EVALUATING THE EFFECTS OF ENVIRONMENTALLY ACCEPTABLE CLAY

STABILIZER ON BANDERA SANDSTONE

A Thesis

by

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ABSTRACT

Fines migration and clay swelling are major problems encountered in sandstone formations in the petroleum industry which leads to a decline in the level of productivity in the reservoirs. Inorganic salts such as KCl, NH_4Cl, and NaCl are used in such reservoir formations to mitigate clay particles from migrating and swelling.

The uses of these inorganic salts have temporary short term effects in the reservoirs. Cationic inorganic and organic polymers are being designed and developed to work as clay stabilizers by having a more permanent effect on these reservoirs.

Capillary suction time (CST) tests were used to evaluate existing industry-used clay stabilizers and the cationic inorganic (Al/Zr) polymer with the use of bentonite clay, and also as a screening test to qualitatively select clay stabilizing additive concentrations to be used for further tests. Coreflood experiments were done using an inorganic (Al/Zr) polymer compound at concentrations of 1, 2, and 4 wt% on Bandera sandstone core samples with temperatures ranging from 77 to 300°F.

Coreflood experiments were initially done at a temperature of 77°F and the effectiveness of the cationic inorganic polymer on Bandera sandstone core samples was analyzed and a 2 wt% concentration was determined to work best in mitigating fines migration, clay swelling, and sand production. The 2 wt% concentration of the clay stabilizing additive was also seen to work effectively at temperatures of 200°F and 300°F.

Acidizing treatments were done following a preflush of the cationic clay stabilizer on the Bandera sandstone core sample showing the stability of the clay stabilizer even after stimulation treatment.

DEDICATION

This thesis is dedicated to God Almighty for the gift of life, and the opportunity to attend such a prestigious university to study a fulfilling course.

To my parents, Sir and Lady E. E. Emecheta, my brother, and sisters for their relentless prayers and words of encouragement.

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1. INTRODUCTION – LITERATURE REVIEW

The majority of formations, approximately 97% of all petroleum reservoirs, contain clay minerals (Berry, Boles et al. 2008). These clay minerals are either naturally occurring, originally deposited during sedimentation (detrital clay), or precipitated from fluids flowing through the matrix (authigenic clay) being used to recover the hydrocarbons (Mohan, Vaidya et al. 1993). Clay minerals are implicated in oilfield applications like drilling operations. The presence of authigenic and detrital clays can cause loss of permeability by several mechanisms (Mohan, Vaidya et al. 1993). The reaction of water with these clay minerals tends to cause fines dispersion and clay swelling (Azari and Leimkuhler 1990). Inadequacy in the prevention of these effects can lead to significant loss in productivity by reducing reservoir permeability by more than 90% (Zhou, Gunter et al. 1995).

Laboratory and field studies indicate that almost every operation in the field is a potential source of damage to the formation hence reducing well productivity (Krueger 1988). Formation damage is an operational and economic problem that causes a decrease in permeability of petroleum bearing formations which occurs during the oil and gas production, drilling, hydraulic fracturing, or workover operations (El-Monier and Nasr-El-Din 2013). Formation damage is usually difficult and costly and the basic approach would be to prevent such damage (Ezeukwu, Thomas et al. 1998, Gabrieladn Inamdar 1983, Porter, K. E. 1989, Vitthal, Sharma et al. 1988). A widespread knowledge of how formation damage occurs is the first step in the prevention of well damage (Fink, J. K. 2012, Raible and Gall 1985, Sharma, Yortsos et al. 1985). Operators in the oil and gas industry have sought to extend the useful lives of wells in sandstone reservoirs and to avoid early abandonment when productivity decreases as a result of formation damage or low natural permeability (Borchardt, Roll et al. 1984).

Fine particles that may contribute to permeability impairment include clay minerals, quartz, amorphous silica, and carbonates (Chen, D, B. Zhou et al. 1986). Clay minerals

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are small and structurally quite flat with wide surface areas, giving them the tendency to react readily with fluids introduced into the porous media (Ohen and Civan 1989). Sandstone formations contain different amounts of clay minerals and particles that are attached to sand grains (Christani, Ferrara et al. 2011, Rodriguez and Bryant 2007, Roque, Chauveteau et al. 1995). During oilfield operations, fines weakly attached by physiochemical forces to the pore walls are released as a result of the flowing fluid's drag forces (Crocker, Donaldson et al. 1983).

Clay minerals are negatively charged, a quality that makes them sensitive to fluids, and provides the mechanism by which clay stabilizers operate (Nasr-El-Din, Al-Mulhem et al. 1999). To control and prevent the effects of these clays and fines in the formation, clay stabilizers are incorporated into the treatment fluids used in oilfield operations (Christian and Ayres 1974, O'Neil et al. 2013, Wilcox and Jarrett 1988).

Clay particle migration is the most common mechanism of permeability reduction in most sandstone formations because they contain very little to almost no swelling clays (Crowe, C. W. 1990). Bandera sandstones contain very little to no swelling clays and a considerable amount of migratory or dispersible clays such as kaolinite, which is sensitive to sudden changes in salinity (Khilar and Fogler 1983). From the chemical or physiochemical point of view, temperature is an important factor for rock/fluid interactions (Devine, C. S. 2005). Changes in temperature might induce organic or inorganic precipitation (Ohen and Civan 1989). For water-sensitive formations, the effect of temperature is significant (Musharova, Mohamed et al. 2012). Schembre, Tang et al. (2006) concluded that permeability reaction increases as temperature increases, and fines migration occurs continuously at higher temperatures and vary with solution pH and ionic strength (Nguyen, Weaver et al. 2005, Rieke 1972). Fines released from the pore walls take place under conditions of elevated temperature, high pH, and moderate aqueous phase salinity.

Clay stabilizers are chemical additives used in stimulation treatments to prevent the migration or swelling of clay particles in reaction to water-based fluid (Coulter,

Copeland et al. 1979). Clay stabilizers are mostly used in fracturing and acidizing treatments. Acid stimulation provides a cost-effective method of increasing production and accelerating reserves. Acid plays a significant role in boosting the hydrocarbon production in oil and gas fields. When clay stabilizers are used in stimulation operations, they should be chemically stable in acids and high pH environments for fracturing treatments. Various clay stabilizers are used to prevent the damage caused by these clay minerals (Gruesbeck and Collins 1982).

Experimental studies done by Tague and Lewallen (2000) state that the design of an enhanced clay stabilizer be based primarily on its ability to control smectite and illite clays, and as a secondary consideration, to maintain a water-wet formation. They further explained that the clay stabilizer should be water soluble and adsorb to clay surfaces in a permanent way because of the presence of multiple cationic sites on the polymer chain. This will make clays insensitive to swelling in fresh water (Grayeff, S. G. 2004, Leone and Scott 1988).

Clay stabilizing additives can be grouped into two basic categories: temporary or permanent (Himes and Vinson 1991). They can be also categorized into inorganic and organic clay stabilizers (Zhou, Gunter et al. 1995). The use of inorganic salts, such as potassium chloride (KCl) and sodium chloride (NaCl) as temporary clay stabilizers during hydrocarbon well drilling, completions, and servicing operations, has been in practice for many years (Himes, Parker et al. 1990). Experimental work done byNasr-El-Din, Al-Mulhem et al. (1999) indicate that the critical salt concentration (CSC) of KCl brine is nearly 5 wt%. With the injection of brines of lower salt concentrations, migration of fines particles was observed and this led to loss of permeability (Hesterberg and Reed 1991).

The water sensitivity of sandstone is a colloidal phenomenon because the permeability of the sandstone is decreased rapidly and significantly after the sandstone is in contact with fresh water (Khilar and Fogler 1983). Berry, Boles et al. (2008) showed that the ionic liquid at concentrations of 2 and 4 wt% performed better at mitigating fines

migration and inhibiting clay swelling in the sandstone core sample than quaternary amine did.

Cationic polymers have become widely used in preventing permeability damage caused by clay swelling and fines migration with a permanent effect (Mahmoud, Nasr-El-Din et al. 2011, Saldungaray, Caretta et al. 2001). El-monier and Nasr-El-Din (2010) did different coreflood experiments with concentrations of 0.5, 1, and 4 wt% at 200ºF to determine the optimum concentration of a clay stabilizing additive on Berea sandstone. Core effluent samples were collected from each experiment and tested. The minimum amount of fines and little precipitation of chemicals from the stabilizer were observed when used at a concentration of 1 wt%, indicating optimal effectiveness of the clay stabilizing additive at this concentration when compared to the other concentrations tested.

The COP clay stabilizers that have been developed and are widely used in controlling clay swelling and fines migration undergo decomposition reactions in high pH and high temperature environments (Stanley, Ali et al. 1995). The explorations of deep hydrocarbon producing formations have led to the need for evaluating acid treatment operations, especially under high temperature and pressure conditions (Qiu, Gherryo et al. 2008). Musharova, Mohamed et al. (2012) investigated the impact of temperature on fines migration in sandstone formations, and they showed that high salt concentrations or salt containing high valence cations will be required to mitigate fines migration due to pH changes at higher temperatures. Reservoirs with higher temperature are more susceptible to formation damage (Hibbeler, Garcia et al. 2003).

The project area of research is focused on the design and evaluation of environmentally acceptable clay stabilizers (cationic inorganic polymers – CIP) for sandstone formations, putting into consideration reservoirs at high temperatures (temperatures greater than 180ºF). Fines migration, clay swelling, and sand production are associated with sandstone reservoirs (Howard, Hinkel et al. 2012). These problems, if left unaddressed, will continue to cause decline in petroleum reservoir productivity (Thomas and Crowe

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1978). A greater knowledge of the reaction between the clay/sand particles and fluids, the proper design of clay stabilizing additives, and the application of these additives to increase hydrocarbon recovery is still needed in the petroleum industry (Hsi, C. D. 1984, Simon and Anderson 1990, Somerton and Radke 1983). Laboratory experiments will be conducted using the coreflood setup in evaluating the effect of industry provided clay stabilizers on Bandera sandstone (Miranda and Underdown 1993). Initial tests will be done at temperatures of 77ºF and additional tests will be done on the most effective stabilizing additive concentration at higher temperatures up to 200ºF and 300ºF to evaluate the stability of the additive at an elevated temperature. Acid treatments will also be done on the Bandera sandstone cores following a preflush of the clay stabilizer to determine its effectiveness after stimulation treatment.

2.   FINES MIGRATION AND CLAY SWELLING

2.1   INTRODUCTION

The majority of hydrocarbon producing formations contain clay minerals, and the reaction of water (low salinity fluids) with these clay minerals tends to cause fines dispersion and clay swelling (Kaufman et al. 2008). The phenomenon of colloidal induced fines migration has significant importance in the petroleum industry as the release of these fines can migrate and plug areas in the formation causing damage in the formation thereby leading to the reduction in production (Khilar, Vaidya et al. 1990). Fines can be said to be small or tiny components of rock that can move within or through pores of the rock (Chalk, P. N, Gooding et al. 2011). Clay fines migration vary with mineralogy, morphology, abundance, and distribution (Zaltoun and Berton 1992). Water sensitivity of sandstones, a problem in colloid chemistry, is a situation where the permeability of sandstones containing clay minerals decrease significantly and rapidly when fresh water replaces salt water originally present in the sandstone formation (Khilar and Fogler 1984). As stated by Zhou, Gunter et al. (1995), the hydration of interlayer cations and the formation of diffuse double layers result in the expansion of structural layers, thereby resulting in clay swelling. From many laboratory tests and field cases, clay swelling has been continually proven to cause extreme damage to reservoir permeability (Huerta and McQuarrie 1994, Zeinijahromi et al. 2011). Clay minerals are especially susceptible to migration because of their physical size and surface properties. From more studies based on the work by Zhou, Gunter et al. (1995), most clay minerals (including silica and/or silicate sands) carry a negative surface charge when immersed in aqueous solution of pH 5 and/or above. As a result of this negative charge, clay particles detach from themselves and the matrix, inducing migration under hydrodynamic drag (Kia, Fogler et al. 1987). Further experimental studies show that fines migration is affected by salt concentration, type and valence of cations, pH, flow rate, mineral composition, and wetting status of fines (Chang, F. and F. Civan 1991). A critical salt

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concentration (CSC) was found to exist in the water sensitivity of sandstones (Matthews, Matthews et al. 1993, Underdown et al 1993). In reservoir formations containing significant amounts of clay particles such as smectite/montmorillonite, swelling of these clay particles is noticeable and causes formation damage Muecke, T. W. 1979).
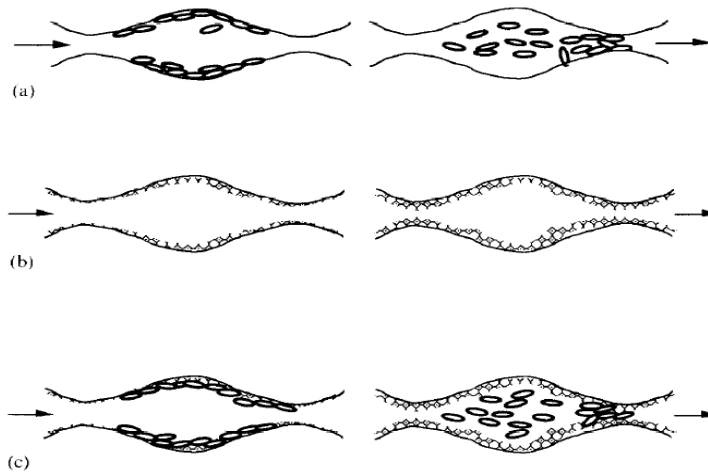
Fig. 2.1 – Mechanisms of permeability reduction (K.K Mohan, R.N Vaidya, et al 1993)
        a – Migration
        b – Swelling
        c – Swelling-induced migration

In order to comprehend the mechanism of fines migration (as shown in Fig. 2.1), the DLVO (Derjaguin, Landau, Verwar and Overbeek) theory is used. The theory explains the stability of colloidal systems (Fig. 2.2) resulting from the balance of attractive and repulsive forces (Schembre and Kovscek 2004). Forces acting between two charged colloidal particles in an electrolytic solution are either attractive (F_A) or repulsive (F_R). The balance of both forces determines the stability of the colloidal system (Ahmadi M, A Habibi et al. 2011, Gravelle, Peysson et al. 2011). The interaction forces between particles (F_T) can be expressed as:

$$F_T(h) = F_A(h) + F_R(h) \qquad (1)$$

Where: (h) is the interparticle distance (Schembre and Kovscek 2004).

