COMPARATIVE ANALYSIS OF AMINOPOLYCARBOXYLATE CHELANTS FOR EFFECTIVE IRON CONTROL IN ACIDIZING OPERATIONS

A Thesis

by

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ABSTRACT

Acidizing in the oil and gas industry is a stimulation operation with a purpose of improving a well's productivity or injectivity. The main problems resulting from this process come from the fact that acid is corrosive and a very reactive chemical. While it is mixed and pumped to the formation, it dissolves iron compounds from mixing tanks, equipment and flow lines. Iron content may increase as it reacts with formation. Live acid is the best dissolver to most iron compounds; however, problems arise when acid reacts with formation. As a result of acid stimulation process, pH of spent acid rises from zero and becomes no longer suitable dissolver to iron compounds. Unless acid contains an effective iron-controlling system, all iron in partially-spent acid will precipitate, plug formation, and cause severe formation damage.

Aminopolycarboxylate chelating agents have been used extensively in controlling iron precipitation. When iron presents in acid, these chelants interact with it and form water-soluble complexes, thus eliminate any problem that can be expected as a result of iron precipitation.

This work evaluates the performance of various chelants as iron-control agents, and their optimum versus theoretical molar ratios at different temperatures and pH environments during acidizing with different levels of iron concentrations in acid. It also addresses the impact of acid additives on the performance of different chelants, as well as their impact on carbonate cores.

Iron precipitation was monitored at the absence of a chelating agent in acid to demonstrate severity of precipitation problem at various pH environments and temperatures. Chelants were investigated at pH values of 0 to 4.5 to mimic carbonate acidizing, and at a temperature range of 71 to 300˚F. Impact of acid additives such as corrosion inhibitors, surfactants, H_2S scavengers, and polymers on chelation performance was investigated. Core-flooding was conducted on

carbonate cores that were flooded by acid containing the chelant to determine its influence on the permeability of cores. Chelants were tested at various mole ratios relative to iron concentration to determine optimum molar ratios, which will demonstrate how each chelant prefers to chelate iron versus other divalent cations in acid.

Precipitation was investigated by monitoring iron concentration in solution using inductively coupled argon plasma emission spectroscopy (ICAP). Precipitates were filtered and analyzed using x-ray diffraction (XRD), X-Ray Fluorescence (XRF) and Scanning Electron Microscopy- Energy Dispersive Spectroscopy (SEM-EDS).

DEDICATION

To my beloved father and mother for their advice, endless love, encouragement and prayers day and night, you are always first priority and I always love you and pray for you.

To my sister, Reham, and my brother, Mohammed for their help and support emotionally and sometimes technically, I love you.

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NOMENCLATURE

NTA	Nitrilotriacetic Acid
EDTA	Ethylenediaminetriacetic acid
HEDTA	Hydroxyethyl Ethylenediaminetriacetic acid
DTPA	Diethylenetriaminepentaacetic acid
XRD	X-Ray Diffraction
XRF	X-Ray Fluorescence
ICAP	Inductively Coupled Argon Plasma Emission Spectroscopy
SEM-EDS	Scanning Electron Microscopy-Energy Dispersive Spectroscopy
TDS	Total Dissolved Solids
PPM	Parts Per Million
pKa	Negative log of the acid dissociation constant or K_a value
Eh	Reduction potential

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CHAPTER I

INTRODUCTION & LITERATURE REVIEW

The Problem

Acid stimulation fluids, due to its high corrosivity, raise more severe issues than non-acidic stimulation fluids. Acids dissolve iron compounds from any material contacted while mixed in tanks, pumped in pipelines, and sometimes as it reacts with the formation. If acid does not contain an effective iron control system, dissolved iron precipitates. This precipitate may then accumulate as it is carried toward the wellbore during flow-back. This accumulation of solids may plug natural and created permeability (recently opened flow channels by the acid) and have a detrimental effect on the recovery of the treating fluid and production. Moreover, if carried to the surface, it can cause serious separator clogging and flow assurance issues.

Acid corrosion inhibitors control the reaction of acid on the metal contacted; however, they do not prevent the reaction of the acid with iron compounds (rust, mill scale, siderite, and other iron compounds) to an appreciable extent; they just help limiting the reaction. Furthermore, inhibition of corrosion of tubular is not at 100%, as there is minimum corrosion allowance that depends on the type of tubular.

Iron content of the acid can possibly reach and exceed 100, 000 mg/l (ppm) by the time it reaches the formation (W. Dill & Smolarchuk, 1988). This will depend on the condition of the pipe, the amount of pipe surface area contacted, concentration of acid used, and the temperature. Present conditions can dictate a pre-clean job (Pickling) prior to formation stimulation operation.

Containing iron in solution, acid flows into the formation, and dissolves additional iron before it is spent. After reaction with the reservoir rock, the spent acid is expected to contain more

than 400,000 mg/L of total dissolved solids (TDS). High ionic strength makes the solution much more susceptible to precipitation (W. Dill & Smolarchuk, 1988).

Nature of Iron

Iron, in its free metallic state, has a zero-oxidation state and is represented as Fe^0. Iron can exist as divalent, trivalent or hexavalent cation with one of three oxidation states of +2, +3 and +6, respectively. The +6 oxidation state (hexavalent) is considered rare, however, it is represented in a few cases in which coordination and chelation compounds are formed with iron. The +2 and +3 oxidation states correspond to the ferrous ion, Fe^{++}, or "iron (II)", and ferric ion, Fe^{+++}, or "iron (III)", respectively. Iron (II) is easily oxidized to iron (III) by air or oxidizing agents. The oxidation state of iron depends on the oxidizing or reducing nature of the medium in which it exists as well as the type of anion to which it is associated. In an oxidizing medium or in the presence of air at surface conditions, the ferric — iron (III) — ion is more dominant, whereas under reducing medium or in an anaerobic condition downhole, iron (II) is more dominant. During acidizing treatments, anaerobic reduction is very important since dissolved iron (II) and iron (III) are in intimate contact with metallic iron tubing. Thus, iron (III), occurring from rust dissolution in acid, tends to be converted to iron (II) while acid is pumped down hole during matrix acidizing treatments (Smith, Crowe, & Nolan, 1969).

Sources of Iron

Down-hole: Tubulars and formation

Hall and Dill (1988) studied millscale (Fe_3O_4) in new 2-7/8 in., 6.5 lb/ft tubing and they found out that 690 gal of 15 wt% HCl after contact with 10,000 ft. of pipe contained 85,938 mg/L total iron of which almost two thirds was ferric iron, Fe (III), and one third was ferrous iron, Fe (II).

Rust contains three iron oxide layers. The outer layer is primarily ferric oxide, Fe_2O_3, while the layer closest to the steel is ferrous oxide, FeO. The intermediate layer is a mixture of both iron oxidation states and can be represented as Fe_3O_4 or $FeO.Fe_2O_3$ with the ratio of iron (III) to iron (II) of two to one. If HCl was in contact with enough $FeO.Fe_2O_3$ to give a solution containing 45,000 mg/L total iron, then the solution will contain two-thirds of the iron in solution, 30,000 mg/L, iron (III) and one-third, 15,000 mg/L, iron (II). The leading edge of the acid can become loaded with dissolved iron during acid injection. Therefore, Gougler, Hendrick, and Coulter (1985) advocate cleaning the tubulars prior to acidizing the formation to reduce the iron load introduced into the formation. Moreover, it is highly recommended that the leading edge of the acid should not be allowed to enter the formation otherwise there is very high potential for severe formation damage (Taylor, Nasr-El-Din, & Saleem, 2001).

Different formation waters were analyzed, and it was found that 57 mg/L to 2075 mg/L of ferrous iron may be in solution (Hall & Dill, 1988).

Table 1 shows some, not all, iron-containing minerals, their chemical formula, iron oxidation state, and where they are most likely to be found. Practically almost all mineral forms of iron are soluble in hydrochloric acid. Once an iron-containing mineral is dissolved in acid, the oxidation-reduction potential existing in the solution determines the behavior of iron (Smith et al., 1969).

While iron-containing compounds such as magnetite and hematite are soluble in acid, pyrite, for example, is relatively insoluble in acid. When acid reacts with the formation, it may spend on rapidly soluble minerals in the formation and produce relatively insoluble or slowly soluble compounds. The released solids may plug flow channels, create precipitation problems, and increase the rate of production decline following acid stimulation. This damage can be minimized

by using the lowest concentration of acid that will effectively stimulate the formation (W. R. Dill & Fredette, 1983).

Mineral	Chemical Formula	Iron Oxidation State	Commonly found in
Ankerite	$Ca(Mg,Fe)(CO_3)_2$	Fe^{+2}	Carbonate Formations
Chlorite		Fe^{+2}, Fe^{+3}	Clays in sandstone
Hematite	Fe_2O_3	Fe^{+3}	Flowline rust, and Sandstone formations
Limonite	$2Fe_2O_3 \cdot 3H_2O$	Fe^{+3}	Sandstone formations
Magnetite	Fe_3O_4 or $FeO.Fe_2O_3$	Fe^{+2}, Fe^{+3}	Pipeline millscale, rust, and Sandstone formations
Pyrite and Marcasite	FeS_2	Fe^{+2}	Carbonate Formations; especially Limestone
Pyrrhotite	FeS	Fe^{+2}	Carbonate Formations; especially Limestone
Siderite	$FeCO_3$	Fe^{+2}	Carbonate Formations

Table 1— Iron-containing minerals (Adapted from (Smith et al., 1969))

Surface facilities

Acid also dissolves rust in storage and mixing tanks as well as flowlines in surface facilities. This dissolution results in a mixture of iron (II) and iron (III) in solution, but dissolved oxygen in the acid will rapidly oxidize iron (II) to iron (III). Iron in the acid before injection will be present as ferric iron (Fe III) unless iron reducing additives such as erythorbic acid reduce this iron (III) to iron (II).

Iron precipitation

The amount of iron that is loaded in the acid and needs to be controlled in an acidizing operation is difficult to accurately predict due to several variables involved such as those listed by (Hall & Dill, 1988):

1. Condition of the tubulars
2. Amount of tubular surface area
3. Type of iron compounds
4. Temperature
5. Type and concentration of acid
6. Contact time
7. Type of production
8. Amount of iron in the formation
9. Other acid-reactive components of the formation.

In a sweet environment, absence of H_2S, common cause of iron precipitation is the formation of insoluble iron hydroxide as the pH rises as a result of HCl reacts with the formation and the acid becomes spent. Classically, ferric hydroxide, $Fe(OH)_3$, is blamed as the most damaging iron precipitant following acid treatment. Both iron (II) and iron (III) can precipitate, but iron (III) precipitates first from spent acid since it comes out of solution at a pH of about 1 under the conditions of experiment presented in the paper by Taylor and Nasr-El-Din (1999). Iron (II), on the other hand, does not normally precipitate in the form of hydroxide at a pH values below 6 (Hall & Dill, 1988).

In formation water, ferrous iron will remain in solution at the pH of the natural formation environment. However, when an aerated fluid, such as injected fluid, mixes with the formation

water, it oxidizes the ferrous iron to ferric iron, which will then precipitate. This precipitation is considered detrimental to the stimulation operation (W. R. Dill & Fredette, 1983).

Down-hole conditions tend to convert ferric iron to ferrous iron, $Fe^{0} + Fe^{+++} \rightarrow Fe^{++} + e^{-}$, obviously, if iron (II) is the species present, there will not be a ferric hydroxide precipitation. Oilfield tubing contributes to reduction of the ferric ions to ferrous ions in acid solution. Iron (III) dissolved within the formation cannot be converted to iron (II) since there is no free iron to bring about the transition, thus iron (III) dissolved remains that way in solution and potentially can cause severe depositional problems (Smith et al., 1969).

Assem, Nasr-El-Din, and De Wolf (2013) studied the formation damage caused by iron precipitation in low and high permeability Indiana limestone. Rady and Nasr-El-Din (2015) indicated that iron deposition problems are even more severe in sandstone and dolomite formations.

Backflow

The iron (II) remaining in the solution can also trigger problems in the surface facilities. The acid-stimulated wells are flowed back into a separator, in order to protect the environment. In case of the absence of an efficient iron control system in the solution or the improper selection of the system, a great quantity of iron-rich sludges of volumes exceeding 1.9 m^3 will deposit and plug the bottom nozzles of the separator leading to separator failure (Pourabdollah, 2017).

Iron-control Agents

How effective an iron control system in acidizing is determined by a set of properties. In this work we describe these properties to be able to make a judicial pick of the most effective system. Iron control agents are frequently misused and overused due to the attitude “It won’t hurt,

and it might help" because as a matter of fact, it does hurt if improper selection is made thoughtlessly or if it was used excessively (Smith et al., 1969).

Chelating Agents

Chelating Agents, with the name derived from the Greek word chele, meaning "claw.", are widely-used organic compounds that contain two or more electron donating groups that can act as a Lewis bases and bind tightly to metal ions by forming coordinate bonds through electron donation. Multiple coordinate bonds from a single molecule, a ploydentate ligand, create one or more heterocyclic rings or chelate rings, hence the name *chelating agents*. These ligands are called chelating agents, sequestering agents, chelants, chelons, or chelators. The strength of chelating agents is generally measured by its stability constants with the ion of interest. Generally, if a chelating agent exhibits higher stability with iron (Fe), for example, than another chelating agent, it will also show higher stability with other ions compared to this same chelating agent. Both iron (II) and iron (III) form stable complexes with chelating agents.

An effective complex must be soluble in both live and spent acid, and more stable than the insoluble ferric hydroxide. It also makes perfect sense that an iron-control agent should not form insoluble reaction products with other ions present in the solution. Finally, an iron-control agent has to be effective at bottom-hole temperature.

Aminopolycarboxylic Acids

The class of chelating agents, that is widely used in oil industry, is Aminopolycarboxylic acids which, as the name refers, have two or more nitrogen atoms in the center of the molecule with multiple carboxylic acid functional groups that act as the claws that catch and bind to the metal ion in the chelation process. This process results in the formation of stable metal-chelant complexes isolating the metal ion from any further reactions, and utilizing this technique, APCA's

have many applications throughout the oil and gas industry including standalone stimulation fluids, iron control, and scale removal. (Almubarak, Ng, & Nasr-El-Din, 2017; Kamal, Hussein, Mahmoud, Sultan, & Saad, 2018). Mellor (1964) indicated that stability of these complexes depends on the size of the ring formed during chelation, the number of rings formed, the basic strength of the chelating molecule, the effect of substitution in chelating molecule, the nature of the donor atom, and the central metal atom. However, the thermal stability of the aqueous solutions of chelating agents is a concern at temperature above 350°F (Sokhanvarian, Nasr-El-Din, & De-Wolf, 2013; Sokhanvarian, Nasr-El-Din, Wang, & De Wolf, 2012)

Aliphatic polycarboxylic amino acids are produced by using an alkali cyanide, formaldehyde, and a primary or secondary aliphatic amine. (Bersworth, 1946) accomplished this by preparing a solution in which aliphatic amine and alkali metal cyanide are both always present, and gradually introducing about one mol of formaldehyde for each amino-hydrogen of the amine to be substituted. It is essential that produced ammonia will be as completely removed as possible before more formaldehyde is added. Finally, adding roughly the same total molal quantity of an alkali metal cyanide at such a rate that leaves the cyanide in excess over the formaldehyde. The solution is agitated constantly, and heated to a proper temperature. Young (1957) pointed that increasing the quantity of alkali metal cyanide and formaldehyde reacted with the aliphatic amine over the theoretically required amount to replace each replaceable hydrogen atom on the amine, increase the production of the desired amino polycarboxylic acid or the chelation value per unit of aliphatic amine reacted while still using the same amount of the amine.

