EVALUATION OF A NEW LIQUID BREAKER FOR

POLYMER BASED IN-SITU GELLED ACIDS

A Thesis

by

GAMZE AKSOY

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

August 2011

Major Subject: Petroleum Engineering

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Approved by:

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

Evaluation of a New Liquid Breaker for Polymer Based In-Situ Gelled Acids.

(August 2011)

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Chair of Advisory Committee: Dr. Hisham A. Nasr-El-Din

A solid breaker is used to reduce the viscosity of the gel at pH range of 4-5 for in-situ gelled acids with Zr^{4+} cross-linkers utilize. However, the literature survey confirmed that solid breakers caused a premature reduction in the fluid viscosity resulting in a less than desirable productivity. Therefore, an effective liquid breaker that is based on tetrafluoroboric acid was developed.

This study was conducted to evaluate this new breaker system under the following conditions: breaker concentration (0-200 ppm), and acid injection rate (0.5-10 cm^3/min).

The major findings from the performed viscosity measurements and single coreflood experiments can be summarized as follows: the crosslinking of the polymer occurred at a pH value of 1.8. At a pH of less than 2, doubling the breaker concentration did not affect the viscosity of the acid. However, at a pH of greater than 2, the viscosity of acid was reduced by 30%. At a breaker concentration of 0 ppm, the appearance of Zr in the core effluent sample was delayed by 0.25 PV compared to the reaction product, while at 100 ppm, Zr was delayed by 0.75 PV. At 200 ppm breaker, no Zr ions were

detected in the effluent samples. Additionally, it was observed that as the breaker concentration increased, more Zr remained inside the core, as ZrF_4, which is water-insoluble. Increasing the breaker concentration from 100 to 200 ppm reduced the final normalized pressure drop by 50% at injection rate of $2.5cm^3/min$. Permeability reduction due to gel was reduced by increasing the acid injection rate.

DEDICATION

This thesis is dedicated to my parents for their unlimited support and encouragement.

ACKNOWLEDGEMENTS

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CHAPTER I

INTRODUCTION

1.1. Matrix Acidizing and Methods to Control Acid Placement

Matrix acidizing is a stimulation method to improve the well performance in carbonate reservoirs. It is conducted by pumping the acid at a pressure between pore pressure and fracture pressure. Acid prefers to flow through the high permeability regions of the formation leaving the low permeability regions untreated. Therefore, the success of acidizing treatments is measured by how good the treatment fluid is placed. This is because accurate and efficient acid diversion improves the permeability around the wellbore (Sengul and Remiso 2002).

Jin et al. (2007) indicated that creating wormholes is the objective of matrix treatments in carbonate reservoirs. The length of wormholes is controlled by reaction rate and leak off. Once wormholes stop extending, as more acid is pumped, they will become wider. After this point, the acid should be diverted.

Chang et al. (2007) classified the acid diversion techniques into two categories: mechanical and chemical techniques. Mechanical methods such as ball sealers, coiled tubing and packers are practical but are more expensive and time consuming than chemical methods and are not suitable and effective for open-hole completions. Also, mechanical methods divert the stimulation fluids inside the wellbore, however, once the

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

fluids enter the formation, there is no control. On the other hand, if the proper chemical diverter is selected considering the fluid and rock interactions, chemical methods of diversion are more effective inside the formation (Beheiri and Nasr-El-Din 2007). **Fig. 1.1** shows the methods to divert the acid.

HCl is the most common stimulation fluid since it is cheap and has high rock dissolving power. However, high HCl/carbonate reaction brings a problem. Deep penetration of the acid is prevented because of fast HCl spending (Buijse et al. 2004). To obtain an efficient penetration depth, acids are retarded by gelling, foaming, or emulsifying the acid and by crosslinking suitable acid gelling agents. Among these applications, a high viscosity that is necessary to divert the acid into the low-permeable zones is provided by only crosslinking the acid with the gelling agent (Deysarkar et al. 1984; Jones et al. 1996).

Diversion Methods

Mechanical Methods	Chemical Methods
* Coiled Tubing	* Foamed Acid
* Packers	* Emulsified Acid
* Ball Sealers	* Gelled Acid
* Bridge Plugs	* In-Situ Gelled Acid
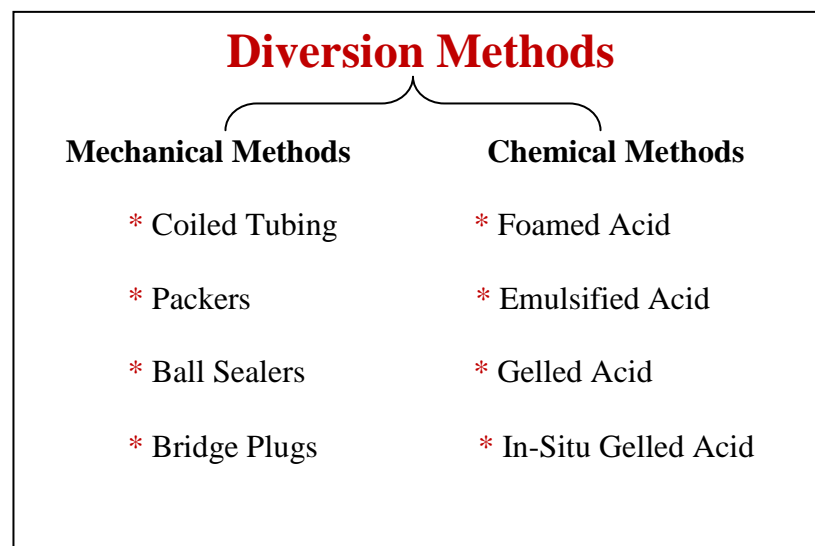
Fig. 1.1—Diversion methods.

1.2. Previous Work

In-situ gelled acid systems are composed of a polymer, a cross-linker, a breaker, and other chemicals (Yeager and Shuchart 1997; Nasr-El-Din et al. 2002). Hill (2005) stated that at pH value around 2 or greater, any water-soluble polymer, which has carboxyl groups can crosslink to the zirconium or ferric ions. According to Abdel Fatah et al. (2008), diversion of the fresh acid to the damaged parts of the formation is caused by the gel which is a product of the polymer and the cross-linker at a certain pH value. Initially, the in-situ gelled acid had a pH value of nearly zero. **Fig. 1.2** illustrates the mechanism of acid diversion schematically. As the acid reacts with the formation, the pH value increases. Around a pH of 2, the polymer that contains the carboxyl groups will crosslink in the presence of zirconium or ferric ions. The viscosity of the gel decreases as the cross-linker and the polymer decompose at pH values greater than 4 (MaGee et al. 1997; Saxon et al. 2000). Nasr-El-Din et al. (2002) mentioned two mechanisms that trigger the breaker: reducing the valence of the multi-valent cation and/or forming a more stable compound with the cross-linker.

There are several studies examined the in-situ gelled acids. Mohamed et al. (1999) conducted the matrix acidizing treatments for more than 80 seawater injectors and saltwater disposal wells. The ratio of the volume of regular acid to in-situ gelled acid is important and it is recommended to use low HCl concentrations. In-situ acid systems can be used at HTHP wells. Well designed treatments were successful at temperatures up to 176°F (Buijse et al. 2000). Lynn and Nasr-El-Din (2001) examined these acids at high temperatures. They found polymer residue inside the wormholes created by the

acid. Not only that, they found the permeability enhancement was affected by injection rates. Taylor and Nasr-El-Din (2002) showed that the polymer was found to be the primary source of the decrease in permeability. They also indicated that a significant amount of cross-linker remained inside the cores. Gomaa et al. (2011) studied the diversion of in-situ gelled acids with different injection rates. They found that in-situ gelled acid can divert the acid and enhance the permeability for low permeability contrast, however, for high permeability contrast, in-situ gelled acid diverted the acid with injection rate lower than 10 cm^3/min.
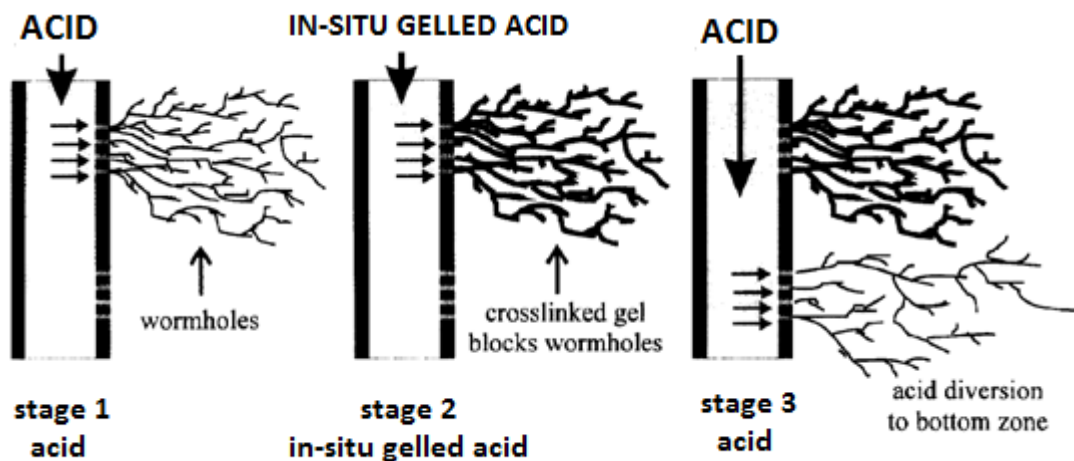
Fig. 1.2—Acid diversion by in-situ gelled acid (MaGee et al. 1997).

A breaker is one of the necessary components of the crosslinked system since it reverses the crosslinking reaction. Haldar et al. (2004) studied breaker optimization and found that as the concentration of breaker increases, the fluid viscosity decreases. Higher temperature also increases the need for more breaker. Boles et al. (1996) stated that

fluoride, phosphate, sulfate ions and multi-carboxylated compounds are known to have the ability to complex with zirconium and titanium cross-linkers. Coating the fluorspar with a wood resin material is desirable to delay the time of the breaker because the release of fluoride ions breaks the bonds between the polymer and cross-linker when it is introduced to the crosslinked polymer gel. Kalfayan and Martin (2009) stated that fluoride breaker decreases the gel viscosity and improves cleanup after the treatment is finished. The concentration of the breaker, acid, and the bottomhole temperature are the factors that affect the speed of the breaking mechanism. Therefore, for each treatment, the breaker loading should be designed carefully. The integrity of the polymer molecules will not be affected by the breaker in both cases.

1.3. Statement of the Problem

Taylor and Nasr-El-Din (2002) indicated that solid breakers are not effective because the gel remains inside the core, which causes a reduction in the permeability. Solid breakers are composed of particles of fluoride ions, which are capable of complexing with the crosskinking compound of the in-situ gelled acids. These fluoride particles are coated with a water insoluble wood resin gel, which delays the release time of the particles; therefore, in-situ gelled viscosity reduces at a retarded rate (Boles et al. 1996). Solid breakers are not soluble and do not disperse well in the acid solution. Larger particles go inside the formation and cause formation damage. The precipitation of coating material causes ineffective acidizing treatments. They also do not generate stable breaking times, which is important because early break can cause premature reduction in acid viscosity resulting in a less than desirable productivity (DeBenedictis et al. 2010). There is a need

for a new crosslinked acid breaker system that is efficient at reducing the viscosity of crosslinked gel.

1.4. Mechanism of New Liquid Breaker

The new liquid breaker is based on tetrafluoroboric acid. There are two methods to produce the breaker: the tetrafluoroboric acid is added directly to the solution or the tetrafluoroboric acid is generated in-situ. The second method is done by mixing hydrochloric acid, ammonium bifluoride, and boric acid together so that the tetrafluoroboric acid can be produced by the reaction of the components. Hydration and crosslinking of the polymer is not affected by the new breaker, since it is generated very slowly in the beginning at the ambient temperature. The tetrafluoroboric acid decomposes into HF and BF_3 (Eq. 1). Hydrafluoric acid (Eq. 2) releases fluoride ions, which ties up the zirconium ions. This breaks the bond between zirconium - polymer crosslink. The acid viscosity decreases for easier spent acid recovery. The mechanism of the breaker and the time to break down the gelled acid solution are affected by the increase in temperature and acid reaction rate (De Benedictis et al. 2010).

$$HBF_4 \rightleftharpoons HF + BF_3 \tag{1}$$
$$HF \rightleftharpoons H^+ + F^- \tag{2}$$

The new liquid breaker system is easier to mix than the solid breakers. Since solid breakers are coated with non-soluble materials, it is not effective to mix them with the acid solution. The coating material precipitates in the acid system and causes problems. Adequate dispersion of the solid breaker is difficult compared to the new

liquid breaker. Timing is an important factor for the breakers performance. A well dispersed liquid breaker enables operator to control how the treatment fluid is broken. In-situ gelled acids that break too slowly can cause slow recovery of the solution from the formation. Under normal circumstances, when the pumping process is stopped, the in-situ gel starts to break (De Benedictis et al. 2010).

1.5. Objectives

The objective of this study is to: 1) evaluate the new liquid breaker, 2) determine the pH value of polymer crosslinking, 3) describe the effect of breaker concentration, and 4) describe the effect of injection rate. These objectives were achieved by conducting viscosity and coreflood experiments, monitoring the pressure drop across the cores, and measuring the calcium and zirconium ions concentrations, pH, and density from the core effluent samples.

CHAPTER II

EXPERIMENTAL STUDIES*

2.1. Materials

CAS hydrochloric acid was used in this work and was found to have the concentration of 36.8 wt%. Calcium carbonate powder was used to neutralize the live acid. Pink Desert limestone cores (1.5-in. diameter and 6-in. length) had the properties given in **Table 2.1**. Deionized water was obtained from a water purification system (Barnstead EASYpure PoDi-model D13321), which had a resistivity of 18.2 MΩ.cm at room temperature. A digital density meter (DMA 35) was used for the density measurements. Polymer, cross-linker, breaker and other additives were all oilfield chemicals, and were used without further purification. The in-situ gelled acid system includes polyacrylamide based polymer (the gelling material used to increase the viscosity of the in-situ gelled acid), zirconium based crosslinker (crosslinking compound of the gel is used to connect the polymer chains with each other at pH level of 2, producing high viscosity), breaker (tetrafluoroboric acid used to reduce the viscosity of crosslinked gel caused by zirconium ions), corrosion inhibitor and buffer.

TABLE 2.1—PROPERTIES OF THE CORES				
Core	**Lithology**	**Porosity Range, vol %**	**Diameter, in.**	**Length, in.**
1 - 9	Pink Dessert Limestone	33 - 41	1.5	6

2.2. Measurements

Viscosity measurements at high temperatures were made using a M5600 viscometer at 300 psi pressure. Viscometer measurements at room temperature were made using a rotational viscometer. All acids were prepared using a magnetic stirrer. The core flood setup, as shown in **Fig. 2.1**, was constructed to simulate the matrix stimulation treatment. A back pressure of 1,000 psi was applied to keep CO_2 in solution. Pressure transducers were connected to a computer to monitor and record the pressure drop across the core during the experiments. The pH values for the collected samples were measured using an Orion 370 PerpHecT Ross Electrode, while calcium and zirconium concentrations for the collected samples were measured using an inductively coupled plasma optical emission spectrometer (Optima 7000 DV type). The cores scanned with X-ray Computed Tomography (CT) before and after acid injection. The CT number was found to be from 2000 to 2200 for the water saturated cores before acid injection, which indicates that all the used cores had one pore level of heterogeneity.

2.3. Procedure

2.3.1. Acid Preparation

All in-situ gelled acids were prepared based on 5 wt% HCl as recommended by Gomaa and Nasr-El-Din (2010). **Table 2.2** shows the acid formula used in these tests. It is important to highlight that the acid formula used is the same acid formula typically used in the field when the zirconium (IV) system is used. Acids were prepared by mixing the corrosion inhibitor and HCl acid with water, then polymer was added to the acid slowly. After that, zirconium cross-linker and buffer were added to the solution and mixed for 30 minutes. The breaker at different concentrations was the last chemical added to the acid solution just before neutralization process. Solutions were slowly neutralized with calcium carbonate powder to various pH values. The apparent viscosity of the solutions with the different breaker concentrations was measured as a function of the equilibrium pH values.
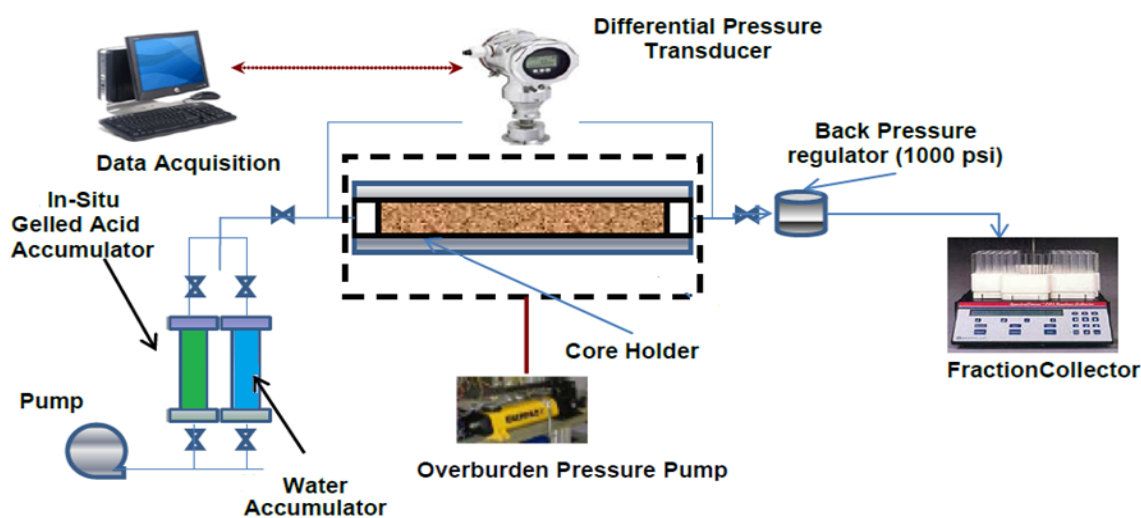
Fig. 2.1—Core flood setup.

