# EVALUATION OF MULTI-STAGE SANDSTONE ACIDIZING USING AN ORGANIC MUD ACID AND A CLAY STABILIZER

A Thesis

by

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# ABSTRACT

Acidizing sandstone reservoirs is a complex process. If not fully studied, it could lead to formation damage. A combination of HCl/HF has been widely used to stimulate sandstone reservoirs. However, the success rate is low due to the complexity of the reactions involved in this process. These reactions result in potentially damaging precipitation and cause formation damage. The problem is more severe when dealing with Bandera sandstone formations that contain a high concentration of carbonate minerals and clay particles. The purpose of this study is to present and evaluate multi-stage acid injection into the Bandera sandstone cores to remove formation damage.

In this study, coreflood experiments were conducted on Bandera sandstone cores (1.5 in. × 6 in.) at a flow rate of 4 $cm^3$/ min and temperature of 140°F. A mixture of formic acid and HF was used as an organic mud acid. Preflush of hydrochloric and formic acid was employed to remove carbonate minerals. Bandera sandstone cores contain a considerable amount of HCl sensitive clays. So another stage was employed to cover clay minerals and prevent HCl attack on the surface of clay particles. Different clay stabilizers as well as preflush pore volume were examined in this study. At the end, this multi-stage treatment design was tested on a Berea sandstone core to investigate the impact of mineralogy. During each experiment effluent samples were collected. Samples were analyzed using Inductively Coupled Plasma (ICP) and Scanning Electron Microscopy (SEM) to investigate reaction kinetics and chemistry of precipitation.

Chemical analysis confirmed incompatibility of HCl with clays in Bandera cores at 140°F. Clay stabilizer CSA showed the ability to prevent HCl attack on the clay particle's surface. As a result, a coreflood experiment conducted using CSA led to permeability improvement. The result of the coreflood experiment conducted using CSC indicated that this chemical is able to exchange cations with clay particles, however permeability decreased due to an insufficient injection of preflush. As in another experiment, increasing preflush pore volume using CSC resulted in permeability improvement. CSB completely failed to cover clay minerals and permeability decreased drastically at the end of the treatment.

# DEDICATION

Dedicated to

My parents, my lovely sisters, and my brother.

# ACKNOWLEDGEMENTS

I would like to express my sincere gratitude and deep regard to my supervisor, Dr. Nasr-El-Din, for the guidance, support, and patience he provided throughout the course of this thesis. The blessing, help and guidance given by him shall carry me a long way in the journey of life on which I am about to embark.

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# 1. INTRODUCTION

## 1.1 Matrix Acidizing

Matrix acidizing has been used as a means to remove formation damage and improve well performance. Formation damage occurs during drilling, completion, or work over and as a result there is a zone with permeability less than the permeability of the undamaged zone. This area is also known as skin zone and is presented in literature as “skin effect”. Based on the type of operation conducted on the well, the skin zone could have different radius of penetration inside the formation. **Figure 1.1** illustrates the zone of altered permeability.

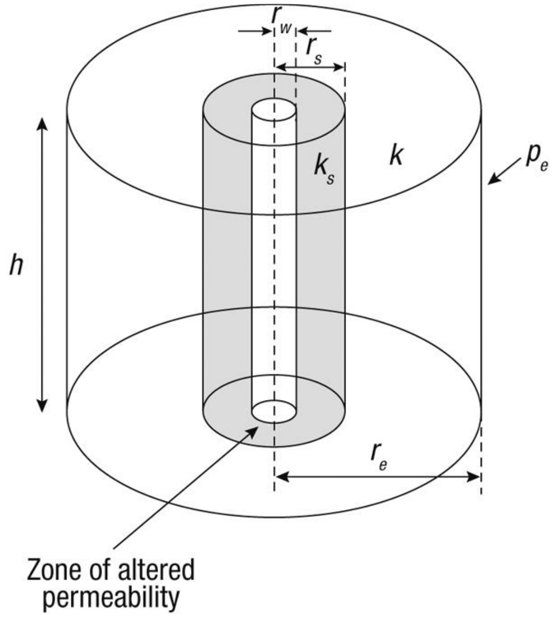

**Figure 1.1- Formation damage around the wellbore**

Most of the pressure drop inside the reservoir occurs in the area near the wellbore and as a result, a reduction in permeability in this area will reduce well performance significantly. Hence, there is a need to take action and eliminate the effect of this area on well productivity/injectivity. There are two approaches to eliminate this skin effect including hydraulic fracturing and matrix acidizing. In hydraulic fracturing the objective is to bypass the damaged zone completely by creating long fractures that connect the wellbore to the virgin zone directly, this way the skin zone is eliminated completely. In matrix acidizing, the purpose is to remove the formation damage and improve permeability of the area around the wellbore. However, based on the type of the formation the approach for permeability improvement will be different. In matrix acidizing the idea is to inject chemicals into the formation to dissolve minerals in the damaged zone, and as a result create porosity and improve permeability. These chemicals encompass a wide range including different types of acids, chelating agents (Mahmoud et al. 2011b), clay stabilizers and so on.

## 1.2 Theoretical Background

### 1.2.1 Sandstone Mineralogy

Sandstone reservoirs are mainly composed of sand. Sand or quartz is silicon dioxide ($SiO_2$). These sand particles are attached to each other via cementing materials. The quality of these cementing materials determines whether the formation is consolidated or unconsolidated. **Figure 1.2** shows a simple schematic of sand particles attached to each other and cementing materials. There is no pure sandstone formation. **Table 1.1** lists other possible minerals present in sandstone formations.

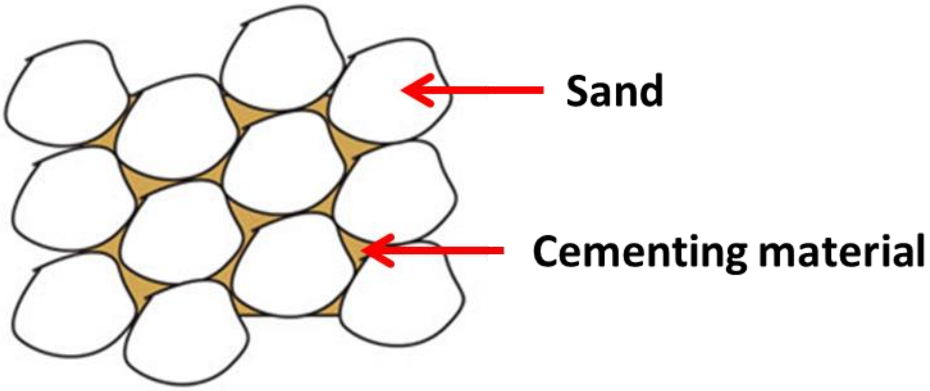

**Figure 1.2- Sand particles attached to each other with cementing materials**

**Table 1.1—Minerals Present In Sandstone Formations**

| Minerals | Type | Chemical composition |
|---|---|---|
| Sand | Quartz | $SiO_2$ |
| Carbonates | Calcite<br>Dolomite | $CaCo_3$<br>$CaMg(Co_3)_2$ |
| Clays | Chlorite<br>Illite<br>Smectite<br>Kaolinite | $MAl_XSi_Y(OH)$ |
| Feldspars | Na-Feldspar<br>K-Feldspar<br>Ca-Feldspar | $MAl_XSi_YO_Z$ |

Carbonate minerals are commonly calcite and dolomite. The main acid used to dissolve these minerals is HCl. It can dissolve these minerals and the reaction product is soluble in water or spent acid. However, when they react with HF, the reaction product is not soluble is the aqueous phase (Smith and Hendrickson 1965).

Clays and feldspars are layered alumino silicates. The main difference between these two types of minerals is that clays are hydrated alumino silicates. However, feldspars do not have hydroxyl group. Feldspars are mainly 3 types: sodium, potassium, or calcium feldspars. (Hughes 1950).

**Table 1.1** lists the mineralogy of sandstone formations in general. However, the concentration of these minerals is different for various types of sandstone formations. More specifically, four different categories of sandstone formations exist: Berea, Scioto, Kentucky, and Bandera. **Table 1.2** lists the minerals present in each one of these types of sandstone rocks.

**TABLE 1.2 Mineral Compositions For Different Sandstone Cores**

| Mineral | Berea | Scioto | Kentucky | Bandera |
|---|---|---|---|---|
| Quartz | 87 | 70 | 66 | 57 |
| Dolomite | 1 | -- | -- | 16 |
| Calcite | 2 | -- | -- | -- |
| Feldspar | 3 | 2 | 2 | -- |
| Kaolinite | 5 | Tr | Tr | 3 |
| Illite | 1 | 18 | 14 | 10 |
| Chlorite | 2 | 4 | -- | 1 |
| Plagioclase | -- | 5 | 17 | 12 |

### 1.2.2 Sandstone Acidizing

Acidizing sandstone reservoirs is a complex process and needs to be conducted in a multi-stage process. The purpose of sandstone acidizing is not to create wormholes, but to dissolve minerals and remove formation damage.

The abundant mineral in sandstone cores is quartz. Therefore, there is no doubt that HF is the main acid used to dissolve quartz and alumino silicates. However, the presence of carbonate minerals might be a source of formation damage when using HF. If HF is introduced in the formation containing calcite or dolomite, it will react with these minerals. The reaction product, i.e. $CaF_2$ or $MgF_2$, is not soluble in the aqueous phase and therefore it will precipitate and cover the rock surface. The reaction of HF with calcite and dolomite is written in **Equations 1.1** and **1.2**, respectively (Mahmoud et al. 2011a).

$$2HF + CaCO_3 \rightarrow CaF_2 + H_2O + CO_2 \qquad (1.1)$$

$$4HF + CaMg\,(CO_3)2 \rightarrow CaF_2 + MgF_2 + 2H_2O + 2CO_2 \qquad (1.2)$$

To avoid the precipitation, another step is required to remove carbonate minerals first. HCl is the best choice to dissolve and remove calcite and dolomite. The reaction products, i.e. $CaCl_2$ and $MgCl_2$, are soluble in the aqueous phase. (**Equations 1.3** and **1.4**)

$$2HCl + CaCO_3 \rightarrow CaCl_2 + H_2O + CO_2 \qquad (1.3)$$

$$4HCl + CaMg\,(CO_3)2 \rightarrow CaCl_2 + MgCl_2 + H_2O + CO_2 \qquad (1.4)$$

HCl degrades the Bandera sandstone core due to presence of more than 14 wt% clay particles. (Thomas et al. 2001). So another step is required before HCl injection to avoid the reaction of HCl with clay minerals. The idea here is to inject a chemical known as clay stabilizer before HCl injection. This chemical attaches to clays and covers the clay surface. However, it needs to be tested in the lab to avoid formation damage (Nasr-El-Din et al. 1999). The chemistry of clay stabilizers and how they attach to clay particles will be discussed later.

So far, there are three sequential stages to acidize Bandera sandstone cores:

1) Clay Stabilizer
2) HCl
3) HF

However, the treatment plan is not complete yet. HF is a weak acid. its dissociation equation and dissociation constant are given in **Equation 1.5** (Perrin. 1981)

$$HF \leftrightarrow H^{+} + F^{-} \ (pKa, HF = 3.17) \ \ldots\ldots \ (1.5)$$

As a weak acid, HF should never be injected alone. Another acid is needed to inject with HF to keep the pH low. This way, reaction products will remain soluble in spent acid (Yang et al. 2012). HCl is mostly used with HF to serve as a strong acid. However, HCl is corrosive especially at high temperature and will cause a lot of problems due to corrosion. Therefore, instead of HCl, organic acids will be used. The mixture of HF and organic acid that is used as main stage in acidizing sandstone reservoirs is known as organic mud acid. HCl will also be replaced by a mixture of HCl and formic acid to avoid corrosion. Ammonium chloride is used as a preflush to replace $Na^+$ and $K^+$ to avoid precipitation of fluosilicate salts (Gdanski 1998).

The complexity of sandstone acidizing is not because of the high order of heterogeneity. Reaction of HF with alumino silicates consists of three different stages of chemical reactions. These chemical reactions occur at different conditions and follow each other. (Gdanski 1999)

The primary reaction of HF with alumino silicates can be written in a general form, as shown in **Equation 1.6** (Gdanski 2000). Based on this equation all cations, M, such as $Na^+$ or $Fe^{2+}$, will require consumption of acid in order to maintain stoichiometric balance.

$$(5+x)HF + M - Al - Si + (3-x+1)H^+ \rightarrow$$

$$HSiF_5 + AlF_x^{(3-x)+} + M^+ + water \ldots\ldots\ldots\ldots\ldots \text{(1.6)}$$

The rate law of the primary reaction of HF with aluminosilicates is independent of HCl concentration and the second order in HF concentration.

The secondary reaction of HF with aluminosilicates is the reaction of fluosilicic acid with aluminoisilicates and its general form is shown in **Equation 1.7** (Gdanski 1999).

$$x/_5\, HSiF_5 + M - Al - Si + (3-x+1)H^+ + water \rightarrow$$

$$AlF_x^{(3-x)+} + M^+ + silica\ gel \ldots\ldots\ldots\ldots\ldots \text{(1.7)}$$

The reaction with the aluminosilicates to release the cations can be viewed as the acid dissolving the metal oxides. In this reaction, all portions of the clays are removed except the silicon, which results in an amorphous and chemically complex silica gel film. Also important, above 125°F this reaction goes to completion and substantial precipitation of potassium and sodium fluosilicates could occur.

The tertiary reaction of HF with aluminosilicates was first reported as **Equation 1.8** (Shuchart and Buster 1995).

$$AlF_2^+ + M - Al - Si + (3+1)H^+ + water \rightarrow$$
$$2AlF^{2+} + M^+ + Silica\ gel \ldots\ldots (1.8)$$

This reaction is quite slow on feldspars, and on clays it depends on temperature. In all three reactions of HF with aluminosilicates, x is the number of fluoride required to dissolve aluminum.

### 1.2.3 Clay Minerals

Clays are hydrated aluminosilicates meaning that these minerals are composed of two oxides, aluminum oxide and silicon dioxide. They also have a group of hydroxide. All clays have 4 main properties:

1. They are small particles. Their size is between 2 to 4 microns.
2. They have a huge surface area.
3. They are negatively charged.
4. They have the ability to exchange ions.

Four main types of clays are present in sandstone formations, kaolinite, illite, smectite and chlorite. Kaolinite causes fines migration when it comes into contact with fresh water or high pH fluids. Chlorite contains a large amount of iron. To avoid problems associated with chlorite, an iron controlling agent is required. Illite is a needle shape clay particle which is sensitive to HCl attack. HCl attacks illite structure and breaks down the layered structure of this clay and causes pore throat blockage. Fresh water causes smectite to swell. Smectite absorbs water into its structure due to presence of OH bond between layers.

Clay particles present in sandstone reservoirs are initially agglomerated or flocculated (Hill 1982). A sudden change in Salinity or pH of the surrounding environment makes them to disperse and block the pore throat (Zhou et al 1995).

If the salinity of the permeating fluid falls below critical salt concentration, clay particles will be dispersed. This specific value is termed “critical salt concentration”. The results of a standard water shock experiment are shown in **Figure 1.3** (Khilar and Fogler 1983). The normalized permeability drops from 1 to about 0.01 after only 2 or 3 pore volumes of fresh water were injected into the core. However, reversing the flow direction increases permeability temporarily. The permeability restoration with countercurrent flow reversal can be explained by assuming that clay particles come off the pore walls and migrate in the direction of flow until they are trapped by a pore throat. (**Figure 1.4**)

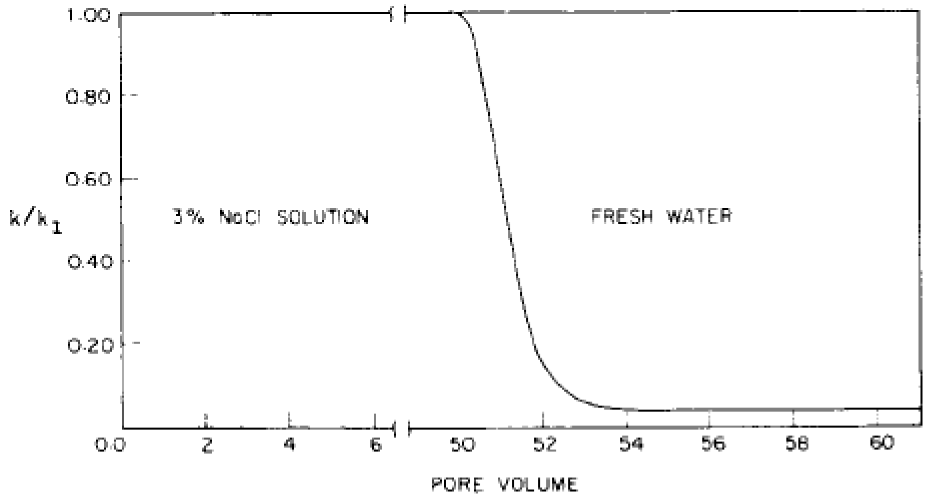

**Figure 1.3- Permeability reduction in a typical water shock experiment (Khilar and Fogler 1983)**

Swelling clays have a deficiency in their structural charge. The interlayer cations get hydrated and the structural layers get expanded and swelling occurs.

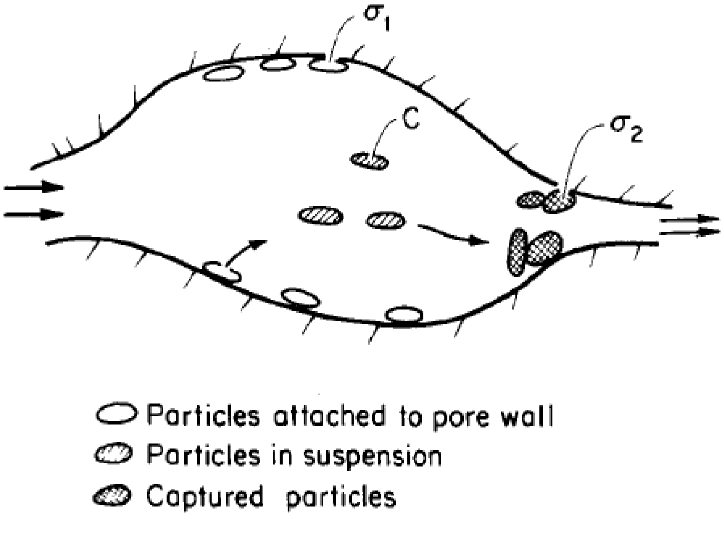

**Figure 1.4- Pore body and pore throat in the presence of clay particles (Khilar and Fogler 1983)**

Two main layers present in clay’s structure are tetrahedral and octahedral layers. Tetrahedral is the silicon-oxygen tetrahedral. Three later clays have two tetrahedral layers and one octahedral layer in between.

