AN EXPERIMENTAL INVESTIGATION OF THE SHALE INHIBITION PROPERTIES OF A QUATERNARY AMINE COMPOUND

A THESIS SUBMITTED TO
THE GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES
OF
MIDDLE EAST TECHNICAL UNIVERSITY

BY

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IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR
THE DEGREE MASTER OF SCIENCE
IN
PETROLEUM AND NATURAL GAS ENGINEERING

FEBRUARY 2013

Approval of the thesis:

AN EXPERIMENTAL INVESTIGATION OF THE SHALE INHIBITION PROPERTIES OF A QUATERNARY AMINE COMPOUND

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I hereby declare that all information in this document has been obtained and presented in accordance with academic rules and ethical conduct. I also declare that, as required by these rules and conduct, I have fully cited and referenced all material and results that are not original to this work.

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ABSTRACT

AN EXPERIMENTAL INVESTIGATION OF THE SHALE INHIBITION PROPERTIES OF A QUATERNARY AMINE COMPOUND

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February 2013, 76 pages

Depleting oil reserves and increased costs of the oil and gas recoveries have created the need to drill in challenging formations. When drilled through, shale formations in particular always generated a wide variety of problems if conventional water-based muds are used. Furthermore, the complexity and variations in shales have compounded the task of developing suitable drilling fluids. In light of these problems, the study of shale properties and their interactions with fluids will continue to be a much-needed source of information in drilling industry.

In this study a low molecular weight quaternary amine compound, which is provided by KarKim Drilling Fluids Inc., and its mixtures with sodium and potassium chloride is investigated in the aspects of capillary suction times, hot rolling recoveries, methylene blue capacities and one-dimensional free swelling properties in order to compare performances of salts and amine compound.

For all test methods quaternary amine concentration from 1% to 6% by volume were studied and seen that less amount of quaternary amine compound is needed in order to obtain close shale recoveries and shale volume change potential if compared with sodium and potassium chloride. This prevents the usage of high concentration of chlorides and hence provides environmental sensitiveness.

Furthermore, it was concluded that combining an amount of salt with quaternary amine compound gives the system enhanced shale inhibition properties.

Key words: *Drilling, drilling fluid, quaternary amine compound, clay, shale inhibition.*

ÖZ

KUVATERNER AMİN BİLEŞİĞİNİN KİL BASKILAMA ÖZELLİKLERİNİN DENEYSEL OLARAK İNCELENMESİ

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Şubat 2013, 76 sayfa

Tükenen petrol rezervleri ve artan petrol ve gaz kazanım maliyetleri daha zorlu formasyonların sondajı ihtiyacını yaratmıştır. Geleneksel su bazlı sondaj çamuru kullanılarak kazılan şeyl formasyonları genel olarak çeşitli problemlere yol açmaktadır. Ek olarak, killerin karmaşıklığı ve çeşitliliği uygun sondaj akışkanını geliştirmeyi zorlaştırmaktadır. Bu sorunların altında, kil özellikleri ve kil-akışkan etkileşimleri sondaj endüstrisinde daha çok ihtiyaç duyulan bilgi olmaya devam etmektedir.

Bu çalışmada KarKim Sondaj Akışkanları A.Ş. tarafından sağlanan düşük molekül ağırlıklı bir kuvaterner amin bileşiği ve bu bileşiğin sodyum ve potasyum klorür tuzlarıyla karışımları, tuz ve amin bileşiğinin performans kıyaslamalarını yapabilmek için kepiler emilme süreleri, sıcak şartlandırma geri kazanımları, metilen mavisi kapasiteleri ve tek boyutlu serbest şişme özellikleri açısından incelenmiştir.

Bütün test yöntemleri için kuvaterner amin konsantrasyonu hacimce %1 ile %6 arasında tutulmuş ve yaklaşık ayni kil geri kazanımı ve kil hacim değiştirme potansiyeli sonucu elde etmek için sodyum ve potasyum klorüre kıyasla daha düşük miktarda kuvaterner amine ihtiyaç duyulduğu saptanmıştır. Bu durum yüksek miktarda klor kullanılmasını engellemekte ve bu sayede çevreye daha hassas olunmasını sağlamaktadır.

Ek olarak, belirli bir miktar tuz ile kuvaterner amin bileşiğinin beraber kullanılmasının sisteme gelişmiş baskılama özellikleri kattığı sonucuna varılmıştır.

Anahtar Kelimeler: *Sondaj, sondaj akışkanı, kuvaterner amin bileşiği, kil, şeyl baskılama*

To my family...

ACKNOWLEDGEMENTS

I would like to thank to my supervisor Prof. Dr. Mahmut PARLAKTUNA for his guidance through the course of this research.

I wish to thank my co-supervisor Assoc. Prof. Dr. İ. Hakkı GÜCÜYENER for his guidance, encouragements and invaluable advices. He truly played an important role in each step of this research and helped to shape most of the thesis. Without his help, this work would not have been possible.

I would like to thank KarKim Drilling Fluids Inc. for providing laboratory, equipment and the additives used in the experimental work. I would also like to express my sincere thanks to Ahmet AY, Metehan ALAKARA, Gökhan BAĞATIR and my other colleagues working in KarKim Drilling Fluids Inc. for sharing their knowledge and help.

I also would like to thank my classmates Tuğçe BAYRAM ERTÜRK, S. Aslı GÜNDOĞAR, Gülcan TÜRKARSLAN and Sinem Setenay ERDOĞAN. They did never hesitate to offer their sincere help.

I wish to express my gratefulness to my dear friend John ANGLISS for his valuable helps.

Finally, special thanks to my family, the completion of this work would not be possible without their encouragement, understanding and endless patience.

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CHAPTER 1

INTRODUCTION

Since the beginning of the drilling industry, people had been mainly focused on how to drill hydratable shales without facing problems such as stuck pipe, hole enlargement and washouts, tight hole, accumulation of fill on the hole bottom after trips, solids build up in mud and poor cementing jobs, which cover 90% of wellbore instability problems and cost annually $500 million (Mody and Hale 1993; Chenevert and Pernot 1998). In addition to these problems, it is realized that in the production stage of a well, clays start to migrate when exposed to the produced reservoir fluid. After a while they accumulate in the pore throat openings and this situation reduces production rates.

Oil-based muds were seen as the best solutions for well bore stability problems at the beginning with their ability to eliminate the flow of water and ions into the shales. Although oil-based muds ensure the best wellbore stability, increasing environmental awareness restricts them to be used and most of the time water based fluids have been preferred.

Additives used in water based muds as clay hydration suppressants can be classified in two categories as clay-controlling additives and clay stabilizers.

Salts like sodium chloride and potassium chloride are often used as clay controlling additives for their ability to retard clay hydration. These salts are only effective for as long as the mud retains them. On the other hand when the salt concentration depletes or the mud is changed with fresh water, clays will hydrate or swell and this causes stability problems.

In addition, high concentrations of salts are required to retard the osmotic hydration by increasing the ionic content of the water phase. However, in many jurisdictions environmental regulations prohibit the use of salt brines containing more than 3000-ppm chloride. This situation makes brines to be transported in order to dispose properly. This increases drilling costs in great aspects.

Furthermore, one of the mechanisms lying under the hydration controlling ability of these types of additives is cation exchange reaction. Cation exchange reactions reduce the volume of available water adsorbed by hydratable cations on the surface of the clay. Hence, these salts are only effective when swelling clays have a minimum number of exchangeable cations.

In this study an alternative cation source (quaternary amine) to potassium chloride is investigated. Solutions were formulated to compare the shale inhibition properties of sodium and potassium chloride with quaternary amine and quaternary amine/salt combinations.

In order to compare shale inhibition properties of quaternary amine with sodium and potassium chloride, formerly x-ray diffraction (XRD) analyses were made to shale sample to identify the contents of the exposed sample. Laterally, capillary suction time tests were investigated in order to check compatibility of different concentrations of salt, quaternary amine and quaternary amine/salt combinations with shale sample.

In order to get information about long-term interactions between brines and solutions with shale sample, hot rolling dispersion tests were applied. It is screening method that reveals from which solutions more recoveries can be obtained.

Furthermore, methylene blue tests were investigated in order to get the amount of reactive clays. With the help of these tests increasing or decreasing numbers of the negatively charged surfaces of the clay minerals can be obtained.

Lastly, in order to see volume-changing potential of the shale sample when subjected to submergence in solutions, one-dimensional free swelling tests were applied to solutions.

CHAPTER 2

LITERATURE REVIEW

2.1. Structure of Clay Minerals

Two main components form clay minerals. While tetrahedral sheet is composed of silicone dioxide, octahedral sheet is composed of aluminum hydroxide or magnesium hydroxide.

Silica tetrahedron has four sides and this is the reason why it is called tetrahedron as like octahedron unit has eight sides. In tetrahedral units four oxygen atoms are bonded a silicon atom, which takes place in the center of this structure. This means center silicon atom has equal distances to all four oxygen atoms. When tree of four oxygen atoms of a tetrahedral unit are shared, a sheet is created. Figure 1 shows a single tetrahedron and a tetrahedral sheet.

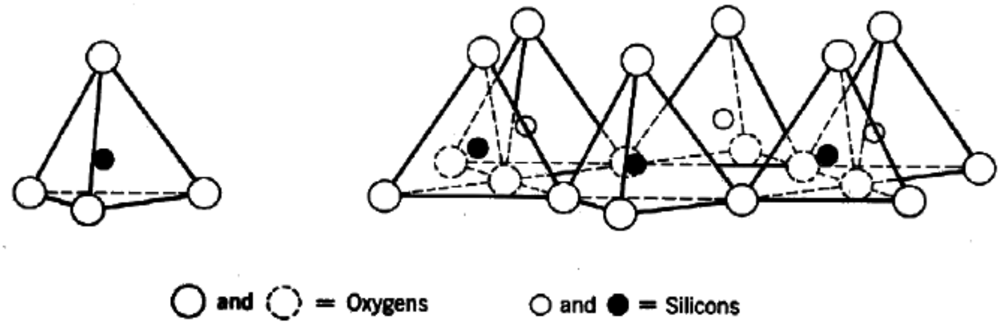


Figure 1: Structure of silica tetrahedral unit as single and sheet (Grim 1962)

The aluminum or magnesium atom in the center is bonded to six hydroxyl ions to form an octahedral unit. When each octahedron shares all six of its oxygen atoms, a sheet is formed as shown in Figure 2.

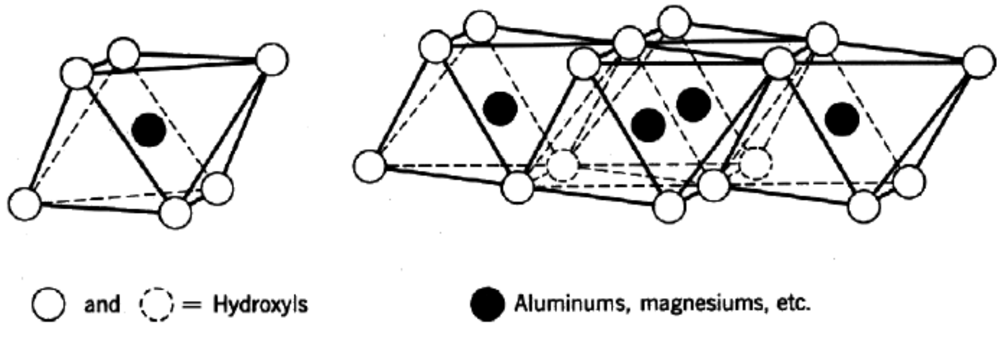


Figure 2: Structure of alumina or magnesia octahedral unit as single and sheet (Grim 1962)

Due to the great hydration tendencies of smectite clays, sodium montmorillonite, which is a member of smectite family, was chosen to investigate in this study.

2.1.1. Structure and Properties of Na-Montmorillonite

Montmorillonite is generally accepted to be 2:1 clay, meaning that its central octahedral alumina sheet lies in-between two tetrahedral silica sheets. All the end points of tetrahedral sheets directed to the center of the unit so that the hydroxyl tips of the octahedrons can form a layer with the oxygen tips of the tetrahedrons. Figure 3 shows a diagrammatic sketch of this structure (Grim 1962).

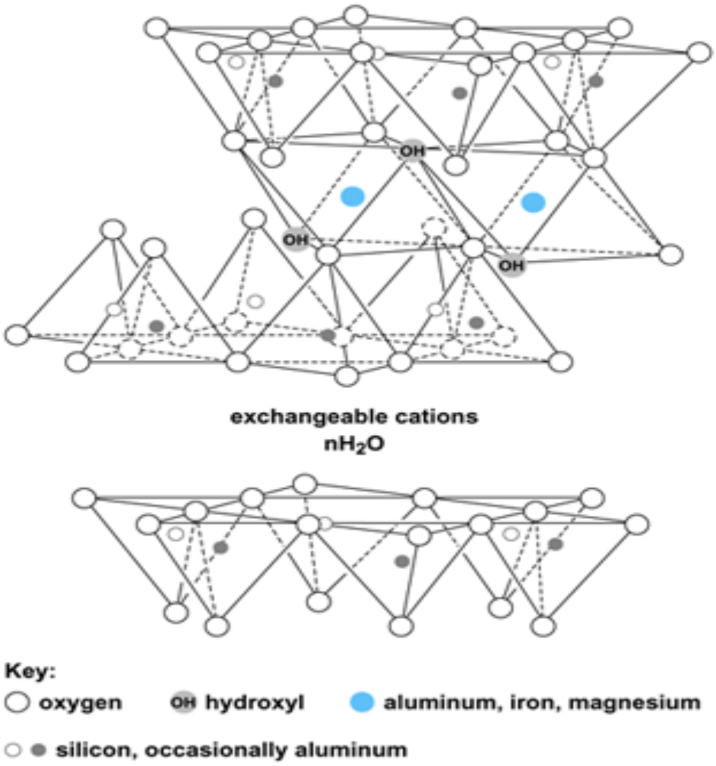


Figure 3: Diagrammatic Sketch of the Structure of Na-Montmorillonite (Grim 1962)

2.1.2. Isomorphous Substitution

Isomorphous substitution is the replacement of a metal ion with an ion of lower charge valency. For instance, Al^{+3} can replace Si^{+4} in the tetrahedral sheet and Mg^{+2} can replace Al^{+3} in the octahedral sheet. These substitutions create negatively charged surfaces as shown in Figure 4. These negative charges are balanced by the cations, which are adsorbed by the layers. Adsorbed cations take places between the layers to form chemical bonding between layers.

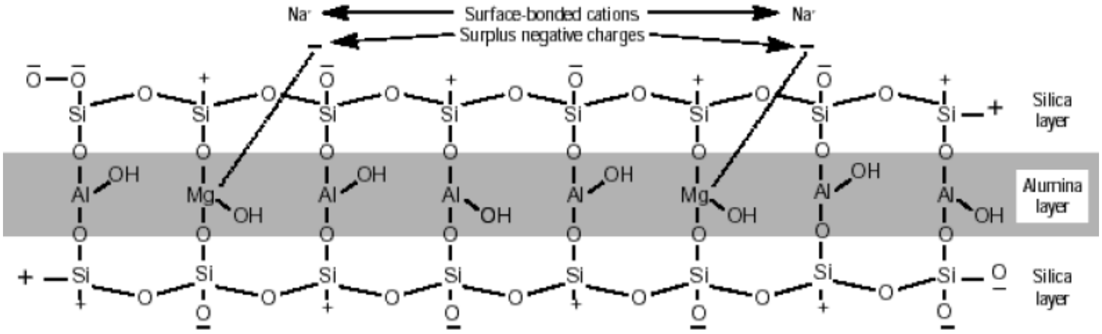


Figure 4: Forming of a negatively charged particle with the substitution of Mg^{+2} for Al^{+3} (van Olphen 1977)

2.1.3. Electrical Double Layer

In clay sols, particles are negatively charged because of the isomorphous substitution. These negative charges must be balanced with oppositely positive charges. This is the reason why unit layers adsorb cations. When clay particles interact with water, although counter ions are attracted by the opposite sign surface, they have also tendency to diffuse away through the bulk solution, where they are in low concentration. This situation causes a diffuse electrical double layer on the surfaces of the clay particle.

Electrical double layer contains two parts called Stern and diffuse layers. These layers are separated by Stern plane. Figure 5 describes the place of the Stern plane. Ions attracted to the surface charge create a diffuse layer, which screens the Stern layer electrically.

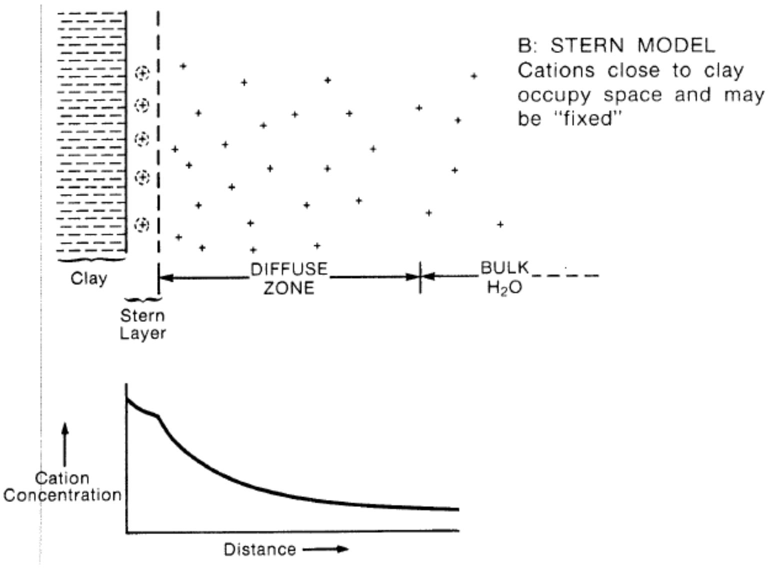


Figure 5: Illustration of the electrical double layer (van Olphen 1977)

2.1.4. Cation Exchange and Cation Exchange Capacity

Exchangeable cations are available cations in a solution that can be exchanged with the compensating cations on the layer surfaces in the presence of water. Ca^{+2}, Mg^{+2}, H^+, K^+, NH_4^+ and Na^+ are the most frequently seen exchangeable cations. Exchangeable cations are also anchored around the outside of the structural units as like between the basal spacing. During and after cation exchange process, the structure of the clay mineral does not change.

To quantify the amount of exchangeable cations, a term referred as the "cation exchange capacity" (CEC) is defined, which corresponds to the amount of the exchangeable cations in milliequivalents per 100gr dry clay at pH 7. Clays contain large quantities of negative charges on their surfaces have high cation exchange capacities.

According to the type of ions they contain, their size and degree of hydration, concentration and valence, and the kinds of clay minerals coming into play, the replacement power of cations varies. When under normal circumstances monovalent and divalent cations are mixed, their power of replacement is, in descending order:

$H^+ > Al^{+3} > Ca^{+2} > Mg^{+2} > K^+ > NH_4^+ > Na^+ > Li^+$

(Gucuyener 2012)

2.2. Properties of Clay-Water Systems

Repulsive and attractive forces are acting forces on the clay particles.

2.2.1. Repulsive Forces

Interaction of the diffuse counter-ion layers of clay particles increases with decreasing distance between the particles. Increasing interaction causes changes in ion distribution in the electrical double layer of each particle.

Because electrolytes makes the electrical double layer compacted, particles can approach closer to each other. This compaction is dependent on salt concentration and the valance of the counter ions.

2.2.2. Attractive Forces

van der Waals forces are a type of attractive force on the atomic and molecular level named after Johannes van der Waals (1837-1923). They are much less powerful than valence bond forces, being inversely proportional to the 7th power of the distance separating the molecules or atoms. van der Waals forces are the forces which cause molecular crystals to gain lattice energy. These forces are caused by three factors:

1. Dipole-dipole interaction, when two molecules with unchanging dipole moments are electrostatically attracted
2. Dipole-induced dipole interactions, when one molecule’s dipole causes a nearby molecule to itself become polarized
3. The dispersion forces caused by small momentary dipoles in atoms (Daintith 2008).

2.2.3. Association of Clay Particles

van Olphen classified the geometry of particle association into three kinds: face-to-face (FF), edge-to-face (EF) and edge-to-edge (EE). He considered that EE and EF associations lead to flocculation of viscous gels, and that FF associations lead to less viscous oriented aggregates (Figures 6-7). Dispersion is the term used to describe the disassociation of flocculated particles. Thus, the terms “flocculation-deflocculation” and “aggregation-dispersion” refer to different geometries of clay platelet association. The viscosity or gel forming tendencies of clay minerals are determined by the type of associations, which depend on the clay concentration and electrolyte concentration (Figure 8). Flocculation most commonly occurs in relatively low salinity suspensions. At high salinities, aggregation also occurs, causing lower viscosities (Eslinger and Pevear 1988).

