FORMATION DAMAGE DUE TO IRON PRECIPITATION IN ACIDIZING OPERATIONS AND EVALUATING GLDA AS A CHELATING AGENT

A Thesis

by

ROHIT MITTAL

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

December 2011

Major Subject: Petroleum Engineering

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Approved by:

Chair of Committee,	Hisham A. Nasr-El-Din
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ABSTRACT

Formation Damage due to Iron Precipitation in Acidizing Operations and Evaluating GLDA as a Chelating Agent.

(December 2011)

Rohit Mittal, B.Tech., Indian Institute of Technology Guwahati
Chair of Advisory Committee: Dr. Hisham A. Nasr-El-Din

Iron control during acidizing plays a key role in the success of matrix treatment. Ferric ion precipitates in the formation once the acid is spent and the pH exceeds 1-2. Precipitation of iron (III) within the formation can cause formation damage. Chelating agents such as EDTA and NTA are usually added to acids to minimize iron precipitation. Drawbacks of these chelating agents include limited solubility in strong acids and poor environmental profile. Hydroxy EDTA was introduced because of its higher solubility in 15 wt% HCl. However, its solubility in 28 wt% HCl is low and it is not readily biodegradable.

In this study we studied the formation damage caused by iron precipitation in acidizing operations and tested the chelate L-glutamic acid, N,N-diacetic acid (GLDA). This chelant is soluble in higher concentrations of HCl. It is readily biodegradable, and is an effective iron control agent. A study was conducted to study the concentration of iron at different pHs ranging from 1-4 without the presence of any chelating agent at room temperature. A similar study was conducted in the presence of a chelating agent.

To simulate field conditions, coreflood tests were conducted on Indiana Limestone, Austin Chalk and Pink Desert. Tests were conducted with and without the chelant. Samples of core effluent were collected and iron and calcium concentrations were measured using atomic absorption spectroscopy (AA). The cores were scanned using X-ray before and after acid injection.

Results indicated that precipitation of iron can cause serious reduction in core permeability. The chelate was found to be very effective in chelating iron upto 300°F. No permeability reduction was noted when GLDA was added to the acid. Material balance calculations show that significant amount of the iron that was added to the injected acid was produced when GLDA was used. This chelant is effective, environmentally friendly and can used up to 300°F.

DEDICATION

This thesis is dedicated to my parents for their never ending support and encouragement.

ACKNOWLEDGEMENTS

I would like to express my largest gratitude to my supervisor, Dr. Nasr-El-Din, for his guidance, knowledge, and supervision he provided throughout my graduate study.

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I would also like to thank Akzo Nobel for providing me financial support during my education.

My officemates, classmates, and lab mates have always been there for their support, friendship, and help. I would like to thank them.

Finally, I would like to thank to my parents for their never ending support and encouragement.

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CHAPTER I

INTRODUCTION AND LITERATURE REVIEW

Stimulating wells with acids was first reported in the year 1896 (Walker et al. 1991). The aim was to dissolve large amounts of rock near the wellbore region to remove any damage done to the permeability of the rock. Though its success has made it possible to be followed even today, it has many disadvantages. One of them is the high solubility of iron (III) in live acid. This iron comes from sources that include storage tanks, pipelines, and tubulars. As the acid spends on the rock, the pH of the acid starts increasing as the acid reacts with the carbonate in the rock. As the pH crosses 1, ferric hydroxide starts precipitating from the solution. By a pH of 2, most of the ferric is precipitated (Taylor et al. 1999). This precipitate blocks the pores and significantly reduces the permeability of the near wellbore rock. If the well is sour, the presence of hydrogen sulfide (H_2S) leads to formation of further precipitates – elemental sulfur (S_8) and iron sulfide (FeS) — that cause even more damage. This damage is very difficult to remove. It has been recommended that the tubing be pickled with acid before acidizing the formation to reduce the damage as much as possible (Gougler et al. 1985).

Since a large amount of iron is dissolved in live acid before it reaches the formation and then re-precipitated within the formation, it has attracted considerable research in the industry.

This thesis follows the style of *SPE Production & Operations*.

Table 1.1 – Comparison between different chelating agents used in the industry

Sequestering Agent	**Advantages**	**Disadvantages**	**Amt. Req. in 1000 gal 15% HCl to sequester 5,000 ppm Fe(III) for Minimum of 2 days at 150°F**
Citric Acid	Effective up to 200°F	Will precipitate as calcium citrate when excess quantities are used.	175 lb
Citric-Acetic acid mixture	Very effective at lower temperature	When indicated amount is used, calcium citrate will precipitate unless at at least 2,000 ppm Fe(III) is present in spent acid. Efficiency decreases rapidly at temperatures above 150°F	50 lb (citric acid) 87 lb (acetic acid)
Lactic Acid	Little chance of calcium lactate precipitation if excessive quantities are used.	Not very effective above 100°F	190 lb at 75°F
Acetic Acid	No problem from possible precipitation as calcium acetate.	Effective only to about 160°F	435 lb
Gluconic Acid	Little chance of calcium gluconate precipitation	Effective only to about 150°F. Expensive on a cost performance basis.	350 lb
EDTA Na_4	Large excesses may be used without precipitation of calcium salt. Effective at temperature upto 200°F	More expensive to use than many of the other agents.	296 lb
EDTA Na_3	May be used in considerable excess without precipitation as calcium salt. Effective up to 200°F	Less expensive than EDTA but still more expensive than citric acid.	250 lb

Smith and Mancillas (1969) first analyzed sequestering agents/chelating agents that could be used in the field to stop the precipitation of ferric compounds. They gave the thermal and solubility limits of chelating agents and indicated how much iron they could chelate. **Table 1.1** tabulates their findings.

However, chelating agents do not solve all the problems. Dill and Fredette (1983) found about inability of chelating agents to prevent iron precipitation and fines migration during acidizing. In sour conditions, the chelating agents do not work. In conditions where oxidizing agents are present, they do not work. Alternate measures were provided to solve these problems.

Since chelating agents have various limitations of temperature and solubility, it was important to understand the need for right selection(s) of chelating agent depending upon field conditions. Ewing et al. 1983 experimented with different blends of chelating agents to chelate iron. They identified the limitations of individual chelating agents and how combining different chelating agents may mitigate their weakness and provide a cumulative benefit. For example, citric acid is a good chelating agent, but if used in higher concentrations, it precipitates as calcium citrate. EDTA is an effective chelating agent but is expensive. Acetic acid does not really work as a chelating agent, but works as buffering agent and keeps the pH low. A blend of three serves to work around their individual weaknesses and provides more chelating power than any two together. They tested various ratios of the three starting from 1:0:0 to 3:2:2 (LCA/NTA/AA) at various HCl concentrations ranging from 7.5% to 20%.

In 1988, Hall et al. identified the challenges in estimating the amount of iron control agent that must be used to prevent the precipitation of iron. They identified, amongst others, factors like condition of the tubular, amount of tubular surface area, type of iron compounds, temperature, acid type and its concentration, contact time, type of production, amount of iron in the formation and other acid-reactive components in the formation that affect the amount of iron control agent that must be used. Also, whether a well is an injection well or a producer well affects the amount of iron to be chelated. Injection wells have more ferrous oxide (FeO) than producer wells. They suggested that a pre-flush, such as acetic acid, should be considered to minimize the contact time between treating acid and to maintain a low pH.

In 1999, Taylor et al. conducted a systematic study of iron control chemicals that are used in the industry. They studied the precipitation of iron by measuring the amount of iron in solution. Their work compared the precipitation of iron without the presence of any chelating agent, in the presence of chelating agents and in the presence of salts. Chelating agents studied were citric acid, nitrilotriacetic acid (NTA), acetic acid and ethylenediamine tetra-acetic acid (EDTA). Time dependence precipitation was also studied. This study was the first of its kind, where the amount of iron precipitated was quantitatively studied with respect to pH and time. They found that most of the iron precipitated in the formation by a pH of 2 rather than 3 as was reported before. They also reported a lower solubility of iron (III) hydroxide at higher temperatures. Finally, they reported the positive effect of combining acetic acid and citric acid as chelating agent at 185°F.

Over the years, environmental concerns have become important and therefore industry is willing to conduct more research on more environmentally friendly chelating agents. In early 2000s, (Frenier et al 2000; Frenier et al 2003) hydroxyethyliminodiacetate (HEIDA, HEDTA) salts were reported as having both a higher solubility and possessing a favorable biodegradability profile. However, they had a poor aquatic toxicity profile. LePage et al (2009) reported a new chelating agent GLDA, which is much more biodegradable than any other conventional chelating agents, including hydroxyethyliminodiacetate (HEIDA). However, GLDA is not as strong a chelating agent as EDTA and N-hydroxyethylenediaminetriacetic acid (HEDTA), but is much more soluble in acid than any of the known chelating agents.

The objective of this study is to understand under simulated reservoir conditions, the damage caused by iron in acidizing operations with varying parameters and the effect of using GLDA as a chelating agent.

The effect of following parameters has been studied:

1. Temperature
2. Permeability
3. Acid/GLDA Concentration
4. Flow Rate

CHAPTER II

IRON PRECIPITATION AS A FUNCTION OF PH AT ROOM CONDITIONS

Introduction

As the live acid is spent on the carbonate rock, the pH of the acid goes up. In the case of carbonates, the pH of spent acid is around 4-5 due to buffer formed by the dissolved carbon dioxide that is released when HCl reacts with calcite. As the pH increases, the solubility of ferric hydroxide decreases and it precipitates in the formation. A study was conducted to understand the precipitation of iron with respect to pH. Experiments were done at room temperature and at a pressure of 1 bar. The tests were conducted using 5 wt% HCl containing 10,000 ppm of ferric ions. Experimental results showed the precipitation of iron started around a pH of 1.5 and most of it precipitated by a pH of 2.6 without the presence of GLDA. In the presence of GLDA, very little or no precipitation was observed even the samples were allowed to rest for days.

For the purpose of experiments, a 36.5 wt% of HCl stock was used. To measure the pH, an Oakton pH 510 pH meter was used. For creating a 10,000 ppm acid solution, pure ferric chloride was ordered from Sigma-Alderich.

Experimental Procedure/Methods

Procedure for preparing 5 wt% HCl containing 10,000 ppm Fe(III)

$FeCl_3$, when dissolved in acid, contributes to the acidity of the solution. Due to the coupled nature of the mixture, simultaneous equations (as described in the following pages) were solved to arrive at the following amounts that must be used to prepare 1 kg of 5% HCl (10,000 Fe(III)).

Let x gms of HCl, y gms of water and n gms of $FeCl_3$ be required for creating the required HCl and iron concentration. Using the principle of mass balance, three equations were derived to find the values of x,y and n. These values were used to prepare the acid. The concentration of HCl in the original packaging is 36.5% ($f=0.365$). It was assumed that all $FeCl_3$ dissociates into Fe^{3+} and 3 Cl^- ions in the solution (Taylor et al. 1999).

A mass balance on HCl gave the first equation:

$$\frac{\left[\left(\frac{x}{36.5} * f + \frac{3n}{162.6}\right) * 36.5\right]}{(x+y+n)} = Required\ HCl\ concentration$$

In the above equation, the numerator in parenthesis (i.e the numerator without multiplying 36.5) on the left hand side represents the moles of Cl^- ions coming from HCl and $FeCl_3$. The whole numerator on the left hand side represents the total weight of HCl (in gms) in the solution since the number of moles of Cl^- is equal to the number of moles HCl. Dividing the weight of HCl by the total weight, the denominator, we get the required fraction of HCl. This is the first equation.

Doing a mass balance on Fe(III) gave the second equation:

$$\frac{\left(\frac{n}{162.6} * 56\right)}{(x+y+n)} = \frac{10\ gms(= 10{,}000\ mg)}{1000\ gms\ (= 1\ kg)}$$

Here, the numerator on the left hand side represents the weight of Fe(III) in $FeCl_3$. We divide this by the total weight and equate it to the required iron concentration in the solution (10,000 ppm or mg/kg). This is the second equation.

The third equation can be found by taking the total mass of the prepared solution to be 1 kg. Therefore, the third equation can be written as follows:

$$(x + y + n) = 1000 \ (gms)$$

Using the values of x,y and n and the density of HCl (1.1803 gms/cc), the following procedure was determined to prepare the acid solution containing 10,000 ppm iron.

1. Take y gms of water and add x gms of 36.5% HCl to it.
2. Add n gms of Ferric Chloride in the solution.
3. Add y gms of water.
4. Finally bring the HCl concentration to the required concentration by adding x gms of 36.5 wt% HCl to the solution.

pH meter calibration

A good pH meter calibration is extremely important as the experiment requires an accurate measurement of pH. Calibration of the Oakton pH 510 meter was done using 3 buffer solutions of pH 4,7,10. Often, the pH meter was calibrated repeatedly 2-3 times until the difference between the measured and the actual pH of the buffer solution was less than 0.05 unit after calibration.

Experiment 1: No GLDA

Two procedures were used to collect the data. One of the procedures was given by Talor et al. (1999) to understand the precipitation of iron with respect to pH.

Procedure 1

1. 30 ml of 5% HCl solution containing 10,000 ppm, Fe (III) was taken in a beaker and stirred continuously with the help of magnetic stirrer.
2. A pH meter continuously measured the pH of the solution.
3. Calcium carbonate was added in small amounts until the pH reached the desired value. In case the pH value overshot the desired value, time was given to it to stabilize as the pH came down with time.
4. After some time, as the pH came down, more calcium carbonate was added.
5. Steps 4-5 were repeated until the pH remained constant (± 0.05) for at least 15 minutes.
6. The contents of the beaker was transferred in a test tube and centrifuged for 5 minutes.
7. The supernatant from the test tube was then immediately diluted by serially diluting the sample first 10 times and then 100 times.
8. Steps 1-6 were repeated at different pH values between 1.3 and 4.
9. Iron (Fe([III]) concentration of the diluted samples was measured suing atomic absorption technique.

Procedure 2

35 g of 5% HCl containing 10,000 ppm Fe(III) was taken in several test tubes. Amount of calcium carbonate to neutralize 105% of the acid was determined using stoichiometric calculations. Calcium carbonate was added in small increments to each test tube that corresponded from 80% neutralization to 105% neutralization of the acid. Equilibrium was allowed to attain in the tubes for 6-8 hours. pH of the tubes after 6-8 hours was measured and then Fe (III) concentration was measured as described in procedure 1 (Steps 6-9).

Comparison of Procedures

While conducting procedure 1, it was observed that the pH of the acid solution after adding calcium carbonate did not remain stable. The pH continuously decreased for a long amount of time. This effect was more pronounced when the pH of the solution was initially around pH 2.5 after adding calcium carbonate. The apparent stabilization of pH if the pH did not change much for 15 min (<0.05) could in fact still be in progress to equilibrium, since it was found that the pH changed (decreased) by a significant amount if measured again after 6 hours. Sometimes, the difference was more 1 unit of pH. In method 1, there is active mixing while in method 2, there is only passive mixing due to diffusion. However, since the tube was shaken after adding calcite, it is assumed that sufficient mixing took place during the course of 5-7 hours. For the purpose of our research, the results of the second procedure will be used.

Experiment 2: GLDA present

The following procedure was followed to collect data points:

1. Approximately 30 ml acid was taken in a beaker. GLDA (trisodium salt) was added corresponding to 4.4 wt% of solution.
2. The solution was continuously stirred using a magnetic stirrer while a pH meter measured the pH.
3. Calcium carbonate was added in small amounts until the desired pH was reached and held stable for 10-15 minutes.
4. The beaker was emptied into a test tube.
5. Steps 1-4 were repeated until a desired number of pH points between pH 1.45 - 4.0 were collected.
6. The tubes were centrifuged at 4,500 rpm for 5 minutes.
7. The supernatants of the samples were serially diluted 1000 times.
8. The iron concentration was measured using atomic absorption spectroscopy technique.
9. For the case of GLDA:Fe(III) mole ratio - 2:1, GLDA was added corresponding to 8% of the solution weight and steps 1-8 were repeated.

In the case of acid with GLDA, it was seen that the pH stabilized quickly after adding calcium carbonate and remained so even hours later. Therefore, data points in the case of GLDA were collected using the above procedure.

Results

Figure 2.3 and **Table 2.2** show that in the case of GLDA, there is little or no precipitation. In the case of iron precipitation without GLDA, precipitation started around pH 1.5 and was essentially complete by a pH of 2.6 as shown in **Figure 2.1**. Also, it was seen that a small amount of Fe(III) (<100 ppm) remained in the acid even until a pH of 4.8. **Table 2.1** tabulates the iron in the solution vs measured pH. **Figure 2.2** gives a comparison of the results from the two procedures. They are more or less comparable but however, indicate a possible time dependence of precipitation. This could be investigated further.

Table 2.1 – Iron in solution as measured by atomic absorption spectroscopy w/o GLDA

pH	Fe(III)
0.84	11590.00
0.99	11030.00
1.21	11490
1.48	9582
1.55	11270
1.61	11110
1.63	10210
1.63	10450
1.94	7217
1.98	7762
2.14	4472
2.65	905
3.78	211.8
4.21	62
4.78	70.3

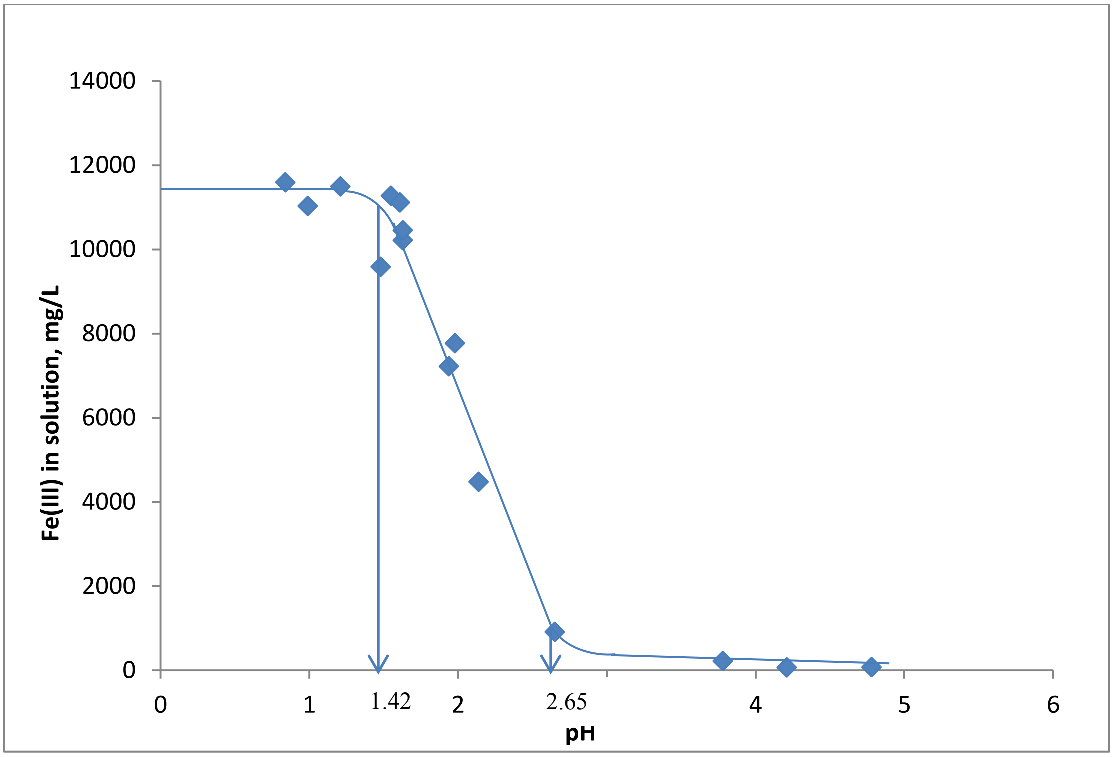

Figure 2.1 – Dissolved Fe(III) vs pH at room temperature

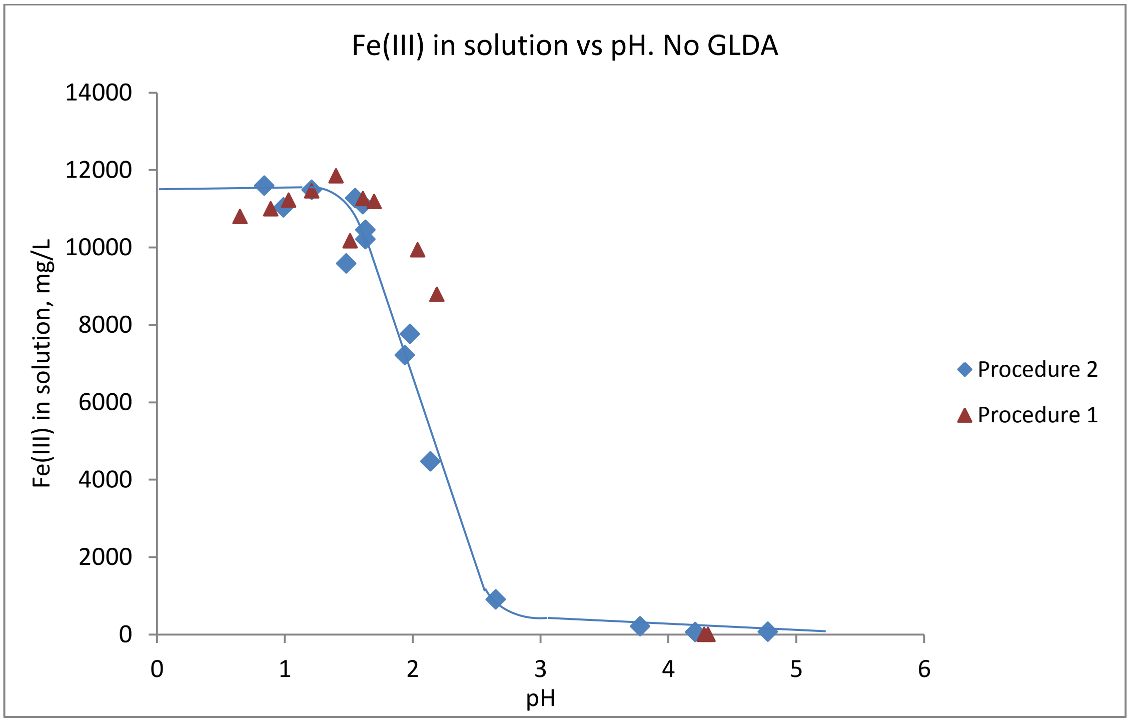

Figure 2.2 – Comparison of results for two procedures for dissolved iron vs pH

Table 2.2 – Iron as measured by atomic absorption spectroscopy w/ GLDA

pH	Fe(III)
0.86	11210
1.2	11800
1.59	11840
1.81	11180
1.99	11950
2.15	11610
2.32	11530
2.42	12340
2.54	11690
2.76	12320
2.92	12300
3.09	12350
3.31	11550
3.58	12400
4	11730
5.22	11700

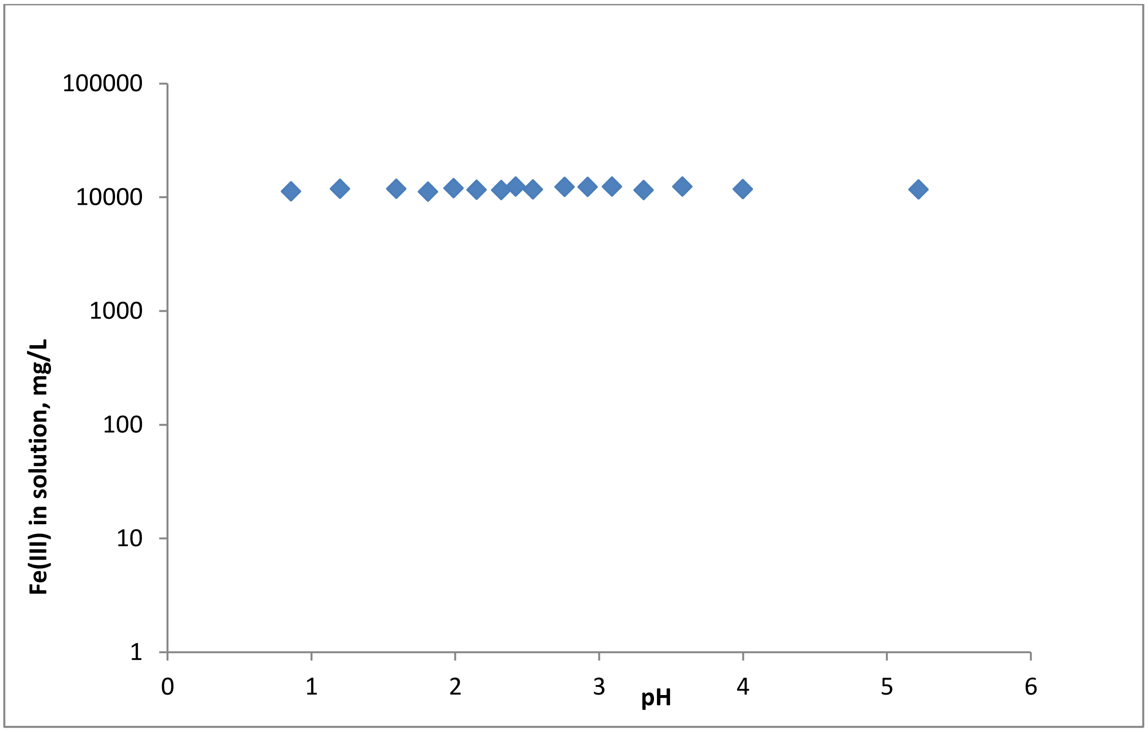

Figure 2.3 – Dissolved iron in solution vs pH with 8 wt% GLDA

CHAPTER III

PRELIMINARY STUDY: FORMATION DAMAGE AND EFFECT OF CHELATING AGENT (GLDA)

After doing a preliminary study on the precipitation of iron and the ability of GLDA to chelate iron at room temperature, coreflood experiments were conducted at 200°F and 300°F with Indiana limestone that had low permeability. It was found that almost all the iron precipitated in the formation when there was no GLDA present. This led to formation damage and the permeability reduced by a factor of 1.8. In the second experiment, GLDA was able to bring out 44-48 wt% of the iron that was entered the core. Further, there was a net stimulation (increase in permeability) of the core and the permeability increased by 22%. To understand the effect of temperature, experiments were also conducted at 300ºF with varying concentration of GLDA. To understand the changes in the core before and after the treatment, the cores were scanned using computer topography (CT Scan). Also, to understand the precipitation of iron within the core, the cores were cut into small cylindrical disks and analyzed for total iron content which will be analyzed in further chapters.

