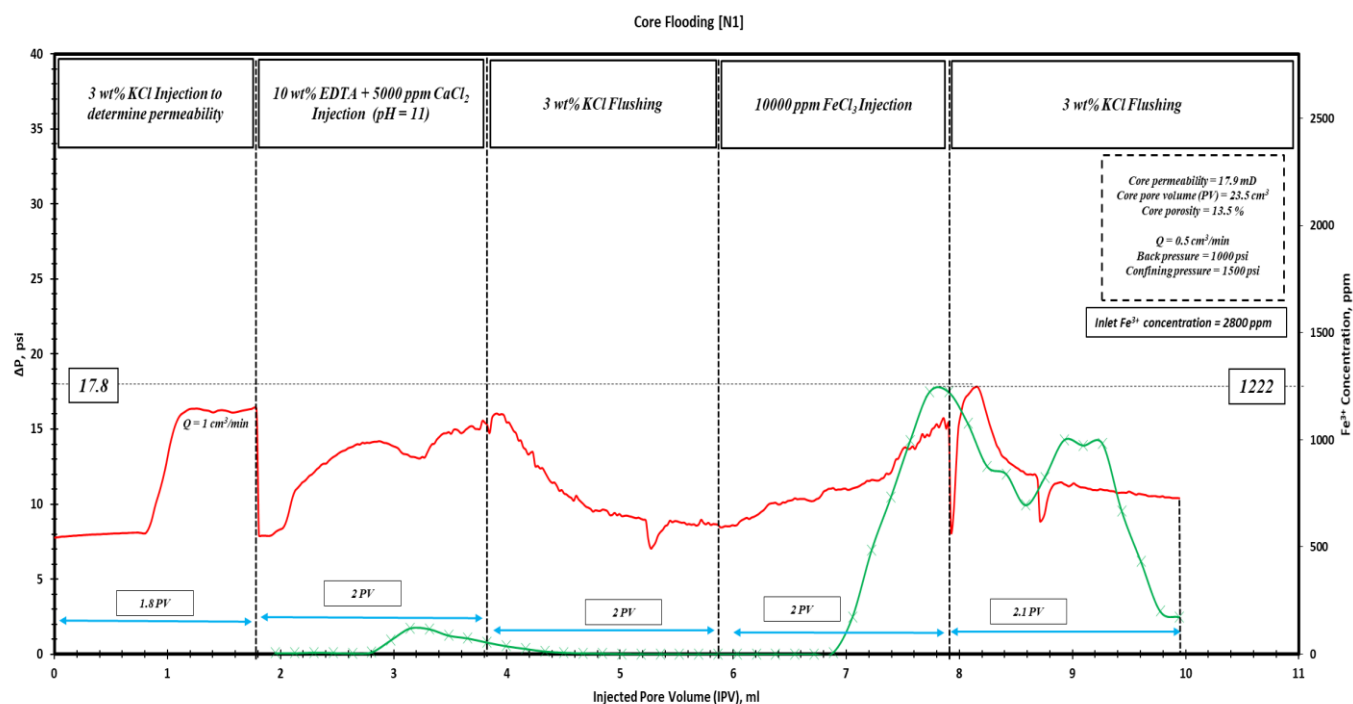


Figure 58 – Coreflooding data and Fe³⁺ concentration during the experiment using 10 wt% EDTA with Mg²⁺ at 77°F

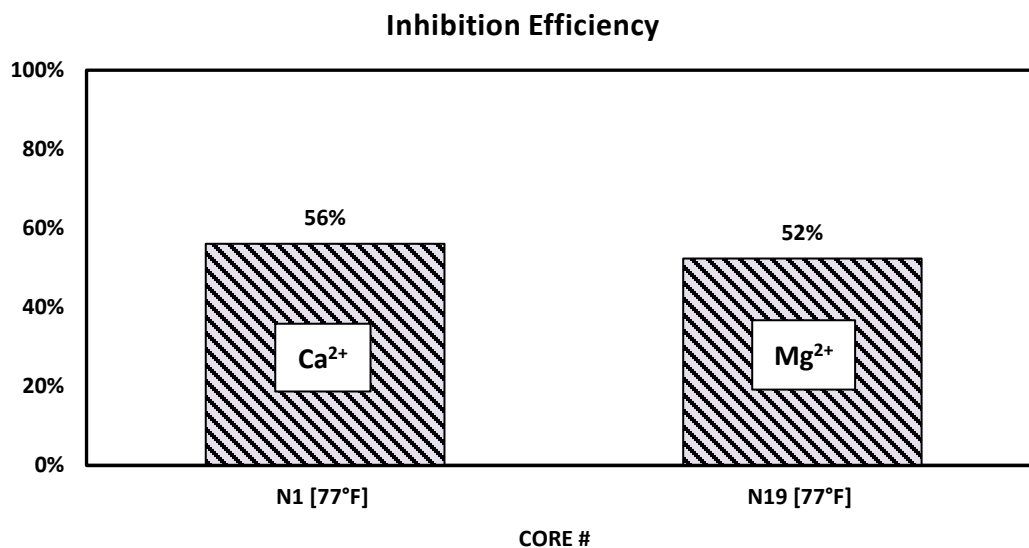


Figure 59 – Effect of cations on inhibition efficiency of 10 wt% EDTA at 77°F

The permeability loss again was determined with the ratio of K_{final} and K_{initial} . The slight difference between inhibition efficiencies also reflected to the permeability decrease in the same manner. Having Ca²⁺ in EDTA resulted in 4% more inhibition efficiency (Figure 59), almost 100 ppm of more iron (III) chelation than Mg²⁺. Hence, the decrease in permeability was 44% and 50% in Ca²⁺ and Mg²⁺ respectively (Figure 60).

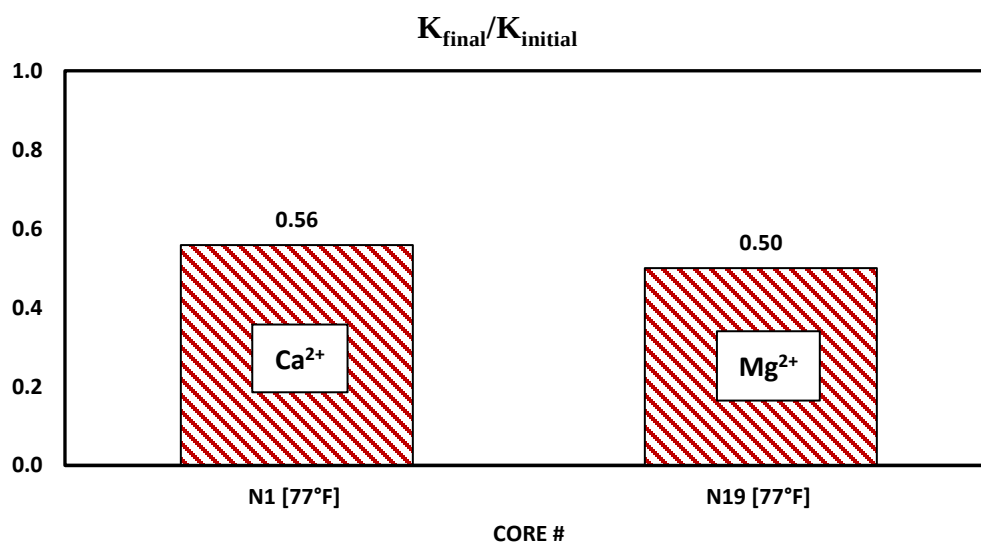


Figure 60 – Permeability change K_f/K_i (effect of cations)

4.1.6 Effect of soaking time on EDTA adsorption

Further in this work the effect of additional soaking inhibitor time for 10 and 20 wt% EDTA was examined. Soaking time of one hour and two hours for 10 wt% EDTA [N5 and N18 cores] and two hours for 20 wt% EDTA at 77°F [N17 core]. The initial permeability of rock samples used in these experiments are shown in **Table 28**.

Table 28 – Initial rock permeability and initial iron (III) concentration (soaking time)

Core #	Initial rock	Initial Fe ³⁺
	permeability, mD	concentration, ppm
N5	11.1	2800
N17	12.5	2800
N18	11.0	2800

The effect of one hour soaking time on 10 wt% EDTA at ambient temperature resulted in maximum 522 ppm of Fe³⁺ concentration (**Figure 61**) while two hours of soaking time yielded the maximum of 406 ppm of Fe³⁺ ions (**Figure 62**) in effluent samples. As mentioned earlier in Chapter 4 (section 4.1.2), the maximum observed concentration of ferric ions with 10 wt% EDTA at ambient temperature was 550 ppm. The results shows that soaking time of one hour for 10 wt% EDTA complexed 28 ppm more ferric ions. However, the effect of the two hours soaking time was more notable as this time allowed to 10 wt% EDTA to complex additional 61 ppm compared with 10 wt% without any soaking time. Therefore, two hours soaking time was tested using 20 wt% EDTA as well. The alteration of ferric concentration throughout the experiment is shown

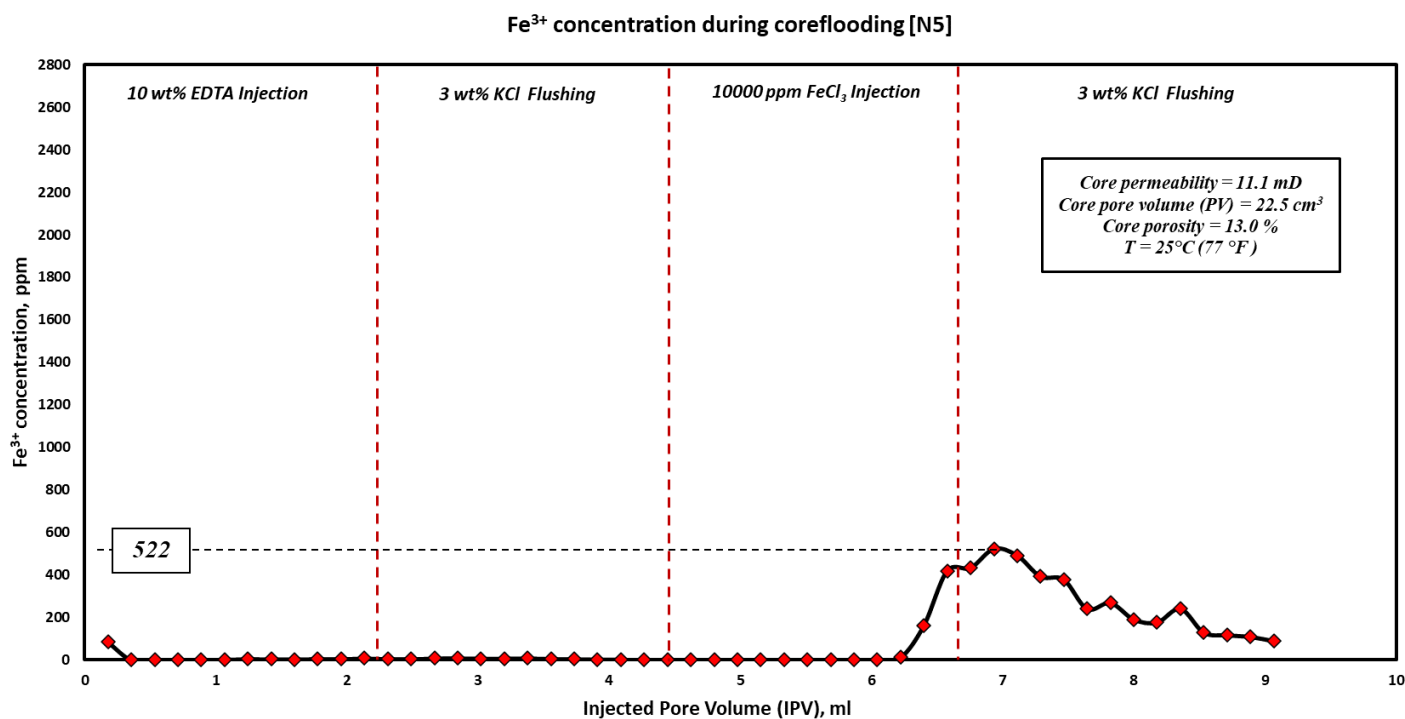


Figure 61 – Fe³⁺ concentration for 10 wt% EDTA at 77°F (1h soaking time)

