DISPERSION AND FILTER CAKE REMOVAL OF MANGANESE TETROXIDE-BASED DRILLING FLUIDS

A Dissertation

by

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ABSTRACT

Linear and other structures of particle aggregations were identified in Mn_3O_4-based filter cake. Several dispersants showed high potential to disperse manganese tetraoxide particles in water-based drilling fluids. Groups A and B dispersants showed particle settling times of 24 and 1 to 3 hrs, respectively. Laser particle analysis showed that aggregation of particles was reduced in the presence of lignosulfonate based dispersant. Zeta potential measurements showed a region of dispersion stability at pH of 6 to 11 based on Mn_3O_4/C31 dispersant aqueous solutions. Zeta potential and transparency experiments showed that the optimum dispersant concentration was below 1 wt% and nearly 0.5 wt% based on Mn_3O_4/dispersant aqueous solutions. SEM images of filter cake showed that the aggregation of particles was reduced when acrylic/maleic-based dispersant was used in clay contaminated drilling fluids. In most cases, the rheological behavior and sagging tendency of the contaminated and non-contaminated drilling fluids (17.5 and 20 lbm/gal) before/after heat aging at 400°F were improved in the presence of dispersants. The presence of NaCl and $CaCl_2$ had varying interactions with compatibility and particle settling.

Dispersants for oil-based systems were sorted in **Appendix B** by the highest potential to disperse manganese tetraoxide particles in mineral oil-based solutions. Particle settling indicated that the optimum concentration for dispersants were nearly between 0.2 and 2 wt% based on Mn_3O_4/dispersant S9 mineral oil-based solutions. Viscosity measurements showed a lower viscosity of 13.8 lbm/gal Mn_3O_4 oil-based drilling fluids at 1 wt% dispersant S9 than that of drilling fluids at 0.25 wt%. In most cases, the rheological behavior and sagging tendency of the contaminated and non-contaminated drilling fluids (17.5 and 20 lbm/gal) before/after heat aging at 400°F were improved in the presence of dispersants. Ilmenite and API barite oil-based drilling fluids showed higher sagging tendencies than those of manganese tetraoxide oil-based drilling fluids, indicating dispersant S5 was more effective with manganese tetraoxide fluids although the three drilling fluids have nearly similar rheological behavior.

Glycolic or HCl acids (4 wt%) dissolved 75 wt% of manganese tetraoxide particles. The dissolved manganese ions were higher with glycolic acid (i.e. 10,000 mg/l) than that of HCl acid (8,500 mg/l). The reaction time when using

HCl was nearly 5 times faster than that of glycolic acid reaction with manganese tetroxide particles. The Mn_3O_4-based filter removal efficiency was nearly 90 wt% when glycolic acid was used in the single or two-step procedure to dissolve the filter cake. Glycolic acid concentrations were 7 and 10 wt% during the single and two-step filter cake removal procedures, respectively. The removal efficiencies by flow rate were higher with sandstone core samples (i.e. 125 vol%) than those of limestone core samples (i.e. 100 vol%).

DEDICATION

For the sake of Allah.

ACKNOWLEDGEMENTS

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CHAPTER I

INTRODUCTION: THE IMPORTANCE OF RESEARCH

High-density drilling fluids are desirable because they provide the necessary column weight in deep drilling. The control of downhole pressure while drilling is an important function of the drilling fluids. Different weighting materials have been used to increase the density of oil and water-based drilling fluids. Conventional weighting materials such as calcium carbonate or barite have been used for many years because of their availability and lower cost. Barite, however, is not soluble in HCl and, therefore, can damage the formation if it invaded the formation. In addition, barite can result in excessive equivalent circulating density because of frictional pressure loss (Ezell and Harrison 2008). Calcium carbonate, on the other hand, has a low specific gravity of 2.7, resulting in using a substantial amount of solids to meet the downhole pressure requirements and, therefore, its application for deep drilling is limited.

Other materials such as iron oxides, iron carbonate, ultrafine-grind barite, and manganese tetraoxide have been introduced, laboratory-tested, and applied in several field treatments. For instance, Menzel (1973) introduced a synthetic iron oxide to replace barite with a specific gravity of 4.7. Because of the small particle size, the abrasion of the synthetic iron oxide is similar to barite's and lower than that of natural iron oxides. Because of the chemical composition (85 wt% Fe_2O_3), the material is soluble in HCl up to 85%. The particle size distribution of the proposed synthetic iron oxide does change during drilling, which results in stable and constant rheological properties. Sloan et al. (1975) investigated the use of iron carbonate to replace barite and formulate drilling fluid up to 19 lbm/gal. The new material showed a significant enhancement in solubility using dilute hydrochloric acid and coreflooding. In their lab studies, iron carbonate fluids did not result in damaging the Berea sandstone cores by particulate invasion or by filter cake buildup. The filter cake was effectively removed using the subsequent acidizing treatment. Walker (1983) provided data on using mined iron oxide, refined iron oxide, and iron oxide-barite blends in drilling nine wells in Louisiana and Texas. The data showed enhanced performance for the drilling muds containing iron oxide. However, other

problems such as abrasion, pump wear, efficiency of wetting, and material stains were noticed.

The microsized manganese tetraoxide (Mn_3O_4) particles have been used to design high density fluids as an alternative to barite-weighted drilling fluids, which can be utilized to drill deep and high temperature wells. Acid solubility is one of the main advantages of manganese tetraoxide particles (Al Moajil and Nasr-El-Din 2013; 2014).The microsize and high density (SG of 4.8) properties make manganese tetroxide particles an appropriate weighting agents for drilling fluids in HP/HT drilling. They have been used in water-based drilling fluids to reduce equivalent circulating density and are considered as less damaging compared to other weighting agents (Al-Yami et al. 2010).

Mn_3O_4 particles have been used in cementing, drilling, and completion fluids. Statoil drilled the reservoir section of the Gullfaks field using potassium formate drilling fluids weighted with Mn_3O_4 to 14 lbm/gal (Howard 1995; Svendsen et al. 1995). In 2004, an oil-based drilling fluid weighted with Mn_3O_4 was used for drilling in the North Cormorant field in the North Sea (Franks and Marshall 2004; Kleverlaan and Lawless 2004). Moroni et al. (2008) used Mn_3O_4 as a weighting material for invert-emulsion fluids (11.7 lbm/gal) and showed low-sag characteristics and low-filming tendency. Potassium formate drilling fluids (13.1 lbm/gal) weighted with Mn_3O_4 were used to drill exploratory wells in the Raudhatain field in North Kuwait. These drilling fluids replaced oil-based muds that were used to drill these wells because they provided better-quality logs. Successful field drilling operations at HP/HT in Kuwait conditions using potassium formate/manganese tetra-oxide drilling fluids showed that using these fluids resulted in improved drilling characteristics and imaging log quality (Al-Saeedi et al. 2010; Al-Muhailan et al. 2014; Al-Foudari et al. 2015). The weighting material (Mn_3O_4) was allowed as a part of a drilling fluid with a density of 17.8 lbm/gal for the first time in this field. The results were also supported by the field application in Saudi Arabia, reported by ElBialy et al. (2011).

The Settling of Solids in Drilling Fluids and Effect of Contaminations

A particle's tendency to aggregate, the negative surface charge on manganese tetraoxide particles, its magnetic properties, the presence of biopolymers, and cement contamination are factors that can promote sagging tendency in manganese tetraoxide-based drilling fluids. The settling velocity of

smaller sized particles in an aqueous solution is expected to be lower than the settling velocity of larger sized particles, and thus, a lower sagging tendency is expected. However, solid particles may exhibit aggregation tendency under van der Waals attractions and hydrodynamic forces. Carbajal et al. suggested that the negative surface charge of manganese tetraoxide particles promote dispersion in aqueous solutions because of repulsive forces (2009). Barite particles do not have this advantageous surface property. However, the micronized manganese tetraoxide particles (1 micron) attract to biopolymers present in the drilling fluid such as starch. Manganese tetraoxide particles aggregate to larger size particles (up to 30 microns).

The flocculation of manganese tetraoxide particles accelerate particle settling in solutions and, thus, negatively affect the rheological behavior and sagging tendency of the drilling fluid. Thus, it would cause operational problems during drilling such as stuck pipe, well control, and drilling fluid losses. **Fig. 1** shows scale in a drill pipe caused by a manganese tetraoxide-based drilling fluid contaminated with cement.

Fig. 1—Deposit and scale in drill pipe (Al-Muhailan et al. 2014).

Settling of manganese particles in a drill pipe tool joint caused difficulties in opening drill pipe connections. Controlling the settling of weighting material in the drilling fluids is a challenge that would reduce several operational problems during drilling such as insufficient drilling fluid density for well control,

hindering proper casing running, and incomplete displacement during cementing operations (Omland et al. 2007; Carbajal et al. 2009; Al-Muhailan et al. 2014).

The presence of cement contamination promotes particle settling and caused scaling problems in drill pipes (Carbajal et al. 2009; Al-Muhailan et al. 2014). Although the microsized particles of manganese tetraoxide are considered an advantage over the other conventional weighting material, small sized solid particles may exhibit aggregation tendency under van der Waals attractions and hydrodynamic forces.

The stability of emulsions, suspensions, and colloidal particles depend on the balance between repulsive and attractive forces. Manganese tetraoxide particle flocculation may be controlled by magnetic properties, surface charge, presence of adsorbed polymers, and contaminations. Magnetic solid particles (i.e. spherical) have a tendency to aggregate and form a linear chain due to dipole-dipole interactions (van Netten et al. 2013). Colloidal particles tend to agglomerate, forming a structure that depends on the aggregation process and type of attractive forces (e.g. van-deer Waals and interactions with non-adsorbing polymer). The mass of aggregation can be estimated through a power law that depends on the radius of gyration and mass factual coefficient. In the presence of repulsive forces (e.g. electrically charged particles and polymer adsorbed on the particle surface), the coagulation process complexes and slows the aggregation process (Bossis et al. 1991; Kovalchuk and Starov 2012; van Netten et al. 2013).

Drilling fluids with high gel strengths are generally thought to have low sag potential, but this is not the case for most oil-based drilling fluids. This could be because a comprehensive rheology study of the drilling fluids is needed, in addition to the standard API gel strength testing (Saasen 2002). Sag can cause many drilling problems such as variations in drilling fluid weight, well-control situations, downhole fluid losses, and stuck pipe (Bern et al. 1996). The problem is more common in deviated wellbores because the particle-settling rates in inclined fluid columns are greater than those in vertical columns due to the boycott effect (Bern et al. 1996). Sag is the settling of drilling solids in the drilling fluid that are defined as the appreciable density differences between the top and bottom columns of the drilling fluid when they remain static for a period of time (Bern et al. 1996). Settling that occurs in a drilling fluid, while it is static, depends on the fluid gel strength and the density, size, shape, and concentration

of the particles. Dynamic sag depends both on the flow properties such as shear rate and the fluid properties such as the network structure at these shear rates (Jachnik and Robinson 1999). Sag is considerably higher in oil-based drilling fluids because of differences in the gelling mechanisms between water and oil-based systems (Taugbol et al. 2005). In deep and high temperature wells, sag tendency is much higher because high-density weighting agents at high concentrations are required in the drilling fluids to balance formation pressures. Due to a higher density and concentration, weighting particles have a tendency to settle down because of gravity, causing sag. Dispersants are used to keep particles suspended in the solution and lower the sag tendency of the drilling fluid.

Dispersants in Drilling Fluids

The main factors that control type, rate, and mass of manganese tetraoxide particles aggregates are related to the magnetic properties of the particles (van Netten et al. 2013), high surface area, spherical shape, particle size, surface charge, presence of adsorbed/non-adsorbed polymers (Bossis et al. 1991; Kovalchuk and Starov 2012), and drilling fluid contaminations. Therefore, developing an efficient dispersant is crucial for maintaining the weighting material and other solid particles in the fluid to prevent the flocculation of solids.

Surfactants and polymers are used in drilling and cementing fluids as fluid loss control agents, viscosity-generating agents, emulsifiers, interparticle forces reduction, defoaming agents, and dispersants. Dispersants are compounds that maintain particle suspension in a liquid medium by providing repulsive forces. They can delay or prevent particle flocculation. Dispersants range from low molecular weight surfactants such as lignosulfonates to high molecular weight polymers such as polyacrylates. Applications for dispersants in the oil industry include: oil-spill treatments, cementing, drilling fluids, sulfur, and asphalt depositions. Sulfonated lignin is non-toxic and is a PLONOR listed product (Petrille et al. 1996). Lignosulfonates have been used to disperse hematite slurries. The distribution of unpolar and polar groups, including the hydroxyl and sulfonic acid groups formed at the degradation, controls the properties of a particular lignosulfonate (Jennings 1978). Dispersants such as polyacrymides are used for shale stabilization. Dispersants obtained by heat treating an aqueous mixture of pyrogallol and an alkali metal hydroxide in the presence of

iron can be used to disperse clay particles in the drilling fluid. Dispersants in drilling fluids prevent solid flocculation and improve fluid mobility and rheological properties. In cementing applications, preventing flocculation using dispersants is important for the hydration reaction of the aggregated cement. Anionic dispersants (thinners) are used to reduce yield point and gel strength because they attract to charged clay particles. Dispersants, such as lignosulfonates, polyacrylates, lignites, and maleic anhydride, are common dispersing agents. A combination of dispersant systems has been used such as the combination of a sulfonated polystyrene maleic anhydride copolymer and ferrochrome lignosulfonate. A mixture of sulfonated styrene-maleic anhydride copolymer and polymers prepared from acrylic acid or acrylamide is nontoxic to aquatic life (Chesser and Enright 1980; Wilcox and Jarrett 1988). Chrome and ferrochrome lignosulfonates contain heavy metals which may cause environmental problems and are not as effective in seawater. Dispersants which contain polyacrylic acid and the copolymer of itaconic acid and acrylamide are effective in freshwater and seawater up to 400°F. Dihydroxy benzene dispersants are used in low pH drilling fluids. With high solid content fluids and high temperature applications, the effectiveness of the deflocculation process may require an optimized chemical selection and mixing design. In addition, the selection of proper dispersants requires the consideration of the type of drilling fluid, thermal stability requirement, pH of fluid, and biodegradability in aquatic environments. For example, ferrochrome lignosulfonate, a dispersant for an aqueous drilling fluid, will break at high temperatures, resulting in the gelling of the fluid and, thus, is not appropriate for high temperature applications. Polyacrylic acids having molecular weights less than 8,000 are very effective dispersants at low concentrations but are sensitive to drilled solid contamination and high temperatures which may reduce their dispersing capabilities. Neutralizing polyacrylic acid with alkylamine will reduce the sensitivity to drilling contaminations and enhance its thermal stability (Robert B 1961; Kablaoui and Kolaian 1972; Villa and Zeiner 1985; Garvey et al. 1989; Houwen 1993; Mueller and Bray 1993; Schlemmer et al. 1994; Deville et al. 2011; Huang et al. 2011; van Zanten 2011; De Stefano et al. 2013).

Low-molecular-weight copolymers of acrylic acid and salts of vinyl sulfonic acid have been described as dispersants and high-temperature deflocculants for the stabilization of the rheological properties of aqueous, clay-based drilling

fluids subjected to high levels of calcium ion contamination (Portnoy 1987). Complexes of tetravalent zirconium and ligands selected from organic acids such as citric, tartaric, malic, and lactic acid and a complex of aluminum and citric acid are suitable dispersants for bentonite suspensions (Lawson and Hale 1989). A mixture of a sulfonated styrene-maleic anhydride copolymer and polymers prepared from acrylic acid or acrylamide and their derivatives are effective dispersants for drilling fluids. The rheological characteristics of aqueous well drilling fluids are enhanced by incorporating the fluids into small amounts of sulfonated styrene-itaconic acid copolymers and an acrylic acid or acrylamide polymer (Burrafato and Carminati 2005). The complexity of developing an effective dispersant may increase in the presence of contaminations such as salts, cementing, and clay content. A high salt concentration has a negative effect on the clays added to the drilling fluid such as bentonite. The presence of salts dehydrates the clay, and, as a result, the viscosity of the drilling fluid decreases (Chaney 1942).

Polyacrylic acids having molecular weights less than 8,000 are reported to be very effective dispersants at low concentrations but are sensitive to drilled solids contamination and high temperatures which may reduce the dispersing capabilities (Garvey et al. 1989). Thus, selection of proper dispersants may be required to consider the presence of contaminations. Salt water, rock salt, and montmorillonite clay particles are common sources of drilling fluids contamination (Chaney 1942). The presence of cement contamination promoted manganese tetraoxide particle settling and caused scale problems in drill pipes (Al-Muhailan et al. 2014). Cement contamination affects the properties of a drilling fluid. The chemical interaction between cement and bentonite leads to a thickening of the drilling fluid, especially under HT/HP conditions (Hilscher and Clements 1982). Calcium hydroxide present in cement slurries may modify drilling fluid properties. The hydroxyl ions increase the pH of the drilling fluid, and the calcium ions present form toberomite in the presence of bentonite. Toberomite forms due to an ion exchange between Na^+ ions in the clay and Ca^{+2} ions in the solution. As a result, the drilling fluid may have cement like characteristics (i.e. solidification), especially in the presence of calcium lignosulfonate (Carney et al. 1988). The drilling fluid becomes thixotropic and very sensitive to salt contamination. Adding effective dispersants keeps the clay particles dispersed and reverses the effects of cement. Contamination with clay

particles can occur during drilling and depends on the formation composition. High salt concentration has a negative effect on the clays added to the drilling fluid (e.g. bentonite). It represses the ionization of the clays by mass action, which may result in clay flocculation. The salt also dehydrates the clay, and, as a result, the viscosity of the drilling fluid decreases (Chaney 1942). Additives such as xanthan gum and lignosulfonates are known to adsorb on the clay platelets, offering a steric hindrance for the attractive forces to disperse clay particles (Walker 1975).

