

**CALCIUM SULFATE FORMATION AND MITIGATION WHEN SEAWATER  
WAS USED TO PREPARE HCL-BASED ACIDS**

A Thesis

by

JIA HE

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

December 2011

Major Subject: Petroleum Engineering

Calcium Sulfate Formation and Mitigation when Seawater Was

Used to Prepare HCl-Based Acids

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December 2011

Major Subject: Petroleum Engineering

**ABSTRACT**

Calcium Sulfate Formation and Mitigation when Seawater Was  
Used to Prepare HCl-Based Acids. (December 2011)

Jia He, B.S., China University of Petroleum

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

It has been a practice to use seawater for preparing acid in offshore operations where fresh water is relatively expensive or logistically impossible to use. However, hydrochloric acid will release calcium ion into solution, which will combine with sulfate ion in seawater (greater than 3000 ppm) and calcium sulfate will precipitate once it exceeds its critical scaling tendency. A few studies have provided evidence for this problem and how to address this problem has not been fully examined.

Core flood tests were conducted using Austin Chalks cores (1.5 in. × 6 in. and 1.5 in. × 20 in.) with permeability 5 md to investigate the effectiveness of scale inhibitor. A synthetic seawater was prepared according to the composition of seawater in the Arabian Gulf. Calcium, sulfate ions, and scale inhibitor concentrations were analyzed in the core effluent samples. Solids collected in the core effluent samples were analyzed using X-ray photoelectron spectroscopy (XPS) technique and thermodynamic calculation using OLI Analyzer software were conducted to identify the critical scaling tendency of calcium sulfate at different temperatures.

Results showed that calcium sulfate precipitation occurred when seawater was used in any stage during matrix acidizing including preflush, post-flush, or in the main stage. Injection rate was the most important parameter that affected calcium sulfate precipitation; permeability reduction was significant at low flow rates, while at high rates wormhole breakthrough reduced the severity of the problem.

More  $\text{CaSO}_4$  precipitated at high temperatures, accounting for more significant permeability reduction in the cores. The values of critical scaling tendency at various temperatures calculated by OLI ScaleChem 4.0.3 were believed to be 2.1, 2.0, and 1.2 respectively.

A scale inhibitor (a sulfonated terpolymer) was found to be compatible with hydrochloric acid systems and can tolerate high concentration of calcium (30,000 mg/l). Analysis of core effluent indicated that the new treatment successfully eliminated calcium sulfate scale deposition. The concentration of scale inhibitor ranged from 20 to 250 ppm, depending on the scaling tendencies of calcium sulfate.

This work confirms the damaging effect of preparing hydrochloric acid solutions using seawater on the permeability of carbonate cores. Therefore, it is recommended to use fresh water instead of seawater to prepare HCl acids whenever possible. If fresh water is not available, then a proper scale inhibitor should be added to the acids to avoid calcium sulfate precipitation.

## **DEDICATION**

I would like to dedicate this thesis to my parents and wife who have always given me strength to achieve my goals.

## **ACKNOWLEDGEMENTS**

I would like to thank my committee chair, Dr. Hisham Nasr-El-Din for his support, supervision, and assistance in this thesis. Thanks also go to my two committee members, Dr. Mahmoud El-Halwagi and Dr. Daniel Hill, for their cooperation and support throughout the course of this research.

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## 1. INTRODUCTION

The potential of calcium sulfate precipitation is greatly increased when seawater is used for matrix acidizing treatments (Oddo et al. 1991; Nasr-El-Din et al. 1996; He et al. 2011). In those processes, calcium concentration is greatly increased due to the reaction of the hydrochloric acid with calcite in the carbonate reservoir rocks. High calcium concentration will combine with high concentration of sulfate in seawater and significantly increase the scaling tendency of calcium sulfate. Besides, the solubility of calcium sulfate drops greatly once acid spends (Flint 1968; Kruchenko and Beremzhanov 1976; Li and Demopoulos 2002). Those two factors account for the precipitation of calcium sulfate out of solution once it exceeds the value of critical scaling tendency of calcium sulfate (Yeboah et al. 1993a, b; Raju and Nasr-El-Din 2004).

Calcium sulfate will deposit in the stimulated flow channels (Delorey et al. 1996), possibly cause blockage of pore throats and severely impair the formation permeability (Tahmasebi et al. 2007); hence decrease well injectivity or productivity (Smith et al. 1968; Shen and Crosby 1983). Even worse, the nucleation and precipitation process of calcium sulfate during acidizing treatments may affect the acid reaction with carbonate rocks and cause limited acid stimulation effect (He et al. 2011).

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This thesis follows the style of *Society of Petroleum Engineers*.

The most common calcium sulfate scale minerals found in the oilfield include: anhydrite ( $\text{CaSO}_4$ ), hemihydrate ( $\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$ ) and gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) (Kan et al. 2005; Schausberger et al. 2009). Gypsum is the stable form below  $45^\circ\text{C}$  while anhydrite is the stable form above  $93^\circ\text{C}$  (Furby et al. 1967). The solubility of calcium sulfate in brines is influenced by many factors with ionic strength and temperature being the most important ones (Abu-Khamsin and Ahmad 2005). Temperature tends to greatly reduce the solubilities of all forms of calcium sulfate while the solubilities increase at higher ionic strengths (Meijer and Van Rosmalen 1984).

Because of the complexity of scale formation and the difficulty to precisely conduct thermodynamic calculation to predict scaling, various models have been developed, including: EQ 3/6, PHREEQC, ScaleChem, ScaleSoftPitzer, OKSCALE (Frenier and Murtaza 2008). To obtain precise thermodynamic properties of calcium sulfate in brines, ScaleChem 4.0.3 was used in this work (Millan et al. 2004; Amiri and Moghadasi 2010; Lopez-Salinas et al. 2011).

Typically, the application of scale inhibitors has been one of the best economical methods to mitigate calcium sulfate (Yuan 2004; Fan et al. 2010; Hoang et al. 2009). The use of scale inhibitors may act either as chelating agents to form soluble complex (Moore et al. 1972; Jamialahmadi and Mueller 1991; Al-Khaldi et al. 2011), or as threshold inhibitors which block the development of the supercritical nuclei (He et al. 1994; Tomson et al. 2003), or as retarders of the growth of the calcium sulfate crystals (Amjad and Hooley 1986; Amjad 1988; Liu and Nancollas 1973). By simply adding an acid-soluble and effective scale inhibitor into the acid system, mineral scale formation

can be prevented during the process of acid stimulation (Smith et al. 2000; Sam 2003; Nasr-El-Din et al. 2004). In addition, combining scale inhibition and acid stimulation into a single package inherently reduces well intervention costs and well downtime, and therefore achieves significant economic benefits (Smith et al. 2001).

A sulfonated polymer-based scale inhibitor was selected because of its higher calcium tolerant compared with phosphate scale inhibitors (Jordan et al. 1995) and superior inhibitor retention efficiency. Besides, the sulfonate groups are strongly ionized, which are expected to promote stronger electrostatic interactions between polymer and the surface of calcium containing crystals and better inhibit scale formation (Lioliou et al. 2006).

In the following sections, a detailed literature review is firstly presented on the scaling problems in oil fields and studies of solubility of calcium sulfate. Then the experimental work and results will be thoroughly discussed. The conclusions and suggestions based on our laboratory tests and modeling analysis will be presented finally.

This study is focused on the effect of preparing acids using seawater on permeability of carbonate cores under different injection rates and temperatures and how much calcium sulfate will precipitate in the cores under certain conditions. The objective is to identify the damaging effect of preparing hydrochloric acid using seawater and eliminate the precipitation of calcium sulfate during acid treatments by applying an acid-compatible scale inhibitor into acid.



## 2. LITERATURE REVIEW

In this section, literature review on scaling problems caused by incompatible fluids mixing is presented. The considerable experimental work and models to predict scale formation are reviewed. Besides, methods to inhibit scale formation are also discussed.

### 2.1 The Scaling Problem

The scaling phenomenon, the precipitation and deposition of sparingly soluble salts in process equipment, is a common problem in many industrial processes, especially in oil production. Well production and injection rates and capacities thus drop, with consequent economical loss. In some cases, the choke of the flow line is so large that the well needs to be closed. Scaling can also cause safety problems, such as blockage and failure of valves. A brief literature review on scale formation due to incompatibility fluids mixing was conducted.

Lindlof and Stoffer (1983) described the problems of sulfate scale in Ghawar field where seawater was injected to maintain reservoir pressure. Three water systems with a possible incompatibility problem were carefully examined and results showed that sulfate scale precipitated in the wellbore where seawater and formation water mixed intimately under turbulent flow conditions.

Oddo (1991) reported the  $\text{CaCO}_3$  and  $\text{CaSO}_4$  scaling problems in and around the submersible pumps encountered in wells offshore Indonesia. Twenty-four well brines

were analyzed on-site to accurately determine brine chemistries and scale samples were analyzed to determine exact composition. Well histories were studied to find correlations of procedures which led to scaling problems and saturation indices were calculated to give insights into the causes of the intermittent scale formation.  $\text{CaSO}_4$  scale was determined to be a result of the over-flush of the seawater KCl solution after an acid stimulation treatment and  $\text{CaCO}_3$  forms due to the increased temperature or the decreased pressure and gas separation in or near the submersible pumps.

Bayona (1993) described abnormal reduction in well injectivity associated with seawater injection program of the North Uthmaniyah section of the Ghawar Field in Saudi Arabia. The major cause of losses of well injectivity is due to the introduction of iron corrosion products generated in the piping system.

Paulo et al. (2001) identified location of sulfate scale formation due to brine mixing in the Alba field in the North Sea. Three principal zones with position relatively to injection wells are identified based on theoretical analysis to the production data and produced brine compositions of each well.

Moghadasi et al. (2003) reported calcium and strontium scale deposition in the Iranian offshore of Siri field in the southern Persian Gulf where sea water injection was the primary oil recovery mechanism and pressure maintenance means. Carefully study showed that the deposits are seldom pure calcium sulfate or calcium carbonate, the quantity and morphology of which were greatly affected by conditions such as large degree of supersaturation, presence of impurities.

Raju and Nasr-El-Din (2004) conducted field tests to assess compatibility of formation water with seawater and formation of calcium sulfate scale. Field results indicated that seawater was not compatible with formation water, while injection of compatible aquifer buffer zone significantly reduced this problem. Injection of 70 vol% of seawater was believed to generate highest scale amount. The critical saturation index and amount of  $\text{CaSO}_4$  scale correlated with OKSCALE scale program were found to be 0.25 and 450 mg/L respectively.

Raju (2009) provided an overview of the scaling problems in Saudi Aramco and how Saudi Aramco had mitigated the scaling challenge through careful selection of injection water throughout the field lifetime. Calcium carbonate scale was believed to be the most common scale in Saudi Aramco due to pressure drop and pH changes while sulfate scales resulted by seawater injection were also a significant challenge to oil industry.

## **2.2 Scale Prediction**

### **2.2.1 Laboratory Study**

Extensive experimental work has been conducted to study the scale formation in oil fields. The kinetic and thermodynamic studies are both reviewed.

Fulford (1967) examined the effects of brine concentration and pressure drop on gypsum scaling in oil wells. The study revealed that the amounts of scale formed at a given pressure drop and temperature depend on the amount of sodium chloride and other salts dissolved in solution. The quantity of gypsum deposited increased with salt

concentration to a maximum, and then decreased until, with strong brines, no scale is formed. Calculations shown that pressure drop can be a major cause of gypsum scale in oil wells producing from formations containing anhydrite.

Nancollas and Gill (1979) studied transformations that take place between the dehydrate, hemihydrate and anhydrite phases of  $\text{CaSO}_4$  as a function of temperature from 90 to 150 °C and liquid phase composition during scale formation. The growth and dissolution rates of anhydrite follow a kinetic equation second-order in super-saturation and under-saturation, respectively. In contrast, the dissolution of hemihydrate follows a rate equation first-order in under-saturation, and the phase transformations are influenced greatly by temperature changes. Moreover, the rate of dissolution of the anhydrite is considerably less than the rate at which the hemihydrate dissolves under similar conditions of under-saturation and fluid dynamics.

Zhang (1990) investigated the growth rate of calcium sulfate dehydrate using the constant composition method over a range of calcium/sulfate molar ratios in supersaturated solutions. The rate increased with decreasing  $\text{Ca}^{2+}/\text{SO}_4^{2-}$  molar ratio. They concluded that the rate of crystal growth is not merely a function of the thermodynamic driving forces but also depends upon the relative concentrations and characteristics of individual lattice ions.

Chong and Sheikholeslami (2001) conducted a study on effect of co-precipitation of calcium carbonate and calcium sulfate in a solution having  $\text{CaCO}_3$  as the dominant salt at 60, 70 and 80 °C. Presence of  $\text{CaSO}_4$  from 0.002 to 0.01 M increased the calcium carbonate solubility product more than an order of magnitude. In solutions with minute

amounts of sulfate (0.002M), the  $\text{CaSO}_4$  solubility product in the mixture was much less than that of pure salt. However, further increases in the sulfate concentration to 0.01 M increased the  $\text{CaSO}_4$  solubility constant in the mixture to that of pure salt. Experimental results suggested that thermodynamic data for pure salts are not extendable to co-precipitation.

Sheikholeslami and Ong (2003) further examined kinetics and thermodynamics of co-precipitation of calcium carbonate and calcium sulfate at salinities up to 1.5 M. Kinetics of pure  $\text{CaSO}_4$  precipitation was found to be strongly affected by the level of salinity; however, salinity level had no significant effect on kinetics of  $\text{CaCO}_3$  precipitation. The reaction rate of pure  $\text{CaSO}_4$  is found to be faster compared to the mixed system. Thermodynamic solubility constants ( $k_{sp}$ ) of the pure salts were not affected by different salinity levels; however, the salinity level affected  $k_{sp}$  in mixed salt systems.

Ahmi and Gadri (2004) studied the kinetics of formed gypsum from the measurements of the induction period for the gypsum nucleation. It was observed that the induction period depends highly on temperature, supersaturation, and the lattice cation/anion molar ratio, from which homogeneous and heterogeneous nucleation mechanisms can be distinguished. The activation energy of gypsum nucleation, interfacial tension between gypsum and aqueous solution, and the critical radius were determined. The limit between homogeneous and heterogeneous nucleation was estimated in an interval of supersaturation ranging between 3.5 and 4.

Abu-Khamsin and Ahmad (2005) conducted core flood study on precipitation of calcium sulfate in sandstone cores. The brine was formulated by mixing a calcium rich solution with a sulfate rich solution at the core inlet. Experimental parameters including temperature, pressure, degree of supersaturation, and flooding velocity were to generate reaction rate equations. Precipitation rate of calcium sulfate increased at higher temperatures, higher flood velocities, and greater brine supersaturation. The reaction's activation energy was estimated at 26.2 kJ/mol.

Tahmasebi et al (2007) conducted an experimental and theoretical study to determine the permeability reduction due to calcium sulfate deposition in porous media. In his study, brine solutions containing calcium and sulfate ions were injected in a packed glass beads porous media at elevated temperatures and various flow rate and brine concentrations. A novel empirical equation to predict the permeability reduction and mobility reduction due to calcium sulfate scale formation was suggested based on experimental parameters.