Montmorillonite, as shown in **Figure 1.5**, has magnesium between the layers.

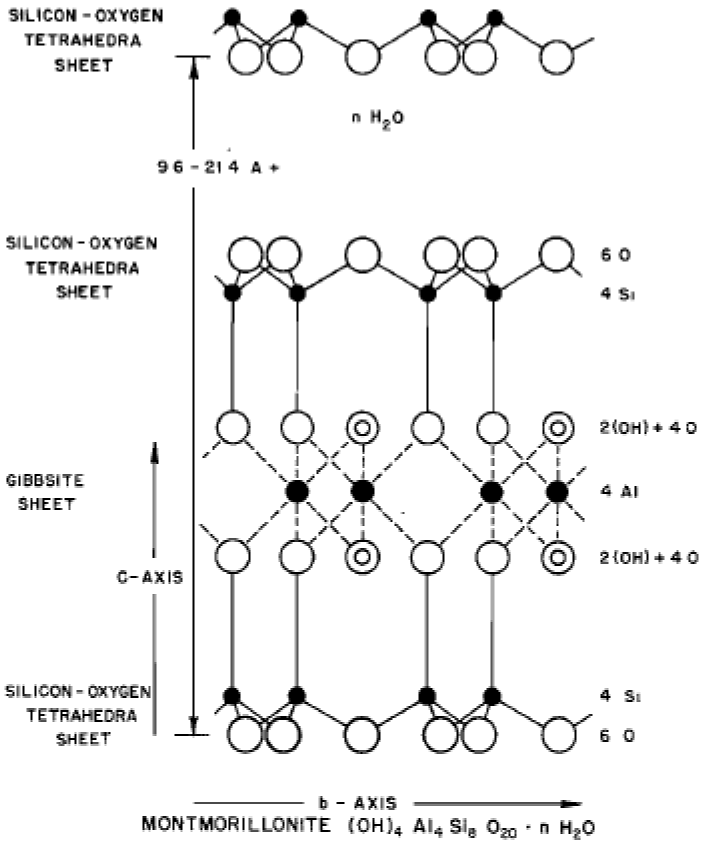

**Figure 1.5- Schematic crystal structure of montmorillonite (Hughes 1950)**

Substitution of cations is more in illite. The general formula of illite was proposed by Grim as $(OH)_4\ K_y\ (Al_4\ Fe_4\ Mg_4)\ Si_{8-y}\ Al_yO_{20}$, with the value of y varying from 1 to 1.5 (Hughes 1950). **Figure 1.6** shows the structure of illite.

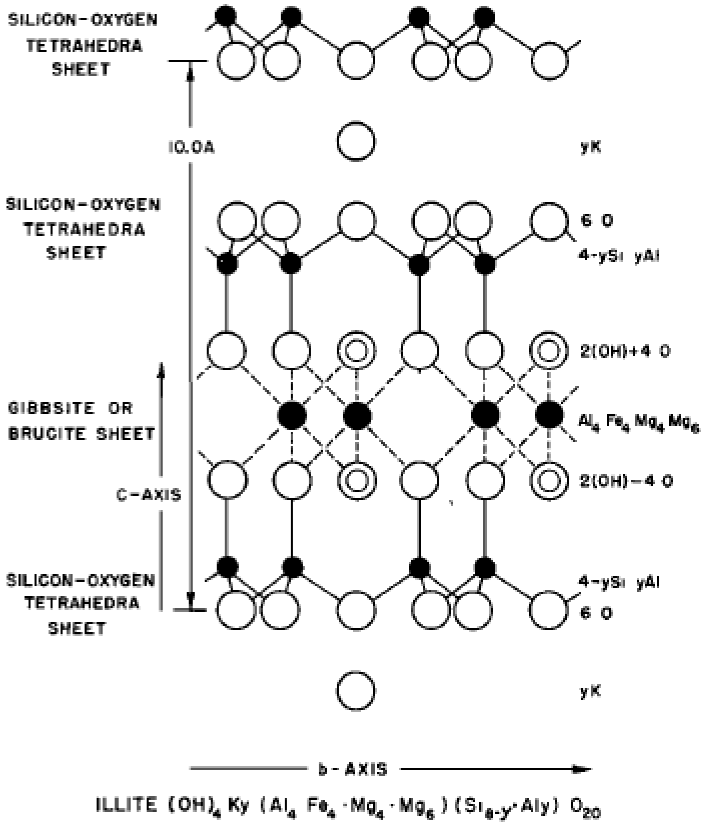

**Figure 1.6- Schematic crystal structure of illite (Hughes 1950)**

Kaolinite has no substitution in its structure and as a result, it is chemically stable. Kaolinite is a decomposition product of many aluminum silicates. The formula is given as $(OH)_8\ AL_4\ Si_4\ O_{10}$. **Figure 1.7** shows the structure of kaolinite.

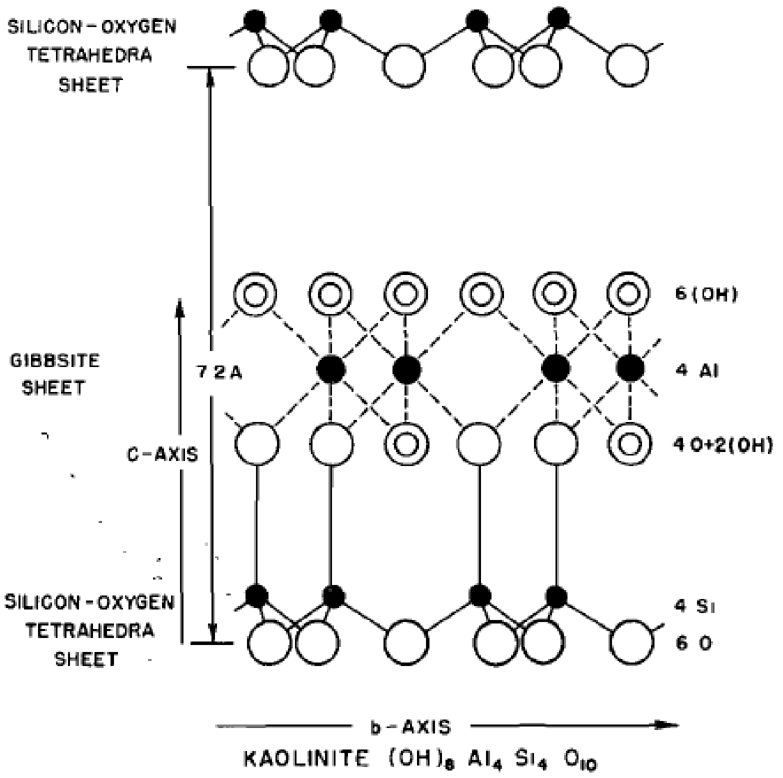

**Figure 1.7- Schematic crystal structure of kaolinite (Hughes 1950)**

Research has shown that clay particles are also sensitive to HCl. Illite and chlorite are the two main groups of clays that can have their structures degraded by HCl. HCl will leach Fe, Mg, and Al from chlorite clays by destroying the crystal structure and rendering the remaining material amorphous or non-crystalline (Simon and Anderson 1990).

To solve this problem, clay stabilizers are used to protect clay particles. The stabilizers are cationic solutions mainly $Al^{3+}$ and $Zr^{4+}$. El-Monier and Nasr-El-Din, presented new type of Al/Zr based stabilizers that is effective during and after acid treatment (El-Monier and Nasr-El-Din 2011).

## 1.3 Problem Statement

As mentioned in the previous section acidizing sandstone reservoirs has a long history and it has been an issue for many years. However, no unique solution has been presented for this challenge. Different methods that are successful in some cases, has led to formation damage rather than well stimulation and permeability improvement in others.

The main problem with sandstone acidizing is the complexity of minerals present. Each mineral has its own properties and needs to be treated differently. Exposing these minerals into one chemical will result in reaction products that might not be compatible with each other. As a result, it is almost impossible to find one chemical that is compatible with all minerals and serves as a stimulating fluid as well. Different concentrations of these minerals in different sandstone formations is another problem that makes sandstone matrix acidizing more challenging.

Sandstone acidizing is composed of three main stages including preflush, main stage and postflush. Preflush and postflush mostly consists of HCl to remove carbonate minerals and to keep the environment acidic. This way the reaction product will be soluble in spent acid. The main stage is mainly HF to dissolve aluminosilicates. However, the presence of clays and clay minerals that are not compatible with HCl results in a failure in matrix acidizing. Most of the works presented in the literature have been conducted on Berea sandstone, which has the lowest amount of clay minerals. Bandera sandstone, on the other hand, contains 14 wt% clay minerals which need to be considered as a source of formation damage. HCl will degrade clay particles and cause silica gel to precipitate and reduce the permeability. Clay stabilizers are the chemical used to avoid formation damage due to HCl attack on the surface of clay particles.

## 1.4 Research Objective

The objective of this research study is to present and evaluate a newly developed method for sandstone matrix acidizing. The main focus is on Bandera sandstone which was not addressed in the literature as much as Berea sandstone. The new method is a multi-stage treatment design that consists of the following stages:

1) Injection of brine
2) Injection of brine and clay stabilizer
3) Injection of HCl and formic acid
4) Injection of HF and formic acid
5) Injection of brine

In this study new types of clay stabilizers were utilized to assess their efficiency to cover clay particles and avoid formation damage. Different factors affecting success or failure of this treatment design were investigated. These factors include: type of the clay stabilizer, concentration of clay stabilizer, preflush pore volume and mineralogy of the rock. The objective is accomplished by conducting coreflood experiments and analyzing effluents collected during the experiment.

# 2. EXPERIMENTAL SETUP AND CONDITION

## 2.1 Coreflood Apparatus

**Figure 2.1** illustrates the coreflood setup utilized during this research study. This setup is composed of the following items:

1- Core holder
2- Pressure transducer
3- Backpressure regulator
4- Accumulators
5- Syringe pump
6- Data acquisition system
7- Enerpac pump
8- Heater
9- Sampler

The core holder is the main part of the system; the core is placed inside under a specific confining (overburden) pressure. **Figure 2.2** shows the core holder used for coreflood experiments appropriate for cores with the dimension of 1.5 in. in diameter and 6 in. in length. It is manufactured by Phoenix Instruments and is made of hastelloy. As can be seen in Figure 2.2, it is made up of three parts. The main body where the core is placed, the inlet, and outlet cap.

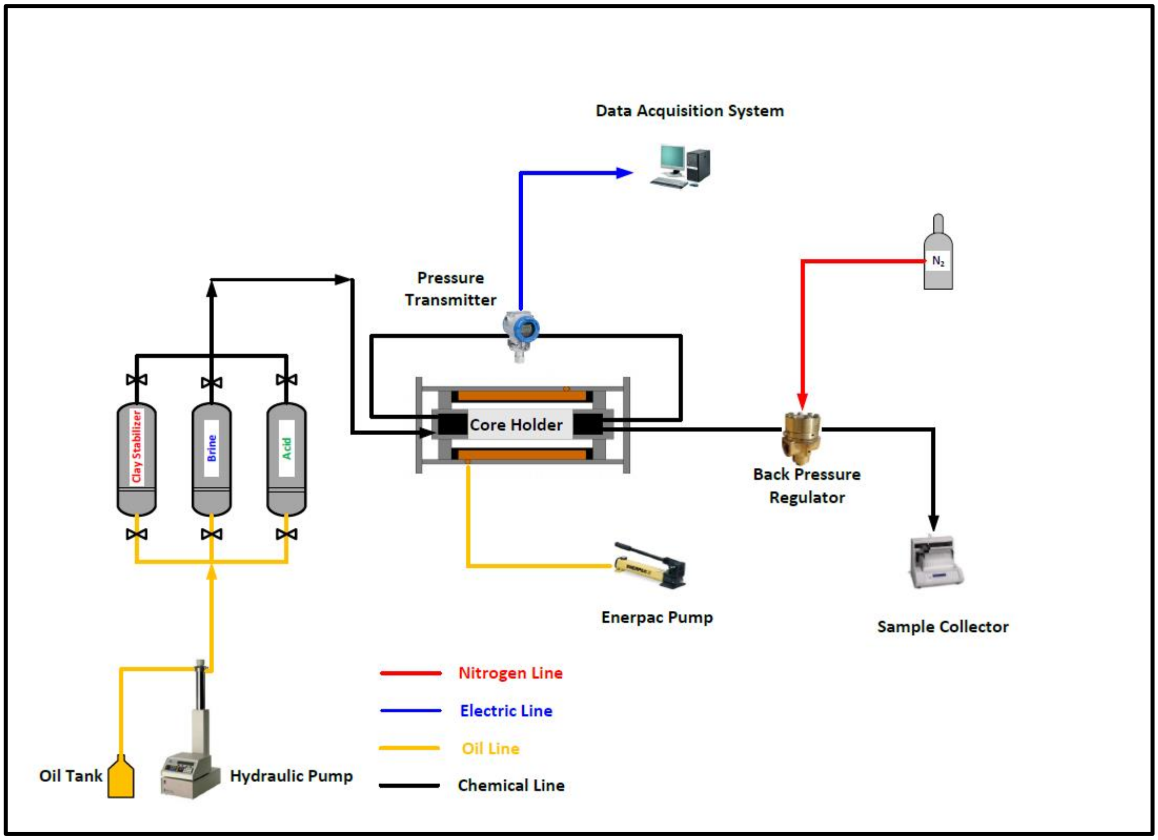

**Figure 2.1- Coreflood setup**

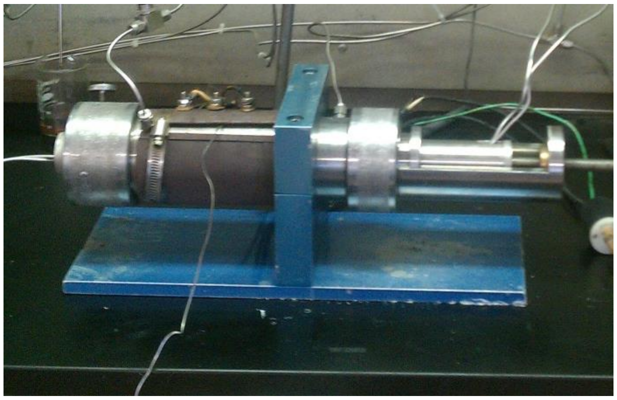

**Figure 2.2- 6 in. core holder**

The pressure transducer is used to measure the pressure drop across the core during the experiment. **Figure 2.3** shows the type of transducer used in this study.

**Figure 2.3- Pressure transducer**

The back pressure regulator is also used to control the pressure at the outlet of the core (downstream pressure). Setting the back pressure to 1200 psi or more keeps $CO_2$ in solution inside the core, and as a result it prevents drastic changes in pressure drop response. It also avoids the formation of a buffer during the experiment inside the core (**Figure 2.4**).

Figure 2.4- Back pressure regulator

Accumulators are used to place deionized water (DI), brine, acid, or other chemicals. **Figure 2.5** shows three accumulators employed for the coreflood setup. The accumulator on the left is used to place brine. The one in the middle is just for deionized water. The accumulator on the right is made of hastelloy and designed just for acid. Acid is never placed in accumulators in the middle or left. The core holder is connected to these accumulators, which contained various brines and the clay stabilizer solution. These vessels were connected in parallel and controlled by valves.

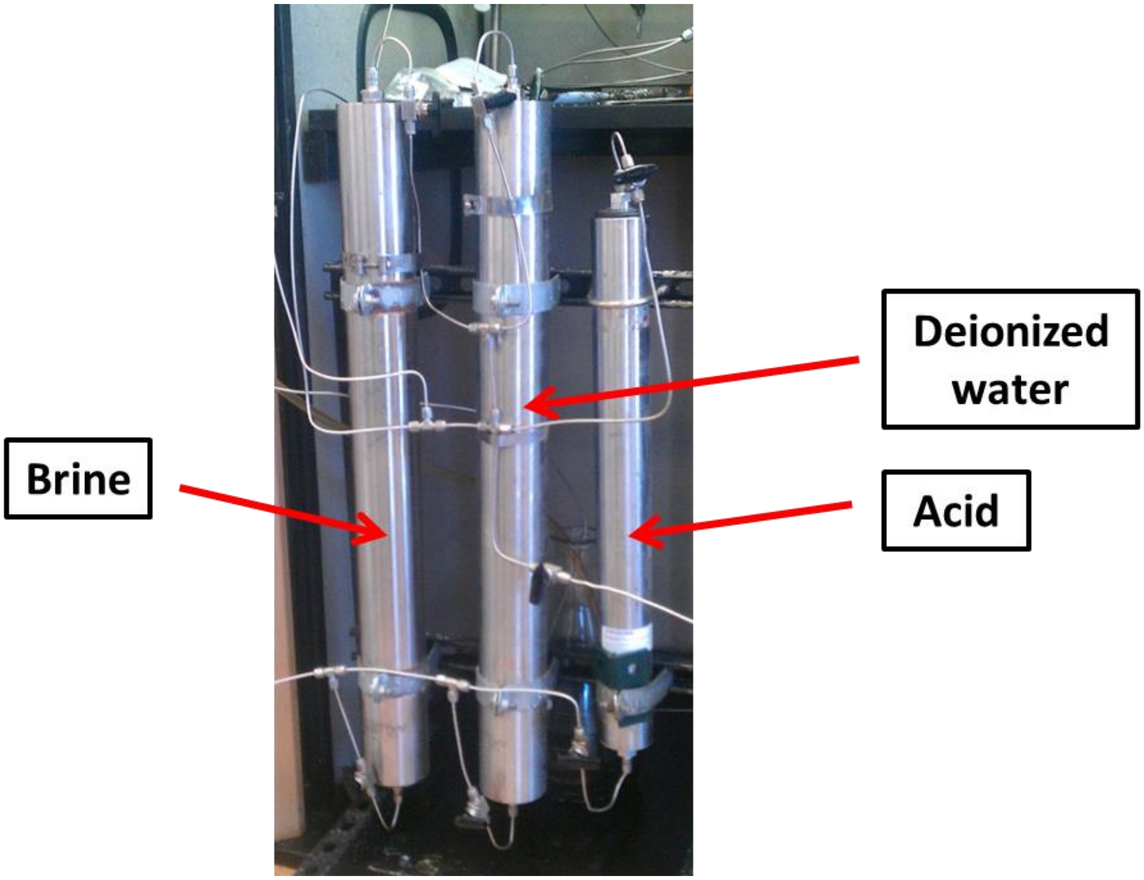

**Figure 2.5- Accumulators**

The syringe pump is also used to inject the intended fluid into the core during the experiment. The fluid can be pumped either on a constant flow rate or constant pressure status based on the experiment design. All experiments in this study were conducted with constant flow rate of 4 $cm^3$/min. **Figure 2.6** shows Teledyne ISCO used as a syringe pump for the coreflood setup.