Dissolution of Filter Cake

Conventional techniques and cleaning fluids used to remove the filter cake/damage created by drilling fluids are not efficient when these drilling fluids are based on weighting materials such as manganese tetraoxide (Mn_3O_4). This is because of the complexity of chemical reactions between acids/chelating agents and manganese tetraoxide particles (Al Moajil and Nasr-El-Din 2013). Mn_3O_4 particles used in drilling fluids are spherical in shape, have a sub-micron particle size, and have a specific gravity of 4.8. The possibility of filter cake/formation damage generated by Mn_3O_4-based fluids has been reported in the literature, and it is mainly because of Mn_3O_4 particle agglomeration and their interactions with the adsorbed polymers used prepare the drilling fluid. Biopolymers (e.g. starch) present in the filter cake cover manganese tetraoxide particles, and they tend to aggregate. Accumulation of these aggregates may cause formation damage (Al Moajil and Nasr-El-Din 2013).

The cleanup of Mn_3O_4-based filter cake is challenging. Mn_3O_4 is a strong oxidizing agent and can be used as a catalyst. Its active phase is composed of an octahedral Mn_2O_3 phase and a tetrahedral MnO phase, which results in complex interactions with most cleaning fluids. For example, EDTA at high pH (12) and acetic, propionic, butyric, and gluconic acids at low pH (3-5) showed very low Mn_3O_4 particles solubilities. Citric acid is recommended in the literature as a cleaning fluid (Svendsen et al. 1995). However, a recent publication reported that citric acid will produce insoluble manganese citrate [$Mn_3(C_6H_5O_7)_2 \cdot 10H_2O$] when reacted with a manganese tetraoxide-based filter cake (Al Moajil and Nasr-El-Din 2013). Oxalic and tartaric acids will react with Mn_3O_4 particles completely. However, a large amount of a white precipitate will produce. High pH fluids, such as diethylene triamine pentaacetic acid (DTPA)

may produce damaging Mn (silicates) when reacted with a Mn_3O_4-based filter cake in sandstone formations (Al Moajil and Nasr-El-Din 2013).

Manganese forms different salts with organic acids that are water soluble or insoluble. Many manganese salts of mono- and dibasic carboxylic acids are known, and compounds of Mn (II), (III), and (IV) exist. The formation of these salts depends on the stoichiometry of the manganese oxides to acids (Hawley 2001; Kemmitt 2001). The rate of reaction of manganese oxides with organic acids depends on the structure of the acid, the ability of the acid to chelate multivalent cations, and the stoichiometry of the reactants (Kemmitt 2001). In the case of acetic acid, there is no secondary function that is able to chelate. Therefore, the solubility of Mn_3O_4 in acetic acid is low. α-hydroxy monoacids (e.g. lactic and glycolic acids) react more slowly than diacids. The reaction of diacids depends on the resulting chelate ring size, so oxalic acid (five-membered ring) is the fastest, followed by malonic acid (six-membered ring). Malic and tartaric acids contain α-hydroxyls, form complexes analogous to lactic acids, and have a reaction rate is close to that of diacids (Kemmitt 2001).

CHAPTER II

DISPERSION OF MN3O4 WATER-BASED DRILLING FLUIDS:

EFFECT OF SALT AND CEMENT[*]

Overview

The settling of manganese tetraoxide particles in drilling fluids was reported to cause operational problems, particularly in the presence of cement contaminations (Al-Muhailan et al. 2014). The aggregation of manganese tetraoxide particles and cement contamination caused stuck pipe, well control, false bit gain, and scale problems. This affects the rheological behavior and sagging tendency of the drilling fluid adversely. Dispersants are used in drilling fluids to prevent solid flocculation. Manganese tetraoxide is a strong oxidizer and may interact differently with dispersants. Thus, a thorough investigation on appropriate dispersants for cement contaminated Mn_3O_4 water–based fluids was conducted.

The dispersion of Mn_3O_4 particles in aqueous solutions was evaluated through visual transparency testing and a PC-2200 Spectrek laser particle analyzer. More than 400 companies were contacted globally, and nearly 60 dispersants were obtained. A Mastersizer 2000 was used to obtain the particle size distribution and specific surface area of Mn_3O_4 particles. A TGA and variable speed mixers were used to assess the thermal stability and compatibility. HP/HT fluid loss, viscosity, and sagging tendency were evaluated using a HP/HT dynamic filter press, a Fan 35A viscometer, and density variation measurements. The effect of $CaCl_2$ was considered in the experimental study. The drilling fluids were aged using a hot rolling oven up to 400°F.

The dispersion of high density water-based drilling fluids up to 20 lbm/gal that are-based on Mn_3O_4 particles as a weighting material in the presence of cement contamination was investigated. The objectives were to: (i) examine more than 60 commercially potential chemicals as dispersants, (ii) conduct particle settling, compatibility, and thermal stability testing, (iii) compare the

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rheological behavior/sagging tendency of the drilling fluid and filter cake micro-structure after heat aging at 400°F, and (iv) examine the effect of cement and $CaCl_2$ on the drilling fluid behavior and dispersion of manganese tetraoxide particles. The dispersants examined are listed in **Appendix A** and, thus, would help the reader to identify proper/improper dispersants-based on the results of this study.

Linear and non-linear structures of particle aggregations were identified in Mn_3O_4-based filter cake. Dispersants examined were categorized into groups A, B, and C. Groups A and B dispersants showed settling times of 24 hours and 1-3 hrs, respectively. More than 25 dispersants were assigned to groups A and B. Laser particle analysis showed that aggregations of particles were reduced in the presence of a lignosulfonate-based dispersant. Acrylates- and lingosulfonates-based dispersants were compatible with water-based fluids and thermally stable up to 400°F and in the presence of $CaCl_2$. Both dispersants reduced the sag factor and fluid loss for drilling fluids in the presence of cement contamination. The shear stress/rate relationship and viscosity measurements showed that the rheological behavior of drilling fluids dispersed with either dispersants were improved. The dispersants was chosen were non-toxic to aquatic organisms and biodegradable. The examined drilling fluids were high density fluids up to 20 lbm/gal appropriate for deep drilling.

Material and Experimental Procedure

Water-based drilling fluid compositions used in this study are shown in **Tables 1** to **4**. Bentonite is an aluminum phyllosilicate clay used as a viscosity additive and for filtration control. Bentonite is also used to cool and lubricate cutting bits. Sodium hydroxide was used to increase the pH of the drilling fluid. A mixture of lignitic earth and synthetic maleic anhydride provide filtration control and rheological stability. A synthetic copolymer of acrylamide-2-acrylamido-2-methylpropanesulfonic acid was used as a filtration control additive and drilling fluid lubricant. An acrylamide polymer is used as a preferred thickening agent in drilling fluids. Manganese tetroxide was used as a weighting agent. Most drilling fluid additives were obtained from a local service company. Drilling fluid contamination samples, such as cement (Portland cement with 1-5 wt% quartz) and rock salt (potassium chloride), were obtained from a local service company. Dispersants were added to the drilling fluids at concentrations of 5-15 g/l.

Cement and rock salt contaminates were added at an amount of 69.5 and 19.5 g, respectively.

Material	Amount
Deionized Water	240 g
Bentonite	4.89 g
Sodium hydroxide	0.489 g
Lignite/maleic anhydride copolymer	4.89 g
Acrylamide-methylpropane sulfonic acid	1.95 g
Acrylamide polymer	1.95 g
Manganese tetraoxide	469.1 g

Table 1—Composition of Mn_3O_4 water-based drilling fluid (17.5 lbm/gal)

Material	Amount
Deionized Water	279 g
Bentonite	5 g
Sodium hydroxide	0.5 g
Lignite/maleic anhydride copolymer	5 g
Acrylamide-methylpropanesulfonic acid	1 g
Acrylamide polymer	1 g
Manganese tetraoxide	348.5 g

Table 2—Composition of Mn_3O_4 water-based drilling fluid (15 lbm/gal)

Material	Amount
Deionized Water	287.7 g
XC-Polymer	1 g
Starch	6 g
Polyanionic cellulose	0.75 g
Potassium chloride	41 g
Potassium hydroxide	0.3 g
Calcium hydroxide	0.25 g
Calcium carbonate (fine)	3.5 g
Calcium carbonate (medium)	1.5
Manganese tetraoxide	202 g

Table 3—composition of Mn_3O_4 water-based drilling fluid (12.7 lbm/gal)

Material	Amount
Deionized Water	206 g
Bentonite	4.89 g
Sodium hydroxide	0.489 g
Lignite/maleic anhydride copolymer	5.87 g
Acrylamide-methylpropane sulfonic acid	1.95 g
Acrylamide polymer	1.95 g
Manganese tetraoxide	595.43 g

Table 4—Composition of Mn_3O_4 water-based drilling fluid (20 lbm/gal)

Dispersants were obtained from several manufactures and companies worldwide including: Tetra Technologies, AkzoNobel, Oil Chem Technologies, Flotec, Clariant, Sasol, Trican, BASF, Cargill, Halliburton, Rhodia, Borregaard, Expo Chemical Company, Georgia-Pacific, Stepan, Huntsman Corporation, Ciba Specialty Chemicals, Omnova Solutions, Asahi Kasei Corporation, and International Specialty Products. More than 400 companies have been contacted to provide dispersants. The targeted dispersants were non-toxic to aquatic

organisms, ionic or non-ionic, had the affinity to absorb on the surface of Mn_3O_4 particles, and were stable in alkaline media and in the presence of salts. Nearly 60 dispersants were obtained and tested. **Appendix A** shows the list of dispersants, health, flammability, reactivity, and other information.

Compatibility and solubility testing were conducted by preparing and mixing dispersant aqueous solution using at 80 rpm for 20 minutes using a variable speed mixer. Then, the solution was allowed to remain still for 2 hours. Finally, visual observations of solubility and compatibility were recorded. The solution volume was 250 cm^3, and the dispersant concentration was 1.6 wt%.

Viscosity measurements of the water-based drilling fluid with contaminants were conducted using a Fann 35A Viscometer. Fluid loss was collected for 30 minutes using static and dynamic HP/HT filtration testing at 265°F, 200 rpm, and 10 micron ceramic disc. Static sag was measured using aging cells. The cells were placed at an angle of 45° and temperature of 300°F for 16 hrs. A 10 cm^3 syringe and a balance were used in density measurements, and the sag value was calculated using **Eq.1**

$$Static\ Sag\ value\ = \frac{Density\ of\ bottom\ layer}{\sum(Densities\ at\ bottom\ and\ top\ layers)} \dots\dots\dots\dots\dots\dots\dots\dots (1)$$

Dynamic sag was measured using a Fann 35A Viscometer at 120°F with a horse shoe installed. The densities were measured initially and after 30 minutes of settling. The dynamic sag value was calculated from the difference in density measurements.

Settling tests and particle size analysis were conducted using visual observations and a laser particle analyzer to study the particle dispersion and settling velocity. Samples of the drilling fluids were diluted with deionized water until the samples were transparent. Dispersant was then added at a concentration of 0.1 wt%. Finally, the fluids were analyzed using a Spectrek PC-2200 laser particle analyzer. The particle settling measurements of dispersant solutions in the presence of Mn_3O_4 particles were conducted at 1.6 wt% dispersant concentration. The procedure that followed was to prepare 10 g of dispersant solution in a 10 cm^3 graduated cylinder (ID = 13.9 mm). Then, 2 g of Mn_3O_4 particles were added to the dispersant solution and mixed thoroughly until the solid particles are dispersed in the solution. The liquid level was fixed at 10 cm^3. Volumetric readings of the changes in particle settling were taken as a

function of time. At 75% solution transparency, the settling time was recorded. The solution transparency increases as the particles are settling. The dispersion of solid particles is higher at lower transparencies (**Fig. 2**). The solution transparency indication was calculated using **Eq. 2**:

$$Transparancy\ Indication, \% \ = 1 - \left(\frac{volume\ of\ settled\ solids\ layer}{total\ volume}\right) \times 100\dots\dots\dots\dots\dots\dots\dots\ (2)$$
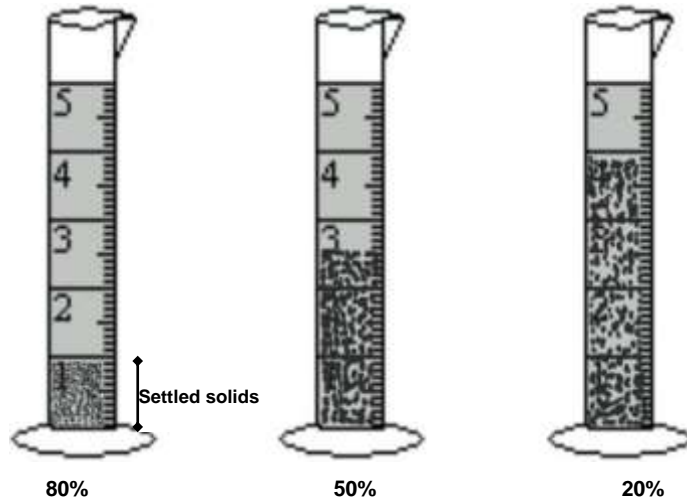
Fig. 2—Illustrative drawing of dispersant solutions at 20, 50, and 80% transparency.

Compatibility of Dispersant Solutions

Several dispersants that have been studied were incompatible with an aqueous system or generated foam upon mixing. For example, dispersants C26 and C28 are nonionic and ionic lignosulfonates, respectively. They were soluble with aqueous solutions at a 1.6 wt% dispersant concentration. Both C26 and C28 dispersants show a similar particle settling time of 0.6-0.75 hours using micronized manganese tetraoxide. Dispersant C28 generated a lot of foam compared to dispersant C26 (**Fig. 18)**. Thus, dispersant C26 is favored because of the anticipated high foam generation with dispersant C28. Drilling fluids that generate foams may result in operational problems such as false bit gain information. Dispersants C46 and C54 are both polymers-based on ethoxylated alcohols. Dispersant C54 precipitated at 1.6 wt% concentration. Thus, dispersant C46 is favored because of the anticipated lower solubility in water

with dispersant C46. The colors of dispersant solutions were clear, yellow, or dark. Detailed compatibility observations such as color, solubility, and foam generation were recorded for over 60 dispersants.
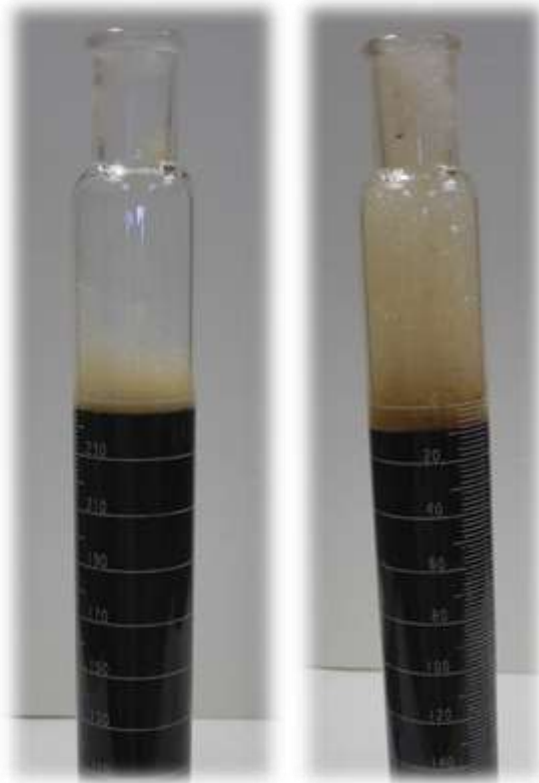
Fig. 3—Foam generation in C26 and C28 dispersants solutions at 1.6 wt% dispersant concentration.

Particle Size Analysis and Manganese Tetraoxide Aggregates

The particle size distribution for manganese tetroxide particles was 0.4, 1.09, and 2.87 µm at D10, D50, and D90, respectively, at a refractive index of 2.39 using a Mastersizer 2000. Three drilling fluid samples with compositions shown in Tables 1 to 3 were diluted until they became transparent. The drilling fluids were prepared with no contaminations. Dispersant B15, an anionic lignosulfonate, was added at a concentration of 0.1 wt%. The particle size was measured using a laser particle counter. Drilling fluids with higher densities showed higher solid concentrations and average particle sizes. Average particle

sizes of 11.8, 21.9, and 30.1 microns were measured for diluted samples 1, 2, and 3, respectively. Drilling fluid samples with dispersant added showed lower average particle sizes (

Table 5). This indicated that dispersant B15 improved the dispersion of solid particles in the three drilling fluid samples. Dispersant B15 was calcium lignosulfonate. The concentrations of solids were reduced from 16.6, 3.46, and 0.65 ppm to 5.53, 0.42, and 0.17 ppm for drilling fluids 1, 2, and 3, respectively. This indicated that the dispersion of particles have improved upon the addition of dispersant.