Fan et al (2010) quantitatively evaluated the precipitation kinetics of calcium sulfate in the presence and absence of scale inhibitors. The nucleation kinetics of calcium sulfates in 0 -3.2 M NaCl solutions was determined from 0 to 200 °C at various supersaturation conditions. A semi-quantitative model was developed to predict precipitation kinetics of calcium sulfate as a function of temperature, pH, saturation index, and scale inhibitor concentration.

### ***2.2.2 Model Development***

Numerous programs and calculation models have been developed to predict scale deposition. Most of the models available yield scale potential based on several parameters such as ion concentrations, temperature, pH, pressure, carbon dioxide partial pressures, organic acids, etc. Kinetic studies are incorporated into some models as well.

Vetter and Phillips (1970) proposed a simple thermodynamic relation to calculate the solubility of different  $\text{CaSO}_4$  compounds in NaCl brines at different pressures and temperatures. Although this method has its limitations, the calculated solubility is as accurate as the experimentally determined concentration. Results shown that pressure drops are believed to be particularly important to determine where the scale is deposited. The area behind the sand face is one of the critical locations where scale deposits. The pressure at which the solubilities of  $\text{CaSO}_4$  in water and in brine are equal depends on the NaCl concentration.

Vetter et al (1982) reported a new scale prediction model to predict the co-precipitation of  $\text{CaSO}_4$ ,  $\text{SrSO}_4$ , and  $\text{BaSO}_4$  at various locations in field operations as mixtures of injection and reservoir waters flow through injection wells, reservoir, and production wells into surface facilities. The scale component with the smallest solubility product precipitated first, which is followed by the precipitation of second smallest solubility product. The composition of solution was adjusted after the previous precipitation. The model used comprehensively data of actually measured solubility in oil field brines at various temperatures and pressures. The solubility at extreme conditions was calculated using thermodynamic parameters.

Atkinson et al (1991) developed the OKSCALE program to predict sulfate scaling problems in single brines or brine mixtures. The effects of temperature, pressure and ionic strength were considered using the classical thermodynamic approach. The activity coefficients needed were calculated with a modified Pitzer equation. The important effect of  $\text{MgSO}_4$  ion association was considered explicitly and all the possible sulfate scales were considered simultaneously. The effect of pressure was small and was ignored under most practical applications.

Yuan and Todd (1991) developed a model for predicting the scaling tendencies of barium, strontium, and calcium sulfates resulting from the mixing of incompatible injected and formation waters and from temperature and pressure effects. The model based on the Pitzer equation was capable of predicting the scaling tendencies of  $\text{BaSO}_4$ ,  $\text{SrSO}_4$ , and  $\text{CaSO}_4$  at various water compositions, temperatures, and pressures covering oil field conditions. The simultaneous co-precipitation of those sulfate minerals was considered and the model can determine whether the  $\text{CaSO}_4$  scale was in the form of anhydrite or gypsum and their corresponding sulfate scaling tendencies.

Yeboah et al (1993) developed OSPMod program to predict carbonate and sulfate scales in oil field conditions. Experimental solubility data in single and mixed as well as natural oil field brines was used to determine the thermodynamic scaling potential. Once the scaling potential has been established to exist, flow characteristics and kinetic data were used to kinetically predict the scale deposition profile as a function of position and time. The critical saturation indices of scale forming salts were



determined by correlating the predicted saturation indices of actual wells with field observations. The scale formation within rocks was not considered in this model.

Oddo and Tomson (1994) developed an updated Oddo-Tomson saturation index method to calculate calcium carbonate and sulfate minerals. Experimental solubility data and pressure data from the literature or calculation were used in nonlinear least-squares fit to determine the conditional constants and associated errors. Then the function form of the derived equations can be determined. The recommended saturation index equations can be used to calculate saturation index of common sulfate minerals, including three different calcium sulfate forms.

Bedrikovetsky et al (2003) mathematically modeled  $\text{BaSO}_4$  scaling process based on core flood tests, which consists of the sequence of diffusivity tests, of transient tests with chemical reaction, and of steady state tests on simultaneous injection of both injected and formation waters. Diffusivity tests were used to determine the diffusion efficient, and steady state tests allowed determination of chemical reaction rate constant versus velocity. Mathematical modeling data was compared with transient test data to validate its results of steady state test. The key finding in the study was the proportionality between chemical reaction constant and flow velocity in the range of experimental conditions.

García et al (2005) proposed an extended UNIQUAC model to predict sulfate scaling minerals by incorporating pressure parameters. The improved model had been used for correlation and prediction of solid-liquid-equilibrium (SLE) of scaling minerals ( $\text{CaSO}_4$ ,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ,  $\text{BaSO}_4$  and  $\text{SrSO}_4$ ) at temperatures up to  $300^\circ\text{C}$ , pressures up to

1000 bar and concentrations up to saturation. More than 4200 SLE measurements had been collected and analyzed with only reliable data for parameter estimation. The figures presented shown that the extended UNIQUAC model could obtain accurate results even at very high temperatures and pressures. Most of the data used for parameter estimation can be reproduced by extend UNIQUAC model within experimental accuracy. The simplicity of the model made it an appropriate choice to study sulfate scaling minerals as it only contains binary interaction parameters which can be applied to any multi-component system.

Kan et al (2005) proposed a scale prediction program - ScaleSoftPitzer based on Pitzer equation. In his study, a new high temperature and high pressure flow-through apparatus was developed to measure mineral salt solubilities under extreme oil and gas production conditions, i.e., high temperature, pressure, TDS, and the presence of methanol and ethylene glycol. New solubility data illustrated the validity of the Pitzer activity correction of mineral salt solubilities.

From the literature review, it can be seen that the scaling problems have been extensively studied at various conditions. However, in the case of preparing HCl using seawater for matrix acidizing treatment, few experiment studies and prediction models have been developed. Therefore, core flooding tests will be conducted to generate sufficient data that will help study the process of calcium sulfate deposition in porous media. Thermodynamic studies are included whenever necessary.

### 3. STUDIES ON SOLUBILITY OF CALCIUM SULFATE

In this section, theoretical studies on solubility of calcium sulfate solubility are presented. Various parameters, including temperature, pressure, pH, ion composition, etc., are covered in this section.

#### 3.1 Introduction

The most common calcium sulfate scale minerals found in the oilfield include anhydrite ( $\text{CaSO}_4$ ), hemihydrate ( $\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$ ) and gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) (Kan et al. 2005; Schausberger et al. 2009). If a solution is supersaturated with respect to one or more calcium sulfate minerals, precipitation can occur according the reaction:



where  $x$  equals to 0,  $1/2$ , or 2.

Calcium sulfate will precipitate once it exceeds its solubility limit in solution, and it will precipitate until the product of the ion concentrations equals the solubility product. The solubility of calcium sulfate affected by various parameters with the temperature and ion strengthen being the most important ones. In the following section, various factors that affect the solubility of calcium sulfate will be discussed.

#### 3.2 Factors Affecting Solubility of Calcium Sulfate

The solubility of calcium sulfate can be affected by various factors, including temperature, ionic strength, pressure, and mixing of fluids.

### ***3.2.1 Effect of Temperature***

Solubility of gypsum tends to increase a little up to about 40 °C and then decrease slowly with temperature increment. The solubilities of anhydrite and hemihydrate decreased with the increased temperature. In the literature, studies show that gypsum is the stable form below 45 °C and anhydrite is the most stable form above 93 °C. The hemihydrate is metastable at all temperatures.

In standard seawater solutions, the solubilities of all three calcium sulfate forms increase at increasing ionic strength of the solution, without severely affecting the shape of solubility lines.

### ***3.2.2 Effect of Ionic Strength***

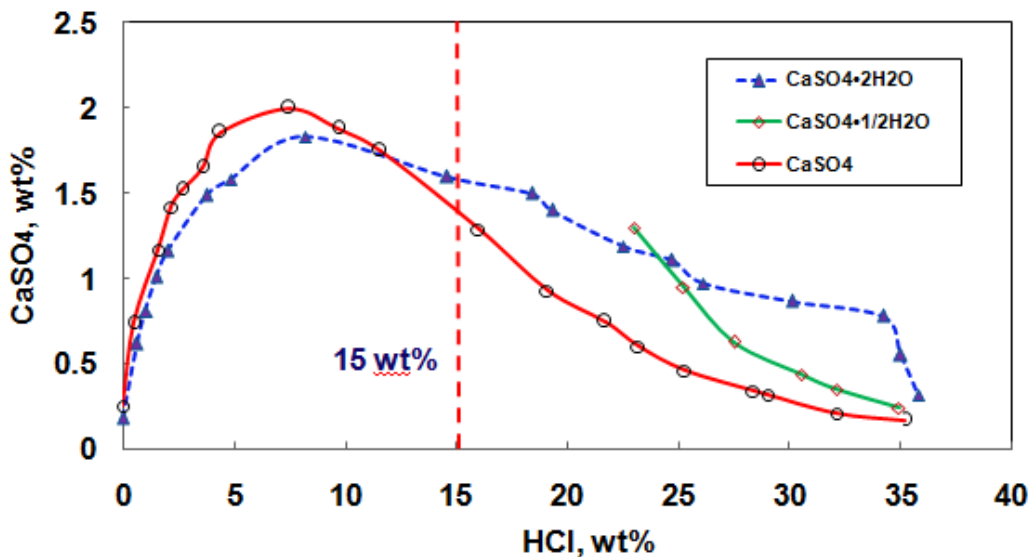
The solubility of calcium sulfate tends to increase at higher ionic strength without changing the shape trend of temperature effect. At lower ionic strength, the solubility seems to increase significantly with the increment of ionic strength but tends to stabilize at higher ionic strength.

### ***3.2.3 Effect of Pressure***

A drop in pressure can cause calcium sulfate deposition. The reason is quite different from that for calcium carbonate. The presence or absence of CO<sub>2</sub> in solution has little to do with calcium sulfate solubility.

### 3.2.4 Effect of Mixing Fluids

The solubility of calcium sulfate in HCl is quite different from that in brine, which was shown in **Fig. 1**. The solubility of gypsum initially increases, attaining a maximum 1.8% wt% in the solution with 8% HCl, and then falls. The solubility of anhydrite rises sharply, reaching 2.0 wt% in 7.5% acid solution, and then decreases. The solubility of hemihydrates was determined only in the solution where it is stable during the period required for equilibrium. It can be seen that when the acid concentration drops from 15wt% to 0, the solubility of calcium sulfate decreases greatly, from around 1.5wt% to 0.2wt%.

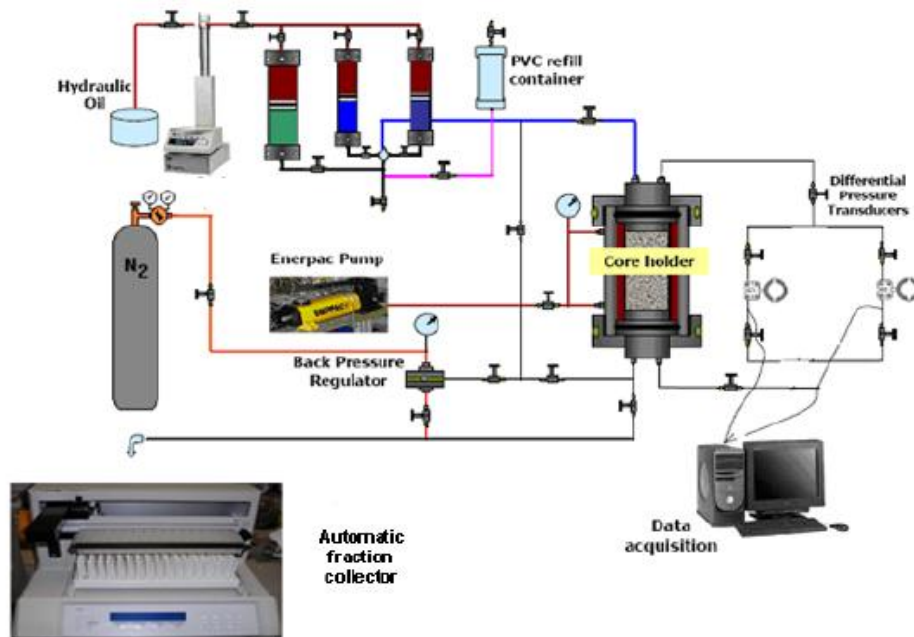


**Fig. 1**—Solubility of calcium sulfate in HCl at 25 °C

## 4. EXPERIMENTAL SET-UP FOR CORE FLOOD TESTS

### 4.1 Experimental Systems

The core testing system consists of a core holder connected to three separate pumps supplying for acid, fresh water and seawater, a pressure transducer measuring the overall pressure drop, a pump to apply an overburden pressure over the rubber sleeve containing the core sample, a backpressure system, and an effluent fluid collection container. The schematic of the experimental system set-up is shown in **Fig. 2**.



**Fig. 2—Core flooding set-up mainly consists of three supplying pumps, pressure regulator, core holder, and pressure transducers.**

## 4.2 Fluid Preparation

Synthetic seawater was prepared according the composition of seawater in Arabian Gulf at Kuwait as shown in **Table 1**. The sulfate concentration determined by spectrophotometer apparatus was about 3500 mg/l and calcium concentration analyzed by atomic absorption apparatus was about 540 mg/l in the synthetic seawater. The synthetic seawater was used for core porosity and permeability measurements and for initial saturation of the core.

**TABLE 1—COMPOSITION OF SEAWATER**

Ion concentration, mg/L	Arabian Gulf at Kuwait
Chloride (Cl <sup>-</sup> )	23,000
Sodium (Na <sup>+</sup> )	15,850
Sulfate (SO <sub>4</sub> <sup>2-</sup> )	3,200
Magnesium (Mg <sup>2+</sup> )	1,765
Calcium (Ca <sup>2+</sup> )	500
Bicarbonate (HCO <sub>3</sub> <sup>-</sup> )	142

15 wt% hydrochloric acid was prepared either in fresh water or in seawater to examine effect of acid preparation methods on core flood reaction process and corrosion inhibitor was added to acid. The same volume of acid was injected in all core flood tests for comparison analysis.

### 4.3 Experimental Procedure

Once the cores were saturated with seawater for about 12 hours, they were loaded on the core holder and pressurized with a confining pressure 1,000 psi. Cores were injected at a constant flow rate, and 10 ml acid was injected. Note that an additional experiment that used fresh water to preflush and post-flush the core was conducted for comparison analysis.

A flooding test was terminated when constant pressure drop, constant pH value, constant  $\text{Ca}^{2+}$  concentration, and constant  $\text{SO}_4^{2-}$  concentration were determined. The  $\text{Ca}^{2+}$  concentration of effluent samples was analyzed by atomic absorption apparatus. A spectrophotometer was used to analyze  $\text{SO}_4^{2-}$  concentration and pH value was determined by pH meter. Some selected cores were analyzed by CT scan technique before and after core flood tests to examine the calcium sulfate precipitation in the cores.