2.3.2. Core Preparation

Core preparation was performed through the following steps:

1- Cylindrical cores with a 1.5 in. diameter and 6 in. length were cut from a Pink Desert limestone block, **Table 2.1**.

2- Cores were dried inside an oven set at 257 °F for 5 hours and weighed dry and were saturated with deionized water under vacuum for 24 hours. The core porosity was calculated from these measurements.

3- The core was placed inside the core holder, water was injected at different flow rates (0.5, 2.5, and 10 cm^3/min), and the pressure drop across the core was monitored to calculate the core initial permeability.

4- In-situ gelled acid was injected at a constant flow rate while the pressure drop across the core was monitored.

5- Effluent samples from the cores were collected throughout the experiment by using an automatic fraction collector.

6- pH value, density and the concentrations of calcium and zirconium ions were determined from the collected effluent samples.

Concentration	Component
TABLE 2.2—FORMULA OF THE IN-SITU GELLED ACID	
5 wt%	Hydrocloric Acid
20 gal/Mgal	Acid Gelling Agent: A mixture of Acrylic polymers (30-60 wt%), Distillates,petroleum, hydrotreated middle (10-30 wt%), Nonylphenolethoxylate (1-5 wt%).
4 gal/Mgal	Corrosion Inhibitor:A mixture of Methanol (1-5 wt%), Isopropanol (1-5 wt%), Formic Acid (30-60 wt%), Organic sulfur compound (1-5 wt%), Quaternary ammonium compound (1-5 wt%), Haloalkylheteropolycycle salt (10-30 wt%), Aromatic aldehyde (10-30%), Oxyalkylated fatty acid (10-30 wt%), Benzyl chloride (10-30 wt%).
4.5 gal/Mgal	Cross-linker : Mixture of aluminum and zirconium salts in water.
0-200 ppm	Breaker : Tetrafluoroboric acid
2 gal/Mgal	Buffer : Poly (oxy-1,2-ethanediyl)

2.3.3. Injection Sequence

Before starting the acid injection, water was injected into the cores with the selected flow rate. This was done to ensure that the core was fully saturated with water. After reaching a stable pressure drop across the cores, in-situ gelled acid was injected at a constant flow rate which was followed by the injection of water.

In this study, two different sets of core flood tests were conducted to assess the effect of breaker concentration in the performance of the in-situ gelled acid. The first set injected 0.5 PV of acid into the cores 1-7. For cores 1 and 2, the acid was injected without breaker at flow rates of 2.5 and 10 cm^3/min. In-situ gelled acid with 100 ppm breaker was injected into cores 3, 4, and 5 at flow rates of 0.5, 2.5, and 10 cm^3/min, respectively. For cores 6 and 7, the acid solution with 200 ppm breaker was injected at flow rates of 2.5 and 10 cm^3/min. For the second test set, two experiments were

conducted using cores 8 and 9. In-situ gelled acid was prepared with 100 ppm breaker and was injected until breakthrough at flow rates of 2.5 and 5 cm^3/min, respectively.

CHAPTER III

RESULTS AND DISCUSSIONS*

3.1. Inefficiency of the Solid Breakers

Solid breakers are not effective in reducing the viscosity of the crosslinked acid. **Figs. 3.1** and **3.2** show the effect of a solid breaker at high temperatures. The measurements were done with a HPHT viscometer at 300 psi. The viscosities of partially neutralized in-situ gelled acid with and without breaker were presented in **Fig. 3.1**. At temperatures lower than 250^oF, using breaker reduced the viscosity of the gel slightly. However, at temperatures higher than 250^oF, there is almost no change in the viscosity whether the breaker was used or not. **Fig. 3.2** shows the rheological properties of partially neutralized acid. At this pH level, the viscous modulus was supposed to be dominant over the elastic modulus; however, even at higher temperatures, solid breaker has nearly no effect on the system.

3.2. Determination of pH at Gelation

Crosslinking occurs when the carboxyl group releases hydrogen ions. This allows the multivalent cation to crosslink with the polymer and produce the crosslinked network to

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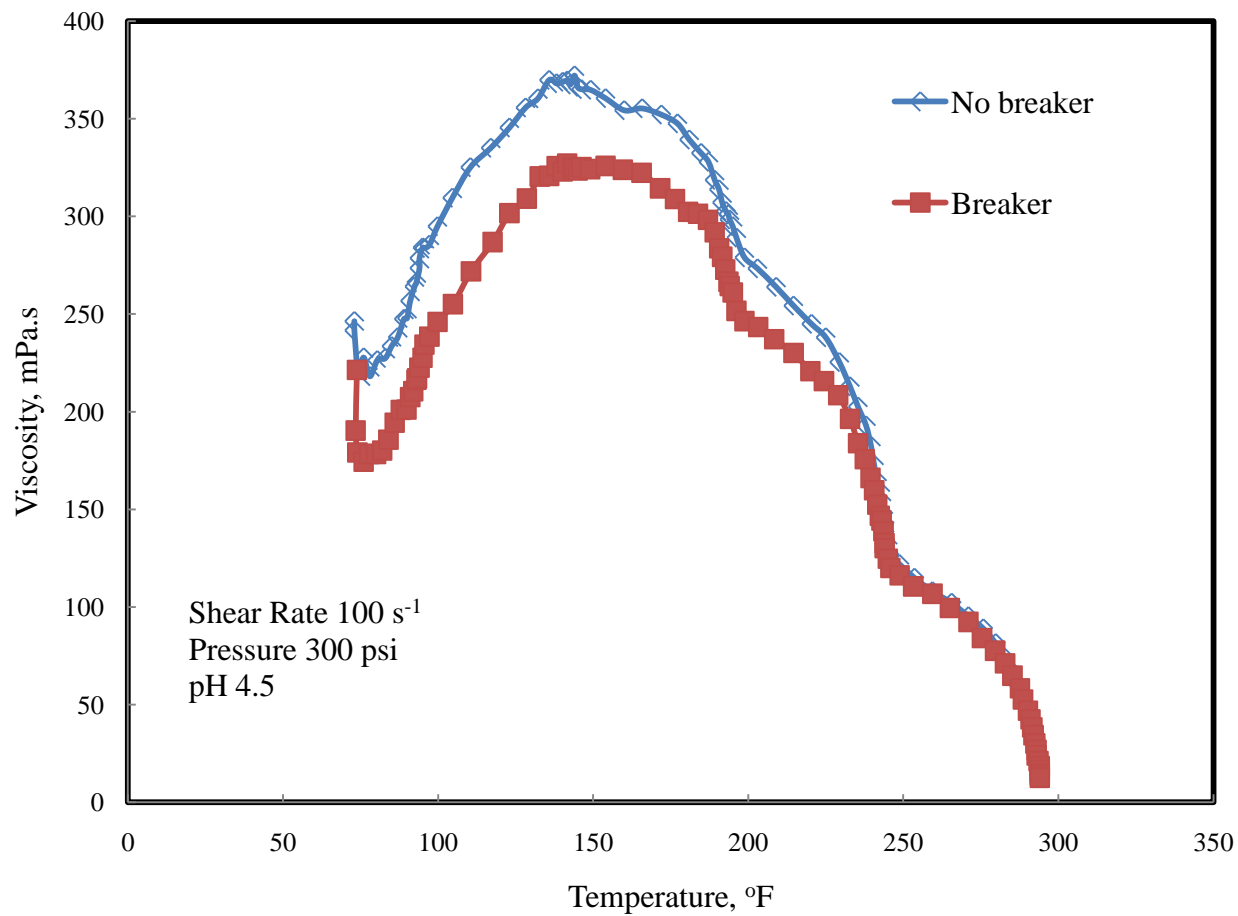
Fig. 3.1–The effect of solid breaker on viscosity at high temperatures (Shear rate = 100 s^{-1}, pH=4.5, Pressure 300 psi).
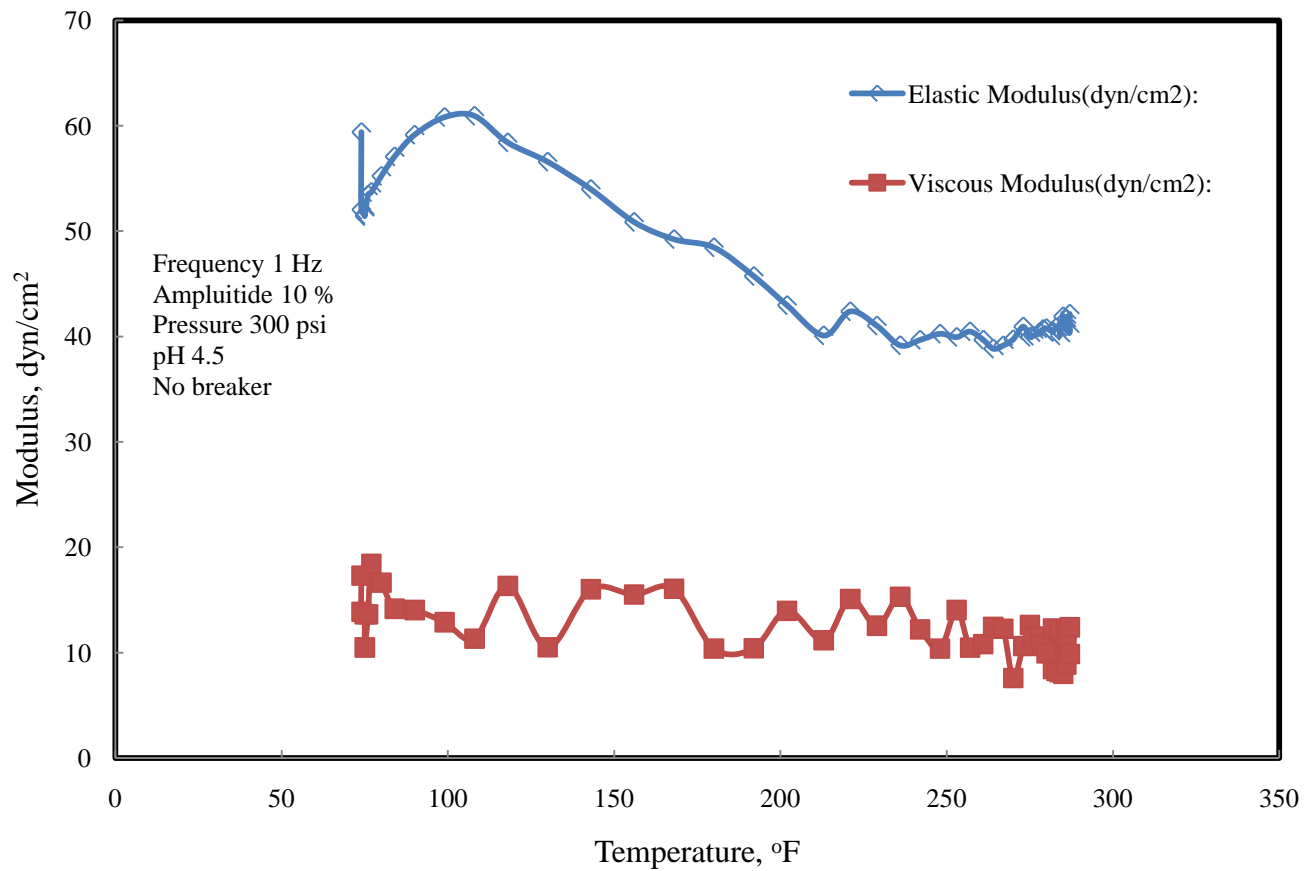
Fig. 3.2–The effect of solid breaker on rheological properties at high temperatures (pH=4.5, Pressure 300 psi).

enhance the viscosity of the solution. The pK_a measurement is used to determine at which pH value crosslinking occurs. This study was done by recording the pH while adding the sodium hydroxide to acid solutions. **Fig. 3.3** shows the pH values as a function of sodium hydroxide volume added for two solutions. The first solution contains only 5 wt% HCl while the second solution contains 5 wt% HCl and polymer.

In the test with the first solution when sodium hydroxide added, the pH increased slowly until it reached to pH level of 2. Then, it increased rapidly from pH 2 to 12. There was no fluctuation and the pH increased all the time. For the second solution which contained 5 wt% HCl and polymer, the pH increased similarly to the first solution until it reached a pH value of 1.8. The pH curve then deviated from the first solution. A fluctuation in the pH value was observed at a pH around 2 and a maximum pH was reached around 9. The region where the fluctuation was seen is the cross-linking region. Hydrogen ions were released from carboxyl group on the polymer at exactly a pH value of 1.8.
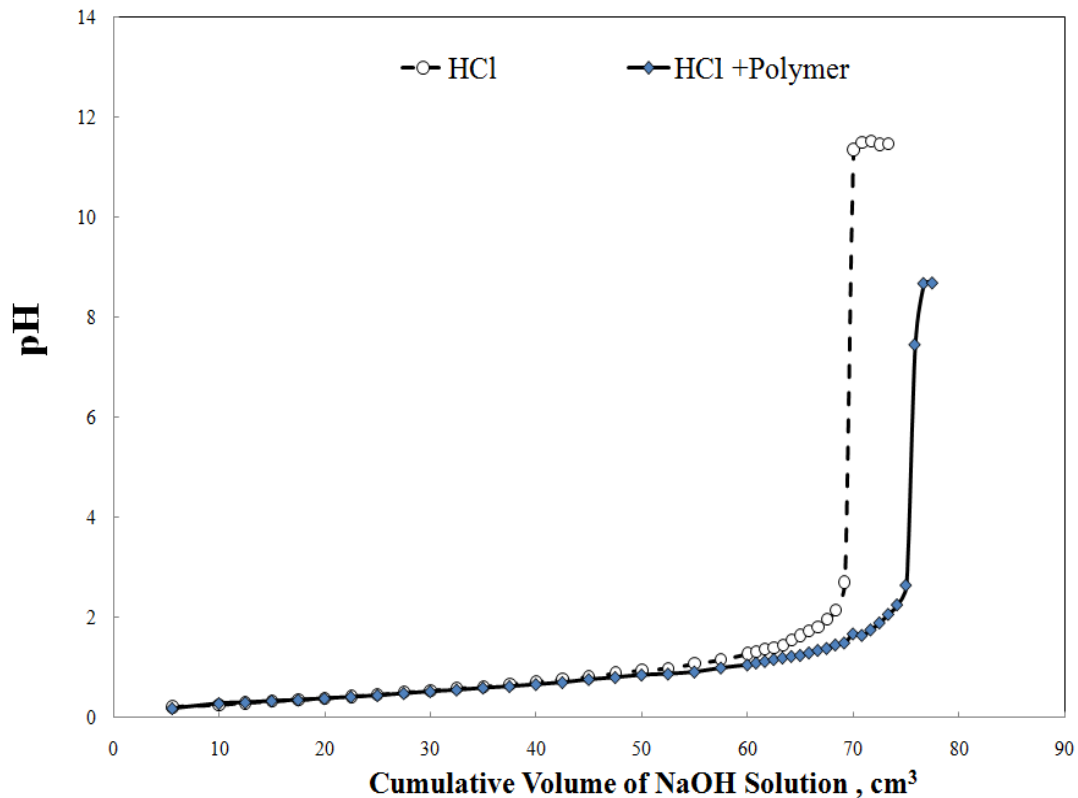
Fig. 3.3—pH values as a function of NaOH solution (0.5 M).

