A NEW APPLICATION OF POTASSIUM NITRATE AS AN ENVIRONMENTALLY FRIENDLY CLAY STABILIZER IN WATER-BASED DRILLING FLUID

A Thesis

by

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ABSTRACT

The application of potassium chloride (KCl) as a temporary clay stabilizing additive in water-based drilling fluids is problematic in chloride-sensitive formations. However, failure to utilize clay stabilization leads to additional costs to drilling operations due to wellbore stability and drilling fluid residual problems. In addition, the chloride ions can be defined as a contaminant in land operations, with the potential to inhibit the growth of vegetation and the potential to pollute aquifers. The purpose of this study is to propose a new, high performance water-based fluid system using potassium nitrate instead of potassium chloride as the clay stabilizing additive for drilling applications.

Water-based drilling fluids using potassium nitrate and potassium chloride, respectively, were prepared with a density of 1.3 S.G. using various weighting materials. Capillary suction time (CST) test was used to optimize the potassium salt concentration in drilling fluids for effective clay swelling inhibition. HPHT filtration tests under static and dynamic conditions were conducted at 250°F and 300 psi. Berea sandstone cores with an average porosity of 23 vol% and an average permeability of 50 md were used in the filtration tests. The rheological properties, the volume of filtrate, and the filter cake thickness of the water-based drilling fluids were determined and compared.

The CST tests show that potassium nitrate performs comparably to potassium chloride as a clay stabilizer. However, the water-based drilling fluid containing potassium nitrate has better rheological properties than that containing potassium chloride. The HPHT filtration press tests show that water-based drilling fluid with potassium nitrate has a low filtration volume, less than 1 mL out of a total solution of 200 - 250 mL, when using barite as the weighting material. This paper not only highlights the successful replacement of KCl by KNO₃ to achieve good rheological properties in water-based drilling fluids, but also shows that KNO₃-based drilling fluids are more economical as well as environmentally friendly than KCl-based drilling fluids in drilling waste management.

DEDICATION

To my family.

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NOMENCLATURE

CSC Critical Salt Concentration CST Capillary Suction Time Hounsfield Units HU HPHT High Pressure/High Temperature PHPA Partially Hydrolyzed Polyacrylamide/Polyacrylate PV Plastic Viscosity S.G. Specific Gravity YP Yield Point

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1. INTRODUCTION AND LITERATURE REVIEW

1.1 Water-Sensitive Problems in Clay-Rich Reservoirs

Water-sensitive clays undergo an ion-exchange process when insufficient concentration of salt is present in the water. This salt insufficiency results in an imbalance in their ionic stability leading to clay swelling, clay migration and even breakdown of the rock structure (Bakly and Samir 2007). Conway et al. (2011) showed that there are two factors, stabilizer type and concentration, which have a major impact on the extent of clay stabilization. Investigation of water sensitive reservoir rocks began nearly sixty years ago. The term "water sensitivity" refers to the phenomenon of reduction in permeability caused by the swelling of indigenous clays or by the dispersion and movement of indigenous particles.

1.2 Clay Migration and Swelling Mechanism

The majority of hydrocarbon producing formations contain clay minerals, and the reaction of water (low salinity fluids) with these clay minerals tends to cause fines dispersion and clay swelling.

Fines can be said to be small or tiny components of rock that can move within or through pores of the rock. The characteristics of the fines migration vary with mineralogy, morphology, abundance, and distribution. The phenomenon of colloidal induced fines migration has significance in the petroleum industry as the release of these fines can migrate and block pore throats causing formation damage thereby leading to reduced production (Khilar et al. 1990). Clay minerals are especially susceptible to migration because of their physical size and surface properties. According to Zhou et al. (1995), most clay minerals (including silica and/or silicate sands) carry a negative surface charge when immersed in aqueous solution of pH 5 or above. As a result of this negative charge, clay particles detach themselves from the matrix, inducing migration under hydrodynamic drag. Further experimental studies showed that fines migration is affected by salt concentration, type and valence of cations, pH, flow rate, mineral composition, and wetting status of fines.

As stated by Zhou et al. (1995), the hydration of interlayer cations and the formation of diffuse double layers result in the expansion of structural layers, thereby resulting in clay swelling. From many laboratory tests and field cases, clay swelling has been continually proven to cause extreme damage to reservoir permeability. A concept known as critical salt concentration (CSC) is found to exist in the water sensitivity of all sandstones. In reservoir formations containing significant amounts of clay particles such as smectite/montmorillonite, swelling of these clay particles is noticeable and causes formation damage.

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Fig. 1—Mechanisms of permeability reduction. (a) Migration, (b) Swelling, (c) Swelling-Induced Migration. After Mohan et al. (1993).

1.3 Drilling Fluids and Clay Reactions

Historically, wellbore instability problems have occurred because of an insufficient understanding the interaction between the drilling fluid and the clay reactions (Bakly and Samir 2007).

Drilling fluids are a mixture of solids, liquids, and chemicals, with the liquid being the continuous phase to stabilize the wellbore (Elkatatny et al. 2012). Various drilling fluids have been suggested for dealing with troublesome water-sensitive reservoirs. The nature of the clay/drilling fluids interface is strongly influenced by physical and chemical interaction of solute species in the drilling fluid with the clay surface and/or dilution of bound water by drilling fluid solvent (Schlemmer et al. 2003).

Unlike when drilling with oil-based drilling fluids, water-based drilling fluids react with the formations (Kjøsnes et al. 2003). When drilling is expected to encounter water-sensitive zones, the selection of the fluid becomes even more important. To maintain a stable borehole through such zones, inhibitive drilling fluids will often be required (O'Brien and Chenevert 1973).

1.4 Function of Potassium Salts in Drilling Fluids

The development of a water based drilling fluid that could effectively minimize operational problems while drilling these wells was and continues to be a major challenge (Donham and Young 2009). Oil-base fluids have been used to drill watersensitive formations, however, the use of oil-based drilling fluids is expensive and present environmental problems, particularly for offshore use (Clark et al. 1976). The use of oil-based drilling fluids also results in the discharge of contaminated cuttings overboard, causing damage to benthic communities (Reid and Minton 1992).

Recently, potassium-based drilling fluids have become widely accepted for drilling water-sensitive reservoirs which contain large quantities of smectite or interleaved clays in the total clay fraction. Clay stabilizers are additives used in waterbased drilling fluid to prevent the swelling or migration reactions between water and clay in pay zones. Cation exchange reactions can usually achieve an adequate degree of clay stabilization. In the case of potassium enabled inhibition this is achieved by the replacement of native sodium (Na⁺) and calcium (Ca⁺) by K⁺. The low hydration energy and small size of the potassium ions enable K⁺ to fit into the gaps in the silica layers within the clay crystal. K⁺ replaces Na⁺ and Ca⁺, becomes tightly fixed by attractive forces, and binds the clay sheets together, thus reducing interlayer swelling. Compared to available alternatives, lower cost, greater availability, and better thermal stability favor the use of potassium salts.

The benefits of potassium ions in suppressing the hydration and swelling of clay minerals have long been recognized and applied in drilling (Mondshine 1973). The native potassium ions (K^+) attach to clay surfaces and lend stability to reservoir rocks exposed to drilling fluids by the bit. The ions also help hold the cuttings together, minimizing dispersion into finer particles.