One of the biggest concerns about chelants, like EDTA, is that some are not or only slowly biodegradable which raise a lot of environmental issues that eventually limit their uses and applications (Nowack & VanBriesen, 2005).

Types of Aminopolycarboxylic Acids (APCA)

The performance of five different chelating agents, described in **Table 2**, and **Table 3**, will be discussed in a comparative analysis.

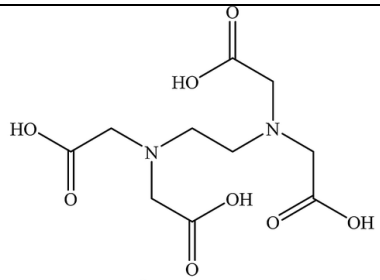
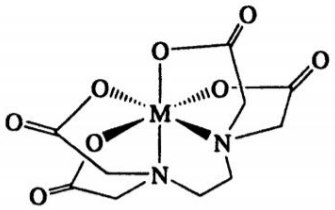
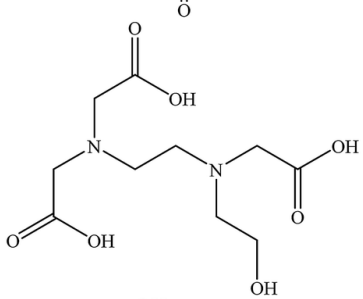
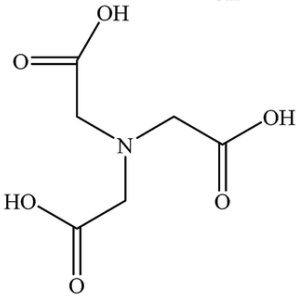
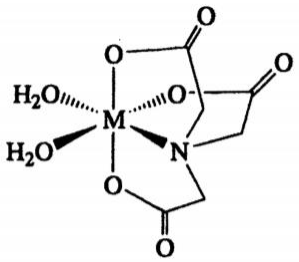
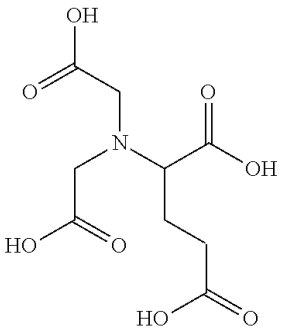
Acronym	Name	Structure	Metal-Chelant Complex
EDTA	Ethylenediaminetetraacetic acid		
HEDTA	N-(hydroxyethyl)-ethylenediaminetriacetic acid		
NTA	Nitrilotriacetic acid		
GLDA	Glutamic acid, N, N-diacetic acid		

Table 2—Studied Aminopolycarboxylate chelating agents (APCs)

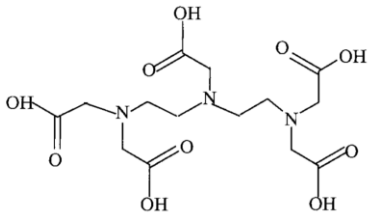
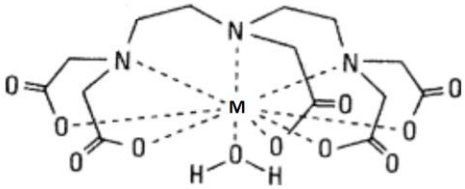
Acronym	Name	Structure	Metal-Chelant Complex
DTPA	Diethylenetriaminepenta acetic acid		

Table 2 continued—Studied Aminopolycarboxylate chelating agents (APCs)

Chelant	Stability Constant (K)		MW		pK_{a1}	pK_{a2}	pK_{a3}	pK_{a4}	pK_{a5}
	Iron (II) Fe^{2+}	Iron (III) Fe^{3+}	Acid	Na Salt					
EDTA	14.3	25.7	292	380	10.2	6.1	2.7	2.0	—
HEDTA	12.2	19.8	278	344	9.8	5.4	2.6	—	—
NTA	8.3	15.9	191	257	9.7	2.5	1.8	—	—
GLDA	8.7	15.2	263	351	9.4	5	3.5	2.6	—
DTPA	16.5	28	393	503	10.5	8.5	4.3	2.6	1.8

Table 3—Stability Constants (at 77 °F) to iron ions, Nolecular weights, and pK values of Studied Aminopolycarboxylate chelating agents

H_4EDTA (Ethylenediaminetetraacetic acid)

EDTA is a hexadentate aminopolycarboxylic acid that has been used in a variety of applications (Oviedo & Rodríguez, 2003). Although it has high stability constants with iron ions, it has two major issues in its application as iron control agent. Although at a laboratory scale, degradation of EDTA has been achieved; in natural environments studies detect poor biodegradability. EDTA is considered to be a persistent substance in the environment and, therefore, its contribution to heavy metals bioavailability is a major concern (Allard, Renberg, & Neilson, 1996; Bolton, Li, Workman, & Girvin, 1993; Madsen & Alexander, 1985; Nowack &

VanBriesen, 2005). Considering this along with its high chelating strength, EDTA earned a strict scrutiny in Europe in the late 1980s (Grundler, van der Steen, & Wilmot, 2005), and was prohibited in some countries (Kolodynska, Jachula, & Hubicki, 2009). Moreover, it has very limited solubility in acid solutions, as shown in **Fig. 1**, due to its ampholytic nature (BAILAR, 1953; Martell, 1952; Yoe, 1953); 8 gpt in 28 wt% HCl (Wayne W. Frenier, Wilson, Crump, & Jones, 2000). Recently, Li et al. (2018) claimed that EDTA helped in efficiently inhibiting FeS scale formation by complexing ferrous ions, however, Taylor and Nasr-El-Din (1999) concluded that EDTA is not an effective iron control chemical because of its low iron carrying capacity. These disadvantages have forced researchers to look for alternate chelants.

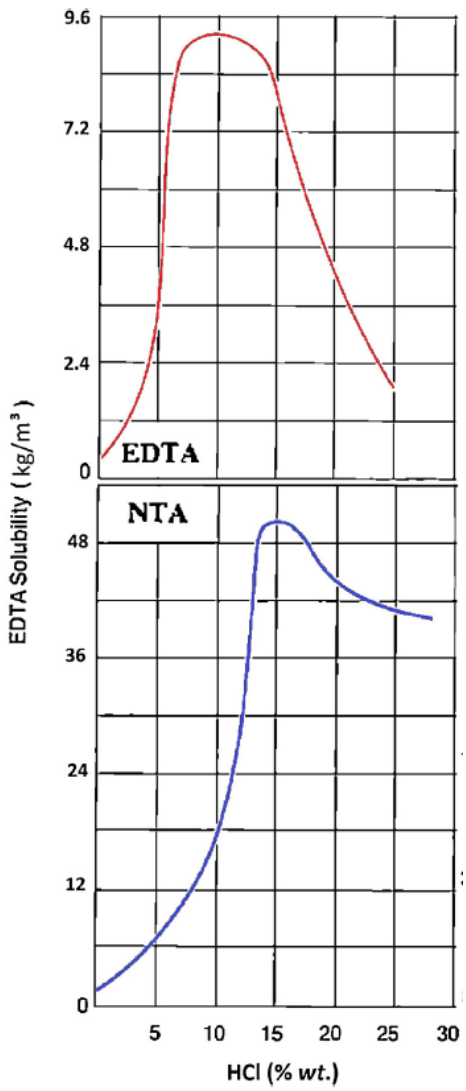


Fig. 1—Solubility of EDTA and NTA (Reprinted from (W. R. Dill & Fredette, 1983)

EDTA was patented in Germany in 1935 by F. Munz. The molecule is a substituted diamine usually marketed as its sodium salts. It is a powerful complexing agent of metals and a highly stable molecule, offering a considerable versatility in industrial and household uses (**Table 4**). Since it is applied predominantly in aqueous medium, it is released into the environment through wastewaters.

Use	% of world market
Detergents	33
Water treatment	18
Pulp and Paper Industry	13
Photography	5
Metal Cleaning	5
Cosmetics, foodstuffs, pharmaceuticals	5
Agrochemicals	4
Textile Industry	4
Printing inks	3
Concrete admixtures	2
Miscellaneous	12

Table 4— Industrial and houshold uses of EDTA and its ligands (Adapted from (Oviedo & Rodríguez, 2003))

The tetrasodium salt of EDTA is very soluble in water. However, if the sodium salts are placed in hydrochloric acid, the acid form of EDTA is formed and the problem of solubility is still encountered.

$$\mathrm{Na_4EDTA} + 4\,\mathrm{HCL} \rightarrow \mathrm{EDTA} \downarrow + 4\,\mathrm{NaCl}$$

If a concentration of the sodium salt of EDTA is used that forms more than the solubility limit of the solution, excess EDTA will precipitate.

NTA (Nitrilotriacetic Acid)

Nitrilotriacetic acid, NTA, a quadridentate aminopolycarboxylic acid, was the first chelating agent to be synthesized by reacting chloroacetic acid and ammonia (Heintz, 1862), and was the first aminopolycarboxylic acid to be produced commercially in 1936 at I.G. Farbenindustrie in Germany (Nowack & VanBriesen, 2005; Warren, 1974). NTA is used for well stimulation, iron control, and scale removal. In addition to being a chelating agent, NTA is also used as a

replacement for phosphates in detergents. Its structure consists of three acetic acid “arms” and a central nitrogen atom, all of which are responsible for the denticity of NTA.

One major concern about NTA is that it is a known animal carcinogen when present in drinking water or diet; it led, as a result of extensive tissue damage, to kidney tumors in rats and mice, and tumors of the efferent urinary passages in rats (Leibold et al., 2002). This issue causes some restrictions in its applications (Kolodynska et al., 2009). Moreover, it has a low stability constant with most cations.

Bunescu, Besse-Hoggan, Sancelme, Mailhot, and Delort (2008) highlighted the fact that NTA is rarely encountered in soils, sediments, natural waters, and wastewater treatment plants, although about 20,000 tons was used in Europe only in 1999. Keeping this enormous use in mind, they concluded that NTA is somehow efficiently removed from existence by means of photodegradation and biodegradation mechanisms. Although, NTA does not absorb solar light, some of its complexes, specifically the iron complex nitrilotriacetic acid-Fe(III) (FeNTA), can absorb solar light and undergo an efficient photoredox process that leads to the reduction of the metal and the oxidation of the ligand NTA. In addition, NTA was found to be biodegraded by Pseudomonas to CO_2, NH_3, and H_2O, than other commonly used chelating agents such as EDTA and HEDTA (Bunescu et al., 2008; Warren, 1974).

Advantages of using NTA vs. EDTA includes the fact that NTA is readily soluble in concentrations of HCl that exceed about 5 wt%, as shown in **Fig. 1**. Furthermore, the molar mass of NTA is less than that of EDTA. Therefore, given same weight of the two chelants, more iron is chelated by NTA. Another advantage of using NTA over EDTA was the lower breakthrough volumes of acid and subsequently the lower time of acidizing processes, and lower chance of post-acidzing damage. (Pourabdollah, 2017)

Hydroxyethyl ethylenediaminetriacetic acid (HEDTA or EDTA-OH)

Hydroxyethyl ethylenediaminetriacetic acid (HEDTA) is one of the hydroxyaminopolycarboxylic acids (HACA) such as hydroxyethyliminodiacetic acid (HEIDA) as well as other types of chelating agents. HEDTA has similar molecular structure to EDTA with a hydroxyethyl group in place of one acetic acid group transforming the chelant to be quinquedentate. This minor change in chemical formula improves the solubility (**Table 5**), but lowers the stability constant to iron ions. (W. W. Frenier, Rainey, Wilson, Crump, & Jones, 2003; Wayne W. Frenier et al., 2000).

Chelant	15 wt% HCl		28 wt% HCl	
Tetrasodium EDTA	50 gal/1000	2.5% active	8 gal/1000	0.4% active
Trisodium HEDTA	> 115	5.8	22	1.1

Table 5—Maximum Solubility of chelants in HCl (Adapted from (Wayne W. Frenier et al., 2000))

HEDTA has also been used for iron control as well as scale removal (Frenier1986, 2001). However, it faces similar biodegradability issues as EDTA due to the presence of two nitrogen atoms in its structure.

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

GLDA synthesis was patented by Heus, Lammers, and Volmer (2008). It was presented as an environmentally friendly stimulation fluid with high solubility in both water and acid solutions (De Wolf et al., 2014; LePage, De Wolf, Bemelaar, & Nasr-El-Din, 2011; Mahmoud, Nasr-El-Din, De Wolf, & LePage, 2010); This is because of the larger groups attached to the iminodiacetic

acid part which reduces the likelihood of crystallization and therefore increasing solubility. It was also proposed as iron-control agent (Mittal, 2012). It's readily biodegradable as it is manufactured from L-glutamic acid or monosodium glutamate, but it has relatively low stability constants with iron cations (Begum et al., 2012).

Diethylenetriaminepentaacetic acid (DTPA)

DTPA is an octadentate chelant with highest stability constant with iron ions among the studied chelating agents. It's a common sulfate scale removal (Putnis, Putnis, & Paul, 1995). However, it faces both biodegradability and solubility issues in water and acid solutions (Sýkora, Pitter, Bittnerová, & Lederer, 2001).

CHAPTER II

STATEMENT OF PURPOSE

Detailed literature studies have been made in the area of iron control prior to acidizing operations. There are gaps in literature that needs to be addressed. The type and the concentration of chelators must be reconsidered based upon the formation and well characteristics. This simple procedure will reduce the cost of acid stimulation jobs and after-production operations, significantly. In this work, the effectiveness of the various systems is described so that a judicial selection of the most effective system can be made. This research recommends the best chelant that can work under the expected acidizing conditions by comparing the performance of five chelants at different pH values, temperatures, iron concentrations, acid additives, and Chelant:Iron molar ratios through a parametric analysis. The effect of iron-controlling chelants on the permeability of carbonate cores was also investigated. Results can be used to design more efficient acidizing fluids.