**Figure 2.6- Syringe pump**

**Figure 2.7** shows the Enerpac pump used to apply the over burden pressure around the core while conducting the coreflood experiment. In all experiments, an overburden pressure of 2000 psi was fixed to squeeze the rubber sleeve around the core and represent reservoir conditions.

**Figure 2.7- Enerpac pump to supply overburden pressure**

The data acquisition system records the pressure drop response during the experiment. It consists of a signal processing board and a computer installed with LabView software. The pressure drop measured by the pressure transducer is transmitted to the software and recorded there. **Figure 2.8** also shows the signal processing board.

A heater is connected to the core holder to conduct the experiment at the temperature of interest. It is important to open the valve that controls the overburden pressure whenever the heater is on. The temperature was set to 140°F in all coreflood experiments in this research study.

A sample collector is used to collect fluid from the outlet of the core. Effluent samples are useful for further analysis and interpretation of results obtained. **Figure 2.9** demonstrates the sampler used while running the coreflood.

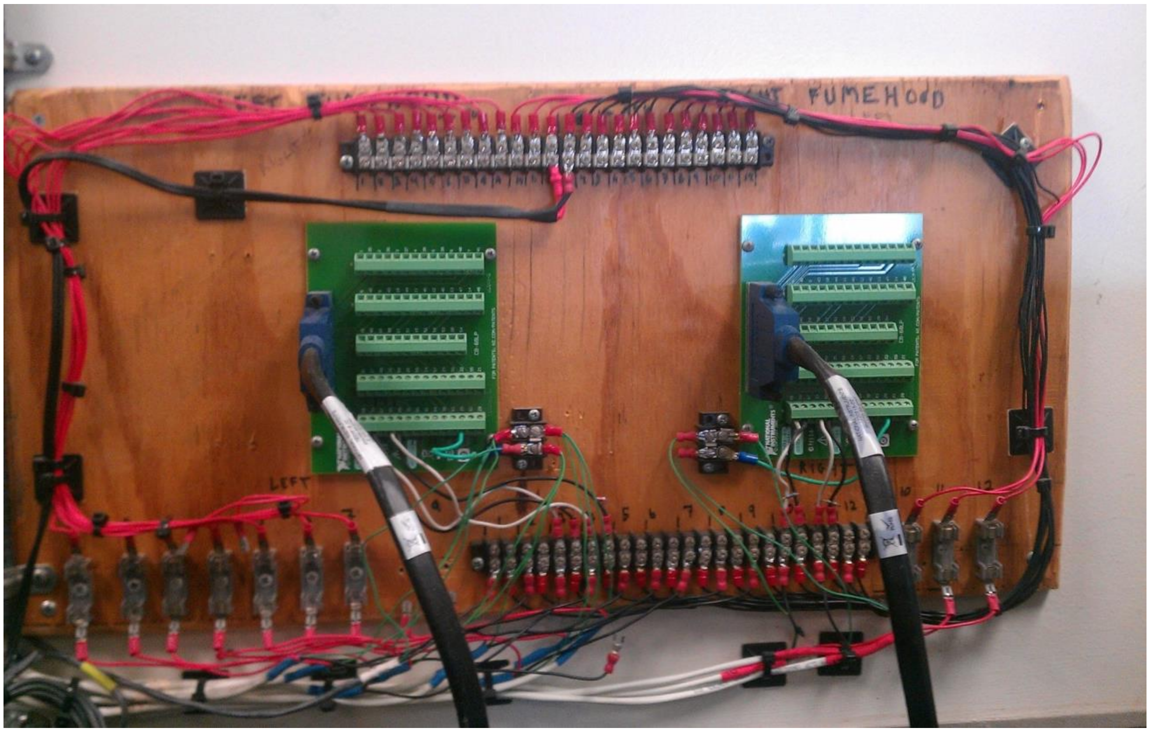

**Figure 2.8- Signal processing board**

**Figure 2.9- Sample collector**

## 2.2 Inductively Coupled Plasma (ICP)

Inductively Coupled Plasma (ICP) is the equipment used to measure the concentration of cations present in the effluent samples taken during the experiment. Inductively coupled plasma optical emission spectrometry is an analytical technique used for the detection of trace metals. It is a type of emission spectroscopy that uses the inductively coupled plasma to produce excited atoms and ions that emit electromagnetic radiation at wavelengths characteristic of a particular element. The intensity of this emission is indicative of the concentration of the element within the sample. The Optima 7000 DV is the ICP machine utilized in this study. It is shown in **Figure 2.10**.

The limitation of ICP is the maximum concentration of cations that can be measured. This value is 35 mg/L. For this reason all samples are diluted first before ICP analysis. To use ICP three steps are required:

1) Blank analysis
2) Standard analysis
3) Sample analysis

The blank is deionized water which is used to determine and set the zero value. Standards are used to calibrate the optima 7000 DV for each cation that is of interest. After calibration each sample is analyzed and concentrations are reported. Winlab32 is the software connected to the ICP and reports the amount of cations in each sample. **Figure 2.11** shows Winlab32 ICP software.

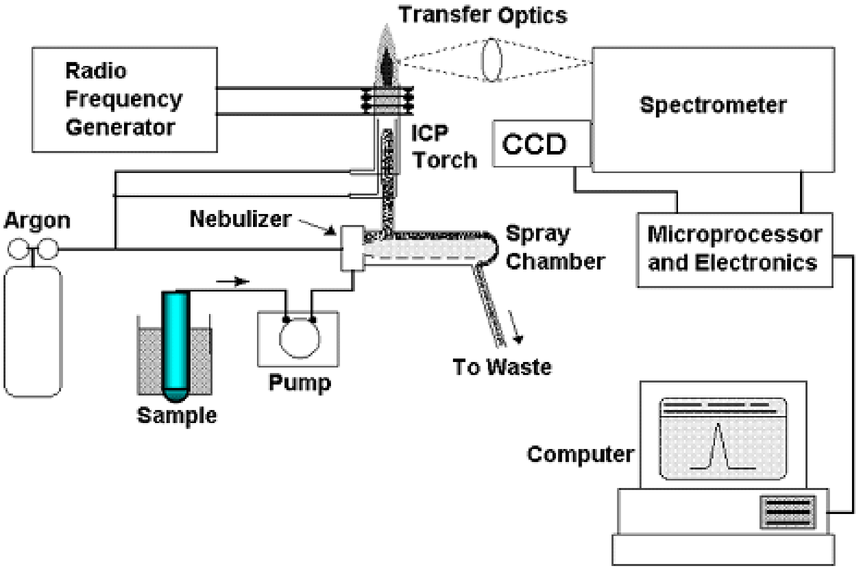

Figure 2.10- Major components and layout of a typical ICP-OES instrument

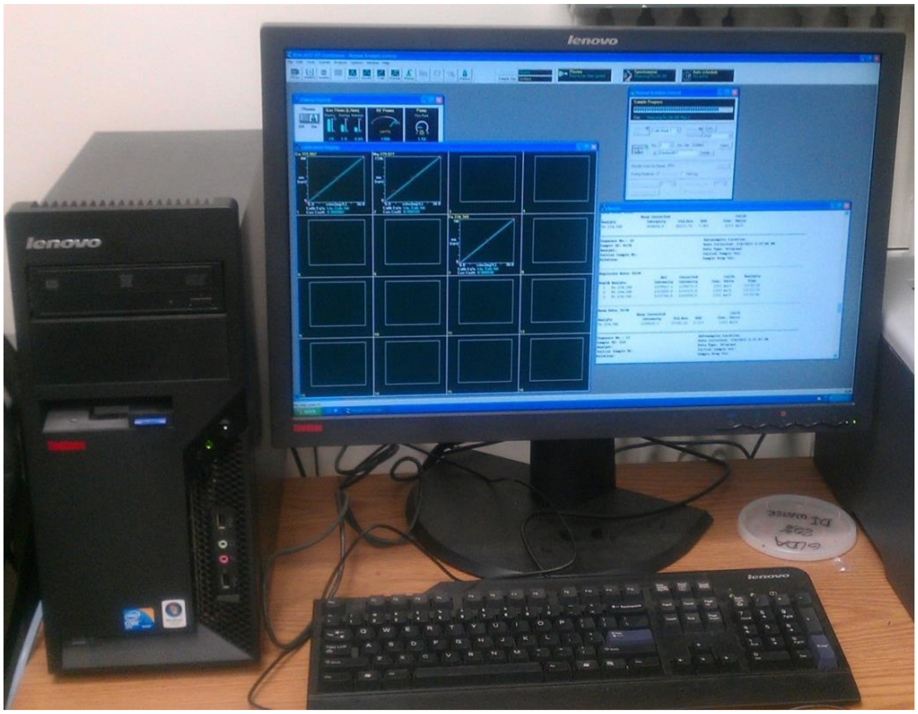

Figure 2.11- Winlab 32 ICP software

## 2.3 Scanning Electron Microscopy (SEM)

A scanning electron microscopy (SEM) is a type of electron microscope that produces images of a sample by scanning it with a focused beam of electrons. The electrons interact with electrons in the sample, producing various signals that can be detected and that contain information about the sample's surface topography and composition. SEM can achieve resolution better than a nanometer. **Figure 2.12** shows the Evex Mini SEM used in this study.

**Figure 2.12- Eves Mini SEM**

In this study SEM is used to analyze core samples and precipitation observed in the effluent samples. To do so, the samples need to be prepared first. The samples were first prepared by crushing them into fine particles. Then the broken pieces were mounted on a double stick carbon tape and coated with a thin film of gold. To coat the samples with gold, MSC-1000 Mini sputter coater was utilized. **Figure 2.13** shows the sputter coater used for this purpose.

**Figure 2.13- MSC-1000 Mini-Sputter Coater**

The coated samples were then inserted in the SEM specimen chamber and examined at 20 kV beam acceleration potential. **Figure 2.14** illustrates the chamber next to the camera where samples were inserted. SX-3000 is the software used to provide the image and EvexNanoAnalysis was used as software to run the elemental analysis.

**Figure 2.14- SEM Chamber**

# 3. EXPERIMENTAL PROCEDURE

This section describes the experimental procedure to conduct the coreflood experiments. It includes core plug preparations as well as pre-experiment measurements of core properties, acid injection, and post experiment analysis. To measure porosity and initial permeability of the core, it needs to be saturated first before acid injection.

## 3.1 Material

Formic acid 88% was obtained from Mallinckrodt Chemicals. Hydrochloric acid with a purity of 36.5% was also obtained from Macron Chemicals. Ammonium chloride was obtained with purity more than 99.5 wt% from Macron Chemical Fines. Ammonium bifluoride and corrosion inhibitor both were supplied by Schlumberger.

Three clay stabilizers were obtained from MaxFlo Oilfield Chemical Solutions. These chemicals will be referred to as CS-A, CS-B, and CS-C. The chemicals are proprietary clay stabilizers, were supplied in a liquid form, and were used without purification.

Core samples used in this study are both Berea and Bandera sandstone cores. Core plugs were cut in cylindrical form from Berea and Bandera sandstone outcrops in the size of 1.5 in. in diameter and 6 in. in length.

Distilled water with a resistivity of 18.3 MΩ.cm at room temperature was used to prepare all solutions.

## 3.2 Core Preparation

Core plugs were cut from Berea and Bandera sandstone outcrop blocks. Then they were placed in the oven for 6 hours at temperature of 250°F to dry completely. The weight of dried core was measured and used to measure the pore volume of core plugs. After that, the cores were saturated with brine (ammonium chloride 5 wt%). To do so, cores were connected to vacuum pump shown in **Figure 3.1**.

The saturated cores were weighed again. The weight difference divided by the density of the brine used to saturate the core plug gives the pore volume. (**Equation 3.2**) Porosity is obtained by dividing pore volume by bulk volume. (**Equation 3.3**)

$$V_{Bulk} = A.L = \frac{1}{4}\pi D^2 .L \quad \text{.......} \quad (3.1)$$

$$V_{Pore} = \frac{M_{saturated} - M_{dry}}{\rho_{brine}} \quad \text{.......} \quad (3.2)$$

$$\phi = \frac{V_{Pore}}{V_{bulk}} \times 100\% \quad \text{.......} \quad (3.3)$$

## 3.3 Fluid Preparation

Organic mud acid used in this study is a mixture of 1 wt% HF and 9 wt% formic acid. To prepare the HF, HCl and ammonium bifluoride were mixed based on the following equation. (**Equation 3.4**)

$NH_4HF2 + HCl \rightarrow 2HF + NH_4Cl$................................................................. (3.4)

Corrosion inhibitor was also added to the acid mixture to prevent corrosion of the coreflood system.

Using 300 g of organic mud acid, below is the calculation to find out the amount of each chemical required.

- ✓ **Ammonium bifluoride**:

300 g × 1 wt% = 3 g HF

3 g / (20 g/mol) = 0.15 mol

Based on Eq. 3.4, 0.075 mol of ammonium bifluoride is required.

Weight of pure ammonium bifluoride = 0.075 mol × 57 (g/mol) = 4.275 g

- ✓ **Hydrochloric acid:**

Based on Eq. 3.4, 0.075 mol of pure HCl is required.

Weight of pure HCl = 0.075 mol × 36.5 (g/mol) = 2.7375 g

Weight of HCl solution = 2.7375 g / 36.5% = 7.5 g

Volume of HCl solution = 7.5 g / (1.18 g/ml) = 6.36 ml

- ✓ **Formic acid:**

Weight of pure formic acid = 300 g × 9 wt% = 27 g

Weight of formic acid solution = 27 g / 88 wt% = 30.68 g

Volume of formic acid solution = 30.68 g / (1.2 g/ml) = 25.56 ml

Corrosion inhibitor is also 0.1 wt% which is 0.3 g. At the end, water is added to make the mixture 300 g.

Using 300 g of the preflush acid mixture, below is the calculation to find out the amount of each chemical required. The preflush acid used is a mixture of HCl and formic acid.

- ✓ **Hydrochloric acid**:

  Weight of pure HCl = 300 g × 5% = 15 g

  Weight of HCl solution = 15 g / 36.5% = 41.09 g

  Volume of HCl solution = 41.09 g / (1.18 g/ml) = 34.82 ml

- ✓ **Formic acid**:

  Weight of pure formic acid = 300 g × 5 wt% = 15 g

  Weight of formic acid solution = 15 g / 88 wt% = 17.05 g

  Volume of formic acid solution = 17.05 g / (1.2 g/ml) = 14.2 ml

## 3.4 Initial Permeability Measurement

The first coreflood experiment is conducted on each core to measure the initial permeability. This value will be used to compare initial and final permeability and to evaluate the efficiency of a multi-stage stimulation treatment design. To measure initial permeability, a core sample saturated with 5 wt% ammonium chloride is inserted inside core holder. Then, the accumulator is filled with brine. Brine is injected into the core until pressure drop across the core becomes stable. Darcy’s equation (**Equation 3.5**) governs fluid flow in porous media and is the main equation used to measure permeability in the coreflood experiments. To measure initial permeability, brine is injected into the core with a constant flow rate using hydraulic pump. The area, length, and viscosity of brine are the known parameters. A pressure transducer will determine pressure drop across the core. Permeability is measured using Darcy's equation and known parameters. (**Equation 3.6**)

$$Q = \frac{K.A}{\mu} \times \frac{\Delta P}{L} \quad \text{.......} \quad (3.5)$$

$$K = \frac{Q.L.\mu}{A.\Delta P} \quad \text{.......} \quad (3.6)$$

**Figure 3.1** shows a typical graph of pressure drop response during the coreflood experiment at a constant flow rate.

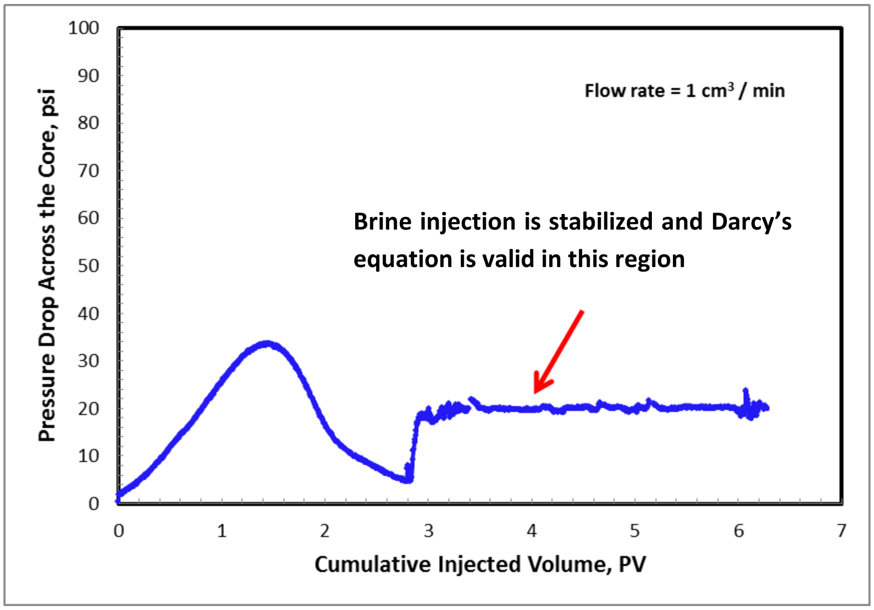

**Figure 3.1- Pressure drop response during brine injection with the flow rate of 1 $cm^3$/min into the saturated core to measure the initial permeability**

The initial permeability of all cores used in this study was measured based on the procedure explained above. **Table 3.1** lists initial porosity, initial permeability, and pore volume of the cores subjected to the newly developed acid treatment.