The list of parameters, nomenclature, and greek symbols can be seen in Tables 4.4-4.6.

The interaction between a clay particle and a pore surface is described by the following:

$$V_t(h) = V_{LVA}(h) + V_{DLR}(h) + V_{BR}(h) + V_{HR}(h) + V_{IHL}(h) \qquad (2)$$

Where: V_t is total potential

V_t = positive (+ve) = unstable (repulsive)

V_t = negative (-ve) = stable (attractive)

The London Van der Waals (V_{LVA}) is an attractive force which plays an important role with regards to intergranular and wetting behavior and is expressed as (Musharova, Mohamed et al. 2012):

$$V_{LVA}(h) = -\frac{A}{6}\left[\frac{2(H+1)}{H(H+2)} + \ln\left(\frac{H}{H+2}\right)\right] \qquad (3)$$

Where: A is Hamaker constant

H is ratio of separation particle radius, h/r_p

The Double layer term is a repulsion force, calculated assuming a constant charge condition and is expressed as (Schembre, Tang et al. 2006):

$$V_{DLR}(h) = \frac{\varepsilon\, rp}{4}(\Phi_{01}{}^2 + \Phi_{02}{}^2)\left[\left(\frac{2\Phi 01\Phi 02}{\Phi 012 + \Phi 022}\right)\ln\left(\frac{1+\exp(-kh)}{1-\exp(-kh)}\right) - \ln[1-\exp(-2\kappa h)]\right] \qquad (4)$$

Where: k is the Debye-Huckel reciprocal length

ε is dielectric constant on the medium

Φ_{oi} is the surface potential of the wall (i = 1) and particle (i =2)

The Debye-Huckel reciprocal length term is expressed as (Schembre, Tang et al. 2006):

$$k = \sqrt{\frac{2e^2 n_b}{\varepsilon kT}} \qquad (5)$$

Where: n_b is the total ion density

The Born repulsion (V_{BR}) measures the short range molecular interaction resulting from the overlap of electron clouds, and is expressed as (Kia, Fogler et al. 1987):

$$V_{BR} = \frac{A\delta}{7560}\left[\frac{8rp+h}{(2rp+h)7} + \frac{6rp-h}{(h)7}\right]$$

(6)

Where: δ is the collision diameter
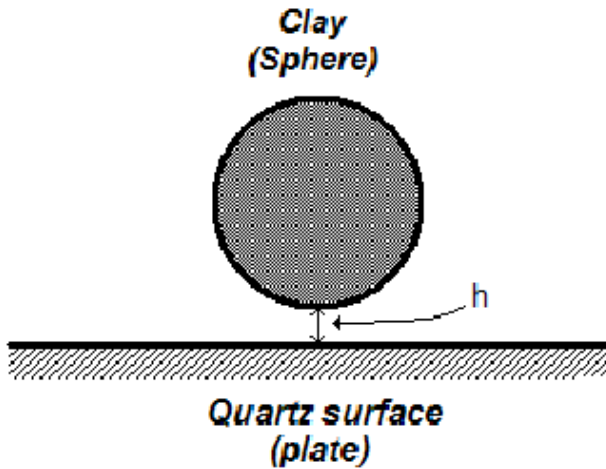
Fig. 2.2 – Sphere-plate system for modeling fines stability
(Schembre and Kovscek 2004)

2.2 CLAY MINERALS

Clay is a general term including many combinations of one or more clay minerals with traces of metal oxides and organic matter. The term "clay" is applied both to materials having a particle size of less than 2 micrometers and to the family of minerals that has similar chemical compositions and common crystal structural characteristics. Clay minerals are hydrous aluminum phyllosilicates. Table 2.1 shows the clay mineral silicate

groups. Clay deposits may be formed in place as residual deposits in soil, but thick deposits usually are formed as the result of a secondary sedimentary deposition process after they have been eroded and transported from their original location of formation (Zhou, Cameron et al. 1997). Clay minerals are very common in fine grained sedimentary rocks such as shale, mudstone, and siltstone (Baghdikian, S Y, M. M. Sharma et al. 1989).

The characteristics common to all clay minerals are derived from their chemical composition, layered structure, and size:

- Clays are fine-grained sediments (tiny particles), ranging from 2-4 micron in size.
- Clays are plate-like in structure
- Clays are hydrated aluminum silicates
- Clays exhibit ion exchange capacity
- Clays have large surface area
- Clays are negatively charged
  (The presence of surface and broken - edge -OH groups gives clay particles their electronegativity)

There are four (4) main groups of clays of interest to the petroleum industry:

- Kaolinite [$Al_2Si_2O_5(OH)_4$]
- Illite [$(K,H_3O)(Al,Mg,Fe)_2(Si,Al)_4O_{10}[(OH)_2,(H_2O)]$]
- Chlorite [$(Mg,Fe)_3(Si,Al) O_{10}(OH)_2 \cdot (Mg,Fe)_3(OH)_6$]
- Smectite [$(Na,Ca)_{0.33}(Al,Mg)_2(Si_4O_{10})(OH)_2 \cdot nH_2O$]

2.2.1   KAOLINITE

Kaolinite is one of the most common minerals. It occurs in abundance in soils that have formed from chemical weathering of rocks (Fig. 2.3). It is a layered silicate mineral with one tetrahedral sheet linked through oxygen atoms to one octahedral sheet of alumina octahedral (Cerda, C. M 1987). It has a low shrink-swell capacity and a low cation exchange capacity. It is soft, earthy, and usually white.
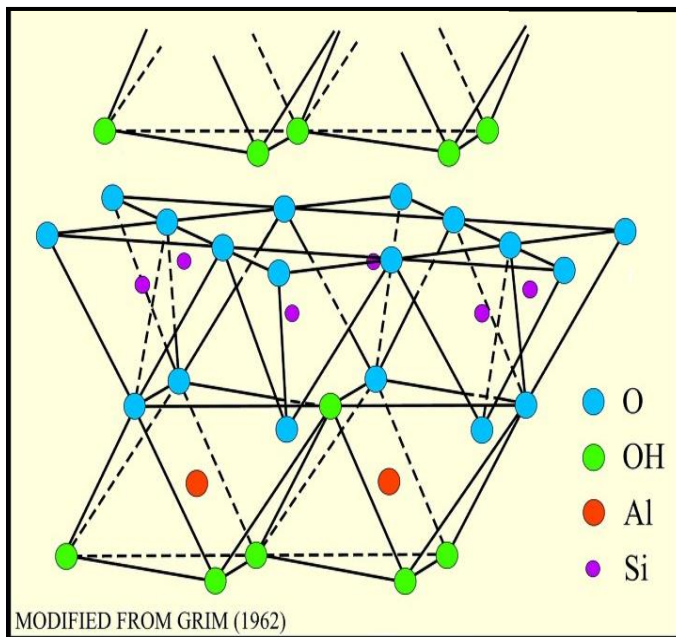
Fig. 2.3 – Structure of Kaolinite Layer

2.2.2   ILLITE

Illite, also called hydromica or hydromuscovitte, is a layered alumino-silicate non-expanding mineral. It has a structure constituted by the repetition of tetrahedron-octahedron-tetrahedron (TOT) layers (Fig. 2.4). It occurs as aggregates of small monoclinic grey to white crystals. It is common in sediments, soils, argillaceous

sedimentary rocks, and some low grade metamorphic rocks. The cation exchange capacity is higher than that of kaolinite but lower than that of smectite.
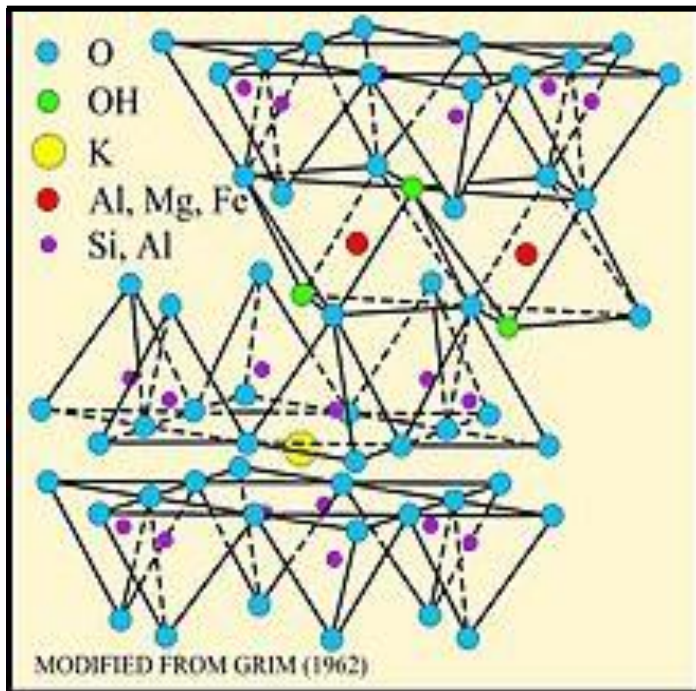
Fig. 2.4 – Structure of Illite Layer

2.2.3   CHLORITE

Chlorite naturally occurs in a variety of forms and in different locations. It is commonly found in igneous rocks as an alteration product of mafic minerals such as biotite. It is a common metamorphic mineral, usually indicative of low-grade metamorphism and is associated with hydrothermal ore deposits. Chlorites have a tetrahedral-octahedral-tetrahedral sandwich structure, commonly referred to as talc layer (Fig. 2.5). Chlorite is very soft and can be easily scratched.

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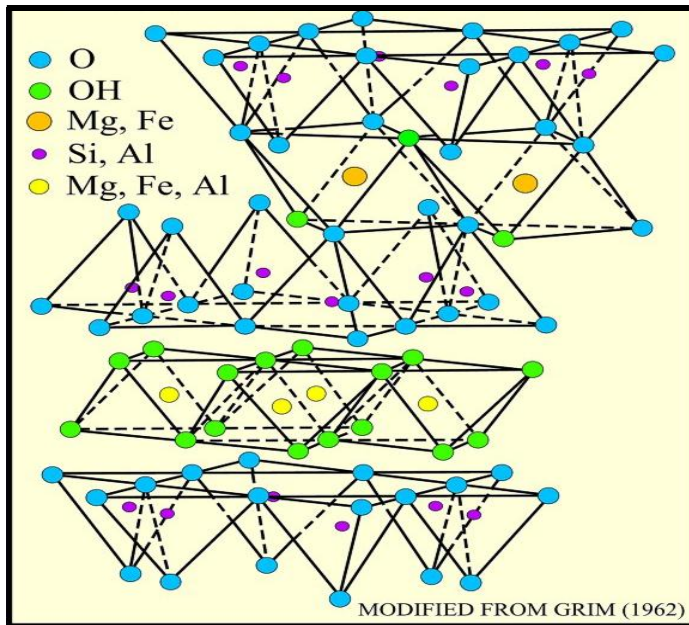
Fig. 2.5 – Structure of Chlorite Layer

2.2.4 SMECTITE

Smectite is the main constituent of the volcanic ash weathering product, bentonite. The water content is variable and it increases greatly in volume when it absorbs water. It has two (2) tetrahedral sheets sandwiching a central octahedral sheet. Smectite is a very soft mineral that typically forms in microscopic crystals (Fig 2.6). Its cation exchange capacity is higher than that of Illite.
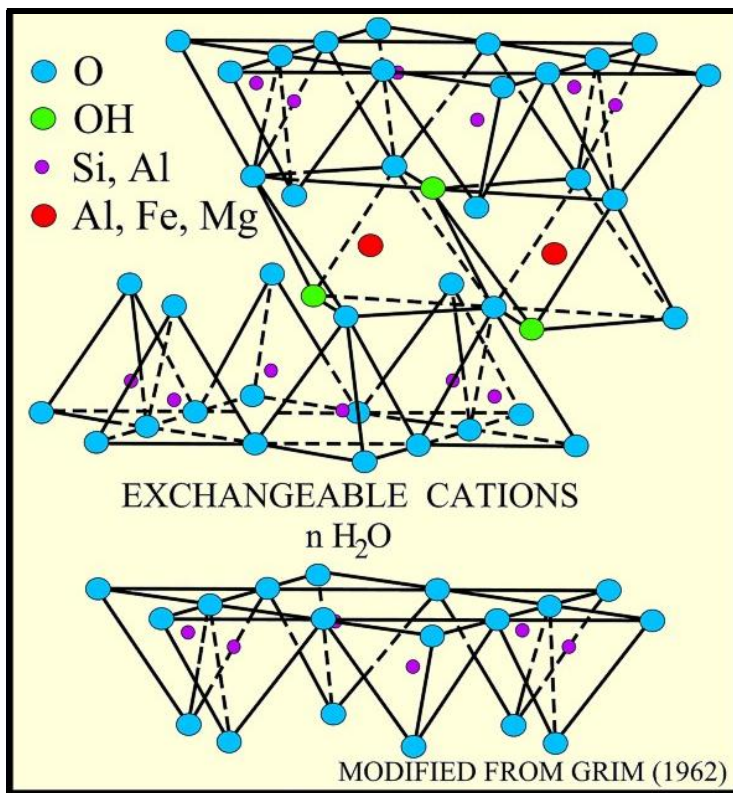
Fig. 2.6 – Structure of Smectite Layer

Table 2.1 – Silicate Clay Mineral Groups

Group	Layer Type	Layer Charge (x)	Chemical Formula
Kaolinite	1:1	<0.01	$Al_2Si_2O_5(OH)_4$
Illite	2:1	1.4-2.0	$(K,H_3O)(Al,Mg,Fe)_2(Si,Al)_4O_{10}[(OH)_2,(H_2O)]$
Chlorite	2:1	Variable	$(Mg,Fe)_3(Si,Al) O_{10}(OH)_2 \cdot (Mg,Fe)_3(OH)_6$
Smectite	2:1	0.5-1.2	$(Na,Ca)_{0.33}(Al,Mg)_2(Si_4O_{10})(OH)_2 \cdot nH_2O$

*The Chemistry of Soils – Oxford University Press

2.3   EFFECTS OF LOW SALINITY AND HIGH PH FLUIDS

Fines migration, which is considered a damage mechanism, involves the movement of rock particles through and within the pore matrix of the rock. Critical salt concentration (CSC) is said to be the concentration of the flowing solution above which there will be no damage due to changes in salt concentration. It is also defined as the salt concentration below which there is loss of permeability (Bishop S. R. 1997). Studies by Khilar and Fogler (1984) explore the importance of CSC by conducting experiments on reservoir core samples and switching the flow from salt water to fresh water. This switch caused the release of clay particles from the pore wall which migrated in the direction of the flow, eventually getting trapped at the pore throats which resulted in blockage, thereby decreasing permeability.