Material	Average Particle size, microns	Total Suspended Solids, ppm
Drilling fluid 1 (Table 1)	30.1	16.66
Drilling fluid 2 (Table 2)	21.9	3.46
Drilling fluid 3 (Table 3)	11.8	0.65
Drilling Fluid 1 + dispersant B15	24	5.53
Drilling Fluid 2 + dispersant B15	10.9	0.42
Drilling Fluid 3 + dispersant B15	7.7	0.17

Table 5—laser particle counter results for mn3o4 water-based drilling fluids

Settling and Aggregations of Manganese Tetraoxide Particles

The settling and aggregations of Mn_3O_4 particles were studied through settling tests and a scanning electron microscope (SEM). The dispersion of Mn_3O_4 particles in aqueous solutions was evaluated from settling times of Mn_3O_4 particles (Fig. 2). The description of several dispersants tested are summarized in Appendix A. The dispersants were divided into groups-based on the settling time results at a 1.6 wt% dispersant concentration. Group A dispersants (i.e. A1-A12) provided the highest capability to disperse manganese tetraoxide particles in aqueous solutions. The settling times of manganese tetraoxide particles were over 24 hours (**Fig. 4**). The chemical ingredients of these dispersants may contain ethoxylated alcohols or phenols that are based on phosphate esters, phosphoric acids, sodium salts, maleic acids, sulfated polyethylene glycol ether, ether phosphates, sulfonated acrylate, or sodium salt of alkylbenzene sulfonated

compounds. Thus, dispersants A1-A12 are mainly phosphate, sulfate, or sulfonated-based compounds. The second group of dispersants were numbered from B13-B25. Fig. 4 shows that the settling times of manganese tetraoxide particles were between 1-3 hours for group B dispersants at 1.6 wt% concentrations. The chemical ingredients of these dispersants may contain carboxylic acids-based ethoxylated alcohols and phosphate esters, lignosulfonate salts, polyethylene glycol, or polyglycol ethers. The settling times of the remaining dispersants (i.e. Group C) were less than one hour (Fig. 4).

Linear and other structures of manganese tetraoxide aggregates were identified from the filter cake SEM images. **Fig. 5(a-c)** shows the linear aggregation of manganese tetraoxide particles in the filter cake. The linear-chain aggregation is because of the magnetic properties of the spherical particles. The linear-chain aggregates can form because of the magnetic dipole-dipole interactions and Brownian motion. An induced dipole-dipole interactions would further have a greater influence on the linear aggregation and control the orientation, and length of aggregates (Martínez-Pedrero et al. 2009; van Netten et al. 2013). **Fig. 5(d, f)** shows round and other structures of particles aggregations, probably inside a medium adsorbed polymers. Attractive and repulsive forces such as van deer Waals, the presence of adsorbed polymers, and electrically charged particles can attract adjacent aggregates and complicate the aggregation process, giving the particles more time to rearrange inside the aggregate (Martínez-Pedrero et al. 2009; Kovalchuk and Starov 2012). The distribution of particle sizes in the Mn_3O_4-based filter cake promoted the capture of smaller particles by larger particles as shown in Fig. 5(d, f). Mathieu and Martel (2009) suggested that the particle size is a factor that modifies the balance between magnetic potential and other colloidal potentials. The influence by repulsive forces between particles can be dominated by the attractive interactions between small and larger particles. This results in a side-by-side configuration of small particles on the surface by larger particles (Mathieu and Martel 2009).
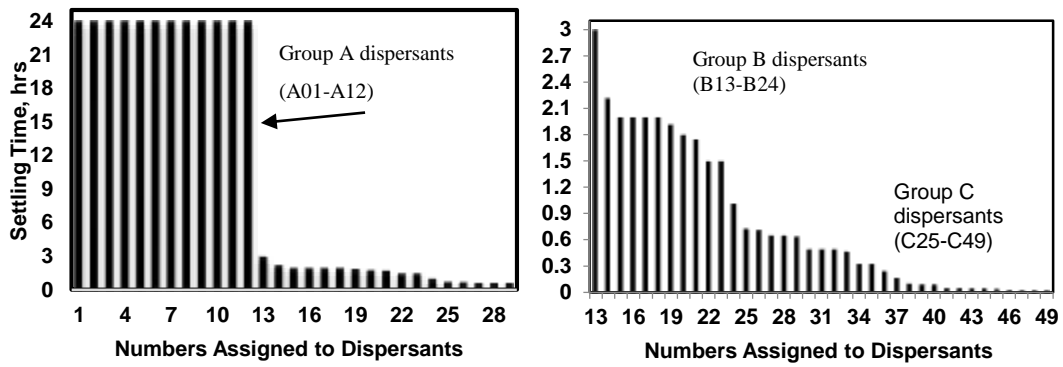
Fig. 4—Settling times of Mn$_3$O$_4$ particles in 1.6 wt% dispersant solutions. Refer to Appendix A for dispersant information.
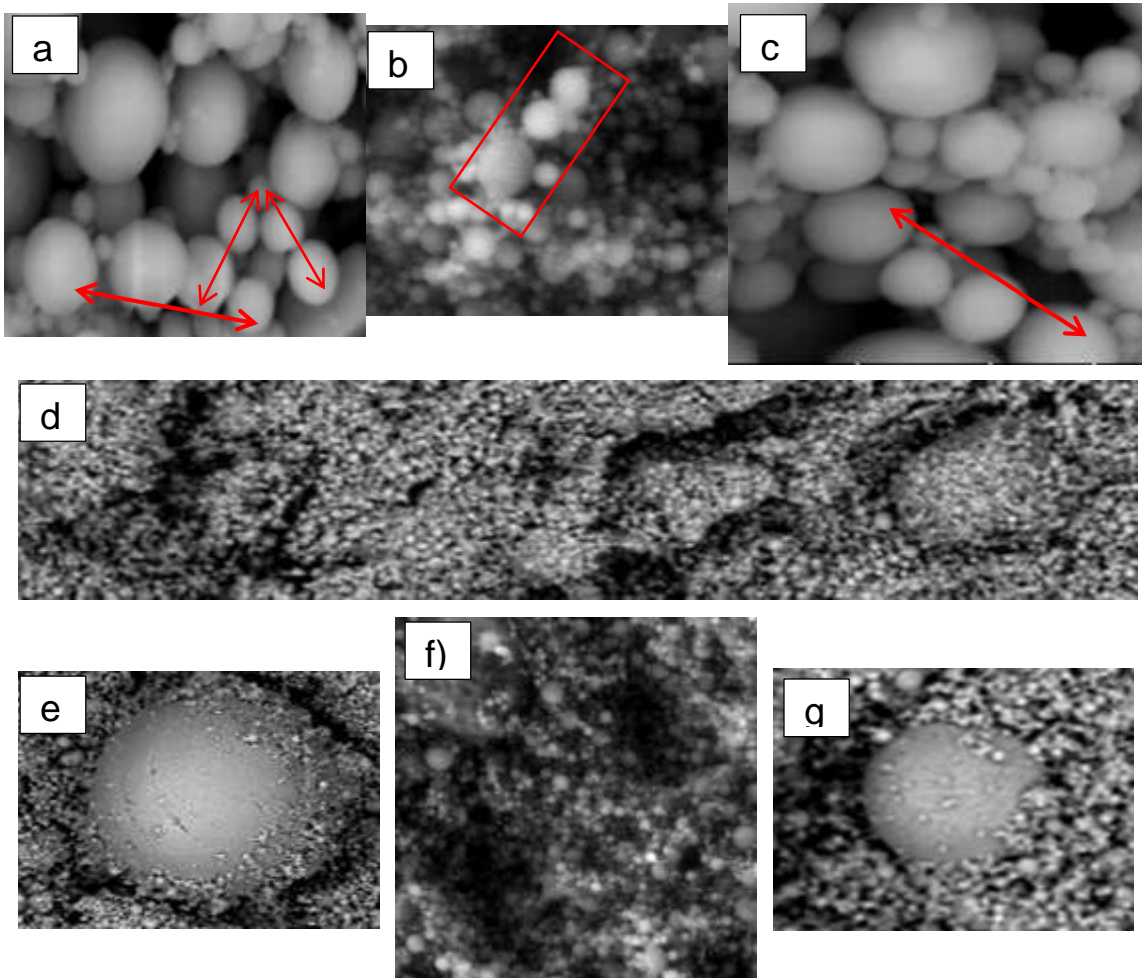
Fig. 5—SEM images of manganese tetraoxide-based filter cake. Magnifications: a) 40,000x, b) 2,000x, c)40,000x, d)20,000x, f) 2,000x, g) 20,000x.

Effect of CaCl$_2$ on the Dispersion of Manganese Tetraoxide Particles

Salinity and high pH reduced the settling time of manganese tetraoxide particles with several dispersant solutions. The settling time of manganese tetraoxide particles was reduced from 24 hours to 1.5 hours when the pH was increased from 7 to 11 at a 1.6 wt% dispersant concentration (i.e. dispersants A07 and A10). Both dispersants were based on nonylphenol ethoxylate phosphate esters. At a concentration of 10 wt%, CaCl$_2$ was added to the dispersant solution, and the pH was increased to 11 using NaOH. The settling time of manganese tetraoxide particles was reduced from 24 hours to 1.5-2 hours for dispersants A02 and A07-A12. Dispersant A01 showed the longest settling time of 5-6 hours at a 1.6 wt% concentration. Dispersant A01 was based on a sulphonated/acrylate copolymer, while dispersants A07 to A12 were based on ether phosphate, nonylphoenol ethoxylated phosphate esters, alcohol phosphate esters, and phosphoric acid. The performance of dispersant solutions in the presence CaCl$_2$ was reduced, even at lower dispersant and CaCl$_2$ concentrations. The settling time of manganese tetraoxide particles was reduced from 24 hours to less than 1 hr. at 5 wt% CaCl$_2$ and 0.5 wt% dispersant concentration (e.g. dispersants A07 to A10) at pH of 9. The presence of 5 and 10 wt% CaCl$_2$ at a pH of 9 to 11 precipitated when using dispersants A07 to A12. The solubility was higher with dispersant A01 (**Fig. 6**). The performance of dispersant A01 to disperse manganese tetraoxide particles was the highest in the presence of calcium chloride (**Fig. 7**).

No salt   10 wt% CaCl$_2$ No salt   10 wt% CaCl$_2$ No salt   5 wt% CaCl$_2$
Dispersant A01   **Dispersant A09**   **Dispersant A11**
1.6 wt% dispersant   **1.6 wt% dispersant**   **0.5 wt% dispersant**
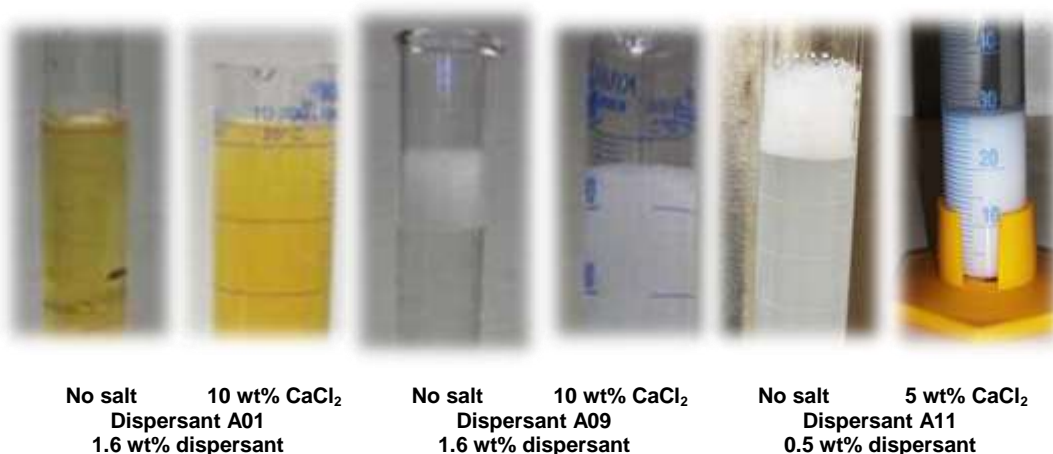
Fig. 7— Effect of 10 wt% CaCl$_2$ on the settling times of Mn$_3$O$_4$ particles at 1.6 wt% dispersant solutions at pH of 11.

Thermal Stability of Dispersant Solutions

Thermal stability curves for dispersants A01, B15, and C25 were generated (**Fig. 8**). They are based on sulphonated acrylate copolymer, ionic lignosulfonate, and nonionic lignosulfonate, respectively. The settling time results were 24, 2, and 0.75 hrs, respectively at a 1.6 wt% dispersant concentration. At 500°F, the weight loss of dispersants B15 and C25 was 10 wt%. A higher weight loss (e.g. ~30 wt%) was observed at very high temperatures (i.e. 700°F). At 290°F, the weight loss was 40% for dispersant A01. The solid content of dispersant A01 as received was 40% as reported in the material safety data sheet. Thus, the weight loss reported at 400°F was 60 wt%. This explains the larger weight loss compared to those of dispersants B15 and C25 (Fig. 8). Lignosulfonates structures include a branched three-dimensional phenolic structure including three main phenyl propane units. They are obtained by complex condensation of the phenyl propane units. Thus, they are thermally stable compounds (Domburg et al. 1970; Brebu and Vasile 2010). The highest thermal stability were with dispersants B15 and C25, while the highest settling time was obtained when using dispersant A01.

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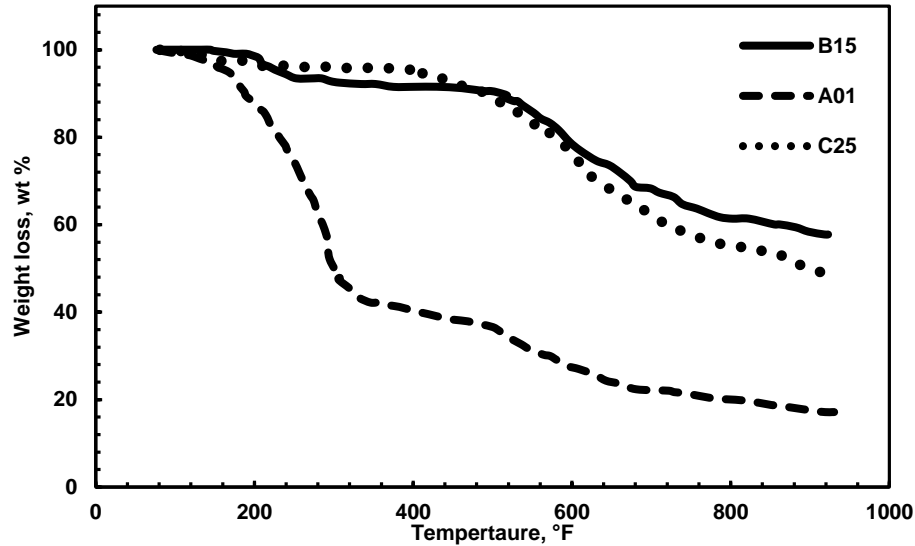
Fig. 8—Thermal Stability for dispersants A01, B15, and C25 obtained by thermogravimetric analysis (TGA), heating rate: 50°F/min.

Sagging Tendency and Fluid loss Comparison

Sag is a measure of the variation of drilling fluid densities as the weighting material is settling. The presence of contaminants have increased the sagging tendency for Mn_3O_4 water-based drilling fluids (**Fig. 9**). However, adding dispersants improved the results. The sag values of the cement and rock salt contaminated drilling fluids were lowered when adding dispersants A01, B03, or C25 (Fig. 9). Sag values were measured in non-contaminated drilling fluids (17.5 and 20 lbm/gal) at a 5 g/l dispersant concentration (**Fig. 10**). The drilling fluids were heat aged and rolled for 16 hours at 400°F. The results showed lower sagging tendency for the drilling fluids in the presence of dispersants. Dynamic sag values for 13.7 lbm/gal drilling fluids were measured at 120°F using a Fan 35A viscometer and a sag shoe. The sag values were nearly 0.53, 0.51, 0.52, and 0.52 for non-contaminated fluids with no dispersant and with dispersants A01, B18, and C59, respectively.