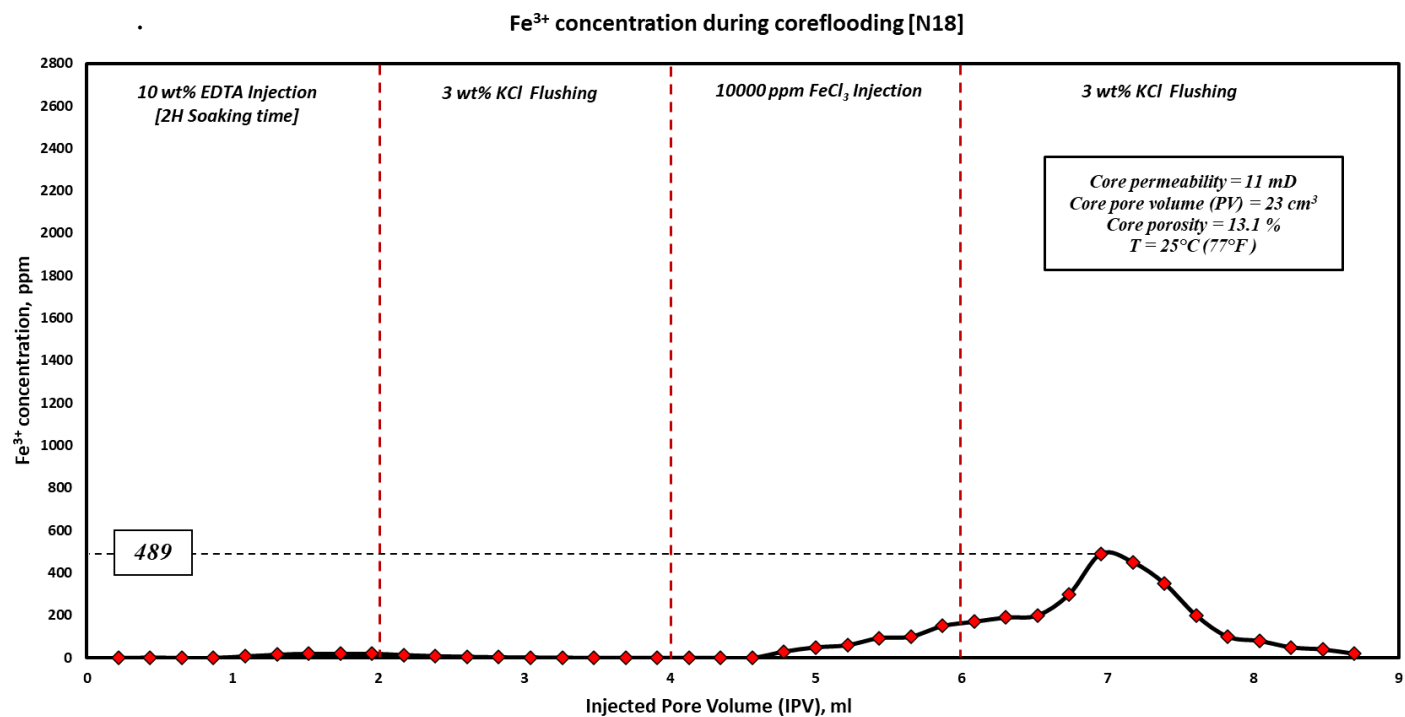


Figure 62 – Fe³⁺ concentration for 10 wt% EDTA at 77°F (2h soaking time)

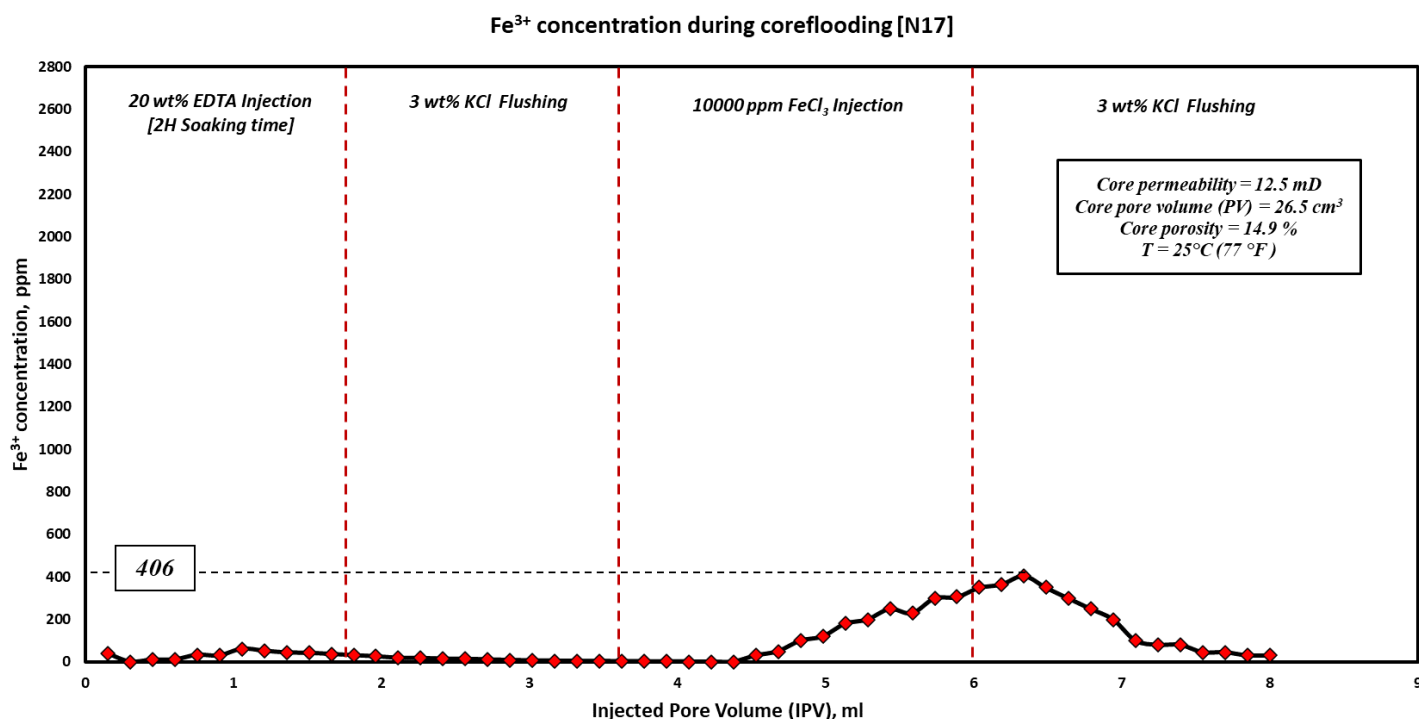


Figure 63 – Fe³⁺ concentration for 20 wt% EDTA at 77°F (2h soaking time)

in **Figure 63**. Compared to 20 wt% without soaking time, two hours soaking time resulted in chelation of 46 ppm more iron (III) ions.

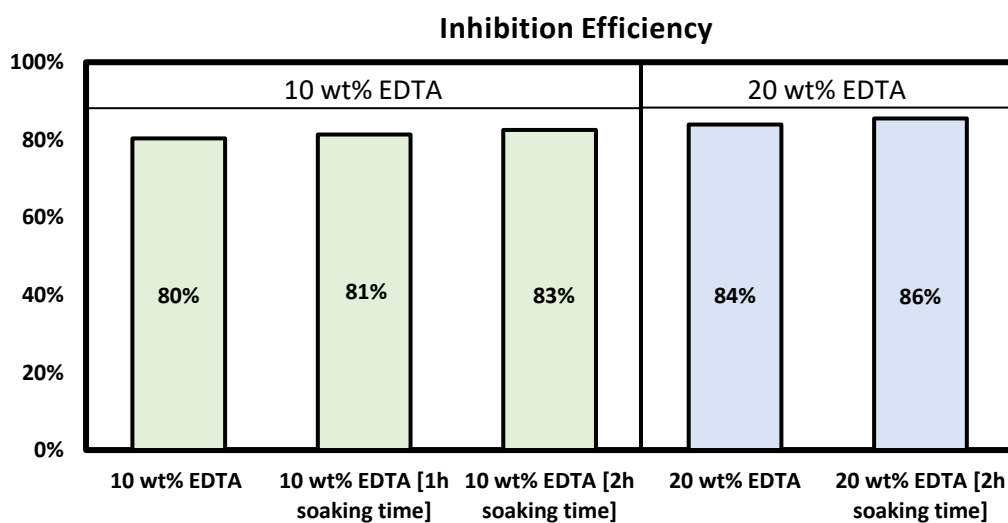


Figure 64 – Comparison of inhibition efficiencies (without/with soaking time)

Figure 64 summarizes all inhibition efficiencies of 10 wt% EDTA and 20 wt% EDTA with and without impact of soaking time. One hour and two hours of soaking time gave addition 1% and 3% efficiency respectively. In case of 20 wt% of EDTA, two hours of soaking time improved inhibition efficiency by 2%. **Figure 65** represents initial ferric concentration and corresponding maximum final ferric concentrations for the mentioned cases above.

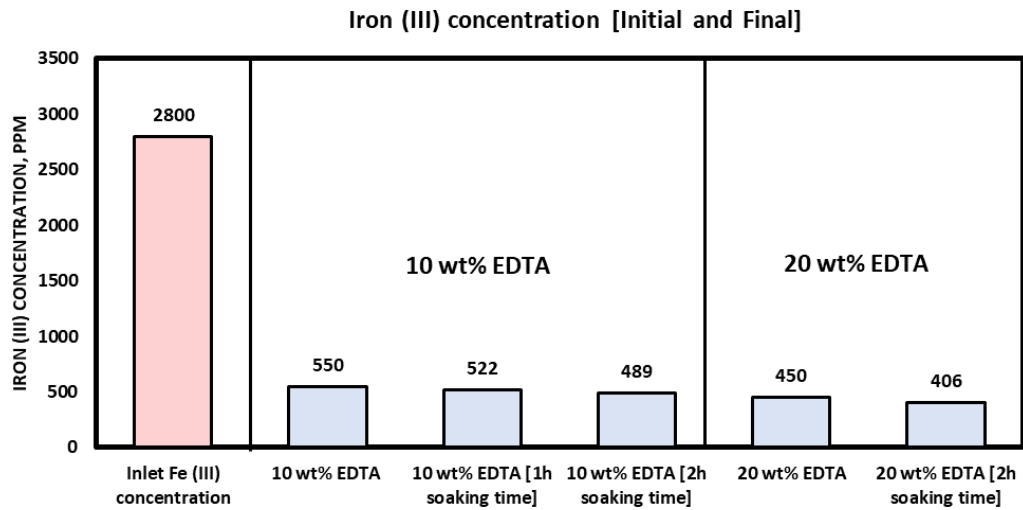


Figure 65 – Initial and final Fe^{3+} concentration

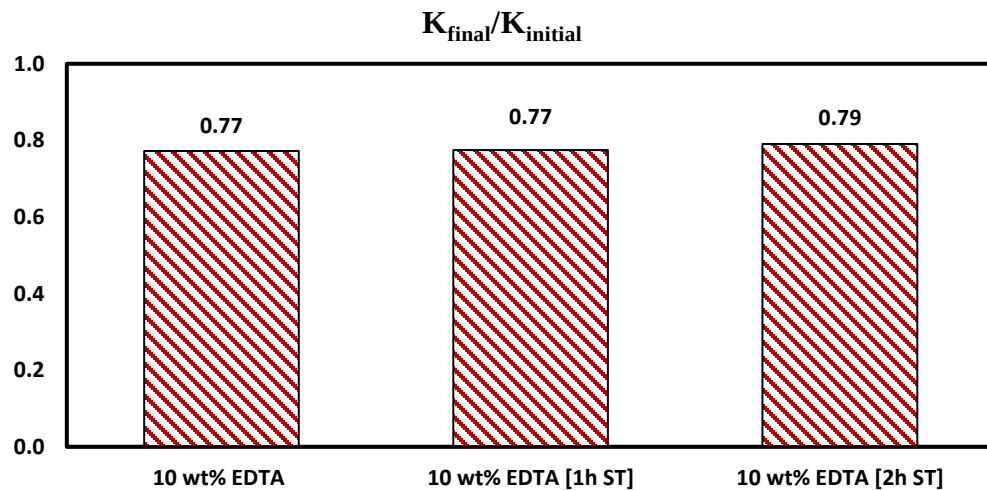


Figure 66 – Permeability change K_f/K_i [10 wt% EDTA]

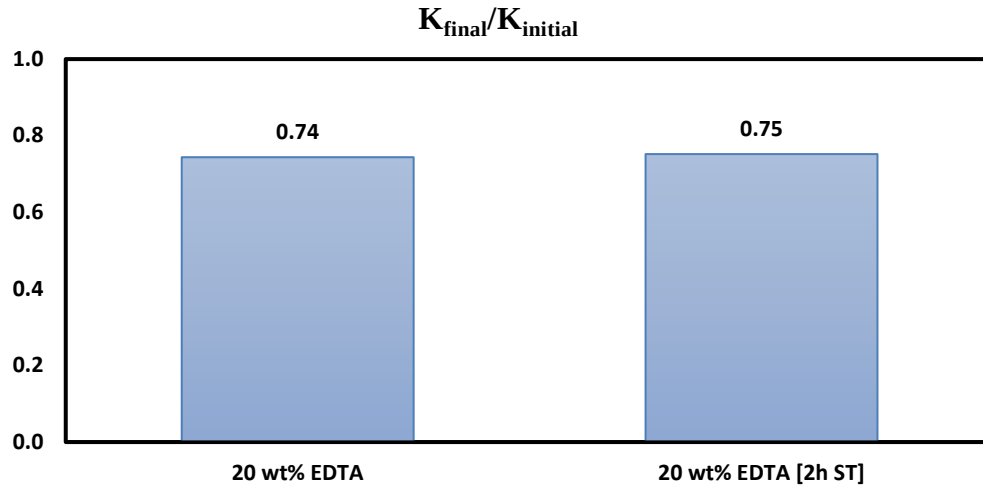


Figure 67 – Permeability change K_f/K_i [20 wt% EDTA]

Figure 66 and **Figure 67** compares the permeability changes for the cases with and without soaking time of EDTA. It is evident that having small percentage of more inhibition efficiencies reflected on the permeability loss and very small improvements on final rock permeability. Overall, it can be concluded that soaking time did not show profound impact on EDTA adsorption.