3.3. Viscosity Measurements

The viscosity behavior of in-situ gelled acid was studied with different breaker concentrations at atmospheric pressure and room temperature. Live acid solutions were neutralized by adding calcium carbonate powder. The pH was recorded and the viscosity of the solution was measured. **Fig. 3.4** shows the apparent viscosity as a function of equilibrium pH for in-situ gelled acids at breaker concentrations of 100 and 200 ppm. For the 100 ppm breaker concentration, the viscosity started to increase at a pH of 2.3 and reached the maximum viscosity value of 405 mPa.s at a pH of 3.75. After that, the

viscosity decreased to 316 mPa.s at pH 4.5. For the 200 ppm breaker concentration, the viscosity started to increase at a pH of 2.55 and reached the maximum viscosity value of 209 mPa.s at pH 4.2. As the breaker concentration increases from 100 to 200 ppm, at pH level 2 to 5 range, the viscosity decreases. Adding too much breaker will affect the diversion of the acid treatment. **Table 3.1** shows a non-Newtonian, shear-thinning effect of the polymer based in-situ gelled acid. As the shear rate increases from 0.1 to1,000 s^{-1}, the viscosity of the solution decreases. The relationship between the viscosity and the shear rate can be described by the power-law model, Eq. 3:

$$\mu = K\dot{\gamma}^{(n-1)} \tag{3}$$

where μ is the fluid viscosity (mPa.s), $\dot{\gamma}$ is the shear rate (s^{-1}), n is the power-law index (-), and K is the power-law consistency index ($mPa.s^{n}$).
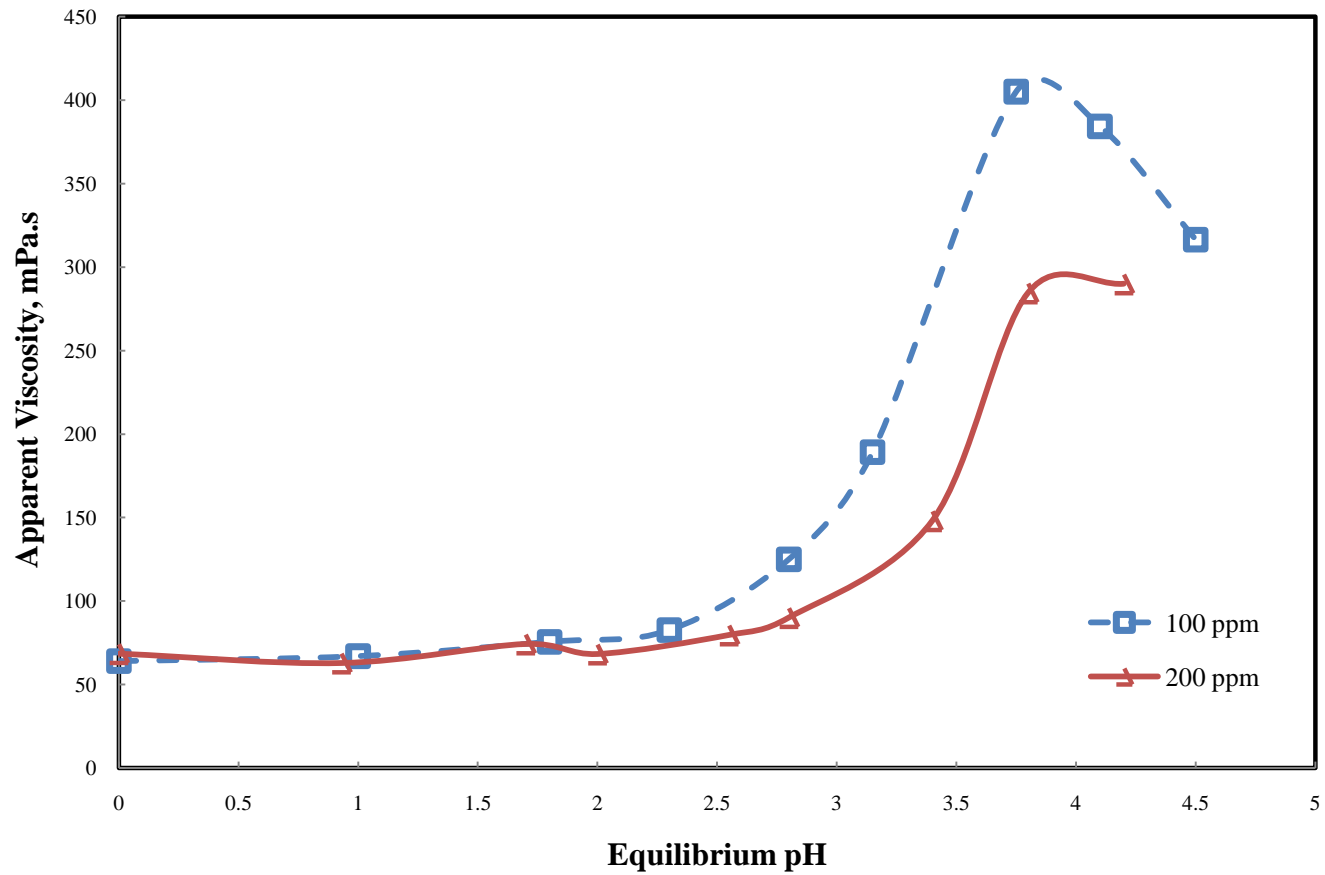
Fig. 3.4—Apparent viscosity versus equilibrium pH with 100 and 200 ppm breaker concentrations (100 s^{-1}).

TABLE 3.1—POWER-LAW PARAMETERS OF IN-SITU GELLED ACID AT DIFFERENT pH VALUES NEUTRALIZED BY $CaCO_3$ AND AT DIFFERENT BREAKER CONCENTRATIONS

Breaker Concentration (ppm)	pH	K, mPa.s^n	n	R^2
100	live	1742.5	0.320	0.9222
	1	1131.8	0.418	0.9515
	2.3	767.7	0.528	0.9909
	2.8	2621.3	0.381	0.9726
	3.15	3842.5	0.373	0.9927
	3.75	8511	0.321	0.9483
	4.1	8614.4	0.276	0.9324
	4.5	10215	0.190	0.9432
200	live	596.4	0.54	0.9587
	0.93	1661.4	0.354	0.9711
	1.7	1198.7	0.426	0.9800
	2	1138.3	0.440	0.9223
	2.55	1501.8	0.401	0.9876
	2.8	1622.1	0.416	0.9766
	3.4	2845.7	0.389	0.9628
	3.8	10256	0.248	0.9840
	4.2	11687	0.220	0.9957

3.4. Core Flood Studies

Experiment #1

A 0.5 PV slug of acid was injected through core 1 at an injection rate of 2.5 cm^3/min and at room temperature. In this test, no breaker was added to the acid. **Fig. 3.5** shows the change in pressure drop across the core as a function of cumulative injected volume. The initial pressure drop was 23 psi. As the acid entered the core, the pressure drop increased to about 260 psi due to higher acid viscosity. Then, the pressure drop decreased and

increased in one cycling behavior. The cycling behavior of in-situ gelled acid described by Gomaa et al. (2011) as evidence of acid diversion. In-situ gelled acid was changing its path inside the core and this is because the pressure drop was changing. However, water injection was started and the pressure drop decreased instantly to 43 psi due to the low water viscosity. Since the gel remained inside the core, the pressure drop increased again to 356 psi. Some of the gel was removed slowly by continued waster injection. Then, the pressure drop decreased slowly and stabilized at 215 psi. The core permeability reduced from 38 to 3.8 mD. It can be concluded that since the pressure drop increased ten times due to the gel inside the core, the permeability of the core decreased almost 10 times and caused formation damage.

Fig. 3.6 shows the pH and density values measured from the collected effluent samples. After injection of 0.5 PV of acid followed by 1.5 PV of water, the reaction product started to be released from the core. Also, at the same time the density started to increase, calcium and zirconium were detected in the effluent (**Fig. 3.7**). Increase in density represents calcium presence in the core effluent samples. Zirconium in the effluent samples was detected later, since zirconium was delayed because of the gel by 0.25 PV.

Fig. 3.5—Pressure drop across core # 1 versus cumulative injected acid volume, in-situ gelled acid was injected at 2.5 cm³/min and breaker concentration is 0 ppm.

Fig. 3.6—pH and density values of the core effluent samples, Experiment #1, in-situ gelled acid was injected at 2.5 cm^3/ min and breaker concentration is 0 ppm.

**Fig. 3.7—Ca and Zr concentrations of the Experiment #1,
in-situ gelled acid was injected at 2.5 cm³/min and breaker concentration is 0 ppm.**

Experiment #2

Fig. 3.8 shows the pressure drop across core 2 during injection of the in-situ gelled acid without a breaker, followed by water at 10 cm^3/min and at room temperature. The initial pressure of the core was 87 psi. As 0.5 PV of acid was injected into the core, the pressure drop rapidly increased to 663 psi. After that, due to the water cleanup, the pressure drop decreased to 393 psi. After reaching 795 psi, the pressure started to stabilize at 10 PV of water was injected into the core for clean up. The final pressure drop was recorded at 469 psi. The pH, density, Ca, and Zr concentrations measurements were nearly the same as shown in **Figs. 3.9** and **3.10**.

At the end of the experiment, the pressure drop increased five times causing formation damage. This means that the permeability of the core decreased five times. The initial permeability of core 2 decreased from 38 to 7 mD. It can be concluded that when the injection rate was increased from 2.5 to 10 cm^3/min, the damage has been decreased from 90% to 81%.
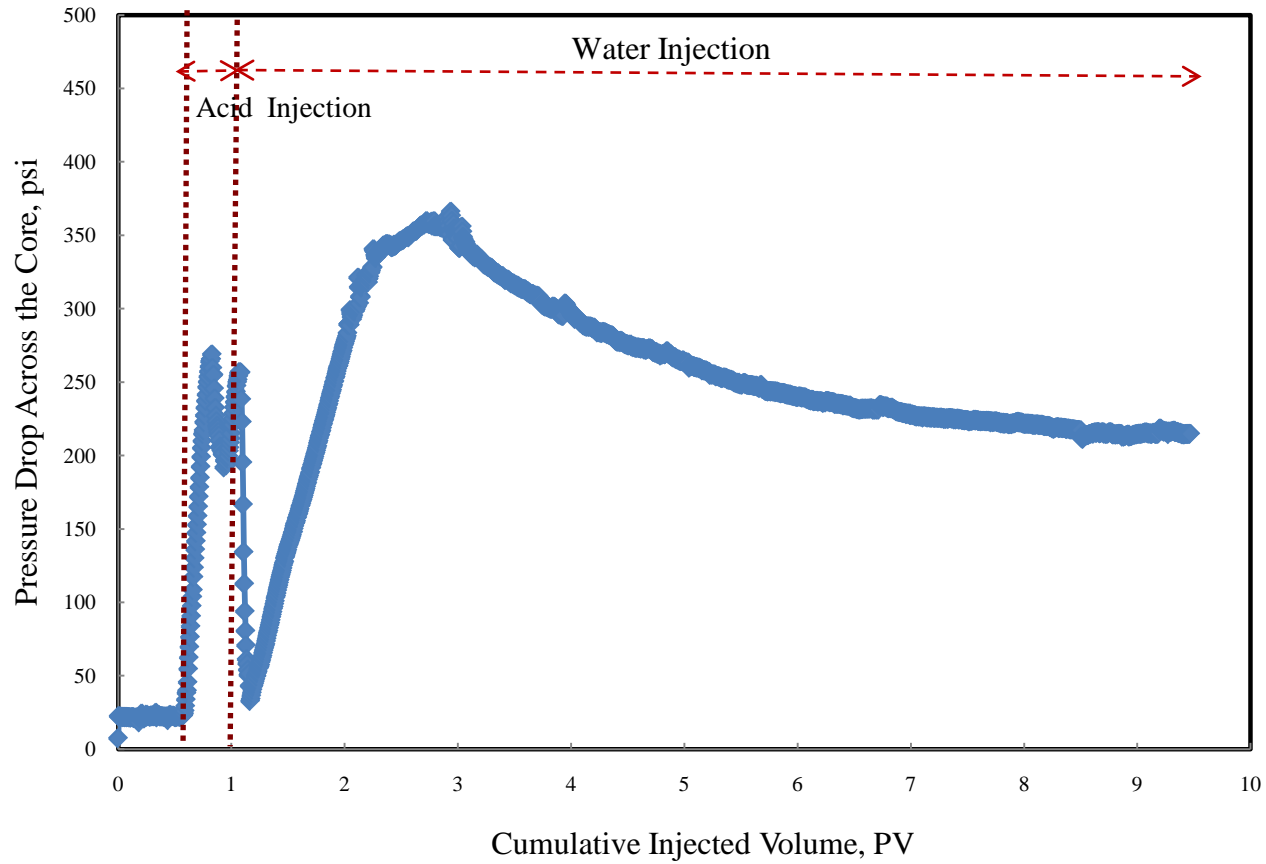
Fig. 3.8—Pressure drop across core # 2 versus cumulative injected acid volume, in-situ gelled acid was injected at 10 cm^3/min and breaker concentration is 0 ppm.
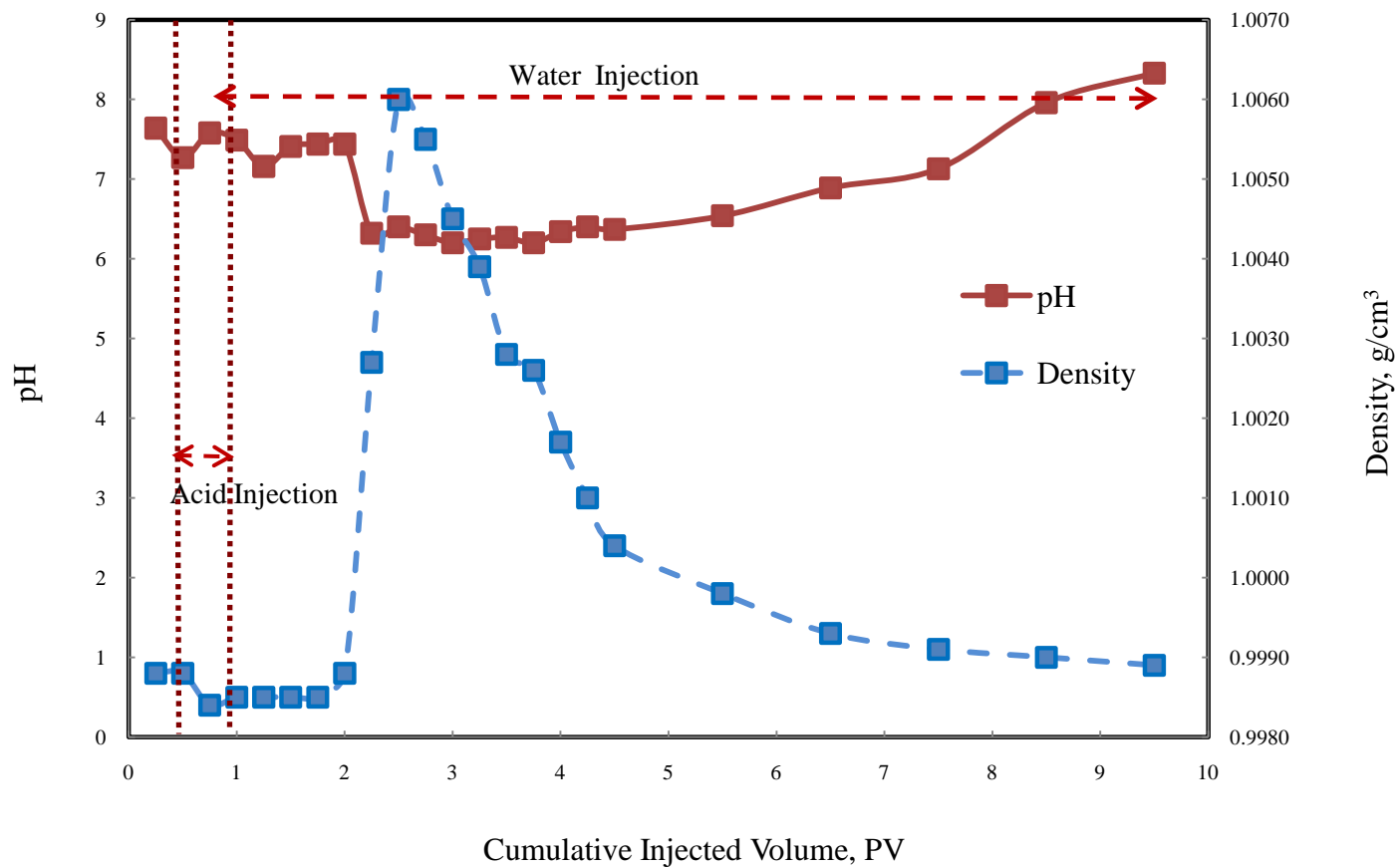
Fig. 3.9—pH and density values of the core effluent samples, Experiment #2, in-situ gelled acid was injected at 10 cm^3/ min and breaker concentration is 0 ppm.
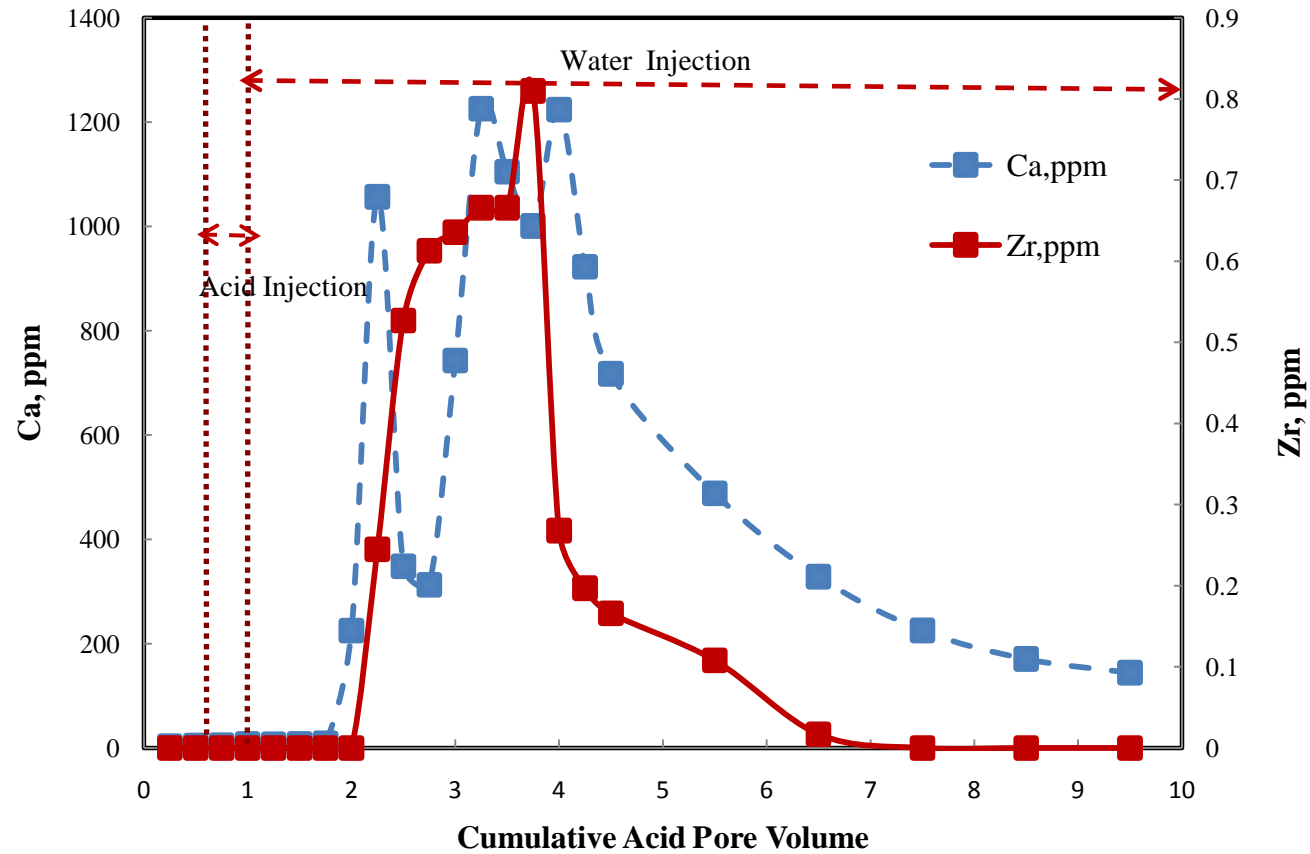
**Fig. 3.10—Ca and Zr concentrations of the Experiment #2,
in-situ gelled acid was injected at 10 cm³/min and breaker concentration is 0 ppm.**