Fluid loss values increased in contaminated drilling fluids, especially in the presence of cement contaminated drilling fluids (**Fig. 11**). Adding dispersants A01 and B15 reduced the fluid loss values (**Fig. 12**). The fluid loss values were measured from HP/HT filtration experiments at 265°F, 500 psi, and using 10 micron ceramic disk at static and dynamic (200 rpm) conditions.
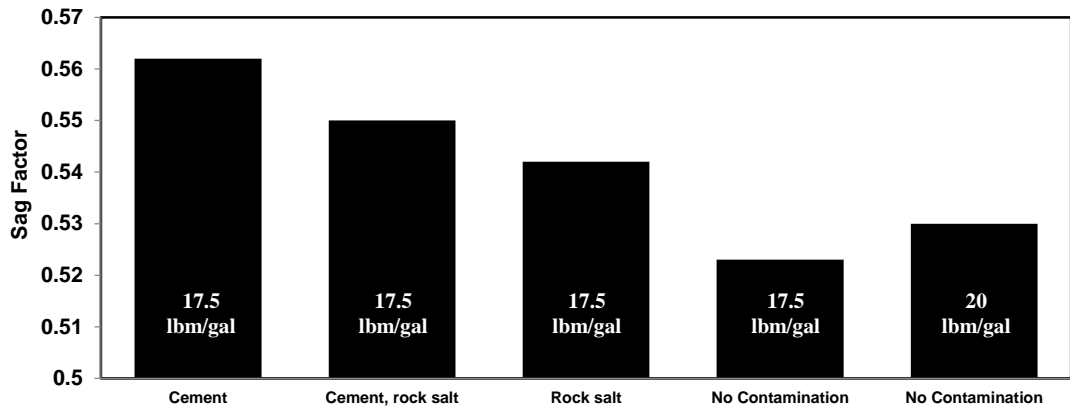
(a)
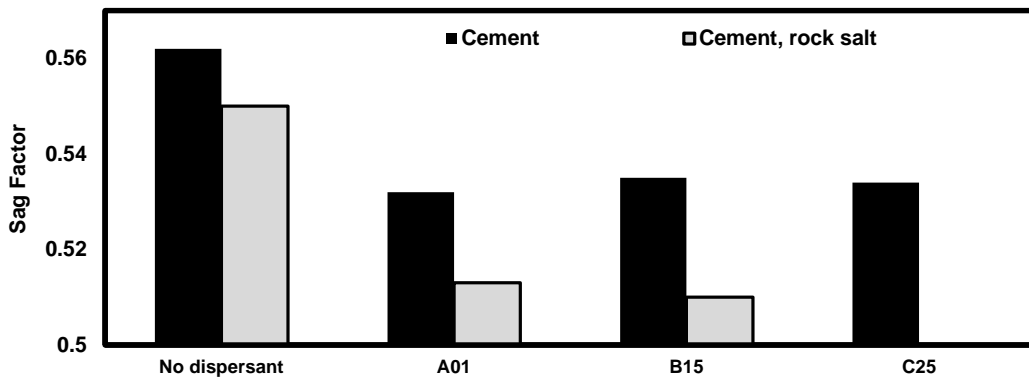
(b)
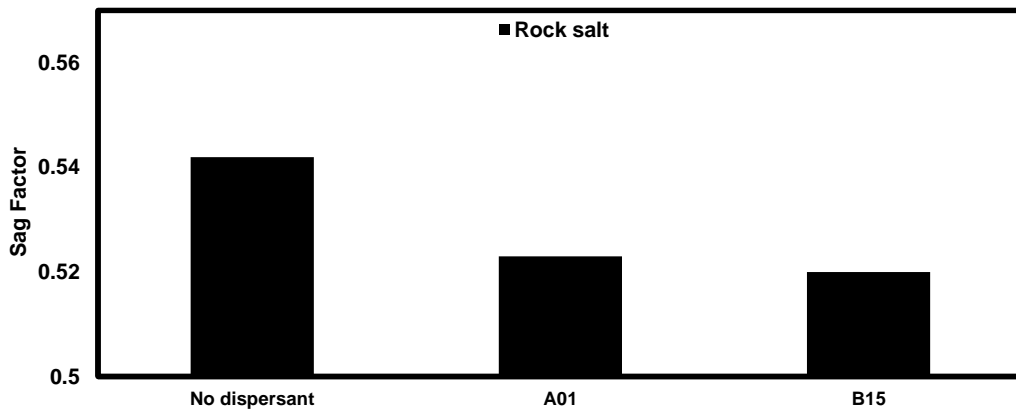
(c)

Fig. 9—Sag values for dispersed and/or contaminated water-based drilling fluids (17.5 lbm/gal) after heat aging at 400°F for 16 hrs. Dispersant concentration was 8 g/l water.
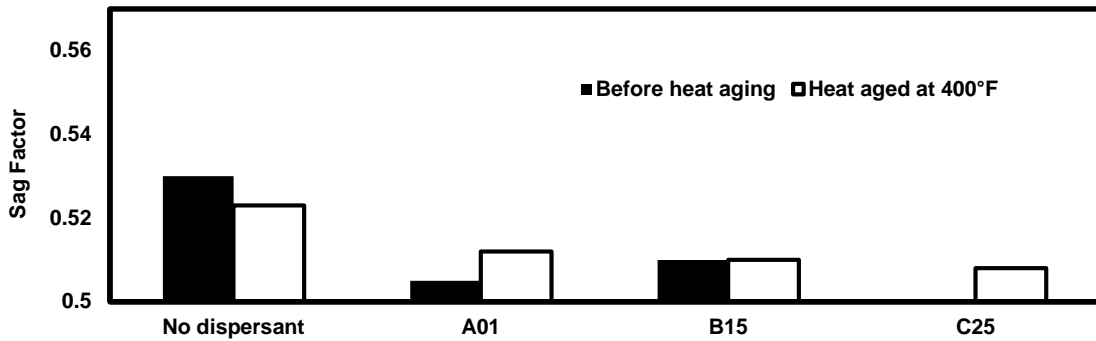
(a)
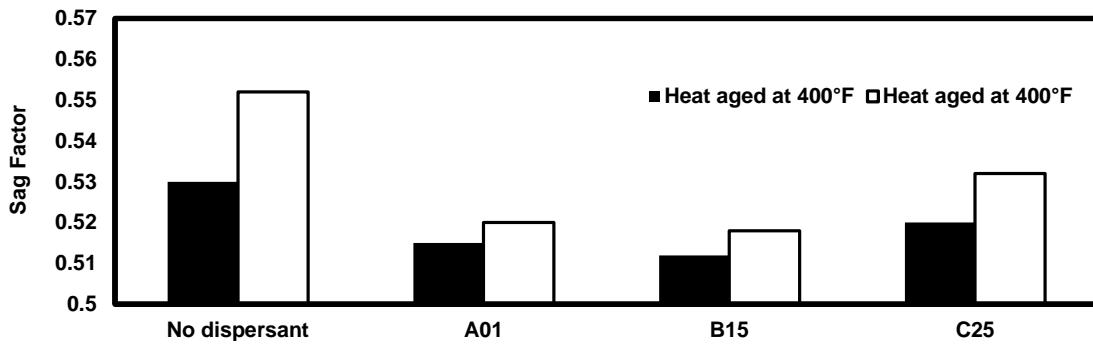
(b)

Fig. 10—Sag values for non-contaminated water-based drilling fluids: a) 17.5 and b) 20 lbm/gal after heat aging at 400°F for 16 hrs. Dispersant concentration was 5 g/l water.
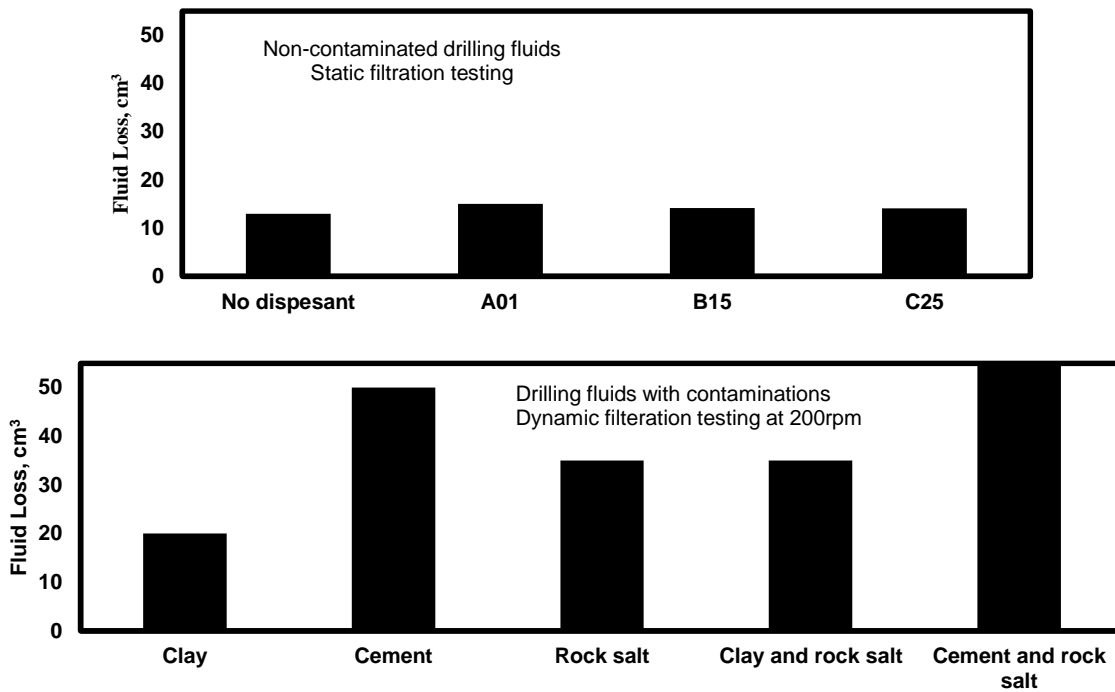
Fig. 11—Fluid loss for water-based drilling fluids (17.5 lbm/gal) using static and dynamic HP/HT filtration test at 265°F, and 10-micron ceramic. Dispersant concentration was 5 g/l water.

24
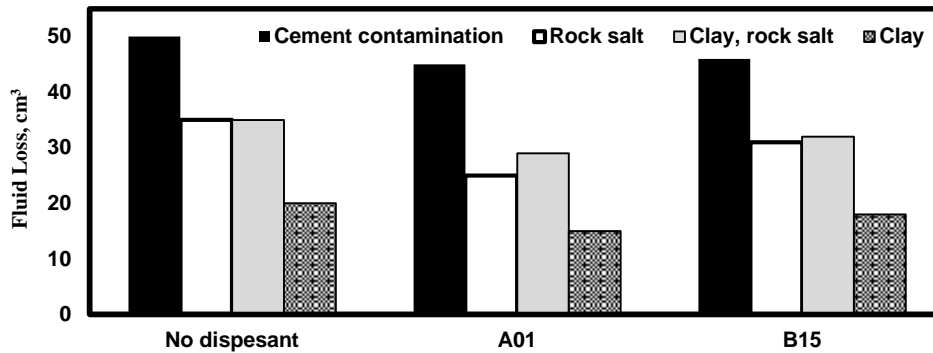
Fig. 12—Fluid loss for water-based drilling fluids (17.5 lbm/gal) using dynamic HP/HT filtration test at 265°F, 200 rpm, and 10-micron ceramic disc. Dispersant concentration was 5 g/l water.

Rheological Behavior of Contaminated Mn_3O_4 Water-Based Drilling Fluids

The dispersants that showed longer particle settling times (e.g. A1 and B15) have generally reduced the rheological behavior of the drilling fluids, especially in the presence of cement contamination. **Appendix D** and **Figs. 13** and **14** show that the shear stress values were reduced in cement/rock salt contaminated manganese tetraoxide water-based drilling fluids (17.5 and 20 lbm/gal) before and after heat aging at 400°F when dispersants were added (e.g., A01, B15, and C25). The presence of contaminations resulted in higher rheological properties (**Fig**. **15** and Appendix D). In non-contaminated drilling fluids, the rheological behavior were also improved when dispersants were added. **Fig. 16** and Appendix D shows that shear stress values of non-contaminated drilling fluids (17.5 and 20 lbm/gal) were slightly reduced before/after heat aging at 400°F when dispersants were added (i.e. A01 and B15).
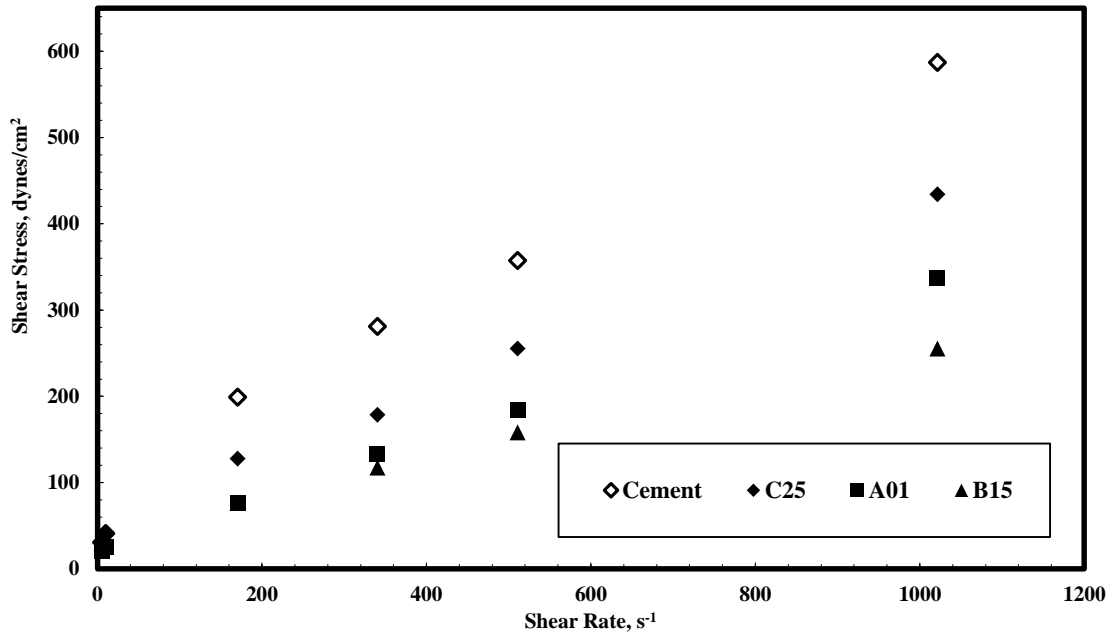
Fig. 13—Shear stresses for 17.5 lbm/gal water-based drilling fluid contaminated with cement. Dispersant concentration was 8 g/l water.
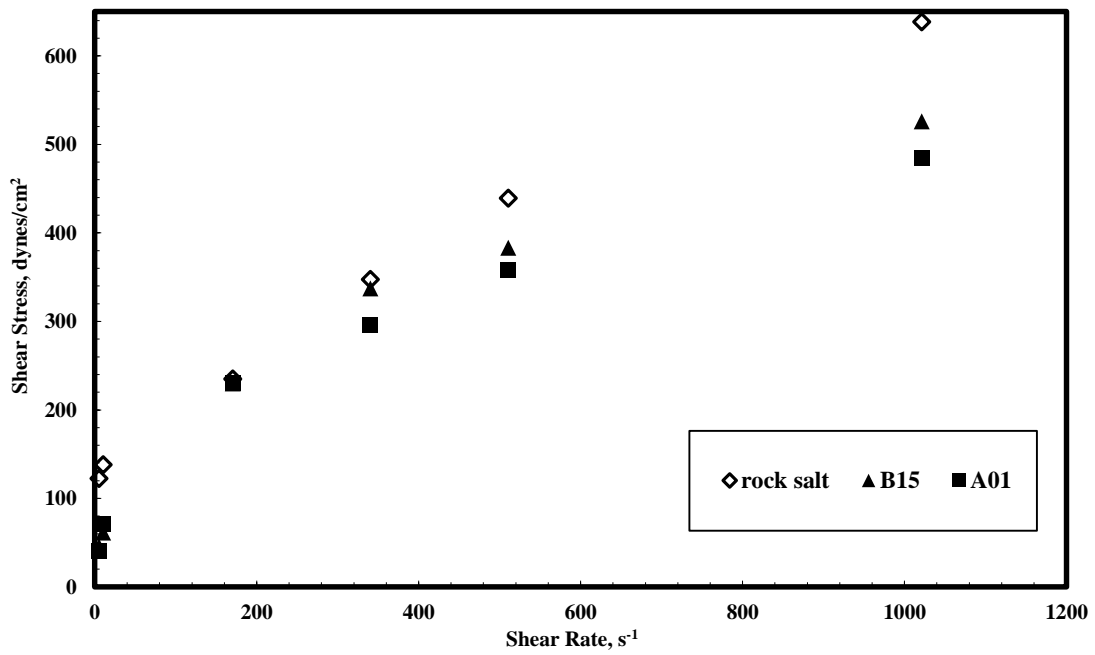
Fig. 14—Shear stresses for 20 lbm/gal water-based drilling fluid contaminated with cement and rock salt after heat aging. Dispersant concentration was 15 g/l water