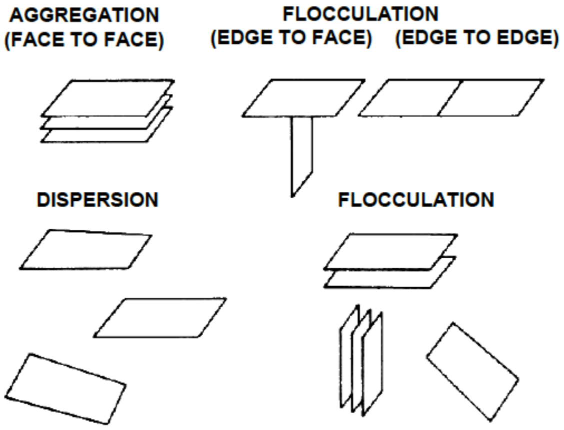


Figure 6: Modes of Particle Association in Clay Suspensions (Grim 1962)

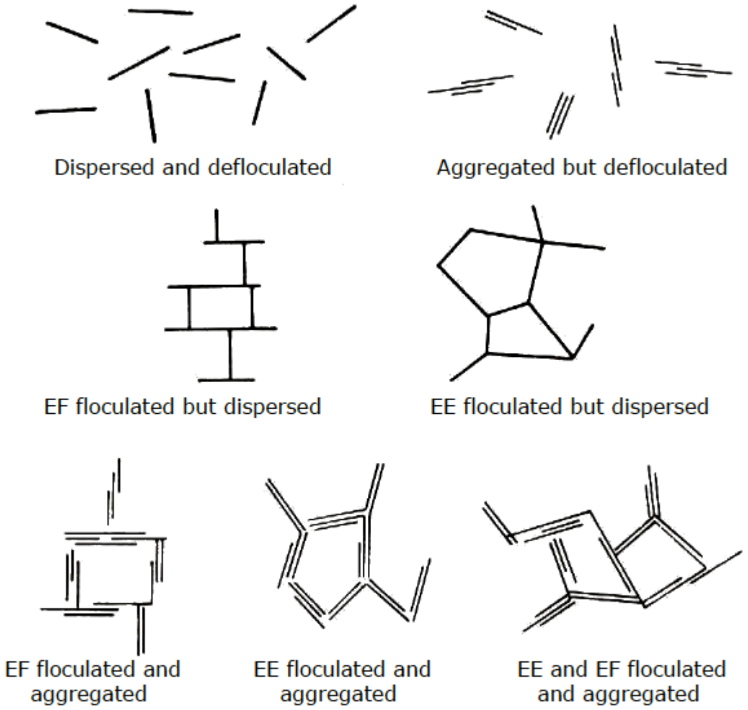


Figure 7: Clay particle associations (Grim 1962)

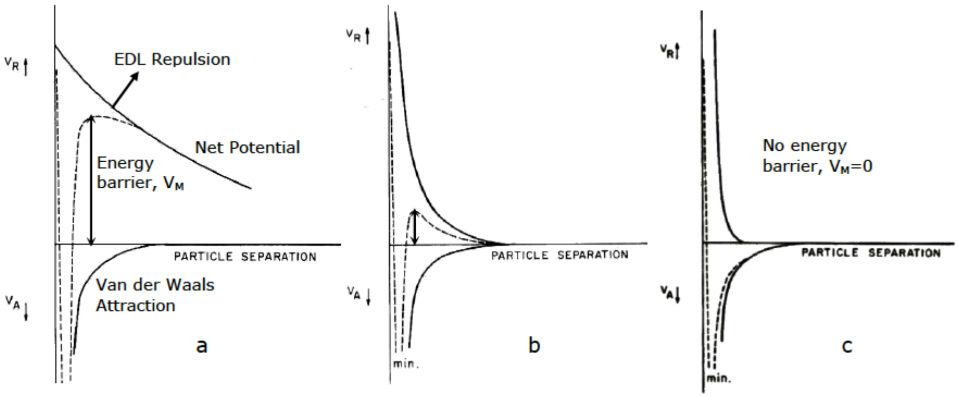


Figure 8: Resultant interaction energy as a function of particle separation in low (a), intermediate (b) and high (c) salt concentrations (van Olphen 1977)

2.2.4. Clay Hydration

Hydration of clay is double staged process. First step of this progress is ion hydration. At the second stage osmotic swelling occurs.

2.2.4.1. Ion Hydration

As montmorillonite clays interact with water or water vapor, up to four monolayers of water penetrate between clay layers –around the counter cation in basal spacing (Figure9-10)– or between flat surfaces of the neighboring particles. This makes clay particles swell. Three forces, that are effective in the separation of clay layers, are the attractive van der Waals forces, the electrostatic interaction of charged surfaces and cations, and the adsorption energy of water, which dominates the process. From the net interaction energies, the operative forces in clay swelling are determined to be in the order of a few thousand atmospheres for the entrance of consecutive layers, which indicates that the last layers of adsorbed water in clay sediment are not likely to be completely removed by overburden pressure. (Hensen and Smit 2002; Mering 1946; van Olphen 1977)

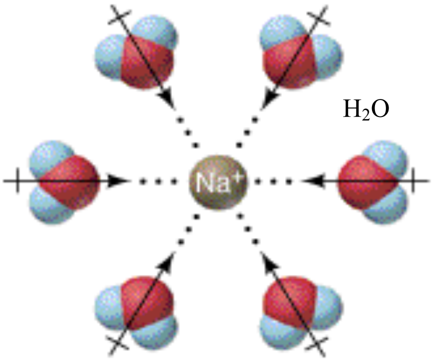


Figure 9: Ion Hydration

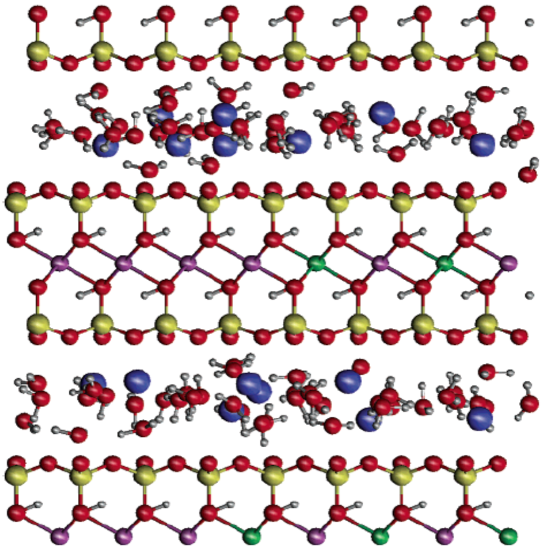


Figure 10: Atomistic Model of the One-Layer Hydrate of Sodium Montmorillonite
(O: Red, H: White, Si: Yellow, Na: Blue, Al: purple and Mg: Green) (Boek, Coveney, and Skipper 1995)

2.2.4.2. Osmotic Swelling

The big differential between ion concentrations at the surface of the clay and concentrations in pore water causes the second stage of clay swelling. As the spacing between individual clay layers increases with ion hydration, the surface hydration energy becomes less significant and the electrical double layer repulsion resulting from the different nature of the forces turns out to be the essential repulsive force between the plates. The distance between plates might increase until the plates become completely disassociated. These forces arise from a balance of electrostatic and van der Waals forces, and the osmotic pressure exerted by interlamellar cations (Cases et al. 1992).

2.3 Inhibition Methods

To overcome the problems caused by hydratable shales, oil phase drilling fluids began to be used in the middle 1930's. Because of the oil wetting property of the oil-based mud (OBM), water sensitive shales remain stable. Also, OBM minimizes ion transfer between mud and formation by acting as a semi-permeable membrane and this reduces clay's adsorption energy.

Although using oil-based mud seems to solve all the hole stability problems (Kersten 1946), OBM does not completely finish the ion transfer and in some cases problems caused by shale hydration still continue (Browning and Perricone 1963). Furthermore, if recent environmental restrictions and high operational costs of OBM are taken into account, it can be seen why drilling industry pushed forward to find other water-based solutions.

In this point of view in 1960's, lignosulfonate muds were introduced to the drilling industry (Browning and Perricone 1963). First pioneers of lignosulfonate muds, however, contain an amount of oil and environmentally non-acceptable additives such as chrome lignosulfonate. Also, these systems rely on swelling property of sodium bentonite. Because of this reason, in the present day water based mud systems are classified in two main subclasses, which are inhibitive and non-inhibitive systems. Non-inhibitive systems, under which bentonite, lime and lignosulfonate muds take place, do not suppress clay swelling. Conversely, inhibitive fluids retard or prevent clay swelling.

Clay suppressants used in inhibitive fluid solutions are divided into two subgroups by their ability to retard or prevent swelling as temporary and permanent stabilizers.

2.3.1 Potassium Fixation

In the beginning of 1970's, industry met with potassium chloride as the most effective clay suppressant (O'Brien and Chenevert 1973).

The answer how potassium chloride works is related with the clay chemistry. Potassium ion is in the proper size to fit the space between tetrahedral sheets of clay platelets, which are negatively charged because of the isomorphous substitution in the octahedral layer. When potassium ion is in the lattice space with the help of cation exchange, it is as close as to the center of negative charges. So that unlike other exchangeable cations, clays are held with a greater bonding energy, i.e. cationic potassium ion can hold negatively charged platelets together. Higher affinity of potassium to cation exchange than sodium and calcium ions on montmorillonite or interlayered clays results a type of clay, which performs just surface swelling. This K-montmorillonites cannot swell as much as Na-montmorillonite clays.

A few years after O'Brien's survey, which supported the place of potassium chloride in drilling technology, Clark et al published their studies that covers the usage of potassium chloride in the laboratory and at the field with a newly introduced high molecular weight partially hydrolyzed polyacrylamide (PHPA) (Clark et al. 1976). This co-polymer is absorbed on the clay surfaces and makes a barrier to keep drilled cutting in a fixed shape. Also, this barrier prevents the clay-water interaction. Both laboratory and field applications have better clay inhibition results compared with just potassium chloride usage itself. It is seen that, however, the shale inhibition of this system is not enough and the success of this system highly depends on the availability of an efficient solid control system. Also in 90's, the glycol and poly-glycol combination with KCl and KCl/polymer systems were presented and again the level of inhibition was not enough.

The discovery of the permanent formation damage caused by migrated clay fines was also in the first half of the 70's. KCl/polymer system apparently had solved this problem. It was understood, however, that potassium exchange is a reversible reaction, i.e. if enough cationic ions exist in the system, they can exchange with fixed potassium in the lattice space, even if these ions has smaller affinity than potassium ion has. In addition, although potassium chloride is very effective to reduce swelling and hydration ability of smectites and most of the clays, it shows insufficient effects on illite and even worse, causes more swelling of kaolinite (Van Oort 1997).

2.3.2 Amine Fixation

In the mid. 80's, because of these disadvantages of potassium chloride, new approaches were needed. For this reason, amine derivatives started to be seen more frequently in drilling market. Since 1950's, several studies had been conducted to understand how amine compounds adsorbed onto clays. It was seen that, like other simple cations, cation exchange plays very important role for adsorption. In addition, numerous investigations had been done on amine derivatives (mostly polyamines) - clay interactions to examine the inhibition mechanism. Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), electron microscopy (SEM/TEM), zeta potential analysis (ζ-Potential), thermo gravimetric analysis and bulk hardness testing are some of the applied techniques (McAtee 1959; Laura and Cloos 1975; Williams Jr and Underdown 1981; Yukselen and Kaya 2003; Souza and Nascimento 2008; Blachier et al. 2009; Zhong et al. 2011; Wang et al. 2011).

In 1982, Hill classified clay stabilization chemicals as brines, inorganic cationic polymers, cationic surfactants and organic cationic polymers. In his study, short-term stabilizing effect of potassium chloride and ammonium chloride were mentioned. Amine salts, like ammonium chloride was found to be a crucial troublemaker because of its free liberation of ammonia gas with increasing pH. Another ammonia-based salt, diammonium phosphate, seemed to be a good clay inhibitor, but this salt had a limited market because of its temperature and performance limitations (Schlemmer et al. 2003; A. Patel et al. 2007). Hill also supported that polyvalent inorganic cations, such as zirconium oxychloride and hydroxyl-aluminum, are effective for clay stabilization by masking anionic sights of clays, therefore reducing cation exchange capacity (Reed 1971). However, because of complexity of usage and acid solubility of these materials, they have not been widely used. From that study, brief information about cationic surfactants like fatty quaternary amines and amine salts can be found. Although these surfactants present good clay inhibition property, they are undesirable materials to be used because they change wettability of the rock from water wet to oil wet for clay inhibition (Hill 1982). In addition, in 1990 Beihoffer et al. indicated in a challenging study that these surfactants creates foaming problem.

Early developed polyamines allow users to apply it in all formation types because they do not require a pH range and limestone, dolomite, anhydrate and common contaminants do not affect the polymers. In addition, they can be used both in fresh water, seawater and solutions of ammonium chloride, potassium chloride, calcium chloride and hydrochloric acid. Furthermore, due to intense polarities, polymers are not hydrocarbon soluble. That's why, in production stage, it is not possible to be taken away from clay surfaces by crude oil and produced formation fluid, unlike potassium chloride. Like this property, acid treatment does not disturb clay fixation. Finally, to fix clays, very little amount of polymer is needed when compared with potassium chloride. This provides simplicity to use and environmentally friendliness because of the lower chloride content (McLaughlin, Elphingstone, and Hall 1976). In contrast, according to the study made by Retz et al. in 1991, LC_{50} values, which indicate the toxicity of the polymer samples, of most ammonium salts and quaternary amines are lower than 30,000-ppm limitation. The lower the LC_{50} values, the greater toxicity of the polymer. Also it was concluded that, there is no relation between toxicity and charge density and molecular weight. (Retz et al. 1991; Hemphill et al. 1992)

As mentioned before, in 1990 Beihoffer et al. published their study, which brings a new point of view to amine-clay relationship. They noticed that, the smaller the chain length (molecular weight) of polyamine, the better polymer adsorption occurs and hence the better clay inhibition it provides (T W Beihoffer, Dorrough, and Schmidt 1990). Correspondingly, some other scientists confirmed this information by using adsorption isotherms and XRD results. Adsorption isotherms are plotted with respect to the adsorbed amount, which is calculated from the difference between initial and equilibrium amine concentrations. The concentrations were determined by Total Carbon Analyzer (Lin et al. 2001; Souza et al. 2006; Souza and Nascimento 2008; Blachier et al. 2009; Wang et al. 2011). Furthermore, some other scientists reported that high molecular weight polyamines are found to block permeability (R.E. Himes, Vinson, and Simon 1991; Zhou, Gunter, and Jonasson 1995; Schlemmer et al. 2003). According to Beihoffer et al., combination of quaternary amine with potassium chloride provides greater shale recoveries than with either component alone. However, quaternary amines have an handicap that they are not compatible with most of the conventional viscosifiers and fluid loss control agents, such as xanthan gum, CMC, PAC, polyacrylates etc. The reason of this situation is the anionic structures of such polymers. Cationic clay inhibitor reacts with the anionic polymer and causes precipitation. To overcome this, in his early studies Beihoffer used non-ionic viscosifiers and fluid loss agents, e.g. hydroxylethyl cellulose and pre-gelatinized starches. In the later studies, it is noticed that precipitation reaction can be reduced or completely eliminated by increasing the ionic content with the use of an electrolyte, e.g. sodium chloride, potassium chloride etc. (Retz et al. 1991; Welch and Lee 1992; Thomas W. Beihoffer et al. 1992). This situation, however, affects environmental concerns because of the chloride contents.

The reasons why most of the organic cationic polymers are not widely used today are their high marine toxicity level, pH dependency and high consumption rates causing high cost. Also, some quaternary amine products highly flocculate high-solid fluids. However, quaternary hydroxy amines like β-hydoxyethyltrimethylammonium chloride, which is non-toxic and has been used medically, continues to be widely used with the disadvantage of low level of inhibition (Schlemmer et al. 2003; A. Patel et al. 2007).

In 1993 Bruton et al. studied to find a totally environmental solution and the final product must be compatible with anionic conventional drilling fluid additives. They produced a low molecular weight synthetic amino acid, because amino acids are the main components of natural proteins so environmentally friendly and also because of their amphoteric property, i.e. they contain carboxyl and amine groups, amino acids acts like both anionic and cationic. Although amino acid molecules are primarily positive in an acidic solution, the molecules are primarily negative in alkaline environments.

This property of amino acids makes them compatible with both anionic and cationic substances. However, authors also noted as the pH increases above 7, cationic strength and cationic effect, which means clay inhibition property, decreases. In 1995 Stamatakis et al. also emphasized that because of the amphoteric nature of amino acids, their inhibition characteristics are somewhat less than those of truly cationic materials (Stamatakis et al. 1995). For this reason best pH range for amino acid are 7 to 9. In addition to their pH handicap, amino acids may increase the usage of fluid-loss-control additives at the fields (Bruton and Mclaurine 1993). Today these poly-amino acids are used in “drilling-in fluids” (Schlemmer et al. 2003).

In 1998 Brady et al. introduced two effective amine glycols. These non-cloud point glycols provide shale inhibition by bounding amine groups to shale surfaces (Brady et al. 1998). However, in some field applications bit and collar balling had been observed in the presence of glycol (Schlemmer et al. 2003). Also, shale inhibition properties of these types of glycols are found to be below average (A. D. Patel 2009; A. Patel et al. 2007).

In the early 2000’s, novel amine ingredients were presented (Schlemmer et al. 2003). These amines are polyether diamines (poly(oxyalkylene) amine) (POAM). Besides this polymer has inhibition property of other indicated amines, the molecules of POAM struggle with water molecules to be anchored to the clay’s reactive sites. This gives hydrophobicity to clay mineral and again reduces swelling property. Also, POAM provides excellent shale inhibition property with low marine toxicity, high temperature stability, pH independency and compatibility with other mud ingredients through its amphoteric property (Qu et al. 2009; A. D. Patel 2009).

In addition to this development, in 2006 Young and Stamatakis introduced lipophilic amines as shale inhibitors (Young and Stamatakis 2006). These amines are excellent shale inhibitors at or below 9.5 pH. Although these lipophilic amines sometimes act like a surfactant and cause foaming, using defoamers can solve this problem (A. Patel et al. 2007)

In 2009 Patel et al. classified amines as monocationic, oligomeric and polycationic amines. This classification simply can be found in Tables 1-3.

Table 1: Monocationic Amine Shale Stabilizers (A. D. Patel 2009)

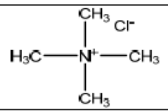
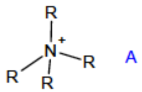
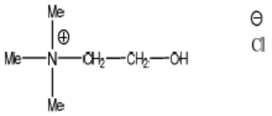
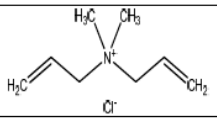
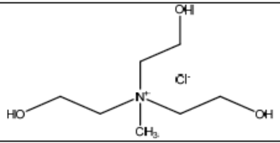
Name	**Structure/Composition**	**Function/Limitation**	**HS&E/Toxicity**
Ammonium Chloride	NH_4Cl and other salts	pH and temperature limitations	Obnoxious odor, toxic
Tetramethyl Ammonium Chloride (TMAC)		pH and temperature limitations	Marine toxicity, bad odor
Tetraalkyl Ammonium Salts		Formulation limitations, foaming, incompatibility	Marine toxicity
Choline Chloride		Compatible with additives, limitation in shale inhibition, ammonia odor	Biodegradable, non-toxic to marine
Dimethyl diallyl ammonium chloride		Limited inhibition, odor	Monomer toxic
Triethanol amine methyl chloride		Limited inhibition	Non-toxic to marine

Table 2: Oligomeric Cationic Amine Shale Stabilizers (A. D. Patel 2009)

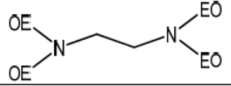
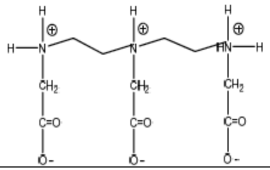
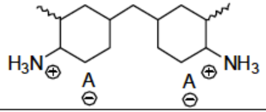
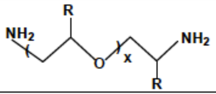
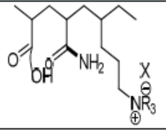
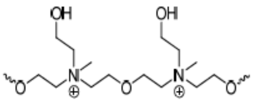
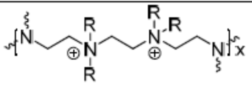
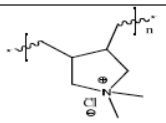
Name	Structure/composition	Function/limitation	HS&E/toxicity
Ethoxylated Diamine		Poor inhibition	
Amphoteric Amines		Limited inhibition, solid tolerance, ineffective in high active solids	No marine toxicity
Hexamethylene diamine/Salts Cyclohexyldiamines	NH_2- $(CH_2)_6$ –NH_2	Inhibition limited, no optimization	Odor, some toxicity
Polyethylene imine salts		Excellent inhibition, requires neutralization, foaming	Not toxic to marine
Oligomeric ether amines/salts		Excellent inhibition	Not toxic to marine, microtox issue
Oligomeric imine chemistry	$RNH-(CH_2)_x-NR-(CH_2)_x-NHR$	Limitation in inhibition	Toxicity issues

Table 3: Polycationic Amine Shale Stabilizers (A. D. Patel 2009)

Name	Structure/composition	Function/ limitation	HS&E/toxicity
Polycationic PHPA		Limited shale inhibition, good encapsulation, compatibility issue, mud formulation issue	Toxic to marine environment
Polytriethanol-aminemethyl quaternary amine		Limited shale inhibition	Toxicity issues
Polycationic polyimine		Limited shale inhibition, compatibility issues	Toxicity to marine
Poly dimethyldiallyl-ammonium chloride (PolyDMDAAC)		Compatibility issues, fluid formulation limitations	Toxicity issues

Guerrero et.al tried to understand shale inhibition property of different amines in their study in 2006 (Guerrero, Guerrero, and Warren 2006). Like this study, they also used capillary suction tests (CST) to clarify correct amine concentrations. They also applied shale dispersion tests to make CST results more rigid. They saw an increasing trend with the increasing smectite content.

Since the beginning of 90’s many field studies had been conducted on amine chemistry. These studies illustrated that during shale drilling operations, using amine based polymers increases penetration rates, decreases bit balling and torque & drag, and eliminates the risk of differential sticking. Also, caliper logs showed better hole sizes than conventional drilling fluids. In addition, total mud costs are lower when compared to oil-based mud (Ronald E Himes, Parker, and Schmelzl 1990; Hemphill et al. 1992; Welch and Lee 1992; T W Beihoffer et al. 1992; Moroni and Denax 2009)

CHAPTER 3

STATEMENT OF THE PROBLEM

While drilling hydratable shales with conventional water based drilling fluids, several problems will be encountered. Wellbore instability due to hydration of clays contained in shales will cause waste of equipment, time and money and under certain circumstances loss of the well.

Oil based drilling fluids might be a solution to these problems, but they are passed over because of their high cost and the environmental problems they cause. Instead, with correctly administered shale hydration inhibitors, water based drilling fluids are generally used.

The scope of this study is to understand the interaction between quaternary amine and sodium montmorillonite mineral and bring a noticeable perspective to shale hydration inhibition properties of quaternary amine compound. Furthermore, this study experimentally evaluates both potassium chloride and quaternary amine as shale hydration suppressant.