In this case, permeability reduction is dictated by the detachment of clay particles from the surfaces which are afterwards plugged in narrow pore throats. The evidence of the flow of fresh (low salinity) water causing release of clay particles strongly indicates that the release phenomenon is dependent on salt concentration. This detachment is governed by the balance of Van der Waal's force of attraction and electrostatic force of repulsion between the surface and clay particles.

A vital process that governs this occurrence is the exchange of hydrogen ions. Studies done by Mohan, Vaidya et al. (1993) show that when the salt concentration is decreased, a pH transient is set up in the core. Speedy reduction in salinity causes the transient to resemble a sharp wave with peak attaining values of pH $\sim$ 10.5 (for injection of deionized water at a neutral pH). This increase in pH incites clay particles to develop high negative potentials, causing them to detach from the surface and migrate in the direction of the flow where they plug the pore throats Gdanski, R. 2002). These studies show that the dispersion of clay particles is minimized at low pH, also leading to the prevention of damage during water shock, with acidic solutions.

It was observed that the double layer repulsion charge on a clay particle increased with an increase in pH and a decrease in salinity (El-Monier and Nasr-El-Din 2011). The fines detaching from the pore walls, becoming mobile in the injected fluid, and leading to significant loss in permeability is as a result of this increase in repulsion.

2.4   EFFECT OF HIGH TEMPERATURE

Temperature is an important factor for rock/fluid interactions which governs the stability of colloidal suspension of clay particles. Schembre et al. (2006) showed that permeability reduction is observed with temperature increase and fines migration occurs repeatedly at a particular temperature that varies with solution pH and ionic strength. It was found that fines release from pore walls takes place under conditions of elevated temperatures, high pH, and reduction in salinity (Byrne and Waggoner 2009, Young, McLaughlin et al, 1980). A rise in temperature increases the value of the zeta potential (the potential difference between the dispersion medium and the stationary layer of fluid attached to the dispersed particle) and proffers to the dispersion of clay particles (Tchistiakov 2000).

It was also observed that the forces between the clay and surface become repulsive at temperatures higher than room temperature. A high percentage reduction in permeability was noticed when fines are collected in the effluent samples.

The stability or detachment of clay particles in a reservoir formation is determined by the balance of forces acting on the clay particle in the reservoir. Experimental studies by Musharova, Mohamed et al. (2012) showed that the application of the DLVO theory to clay-matrix systems identified double-layer repulsion forces, among other existing attractive and repulsive forces, as most affected by temperature change.

3. CAPILLARY SUCTION TIME (CST) TEST

3.1   INTRODUCTION

Clay stabilizers play a major role in mitigating fines migration and clay swelling, which in turn increases the rate of production in hydrocarbon producing wells. Capillary Suction Time (CST) is a filtration method used in determining the effectiveness of surfactants and polymers in preventing the swelling of clays. The CST testing is a moderately rapid method of tests used to determine the sensitivity of rock core samples to potential base fluids for operational purposes. The CST test acts as a screening test which aids in narrowing down the types of clay stabilizer concentrations to be further tested for use in the industry.

The Capillary Suction Time (CST) Test is a method used to compare the effects of aqueous fluids on the tendency for clay swelling and/or dispersion. The test gives the time of movement of a water front between two (2) electrodes. It is composed of 2 separate components: the acrylic filtration unit with the electrodes and a timer. The CST automatically measures the time for filtration to advance between the two (2) electrodes. The CST studies the filtration of an aqueous system utilizing the capillary suction pressure of a porous paper to affect the filtration rate. The suspension is filtered under the effect of capillary pressure. The rate at which the filtrate is absorbed away from the suspension is determined by the degree of stabilization of the clays in the sample. The measured time of the movement of the water front is related to the ability of the fluid to flocculate clays in the sample. The longer the time of the water front movement, the higher the water sensitivity of the sample, that is, the higher the flocculation. In other words, the longer the time of the water front movement, the poorer the clay control of the fluid.

Both inorganic salts and polymers were used in this study. Results showed that the use of 4 wt% KCl worked well in mitigating clay particles to ease fluid flow, but this is more

on a temporary basis. At 2 wt%, the inorganic polymer compound, Clay Secure A (CS-A) was also seen to work effectively. Being a small scale test, in determining the potency of the clay stabilizer using the CST, the use of at least 1 wt% should show significant effect on the clay compared to control test results gotten without the use of the stabilizer. (Berry et al. 2008; Howard et al. 2012; O'Neil et al. 2013)

3.2   EXPERIMENTAL STUDIES

This is the set-up of the CST consisting of two electrodes located 0.5 cm and 1.0 cm from the edge of the funnel. The set-up is connected to a timer. Fluid contact with the first electrode starts the timer while fluid contact with the second electrode stops the timer. Fig. 3.1- shows a schematic diagram of the CST set-up.
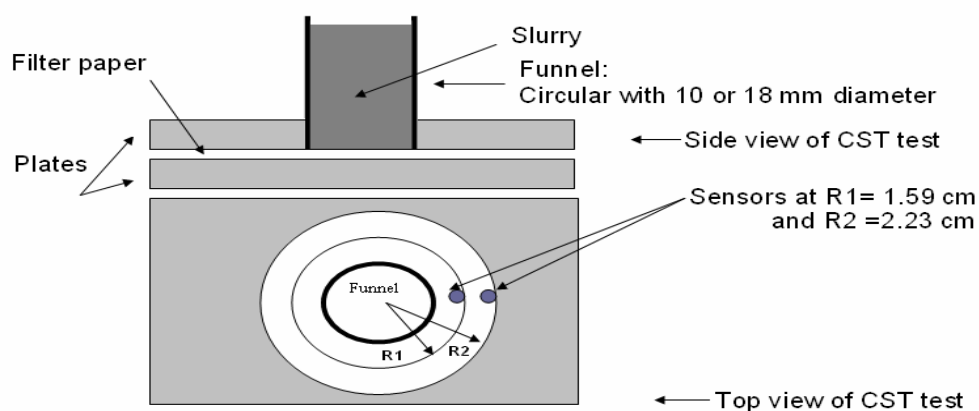
Fig. 3.1 – Schematic Diagram of Capillary Suction Timer

3.2.1 SAMPLE PREPARATION

Bentonite clay sample was used in this stage of the experiment. Inorganic salts and CS-A are prepared at concentrations ranging from 0.1 to 5 wt%.

The choice of a cationic inorganic polymer (CIP) as a clay stabilizer of reference is because of its relative affordability and its ease of application in the oil field, making it possible for large areas of the formation to be effectively treated.

3.2.1.1 BENTONITE

Bentonite is impure clay consisting mainly of montmorillonite. It is an absorbent aluminum phyllosilicate (Casás, L. M., M. Pozo, et al. 2013). Bentonite is usually formed from weathering volcanic ash, mostly in the presence of water. Two main classes of bentonite exist for industry purposes namely; sodium (Na) bentonite, and calcium (Ca) bentonite (Fig. 3.2).

Sodium bentonite expands when wet, absorbing much water in its dry mass. It is often used as a constituent of drilling mud for oil and gas wells because of its excellent colloidal properties.

Calcium bentonite is known for its adsorbent tendency of ions in a solution. It can be converted to sodium bentonite, which is known as sodium beneficiation or sodium activation.
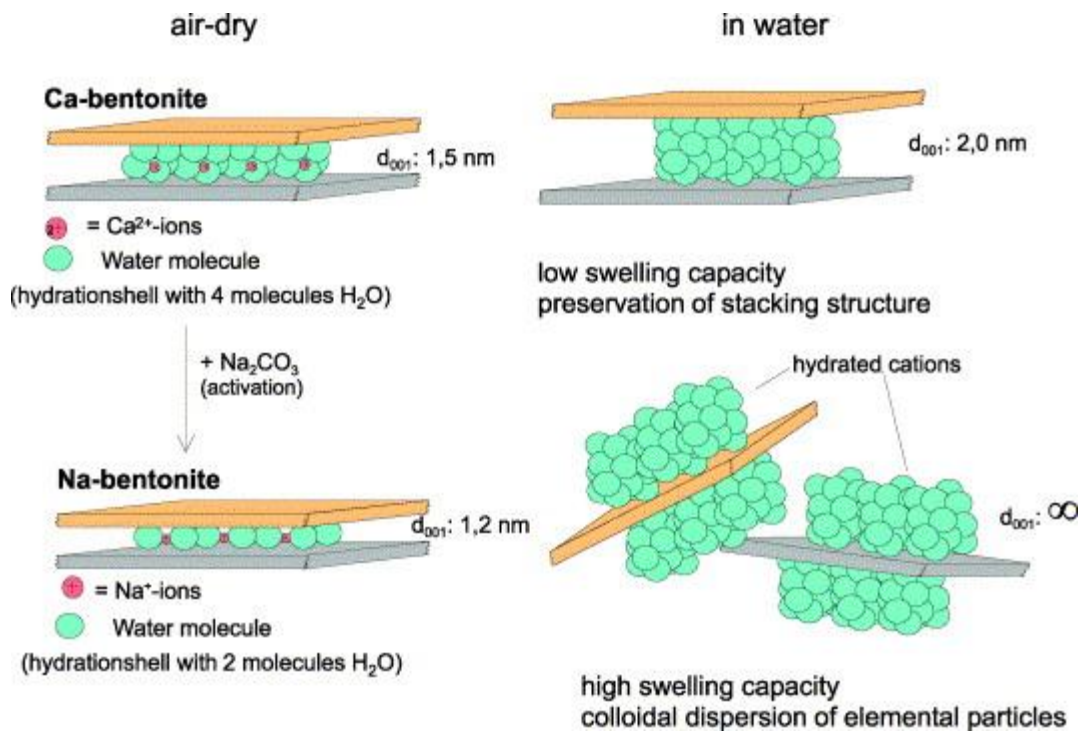
Fig. 3.2 – Behavioral Structures of Bentonite

3.2.2   TEST RUN

Deionized (DI) water alone with the clay sample is run as a standard test to determine if the clay sample requires the need for the addition of the stabilizer.

Ten (10) grams of the crushed sample is measured out and put in a beaker with 'x' wt% of the clay stabilizer plus DI water (100 ml) and mixed for 5 mins (or until an even slurry is attained) with a magnetic stirrer. The mixer is stopped and 5 ml of the slurry is injected in the funnel which rests on standard porous filter paper. Tables 3.1 and 3.2 show the materials and properties used for the experiment respectively.

The same procedure is followed using potassium chloride (KCl), choline chloride, and CS-A. (E.g. DI water + 10g bentonite + 2 wt % KCl)

Capillary Suction Test Timer (Fig. 3.3) from OFI Testing Equipment Inc. (Ofite) was used in these series of experiments with Standard CST Paper; Whatman #17; Chromatography Grade .

Fig. 3.3 – CST Timer

Table 3.1 –Materials used for Capillary Suction Time (CST) Test

Equipment	Stabilizers
Magnetic stirrer	KCl
Filter Paper	Choline chloride
Beaker	CS-A
Weighing scale	
Pipette	
Capillary Suction Time Tester	

In addition to bentonite and DI water

Table 3.2 – Properties of Stabilizer used – at 77°F

CS-A
Density, g/cc………………………………………………………………1.36
pH……………………………………………………………………2.29
Viscosity, cp………………………………………………………14.87

Fig. 3.4 – CS-A + Clay (mixing)

Fig 3.4 shows the evenness of the mixing slurry used for the experiment.

Fig. 3.5 – CS-A + Clay (settled)

Fig. 3.5 shows the settled slurry mixture with the effective clay stabilizer.