## 5. CALCIUM SULFATE FORMATION

In this section, core flood tests were conducted to examine formation damage due to calcium sulfate precipitation during matrix acidizing treatments. Austin chalk cores (1.5 in. × 6 in. and 1.5 in. × 20 in.) with an average porosity 19 vol% and permeability of 10 md were used. All cores were dried at 100°C for 4 hours and weighed and then saturated with either seawater or deionized water to calculate the pore volume and porosity of the cores, **Table 2**.

### 5.1 Results of the Base Case at 0.5 cm<sup>3</sup>/min

A core flood was conducted to determine the effect of acid prepared in deionized water on the core permeability. In this experiment, only deionized water was used in the pre and post flushes and to prepare the acid. The core was initially saturated with deionized water. The pressure drop across the core is shown in **Fig. 3**. The initial increase in the pressure drop was due to the release of CO<sub>2</sub> which was due to the reaction of HCl with the calcite rock. The back pressure of a 1000 psi cannot keep all CO<sub>2</sub> in solution. At the end of the experiment, the permeability of the core increased from 8.5 to 11 md, indicating that there was acid stimulation effect.

TABLE 2—CORE FLOOD DATA TO EXAMINE FORMATION OF CALCIUM SULFATE

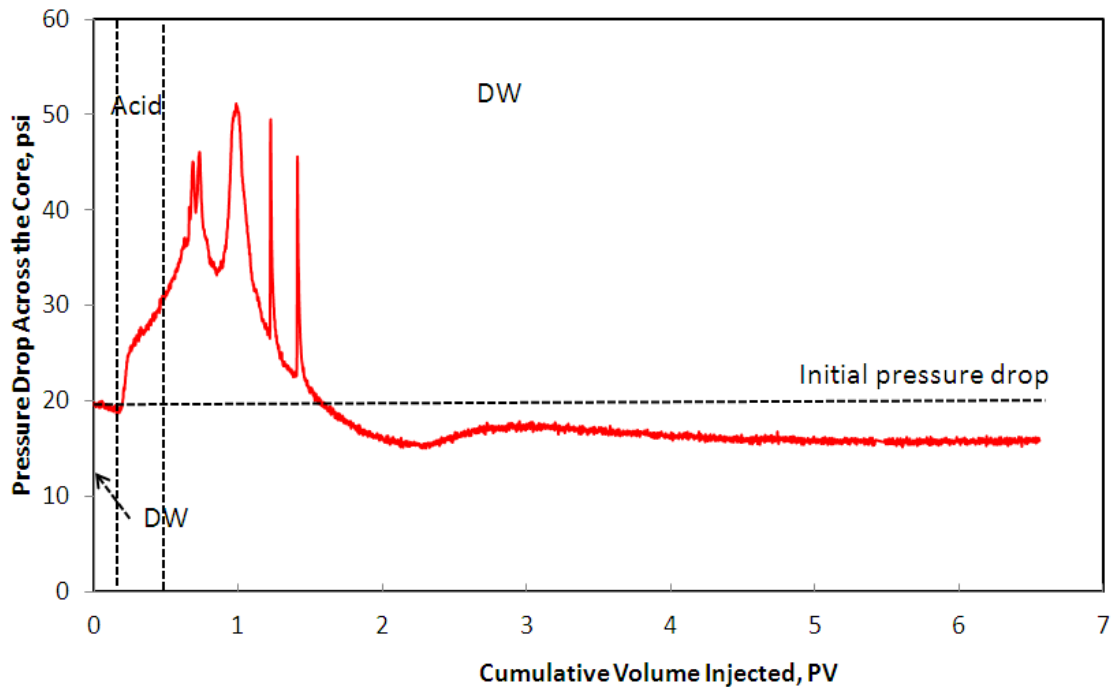
Run	Flow rate, cm <sup>3</sup> /min	Core Length, in.	Temp., °F	Pre flush	Acid mixing fluid	Post flush	Pore Volume, cm <sup>3</sup>	Porosity, fraction	Initial Permeability, md
1 <sup>a</sup>	0.5	6	77	DW	DW	DW	34.58	0.232	8.5
2	0.5	6	77	SW	DW	SW	34.38	0.231	9.6
3	0.5	6	77	SW	SW	SW	30.42	0.175	7.3
4	1.0	6	77	SW	DW	SW	32.58	0.219	8.2
5	1.0	6	77	SW	SW	SW	42.23	0.284	11
6 <sup>a</sup>	1.0	6	77	DW	DW	DW	33.46	0.225	4.2
7	5.0	6	77	SW	DW	SW	33.02	0.222	7.7
8	5.0	6	77	SW	SW	SW	33.79	0.227	9.4
9	1	20	77	SW	SW	SW	110.45	0.191	4.1
10	1	20	150	SW	SW	SW	115.81	0.2	12.8
11	1	20	210	SW	SW	SW	127.86	0.221	14.5
12 <sup>b</sup>	1	20	210	DW	DW	DW	120.85	0.209	3.1

SW = Seawater

DW = Deionized water

a: base case for 6 in. cores were saturated with deionized water before preflush

b: base case for 20 in. cores were saturated with deionized water before preflush



**Fig. 3—Pressure drop across core #1 at 0.5 cm<sup>3</sup>/min (the acid was prepared in deionized water and the core was saturated with deionized water).**

## 5.2 Effect of Mixing Seawater on Permeability of Carbonate Cores

Core flood tests at 0.5 cm<sup>3</sup>/min were conducted to examine the effect of preparing hydrochloric acid with seawater on core permeability. Two core flood experiments were conducted. In both cases, the cores were saturated with seawater. In the first experiment, the acid was prepared with deionized water, whereas in the second test, the acid was prepared using seawater. Seawater was used in the preflush and post-flush in the two experiments. The pressure drop responses for the two tests are given in **Figs. 4 and 5**. The concentrations of calcium and sulfate ions in the core effluent samples are shown in **Figs. 6 and 7**. The permeability of carbonate cores decreased from

9.6 to 7.5 md when seawater was used in the pre and post flushes, **Table 3**. The permeability of carbonate cores decreased from 7.3 to 6.8 md (**Table 3**), indicating that calcium sulfate precipitated inside the core, which reduced the stimulation effect of the acid. A significant permeability reduction was observed when the acid was prepared in deionized water and seawater was used in the preflush and post-flush stage. This is because of the solubility of calcium sulfate increases at higher ionic strength of the salinity water (Meijer and Van Rosmalen 1984)

For the acid prepared in deionized water (**Fig. 6**), calcium sulfate precipitation occurred when seawater was used in the preflush and post-flush stages. The decrease in the concentration of sulfate was not clearly due to precipitation of calcium sulfate because there is no sulfate ion in the acid. However, material balance calculation showed that 15 wt% of the injected sulfate retained in the core (**Table 3**). More calcium sulfate precipitated when acid prepared in deionized water was mixed with seawater in the preflush and post-flush stage because of lower solubility of calcium sulfate in fresh water. This result was consistent with the material balance calculation that more sulfate retained in the core when the acid was prepared in deionized water.

TABLE 3—MATERIAL BALANCE AND PERMEABILITY CHANGES

Run	Flow rate, cm <sup>3</sup> /min	Core Length, in.	Temperature, °F	Acid mixing fluid	Sulfate injected, mg	Sulfate collected, mg	Sulfate difference, wt%	K, before injection of acid, md	K, after injection of acid, md
1 <sup>a</sup>	0.5	6	77	DW	0	0	0	8.5	11
2	0.5	6	77	DW	640	546	15	9.6	7.5
3	0.5	6	77	SW	733	653	11	7.3	6.8
4	1.0	6	77	DW	1,387	1,218	12	8.2	12
5	1.0	6	77	SW	1,156	1,047	9	11	11.2
6 <sup>a</sup>	1.0	6	77	DW	0	0	0	4.2	32
7	5.0	6	77	DW	935	917	2	7.7	148.9
8	5.0	6	77	SW	1,205	1,108	8	9.4	163.7
9	1.0	20	77	SW	1,022	965	6	4.1	5.8
10	1.0	20	150	SW	1,589	1,478	7	12.8	4.9
11	1.0	20	210	SW	1,053	915	13	14.5	5.3
12 <sup>b</sup>	1.0	20	210	DW	0	0	0	3.1	3.6

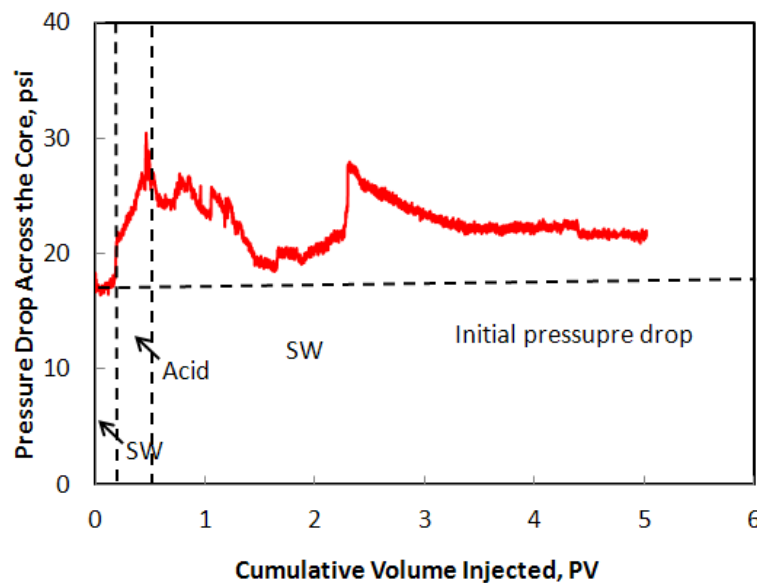
SW = Seawater

DW = Deionized water

a: base case for 6 in. cores were saturated with deionized water before preflush

b: base case for 20 in. cores were saturated with deionized water before preflush

In the case of acid prepared in seawater (**Fig. 7**), pH values after spent acid breakthrough were between 6 and 7, indicating that HCl was completely spent in the core. Calcium concentration increased from 315 to 37,000 mg/l after spent acid breakthrough while the sulfate concentration decreased to 1,800 mg/l after maintaining a constant value of 3,500 mg/l. The increase in the calcium ion concentration was due to the reaction of HCl with calcite. The decrease of sulfate concentration was attributed to two factors: calcium sulfate deposition and second, lower sulfate concentration (2187 mg/l) in acid. However, the extent of reduction in the sulfate concentration (1,800 mg/l) was lower than that in the injected acid. The result also suggests that calcium concentration given in **Fig. 7** was less than that produced by the reaction of the acid with calcite. Finally, both calcium and sulfate concentrations gradually reached their levels in seawater.



**Fig. 4—Pressure drop across core #2 at 0.5 cm<sup>3</sup>/min (acid was prepared in deionized water).**

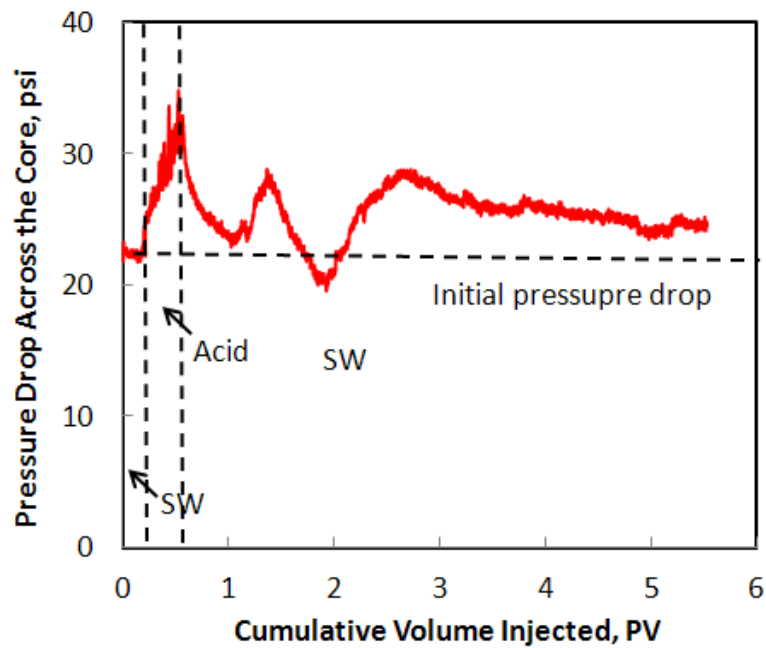


Fig. 5—Pressure drop across core # 3 at  $0.5 \text{ cm}^3/\text{min}$  (acid was prepared in seawater).

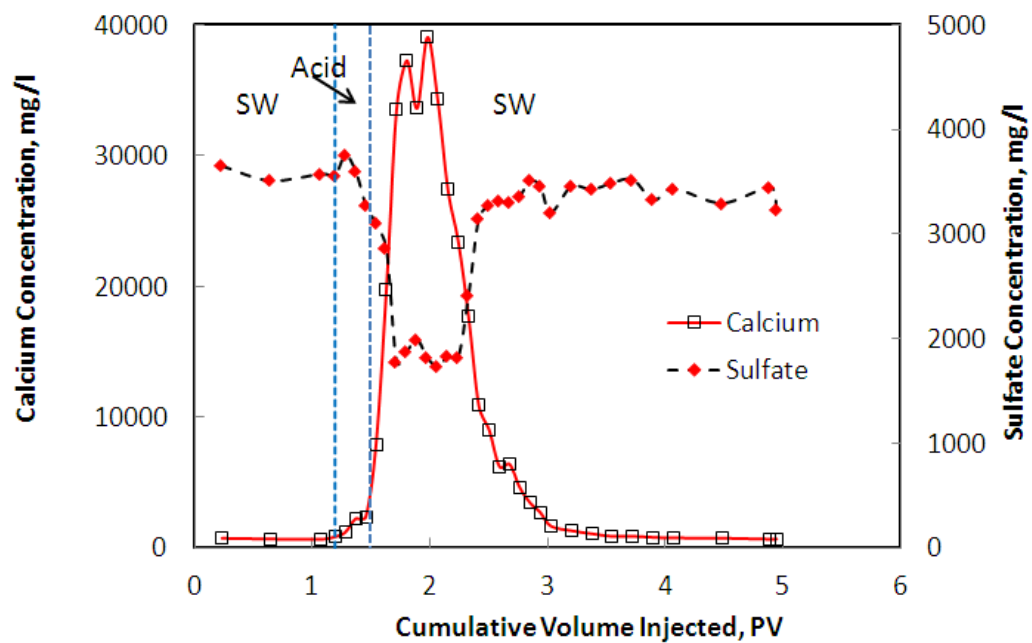
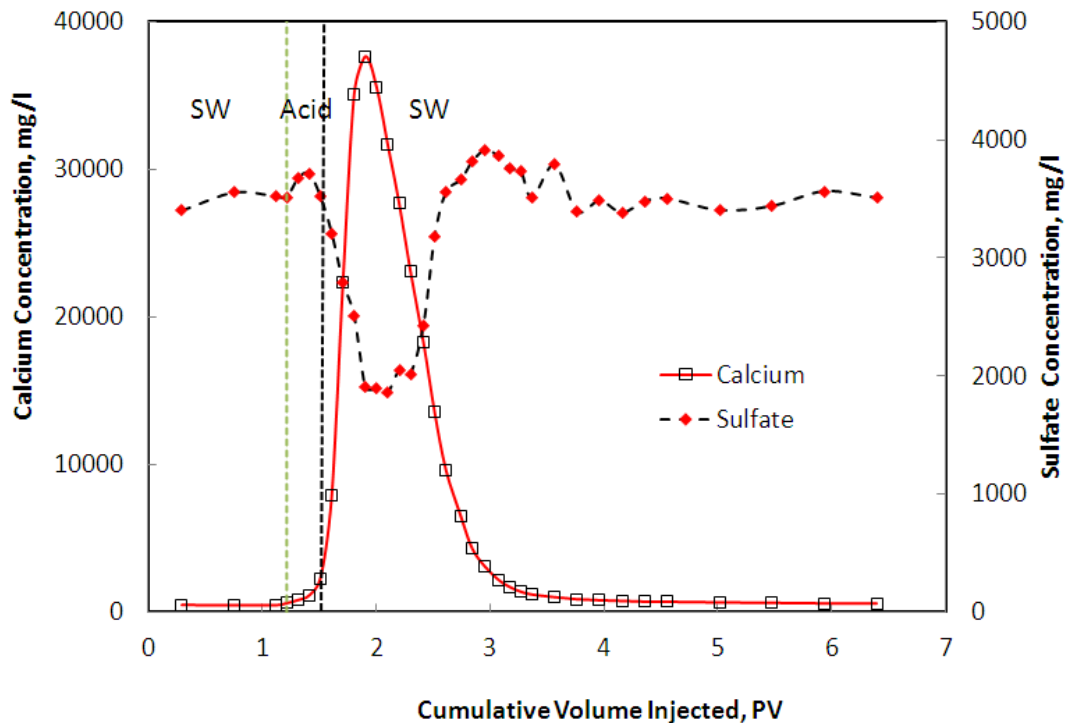


Fig. 6—Ion concentration in core # 2 (acid was prepared in deionized water).