CHAPTER 4

EXPERIMENTAL METHODS AND EQUIPMENT

4.1. Introduction

Sodium montmorillonite used for this investigation was obtained from Karakaya Bentonit Sanayi ve Tic. A.Ş., which produced from Reşadiye, Tokat in Turkey. and meet API 13A Section 4 specifications.

Quaternary amine obtained from KarKim Drilling Fluids Inc. (KAR-GUARD) and specifications can be found in Table 4. Positively charged polyatomic ions of structure NR_4^+, R being an alkyl or an aryl group, are known as quaternary amines (Figure 11).

Potassium chloride and sodium chloride salts used for the experiments were the products of Merck Chemicals (Table 5).

Table 4: Properties of Quaternary Amine (KAR-GUARD)

Appearance	:	Amber Liquid
pH (1% by Volume Solution)	:	5.0 – 6.5
Specific Gravity	:	1.08 – 1.10
Flash Point	:	>212^o F (100^o C)

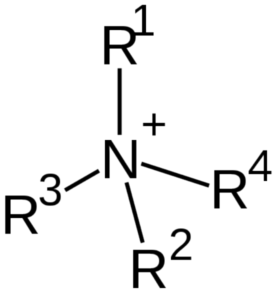


Figure 11: General Structure of Quaternary Amine

Table 5: Properties of KCl and NaCl

		KCl	NaCl
Solubility in water (g/l) (20° C)	:	347	358
Melting Point (° C)	:	773	801
Molar Mass (g/mole)	:	74.55	58.44
Density (g/cm^3)	:	1.98	2.17
Bulk Density (kg/m^3)	:	1000	1140
pH value (50g/l water, 25° C)	:	5.5 – 8.0	5.0 – 9.0
Boiling Point (° C)	:	1413	1461

4.2. Description of Equipment

4.2.1. Sieve Shaker

RETSCH AS 200 shaker was used to screen samples up to 44 micron (325 mesh/no). For hot roll dispersion test, samples are also screened with the same equipment (Figure 12).

Figure 12: RETSCH AS 200 Sieve Shaker

4.2.2. pH Meter

pH meters are used to measure the concentration of hydrogen ions in liquids. pH can be measured using a pH meter, which is a glass electrode connected to an electronic meter. The pH meter reads pH by measuring the activity of hydrogen cations. The probe produces a small amount of voltage which is converted using this instrument into pH units. Using an ECO TEST R digital pH meter (figure 13), the pHs of the different mixtures were able to be determined. This pH meter can measure the entire pH scale from zero to fourteen with an accuracy of ±0.01.

Figure 13: ECO TEST R digital pH meter

4.2.3. Capillary Suction Timer

The Capillary Suction Timer consisted of two different parts, the acrylic filtration unit and the electrodes and timer. The aqueous system to be tested is sampled, and this is inserted into the sample cylinder. The filtrate moves radially in a near-elliptical pattern. The timer is activated by the liquid reaching the first set of electrodes (Figure 14), and stops timing when the liquid reaches the third electrode, switching the finish lamp on and playing an audible signal. The counter then indicates the CST reading to the nearest tenth of a second. CST instrument was obtained from Venture Innovations Inc. (Figure 15). Special CST papers were obtained from OFI Testing Equipment Inc.

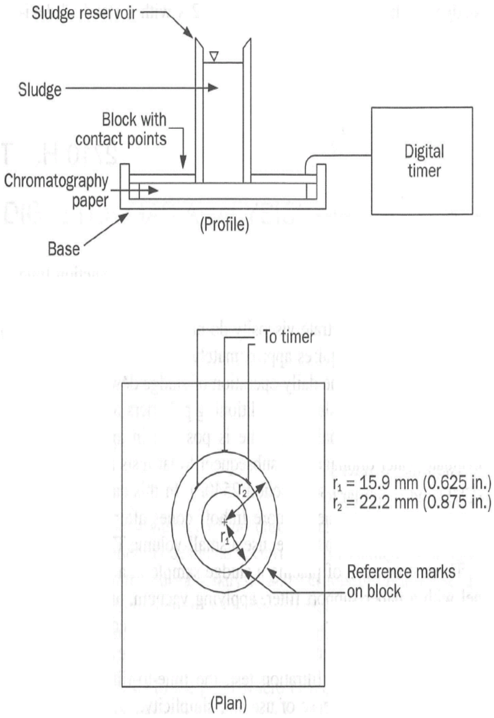


Figure 14: Schematic of Capillary Suction Timer

Figure 15: Capillary Suction Timer

4.2.4. Drying Oven

NUVE FN120 Dry Heat Sterilizer (Figure 16) was the drying oven used for the sample drying in preparation process. In addition to that drying oven was also responsible to dry the samples, which were recovered from hot rolling dispersion tests.

Figure 16: NUVE FN120 Drying Oven

4.2.5. Multi Mixer and Mixer Cups

FANN Five Spindle Multi-Mixer ® Model 9B (Figure 17), which conforms API Specification 13A related with mixing water and oil based muds, was used for the mixing/agitating purposes of the solutions to have homogeneous mixtures. This multi mixer has 5 spindles and placing a mixing cup to any spindle runs the motor automatically. The motor stops when the last cup is taken from its place.

Figure 17: FANN Five Spindle Multi-Mixer® Model 9B and Mixer Cups

4.2.6. Roller Oven and Aging Cells

FANN Roller Oven (Figure 18) was used to simulate down-hole and circulation conditions in the laboratory. The aging cell (Figure 19) is a vessel which subjects fluid samples to high temperatures while maintaining them in liquid states. They can be used to simulate static aging conditions, or dynamic aging conditions in a roller oven. This process completed all chemical reactions between screened bentonite pieces and freshly prepared solutions. In addition, by this way solutions were allowed to develop its rheological and filtration properties.

Figure 18: FANN Roller Oven

Figure 19: Fann Aging Cell

4.2.7. Methylene Blue Test Kit

Methylene blue test kit contains:

- 0.01 milliequivalent methylene blue solution
- 3% hydrogen peroxide solution
- 5 N sulfuric acid
- 5 cm^3 syringe
- 250 cm^3 Erlenmeyer flask
- 50 cm^3 graduated cylinder
- Stirring rod
- 1 cm^3 pipette
- 10 cm^3 pipette
- 325 Watt hot plate
- 3.5 inch diameter filter paper

Figure 20: FANN Methylene Blue Test Kit

4.3. Description of Experiments and Procedures

4.3.1. Sample Preparation

Steps of procedure utilized for sample preparation are as follows:

1. Sodium montmorillonite rock pieces were dried for not less than 24 hours with NUVE FN 120 drying oven.

2. After crushing, the samples were screened trough sieves No. 5, 10, 200 and 325; i.e. 4000, 2000, 74 and 44 microns respectively. While coarse samples –taken from under No.5 above No.10– were used for hot rolling dispersion tests, fine samples –taken from under No.200 above No.325– were used for capillary suction time, methylene blue capacity and one-dimensional free swell tests.

3. No further purification was applied to the sample.

4.3.2. Capillary Suction Time Test

One way in which the compatibility between the fluid and rock can be tested is through capillary suction time tests. Developed in 1967 for drilling fluids, capillary suction tests serve to determine the time to move a waterfront between two electrodes. The time of waterfront movement is an indication of fluid's ability to flocculate or disperse clays. Hence, the amount of dispersion will become larger as with increasing duration of waterfront movement, which means that long CST times point out poor clay control of the fluid. Since fluid pH and formation grain size are influencing factors for capillary suction time, they were kept constant while performing the tests.

Steps of procedure utilized for running CST tests are as follows(Hart 1989):

1. Sodium and potassium chloride brines were mixed as 3%, 6%, 9%, 12% and 15% by weight.
2. Amine solutions were mixed as 1-laboratory barrels ($350cm^3$) by using multi mixer as 1%, 2%, 3%, 4%, 5% and 6% by volume. If sodium chloride or potassium chloride exists in the composition, first brines were mixed as 6% salt content by weight.
3. pH was adjusted to 9.5 with sodium hydroxide solution.
4. Fine bentonite samples were added while the solutions were mixing.
5. Suspensions mixed for 20 minutes.
6. Mixtures were poured to ageing cells to be aged for 16 hours under 120^oF temperature in roller oven.
7. At the end of 16 hours samples were opened and $3cm^3$ of them had been taken while mixing to perform CST tests.
8. The time indicated by instrument was noted.
9. CST tests were carried out for 3 times with different $3cm^3$ for every sample.
10. Mean values of the times were computed and the standard deviations were found.
11. The results obtained for deviation added to and subtracted from mean values to find minimum and maximum expectations of CST values respectively to eliminate the trivial CST results.
12. Data between minimum and maximum values were taken into consideration and averages calculated again with these values.
13. When only sodium and potassium chloride are employed step 6, 9, 10, 11 and 12 were skipped.

4.3.3. Hot Roll Dispersion Test

Hot rolling dispersion test is a screening method, which obtains information from the long-term interactions between shale samples and fluid. The results of this test are good indication of the capability of the fluid to suppress swelling of the clay content of the shale samples.

Steps of procedure utilized for running Hot Roll Dispersion tests are as follows (American Petroleum Institute 2001):

1. Sodium chloride (NaCl) and potassium chloride (KCl) brines were mixed as 3%, 6%, 9%, 12% and 15% by weight when they were tested alone, while quaternary amine solutions were mixed as 1%, 2%, 3%, 4%, 5% and 6% by volume. If salt and quaternary amine were used together 6% by weight salt and 1%, 2%, 3%, 4%, 5% and 6% by volume quaternary amine were mixed.

2. pH was adjusted as 9.5 for all brines and solutions with sodium hydroxide solution.

3. Solutions were poured to hot rolling aging cells.

4. 30 grams of coarse bentonite samples were added to the aging cells. When roller oven was at temperature of 120^{o} F.

5. Aging cells were placed to roller oven.

6. After 16 hours aging, cells were opened and the contents were poured through the sieves No. 10 and 20, 2000 and 841 microns respectively.

7. After washing the sieves with 10% by weight potassium chloride brine; recovered shale samples, which were collected from both sieves, were dried at 120^{o} C and the weighs were noted after weighting.

4.3.4. Methylene Blue Capacity

Methylene blue test (MBT) is performed to determine the methylene blue capacity of a drilling fluid, which indicates the amount of reactive clays (bentonite or drilled solids) it contains. To assess the value of total exchange capacity (CEC) of the solids in the drilling fluid, a good indicator and estimate would be the value of the methylene blue capacity, which does not always mean that the methylene blue capacity and the cation exchange capacity are equivalent.

Due to the cationic properties of methylene blue dye, it sticks to the negatively charged surfaces. Hence, whenever methylene blue dye is added to clay suspensions and one drop of final mixture is placed on a filter paper, blue/dark blue point is seen. However, if there is not enough negatively charged surface for methylene blue to stick a light blue tint will appear on the filter paper if same procedure applied. The methylene blue capacity is noted to be generally less than the actual cation exchange capacity.

Followed test procedure, which is also schematically sketched in Figure 21, to determine methylene blue capacity of mixed amine-brine-bentonite suspensions is as follows (American Petroleum Institute 2001):

1. 10m^3 of distilled water poured into the Erlenmeyer flask.

2. 5 cm^3 of mixed slurry transferred into the flask.

3. 15 cm^3 of 3% hydrogen peroxide and 0.5 cm^3 of 5N sulfuric acid added to the flask.

4. Gently boiled for 10 minutes, then diluted to 50 cm^3 with deionized water.

5. Methylene blue was added to the flask in increments of 0.5 cm^3. After each addition contents of the flask was swirled for about 30 seconds. While the solids still suspended, one drop of liquid was removed with dropper and placed to filter paper.

6. When a lighter blue tint spreading from the spot was detected, flask was shaked an additional 1-2 minutes and placed another drop on the filter paper. If the blue ring was again evident it

was accepted as the endpoint. If it didn't appear, continued as before until a drop taken after 2 minutes show the blue tint.

7. Methylene blue capacity reported as the value of added methylene blue in cm^3

This method was applied for all of the slurries, whose pHs were initially adjusted to 9.5 before bentonite addition. Same concentrations were tested with the concentrations investigated for capillary suction time test.

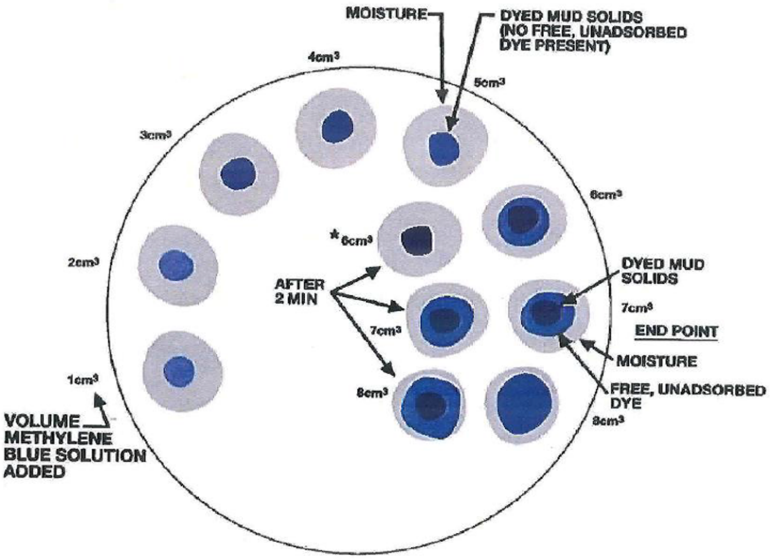


Figure 21: Schematic Sketch of MBT test procedure

4.3.5. One-Dimensional Free Swell Test

One-directional free swell (differential free swell) is an increase in soil volume free of external constraints while submerged in water or a solution of polymers. This increase is a parameter that can be used as a direct indicative of the overall volume change potential of clay minerals. Therefore, free swell is an appropriate approach to evaluate swelling potential of clays with a reasonable degree of accuracy.

Following test procedure is developed from IS 2720 (Part 40) standards:

1. Brines and amine solutions were mixed with the same procedures with capillary suction time tests.
2. 10 grams of fine bentonite sample were poured to 100 cm^3 graduated cylinders.
3. pHs of the brines and solutions adjusted as 9.5 with sodium hydroxide solution.
4. Brines, amine solutions and combined solutions were also poured to 100 cm^3-graduated cylinders.
5. Suspensions were allowed to free swell for 24 hours.
6. The readings after 24 hours were recorded.

7. Diesel, being a non-polar liquid does not cause any volume change in the bentonite samples. Because of this reason one sample was left to swell in diesel oil to calculate free swelling indexes by using the following formula:

$$FSI = \frac{(Vr - Vd)}{Vd} \times 100$$

where,

FSI = free swelling index, percent

Vr = the volume of bentonite specimen read from the graduated cylinder containing solution

Vd = the volume of bentonite specimen read from the graduated cylinder containing diesel oil

CHAPTER 5

RESULTS AND DISCUSSIONS

The results of the experiment and observations on it are detailed in this chapter, which contain XRD analysis, capillary suction time, hot roll dispersion, methylene blue and free swell test results as functions of additives used.

5.1. X-Ray Diffraction Analysis

Since screening samples eliminate some impurities, two XRD results obtained from course and fine bentonite pieces (Appendix A).

XRD results indicate that course samples contain 77% clay and all of the clay minerals are sodium smectite. Mica (muscovite), calcite, feldspar, quartz and zeolite are the other components of fine bentonite samples.

Although zeolites, like clays, are alumino-silicates, their crystalline structure is considerably different. Most clays are composed of layers of crystals, so as water is absorbed and removed between the layers, they exhibit a degree of shrinking and swelling. Zeolites, in contrast, are rigid, with a three-dimentional crystal structure resembling a honeycomb, with a series of connected tunnels and cages. While water can move into and out of these pores, zeolites do not swell and remain in a rigid shape.

79% of fine samples are clay and like course samples, all of the clay minerals show that the sample contains only sodium smectite. From random oriented XRD diffraction patterns it can be said that the rest of the sample consists zeolite, mica (muscovite) and calcite.

5.2. Capillary Suction Time

Capillary suction time tests were performed with changing sodium chloride and potassium chloride concentrations as 3%, 6%, 9%, 12% and 15% by weight and changing quaternary amine concentration as 1%, 2%, 3%, 4%, 5% and 6% by volume at the same bentonite sample concentrations with the increase rate as 10, 20, 30, 40, 50 and 60 lb/bbl to see the changes in capillary suction times. Bentonite concentrations were kept constant for each curve as like pH was adjusted to 9.5 with sodium hydroxide for all samples.

When comparing the capillary suction times of base solution, i.e. no bentonite content, while sodium and potassium chloride gave stabilized CST values. On the other hand quaternary amine gave an increasing trend (Figure 22-24).

When only salts were utilized, capillary suction times decreased exponentially when salt concentrations were increased at the same bentonite contents. This is the reason of the ability of electrolytes to compress electrical double layer. In addition, potassium fixation is the key feature when discussing why the CST values of potassium chloride are lower than sodium chloride (Figure 25-30).

Although, Figure 25-36 indicate that using only quaternary amine gave a bit higher capillary suction times than only salt usage. Following the completion of the cation exchange process, excess quaternary amine molecules available in solution are responsible for this increase in capillary suction time (Figure 24). Also, as bentonite concentration was increased, the distances between the colloidal particles were decreased and because of this reason gel strength increased with the assistance of van der Waals forces. After reaching the critical concentration, the gel strength still increased however oppositely capillary suction times decreased. This situation is the indication of aggregation as Wilcox et al. explained (Wilcox, Fisk, and Corbett 1987). This must be the reason why no more than 20 lb/bbl bentonite can be added to 1% volume quaternary amine solution. Furthermore, 2% concentration could not handle 60 lb/bbl bentonite.

Results of capillary suction time tests are available in Appendix B in more details.

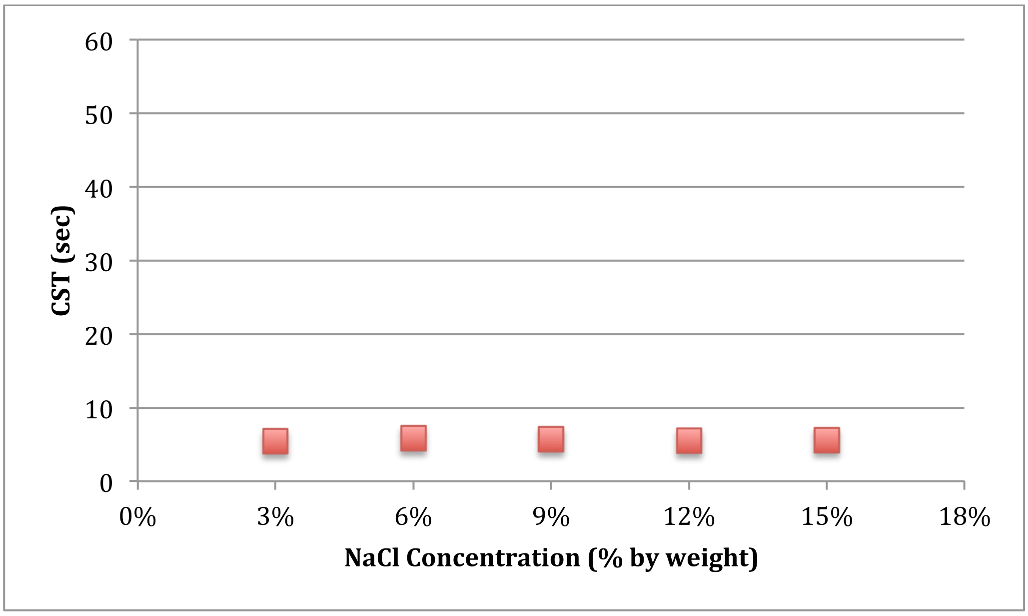


Figure 22: CST Values for Increasing Sodium Chloride Concentration with no Bentonite Content

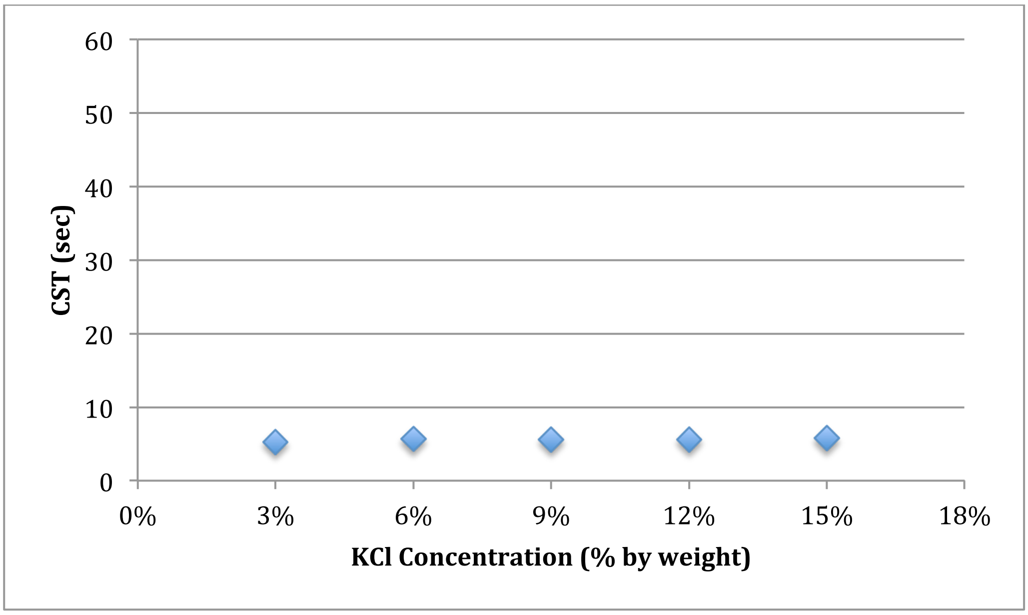


Figure 23: CST Values for Increasing Potassium Chloride Concentration with no Bentonite Content