3.3   RESULTS
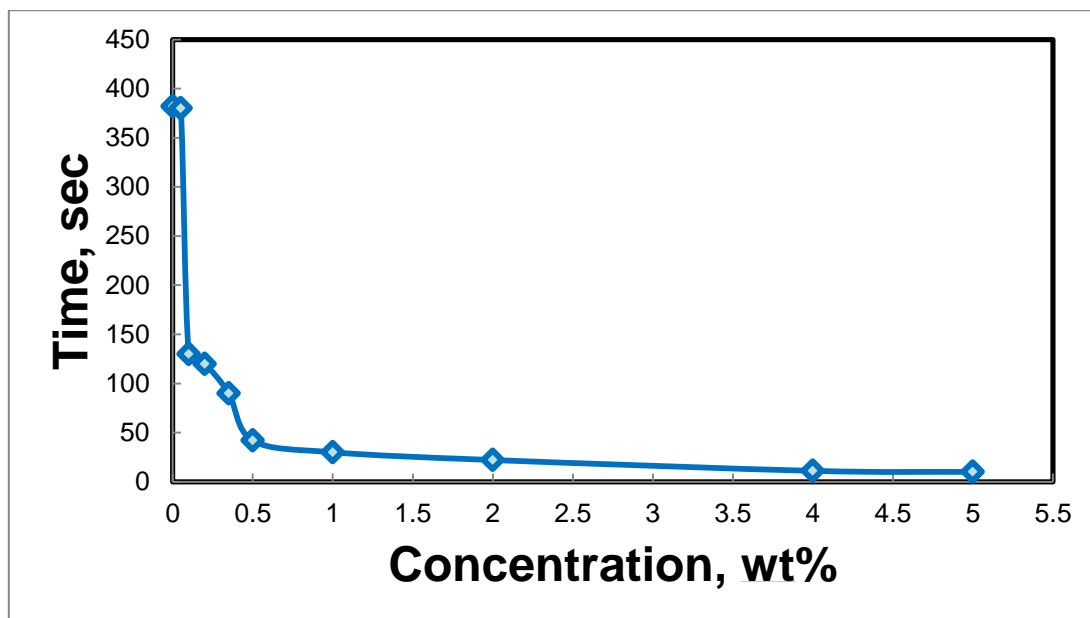
Fig. 3.6 – Capillary Suction Time (CST) test on KCl
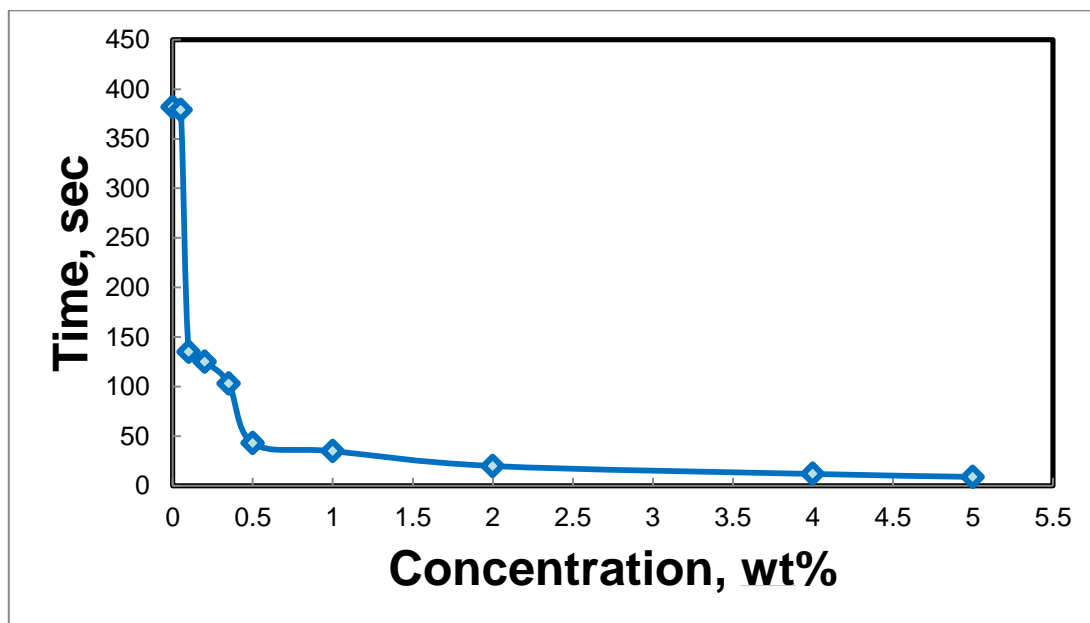
Fig. 3.7 – Capillary Suction Time (CST) test on Choline Chloride
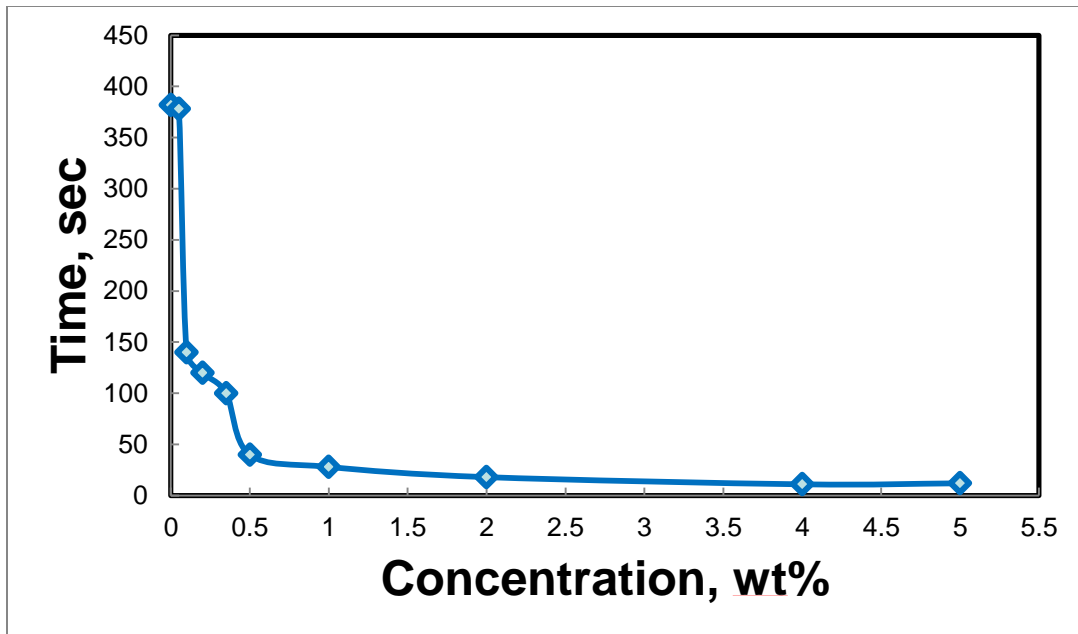
Fig. 3.8 – Capillary Suction Time (CST) test on CS-A

- The CST does not determine the level of concentration of the stabilizer, it only determines if the stabilizer should be used when treating the formation. Figs. 3.6 to 3.8 show the effectiveness of the clay stabilizers

- With the use CST for clay stabilizer comparison, the use of at least 1 wt% should show significant effect on the clay compared to control test results gotten without the use of the stabilizer.

- As little as 1 wt% of both KCl and choline chloride showed to be very effective but this is more of a temporary effect.

- CS-A also showed good comparison and a positive effect in coagulating clay particles to enable fluid flow and this polymer can be used to produce a more permanent effect.

4. CLAY STABILIZER

4.1   INTRODUCTION

Clay stabilizers are chemical additives used in stimulation treatments to prevent the migration or swelling of clay particles in the reaction to water-base fluid. These clay stabilizers are routinely included in aqueous stimulation and completion fluids in order to prevent damage to the formation. These clay stabilizing additives, as mentioned earlier, can either be of temporary protection or permanent protection (Baltz T. H, R. E Himes et al. 1989). When clay stabilizers are used in stimulation operations, they should be chemically stable in acids and high pH environments for fracturing treatments. Various clay stabilizers are used to prevent the damage caused by these clay minerals (Bazin B, E. Souto et al. 1994). Water sensitivity of sandstone formations play an important role in the ability of clays to exchange cations on the surface (Thomas and Crowe 1978). Experimental studies show that exposure to monovalent cations (Na^+, Li^+) increases the tendency of clays to migrate or swell, while exposure to polyvalent cations (Ca^{++}, Mg^{++}, Zr^{+4}) decreases their water sensitivity (Thomas and Crowe 1978).

The mechanism of clay stabilization with the use of Zirconium (Zr^{+4}) and Aluminum (Al^{+3}) is initiated by hydrolyzing to yield highly charged oligomers that permanently exchange with cations on the surface of the clay. This exchange causes the clay particles to become insensitive to other cations, e.g. Na^+, that would normally cause migration or swelling (Bennion D. B, F. B. Thomas et al. 1992).

Clay stabilizing additives were given a comprehensive review by Zhou, Gunter et al. (1995) where clay stabilizers were divided into the following classes:

- Simple inorganic salts (KCl, NaCl)
- Cationic inorganic polymers (ZrOCl)
- Simple organic compounds (di-2-methylbutylammonium chloride)
- Organic cationic polymers (polydiallaydimethylamine chloride)

- Anionic organic polymers (carboxymethylcellulose)
- Non-ionic organic polymers (polyacrylamide)

Clay stabilizers should be chemically stable (in acids used for stimulation and high pH environments) and thermally stable under reservoir pressure and temperature. Clay stabilizers must also meet the following criteria in order to effectively stabilize fine particles (Nasr-El-Din, Al-Mulhem et al. 1999):

i. They must be non-wetting on the sandstone surfaces to reduce water saturation.
ii. They must be cationic (have positive charges) to neutralize the negative charges of clays.
iii. They must have low uniform molecular weight (to prevent plugging of pores).
iv. They must resist wash-off by fluids flowing through the reservoir (e.g. brine)

According to Zhou, Gunter et al. 1995, the economic success in applying clay stabilizers is entirely based on the understanding of the formation, possible formation damage, and choice of clay stabilizer. For the efficient and successful use of the clay stabilizers, it is very vital to evaluate the applicability and limitations of such chemical compounds.

CS-A is an Al/Zr compound which falls into the class of Cationic Inorganic Polymer (CIP). It is effective in preventing both fines migration and clay swelling, and its selection as a case study is as a result of its relatively affordable nature in addition to its ease of application in the field, thereby making it very possible for large areas of the formation to be effectively treated (Bedrikovetsky, P. G, A. V. Junior et al. 2011). CIP's are effectively used as pre-treatment for thermal recovery processes and as post-flush for acid treatment (Zhou, Gunter et al. 1995).

From experiments done in chapter 3 using the capillary suction time (CST) test, which is a screening test, it was decided to use 2 wt% of the clay-stabilizing additive (CS-A) for further laboratory experiments.

4.2   CORES AND SOLUTION PREPARATION

4.2.1   MATERIALS

Bandera sandstone cores, 6 by 1.5 in. with permeabilities ranging from 13 to 33 md were used for these experiments.

Sodium Chloride (NaCl) inorganic salt was used to prepare the brine at a concentration of 5 wt%. Previous experimental studies show the critical salt concentration placement to be between 3 and 4 wt%. The use of 5 wt% NaCl was to give a safe platform to the experiment so as not to induce fines migration or clay swelling prior to the main run of the experiment. Table 4.1 shows the mineral composition of the Bandera sandstone core sample used. Figs. 4.1 and 4.2 show the Scanning Electron Microscopic and Spectrum Images of the Bandera sandstone core before treatment.

Table 4.1 – Mineral Composition of Bandera Sandstone Core Sample

Mineral	Composition
Quartz	57
Dolomite	16
Calcite	-
Feldspar	-
Kaolinite	3
Illite	10
Chlorite	1
Ca-Feldspar	12
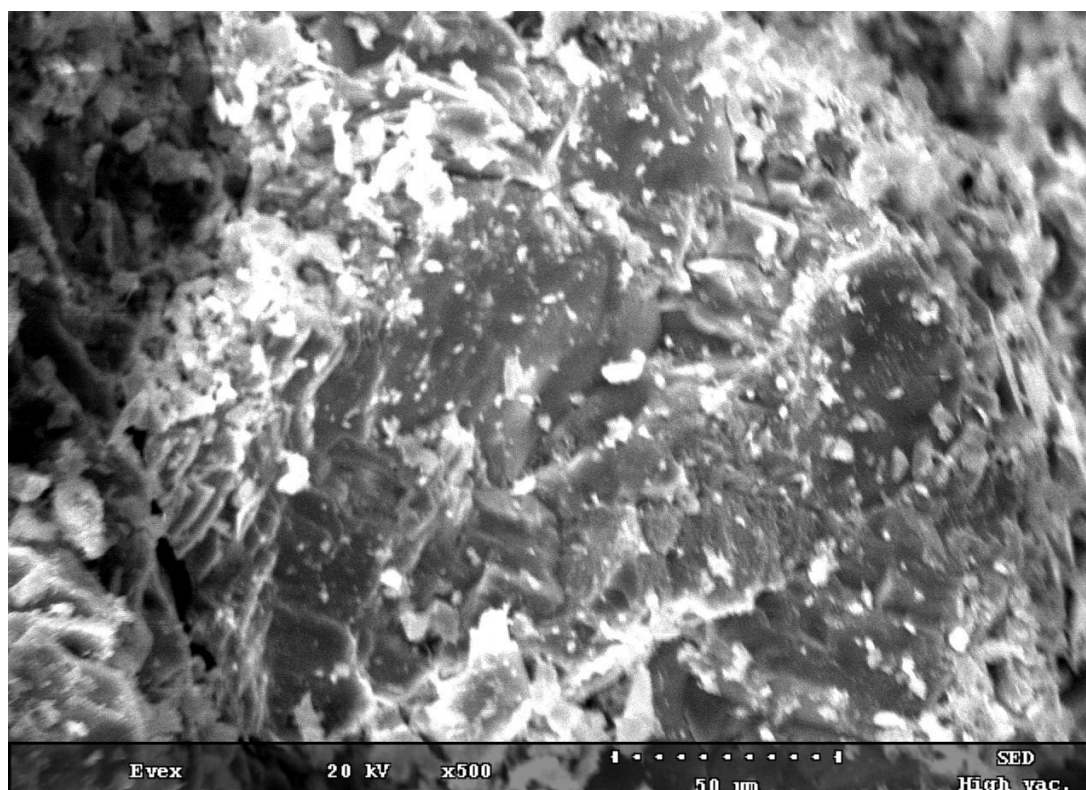
Fig. 4.1 – Scanning Electron Microscope Image of the Bandera Sandstone Core before Treatment
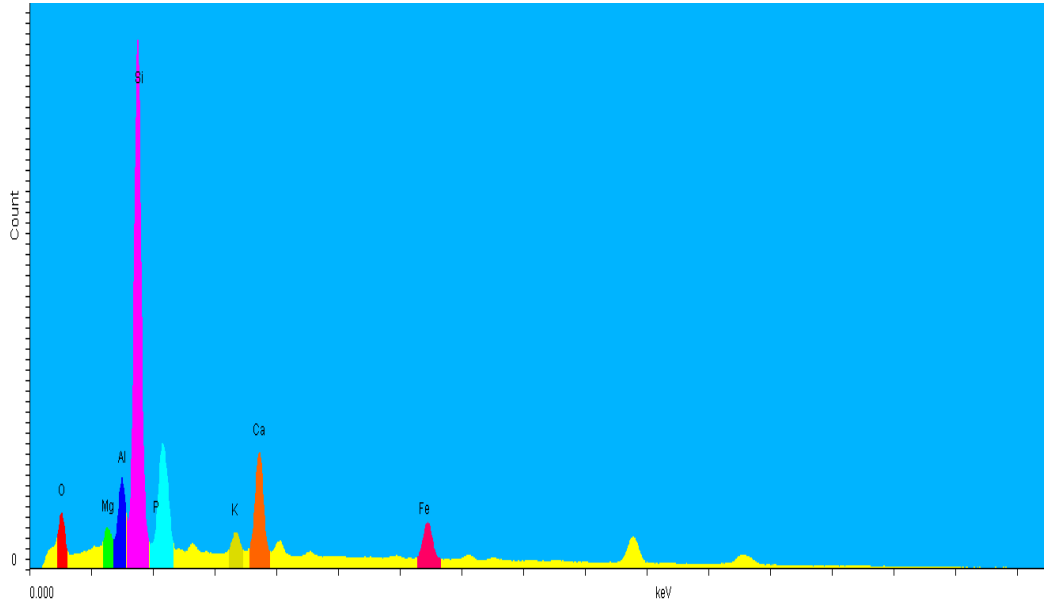
Fig. 4.2 – Spectrum Image of Elements in Core before Treatment