Potassium ions retard the expansion of swelling clay (smectites) and, hence, of shales containing these minerals. High salt levels also promote clay flocculation by collapsing extended electrical double layers. The superiority of potassium in this role is due to the size and low hydration energy of the potassium ion. Potassium can enter into the clay lattice, forcing ejection of connate water, become tightly fixed by attractive forces, and thus bind the clay sheets together. The use of potassium as an exchange ion to stabilize drilled shales has been accepted worldwide. Potassium is an effective clay swelling/hydration inhibitor, where the concentration of potassium to achieve the desired result is often a function of the shale being drilled. The potassium ion replaces native sodium and calcium ions in clay to prevent hydration of the clay. Potassium is widely

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used internationally, and comes from many sources, including potassium chloride, potassium carbonate, potassium acetate, and potassium hydroxide. However, the formation will be damaged from filtrate invasion of potassium formate drilling fluids.

1.5 Application of Potassium Chloride as Clay Stabilizer in Drilling Fluids

Potassium chloride (KCl) is often used as the supply of potassium in water-based drilling fluids. The chloride ion however can be defined as a contaminant in land operations, with the potential to inhibit the growth of vegetation, and it can also be considered a potential pollutant to aquifers (Dow et al. 2012).

The KCl/polymer system was developed to stabilize water-sensitive shales by means of potassium ion inhibition. The inhibitive nature of this system minimizes the hydration of shales, which minimizes hole enlargement, stabilizer balling, sloughing shale, and reduction of permeability in productive zones. KCl is much more effective for stabilizing the shale specimens than equal concentrations of sodium chloride. This system works best when polymers are used for encapsulation. KCl replaces Na⁺ with K⁺ to thus prevent swelling of clay in pay zones.

Since some shales are more water-sensitive than others, the concentration of KCl required to inhibit these shales varies. During drilling operations, shale cuttings should be monitored continuously for inhibition. If the concentration of KCl in the system is insufficient, shale cuttings will be soft and mushy. If the concentration of KCl is sufficient, they will retain their integrity. Older shales which contain nonswelling clay

usually require 10 to 15 lb/bbl KCl while younger shales containing hydratable clay may require 30 to 50 lb/bbl.

Most data to date indicate that a 3 to 5 wt% KCl concentration is sufficient to provide inhibition of clay swelling and hydration. Attempts have been made to increase the inhibitive effect by increasing the KCl concentration up to 15% (57.6 lbm/bbl), but improved clay stability has not always been achieved. Commercially available organic and inorganic potassium salts have been used at a concentration of 0.67 mole/liter (corresponding to 5% w/w concentrations of potassium chloride).

The polyacrylamide/KCl fluids can be formulated in freshwater and seawater using 0.25 to 0.75 lb/bbl of polyacrylamide and 10 to 60 lb/bbl of potassium chloride depending on the shale to be drilled. In addition, glycols are effective in increasing shale strength and reducing pressure propagation only when the potassium ion is also present.

KCl fluids not only use a wide variety of KCl concentration from 3 to 15 wt%, but also a wide variety of types and concentrations of polymers. To be economical, concentration of drilling solids should be low and efficient solids control practices must be used. Determining the concentration of inhibitors is not straightforward. It depends on in-situ stresses, sand pore pressure, shale mineralogy, permeability, diffusion coefficient, strength, stiffness, borehole pressure, other drilling fluid constituents, time exposure, etc.

Many laboratory tests and field case histories have shown increased clay swelling/hydration inhibition with the addition of a partially hydrolyzed polyacrylamide/polyacrylate (PHPA) copolymer to a KCl fluid. The performance of PHPA polymers is significant in encapsulating cuttings and improving solids removal efficiency. High-molecular-weight linear polymers, such as PHPA, adsorb on mineral surfaces to form a slick, robust coating that provides a degree of mechanical integrity to shale softened by the ingress of fluids filtrate.

By bonding on sites that would otherwise react with water, these polymers inhibit the dispersion (physiochemical breakdown) of cuttings and formation solids into the fluid system. For their high molecular weight, these molecules are considerably longer than they are wide or thick. At small concentrations (0.2 to 3.0 lbm/bbl), they impart a high level of cuttings encapsulation to water-base fluids (even in freshwater). This system is adequate for drilling in many areas but still causes severe hole problems when used in very reactive shales.

An adequate degree of shale stabilization can usually be achieved by cation exchange reactions, usually the replacement of Na⁺ by K⁺. KCl is more effective at reducing linear swelling than equivalent concentrations of other salts as shown in **Figure 2**. The same phenomenon is shown in volumetric swelling tests on confined specimens of Pierre shale. The potassium ion is more effective because of its low hydration energy and its small size, which enable it to fit into the holes in the silica layers in the clay crystal, thus reducing interlayer swelling.

The concentration of KCl required to suppress swelling depends on the cation exchange capacity of the shales, and the exchange constants of the ions involved. Steiger (1982) found that shales high in montmorillonite required up to 90 lb/bbl (256 kg/m³), whereas illitic shales required only 20 lb/bbl (57 kg/m³). Because of its stability in high-

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salinity brines, polyanionic cellulose is commonly used to provide filtration control in KCl fluids.



Fig. 2—Effect of cation concentration and species on linear swelling.

The performance of KCl fluids is greatly increased by the addition of certain long-chain anionic polymers that coat the shale surface, and thus protect the walls of the hole from disintegration (**Figure 3**). The most likely explanation of the coating action is that the negative sites on the polymer chain are attracted to the positive sites on the clay crystal edges. Tests in a model bore hole have shown that PHPA is the best polymer for maintaining hole stability in an illitic (Atoka) shale. And 10.5 lb/bbl (3%) KCl was added to prevent swelling.

A similar test showed that PHPA was the best polymer to prevent erosion of amontmorillonitic shale, but 10% KCl was necessary to prevent swelling. Strain-gauge tests have shown that PHPA does not inhibit swelling—that function was fulfilled by the KCl. As already mentioned, the optimum concentration of KCl depends on the CSC required by the shale. Hole stability can often be maintained with KCl alone, but considerably higher concentrations are required if the PHPA is omitted.



Fig. 3—Effect of KCl and polymer solutions on linear swelling.

The cuttings stability problem, however, is well-understood and has been tackled successfully using 'inhibitive' fluids which incorporate salts that minimize clay hydration such as KCl (van Oort 1994). Potassium chloride is used at 2 to 60 lb/bbl. It is used to mitigate fines migration and clay swelling (Al-Yami and Nasr-El-Din 2007).

KCl is used extensively for its capacity to inhibit shales. It is available commercially as a high-purity, dry, crystalline inorganic salt. The superior performance and low cost of KCl make it by far the best common inorganic salt to use in an inhibitive fluids system.

For more than the past five decades, high concentration of potassium chloride through a variety of mechanisms might be claimed to somehow retard swelling. In the late 1960s and early 1970s, KCl/polymer fluids became popular. A variety of polymers in combination with KCl has been evaluated to achieve a higher level of shale inhibition as compared with KCl alone. The disadvantage of these KCl/polymer-based drilling fluids is their dependency on electrolytes for optimum shale inhibition. Glycol and polyglycol in combination with KCl and a KCl/polymer system were applied in the field in the 1990s with limited success. Until the mid-1990s, the fully formulated silicatebased drilling fluids using high concentrations of potassium/silicate were applied. In 2007, high performance water-based fluids using ammonium performed like an oil-based fluids in laboratory testing as well as in offset wells was applied.