**Fig. 7—Ion concentration in core # 3 (acid was prepared in seawater).**

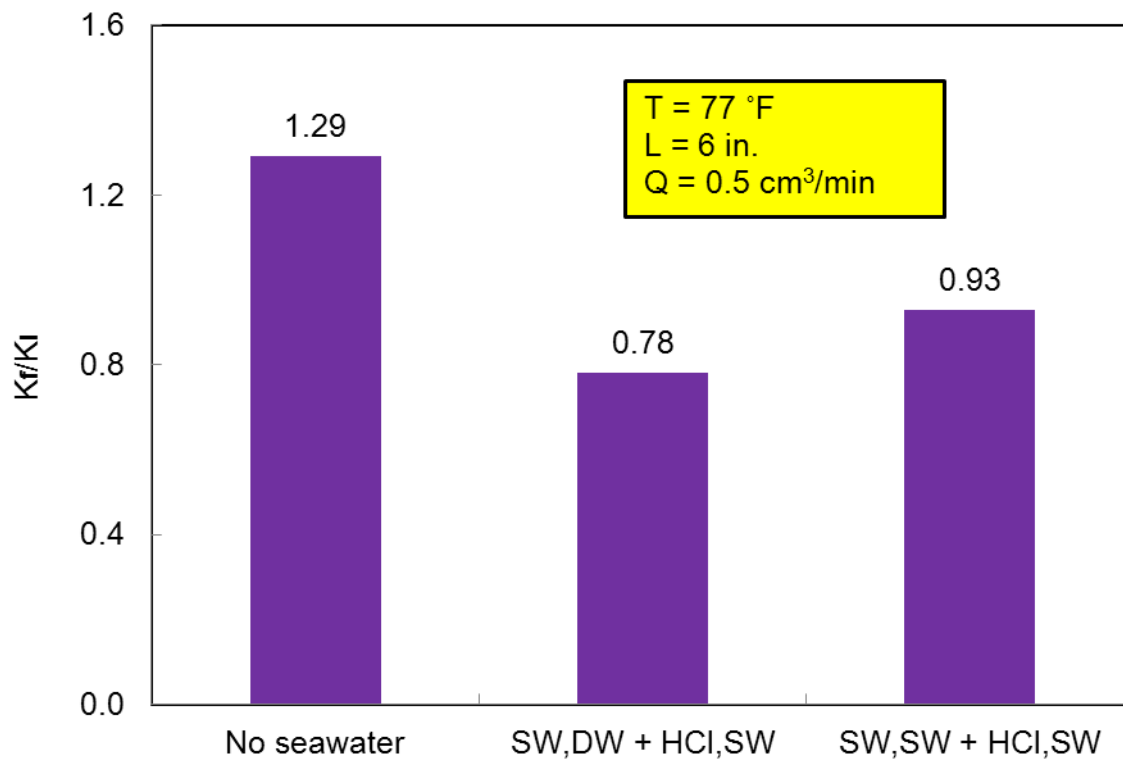
Based on these results, calcium sulfate precipitated whether seawater was used in the preflush and post-flush stage or was used to prepare the main acid stage. Permeability loss occurred in all tests that included seawater.

### 5.3 Effect of Injection Rate

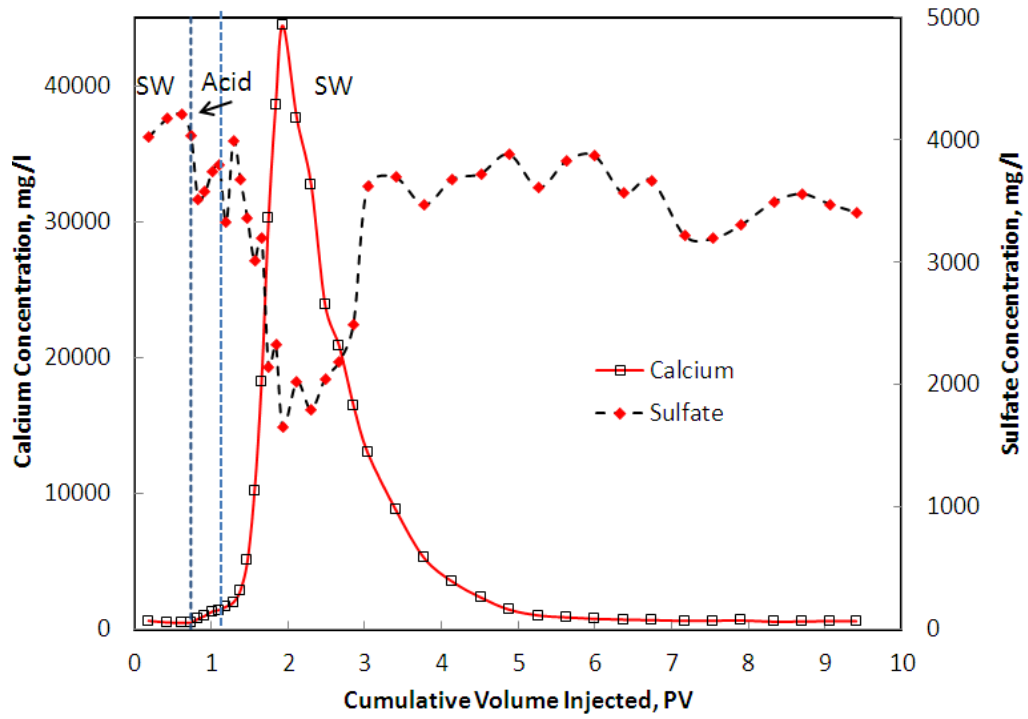
At  $0.5 \text{ cm}^3/\text{min}$ , the effect of calcium sulfate precipitation on acid stimulation was not significant due to acid face dissolution occurred in all three tests, **Fig. 8**. Core flood tests at higher injection rates were conducted to quantify how much precipitation of calcium sulfate would reduce the outcome of acid treatment, especially when there are wormholes produced inside the carbonate cores. Both acid prepared in seawater and



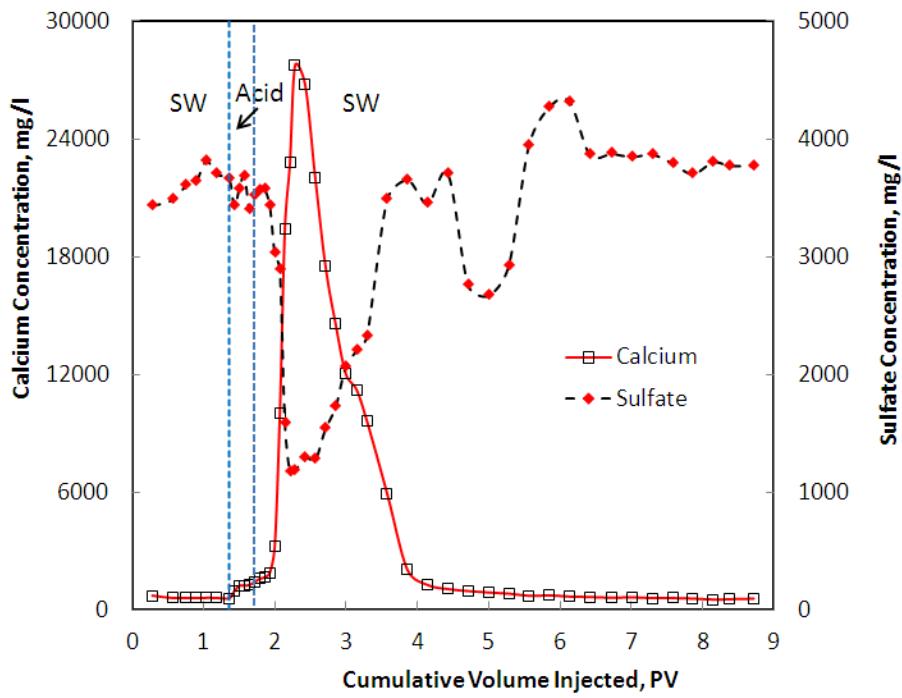
deionized water were examined. At  $1 \text{ cm}^3/\text{min}$ , calcium concentration increased from zero to 44,000 (in case of acid prepared in deionized water, **Fig. 9**) and from 315 to 28,000 mg/l (in case acid was prepared in seawater, **Fig. 10**). The sulfate concentration decreased from 2187 to 1,500 mg/l due to calcium sulfate precipitation after maintaining a constant value of 3,500 mg/l in **Figs. 9 and 10**. And after that they both gradually reached to the sulfate concentration in the injected acid. The pH values both varied between 6 and 7 after spent acid breakthrough.



**Fig. 8—Permeability changes at  $0.5 \text{ cm}^3/\text{min}$ .**

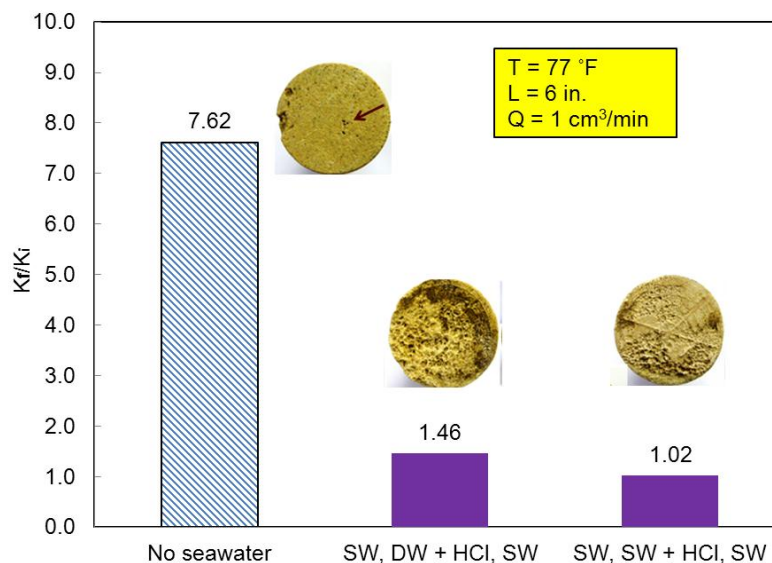


**Fig. 9—Ion concentration in core # 4 (acid was prepared in deionized water).**



**Fig. 10—Ion concentration in core # 5 (acid was prepared in seawater).**

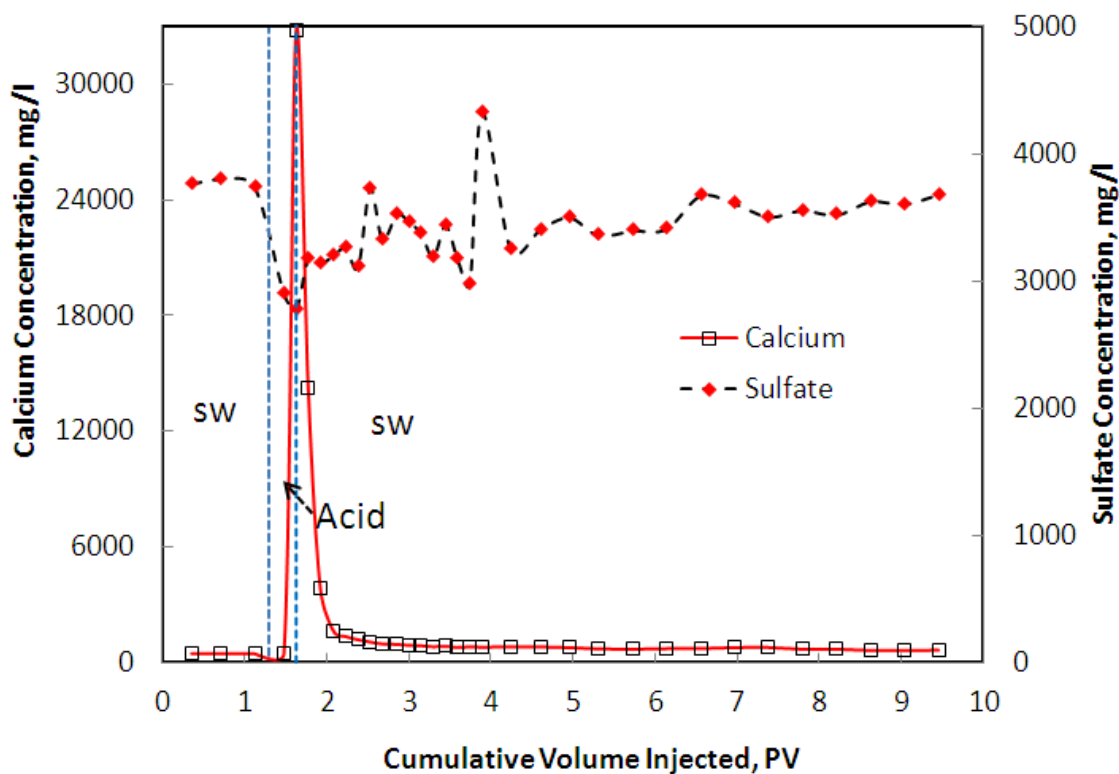
In **Fig. 11**, the permeability of carbonate core increased from 4.2 to 32 md (**Table 3**) when deionized water was used in the preflush, main acid, and post-flush at 1 cm<sup>3</sup>/min. Acid stimulation effect was almost completely reduced from 7.62 to 1 when seawater was used to either prepare the acid or preflush the cores. Two factors accounted for the significant reduction in acid stimulation effect. First, precipitation of calcium sulfate blocked the fluid pathways in the carbonate cores. Second, calcium sulfate deposition diverted acid solution, which resulted acid face dissolution. This face dissolution consumes much of acid at the core inlet and made acid stimulation less effective. When acid was prepared in seawater, acid face dissolution was more severe because calcium sulfate instantly precipitated after the acid reacted with calcite. However, material balance calculations (**Table 3**) showed that more calcium sulfate precipitated when the injected acid was prepared in deionized water, which confirmed the results obtained at 0.5 cm<sup>3</sup>/min.