4.1.7 Inhibition efficiency of 20 wt% DTPA

After finalizing the experiments with EDTA, it was concluded that 20 wt% EDTA was the best-adsorbed chelating agent concentration. It is worth to mentioning that DTPA usually shows the same trends as EDTA and because of the fact DTPA experiments with 20 wt% was conducted at 77°F [N15 core sample] and 120°F [N16 core sample]. **Table 29** details the initial ferric concentration and initial permeability of the rock samples. As represented in **Figure 68**, during the experiment performed at ambient temperature condition, maximum ferric concentration in effluent samples was 409 ppm which was almost as same as 20 wt% EDTA. However, at 120 °F (**Figure 69**), there was slight

difference of maximum ferric concentration as it was almost 400 ppm in case of 20 wt% EDTA and 606 ppm using 20 wt% DTPA.

Table 29 – Initial rock permeability and initial iron (III) concentration (20 wt% DTPA)

Core #	Initial rock permeability, mD	Initial Fe ³⁺ concentration, ppm
N15	49.7	2800
N16	48	2800

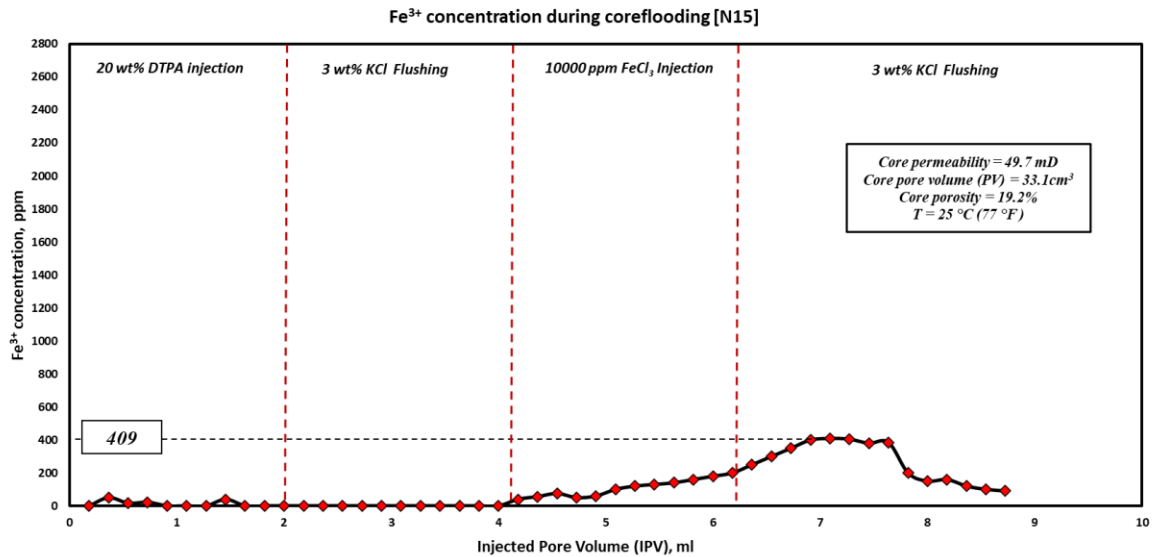


Figure 68 – Fe³⁺ concentration using 20 wt% DTPA at 77°F

Figure 70 shows inhibition efficiencies for 20 wt% DTPA at ambient temperature and 120°F which can be taken into account almost the same percentage of inhibition with 20 wt% EDTA. Further the permeability changes were determined, and it was concluded that the inhibition efficiency of both EDTA and DTPA are almost the same and this trend reflected on permeability change in the same manner.

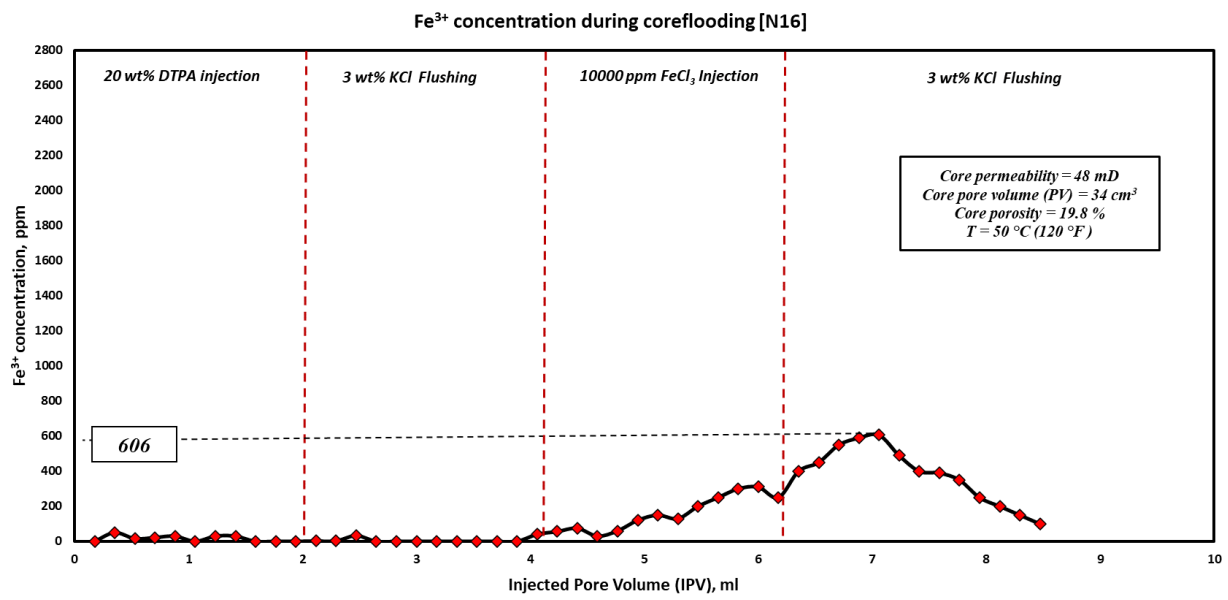


Figure 69 – Fe³⁺ concentration using 20 wt% DTPA at 120°F

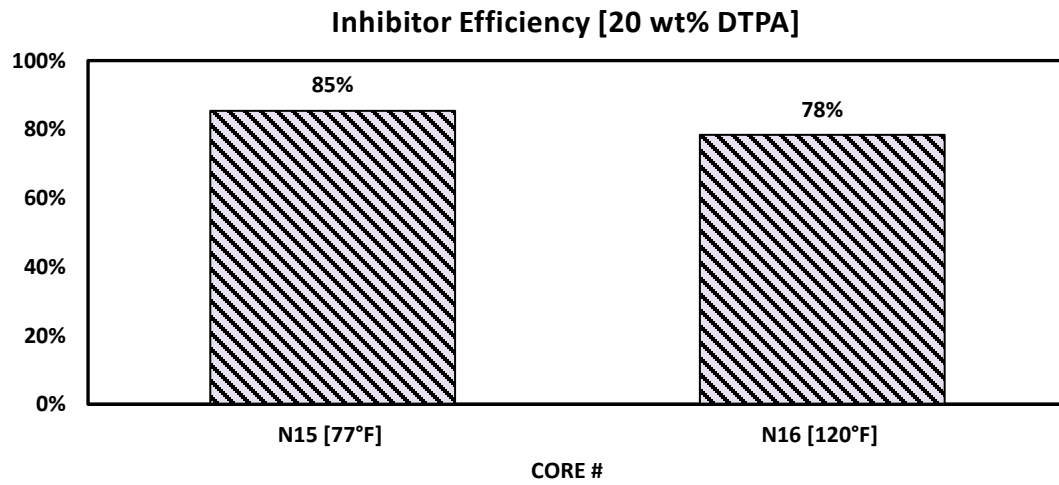


Figure 70 – Inhibition efficiency of 20 wt% EDTA

4.2 Electrostatic interaction (solid/solid interaction)

Chemical interactions happen during water injection operation significantly affect the pH environment of the reservoir formation and causing precipitation of unwanted solid particles such as solid crystals of different scales (in our case ferrous and/or ferric ions). In this section, the results of series of zeta potential measurements conducted to analyze the behaviour and precipitation of iron (II) and iron (III) on calcite mineral in varying pH environments using the theory of surface charge will be discussed. Additionally, the effect of different types and concentrations of salts on iron (III) precipitation will be discussed within the framework of this section.

4.2.1 Calcite mineral surface charge investigation

The zeta potential measurements started with determining the surface charge of calcite minerals in pH environments from 1 to 13. The surface charge alteration of calcite minerals almost replicates the studies performed on calcite mineral in the literature [100], [101]. The surface charge of calcite minerals is reported to be a strong function of pH environment [102]. **Figure 71** illustrating the zeta potential values of calcite particles. In the acidic region (pH 1-4) it is observed that there is an increase toward negative zeta potential side and may be attributed to protonation. The reduction in the zeta potential value from 4 to 7 can be because of double layer compression. Between pH value from 7 to 8 it is observed that there is double layer collapse while from 8-12 the further decrease might be because of adsorption of OH^- on calcite particle surface. In the region of pH 12-13, this can be due to compression of double layer.

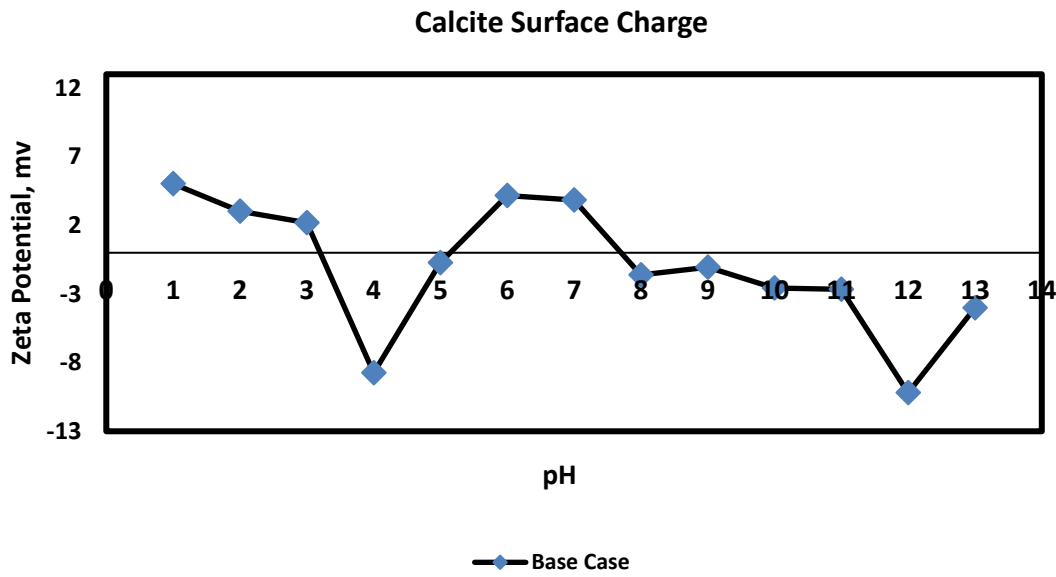


Figure 71 – Surface charge of calcite mineral as a function of pH

4.2.2 Precipitation of iron (III) on calcite mineral

Further, using zeta potential in varying pH environments it was determined that at which pH environments, different concentrations of Fe^{3+} ions will precipitate. As mentioned before in **Chapter 3 (Section 3.2)**, zeta potential values in between -5 mV and 5 mV indicate high possibility of instability and particle precipitation. To study the precipitation of ferric ions five different concentrations of iron was prepared. In the case calcite mineral, it was observed that calcite particles are not stable enough in every pH environment, since zeta potential values were varying in between -10 mV and 10 mV and addition of Fe^{3+} forms even high instable region experiencing with iron (III) precipitation. For analyzing the results, the ferric concentrations were grouped in two categories in which ferric concentrations was lower than 1600 ppm and higher than 5000 ppm. **Figure 72** shows the behavior of 100 ppm, 500 ppm and 1500 ppm of Fe^{3+} on calcite surface. Generally, it has been reported that iron (III) is readily precipitate once pH of the

environment reaches 1 [69][103]. Red-dotted lines in **Figure 72** indicates the zeta potential region of -5 mV and 5 mV. Results with low ferric concentrations almost supports the fact that ferric ions tend to be precipitated in all pH environments starting from 1 up to 13. It is evident that iron (III) system, in some pH values, showed higher zeta potential with around -10 mV and 10 mV. However, it can be concluded that regardless of iron (III) concentration, iron (III) ions promoting precipitation on calcite surface in whole range of pH environments.