Experiment #3

In-situ gelled acid with 100 ppm breaker concentration was injected into core 3 at an injection rate of 0.5 cm^3/min and at room temperature. The initial core pressure was 11 psi and as the acid entered the core, the pressure drop increased to 204 psi due to the acid viscosity (**Fig. 3.11**). After that, the pressure drop decreased showing cycling behavior which indicates that acid was diverted inside the core and stabilized at 87 psi. The final permeability of the core was measured as 1.9 mD, where the initial permeability was 15 mD.

  Fig. 3.12 shows the pH values and density for the core effluent samples as a function of the cumulative injected volume. After injection 0.5 PV of acid, the pH decreased to the value of 5.7. The increase in density values represents the presence of calcium in the samples. At the same time the calcium was detected, the density values started to increase (**Fig. 3.13**). Zirconium was detected later than calcium, since zirconium was delayed because of the gel formed inside the core.
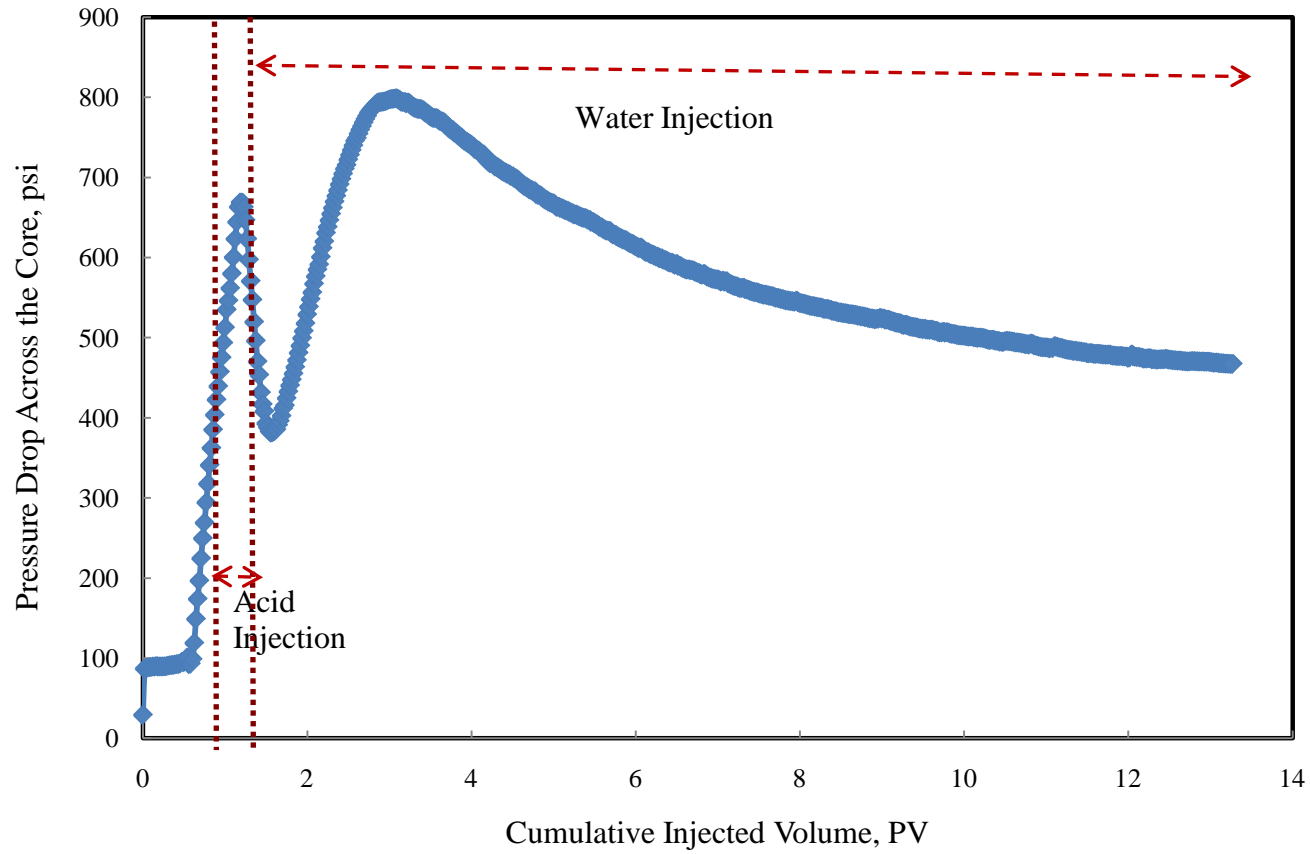
Fig. 3.11—Pressure drop across core # 3 versus cumulative injected acid volume, in-situ gelled acid was injected at 0.5 cm^3/min and breaker concentration is 100 ppm.
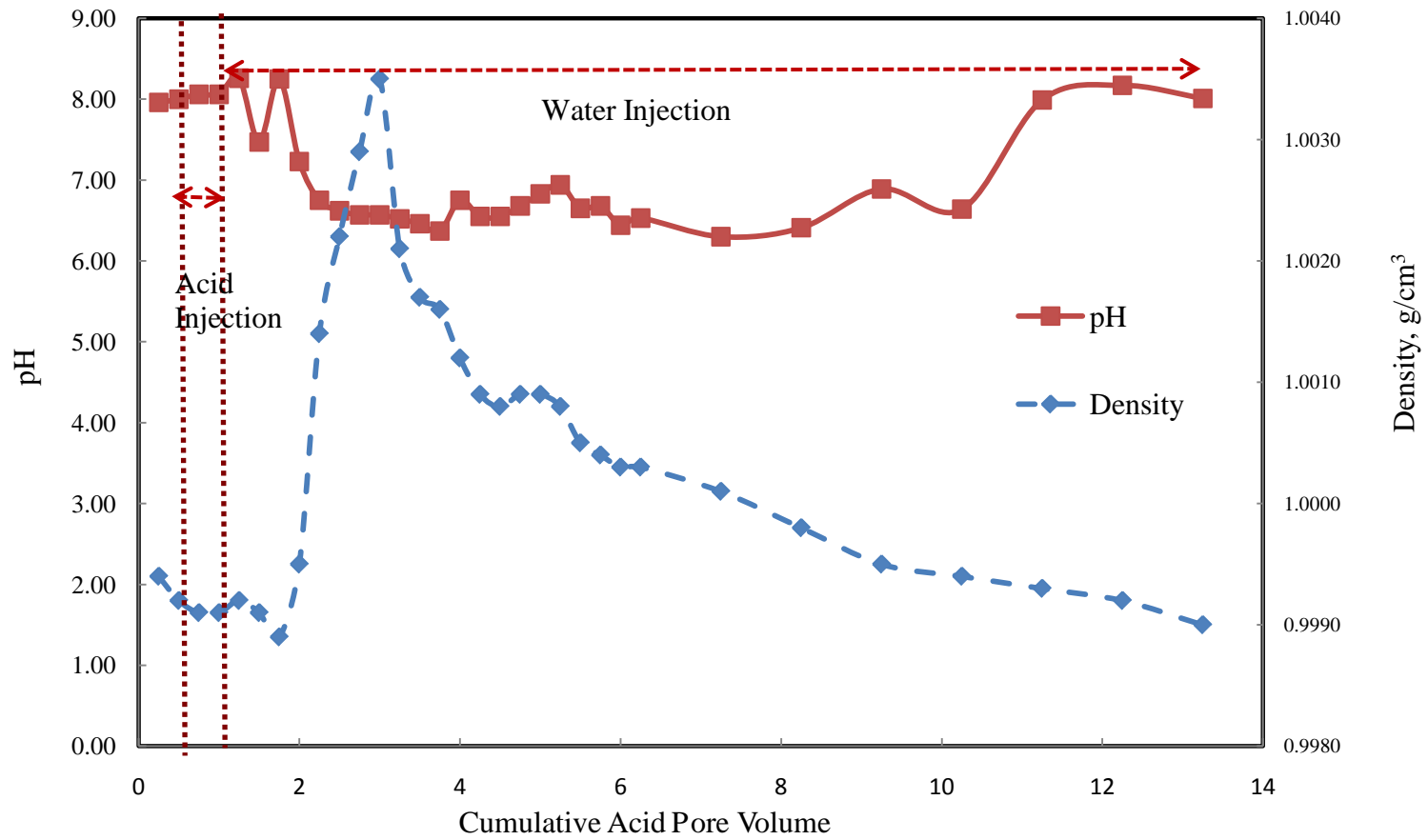
Fig. 3.12—pH and density values of the core effluent samples, Experiment #3, in-situ gelled acid was injected at 0.5 cm^3/ min and breaker concentration is 100 ppm.
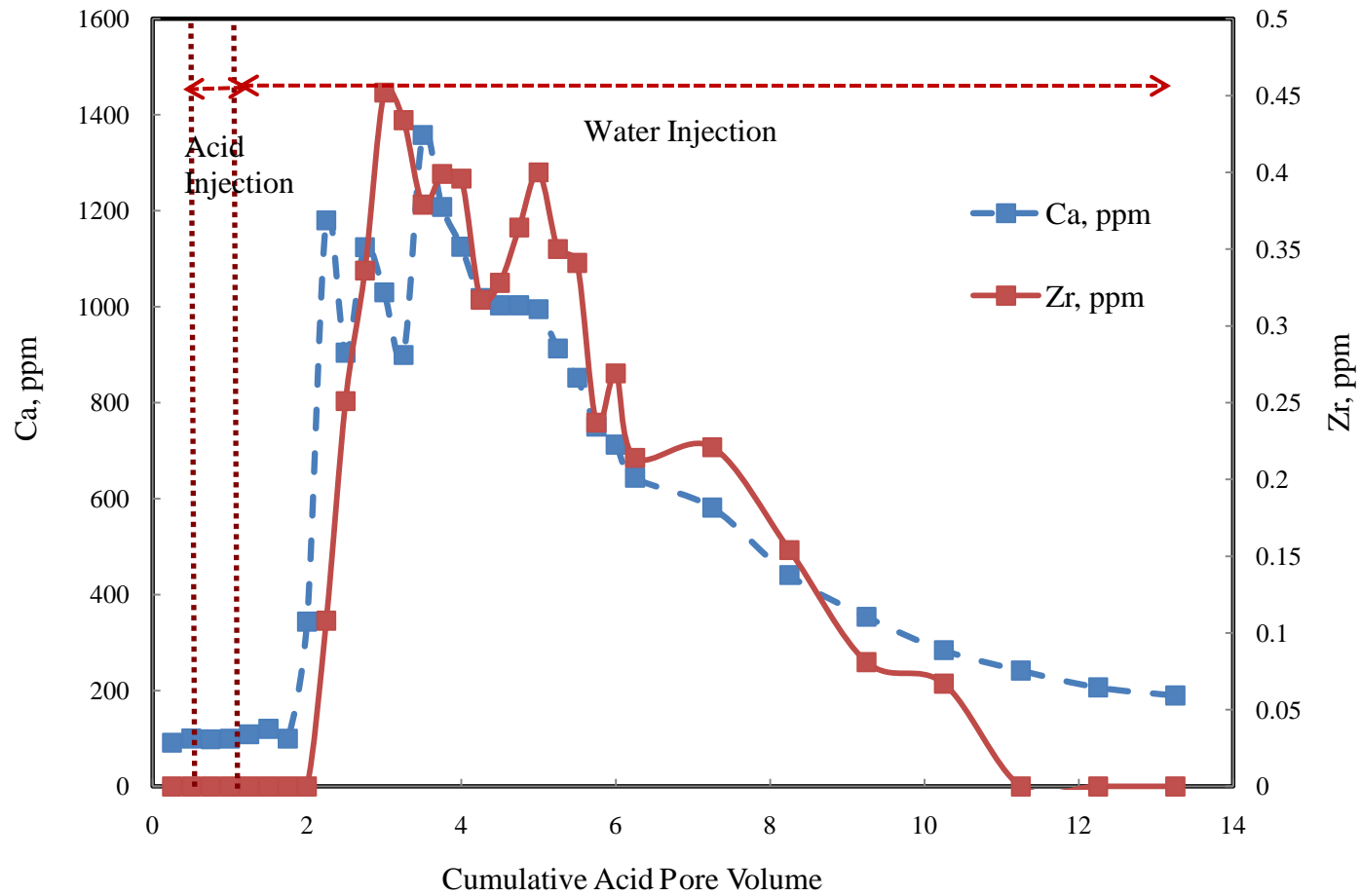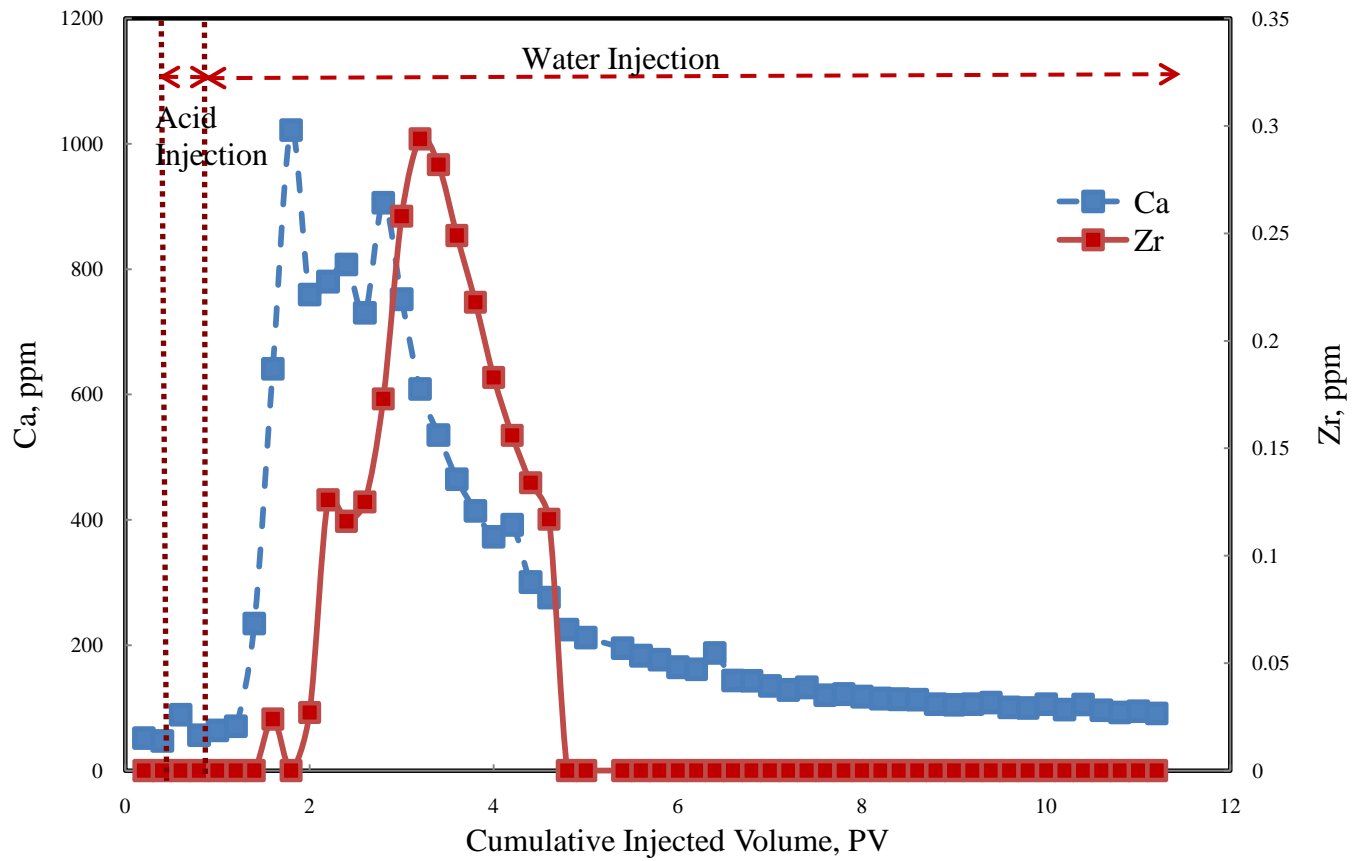
**Fig. 3.13—Ca and Zr concentrations of the Experiment #3,
in-situ gelled acid was injected at 0.5 cm³/min and breaker concentration is 100 ppm.**