Experimental Procedure

Task 1: Find the permeability before stimulation

The core was saturated with 5% NaCl brine by flowing it through the core at a flow rate of 1 cc/min until the pressure drop across the core stabilized.

The core permeability was calculated using the Darcy equation for laminar flow:

$$k = \frac{L\mu}{\Delta PA} q$$

k : Permeability

q: Flow rate,

L: Length of the core

A: Cross-sectional area

ΔP: Pressure Drop

μ: Viscosity

The units in the above equation is valid for any consistent units. In laboratory units, the following equations hold:

$$K = 122.08 \frac{L\mu}{\Delta Pd} q$$

K: md, L: inches, d: diameter (inch^2), q : cm^3/sec, μ: cp, ΔP: psi

Task 2: Heating the core

°F while brine flowed through the core. The brine was flowed until the pressure drop re-stabilized to another value of pressure drop. The pressure drop falls down because the viscosity of the brine is lower as temperatures increases.

Task 3: Flowing acid through the core

After the pressure re-stabilized after heating, 0.5 PV of 5% NaCl was flowed through the core at 1cm^3/min. Immediately after starting the acid flow, core effluent were collected at a sampling rate of 2 ml per sample.

Task 4: Flushing the core with brine

After 0.5 PV of brine was injected through the core, the core was flushed with 5 wt% NaCl brine until the pressure drop re-stabilized. This final value of pressure drop was used to find the permeability after the acid treatment.

Post Experiment Treatment

Task 1: Dilute the samples

The samples were diluted by a factor of 100 to prepare them for analyzing iron and calcium concentrations using the atomic absorption spectroscopy technique. For this, 0.1 ml of the sample was added to 9.9 ml of de-ionized water.

Task 2: Find the concentration

Calcium and iron concentrations were measured using the AA spectroscopy using the flame technique.

Out of the two experiments, the first one was conducted using acid without adding any chelating agent. In the second experiment, GLDA as a chelating agent was added to make the acid solution 4.3 wt% GLDA.

The weight percentage was calculated by taking GLDA:Fe(III) mole ratio in solution ratio as 1:1.

MW of GLDA monosodium salt: 285

Concentration of iron in acid~ 10,000 mg/L -> 1000 mg/100 g of acid.

Density of 5 wt% acid ~ 1 gm/L

Number of moles of iron in 100 gms of acid = 1000 mg/56 gms

So, in 100 gms of acid:

1000 mg/56 gms moles of Fe = moles of GLDA (For equimolar ratio)

This is equal to 0.017857 moles of Fe = moles of GLDA

Taking into account MW of GLDA, this is = 5.0893 gms of GLDA

GLDA comes in 35.6 wt% solution

Actual GLDA solution required = 5.0893 gms/0.356 = 13.943 gms

Thus, 13.94 gms GLDA solution is required for 100 gms of acid

Thus,113.94 gms of total acid + GLDA contains 13.94 gms of GLDA.

13.94 gms of GLDA / (113.94 gms of solution) = **12.23 wt%**

Pure GLDA = 12.23*0.356 = 4.3 wt%

Results and Analysis

Pressure drop

Figure 3.1 and 3.2 show the pressure drop through the course of the experiment. The figures show the four parts of the experiment: saturating the core to find the porosity of the core, heating the core while passing brine, passing acid and then finally flushing the core with brine.

Experiment 1

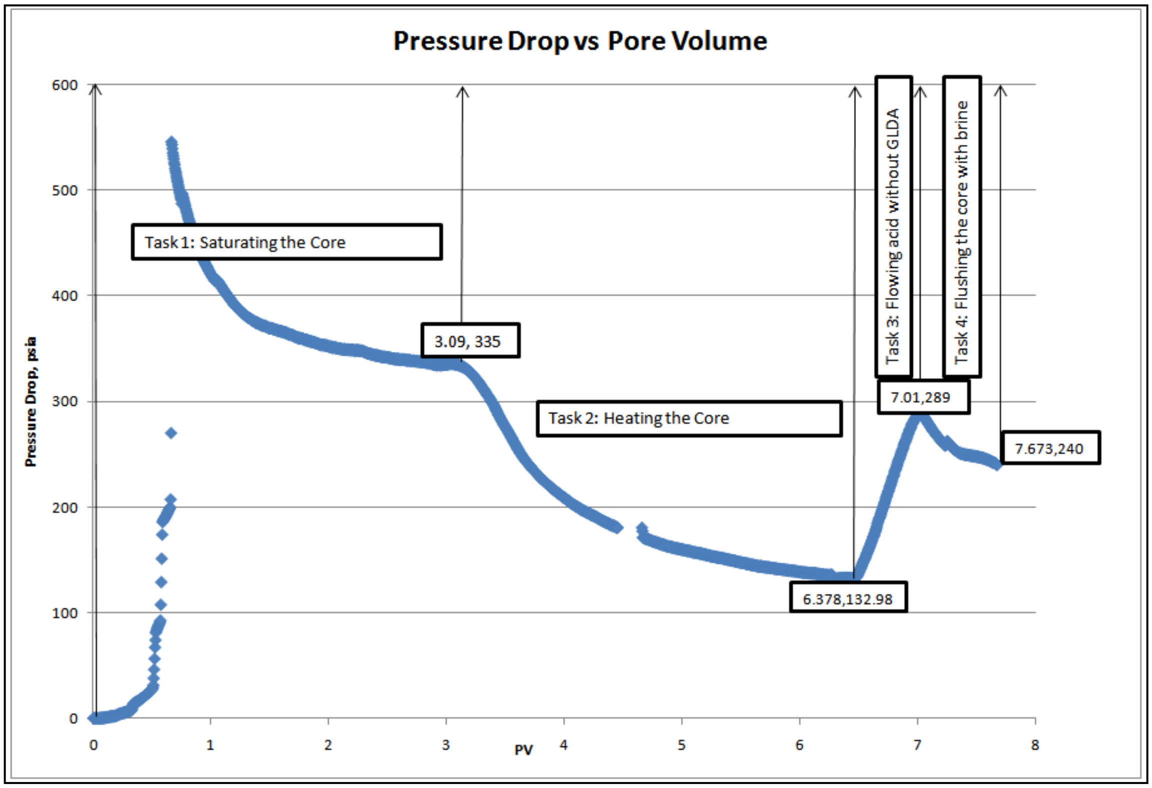

Figure 3.1 – Pressure drop across the core as a function of PV injected in the core in Indiana Limestone core with 5 wt% HCl containing 10,000 ppm of Fe(III) at 200°F

Experiment 2

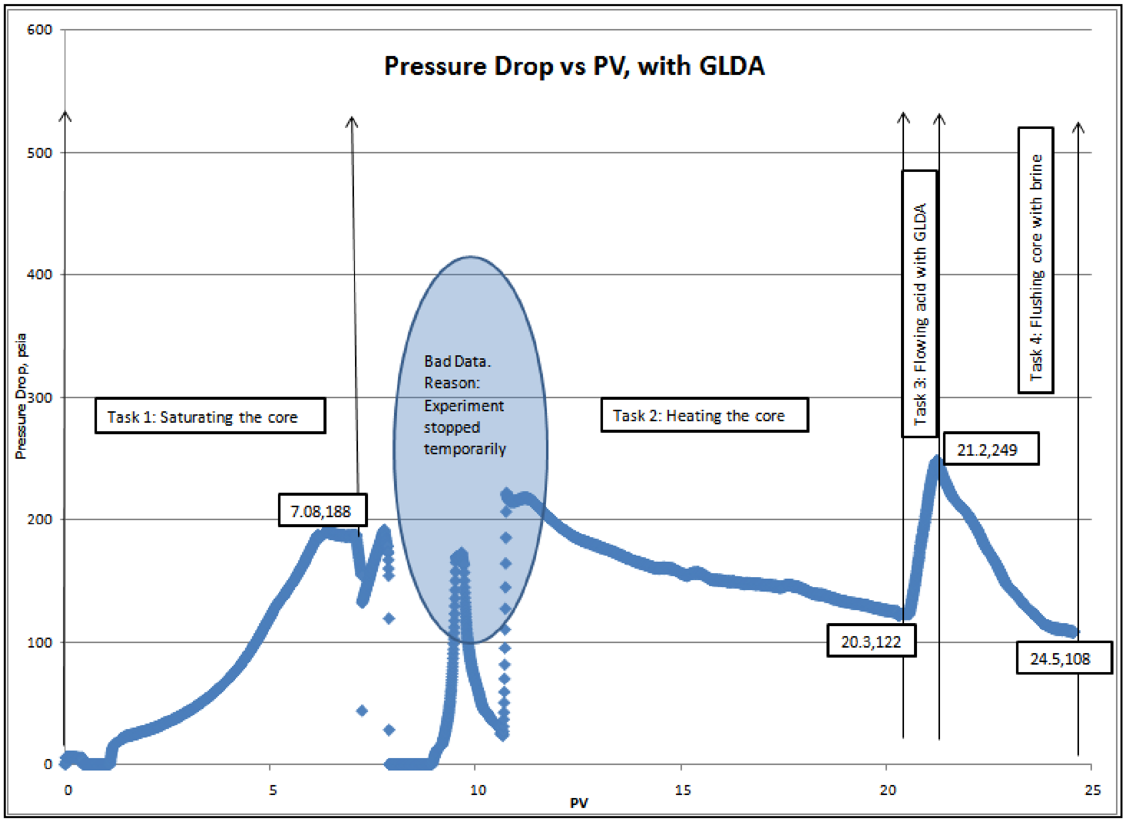

Figure 3.2 – As compared to pressure drop without chelating agent, the final pressure drop is lower after injection of acid

Pressure Drop Comparison

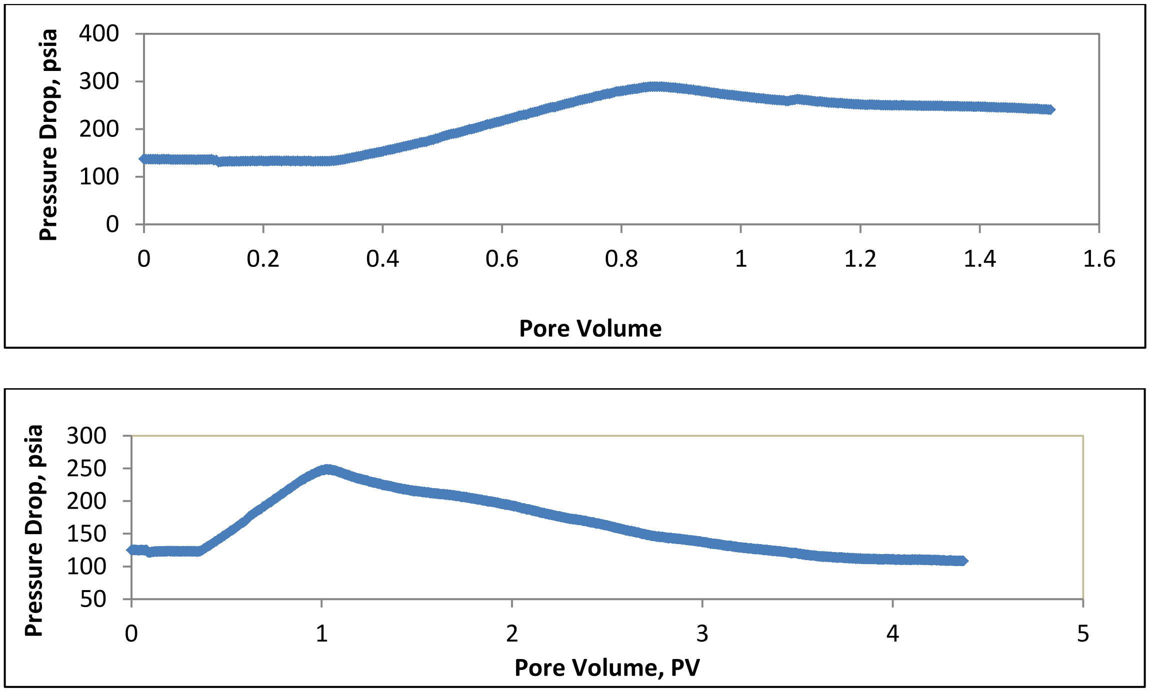

Figure 3.3 – The pressure drop shows a decrease in permeability in absence of GLDA in the upper figure and an increase in permeability in the case of presence of GLDA in the lower figure when 5 wt% HCl containing 10,000 ppm was injected at 200°F

Table 3.1 – Porosity, Permeability increase after the treatment

Experiment	**Porosity** **(Pore Volume, cc)**	**Initial** **Permeability (md)**	**k_2/k_1**
Core 1. w/o GLDA	12.68% (22.02 cc)	0.68	0.554
Core 2, w/ GLDA	09.99% (17.36 cc)	1.21	1.122

Figure 3.3 shows a comparison of pressure drop between the two experiments shows that there was a net increase in permeability in the case of acid containing GLDA. Also, the slope of the pressure drop is higher in experiment 1, not containing GLDA. That is, the pressure drop rose faster without GLDA. **Table 3.1** tabulates the increase in permeability and the initial porosity of the cores.

Iron content

Iron in the samples was measured by atomic absorption spectroscopy using flame technique. The iron concentration was plotted against the core effluent collected in terms of PV of the core. The total iron that came out was found by integrating the curve and finding the area under the curve. The following formula was used to convert from pore volume to actual iron weight that exited the core:

$$Total\ iron\ coming\ out\ (mg) =$$

$$(Area\ under\ the\ curve)\left(in\ \frac{mg.PV}{L}\right) * \frac{Actual\ Pore\ Volume\ (in\ cc)}{PV} * \frac{1\ L}{1000\ cc}$$

Total iron in = PV* (Actual Pore Volume)/1000*10000 mg

Experiment 1

This experiment was conducted without any GLDA in the acid.

Method 1

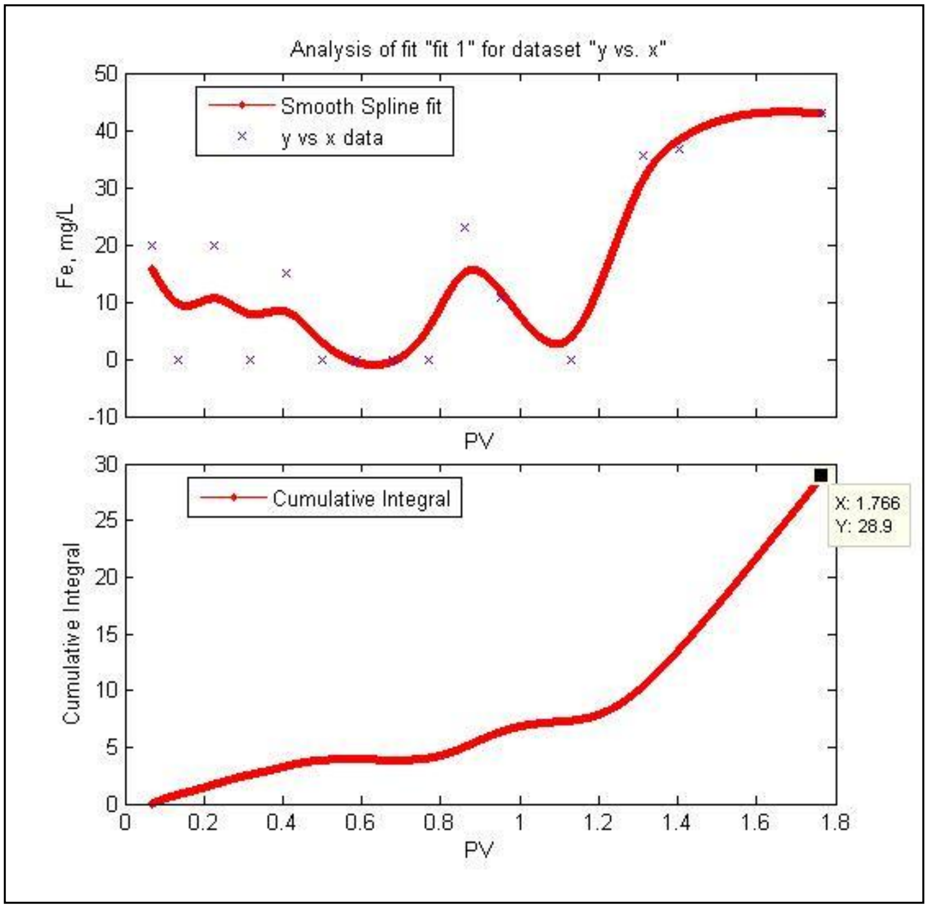

Figure 3.4 – Iron concentration as a function of PV received after the start of treatment and a cumulative integral of total iron that came out without GLDA

Figure 3.4 shows the data fitted using smoothing spline method.

Integral = 28.9

Weight of iron exited = 28.9*22.02/1000 mg = .6364 mg

Total iron in = 0.5*22.02/1000*10000*0.78 = 126.5 mg

Method 2

This method used the interpolant method, which is similar to the trapezoidal way of calculating the integral **(Figure 3.5)**. We see that the integral is almost the same as before, with the difference being less than 2.1%

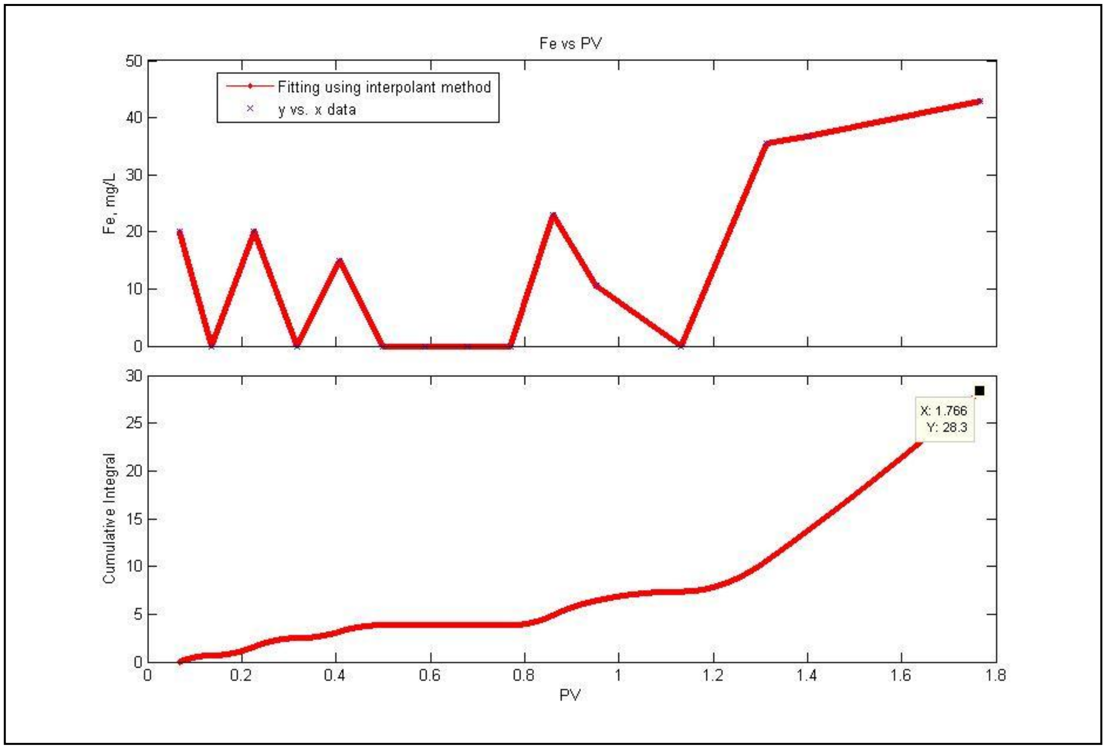

Figure 3.5 – Iron concentration as a function of PV received after the start of treatment (without GLDA) and a cumulative integral of total iron that came out

Experiment 2

This experiment was conducted with GLDA added to the acid.