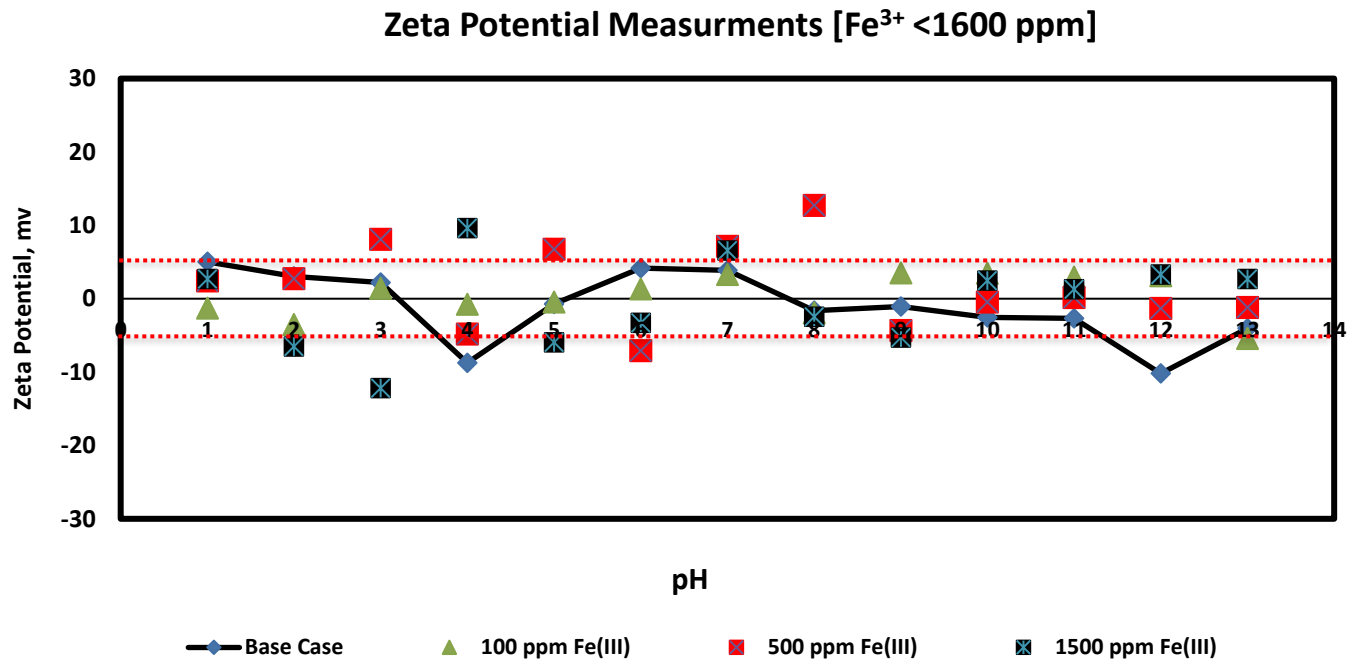


Figure 72 – Zeta potential for Fe^{3+} concentrations < 1600 ppm

The second criteria were ferric concentrations higher than 5000 ppm. 5000 ppm and 10000 ppm of ferric concentration in the calcite system were analyzed. **Figure 73** depicts the behavior of zeta potential values of 5000 ppm and 10000 ppm of Fe^{3+} on calcite

surface. Unlike low iron (III) concentrations, at higher ferric concentrations it much more obvious instability and precipitation. It can be easily concluded that the higher concentrations result in obvious precipitation on calcite minerals surface. However, there is slight fluctuation in pH region of 8-9 in which it can be seen that 10000 ppm ferric gets more stability (-14 mV) in pH value of 8 while 5000 ppm ferric shows same phenomenon (-14 mV) at pH 9. However, to sum up, during well operations, especially in water injection wells, having ferric ions (might come from the injection string as a result of corrosion product) in the solution will cause immediate precipitation.

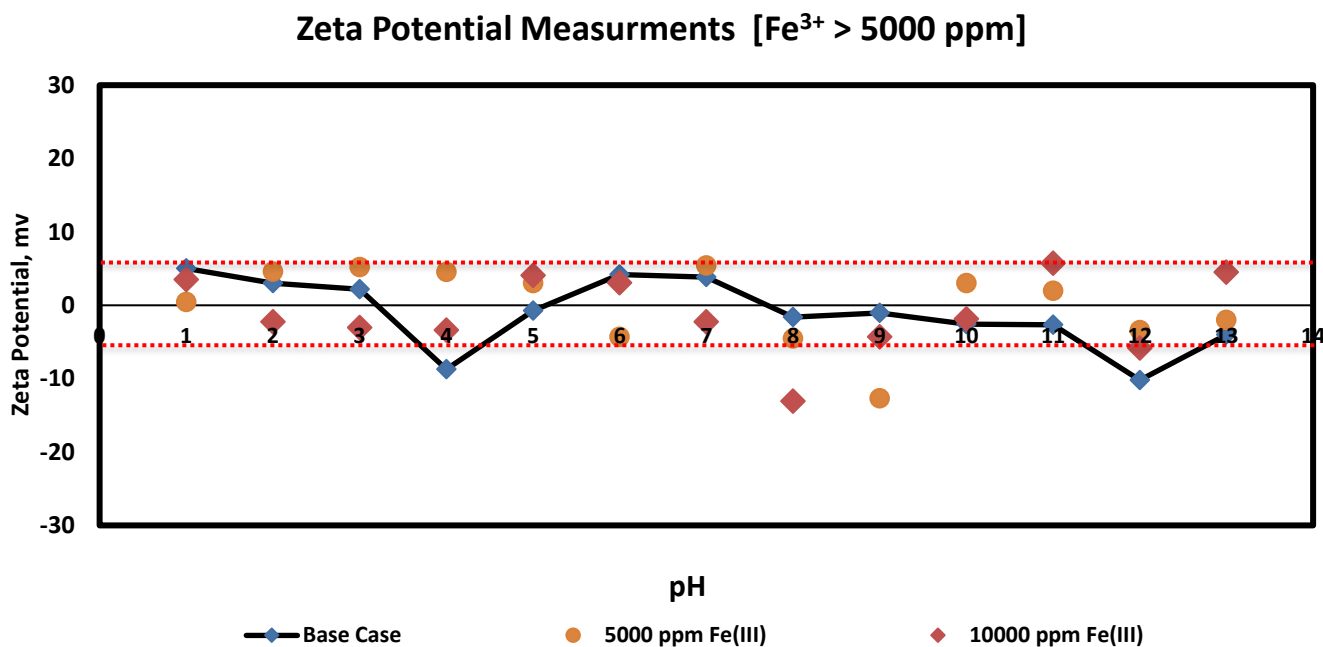


Figure 73 – Zeta potential for Fe^{3+} concentrations > 5000 ppm

4.2.3 Precipitation of iron (II) on calcite mineral

After conducting zeta potential measurements with iron (III) ions, the measurements for calcite minerals were conducted in which iron (II) ions were used. Six different ferrous ions concentrations were used, and they can be divided into two

categories. In the first category, iron (II) concentration was calculated to be lower than 1600 ppm and in the second category ferrous concentration was higher than 3000 ppm. **Figure 74** depicting the change in zeta potential values with an addition of iron (II) ions into calcite system. Unlike ferric ions, it is reported that ferrous ions usually start to precipitate in pH environments higher than 6 [103][73]. However, for calcite particles low concentrations of ferrous ions did not result in high degree of precipitation or instability. Another observation is about changing the charge state. In case of 100 ppm, it is evident that there is fluctuation between positive and negative while as the concentration of ferrous increases toward 500 ppm and 1500 ppm the system becomes predominantly positively charged. In pH environment 1 to 2 and at 4, 100 ppm ferrous concentration showing very zeta potential values very close to zero potential charge. However, as expected, having more concentration of ferrous in the system, in acidic region resulted in higher stability and higher zeta potential values.

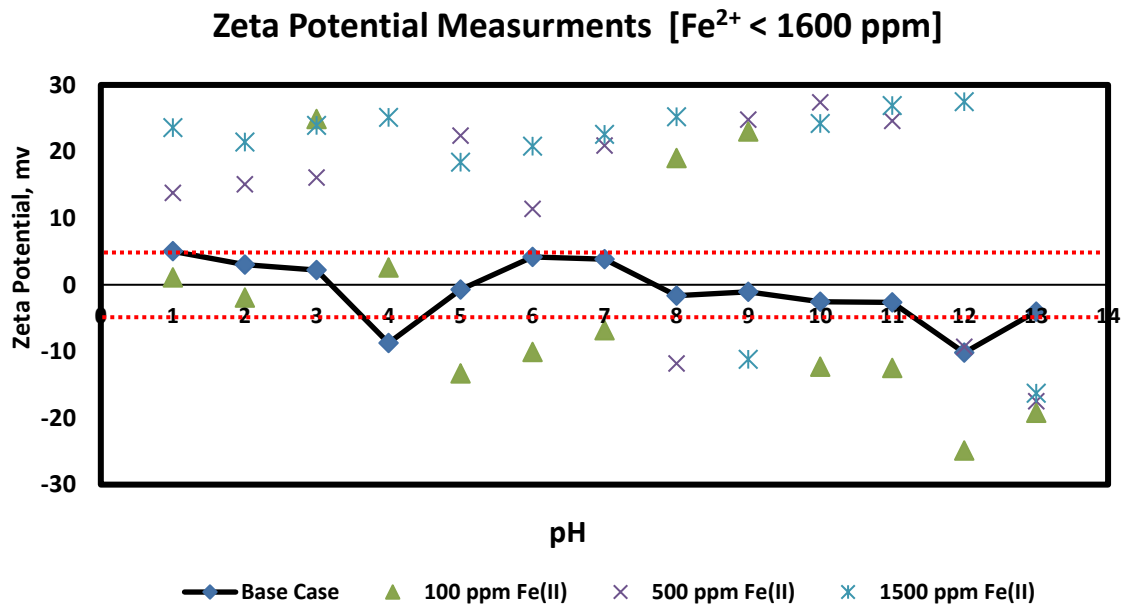


Figure 74 – Zeta potential for Fe^{2+} concentrations < 1600 ppm

The variation of zeta potential values for the second criteria which includes Fe^{2+} concentrations higher than 3000 ppm is shown in **Figure 75**. The phenomenon of dominance by positive charges continued in case of having 3000 ppm or higher concentrations of ferrous in the system. It is obvious that in the pH environments higher than 6 there is a declining trend of zeta potential values toward the zero potential charge with the only exception of pH region of 11-13 for 3000 ppm of Fe^{2+} . This trend shows that unlike ferric ions, the concentration of ferrous ions impacts the stability of the system. Higher concentration of ferrous in the system is giving more instability and lower zeta charges (but do not result in obvious precipitation) while lower concentrations of ferrous ions showing erratic changes on zeta potential charges on calcite surface.