1.6 Application of KNO₃ to Replace KCl

KCl is a common industrial material which is relatively inexpensive. Due to the potential environmental issues in chloride-sensitive zones as well as the logistics of using KCl and the cost of treating residual drilling fluids for this application, many operators have begun to search for alternative clay stabilizer products. Another drawback to the standard KCl-based drilling fluid system is that general hole conditions related to torque/drag and excessive time tripping in and out have affected overall efficiency (Huadi et al. 2010). The first requirement for improving plant growth on drilling fluid and soil mixtures are to remove soluble salts and reduce excessive amounts of exchangeable ions (Miller et al. 1976). Drilling wastes are commonly associated with the use of KCl/polymer fluids and are difficult to treat and remove (Brady et al. 1998).

 KNO_3 could also be used in water-based fluids as the clay inhibitor to avoid active shale swelling. Nitrate (NO_3^-) was chosen to eliminate the negative environmental impact of the chloride ion (Cl^-) seen with the common use of KCl.

Potassium nitrate (KNO₃) can be used with water-based drilling fluid as the clay inhibitor to avoid active clay swelling. Nitrate is better for the environment than chloride; this substitution is highly desirable especially in areas where high chloride ions may be objectionable. KNO₃ also provides the advantages of high water solubility under high temperature conditions as well as the capacity to be used as a tracer ion in drilling fluids. KNO₃ could be used as the K⁺ source for possible plant growth enhancement, particularly in nitrogen deficient soils. Environmentally friendly drilling fluid using NO₃⁻ as plant fertilizer allows for the drilling of wells in delicate ecological environments.

1.6.1 Nitrate Used as Tracer Ion

Nitrate as a tracer ion in drilling fluids offers a simple and inexpensive method to distinguish filtrate from formation water, and provides the information needed to calculate the absolute formation water salinity from drill stem and wireline formation test recoveries. The utility of the nitrate ion as a tracer is partly due to the fact that nitrate in subsurface formations and formation water is rare. Thus, the nitrate concentration in the drilling fluids needs not be very high to be an effective tracer.

1.6.2 High Solubility of KNO₃ at High Temperature

The water solubility of KCl is a weak function of temperature as shown in **Figure 4**, whereas that of KNO₃ is a strong function. Based on this fact, KNO₃ could be more effectively used in water-based drilling fluid under high temperature condition when treated safely.



Fig. 4—Solubility of KNO₃ and KCl.

At 20°C, KCl is more soluble; but at 40°C, KNO₃ has greater solubility. Although the solubility of both salts increased with temperature, a given temperature rise enhances the solubility of the nitrate much more than that of the chloride.

When a mixture of salts is present, the most soluble one suppresses the solubility of the other components, for example KCl is much less soluble in concentrated $MgCl_2$ solution.

1.6.3 Environmentally Friendly Drilling Fluids Using KNO3

 KNO_3 could be used as the K⁺ source for possible plant growth enhancement, particularly in nitrogen deficient soils. It could be used in agriculture as fertilizing because KNO₃ aids vegetable development. It is important to take into account environmentally friendly drilling fluids that allow drilling wells in the delicate ecological environments.

1.6.4 Drawbacks of KNO₃ as an Alternative of KCl

KNO₃ is a strong oxidization agent. It may cause or contribute to combustion by yielding oxygen as a result of redox chemical reaction. Considering the HSE impact, KNO₃ is combustible and could result in toxic fumes and vapor.

It is incompatible with combustible materials and strong reducing agents and finely powdered metals such as boron, chromium nitride, aluminum, titanium, germanium, zinc, zirconium, calcium disilicide, metal sulfides, carbon, sulfur, phosphorus, phosphides, sodium, phosphate, sodium thiosulfate, citric acid, tin chloride, sodium acetate, and throium carbide.

KNO₃ contained within water-based muds provided good inhibition and considerably reduced environmental impact. However, high concentrations of KNO₃ required to successfully inhibit the problematic shales led to new requirements in water treatment. The use of these salts raises a different set of problems which include eutrophication of water courses and lakes and the health implications of high nitrate levels in drinking waters.

2. EXPERIMENTAL SETUP

2.1 Capillary Suction Test

The oil and gas industry has adopted several methods to obtain insight as to how a fluid may affect reservoir material, and the capillary suction time (CST) test has become a standard test method (Pagels et al. 2012). This test was developed in the 1970s to evaluate dewatering of sludges. It was adapted to oil field originally to evaluate watersensitive (clay-rich) formations to drilling.

The CST setup consists of two electrodes located 0.5 and 1.0 cm from the edges of the funnel. The setup is connected to a timer. The fluid in contact with the first electrode starts the timer while the fluid in contact with the second electrode stops the timer. **Figures**. **5 and 6** show the schematic diagram and picture of the CST setup.



Fig. 5—Schematic diagram of a capillary suction timer.



Fig. 6—CST timer (OFI Testing Equipment, Inc. 2014).

2.2 Drilling Fluid Properties Test

A fluid balance (**Figure 7**) was used to measure the density of the drilling fluids. The density is measured in pounds per barrel (ppb) unit. This is necessary because the density of the drilling fluid is an important parameter which determines whether there will be a need for weighting up or further analysis.



Fig. 7—Fluid balance.

The rheological properties of drilling fluids were measured using the Grace M3600 Viscometer (**Figure 8**). The viscometer was calibrated in revolutions per minute (RPM) and the results are in centipoise (cp). This equipment calculated values for the plastic viscosity (PV), yield point (YP), and gel strengths. These three rheological properties are of primary concern in the design and formulation of any type of drilling fluid. Sufficiently low plastic viscosity (PV) values were achieved with appropriate yield point (YP) numbers that aid in the minimization of particled sag and enhanced overall hole cleaning. The gel strength of drilling fluid determines the drilling fluid's carrying capacity, which determines if it can carry cuttings to the surface (Olatunde et al. 2012).

The temperature condition for density measurement is 75°F and the rheological properties measurements were conducted at 120°F. Multiple measurements were conducted to ensure that accurate values could be obtained.



Fig. 8—M3600 grace viscometer (Grace Instrument Industries LLC 2014).

2.3 High-Pressure/High-Temperature (HPHT) Filtration Test

HPHT static filtration tests were used to determine filter cake quality and filtrate volume loss for a drilling fluid under specific testing conditions. Filtration characteristics are affected by the types and quantity of solids and their physical and chemical interactions. Temperature and pressure further affect these solids and their interactions.

HPHT filtration tests were performed using a standard HPHT filter press (Figure9) under static conditions (the temperature was adjusted to 250°F and 300 psi differential pressure) and the filter cakes were allowed to build in a quiescent fluid.



Fig. 9—HPHT filtration press (Fann Instrument Company 2015).

2.4 X-Ray Computed Tomography (CT) Scanning

X-ray computerized tomography (CT) scanning (**Figure 10**) combines a series of X-ray views taken from many different angles and computer processes to create crosssectional images of the filter cake samples. CT scanning is a radiological imaging technique that measure density (Wellington and Vinegar 1987). The objective of the X-ray computed tomography process is to obtain descriptive images of density variations within a sample. CT numbers are normalized values of the calculated X-ray absorption coefficient of a pixel (picture element) in a computed tomogram that provides radio density which is expressed in Hounsfield Units (HU). Because X-ray attenuations are related to density, the CT image gives the density distribution within every point of the object scanned. The radio density refers to a relative inability of X-rays to pass through the material and is proportional to its density (Novelline 2004; Wellington and Vinegar 1987). The average CT numbers increases with the increase intensity. For reference, the CT number of water is 0 HU and air is -1,000 HU (Akin and Kovscek 2003).



Fig. 10—X-Ray computerized tomography (CT) scanning.