As can be seen in Table 3.1, the permeabilities of Berea and Bandera sandstone cores are completely different, revealing the effect of minerals and their concentration on core properties.

**TABLE 3.1 − Core Specifications**

| Core No. | Mineralogy | Dimension, in. × in. | Porosity | Permeability, md | Pore Volume, $cm^3$ |
|---|---|---|---|---|---|
| 1 | Bandera | 1.5 × 6 | 0.189 | 15.69 | 32.86 |
| 2 | Bandera | 1.5 × 6 | 0.192 | 17.6 | 33.3 |
| 3 | Bandera | 1.5 × 6 | 0.197 | 14.3 | 34.2 |
| 4 | Bandera | 1.5 × 6 | 0.183 | 17.7 | 31.86 |
| 5 | Bandera | 1.5 × 6 | 0.172 | 16.17 | 29.86 |
| 6 | Bandera | 1.5 × 6 | 0.166 | 15.23 | 28.83 |
| 7 | Berea | 1.5 × 6 | | | |

After permeability measurement, it is the time to test the novel treatment design. However, this treatment is designed to remove formation damage from the zone of altered permeability (Figure 1.1). To have a representative of this area, each core was damaged first using deionized water. Therefore, another coreflood was conducted to inject deionized water at a temperature of 140°F and flow rate of 4 $cm^3$/min. **Figure 3.2** demonstrates the result of deionized water injection into the Bandera sandstone core.

As can be seen in Figure 3.2, fresh water is not compatible with clays and clay minerals. It disperses fine particles attached to the surface of sands and thus leads to permeability reduction.

This process was conducted for the first three experiments conducted on cores No. 1, 2, and 3. **Table 3.2** shows the permeability of each core after deionized water injection.

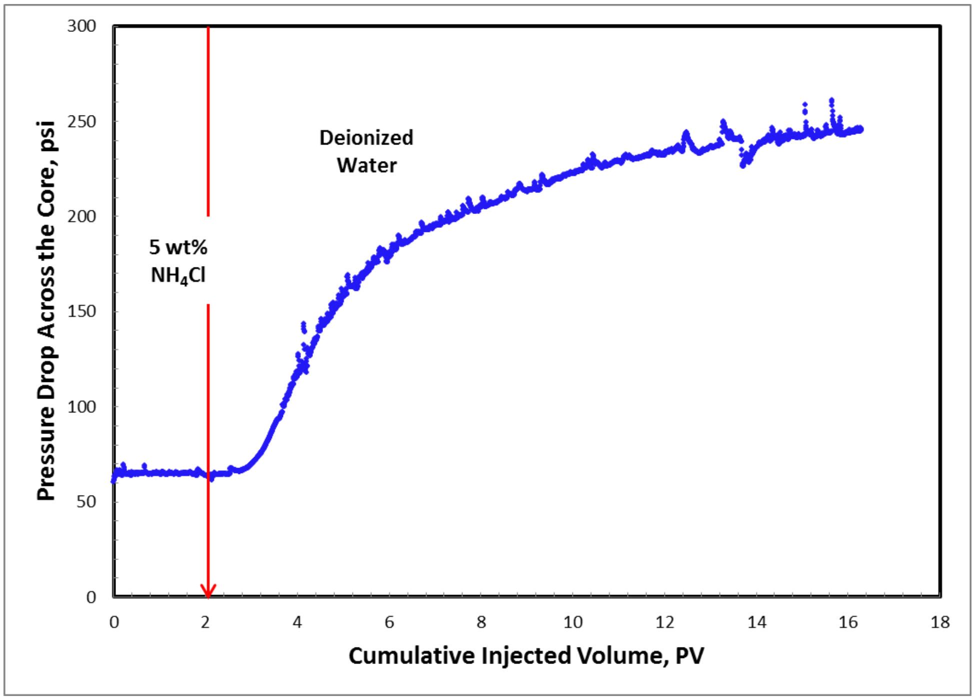

**Figure 3.2- pressure drop response during deionized water injection into the Bandera sandstone core at a temperature of 140°F**

| TABLE 3.2 − Effect of Fresh Water on Bandera Sandstone Cores | | | |
|---|---|---|---|
| **Core No.** | **Mineralogy** | **Initial Permeability, md** | **Damaged Permeability, md** |
| 1 | Bandera | 15.69 | 8.1 |
| 2 | Bandera | 17.6 | 7.3 |
| 3 | Bandera | 14.3 | 6.2 |

## 3.5 Acid Injection

### 3.5.1 Coreflood Experiment on Bandera Sandstone Without Using Stabilizer

To study the effect of HCl attack on clay particles during preflush injection, the first coreflood experiment was conducted on a Bandera sandstone core without using any clay stabilizer. The core was prepared as mentioned in section 3.2 and initial and damaged permeabilities were also measured (Section 3.4 and 3.5). Then, the damaged core was introduced into the acid treatment plan. **Table 3.3** shows the sequence of chemicals injected into the core in this experiment. The experiment temperature was 140°F and the flow rate was 4 $cm^3$/min.

| TABLE 3.3 —Acid Treatment Design for CF-1 | | | |
|---|---|---|---|
| **Brine** | **Preflush (5 PV)** | **Organic Mud Acid (5 PV)** | **Brine** |
| 5 wt% $NH_4Cl$ | 5 wt% HCl +<br>5 wt% formic acid | 1 wt% HF +<br>9 wt% formic acid | 5 wt% $NH_4Cl$ |

First, 5 wt% ammonium chloride was injected into the core until the pressure drop was stabilized. Then, 5 pore volumes of preflush mixture was injected into the core followed by 5 pore volumes of organic mud acid. At the end, 5 wt% ammonium chloride was injected into the core until a stable pressure drop was reached.

Effluent samples were collected while injecting chemicals every 2 minutes. So each tube contains 8 $cm^3$ of effluents representing nearly a quarter of core pore volume. Pressure drop response during the experiment was recorded to interpret the effect of chemical injection into the core. Effluent samples were used to determine concentration of major cations using ICP.

### 3.5.2 Coreflood Experiments on Bandera Sandstones Using the Stabilizers CSA and CSB

To investigate the effect of two different clay stabilizers, two coreflood experiments were conducted on Bandera sandstone cores. In coreflood experiments CF-2 and CF-3, clay stabilizers CSA and CSB were employed, respectively. **Table 3.4** demonstrates acid treatment design for these two experiments. The concentration of CSA used in CF-2 was 2 wt%, and CSB used in CF-3 was 4 wt%.

**TABLE 3.4 —Acid Treatment Design for CF-2 and CF-3**

| Experiment | Brine | Clay Stabilizer (2 PV) | Preflush (5 PV) | Organic Mud Acid (5 PV) | Brine |
|---|---|---|---|---|---|
| **CF-2** | 5 wt% $NH_4Cl$ | 5 wt% $NH_4Cl$ + **2** wt% **CSA** | 5 wt% HCl + 5 wt% formic acid | 1 wt% HF + 9 wt% formic acid | 5 wt% $NH_4Cl$ |
| **CF-3** | 5 wt% $NH_4Cl$ | 5 wt% $NH_4Cl$ + **4** wt% **CSB** | 5 wt% HCl + 5 wt% formic acid | 1 wt% HF + 9 wt% formic acid | 5 wt% $NH_4Cl$ |

In this set of experiments, brine was first injected until pressure drop was stabilized, and then it was switched to the clay stabilizer which was prepared in brine. Two pore volumes of this chemical was injected to ensure it covered all clay minerals inside the core. Then 5 pore volumes of preflush was injected followed by 5 pore volumes of organic mud acid. Both experiments were conducted at a temperature of 140°F and flow rate of 4 $cm^3$/min. Also; samples were collected every 2 minutes for further analysis.

These two experiments were conducted on the cores that were damaged with fresh water first. The objective was to remove formation damage using these two clay stabilizers.

### 3.5.3 Coreflood Experiments on Bandera Sandstones Using Stabilizer CSC with Different Preflush Pore Volume

To study the effect of a new clay stabilizer and preflush volume, two coreflood experiments, CF-4 and CF-5, were conducted on Bandera sandstone cores. Clay stabilizer CSC was used at a concentration of 2 wt% in both experiments. The difference between these two experiments and the previous set of experiments is that the experiments in the previous section were conducted on damaged cores. However, CF-4 and CF-5 were conducted to improve the initial permeability and the cores were not damaged before acid treatment. **Table 3.5** shows chemical injection sequence and pore volume injected.

**TABLE 3.5 —Acid Treatment Design for CF-4 and CF-5**

| | Brine | Clay Stabilizer (2 PV) | Preflush | Organic Mud Acid (5 PV) | Brine |
|---|---|---|---|---|---|
| **CF-4** | 5 wt% $NH_4Cl$ | 5 wt% $NH_4Cl$ + 2 wt% CSC | 5 wt% HCl + 5 wt% formic acid **(5 PV)** | 1 wt% HF + 9 wt% formic acid | 5 wt% $NH_4Cl$ |
| **CF-5** | 5 wt% $NH_4Cl$ | 5 wt% $NH_4Cl$ + 2 wt% CSC | 5 wt% HCl + 5 wt% formic acid **(10 PV)** | 1 wt% HF + 9 wt% formic acid | 5 wt% $NH_4Cl$ |

In CF-5, the preflush pore volume was increased from 5 to 10. The flow rate was 4 $cm^3$/min and temperature was 140°F. Effluent samples were also collected during the experiments to investigate efficiency of clay stabilizer CSC and preflush volume on the outcome of the stimulation.

### 3.5.4 Coreflood Experiments on Berea and Bandera Sandstones Using the Stabilizer CSC

To investigate the effect of mineralogy on matrix acidizing, two coreflood experiments were conducted using clay stabilizer CSC. Coreflood CF-6 was conducted using a Bandera sandstone core and coreflood CF-7 was conducted using a Berea sandstone core. All other experiment parameters (clay stabilizer pore volume, preflush pore volume, temperature, flow rate, clay stabilizer concentration, and so on) were kept constant to observe the effect of different mineralogy on the newly developed acid treatment plan. **Table 3.6** shows the chemical injection sequence for this set of experiments.

**TABLE 3.6 —Acid Treatment Design for CF-6 and CF-7**

| | Mineralogy | Brine | Clay Stabilizer (2PV) | Preflush (10 PV) | Organic Mud Acid (5 PV) | Brine |
|---|---|---|---|---|---|---|
| CF-6 | **Bandera** | 5 wt% $NH_4Cl$ | 5 wt% $NH_4Cl$ + 2 wt% CSC | 5 wt% HCl + 5 wt% formic acid | 1 wt% HF + 9 wt% formic acid | 5 wt% $NH_4Cl$ |
| CF-7 | **Berea** | 5 wt% $NH_4Cl$ | 5 wt% $NH_4Cl$ + 2 wt% CSC | 5 wt% HCl + 5 wt% formic acid | 1 wt% HF + 9 wt% formic acid | 5 wt% $NH_4Cl$ |

First, brine was injected until a stable pressure drop was reached, then 10 pore volumes of preflush was injected followed by 5 pore volumes of organic mud acid. Ultimately, 5 wt% ammonium chloride was injected until pressure drop across the core became stable.

Effluent samples were collected every two minutes during the experiment for further analysis and determination of key positive ions such as Ca, Mg, Si, Al, Fe, and Zr using an Optima 7000 DV ICP-OES system and WinLab 32™ software.

### 3.6 Post Experiment Analysis

- Final Permeability Measurement:

  After the multi-stage acidizing has been completed for each coreflood experiment, another coreflood experiment was conducted to measure the final permeability of the core. To do so, another coreflood setup, which has a different pressure transducer was employed. This pressure transducer is more accurate for low pressure drop and provides more precision.

  Measuring final permeability was conducted at room temperature and 5 wt% ammonium chloride was used as the flowing fluid into the core. An overburden pressure was set to 2000 psi. Back pressure was set to 500 psi.

  Comparing initial permeability, damaged permeability, and final permeability after acid treatment is a good indicator of how successful an acid treatment plan is.

- Aqueous Phase Analysis:

  Samples collected during coreflood experiments are a great source of information to interpret and analyze what chemical reactions occurred. For example, a sudden reduction in the concentration of a specific cation during an experiment might be an indicator of precipitation inside the core.

To measure the concentration of key cations, samples were first diluted to a specific order using deionized water and a pipet. Key elements that are generally of interest in sandstone acidizing are: Ca, Mg, Fe, Al, Si, Zr. In this study, phosphorus was also observed in effluent samples, so it was measured in all experiments to track its presence in effluents.

- Solid Phase Analysis:

Precipitation was observed in the effluent samples of coreflood experiments conducted on Bandera sandstone. Precipitation is a serious issue and the source of this occurrence needs to be addressed. To do so, a scientific approach is to determine the chemical composition of these precipitation. SEM was conducted to determine the minerals and/or elements of precipitation.

The solid phase present inside each tube was first filtered using filter paper and then dried and prepared for SEM analysis.

- Computed Tomography (CT) Scanning:

Computed tomography is a procedure that utilizes a computer-processed X-ray to produce tomographic images or slices of specific areas of the core. It was used to scan the cores before and after acid treatment. It measures CT numbers of each point. The CT number is associated with the mineral present at each location and is related to the density based on the **Equation 3.7** (Akin and Kovscek 2003).

$$\rho_{bulk} = aCTN + b \qquad (3.7)$$

In this equation CTN is the CT number, a is the slope, and b is the intercept of the linear equation relating the CT number and density.

# 4. EXPERIMENTAL RESULTS AND DISCUSSION

## 4.1 Coreflood Experiment on Bandera Sandstone Without Using Stabilizer

The first coreflood experiment (CF-1) was conducted on a Bandera sandstone core. Pressure drop across the core as function of cumulative injected pore volume is shown in **Figure 4.1**. Pressure drop is erratic and inconsistent during preflush (HCl and formic acid). This indicates that HCl is not compatible with clay minerals present in Bandera sandstone cores (i.e. illite and chlorite) at 140°F. Hence, HCl reacts with illite and chlorite and leaches an alumina layer out of the mineral structure. The remaining is an amorphous silica layer that precipitates as silica gel.

HCl attack on the surface of clays leaves portion of carbonate minerals that are not dissolved which is another source of formation damage when organic mud acid is injected into the formation. It is shown in Figure 4.1 that the pressure drop increased from 100 psi to more than 200 psi during the HF and formic acid stage. This is due to precipitation of calcium and magnesium fluoride precipitation. This reaction reduces porosity and as a result, reduces the permeability of the Bandera sandstone core.

**Figure 4.2** is the ICP result showing the concentration of key cations in the effluent samples. During preflush HCl dissolves carbonate minerals and reacts with clay particles.

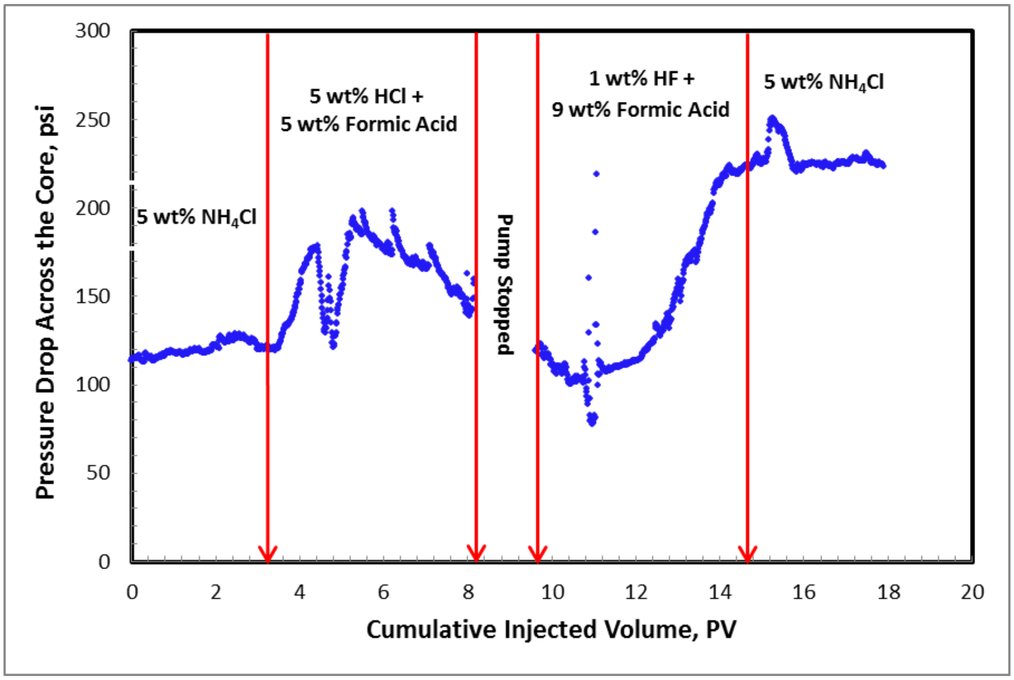

**Figure 4.1-pressure drop response during coreflood experiment CF-1**

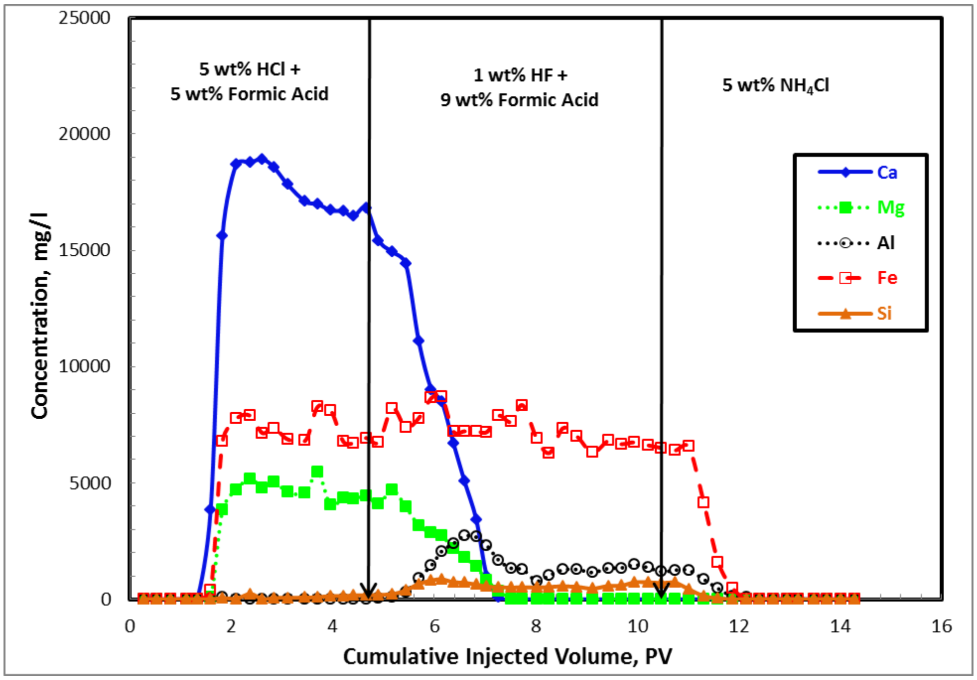

**Figure 4.2- ICP result of coreflood experiment CF-1**

During organic mud acid injection, Ca and Mg concentration in the effluents decreased sharply to zero, which indicates reaction of HF with dolomite and precipitation of $CaF_2$ and $MgF_2$.