4.2.2   CORES PREPARATION

Cores were dried in the oven at 250°F for 6 hours, weighed, saturated with 5 wt% NaCl brine, and weighed again. The difference between the saturated and dry weights was used to calculate the porosity.

$$V_p = \frac{W_{wet} - W_{dry}}{\rho}$$

Where:

V_p: pore volume, cm^3; ρ: brine density, g/cm^3

Initial permeability was measured at room temperature by injecting 5 wt% NaCl brine. Darcy's equation for laminar flow was used:

$$k = 122.08 \frac{L\mu}{\Delta p\, d^2}$$

Where:

k: permeability, md; L: core length, inch, d: core diameter, inch; q: flow rate, cm^3/min;
μ: viscosity, cp; Δp: psia

4.2.3   SOLUTION PREPARATION

One stage of the experiment is done using 2 wt% CS-A prepared in 5 wt% NaCl brine, while a comparison stage of the experiment is done using 2 wt% CS-A prepared in DI water. Table 4.2 shows the properties of the stabilizing solutions used during the experiments.

Table 4.2 – Properties of Stabilizing Solutions at 77ºF

Properties of CS-A as received	
Density, g/cc…………………………………………………………………	1.36
pH……………………………………………………………………………	2.29
Viscosity, cp…………………………………………………………………	14.87
Al conc, ppm………………………………………………………………...	172000
Zr conc, ppm………………………………………………………………...	50490
DI water	
Density, g/cc…………………………………………………………………	0.998
pH……………………………………………………………………………	7.0
Viscosity, cp…………………………………………………………………	1.08
5 wt% NaCl brine	
Density, g/cc…………………………………………………………………	1.034
pH……………………………………………………………………………	5.7
Viscosity, cp…………………………………………………………………	1.17
2 wt% CS prepared in brine	
Density, g/cc…………………………………………………………………	1.04
pH……………………………………………………………………………	4.2
Viscosity, cp…………………………………………………………………	1.123
2 wt% CS prepared in DI water	
Density, g/cc…………………………………………………………………	1.004
pH……………………………………………………………………………	4.24
Viscosity, cp…………………………………………………………………	1.024

4.3   COREFLOOD EXPERIMENT

4.3.1   PROCEDURE

Five sets of coreflood experiments were conducted (Fig. 4.3). The first set was done to determine the initial permeability of the Bandera sandstone core. The second set of experiments was conducted to monitor and assess the damage caused by fresh water. The third set of experiments was done to test the effectiveness of the clay stabilizer and also assess its behavior after injecting fresh water. The goal of the fourth set was to determine the final permeability of the Bandera sandstone core. Flow rate used was 5 ml/min was maintained throughout the experiment. This was assumed to be an ideal rate to so as not to induce mechanical fines migration. An additional set of experiments was done to determine the effectiveness of the clay stabilizer after acid treatment with 5 wt% HCl.

The first and fourth sets of experiments were done at room temperature (without any form of added heat), while the second and third were done at a low temperature of 77ºF.

Experiment set # 1 was done by running simple NaCl [5 wt%] brine through the core in the setup at different flow rates to determine its initial permeability. This will then be compared to the final permeability at the end of the entire experiment.

Experiment set # 2 was achieved by injecting brine into the core until pressure drop stabilization was attained. This was followed by about 3 PV of deionized water. The pressure drop across the core was monitored and recorded.

Experiment set # 3 was carried out by initially injecting brine into the core. This was followed by injecting 2 PV of the clay stabilize and then about 10 PV deionized water. The pressure drop was also monitored and recorded.

Experiment set # 4 was also done by running only 5 wt% NaCl brine through the core in the setup at different flow rates so that the final permeability could be measured to

evaluate either an increase or decrease in the core permeability after treatment with the clay stabilizer and subsequent injection of deionized water.

For experiment set # 5, 5 wt% NaCl brine was injected, followed by 2 PV of 2 wt% CS-A, then about 4 PV DI, followed by 2 PV of 5 wt% HCl, then the flow of DI water.
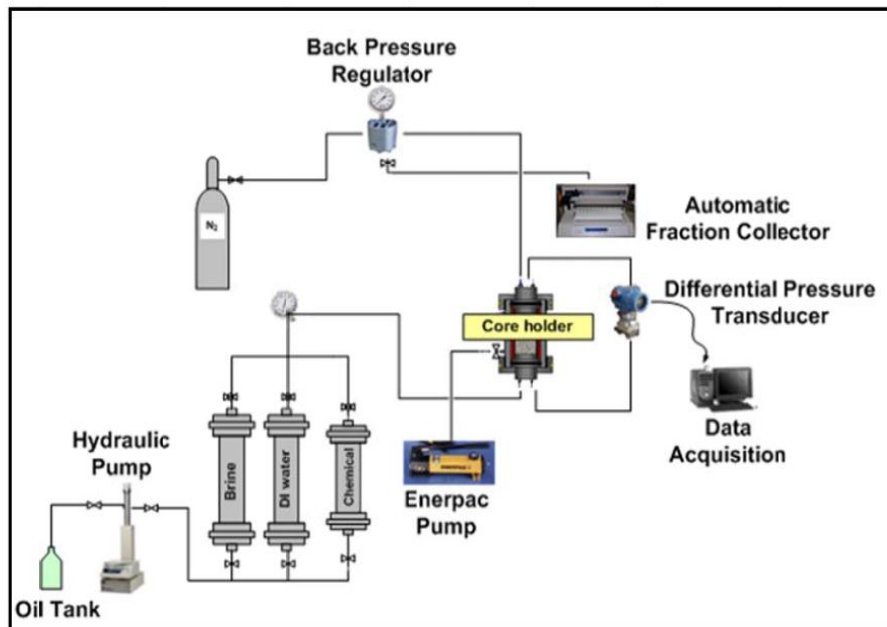

Fig. 4.3 – Coreflood Setup

Experiment set # 2 was done to verify the need for the use of a clay stabilizer in that formation (Fig. 4.4).
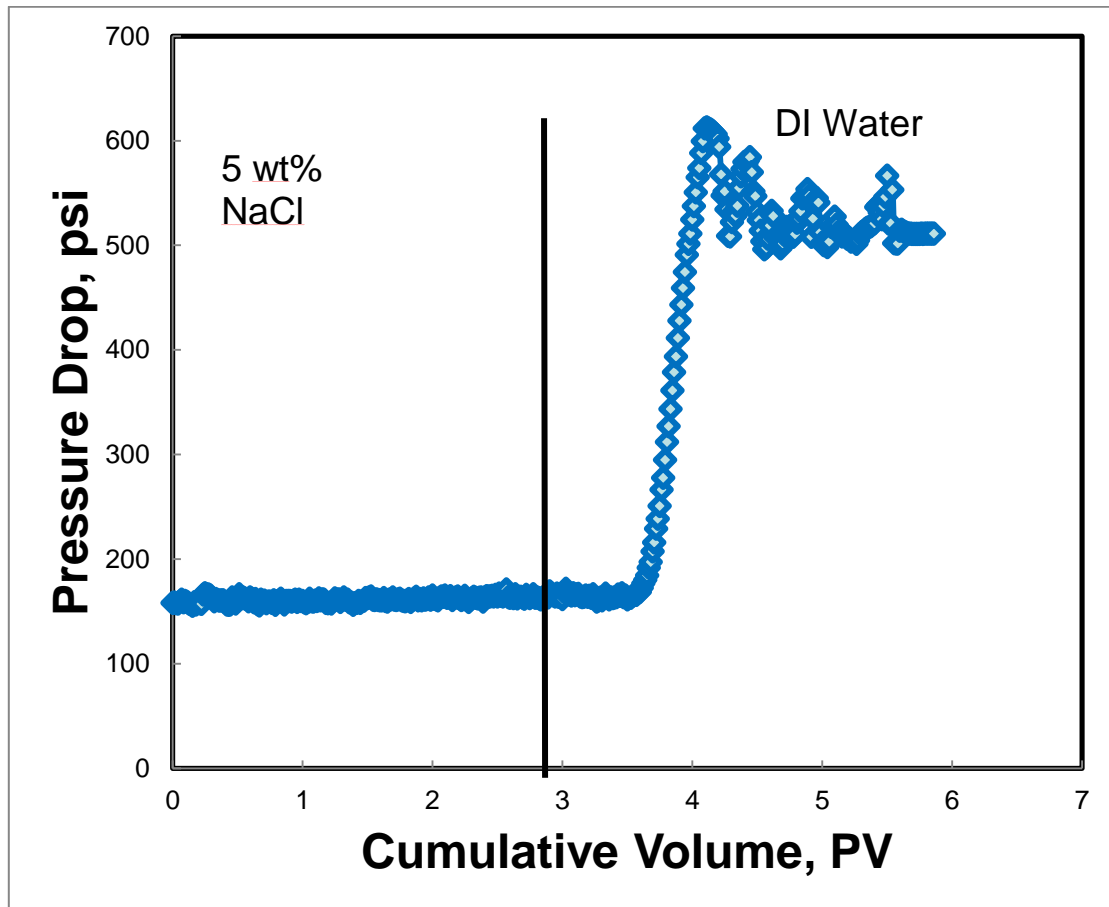

Fig. 4.4 – Pressure drop profile with 5 wt% NaCl, T = 77°F, q = 5 ml/min,

   k_i = 15 md, k_f = 2 md

Fines were noticed from effluent samples collected during the experiment to determine the need for the use of clay stabilizer.

4.4   COREFLOOD RESULTS

Experiment set # 1 indicated a permeability of about 14 md.

From experiment set # 2, there was a constant increase in the pressure drop across the core, indicating fines migration within the core and plugging of pore throats.

For experiment set # 3, results showed the introduction of the clay stabilizer did not significantly increase the pressure drop across the core, which in turn maintained the stability even with the injection of deionized water afterwards. The pressure drop stabilized to about 15 psi.

Experiment set # 4 indicated a permeability of 24 md.

This showed an increase in permeability of about 85% (Fig. 4.5).

The pressure drop profile and permeability measurements show that the clay stabilizer tends to work effectively when prepared in brine.

Fresh water was also used to prepare the clay stabilizer and the results obtained were compared to the results gotten when prepared in brine in order to determine the more effective solution.
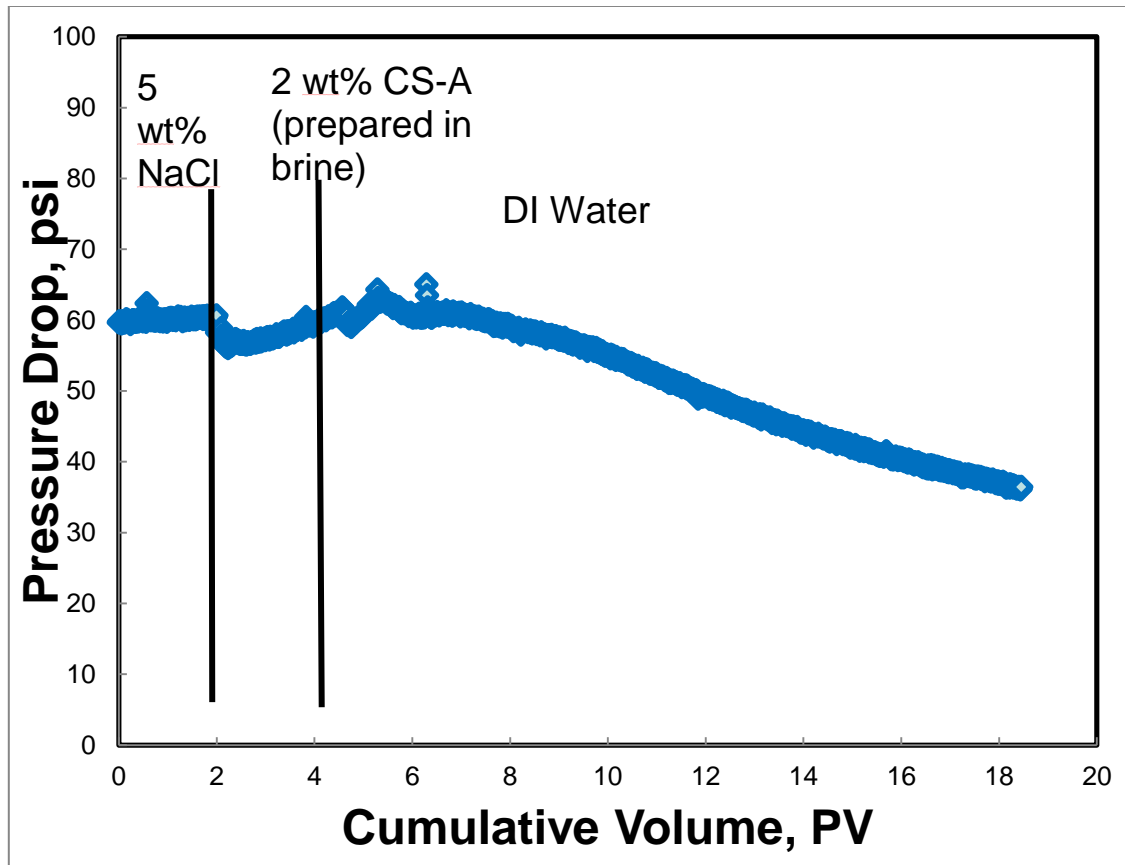
Fig. 4.5 – Pressure drop profile with 5 wt% NaCl (2 PV CS-A), T = 77ºF, q = 5ml/min, k_i = 14 md, k_f = 24 md

4.4.1   ANALYSIS OF CORE EFFLUENT

No fines were noticed in the samples collected during the experiment. Cation concentrations of Al and Zr were measured using Inductively Coupled Plasma (ICP).