3. EXPERIMENTAL PROCEDURES

3.1 Capillary Suction Test

The CST test indicated the time of movement of the water front between the two electrodes. The time of movement of the water front is related to the ability of the fluid to disperse clays in the samples. For the same clay sample in different fluids, the longer the time of liquid front movement, the poorer the clay is controlled by the fluid (the greater dispersion). The objective of this experiment is to compare the abilities of potassium nitrate and potassium chloride as the temporary clay stabilizers in drilling and production operations.

Different concentrations of KCl and KNO₃ solutions were first prepared by dissolving a certain amount of salts into deionized water. The volume of each solution was kept constant as 100 mL and the concentrations of salt solutions varied from 0.05 to 12 wt%. Next, 3 g bentonite were added to each solution and mixed thoroughly. Finally, 5 mL aliquot of the mixed solution was transferred with pipette into the CST tester and the reading was recorded. The CST value of each solution and CST value in the DI water were measured 5 times and averaged to obtain accurate results.

3.2 Drilling Fluid Properties Test

The water-based drilling fluids prepared in the experiment contained:

- 1. DI water (280 g): DI water acted as the continuous phase.
- 2. Bentonite (6 g): the bentonite clay used in the drilling fluid was montmorillonite [(Na, Ca)_{0.33}(Al, Mg)₂(Si₄O₁₀)(OH)₂⋅nH₂O]. It was added to provide a colloidal solid that could improve filter cake quality, increase the hole cleaning properties, reduce water seepage or filtration into permeable formation, form a thin filter cake of low permeability, promote borehole stability in poorly cemented formations, and avoid or overcome loss of circulation.
- 3. Modified starch derivative (6 g): modified starch (treated with a biocide) was used as a fluid loss agent. It has a thermal stability of approximately 250°F.
- 4. Polyanioinic cellulose (0.75 g): polyanioinic cellulose (PAC-R) was used as a secondary fluid loss agent, and it also acted as viscosity modifier.
- 5. Potassium salts (49 g): potassium salts, either KCl or KNO₃, were used for controlling clay swelling and for hydration. KNO₃ may be used with little or no effect on performance if there are environmental restrictions on chloride.
- 6. Potassium hydroxide (0.6 g): potassium hydroxide (KOH) was used for alkalinity control rather than caustic soda because it provides pH control without introducing potentially destabilizing sodium ions.

- 7. Calcium carbonate (15 g fine and 5 g medium): Calcium carbonate (CaCO₃) was particularly beneficial for reducing fluid loss and used to form more-stable external filter cakes. The weighting ratio of calcium carbonate fine size and medium size was 1:3 because this ratio was recommended to rapidly bridge the formation (Cargnel and Luzardo 1999).
- 8. API standard weighting materials (205 g): weighting materials, such as barite (BaSO₄), manganese tetraoxide (Mn₃O₄), and ilmenite (FeTiO₄), were added as needed to increase density and bridge the formation to prevent massive loss circulation. The bridging mechanism will help to create a thin filter cake and prevent thick cake buildup that could cause several operational problems such as torque and drag of string.

Water-based drilling fluids were made up in accordance with the formulas shown in **Tables 1 and 2** with the final stage being the weighting up of fluids to 13 lb/gal. The fluid properties were measured according to the API 13B standard protocol.

	Formula	Formula	Formula	Formula	Formula	Formula
	1	2	3	4	5	6
Water, g	280	280	280	280	280	280
Deformer, g	0.05	0.05	0.05	0.05	0.05	0.05
Bentonite , g	6	6	6	6	6	6
M-starch, g	6	6	6	6	6	6
PAC-R, g	0.75	0.75	0.75	0.75	0.75	0.75
KCl, g	49	49	49	49	49	49
KOH, g	0.6	0.6	0.6	0.6	0.6	0.6
CaCO ₃ (fine), g	-	15	-	15	-	15
CaCO ₃ (medium), g	-	5	-	5	-	5
Barite, g	205	205	-	-	-	-
Mn ₃ O ₄ , g	-	-	205	205	-	-
Ilmenite, g	-	-	-	-	205	205

Table 1— KCl-based drilling fluids with various formulas

Table 2— KNO₃-based drilling fluids with various formulas

	Formula Formula		Formula	Formula	Formula	Formula
	1	2	3	4	5	6
Water, g	280	280	280	280	280	280
Deformer, g	0.05	0.05	0.05	0.05	0.05	0.05
Bentonite , g	6	6	6	6	6	6
M-starch, g	6	6	6	6	6	6
PAC-R, g	0.75	0.75	0.75	0.75	0.75	0.75
KCl, g	49	49	49	49	49	49
KOH, g	0.6	0.6	0.6	0.6	0.6	0.6
CaCO ₃ (fine), g	-	15	-	15	-	15
CaCO ₃ (medium), g	-	5	-	5	-	5
Barite, g	205	205	-	-	-	-
Mn ₃ O ₄ , g	-	-	205	205	-	-
Ilmenite, g	-	-	-	-	205	205

The density was measured at a temperature of 75°F using a fluid balance and rheological property measurements were conducted at 120°F using a Grace M3600 viscometer. Properties of drilling fluids were determined by repeating the measurements and taking the average to minimize errors.

3.3 HPHT Filtration Tests

As shown in Tables 1 and 2, the fluids were selected for static filtration tests to investigate the filtration characteristics. To simulate reservoir rock, Indiana limestone cores with an average porosity of 23 vol% and an average permeability of 100 md were used in the filtration tests.

The drilling fluids were put in the filter press cell, and the cell was placed in the heating jacket. The drilling fluid leak off was measured at 250°F and 300 psi differential pressure over a 30 minutes period. The static HPHT fluid loss was measured using ceramic discs with 10-µm pore throat size. The cumulative filtrate volume was plotted versus time with the dependent variable being the spurt loss volume.

3.4 X-Ray CT Scanning

CT scan settings are provided in **Table 3**. Filter cake that form from the drilling fluid is first dried. It is then placed horizontally on the couch of the CT scanner, the X-ray source and detector rotated continuously, and images were taken using the traversing slice method (Carretero-Carralero et al. 2007). Imagej software was used to reconstruct the images of the core from the multidirectional transmission date. The CT scanning tests were repeated five times to confirm the experimental results.

	<u> </u>
X-Ray Power	150 keV
Camera Exposure	1.8 seconds
Rotation Increment	1.0°
Vertical Step	9.5 mm
Image Display Region	1024×1024 pixels
CT Image Resolution	1 pixel = 0.00138 mm^2
X-Ray Beam Thickness	6 pixels (0.00828 mm)

 Table 3—CT scanning settings

4. RESULTS AND DISCUSSION

4.1 CST Test Results

Table 4 shows the CST values of the clay suspensions spiked with progressively
 increasing concentrations of KCl or KNO₃. Figure 11 is the plot of those CST values versus time in second. Without the addition of KCl or KNO₃, the CST value of clay suspended in only deionized water is as high as 382 s, indicating highly dispersed clay minerals in suspension. As the salt concentration increases, the CST values decrease greatly. The phenomenon of clays swelling and water sensitivity has been controlled significantly when the concentration of potassium salts increases up to 4 wt%. At this point, the CST values decreases from 382 to 8.4 and 9.4 s respectively. Beyond this point, additional salt in solution does not markedly decrease CST value. In fact, at salt concentration of 4 wt% and above, the CST values of KCl and KNO3 solutions are quite similar and the maximum difference of the CST values between KCl and KNO3 solutions is only 1 s. Those confirm that the addition of potassium salts as a temporary clay stabilizer in water-based drilling fluids can effectively prevent the swelling of clay minerals. The function of KNO3 acts similar to that of KCl and can be treated as a potential substitute of KCl in chloride-sensitive formations.