Experiment #4

A 0.5 PV of in-situ gelled acid with 100 ppm breaker concentration was injected at an injection rate 2.5 cm^3/min at room temperature. The initial core pressure was measured as 21psi. As the acid entered the core, the pressure drop increased to the value of 304 psi. Then, due to the water viscosity, the pressure drop decreased to 178 psi and started to increase again. The maximum pressure drop value was 533 psi (**Fig. 3.14**). The permeability of core 4 decreased from 39 to 1.9 mD. The pH, density, Ca, and Zr concentrations measurements were nearly the same as shown in **Figs. 3.15** and **3.16**.
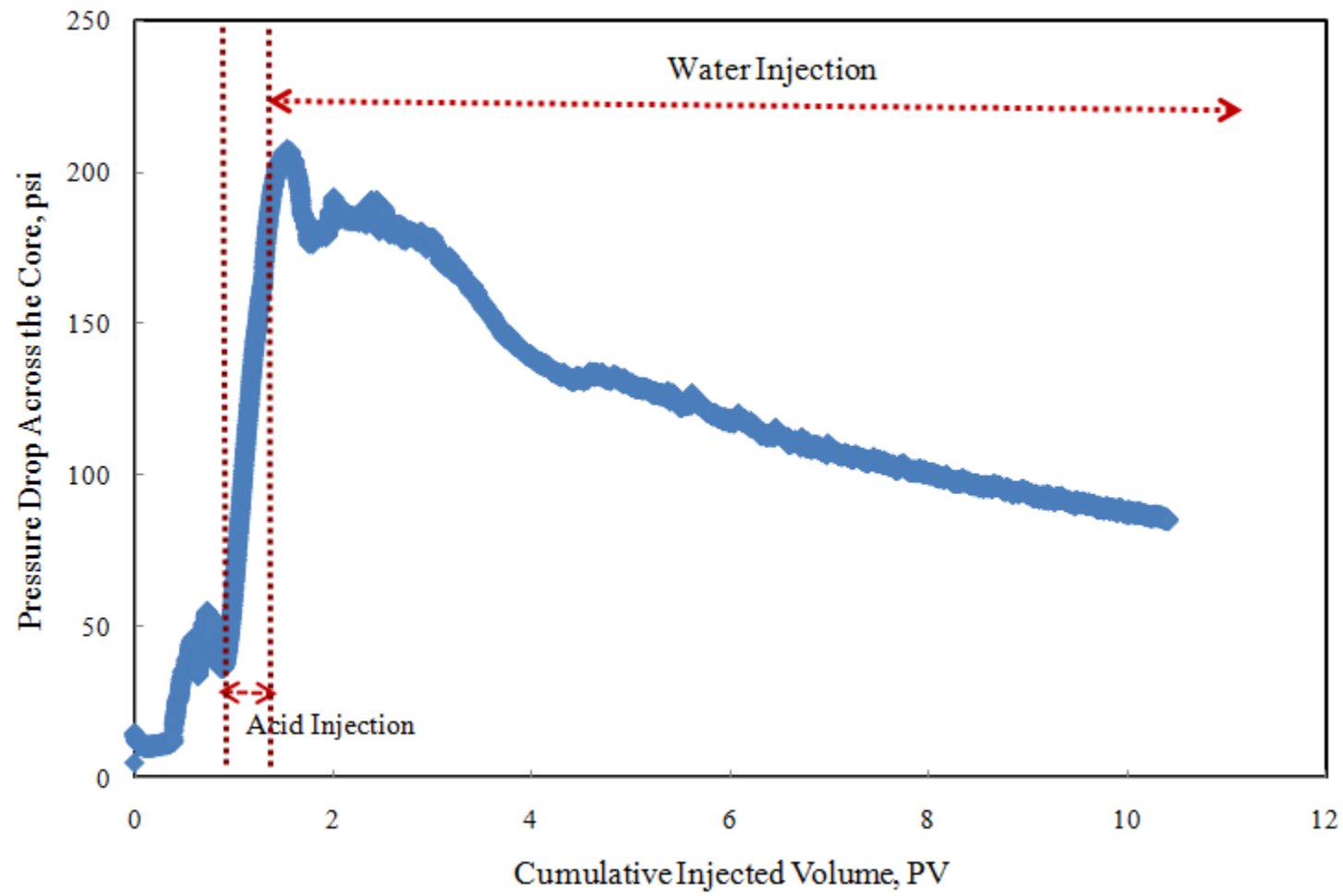

Fig. 3.14—Pressure drop across core # 4 versus cumulative injected acid volume, in-situ gelled acid was injected at 2.5 cm^3/min and breaker concentration is 100 ppm.

Fig. 3.15—pH and density values of the core effluent samples, Experiment #4, in-situ gelled acid was injected at 2.5 cm^3/ min and breaker concentration is 100 ppm.

**Fig. 3.16—Ca and Zr concentrations of the Experiment #4,
in-situ gelled acid was injected at 2.5 cm^3/min and breaker concentration is 100 ppm.**

Experiment #5

Fig. 3.17 shows the pressure drop as a function of cumulative injected volume. The in-situ gelled acid was with 100 ppm breaker concentration at injection rate of 10 cm^3/min and at room temperature. The initial core pressure was 43 psi. With the acid injection entering the core, the pressure drop increased to the value of 668 psi and stabilized at 498 psi as 15 PV of water was injected. The initial permeability of the core was 76 mD and decreased to 6.6 mD. It can be concluded that the gel that formed plugged the core and since the pressure drop increased eleven times, the core permeability decreased eleven times. The pH, density, Ca, and Zr concentrations measurements were nearly the same as shown in **Figs. 3.18** and **3.19**. It can be concluded that, increasing the injection rate enhanced the permeability. For core 2, the pressure drop increased twenty times and the permeability of the core decreased twenty times. When the injection rate was increased, the pressure drop increased twelve times and the permeability decreased twelve times.

Fig. 3.17—Pressure drop across core # 5 versus cumulative injected acid volume, in-situ gelled acid was injected at 10 cm³/min and breaker concentration is 100 ppm.
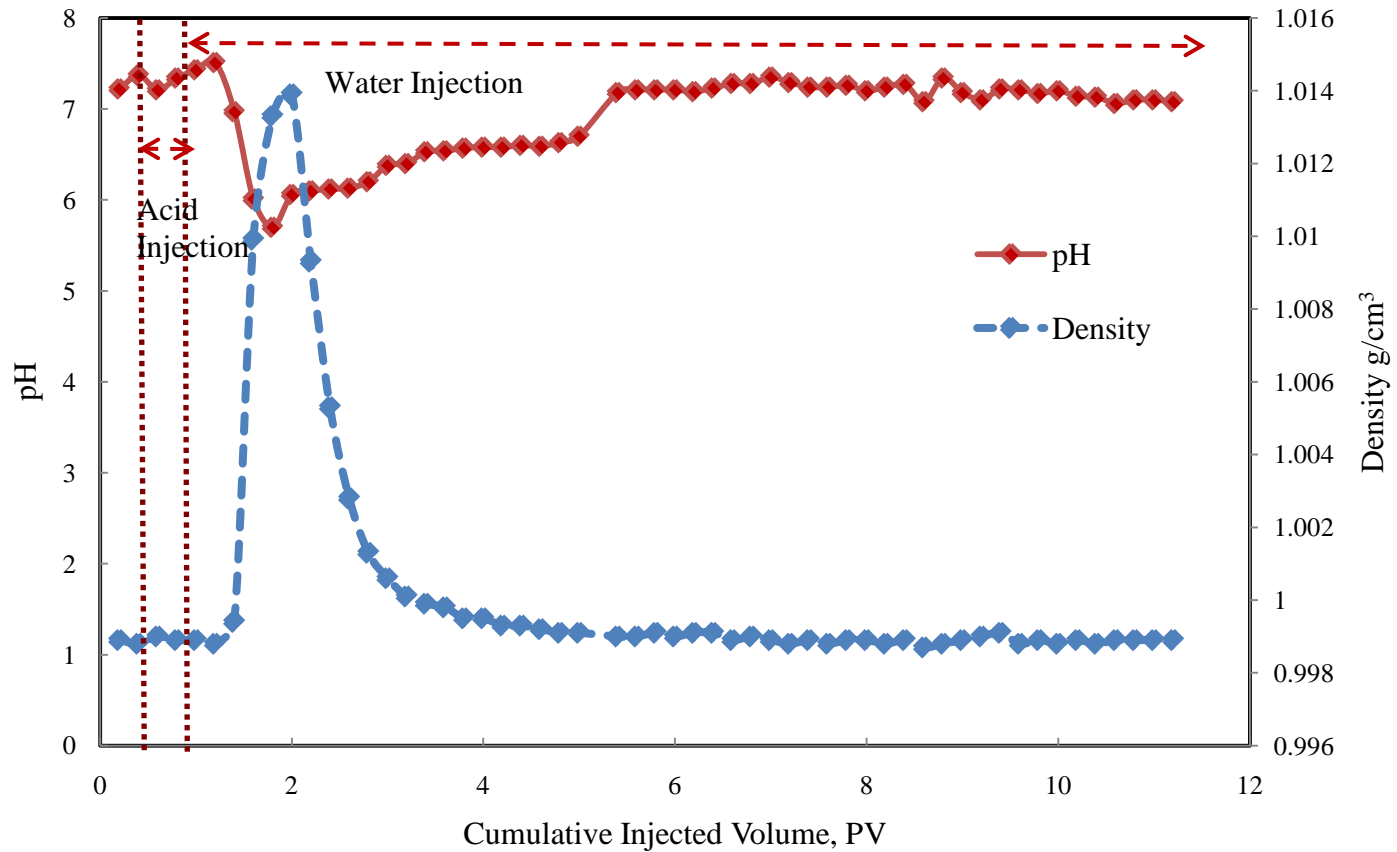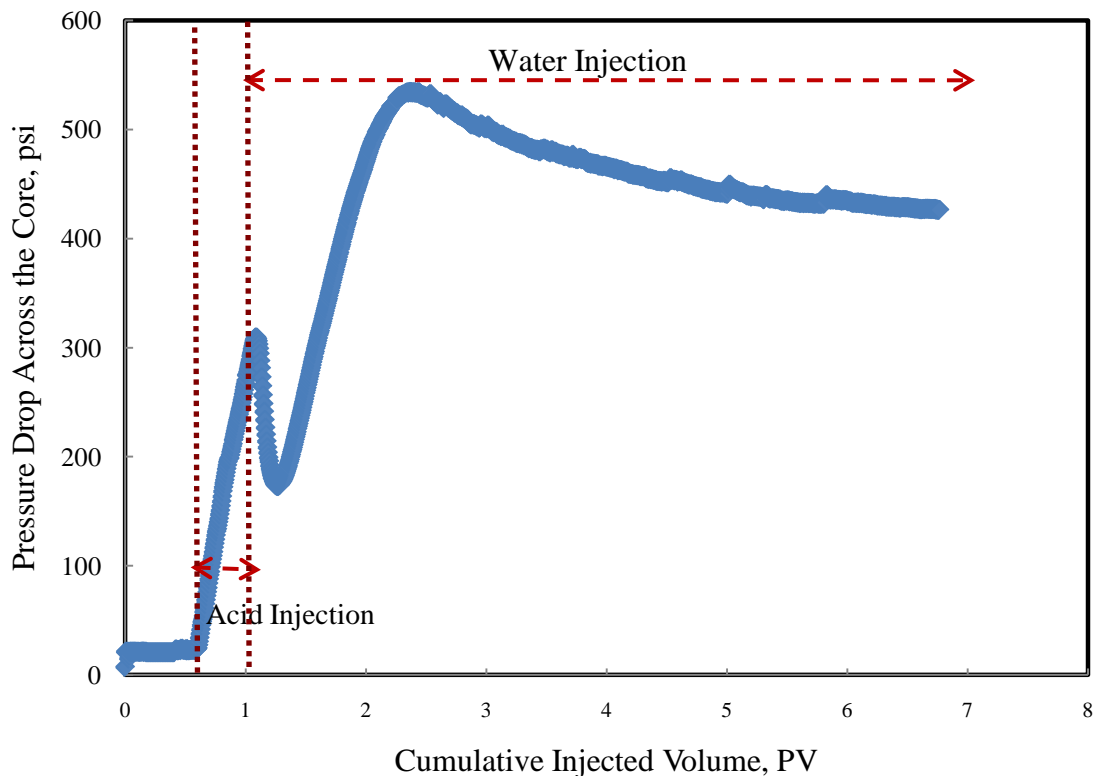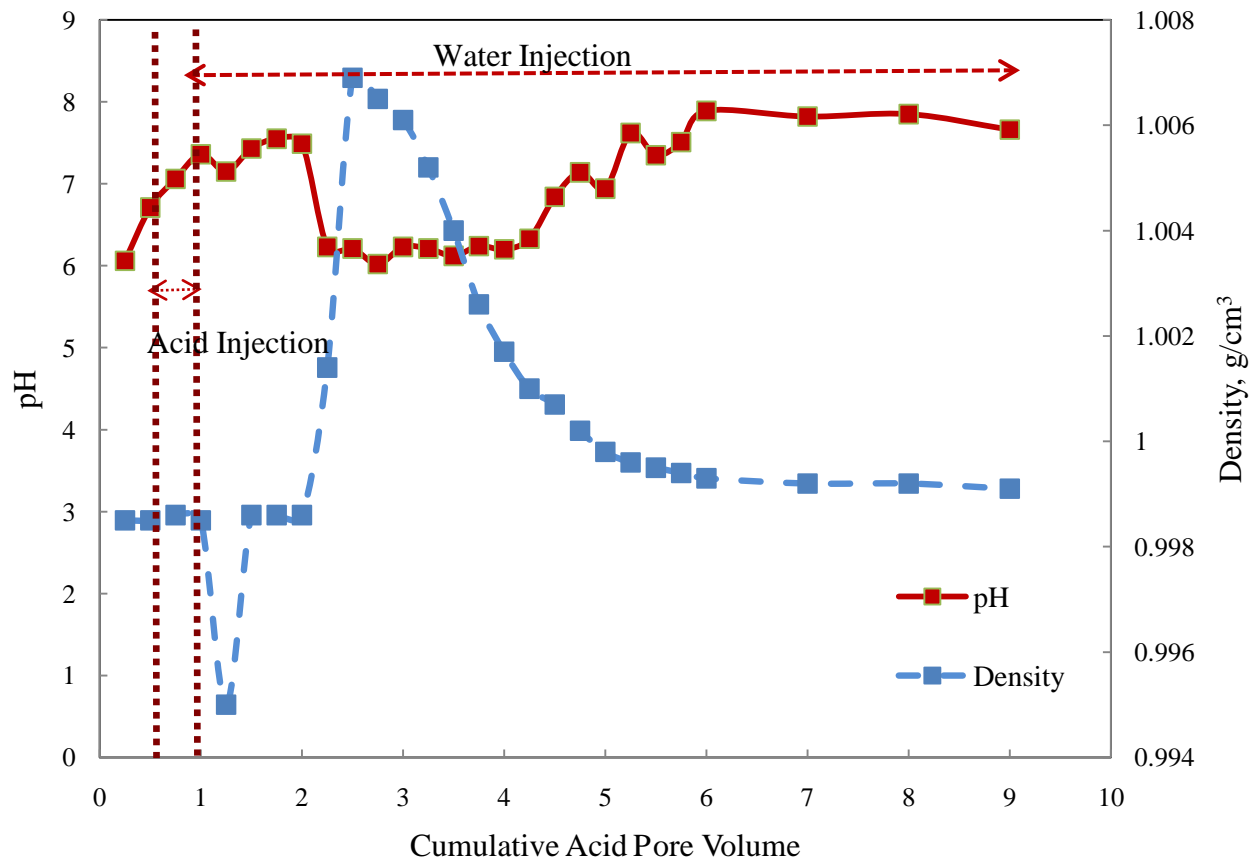
Fig. 3.18—pH and density values of the core effluent samples, Experiment #5, in-situ gelled acid was injected at 10 cm^3/ min and breaker concentration is 100 ppm.
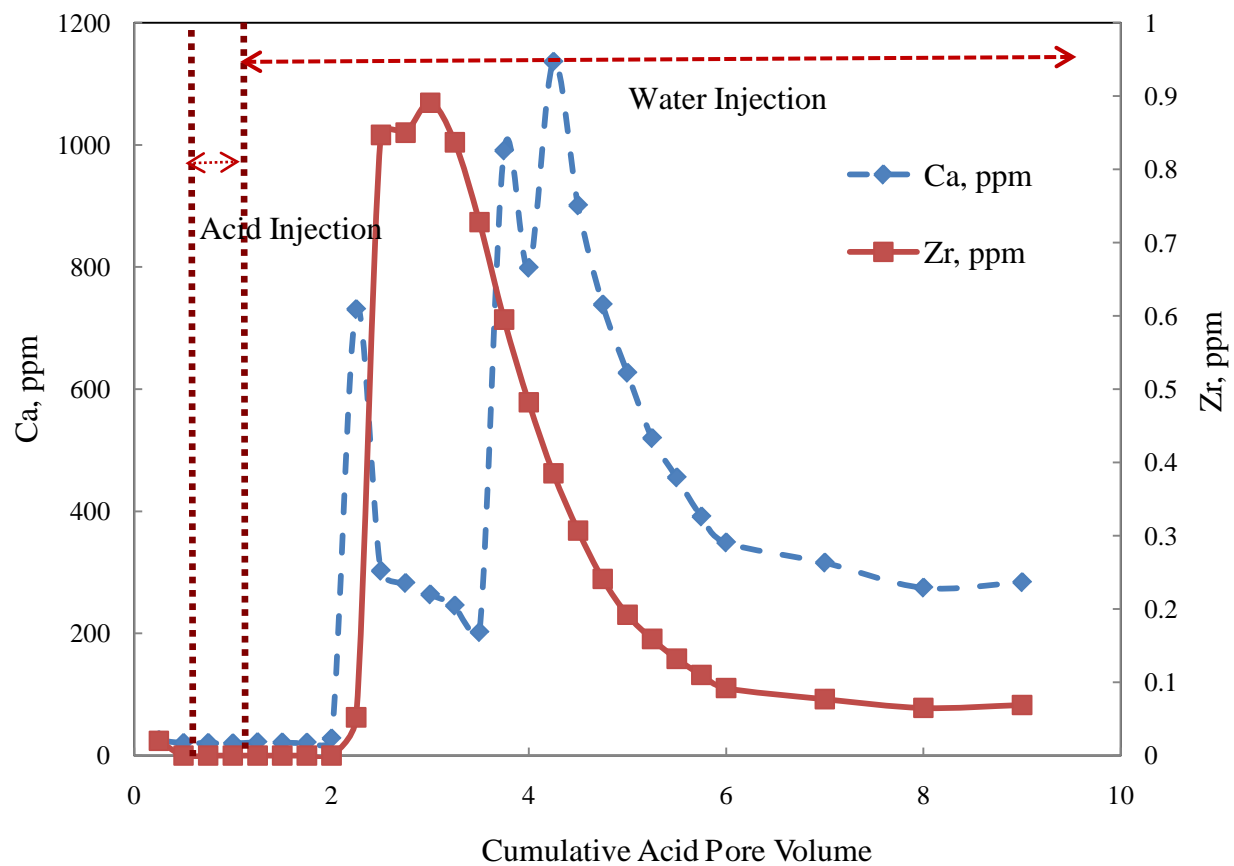
**Fig. 3.19—Ca and Zr concentrations of the Experiment #5,
in-situ gelled acid was injected at 10 cm^3/min and breaker concentration is 100 ppm.**