26
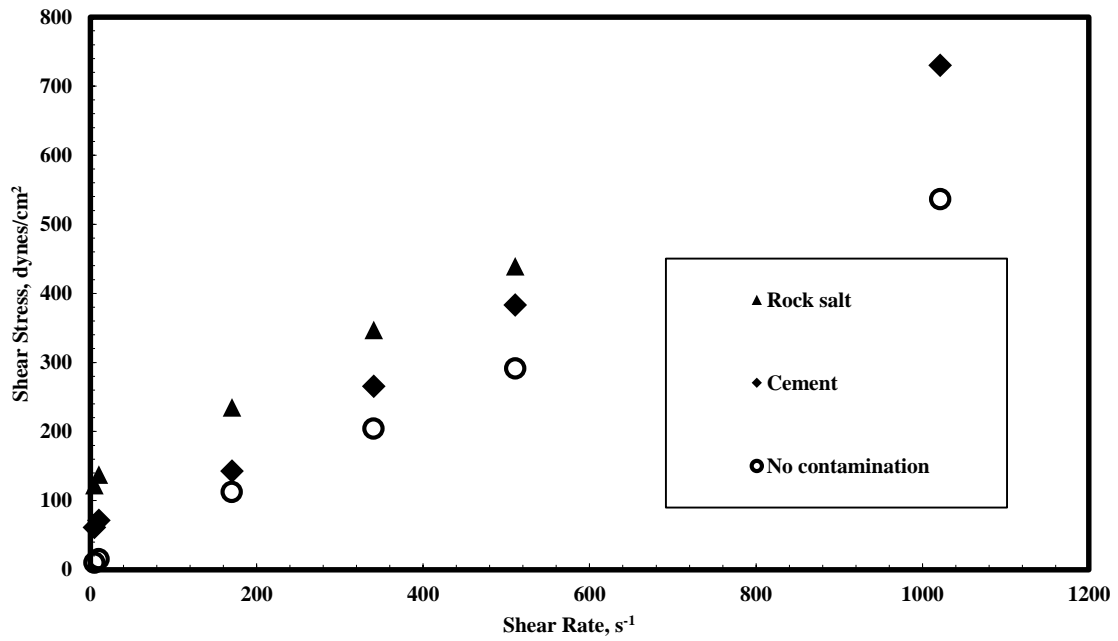
Fig. 15—Shear stresses for contaminated 20 lbm/gal water-based drilling fluids after heat aging at 400°F for 16 hrs. Dispersant concentration was 15 g/l water
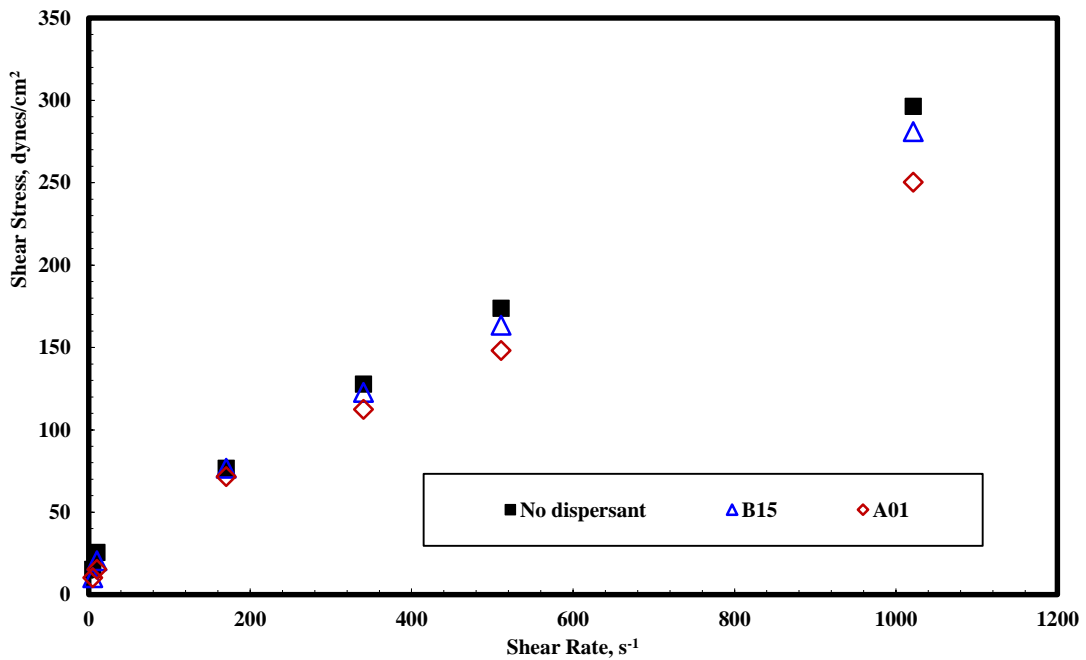
Fig. 16—Shear stresses for non-contaminated 17.5 lbm/gal Mn_3O_4 water-based drilling fluid before heat aging. Dispersant concentration was 5 g/l water.

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Conclusions

The dispersion of manganese tetraoxide particles in water-based drilling fluids (12.7 to 20 lbm/gal), applicable for high temperature drilling, has been studied. More than 50 commercially available chemicals were examined. Appendix A and Fig. 4 summarize the dispersants chemical ingredients, compatibility with water, and particle settling results. Linear and other structures of manganese tetraoxide aggregates have been identified in the filter cake SEM images. Laser particle analysis showed that aggregations of particles were reduced in the presence of dispersant B15. Group A and B dispersants showed particle settling times of 24 and 1-3 hrs, respectively (Appendix A). The remaining dispersants showed shorter particle settling times. Dispersants A01 and B15 reduced the sag factor and fluid loss for the drilling fluids in the presence of cement contamination. Dispersants A01 and B15 are based on anionic lignosulfonate and acrylate copolymer, respectively. The rheological behavior of drilling fluids dispersed with either dispersant A01 or B15 was improved in the presence of cement and rock salt contamination. Dispersant A01 showed the longest particle settling time in $CaCl_2$ solutions. Several dispersants precipitated and showed shorter particle settling times in 5 and 10 wt% $CaCl_2$ solutions. Based on the experimental results, the following conclusions can be drawn:

1. Several types of dispersants can be recommended for manganese tetraoxide water-based drilling fluids such as:
    i. Sulphonated copolymers of acrylic and maleic acids
    ii. Calcium/iron lignosulfonates
    iii. Nonylphenol ethoxylated fatty alcohols/acid/esters containing phosphate or sulfate functional groups
2. Divalent salts may reduce the dispersion of manganese tetraoxide. Thus, testing dispersants in the presence of divalent salts is important to ensure the effectiveness of dispersion process.
3. The quality of manganese tetraoxide particles (i.e. narrow PSD) can minimize the particle aggregation caused by the particle size.

CHAPTER III

DISPERSION OF MN3O4 WATER-BASED DRILLING FLUIDS:

EFFECT OF CLAY AND SALT[*]

Overview

Managing the solid flocculation in high-density drilling fluids is a challenge in drilling operations. A weighting material such as manganese tetraoxide is used to formulate drilling fluids at density requirements for deep drilling because of its high specific gravity (4.8 g/cm^3). The microsized Mn_3O_4 particles, surface charge, and presence of biopolymers increase the tendency to agglomerate and, thus, promote sagging in manganese tetraoxide-based drilling fluids. Developing a good dispersant is then critical for a successful drilling operation, especially in HP/HT conditions.

The dispersion of Mn_3O_4 particles in aqueous solutions was evaluated through visual transparency testing and a PC-2200 Spectrek laser particle analyzer. A Mastersizer 2000 was used to obtain the particle size distribution and specific surface area of Mn_3O_4 particles. TGA and variable speed mixers were used to assess the thermal stability and compatibility. Rheology and sagging tendency were evaluated using a Fan 35A viscometer and density variation measurements. The microstructure of Mn_3O_4-based filter cake was interpreted through SEM to identify the aggregation of solid particles. The effect of $CaCl_2$ was considered in the experimental study. The drilling fluids were aged at 400°F.

Dispersants for high density water-based drilling fluids (12.7 to 20 lbm/gal) using Mn_3O_4 particles as a weighting material were tested with the following objectives: (1) studying the compatibility of the dispersant with freshwater at a pH range 9 to 10, (2) studying the dispersion of Mn_3O_4 using zeta potential and particle settling testing, (3) investigating the thermal stability of the dispersed drilling fluid at elevated temperatures (e.g. 400ºF), and (4) examining the

effectiveness of the dispersant in the presence of contaminating rock salt and clay particles.

Several dispersants showed high potential to disperse manganese tetraoxide particles in water-based drilling fluids. Appendix A sorts the dispersants by the longest particle settling time. Zeta potential measurements showed a region of dispersion stability from a pH of 6 to 11 for lignosulfonate and sulfonic acid-based dispersants. Zeta potential and particle settling tests indicated that dispersion with acrylic/sulfonic copolymer is more effective than benzene sulfonic acid. Zeta potential absolute values increased with temperature in sulfonic acid-based dispersant (i.e. 77 and 120°F). Zeta potential and transparency experiments showed optimum dispersant concentration was below 1 wt% and nearly 0.5 wt%. TGA analysis showed that the acrylates and lignosulfonate-based dispersants were thermally stable between 300 and 500°F. SEM images of filter cake showed that the aggregation of particles was reduced when acrylic/maleic-based dispersant was used in clay contaminated drilling fluid. In most cases, the rheological behavior of the contaminated and non-contaminated drilling fluids (17.5 and 20 lbm/gal) before/after heat aging at 400°F was improved in the presence of dispersants. Dispersant solutions with NaCl had varying compatibility and particle settling interactions. The settling times of manganese tetraoxide particles were lower, higher, or did not change for several dispersants' solutions when NaCl was added. The sagging tendency of contaminated and non-contaminated drilling fluids was improved in the presence of dispersants. For instance, the sag factor was reduced from 0.55 to 0.51 in clay and rock salt contaminated drilling fluids when acrylic/maleic acid copolymer was used.

Material and Experimental Procedure

Water-based drilling fluid compositions used in this study are shown in **Table 6**. Bentonite is an aluminum phyllosilicate clay used as a viscosity additive and filtration control. Bentonite is also used to cool and lubricate cutting bits. Sodium hydroxide was used to increase the pH of the drilling fluid. A mixture of lignitic earth and synthetic maleic anhydride provided filtration control and rheological stability. A synthetic copolymer of acrylamide/methylpropane sulfonic acid was used as a filtration control additive and drilling fluids lubricant. An acrylamide

polymer is used as a preferred thickening agent in drilling fluids. Manganese tetroxide particles was used as a weighting agent.

Materials	Amount per 350 cm^3	Materials	Amount per 350 cm^3		
Drilling Fluid No.	1		2	3	4
Density	12.7 lbm/gal	Density	15 lbm/gal	17.5 lbm/gal	20 lbm/gal
Deionized Water	287.7 g	Deionized Water	279 g	240 g	206 g
Defoamer	0.08 g	Bentonite	5 g	4.9 g	4.9 g
XC-Polymer	1 g	Sodium hydroxide	0.5 g	0.5 g	0.5 g
Starch	6 g				
Polyanionic cellulose	0.75 g	Lignite/maleic anhydride copolymer	5 g	4.9 g	5.9 g
Potassium chloride	41 g				
Potassium hydroxide	0.3 g				
Calcium hydroxide	0.25 g				
Calcium carbonate (fine/medium)	3.5/1.5 g	Acrylamide-methylpropanesulfonic acid	1 g	2 g	2 g
Calcium carbonate (medium)	1.5 g				
Sodium sulfite	0.75 g	Acrylamide polymer	1 g	2 g	2 g
Manganese tetraoxide	202 g	Manganese tetraoxide	348.5 g	469.1 g	595.4 g

Table 6—Composition of Mn$_3$O$_4$ water-based drilling fluid

The particles were spherical with specific area of 1.52 m^2/g and d50 of 1.091 μm (**Fig. 17**) Drilling fluid additives, clay, and rock salt contaminations were obtained from a local service company. The clay contamination was a mixture of clays and fines (e.g., quartz; cristobalite, illite, mixed layer clay; kaolinite, and chlorite). Rock salt was potassium chloride. Clay and rock salt contaminates were added at an amount of 69.5 and 19.5 g. Dispersants were added to the drilling fluids at concentrations of 5-15 g/l. Dispersants were obtained from several manufacturers and chemical companies worldwide. More than 50 dispersants were obtained and tested. Dispersants were classified into groups A, B, and C based on the particle settling velocities. **Appendix A** summarizes the chemical ingredients for dispersants, compatibility with water, and Hazard information.

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D10 = 0.40 µm
D50 = 1.09 µm
D90 = 2.87 µm

Particle Size, µm

Volume, %
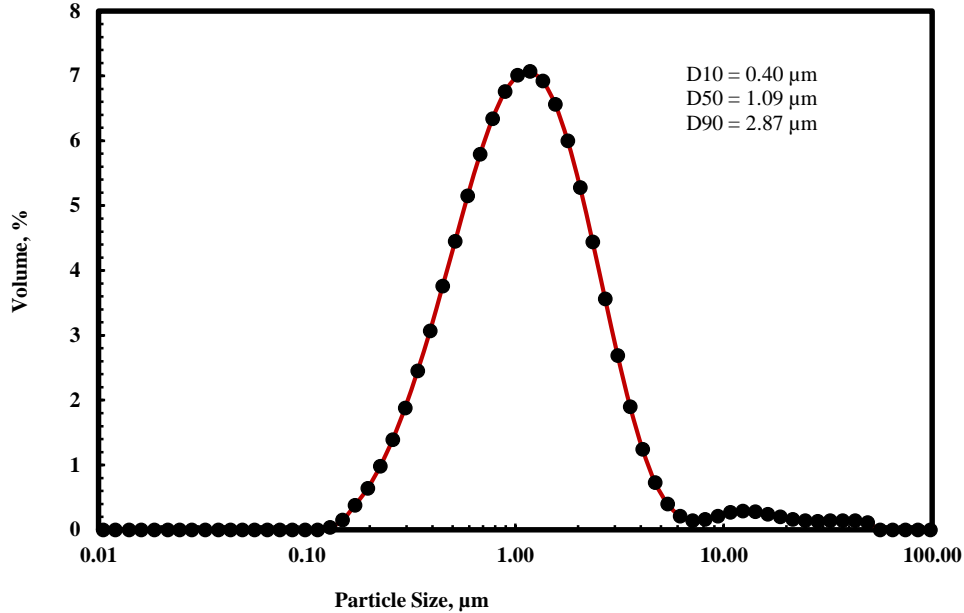
Fig. 17—Manganese tetraoxide particle size distribution.

The compatibility and solubility testing was conducted by preparing and mixing 1.6 wt% dispersant aqueous solutions at 80 rpm for 20 minutes using a variable speed mixer. Solution volume was 250 cm^3. Then, the mixture was allowed to remain still for 2 hours. Visual observations of compatibility were recorded.

The rheology measurements of the water-based drilling fluids with contaminants were conducted using a Fann 35A viscometer. ZetaPALS by Brookhaven Instrument Corporation was used for zeta potential measurements. A dispersant solution was prepared using deionized water that contained 5 wt% Mn_3O_4. Then, 1.6 cm^3 was poured into the sample cell after the solution was mixed. The electrodes were then inserted into the sample for zeta potential measurements, and the pH was controlled using potassium hydroxide.

The particle settling tests of dispersant solutions in the presence of Mn_3O_4 particles were studied as a function of concentration and settling time. The procedure that followed was as follows: 2 g of Mn_3O_4 particles were added to a dispersant solution in a 10 cm^3 graduated cylinder (ID = 13.9 mm) and mixed thoroughly until the solid particles were dispersed in the solution, and the initial volume was recorded. During the experiment and while the solid particles were

settling, a volumetric reading of the solution clarity indication was taken as a function of time. Initially, the color of solution was opaque because solid particles were dispersed in the solution. When all the solids were settled in the cylinder, the solution became lighter in color. The dispersion of solid particles is, therefore, higher at lower transparency. An illustrative schematic of the transparency measurement is shown in Fig. 2. Transparency indication was calculated using Eq. 2. Static sag was measured using aging cells. The cells were placed at an angle of 45° and a temperature of 300°F for 16 hrs. A 10 cm^3 syringe and a balance were used in density measurements, and sag value was calculated using Eq.1.

Compatibility and Particle Settling

Extensive compatibility testing such as foam generation, precipitations, and phase separation were recorded on over 50 dispersants aqueous solutions to identify compatible dispersant solutions (Appendix A). Dispersants C51 to C58 were not compatible at 1.6 wt% dispersant concentration because of precipitation or phase separation. Dispersants C30 and C31 were based on ether carboxylate polymer and benzene sulfonic acid, respectively. They were compatible with aqueous solutions. Dispersant C31 generated little foam (Fig. 18). Both C30 and C31 dispersants showed similar settling velocities of manganese tetraoxide particles. Dispersant C30 would be favored because of anticipated foam generation with dispersant C31. Drilling fluid that generated a lot of foams may result in operational problems such as false bit gain information. Dispersant C54, an ethoxylated alcohol, precipitated and, thus, is not recommended for water-based drilling fluids. Most tested dispersants were compatible with aqueous solutions such as dispersants A01, A05, A10, B13, and C26 (Fig. 19). Detailed compatibility observations such as color, presence of precipitation, foam generation, and solubility were recorded for over 50 dispersants (Appendix A).