CHAPTER III

OBJECTIVES

- To evaluate iron precipitation problem in the absence of chelating agent.
- To study different Chelating Agents including:
    - Tri-sodium Nitrilotriacetic Acid (NTA.Na3)
    - Tetra-sodium glutamic acid, N, N-diacetic acid (Na4.GLDA)
    - Tri-sodium hydroxyethyl ethylenediaminetriacetic acid (Na3.HEDTA)
    - Protonated Diethylenetriaminepentaacetic acid (DTPA)
    - Tetra-sodium ethylenediaminetriacetic acid (Na4.EDTA)
        - Evaluate their ability to control iron (Fe) at different encountered pH environments during acidizing.
        - Determine thermal stability of different chelating agents.
- To improve the performance of trisodium NTA at high temperatures.
- To study the impact of acid additives on the chelation performance of different chelants.
- To study the impact of the studied chelating agents on the permeability of carbonate cores.
- To study the performance of chelants on different initial iron concentrations (2000 ppm, and 4000 ppm)

CHAPTER IV

MATERIALS

- An industry grade concentrated Hydrochloric Acid (HCl) solution of 37 wt% obtained from bio bioscientific at Texas A&M University.
- Calcium Carbonate ($CaCO_3$) (CAS Number: 471-34-1), +99% purity powder, was obtained from Alfa Aesar.
- Ferric tricholride anhydrous ($FeCl_3$) (CAS Number: 7705-08-0), 98% crystalline, was obtained from Alfa Aesar.
- Chelating Agents:
    - Solution of monohydrate trisodium nitrilotriacetic acid (NTA), 43.9 wt%, was obtained from Ascend Performance Materials.
    - Trisodium hydroxyethyl ethelenediaminetriacetic acid (HEDTA) in crystalline powder form was obtained from Akzo Nobel Functional Chemicals.
    - Tetrasodium salt of ethelenediaminetetraacetic acid (EDTA) was obtained from Fisher Scientific Chemicals.
    - Tetra-sodium glutamic acid, N, N-diacetic acid (GLDA) in microgranular form was obtained from Akzo Nobel Functional Chemicals.
    - Diethylenetriaminepentaacetic acid (DTPA) (CAS Number: 67-43-6), +98% purity, was obtained from Alfa Aesar.
- Three cylindrical cores of 6 in. length and 1.5 in. diameter were cut from Indiana Limestone. XRF elemental analysis of the core is shown in **Table 6.** The mineralogy of the core, as obtained from X-Ray Diffraction (XRD) analysis, is listed in **Table 7**.

- Sodium Chloride (NaCl) crystals of +99% purity obtained from Macron Fine Chemicals.
- De-ionized (DI) water having a resistivity of 18.2 MΩ.cm at room temperature were used to prepare the brine, and acid. The brine viscosity and density at 200°F and 14.7 psi was measured to be 0.385 cp and 1.01 g/cm^3.
- An industry grade corrosion inhibitor CI-27, obtained from Baker Hughes, 0.5% by volume, was added.
- Non-ionic surfactant (ETHOMEEN C/12) was obtained from Akzo Nobel Functional Chemicals.

Element	wt%
Ca	97.78
Mg	0.86
Si	0.49
Al	0.27
Fe	0.25
S	0.04
K	0.14
Cl	0.06
Sr	0.07
Mn	0.02

Table 6—XRF Analysis of Low Perm Indiana limestone Core

Mineral	Concentration (wt%)
Calcite	99.6
Quartz	0.4

Table 7—Mineralogy of Low perm Indiana Limestone, as obtained from X-Ray Diffraction (XRD) analysis

CHAPTER V

EQUIPMENT

- The coreflood setup, as described in **Fig. 2,** consisted of the following parts:
    i. Three accumulators used to contain the acid and its additives, DI water, and 5 wt% NaCl brine.
    ii. Teledyne ISCO D500 precision syringe pump used to inject fluids at the desired flow rate with a maximum injection pressure of 2,000 psi.
    iii. Corrosion resistant lines made of Hastelloy-B alloy used for transmitting injection and production fluids.
    iv. Core holder made of Hastelloy-B alloy used to hold the core horizontally while contained within an oven at the necessary reservoir temperature.
    v. Overburden pump used to apply overburden pressure by pumping hydraulic oil onto the rubber sleeve that contains the core.
    vi. Backpressure regulator used to apply the necessary initial pore pressure and the pressure at the core outlet, using nitrogen (N_2).
    vii. Thermocouples at the inlet and outlet used to measure fluids' temperatures while fluids enter and exit the core and ensure they are at required temperature.
    viii. Pressure transducer used to measure the pressure drop across the core.
    ix. LabVIEW^{TM} software used to record data of pressure drop across the core, pumping rate, and other parameters.
- X-Ray Diffraction (XRD)
- X-Ray Fluorescence (XRF)

- Inductively Coupled Argon Plasma Emission Spectroscopy (ICAP).
- Scanning Electron Microscopy-Energy Dispersive Spectroscopy (SEM-EDS)
- pH meter with a special high temperature electrode.

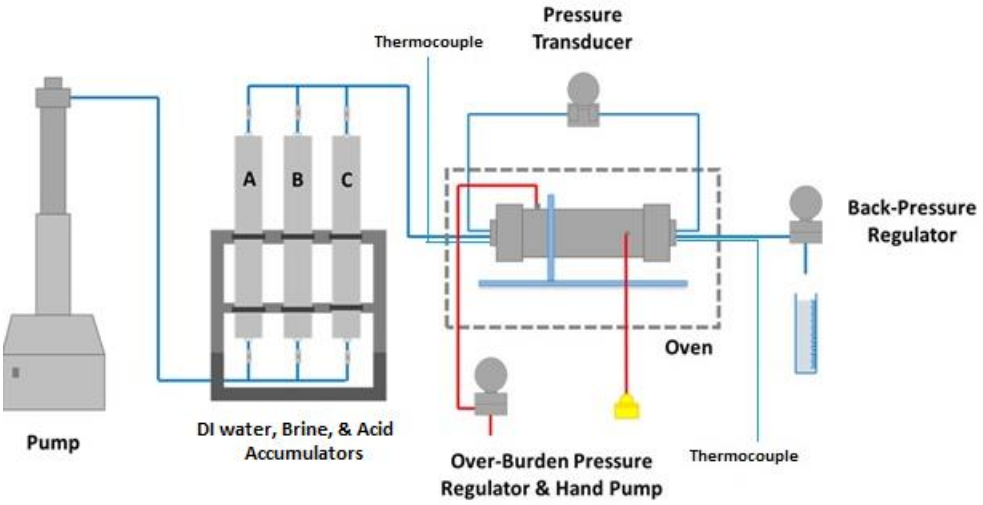


Fig. 2— A schematic diagram of laboratory coreflood setup used in the experimental study (Reprinted from (Kumar, Muhemmed, & Nasr-El-Din, 2020))

CHAPTER VI

METHODOLOGY

Test-tube runs

The testing procedure is illustrated schematically in **Fig.** 3, and defined as follows. The first step was to determine the exact concentration of the used Hydrochloric acid. Concentration was calculated to be 37.67 wt%.

1. 500 ml of acid solution of known concentration (5 wt% HCl) containing 2000 ppm (mg/kg) or 4000 ppm Fe III, and iron-control additives was prepared and divided into around 25 subsamples.
    a. Iron was added to solution in the form of ferric chloride (Anhydrous) $FeCl_3$.
    b. Iron-control chemicals will be added to acid solutions at a molar ratio of 1.0. At a molar ratio of 1.0, there are equal numbers of iron and iron-control molecules in solution, and this is the theoretical amount required to keep all of the iron in solution.
2. To each of these samples, a calculated amount of calcium carbonate, representing reservoir rock, was added to make a different pH step.
3. Samples were then kept in water baths at temperatures 150˚F, and 210˚F to test the performance of the chelants at elevated temperature.
4. pH values were measured at high temperature (150˚F, and 210˚F) using a special high temperature electrode.

5. Depending on the iron-control additive, a precipitate sometimes formed so samples were centrifuged for 20 minutes at 2000 rpm, filtered, and then were diluted to match detection limits of ICAP.
    a. Iron concentrations was measured by inductively coupled argon plasma emission spectroscopy (ICAP). Results of iron concentration generally had a relative standard deviation of 4.4% for the acid sample.
    b. Precipitates, when formed in adequate amounts, were analyzed using x-ray diffraction (XRD), and x-ray fluorescence (XRF).

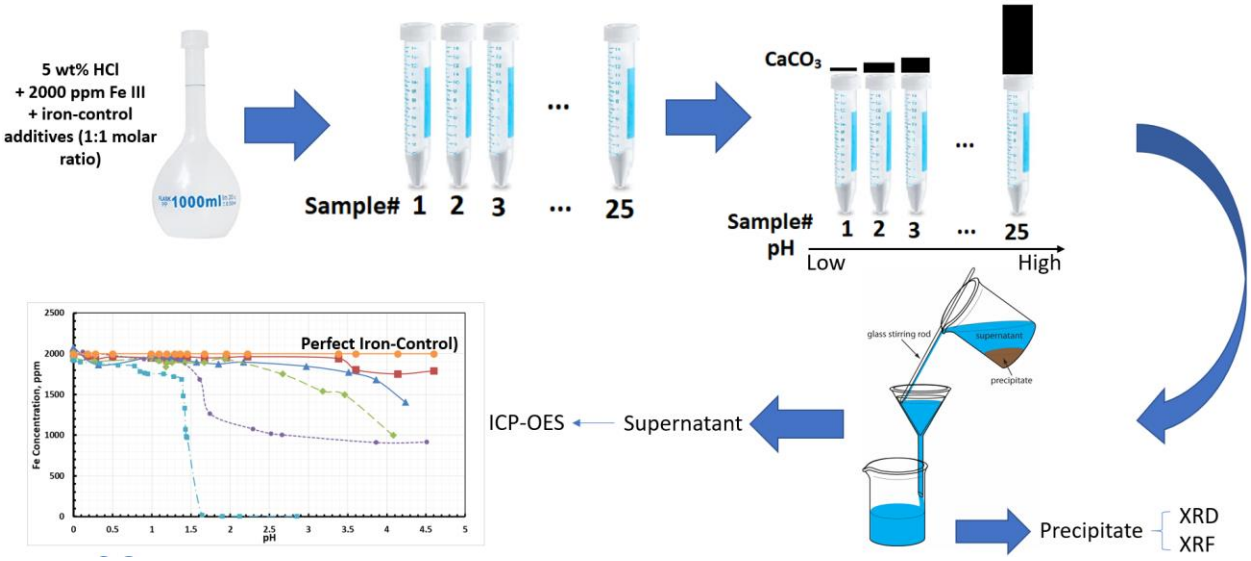


Fig. 3—Schematic of the test-tube run

Coreflood runs

1. The carbonate cores were first dried by putting them overnight in a conventional oven at 250°F. Dry weights of the cores were recorded.
2. The cores were then vacuumed with 5 wt% NaCl solution for six hours.

3. To ensure complete water saturation, the cores were loaded horizontally onto the coreflood system, and injected with brine at multiple rates, and assessed for stability in the pressure drop measurements at each rate.
4. The pore volumes were estimated using the saturation method.
5. A back-pressure of 1,100 psi was applied to keep most of CO_2 in solution. Overburden pressure was maintained at 1,800 psi.
6. During coreflood runs, pre-flush of brine was injected while the core was heated to the desired temperature (200°F).
7. Initial permeability was measured when pressure stabilized.
8. Half pore-volume of the acid solution was injected then the cores were flushed again with 5 wt% NaCl brine.
9. Pressure drop across the core was plotted using LabVIEW™ software.
10. The total iron concentrations of the core effluent samples were measured using the Optima 7000 ICP-OES Spectrometer.
11. Final permeability was measured when pressure stabilized. Percentage improvement in permeability after acidizing operation was determined by Eq.1:

$$\%improveent\ in\ permeability = \frac{k_{final} - k_{initial}}{k_{initial}} = \frac{\Delta P_{initial} - \Delta P_{final}}{\Delta P_{final}}, \quad \text{.....(1)}$$

CHAPTER VII

RESULTS AND DISCUSSION

Experiments at 2000ppm Fe(III) concentration

In the absence of chelating agents

In order to investigate the problem of iron precipitation in acidizing operation, and how important an iron-control agent can be, we performed the experiments without adding any iron control agents and under the same experiment conditions discussed in the methods section.

At room temperature

Iron precipitation begun when the pH increased to 1.45, and was complete by pH 2.42 as shown in the following **Table 8**, and **Fig. 4**, and **Fig. 5**.

pH (Room Temperature)	$CaCO_3$ added (g)	Fe Concentration (ppm) (Room Temperature)
0	0	2017.5
0.39	1.65	1995
0.64	1.9	1981.5
0.87	2	1960.5
1.08	2	1950
1.15	2.05	1882.5
1.21	2.058	1860
1.25	2.005	1854
1.45	2.06	1851

Table 8— Amount of $CaCO_3$ added to each sample (25 ml), and Measured Fe concentration using ICAP at 77 ˚F

pH (Room Temperature)	$CaCO_3$ added (g)	Fe Concentration (ppm) (Room Temperature)
1.58	2.059	1816.5
1.68	2.0555	1686
1.7	2.077	1479.3
1.72	2.074	1330.2
1.73	2.07	1070.1
1.74	2.1	982.8
1.75	2.102	970.5
1.94	2.2	16.95
2.2	2.5	3.45
2.42	2.4	3
3.15	2.85	2.25

Table 8 continued— Amount of CaCO3 added to each sample (25 ml), and Measured Fe concentration using ICAP at Room temperature

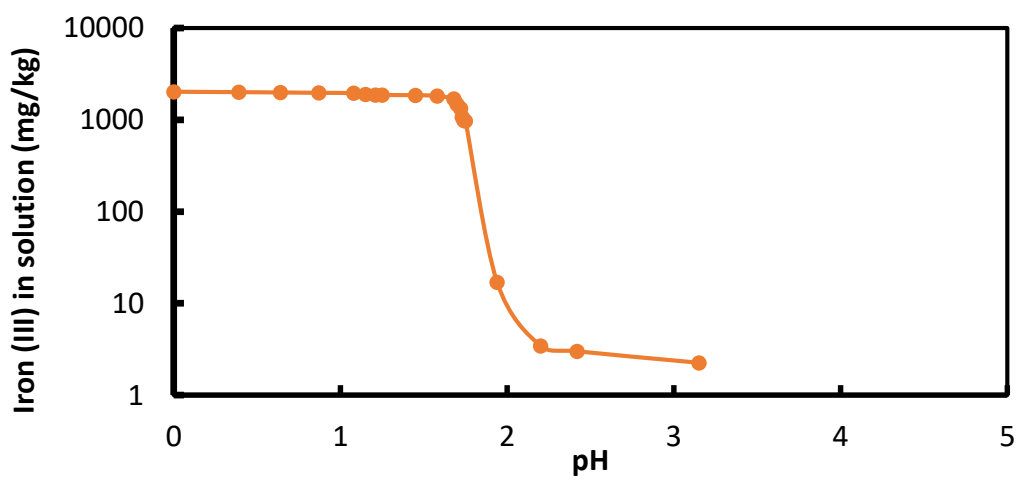


Fig. 4— Iron (III) Solubility vs. pH with no Iron-control agent (semi-log graph)