<u>Method 1</u>

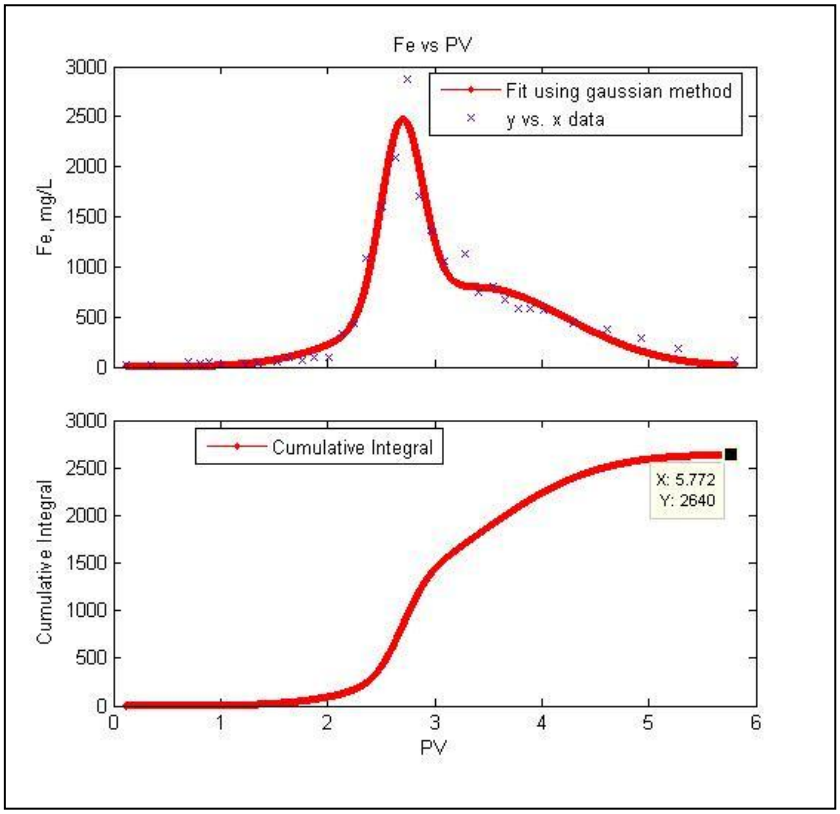

Figure 3.6 – Iron concentration as a function of PV received after the start of treatment (with GLDA) and a cumulative integral of total iron that came out

<u>Method 2</u>

This method used the interpolant method, which is similar to the trapezoidal way of calculating the integral **(Figure 3.7)**. We see that there is little difference compared to the smoothing spline method **(Figure 3.6)**, with the difference around 4.6%.

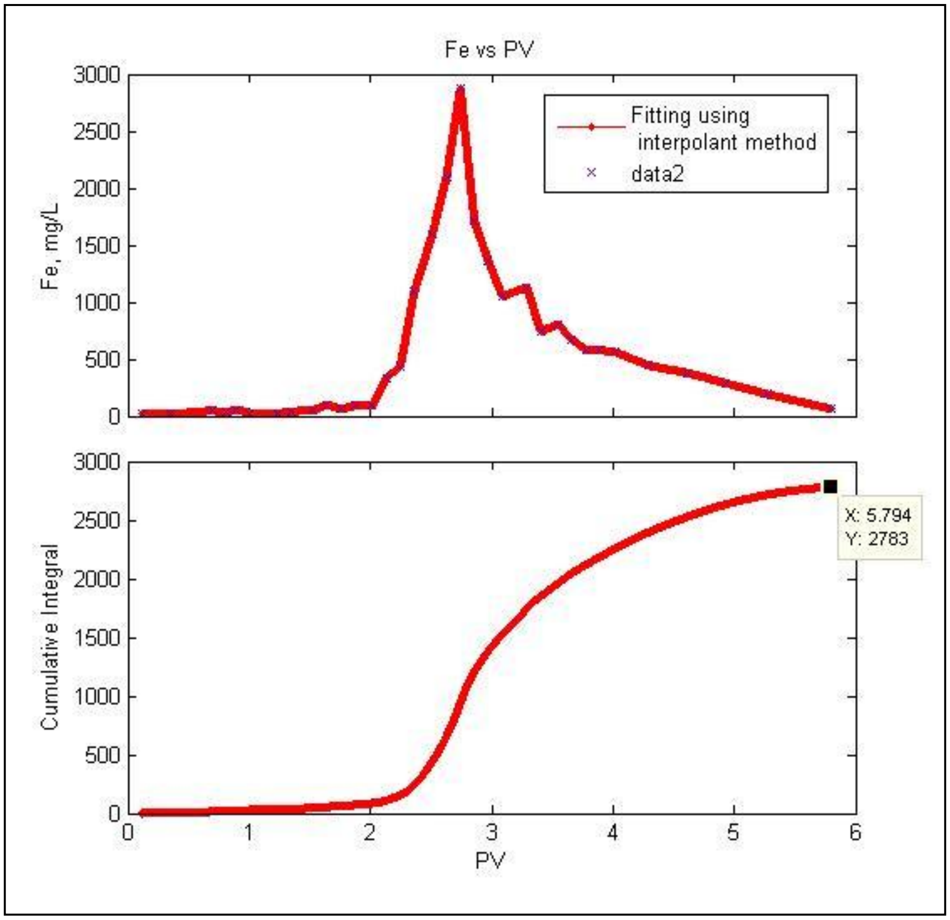

Figure 3.7 – Iron concentration as a function of PV received after the start of treatment (with 1:1 GLDA) and a cumulative integral of total iron that came out

Integral = 2640 (From method 1)

Total iron that exited = 2783*17.36/1000= 46 mg

Total iron that went in = 0.5*17.36/1000*10000*0.88 (because 78% of solution was original acid with 10,000 ppm Fe) mg/L = 76.82

Comparison between experiment 1 and 2:

Table 3.2- Comparison of iron coming out of the core between with and without GLDA

Experiment/Core	Iron in, mg	Iron out, mg	Percentage out
Core 1 w/o GLDA	126.5	.6364	0.05%
Core 2 w/ GLDA	76.82	46	59%

Table 3.2 shows that almost all the iron precipitated in the solution in the case of acid being pumped without any GLDA. In the case of acid being pumped with 4.35 wt% GLDA, almost half the acid was recovered.

pH of effluent samples

The pH of the samples collected was measured using an Oakton pH 510 double junction pH meter. **Figure 3.8** shows the variation in pH.

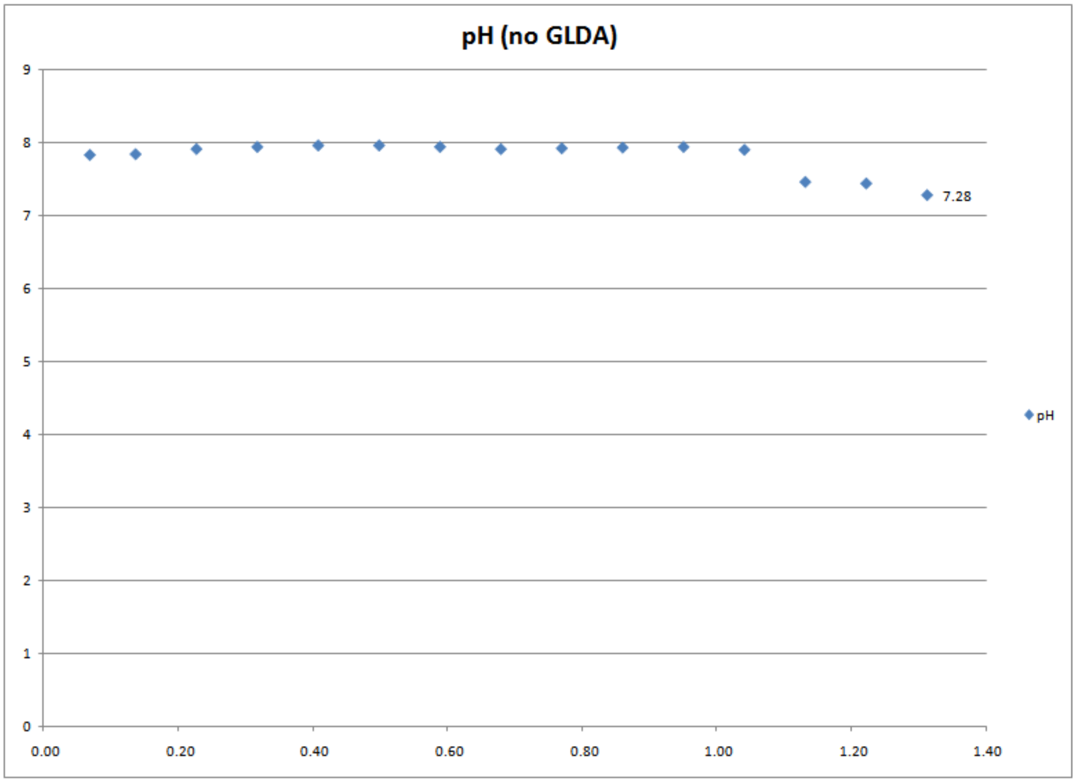

Figure 3.8 – pH remains nearly constant (without GLDA) throughout the samples that were collected. A notable thing is the decrease towards the end

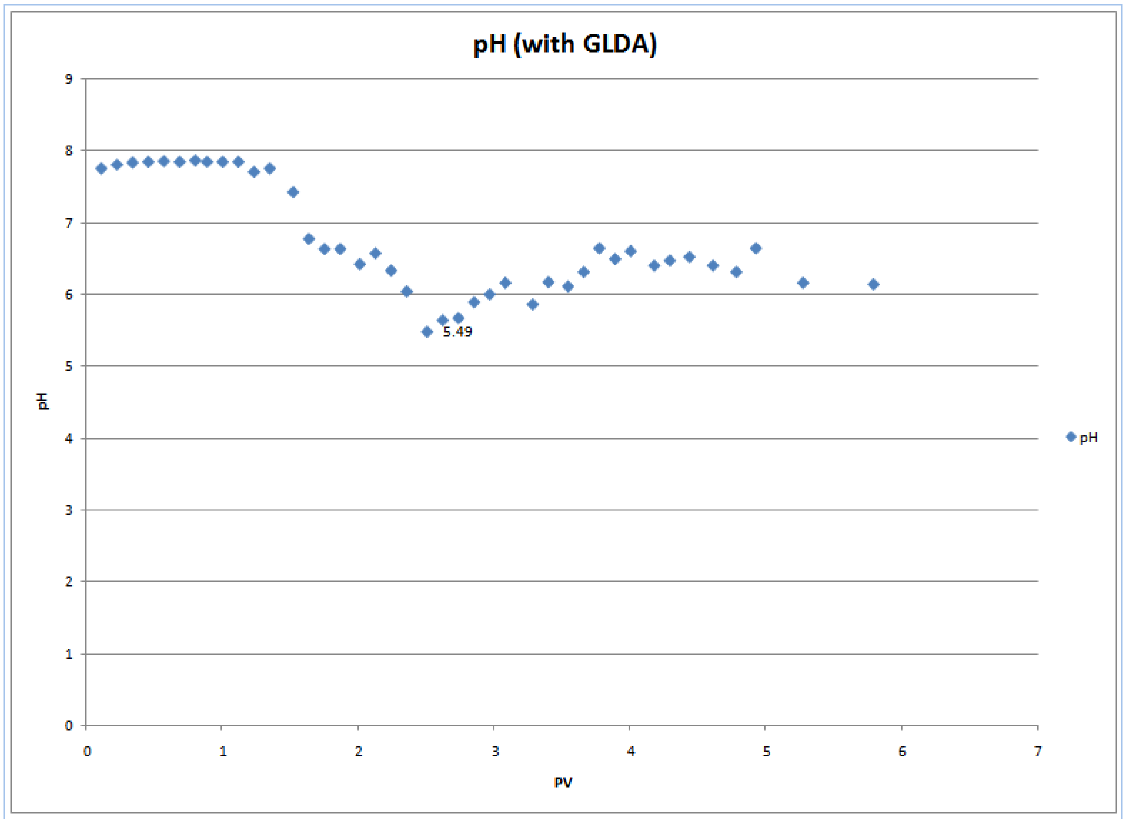

Figure 3.9 – The lowest pH (with GLDA) was seen when nearly 3 pore volumes were collected after the start of the treatment

As we can see from **Figure 3.9**, the pH in the case of no GLDA shows a nearly constant pH and indicates that the acid was spent completely and also a dilution effect due to flushing by brine.

In the case of acid pumped with GLDA, there is a drop in pH and then it goes up again. This difference in pH in the case of GLDA could be attributed to incompletely dissociated GLDA.

The tasks procedures followed above form a basis for the experiments in the remainder of the thesis. However, for calculating the iron recovery, the iron concentration will be multiplied by the sample volume.

CHAPTER IV

PART I – UNDERSTANDING THE DAMAGE CAUSED BY IRON – EFFECT OF HIGHER ACID CONCENTRATION

In this study, the effect of acid concentration on stimulation and iron precipitation distribution was studied. Indiana Limestone cores of approximately 1 md permeability were used for these experiments. Half a pore volume of 10 wt% HCl, 10,000 ppm Fe(III) was flowed through the core at 200°F as compared to the 5 wt% HCl in the previous experiments. Before and after this treatment, 5 wt% NaCl brine was used to saturate the cores.

To find the amount of iron in the cores, the pieces of the core were dissolved in a known of volume of HCl solution.

The solution was then diluted and analyzed using ICP-MS. Since the lengths of the cores were unequal, the value of total iron in the pieces was normalized by dividing by the length of piece of the core. This gave a value in mg/inch of the core. These values were then compared by plotting them against the distance from the inlet of the core.

It was observed that nearly an inch of the core got cut away due to the cutting process.

In this study, two experiments were conducted. In the first experiment, 10 wt% HCl was flowed containing 10,000 ppm of acid without the presence of GLDA. In the second experiment, GLDA was added totaling to 8% of the acid solution (25 wt% GLDA solution containing 35.6 wt% GLDA), which is detailed in Chapter X.

The following are the details of the experiment:

Core used: Indiana Limestone

Dry Weight: 380 gms

Wet Weight: 405.18 gms

Pore Volume = Wet Weight – Dry Weight = 25.17 cc

Permeability: 1.4 md at 1500 psi overburden pressure (233 psi pressure drop across the core at 1 cc/min with an overburden pressure of 1500 psi)

For the treatment, the core was initially saturated with 5 wt% NaCl brine until the pressure was stabilized. The pore volume was measured and permeability was noted by measuring the pressure drop. The core was then heated using a heat jacked at 200ºF until the pressure stabilized. Then, half a pore volume of 10 wt% HCl with 10,000 ppm Fe was flowed through the core at 200ºF.

Finally, core effluents were collected in sample test tubes and measured for iron concentration.

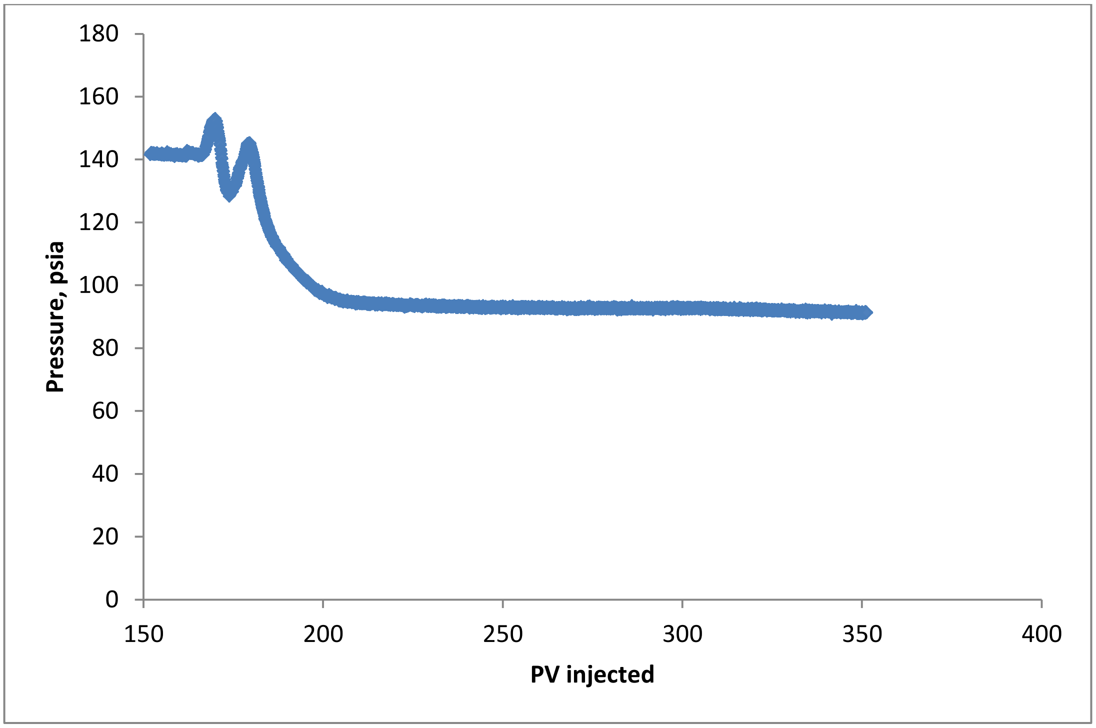

Figure 4.1 – Pressure drop across the core during and after the treatment with 10 wt% HCl and 10,000 ppm of Fe at 200°F

Figure 4.1 shows that the ratio of the final to initial permeability is nearly 1.55. This means that the permeability increased by nearly 55% despite the damage due to iron precipitation in the core.

The core effluent from the core showed little or no iron indicating that all the iron got deposited in the core.

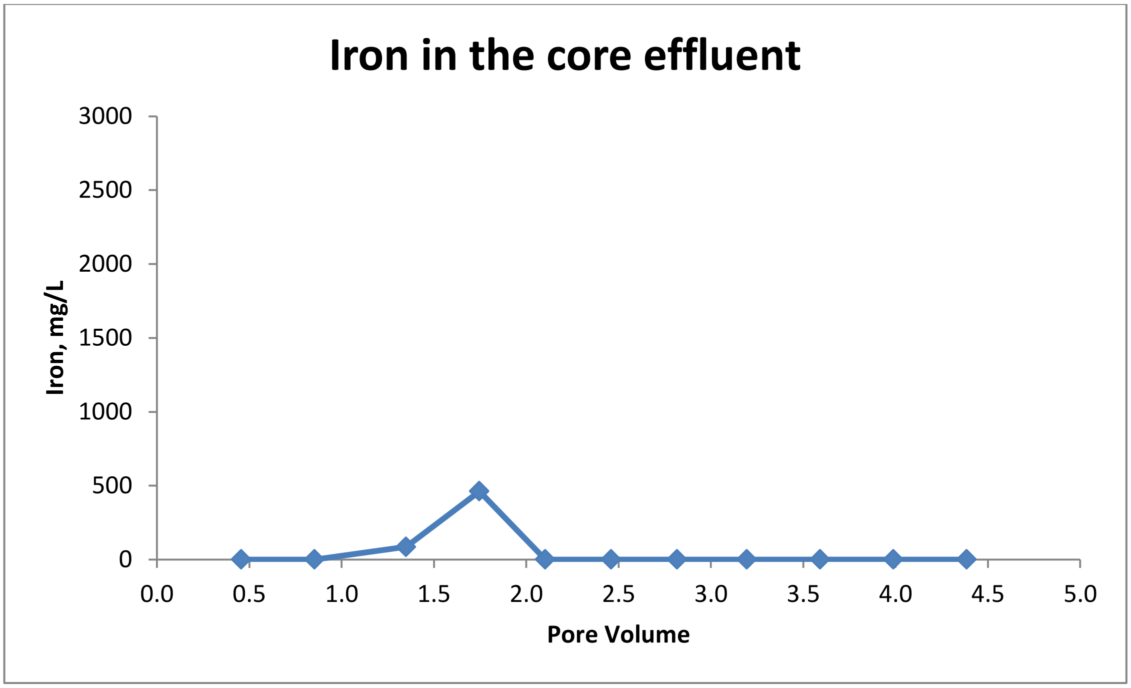

Figure 4.2 – Iron in the core effluent shows that almost all the iron was precipitated in the core

Figure 4.2 shows that most of the iron was precipitated in the core. The above corresponds to just nearly 5 mg of iron in the core effluent, or just under 4.2% of the iron injected.

To understand the deposition of iron in the core, the core was cut and iron was measured in each piece after dissolving it in hydrochloric acid.

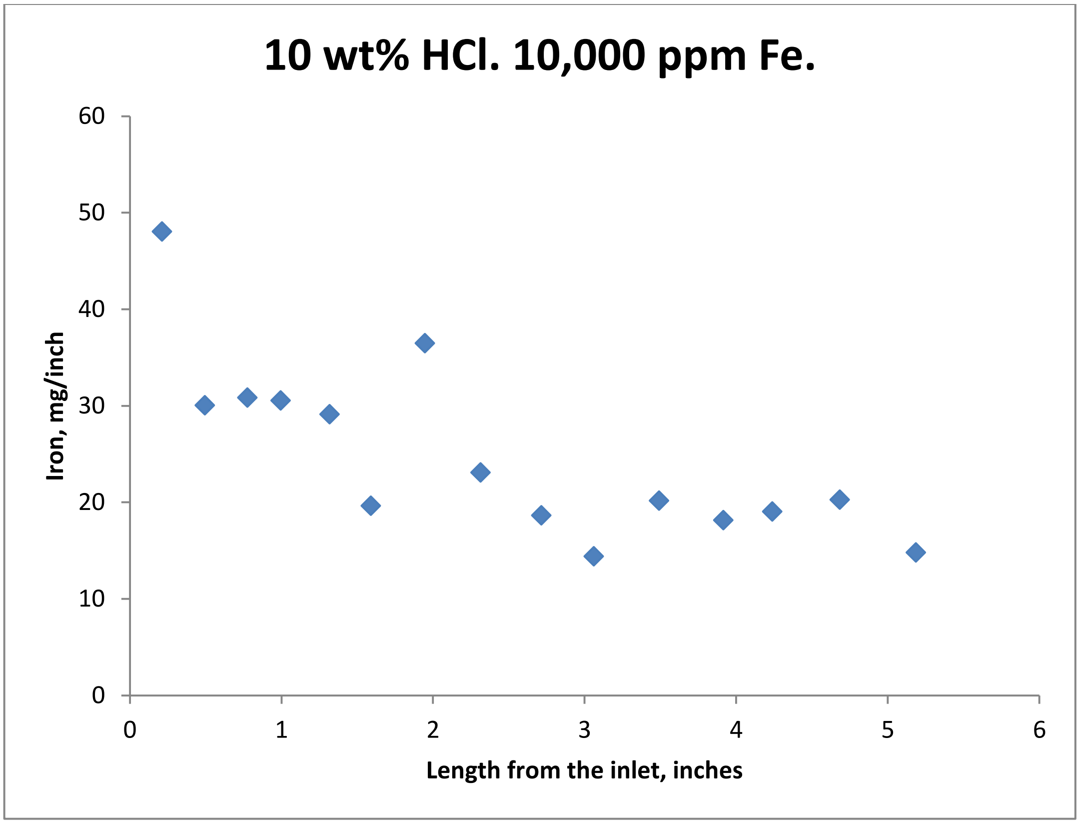

Figure 4.3 – Deposition of iron in the core as a function of length

Figure 4.3 shows that there is a significant amount of iron that got deposited at the face of the core.

CT scan of the core was done to understand the formation of wormhole in the core. **Figure 4.4** shows significant formation of wormholes in the core. This could be a possible reason that explains that there was no net damage to the core. Thus, it can be seen that the formation of wormhole by 10 wt% HCl at 200ºF offsets the damage caused by pore plugging by iron precipitation in the core.