Dispersant C30
Polyether-carboxylate polymer

Dispersant C31
Dodecyl benzene sulfonic acid
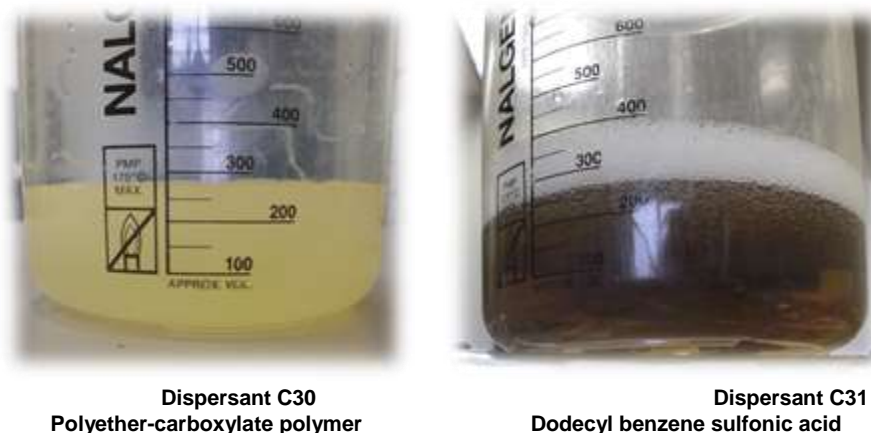
Fig. 18—Compatibility of dispersant solutions at 1.6 wt% dispersant concentration.

Fig. 19—Compatibility of dispersants solutions (1.6 wt%). From left to right are dispersants A01, A05, A10, B13, and C26.

The highest dispersion efficiency based on the manganese tetraoxide particle settling time was observed for dispersants from group A. At 75% transparency, the settling times of manganese tetraoxide particles for group A dispersants were 24 hrs. The settling times of manganese tetraoxide particles were 1-3 hours for group B (**Table 7**). The chemical ingredients of group A dispersants may contain ethoxylated alcohols or phenols that are based on phosphate esters or phosphoric acids, sulfated glycols and ethers, ether

phosphates, and acrylic/maleic acids copolymer. Dispersants B13-B24 may contain ethoxylated fatty carboxylic acids, phosphate esters, lignosulfonate salts, or polyglycol ethers. The remaining dispersants showed lower settling times of manganese tetraoxide particles and/or incompatibilities with aqueous solutions.

Dispersant	Settling time, hrs	Dispersant	Settling time, hrs	Dispersant	Settling time, hrs
A01 to A12	24.0	C30 to C32	0.5	C44 to C46	0.05
B13	3.0	C33	0.47	C47 to C50	0.03
B14	2.2	C34 and C35	0.33	C51	1
B15 to b18	2	C36	0.25	C52	0.17
B19	1.9	C36	0.25	C53	0.05
B20 and B21	1.8	C37	0.17	C54	0.04
B22 and B23	1.5	C38	0.11	C55	0.03

Table 7—Settling times of Mn_3O_4 particles at 75% transparency

Zeta Potential Measurements and Dispersant Concentration

Transparency and zeta potential measurements were conducted to investigate the optimum dispersant concentration. Zeta potential measurements were nearly (-20 and -35 mV) in dispersant-free Mn_3O_4 aqueous solutions at pH of 7 and 9-10, respectively. The literature has reported similar values for zeta potential (Morimoto and Kittaka 1974; Kittaka et al. 1987). These values indicate that the surface of manganese tetraoxide particles was negatively charged. Increasing the absolute values of zeta potential increases the degree of electrostatic repulsions between particles and, thus, favors particle dispersions. The presence of a dispersant in the drilling fluid is expected to increase the zeta potential value, providing higher dispersion capacity.

Several factors were examined to investigate their effect on the zeta potential, such as pH, temperature, and dispersant concentration. **Fig. 20** shows the zeta optional measurements over a pH range from 2-14 when the Mn_3O_4 particles were mixed with dispersant C31 aqueous solutions at three concentrations (0.2, 0.5, and 1 wt%). The results indicate three distinguishing

regions of pH: 2-4, 4-10, and 10-14. Minimum values of zeta potential (i.e. maximum absolute zeta potential values) were observed below a pH of 4 at the three concentration levels followed by a stable region between a pH of 4 to 10. Above a pH of 10, zeta potential absolute values increased with pH (i.e. absolute values of zeta potential were decreased). It was also observed that at 0.2 and 0.5 wt%, the zeta potential stabilized at lower values (-72 and -75 mV) than that of 1 wt% (-62 mV), indicating the impact of the dispersant concentration. Thus, the repulsive forces generated using 0.2 and 0.5 wt% dispersant solutions were higher in magnitude than with 1 wt% dispersant C31 solution. **Fig. 21** illustrates the measurements of zeta potential as a function of dispersant C31 concentration over three pH ranges. The results showed the minimum zeta potential values were obtained at 0.5 wt% dispersant concentration. The absolute values of zeta potential decreased with pH.
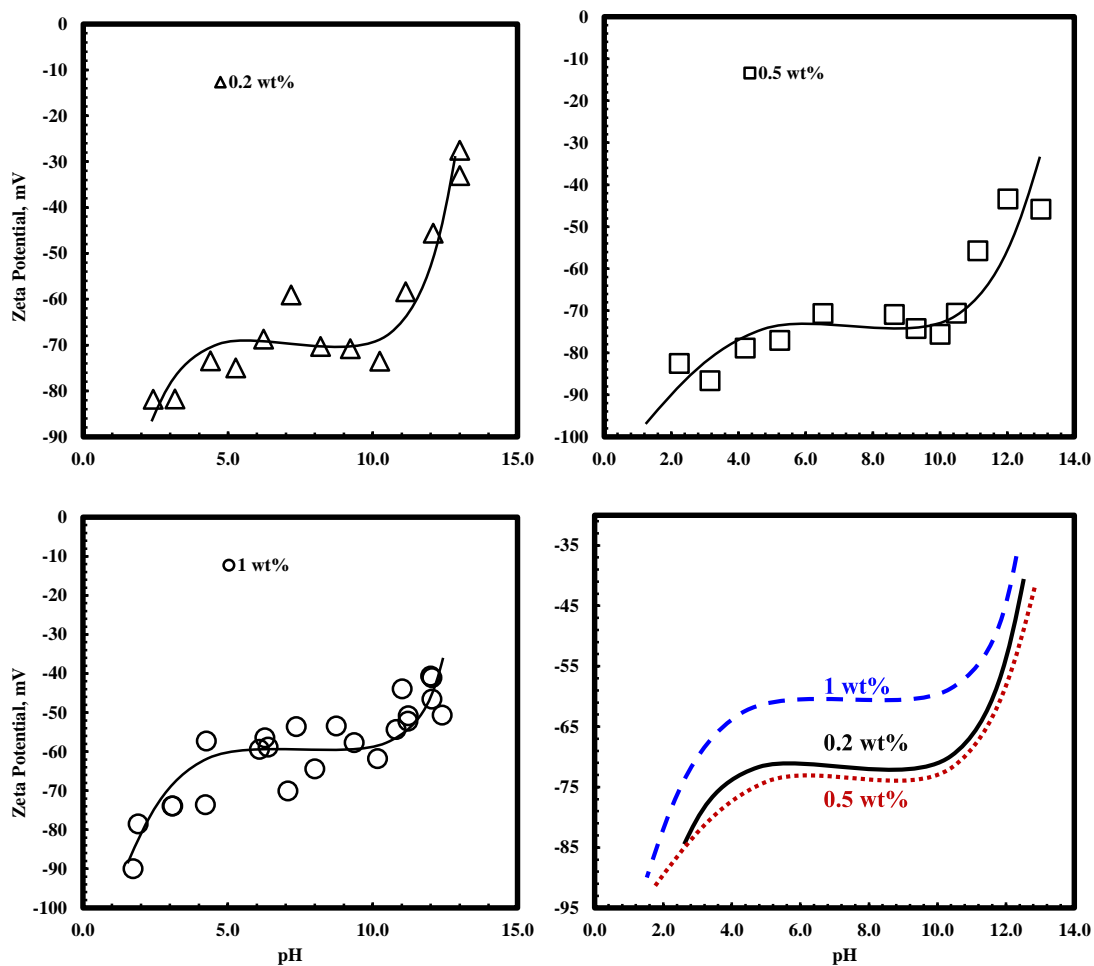
Fig. 20— Zeta potential of manganese tetraoxide-based solutions with dispersant C31 at 0.2, 0.5, and 1 wt%, pH of 2-12.
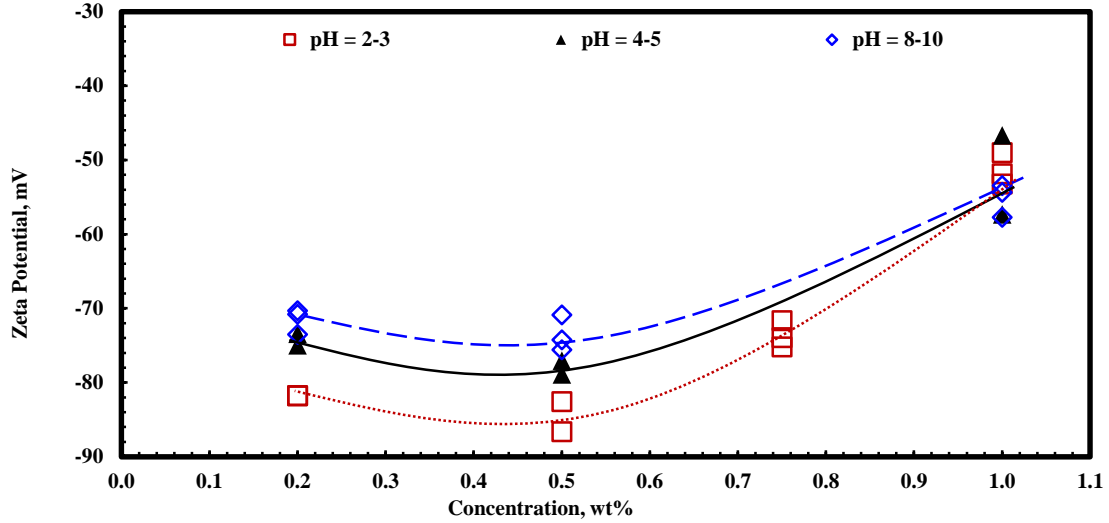
Fig. 21— Zeta potential of manganese tetraoxide-based solutions with dispersant C31 at 77°F, pH = 2-10.

Fig. 22 shows the zeta potential measurements as a function of concentration at 77 and 122°F with dispersant C31 solutions. The minimum zeta potential values were measured at 0.5 wt% dispersant concentration. Thus, the optimum concentration for the minimum zeta potential and maximum dispersion was nearly 0.5 wt%. The absolute values of zeta potential increased with temperature (Fig. 22). At both 77 and 120°F, the zeta potential values were (-85 mV) and (-90 mV) at 0.5 wt% of dispersant, respectively, which were higher in magnitude than manganese tetraoxide dispersant-free solutions. Glaze and Frankel (2000) reported that spherical particle temperature is a strong function of dispersion.
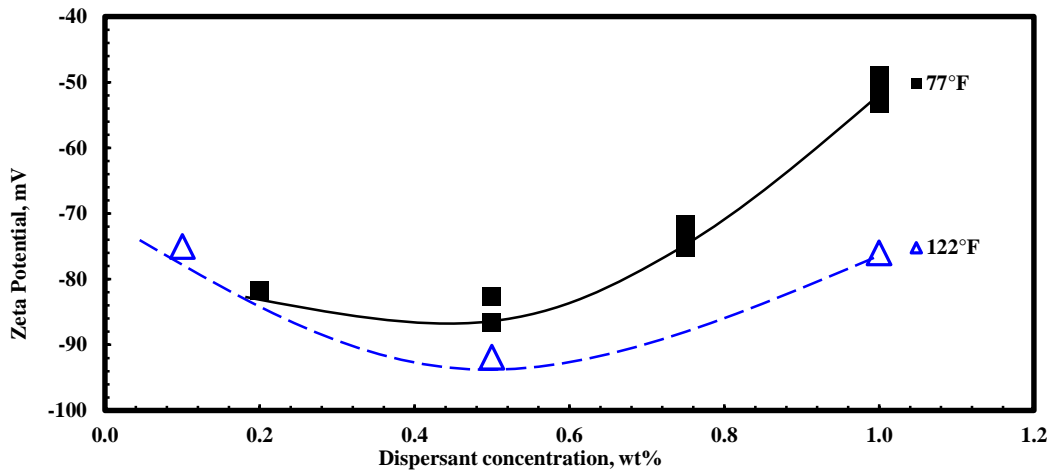
Fig. 22— Zeta potential of manganese tetraoxide-based solutions with dispersant C31 at 77 and 122°F, pH = 2-4.

Fig. 23 shows the zeta potential measurements for dispersant B17 at concentrations of 0.5 and 1 wt%. Lower zeta potential absolute values were observed at lower pH values with a stable region at higher pH values. Stability regions for dispersants B17 and C31 were at pH values of 6-11 and 4-10, respectively (Figs. 20 and 23). Minimum values of zeta potential (i.e. maximum absolute values) were associated with 0.5 wt% dispersant concentration for both B17 and C31 (Figs. 21 and 23).
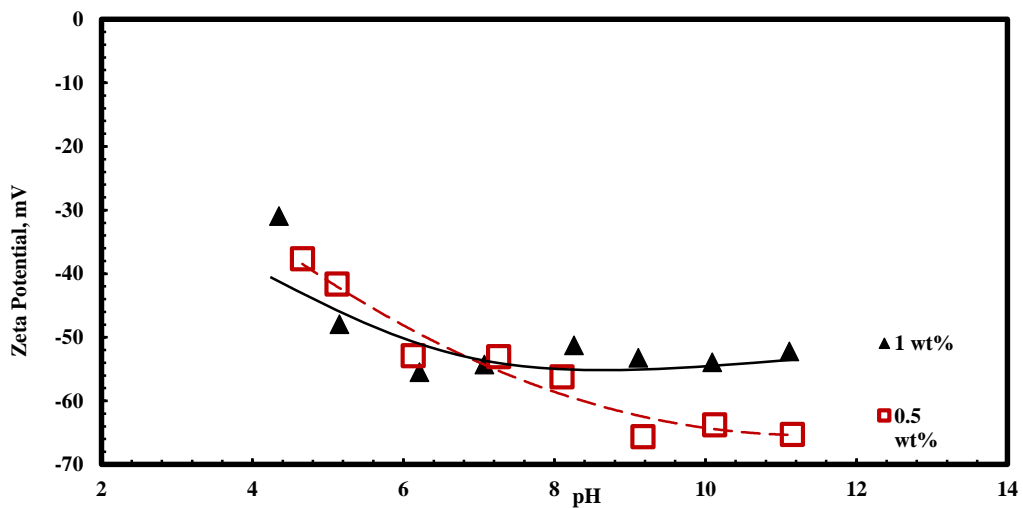
Fig. 23— Zeta potential of manganese tetraoxide-based solutions with dispersant B17 at 0.5 and 1 wt%.

Fig. 24 compares the zeta potential values of dispersants B18 and C31 as a function of the dispersant concentration at 77°F and pH range of 8-10. The minimum value of zeta potential (i.e. maximum absolute value) was observed at nearly 0.5 wt% for both dispersants. The absolute zeta potential values of dispersant B18 were higher than those of C31, which indicated that higher dispersion could be obtained with dispersant B18 rather than C31. The particle settling time results showed that longer particle settling could be achieved with dispersant B18 rather than C31. The main active components in dispersant B18 and C31 were based on acrylic copolymer and dodecyl benzene sulfonic acid, respectively. Dispersant B17 was an anionic lignosulfonate.
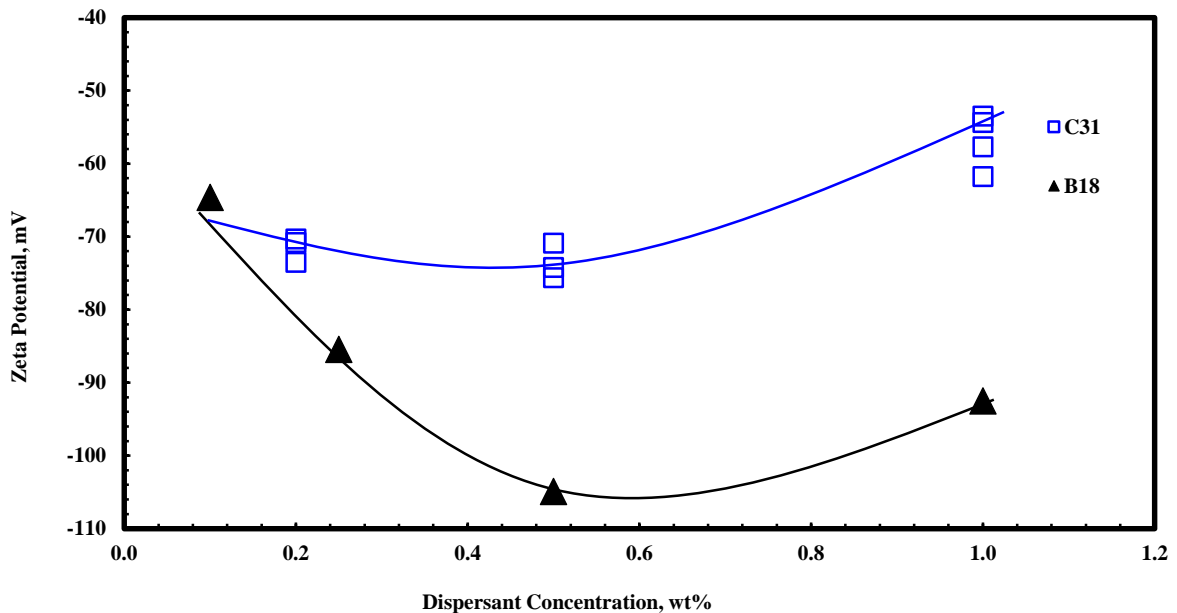
Fig. 24— Zeta potential of manganese tetraoxide-based solutions with dispersants B18 and C31 at 77°F. The pH values were 8-10.