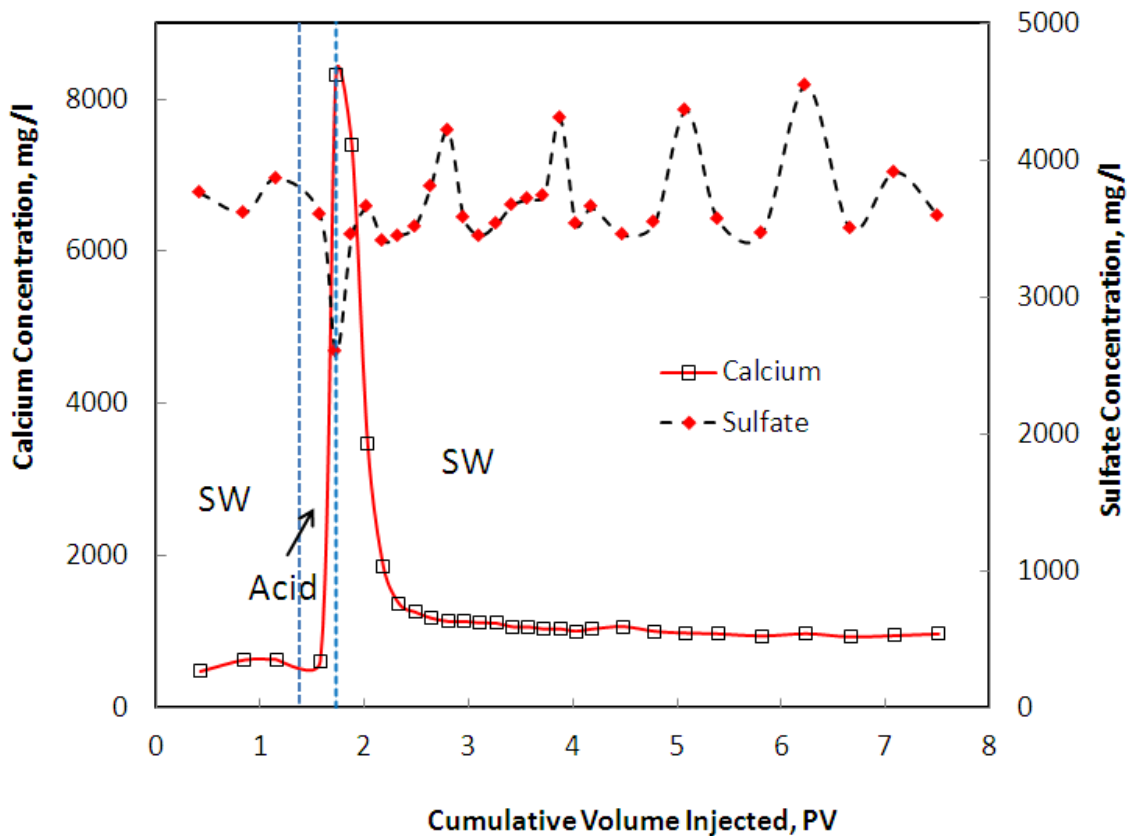
**Fig. 11—Permeability ratio obtained with different waters at 1 cm<sup>3</sup>/min.**

#### 5.4 XPS Analysis of Calcium Sulfate

Core flood tests at 5 cm<sup>3</sup>/min which were believed to produce wormhole breakthrough in the cores were conducted to collect precipitation of calcium sulfate in the effluent samples. At 5 cm<sup>3</sup>/min, calcium concentration increased from 500 to 33,000 (acid prepared in deionized water, **Fig. 12**) and from zero to 8,000 mg/l (acid prepared in seawater, **Fig. 13**) after spent acid breakthrough. The sulfate concentration decreased to 2,600 mg/l after maintaining a constant value of 3,500 mg/l in **Figs. 12 and 13**. And after that they both gradually reached to the normal concentration level. The pH values dropped to 1 in both cases after acid breakthrough, indicating the presence of a low concentration of HCl in the effluent samples.

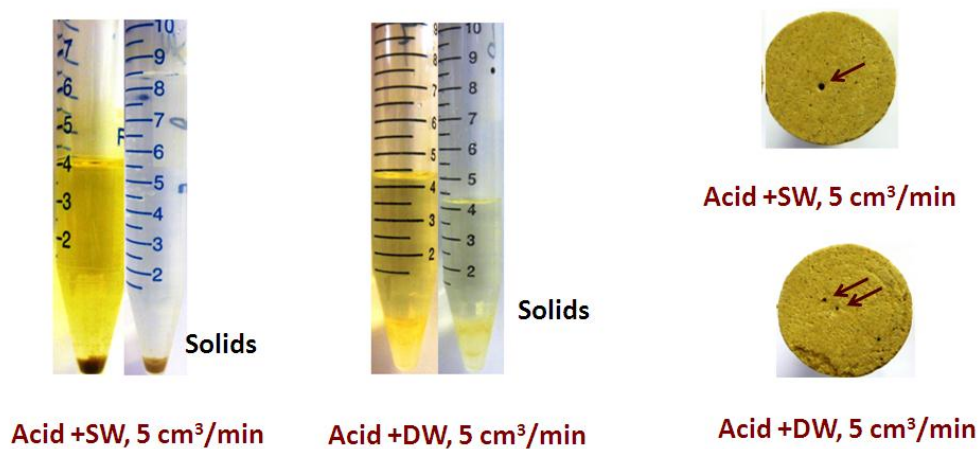


**Fig. 12—Ion concentration in core # 6 (acid was prepared in deionized water).**

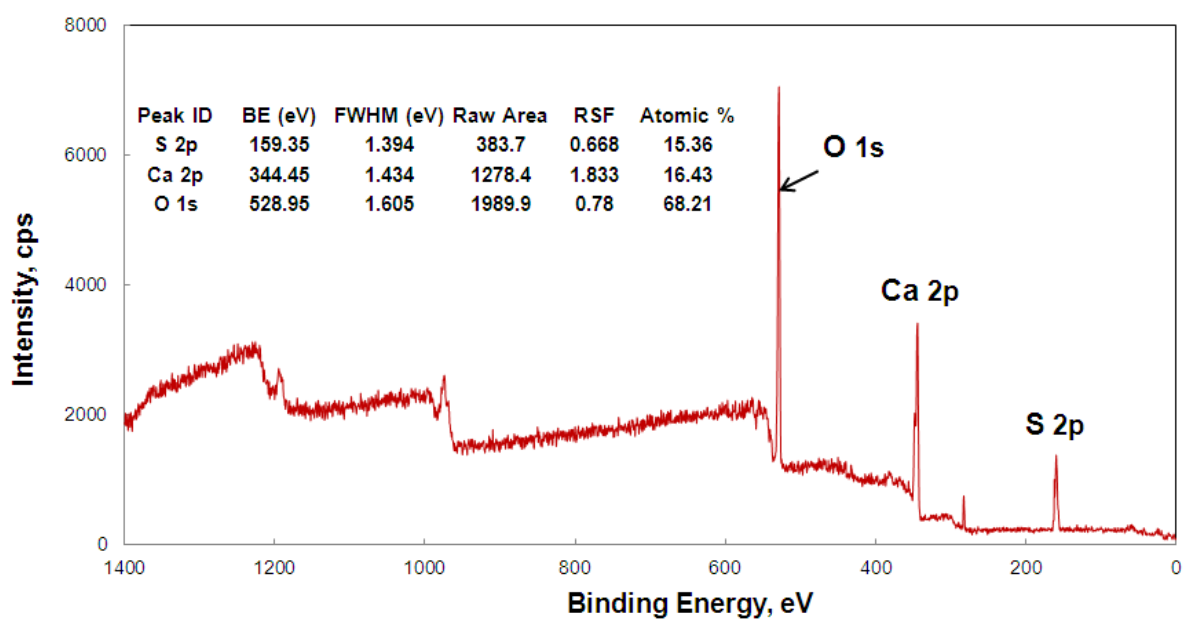


**Fig. 13—Ion concentration in core # 7 (acid was prepared in seawater).**

**Fig. 14** shows that solids were collected in the first two samples after acid breakthrough and wormholes were observed in the outlet of cores. Even under acidic conditions, calcium ion will combine with sulfate ion, depositing calcium sulfate. All the precipitations collected at  $5 \text{ cm}^3/\text{min}$  were dried and then analyzed using X-ray photoelectron spectrometer (XPS) (**Fig. 15**). Calcium, oxygen, and sulfur were identified in the solids and atomic concentration ratio of these elements was 16.43:68.21:15.36 (appropriately 1:4:1), indicating that calcium sulfate was collected.



**Fig. 14—Wormholes in the outlet and precipitation were observed at 5 cm<sup>3</sup>/min.**



**Fig. 15—Precipitation of calcium sulfate collected at 5 cm<sup>3</sup>/min flow rate was analyzed using XPS.**

## 5.5 Effect of Temperature

The solubility of calcium sulfate in brine significantly decreases at higher temperatures (Abu-Khamsin and Ahmad 2005). Core flood tests at 150 and 210°F were conducted at 1 cm<sup>3</sup>/min longer cores to examine the effect of temperature on precipitation of calcium sulfate. Cores with 20 in. length were used in these tests because this length allowed more time for mixing spent acid with seawater and provided more precise results for thermodynamic calculations. Acid was prepared in seawater in these tests.

The sulfate ion concentration profiles at various temperatures are compared in **Fig. 16**. Sulfate concentration decreased to 3,000 mg/l after maintaining a constant value of 3,500 mg/l at 77°F; while at 150°F, the sulfate concentration decreased to 2,000 mg/l, indicating that more calcium sulfate precipitated in the core. At 210°F, the sulfate concentration decreased to 3000 mg/l right after the beginning of pumping post-flush, showing that calcium sulfate precipitated due to the lower solubility of calcium sulfate at higher temperatures.

An additional core flood test was conducted at 210°F using deionized water to preflush, prepare the acid and post-flush. The objective of this test was to assess the effect of calcium sulfate precipitation on the permeability of carbonate cores at higher temperatures. **Fig. 17** shows that permeability reduction was significant because of precipitation of larger amounts of sulfate in the core.

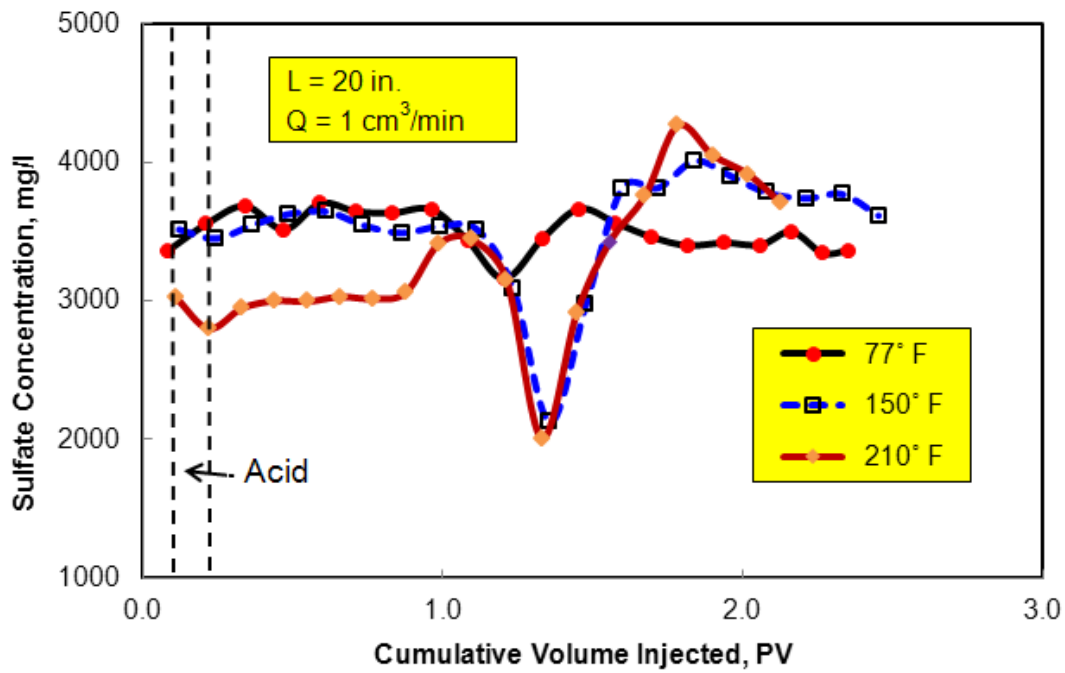


Fig. 16—Comparison of sulfate ion concentration changes at various temperatures.

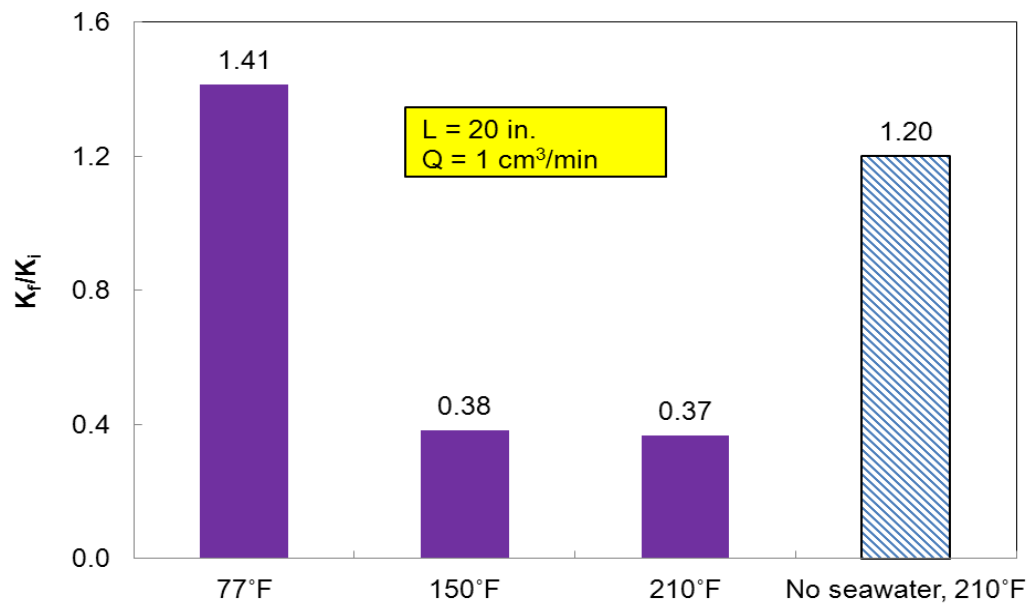


Fig. 17—Permeability changes at various temperatures.