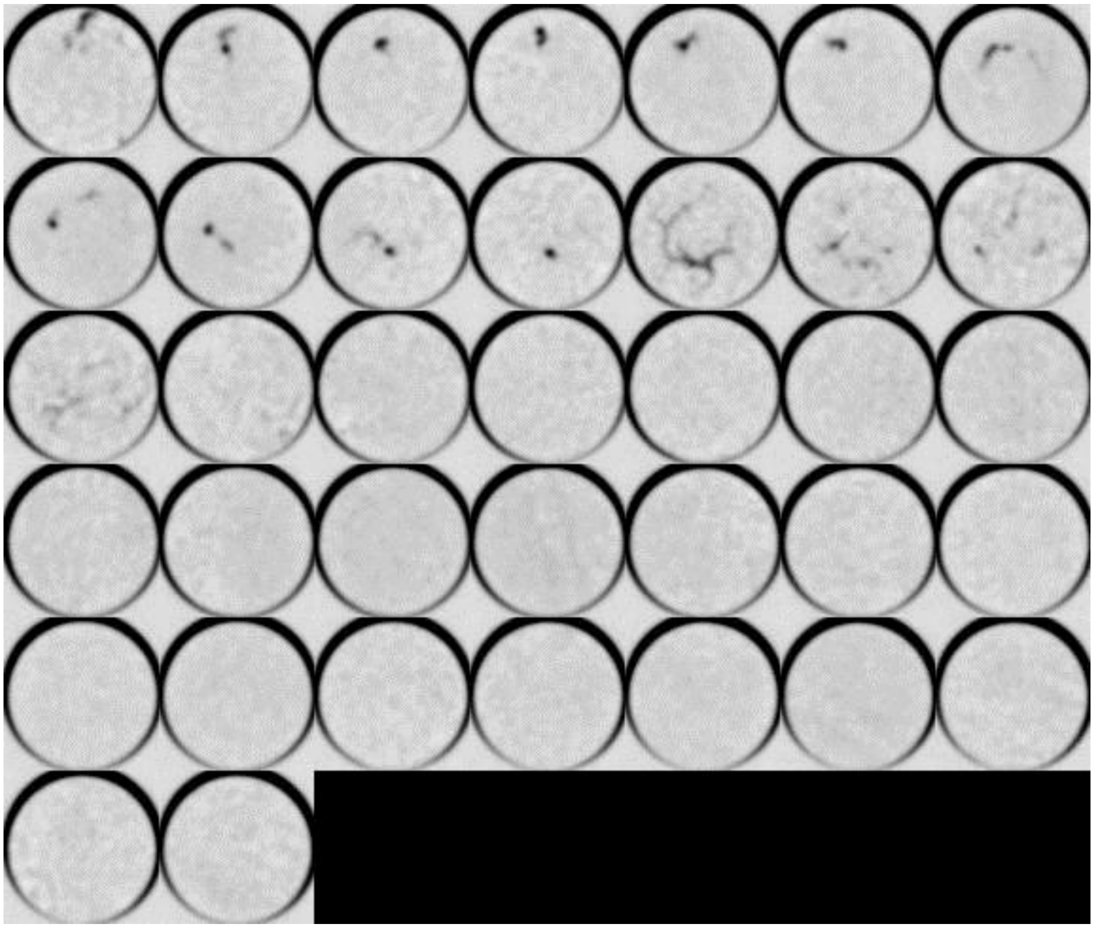

Fig. 4.4 – The CT scan shows formation of wormholes in the core

Figure 4.5 and **4.6** show the images of the core inlet face after the treatment.

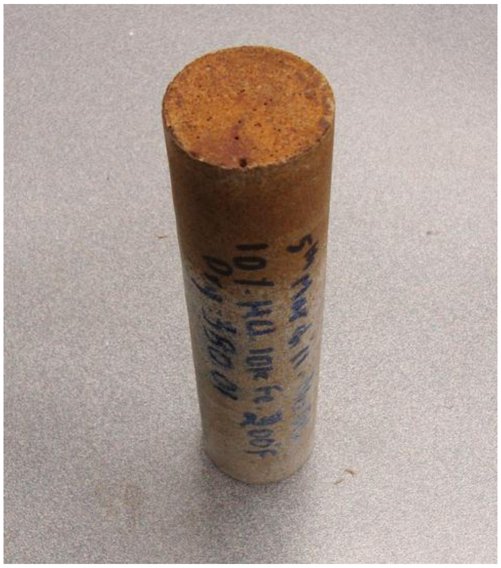

Figure 4.5 – The core shows significant iron deposit on the top as well as the sides

Figure 4.6 – Inlet face of the core shows the formation of wormhole

CHAPTER V

UNDERSTANDING EFFECT OF TEMPERATURE ON IRON PRECIPITATION IN THE CORE WITHOUT CHELANT

In this study, the effect of temperature on the core stimulation and iron distribution was studied. Indiana Limestone cores of approximately 1 md permeability were used for these experiments. Half a pore volume of 5 wt% HCl, 10,000 ppm Fe(III) was flowed through the core at 300ºF. Before and after this treatment, 5% NaCl brine was used to saturate the cores.

To find the amount of iron in the cores, the pieces of the core were dissolved in a known of volume of HCl solution. Typically, the solution was made using 100 ml of water and 40-60 ml of 36.5 wt% HCl. However, the exact the concentration of HCl was immaterial. To find the amount of iron in the sample, only the concentration and the volume of the sample is required.

The solution was then diluted and analyzed using ICP-MS. Since the lengths of the cores were unequal, the value of total iron in the pieces was normalized by dividing by the length of piece of the core. This gave a value in mg/inch of the core. These values were then compared by plotting them against the distance from the inlet of the core.

It was observed that nearly an inch of the core got cut away due to the cutting process.

The following are the experiment details:

Core: Indiana Limestone

Dry Weight: 388 gms

Wet Weight = 413 gms

Pore Volume = Wet Weight – Dry Weight = 25.02 cc

The core was saturated by flowing brine through the core at a constant flow rate for 3-4 hours until the pressure was stabilized. The permeability was also found in a similar fashion. The pressure drop was 215 psi at 1 cc/min at an overburden of 1500 psi. The calculated permeability was thus 1.524 md. For the treatment, 13 ml of acid was flowed at 1 cc/min at 300ºF. The pressure drop was recorded against time. **Figure 5.1** shows a graph of pressure drop during the treatment.

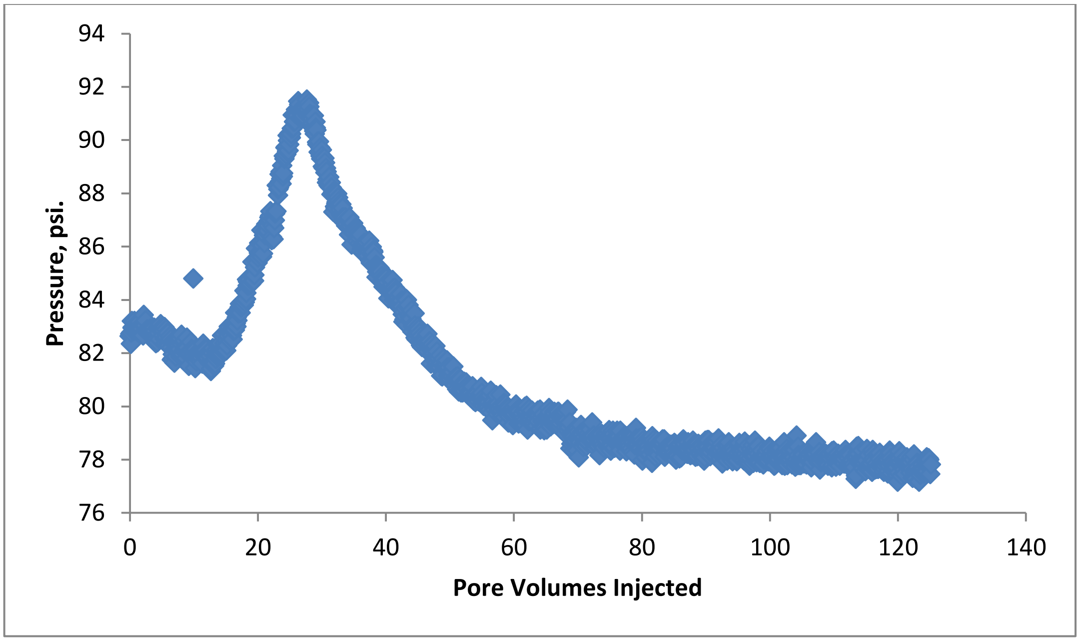

Figure 5.1 – Pressure drop against pore volumes of fluid injected shows a lower pressure drop after the treatment when 5 wt% HCl containing 10,000 ppm Fe(III) at 300°F was injected

The pressure drop shows that the permeability improves during the treatment. The permeability after the treatment is about 5% higher than before. Even though there was a lot of iron deposited in the core, stimulation due to higher reaction rates at higher temperature compensated for the damage done to the core due to iron precipitation. As compared to the higher temperature, at 200ºF, it was observed that the permeability damage was considerable: the final permeability being about 40% lower than the initial permeability. **Figure 5.2** shows the distribution of iron in the core after the treatment at 300ºF. **Figure 5.3** shows the distribution at 200ºF as in Chapter IV containing less iron. This comparison is error prone due to iron getting washed off during cutting, difference in condition of the saw (more or less rust) used for cutting. **Table 5.1** tabulates the results.

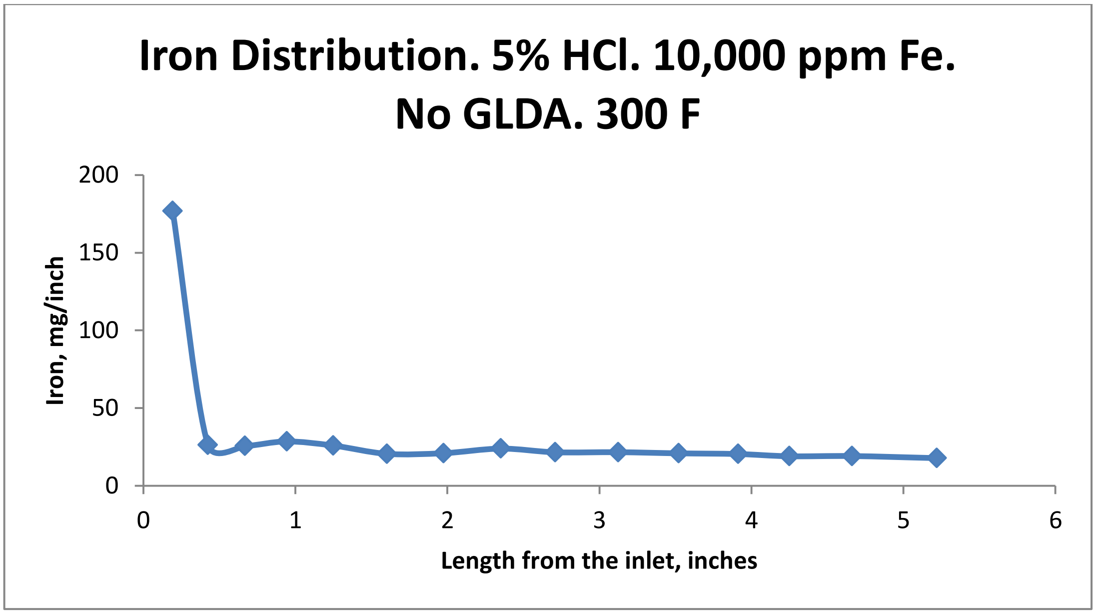

Figure 5.2 – Iron distribution in the core shows a very high iron deposition at the face

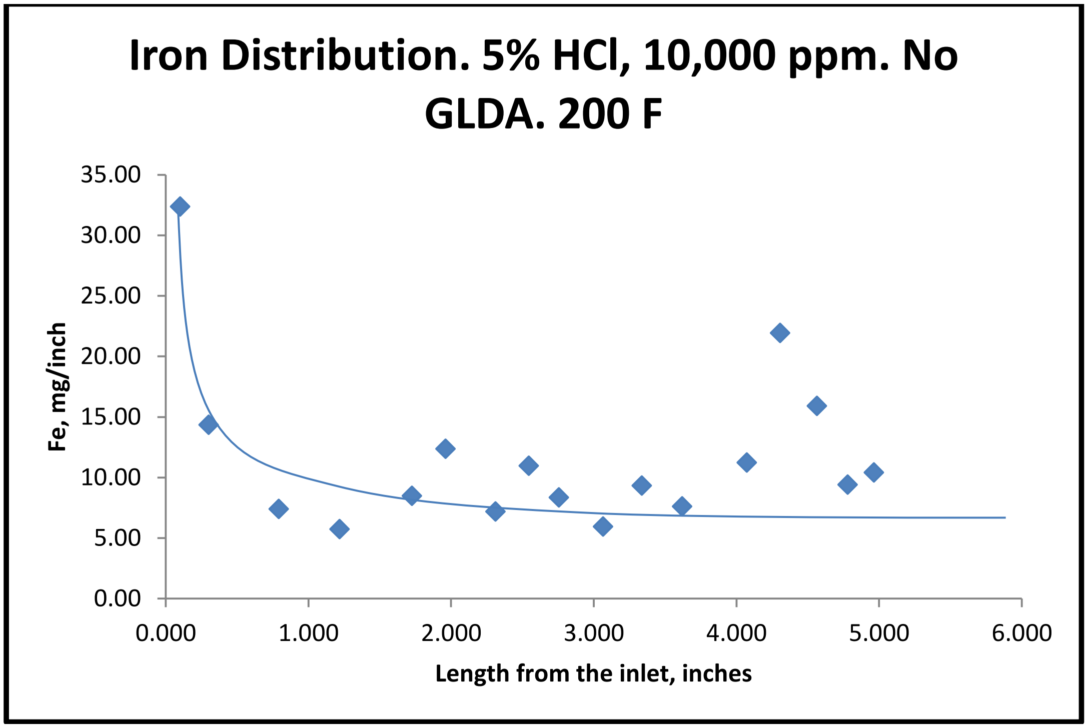

Figure 5.3 –Iron deposition is lower at 200ºF than at 300ºF

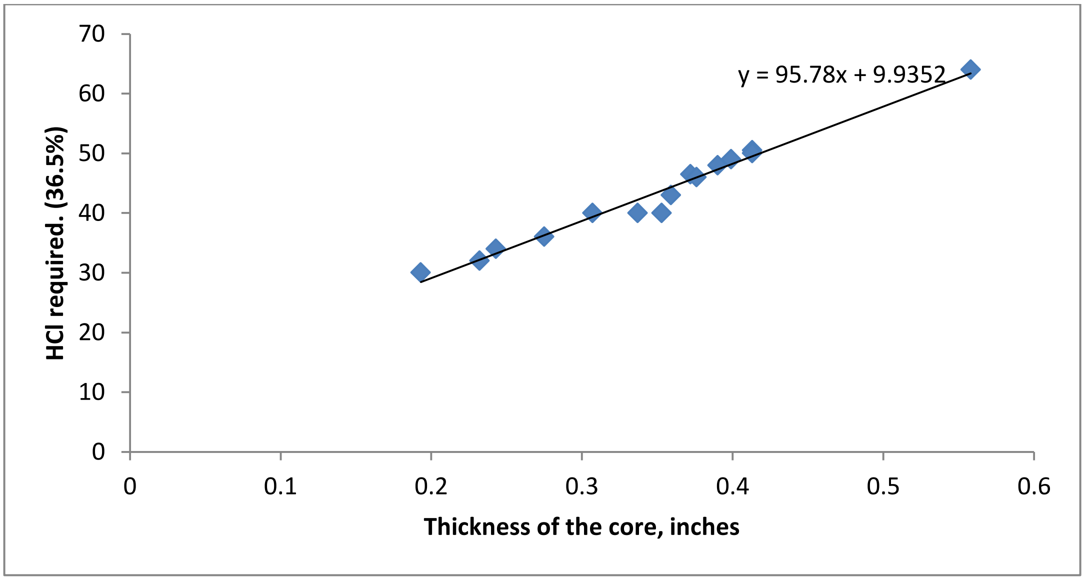

Figure 5.4 – The above graph shows the amount of HCl (36.5%) required to completely dissolve the core using experimental data

Table 5.1 – This table shows the calculations done to find the concentration of iron in the pieces of the core

Piece Number	Length (inches)	Length (inches)	Predicted HCl	Actual amount of HCl (ml)	Dilution Factor	Measured Iron (mg/L)	Actual Iron (mg/L)	Iron Content (mg)	Iron/Length (mg/L)
1	0.193	0.193	30.13	30	10	113.7	1137	34.11	176.735751
2	0.232	0.425	33.60	32	10	18.99	189.9	6.0768	26.1931034
3	0.243	0.668	34.57	34	10	18.28	182.8	6.2152	25.5769547
4	0.275	0.943	37.41	36	10	21.79	217.9	7.8444	28.5250909
5	0.307	1.25	40.25	40	10	19.86	198.6	7.944	25.8762215
6	0.353	1.603	44.34	40	10	18.14	181.4	7.256	20.5552408
7	0.372	1.975	46.02	46.5	10	16.77	167.7	7.79805	20.9625
8	0.376	2.351	46.38	46	10	19.54	195.4	8.9884	23.9053191
9	0.359	2.71	44.87	43	10	18	180	7.74	21.5598886
10	0.413	3.123	49.66	50.5	10	17.67	176.7	8.92335	21.6061743
11	0.399	3.522	48.42	49	10	17	170	8.33	20.877193
12	0.39	3.912	47.62	48	10	16.6	166	7.968	20.4307692
13	0.337	4.249	42.92	40	10	16	160	6.4	18.9910979
14	0.413	4.662	49.66	50	10	15.8	158	7.9	19.1283293
15	0.558	5.22	62.54	64	10	15.51	155.1	9.9264	17.7892473

The column 'Predicted HCl' in **Table 5.1** shows the amount of HCl that must be put in to dissolve the entire piece of core. This value was found empirically using the previous experiments data by linearly regressing the amount of HCl required to dissolve against the thickness of the core. **Figure 5.4** shows the regressed relation. To understand the structure of the core, CT scans of the cores were done. These scans show the wormhole formation in the core. **Figure 5.5** shows the CT scan of the core. **Figure 5.6 and 5.7** shows pictures of the inlet face after the treatment.

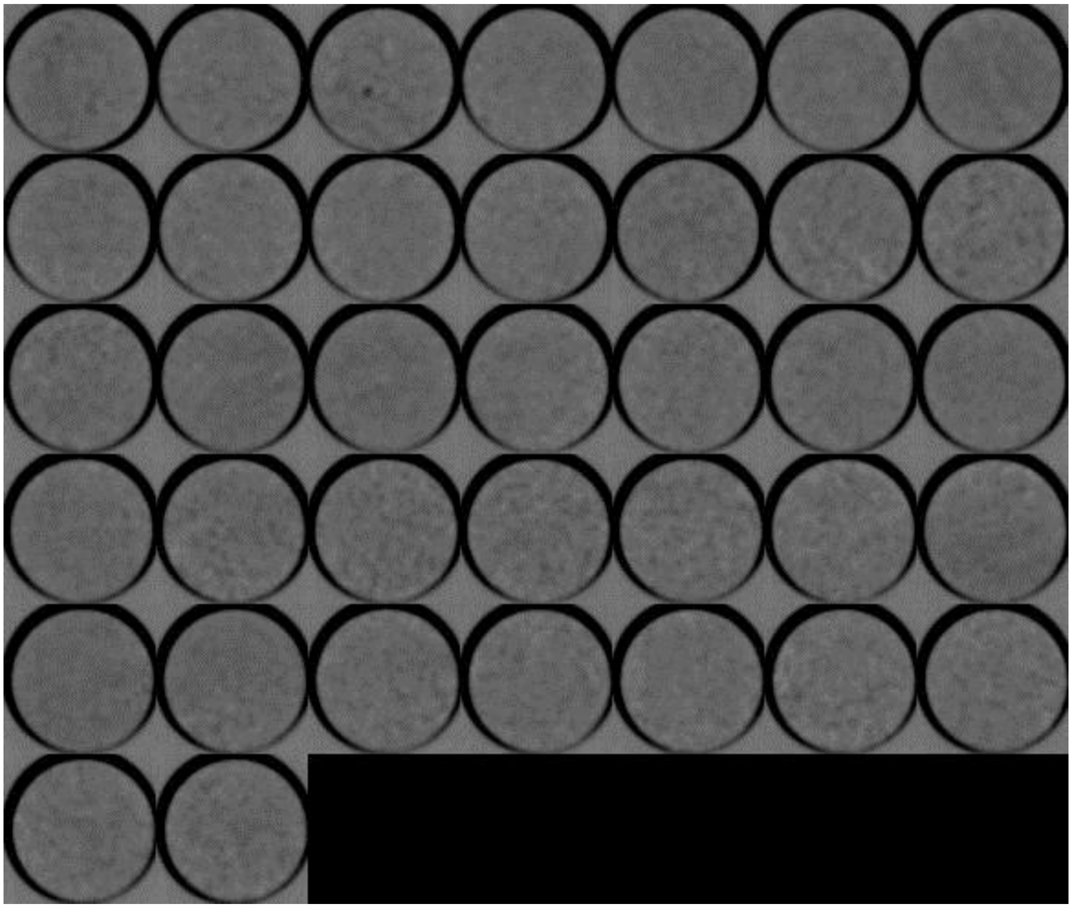

Figure 5.5 – CT scan of the core shows little formation of significant wormholes

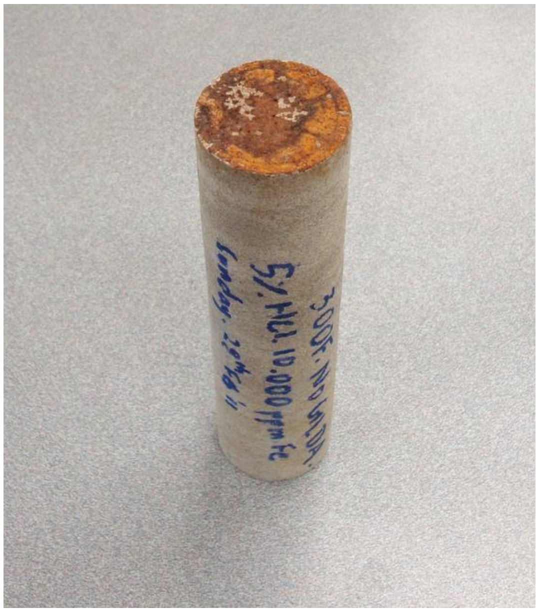

Figure 5.6 – The core after treatment. The red inlet face shows the iron deposition on the core face

Figure 5.7 – The top view of the core in detail shows formation of small wormhole openings that the CT scan failed to capture

As we see in pressure drop graphs, there was no net damage caused to the core by the injection of 5% HCl containing 10,000 ppm of Fe at 300ºF. However, we know that iron causes significant damage to the core. Therefore, to understand the reduction in stimulation caused by iron at 300ºF, an experiment was undertaken with the same experiment description but without putting iron with the 5% acid at 300ºF. **Figure 5.8** shows the pressure drop in the during the stimulation treatment without the presence of iron.