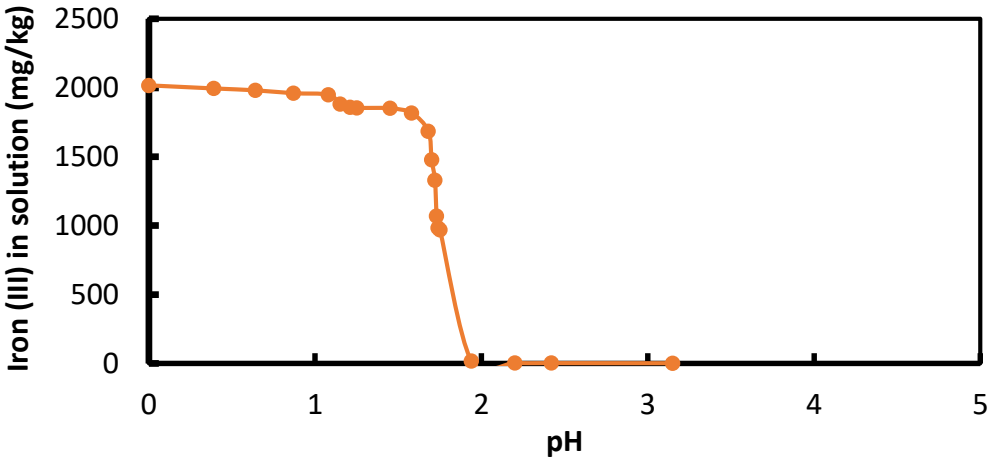


Fig. 5— Iron (III) Solubility vs. pH with no Iron-control agent

At 150˚F and 210˚F

As shown from **Fig. 6**, and **Fig. 7**, at 150˚F and 210˚F, iron precipitation begun at pH 0.68 and 0.3 respectively, and current work is running on the complete curve for iron precipitation at elevated temperatures.

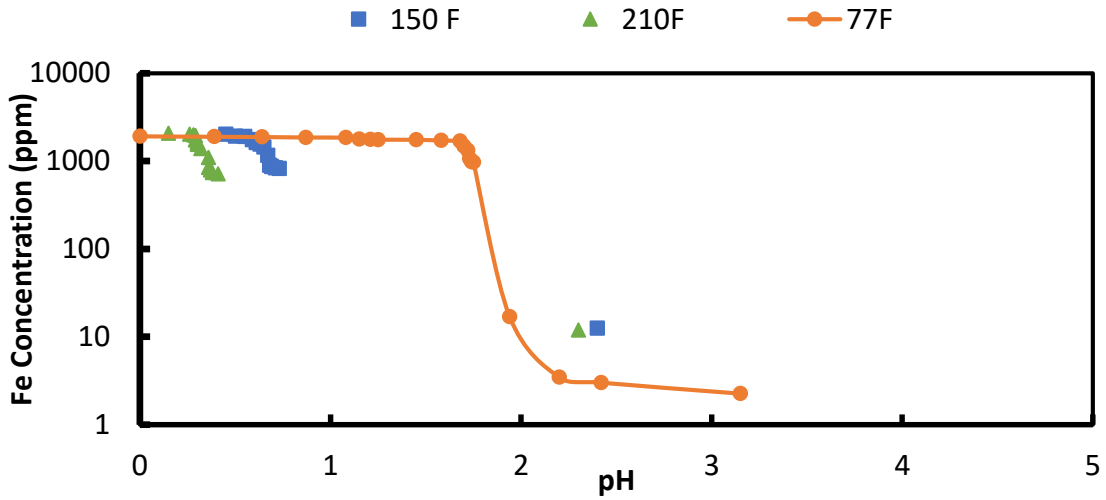


Fig. 6— Iron (III) Solubility at 150˚F, and 210˚F with no iron-control agent (semi-log graph)

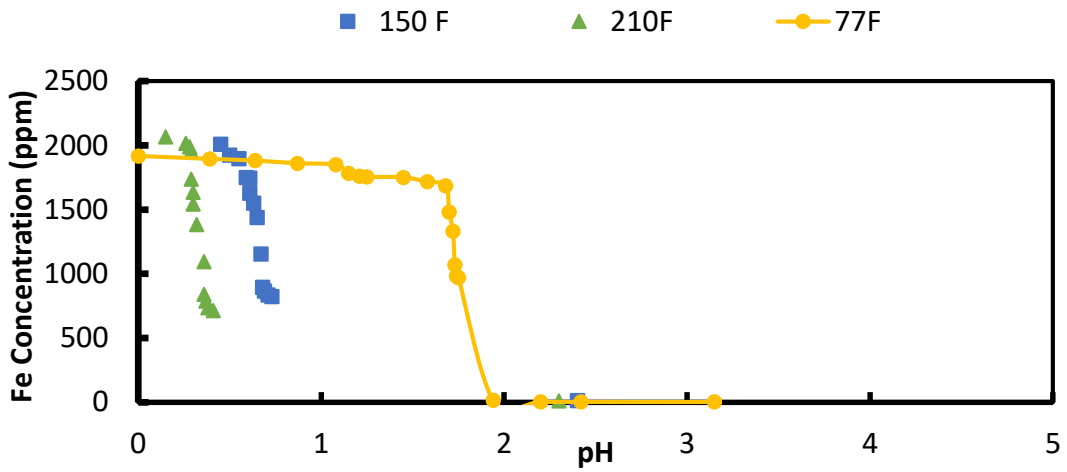


Fig. 7— Iron (III) Solubility at 150˚F, and 210˚F with no iron-control agent

Tri-sodium Nitrilotriacetic Acid ($NTA.Na_3$)

At room temperature, NTA managed to complex all iron in 5% HCl acid. Keeping in mind that the maximum pH of spent acid is in the range of pH 4-5 (pH 4.5), we can conclude that monohydrate tri-sodium NTA can control iron in acidizing.

Samples were kept in a water bath of 150˚F for 4 hours. Precipitation was noticed at samples of pH 3.41 and 4.8. Precipitate was filtered and dried in oven for one day. Then, it was prepared for XRD and analysis showed a mixture of Calcium Carbonate ($CaCO_3$), and iron compounds ($FeCl_3$, $FeCl_2$, and FeOOH). We ran ICP to pH 4.8 sample, Fe concentration after heating to 150˚F reduced to 1300 ppm, i.e., 35% of Fe in solution precipitated.

Finally, samples were kept in a water bath of 210˚F for 4 hours. A lower value of pH (pH = 3.11) showed reddish precipitation. Samples of pH 3.41 and 4.8 showed more precipitation. Precipitate was filtered and dried in oven for one day. Then, it was prepared for XRD and analysis should a mixture of Calcium Carbonate ($CaCO_3$), and iron compounds ($FeCl_3$, $FeCl_2$, and FeOOH).

Na_3NTA showed no solubility problems in 5 wt% HCl. At room temperature, Na_3NTA completely chelates Fe^{3+} at pH values up to 3.5, and its performance is lowered at higher pH values

(pH > 3.5) to around 92.5% chelation at pH = 4.6. At 150˚F, Na_3NTA completely chelates Fe^{3+} at pH values up to 3. At higher pH (pH > 3), its performance starts to decline until it reaches around 74% chelation at pH = 4.24. At 210˚F, Na_3NTA completely chelates Fe^{3+} at pH values up to 2.3. At higher pH (pH > 2.3), its performance starts to decline until it reaches around 53% chelation at pH = 4.08. Results are shown in **Table 9**, and **Fig. 8**.

Formation of a precipitate is a function of both pH, and temperature. In these experiments on Na_3NTA, A precipitate formed at room temperature, and pH = 4.1. At Temperature of 150˚F, precipitate formed at pH = 3.41. At Temperature of 210˚F, precipitate formed at pH = 3.11.

pH (77˚F)	Fe Concentration, ppm (77˚F)	pH (150˚F)	Fe Concentration, ppm (150˚F)	pH (210˚F)	Fe Concentration, ppm (210˚F)
0	2091	0	2121	0	2121
0.18	2059.5	0	2067	0	2136
0.28	2022	0	2061	0	2052
0.5	2050.5	0	2200.5	0	2068.5
0.99	2038.5	0.32	1974	0.27	2025
1.09	2038.5	1	2079	0.99	2061
1.19	2001	1.09	2053.5	1.09	2026.5
1.29	2044.5	1.25	2067	1.18	1951.5
1.36	2035.5	1.26	2047.5	1.19	2002.5
1.45	2052	1.37	2041.5	1.26	2008.5
1.67	2038.5	1.57	2013	1.42	2005.5
1.95	2043	1.85	1987.5	1.67	2004
2.22	2053.5	2.17	2011.5	1.93	2053.5

Table 9—ICP Measured Fe concentration at Room Temperature, 150˚F, and 210˚F for 5 wt% HCl + 2000 ppm Fe(III) + NTA at 1:1 mole ratio to Fe(III)

pH (77˚F)	Fe Concentration, ppm (77˚F)	pH (150˚F)	Fe Concentration, ppm (150˚F)	pH (210˚F)	Fe Concentration, ppm (210˚F)
3.38	2031	2.97	1957.5	2.67	1855.5
3.6	1885.5	3.51	1876.5	3.18	1635
4.14	1831.5	3.86	1780.5	3.46	1588.5
4.6	1872	4.24	1487.4	4.08	1057.5

Table 9 continued—ICP Measured Fe concentration at Room Temperature, 150˚F, and 210˚F for 5 wt% HCl + 2000 ppm Fe(III) + NTA at 1:1 mole ratio to Fe(III)

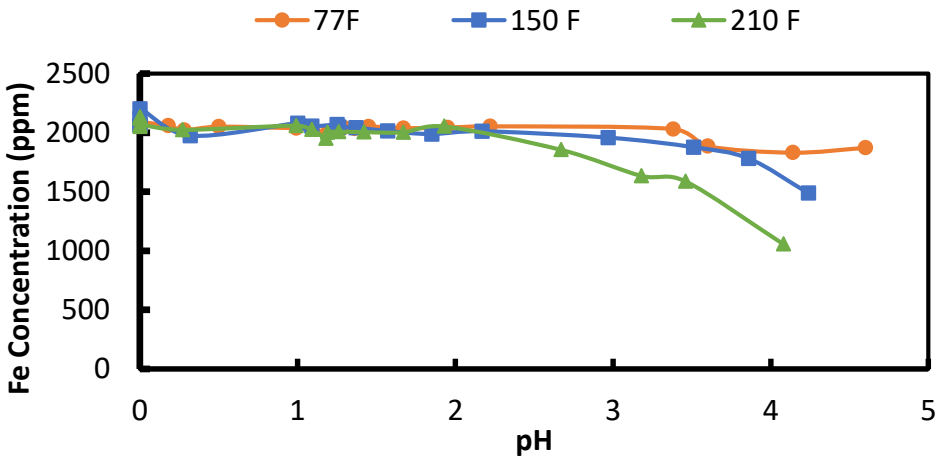


Fig. 8— Iron in Solution vs. pH for Na_3NTA (Room Temperature, 150 ˚F, and 210˚F)

Tri-sodium hydroxyethyl ethylenediaminetriacetic acid (Na_3.HEDTA)

Study of tri-sodium HEDTA showed good performance at room temperature as a chelating agent.

Samples were kept in a water bath of 150˚F, and 210˚F for 4 hours. pH values were measured at high temperature (150˚F, and 210˚F) using a special high temperature electrode. At 150˚F, little precipitation was noticed after pH = 5. Completely spent acid, pH=5.57, show a chelation performance of 91 %. At 210˚F, more precipitation was noticed after pH = 5. Completely spent acid, pH=5.31, showed decline in chelation performance to 81.5 %.

Na_3HEDTA showed no solubility problems in 5 wt% HCl. At room temperature, Na_3HEDTA has efficiently chelated Fe at pH values up to 3.3, Chelation performance encountered a minor decline and reached a minimum of 88.5 % chelation at pH = 4.92. However, at pH = 4.92, No precipitate was noticed in the samples. Hence, a larger sample will be prepared to check the formation of any precipitation at high pH values. At 150˚F, Na_3HEDTA showed minimum chelation performance of 90% at pH=5.6. At 210˚F, Performance dropped to 80% chelation at pH=5.3. Results are shown in **Table 10**, and **Fig. 10**.

pH (Room Temperature)	Fe Concentration, ppm (Room Temperature)	pH (150˚F)	Fe Concentration, ppm (150˚F)	pH (210˚F)	Fe Concentration, ppm (210˚F)
0.38	1959	0	2019	0	1881
0.55	1894.5	0	1935	0	1953
0.79	1969.5	0.04	1921.5	0	1914
1.09	1960.5	0.35	1933.5	0.19	1950
1.18	1980	0.48	1938	0.27	1986
1.49	1981.5	0.95	1924.5	0.88	1974
1.95	1929	1.67	1894.5	1.64	1962
2.75	1933.5	2.64	1908.75	2.6	1917
3.03	1939.5	3.42	1923	3.59	1842
3.31	1980	4.04	1891.5	4.51	1792.5
3.9	1983				
4.87	1759.5				

Table 10—ICP Measured Fe concentration at Room Temperature, 150˚F, and 210˚F for 5 wt% HCl + 2000 ppm Fe(III) + HEDTA at 1:1 mole ratio to Fe(III)

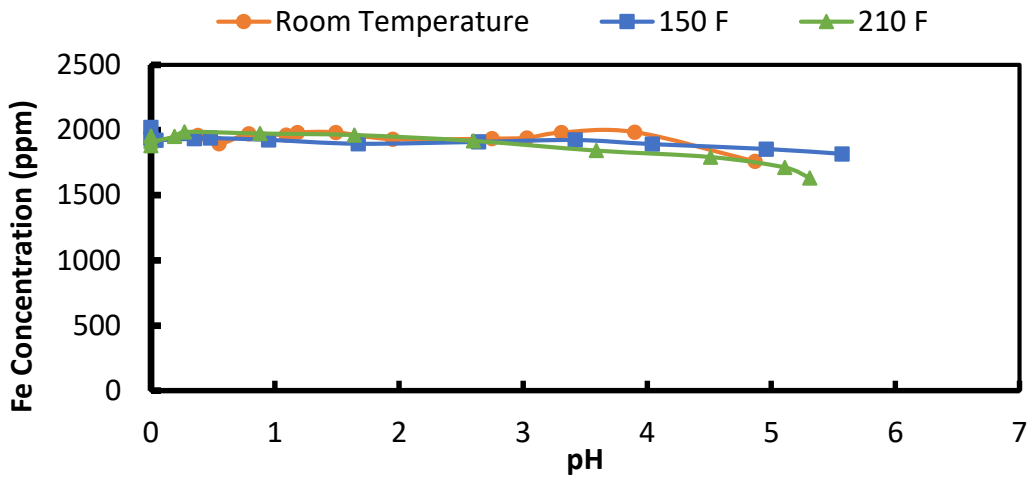


Fig. 9— Iron in Solution vs. pH for Na_3HEDTA (Room Temperature, 150 ˚F, and 210˚F)

Ethylenediaminetetracetic acid (Na4.EDTA)

In such low iron concentration (2000 ppm), equimolar experiments on tetrasodium ethylenediaminetetraacetic acid showed good solubility in live and partially spent acid.