4.4.2 INDUCTIVELY COUPLED PLASMA (ICP)

Inductively Coupled Plasma (ICP) is a type of mass spectrometry plasma source in which energy is supplied by electric currents produced by electromagnetic induction (Fig. 4.6). ICP is capable of detecting metal and non-metals at concentrations as low as one part per trillion. With the use of ICP, emission scans of cations in the core effluents were made to determine the identity and quantity of cations removed from the core sample.

The ICP is sustained in a torch that comprises of three (3) concentric tubes. The end of the torch is placed inside an induction coil supplied with electric current. Argon gas is introduced between the two (2) outer most tubes of the torch and an electric spark is applied for a short time to introduce free electrons into the gas stream.

The gas flow passes through the center of the plasma where it forms a channel that is cooler than the surrounding plasma. Samples to be analyzed are introduced into this central channel in a liquid form by passing the liquid sample through. Once in the central channel of the ICP, the sample evaporates and any solids dissolved in the liquid vaporize then break into atoms.
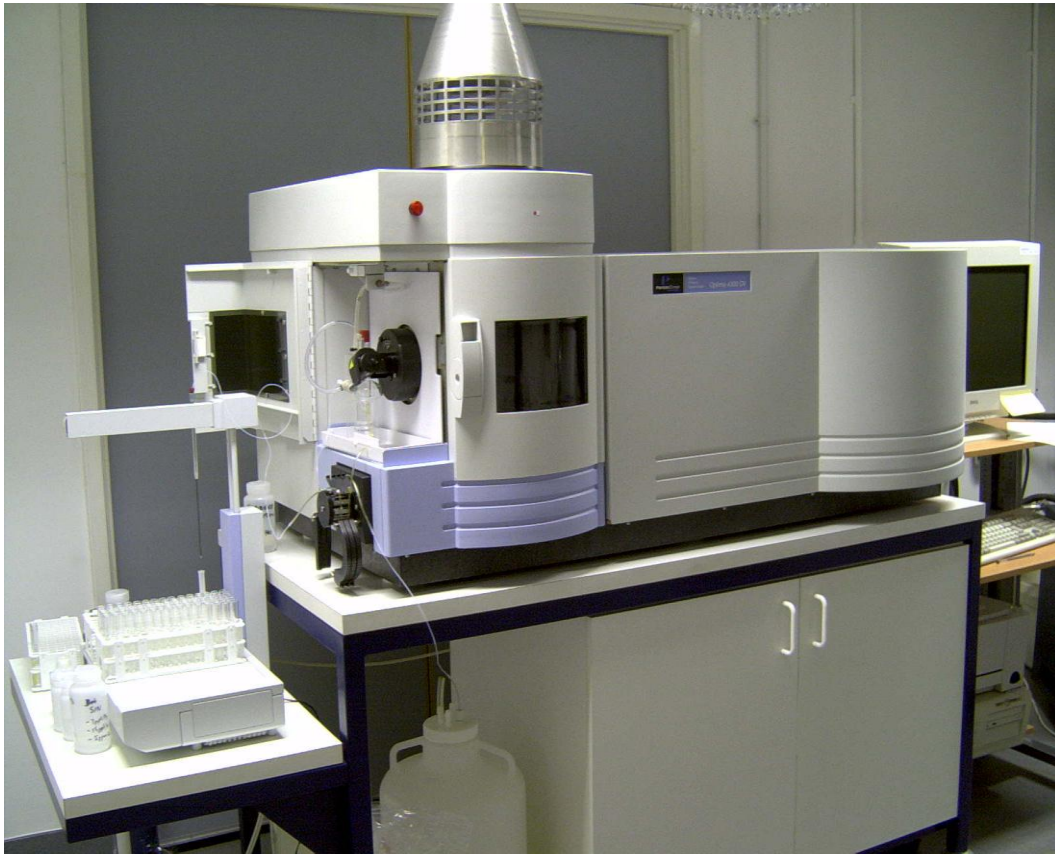
Fig. 4.6 – Inductively Coupled Plasma (ICP)

Effluent samples collected during the coreflood experiment were analyzed using the ICP. Some Al and Zr elements were detected in the ICP, but the remaining amount of Al and Zr in the core was approximately more than 60% (Fig. 4.7).
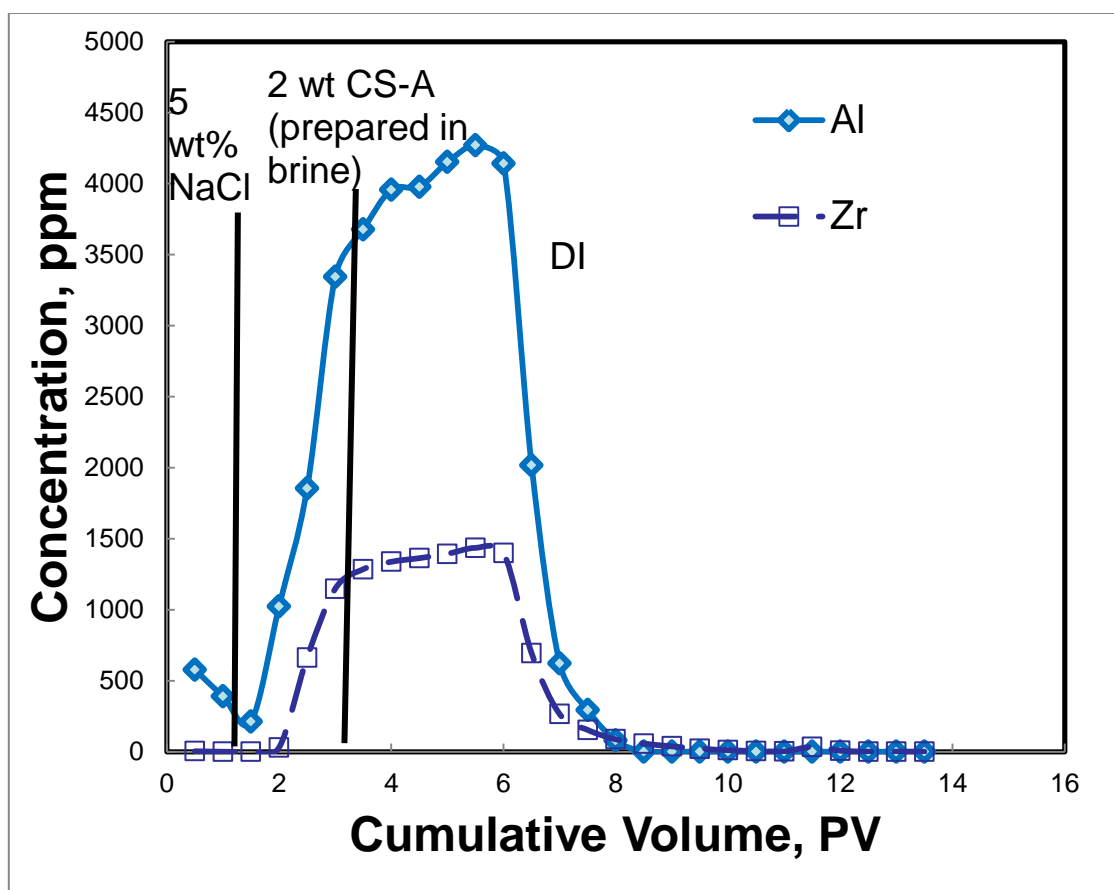
Fig. 4.7 – ICP Analysis – Al, Zr concentrations with 2 wt% CS-A

T = 77ºF
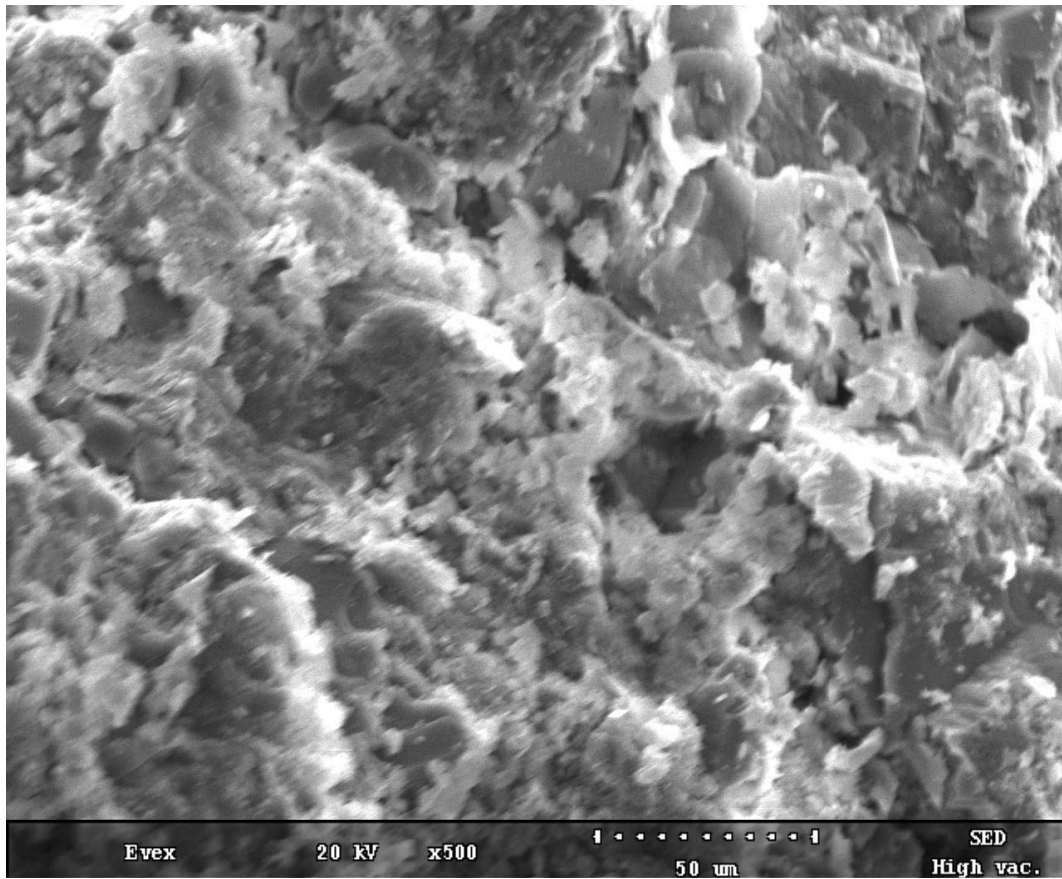
Fig. 4.8 – Scanning Electron Microscopic image of the Bandera sandstone core after treatment
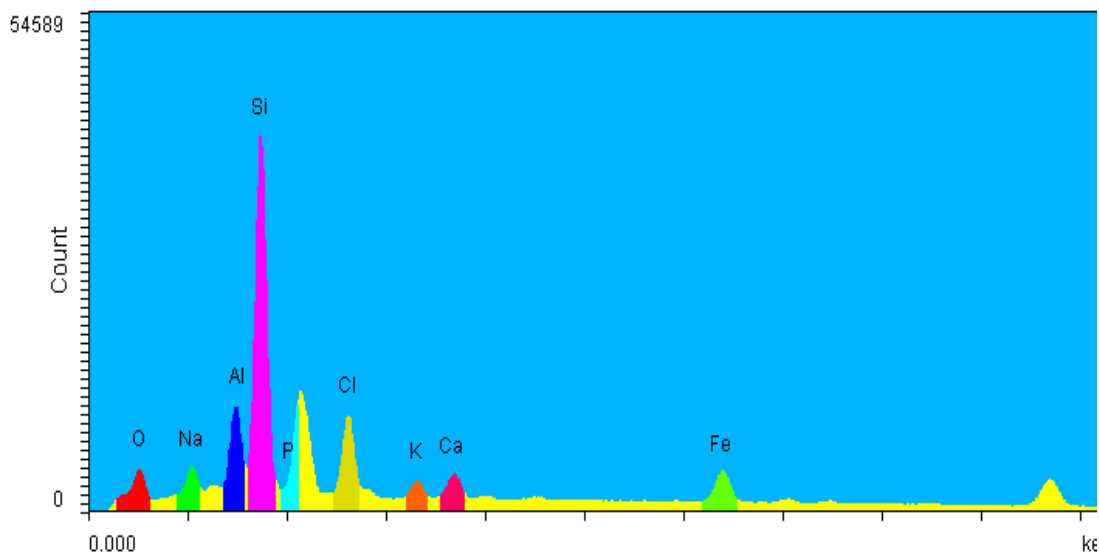
Fig. 4.9 – Spectrum image of elements in the core after treatment

Figs. 4.8 and 4.9 show the Scanning Electron Microscopic and Spectrum Images of the Bandera sandstone core after treatment.