Transparency and particle settling experiments were conducted for three dispersants from group B (i.e., B15, B16, and B25) at different dispersant concentrations (**Fig. 25**). The results indicated that the dispersion of manganese tetraoxide particles decreased with increasing dispersant concentration. The results show that the optimum dispersant concentration is below 1 wt%. Fig. 25 showed that solution transparency increased with time at dispersant concentrations below 1 wt%. Dispersants B15 and B16 were anionic lignosulfonates, while dispersant C25 was a nonionic lignosulfonate.
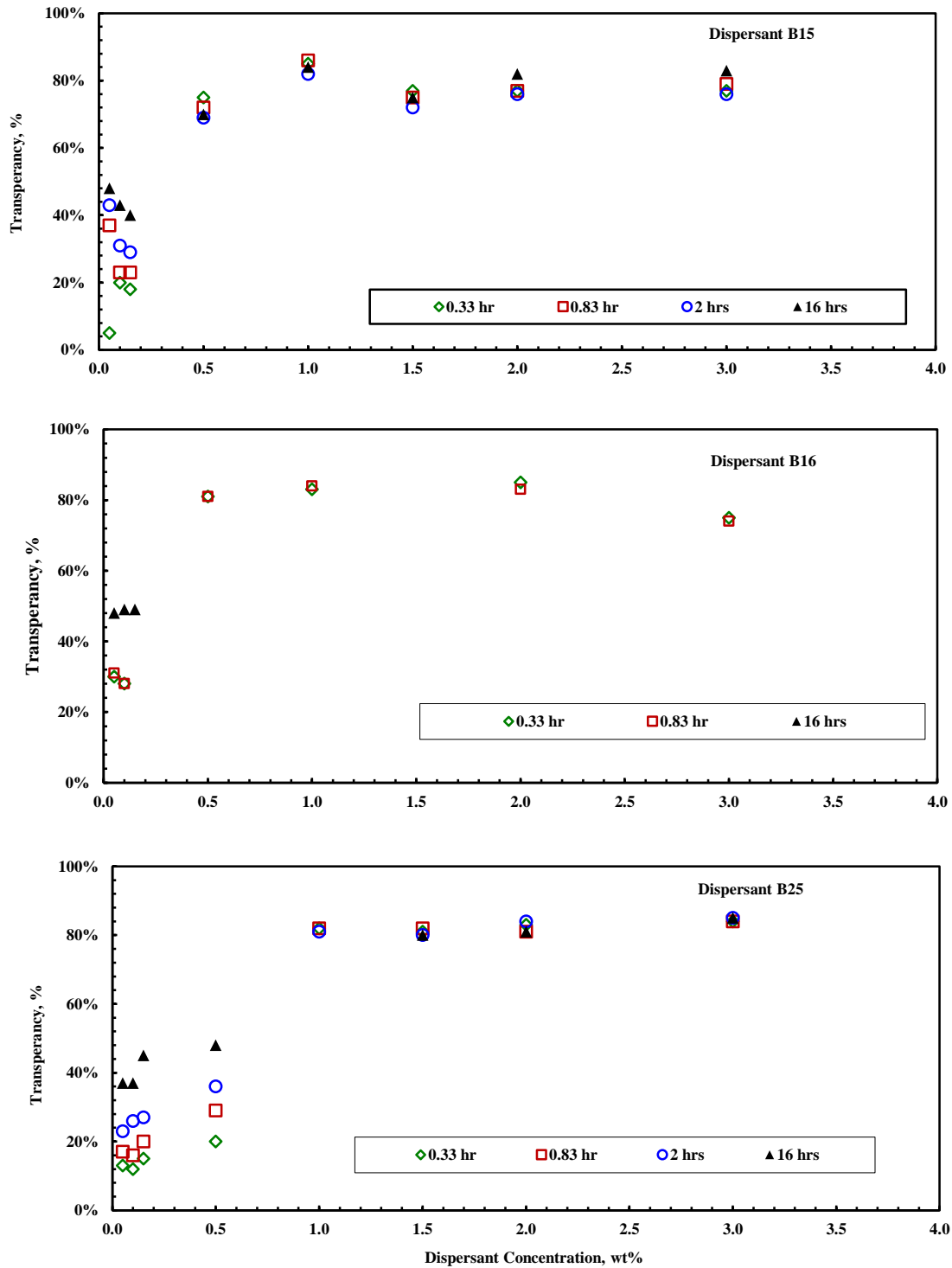
Fig. 25—Solution transparency of manganese tetraoxide-based fluids with dispersants B15, B16, and B25 at settling times of 0.33 to 16 hrs.

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Effect of NaCl on Particle Settling

Dispersant solutions with NaCl had varying interactions with compatibility and particle settling. Dispersants with the longest particle settling at 0.5 wt% dispersant concentration in the presence of sodium chloride were dispersants A02, A09, A11, A13, A14, B15, C25, and C30. They were mainly phosphate-based alcohols/ethers/esters, copolymers, and lignosulfonates.

Dispersants A01, A13, A14, B15, B18, C31, C62, C68, and C77 were compatible with 5 wt% NaCl and 0.5 wt% dispersant concentration. Dispersants A02, A05, A11, C25, C27, C34, C43, and C50 were found compatible with 12 wt% NaCl with little foam generation in some dispersant solutions. Dispersants A05, A09, B17, C30, C33, C35, and C73 solutions precipitated at least with 12 wt% NaCl. Dispersant solution (A06) precipitated in the presence of NaCl, while dispersant C31 solution did not precipitate (both dispersants were based on benzene sulfonic acid, and A06 contains sodium salt). A similar observation was noticed with dispersants A09 and A011, while the ingredients of both dispersants are based on phenol ethoxylated phosphate esters with a varying number of ethylene oxide monomer units. Lignosulfonate dispersants (i.e., B15, B17 and B24) were found compatible at 5 wt% NaCl but precipitated at 12 wt% NaCl.

The settling times of manganese tetraoxide particles were lower, higher, or did not change for several dispersants solutions before and after the addition of sodium chloride. The particle settling times were lowered for dispersants A01, A05, A06, and A09 from 24 hours to less than 4 hours when NaCl was added (**Fig. 26** and **27**). The ingredients of these dispersants were based on acrylate/maleic sulphonated copolymer, ethoxylated sulfated polymer, benzene sulfonic acid, and ethoxylated phosphate ester, respectively. However, the particle settling times were increased for dispersants B15, C25, C30, and C36 in the presence of NaCl (Fig. 26 and 27). Dispersants B15, C25, C30, and C36 are mainly based on sulfonated polymers (e.g. lignosulfonates). The remaining dispersant solutions showed similar particle settling times before and after adding NaCl such as other phosphate-based dispersants (e.g. A02 and A11). The dispersant solutions with the highest particle settling times in the presence of NaCl were dispersants A02, A11, A13, A14, B15, C25, and C30 (Fig. 26 and 27). The ingredients of these dispersants were based on ether phosphate, phosphoric acid/phosphate ester ethoxylated alcohols, maleic acid copolymers, and lignosulfonates.
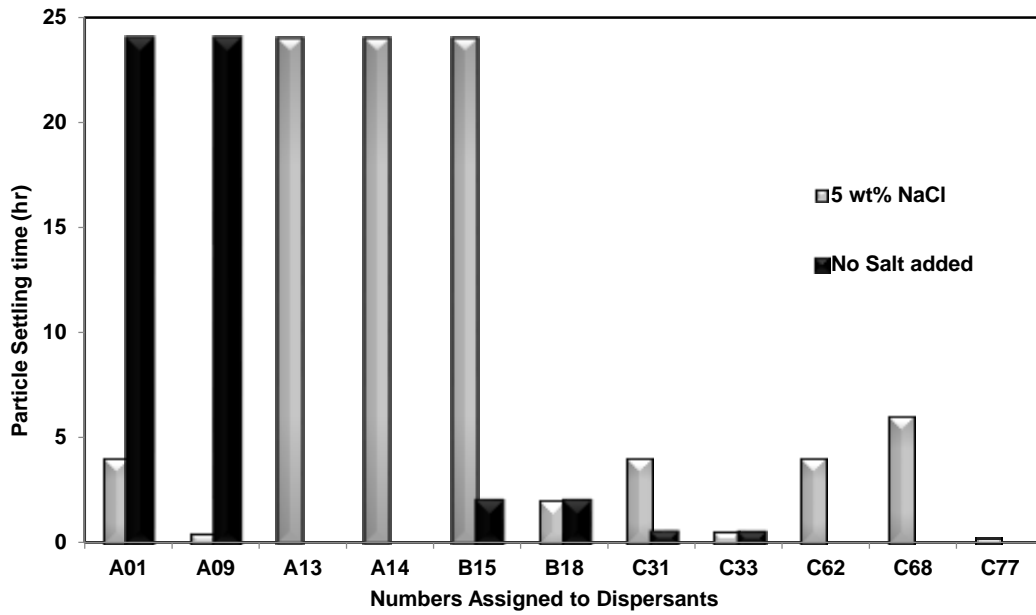
Fig. 26— Manganese tetraoxide particle settling times in 0.5 and 1.6 wt% dispersant solutions, 5 wt% NaCl, pH = 9-10. More details about the dispersants are given in Appendix A.
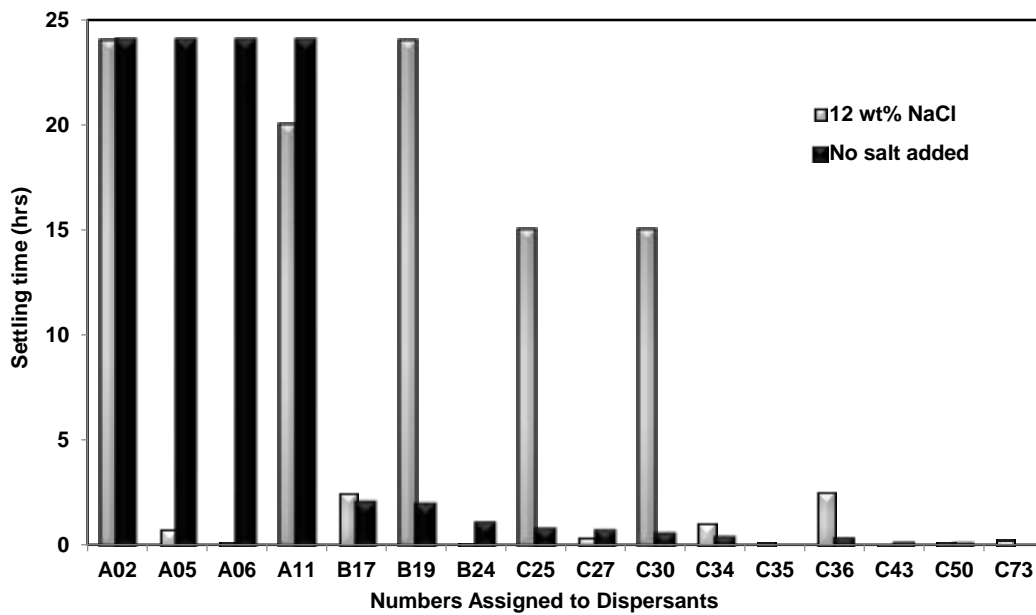
Fig. 27— Manganese tetraoxide particle settling times in 0.5 and 1.6 wt% dispersant solutions, 12 wt% NaCl, pH = 9-10. More details about the dispersants are given in Appendix A.

Sagging Tendency of Mn$_3$O$_4$ Water-based Drilling Fluids

Sag is an indication of solid particle settling in drilling fluids. The sag testing results of water-based drilling fluids weighted with manganese tetraoxide particles are summarized in **Table 8**.

The sag factor was increased with drilling fluid (17.5 to 20 lbm/gal). The presence of clay and rock salt contaminations increased the sagging tendency of drilling fluids (Table 8). Drilling fluids with dispersants added (e.g. A01 and B15) lowered the sag factor from 0.52-0.53 to 0.505 in non-contaminated drilling fluids before and after heat aging at 300-400°F. Drilling fluids with higher density (20 lbm/gal) were heat aged at 450°F; then, a decrease in sag factor from 0.55 to 0.52 was noted when dispersants were added (Table 8). In clay and rock salt contaminated drilling fluids, the sag factor was reduced to nearly 0.52 when dispersants A01 and B15 were added (Table 8). Dynamic sag values were also calculated for 13.7 lbm/gal drilling fluids at 120°F using a Fan 35 viscometer and sag shoe. The dynamic sag factor was reduced from 1.5 to 0.35 lbm/gal when dispersant A01 was used.

Filter Cake Micro Structure

Environmental scanning electron microscope (ESEM) images were taken for the Mn$_3$O$_4$-based filter cake generated with 17.5 lbm/gal water-based drilling fluid contaminated with clay. **Fig. 28a** represents the filter cake when no dispersant was added, while **Fig. 28b** shows the filter cake in the presence of dispersant A01. Spherical particles were manganese tetraoxide with an average diameter of 1-2 µm. Two main observations can be drawn from the images: (1) the cross sectional microstructure in Fig. 28b showed more uniformity in particle distribution. (2) the filter cake image in Fig. 28a showed Mn$_3$O$_4$ particles aggregated forming round-like structures with cavities in between, while Fig. 28b shows Mn$_3$O$_4$ particles arranged with no cavities. This indicated that the addition of dispersant A01 reduced aggloromations and stickiness of particles. The spaces between particles represent adsorbed polymers present in the filter cake.

Drilling fluid density, lbm/gal	Dispersant	Contamination	Heat aging/rolling	Sag factor
17.5	---	---	16 hours @400°F	0.523
20	---	---	16 hours @400°F	0.53
20	---	---	16 hours @450°F	0.552
17.5	---	---	16 hours @400°F	0.523
17.5	---	Clay	16 hours @400°F	0.53
17.5	---	Clay, rock salt	16 hours @400°F	0.553
17.5	---	Rock salt	16 hours @400°F	0.542
17.5	---	---	16 hours @400°F	0.523
17.5	A01	---	---	0.505
17.5	B15	---	---	0.51
17.5	B15	---	16 hours @325°F	0.506
17.5	C25	---	16 hours @325°F	0.504
17.5	A01	---	16 hours @400°F	0.512
17.5	B15	---	16 hours @400°F	0.51
17.5	C25	---	16 hours @400°F	0.508
17.5	C25	---	16 hours @300°F	0.502
17.5	B15	---	16 hours @300°F	0.506
20	---	---	16 hours @400°F	0.53
20	A01	---	16 hours @400°F	0.515
20	B15	---	16 hours @400°F	0.512
20	C25	---	16 hours @400°F	0.52
20	---	---	16 hours @450°F	0.552
20	A01	---	16 hours @450°F	0.52
20	B15	---	16 hours @450°F	0.518
20	C25	---	16 hours @450°F	0.532
17.5	---	Clay	16 hours @400°F	0.53
17.5	A01	Clay	16 hours @400°F	0.521
17.5	B15	Clay	16 hours @400°F	0.523
17.5	---	Clay, rock salt	16 hours @400°F	0.553
17.5	A01	Clay, rock salt	16 hours @400°F	0.513
17.5	B15	Clay, rock salt	16 hours @400°F	0.51
17.5	---	Rock salt	16 hours @400°F	0.542
17.5	A01	Rock salt	16 hours @400°F	0.523
17.5	B15	Rock salt	16 hours @400°F	0.52

Table 8—Sag factor of manganese tetraoxide water-based drilling fluids
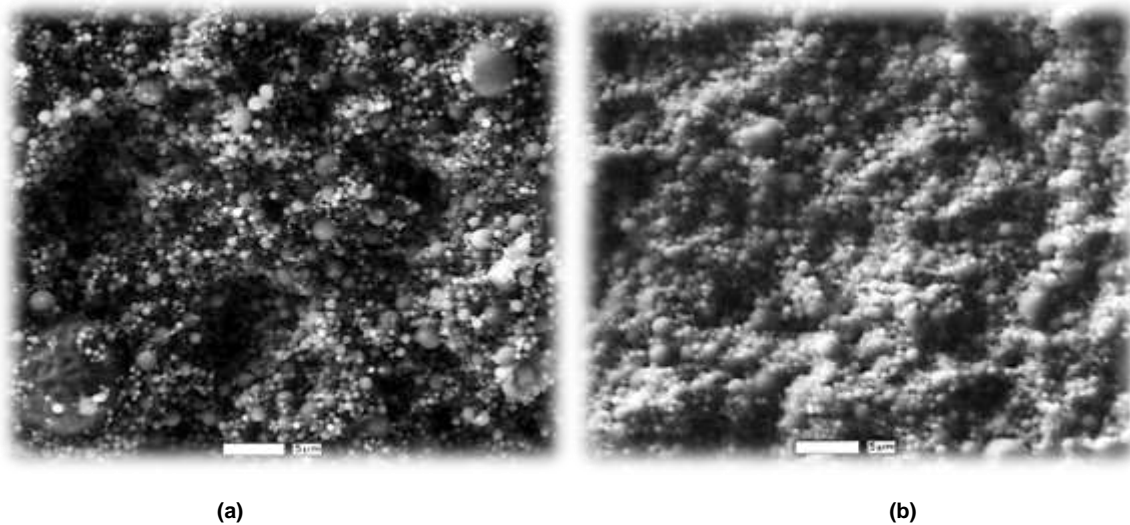
Fig. 28—SEM images of filter cake created by 17.5 lbm/gal Mn$_3$O$_4$ water-based drilling fluids in the presence of clay as containment: a) No dispersant added, b) dispersant A01 was added. Magnification 2000X.