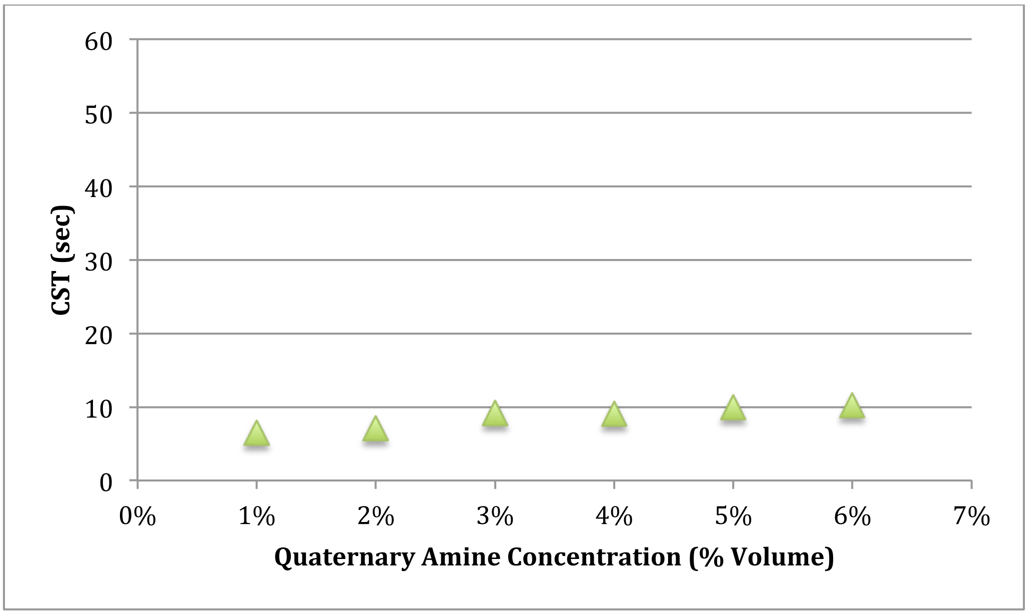


Figure 24: CST Values for Increasing Quaternary Amine Concentration with no Bentonite Content

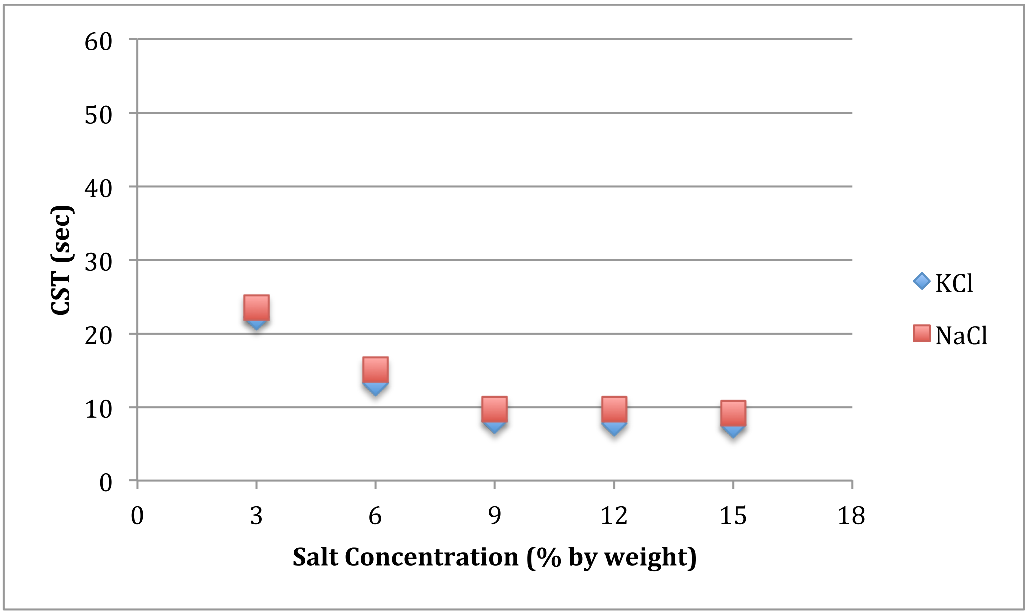


Figure 25: CST Values for Increasing Salt Concentration with 10 lb/bbl Bentonite Content

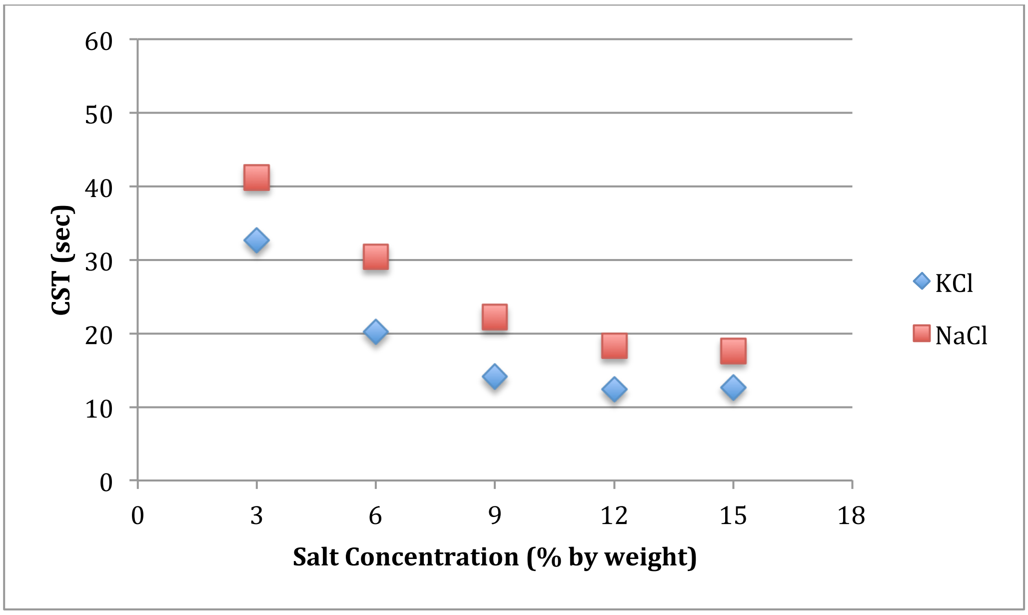


Figure 26: CST Values for Increasing Salt Concentration with 20 lb/bbl Bentonite Content

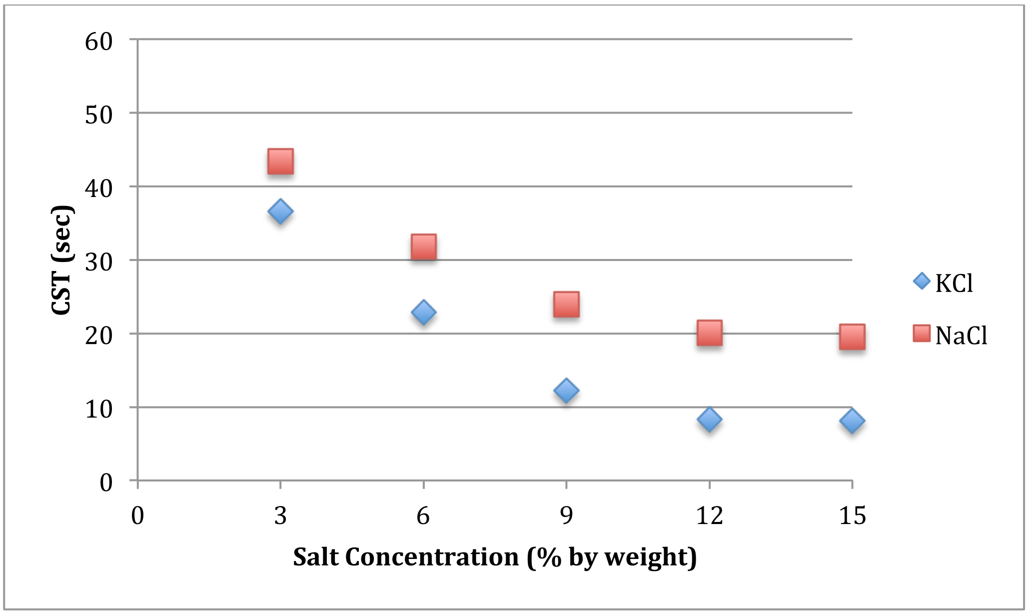


Figure 27: CST Values for Increasing Salt Concentration with 30 lb/bbl Bentonite Content

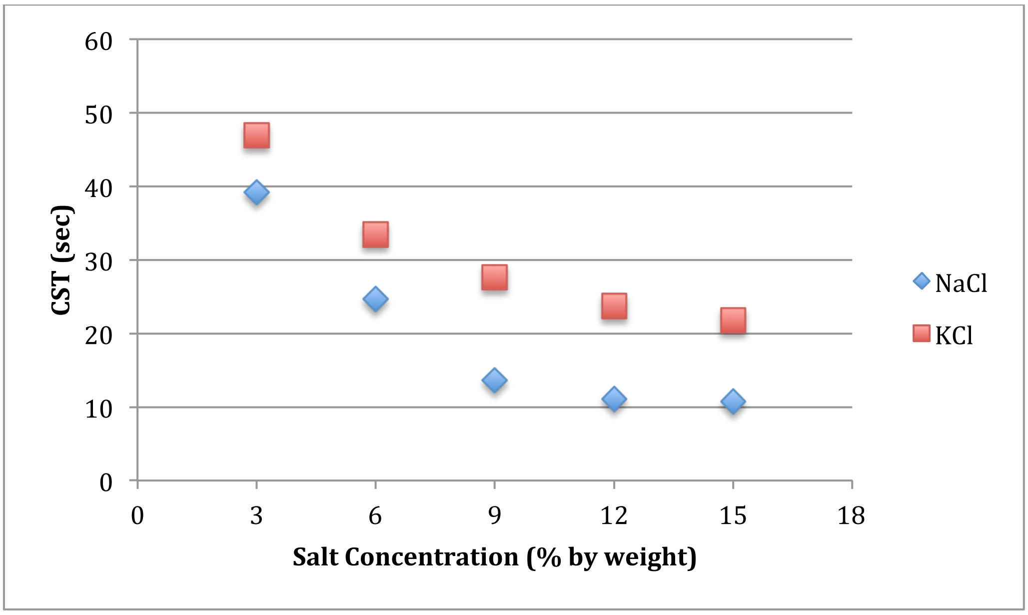


Figure 28: CST Values for Increasing Salt Concentration with 40 lb/bbl Bentonite Content

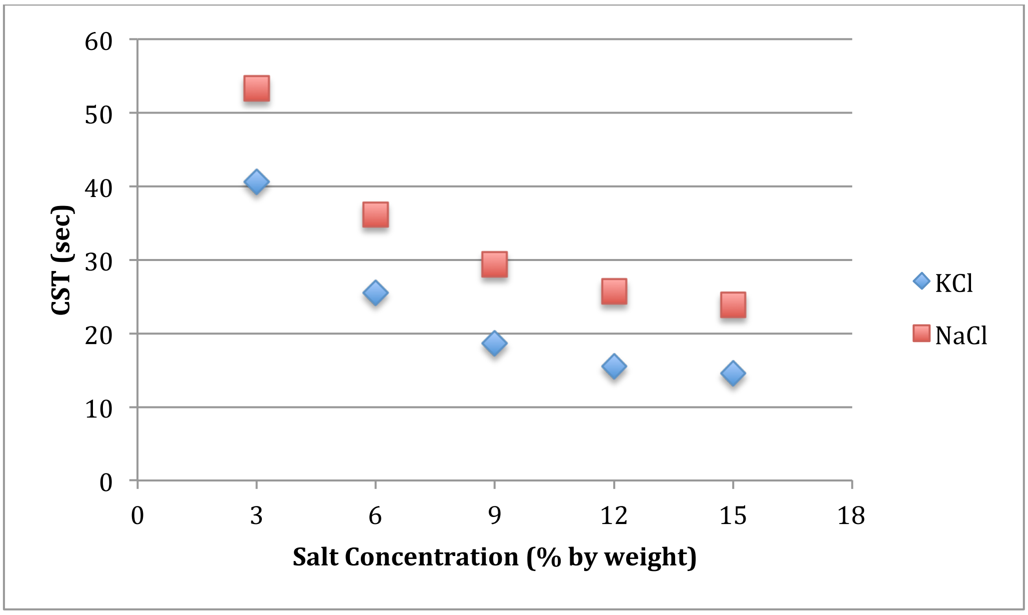


Figure 29: CST Values for Increasing Salt Concentration with 50 lb/bbl Bentonite Content

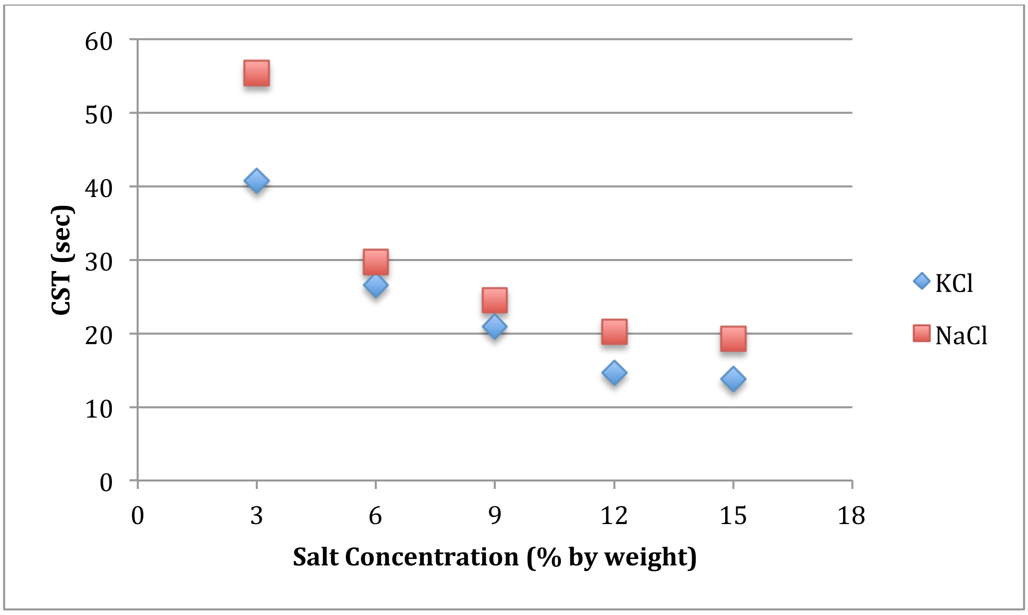


Figure 30: CST Values for Increasing Salt Concentration with 60 lb/bbl Bentonite Content

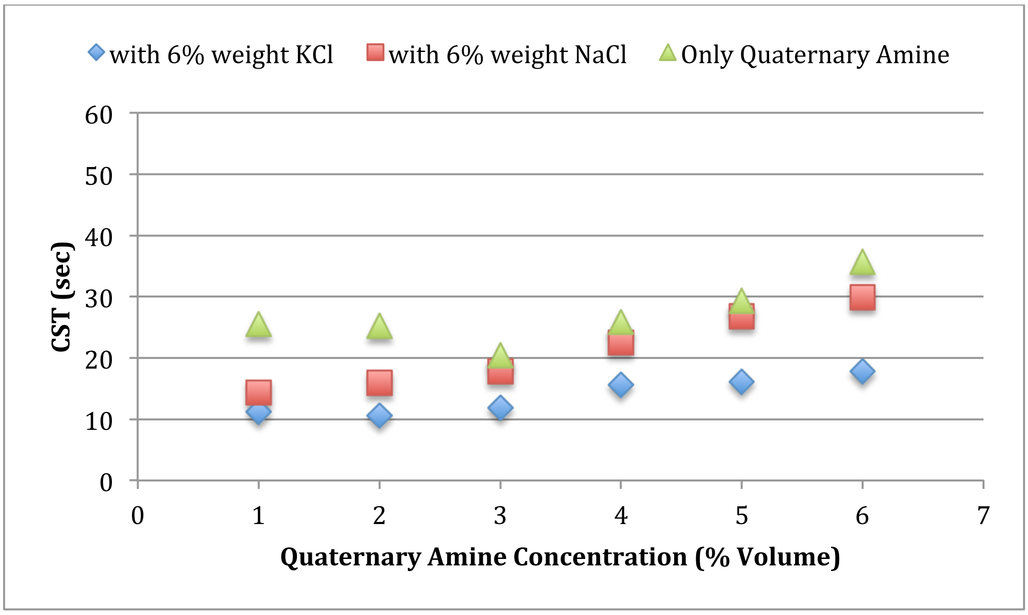


Figure 31: CST Values for Increasing Quaternary Amine with 10 lb/bbl Bentonite Content

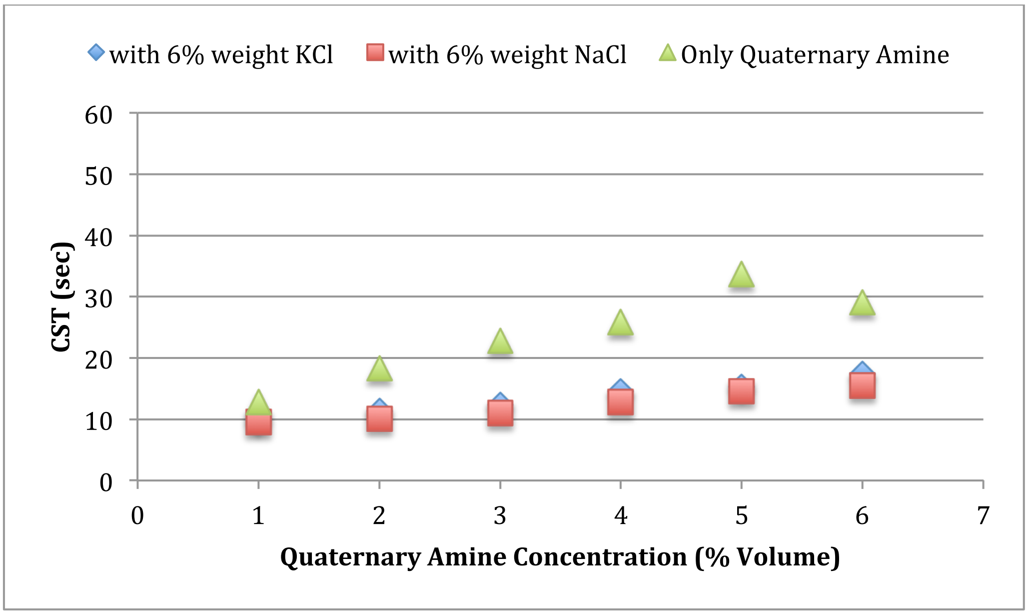


Figure 32: CST Values for Increasing Quaternary Amine with 20 lb/bbl Bentonite Content

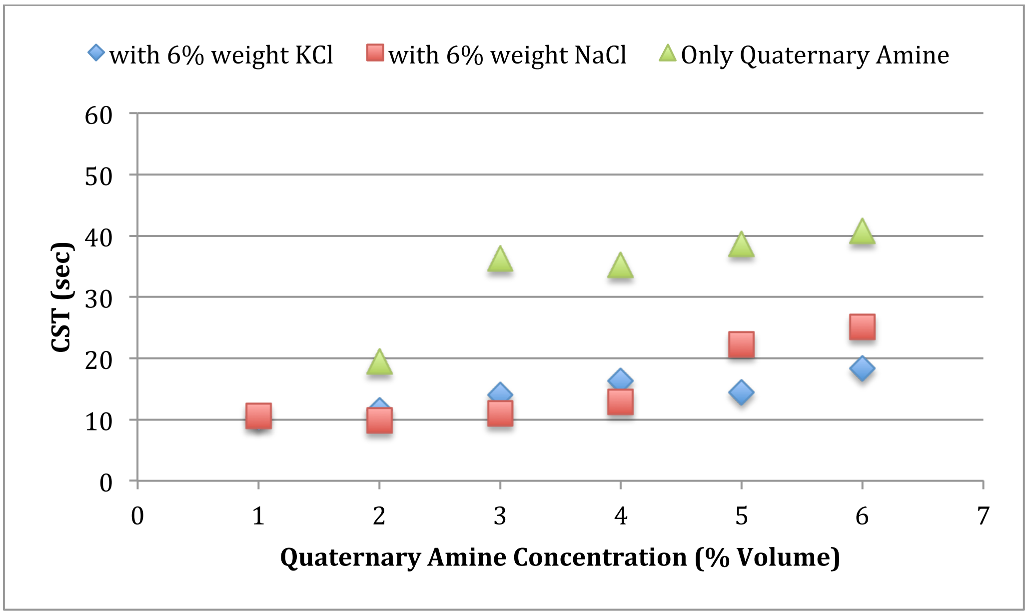


Figure 33: CST Values for Increasing Quaternary Amine with 30 lb/bbl Bentonite Content

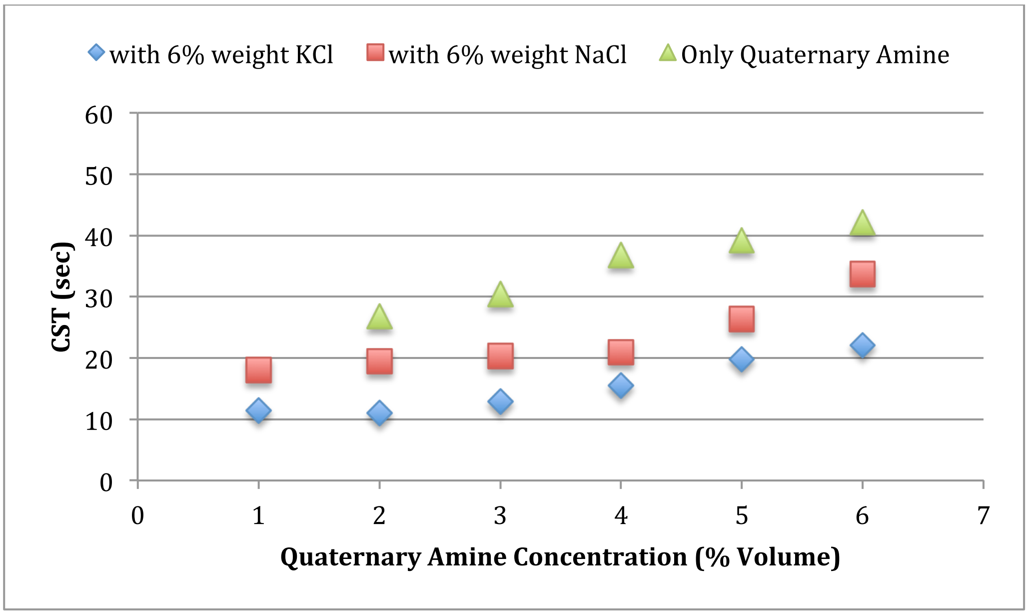


Figure 34: CST Values for Increasing Quaternary Amine with 40 lb/bbl Bentonite Content