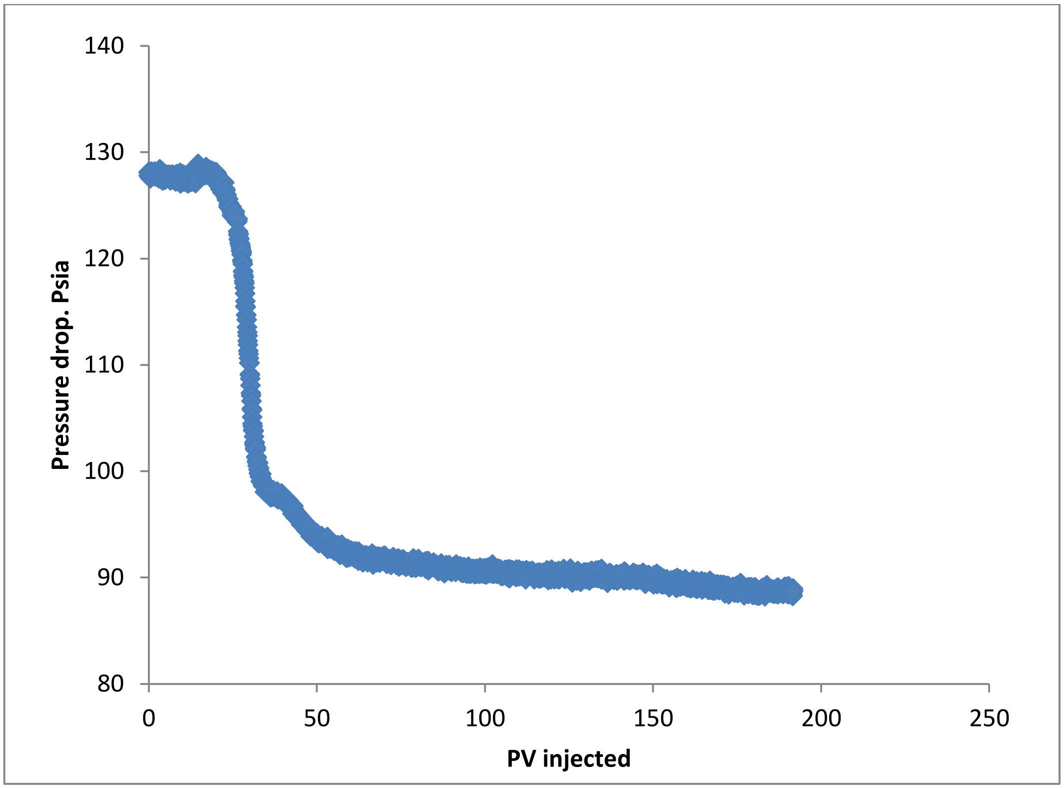

Figure 5.8: The above figure shows the pressure drop across the core when 5% HCl is injected at 300ºF with no iron

Figure 5.8 shows that there is a significant drop in the pressure drop across the core. The final permeability is about 45% percent higher than the original permeability.

Thus, by pumping in iron dissolved with the acid, the stimulation effect was reduced by about 37% measured in terms of permeability improvement.

CHAPTER VI

UNDERSTANDING THE DEPENDENCE OF PERMEABILITY ON IRON PRECIPITATION IN THE CORE

To understand the precipitation of iron better in the core, it is important to estimate the distribution of iron within the core. For this purpose, the core cut along its length into small pieces and the amount of iron was found in each one of them. Three different cores were taken for experiment: Indiana Limestone, Pink Desert core and an Austin Chalk core. The permeability of these cores were approximately 1md, 60md and 5 md respectively. Half a pore volume of 5 wt% HCl, 10,000 ppm Fe(III) were flowed through these cores in seperature coreflood experiments. Before and after this treatment, 5 wt% NaCl brine was used to saturate the cores.

To find the amount of iron in the cores, the pieces of the core were dissolved in a known of volume of HCl solution. Typically, the solution was made using 100 ml of water and 40-60 ml of 36.5 wt% HCl. However, the exact the concentration of HCl was immaterial since only the volume of the acid solution is required, which multiplied by iron concentration gives the total iron in the solution.

The solution was then diluted and analyzed in the atomic absorption unit and using ICP-MS. Since the lengths of the cores were unequal, the value of total iron in the pieces was normalized by dividing by the length of piece of the core. This gave a value in mg/inch of the core. These values were then compared by plotting them against the distance from the inlet of the core. It was observed that nearly an inch of the core got cut away due to the cutting process.

Indiana Limestone Core

Average Permeability: 1 md

Pore Volume: ~ 22 cm^3

Figure 6.1 to 6.4 shows the photographs of the cut pieces of the core. **Figure 6.1** and **6.2** show the core photographs in which no GLDA was used. **Figure 6.3 and 6.4** show the cores in which GLDA was used in 2:1 GLDA:Fe(III) molar ratio.

Figure 6.1- Slices of Indiana Limestone core in which no GLDA was flowed. The consecutive inlet faces of the core are shown starting from the top left and continuing on the right

Figure 6.2 – Slices of Indiana Limestone core in which no GLDA was flowed stacked together and the length measured using a vernier caliper. The main scale of the vernier caliper shows 5 inches

Figure 6.3 –Slices of Indiana Limestone core in which GLDA (2:1 concentration) was flowed with acid at 300°F

Figure 6.4 – Slices of Indiana Limestone core in which GLDA (2:1 concentration) was flowed stacked together

Table 6.1 – Data for the cut core (Indiana Limestone). No GLDA was flowed with the acid at 200ºF

	Thickness of the core (inches)	Length From Inlet (inches)	Acid Volume (100 ml DI water)	Fe Concentration (mg/L)	Total Iron (mg)	Iron per Unit Length (mg/inch)
1	0.185	4.966	130.0	14.820	1.927	10.41
2	0.215	4.781	130.0	15.560	2.023	9.41
3	0.258	4.566	163.0	25.150	4.099	15.89
4	0.235	4.308	158.0	32.630	5.156	21.94
5	0.452	4.073	164.0	30.920	5.071	11.22
6	0.283	3.621	140.0	15.370	2.152	7.60
7	0.271	3.338	145.0	17.440	2.529	9.33
8	0.310	3.067	129.5	14.220	1.841	5.94
9	0.212	2.757	140.0	12.650	1.771	8.35
10	0.233	2.545	140.0	18.250	2.555	10.97
11	0.350	2.312	140.0	17.960	2.514	7.18
12	0.235	1.962	140.0	20.740	2.904	12.36
13	0.508	1.727	160.0	26.940	4.310	8.49
14	0.427	1.219	130.0	18.850	2.451	5.74
15	0.491	0.792	139.5	26.060	3.635	7.40
16	0.200	0.301	140.0	20.500	2.870	14.35
17	0.202	0.101	130.5	50.110	6.539	32.37
	5.067					

Table 6.2 – Data for the cut core (Indiana Limestone). Acid contained GLDA at a mole ratio of 2:1 (GLDA:Fe) at 200°F

	Thickness of the core (inches)	Length From Inlet (inches)	Acid Volume (100 ml DI water)	Fe Concentration (mg/L)	Total Iron (mg)	Iron per Unit Length (mg/inch)
1	0.112	0.056	120	8.943	1.07316	9.58
2	0.112	0.168	135	6.5	0.8775	7.83
3	0.168	0.336	125	9.851	1.231375	7.33
4	0.165	0.501	135	9.556	1.29006	7.82
5	0.15	0.651	140	8.018	1.12252	7.48
6	0.231	0.882	140	11.78	1.6492	7.14
7	0.354	1.236	160	13.75	2.2	6.21
8	0.464	1.7	160	16.33	2.6128	5.63
9	0.511	2.211	160	16.7	2.672	5.23
10	0.438	2.649	150	16.56	2.484	5.67
11	0.436	3.085	144	12.39	1.78416	4.09
12	0.253	3.338	144	10.62	1.52928	6.04
13	0.264	3.602	130	14.28	1.8564	7.03
14	0.253	3.855	131	12.91	1.69121	6.68
15	0.291	4.146	130	10.56	1.3728	4.72
16	0.38	4.526	139	16.17	2.24763	5.91
17	0.406	4.932	140	15.73	2.2022	5.42
	4.988				**29.896295**	

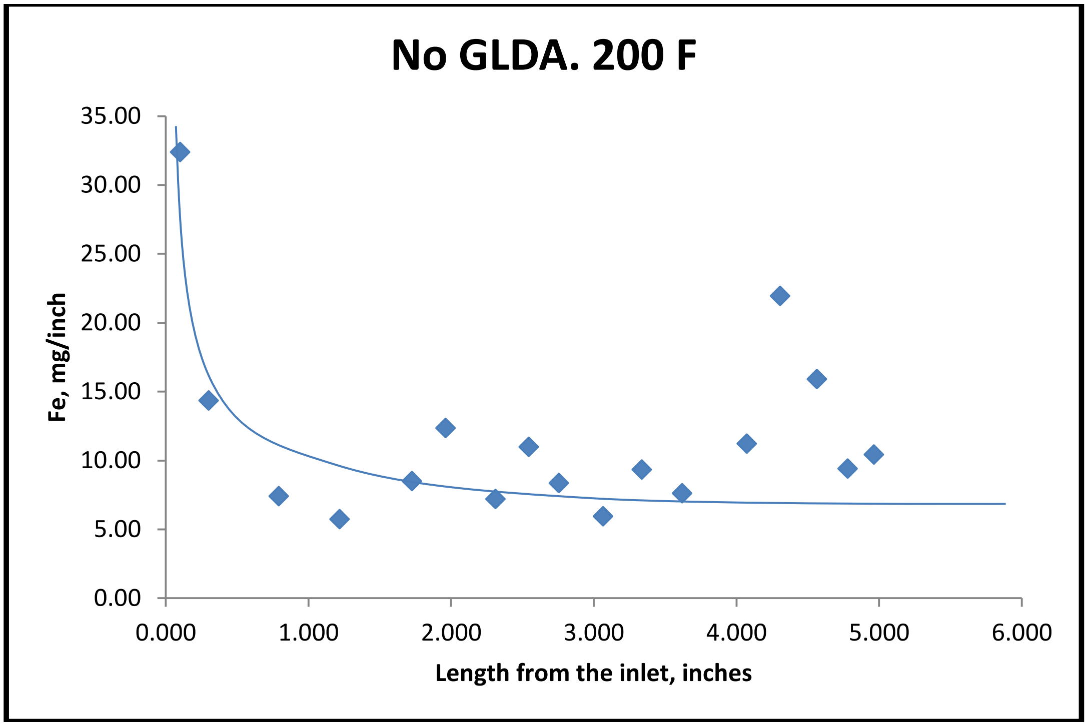

Figure 6.5 – Distribution of iron in the Indiana Limestone core as a function of the distance from the inlet for core in which no GLDA was used

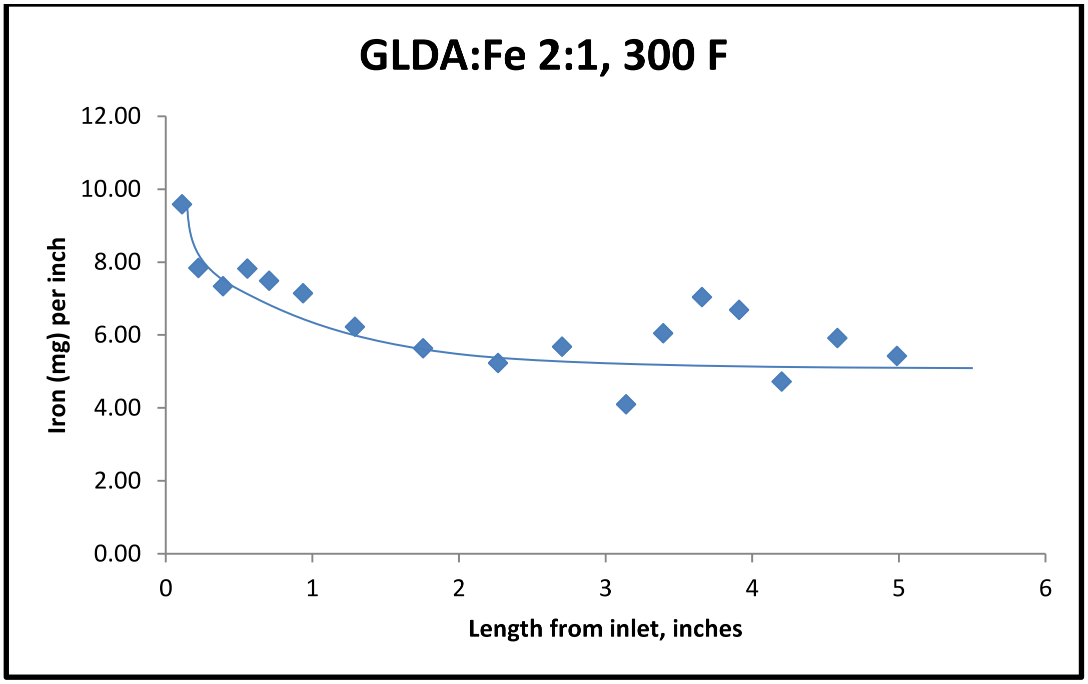

Figure 6.6 – Distribution of iron in the Indiana Limestone core as function of the distance from the inlet for the core in which GLDA was used in the concentration of 2:1 at 300ºF

Table 6.1 tabulates the concentration of iron as a function of length from the inlet when no GLDA was used. **Table 6.2** tabulates the same results but with GLDA used in the molar 2:1 GLDA:Fe(III) ratio. **Figures 6.5 and 6.6** show the iron concentration as a function of length in graph form.

Austin Chalk

Permeability: 5.55 md

Pore Volume: 43 cm^3

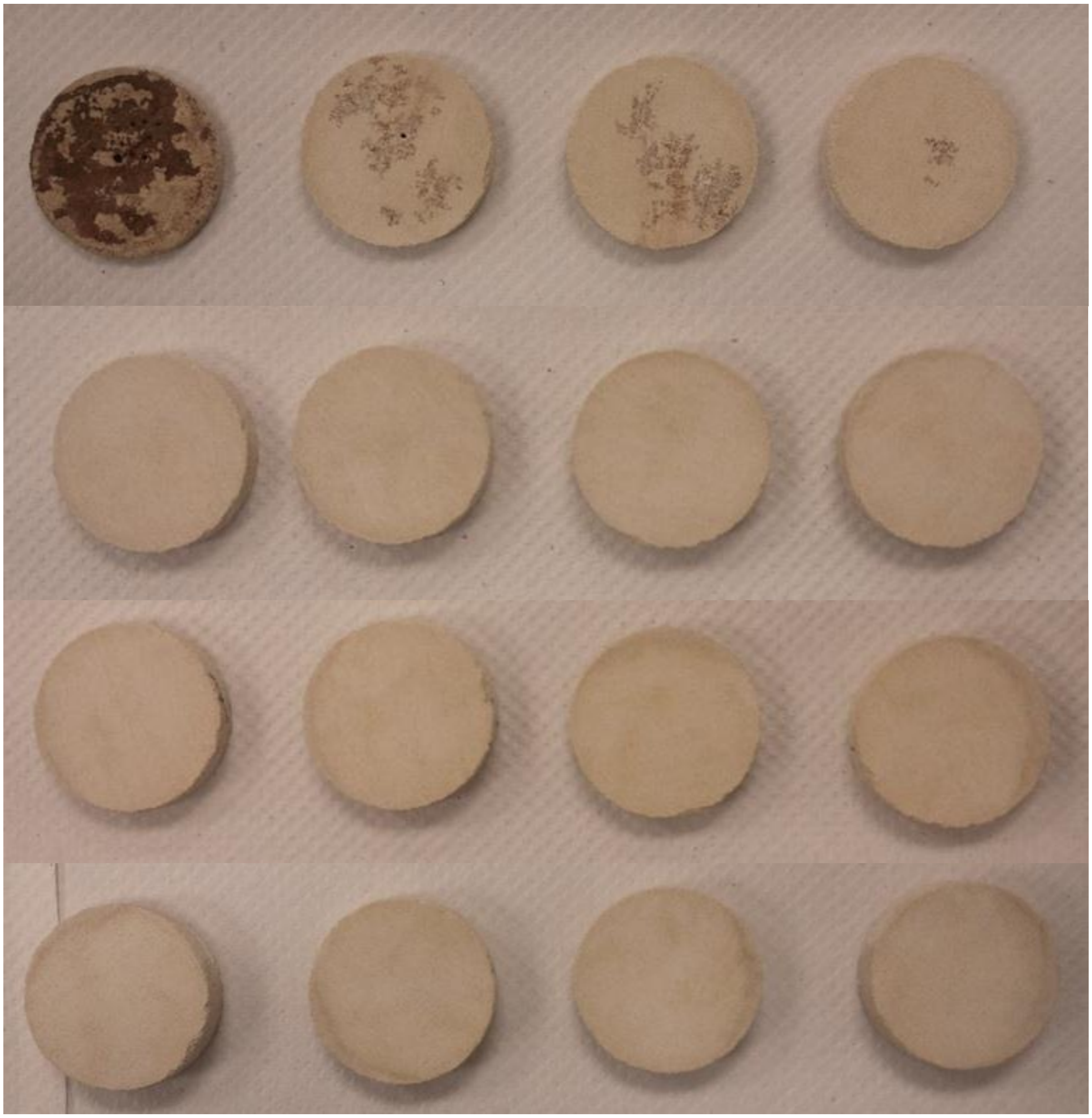

Figure 6.7 – The first 4 core slices show visible marks of iron precipitation in the core in Austin chalk

The core was cut into smaller slices using an iron saw. The slices were numbered as they were cut. The cut slices are shown in **Figure 6.7**. **Table 6.3** is a summary of the core slices weight and widths. The cores were weighed and then dissolved in HCl. The table then shows the amount of HCl each core was dissolved in and the concentration of iron as measured in ICP-MS after dilution. Then, the total iron in each core was normalized with respect to the core width. **Table 6.3** tabulates all of these results.

In **Table 6.3**, the dilution was done by taking 0.5 of the acid solution and diluted with 9.9 ml of deionized water. This gave a dilution factor of 10.4/0.5 = 20.8.

Figure 6.8 shows a graph of iron concentration against the distance from the inlet using results from **Table 6.3**. As can be seen from the graph, the second point seems to be a likely experimental error.

Table 6.3 – This table gives the weight of each core and the volume of acid it was dissolved in. Finally, it gives the iron distribution in the core

Sample	Width (in)	Distance from inlet		Weight (gms)	Weight/Inch (mg/inch)	Vol. Acid Used (ml)	Dilution Factor	Concentration (mg/L)	Mg of iron	Iron/inch (mg/inch)
1	0.136	0.136	0.068	6.65	48.89	29	20.8	54.9	33.12	**243.76**
2	0.212	0.348	0.242	10.99	51.83	24	20.8	13.95	6.96	**32.83**
3	0.252	0.6	0.474	13.40	53.16	33	20.8	47	32.26	**128.09**
4	0.261	0.861	0.730	14.05	53.84	35	20.8	14.96	10.89	**41.72**
5	0.298	1.159	1.01	15.95	53.53	40	20.8	15.033	12.51	**41.97**
6	0.344	1.503	1.331	18.42	53.56	44	20.8	16.81	15.38	**44.72**
7	0.345	1.848	1.675	18.63	53.99	44	20.8	18.57	17.00	**49.26**
8	0.337	2.185	2.016	18.17	53.91	38.5	20.8	19.75	15.82	**46.93**
9	0.299	2.484	2.334	16.02	53.59	41	20.8	16.8	14.33	**47.91**
10	0.347	2.831	2.657	18.57	53.53	47	20.8	19.83	19.39	**55.86**
11	0.327	3.158	2.994	17.40	53.22	48	20.8	18.62	18.59	**56.85**
12	0.363	3.521	3.339	19.21	52.92	50	20.8	18.43	19.17	**52.80**
13	0.4	3.921	3.721	20.91	52.26	43	20.8	23.15	20.71	**51.76**
14	0.389	4.31	4.115	26.41	67.89	42.5	20.8	19.23	17.00	**43.70**
15	0.36	4.67	4.49	19.35	53.76	41	20.8	19.93	17.00	**47.21**
16	0.437	5.107	4.888	23.07	52.78	54.9	20.8	18.39	21.00	**48.05**

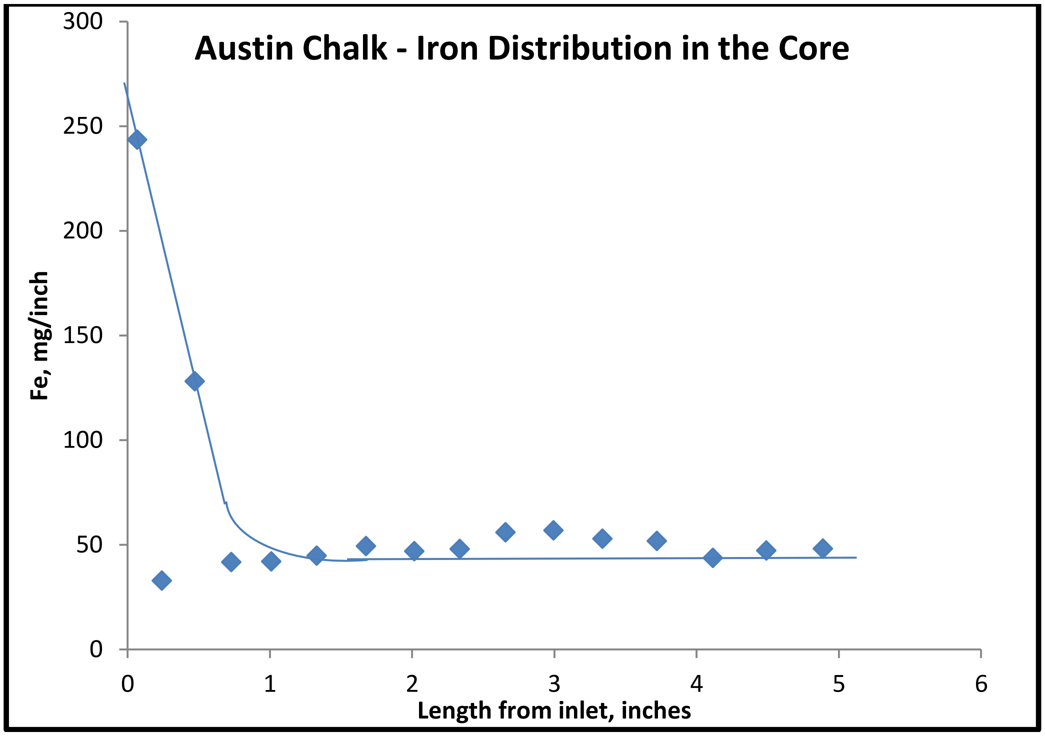

Figure 6.8 – Distribution of iron in the Austin Chalk 6 inch core

Pink Desert

Permeability: 60 md

Pore Volume: 48.97 cm^3

Figure 6.9 shows the cut cores in the order starting from top left:

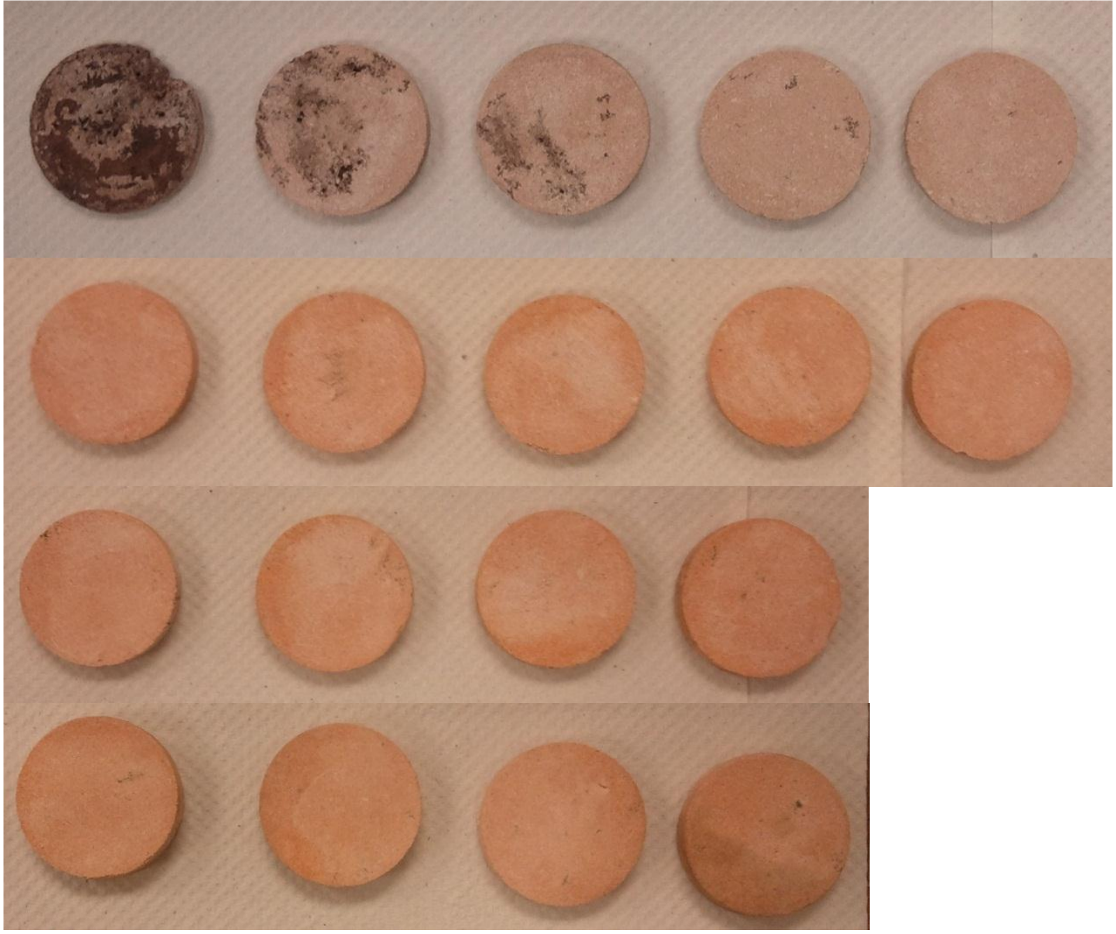

Figure 6.9 – The cut pieces of the Pink Desert core after the treatment

Table 6.4 is a summary of the core weight and widths. The cores were being weighed were then dissolved in HCl. The table then shows the amount of HCl each core was dissolved in and the concentration of iron as measured in ICP-MS after dilution. Then, the total iron in each core was normalized with respect to the core width. **Figure 6.10** shows the results in graph format.