**Figure 4.3** shows the result of the SEM analysis for precipitation that occurred during preflsuh injection (5 wt% HCl + 5 wt% formic acid).

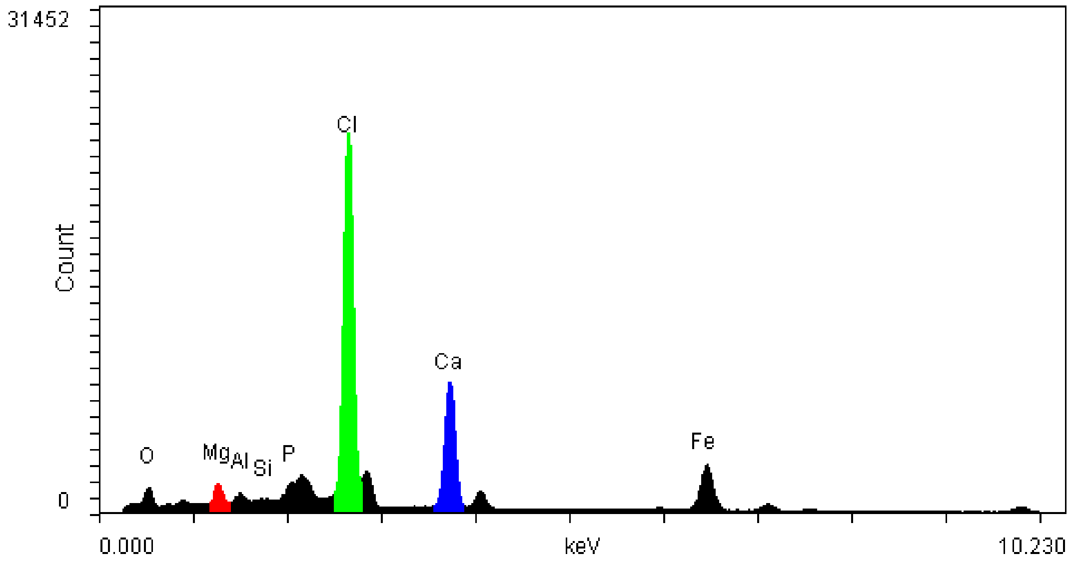

**Figure 4.3- SEM analysis of precipitation occurring during preflush in coreflood experiment CF-1**

The presence of Al and Si is due to HCl attacking the clay particles. Fe is coming either from corrosion or chlorite. **Figure 4.4** demonstrates the result of SEM analysis conducted on precipitation occurring during organic mud acid injection (1 wt% HF + 9 wt% formic acid).

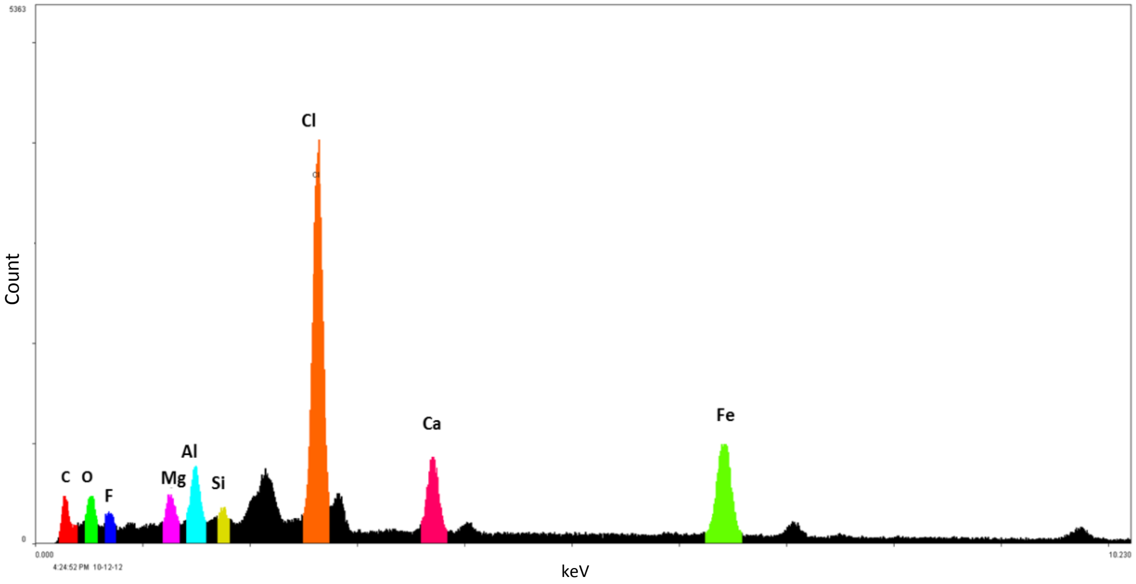

**Figure 4.4- SEM analysis of precipitation occurring during organic mud acid injection in coreflood experiment CF-1**

The presence of calcium, magnesium, and fluoride indicates that $CaF_2$ and $MgF_2$ have been produced during organic mud acid injection. All these results show that clays in Bandera Sandstone cores are sensitive to HCl attack at a temperature of 140°F.

This experiment demonstrates the reason why formation damage occurs rather than permeability improvement in sandstone matrix acidizing. The final permeability after acid treatment decreased from 8.1 to 3.2 md. However, the objective was to restore the initial permeability (15.7 md) after fresh water injection.

## 4.2 Coreflood Experiments on Bandera Sandstones Using the Stabilizers CSA and CSB

Coreflood experiments CF-2 and CF-3 were conducted on Bandera sandstone cores. Both cores were first preflushed using clay stabilizer solution (5 wt% ammonium chloride and 2 wt% CSA or 4 wt% CSB). **Figures 4.5** and **4.6** show the pressure drop response for CF-2 and CF-3, respectively.

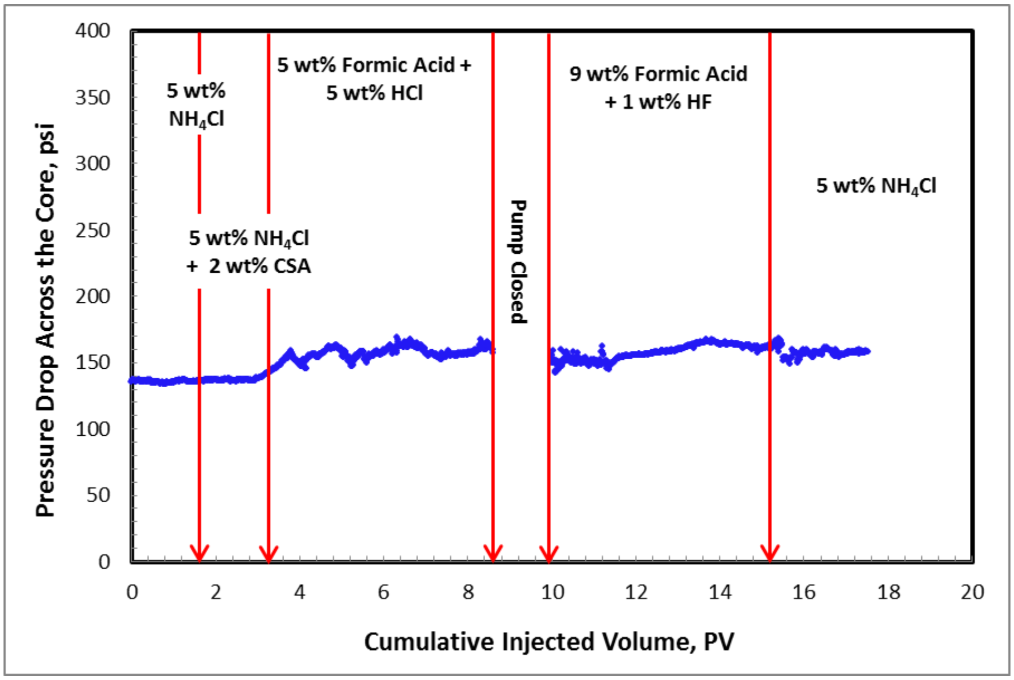

**Figure 4.5- pressure drop response during coreflood experiment CF-2**

As can be seen in the figure above, the pressure drop response during preflush was not as erratic as that in CF-1, indicating clay stabilizer CSA was able to flocculate dispersed clays and exchange enough amounts of positive ions on the surface of clays.

As a result, clay particles were covered by $Al^{3+}$ and $Zr^{4+}$ originating from clay stabilizer CSA. However, pressure drop response in coreflood CF-3 shows a sharp increase during HCl injection. This indicates clay stabilizer CSB was not able to attach to clay particles during HCL injection. In other word, HCl dissolved and removed CSB from the rock surface.

CSA preflush led to a reaction of HCl with carbonate minerals. Therefore, HF did not react with considerable amounts of calcite and dolomite. On the other hand, in coreflood CF-3 when organic mud acid was injected, plentiful amounts of carbonate minerals were still present inside the core. So, the same result as coreflood CF-1 was obtained.

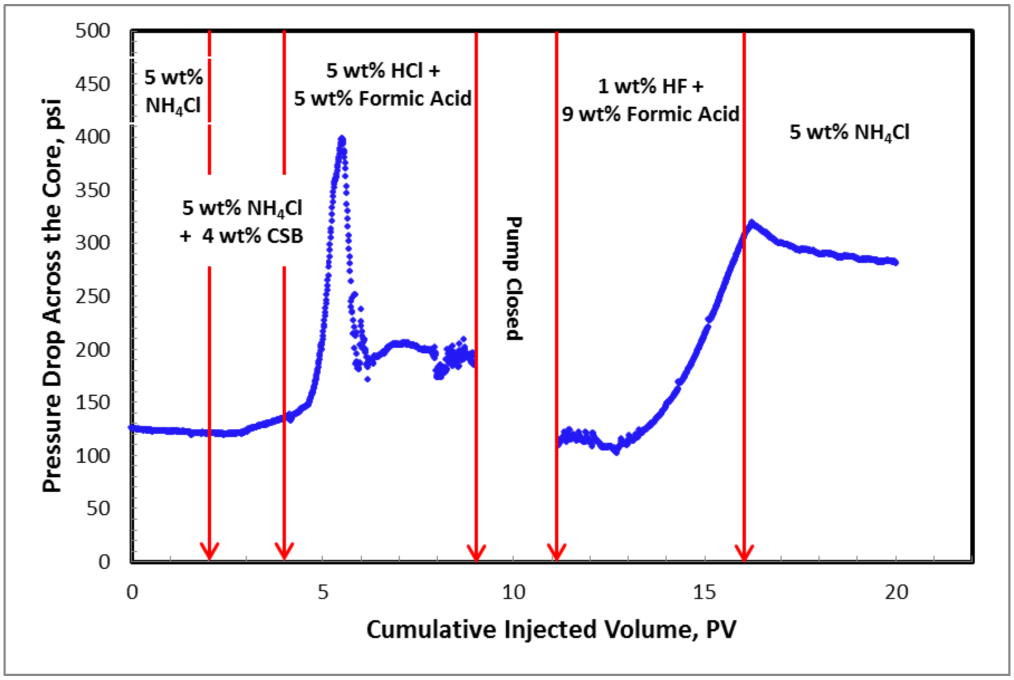

**Figure 4.6- pressure drop response during coreflood experiment CF-3**

Comparing Figures 4.4 and 4.6 shows a similarity between the trend of pressure drop response in corefloods CF-1 and CF-3. In spite of using clay stabilizer CSB, formation damage occurred and permeability decreased from 6.2 to 2.9 md. However, coreflood CF-2 led to permeability improvement and successful matrix acidizing. Permeability increased from 7.3 to 12.9 md. **Figures 4.7.a** and **b** show the ICP result of coreflood experiment CF-2.

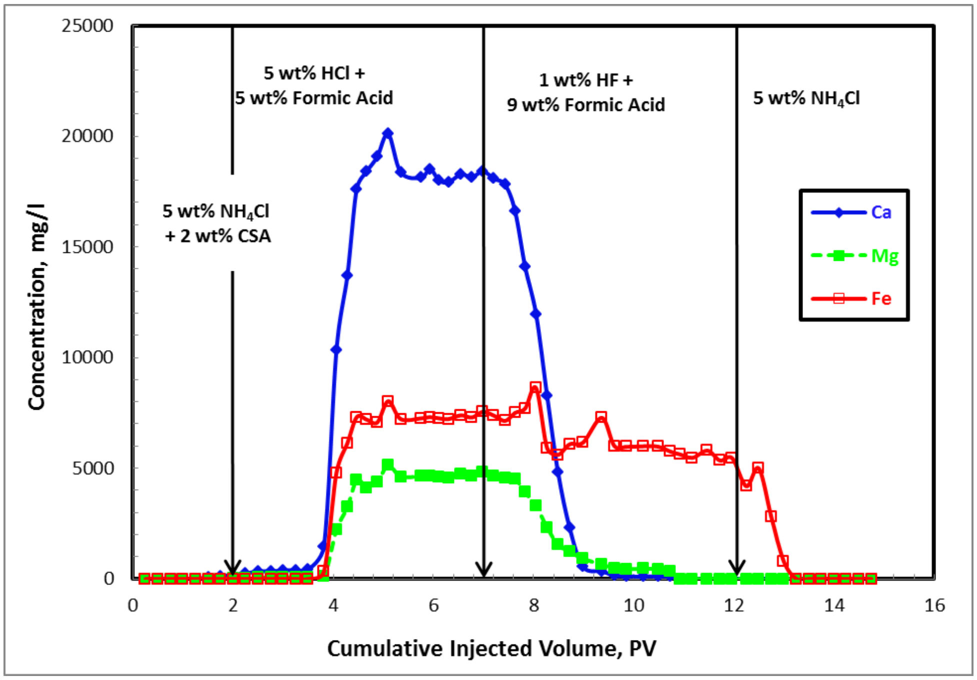

**Figure 4.7.a- ICP result of coreflood experiment CF-2 (Ca, Mg, Fe)**

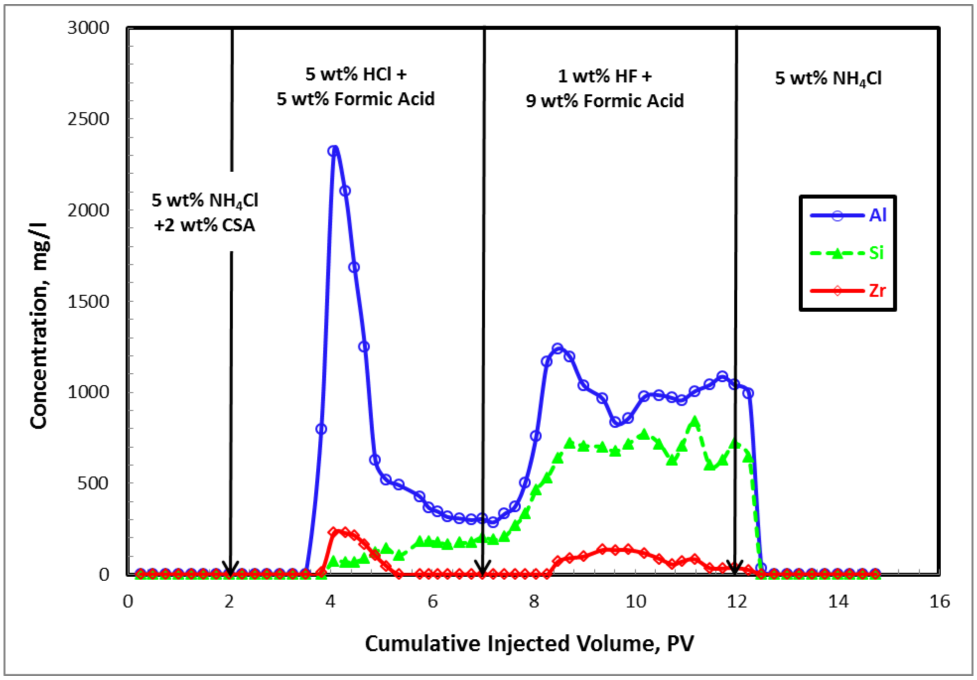

**Figure 4.7.b- ICP result of coreflood experiment CF-2 (Al, Si, Zr)**

As can be seen in **Figure 4.7.a** the amount of calcium and magnesium in the effluent samples in this experiment is more than that in experiment CF-1. Figure 4.7.b depicts a temporary sharp increase in the concentration of aluminum and zirconium during preflush. This increase in the concentration of aluminum and zirconium originates from clay stabilizer CSA. This demonstrates that using 2 wt% of CSA was more than enough to cover and secure clay particles. Another explanation is that HCl might have dissolved a portion of clay stabilizer. The second explanation seems to be more realistic because it confirms the presence of Si in effluent samples in the preflush. It can be concluded that CSA is not able to attach completely to clay particles.

It can be seen that the concentrations of Al and Si show a considerable increase when preflush is changed to organic mud acid, meaning that HF reacts with silica and alumino silicates present in the core. As a result, this stimulation plan improves final permeability.

Although there is permeability improvement, precipitation occurred in the effluent samples collected during CF-2. SEM analysis was conducted to determine elements present to determine the reason of this happening.

**Figures 4.8** and **4.9** show the result of SEM analysis conducted on precipitation during preflush and organic mud acid stages, respectively.