## 5.6 Thermodynamic Calculations

The OLI ScaleChem software was used to calculate the scaling tendency of calcium sulfate at various temperatures and the critical scaling tendency of calcium sulfate was related to the samples that had obvious reduction in sulfate ion concentration. The input data for the OLI ScaleChem software included the ion analysis of the core effluent samples, pressure, temperature, pH, and fluid density. The output of the software included scaling tendency of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ,  $\text{CaSO}_4$ , and  $\text{CaCO}_3$ .

At 77°F, two core effluent samples contained a precipitate. Their scaling tendencies were 2.0 and 2.1, respectively (**Fig. 18**). The value of 2.0 was believed to be the critical scaling tendency for calcium sulfate under experimental conditions at 77°F. The critical scaling tendency of calcium sulfate was computed to be 2.1 at 150°F (**Fig. 19**). In the case of core flood test at 210°F, calcium sulfate began to precipitate even before the breakthrough of spent acid and calculation showed that the value of the critical scaling tendency was 1.2 (**Fig. 20**). The critical scaling tendency at 77 and 150°F agreed well with previous studies (Raju and Nasr-El-Din 2004). Note that the critical scale index is the logarithm of the critical scaling tendency.

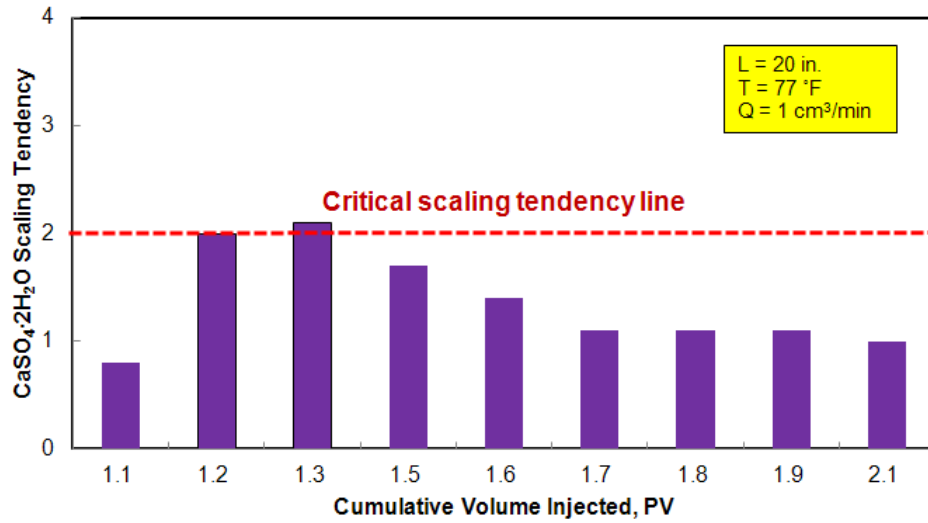


Fig. 18—Saturation index for CaSO<sub>4</sub>·2H<sub>2</sub>O at 77°F.

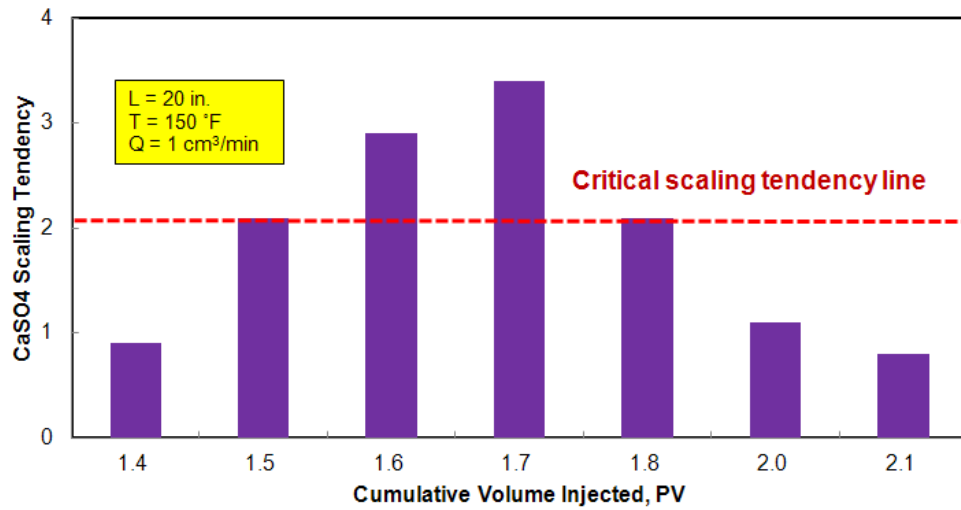
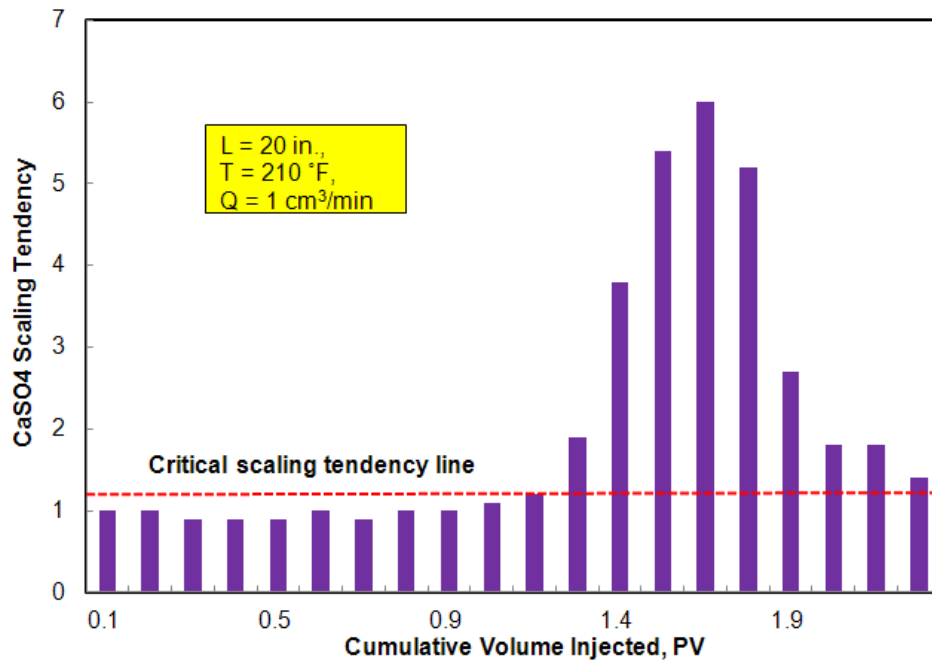


Fig. 19—Saturation index for CaSO<sub>4</sub> at 150°F.



**Fig. 20—Saturation index for CaSO<sub>4</sub> at 210°F.**

### 5.7 Permeability Changes

**Table 3** demonstrates how calcium sulfate precipitation reduced the core permeability after acid injection. At 0.5 cm<sup>3</sup>/min, core permeability increased from 8.5 to 11 md when deionized was used in all treatment stages. The final core permeability decreased from 7.3 to 6.8 md (experiment # 3, **Table 3**) and from 9.6 to 7.5 md (experiment # 2, **Table 3**) when seawater was used. Therefore, precipitation of calcium sulfate in the cores reduced acid stimulation effect. In these 3 core flooding tests, face dissolution occurred to the cores.

At 1 cm<sup>3</sup>/min, permeability increased from 4.2 to 32 md because the wormholes breakthrough the cores without using seawater. When seawater was used in the preflush,

post flush or to prepare the main stage, permeability of carbonate cores slightly increased. Precipitation of calcium sulfate reduced the effect of acid stimulation. At 5 cm<sup>3</sup>/min, the permeability increased significantly because wormhole breakthrough occurred.

In the case of 20 in. core flood tests, permeability increased from 4.1 to 5.8 md at 77°F while it decreased from 12.8 to 4.9 md and from 14.5 to 5.3 md at 150 and 210°F, respectively. For the base case, the permeability increased from 3.0 to 3.6 md at 210°F. More reduction in permeability of carbonate cores was due to two factors. The high reaction rate between acid and calcite at high temperatures, which makes acid treatment less effective, and precipitation of calcium sulfate inside the cores at high temperatures.

## 5.8 Material Balance

Material balance calculations in **Table 3** show how much precipitation retained in the cores. For the 6 in. core flood tests, the retained sulfate was nearly 10 wt% of the injected sulfate. The reduction in the sulfate ion concentration when acid was prepared using deionized water was a slightly more than that prepared in seawater because the solubility of calcium sulfate decreases in less salinity brines.

In the case of 20 in. core flood tests, sulfate retained in the core increased from 6% at 77F to 13% at 210°F. The solubility of calcium sulfate decreased with temperature, which caused a significant reduction in the permeability of the cores at 210°F.

## 6. MIGIGATION OF CALCIUM SULFATE

In this section, a polymer-based scale inhibitor was added into acid to eliminate precipitation of calcium sulfate. The effectiveness and concentration of this scale inhibitor, and whether it is needed in the preflush or post-flush stages were determined.

Austin chalk cores (1.5 in. × 6 in.) with an average porosity 19 vol% and permeability of 5 md were used. All cores were dried at 120°C for 4 hours and weighed and then saturated with either seawater or deionized water to calculate the pore volume and porosity of the cores, **Table 4**. The permeability changes were shown in **Table 5**.

TABLE 4—CORE FLOOD DATA TO MITIGATE CALIUM SULATE

Run	Flow rate, cm <sup>3</sup> /minn	Temperature, °F	Preflush, main stage, post-flush	Scale inhibitor concentration,	Porosity, fraction	Pore volume, cm <sup>3</sup>	Initial Permeability, md
1	1.0	77	DW, DW+HCl, DW	0	0.225	33.46	4.2
2	1.0	77	SW, SW+HCl, SW	0	0.284	42.23	11
3	1.0	77	SW, SW+HCl+SI, SW	20	0.192	33.35	3.8
4	1.0	77	SW, SW+HCl+SI, SW	20*	0.186	32.35	2.7
5	1.0	77	SW, SW+HCl+SI, SW	60	0.184	32.01	3.9
6	1.0	77	SW, SW+HCl+SI, SW	100	0.171	29.73	2.7
7	1.0	150	DW, DW+HCl, DW	0	0.2	34.71	3.7
8	1.0	150	SW, SW+HCl, SW	0	0.196	34.09	6

TABLE 4 Continued

Run	Flow rate, cm <sup>3</sup> /min	Temperature, °F	Preflush, main stage, post-flush	Scale inhibitor concentration,	Porosity, fraction	Pore volume, cm <sup>3</sup>	Initial Permeability, md
9	1.0	150	SW, SW+HCl+SI,	50	0.188	32.60	5.3
10	1.0	150	SW SW, SW+HCl+SI,	100	0.202	35.08	3.6
11	1.0	150	SW SW, SW+HCl+SI,	150	0.204	35.48	4.8
12	1.0	210	SW DW, DW+HCl,	0	0.192	33.32	6
13	1.0	210	DW SW, SW+HCl,	0	0.206	35.75	4.1
14	1.0	210	SW SW, SW+HCl+SI,	50	0.199	34.58	3.7
15	1.0	210	SW SW, SW+HCl+SI,	200	0.193	33.54	4.4
16	1.0	210	SW SW, SW+HCl+SI,	250	0.187	32.46	3.6
17	1.0	210	SW SW, SW+HCl+SI,	500	0.202	35.16	4.4

SW – Seawater

DW – Deionized water

SI – Scale inhibitor

\* In this case, 20 ppm of scale inhibitor was used in the all the stages.

TABLE 5—PERMEABILITY CHANGES

Run	Flow rate, cm <sup>3</sup> /min	Temperature, °F	Preflush, main stage, post-flush	Scale inhibitor concentration,	Initial permeability, md	Final permeability, md
1	1.0	77	DW, DW+HCl,	0	4.2	32
2	1.0	77	DW SW, SW+HCl,	0	11	11.2
3	1.0	77	SW SW, SW+HCl+SI,	20	3.8	4.8

TABLE 5 Continued

Run	Flow rate, cm <sup>3</sup> /min	Temperature, °F	Preflush, main stage, post-flush	Scale inhibitor concentration,	Initial permeability, md	Final permeability, md
4	1.0	77	SW, SW+HCl+SI, SW	20*	2.7	3.3
5	1.0	77	SW, SW+HCl+SI, SW	60	3.9	8.3
6	1.0	77	SW, SW+HCl+SI, SW	100	2.7	25
7	1.0	150	DW, DW+HCl, DW	0	3.7	8.2
8	1.0	150	SW, SW+HCl, SW	0	6	6.8
9	1.0	150	SW, SW+HCl+SI, SW	50	5.3	6.8
10	1.0	150	SW, SW+HCl+SI, SW	100	3.6	7.5
11	1.0	150	SW, SW+HCl+SI, SW	150	4.8	13.6
12	1.0	210	DW, DW+HCl, DW	0	6	7
13	1.0	210	SW, SW+HCl, SW	0	4.1	3.6
14	1.0	210	SW, SW+HCl+SI, SW	50	3.7	3.7
15	1.0	210	SW, SW+HCl+SI, SW	200	4.4	4.6
16	1.0	210	SW, SW+HCl+SI, SW	250	3.6	4.0
17	1.0	210	SW, SW+HCl+SI, SW	500	4.4	4.8

SW – Seawater

DW – Deionized water

SI – Scale inhibitor

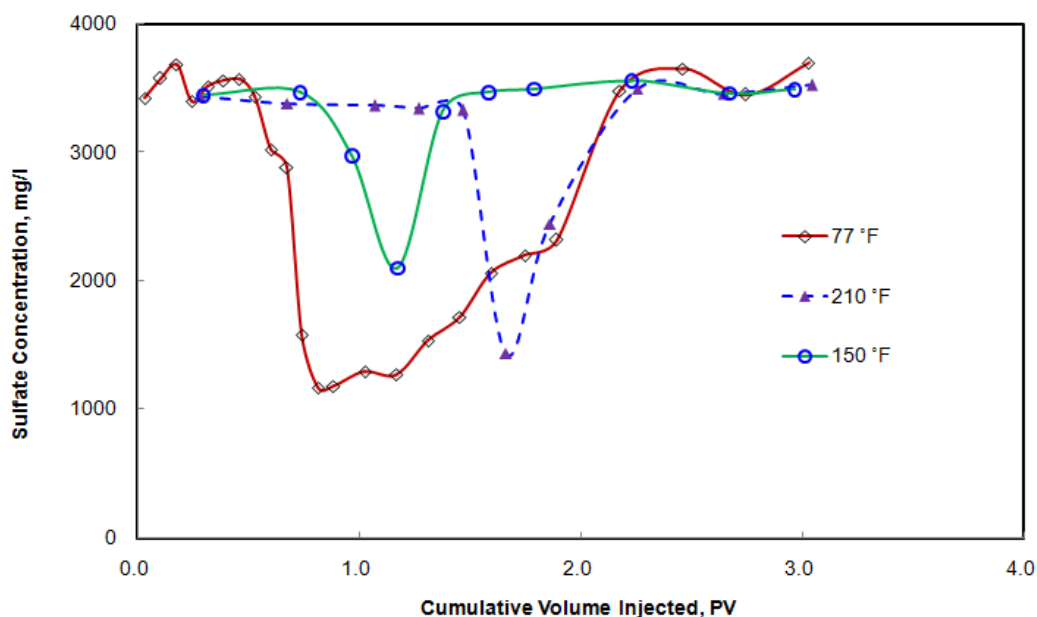
\* In this case, 20 ppm of scale inhibitor was used in the all the stages.