At room temperature, Na4EDTA showed chelation performance until pH of 2, after which it declined to 90% chelation (at pH > 2).

Samples were kept in a water bath of 150˚F, and 210˚F for 4 hours. At 150˚F, Chelation performance dropped at pH > 1.6, to as low as 82.5% chelation at pH=4.75. At 210˚F, Chelation performance dropped at pH > 1.2, to as low as 62.1% chelation at pH=4.53. Results are shown in **Table 11**, and **Fig. 11**.

Na_4EDTA in equivalent moles to 2000 ppm-Fe showed no solubility problems in 5 wt% HCl. This is due to the low concentration of the EDTA formed. (Maximum of 1.015 wt. %). However, higher EDTA concentrations in Acid suffer from low solubility issues, which rules out EDTA Usage as Iron-control agent at higher iron concentrations.

pH (Room Temperature)	Fe Concentration, ppm (Room Temperature)	pH (150˚F)	Fe Concentration, ppm (150˚F)	pH (210˚F)	Fe Concentration, ppm (210˚F)
0	2134.5	0.23	1924.5	0	1824
0.22	2023.5	0.27	1912.5	0.2	1933.5
0.4	2007	0.47	1902	0.38	1872
0.6	2014.5	0.5	1875	0.62	1876.5
0.79	1977	0.65	1896	0.82	1902
0.9	2013	0.78	1926	1.14	1900.5
1.07	1965	0.95	1918.5	3.02	1503
1.12	1999.5	1.17	1905	3.37	1501.5
1.25	1987.5	1.39	1941	3.43	1435.5
1.36	1987.5	1.65	1911	3.57	1446
1.51	1975.5	1.82	1722	4.12	1341
1.65	1980	1.99	1750.5	4.53	1242
1.88	2007	2.27	1756.5		
2.05	1975.5	2.74	1705.5		
2.38	1818	4.51	1681		
2.66	1839	4.75	1650		
2.95	1801.5				
3.25	1788				
4.05	1795.5				
4.95	1800				

Table 11—ICP Measured Fe concentration at Room Temperature, 150˚F, and 210˚F for 5 wt% HCl + 2000 ppm Fe(III) + EDTA at 1:1 mole ratio to Fe(III)

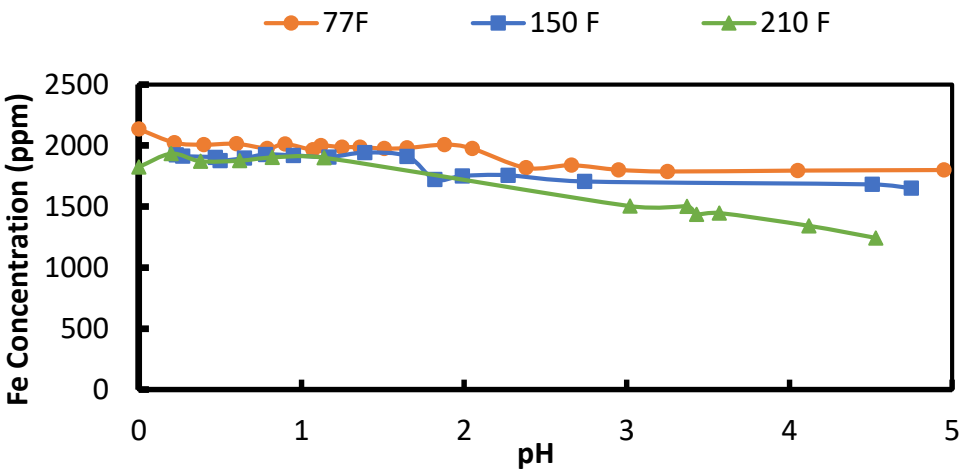


Fig. 10— Iron in Solution vs. pH for Na_4EDTA (Room Temperature, 150 ˚F, and 210˚F)

Tetra-sodium glutamic acid, N, N-diacetic acid (Na4.GLDA)

Na_4GLDA showed no solubility problems in 5 wt% HCl. Study of tetra-sodium GLDA at room temperature, 150˚F, and 210˚F showed drop of iron chelating performance in pH as low as 1.8, iron concentration in solution dropped to less than half of initial concentration as shown in the following **Table 12**, and **Fig. 12**.

XRD showed that the precipitate is not fully crystalline, and couldn't identify it. Precipitate for all high-pH samples were collected to do XRF analysis. XRF analysis showed 17.27 wt% iron as shown in **Table 13**. EDS-SEM showed that the precipitate contains both calcium, and iron with varying percentages. The precipitate also contains Nitrogen, carbon, oxygen, chloride, and sodium.

pH	Fe Concentration, ppm	pH (150˚F)	Fe Concentration, ppm (150˚F)	pH (210˚F)	Fe Concentration, ppm (210˚F)
0.12	2023.5	0	1941	0	1849.5
0.9	1936.5	0.55	1921.5	0.47	1950

Table 12—ICP Measured Fe concentration at Room Temperature, 150˚F, and 210˚F for 5 wt% HCl + 2000 ppm Fe(III) + GLDA at 1:1 mole ratio to Fe(III)

pH	Fe Concentration, ppm	pH (150˚F)	Fe Concentration, ppm (150˚F)	pH (210˚F)	Fe Concentration, ppm (210˚F)
1.28	1950	1.03	1924.5	0.92	1993.5
1.61	1686	1.43	1746	1.53	1836
1.74	1265.55	1.74	1256.1	1.94	1401.75
2.29	1075.65	2.26	1146.9	2.48	1131.15
2.52	1019.55	2.41	1072.8	2.55	1082.25
2.66	1004.25	2.56	1012.95	2.65	1004.4
3.86	910.2	4.19	838.35	4.05	955.2
4.51	913.95	4.61	1045.05	4.55	1327.5

Table 12 continued—ICP Measured Fe concentration at Room Temperature, 150˚F, and 210˚F for 5 wt% HCl + 2000 ppm Fe(III) + GLDA at 1:1 mole ratio to Fe(III)

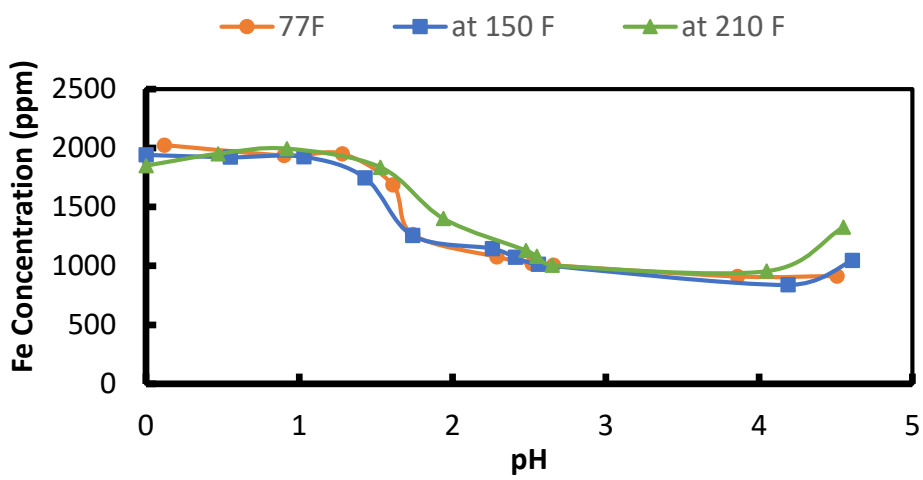


Fig. 11— Iron in Solution vs. pH for Na4EDTA (Room Temperature, 150 ˚F, and 210˚F)

Element	Weight Percent (%)
Ca (%)	46.46
Na (%)	17.8
Fe (III) (%)	17.27

Table 13—XRF elemental analysis of precipitate from Spent 5 wt% HCl with 2000 ppm initial Fe(III) and Na_4GLDA

Element	Weight Percent (%)
Cl (%)	9.22
Mg (%)	4.3
Si (%)	1.89
Al (%)	1.32
K (%)	0.75

Table 13 continued—XRF elemental analysis of precipitate from Spent 5 wt% HCl with 2000 ppm initial Fe(III) and Na4GLDA

Diethylenetriaminepentaacetic acid (DTPA)

Study of DTPA in acid form as an iron control agent encountered some solubility issues that need to be discussed. As shown in **Fig. 13,** while DTPA was completely soluble at original solution of pH=0, It was insoluble at pH between 0 and 1. Clearly at those low pH values HCl is enough to keep iron in solution but chelant precipitation can cause issues. No precipitation was noticed at pH 1 to 2. At pH > 2 a small white precipitation was noticed; this precipitation should be analyzed to see whether it's $CaCO_3$ or DTPA.

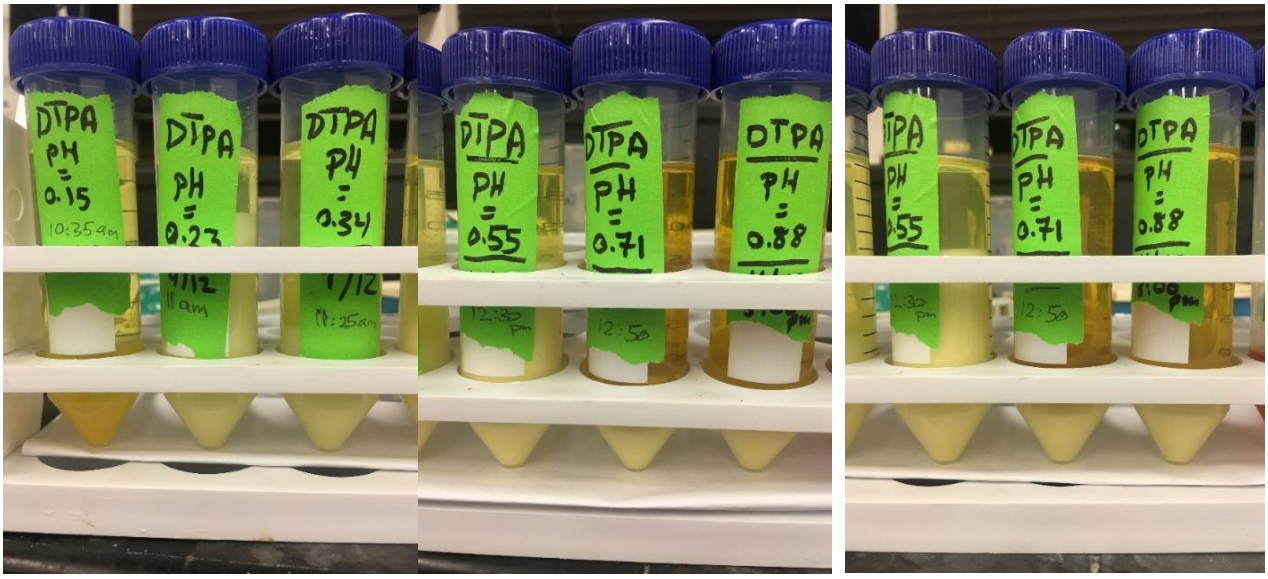


Fig. 12—DTPA at pH range 0 to 1

Unlike Na_3NTA, Samples with DTPA at room temperature showed time dependent precipitation, and also pH values showed minor changes with time. We believe that, unlike Na_3NTA, chelation performance of DTPA is time-dependent.

DTPA's chelation performance change, and pH changes with time is indicated in the **Fig. 14**, and **Fig. 15**. Precipitation continues to form with time, starting at the lowest pH until the sample with pH = 1.5 starts to show precipitation. After 48 hrs, the samples of pH =1.51 precipitate as high as 35 % of Fe initially added after 48 hours, while that of pH = 0.56 precipitate as high as 90 % of the Fe initially added.