Experiment #6

Fig. 3.20 shows the pressure drop across core 6 during injection of the in-situ gelled acid with 200 ppm breaker concentration at injection rate of 2.5 cm^3/min and at room temperature. The initial core pressure was 19.5 psi. A 0.5 PV of acid solution was injected followed by a 4.3 PV slug of water injection. Acid injection caused the pressure drop to increase to 188 psi because of the higher acid viscosity. After that, water injection was started and the pressure drop decreased to 61 psi. After reaching 242 psi, the pressure started to stabilize at 201 psi. The initial permeability of the core was decreased from 42 to 4 mD. The pressure drop increased ten times and as a result, the permeability of the core decreased ten times.

The pH and density values are shown in **Fig. 3.21**. After 0.5 PV of acid followed by 1.5 PV of water, the pH value decreased from 7.4 to 5.9 due to the reaction product leaving the core. At the same time the density started to increase as the Ca concentration increased (**Fig. 3.22**). This indicates the presence of Ca in the samples. However, there was no Zr produced in this experiment indicating that the Zr remained inside the core.
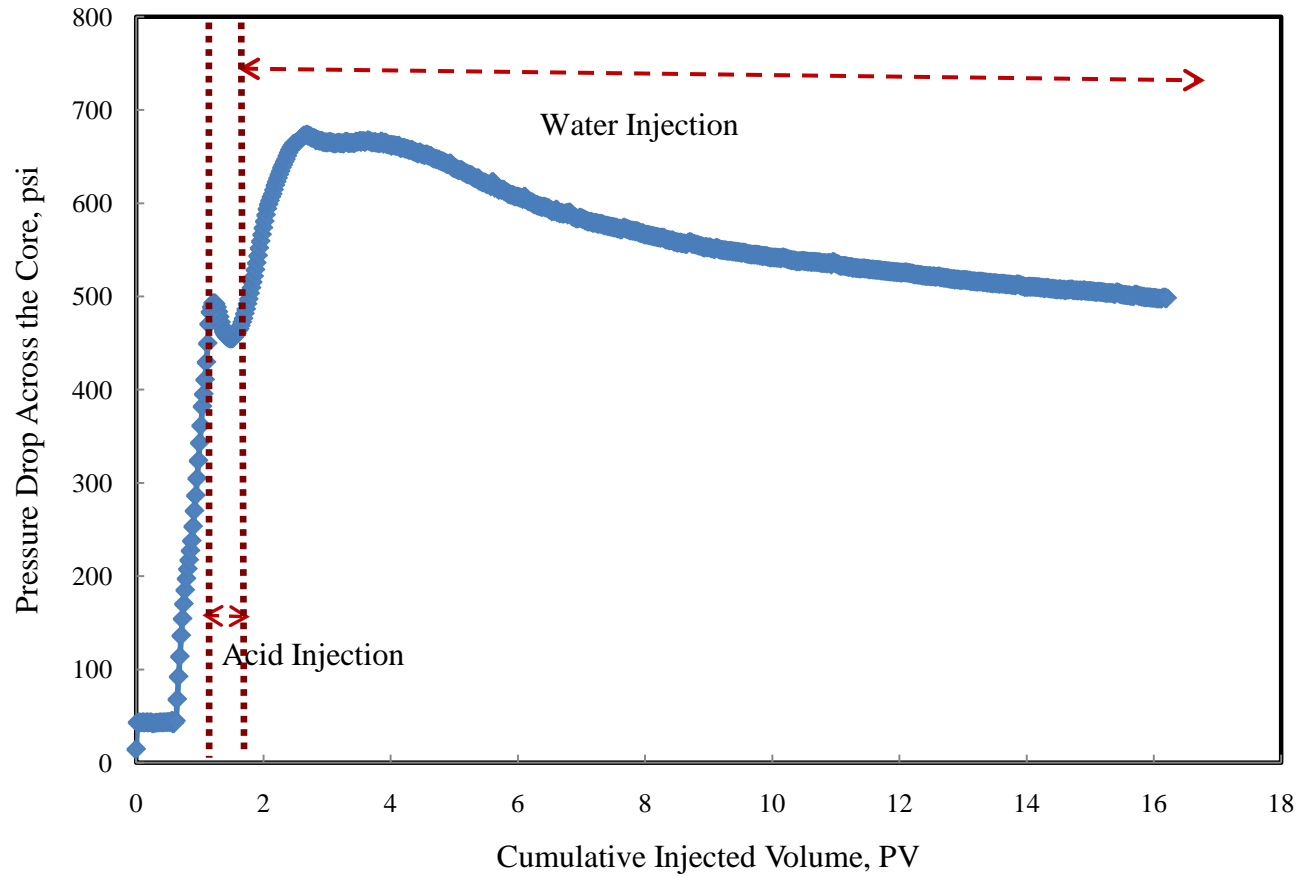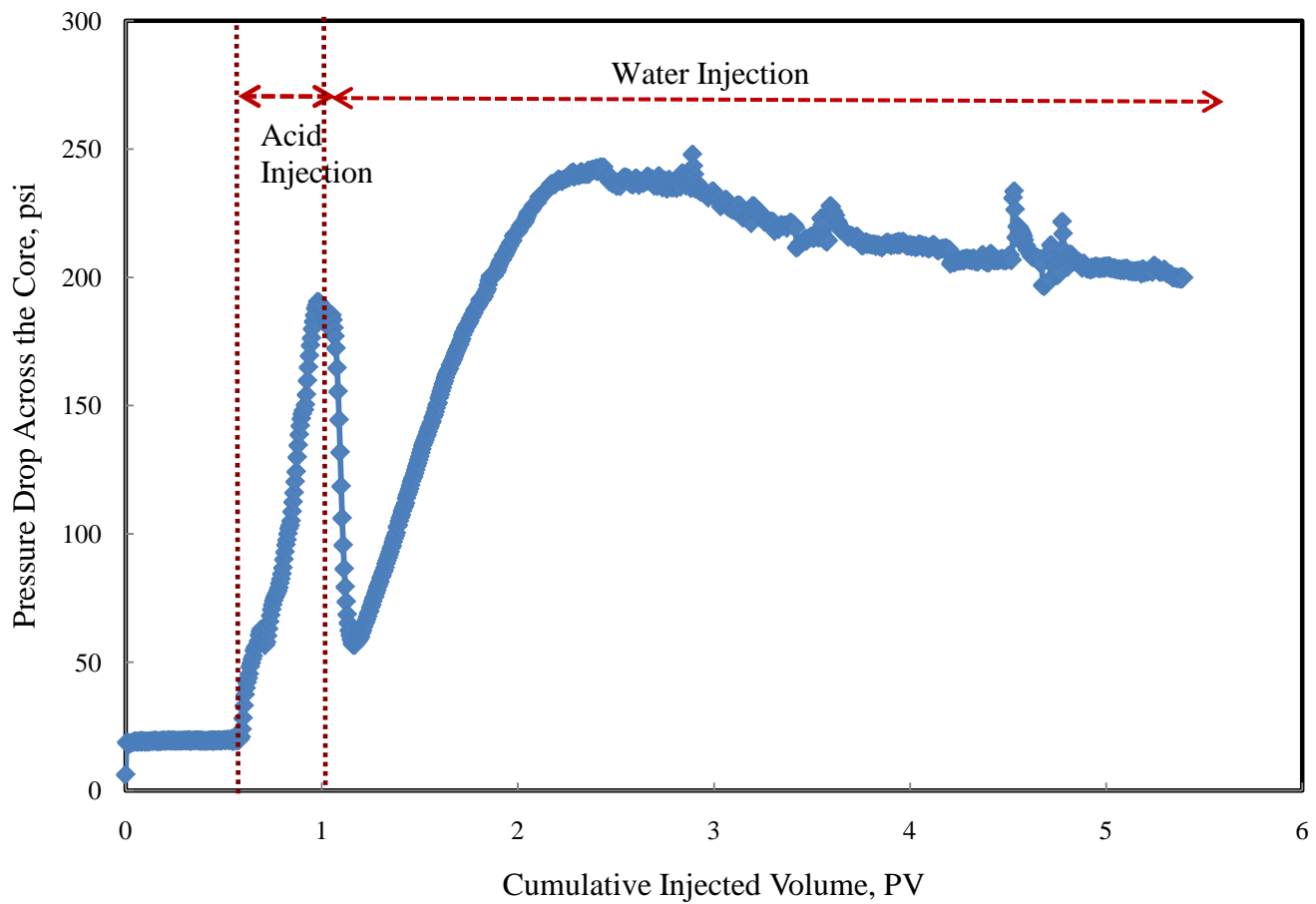
Fig. 3.20—Pressure drop across core # 6 versus cumulative injected acid volume, in-situ gelled acid was injected at 2.5 cm^3/min and breaker concentration is 200 ppm.
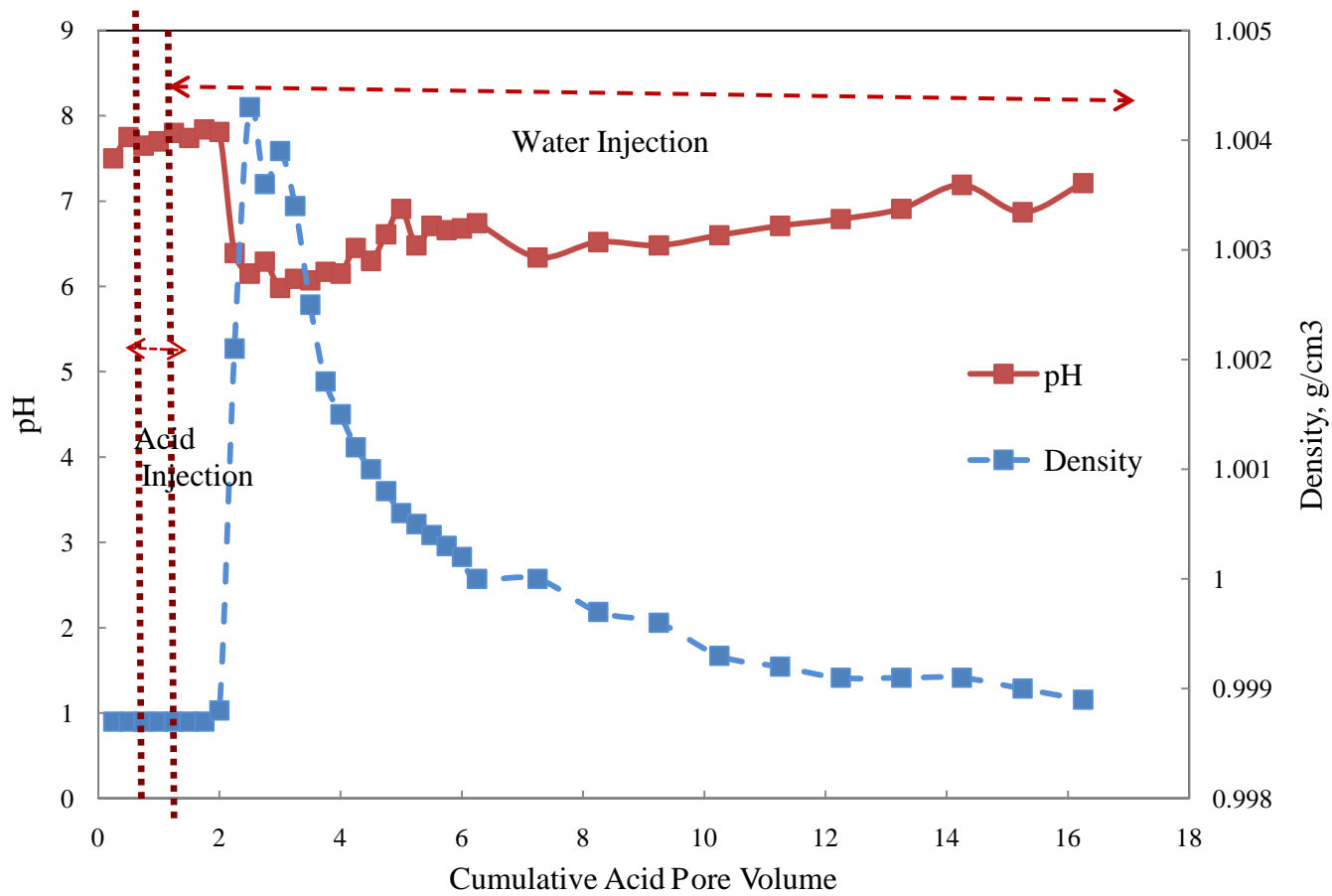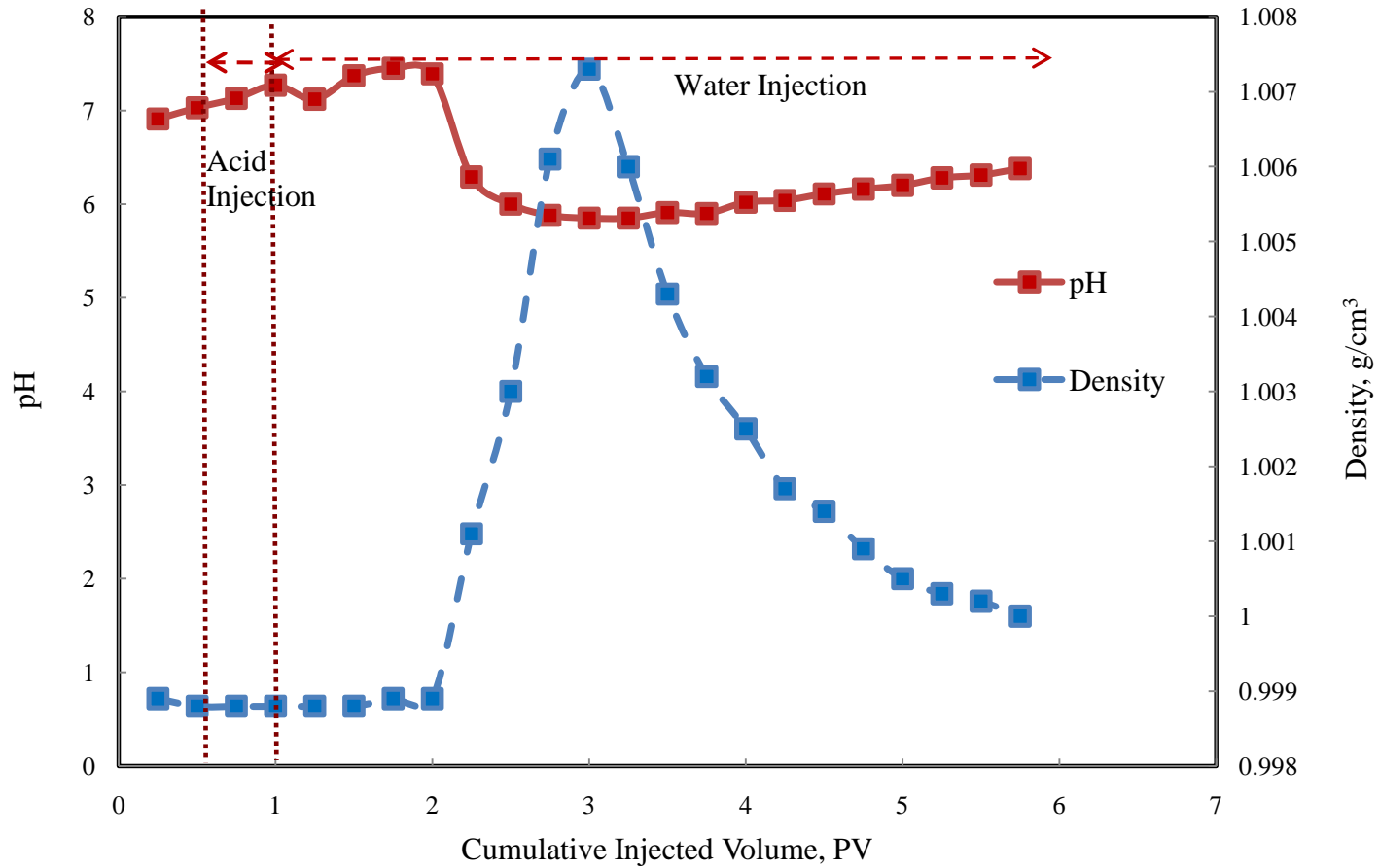
Fig. 3.21—pH and density values of the core effluent samples, Experiment #6, in-situ gelled acid was injected at 2.5 cm³/ min and breaker concentration is 200 ppm.
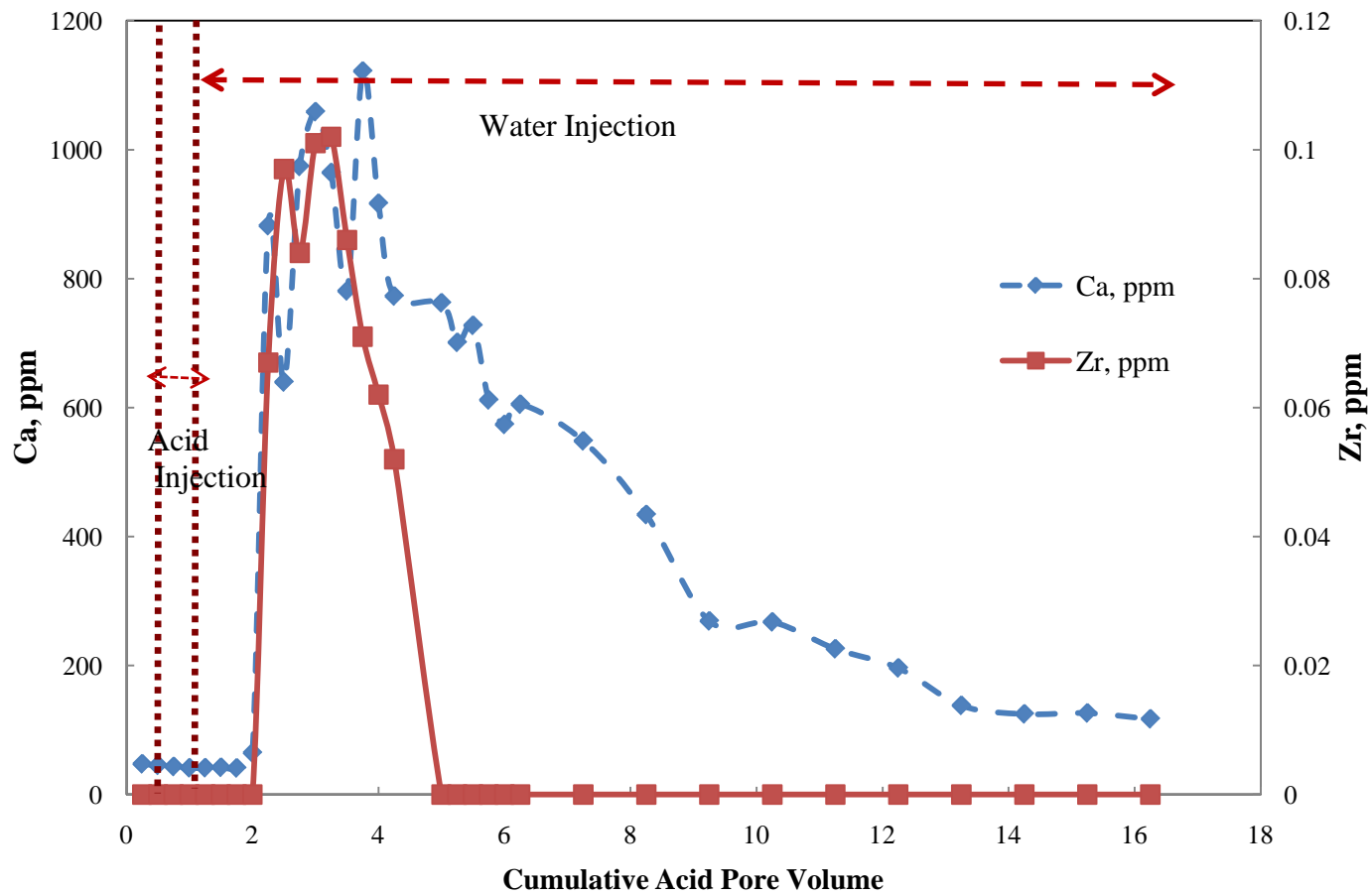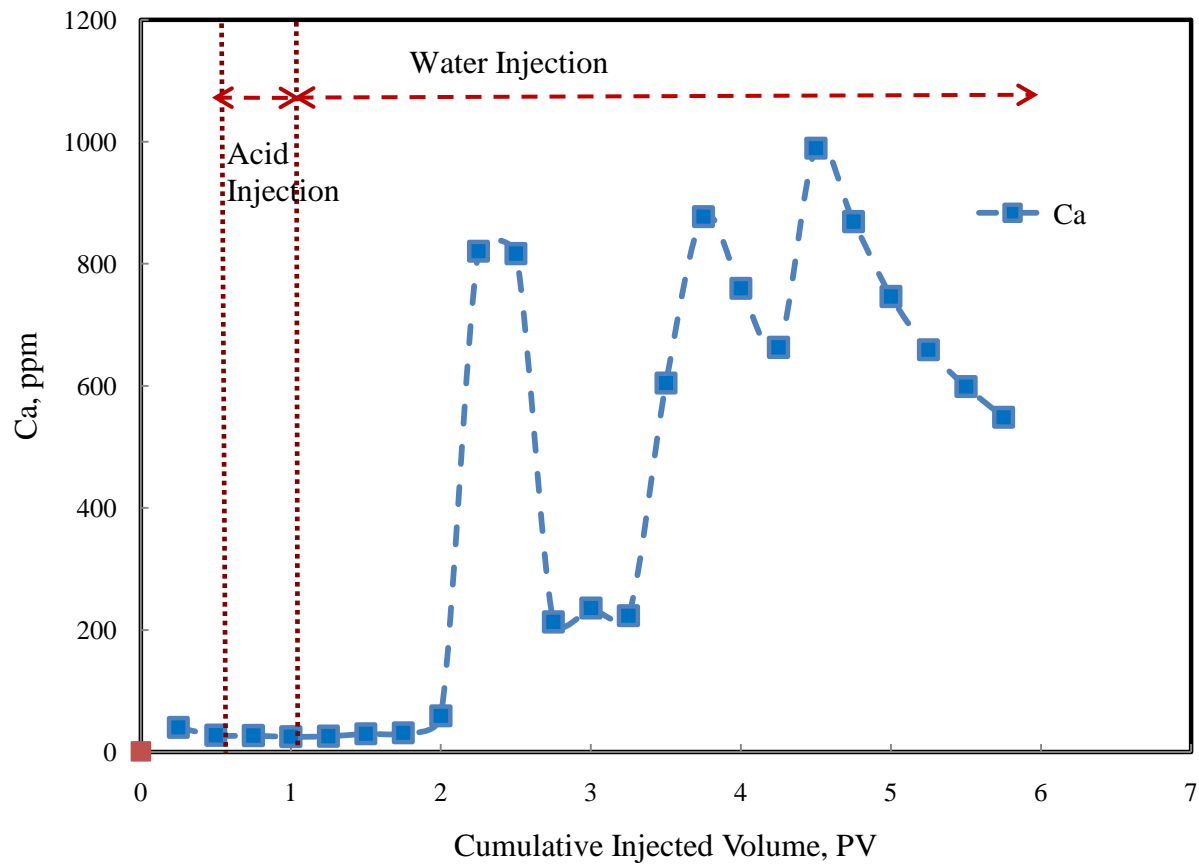
Fig. 3.22—Ca and Zr concentrations of the Experiment #6,
in-situ gelled acid was injected at 2.5 cm³/min and breaker concentration is 200 ppm.