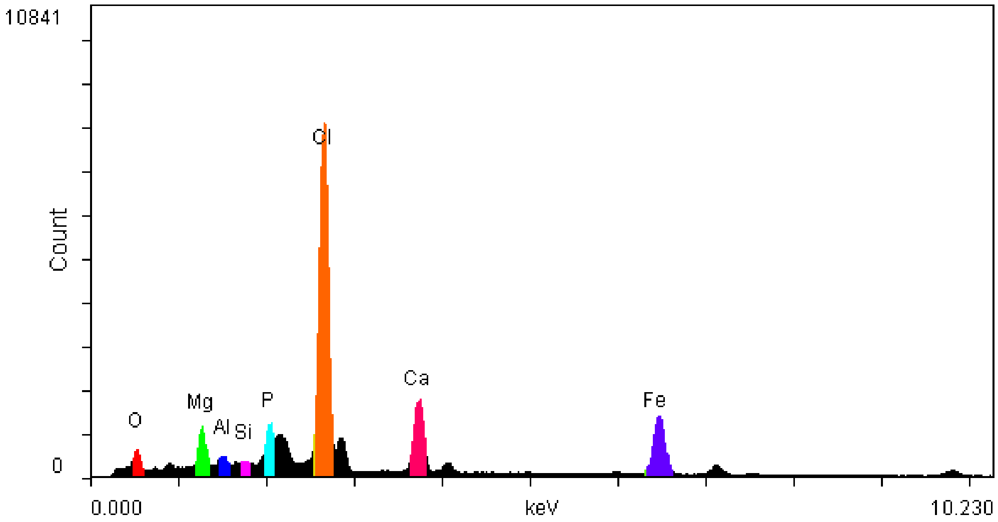

**Figure 4.8- SEM analysis of precipitation occurring during preflush injection in coreflood experiment CF-2**

The presence of Si and Al in solids also confirms the explanation that clay stabilizer CSA is not able to cover clays perfectly. Phosphorus was also detected by SEM analysis, which is not reported in the literature. The presence of phosphorus is discussed later.

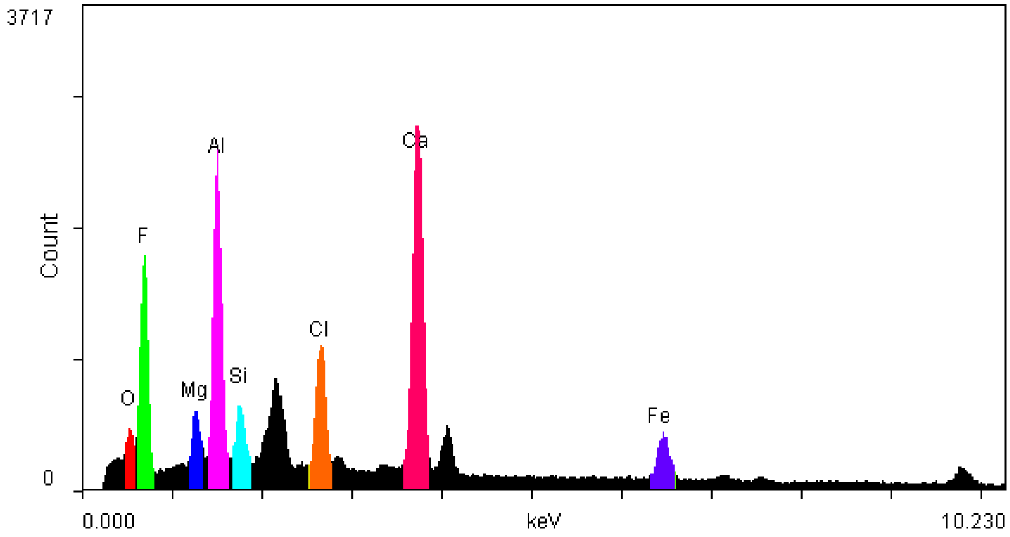

**Figure 4.9- SEM analysis of precipitation occurring during organic mud acid injection in coreflood experiment CF-2**

The presence of Ca, Mg, and F is a sign of precipitation of calcium and magnesium fluoride, demonstrating 5 pore volumes as preflush was not sufficient to dissolve carbonates. Also, Al and F precipitated as complex compounds.

The ICP result of coreflood experiment CF-3 can be seen in **Figures 4.10.a** and **b**. Again, a sharp increase in Zr and Al concentrations originates from clay stabilizer CSB. In coreflood experiment CF-3 the concentration of clay stabilizer increased to 4 wt%. However, the concentration of Zr in effluents is much more than what was expected comparing to that in coreflood experiment CF-2. The amount of Ca and Mg in effluents is less than their concentration in CF-2. Also, Si concentration decreased quickly in the organic mud acid stage.

Final permeability after acid treatment using clay stabilizer CSB in coreflood experiment CF-3 decreased from 6.2 to 2.9 md. The conclusion for CF-3 is that clay stabilizer CSB is inefficient to exchange cations with clays and flocculate dispersed particles.

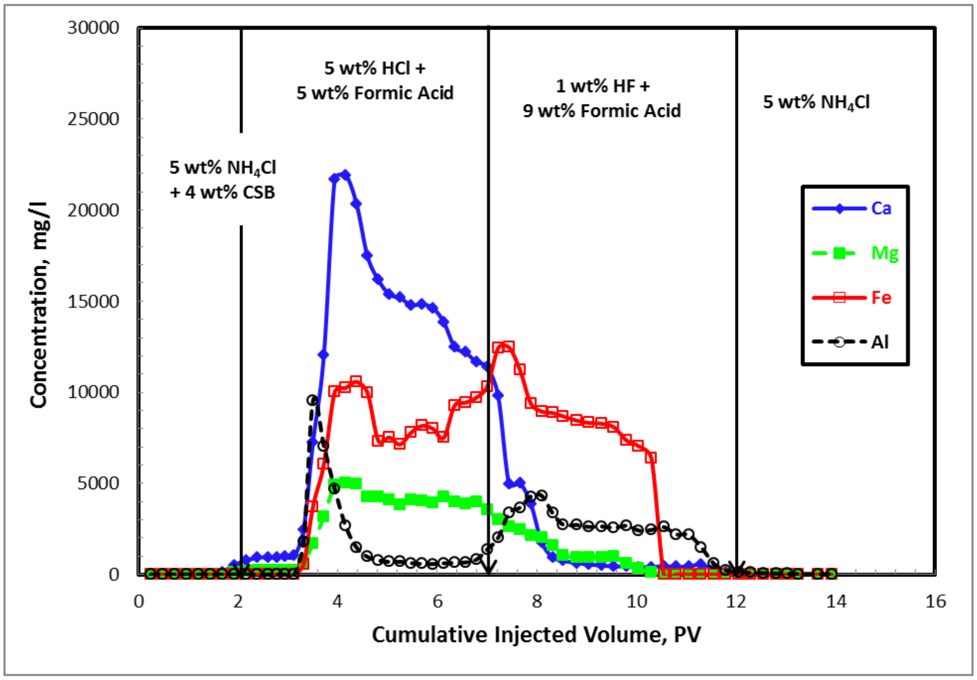

Figure 4.10.a- ICP result of coreflood experiment CF-3 (Ca, Mg, Fe, Al)

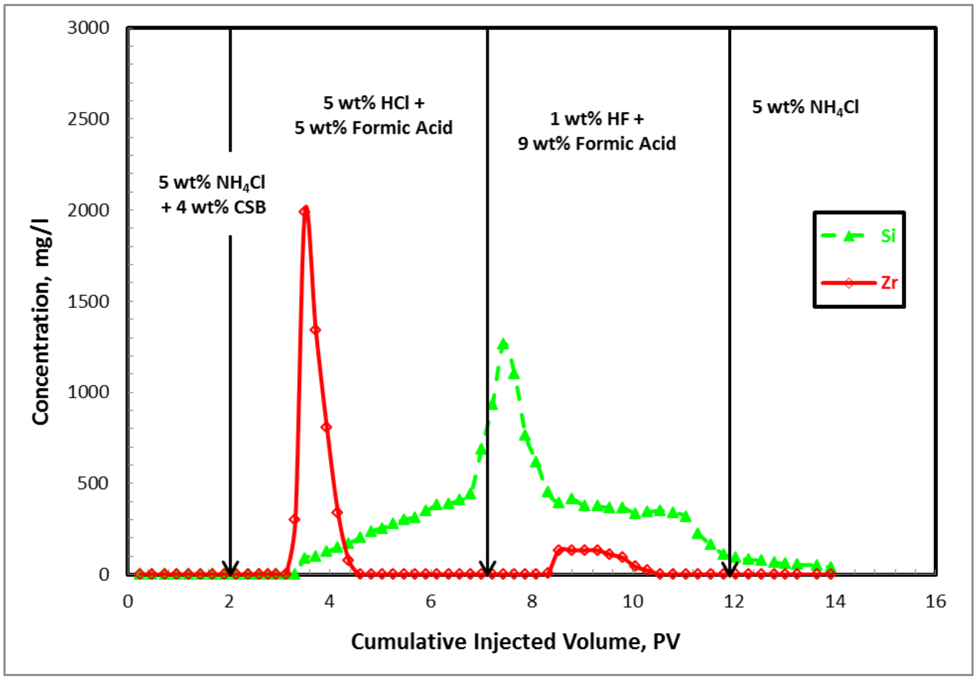

**Figure 4.10.b- ICP result of coreflood experiment CF-3 (Si, Zr)**

As a result, during preflush, HCl will react with illite and chlorite and remains amorphous silica gel. Precipitation occurred again in this coreflood experiment. **Figures 4.11** and **4.12** show the SEM analysis of solids during preflush and organic mud acid stages, respectively. Solids from samples were filtered first using filter paper and then dried.

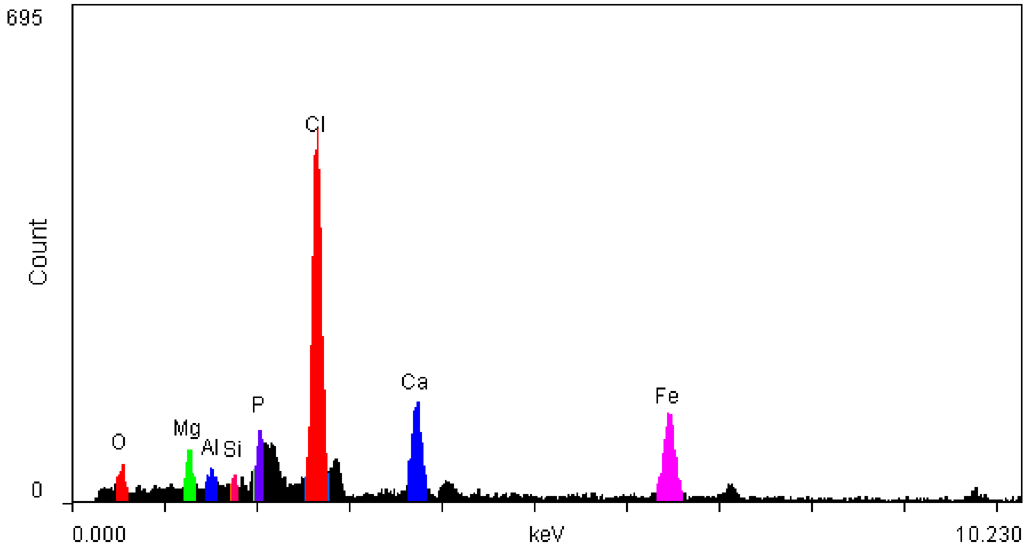

**Figure 4.11- SEM analysis of precipitation occurring during preflush injection in coreflood experiment CF-3**

Precipitation during preflush contains Al and Si which comes from the reaction of acid with clay particles. Phosphorus was also detected in the precipitation as in previous experiment.

Calcium, magnesium and fluoride were all identified in SEM analysis of the precipitation during the organic mud acid stage, meaning HF reacted with calcite and dolomite and the reaction products are $CaF_2$ and $MgF_2$.

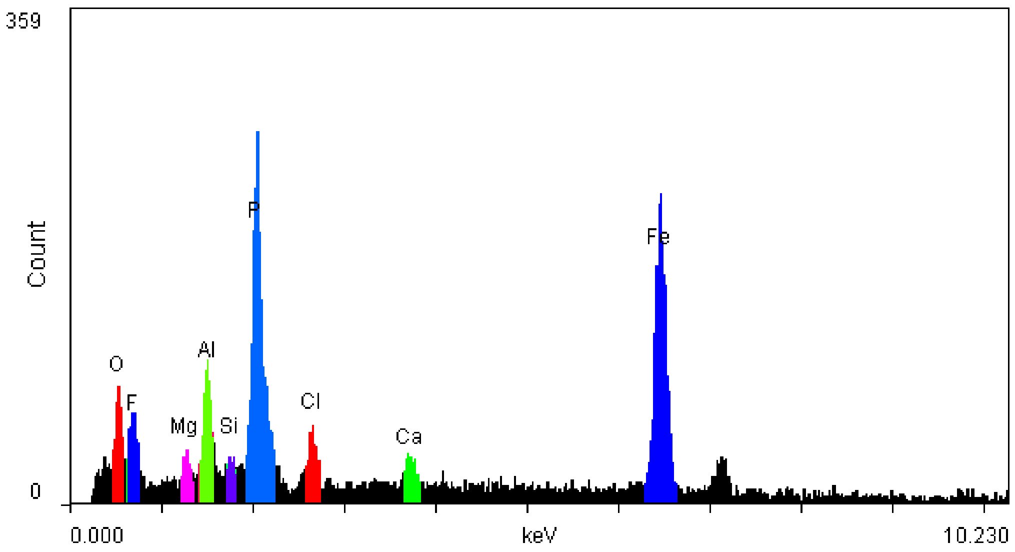

**Figure 4.12- SEM analysis of precipitation occurring during organic mud acid injection in coreflood experiment CF-3**

### 4.3 Coreflood Experiments on Bandera Sandstones Using Stabilizer CSC with Different Preflush Pore Volume

Coreflood experiments CF-4 and CF-5 were conducted on Bandera sandstone cores using clay stabilizer CSC. The main difference between these two experiments is the preflush pore volume. In coreflood CF-4, 5 pore volumes of preflush was used. However, in coreflood CF-5, 10 pore volumes of preflush was injected into the core.

**Figure 4.13** shows the pressure drop response across the core during coreflood experiment CF-4. There is no drastic change or spike in pressure drop during this experiment. It points out that the clay stabilizer CSC was capable of covering clay particles. As a result, HCl did not react with illite and chlorite as it did in CF-1 and CF-3.

**Figures 4.14.a** and **b** show the result of ICP analysis on effluent samples in this experiment.

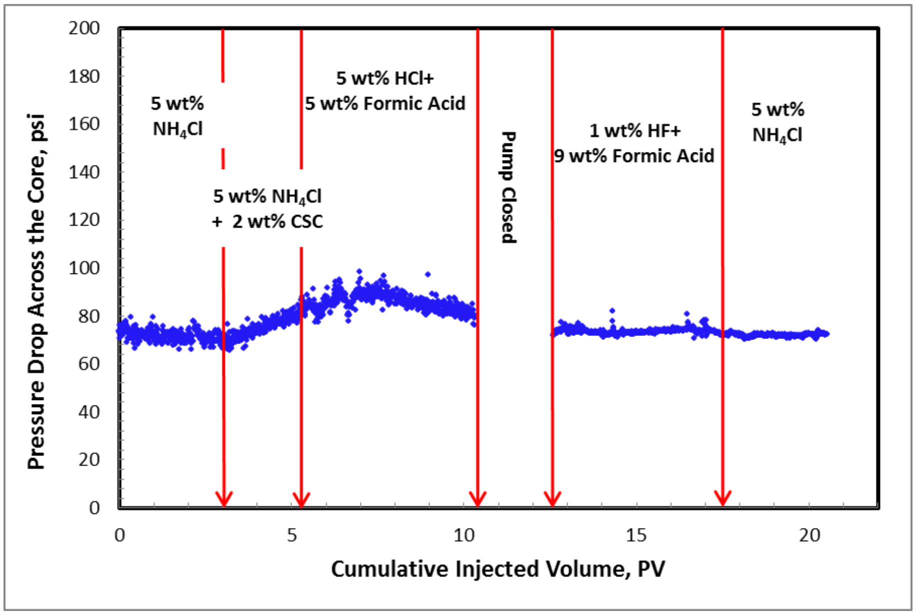

Figure 4.13- pressure drop response during coreflood experiment CF-4

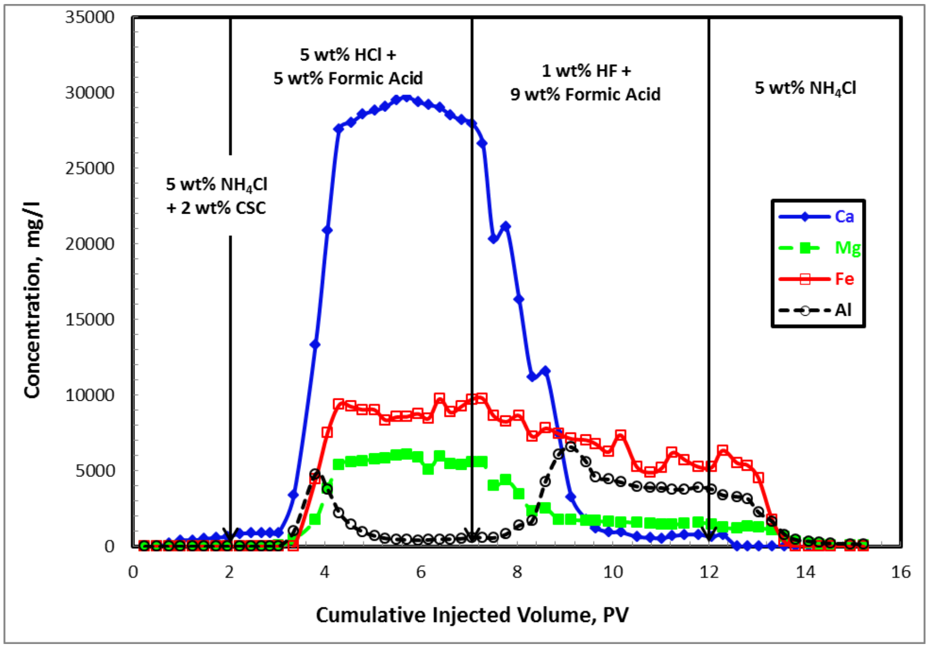

Figure 4.14.a- ICP result of coreflood experiment CF-4 (Ca, Mg, Fe, Al)

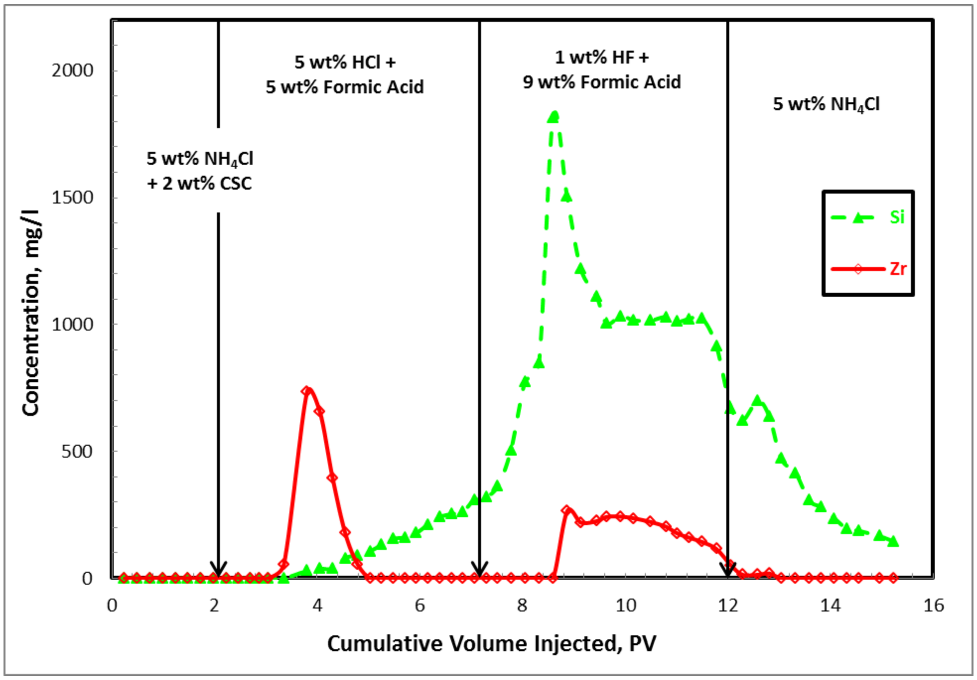

**Figure 4.14.b- ICP result of coreflood experiment CF-4 (Si, Zr)**

After the acid treatment in coreflood experiment CF-4, the final permeability decreased from 17.7 to 14.3 md. ICP results show a decrease in calcium and magnesium concentration when organic mud acid stage started. This demonstrates the presence of carbonates, although 5 pore volumes of preflush were injected. As a result, organic mud acid reacted with dolomite and formation damage occurred. Reaction of HF can also be confirmed by a sharp decrease in Si concentration. As HF was injected into the core, it dissolved and removed alumino silicates. However, due to the presence of dolomite, HF reacted with dolomite and precipitation covered the rock surface. So HF was not able to react with clays, feldspars, or sand particles. As a result Si concentration decreased.