Brine Concentration wt%	CST, s			
Brine Concentration, wt/o	KCl	KNO ₃		
0	382	382		
0.05	360.5	377.9		
0.3	61.6	72.7		
0.5	49.4	61.2		
0.8	39.2	53.3		
1	26.9	36.5		
2	12.0	16.3		
3	10.1	11.9		
4	8.4	9.4		
5	9.3	9.5		
6	8.9	9.1		
7	9.15	8.6		
8	9.5	8.9		
9	9.1	8.75		
10	8.9	8.8		
11	8.8	9.78		
12	9.16	9.18		

Table 4—CST values of KCl and KNO₃



Concentration of Salt Solution, wt%

Fig. 11— The CST values change with the concentration of salt solutions.

4.2 Drilling Fluid Properties

CST results showed that KNO₃ can be an effective substitute for KCl as a temporary clay stabilizer in a simple clay-salt-diH₂O suspension medium. However, it is also necessary to test whether KNO₃ water-based drilling fluids can maintain necessary rheological properties. Various water-based drilling fluids with different formulas were firstly designed with KCl and replaced with KNO₃ as the potassium source. Various weighting materials together with either KCl or KNO₃ were tested to examine impact of the type of weighting materials on rheological properties of water-based drilling fluids. **Tables 5 and 6** show the test results of all water-based drilling fluid with various formulas.

The addition of sized CaCO₃ particles in water-based drilling fluids is a common practice in the field and its main function is to act as the bridging agent to seal formations with low to moderate porosity and permeability to enhance filtration characteristics. Table 5 is the results of water-based drilling fluids with KCl and Table 6 is for the fluids with KNO₃.

	Formula	Formula	Formula 2	Formula	Formula 5	Formula
	1	2	3	4	3	0
Water, g	280	280	280	280	280	280
Deformer, g	0.05	0.05	0.05	0.05	0.05	0.05
Bentonite , g	6	6	6	6	6	6
M-starch, g	6	6	6	6	6	6
PAC-R, g	0.75	0.75	0.75	0.75	0.75	0.75
KCl, g	49	49	49	49	49	49
KOH, g	0.6	0.6	0.6	0.6	0.6	0.6
CaCO ₃ (fine), g	-	15	-	15	-	15
CaCO ₃ (medium), g	-	5	-	5	-	5
Barite, g	205	205	-	-	-	-
Mn ₃ O ₄ , g	-	-	205	205	-	-
Ilmenite, g	-	-	-	-	205	205
Density, lb/gal	13	13	13	13	13	13
PV, cp	21.88	24	31.11	20	26	20.5
YP , lb/100ft ²	27.55	15	18.21	17	17.88	15.26
10 s gel strength, lb/100ft ²	4	2	4	1	3	4
10 min gel strength, lb/100ft ²	6	8	12	4	7	9

Table 5—Rheological properties of KCl-based drilling fluids with various formulas

	Formula 7	Formula 8	Formula 9	Formula 10	Formula 11	Formula 12
Water, g	280 280		280	280	280	280
Deformer, g	0.05	0.05	0.05	0.05	0.05	0.05
Bentonite , g	6	6	6	6	6	6
M-starch, g	6	6	6	6	6	6
PAC-R, g	0.75	0.75	0.75	0.75	0.75	0.75
KNO3, g	49	49	49	49	49	49
KOH, g	0.6	0.6	0.6	0.6	0.6	0.6
CaCO ₃ (fine), g	-	15	-	15	-	15
CaCO3 (medium), g	-	5	-	5	-	5
Barite, g	205	205	-	-	-	-
Mn ₃ O ₄ , g	-	-	205	205	-	-
Ilmenite, g	-	-	-	-	205	205
Density, lb/gal	13	13	13	13	13	13
PV, cp	24.66	28	28.14	20	30	27.87
YP , lb/100ft ²	19.29	11	17.34	13	16	13.54
10 s gel strength, lb/100ft ²	1	1	2	2	2	4
10 min gel strength, lb/100ft ²	3	5	8	4	6	9

Table 6—Rheological properties of KNO₃-based drilling fluids with various formulas

Comparing Formula 1 and 7, with barite is as the weighting material and no CaCO₃ added, the YP of the fluids decreased substantially from 27.55 to 19.29 lb/100 ft² when KCl is replaced with KNO₃ in the fluids. YP in Newtonian fluids is related to resistance of initiation of fluid flow or the stress required in moving the fluid, so it is desirable to have drilling fluids of relatively low YP value to circulate drilling fluids easily. The gel strengths measured at 10 s and 10 min were also decreased substantially from the KCl formula to the KNO₃ formula. The same trend was also observed with the

addition of CaCO₃ into the system, as shown in the data for Formula 2 and 8. The PV value of the fluids slightly increased from 21.88 to 24.66 cp with Formula 1 to Formula 7 and from 24 to 28 cp with Formula 2 to Formula 8. In this case, the replacement of KCl with KNO₃ slightly enhanced the rheological properties of water-based drilling fluids.

When Mn₃O₄ is used as the weighting agent the PV, YP, and gel strengths decreased intermediately in value with the addition of CaCO₃ to the fluid system. In the case of ilmenite as the weighting material, the YP slightly decreased and the PV slightly increased from without CaCO₃ in fluid to with CaCO₃ in fluid. Overall, the addition of KNO₃ as a replacement for KCl can achieve lower YP values and slightly higher value of PV and thus can maintain or even enhance the rheological properties of water-based fluids.

4.3 Filter Loss and Filter Cake Properties

In the previous section, the rheological properties of all tested formulas of waterbased drilling fluids show that KNO₃ can be a good replacement for KCl in the fluids. This section examines whether these drilling fluids achieve high qualify filter cake quality or good filtration characteristics. **Tables 7 and 8** are the filtration characteristics of the water-based drilling fluids with KCl or KNO₃ respectively obtained from HPHT filtration press tests. These results including the spurt loss, total filtrate volume, and the thickness of filter cake.

Table 7—Experimental results of KCI-based drilling fluid HPHT static filter press

	Barite		Mn ₃ O ₄		Ilmenite		
Formula	1	2	3	4	5	6	
Spurt Loss, mL	0.7	1.0	1.1	1.2	1.3	1.1	
The Cumulative	4.0	4.8	7.1	5.0	10.0	8.6	
Filtrate Volume, mL							
The Thickness of	0.13	0.1	0.06	0.09	0.09	0.16	
Filter Cake, in.							

Table 8—Experimental results of KNO₃-based drilling fluid HPHT static filter press

	Barite		Mn ₃ O ₄		Ilmenite		
Formula	7	8	9	10	11	12	
Spurt Loss, mL	2.0	1.4	1.3	0.9	1.4	1.7	
The Cumulative Filtrate Volume, mL	4.8	4.0	8.4	7.6	10.3	8.6	
The Thickness of Filter Cake, in.	0.08	0.08	0.09	0.10	0.10	0.17	

When barite is added as the weighting material and CaCO₃ is not present as bridging material, the spurt loss increased from 0.7 to 2.0 mL and the total filtrate volume increased from 4.0 to 4.8 mL when KNO₃ replaced KCl in the fluids. The same trend in spurt loss and total filtrate volume was observed when CaCO₃ was added as the bridging agent. However, thinner filter cakes were formed in both cased when KNO₃ replaced KCl in the fluids whereas the increment of spurt loss and total filtrate volume was moderate. Good filtration characteristics of optimized water-based drilling fluids were maintained and thinner filter cakes were obtained when KNO₃ acts a substitution for KCl in the fluids. When ilmenite or Mn₃O₄ was the weighting material, the results in Tables 7and 8 show that the spurt loss, the total filtrate volume, and the thickness of filter cake all slightly increased but were kept at very low values. Good filtration characteristics and thin filter cake of optimized water-based drilling fluids were achieved when KNO₃ acts a substitution for KCl in the fluids.