Experiment #7

A 0.5 PV slug of the acid solution with 200 ppm breaker was injected at 10 cm^3/min and at room temperature. **Fig. 3.23** shows the change in pressure drop across the core as a function of cumulative injected volume. The initial core pressure was 59 psi. As the acid entered the core, the pressure drop increased to about 1186 psi slowly due to higher acid viscosity. After that, the pressure drop stabilized at 1133 psi as 5 PV of water was injected for cleanup. The pH, density, Ca, and Zr concentrations were nearly the same as shown in **Figs. 3.24** and **3.25**.
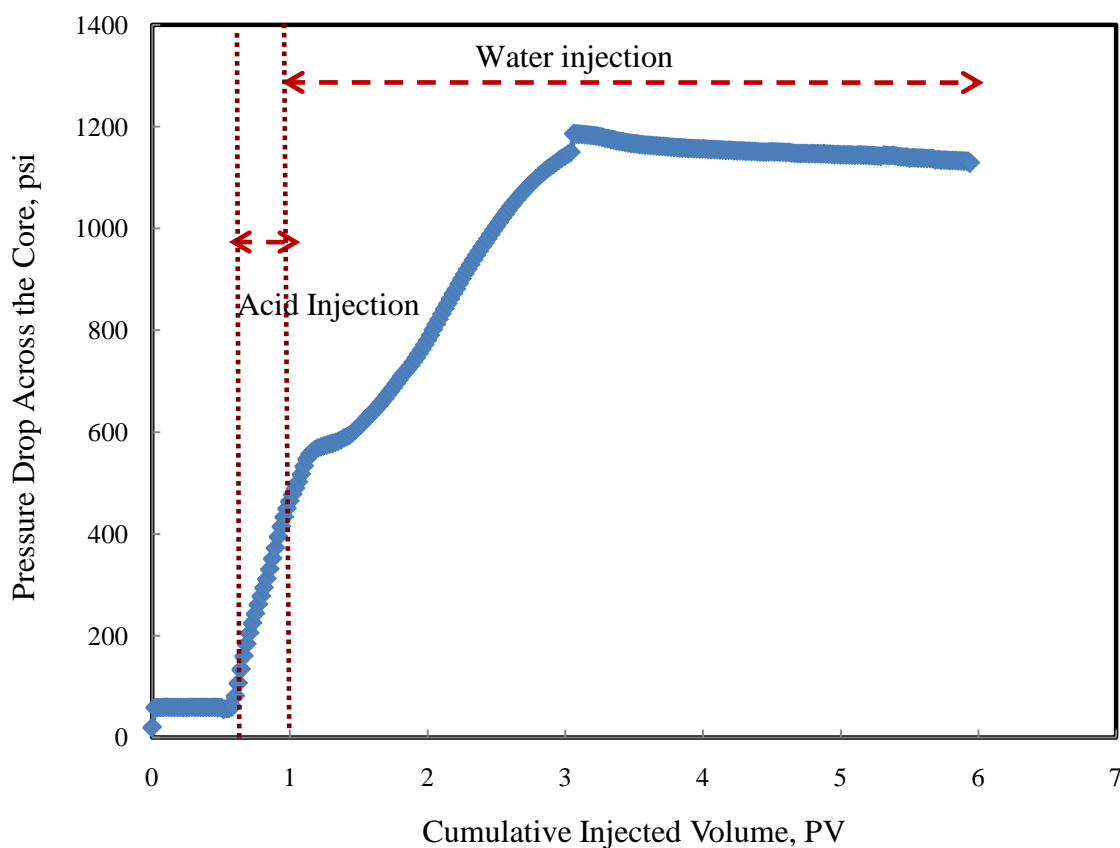
Fig. 3.23—Pressure drop across core # 7 versus cumulative injected acid volume, in-situ gelled acid was injected at 10 cm^3/min and breaker concentration is 200 ppm.

Fig. 3.24—pH and density values of the core effluent samples, Experiment #7, in-situ gelled acid was injected at 10 cm³/ min and breaker concentration is 200 ppm.
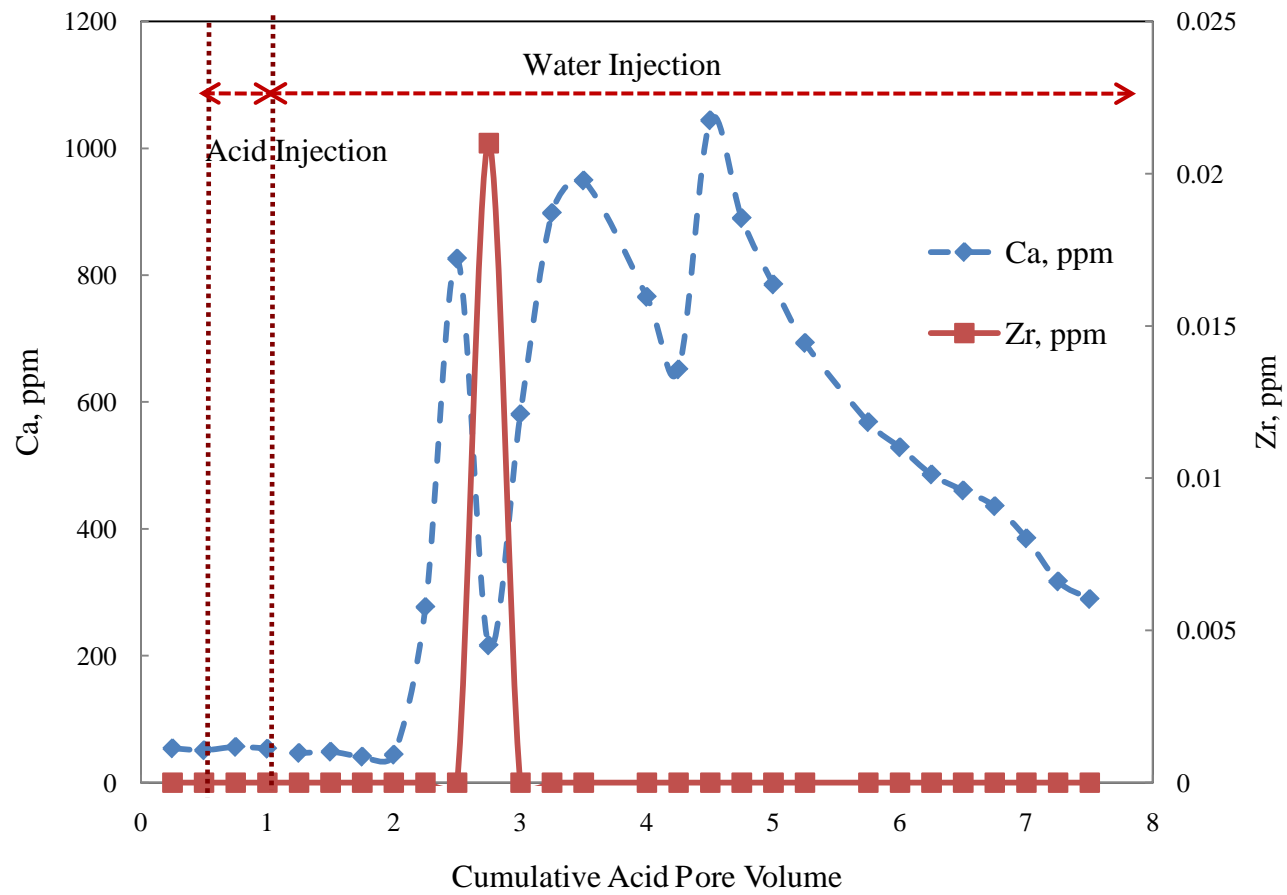
Fig. 3.25—Ca and Zr concentrations of the Experiment #7, in-situ gelled acid was injected at 10 cm^3/min and breaker concentration is 200 ppm.