Table 6.4 - This table gives the weight of each core and the volume of acid it was dissolved in. Finally, it gives the iron distribution in the core

Sample Number	Width (in)	Length from Inlet(in)	Weight (gms)	Weight/Inch (gms/inch)	Volume of Acid (ml)	Dil. Factor	Iron concentration (mg/L)	Total iron (mg)	Iron mg/inch
1	0.125	0.063	5.67	45.37	29	20.8	65.67	39.61	316.90
2	0.198	0.224	9.66	48.79	30	20.8	75.15	46.89	236.84
3	0.253	0.450	12.85	50.79	36	20.8	34.29	25.68	101.49
4	0.209	0.681	10.64	50.90	34.5	20.8	5.765	4.14	19.79
5	0.237	0.904	12.01	50.68	36	20.8	5.942	4.45	18.77
6	0.277	1.161	14.34	51.77	40	20.8	6.062	5.04	18.21
7	0.267	1.433	13.87	51.96	41	20.8	5.415	4.62	17.30
8	0.3	1.716	15.59	51.98	40	20.8	5.897	4.91	16.35
9	0.288	2.010	14.84	51.53	40	20.8	6.69	5.57	19.33
10	0.262	2.285	13.46	51.36	40	20.8	5.767	4.80	18.31
11	0.292	2.562	15.15	51.88	40	20.8	6.968	5.80	19.85
12	0.3	2.858	15.45	51.49	40	20.8	6.655	5.54	18.46
13	0.309	3.163	16.08	52.05	44	20.8	6.451	5.90	19.11
14	0.312	3.473	15.99	51.26	45	20.8	5.338	5.00	16.01
15	0.353	3.806	17.37	49.20	44	20.8	6.475	5.93	16.79
16	0.346	4.155	17.20	49.71	45	20.8	6.694	6.27	18.11
17	0.383	4.520	14.30	37.33	50	20.8	5.142	5.35	13.96
18	0.339	4.881	16.94	49.97	48	20.8	4.408	4.40	12.98

The dilution was done by taking 0.5 of the acid solution and diluted with 9.9 ml of deionized water. This gave a dilution factor of 10.4/0.5 = 20.8

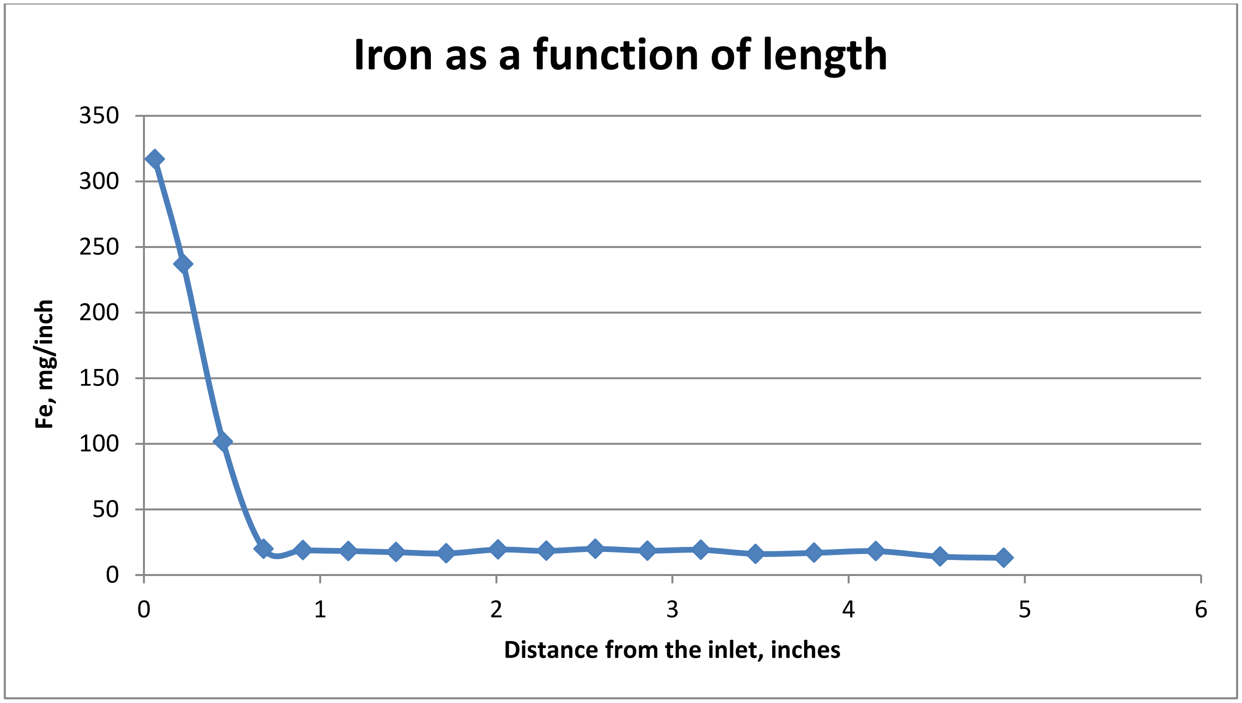

Fig 6.10 – Iron Distribution is lower after the first inch of the core in the case of pink desert

Comparison of iron distribution for different permeabilities

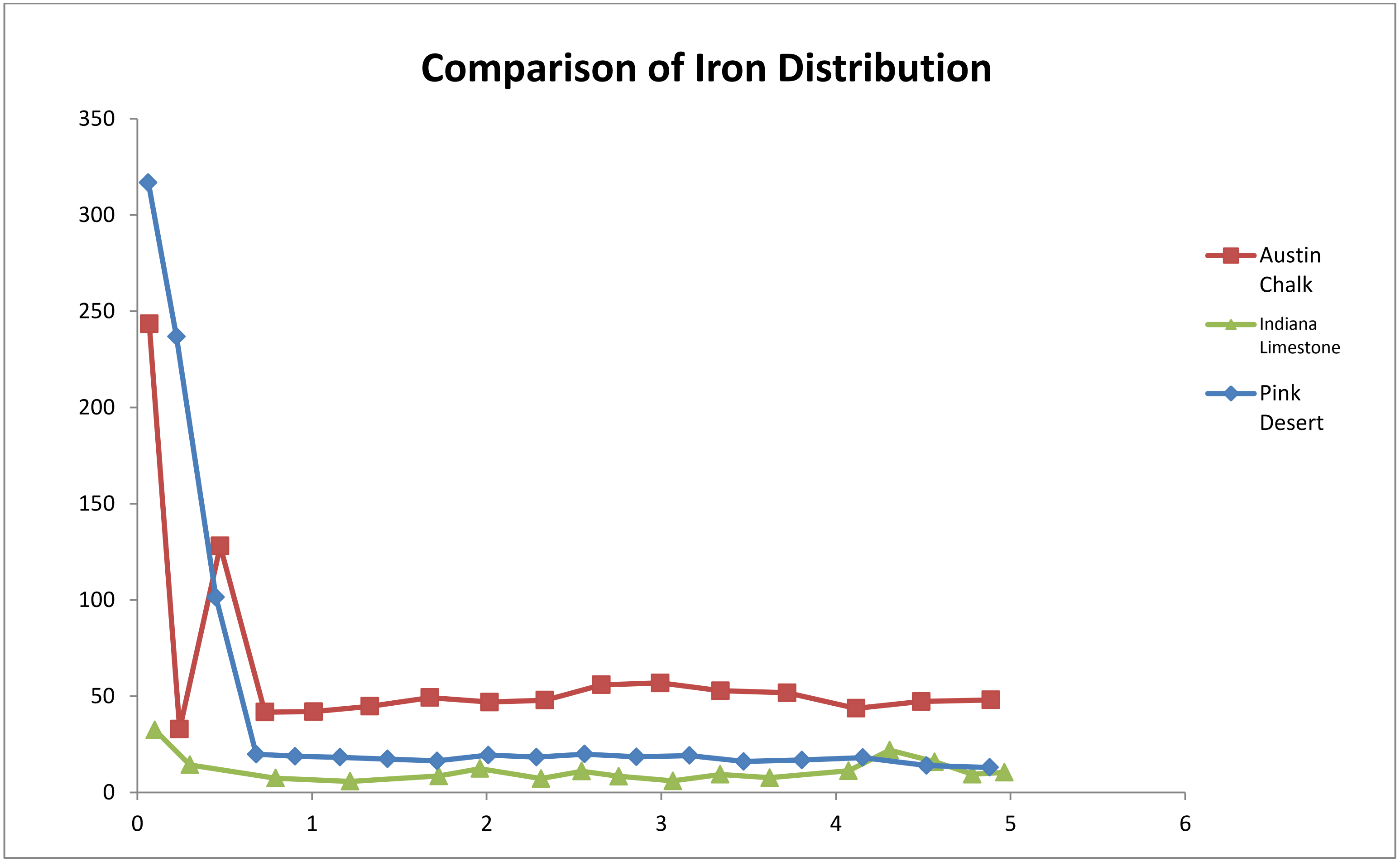

Fig 6.11 – The most permeable rock shows the highest concentration of iron within the first inch of the rock

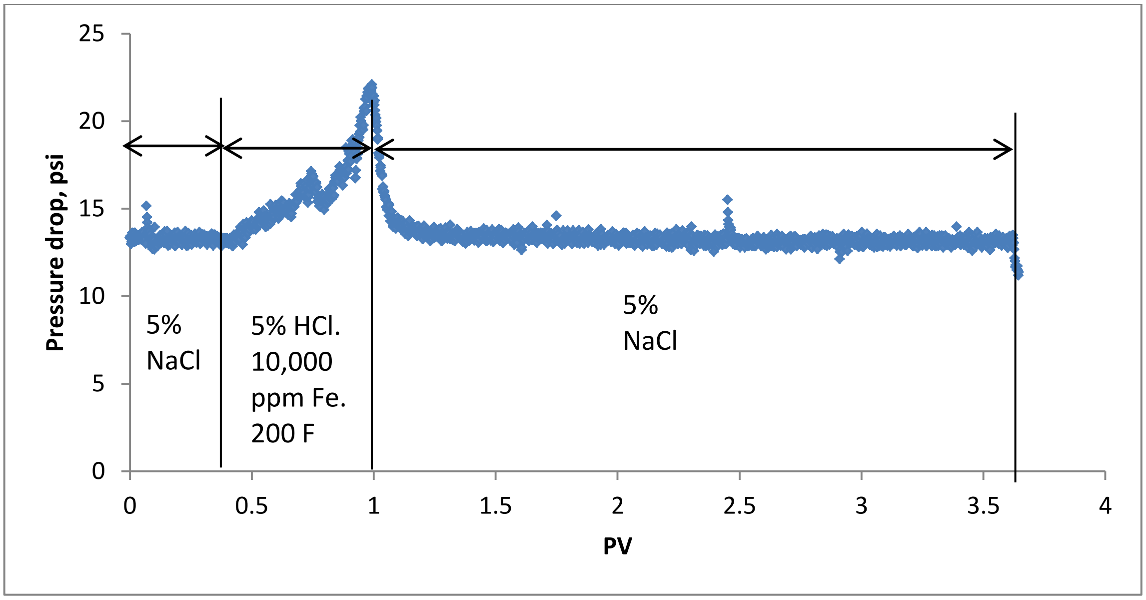

Figure 6.12 – Pressure drop across the Pink Desert Core with 5% HCl, 10,000 ppm Fe at 200°F. No GLDA was present

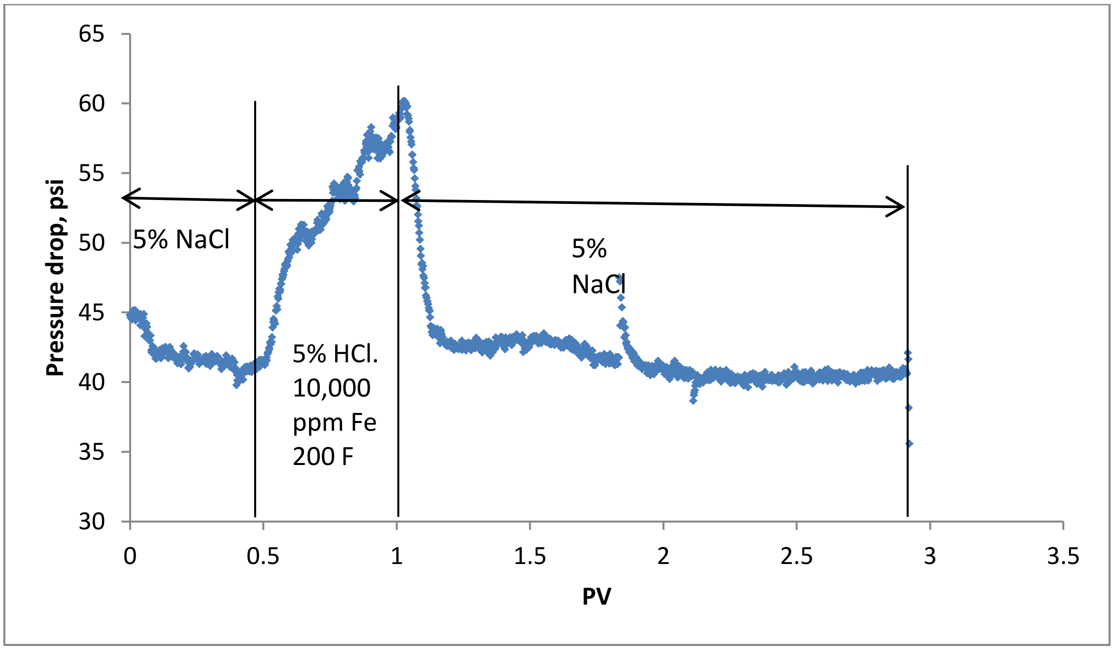

Figure 6.13 – Pressure drop across Austin Chalk core with 5% HCl, 10,000 ppm Fe at 200°F. No GLDA was present

Conclusion

Figure 6.11 shows a comparison of iron concentration in the three kind of rock on the same graph. Iron precipitation is highest within the first inch for all the cores used. However, it was seen that the iron retention is highest in Austin Chalk core. Since Austin Chalk has intermediate permeability, this could indicate an optimum permeability for maximum retention of iron. This could be investigated further. Also, as **Figures 6.12 and 6.13** show, the damage to higher permeability cores in terms of permeability is minimal due to more alternate pathways available for the fluid to flow.

CHAPTER VII

EFFECT OF VARYING FLOW RATE

Flow rate is an important parameter in the successful optimization of acidizing operations. One of the most desirable outcomes of an acidizing operation is creating deep wormholes that bypass the existing zone of damaged permeability. Wormholing in carbonates is a dynamic process that comes about with a concerted effort of physical and chemical processes such as convection, mass transfer and surface reaction. (Gong and El-Rabaa 1999). Flow rate is an important parameter in such processes. It has been reported in literature that (Bazin 2001) there is an optimum flow rate at which least amount of acid is required to break through the core. This is the flow rate at which longest wormholes will form for the same total acid volume. It is proposed in this work that change in flow rate should affect the damage to the core as the flow rate and the distribution of iron in it

An experiment was conducted with an Indiana Limestone core (1 md permeability). 5 wt% HCl containing 10,000 ppm of Fe(III) was injected into the core at 2.4 cc/min at 200ºF. Earlier experiments were conducted at 1 cc/min. Before the treatment, the core was weighed, saturated with 5 wt% NaCl and again weighed to find the pore volume. During the entire treatment, the backpressure was kept at 1000 psi and the overburden was 1500 psi. Pressure drop across the core was recorded through a transducer. Pressure drop is a direct measure of permeability given other parameters remains constant. It was found that unlike 1 cc/min, there was a net increase in permeability of the core **(Figure 7.1)**. Also, the precipitation of iron was deeper than at 1 cc/min. Clearly, 2.4 cc/min is closer to the optimum flow rate than 1 cc/min.

Core effluent samples were taken and tested for iron concentration using the ICP apparatus. The results **(Figure 7.2)** showed that very little iron came out. Most of the iron remained inside the core. Therefore, despite the fact there was increase in permeability, the core was damaged as the iron deposited can cause problems in other treatments. Secondly, the stimulation is suppressed and would have been higher if there was no precipitation of iron. The following graphs show the pressure drop and concentration of iron in the core effluent. **Figure 7.3** shows the CT scan of the core after the treatment showing formation of wormholes.

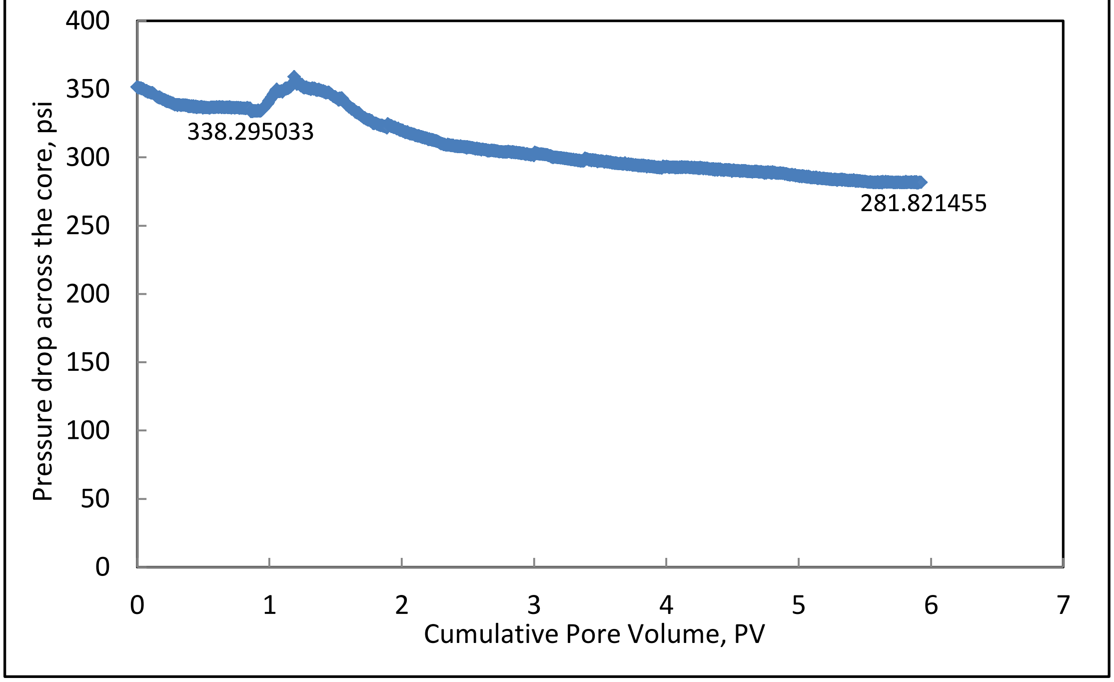

Figure 7.1 – The pressure drop curve shows that there was a net stimulation of the core

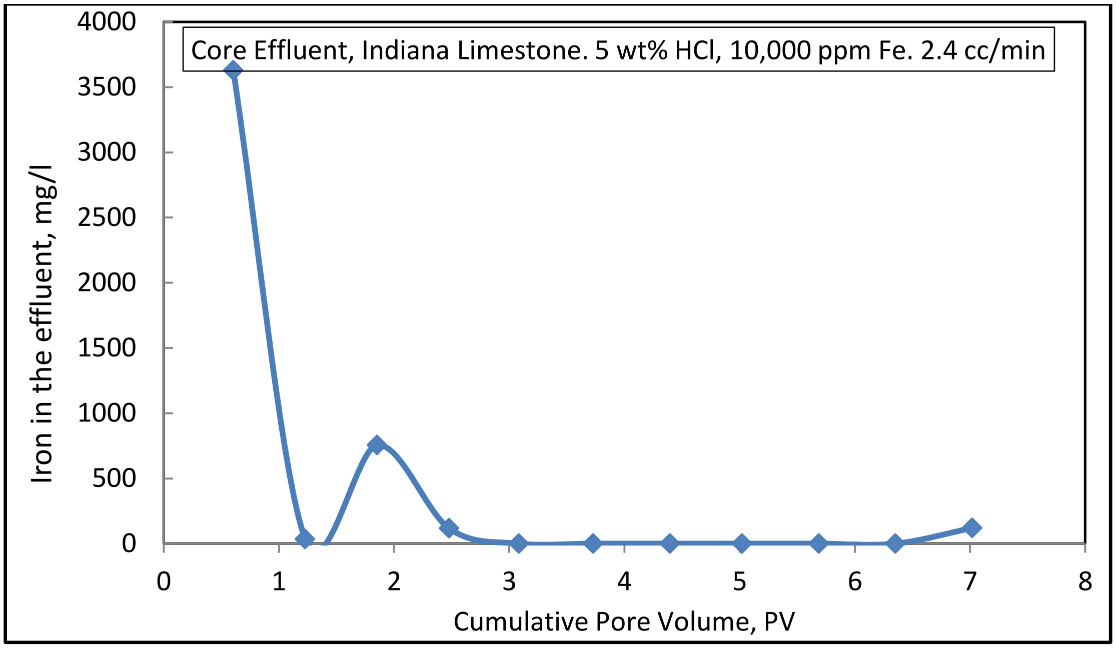

Figure 7.2 – The core effluent graph shows a significant amount of iron coming out of the core at 2.4 cc/min

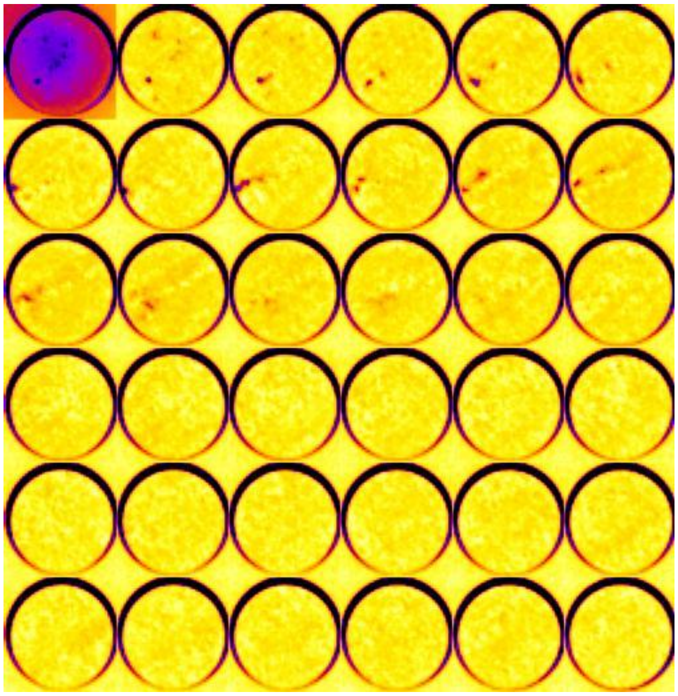

Figure 7.3 – The CT Scan shows that at a higher flow rate, the acid is able to create wormhole through the core bypassing the damage

CHAPTER VIII

PART II - EVALUATING GLDA AS A CHELATING AGENT

EFFECT OF VARYING CONCENTRATION

To understand the effect of concentration of GLDA at 200ºF, a coreflood experiment was conducted in which the amount of GLDA was doubled so that the GLDA:Fe ratio was approximately equal to 2:1. The procedure was the same as followed in Section 3.1.