Tables 7 and 8 also show the effect of $CaCO_3$ on the filtration characteristics of the fluids. It is seen that when using barite as the weighting material, the presence of $CaCO_3$ contributed to slightly higher cumulative filtrate volume. On the contrary, lower cumulative filtrate volume was obtained when using Mn_3O_4 and ilmenite as the weighting material. Photos of the resultant filter cakes from all formulas are provided in **Figures 12 through 23**.



Fig. 12—Filter cake of KCl-based drilling fluid using barite as the weighting material (Formula 1).



Fig. 13—Filter cake of KCl-based drilling fluid using barite as the weighting material (Formula 2).



Fig. 14—Filter cake of KCl-based drilling fluid using Mn₃O₄ as the weighting material (Formula 3).



Fig. 15—Filter cake of KCl-based drilling fluid using Mn₃O₄ as the weighting material (Formula 4).



Fig. 16—Filter cake of KCl-based drilling fluid using ilmenite as the weighting material (Formula 5).



Fig. 17—Filter cake of KCl-based fluid using ilmenite as the weighting material (Formula 6).



Fig. 18—Filter cake of KNO₃-based drilling fluid using barite as the weighting material (Formula 7).



Fig. 19—Filter cake of KNO₃-based drilling fluid using barite as the weighting material (Formula 8).



Fig. 20—Filter cake of KNO3-based drilling fluid using Mn3O4 as the weighting material (Formula 9).



Fig. 21—Filter cake of KNO3-based drilling fluid using Mn3O4 as the weighting material (Formula 10).



Fig. 22—Filter cake of KNO₃-based drilling fluid using ilmenite as the weighting material (Formula 11).



Fig. 23—Filter cake of KNO₃-based drilling fluid using ilmenite as the weighting material (Formula 12).

4.4 CT Images Analysis

Results of filtration tests show use of KNO₃ temporary clay stabilizer in the

fluids made comparable or better filter cakes in terms of thickness when compared to

filter cakes made by use of KCl. CT scan was conducted to further examine the quality of the formed filter cake in above tests. In field conditions, thin and impermeable filter cakes are desirable.

Figures 24-35 show the CT images obtained from the CT scanner. The upper layer and lower layer correspond, relatively, to filter cake and the limestone core. The change in color (from green to red) in the upper layer (filter cake) reveals the change of the density of the filter cake. The radio density refers to a relative inability of X-rays to pass through the material and is proportional to its density. The combination of the CT images and HPHT filtration test provides an efficient method to quantify filtration quality and explain the mechanisms involved (van Overveldt et al. 2012). **Table 9** shows the average CT numbers of the filter cakes for all the tests.

In summary, when barite was the weighting material and CaCO₃ as bridging material was not added, the CT number increased from 7096 to 7844 when KNO₃ replaced KCl in the fluids. Previous results show that the thickness of filter cake decreased from 0.13 to 0.08 in. in the same comparison. Thus, thinner and denser filter cake was formed in KNO₃-based drilling fluid. When CaCO₃ was added as the bridging agent, the same trend was observed but with a higher CT number as the addition of CaCO₃ enhanced the quality of filter cake. In the case of Mn₃O₄ as the weighting agents, the CT number decrease a little bit probably because a less dense and slightly thicker filter cake formed. The same trend as the case of barite was observed when ilmentie was the weighting material. Filter cake formed from KNO₃-based drilling fluid has the highest density indicated by the highest CT number (its average CT number is 7844)

among these drilling fluids that been prepared. When combined with the filtration results, CT results provides strong evidence that barite is the appropriate weighting material due to the superiority of its results compared to manganese tetraoxide and ilmenite.



Fig. 24—CT scanned image for filter cake KCl-based drilling fluid using barite as the weighting material (Formula 1).



Fig. 25—CT scanned image for filter cake KCl-based drilling fluid using barite as the weighting material (Formula 2).



Fig. 26—CT scanned image for filter cake KCl-based drilling fluid using Mn₃O₄ as the weighting material (Formula 3).



Fig. 27—CT scanned image for filter cake KCl-based drilling fluid using Mn₃O₄ as the weighting material (Formula 4).



Fig. 28—CT scanned image for filter cake KCl-based drilling fluid using ilmenite as the weighting material (Formula 5).



Fig. 29—CT scanned image for filter cake KCl-based drilling fluid using ilmenite as the weighting material (Formula 6).



Fig. 30—CT scanned image for filter cake KNO₃-based drilling fluid using barite as the weighting material (Formula 7).



Fig. 31—CT scanned image for filter cake KNO₃-based drilling fluid using barite as the weighting material (Formula 8).



Fig. 32—CT scanned image for filter cake KNO3-based drilling fluid using Mn3O4 as the weighting material (Formula 9).



Fig. 33—CT scanned image for filter cake KNO3-based drilling fluid using Mn3O4 as the weighting material (Formula 10).



Fig. 34—CT scanned image for filter cake KNO₃-based drilling fluid using ilmenite as the weighting material (Formula 11).



Fig. 35—CT scanned image for filter cake KNO₃-based drilling fluid using ilmenite as the weighting material (Formula 12).

Table 7 Average e 1 humbers of filter cakes												
	Filter Cakes formed from KCl-Based Drilling Fluid					Filter Cakes formed from KNO3-Based Drilling Fluid						
Formula	1	2	3	4	5	6	7	8	9	10	11	12
CT Numbers	7096	7795	4553	4624	2756	2895	7844	7914	4153	4455	2826	2989

Table 9—Average CT numbers of filter cakes

4.5 Land Farming of KNO₃ Drilling Residuals

Land farming is a process in which wastes are incorporated into a soil surface to degrade, transform, or immobilize the waste constituents by biological, chemical and physical reactions. Many wells are drilled in agricultural areas, posing concerns to the public with respect to disposal methods for drilling wastes.

Land farming provides a favorable combination of disposal cost, short and long term liability to the generator, and potential environmental impact. It has the following benefits: low capital cost and simple technology, multiple applications on same piece of land, and improved soil characteristics. However, it usually has high maintenance costs (periodic land tilling, fertilizer use). The soluble salts and cation mobility can affect the germination and plant growth, and heavy metals uptake by the plants could be passed along the food chain.

As land farming is an economical technique of drilling waste management, we can make the nontoxic, safer, and more environmentally residuals by using potassium nitrate instead of potassium chloride.

However considering the drawbacks of potassium nitrate, such as combustibility, higher price than potassium chloride, and so on, socioeconomic analyses and technical experiments are needed.

To evaluate the properties of KNO₃ drilling residuals, the following steps should be ordered in **Figure 36** (Wilton et al. 1992):



Fig. 36—Steps for land farming of KNO₃ drilling residuals.

The conclusion is that downhole wastes, when generated with a properly formulated drilling fluid, may be land farmed and have no adverse effects on growth potential when applied at specific loadings.