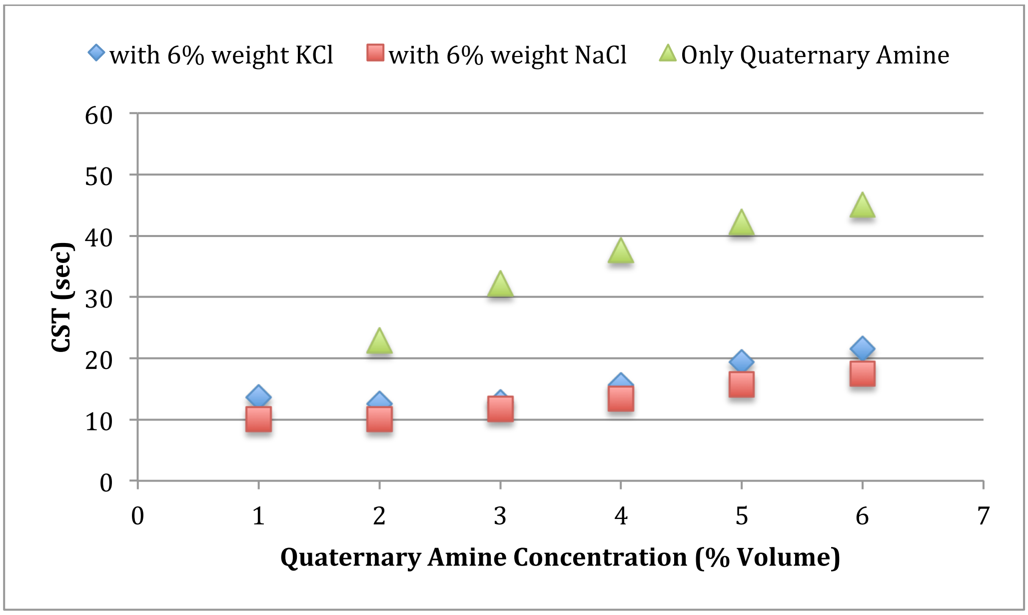


Figure 35: CST Values for Increasing Quaternary Amine with 50 lb/bbl Bentonite Content

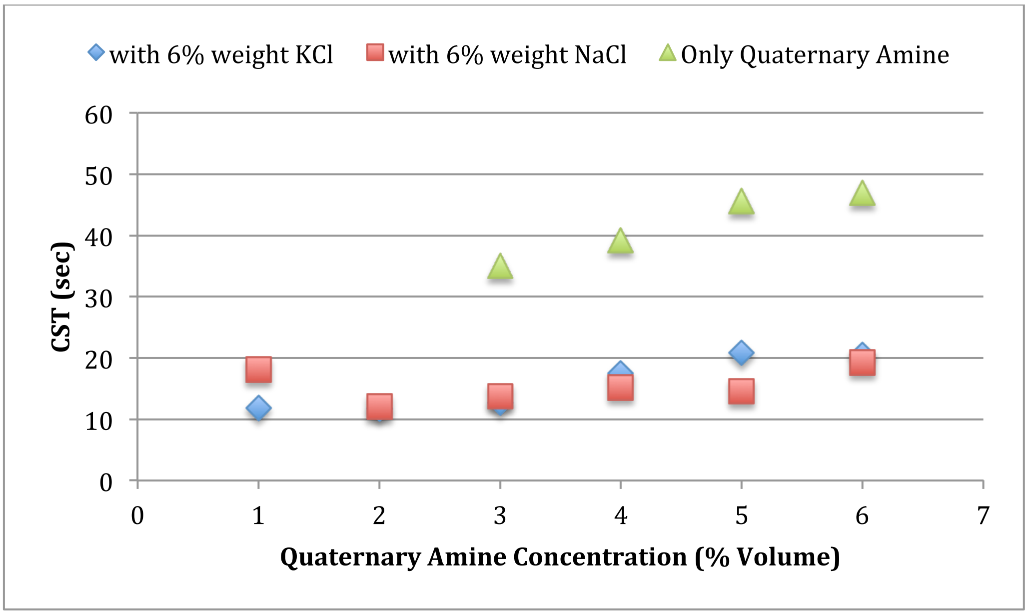


Figure 36: CST Values for Increasing Quaternary Amine with 60 lb/bbl Bentonite Content

5.3. Hot Roll Dispersion

Hot rolling dispersion tests were made to observe long-term interaction between the shale samples and amine solutions. To make suppression comparisons, only sodium chloride (NaCl) and only potassium chloride (KCl) consisting brines were also investigated for hot rolling tests to be taken as references. In addition, for further interpretation 6% (by weight) sodium chloride and potassium chloride brines were mixed with quaternary amine and more hot roll dispersion tests had surveyed with the final mixture. For sodium chloride and potassium chloride solutions 3%, 6%, 9%, 12% and 15% by weight concentrated solutions were used while for amine solutions' concentrations were 1%, 2%, 3%, 4%, 5%, 6% by volume. When the mixture contains both salt and amine, concentration of the salt was kept fixed as 6% by weight.

Expectedly, increasing the concentrations increased the suppression capability of the solutions no matter it contains only salt, only amine or both together. Despite of the fact that, sodium chloride brines results some recoveries, they are very little amount if compared with the bentonite pieces saved by the potassium chloride brines. Cation exchange affinities of potassium ions are greater than sodium ions and this makes potassium ions, which were obtained from potassium chloride, to penetrate to the interlamellar space of the bentonite clay more easily than sodium ions. In addition, ionic sizes of the potassium ions are larger than sodium ions and fits better to the gallery between the platelet. This is the reason why more recoveries were obtained by using potassium chloride brines. This result can be figured out from Figure 37 and 38.

Using quaternary amine solutions alone did not give good results in low concentrations. However, when compared with sodium and potassium chloride brines' recoveries, it can be seen that best recoveries were obtained by quaternary amine. If the specific gravity of the quaternary amine considered, approximately 6.5% by weight of quaternary amine was sufficient to recover nearly all of the bentonite pieces. This result could not be achieved with sodium and potassium salts even in elevated concentrations. This can also be seen if Figures 37-39 are compared.

On the other hand, even in high levels of amine concentrations the clay samples were soft and can be dispersed easily. In addition the shapes of the recoveries were not well defined. Therefore, utilizing quaternary amines with salts is better way to get more recoveries. Figure 40 and 41 show the results of combining 6% by weight brines and quaternary amine together. Both sodium and potassium chloride make the recoveries of quaternary amine climb. Apparently, compressing the double layer of the clays significantly helps amine compounds in great aspects.

Results of hot rolling dispersion tests are available in Appendix C in more details.

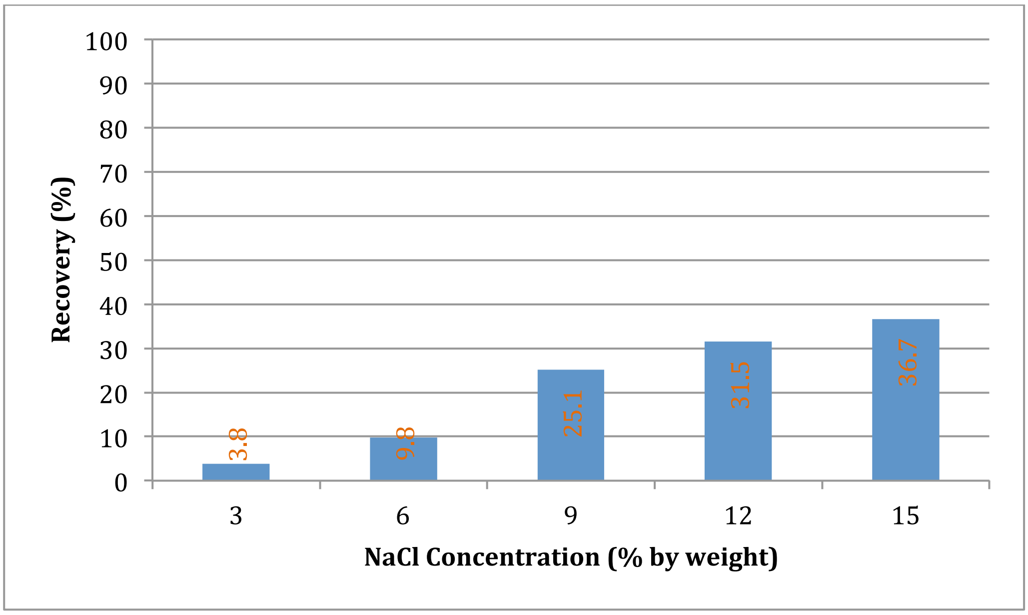


Figure 37: Hot Rolling Recoveries for Different NaCl Concentrations

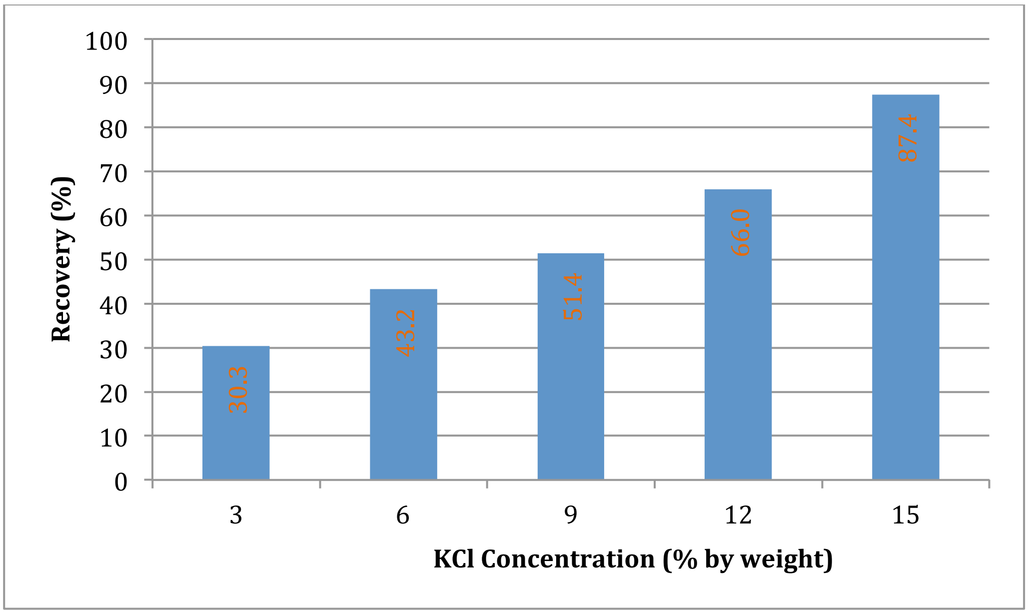


Figure 38: Hot Rolling Recoveries for Different KCl Concentrations

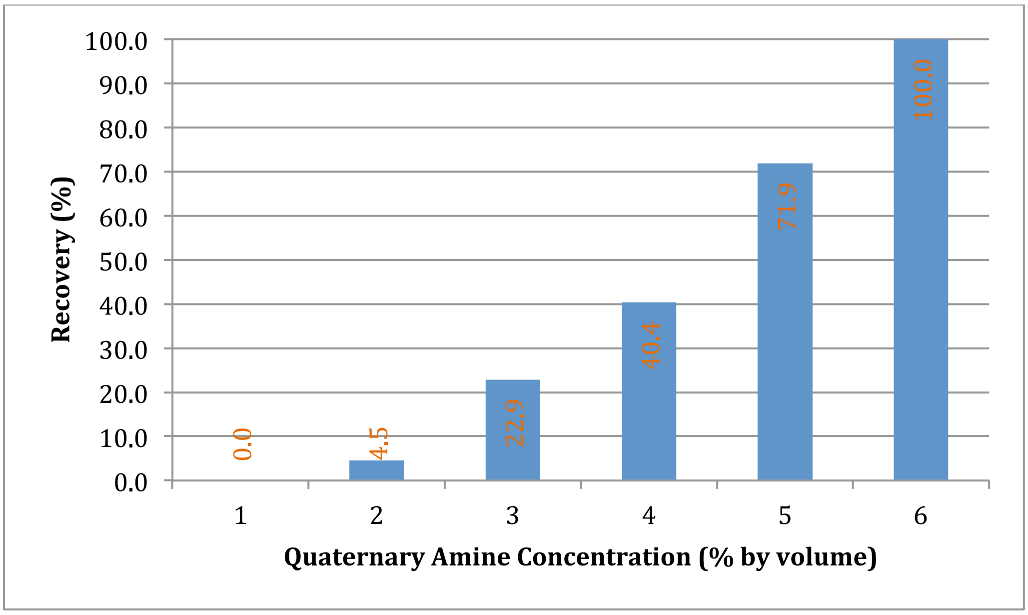


Figure 39: Hot Rolling Recoveries for Different Quaternary Amine Concentrations

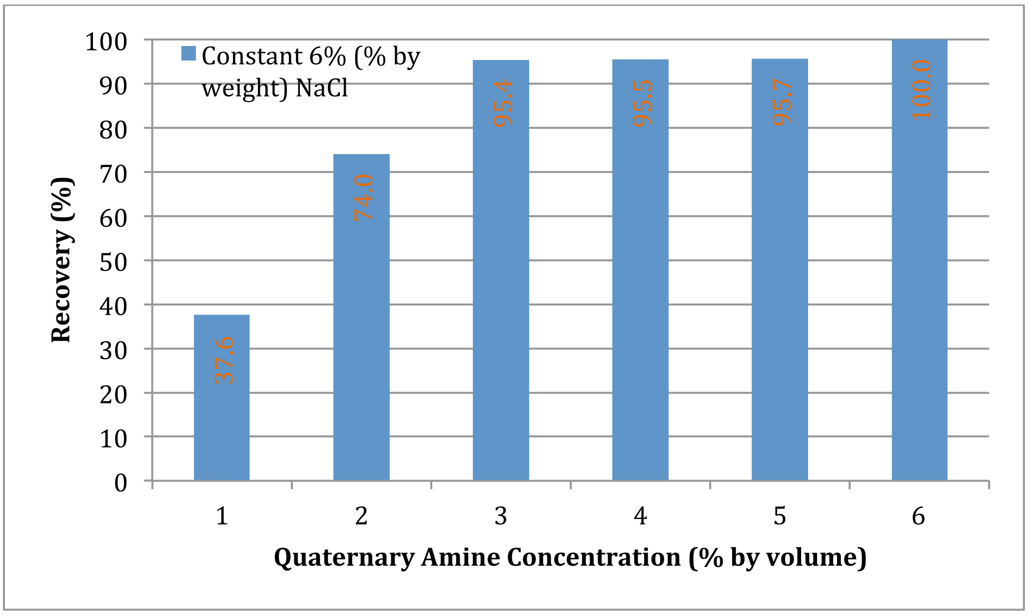


Figure 40: Hot Rolling Recoveries for Constant 6% (by weight) NaCl Combined with Different Quaternary Amine Concentrations

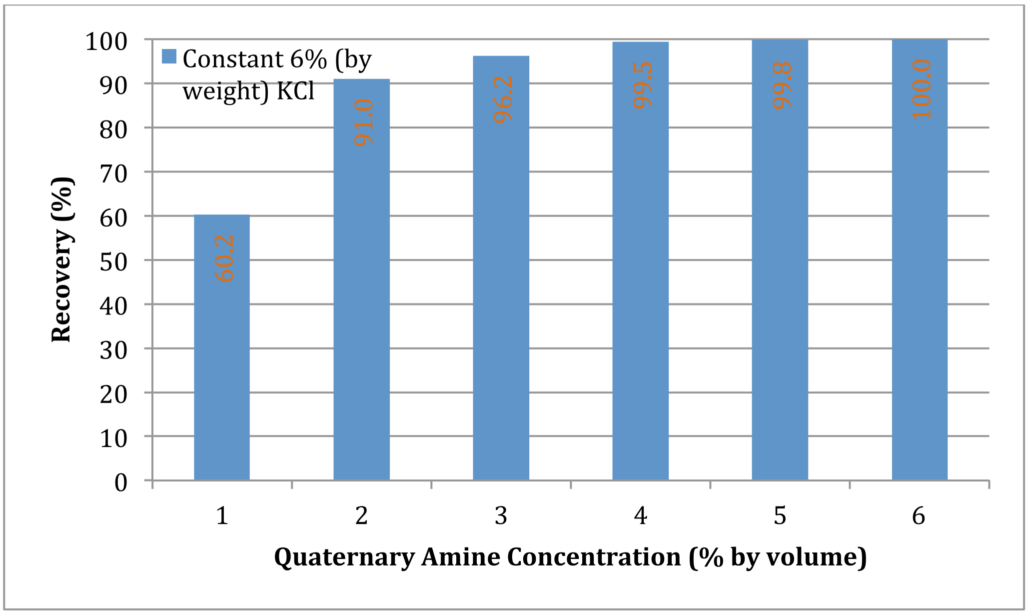


Figure 41: Hot Rolling Recoveries for 6% (by weight) KCl Combined with Different Quaternary Amine Concentrations

5.4. Methylene Blue Capacity

Methylene blue capacity tests were performed to gain a different point of view to shale inhibition mechanism of quaternary amine compound. After mixing the quaternary amine solutions as 1%, 2%, 3%, 4%, 5% and 6% by volume and arranging the pHs to 9.5; 10, 15, 20, 30, 40, 50 and 60 lb/bbl fine bentonite samples were added to each amine solutions separately and left for aging for 16 hours under 120° F. Also, this process was applied to brines, which have concentrations of 3%, 6%, 9%, 12% and 15% by weight, and amine-salt (6% by weight) mixtures.

As presumed, methylene blue capacities decreased exponentially, with increasing quaternary amine content at the same concentration of bentonite. Figures 42 to 47 show the behavior of the solutions when contains 10, 20, 30, 40, 50 and 60 lb/bbl bentonite respectively. Unfortunately, due to the excessive viscosity development, 1% quaternary amine behaviors for more than 20 lb/bbl bentonite could not be obtained when only quaternary amine employed. Furthermore, for 60 lb/bbl bentonite also 2% behaviors could not be concluded since this disproportionate viscosity.

The decrease of the MBT values with increasing quaternary amine content is the reason of the depression of the negatively charged surfaces. Quaternary ammonium cations neutralized negatively charged surfaces and by this way prevented methylene blue dye to be anchored to these surfaces. Consequently, MBT value decreased.

Results of methylene blue capacity tests are available in Appendix D in more details.