Figure 8.1 shows the comparison between pressure drop during the course of the experiment before and after the injection of acid with GLDA.

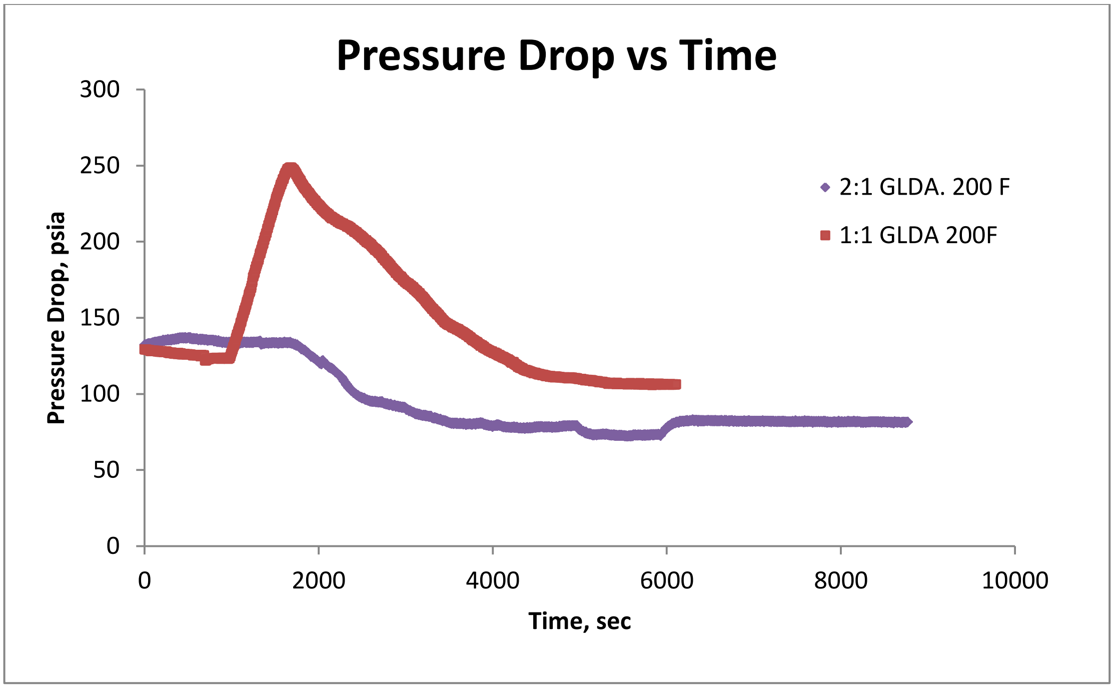

Figure 8.1 – Pressure drop across the core during the course of the experiment for two different concentrations of GLDA shows a lower pressure drop for GLDA concentration of 2:1

It can be clearly seen from the pressure drop curves that the pressure drop is lower in the case of a higher concentration of GLDA indicating a higher final permeability. **Table 8.1** shows the ratio of final and initial permeability after the course of the treatment. The permeability increase in the case of 2:1 GLDA:Fe is 41% higher than 1:1 GLDA:Fe.

Table 8.1 – Comparison of permeability before and after the experiment

Experiment	k_2/k_1
2:1 GLDA	1.63
1:1 GLDA	1.22

Figure 7.2 shows the iron concentration in the outlet effluent as a function of pore volume of fluid injected after the start of injection. The iron concentration in the core effluent is higher in the case of higher GLDA concentration.

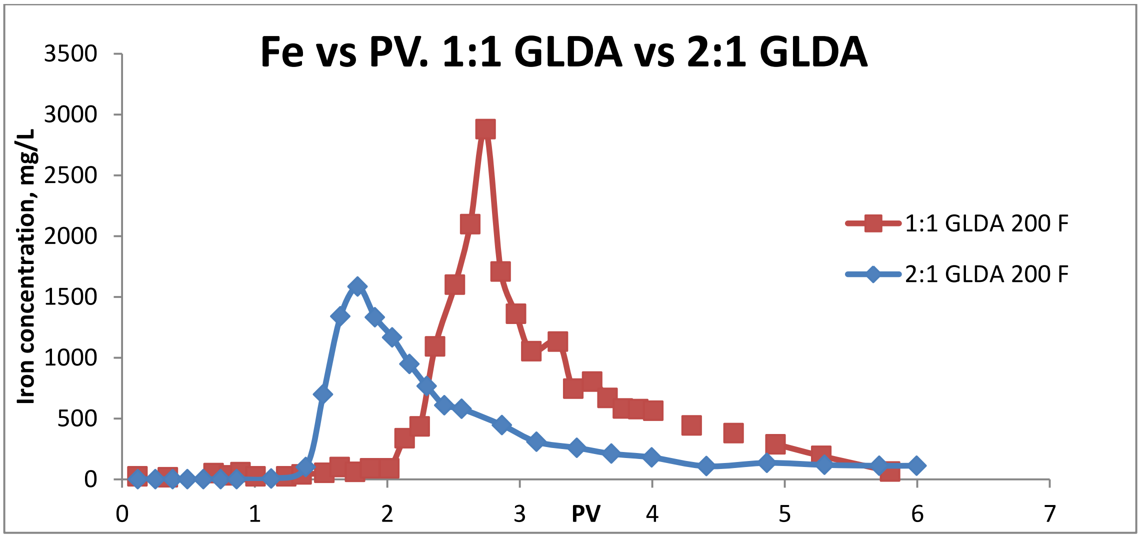

Figure 8.2 – Iron concentration as a function of pore volumes of fluid injected after the start of injection. The peak is higher in the case of 1:1 GLDA due to smaller sampling volume

In **Figure 8.2**, the area under the curve corresponds to the total amount of iron received from the outlet. Another way of finding the total area, which could be more accurate is measuring the iron concentration of each sample and then multiplying it by the volume of the sample. Thought this looks more reliable, it has the risk of not counting that iron which might still come out in small amounts if the experiment had run for many more hours. Though this cannot be done in the lab, under actual field conditions, the well is flowed back for a longer time. If the well is a producing well, it flows back for a much longer time, months and even years together. Thus, curve fitting a curve on this data and finding the area under the curve for (0,∞) could represent a more realistic value of total iron flow back. However, for this thesis, this is calculated by the multiplying the volume of the sample by the iron concentration. **Table 8.2** shows the final recovery of iron in the two cases.

Table 8.2 – Recovery of iron using varying amounts of GLDA

Experiment/Core	Percentage out
2:1 GLDA, 200ºF	60%
1:1 GLDA, 200ºF	59%

Figure 8.3 shows the inlet face of the core after the course of the experiment.

Figure 8.3 – The core on the left had the lower concentration of GLDA (1:1) as compared to the right one (2:1). The core on the right shows a much lower deposit of iron as compared to the left face and thus, a much lower damage

CHAPTER IX

EFFECTIVENESS OF GLDA IN HIGHER PERMEABILITY

In this study, GLDA was injected with acid on higher permeability cores (5 md and 60 md) and the effect of chelation and net stimulation was seen. The cores used were Austin Chalk and Indiana Limestone. It was observed that the net stimulation after the treatment was modest but a large proportion of the iron that went in came out of the core. One of the reason for this could be that extent of damage caused by iron in these cores could be much lesser as compared to tighter cores.

Austin Chalk

Dry Weight: 322.65 gms

Wet Weight: 363.5 gms

Pore Volume = 41 gms

Permeability: 9.4 md

Figure 9.1 shows the core effluent concentration from the Austin Chalk core during the treatment and **Figure 9.2** shows the pressure drop during the treatment.

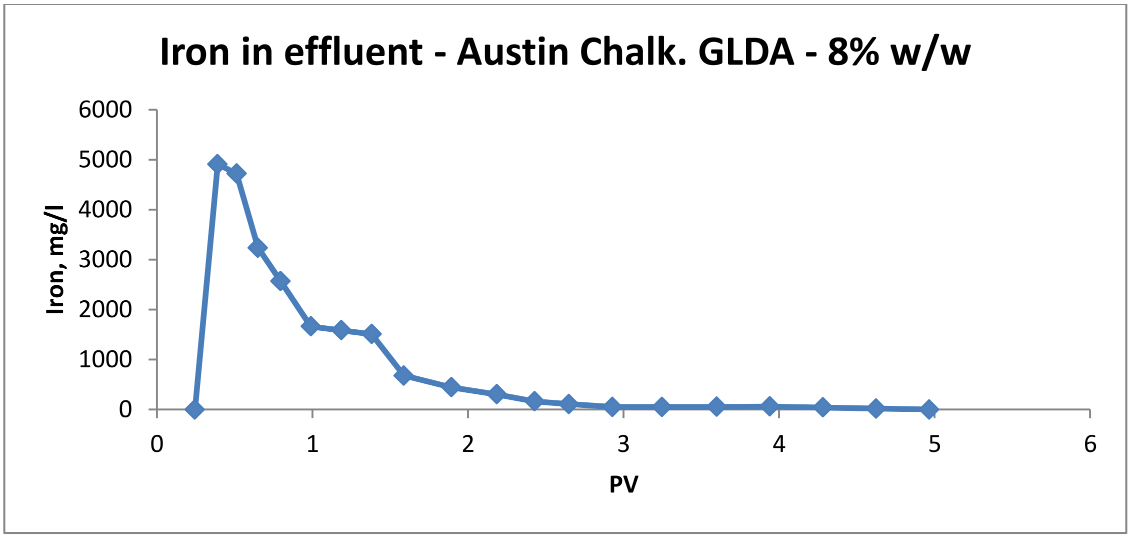

Figure 9.1 – Core effluent iron concentration during the treatment when 5 wt% HCl containing 8 wt% GLDA was injected through an Austin Chalk core at 1 cc/min

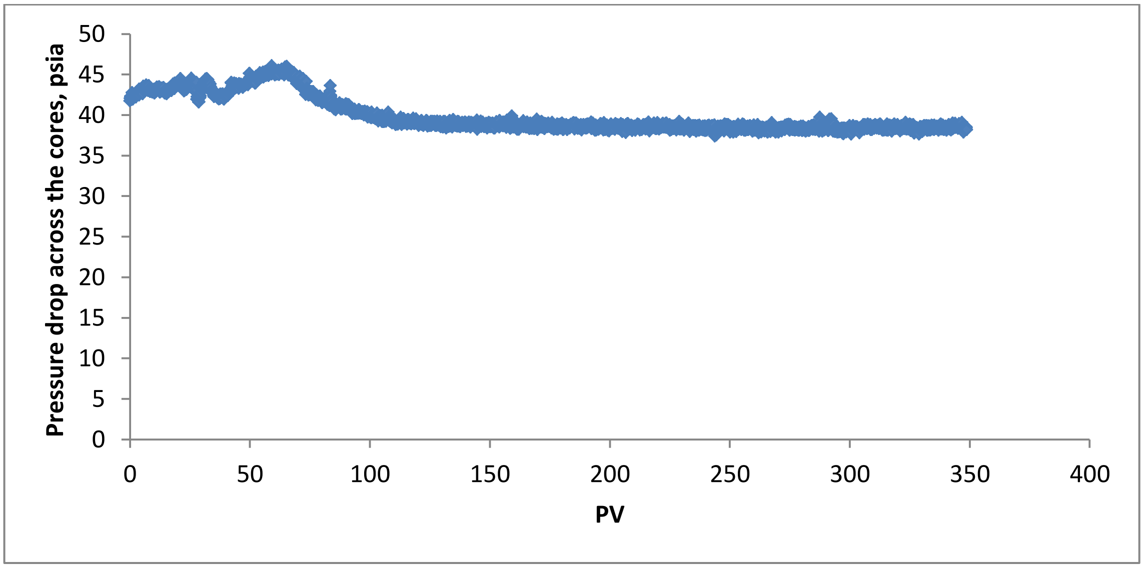

Figure 9.2 – Pressure drop across the core during the treatment when 5 wt% HCl containing 8 wt% GLDA was injected through an Austin Chalk core at 1 cc/min

Volume wise, 77% of the acid is acid containing 10,000 ppm of Fe. This implies that 26.4 ml of acid solution that was pumped in had nearly 204 mg of iron. From **Figure 9.1** - the core effluent graph, it was calculated that 72% of the iron is recovered.

Pink Desert

Dry Weight: 305.9 gms

Wet Weight: 356.9 gms

Pore Volume = 51 gms

Permeability: 94 md

Acid was flowed for about 26 minutes.

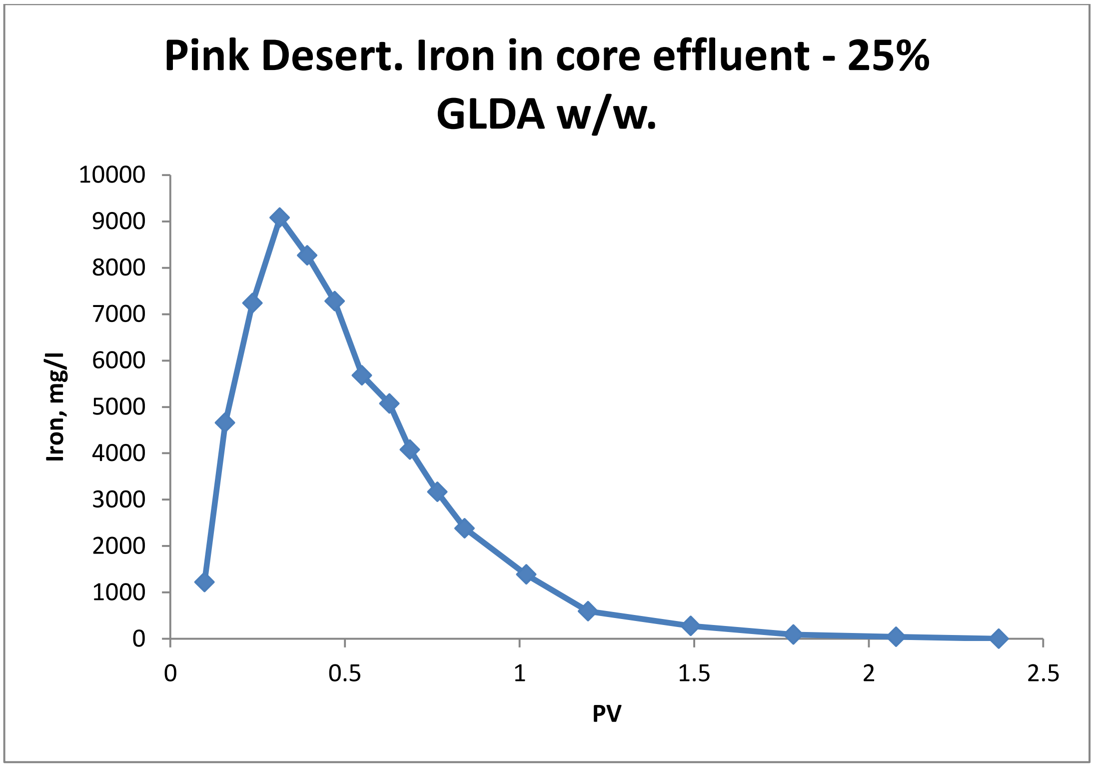

Figure 9.3 – The concentration of iron in the core effluent as a function of pore volume injected after the treatment of the acid containing GLDA

The volume percentage of the acid in the acid solution was nearly 77% which contained 10,000 ppm of Fe. This corresponds to 298 mg of Fe injected.

Figure 9.3 shows the iron concentration of core effluent. It was calculated that nearly 83% of the iron injected was recovered in the core effluents.

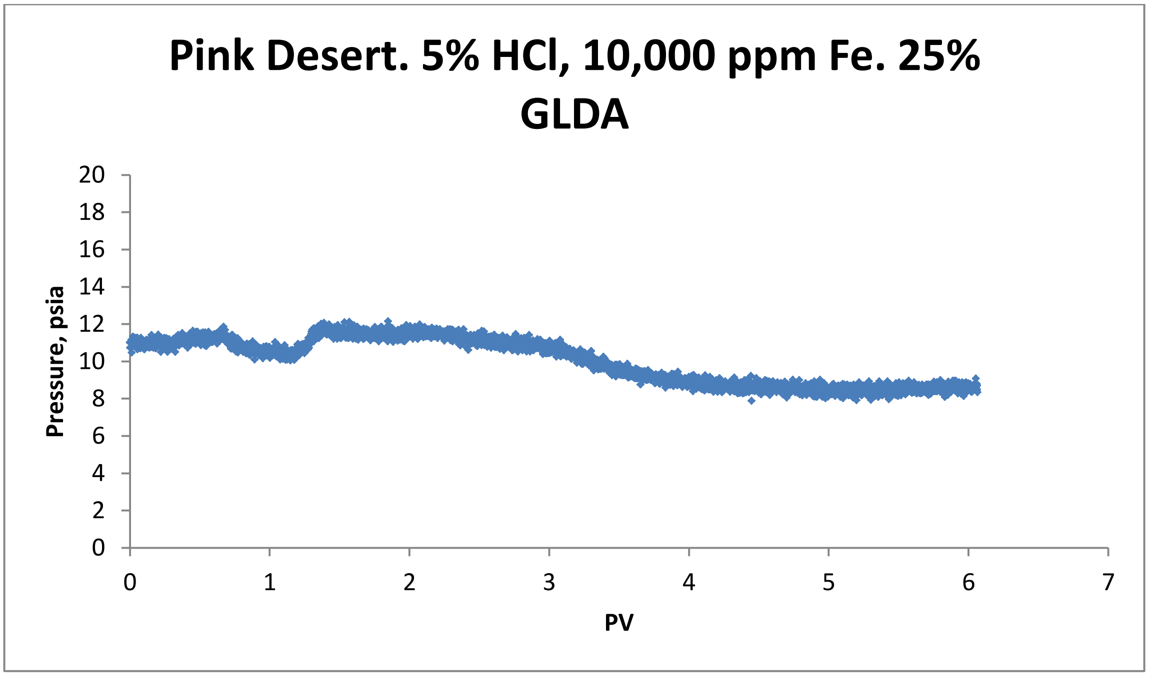

Figure 9.4 – Pressure drop during and after the treatment shows a modest increase in permeability

Figure 9.4 shows the pressure drop during the treatment. The ratio of permeability before and after the treatment is 1.206. Therefore, there is a permeability improvement of nearly 20.6% by this treatment.

In summary, GLDA is able to chelate a large percentage of GLDA back out of the core as core effluent. However, the permeability increase is only modest.

CHAPTER X

EFFECT OF TEMPERATURE ON GLDA PERFORMANCE

To understand the effect of temperature of GLDA at 200ºF and 300ºF, a core flood was conducted with 2:1 ratio of GLDA with 10,000 ppm of iron. The procedure followed was the same as described in Section3.1.

Figure 10.1 shows the comparison between pressure drop during the course of the experiment before and after the injection of acid with GLDA.

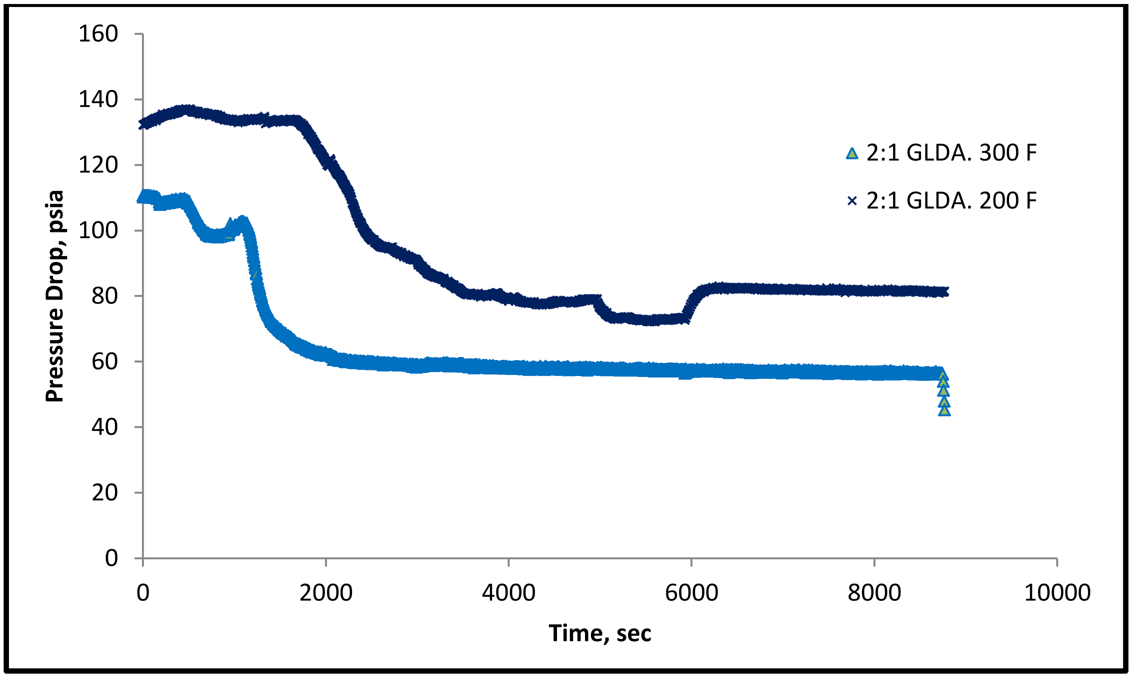

Figure 10.1 – Pressure drop across the Indiana Limestone core during the course of the experiment shows a lower pressure drop at 300ºF

The pressure drop shows that the effect of stimulation is seen much faster in the case temperature being equal to 300ºF as compared to 200ºF. The overall increase in permeability was 63% at 200ºF and 89% for 300ºF. Thus, the core was stimulated by a higher amount in the case of temperature 300ºF.