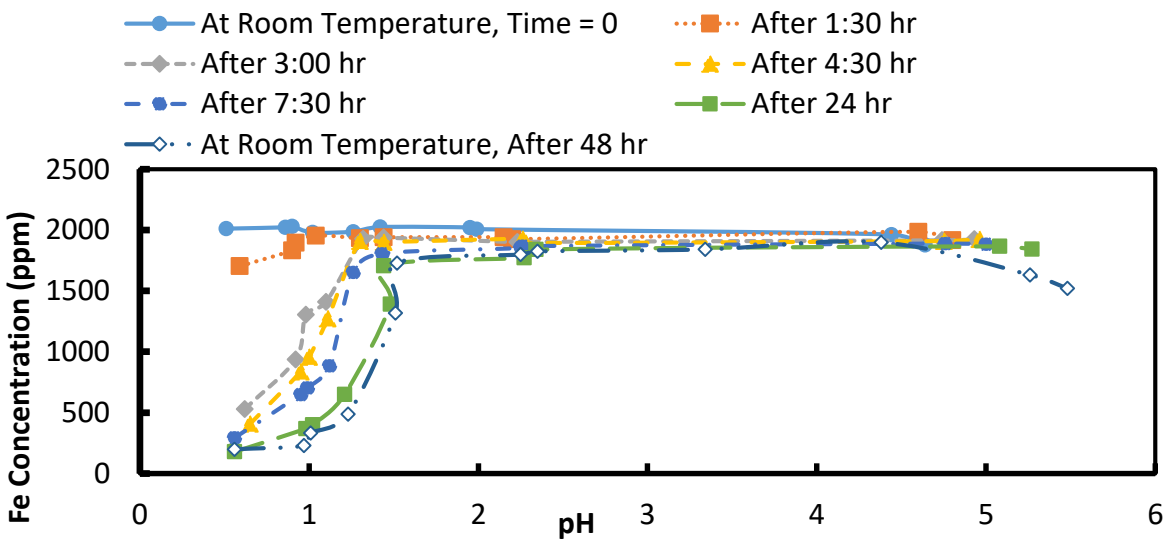


Fig. 13— Iron in Solution vs. pH (DTPA) at various times

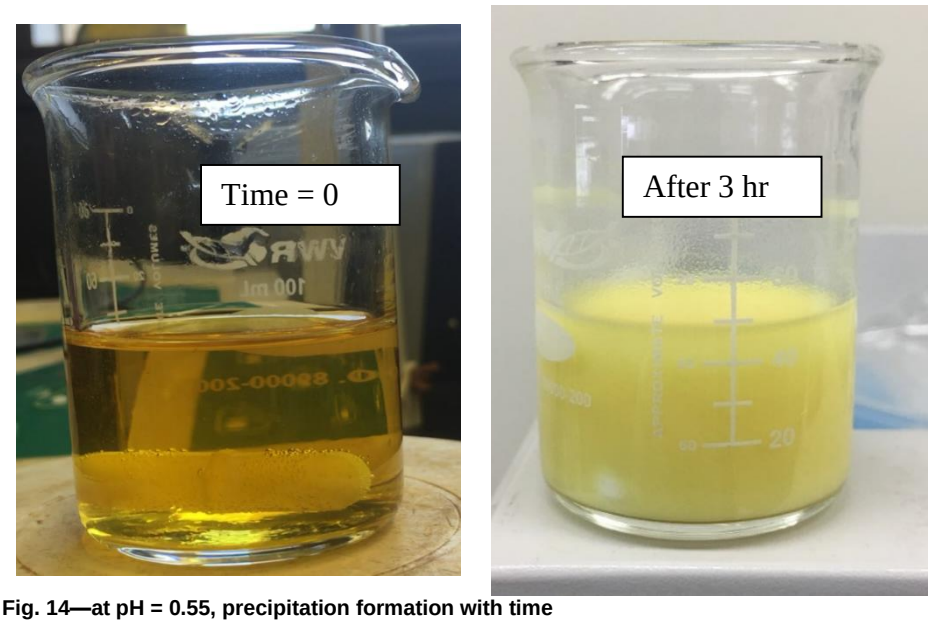


Fig. 14—at pH = 0.55, precipitation formation with time

SEM-EDS (Scanning Electron Microscopy-Energy Dispersive Spectroscopy) as seen from **Fig. 16**, and **Fig. 17** showed that the precipitate contains both calcium, and iron with varying percentages. The precipitate also contains Nitrogen, carbon, oxygen, and chloride. E.g., at pH =0.15, SEM-EDS showed the precipitate to contain as high as 13 wt. % Fe.

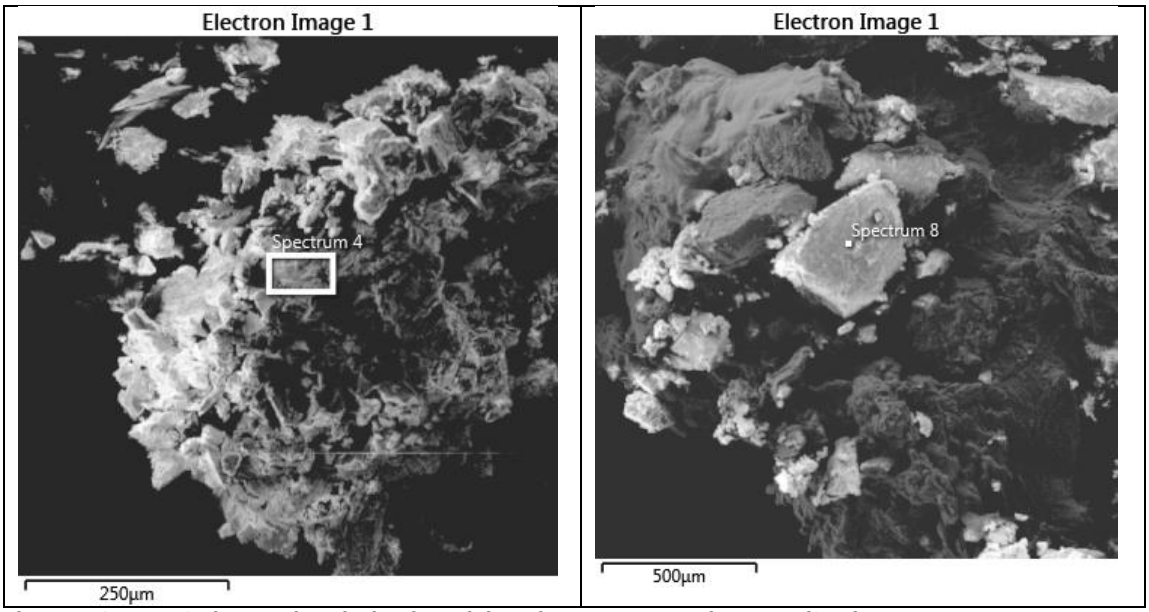


Fig. 15— SEM-EDS elemental analysis of precipitate from DTPA samples at pH (0 - 1)

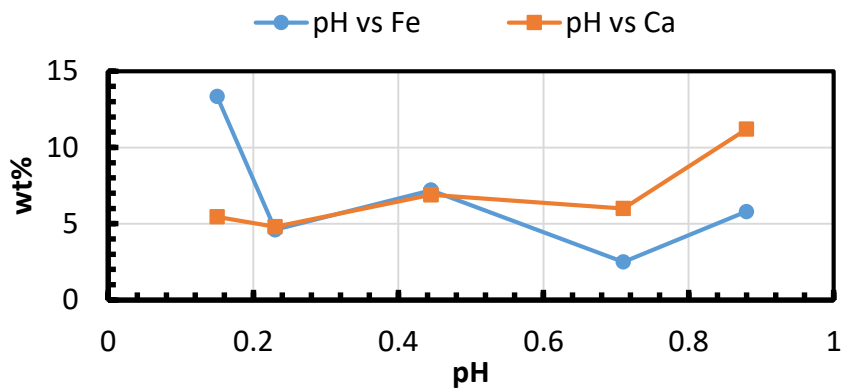


Fig. 16— SEM-EDS wt% iron, and Calcium vs. pH for precipitate from DTPA samples at pH (0 - 1)

Precipitate for all low-pH samples were collected to do XRF analysis. XRF analysis showed 30.5 wt% iron. Results are shown at **Table 14**.

Element	Wt%
Fe (%)	30.58
Na (%)	25.9
Ca (%)	17.14
Cl (%)	13.77

Table 14— XRF elemental analysis of precipitate from low-pH sample with initial DTPA at 1:1 mole ratio

Element	Wt%
Mg (%)	4.8
Si (%)	3.03
Al (%)	1.48
K (%)	1.11
S (%)	0.68

Table 14 continued— XRF elemental analysis of precipitate from low-pH sample with initial DTPA at 1:1 mole ratio

Samples were kept in a water bath of 150˚F, and 210˚F for 4 hours each. All samples were centrifuged then measured for Fe concentration. At 150˚F, DTPA's performance reached its peak at pH = 1.01 with 95 % chelation. At high pH its performance starts to decline until it reaches around 68% chelation at pH = 5.49. At 210˚F, DTPA's performance reached its peak at pH = 0.89 with 93.5 % chelation. At high pH its performance starts to decline until it reaches around 67% chelation at pH = 4.84. Results are shown in **Table 15**, and **Fig. 18.**

Samples were centrifuged for 20 minutes at 2000 rpm, then they were diluted to match detection limits of ICAP.

pH	Fe Concentration, (ppm)	pH (150˚F)	Fe Concentration, ppm (150˚F)	pH (210˚F)	Fe Concentration, ppm (210˚F)
0.15	244.05	0	442.35	0	552.45
0.23	248.1	0.23	522.6	0	844.95
0.34	186.45	0.25	543.6	0.12	930.45
0.55	195.15	0.49	840	0.25	1186.8
0.71	398.55	0.8	1356.9	0.69	1540.5
0.88	464.4	0.86	1355.4	0.82	1705.5
1.02	1878	1.01	1899	0.89	1870.5
1.23	1956	1.71	1927.5	1.63	1830
1.35	1975.5	1.97	1971	1.8	1809.75

Table 15— ICP Measured Fe concentration at Room Temperature, 150˚F, and 210˚F for 5 wt% HCl + 2000 ppm Fe(III) + DTPA at 1:1 mole ratio to Fe(III)

pH	Fe Concentration, (ppm)	pH (150˚F)	Fe Concentration, ppm (150˚F)	pH (210˚F)	Fe Concentration, ppm (210˚F)
1.54	1845	5.31	1692	4.48	1789.5
1.82	1980	5.49	1359.6	4.84	1355.85
1.98	1906.5				
2.07	1798.5				
3.34	1750.5				
4.38	1900.5				
4.85	1989				

Table 15 continued— ICP Measured Fe concentration at Room Temperature, 150˚F, and 210˚F for 5 wt% HCl + 2000 ppm Fe(III) + DTPA at 1:1 mole ratio to Fe(III)

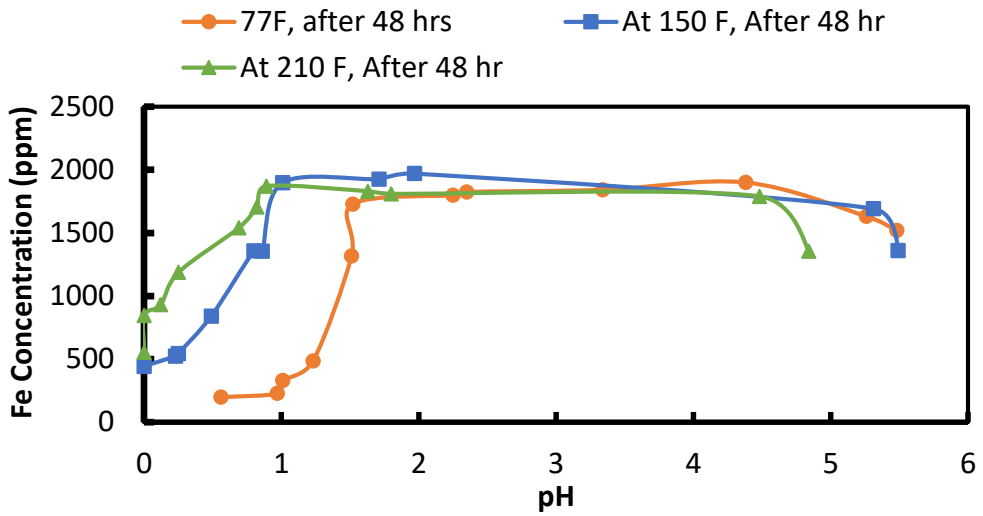


Fig. 17— Iron in Solution vs. pH for DTPA (Room Temperature, 150˚F, and 210˚F)

Table 16 shows comparison between chelation performance at completely spent acid (2000 ppm Fe(III) and 1:1 Fe:Chelant Ratio) for the five chelating agents that were tested in this research.

Chelating Agent	Room Temperature (77˚F)	150˚F	210˚F	Comments & Limitations
Na_3NTA	92.5%	74%	53%	More biodegradable than EDTA and HEDTA Animal carcinogen Limited solubility: Used at maximum iron concentration of 4000 ppm
Na_3GLDA	45.65%	52.25%	66.35%	Insufficient iron-control Environmentally friendly; readily biodegradable
Na_4EDTA	90%	82.5%	62.1%	Solubility issues: Used at maximum iron concentration of 2000 ppm Biodegradability issues
Na_3HEDTA	88.5 %	90%	80%	More soluble which allow it to control higher iron concentrations. Biodegradability issues
DTPA	76%	68%	67.8%	Solubility issues: Unlike Na_3NTA, DTPA has solubility issues at low pH values ($0 < pH < 1$)

Table 16— Chelation Performance at completely spent acid (2000 ppm Fe(III) and 1:1 Fe:Chelant Ratio) for 5 different chelating agents

Attempt to improve Na_3NTA performance

This is done by making a comparison of Na_3NTA performance at various (Na_3NTA: Fe (III)) mole ratios. Performance of trisodium NTA at Mole ratios (NTA: Fe III) of 1:1, 1.1:1, 1.2:1, 1.3:1, 1.4:1, 1.5:1, and 2:1 was compared at temperatures of 77˚F, 150˚F, and 150˚F to find the optimum NTA: Fe III mole ratio for high Iron III chelation in 5 wt% HCl, and 2000ppm Fe III solution.

Investigation of the performance of trisodium NTA at Molar ratios (NTA: Fe III) of 1:1, 1.1:1, 1.2:1, 1.3:1, 1.4:1, 1.5:1, and 2:1 at temperatures of 77˚F, 150˚F, and 150˚F within completely spent acid, and Iron III concentration of 2000ppm showed that:

- A molar ratio of 1.4:1 is optimum at room temperature, and 150˚F; showing chelation performance of 95.3%, and 94.25% respectively.
- A molar ratio of 1.5:1 is optimum at 210˚F; showing chelation performance of 86.71%.

There is no improvement in chelation performance with increasing molar ratio to 2:1, as maximum solubility of NTA in acid might also be exceeded. Results are shown in **Table 17**, and **Fig. 9**.

Mole Ratio	Chelation Performance (%) (Room Temperature 77˚F)	Chelation Performance (%) (150˚F)	Chelation Performance (%) (210˚F)
1.00	89.53	71.13	50.57
1.10	90.67	81.77	68.92
1.20	90.55	89.76	77.95
1.30	90.73	90.51	76.85
1.40	95.34	94.25	83.83
1.50	93.71	90.75	86.71
2	93.65		82.09

Table 17— Chelation Performance of Na3NTA at various mole ratio and temperatures (77˚F, 150˚F, and 150˚F)

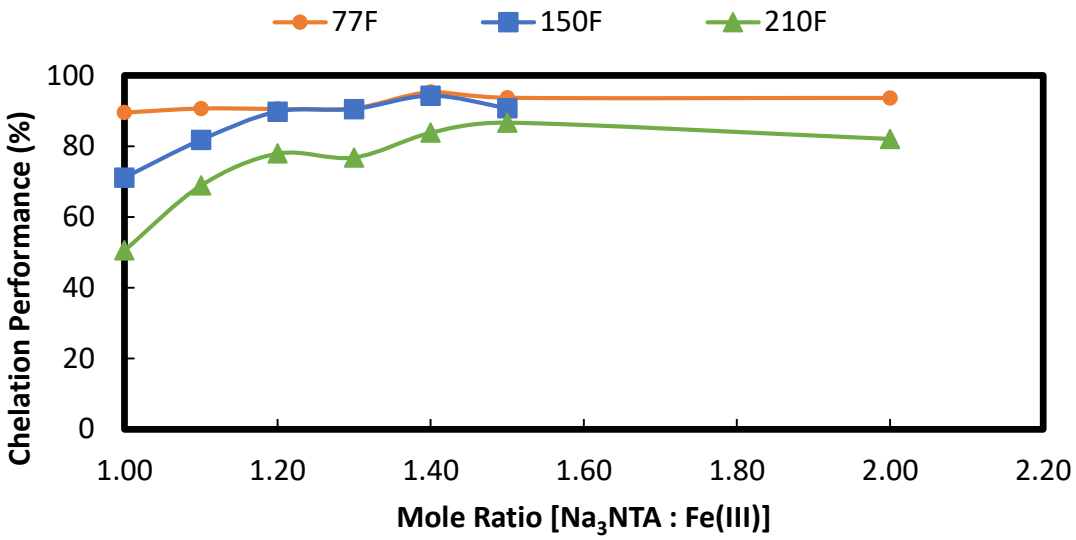


Fig. 18— Chelation Performance of NTA at various mole ratios

Experiments at 4000ppm Fe(III) concentration

NTA

At room temperature, NTA managed to complex all iron in 5% HCl acid up to pH =4.03. The chelation performance declined to a minimum of 97% at pH = 4.7. Samples were kept at water bath of 150˚F, and 210˚F for 4 hours. At 150˚F, Na3NTA completely chelate iron at pH values up to 3.87. At higher pH (pH > 3.87), its performance starts to gradually decline until it reaches around 90.7% chelation at pH = 4.42. At 210˚F, Na3NTA completely chelate Fe3+ at pH values up to 3.53. At higher pH (pH > 3.53), its performance starts to gradually decline until it reaches around 73% chelation at pH = 4. Results are shown in **Fig. 19**.