Drilling waste management practices are subject to all applicable federal and state regulatory requirements:

- The Wyoming Oil and Gas Conservation Commission (WOGCC): Land farming must be approved by the DEQ (Wyoming Department of Environmental Quality).
- The New Mexico Energy, Minerals and Natural Resources Department: Disposal method of land farming for drill cuttings and drilling fluids should meet the new rules. (19.15.2.51 through -55).
- The Railroad Commission of Texas (RCC) and the Texas Commission on Environmental Quality (TCEQ): These institutions provide for various

disposal methods that do not require a permit, including the disposal of certain categories of low-chloride drilling fluid by land farming.

- The Utah Department of Environmental Quality (DEQ): Land farming must be permitted by the Division of Oil, Gas and Mining.
- The Florida Department of Environmental Protection (FDEP): No subsurface formation or zone will be approved for fluid disposal if total dissolved solids of the formation fluid do not equal or exceed 10,000 parts per million (ppm) and chloride content does not equal or exceed 5,000 ppm.

4.6 Potassium Nitrate in a Double Salt Mixture

The optimum concentrations of KCl and KNO₃ are 4 and 7 wt% respectively according to the CST tests. However, the differences between KCl and KNO₃ are relatively small and can be neglected for a concentration of above 4 wt%.

Therefore, KNO₃ can be used as the substitute for KCl at concentration of above 4 wt%, functioning comparably to KCl as the temporary clay stabilizer. Potassium nitrate, as an environmental substitute of KCl, has a higher price than KCl. Considering this, the optimum double salt mixture which contains KNO₃ should be studied to make the KNO₃ more economical as clay stabilizers in drilling and production operations.

To be more economical, an optimum use of potassium nitrate in a double salt mixture should be found, which will undoubtedly make the potassium safer, more environmentally friendly, and even more economical. The properties of some potential double salt mixtures are shown in **Table 10**:

Tuble 10 Troper ites of some potential double sait mixtures.						
Salt	Comments					
Calcium Chloride	Increase the density of solids-free brines; Provide inhibition of swelling					
	clays in water phase of invert emulsion drilling fluids.					
Calcium Nitrate	Nitrate fertilizer.					
Calcium Hydroxide	Manufactures of additives to oils in petroleum refining industry.					
Potassium Sulfate and	Detective fortilizers, but they are not combustible					
Potassium Carbonate	rotassium terunzers, out mey are not compustible.					
Potassium Formate	Potential environmentally deicing salt for use on roads.					
Potassium Silicate	A corrosion inhibitor.					
Magnesium Sulfate,						
Magnesium Chloride and	Be used widely as fertilizer, but they are not combustible.					
Magnesium Nitrate						

Table 10—Properties of some potential double salt mixtures.

The properties of double or triple salts can be measured by doing the CST tests. For the same sample in different fluids, the longer the time of liquid front movement, the poorer the clay control by the fluid (the greater dispersion). Therefore the optimum mixture of double or triple salts has the shortest CST time. The CST values of some double salt mixtures are shown in **Figure 37**.

The mixture of potassium nitrate and another salt performs better than its crystallized form of double salt solution. KCl (4 wt%) and a mixed solution of KNO₃ and Ca(OH)₂ (the molar proportion KNO₃ and Ca(OH)₂ is 1:1) act similar when treating 3 g bentonite in 100 mL solution as the clay stabilizer. The reason is that the Ca²⁺ ion can be exchanged with Na⁺ (that is usually naturally in the clays before a treatment) or K⁺.

The CST time of the 4 wt% mixture solution of the KNO₃ and Ca(OH)₂ solution is shorter than 4 wt% KNO₃ solution. The reason for this is that in the concentration of 4 wt%, the potassium nitrate is better clay stabilizer in alkaline conditions than in acid or neutral condition. Further research should be done to determine whether the pH is a significant factor affecting the swelling control function of clay stabilizers. K^+ double salts should be tested in the future experiments, which means the cations of both salts are all K⁺. Only in that way can it be determined whether there are sufficient amounts of K⁺ that can treat the clay swelling well, and decrease the cost of KNO₃.



Fig. 37—The CST values of double salt mixtures (concentration, 4 wt%).

5. CONCLUSIONS

Potassium nitrate with the proper K^+ concentration matched to the clay's hydration characteristics can be used to inhibit the swelling of bentonite in water media as well as the KCl. KNO₃ based drilling fluid is an excellent environmental alternative to KClbased drilling fluid and can protect water-sensitive formations and minimize or reduce clay-related borehole problems. Environmentally friendly drilling fluid using NO₃⁻ as plant fertilizer allows drilling wells in the delicate ecological environments.

The following are some highlights of the application:

- Comparison of twelve formulas of drilling fluids examined show that the KNO₃based drilling fluid prepared by formula 8 not only has a desirable rheological properties and appropriate density, but also formed a suitable filter cake thickness.
- 2. Considering the formation damage of filter loss, especially to those watersensitive reservoirs, and based on cost-equalized concentrations of additive in water-based drilling fluid, the HPHT filtration test in this study show that barite is the optimum weighting material to perform potassium-based drilling fluids system, which can produce one time lower cumulative volume in 30-minute filtration test than other two weighting materials.
- 3. When using the barite as the weighting material, although the cumulative filtrate volume of KCl-based drilling fluids is lower than KNO₃-based drilling fluids (in

fact, the maximum difference between these two kind of cumulative filtrate volume is only 0.8 mL), the filter cake thickness formed by the KNO₃-based drilling fluids can be 0.05 in. smaller than the filter cake thickness formed by the KCl-based drilling fluids after a 30-minute HPHT filtration test.

REFERENCES

- Akin, S. and Kovscek, A.R. 2003. Computed Tomography in Petroleum Engineering Research. *Geological Society, London, Special Publications* **215** (1): 23-38. <u>http://dx.doi.org/10.1144/GSL.SP.2003.2015.01.03.</u>
- Al-Yami, A.S. and Nasr-El-Din, H.A. 2007. An Innovative Manganese Tetroxide/Kcl Water-Based Drill-in Fluid for HT/HP Wells. Presented at the SPE Annual Technical Conference and Exhibition, Anaheim, California, 11-14 November. SPE-110638-MS. <u>http://dx.doi.org/10.2118/110638-MS.</u>
- Bakly, O. and Samir, A. 2007. Custom Designed Water-Based Mud Systems Help Minimize Hole Washouts in High Temperature Wells- Case History from Western Desert, Egypt. Presented at the SPE/IADC Middle East Drilling and Technology Conference, Cairo, Egypt, 22-24 October. SPE-108292-MS. <u>http://dx.doi.org/10.2118/108292-MS.</u>
- Brady, M.E., Craster, B., Getliff, J.M. et al. 1998. Highly Inhibitive, Low-Salinity Glycol Water-Base Drilling Fluid for Shale Drilling in Environmentally Sensitive Locations. Presented at the SPE International Conference on Health, Safety, and Environment in Oil and Gas Exploration and Production, Caracas, Venezuela, 7-10 June. SPE-46618-MS. <u>http://dx.doi.org/10.2118/46618-MS.</u>
- Cargnel, R.D. and Luzardo, J.P. 1999. Particle Size Distribution Selection of CaCO₃ in Drill-in Fluids: Theory and Applications. Presented at the Latin American and Caribbean Petroleum Engineering Conference, Caracas, Venezuela, 21-23 April. SPE-53937-MS. <u>http://dx.doi.org/10.2118/53937-MS.</u>
- Carretero-Carralero, M.D., Farajzadeh, R., Du, D. et al. 2007. Modeling and Ct Scan Study of Foams for Acid Diversion. Presented at the European Formation Damage Conference, Scheveningen, The Netherlands, 30 May-1 June. SPE-107795-MS. <u>http://dx.doi.org/10.2118/107795-MS.</u>
- Clark, R.K., Scheuerman, R.F., Rath, H. et al. 1976. Polyacrylamide/Potassium-Chloride Mud for Drilling Water-Sensitive Shales. *Journal of Petroleum Technology* 28 (6): 719-727. SPE-5514-PA. <u>http://dx.doi.org/10.2118/5514-PA.</u>
- Conway, M.W., Venditto, J.J.J., Reilly, P.B. et al. 2011. An Examination of Clay Stabilization and Flow Stability in Various North American Gas Shales. Presented at the SPE Annual Technical Conference and Exhibition, Denver, Colorado, USA, 30 October-2 November. SPE-147266-MS. <u>http://dx.doi.org/10.2118/147266-MS.</u>