4.5   COMPARISON WITH FRESH WATER BASE

From the sets of coreflood experiments evaluated in the previous section 4.3, the 2 wt% Al/Zr clay stabilizing compound was prepared in 5 wt% NaCl brine. In this section, another four (4) sets of coreflood experiments were conducted to compare the effectiveness of the clay stabilizing compound when prepared in fresh water. The test was also done at 77ºF to maintain the same testing conditions of the previous test sets to get accurate compared results.

4.5.1   COREFLOOD RESULTS

Experiment set # 1 indicated a permeability of about 11.1 md.

From experiment set # 2, a constant increase in the pressure drop across the core was noticed which indicated fines migration within the core and plugging of pore throats.

For experiment set # 3, results showed the introduction of the clay stabilizer significantly increased the pressure drop across the core, which continued increasing following the injection of deionized water afterwards. The pressure drop gauge range was between 1 – 300 psi. Fines were noticed in the samples collected during the coreflood experiment.

Experiment set # 4 indicated a permeability of 5.82 md.

This showed a decrease in permeability of about 47.5% (Fig. 4.10).
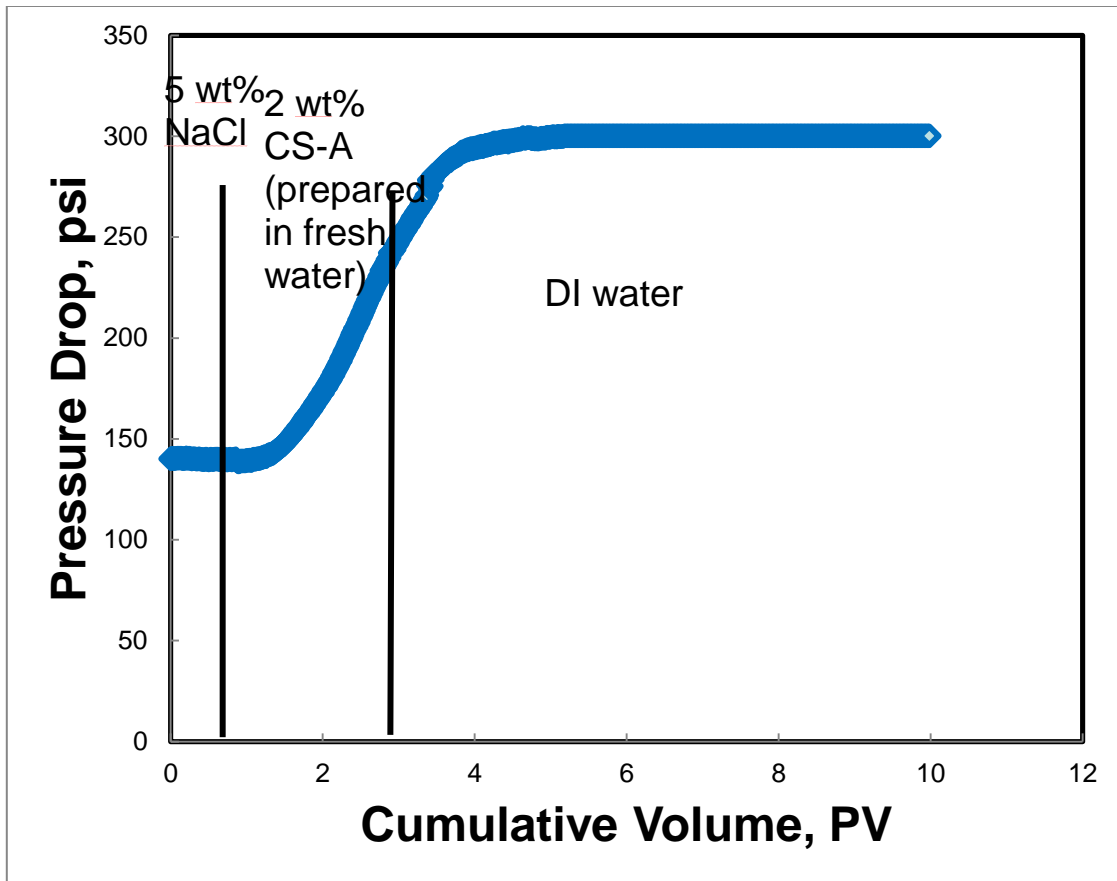
Fig. 4.10 – Pressure drop profile with 5 wt% NaCl (2 PV CS-A), T = 77ºF

q = 5 ml/min, k_i = 11 md, k_f = 5.82 md

4.5.2   ICP ANALYSIS OF SAMPLES

Samples were collected during the coreflood experiment were analyzed using the ICP. Both Al and Zr elements were detected in the ICP, but a great amount of the Al/Zr in the clay stabilizer was retained in the core system (Fig. 4.11).
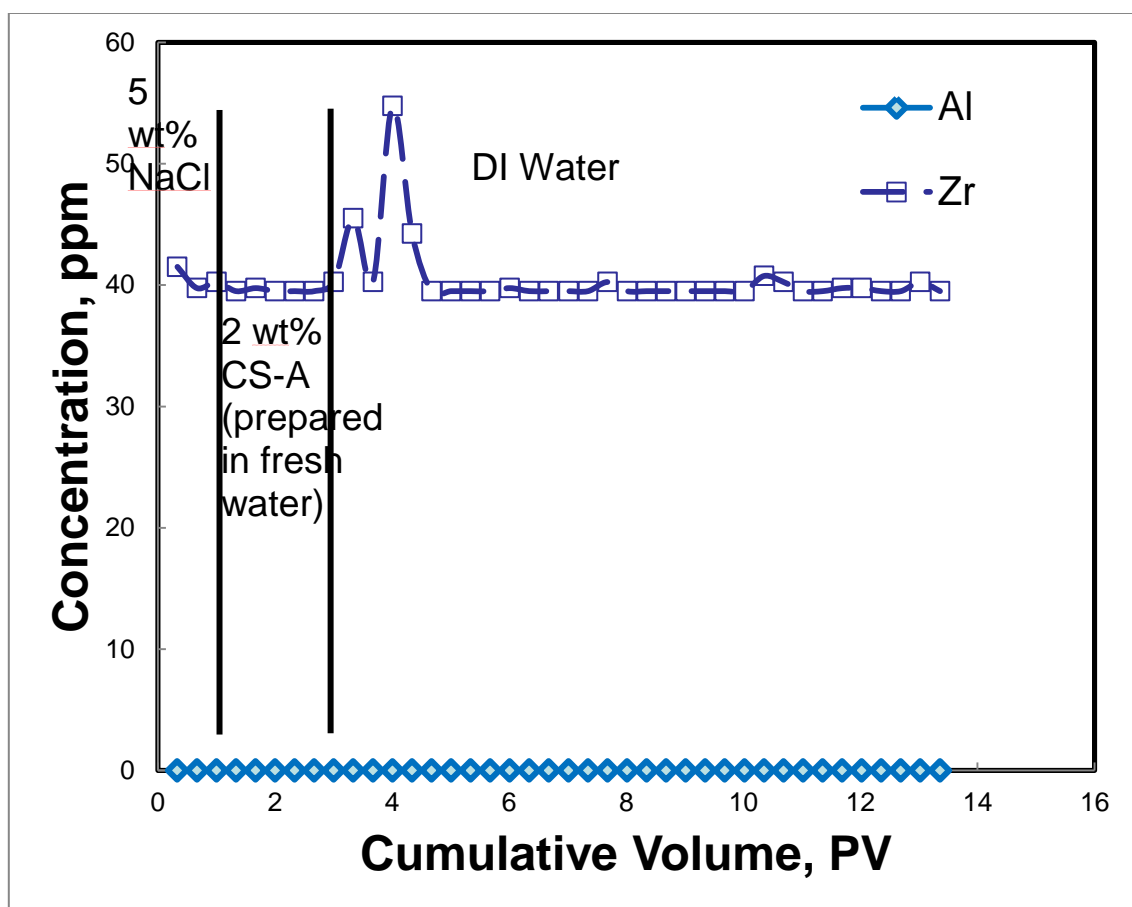
Fig. 4.11 – ICP Analysis – Al, Zr concentrations with 2 wt% CS-A (in Fresh Water)

T = 77°F

4.6   COREFLOOD TEST AT 200ºF TEMPERATURE

Based on the results gotten from previous coreflood experiments indicating that the CS-A clay stabilizer is more effective when prepared in NaCl brine, another experiment was done at a higher temperature to also evaluate the stability of the clay stabilizer.

The CS-A (2 wt% concentration) used for this experiment was prepared in 5 wt% NaCl brine, and the following sets of results were obtained;

Experiment set # 1 indicated an initial permeability of about 22 md.

From experiment set # 2, an increase in the pressure drop across the core was noticed, indicating some sort of instability in the system.

For experiment set # 3, results showed the introduction of the clay stabilizer also increased the pressure drop across the core. Pressure drop increase was also noticed upon the injection of fresh water, but after a while, a sharp decrease in the pressure drop was noticed. This indicated the stabilizer was at work in the system. No fines were noticed in the samples collected during the coreflood experiment.

Experiment set # 4 indicated a final permeability of 24 md (Fig. 4.12).
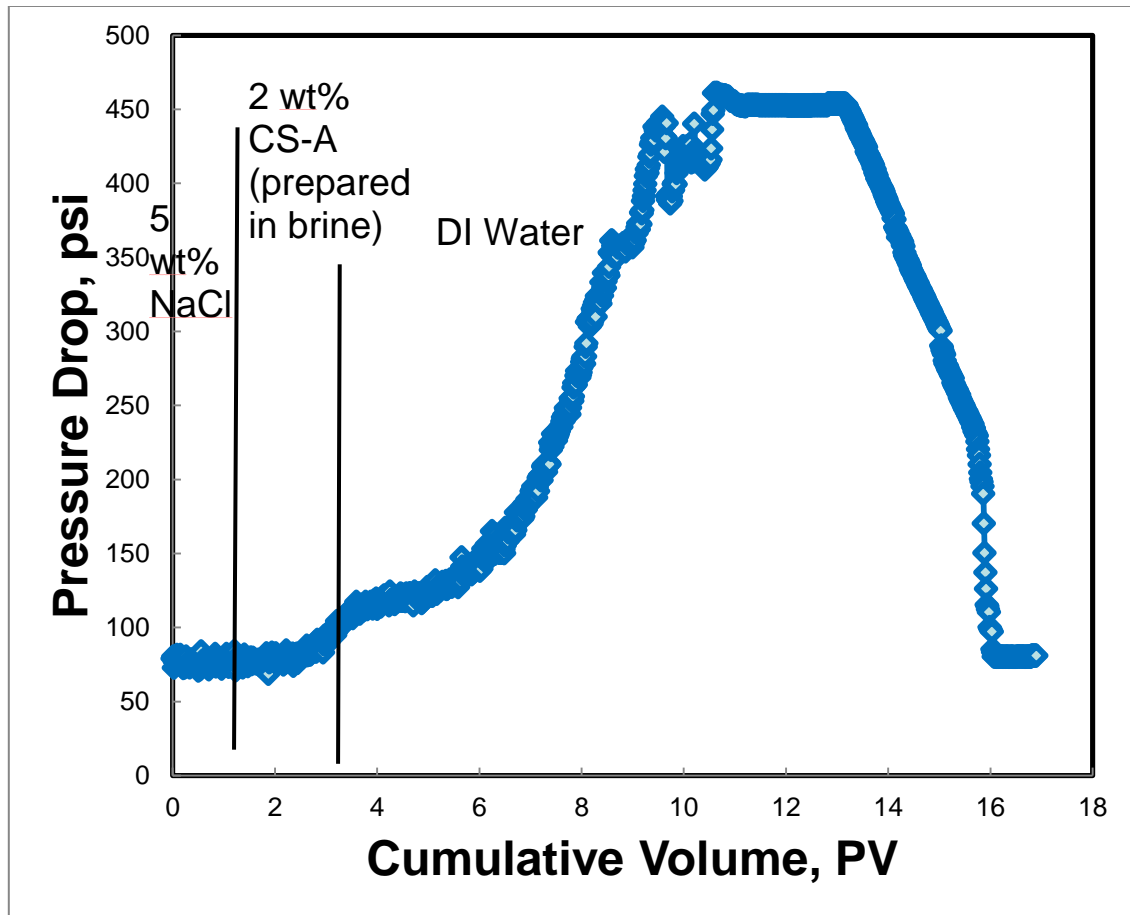
Fig. 4.12 – Pressure drop profile with 5 wt% NaCl, 2 wt% (2 PV) CS-A, T = 200ºF, q = 5 ml/min, k_i = 22 md, k_f = 24 md