In this experiment, precipitation occurred after the samples were collected and cooled down to room temperature. **Figures 4.15** and **4.16** show the results of the SEM analysis on these solids.

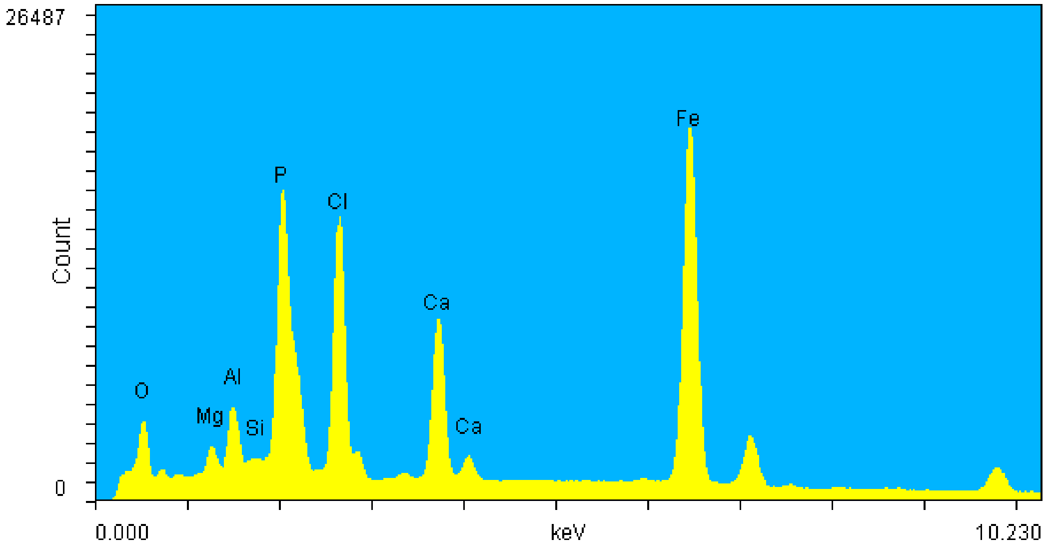

**Figure 4.15- SEM analysis of precipitation occurring during preflush injection in coreflood experiment CF-4**

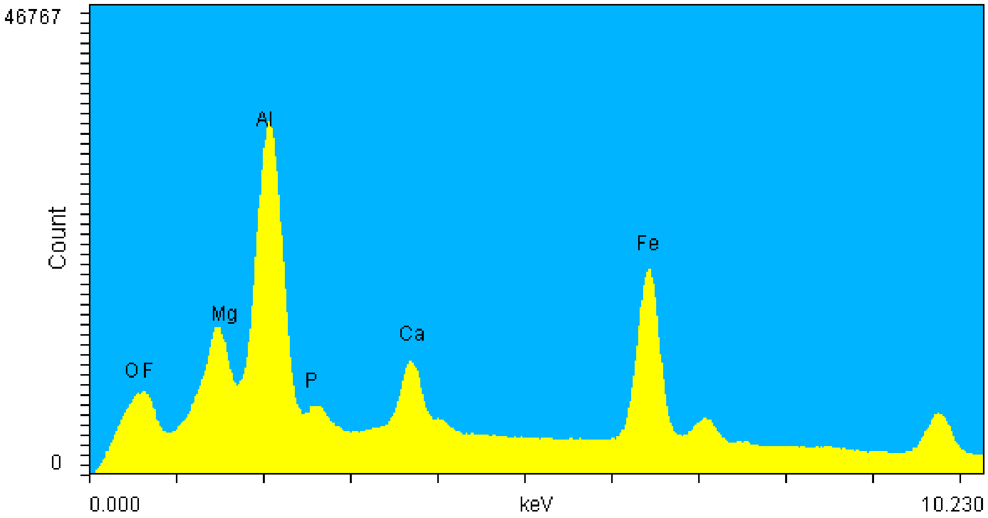

**Figure 4.16- SEM analysis of precipitation occurring during organic mud acid injection in coreflood experiment CF-4**

Precipitation in preflush consisting of Al and Si means that HCl still attacks clay particles. However, SEM results demonstrate that it mostly consists of phosphorus and iron. The presence of phosphorus creates iron phosphate as a compound that precipitates at moderate pH. As mentioned in the previous section, the source of phosphorus and the problems associated with it will be discussed later.

Also, precipitation in the organic mud acid stage mostly consists of aluminum, iron and phosphorus. Again, the presence of phosphorus makes aluminum and iron create chemical bonding with phosphorus and form aluminum and iron phosphate. More importantly, calcium, magnesium, and fluoride were all identified in elemental analysis.

Considering the result of coreflood experiment CF-4, it can be concluded that clay stabilizer CSC worked properly to avoid HCL attack on the surface of clay platelets. However, the problem in this coreflood was an insufficient amount of preflush.

CF-5 was conducted with 10 pore volumes of preflush. **Figure 4.17** demonstrates the pressure drop response in coreflood experiment CF-5. As can be seen, clay stabilizer CSC worked properly again and covered the clay particles from HCl attack.

Injecting 10 pore volumes of preflush removed all carbonate minerals, and as a result, when organic mud acid was injected into the core, it did not react with dolomite. Effluent samples collected during organic mud acid injection showed no precipitation which is a confirmation of the previous statement. Therefore, 10 pore volumes of preflush were enough to remove dolomite minerals inside the core.

The final permeability of the core was increased from 16.17 to 18.3 md. Comparing coreflood experiments CF-4 and CF-5 demonstrates the importance of preflush volume as one of the main factors leading to a successful well stimulation treatment. Using 5 pore volumes of preflush made the final result of matrix acidizing a failure. However, using 10 pore volumes turned it into a successful treatment plan.

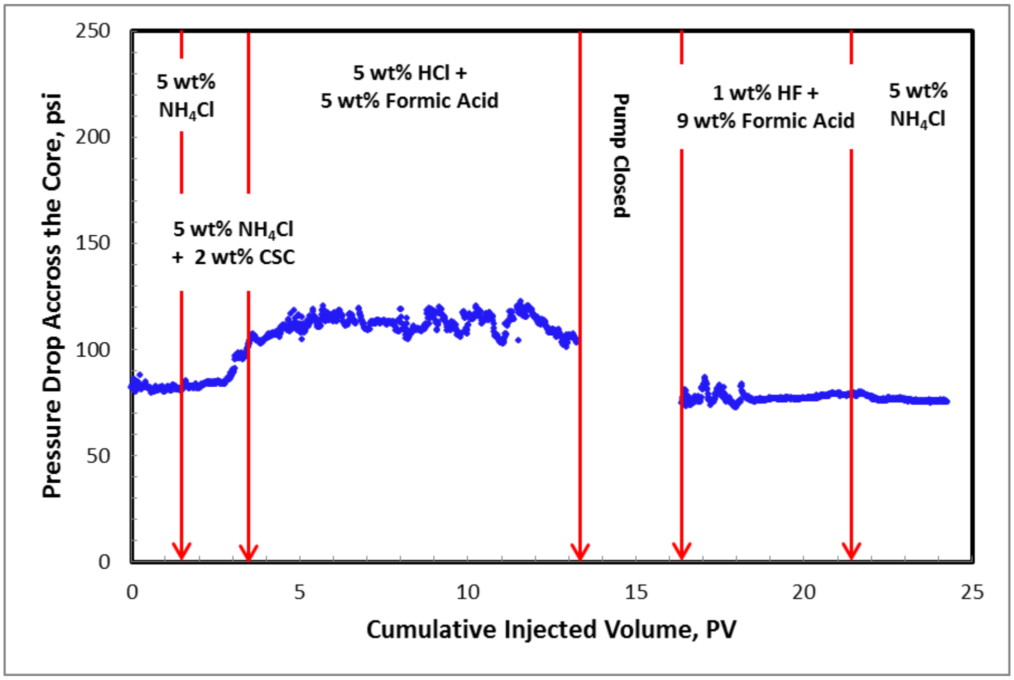

**Figure 4.17- pressure drop response during coreflood experiment CF-5**

**Figures 4.18.a** and **b** show the result of ICP analysis conducted on effluent samples in coreflood experiment CF-5. The amount of calcium and magnesium in the effluent samples are much more than that in coreflood CF-4. This illustrates that using 10 pore volumes of preflush affected the stimulation performance properly. Also, Si concentration during the organic mud acid stage does not show a sharp decrease, meaning HF keeps reacting with alumino silicates.

Although the permeability increased in this experiment, precipitation occurred again in the effluent samples collected. Solids were separated and analyzed using Evex Mini SEM. In spite of previous experiments, in this experiment the precipitation occurred during preflush. **Figure 4.19** shows the result of SEM analysis to determine the type of precipitation in this experiment.

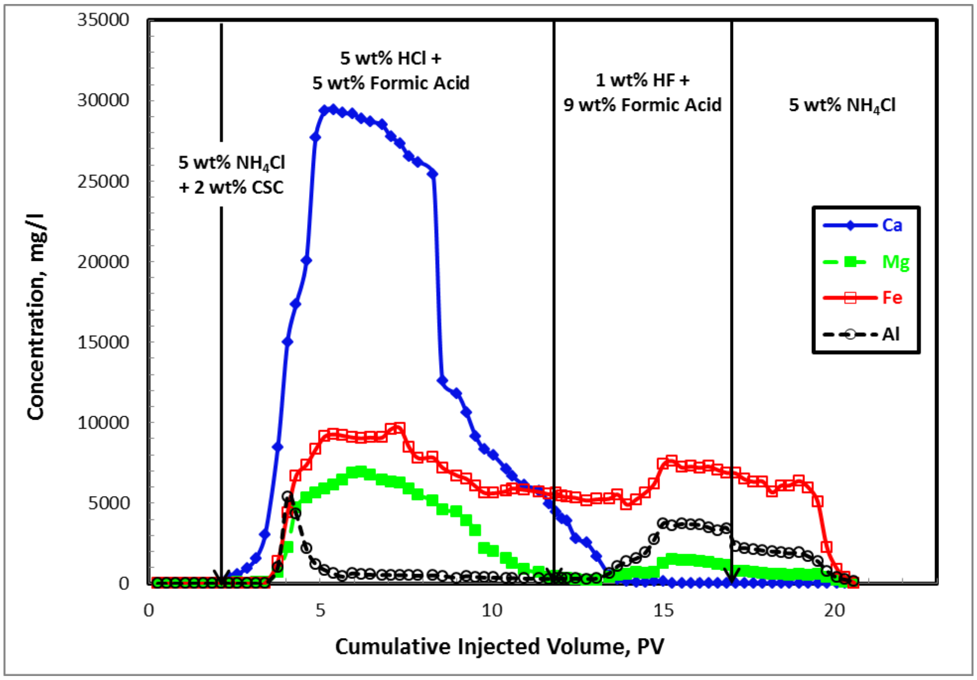

**Figure 4.18.a- ICP result of coreflood experiment CF-5 (Ca, Mg, Fe, Al)**

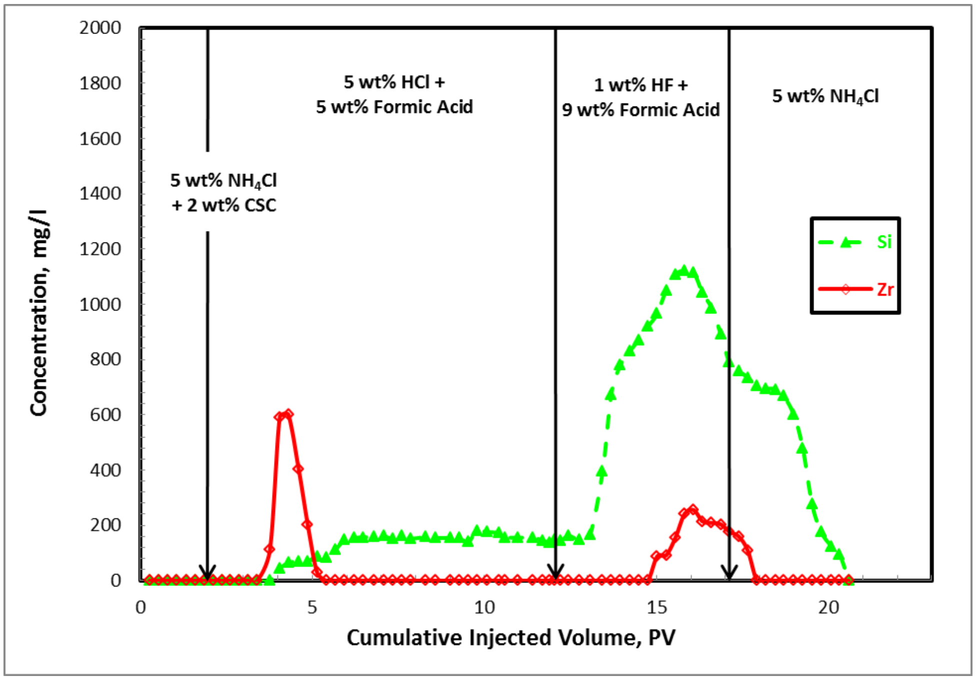

Figure 4.18.b- ICP result of coreflood experiment CF-5 (Si, Zr)

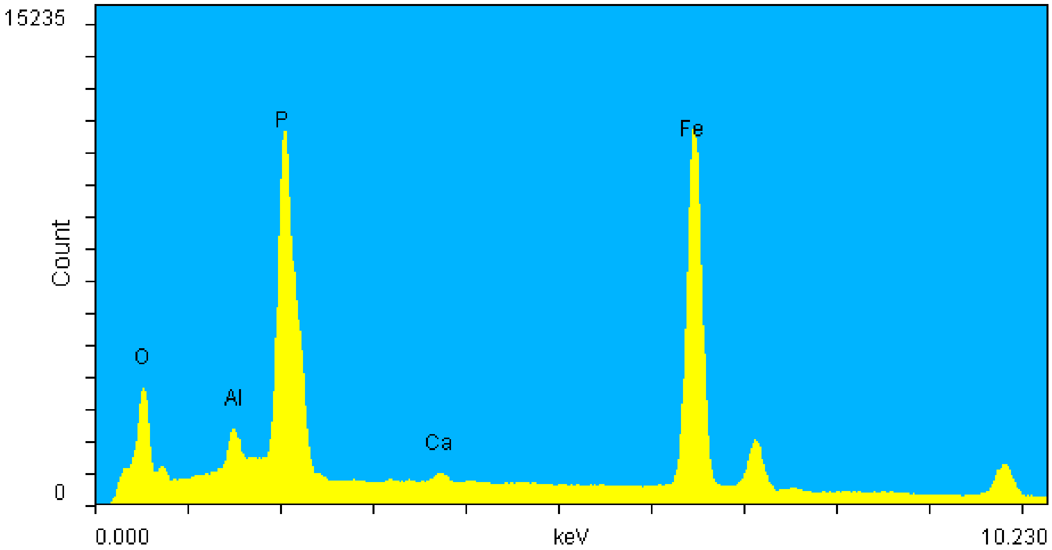

Figure 4.19- SEM analysis of precipitation occurring during preflush injection in coreflood experiment CF-5

As can be seen above, the precipitation contains high amount of phosphorus, which was observed in the previous experiment as well. Aluminum and iron phosphate are the main compounds formed as precipitation in the effluent samples. This type of precipitation occurs due to the presence of phosphorus. The source of this element will be discussed in the next section, in detail.

## 4.4 Coreflood Experiments on Berea and Bandera Sandstones Using the Stabilizer CSC

Two coreflood experiments CF-6 and CF-7 were conducted on Bandera and Berea sandstone cores, respectively. The purpose was to study the effect of mineralogy on the suggested acid treatment plan. Also, the source of phosphorus was investigated.