Table 10.1 shows the permeability of the cores before and after the treatment.

Table 10.1 – Comparison of permeability before and after the experiment

Experiment	**k_2/k_1**
2:1 GLDA	1.89
1:1 GLDA	1.63

Figure 10.2 on the following page shows the concentration of iron that came out as a function of the pore volumes of fluid injected after the start of acid injection.

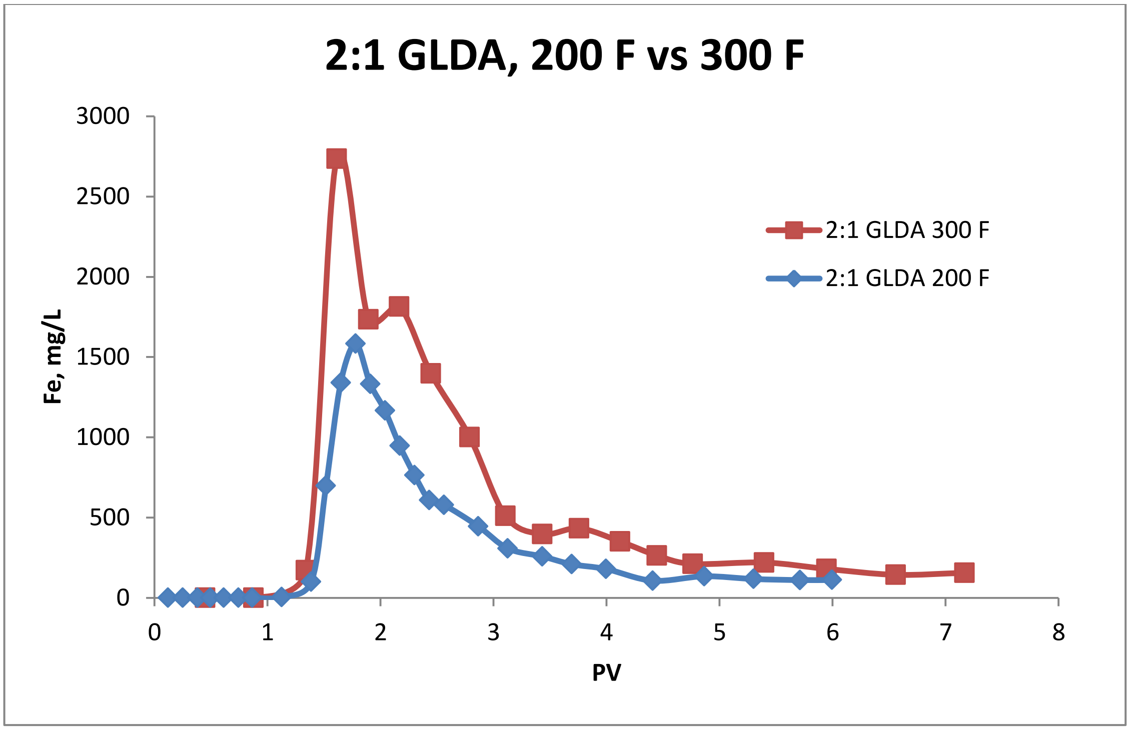

Figure 10.2 – Iron concentration was much higher in the case of higher temperature of 300ºF as compared to 200ºF

The area under the curve gives a measure of the total iron that came out. However, the total iron that came out was calculated by measuring the iron concentration of the effluent samples and then multiplying it by the volume to get the total iron. This gave a lower limit of the iron that got chelated and that came out. **Table 10.2** gives the amount of recovery of iron in these two cases.

Table 10.2 – Recovery of iron using GLDA at varying temperatures

Experiment/Core	Percentage out
2:1 GLDA, 300ºF	88%
2:1 GLDA, 200ºF	60%

Figure 10.3 shows the inlet face of the core after the course of the experiment.

Figure 10.3 – The experiment of the left core was run at a lower temperature as compared to the right one. There is no pronounced visible difference in the precipitation of iron on the face of the cores

CHAPTER XI

EFFECT OF HIGHER ACID CONCENTRATION ON GLDA PERFORMANCE

To show the effect of GLDA on this experiment, an experiment was carried out with 8% GLDA and a higher 10% HCl solution with 10,000 ppm of acid.

As in the previous experiment in Chapter IV, an Indiana Limestone core was used in this experiment whose permeability was found to be about 1.3 md. The pore volume was found to be 23.39 cc.

The effect of this treatment was seen as a significant amount of stimulation of the core. **Figure 11.1** shows the pressure drop curve during the treatment.

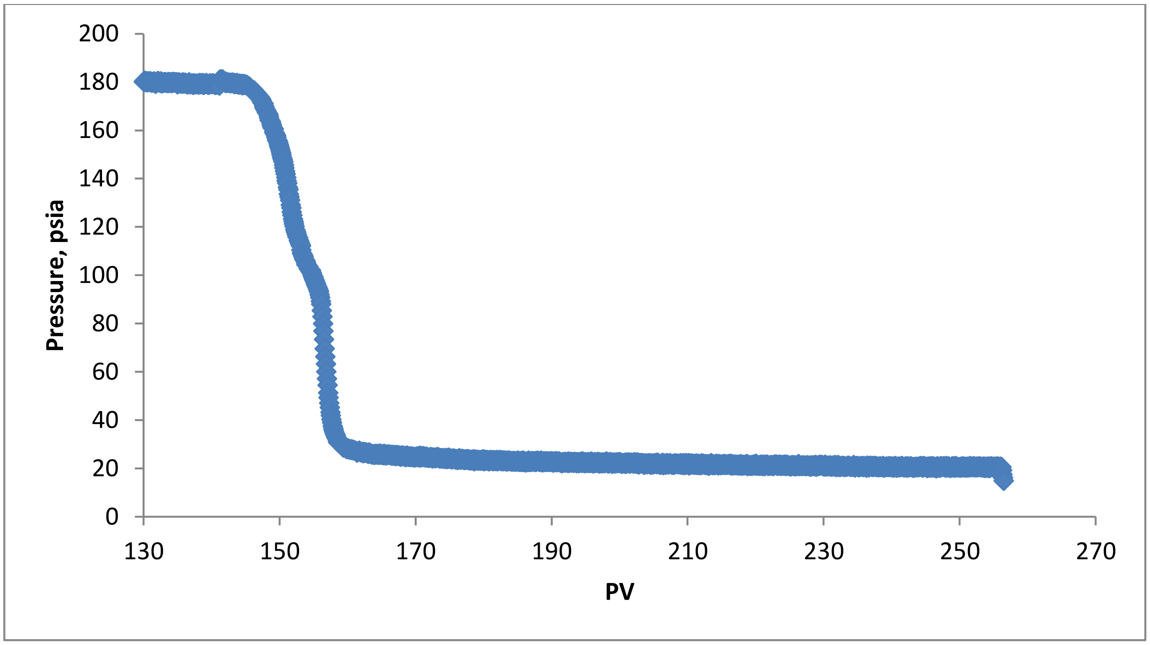

Figure 11.1 – Pressure drop as a function of pore volume of fluid injected in the core when 10 wt% HCl containing 8 wt% GLDA was injected through an Indiana Limestone core at 1 cc/min

From the graph, it can be seen that permeability ratio before and after the treatment is about 9. This is a large amount of stimulation. The permeability increases by 900% by just injecting half a pore volume of acid solution.

To understand how iron got distributed in the core, the core was cut and dissolved in HCl after which the iron was measured. **Figure 11.2** shows the distribution of iron in the core.

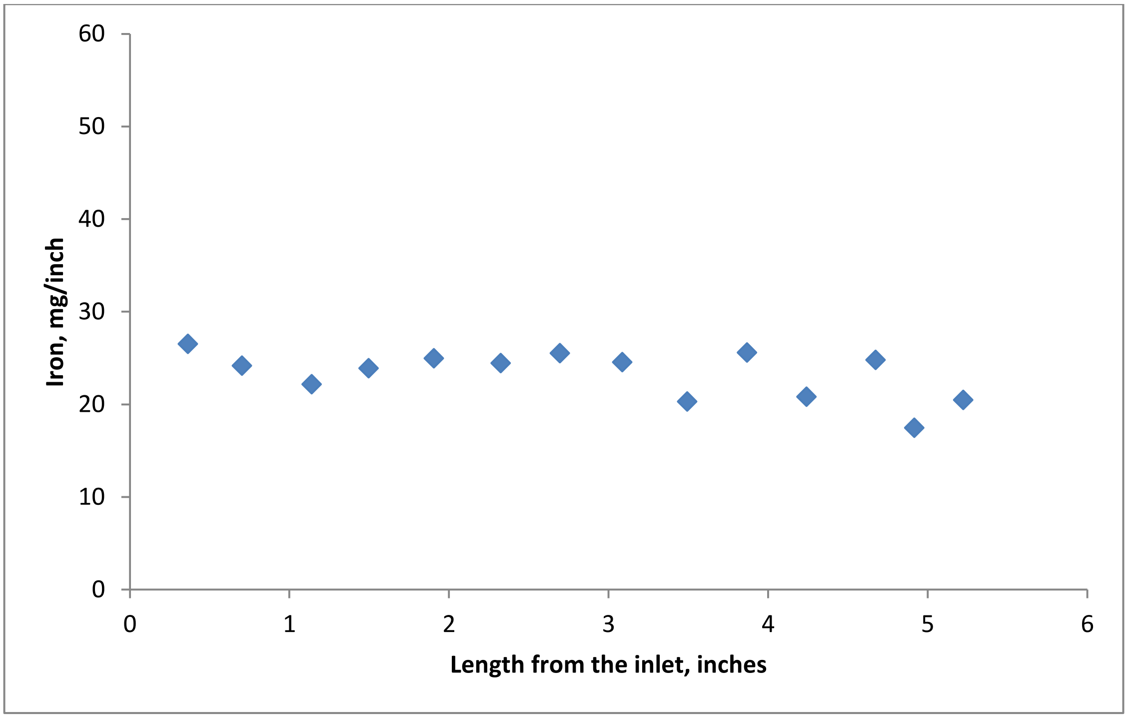

Figure 11.2 – Iron distribution in the core shows a flat distribution, indicating that there may be a little or no deposit in the core

Also, the inlet of the core showed little deposition of iron which shows the the effect of adding GLDA as shown in **Figure 11.3 and 11.4**.

Figure 11.3 – This picture shows the deposit on the core face after the treatment

Figure 11.4 – A close-up of the inlet of the core after the treatment

To understand the net stimulation effect better, CT scan of the core was done to look at the wormhole formation. **Figure 11.5** shows the formation of wormholes in the core.

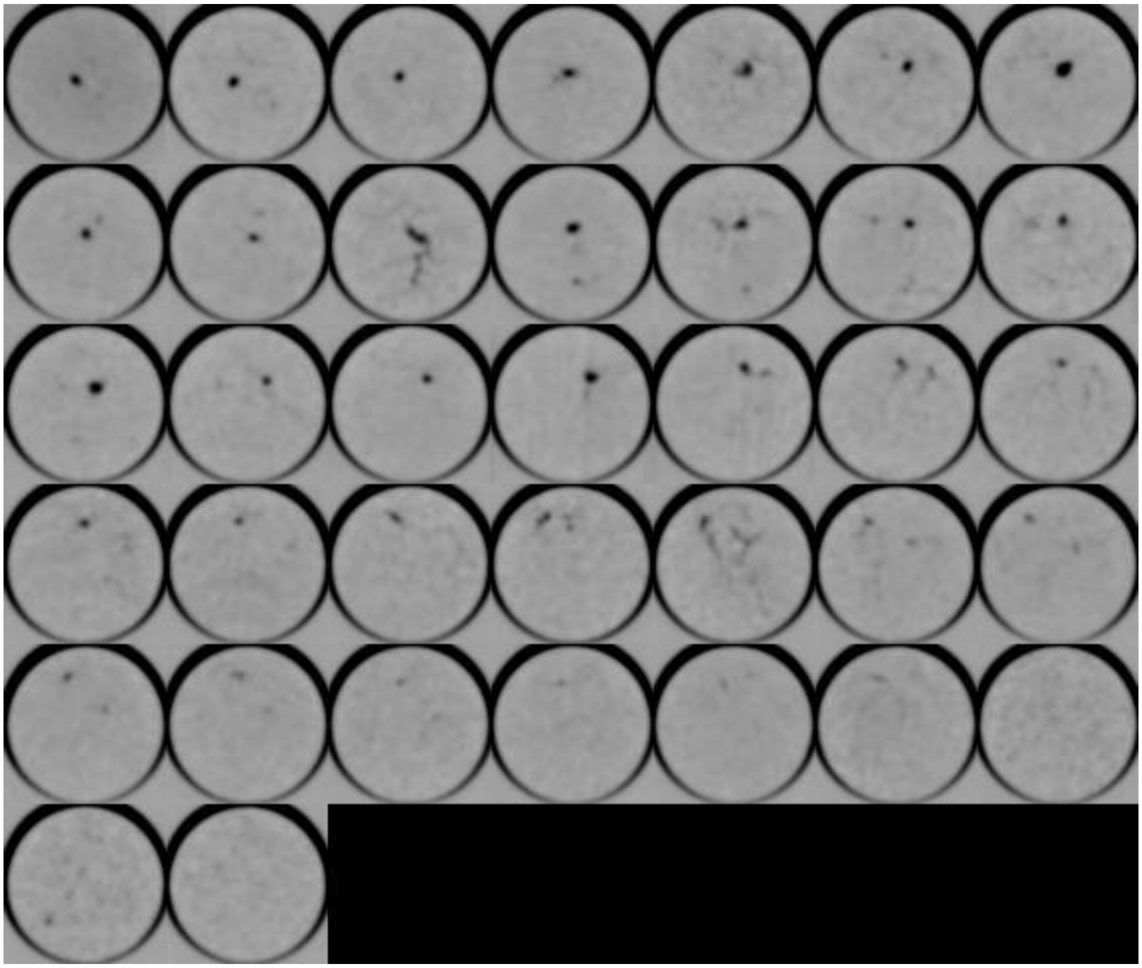

Figure 11.5 – CT Scan of the core shows significant wormhole formation almost until the end of the core

CHAPTER XII

COMPARISON OF PERFORMANCE OF GLDA WITH EDG AS A CHELATING AGENT

GLDA has been established in the previous chapters to be an effective chelating agent. At temperatures as high as 300ºF, it was able to chelate upto 70% of the iron that was injected into the core. It worked well in higher acid concentrations of 10 wt% HCl, where it was able to produce six times increase in permeability. In higher permeability cores, it was able to prevent any damage and bring out a large amount of iron out of core after the treatment.

To compare GLDA with existing chelating agents, a chelating agent was chosen that most closely represented the benefits provided by GLDA. Previous chelating agents have drawbacks that include low acid solubility, non-biodegradability, carcinogenic in nature, harmful to aquatic life among other disadvantages. EDG, also called HEIDA, made by Dr. Wayne Frenier of Schlumberger, was chosen to compare with GLDA. It is biodegradable and has a higher solubility in acid. In our case, we used a 1:1 molar EDG:Fe which corresponds to 3.25 wt% of EDG in 5 wt% HCl was injected through an Indiana Limestone core with an initial permeability of about 1 md at 200ºF.

Figure 12.1 shows the pressure drop across the core during the treatment. The pressure drop curve showed that there was an increase in permeability by 71% as compared to the initial permeability. Also, EDG was able to chelate out nearly 45% of the iron that was injected into the core.

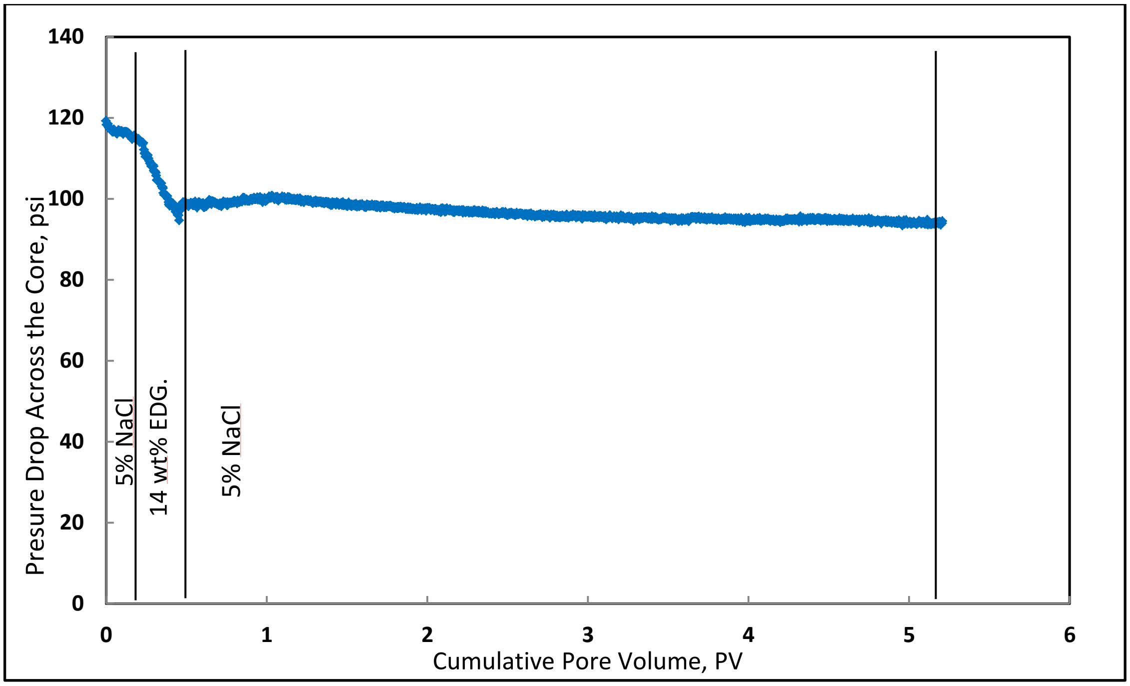

Figure 12.1 – Pressure drop across the core vs cumulative pore volume for 3.25 wt% EDG shows that there was a net stimulation of the core

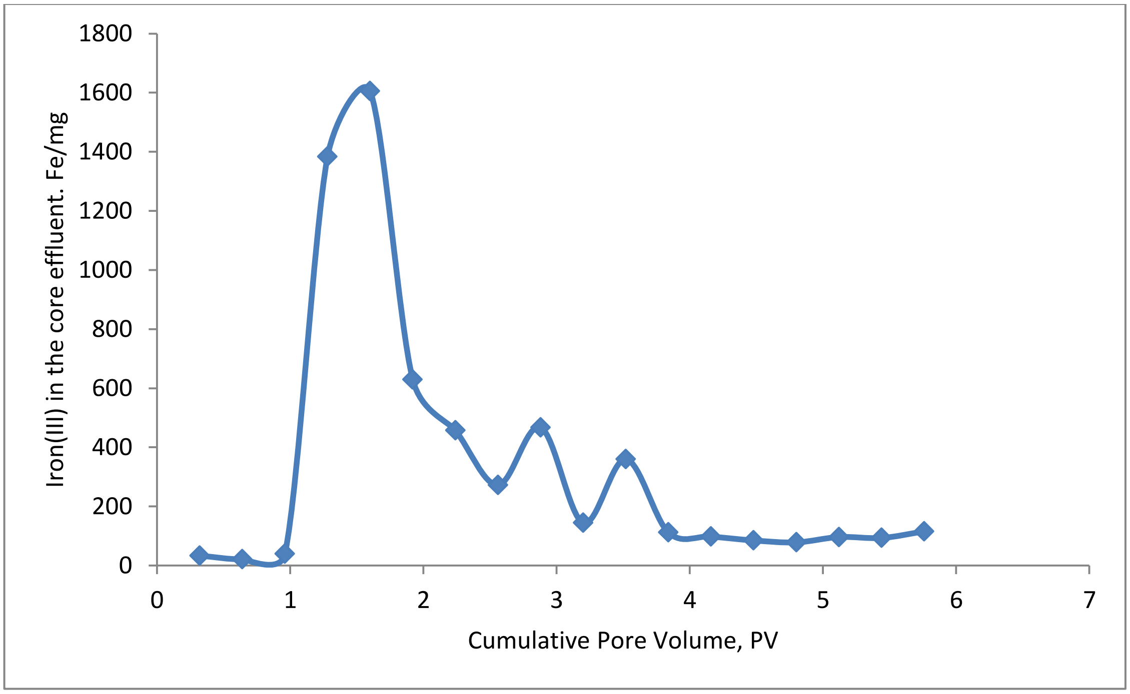

Figure 12.2 – Iron in the core effluent shows that nearly 45% of the iron that was injected was recovered from the core by EDG

Figure 12.2 shows the iron in the core effluent when EDG was used. The performance of EDG was comparable to GLDA for similar temperature conditions. However it is to be noted that the molar ratio of Chelant:Fe(III) was double in the case of GLDA. This means that EDG was better chelating agent on a molar basis. EDG was able to produce marginally more stimulation in terms of permeability and chelated marginally less iron out of the core. However, experiments must be conducted for higher concentrations of EDG and GLDA, preferably until their solubility limit and then compared in future experiments.

CHAPTER XIII

CONCLUSIONS

This work seeks to understand the damage caused by iron precipitation in acidizing operations and to subsequently evaluate GLDA as a chelating agent. In Chapter I, a literature review was conducted. Previous works have focused on experiments at room conditions and gives an overview of previously used chelating agents. In Chapters III-VII, the effect of the damage without presence of any chelating agent has been studied. Work was done on Indiana Limetone, Austin Chalk and Pink Desert Limestone cores using 5-10 wt% HCl containing 10,000 ppm of Fe(III). Experiments indicated that at room conditions, precipitation of iron started around a pH of 1.8 and was essentially complete by pH 2.8. Under simulated reservoir conditions, it was found that iron precipitation can cause a significant damage to core permeability at lower flow rates. Apart from permeability, there is a large retention of iron in the core. This can be damaging to future treatments and in heavy oil production where asphaltene precipitation can take place. It was found that at higher temperatures, acid concentration and flow rate, the damage to permeability was reduced. Iron retention in the core was lower in higher flow rates. This work also showed that the distribution of iron in the core. Iron precipitation is highest within the first inch of the core at lower flow rates.

GLDA was found to be an effective chelating agent. GLDA solubility of 4.3 and 8 wt% was tested. It was able to prevent any damage to the core in the terms of permeability and was able to chelate 40-80% of iron injected under various conditions.

GLDA performance became better at higher temperatures, acid concentrations and permeability. As a final study, GLDA performance was compared with EDG. It was found that 1:1 EDG:Fe molar ratio worked as well as 2:1 GLDA:Fe molar ratio did. This means that EDG is a better chelating agent. However, EDG is limited by its solubility limit in live acid. This means that GLDA is be a potentially better chelating agent in terms of total iron chelating capacity. This needs to be investigated further.

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