ICP Analyses indicating no Aluminum being leached from the core with trace amounts of Zirconium leached from the core (Fig. 4.13).
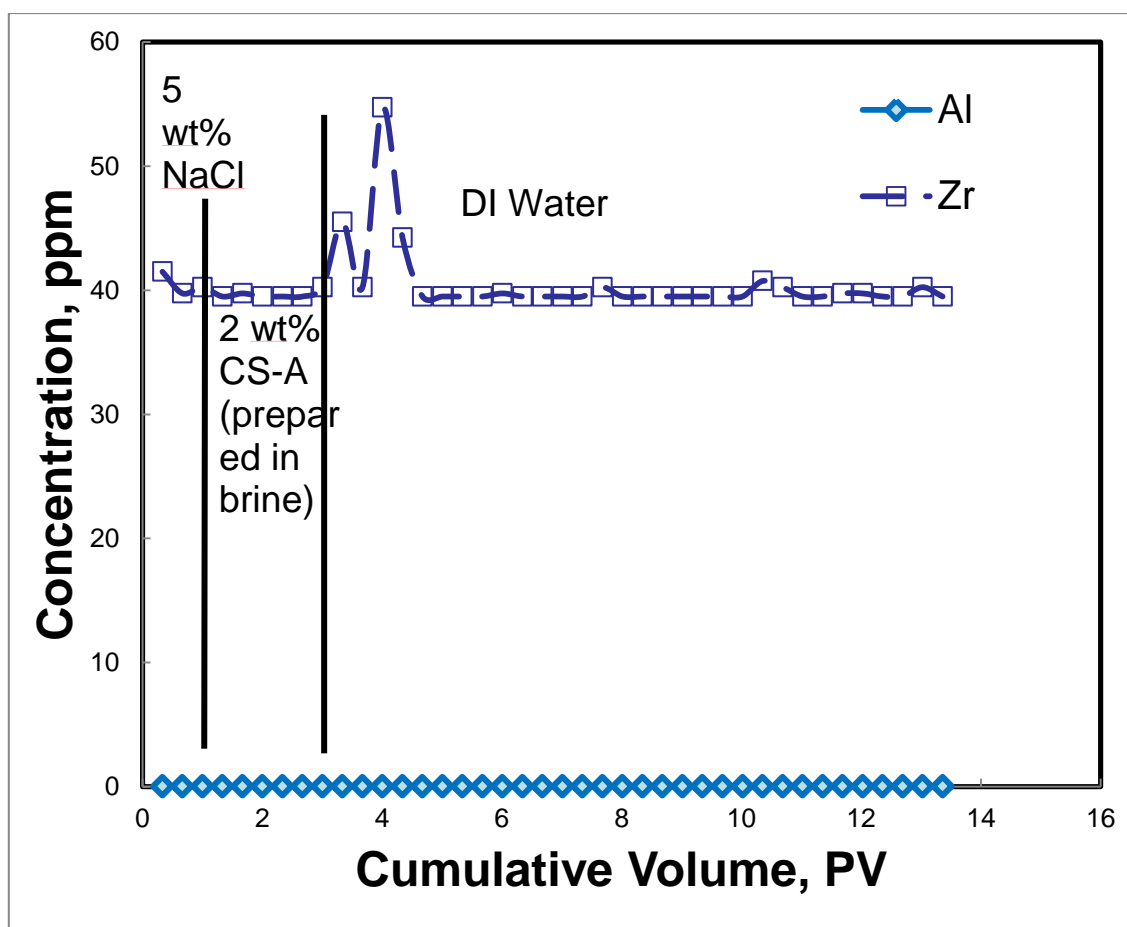
Fig. 4.13 – ICP Analyses – Al, Zr concentrations with 2 wt% CS-A

   T = 200ºF

4.7   STIMULATION TREATMENT WITH ACID

Further experimental testing was done on to study determine the effect of the clay stabilizing (CS-A) solution on the formation after acid (HCl) injection (Kaldayan and Watkins 1990).

The initial permeability of the core was measured to be 17 md. Following the initial flow of 5 wt% NaCl brine through the core, injection of 2 wt% CS-A, then the flow of DI water, 5 wt% HCl was introduced into the system. DI water was once again flowed through the system. Corrosion inhibitor was added to the mixture of HCl to prevent incidences of corrosion.

The pressure drop profile was created and analyzed, indicating an initial increase then a decrease in the pressure drop profile. An increase in permeability was obtained. The final permeability of the core was measured to be 31 md.

No fines were noticed in the core effluent samples collected during the experiment. These effluent samples were analyzed using the ICP which showed no Aluminum was leached from the system and trace amounts of Zirconium was leached.

These results showed that even after acid treatment, the clay stabilizer was retained in the core to keep working effectively (4.14).
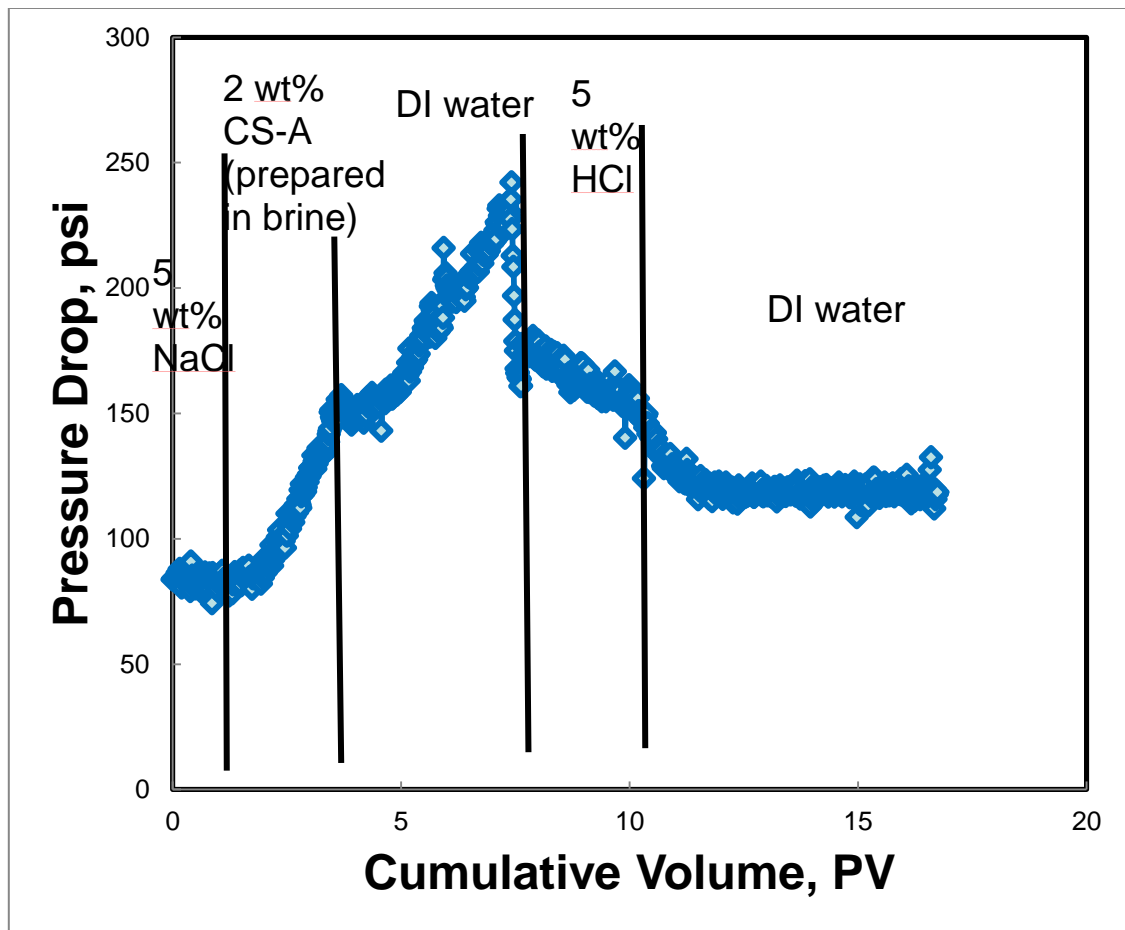
Fig. 4.14 – Pressure drop profile with 5 wt% NaCl, 2 wt% (2 PV) CS-A, 5 wt% HCl (2 PV), T = 300ºF, q = 5 ml/min, k_i = 17 md, k_f = 31 md

ICP Analyses indicating no Aluminum and Silicon were leached from the core, trace amounts of Zirconium also leached from the core, and higher Calcium content being leached from the core. The higher Calcium content shows the effect of the stimulation in the core (Fig. 4.15).
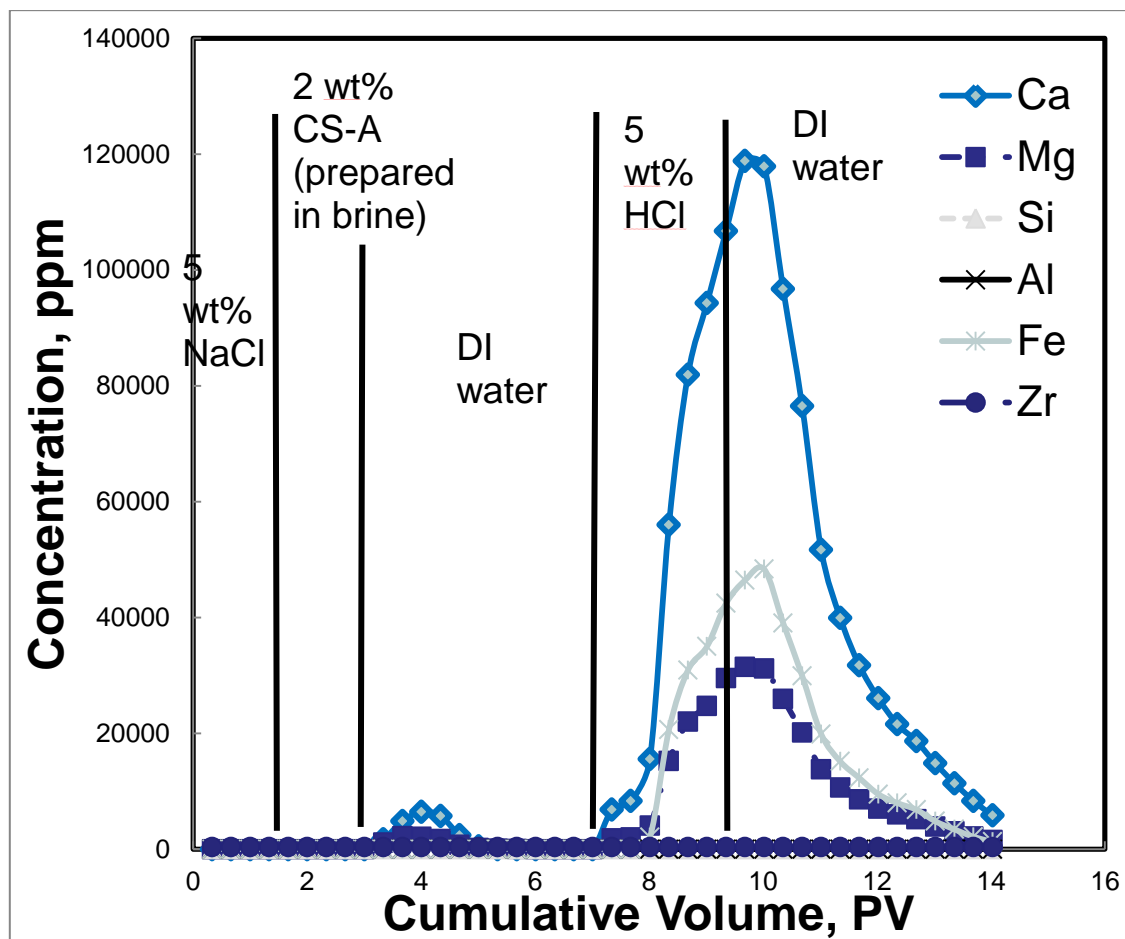
Fig. 4.15 – ICP Analyses – Concentrations with 2 wt% CS-A, 5 wt% HCl
T = 300ºF

Table 4.3 – Permeability before and after Coreflood Experiments

T, ºF	Coreflood Experiment	Initial Permeability, md	Final Permeability, md
77	Stage 1 – 5 wt% NaCl Stage 2 – 2 wt% CS-A (prepared in brine) Stage 3 – DI water	14	24
77	Stage 1 – 5 wt% NaCl Stage 2 – 2 wt% CS-A (prepared in DI water) Stage 3 – DI water	11.1	5.82
200	Stage 1 – 5 wt% NaCl Stage 2 – 2 wt% CS-A (prepared in brine) Stage 3 – DI water	22	24
300	Stage 1 – 5 wt% NaCl Stage 2 – 2 wt% CS-A (prepared in brine) Stage 3 – DI water Stage 4 – 5 wt% HCl Stage 5 – DI water	17	31

5. SUMMARY AND CONCLUSIONS

From the discussion highlighted earlier in this work, fines migration and clay swelling is a serious issue in the oil and gas industry with detrimental effects to the reservoirs, especially clay-containing reservoir formations. The study and use of clay stabilizers, either temporary or permanent, is vital in this area of production chemistry to enhance hydrocarbon production (Table 4.3).

Stated below are the conclusions drawn from the use of the Aluminum-Zirconium (Al/Zr) cationic inorganic polymer (CIP) on Bandera sandstone formation:

- The capillary suction time (CST) test was effective in screening stabilizer concentrations
- The Al/Zr - CIP stabilizer (CS-A) worked well in low temperature conditions
- The Al/Zr stabilizer worked better when prepared in brine (salt water) than compared to the stabilizer prepared in fresh water
- There was no increase in pressure drop during the injection of fresh water after treatment with the Al/Zr-CIP stabilizer (CS-A) when prepared in brine
- In the experimental test run with the CIP stabilizer (CS-A) prepared in fresh water, a constant increase in pressure drop was noticed. This indicated the movement of fines particles within the system which blocked pores, and this resulted to the restriction of fluid flow
- The stabilizer also worked well in high temperature conditions (200ºF, 300°F)
- The clay stabilizer remained in the core even after treatment with acid (HCl) solution
- No fines were noticed in the effluent samples collected during the coreflood experiment with the injection of the clay stabilizer
- Analysis of the effluent samples collected during the coreflood experiment, using the inductively coupled plasma (ICP), showed that more than half of the Al and Zr injected into the system remained in the system.

- The results of the analysis also show that the CS-A remained in the system continued working to keep the fines attached to the reservoir core walls

Table 5.1 – Parameters

k…………………………………………………………permeability, md	
ki…………………………………………………………initial permeability, md	
kf………………………………………………………...final permeability, md	
L…………………………………………………………length, in	
d…………………………………………………………diameter, in	
q…………………………………………………………flow rate, ml/min	
μ…………………………………………………………viscosity, cp	
Δp………………………………………………………..Pressure change, psi	
ρ…………………………………………………………density, g/cm^3	
T………………………………………………………..temperature, °F	

Table 5.2 – Nomenclature

A	Hamaker constant
d	Characteristic dimension
D	Solute diffusivity
e	Electron charge
k	Boltzman's constant
L	Characteristic length
n_b	Total ion density in the bulk
r_p	Particle radius
t	Time
V	Interaction potential
x	Length
z	Valence

Table 5.3 – Greek Symbols

Δ	Collision diameter
E	Electric permittivity or dielectric constant of medium
K	Debye-Huckel reciprocal length
Λ	London wavelength
P	Density
Φ	Porosity
M	Fluid viscosity
Z	Zeta potential
Φ_o	Surface potential

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