## 6.1 In the Absence of Scale Inhibitors

Core flood tests at 1 cm<sup>3</sup>/min were conducted using Austin Chalks cores (1.5 in. × 6 in.) to examine the sulfate concentration profiles in the absence of scale inhibitors over a wide range of temperatures (77 to 210°F) when seawater was used in all the stages (run #2, #8, and #13), **Table 4**.

### 6.1.1 Sulfate Concentration Profiles

At 77°F, a significant sulfate concentration reduction was observed after the injected of acid (**Fig. 21**). Two factors accounted for the decrease of sulfate concentration: first, calcium sulfate deposition and second, lower sulfate concentration (2187 mg/l) in the injected acid.



**Fig 21—Sulfate concentration profiles during acid treatments in the absence of scale inhibitors (77 to 210°F).**



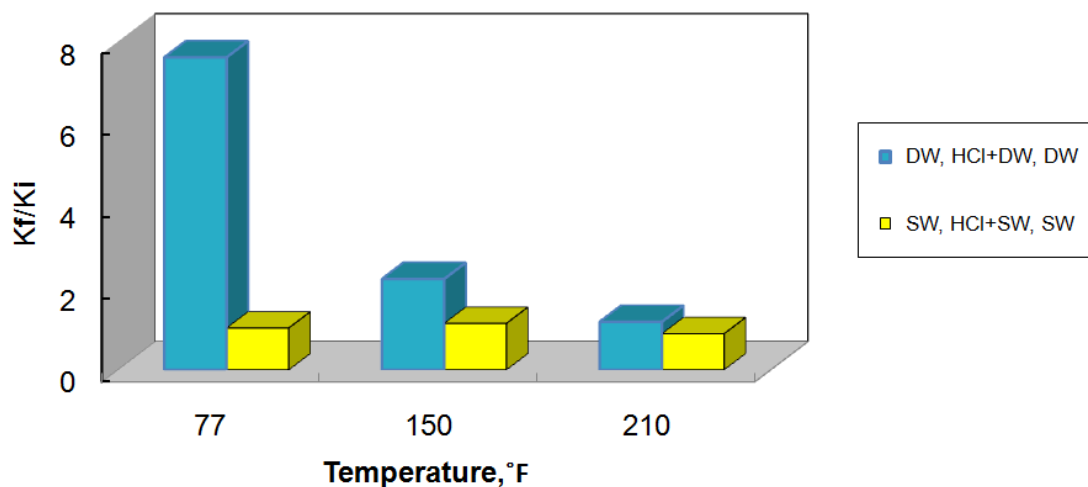
However, the extent of reduction in the sulfate concentration (1,180 mg/l) was much lower than that in the injected acid, indicating that the reduction in sulfate concentration was largely attributed to precipitation of calcium sulfate.

At 150 and 210°F, sulfate concentration was decreased to 2100 mg/l and 1440 mg/l respectively (**Fig. 21**). It is well known that calcium sulfate scale minerals exist mainly three forms in the oilfield, including anhydrite ( $\text{CaSO}_4$ ), hemihydrate ( $\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$ ) and gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) (Kan et al. 2005). All those three forms of calcium sulfate have solubilities which decrease with increasing temperature (Meijer and Van Rosmalen 1984). Gypsum is the stable form below 45°C while anhydrite is the stable form above 93°C (Furby et al. 1967). Hemihydrate tends to exist as a metastable solid phase over the entire temperature range 0 °C to 200 °C (Langelier et al 1950). However, nucleation of anhydrite has been proved to be an extremely slow process in comparison to that of gypsum (Langelier et al 1950; Hasson and Zahavi 1970). Gypsum is more readily to precipitate out of solution in a relatively short reaction period (approximately 30 minutes), which explains the extent of reduction in the sulfate concentration at 77°F was larger than that of sulfate concentration at 150 and 210°F.

### **6.1.2 Permeability Changes**

In the absence of scale inhibitors, the effect of preparing acid using seawater on permeability of carbonate cores (1.5 in. × 6 in.) at 1 cm<sup>3</sup>/min over a wide range of temperatures (77 to 210°F) was shown in **Fig. 22**. At 77°F, the permeability of carbonate core was increased from 11 to 11.2 md when seawater was used in all the stages;

however, the permeability of carbonate core was increased from 4.2 to 32 md when deionized water was used in all the stages, **Table 5**. Calcium sulfate deposition during acid treatments significantly caused formation damage and simultaneously affected the dissolution rate of carbonate reservoir rocks in HCl acid (Anderson 1991; Taylor et al. 2006). The acid stimulation effect, which was defined as the ratio of final permeability and initial permeability of carbonate cores, was reduced from 7.62 to 1.02. At 150 and 210 °F, the acid stimulation effect was decreased from 2.22 and 1.17 to 1.13 and 0.88 respectively. The acid stimulation effects at 150 and 210 °F were not as obvious as that at 77°F, due to high reaction rate of the hydrochloric acid with calcite in the carbonate reservoir rocks (Lund et al. 1973; 1975).



**Fig 22—Effect of mixing seawater on permeability of carbonate cores in the absence of scale inhibitors (77 to 210°F).**

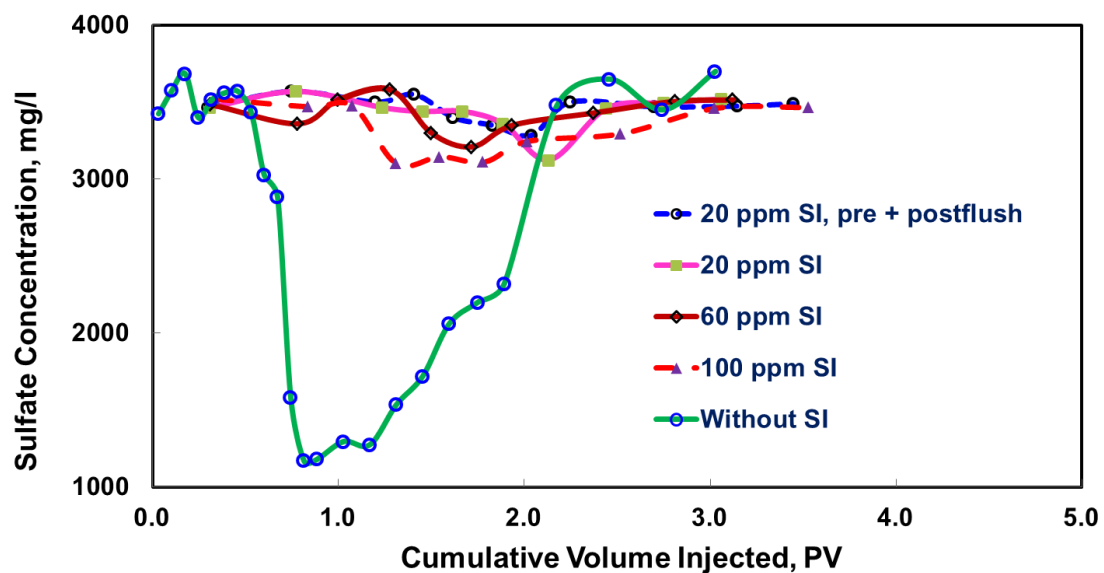
## 6.2 Scale Inhibitor Tests at 77 °F

A sulfonated terpolymer was added to the hydrochloric acid to mitigate calcium sulfate precipitation during acidizing treatments. The effectiveness of different concentrations of scale inhibitor was accessed based on analysis of sulfate concentration in the effluent samples and determination of acid stimulation effect at 1 cm<sup>3</sup>/min.

### 6.2.1 Sulfate Concentration Profiles

Upon the addition of 20 ppm of scale inhibitor at 77°F, sulfate concentration gradually decreased to the value of 3,000 mg/l after the injection of acid and then gradually reached to its normal concentration value (**Fig. 23**). The reduction in sulfate concentration was mainly due to lower sulfate concentration (2187 mg/l) in the injected acid. Sulfate concentration curve demonstrated that the presence of scale inhibitor effectively eliminated calcium sulfate precipitation in the acidizing process. However, the permeability was just increased from 3.8 to 4.8 md, **Table 5**. When 20 ppm of scale inhibitor was used in the preflush, main and post-flush stages, permeability increased from 2.7 to 3.3 md, **Table 5**. The nucleation process of calcium sulfate might affect acid reaction with calcite in carbonate rocks and cause acid treatment less effective. The addition of 20 ppm of scale inhibitor effectively eliminated deposition of calcium sulfate but not effectively inhibited nucleation of calcium sulfate. A series of core flood tests were conducted with an increment of 40 ppm of scale inhibitor added to acid to examine whether the increase of scale inhibitor concentration in acid can restore acid stimulation

effect in comparison with that of deionized water was used in all the stages. It was noted that there was little difference in sulfate concentration curves (**Fig. 23**); however, increase of permeability varied among the different concentrations of scale inhibitor, **Table 5**.



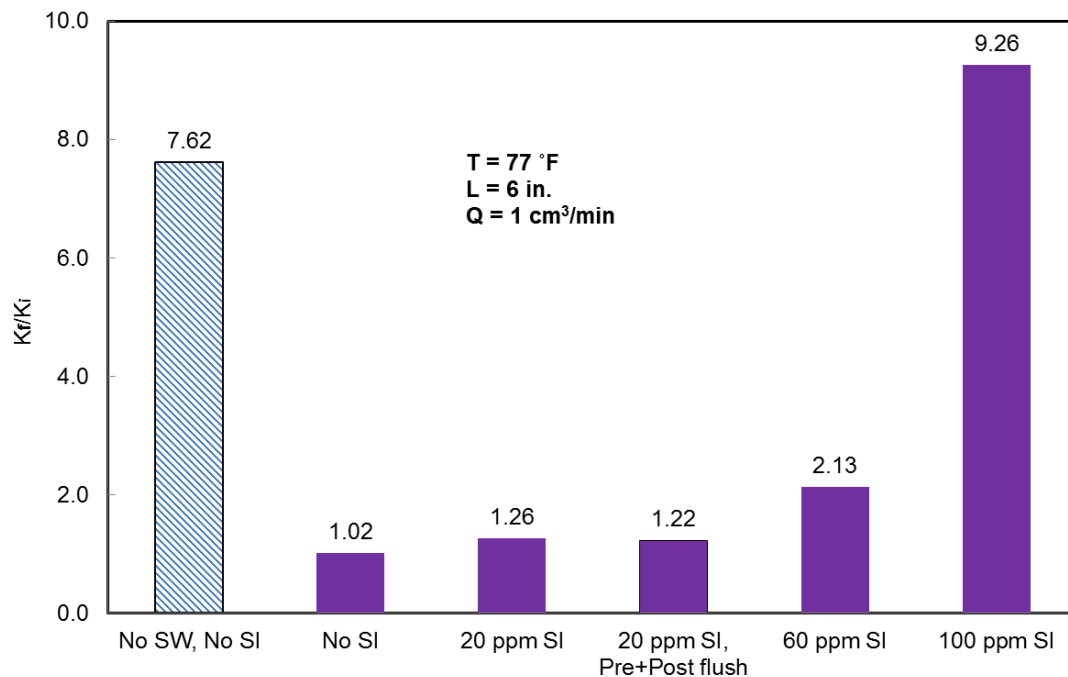
**Fig 23**—Sulfate concentration profiles during acid treatments at 77°F.

### 6.2.2 Permeability Changes and Acid Penetration Distances

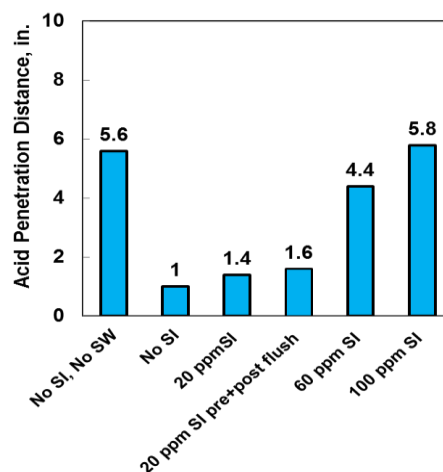
In the presence of different concentrations of scale inhibitor, the effect of mixing seawater on permeability of carbonate cores (1.5 in. × 6 in.) was shown in **Fig. 24**. Acid penetration distances were determined based on the analysis of computed-tomography (CT) scan images of acidized carbonate cores (**Fig. 25**).

The degree of changes in permeability and acid penetration distance varied significantly among the different concentrations of scale inhibitor. For example, acid stimulation effect was increased from 1.02 to 1.26 and acid penetration distance was

increased from 1 to 1.4 in. with the addition of 20 ppm of scale inhibitor in acid. In the case of the addition of 100 ppm of scale inhibitor, acid stimulation effect reached 9.26 and acid penetration distance was 5.8 in., even more than that of deionized water was used in all the stages (7.62 and 5.6 in.). The addition of 100 ppm of scale inhibitor at 77°F was believed to completely inhibit nucleation of calcium sulfate during acidizing treatments and restore the acidizing effect in comparison with that deionized water was used in all the stages.



**Fig 24—Effect of mixing seawater on permeability of carbonate cores at 77°F.**



**Fig 25—Acid penetration distances in the absence and presence of scale inhibitors at 77°F.**

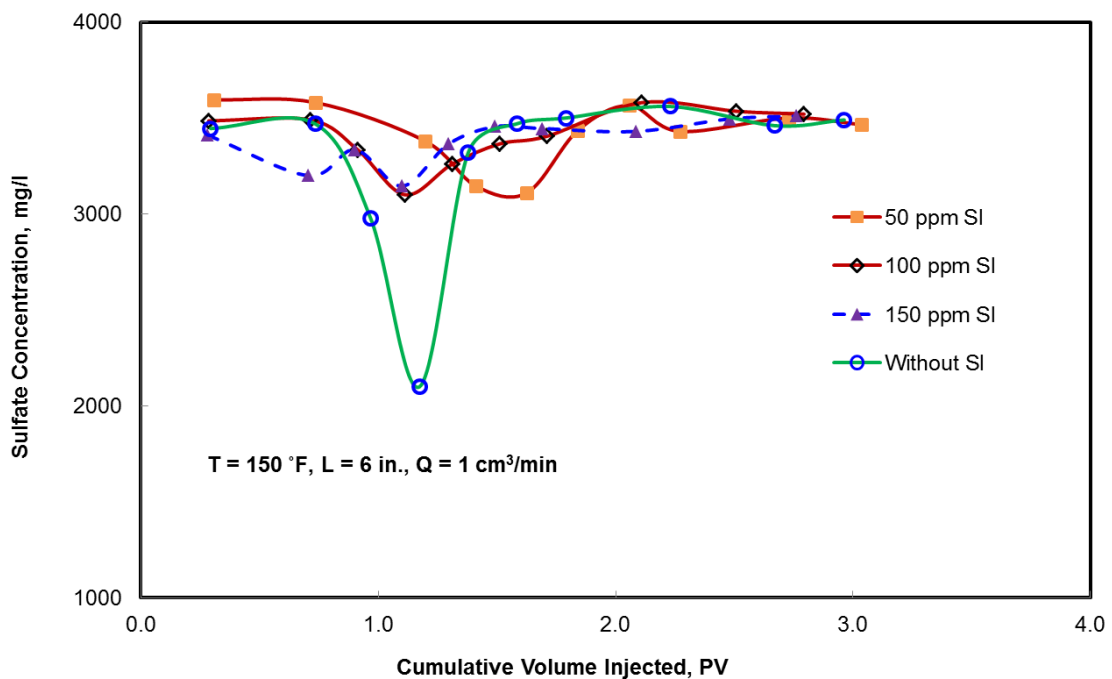
Therefore, it would be reasonable to conclude that by increasing the scale inhibitor dosage in acid the precipitation as well as nucleation of calcium sulfate can be completely inhibited at 77°F. Accordingly, it should be possible to overcome the adverse impact of calcium sulfate on acidizing treatments at 77°F by adding an appropriate dose of scale inhibitor.