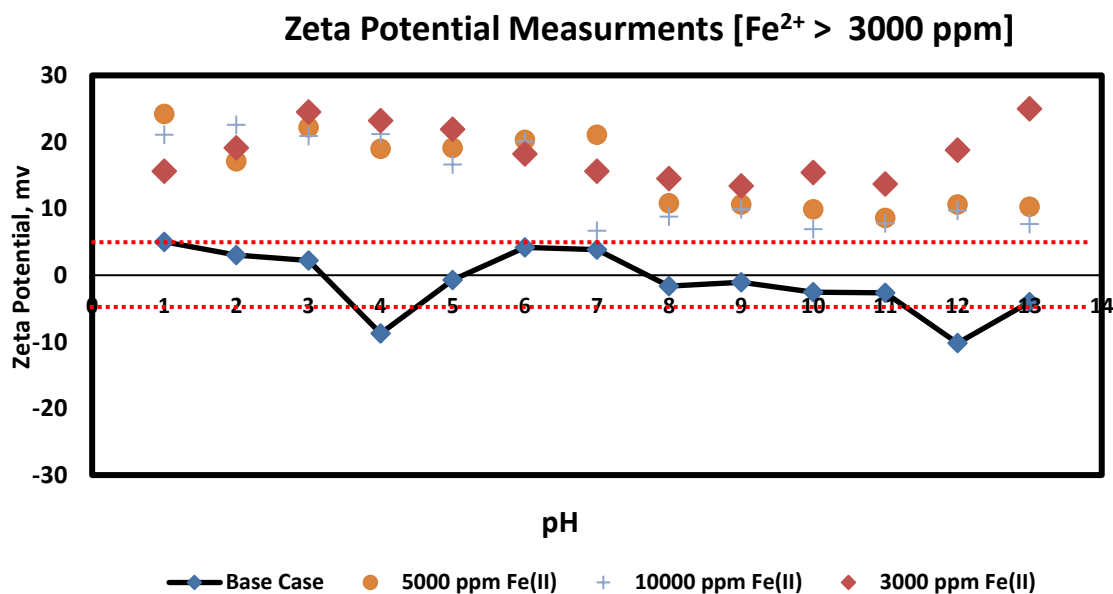


Figure 75 – Zeta potential for Fe^{2+} concentrations > 3000 ppm

4.2.4 Effect of NaCl on iron (III) precipitation

Calcite minerals interaction with 0.1M NaCl and 1M NaCl were firstly determined and shown in **Figure 76**. 0.1 M NaCl representing almost the same mechanism with calcite mineral. However, in pH 5-7, double layer compression can be observed from the trend. Hence, it can be concluded that in the charge development of calcite minerals, 0.1 M NaCl does not have a significant influence. In contrast, 1M NaCl solution impacted zeta potential values giving the system higher stability and changed the system into negative charge dominated. In high pH alkaline region there is an interchanging surface charge. This can be explained by adsorption of OH^- competing with double layer collapse and there is double layer compression from pH 12 to 13.

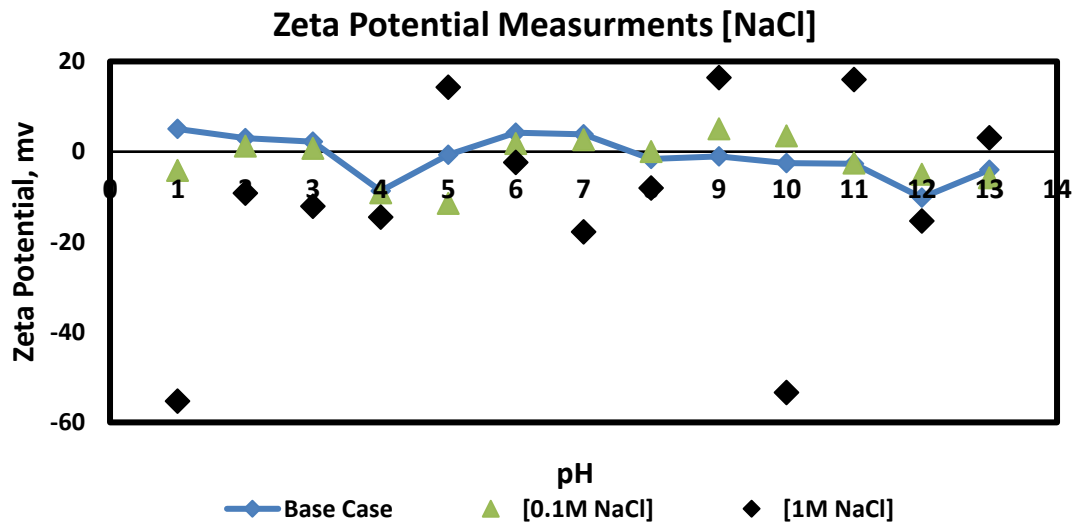


Figure 76 – Zeta potential of calcite suspended in 0.1 M and 1 M NaCl solutions

Further in the measurements, the effect of 0.1 M NaCl and 1M NaCl on alteration of zeta potential charge of the system containing 1500 ppm Fe^{3+} and 10000 ppm Fe^{3+} was analyzed. **Figure 77** showing the impact of 0.1M NaCl on 1500 ppm Fe^{3+} . It is clear from the figure that low concentration NaCl gives the even higher degree of instability and triggers precipitation with the exception of pH 6, where NaCl makes system more stable.

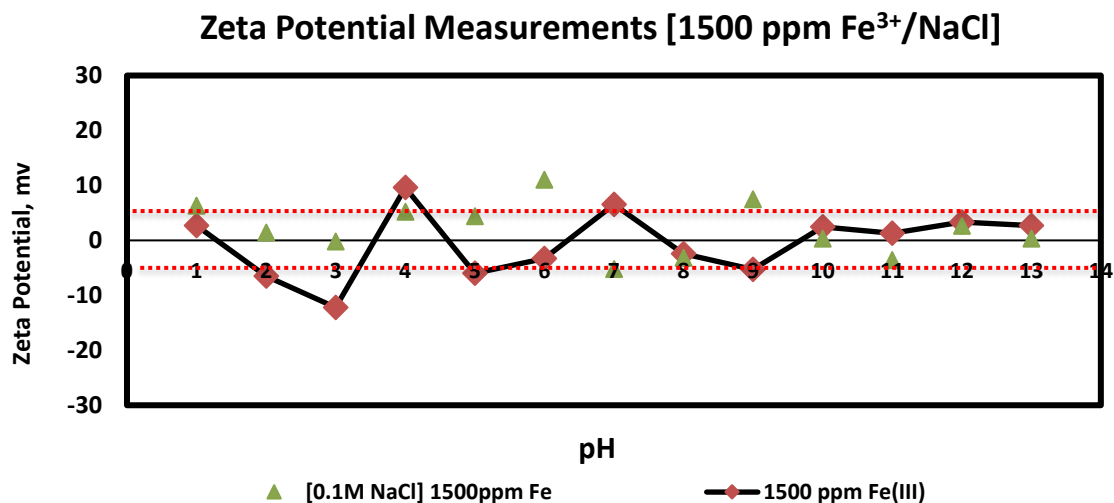


Figure 77 – Effect of 0.1M NaCl on zeta potential of 1500 ppm Fe^{3+} - calcite system

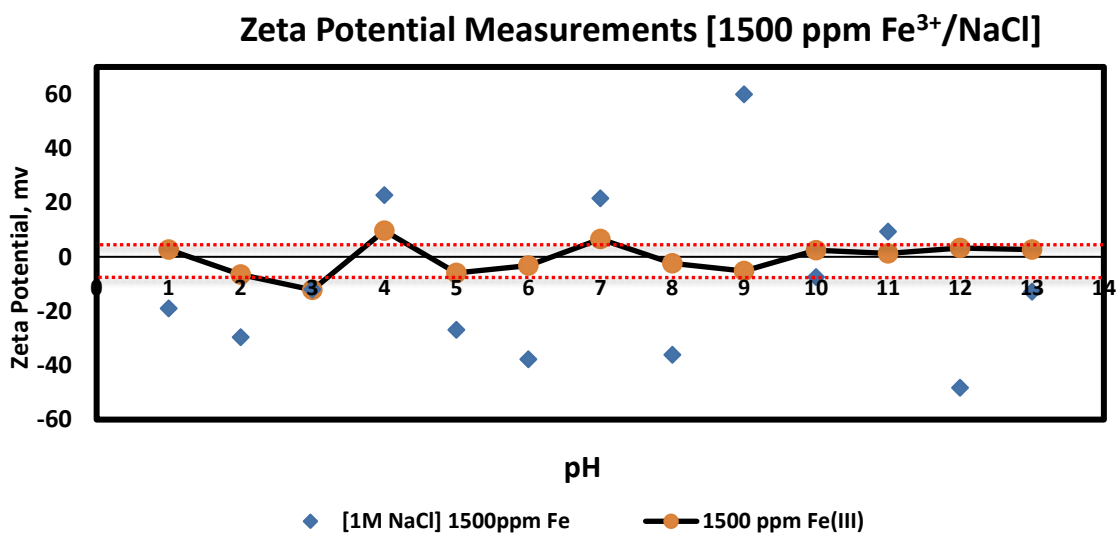


Figure 78 – Effect of 1M NaCl on zeta potential of 1500 ppm Fe^{3+} - calcite system

Figure 78 showing the impact of 1M NaCl on charge development of calcite in case of 1500 ppm Fe^{3+} . Unlike 0.1 M NaCl, in acidic region and near neutral pH environments, 1M NaCl makes the system more stable. However, in the pH environments

between 10-13, near zero potential charge trend continues. **Figure 79** illustrates how 0.1M NaCl influences zeta potential charge of the calcite system that contains 10000 ppm Fe^{3+} . The results propose that 0.1M NaCl affects Fe^{3+} behavior as it forms almost negatively charged more stable system in pH 2, pH 5-6, and pH 11-13. However, the effect of 1M NaCl on the same system is shown in **Figure 80**.

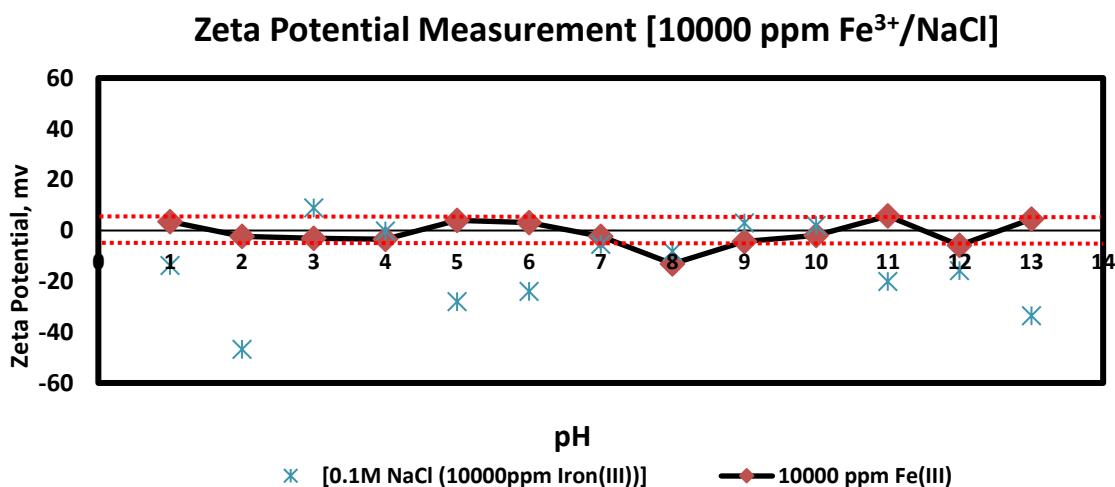


Figure 79 – Effect of 0.1M NaCl on zeta potential of 10000 ppm Fe^{3+} - calcite system

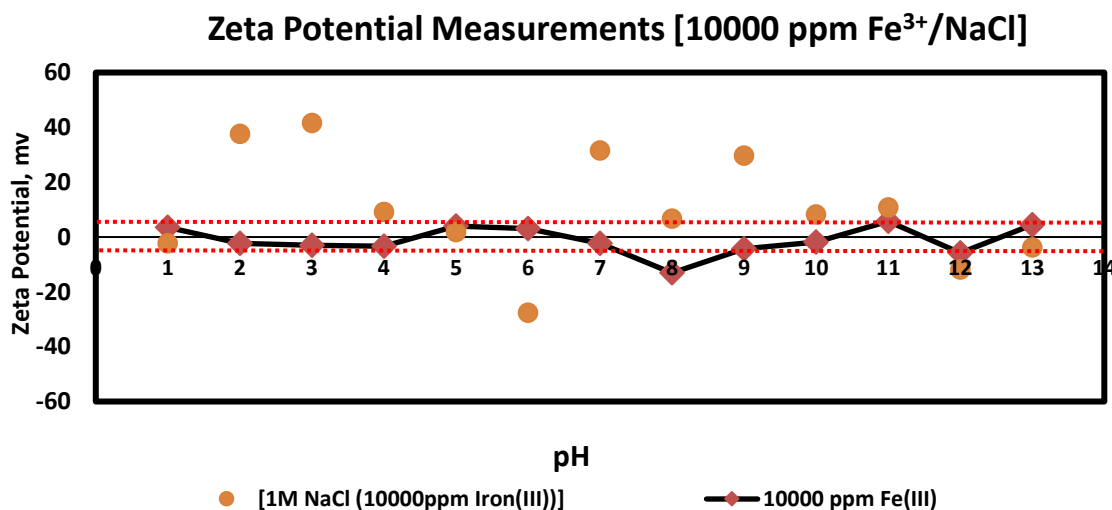


Figure 80 – Effect of 1M NaCl on zeta potential of 10000 ppm Fe^{3+} - calcite system

An interesting trend founded was 1M NaCl creates positively charged systems in pH 2-5 and pH 7-11. In pH 2-3, and pH 7-9, the system shows high stability while 1M NaCl results in ferric precipitation in high alkaline regions.