The final normalized pressure drop is the ratio of the final pressure drop after acid injection to the initial pressure drop before the acid injection at the same injection rate. Based o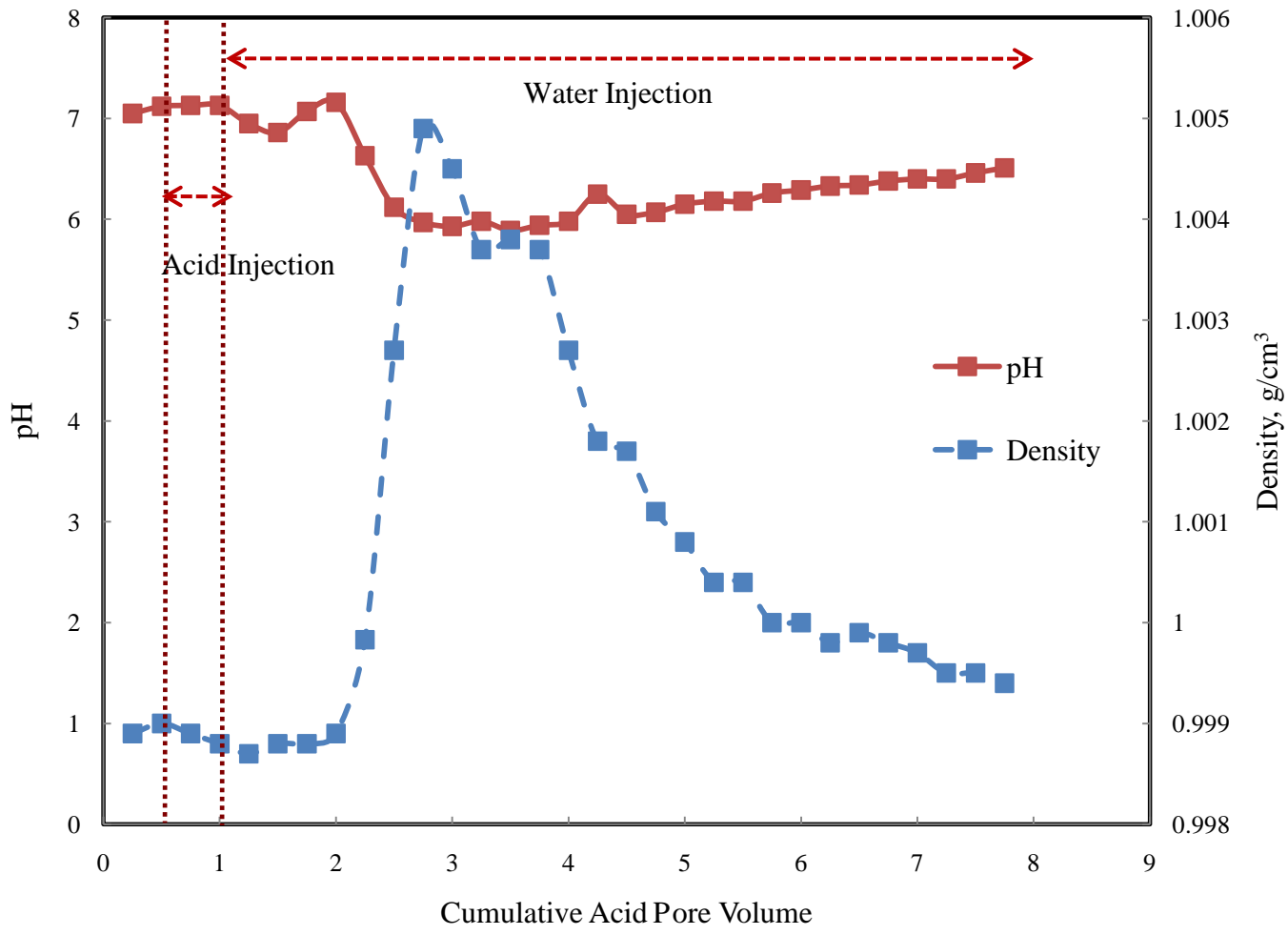n **Table 3.2**, the final normalized pressure drop across the core was significantly increased from 5.4 to 20.3 times. These values represent how the core was damaged, and it was expected to increase since the function of the in-situ gelled acid was to plug the formation. Also, there was no wormhole that can increase the core permeability and the water injection was in the same acid direction (no flow back). However, increasing the injection rate reduces the permeability reduction. At 0 ppm breaker the final normalized pressure drop was reduced from 9.3 to 5.4 when the injection rate was increased from 2.5 to 10 cm^3/min. This was because as the injection rate increased, the viscosity of in-situ gelled acid decreased with also affected the ability to form gel.

At 100 ppm breaker, the final normalized pressure drop was increased from 7.8 to 20.3 when the injection rate was increased from 0.5 to 2.5 cm^3/min. Water was injected in the same acid direction. Therefore, the broken gel was forced to ward the formation. This plugged more pores and caused severe damage. However increasing the injection rate to 10 cm^3/min at the same breaker concentration reduced the final normalized pressure drop to 11.6. Increasing the injection rate reduced the gel viscosity and minimized the core damage. Increasing the breaker concentration from 100 to 200 ppm reduced the final normalized pressure drop by 50% at an injection rate of 2.5cm^3/min, **Table 3.2**. Based on these data, it is recommended to inject the acid solution with the liquid breaker at high injection rates where the noted damage was less.

	Injection Rate, cm³/min	Breaker Concentration	Permeability, md		Permeability Reduction
Core			k_i	k_f	
1	2.5	0	45.49	3.8	0.916
2	10	0	37.64	7	0.814
3	0.5	100 ppm	54.58	1.9	0.965
4	2.5	100 ppm	51.17	1.9	0.963
5	10	100 ppm	76.16	7	0.908
6	2.5	200 ppm	56.47	4	0.929
7	10	200 ppm	55.51	3	0.946

TABLE 3.2—SUMMARY OF ACIDIZING EXPERIMENTS (NON BREAKTHROUGH)

3.5. Analysis of Core Effluent Samples and Material Balance

Effluent samples for all experiments were collected and weighted. Collected volume of effluent samples were calculated from the sample densities. The pH, calcium, and zirconium concentrations were measured in the samples. Zr amounts were calculated by using the concentration of each sample and its volume. The total zirconium in the live acid was 100 ppm. Loss of zirconium inside the core was presented in **Table 3.3**. When the breaker concentration was omitted, zirconium inside the core was removed with a higher injection rate. For experiments 1-2, 97.5 and 96 wt% of zirconium was present in the injected acid left inside the core, respectively. When the acid solution with 100 ppm breaker was injected, the highest injection rate of 10 cm³/min caused more damage where 2.5 cm³/min caused less damage. For experiments 3-5, 98.96, 96.6, and 99.6 wt% zirconium remained inside the core, respectively. The acid solution with 200 ppm breaker caused the highest damage. There was no zirconium in the effluent samples.

	TABLE 3.3—MATERIAL BALANCE CALCULATIONS FOR Zr (FIRST CORE FLOOD SET)		
__Core__	__Injection Rate, cm³/min__	__Breaker Concentration, ppm__	__Zirconium Remained inside the Core, %__
1	2.5	0	97.50
2	10	0	96.00
3	0.5	100	98.96
4	2.5	100	96.60
5	10	100	99.60
6	2.5	200	100.00
7	10	200	99.99

3.6. Breakthrough Acid Injection

Fig. 3.26 shows the pressure drop across core 8 during injection of in-situ gelled acid with 100 ppm breaker concentration at room temperature until acid breakthrough followed by water at 2.5 cm³/min. The initial core pressure was 13 psi. As the acid entered to the core, the pressure drop increased instantaneously to 66 psi. After that, the pressure drop increased in steps of around 31 psi until reaching 1.2 PV. After that, from 1.2 PV to 1.5 PV, the pressure drop increased significantly with the acid injection from 160 to 421 psi which was the maximum value. The amount of the acid injected until breakthrough was 1.5 PV. The pressure drop increased from 13 to 423 psi due to the acid viscosity.

Fig. 3.27 shows the change in the pressure drop across core 9 as a function of cumulative injected volume. In-situ gelled acid was injected until acid breakthrough with 100 ppm breaker concentration at room temperature followed by water at 5 cm³/min. The initial core pressure was 26 psi. The pressure drop increased instantaneously to 985

psi, as the acid entered to the core. After that, the pressure drop decreased to 545 psi at 0.78 PV. From 0.78 to 1 PV, the pressure drop increased in two steps to the value of 642 psi. After 1 PV, the pressure drop decreased slowly to 531 psi. The required acid volume to breakthrough was 1.25 PV.

Based on **Figs. 3.26** and **3.27**, it can be concluded that a larger amount of acid needed to breakthrough if the injection rate is low. For low injection rate, there was high pressure drop before breakthrough. This means the gel structure was strong in the core. However, when the injection rate was increased, this behavior was not observed. At breakthrough, there was a significant enhancement in the permeability for the both cores. **Table 3.4** summarizes the core flood test for the second set.
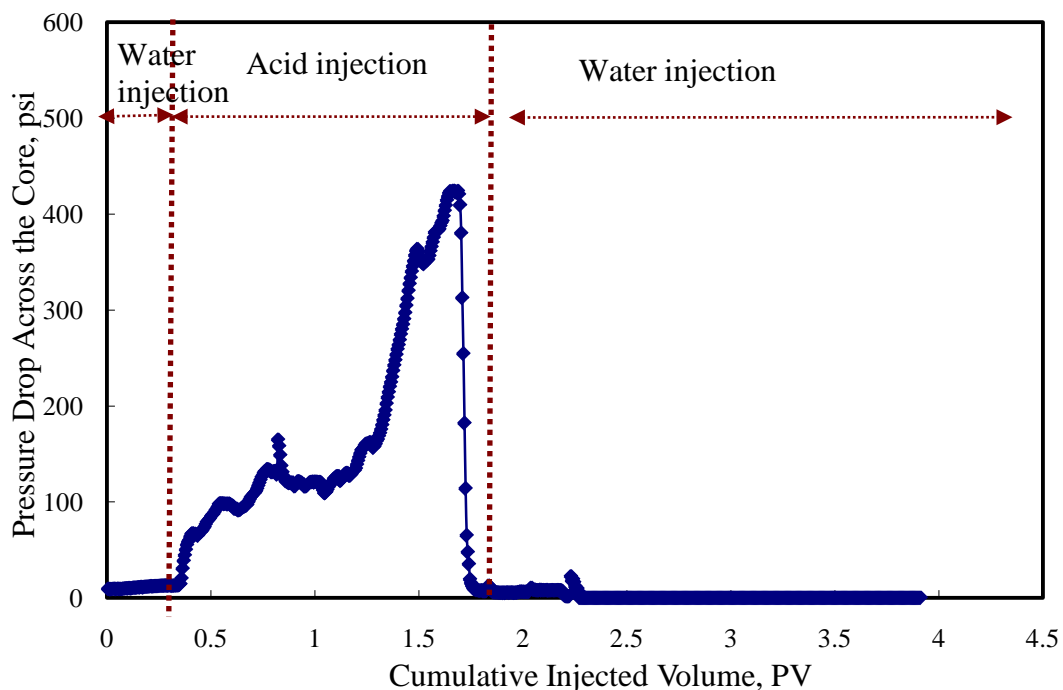
Fig. 3.26—Pressure drop across core # 8 versus cumulative injected acid volume, in-situ gelled acid was injected at 2.5 cm³/min and breaker concentration is 100 ppm until breakthrough.
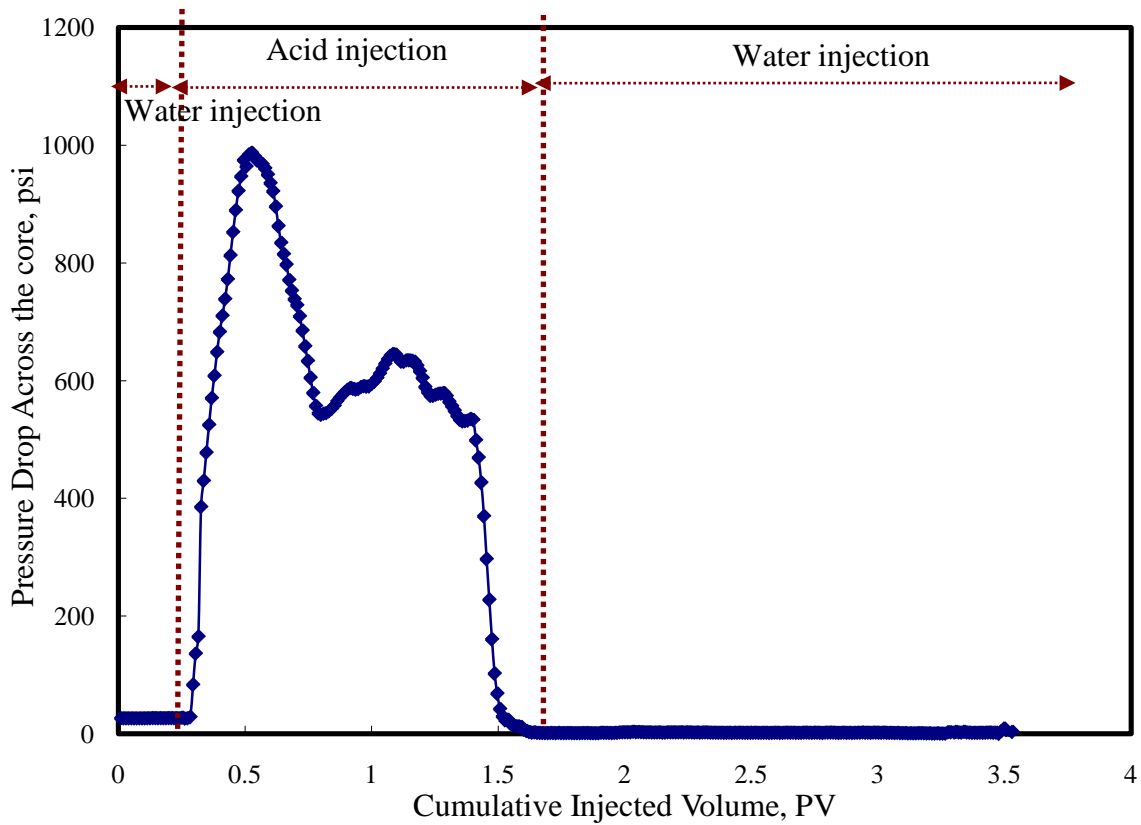
Fig. 3.27—Pressure drop across core # 9 versus cumulative injected acid volume, in-situ gelled acid was injected at 5 cm³/min and breaker concentration is 100 ppm until breakthrough.

Core	Breaker Concentration	Permeability, md		Injection Rate, cm³/min	Temperature, °F
		k_i	k_f		
8	100 ppm	68	Breakthrough	2.5	75
9	100 ppm	63	Breakthrough	5	75

TABLE 3.4—SUMMARY OF ACIDIZING EXPERIMENTS (UNTIL BREAKTHROUGH)

CHAPTER IV

CONCLUSIONS AND RECOMMENDATIONS*

4.1. Conclusions

In-situ gelled acids have been used to divert acids during the matrix acidizing of carbonate formations. Breaker is one of the important components of the in-situ gelled acids. However, a solid breaker is not effective in reducing the viscosity of the crosslinked acid and cannot clean the well after the treatment. Therefore, the effect of a new liquid breaker was examined under different test conditions. Based on the results obtained, the following conclusions can be drawn:

1. The pH profile during neutralization confirmed that the polymer crosslinking action occurred at a pH value of 1.8.

2. At a pH less than 2, doubling the breaker concentration did not affect the viscosity of the acid. However, at pH greater than 2, the viscosity of the acid was reduced by 30%.

3. For the acid without breaker, the Zr in the core effluent sample was delayed by 0.25PV more than the reaction product, while at 100 pm the Zr was delayed by 0.75 PV. However at 200 ppm, no Zr ions were detected in the effluent samples.

4. As the breaker concentration increased, more Zr remained inside the core, as generated ZrF_4, which is water-insoluble.

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5. Increasing the breaker concentration from 100 to 200 ppm reduced the final normalized pressure drop by 50% at injection rate of 2.5 cm^3/min.

6. Permeability reduction due to gel was reduced by increasing the acid injection rate. Therefore, the acid solutions with the liquid breaker should be injected at high injection rates.

4.2. Recommendations for Future Work

The core flood experiments were conducted at room temperature. However, the effect of temperature should be studied. Besides, we did not flow back the cores and this study represents the work for injection wells. This is the reason of high permeability reductions. Production wells also should be studied.

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