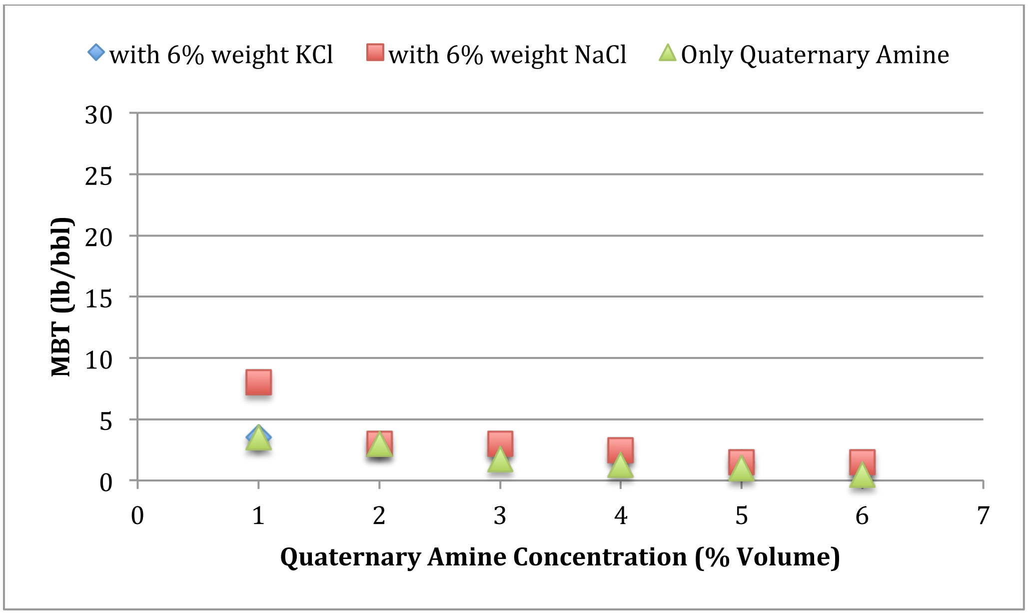


Figure 42: MBT Values for Increasing Quaternary Amine Concentration with 10 lb/bbl Bentonite Content

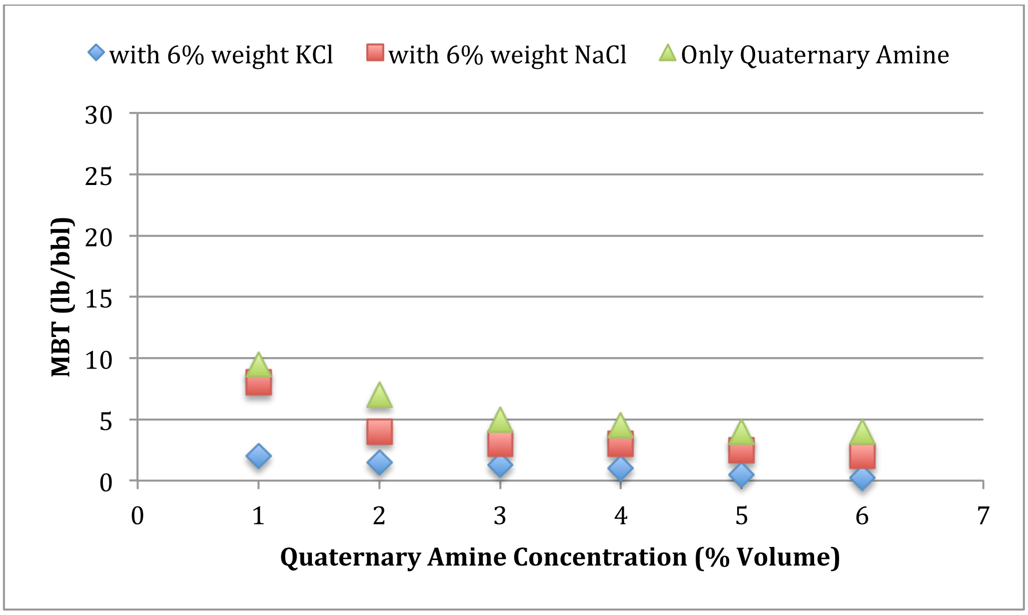


Figure 43: MBT Values for Increasing Quaternary Amine Concentration with 20 lb/bbl Bentonite Content

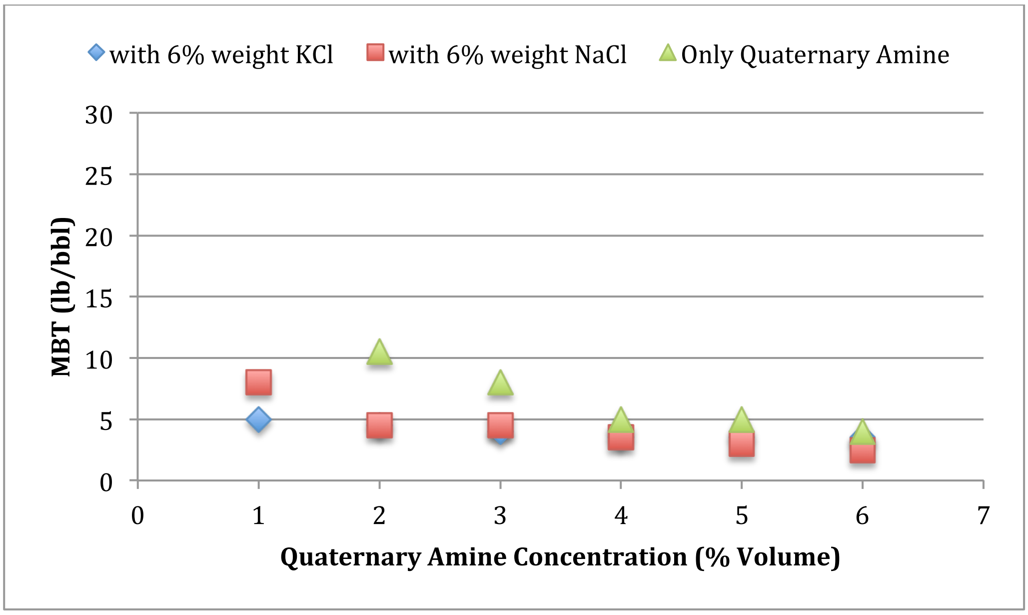


Figure 44: MBT Values for Increasing Quaternary Amine Concentration with 30 lb/bbl Bentonite Content

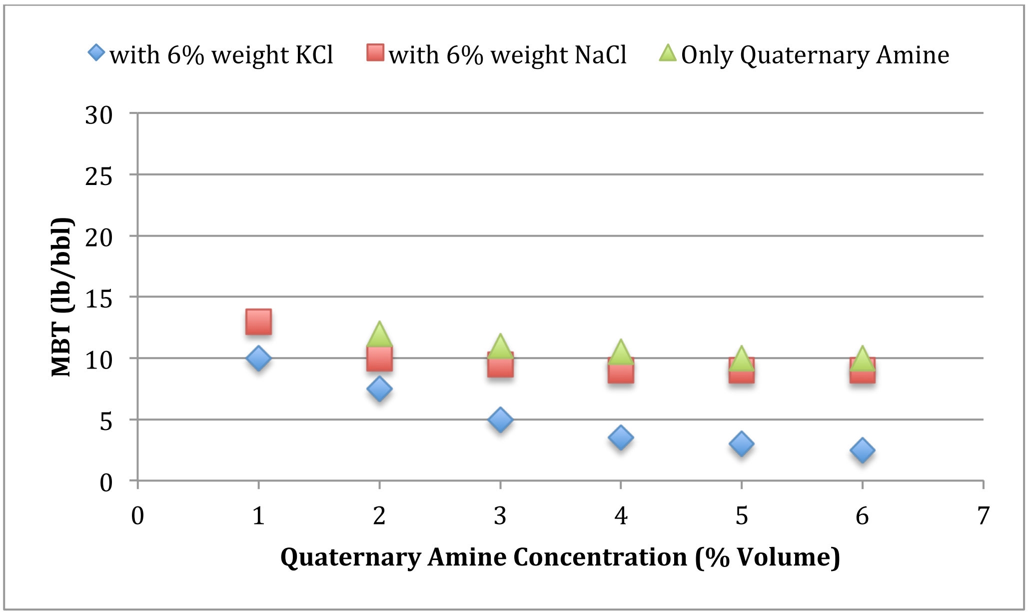


Figure 45: MBT Values for Increasing Quaternary Amine Concentration with 40 lb/bbl Bentonite Content

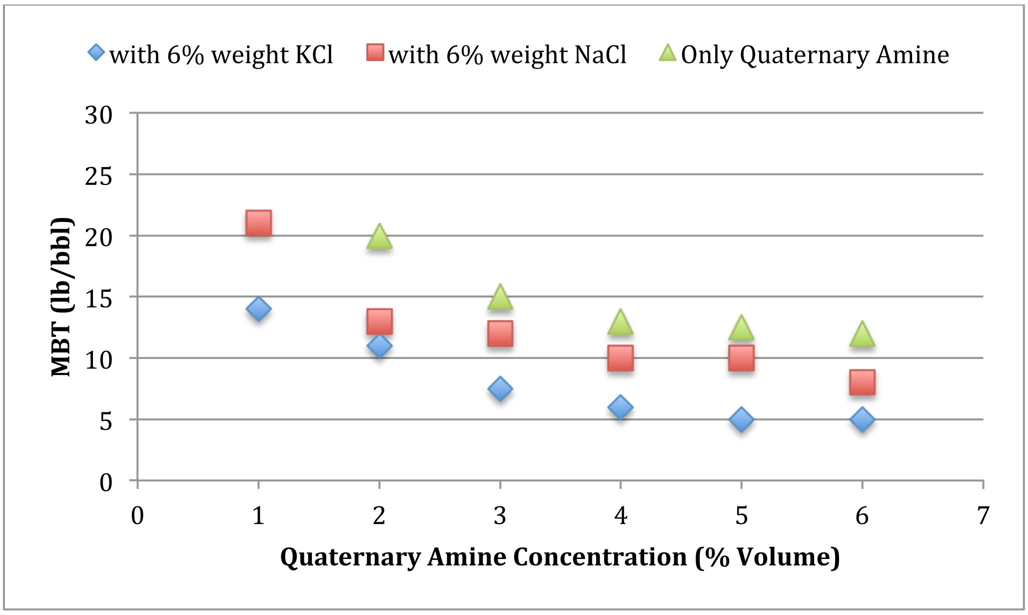


Figure 46: MBT Values for Increasing Quaternary Amine Concentration with 50 lb/bbl Bentonite Content

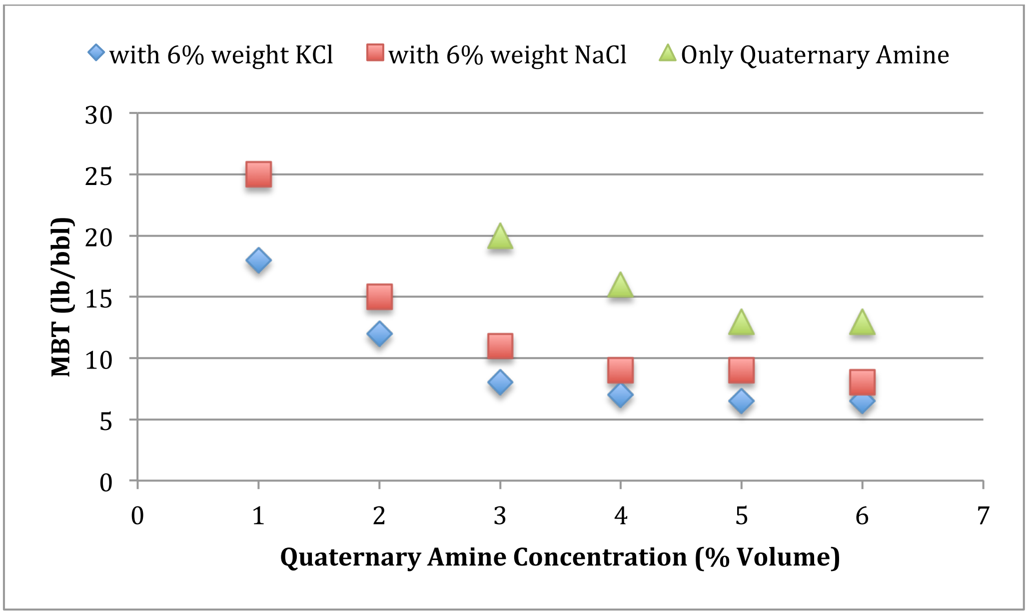


Figure 47: MBT Values for Increasing Quaternary Amine Concentration with 60 lb/bbl Bentonite Content

5.5. One-Dimensional Free Swell Test

In order to interpret the swelling properties of the bentonite pieces in solutions, one-dimensional free swelling tests were performed. The increments of free swelling indexes, which were obtained from one-dimensional free swell, are the direct symptoms of expansion ability of the solid samples.

As shown from Figure 48 and Figure 49 potassium chloride and sodium chloride additions significantly reduced the free swelling index. From related graphs it can be revealed that potassium chloride salt reflects very good shale suppression and it made bentonite pieces not expand as much as sodium chloride salt did. Consequently, lower levels were read from the swell testing measures. This situation is related to the cation exchange and the ionic structure of potassium chloride.

Figures 50 to 52 indicate that quaternary amine addition also leads to significant reduction of free swelling index. This effect of quaternary amine became more apparent when it was used together with sodium chloride and potassium chloride, particularly with the last one.

If Figures 53 to 55 are compared, however, dispersive characteristics of the clays in quaternary amine solutions can be observed from the clouds. Nonetheless, utilizing salts with quaternary amine increased the suppression of expanding, which was already observed in CST and MBT tests. Figure 51 and 52 show this result clearly. As a result, differential-swelling tests supported the results obtained from other surveys subjected to this study.

Results of one-dimensional free swelling tests are available in Appendix E in more details.

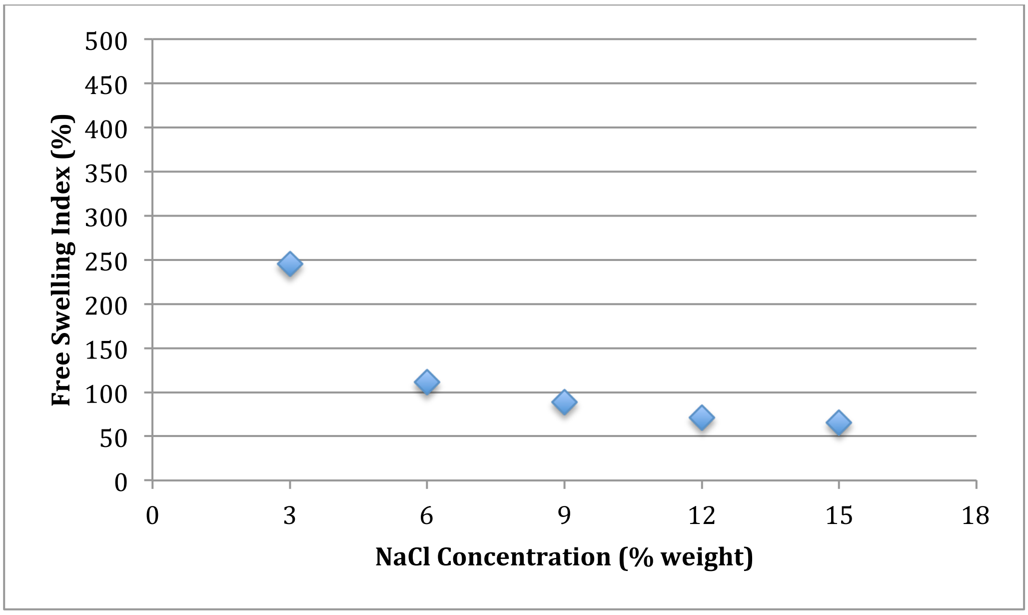


Figure 48: One-Dimensional Free Swell Test Results for Sodium Chloride Concentrations

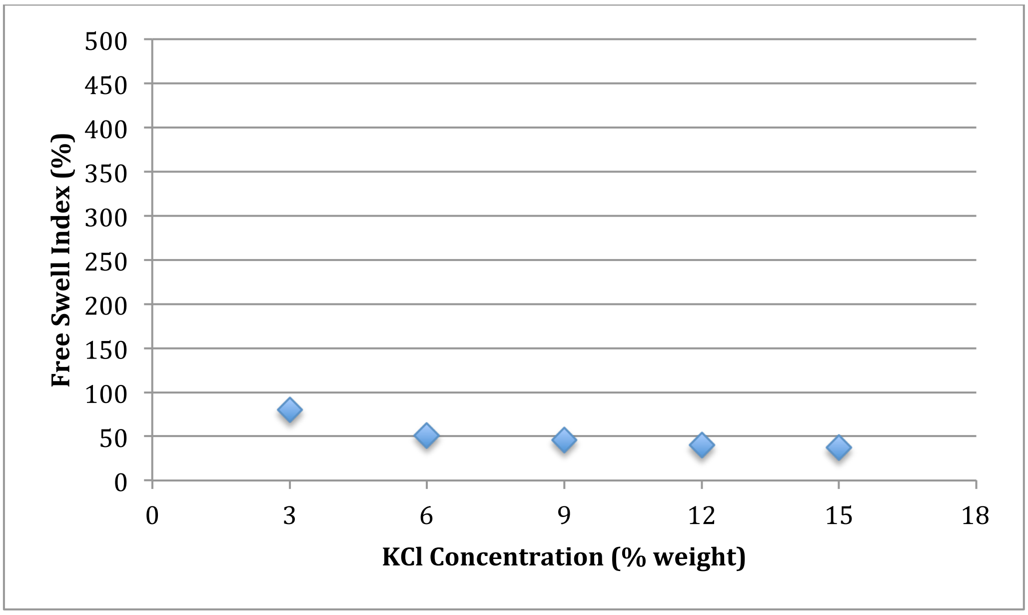


Figure 49: One-Dimensional Free Swell Test Results for Potassium Chloride Concentrations

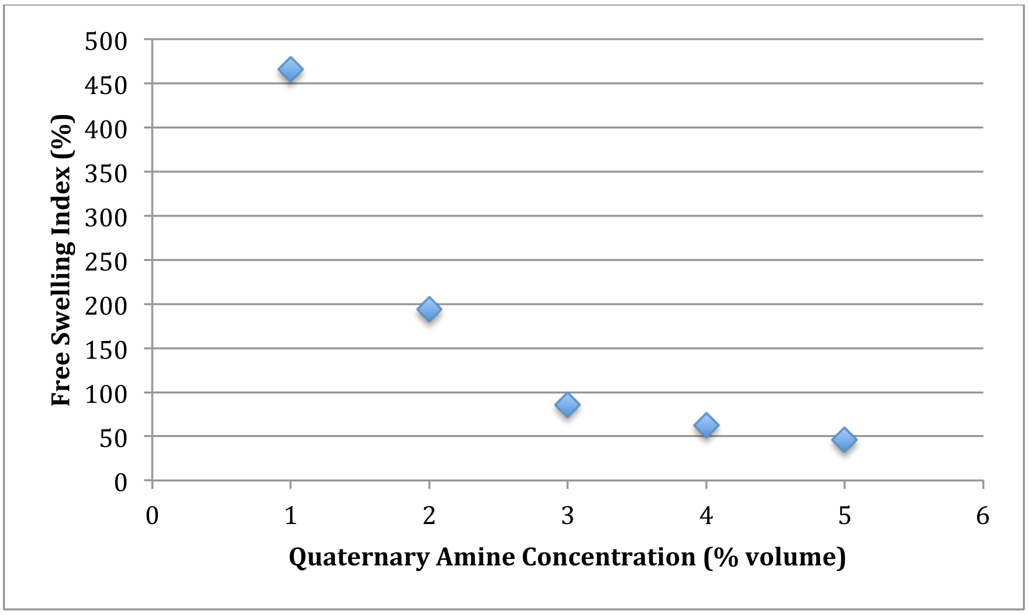


Figure 50: One-Dimensional Free Swell Test Results for Quaternary Amine Concentrations

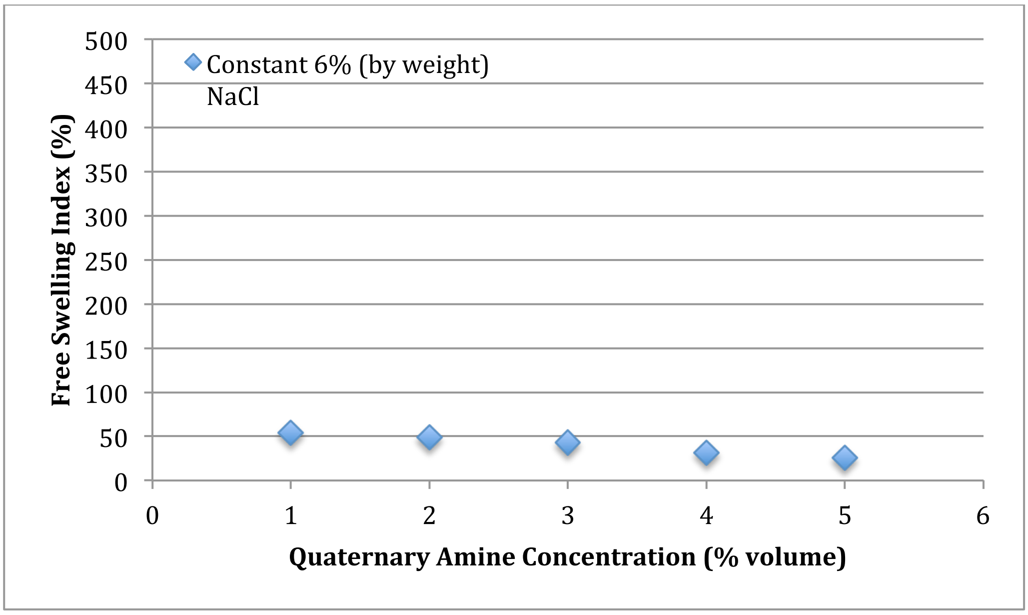


Figure 51: One-Dimensional Free Swell Test Results for Constant 6% (by weight) NaCl Combined with Quaternary Amine Concentrations

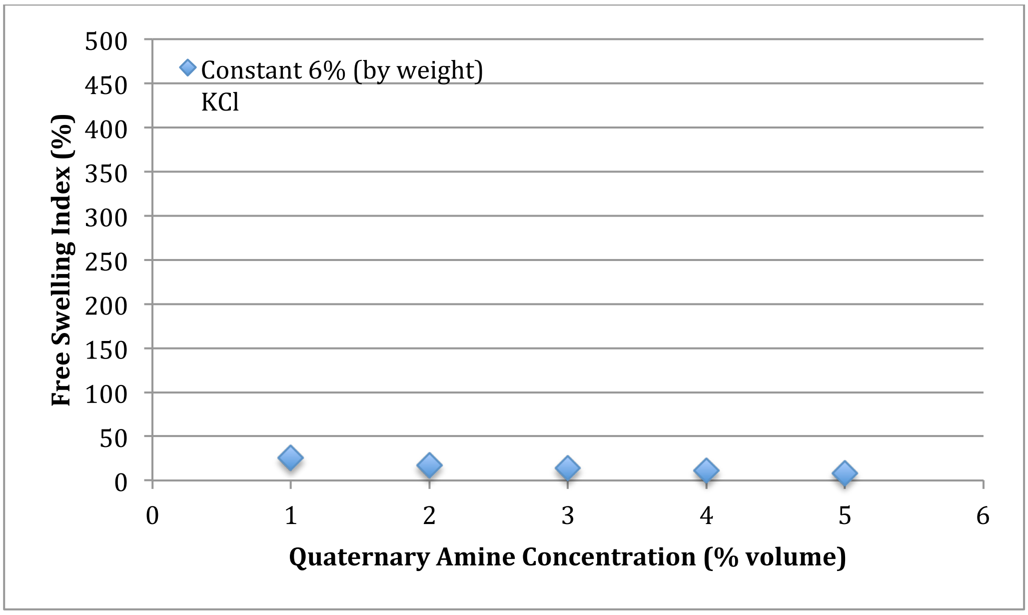


Figure 52: One-Dimensional Free Swell Test Results for Constant 6% (by weight) KCl Combined with Quaternary Amine Concentrations