Based on the results, it can be said that in relatively low concentration of Fe^{3+} , 0.1M NaCl almost does not affect charge development of calcite while 1M NaCl has an impact on charge development of calcite minerals. However, in high concentration of Fe^{3+} , both 0.1M NaCl and 1M NaCl promotes significant changes on surface charge development by creating negative charge dominant (0.1M NaCl), positive charge dominant (1M NaCl) and relatively stable system.

4.2.5 Effect of MgCl_2 on iron (III) precipitation

Calcite minerals interaction with 0.1M MgCl_2 and 1M MgCl_2 were analyzed and are shown in **Figure 81**. The trend indicates that Mg^{2+} adsorbs on the mineral surface. The is a slight decrease in very high acidic regions might be due to compression of double layer. With respect to base calcite case, it can be seen that there is slight increase in high alkaline environment which can be the result of OH^- adsorption on mineral surface. The trends also show interchanging of charges in between pH 8 – 13. However, in the case of 1M MgCl_2 , the system becomes more stable the zeta potential values support this idea in almost all pH environments except pH range between 6-9. It is evident that 1M MgCl_2 creates negatively charged system in acidic region following with double layer's compression in between pH 3 – 4 while double layer's collapse occurred in pH environments from 10 to 13.

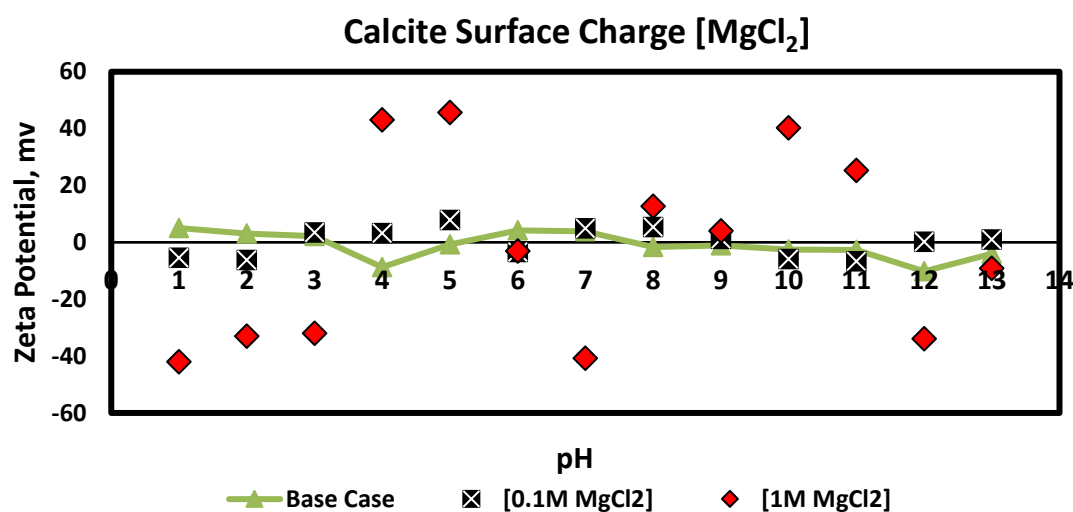


Figure 81 – Zeta potential of calcite suspended in 0.1 M and 1 M MgCl₂ solutions

Measurements were followed with analyzing the effect of 0.1 M MgCl₂ and 1M MgCl₂ on alteration of zeta potential charge of the system containing 1500 ppm Fe³⁺ and 10000 ppm Fe³⁺. **Figure 82** showing the impact of 0.1M MgCl₂ on 1500 ppm Fe³⁺.

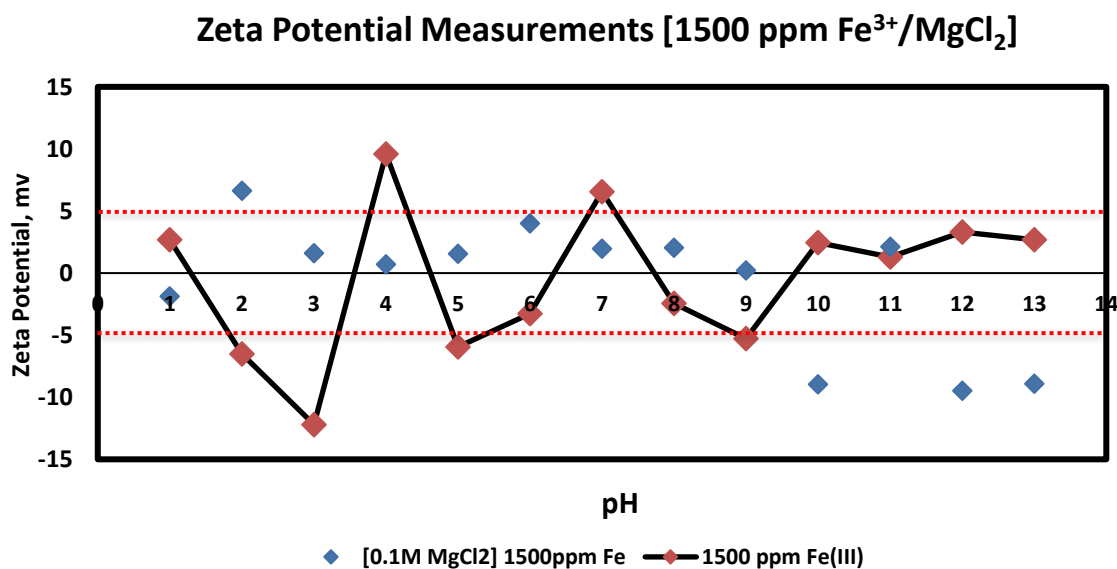


Figure 82 – Effect of 0.1M MgCl₂ on zeta potential of 1500 ppm Fe³⁺ - calcite system

According to the trends, the system having 0.1M MgCl_2 even increases the precipitation of ferric ions in pH environment from 1 to 9. In alkaline regions, 0.1M MgCl_2 turned the calcite surface charge into the negatively charged and more stable system.

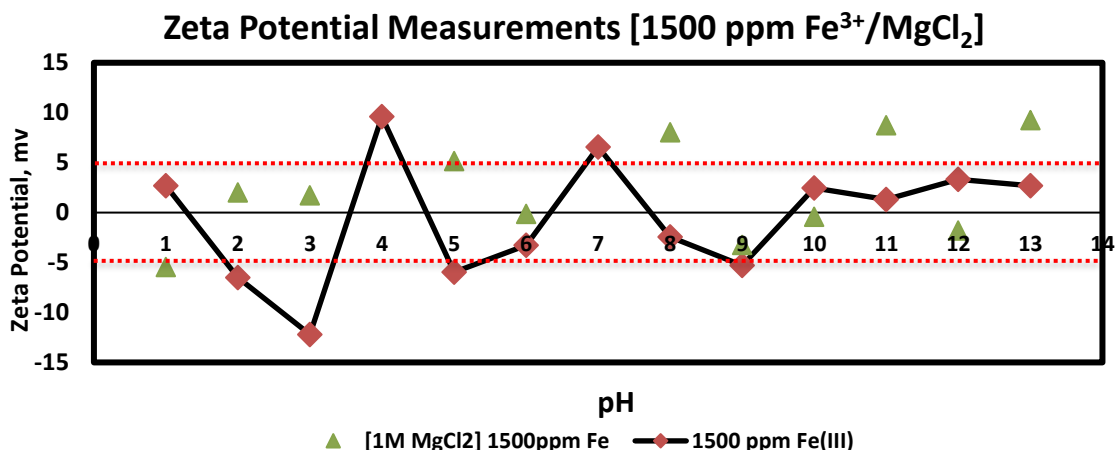


Figure 83 – Effect of 1M MgCl_2 on zeta potential of 1500 ppm Fe^{3+} - calcite system

However, 1M MgCl_2 containing system it is evident from **Figure 83** that having more concentration of Mg^{2+} cations in the system does not affect to the precipitation of ferric ions on calcite mineral as almost for the whole range of pH environments net zeta potential charge of calcite mineral ranging in between -5 mV and 5 mV. **Figure 84** showing that in high Fe^{3+} , calcite surface charge is not affected by 0.1M MgCl_2 , with the exception of high pH environments (pH 10 – 13), 0.1M MgCl_2 increases the stability of the system. **Figure 85** depicting the effect of 1M MgCl_2 on calcite surface charge development. Unlike 0.1M MgCl_2 , with an increase of concentration of MgCl_2 in the system, calcite minerals show higher stability in near neutral pH region. Additionally, it is worth to mentioning that the behavior of the system in high alkaline regions replicates the same trend as low MgCl_2 concentration but with high magnitude of negatively charged system.

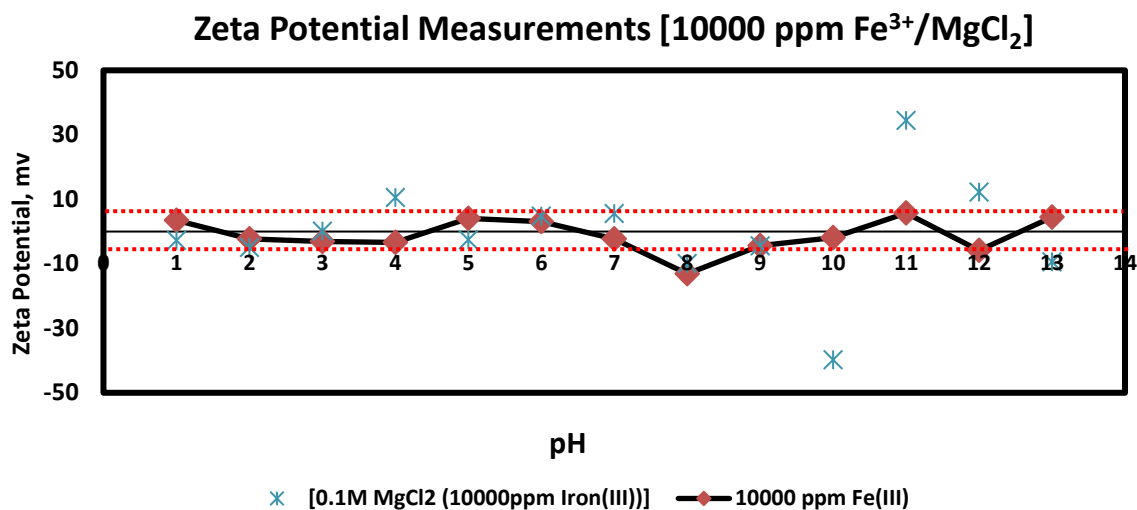


Figure 84 – Effect of 0.1M MgCl₂ on zeta potential of 10000 ppm Fe³⁺ - calcite system

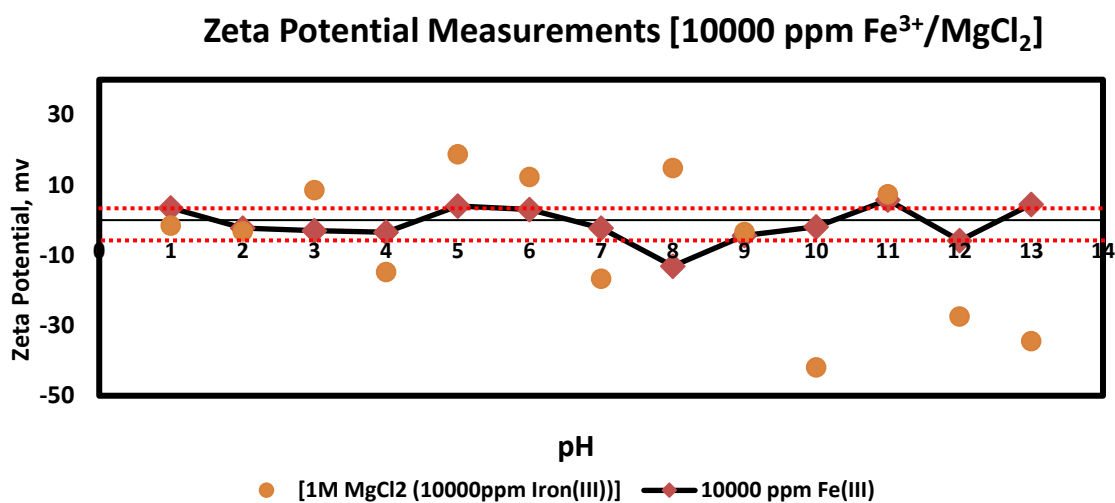


Figure 85 – Effect of 1M MgCl₂ on zeta potential of 10000 ppm Fe³⁺ - calcite system

Obtained results show that generally, MgCl_2 influences charge development of calcite in high pH environment and addition of MgCl_2 to the system forms high stability in alkaline region.