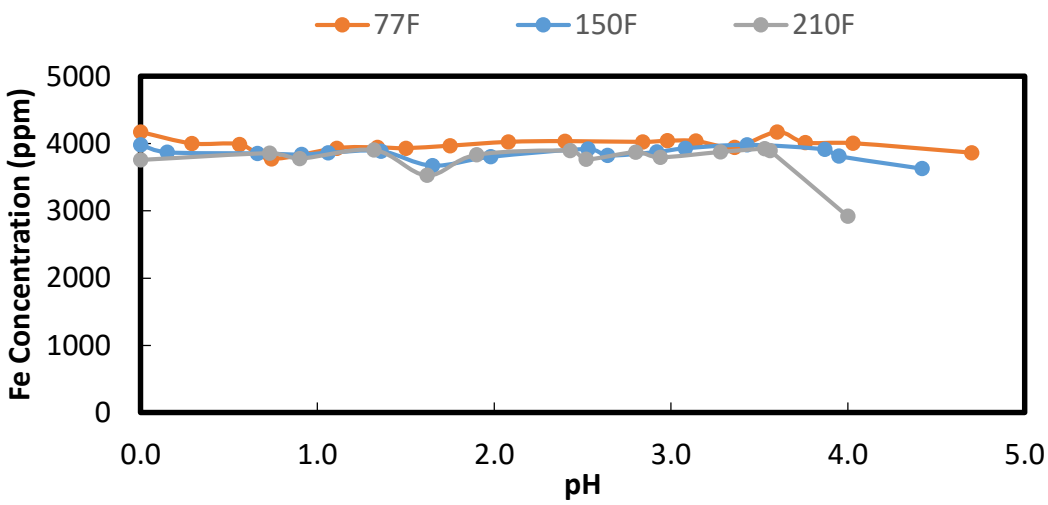


Fig. 19—Iron in Solution vs. pH for Na_3NTA (1-to1 Mole Equivalent) (At 150˚F and 210˚F) (4000 ppm initial iron concentration)

EDTA

Experiments on tetrasodium ethylenediaminetetraacetic acid showed that for mole equivalent of EDTA and Fe III, Na4EDTA concentration will exceed maximum solubility in live 5% HCl solution with 4000ppm Fe III in solution. Precipitation was noticed at the original solution. Precipitate was filtered and dried in oven for one day. XRF analysis was performed on the precipitate to show that it's almost 100% Na4EDTA, and hence, confirm that maximum solubility was exceeded. At room temperature, Iron III in solution dropped at pH = 2.52 to 83% of initial concentration. After this point, there was a slight decline in performance to reach a minimum of 80% at pH = 4.77. At 150˚F, Iron III in solution dropped at pH = 1.6 to 82% of initial concentration. After this point, it slightly declined to a minimum of 78% at pH = 4.44. At 210˚F, Iron III in solution dropped at pH = 1.07 to 81% of initial concentration. After this point, there was a slight decline in performance to reach a minimum of 76% at pH = 3.88. Results are shown in **Fig. 20**.

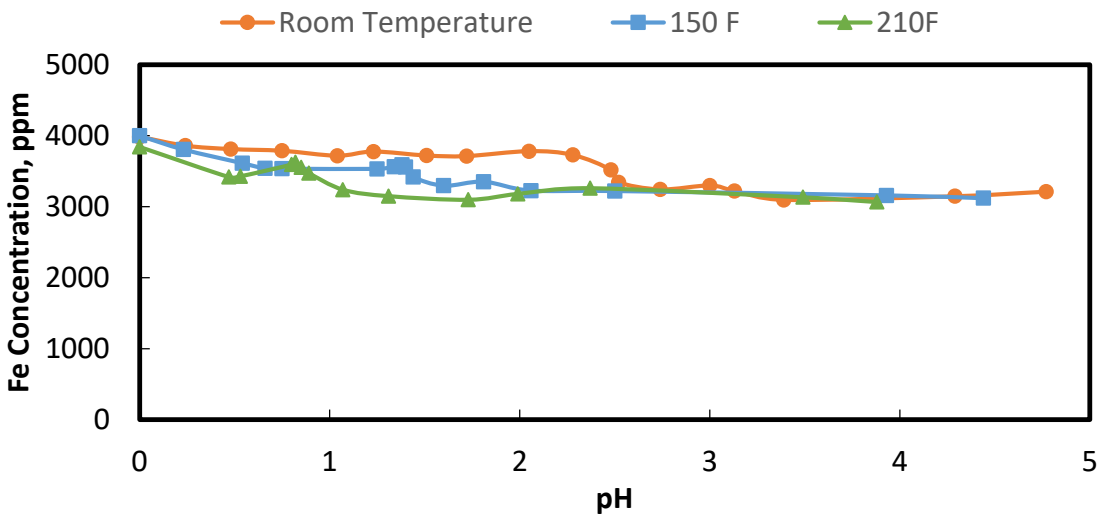


Fig. 20—Iron in Solution vs. pH for Na4EDTA (1-to1 Mole Equivalent) (At 150˚F and 210˚F) (4000 ppm initial iron concentration)

Acid Additives

Corrosion Inhibitor

At 5 gpt of corrosion Inhibitor (CI-27) was added to 5 wt% HCl that contains 2000 ppm of Iron (III). The solution was divided into 5 different samples to which No chelating agent, Na_3HEDTA (1:1), Na_4GLDA (1:1), Na_4EDTA (1:1), and Na_3NTA (1.4:1) was added, respectively. Calcium carbonate was added to completely spend the acid (pH ~ 5) in the five samples and monitor the Iron precipitation in every sample at room temperature 77 ˚F.

Non-Ionic Surfactant

Same steps as CI-27 experiment were repeated using 5 gpt of non-ionic surfactant (ETHOMEEN C/12).

Analysis and Discussion of acid additives experiments

Iron precipitation was quantified by measuring iron concentration in every sample using inductively coupled argon plasma (ICAP) emission spectroscopy. Results in **Fig. 21**, and **Fig. 22**

confirmed our results and showed insignificant interference with the performance of the chelant. NTA and HEDTA were found to be having the best iron-control chelation performance of the five chelating agents tested.

One of the most important and realistic factors in comparing the performance of the chelating agent is the weight ratio Chelant/Iron (mass of chelant required to control unit mass of iron). Keeping this mind, NTA showed the leading performance with weight ratios in the cases of no additives, 5 gpt CI-27, and 5 gpt of ETHOMEEN C/12 to be 6.84, 6.65, and 6.87 respectively, and the second best was HEDTA; with weight ratios of 7.87, 7.08, and 7.18 respectively. To illustrate this in field units; to control 1 liter in acid that contains 2000 ppm Fe(III), 13.5 g of Na_3NTA is required while in case of HEDTA, 15.75 g is required. Weight ratios of the studied chelants are shown in **Fig. 23**.

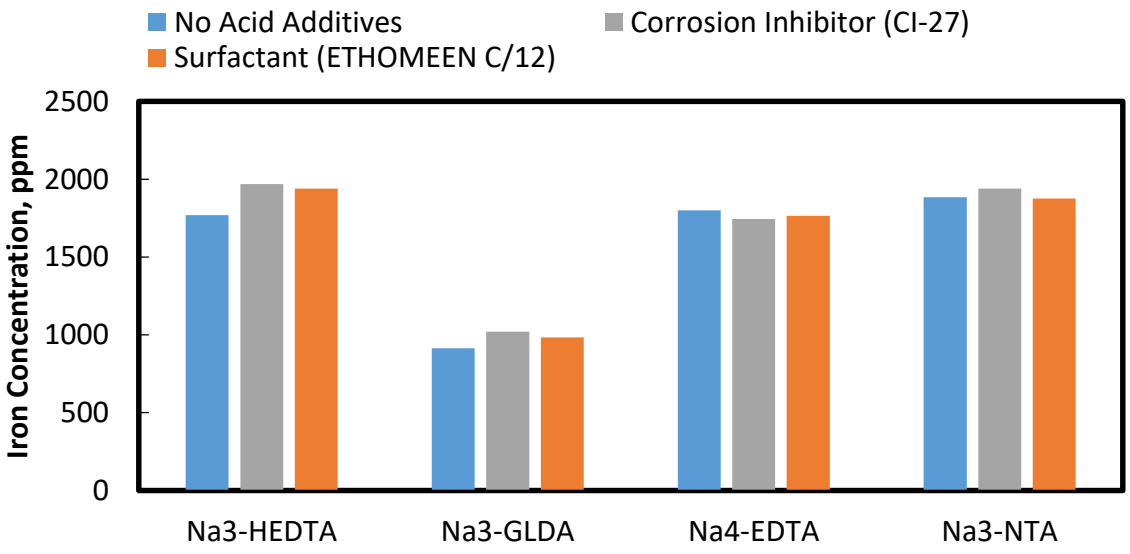


Fig. 21—Effect of Corrosion Inhibitor (5 gpt CI-27), and Non-ionic surfactant (5 gpt ETHOMEEN C/12) on Chelating Agents Performance in spent acid with 2000 ppm initial iron concentration

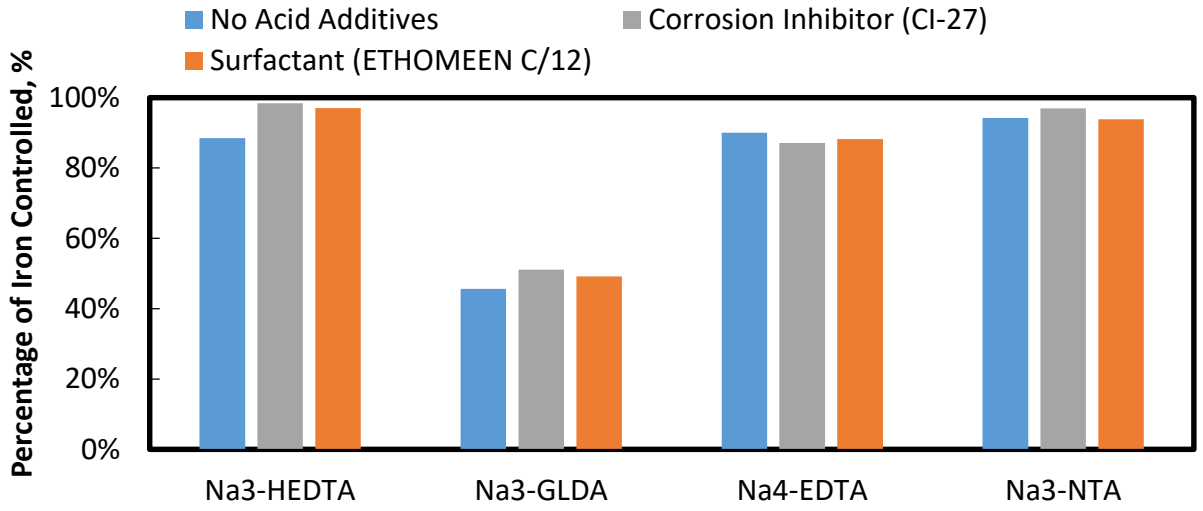


Fig. 22— Effect of Corrosion Inhibitor (5 gpt CI-27), and Non-ionic surfactant (5 gpt ETHOMEEN C/12) on percentage iron controlled (%) in spent acid with 2000 ppm initial iron concentration

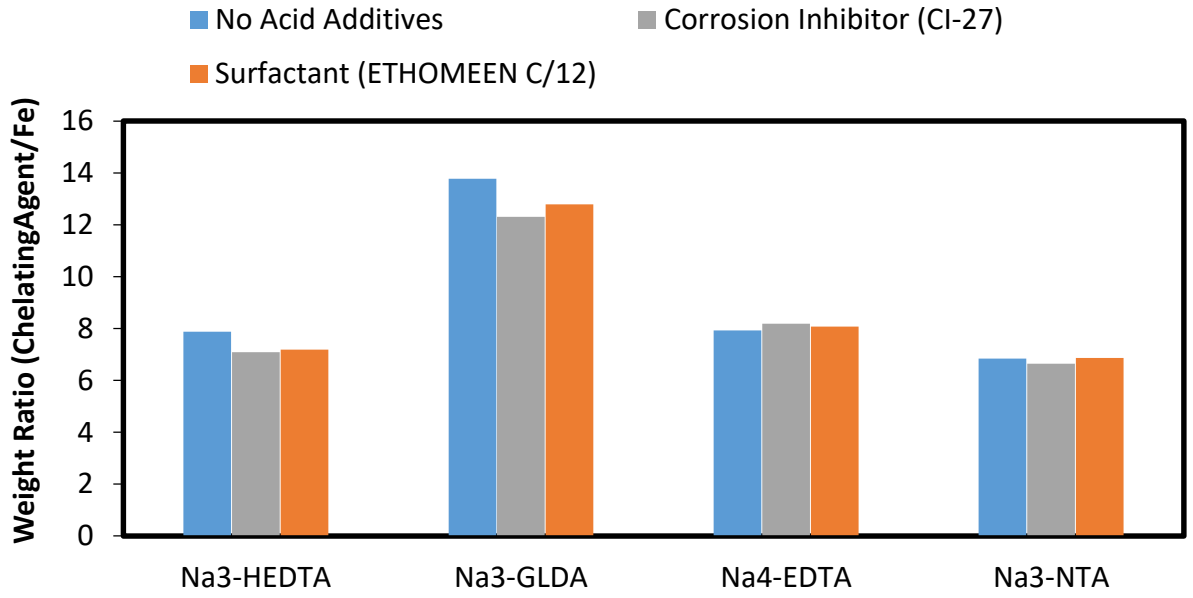


Fig. 23— Effect of Corrosion Inhibitor (5 gpt CI-27), and Non-ionic surfactant (5 gpt ETHOMEEN C/12) on Chelating Agent/Fe Weight Ratio in spent acid with 2000 ppm initial iron concentration

Corefloods

Three coreflood experiments were conducted with 5 wt% HCl and 4000 ppm iron. The first experiment was at the absence of iron in the acidizing solution, the second contained iron but no chelating agents and the third experiment had both iron and chelant (NTA) at 1:1 molar ratio. The brine viscosity and density at 200°F and 14.7 psi was measured to be 0.385 cp and 1.01 g/cm^3.