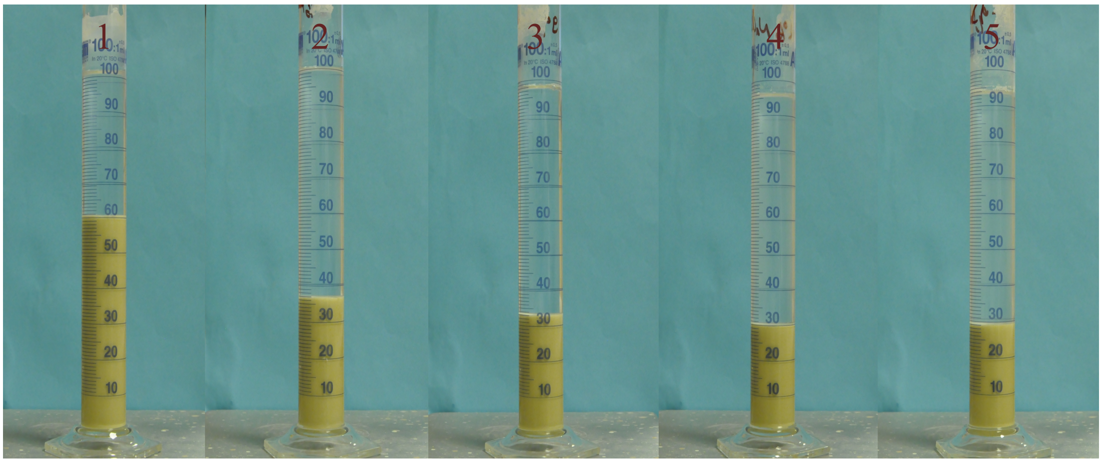


Figure 53: One-Dimensional Free Swell Test Results for 3%, 6%, 9%, 12% and 15% Sodium Chloride by Weight Concentrations

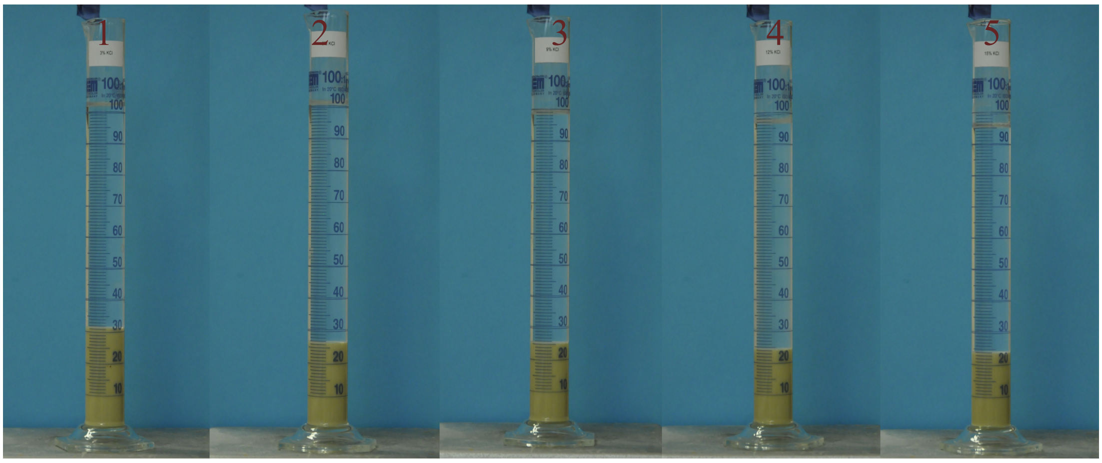


Figure 54: One-Dimensional Free Swell Test Results for 3%, 6%, 9%, 12% and 15% Potassium Chloride by Weight Concentrations

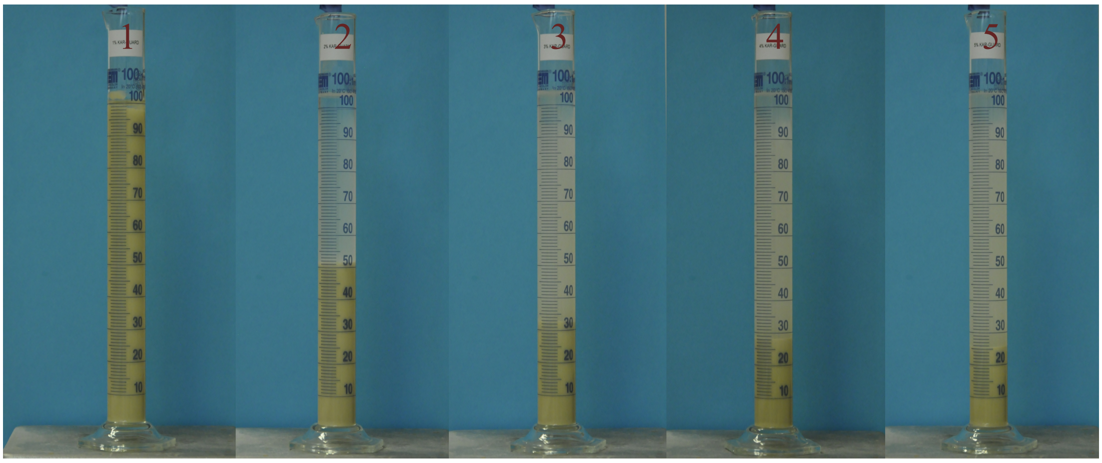


Figure 55: One-Dimensional Free Swell Test Results for 1%, 2%, 3%, 4% and 5% Quaternary Amine by Volume Concentrations

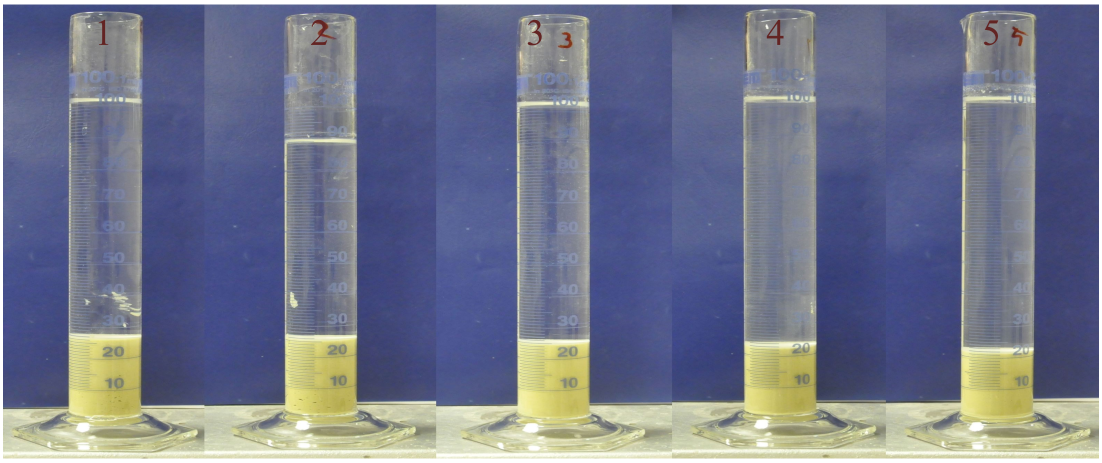


Figure 56: One-Dimensional Free Swell Test Results for 6% Sodium Chloride by Weight with 1%, 2%, 3%, 4% and 5% by Volume Quaternary Amine Concentrations

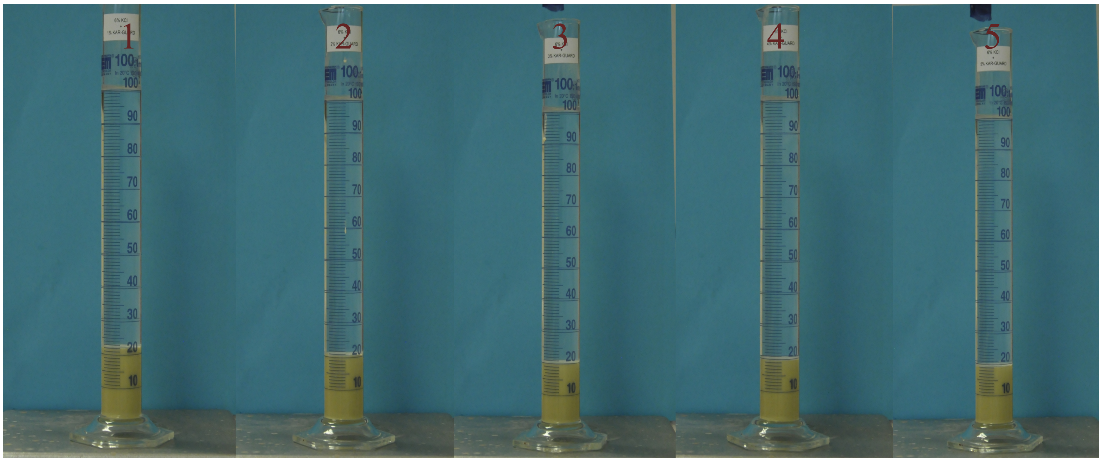


Figure 57: One-Dimensional Free Swell Test Results for 6% Potassium Chloride by Weight with 1%, 2%, 3%, 4% and 5% by Volume Quaternary Amine Concentrations

CHAPTER 6

CONCLUSION

This survey was conducted to examine the behavior and shale suppression properties of quaternary amine and determine the concentration needed when used alone and with salts.

Based upon X-Ray diffraction analysis, capillary suction time, hot rolling dispersion, methylene blue and one-dimensional free swelling tests to the following conclusions are reached:

1. CST test results indicated that capillary suction time decreases with increasing sodium and potassium chloride content due to flocculation.
2. This behavior was reversed for quaternary amine due to the increasing solution viscosity and linkage established by quaternary amine molecules between clay particles.
3. For a given quaternary amine concentration, face-to-face (FF) particle association (aggregation) was approached with increasing bentonite content and full aggregation occurred at a critical value.
4. Quaternary amine with lower concentration compared to sodium chloride and potassium chloride provided higher cutting recoveries as indicated by hot rolling tests.
5. Cutting recoveries were further improved by using quaternary amine with sodium chloride and potassium chloride combination.
6. The cuttings recovered from potassium chloride treated system were well defined with sharp corners compared to those quaternary amine treated system.
7. Methylene blue test is a good tool to determine the replacement power of quaternary amine and potassium chloride. Decreasing trend of MBT with increasing quaternary amine concentration indicated that less exchangeable cations were available on clay surfaces after the quaternary amine treatment. This reduction of cation exchange capacity was more emphasized in combined treatment with quaternary amine and potassium chloride.
8. Potassium chloride provided lower free swelling index than that of sodium chloride. On the other hand, 5% (by volume) quaternary amine provided same free swelling index with 15% (by weight) potassium chloride.
9. Based on less dispersive morphology obtained from potassium chloride treatment than quaternary amine, it was experimentally verified that utilizing potassium chloride with quaternary amine resulted in lowest free swelling index and consequently greatest shale inhibition.

CHAPTER 7

RECOMMENDATIONS

1. In this study, only one type of quaternary amine compound was investigated. Due to the fact that type of amine compound affects amine-smectite association in greater manner, different types of quaternary amines should be studied to have better understanding.

2. Sodium montmorillonite, which is a member of smectite family, was chosen to investigate for this study due to its superior colloidal and expansion features. Different types of clay minerals, such as illite and kaolinite can be surveyed in the same manners to understand the reactions between amine and clay minerals.

3. Swelling tests can be conducted at simulated bottom hole temperature and pressure conditions to evaluate actual performance of quaternary amine and other shale inhibitors.

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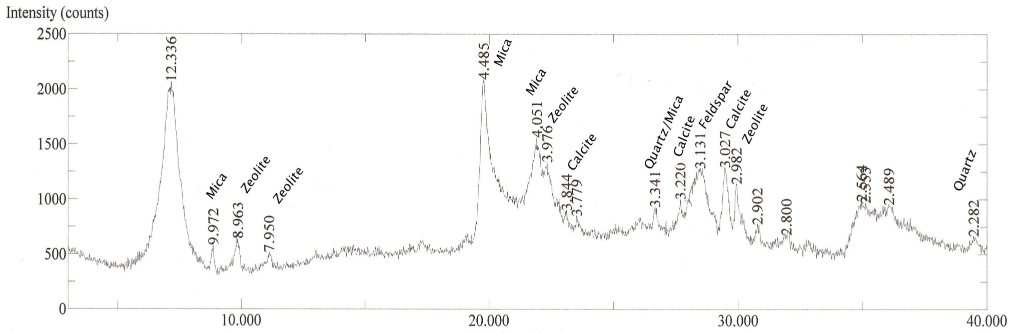
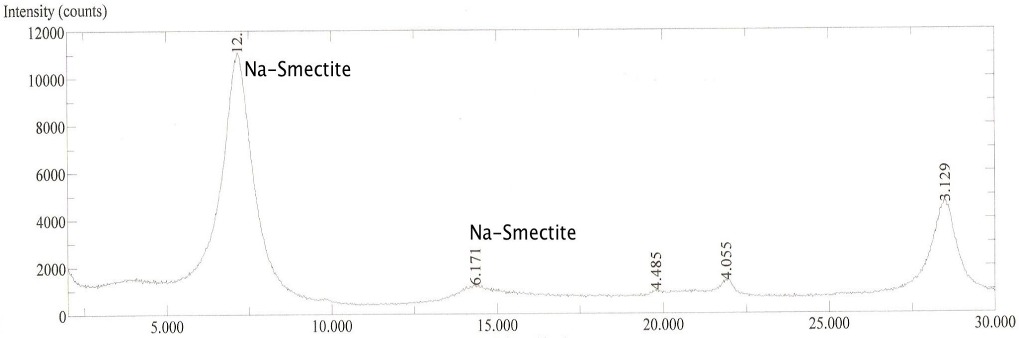
APPENDIX A

X-RAY DIFFRACTION ANALYSIS RESULTS



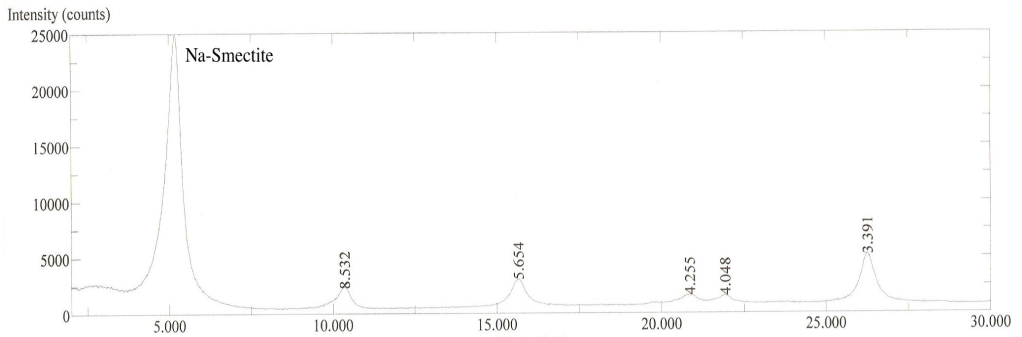
Peak no.	2theta	Flex Width	d-value	Intensity	I/Io
1	7.160	*****	12.3359	2069	99
2	8.860	*****	9.9724	586	28
3	9.860	*****	8.9631	643	31
4	11.120	*****	7.9502	521	25
5	19.780	*****	4.4847	2096	100
6	21.920	*****	4.0515	1570	75
7	22.340	*****	3.9762	1344	65
8	23.120	*****	3.8438	905	44
9	23.520	*****	3.7794	854	41
10	26.660	*****	3.3409	937	45
11	27.680	*****	3.2201	1007	49
12	28.480	0.329	3.1314	1287	62
13	29.480	0.235	3.0274	1294	62
14	29.940	*****	2.9820	1147	55
15	30.780	*****	2.9025	778	38
16	31.940	*****	2.7997	680	33
17	34.960	*****	2.5644	990	48
18	35.120	*****	2.5531	970	47
19	36.060	*****	2.4887	958	46
20	39.460	*****	2.2817	671	33

Figure A.1: Random Oriented X-Ray Diffraction Pattern of Course Bentonite



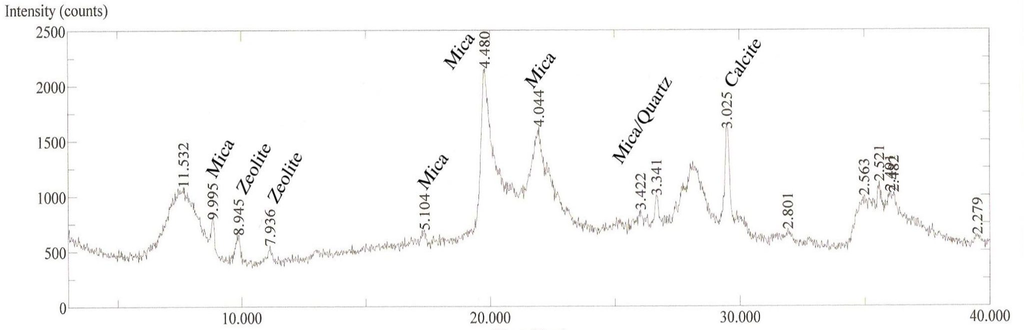
Peak no.	2theta	Flex Width	d-value	Intensity	I/Io
1	7.160	0.706	12.3359	11089	100
2	14.340	*****	6.1714	1239	12
3	19.780	*****	4.4847	1012	10
4	21.900	*****	4.0551	1409	13
5	28.500	0.612	3.1293	4660	43

Figure A.2: Air Dried X-Ray Diffraction Pattern of Course Bentonite



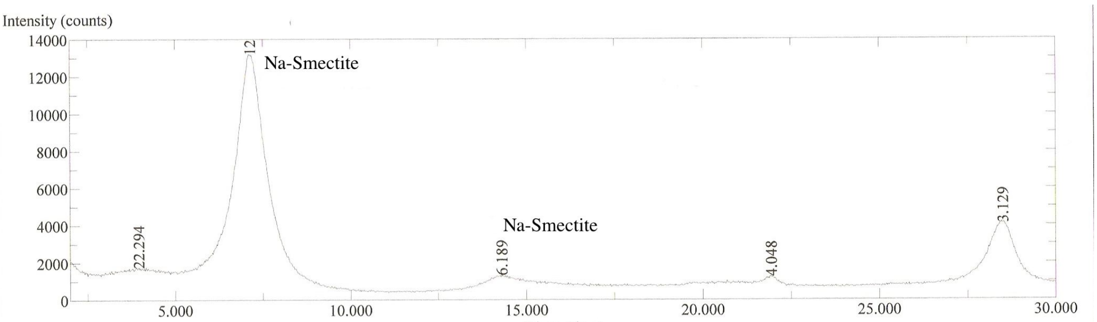
Peak no.	2theta	Flex Width	d-value	Intensity	I/Io	Peak no.	2theta	Flex Width	d-value	Intensity	I/Io
1	5.200	0.353	16.9804	24830	100						
2	10.360	0.329	8.5317	2303	10						
3	15.660	0.376	5.6541	3040	13						
4	20.860	*****	4.2549	1640	7						
5	21.940	*****	4.0478	1579	7						
6	26.260	0.376	3.3909	5193	21						

Figure A.3: Ethylene Glycol Treated X-Ray Diffraction Pattern of Course Bentonite



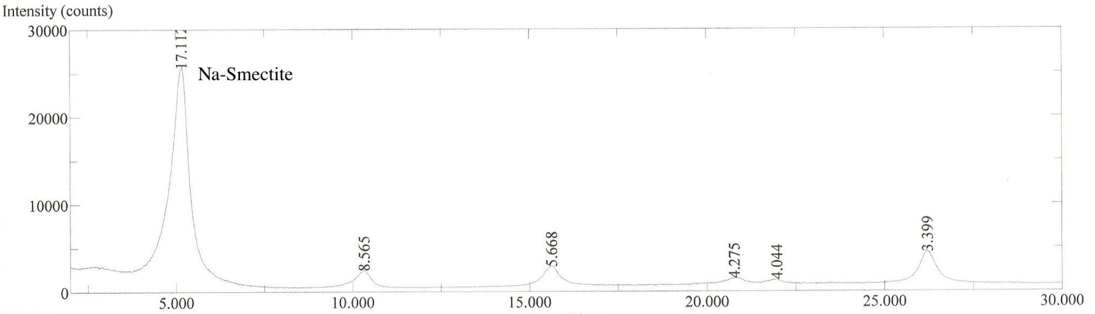
Peak no.	2theta	Flex Width	d-value	Intensity	I/Io	Peak no.	2theta	Flex Width	d-value	Intensity	I/Io
1	7.660	*****	11.5318	1089	51	16	39.500	*****	2.2795	644	30
2	8.840	*****	9.9949	799	37						
3	9.880	*****	8.9450	654	31						
4	11.140	*****	7.9360	557	26						
5	17.360	*****	5.1040	696	33						
6	19.800	*****	4.4802	2161	100						
7	21.960	*****	4.0442	1631	76						
8	26.020	*****	3.4216	877	41						
9	26.660	*****	3.3409	1006	47						
10	29.500	0.188	3.0254	1608	75						
11	31.920	*****	2.8014	699	33						
12	34.980	*****	2.5630	1001	47						
13	35.580	*****	2.5211	1128	53						
14	36.020	*****	2.4913	1036	48						
15	36.160	*****	2.4820	1029	48						

Figure A.4: Random Oriented X-Ray Diffraction Pattern of Fine Bentonite



Peak no.	2theta	Flex Width	d-value	Intensity	I/Io	Peak no.	2theta	Flex Width	d-value	Intensity	I/Io
1	3.960	*****	22.2942	1773	14						
2	7.140	0.635	12.3704	13188	100						
3	14.300	*****	6.1886	1351	11						
4	21.940	*****	4.0478	1272	10						
5	28.500	0.706	3.1293	4101	32						

Figure A.5: Air Dried X-Ray Diffraction Pattern of Fine Bentonite



Peak no.	2theta	Flex Width	d-value	Intensity	I/Io	Peak no.	2theta	Flex Width	d-value	Intensity	I/Io
1	5.160	0.353	17.1119	25600	100						
2	10.320	0.376	8.5646	2466	10						
3	15.620	0.400	5.6685	2912	12						
4	20.760	*****	4.2752	1553	7						
5	21.960	*****	4.0442	1392	6						
6	26.200	0.424	3.3985	4480	18						

Figure A.6: Ethylene Glycol Treated X-Ray Diffraction Pattern of Fine Bentonite

APPENDIX B

CAPILLARY SUCTION TIME TEST RESULTS

Table B.1: CST Values with Increasing Sodium Chloride Concentration for Changing Bentonite Content

		CST (sec)				
	NaCl (% weight)	3%	6%	9%	12%	15%
Bentonite Content	0 lb/bbl	5.4	5.9	5.7	5.5	5.6
	10 lb/bbl	22.2	13.3	8.1	7.8	7.5
	20 lb/bbl	32.7	20.2	14.1	12.4	12.7
	30 lb/bbl	36.6	22.8	12.2	8.3	8.1
	40 lb/bbl	39.2	24.7	13.6	11.1	10.7
	50 lb/bbl	40.6	25.5	18.7	15.5	14.6
	60 lb/bbl	40.8	26.6	20.9	14.7	13.8

Table B.2: CST Values with Increasing Potassium Chloride Concentration for Changing Bentonite Content

		CST (sec)				
	KCl (% weight)	3%	6%	9%	12%	15%
Bentonite Content	0 lb/bbl	5.4	5.9	5.7	5.5	5.6
	10 lb/bbl	22.2	13.3	8.1	7.8	7.5
	20 lb/bbl	32.7	20.2	14.1	12.4	12.7
	30 lb/bbl	36.6	22.8	12.2	8.3	8.1
	40 lb/bbl	39.2	24.7	13.6	11.1	10.7
	50 lb/bbl	40.6	25.5	18.7	15.5	14.6
	60 lb/bbl	40.8	26.6	20.9	14.7	13.8

Numbers in gray cells are taken into consideration to eliminate trivial CST results. Selected numbers are between estimated minimum and maximum values.