4.2.6 Effect of CaCl_2 on iron (III) precipitation

The last set of measurements were conducted to analyze the impact of 0.1M and 1M CaCl_2 to iron (III) precipitation. Firstly, the effect of CaCl_2 on charge development of calcite mineral without any iron (III) were determined. **Figure 86** shows the surface charge alteration of calcite mineral caused by 0.1M CaCl_2 and 1M CaCl_2 . It is very clear from the trend that 0.1M CaCl_2 imitates the behavior 0.1M MgCl_2 . Low concentration of CaCl_2 does not significantly affect to the change of surface charge of calcite mineral. However, 1M CaCl_2 influences the calcite zeta potential charge by forming more stable system in near neutral pH environment (5-6) and slightly alkaline environment (8-10). Between pH 4 and 5 and 7 to 9 there is compression of double layer while in pH 6 to 7 double layer's collapse occurs.

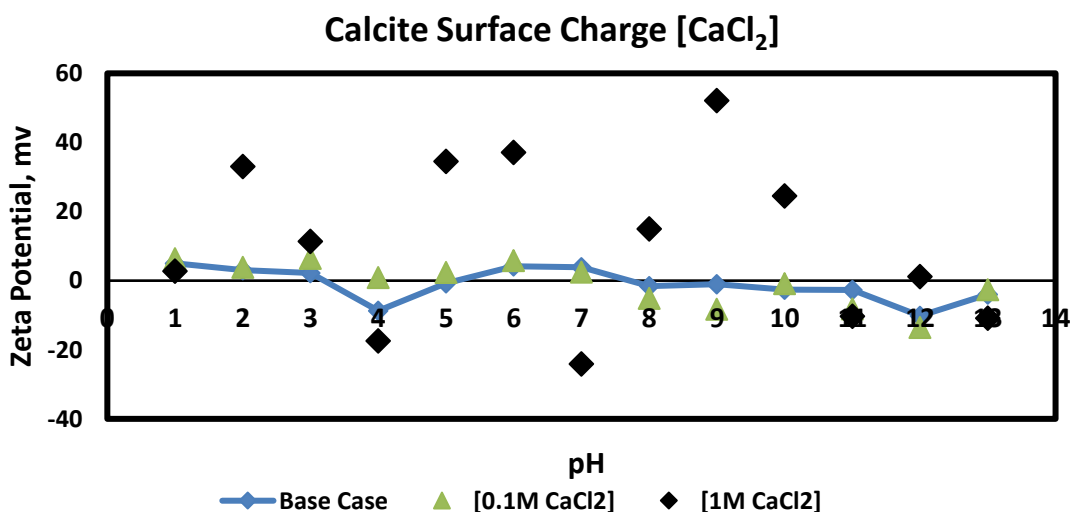


Figure 86 – Zeta potential of calcite suspended in 0.1 M and 1 M CaCl_2 solutions

The impact of 0.1M CaCl_2 on precipitation of 1500 ppm Fe^{3+} on calcite mineral is represented in **Figure 87**. The results indicate that 0.1M CaCl_2 has no significant effect on iron (III) precipitation with comparably lower concentration on calcite mineral. However, 1M CaCl_2 affects the stability of the system (**Figure 88**) by relatively increasing the zeta potential charge in acidic environments and in pH environments in between 7 and 9.

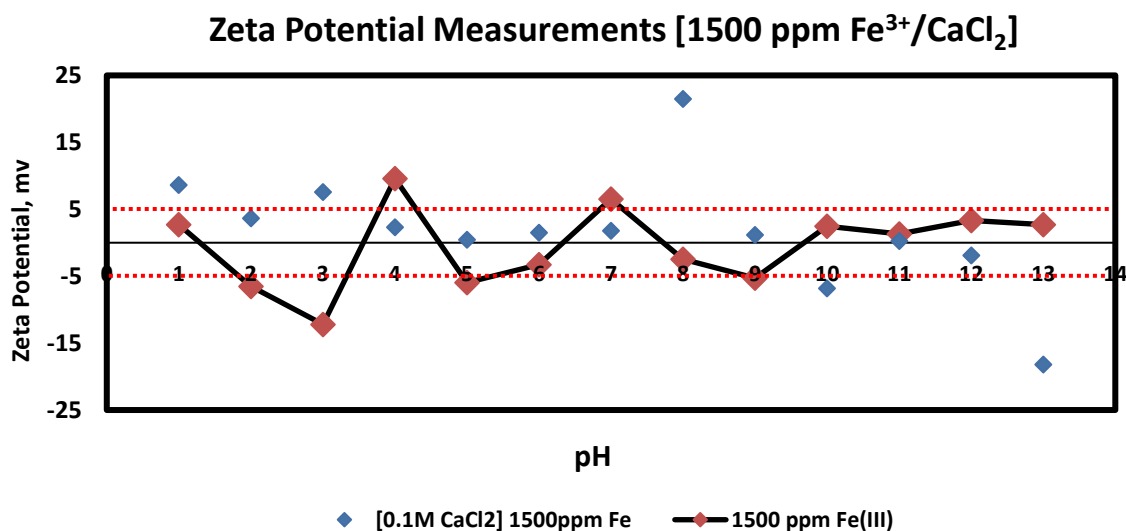


Figure 87 – Effect of 0.1M CaCl_2 on zeta potential of 1500 ppm Fe^{3+} - calcite system

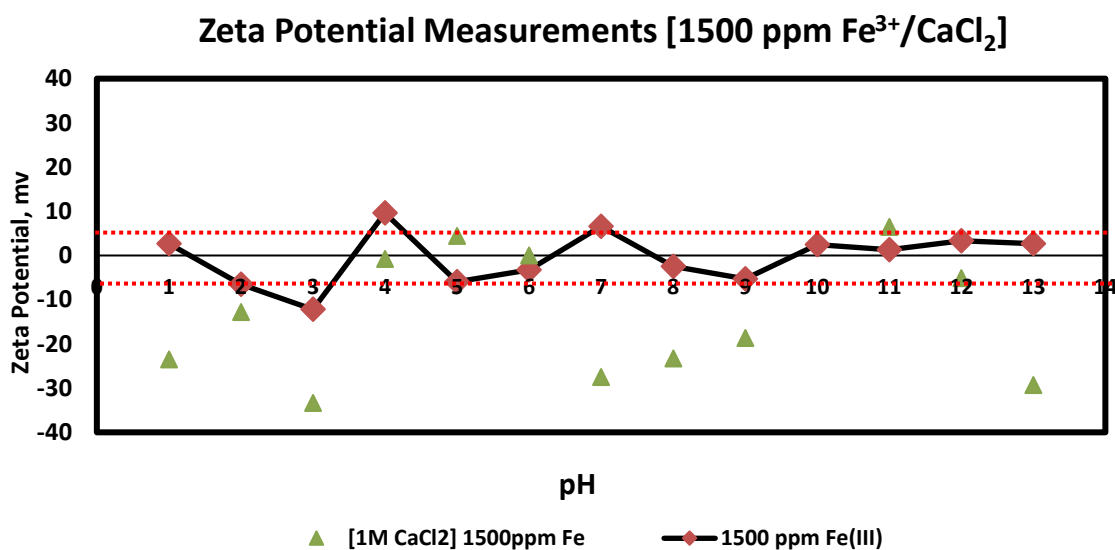


Figure 88 – Effect of 0.1M CaCl_2 on zeta potential of 1500 ppm Fe^{3+} - calcite system

In case of high iron (III) concentration, 0.1M CaCl_2 has a significant impact on ferric precipitation in acidic environment and it reflected in zeta potential values.

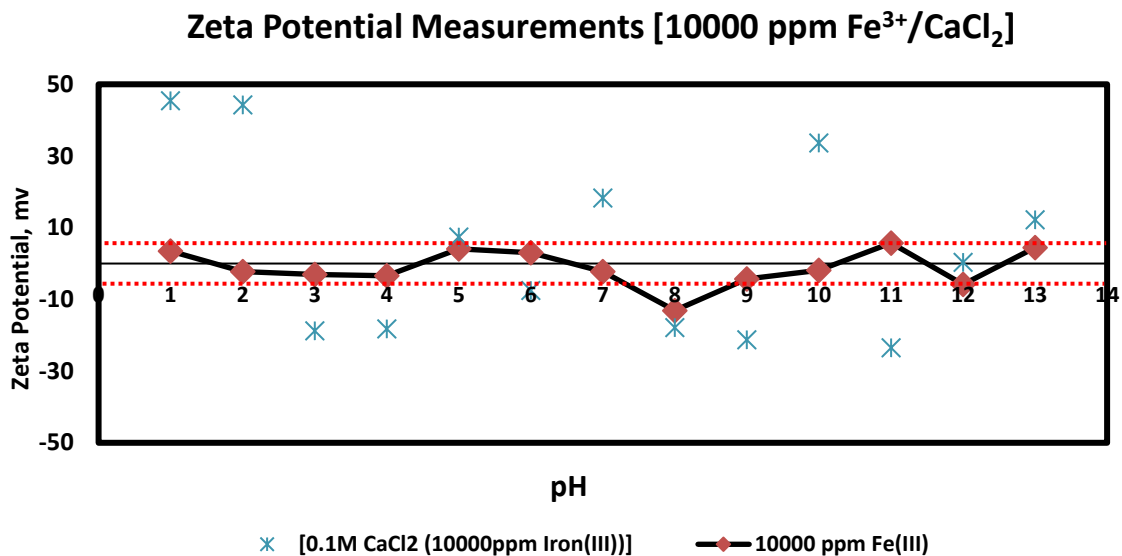


Figure 89 – Effect of 0.1M CaCl_2 on zeta potential of 10000 ppm Fe^{3+} - calcite system

Similarly, 1M CaCl_2 influences the system with the increase of zeta potential values in low pH environments and also in near neutral pH environments ferric ions are not prone to precipitate with the incorporation of high concentration CaCl_2 to the system.

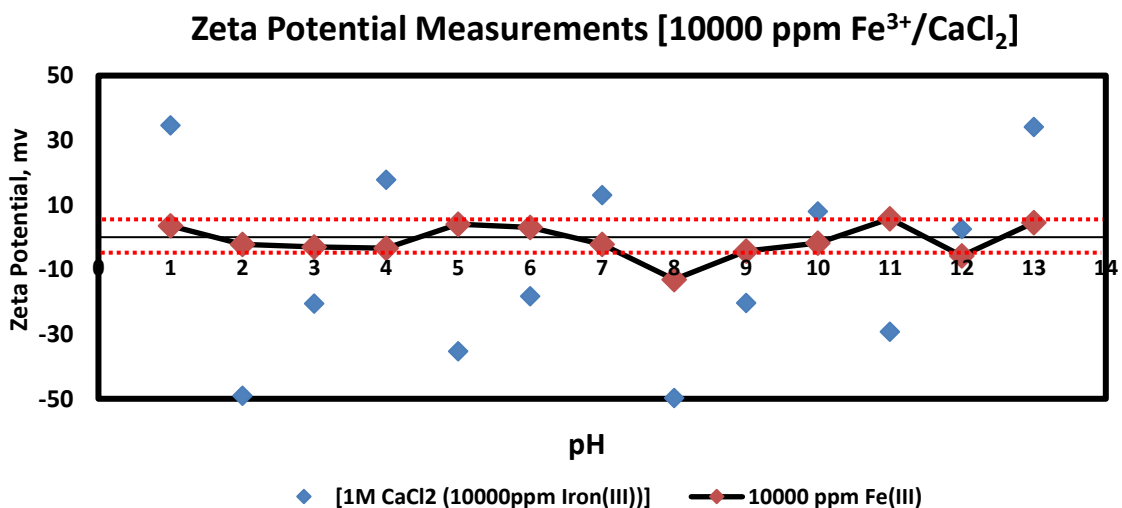


Figure 90 – Effect of 1M CaCl_2 on zeta potential of 10000 ppm Fe^{3+} - calcite system

Results are showing that CaCl_2 with high concentration might form better stability and positively affects of ferric ions in low pH and near-neutral pH environment

4.2.7 Effect of 10 wt% EDTA on iron (III) precipitation

In order to mimic the inhibition mechanism in different pH environments, several experiments were performed using 10 wt% EDTA. However, measurements were conducted in pH environments varying from 4 to 13. This was because of at high EDTA concentrations it was not achievable to prepare for 1-3 pH environments.