Coreflood experiment CF-6 was exactly the same as coreflood experiment CF-5. The purpose was to test the reproducibility of the result and to ensure that the precipitation occurs only during preflush.

**Figure 4.20** shows the pressure drop response during coreflood experiment CF-6. As can be seen, the result of this experiment confirms the result stated in experiment CF-5. Clay stabilizer CF-5 is able to cover the clay particles and avoid HCl attack.

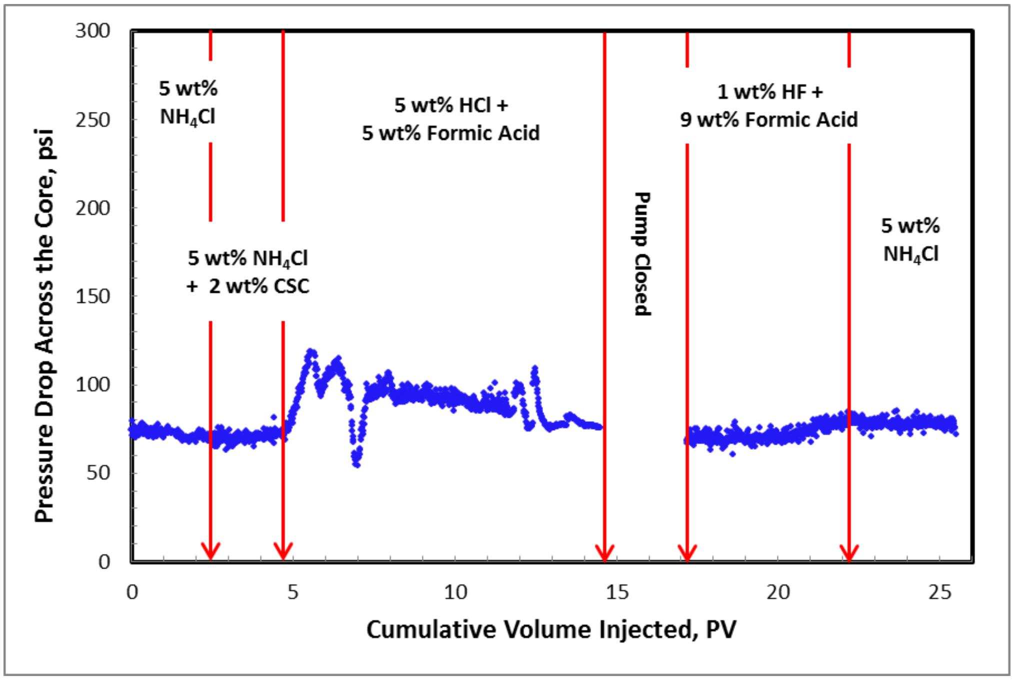

**Figure 4.20- pressure drop response during coreflood experiment CF-6**

Final permeability after acid treatment increased from 15.2 to 17.2 md, meaning using clay stabilizer CSC and 10 pore volumes of preflush resulted in a permeability improvement. Also, precipitation occurred again and it only happened in samples that were collected during the preflush stage. SEM analysis was conducted to observe the nature of the precipitation. **Figure 4.21** shows the SEM results from experiment CF-6 which agrees with the result of coreflood experiment CF-5. Phosphorus is the main reason for precipitation. Because it forms iron and aluminum phosphate.

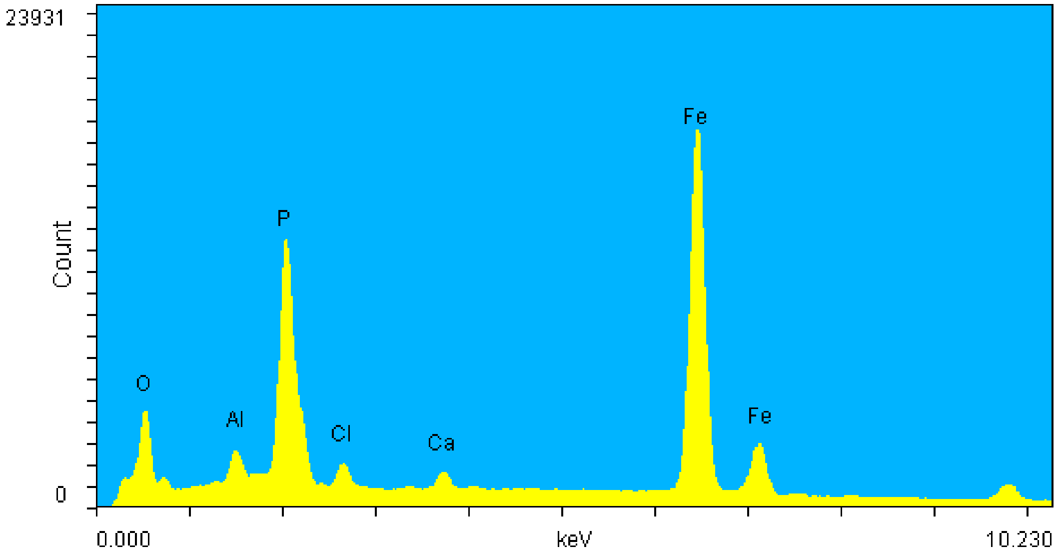

**Figure 4.21- SEM analysis of precipitation occurring during preflush injection in coreflood experiment CF-6**

At this point, it was necessary to find out the source of phosphorus in the effluent samples. To investigate whether it originates from the rock itself, coreflood experiment CF-7 was conducted on the Berea sandstone core while keeping all experiment factors the same as that in CF-6. **Figure 4.22** demonstrates the pressure drop response during the coreflood experiment on the Berea sandstone core. Meanwhile, it was observed that clay stabilizer CSC was able to cover clay particles present in the Berea sandstone cores.

**Figures 4.23.a** and **b** shows the ICP analysis conducted on the effluent samples in the coreflood experiment CF-7. The amount of calcium and magnesium is a lot less than that in the coreflood using Berea. This is due to the mineralogy difference between Berea and Bandera sandstone cores. Berea contains 3 wt%, while Bandera contains 16 wt% carbonate minerals. Also, the silicon concentration in CF-7 reaches the maximum of 2500 mg/L which is more than that in the coreflood experiments using Bandera sandstone cores.

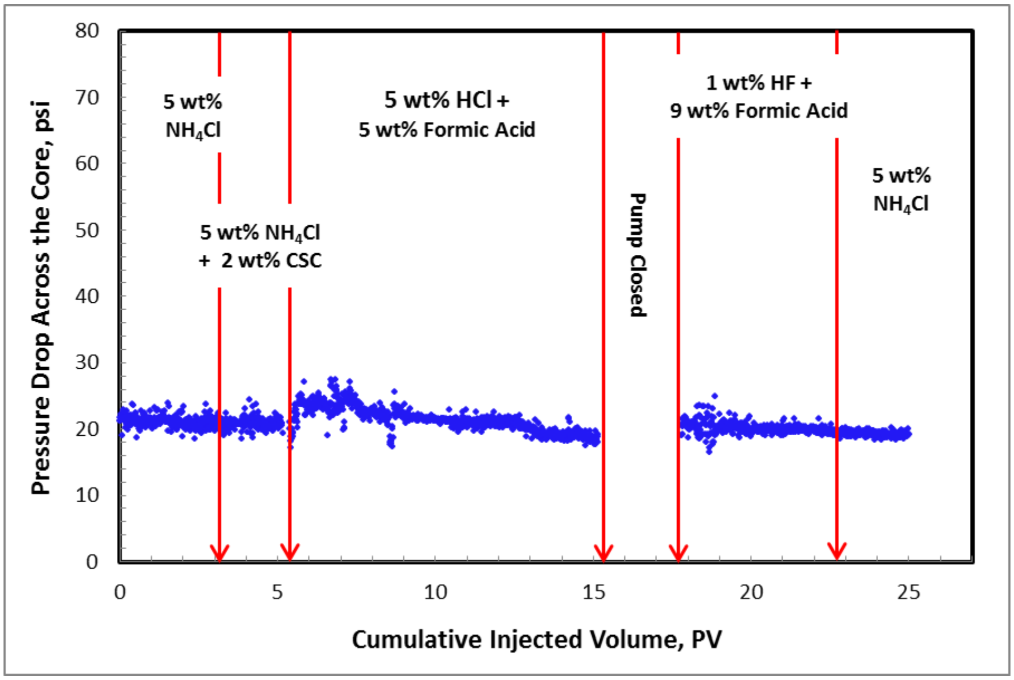

**Figure 4.22- pressure drop response during coreflood experiment CF-7**

The effluent samples were collected and analyzed after the experiment. No precipitation occurred when using the Berea sandstone core. This indicates that phosphorus was coming from minerals present in Bandera sandstone cores in previous experiments. It reveals a new type of formation damage and precipitation regarding sandstone matrix acidizing.

To prove the presence of phosphorus in Bandera sandstone cores, a piece of Bandera core treated in the coreflood experiment CF-6 was crushed and prepared for

SEM analysis. **Figure 4.24** demonstrates SEM analysis for three different spots. The amount of phosphorus at each point is shown in **Table 4.1**.

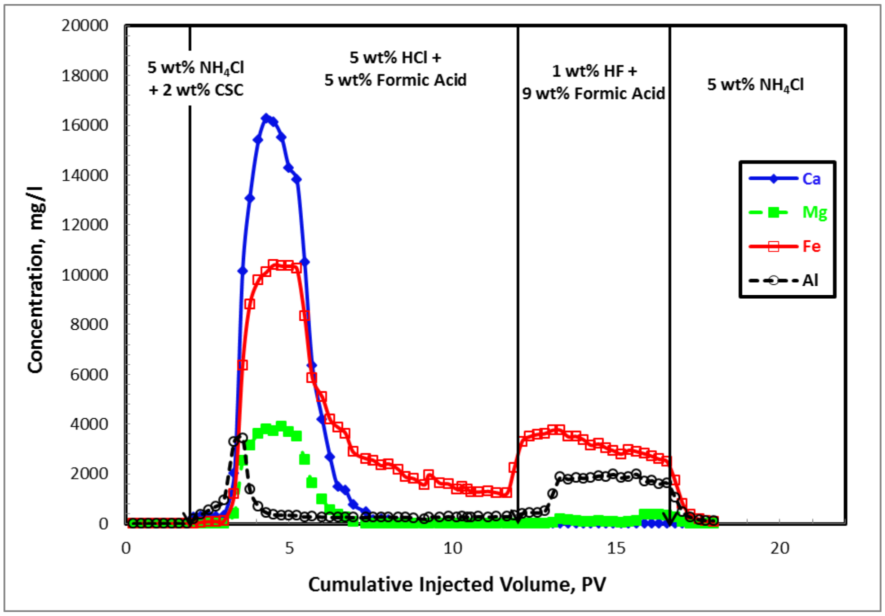

**Figure 4.23.a- ICP result of coreflood experiment CF-7 (Ca, Mg, Fe, Al)**

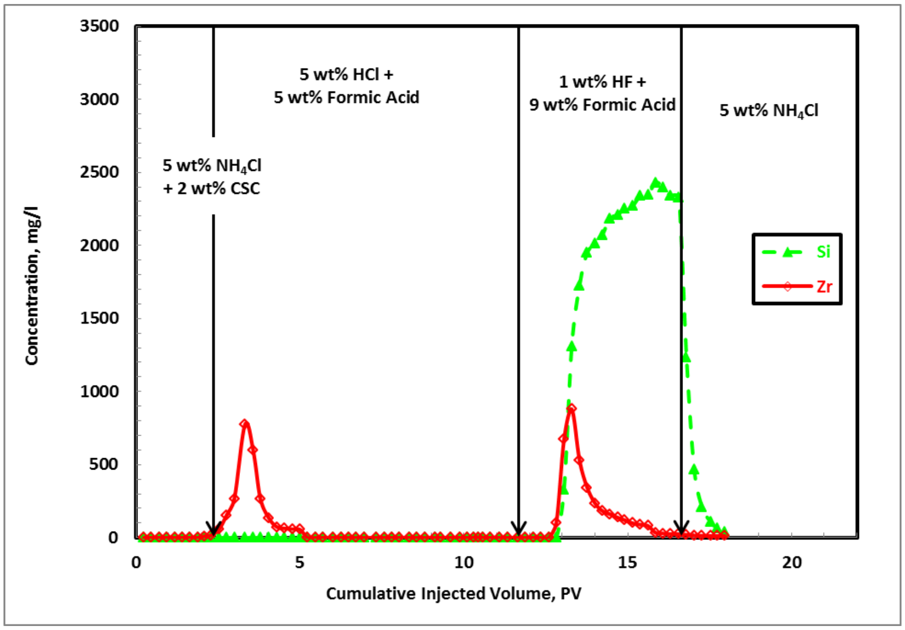

**Figure 4.23.b- ICP result of coreflood experiment CF-7 (Si, Zr)**

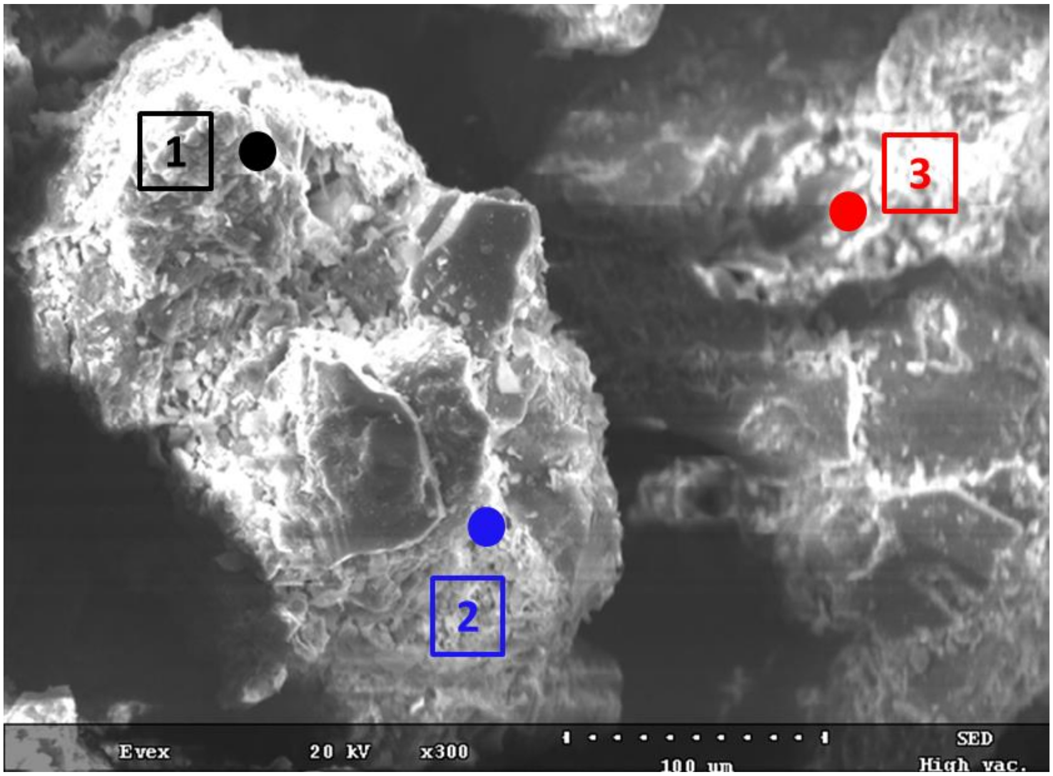

**Figure 4.24- SEM photo of Bandera sandstone core after treatment in the coreflood experiment CF-6**

| TABLE 4.1 —Phosphorous Concentration in Bandera | |
|---|---|
| **Point** | **Phosphorus (wt %)** |
| 1 | 0.87 % |
| 2 | 0.63 % |
| 3 | 0.68 % |

# 5. CONCLUSIONS AND RECOMMENDATIONS

## 5.1 Conclusions

In this study, newly developed clay stabilizers were utilized to cover and secure HCl-sensitive clays such as illite and chlorite. Different clay stabilizers with different concentrations were tested using mainly Bandera sandstone cores. Berea sandstone cores were also tested to investigate the effect of mineralogy on the proposed acid treatment plan. In a set of experiments, clays stabilizers and their concentrations, preflush pore volume, and mineralogy of the core were the main factors determining the success of the treatment plan. Based on the experimental results, the following conclusions were obtained:

1. Injection of deionized water resulted in a permeability reduction of more than 50% at 140°F and flow rate of 4 $cm^3$/min.
2. Illite and chlorite, two main clay minerals present in Bandera sandstone cores, are sensitive to HCl at a temperature of 140°F, even at low concentrations of HCl. In conventional sandstone acidizing, 15 wt% HCl is used as preflush. Using 5 wt% HCl and 5 wt% formic acid did not mitigate fines migration during preflush. Permeability decreased from 8.1 to 3.2 md.
3. Clay stabilizer CSA covered clay particles properly from HCl attack when it was used at 2 wt% concentration. Final permeability increased from 7.3 to 12.9 md.

4. Clay stabilizer CSB did not exchange cations with illite and chlorite even though it was used at 4 wt%. As a result, matrix acidizing was a failure. Final permeability decreased from 6.2 to 2.9 md.
5. Clay stabilizer CSC was able to protect the alumina layer from HCl attack, however the final permeability decreased from 17.7 to 14.3 md. The reason is that an insufficient amount of preflush was injected into the core and precipitation occurred during organic mud acid injection.
6. Increasing the preflush pore volume from 5 to 10 led to permeability improvement rather than formation damage.
7. In all experiments using Bandera sandstone cores, precipitation occurred during the preflush stage and phosphorus was detected using SEM analysis. However, the coreflood experiment on Berea sandstone core resulted in no precipitation, revealing that phosphorus was present in Bandera sandstone core.
8. Precipitation happening during the preflush stage reveals a new type of precipitation and formation damage

## 5.2 Recommendations

One of the main drawbacks of sandstone acidizing is fast reaction of HF with alumino silicates. As a result, the acid will be spent after leaving the first few feet from the wellbore. Retarded systems have been a topic of research for many years. However, they still have the problem addressed in this study. The presence of HCl sensitive clays causes formation damage and the treatment plan will be a failure.

A research study is needed to evaluate the efficiency of a new multi stage treatment plan using a clay stabilizer and retarded HF system. Employing a clay stabilizer avoids the precipitation of silica gel, while utilizing a retarded system avoids consumption of live acid. Coreflood experiments are required to evaluate the feasibility of this multi-stage treatment plan and possible drawbacks.

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