- Donham, F. and Young, S. 2009. High Performance Water Based Drilling Fluids Design. Presented at the Offshore Mediterranean Conference and Exhibition, Ravenna, Italy, 25-27 March. OMC-2009-111.
- Dow, M., Florence, A.S., and Babu, J.V. 2012. Chloride-Free Inhibitive Water-Based Fluid Significantly Improves Environmental Acceptability for Rain Forest Locations. Presented at the International Conference on Health, Safety and Environment in Oil and Gas Exploration and Production, Perth, Australia, 11-13 September. SPE-156824-MS. http://dx.doi.org/10.2118/156824-MS.
- Elkatatny, S., Mahmoud, M.A., and Nasr-El-Din, H.A. 2012. Characterization of Filter Cake Generated by Water-Based Drilling Fluids Using Ct Scan. *SPE Drilling & Completion* 27 (2): 282-293. SPE-144098-PA. <u>http://dx.doi.org/10.2118/144098-PA.</u> PA.
- Fann instrument Company. 2015. Filter Press HPHT 500 ML, <u>http://www.fann.com/fann/products/drilling-fluids-testing/filtration-hpht/fp-hpht-500ml.page</u> (accessed 8 April 2015).
- Grace Instrument Industries LLC. 2014. M3600 VIscometer, <u>http://www.graceinstrument.com/M3600_Viscometer.shtml</u> (accessed 8 April 2015).
- Huadi, F., Aldea, C., MacKereth, B.M. et al. 2010. Successful Kcl Free Highly Inhibitve and Cost Effective Wbm Applications, Offshore East Kalimantan, Indonesia. Presented at the IADC/SPE Asia Pacific Drilling Technology Conference and Exhibition, Ho Chi Minh City, Vietnam, 1-3 November. SPE-132690-MS. <u>http://dx.doi.org/10.2118/132690-MS.</u>
- Khilar, K.C., Vaidya, R.N., and Fogler, H.S. 1990. Colloidally-Induced Fines Release in Porous Media. *Journal of Petroleum Science and Engineering* **4** (3): 213-221. <u>http://dx.doi.org/10.1016/0920-4105(90)90011-Q.</u>
- Kjøsnes, I., Løklingholm, G., Saasen, A. et al. 2003. Successful Water Based Drilling Fluid Design for Optimizing Hole Cleaning and Hole Stability. Presented at the SPE/IADC Middle East Drilling Technology Conference and Exhibition, Abu Dhabi, United Arab Emirates, 20-22 October. SPE-85330-MS. <u>http://dx.doi.org/10.2118/85330-MS.</u>
- Miller, R.W., Pesaran, P., and Honarvar, S. 1976. The Effects of Drilling Fluid Mixtures on Soils and Plant. Presented at the Annual Meeting Papers, Division of Production, Los Angeles, California, 4-7 April. API-76-F001.

- Mohan, K.K., Vaidya, R.N., Reed, M.G. et al. 1993. Water Sensitivity of Sandstones Containing Swelling and Non-Swelling Clays. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **73** (0): 237-254.
- Mondshine, T.C. 1973. A New Potassium Based Mud System. Presented at the Fall Meeting of the Society of Petroleum Engineers of AIME. SPE-4516-MS, Las Vegas, Nevada, 30 September-3 October. <u>http://dx.doi.org/10.2118/4516-MS.</u>
- Novelline, R.A. 2004. *Squire's Fundamentals of Radiology*. 6th. Harvard University Press.
- O'Brien, D.E. and Chenevert, M.E. 1973. Stabilizing Sensitive Shales with Inhibited, Potassium-Based Drilling Fluids. *Journal of Petroleum Technology* **27** (3): 283-293. SPE-4232-PA. <u>http://dx.doi.org/10.2118/4232-PA.</u>
- Olatunde, A.O., Usman, M.A., Olafadehan, O.A. et al. 2012. Improvement of Rheological Properties of Drilling Fluid Using Locally Based Materials. *Petroleum & Coal* **54** (1): 65-75.
- OFI Testing Equipment, Inc. 2014. Capillary Suction Timer, http://www.ofite.com/products/wastewater/product/2117-capillary-suction-timer (access 8 April 2015).
- Pagels, M., Hinkel, J.J., and Willberg, D.M. 2012. Moving Beyond the Capillary Suction Time Test. Presented at the SPE International Symposium and Exhibition on Formation Damage Control, Lafayette, Louisiana, USA, 15-17 February. SPE-151832-MS. <u>http://dx.doi.org/10.2118/151832-MS.</u>
- Reid, P.I. and Minton, R.C. 1992. New Water-Based Muds for Tertiary Shale Control. *SPE Drilling Engineering* **7** (4): 237-240. SPE-23077-PA. <u>http://dx.doi.org/10.2118/23077-PA.</u>
- Schlemmer, R., Friedheim, J.E., Growcock, F.B. et al. 2003. Chemical Osmosis, Shale, and Drilling Fluids. *SPE Drilling & Completion* **18** (4): 318-331. SPE-86912-PA. <u>http://dx.doi.org/10.2118/86912-PA.</u>
- van Oort, E. 1994. A Novel Technique for the Investigation of Drilling Fluid Induced Borehole Instability in Shales. Presented at the Rock Mechanics in Petroleum Engineering, Delft, Netherlands, 29-31 August. SPE-28064-MS. <u>http://dx.doi.org/10.2118/28064-MS.</u>
- van Overveldt, A.S., Guo, H., de Blok, G. et al. 2012. A Ct Scan Study of the Leakoff of Oil-Based Drilling Fluids. Presented at the SPE International Symposium and

Exhibition on Formation Damage Control, Lafayette, Louisiana, USA, 15-17 February. SPE-151856-MS. <u>http://dx.doi.org/10.2118/151856-MS.</u>

- Wellington, S.L. and Vinegar, H.J. 1987. X-Ray Computerized Tomography. Journal of Petroleum Technology 39 (8): 885-898. SPE-16983-PA. <u>http://dx.doi.org/10.2118/16983-PA.</u>
- Wilton, B.S., Bloys, J.B., Watts, R.D. et al. 1992. Drilling Wastes Evaluated in Plant Growth Study. Presented at the SPE Annual Technical Conference and Exhibition, Houston, Texas, 10-12 February. SPE-24566-MS. <u>http://dx.doi.org/10.2118/24566-MS.</u>
- Zhou, Z.J., Gunter, W.O., and Jonasson, R.G. 1995. Controlling Formation Damage Using Clay Stabilizers: A Review. Presented at the Annual Technical Meeting, Calgary, Alberta, 7-9 June. PETSOC-95-71. <u>http://dx.doi.org/10.2118/95-71.</u>