### **6.3 Scale Inhibitor Tests at 150 °F**

It was well-known that the solubility of calcium sulfate decreases greatly with the increment of temperature (Meijer and Van Rosmalen 1984). Temperature tends to decrease the solubility of calcium sulfate and therefore significantly increase the scaling tendency of calcium sulfate (He et al. 2011). A couple of core flood tests at 150°F were conducted to evaluate the inhibition efficiency of this scale inhibitor at higher supersaturated conditions.

### 6.3.1 Sulfate Concentration Profiles

In **Fig. 26**, sulfate concentration curves indicated that the presence of scale inhibitor successfully inhibited calcium sulfate precipitation and little difference was observed on the addition of different concentrations of scale inhibitor. However, the final permeability of carbonate cores was greatly enhanced when the concentration of scale inhibitor was increased from 50 to 150 ppm, **Table 5**.

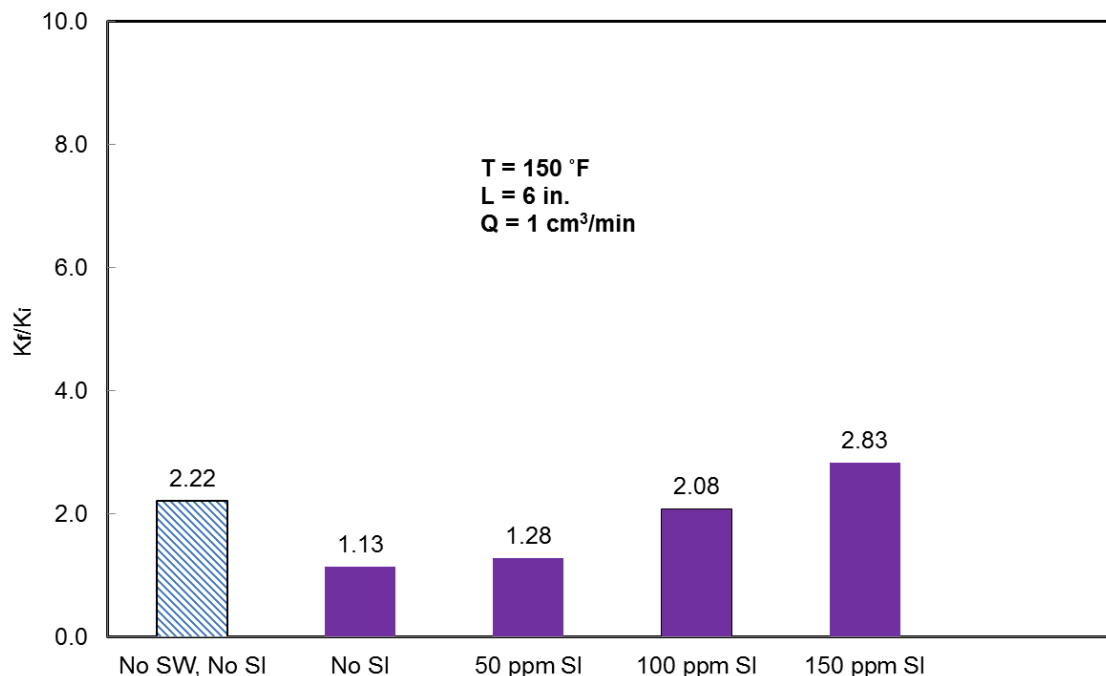


**Fig. 26**—Sulfate concentration profiles during acid treatments at 150°F.

### 6.3.2 Permeability Changes

The effect of mixing seawater on permeability of carbonate cores (1.5 in. × 6 in.) in the absence and presence of scale inhibitors at 150 °F was shown in **Fig. 27**. Acid

stimulation effect was increased from 1.13 to 1.28 with the addition of 50 ppm scale inhibitor and reached 2.83 when 150 ppm of scale inhibitor was added to the acid. At 150 °F, nucleation of calcium sulfate can be successfully inhibited by increasing the scale inhibitor dosage in acid.



**Fig. 27—Effect of mixing seawater on permeability of carbonate cores at 150°F.**

#### 6.4 Scale Inhibitor Tests at 210 °F

A couple of studies have found that it is very difficult to inhibit calcium sulfate scale under highly supersaturated conditions (Vetter 1972; Vetter 1979); for example, when the saturation index of calcium sulfate is above 1 (Fan et al. 2010). Core flood tests at 210 °F were further conducted to examine the inhibition efficiency of this scale inhibitor under highly supersaturated conditions.



#### **6.4.1 Sulfate Concentration Profiles**

Upon the addition of 50 ppm scale inhibitor, sulfate concentration dropped to 2,235 mg/l after the injection of acid in comparison with 1,440 mg/l in the absence of scale inhibitors (**Fig. 28**). In **Fig. 29**, material balance calculation showed that 3% sulfate was decreased in comparison with 7% when no scale inhibitor was applied. At 210 °F, 50 ppm of scale inhibitors was not effectively enough to eliminate calcium sulfate precipitation due to the decreasing efficiency of scale inhibitor with increasing supersaturation (Vetter 1972). By increasing the concentration of scale inhibitor up to 200 ppm, it was noted that sulfate concentration after acid injection was decreased to 2,585 mg/l and generally around 0.4% sulfate was reduced. When the concentration of scale inhibitor was increased to 250 ppm, sulfate reduction was up to 2805 mg/l and 0.2% sulfate was decreased. Generally the same values were obtained when the concentration of scale inhibitor was increased to 500 ppm. It could conclude that the effectiveness of this scale inhibitor depends on the degree of supersaturation and the temperature. More scale inhibitors should be applied to overcome the less effectiveness of this scale inhibitor under highly supersaturated conditions.

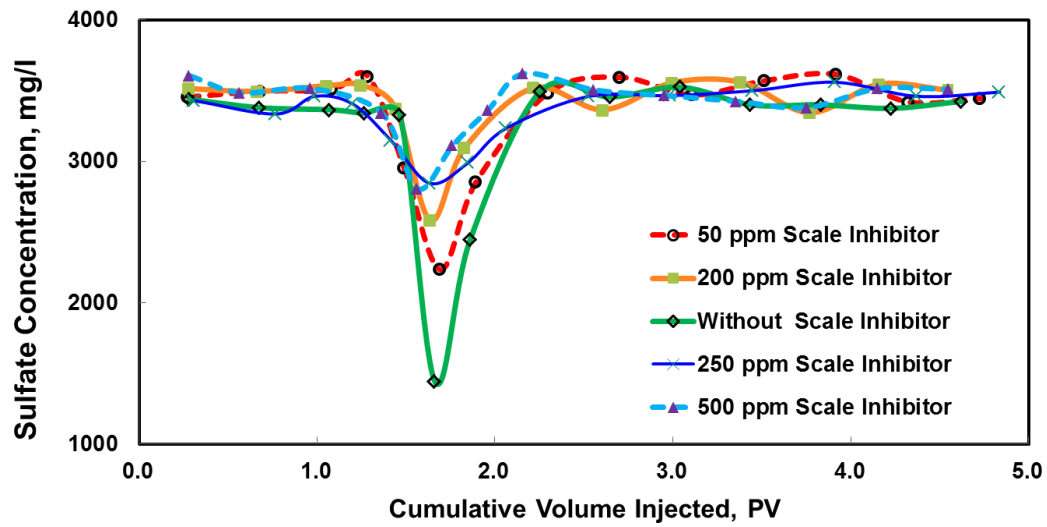


Fig. 28—Sulfate concentration profiles during acid treatments at 210°F.

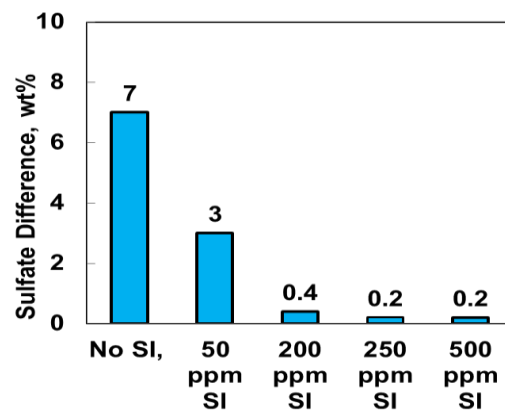
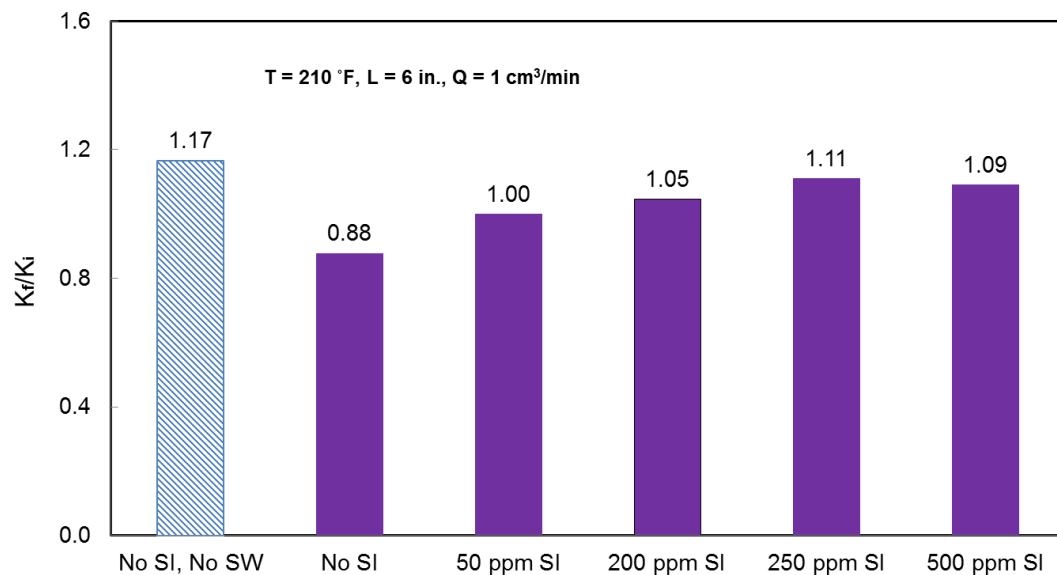


Fig. 29—Sulfate material balance at 210°F.

### 6.4.2 Permeability Changes

The effect of mixing seawater on permeability of carbonate cores (1.5 in. × 6 in.) in the absence and presence of scale inhibitors at 210 °F was shown **Fig. 30**. At 210 °F, there exists a general trend that by increasing concentrations of scale inhibitor the acid stimulation effect was increased. However, the acid stimulation effect with the increment of concentration of scale inhibitor was not as obvious as that at 77 and 150 °F, due to high reaction rate of the hydrochloric acid with calcite in the carbonate reservoir rocks (Lund et al. 1973; 1975).



**Fig. 30—Effect of mixing seawater on permeability of carbonate cores at 210°F.**

### 6.5 Scale Inhibitor Requirements

Based on above discussions, the concentration of scale inhibitor required to completely inhibit precipitation of calcium sulfate ranging from 20 to 200 ppm,

depending on the temperatures. However, the concentration of scale inhibitor that can restore acidizing effect is much higher. All the data are shown in **Table 6**.

**TABLE 6—SCALE INHIBITOR REQUIREMENTS**

No.	Flow rate, cm <sup>3</sup> /min	Temp., °F	Dimension, in.	MIC, ppm	MAC, ppm
1	1	77	6×1.5	20	100
2	1	150	6×1.5	50	150
3	1	210	6×1.5	200	---

MIC: Minimum scale inhibitor concentration to mitigate calcium sulfate deposition

MAC: Scale inhibitor concentration required to restore acidizing effect

## 7. CONCLUSIONS AND RECOMMENDATIONS

### 7.1 Conclusions

Core flood studies were conducted to assess the effect of using seawater in the preflush, post-flush, or to prepare HCl on the permeability of carbonate cores. When seawater was used to prepare HCl for matrix acidizing, the addition of a sulfonated terpolymer into acid was found to be successfully eliminated calcium sulfate precipitation during acidizing process under appropriate supersaturation conditions. The following conclusions can be drawn from this study:

- Calcium sulfate precipitated in cores saturated with seawater, whether the injected acids were prepared in seawater or in deionized water.
- Calcium sulfate scale caused severe loss in the permeability of carbonate cores, especially at high temperatures.
- The critical scaling tendencies for calcium sulfate were 2.0, 2.1, and 1.2 at 77, 150, 210°F, respectively.
- When mixing seawater and acid for matrix acidizing treatments, acid stimulation effect can be increased as much as that deionized water was used in all the stages by addition of appropriate dosage of scale inhibitor into acid.
- The nucleation and precipitation process of calcium sulfate can be completely inhibited by increasing the concentrations of scale inhibitor in acid at 77 and 150 °F. The minimum requirements of scale inhibitor were 100 and 150 ppm respectively.

- The effectiveness of scale inhibitor depends largely on the scaling tendency of calcium sulfate. The higher the supersaturation and the higher the temperature, the less effectiveness of the scale inhibitor becomes. A portion of calcium sulfate will precipitate during acidizing process under highly supersaturated conditions.

## **7.2 Recommendations**

Based on above discussions, it is recommended to use fresh water to prepare HCl acids. If fresh water is not available, then a proper scale inhibitor should be added to the fluids used.

Another concern which was not addressed in this study is the presence of barium and strontium in the formation water. These divalent cations will precipitate barium and strontium sulfates scale during injection of acids which are prepared with seawater. Precipitation of these sulfates will increase the damage that was noted in this paper. More research work is needed to address this concern in the near future.

It should be noted that it is necessary to determine the effectiveness of scale inhibitor under a more wide range of temperatures and supersaturation conditions. The inhibition mechanisms of scale inhibitor should also be fully examined.

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