Table B.3: CST Values with Increasing Quaternary Amine Concentration for 10 lb/bbl Bentonite

	10 lb/bbl Bentonite					
Q. Amine (% volume)	1%	2%	3%	4%	5%	6%
CST1	25.1	25.2	20.4	25.8	30.6	31.5
CST2	26.1	23.8	20.6	25.7	29.3	35.1
CST3	25.5	25.2	20.4	26.0	28.1	36.3
Mean1	25.6	24.7	20.5	25.8	29.3	34.3
St dev.	0.4	0.7	0.1	0.1	1.0	2.0
Max	26.0	25.4	20.6	26.0	30.4	36.3
Min	25.2	24.1	20.4	25.7	28.3	32.3
Mean2	25.5	25.2	20.5	25.8	29.3	35.7

Table B.4: CST Values with Increasing Quaternary Amine Concentration for 20 lb/bbl Bentonite

	20 lb/bbl Bentonite					
Q. Amine (% volume)	1%	2%	3%	4%	5%	6%
CST1	12.7	19.2	23.4	26.0	33.8	29.0
CST2	12.9	33.6	23.0	27.1	34.6	28.7
CST3	14.4	17.5	22.7	25.8	33.6	29.2
Mean1	13.3	23.4	23.0	26.3	34.0	29.0
St dev.	0.8	7.2	0.3	0.6	0.4	0.2
Max	14.1	30.7	23.3	26.9	34.4	29.2
Min	12.6	16.2	22.7	25.7	33.6	28.8
Mean2	12.8	18.4	22.9	25.9	33.7	29.1

Table B.5: CST Values with Increasing Quaternary Amine Concentration for 30 lb/bbl Bentonite

	30 lb/bbl Bentonite				
Q. Amine (% volume)	2%	3%	4%	5%	6%
CST1	19.5	34.9	35.3	38.7	39.1
CST2	19.4	36.5	35.1	39.5	40.8
CST3	18.7	36.1	35.4	37.2	42.3
Mean1	19.2	35.8	35.3	38.5	40.7
St dev.	0.4	0.7	0.1	1.0	1.3
Max	19.6	36.5	35.4	39.4	42.0
Min	18.8	35.2	35.1	37.5	39.4
Mean2	19.5	36.3	35.3	38.7	40.8

Table B.6: CST Values with Increasing Quaternary Amine Concentration for 40 lb/bbl Bentonite

	40 lb/bbl Bentonite				
Q. Amine (% volume)	2%	3%	4%	5%	6%
CST1	25.2	30.4	36.1	39.2	49.0
CST2	26.7	30.6	37.6	28.0	42.0
CST3	26.8	42.0	32.3	39.2	42.2
Mean1	26.2	34.3	35.3	35.5	44.4
St dev.	0.7	5.4	2.2	5.3	3.3
Max	27.0	39.8	37.6	40.7	47.7
Min	25.5	28.9	33.1	30.2	41.1
Mean2	26.8	30.5	36.9	39.2	42.1

Table B.7: CST Values with Increasing Quaternary Amine Concentration for 50 lb/bbl Bentonite

	50 lb/bbl Bentonite				
Q. Amine (% volume)	2%	3%	4%	5%	6%
CST1	23.4	33.1	37.6	40.9	45.1
CST2	22.8	32.2	38.6	42.3	45.1
CST3	23.0	31.7	37.7	43.5	44.7
Mean1	23.1	32.3	38.0	42.2	45.0
St dev.	0.2	0.6	0.4	1.1	0.2
Max	23.3	32.9	38.4	43.3	45.2
Min	22.8	31.8	37.5	41.2	44.8
Mean2	22.9	32.2	37.7	42.3	45.1

Table B.8: CST Values with Increasing Quaternary Amine Concentration for 60 lb/bbl Bentonite

	60 lb/bbl Bentonite			
Q. Amine (% volume)	3%	4%	5%	6%
CST1	35.0	39.2	45.6	49.2
CST2	37.2	43.6	52.0	47.0
CST3	34.0	32.1	36.0	45.4
Mean1	35.4	38.3	44.5	47.2
St dev.	1.3	4.7	6.6	1.6
Max	36.7	43.0	51.1	48.8
Min	34.1	33.6	38.0	45.6
Mean2	35.0	39.2	45.6	47.0

Table B.9: CST Values with Constant NaCl and Increasing Amine Concentration for 10 lb/bbl Bentonite

	6% NaCl (% weight)					
	10 lb/bbl Bentonite					
Q. Amine (% volume)	1%	2%	3%	4%	5%	6%
CST1	14.0	15.9	17.8	22.5	28.4	25.7
CST2	15.0	14.5	18.0	22.4	26.8	29.3
CST3	14.4	15.9	17.8	22.7	25.6	30.5
Mean1	14.5	15.4	17.9	22.5	26.9	28.5
St dev.	0.4	0.7	0.1	0.1	1.1	2.0
Max	14.9	16.1	18.0	22.7	28.1	30.5
Min	14.1	14.8	17.8	22.4	25.8	26.5
Mean2	14.4	15.9	17.8	22.5	26.8	29.9

Table B.10: CST Values with Constant NaCl and Increasing Amine Concentration for 20 lb/bbl Bentonite

	6% NaCl (% weight)					
	20 lb/bbl Bentonite					
Q. Amine (% volume)	1%	2%	3%	4%	5%	6%
CST1	9.4	9.9	11.4	12.9	14.7	15.5
CST2	9.6	10.1	11.0	14.0	15.5	15.2
CST3	11.1	10.7	10.7	12.7	14.5	15.7
Mean1	10.0	10.2	11.0	13.2	14.9	15.5
St dev.	0.8	0.3	0.3	0.6	0.4	0.2
Max	10.8	10.6	11.3	13.8	15.3	15.7
Min	9.3	9.9	10.7	12.6	14.5	15.3
Mean2	9.5	10.1	11.0	12.8	14.6	15.5

Table B.11: CST Values with Constant NaCl and Increasing Amine Concentration for 30 lb/bbl Bentonite

	6% NaCl (% weight)					
	30 lb/bbl Bentonite					
Q. Amine (% volume)	1%	2%	3%	4%	5%	6%
CST1	9.7	9.9	9.6	12.9	22.3	23.4
CST2	10.7	9.8	11.2	12.7	23.1	25.1
CST3	10.5	9.1	10.8	13.0	20.8	26.6
Mean1	10.3	9.6	10.5	12.9	22.1	25.0
St dev.	0.4	0.4	0.7	0.1	1.0	1.3
Max	10.7	10.0	11.2	13.0	23.0	26.3
Min	9.9	9.2	9.9	12.7	21.1	23.7
Mean2	10.6	9.9	11.0	12.9	22.3	25.1

Table B.12: CST Values with Constant NaCl and Increasing Amine Concentration for 40 lb/bbl Bentonite

	6% NaCl (% weight)					
	40 lb/bbl Bentonite					
Q. Amine (% volume)	1%	2%	3%	4%	5%	6%
CST1	16.0	21.1	20.3	20.9	26.4	39.9
CST2	17.5	19.4	20.5	22.4	26.8	33.7
CST3	18.6	19.5	20.2	17.5	26.4	32.9
Mean1	17.4	20.0	20.3	20.3	26.5	35.5
St dev.	1.1	0.8	0.1	2.0	0.2	3.1
Max	18.4	20.8	20.5	22.3	26.7	38.6
Min	16.3	19.2	20.2	18.2	26.3	32.4
Mean2	18.1	19.5	20.3	20.9	26.4	33.7

Table B.13: CST Values with Constant NaCl and Increasing Amine Concentration for 50 lb/bbl Bentonite

	6% NaCl (% weight)					
	50 lb/bbl Bentonite					
Q. Amine (% volume)	1%	2%	3%	4%	5%	6%
CST1	10.3	10.5	12.6	13.4	15.3	17.5
CST2	9.8	9.9	11.7	14.4	15.7	17.5
CST3	12.2	10.1	11.2	13.5	16.7	17.1
Mean1	10.8	10.2	11.8	13.8	15.9	17.4
St dev.	1.0	0.2	0.6	0.4	0.6	0.2
Max	11.8	10.4	12.4	14.2	16.5	17.6
Min	9.7	9.9	11.3	13.3	15.3	17.2
Mean2	10.1	10.1	11.7	13.5	15.7	17.5

Table B.14: CST Values with Constant NaCl and Increasing Amine Concentration for 60 lb/bbl Bentonite

	6% NaCl (% weight)					
	60 lb/bbl Bentonite					
Q. Amine (% volume)	1%	2%	3%	4%	5%	6%
CST1	18.2	12.1	13.6	15.3	14.6	17.4
CST2	18.0	12.0	15.2	16.7	13.6	19.3
CST3	15.9	13.1	13.9	15.1	16.4	21.1
Mean1	17.4	12.4	14.2	15.7	14.9	19.3
St dev.	1.0	0.5	0.7	0.7	1.2	1.5
Max	18.4	12.9	14.9	16.4	16.0	20.8
Min	16.3	11.9	13.5	15.0	13.7	17.8
Mean2	18.1	12.1	13.8	15.2	14.6	19.3

Table B.15: CST Values with Constant KCl and Increasing Amine Concentration for 10 lb/bbl Bentonite

	6% KCl (% weight)					
	10 lb/bbl Bentonite					
Q. Amine (% volume)	1%	2%	3%	4%	5%	6%
CST1	10.2	10.5	11.8	15.6	15.8	17.8
CST2	11.1	10.6	11.9	15.0	16.8	18.2
CST3	11.3	10.2	12.4	16.0	16.1	17.4
Mean1	10.9	10.4	12.0	15.5	16.2	17.8
St dev.	0.5	0.2	0.3	0.4	0.4	0.3
Max	11.3	10.6	12.3	15.9	16.7	18.1
Min	10.4	10.3	11.8	15.1	15.8	17.5
Mean2	11.2	10.6	11.9	15.6	16.1	17.8

Table B.16: CST Values with Constant KCl and Increasing Amine Concentration for 20 lb/bbl Bentonite

	6% KCl (% weight)					
	20 lb/bbl Bentonite					
Q. Amine (% volume)	1%	2%	3%	4%	5%	6%
CST1	9.9	10.9	12.3	12.9	15.3	17.4
CST2	9.9	11.8	12.4	14.4	15.7	16.1
CST3	9.8	11.3	12.5	14.8	15.2	18.0
Mean1	9.9	11.3	12.4	14.0	15.4	17.2
St dev.	0.0	0.4	0.1	0.8	0.2	0.8
Max	9.9	11.7	12.5	14.9	15.6	18.0
Min	9.8	11.0	12.3	13.2	15.2	16.4
Mean2	9.9	11.3	12.4	14.6	15.3	17.4

Table B.17: CST Values with Constant KCl and Increasing Amine Concentration for 30 lb/bbl Bentonite

	6% KCl (% weight)					
	30 lb/bbl Bentonite					
Q. Amine (% volume)	1%	2%	3%	4%	5%	6%
CST1	9.8	11.6	14.8	16.9	15.7	18.7
CST2	10.9	11.5	14.0	16.3	14.6	18.3
CST3	10.4	11.2	14.1	15.1	14.4	17.5
Mean1	10.4	11.4	14.3	16.1	14.9	18.2
St dev.	0.4	0.2	0.4	0.7	0.6	0.5
Max	10.8	11.6	14.7	16.8	15.5	18.7
Min	9.9	11.3	13.9	15.4	14.3	17.7
Mean2	10.4	11.6	14.1	16.3	14.5	18.3

Table B.18: CST Values with Constant KCl and Increasing Amine Concentration for 40 lb/bbl Bentonite

	6% KCl (% weight)					
	40 lb/bbl Bentonite					
Q. Amine (% volume)	1%	2%	3%	4%	5%	6%
CST1	11.6	11.0	13.0	15.1	19.1	22.1
CST2	9.6	10.7	10.3	15.7	18.3	22.0
CST3	11.2	12.3	12.7	15.5	20.5	22.2
Mean1	10.8	11.3	12.0	15.4	19.3	22.1
St dev.	0.9	0.7	1.2	0.2	0.9	0.1
Max	11.7	12.0	13.2	15.7	20.2	22.2
Min	9.9	10.6	10.8	15.2	18.4	22.0
Mean2	11.4	11.0	12.9	15.5	19.8	22.1

Table B.19: CST Values with Constant KCl and Increasing Amine Concentration for 50 lb/bbl Bentonite

	6% KCl (% weight)					
	50 lb/bbl Bentonite					
Q. Amine (% volume)	1%	2%	3%	4%	5%	6%
CST1	14.1	12.4	12.7	14.8	23.8	22.5
CST2	13.6	13.9	12.1	16.1	19.4	20.7
CST3	12.3	12.7	12.8	15.6	19.3	21.6
Mean1	13.3	13.0	12.5	15.5	20.8	21.6
St dev.	0.8	0.6	0.3	0.5	2.1	0.7
Max	14.1	13.6	12.8	16.0	22.9	22.3
Min	12.6	12.4	12.2	15.0	18.7	20.9
Mean2	13.6	12.6	12.8	15.6	19.4	21.6

Table B.20: CST Values with Constant KCl and Increasing Amine Concentration for 60 lb/bbl Bentonite

	6% KCl (% weight)					
	60 lb/bbl Bentonite					
Q. Amine (% volume)	1%	2%	3%	4%	5%	6%
CST1	12.1	11.7	12.5	17.4	20.0	20.6
CST2	10.3	12.3	12.8	17.5	20.8	20.0
CST3	11.5	11.3	14.2	19.9	20.8	20.5
Mean1	11.3	11.8	13.2	18.3	20.5	20.4
St dev.	0.7	0.4	0.7	1.2	0.4	0.3
Max	12.0	12.2	13.9	19.4	20.9	20.6
Min	10.6	11.4	12.4	17.1	20.2	20.1
Mean2	11.8	11.7	12.7	17.5	20.8	20.6

APPENDIX C

HOT ROLL DISPERSION TEST RESULTS

Table C.1: Hot Rolling Recoveries with Increasing Sodium Chloride Concentration (% by weight)

	NaCl				
	3%	6%	9%	12%	15%
1.Sieve (No10)	0.00	0.65	3.49	5.15	7.01
2.Sieve (No20)	1.14	2.30	4.05	4.31	3.99
Total	1.14	2.95	7.54	9.46	11.00
Recovery (%)	**3.80%**	**9.83%**	**25.13%**	**31.53%**	**36.67%**

Table C.2: Hot Rolling Recoveries with Increasing Potassium Chloride Concentration (% by weight)

	KCl				
	3%	6%	9%	12%	15%
1.Sieve (No10)	4.50	11.64	12.57	16.02	22.97
2.Sieve (No20)	4.60	1.33	2.84	3.77	3.25
Total	9.10	12.97	15.41	19.79	26.22
Recovery (%)	**30.33%**	**43.23%**	**51.37%**	**65.97%**	**87.40%**

Table C.3: Hot Rolling Recoveries with Increasing Quaternary Amine Concentration (% by volume)

	Quaternary Amine					
	1%	2%	3%	4%	5%	6%
1.Sieve (No10)	-	0.20	1.09	2.94	9.35	28.07
2.Sieve (No20)	-	1.16	5.77	9.19	12.23	1.92
Total	-	1.36	6.86	12.13	21.58	29.99
Recovery (%)	**0.00%**	**4.53%**	**22.87%**	**40.43%**	**71.93%**	**99.97%**

Table C.4: Hot Rolling Recoveries with Constant NaCl and Increasing Quaternary Amine Concentration (% by volume)

Constant 6% NaCl (% by weight)	Quaternary Amine					
	1%	2%	3%	4%	5%	6%
1.Sieve (No10)	5.86	18.67	27.47	27.68	28.39	30.00
2.Sieve (No20)	5.41	3.53	1.16	0.96	0.33	0.18
Total	11.27	22.2	28.63	28.64	28.72	30.00
Recovery (%)	**37.57%**	**74.00%**	**95.43%**	**95.47%**	**95.73%**	**100.00%**

Table C.5: Hot Rolling Recoveries with Constant KCl and Increasing Quaternary Amine Concentration (% by volume)

Constant 6% KCl (% by weight)	6% KCl + Quaternary Amine					
	1%	2%	3%	4%	5%	6%
1.Sieve (No10)	12.91	26.03	28.32	29.17	29.64	30.00
2.Sieve (No20)	5.15	1.27	0.55	0.68	0.31	0.18
Total	18.06	27.3	28.87	29.85	29.95	30.00
Recovery (%)	**60.20%**	**91.00%**	**96.23%**	**99.50%**	**99.83%**	**100.00%**

APPENDIX D

METHYLENE BLUE TEST RESULTS

Table D.1: MBT Values with Increasing Amine Concentration for Different Bentonite Contents

		MBT (lb/bbl)					
	Q.Amine (% volume)	1%	2%	3%	4%	5%	6%
Bentonite Content	10 lb/bbl	3.5	3	1.75	1.25	1	0.5
	20 lb/bbl	9.5	7	5	4.5	4	4
	30 lb/bbl	-	10.5	8	5	5	4
	40 lb/bbl	-	12	11	10.5	10	10
	50 lb/bbl	-	20	15	13	12.5	12
	60 lb/bbl	-	-	20	16	13	13

Table D.2: MBT Values with Constant 6% Sodium Chloride and Increasing Amine Concentration for Different Bentonite Contents

		6% (by weight) NaCl					
		MBT (lb/bbl)					
	Q.Amine (% volume)	1%	2%	3%	4%	5%	6%
Bentonite Content	10 lb/bbl	8	3	3	2.5	1.5	1.5
	20 lb/bbl	8	4	3	3	2.5	2
	30 lb/bbl	8	4.5	4.5	3.5	3	2.5
	40 lb/bbl	13	10	9.5	9	9	9
	50 lb/bbl	21	13	12	10	10	8
	60 lb/bbl	25	15	11	9	9	8

Table D.3: MBT Values with Constant 6% Potassium Chloride and Increasing Amine Concentration Different Bentonite Contents

		6% (by weight) KCl					
		MBT (lb/bbl)					
	Q.Amine (% volume)	1%	2%	3%	4%	5%	6%
Bentonite Content	10 lb/bbl	3.5	3	2.5	2	1.5	0.75
	20 lb/bbl	2	1.5	1.25	1	0.5	0.25
	30 lb/bbl	5	4.5	4	3.5	3.5	3.5
	40 lb/bbl	10	7.5	5	3.5	3	2.5
	50 lb/bbl	14	11	7.5	6	5	5
	60 lb/bbl	18	12	8	7	6.5	6.5

APPENDIX E

ONE-DIMENSIONAL FREE SWELL TEST RESULTS

Table E.1: One-dimensional Swelling Readings and Free Swell Indexes for Diesel Oil

Content	Reading (ml)	FSI
Diesel	17.5	0.00%

Table E.2: One-dimensional Swelling Readings and Free Swell Indexes for Increasing Sodium Chloride Concentration (% by weight)

Content	Concentration	Reading (ml)	FSI
NaCl	3%	60.5	245.71%
	6%	37.0	111.43%
	9%	33.0	88.57%
	12%	30.0	71.43%
	15%	29.0	65.71%

Table E.3: One-dimensional Swelling Readings and Free Swell Indexes for Increasing Potassium Chloride Concentration (% by weight)

Content	Concentration	Reading (ml)	FSI
KCl	3%	31.5	80.00%
	6%	26.5	51.43%
	9%	25.5	45.71%
	12%	24.5	40.00%
	15%	24.0	37.14%

Table E.4: One-dimensional Swelling Readings and Free Swell Indexes for Increasing Quaternary Amine Concentration (% by volume)

Content	Concentration	Reading (ml)	FSI
Quaternary Amine	1%	99.0	465.71%
	2%	51.5	194.29%
	3%	32.5	85.71%
	4%	28.5	62.86%
	5%	25.5	45.71%

Table E.5: One-dimensional Swelling Readings and Free Swell Indexes for Constant 6% (by weight) Sodium Chloride and Increasing Quaternary Amine Concentration (% by volume)

Content	Amine Concentration	Reading (ml)	FSI
6% NaCl + Quaternary Amine	1%	27.0	54.29%
	2%	26.0	48.57%
	3%	25.0	42.86%
	4%	23.0	31.43%
	5%	22.0	25.71%

Table E.6: One-dimensional Swelling Readings and Free Swell Indexes for Constant 6% (by weight) Potassium Chloride and Increasing Quaternary Amine Concentration (% by volume)

Content	Amine Concentration	Reading (ml)	FSI
6% KCL + Quaternary Amine	1%	22.0	25.71%
	2%	20.5	17.14%
	3%	20.0	14.29%
	4%	19.5	11.43%
	5%	19.0	8.57%