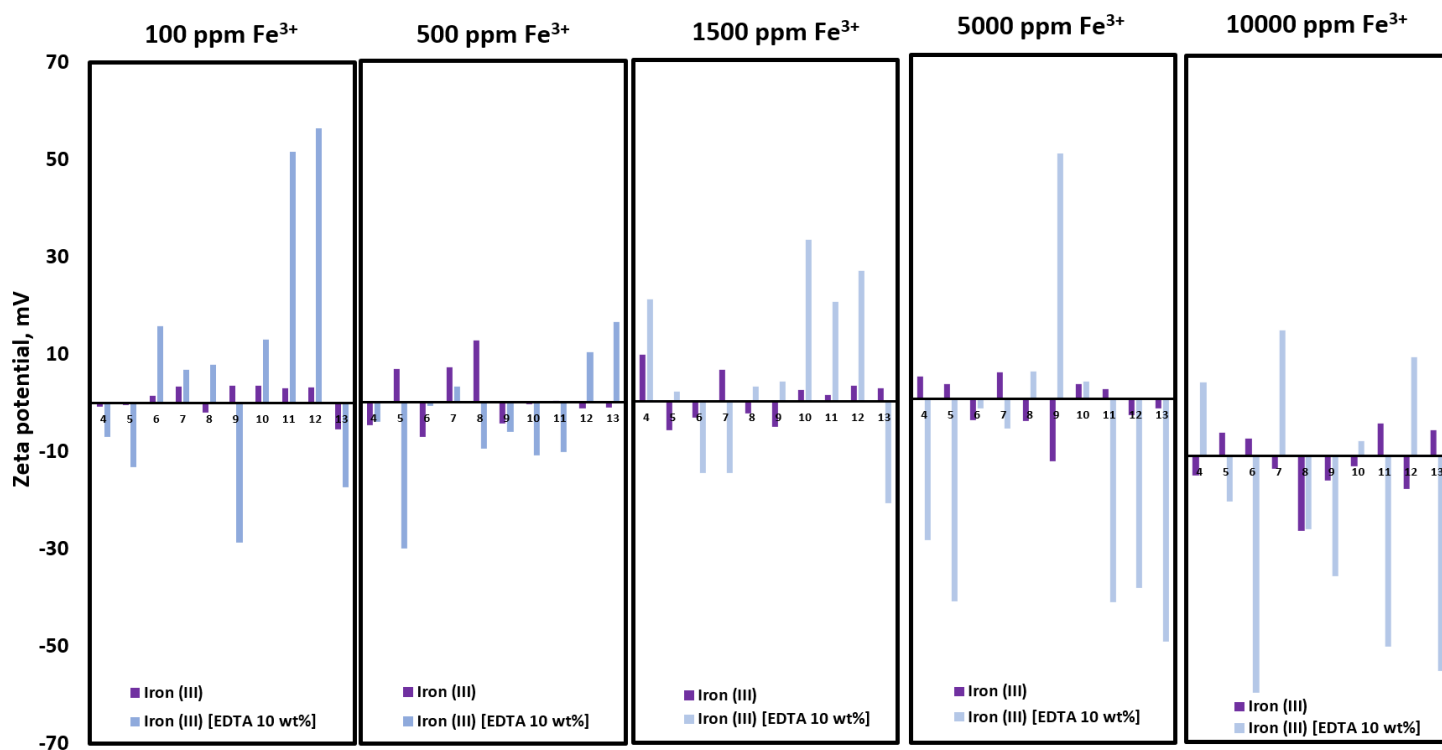


Figure 91 – Effect of 10wt% EDTA on iron (III) precipitation

50 zeta potential measurements were conducted with varying ferric concentrations and 10wt% EDTA (**Figure 91**) used as an inhibitor of Fe^{3+} ions on calcite mineral. One of

the first conclusions made was the increasing inhibition efficiency of 10wt% EDTA as ferric concentration increases in the system. Another notable point is that 10wt% EDTA does not have a profound impact on ferric precipitation in near neutral pH environments (6-8) in almost all concentrations of Fe^{3+} . 10 wt% EDTA has a positive impact on ferric precipitation in high pH environments regardless of iron (III) concentration in the system.

4.3 Iron sulfide scale formation and inhibition

In this section, the results for iron sulfide scale formation and inhibition are discussed. The formation of iron sulfide scale as indicated in **Chapter 3**, was achieved by simultaneous injection of sodium sulfide and ferric chloride into the IL rock samples.

Figure 92 illustrating in-situ formation of iron sulfide scale in rock samples.

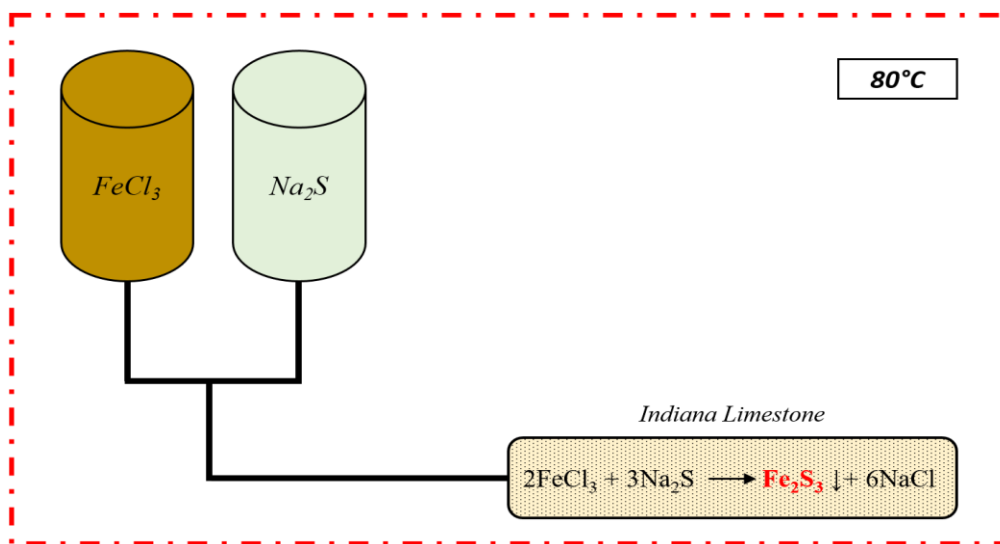


Figure 92 – Reaction of iron sulfide scale formation

4.3.1 Iron sulfide scale formation and inhibition in low permeability rocks

The formation and inhibition of iron sulfide scale in low permeability Indiana rock samples was done by performing two coreflooding experiments. The results of the experiments are shown in **Table 30**. The rock initial permeability for scale formation experiment was determined to be 9 mD. However, final rock permeability was 3.1 mD which reveals that permeability loss due to iron sulfide scale formation was 5.9 mD or 68%. Hence, it is evident that iron sulfide scale is formed and significantly damages the core permeability.

20 wt% EDTA was used as an inhibitor to inhibit the formation of iron sulfide scale. The initial rock permeability used in inhibition experiment was equal to 12.5 mD while having 10.1 mD final permeability. The calculated permeability damage was 2.4 mD with 19% loss.

Table 30 – Permeability alteration of the rocks with and without inhibitors

Core #	Initial rock	Final rock	$K_{\text{final}}/K_{\text{initial}}$
	permeability, mD	permeability, mD	
NF – 1	9	3.1	0.34
NI – 1	12.5	10.1	0.81

CHAPTER 5

CONCLUSIONS & RECOMMENDATIONS

Scale formation is a critical issue in petroleum production systems causing production and economic losses for the oil and gas companies. Evaluation of degree of permeability alteration in near wellbore formation due iron sulfide scale formation and proposing inhibition strategies are worthy tasks.

In this work, dynamic inhibitor adsorption experiments were conducting using coreflooding setup that creates the chance of understanding of dynamic nature of inhibitor adsorption at various temperature conditions. On top of that, use of coreflooding helps us to consider the consequences of precipitation of scale crystals and further scale formation on permeability damage in carbonate formations (Indiana limestone (IL) in this work). Another critical point that should be considered is the interactions occur in case of water injection. Zeta potential measurements further were used to determine impact of interactions to solid precipitation.

The conclusions of this work can be divided into three sections corresponding to phases as follows:

1. Dynamic adsorption of aminocarboxylic acids
2. Evaluation of iron (II) and iron (III) precipitation on calcite mineral
3. Iron sulfide formation and inhibition

Dynamic adsorption of aminocarboxylic acids:

The conducted coreflooding tests revealed that various concentrations of aminocarboxylic acids have different adsorption capabilities that was determined by ferric chelation. The following conclusions were made based on the results of adsorption experiments:

- Regardless of temperature condition, the precipitation of Fe^{3+} is an obvious threat causing severe formation damage in limestone by significantly decreasing the rock permeability.
- Degree of adsorption of chelating agents in carbonate rock samples depends on their concentrations and temperature conditions.
- 10 wt%, 15 wt% and 20 wt% EDTA showed very close inhibition efficiency at ambient temperature conditions.
- However, their adsorption capacity differs at elevated temperature conditions.
- 20 wt% EDTA was seen as a best-adsorbed chelating agent at ambient, medium, and high temperature conditions.
- 20 wt% DTPA resulted in almost the same inhibition efficiency with 20 wt% EDTA at ambient and medium temperature conditions.
- The application of 20 wt% EDTA, however, is more cost-effective choice.
- 5000 ppm MgCl_2 and CaCl_2 slightly decreases the adsorption of EDTA at 77°F.

- The additional soaking time for EDTA did not result in significant adsorption of EDTA at ambient temperature. Therefore, effect of soaking time on EDTA adsorption is not profound.

Evaluation of iron (II) and iron (III) precipitation in calcite mineral:

Zeta potential measurements were performed to analyze the iron precipitation in wide range pH environments on calcite mineral. Based on the analyses on the results several conclusions were made as follow:

- Ferric precipitation inevitable phenomenon happens almost regardless of ferric concentration (higher concentrations triggers a bit more precipitation) on calcite mineral starting from pH environment 1 to 13.
- Ferrous ions, however, shows erratic trends in acidic pH environments and proved to be more stable. Ferrous ions' notable instability starts from neutral pH environment toward the high alkaline regions.
- In relatively low concentration of Fe^{3+} , 0.1M NaCl almost does not affect charge development of calcite while 1M NaCl has an impact on charge development of calcite minerals. However, in high concentrations of Fe^{3+} , both 0.1M NaCl and 1M NaCl promotes significant changes on surface charge development by creating negative charge dominant (0.1M NaCl), positive charge dominant (1M NaCl) and relatively stable system.
- MgCl_2 influences charge development of calcite in high pH environments.
- CaCl_2 with high concentration might form better stability in low pH and near-neutral pH environments.

- 10 wt% EDTA solve the issue of ferric precipitation and significantly impacts charge development of calcite in high pH environments.

Iron sulfide formation and inhibition:

Iron sulfide scale was formed using coreflooding system and inhibition in coreflooding system as well. Several conclusions were made as follow:

- Formation of iron sulfide scale in low permeability limestone core samples can significantly decrease permeability.
- 20 wt% EDTA decreases permeability damage due to iron sulfide scale by 62%.

The following suggestions can be made for further investigations:

- Wide range of EDTA concentrations and their effect on iron precipitation on calcite mineral at different pH environments can be analyzed by performing more zeta potential measurements.
- Adsorption of aminocarboxylic acids on calcite mineral can be more extensively studied using MDS.
- Impact of cations on adsorption of chelating agents can be analyzed and then validated through coreflooding experiments.
- The effect of anionic salts and formation water (using different salinity) on iron precipitation on calcite minerals can be performed using zeta potential.
- During the experiments of iron sulfide scale formation oxygen scavengers is recommended to use to avoid simultaneous formation of iron oxides.

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