Fig. 24 shows the inlet of the three cores. At the first experiment, with clean acid (No Fe III) and no iron-controlling agent, and, as **Fig. 25** shows, pressure drop decreased from 64 psi to 48 psi. This resulted in percentage improvement in permeability of 33.3%. At the second experiment, with iron and in the absence of any iron-control agent more iron precipitated in the core, and, as **Fig. 26** shows, pressure drop decreased by value of only 7 psi; from a pressure drop of 48 psi to 41 psi, which is much less than the clean acid stimulation run. This resulted in percentage improvement in permeability declined to reach only 17 %. At the third experiment, with Na_3NTA, less iron precipitated in the core, and, as **Fig. 27** shows, pressure dropped from 54 psi to 35 psi, which is 3 psi more decrease (19 psi) in pressure drop across the core than the clean acid stimulation run indicating efficient iron control. This resulted in percentage improvement in permeability of 54%. The change in pressure drop, and the improvement of permeability in each of the three experiments, as **Fig. 28**, and **Fig. 29** show, indicated the high importance of NTA as an iron-control additive, in addition to augmenting the stimulation power of the acid.

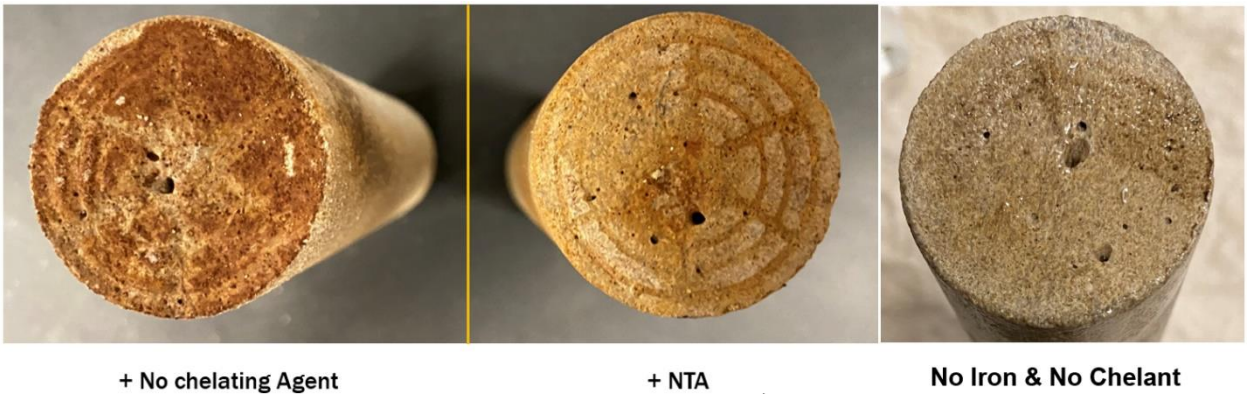


Fig. 24—Cores inlet after acidizing operations with 5 wt% HCl + 4000 ppm Fe(III)

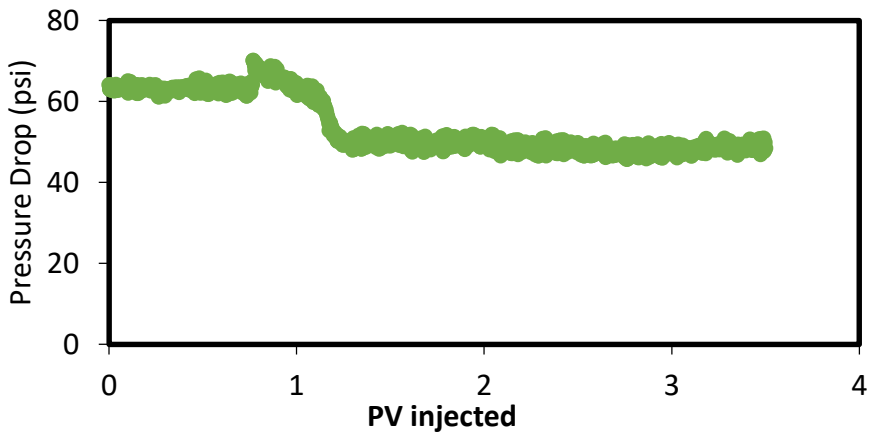


Fig. 25—Pressure Drop across the core for 5 wt% HCl solution with No Fe III at 200 F and No chelating agent

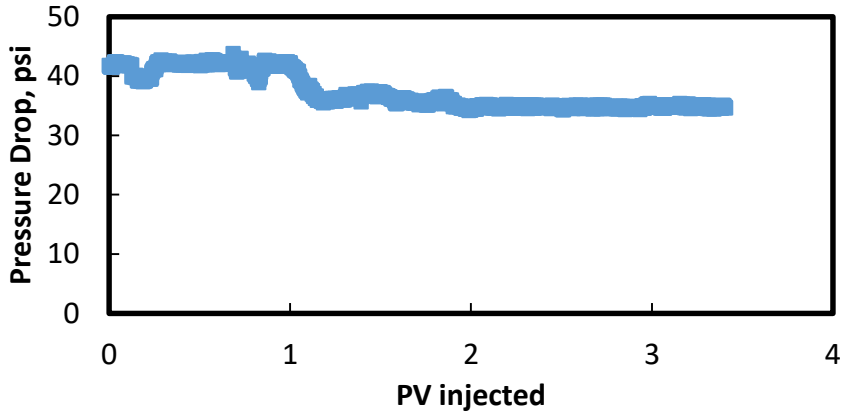


Fig. 26—Pressure Drop across the core for 5 wt% HCl solution with 4,000 ppm Fe III at 200 F and No chelating agent

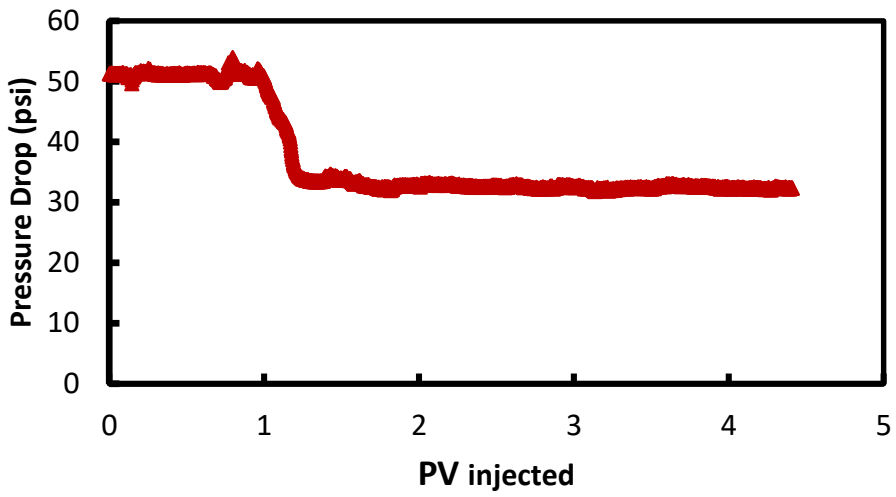


Fig. 27—Pressure Drop across the core for 5 wt% HCl solution with 4,000 ppm Fe III at 200 F and NTA at 1:1 molar ratio

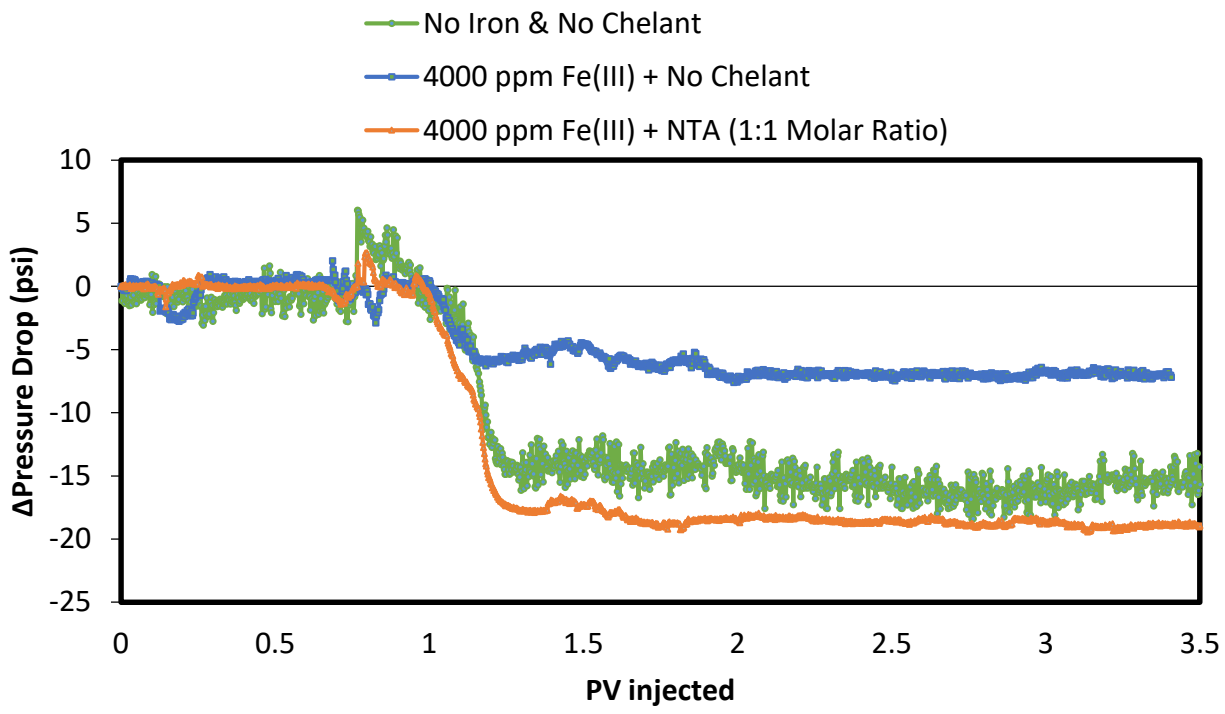


Fig. 28—Change in Pressure Drop across the core for 5 wt% HCl solution at 200 F and No iron & No chelating agent (green), or with 4,000 ppm Fe III and No chelating agent (blue) or with 4,000 ppm Fe III + NTA at 1:1 molar ratio (red)

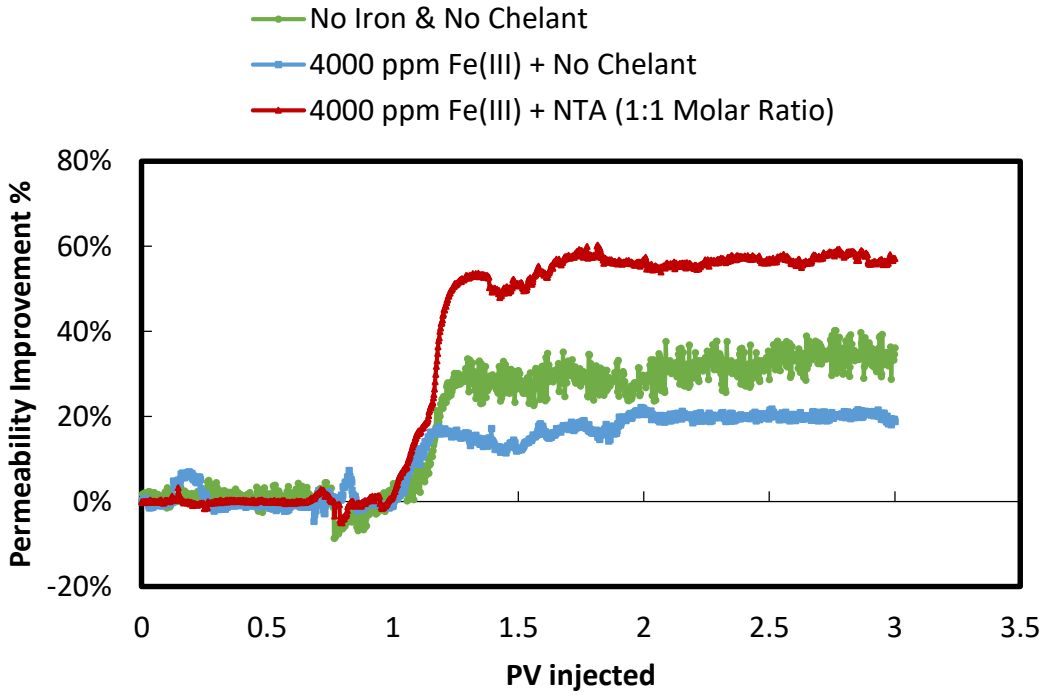


Fig. 29—Improvement in core permeability (%) for 5 wt% HCl solution at 200 F and No iron & No chelating agent (green), or with 4,000 ppm Fe III and No chelating agent (blue) or with 4,000 ppm Fe III + NTA at 1:1 molar ratio (red)

CHAPTER VIII

CONCLUSIONS

1. An effective iron-control agent has to be soluble in acid in all encountered pH, and temperature conditions. Formation of iron precipitate is a function of both pH, and temperature.
2. Na_4GLDA was inefficient in chelating iron with drastic decline in chelation performance to as low as 50% chelation at pH = 2.25 at room temperature.
3. DTPA has severe solubility issues at low pH values ($0 < pH < 1$). In addition, samples with DTPA at room temperature showed time dependent precipitation, and also pH values showed changes with time indicating that chelation performance of DTPA is time-dependent.
4. NTA and HEDTA had the highest performance keeping as high as 80 % of iron in solution, among the five studied chelating agents at 210˚F. NTA is preferred at iron concentrations up to 4000 ppm in 5 wt% HCl due to the facts that less chelant weight is required and NTA is more biodegradable than HEDTA.
5. Using a molar ratio of 1.4:1 to obtain a minimum chelation performance of 86.71% enhances NTA's high-temperature performance.
6. Corrosion inhibitor (CI-27), and non-ionic surfactant (ETHOMEEN C/12) didn't negatively interfere with the performance of these chelants. Effects of other acid additives need to be explored in future work.
7. Coreflood experiments concluded that acidizing will fail with the presence of iron and no-efficient iron control agent. Runs that had NTA added, confirmed the essential role of NTA

as an iron-control additive in acidizing operations in addition to supporting the acid in the stimulation job.

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