Thermal stability of Dispersants A01, B15, and C25

Fig. 8 shows the thermal stability for three selected dispersants: A01, B15, and C25. These dispersants are based on sulphonated acrylate copolymer, calcium lignosulfonate, and anionic lignosulfonate, respectively. The settling time results showed 24, 2, and 0.75 hrs, respectively. From 180 to 300°F, there was a weight loss of 60% for dispersant A01. The solid content of this dispersant was 40% as reported by the vendor. Therefore, the 60% reduction in the weight at this temperature range was because of the evaporation of the aqueous phase/solvent. Between 300 and 500°F, the three dispersants showed a region of thermal stability with a slight reduction in A01. These results are important as it proves the applicability of using these dispersants for HP/HT drilling without the risk of any dispersant decomposing. The three dispersants are then decomposed at extremely harsh conditions. The weight losses were 20, 32, and 46% for dispersants A01, B15, and C25, respectively, at 500 to 900°F.

Rheological Behavior of Mn$_3$O$_4$ Water-based drilling fluids.

The rheological behavior expressed in shear stress and shear rate was examined for high-density manganese tetraoxide water-based drilling fluids (17.5 and 20

lbm/gal). The rheology was measured before/after the drilling fluids were subjected to heat aging at 400°F and 16 hrs.

Fig. 29 and Appendix D shows the rheology measurements for the non-contaminated drilling fluids (17.5 and 20 lbm/gal). Dispersants A01 and B15 were added at 5 and 8 g/l. The results show a slight reduction in the shear stress values when both dispersants were used before/after heat aging at 400°F. The rheology of the drilling fluids (17.5 and 20 lbm/gal) was higher in the presence of clay and rock salt contaminations in some of the tests (**Fig. 30** and Appendix D). The addition of dispersants (e.g., A01, B15, or C25) to the contaminated drilling fluids improved the rheological behavior before/after heat aging in most examined cases (Appendix D and **Figs. 31** and **32**).
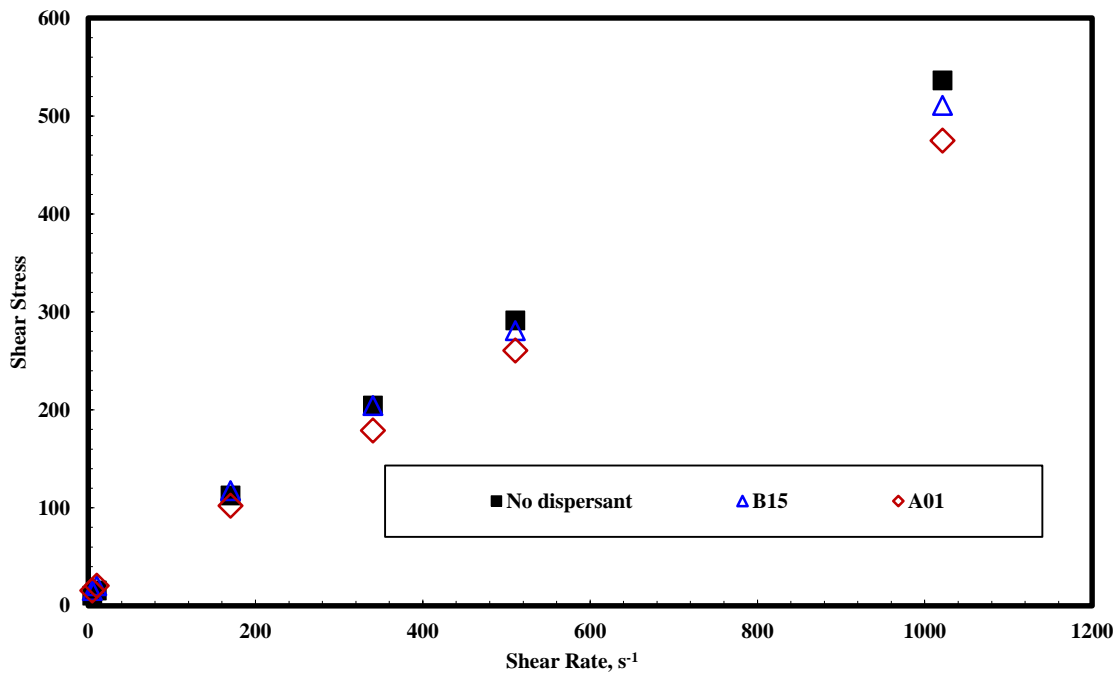
Fig. 29—Shear stresses for 20lb/gal non-contaminated Mn$_3$O$_4$ water-based drilling fluids after heat aging at 400°F for 16 hrs. Dispersant concentration was 8 g/l water.
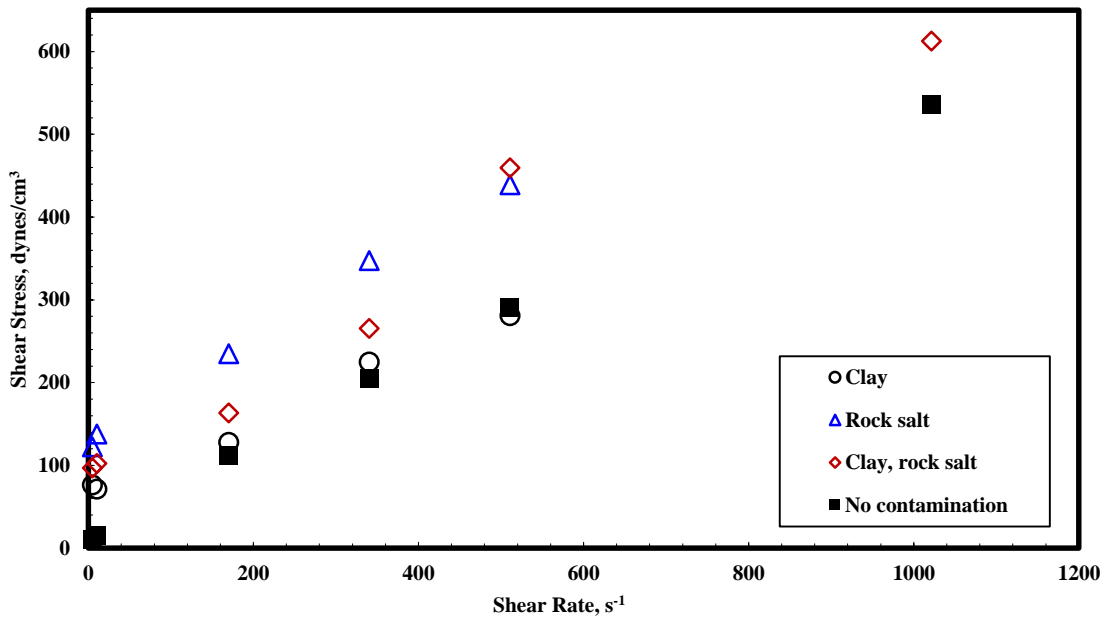
Fig. 30—Shear stresses for contaminated 20 lbm/gal Mn_3O_4 water-based drilling fluids after heat aging at 400°F for 16 hrs.
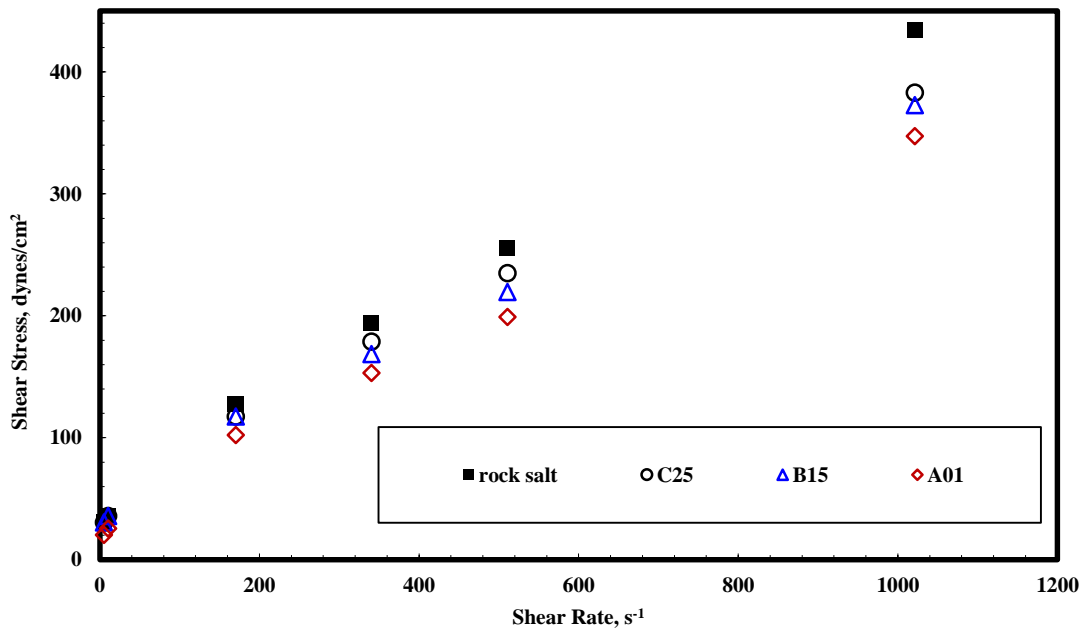
Fig. 31—Shear stresses for rock salt contaminated 17.5 lbm/gal Mn_3O_4 water-based drilling fluids before heat aging. Dispersant concentration was 8 g/l water.
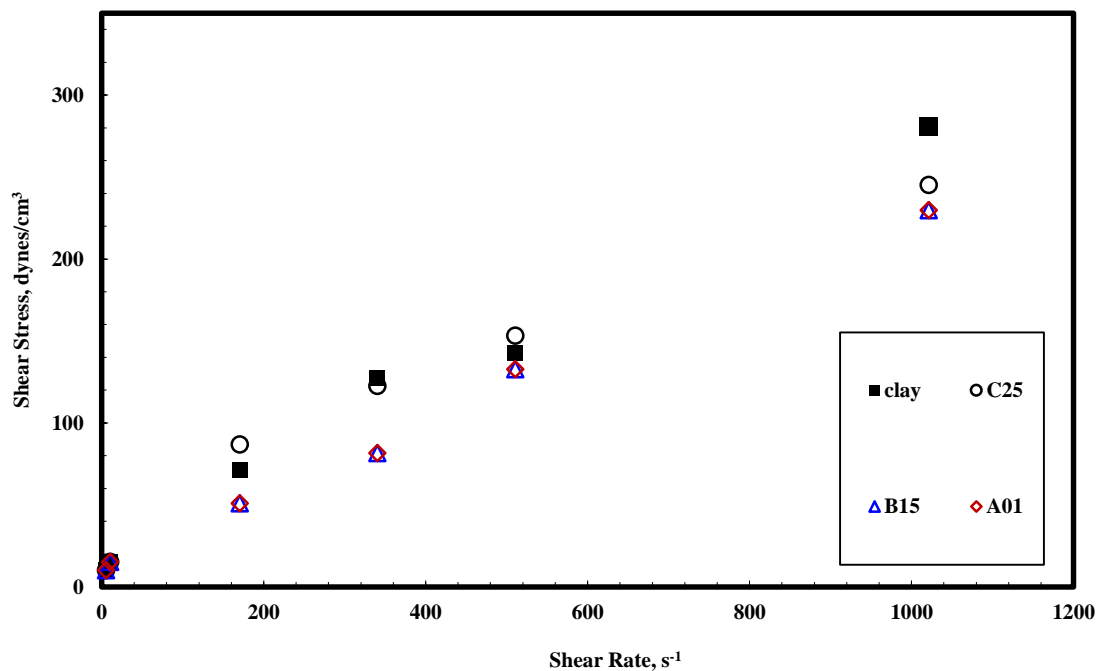
Fig. 32—Shear stresses for clay contaminated 17.5 lbm/gal Mn₃O₄ water-based drilling fluids after heat aging at 400°F for 16 hrs. Dispersant concentration was 8 g/l water.

Conclusions

The dispersion of manganese tetraoxide particles in high density water-based drilling fluids (17.5 and 20 lbm/gal) has been investigated. More than 20 dispersants showed high potential to disperse manganese tetraoxide particles in water-based drilling fluids. Groups A and B dispersants showed the longest particle settling times. Zeta potential measurements showed a region of dispersion stability at a pH of 6 to 11 for lignosulfonate and sulfonic acid-based dispersants (i.e. B17 and C31). Zeta potential and particle settling tests indicated that dispersion with acrylic copolymer (B18) is more effective than that of dodecyl benzene sulfonic acid dispersant (C31). Zeta potential values increased with temperature in the C31 dispersant solution (i.e. 77 and 120°F). Zeta potential and transparency experiments showed that the optimum dispersant concentration was below 1 wt% and nearly 0.5 wt%. TGA analysis showed that the dispersants A01, B15, and C25 were thermally stable between 300 and 500°F. SEM images of filter cake showed that the aggregation of particles was reduced when dispersant A01 was used in clay contaminated

drilling fluid. In most cases, the rheological behavior of the contaminated and non-contaminated drilling fluids (17.5 and 20 lbm/gal) before/after heat aging at 400°F was improved in the presence of dispersants (e.g. A01 and B15). Dispersant solutions with NaCl had varying interactions with compatibility and particle settling. The settling times of manganese tetraoxide particles were lower, higher, or did not change for several dispersant solutions. The sagging tendency of contaminated and non-contaminated drilling fluids was improved in the presence of dispersants. For example, the sag factor was reduced from 0.55 to 0.51 in clay and rock salt contaminated drilling fluids when dispersant A01 was used. Based on the experimental results, the following conclusions can be drawn:

1. Dispersants A1-A14 and B14-B25 showed the highest potential to disperse Mn_3O_4 water-based drilling fluids with chemical ingredients such as:
   a. Acrylic/maleic sulfonated copolymers,
   b. Phenol ethoxylated fatty alcohols with phosphate or sulfate functional groups,
   c. Anionic calcium or iron lignosulfonates,
   d. Phosphate/sulfate-based glycols and ethers.
2. Particle settling and zeta potential measurements are important initial steps to compare the effectiveness of dispersants.
3. The effectiveness of anionic lignosulfonates can be higher than nonionic lignosulfonates.
4. The presence of monovalent salts (i.e. NaCl) may increase or decrease the particle settling velocities in the presence of dispersants.

CHAPTER IV

DISPERSION OF MANGANESE TETRAOXIDE OIL-BASED

DRILLING FLUIDS[*]

Overview

The dispersion of manganese tetraoxide particles in high oil-based drilling fluids (13.8 to 20 lbm/gal), suitable for deep drilling, has been studied. The settling of manganese tetraoxide particles in drilling fluids would cause operational problems during drilling. The rheological behavior and sagging tendency can be adversely affected. Dispersants are used in drilling fluids to prevent solid flocculation. A thorough investigation on appropriate dispersants for Mn_3O_4 oil–based fluids was conducted.

The dispersion of high density oil-based drilling fluids up to 20 lbm/gal that is based on Mn_3O_4 particles as a weighting material in the presence of contaminations was investigated. The objectives were to: (i) examine more than 50 commercially potential chemicals as dispersants, (ii) conduct particle settling and compatibility testing, (iii) compare the rheological behavior/sagging tendency of the drilling fluid and examine the effect of contaminations (iv) investigate optimum dispersant concentrations. The dispersants examined are listed in in Appendix A and, thus, would help the reader to identify proper/improper dispersants based on the results of this study.

The dispersion of Mn_3O_4 particles in aqueous solutions was evaluated through visual transparency and particle settling. More than 400 companies globally were contacted, and over 60 dispersants were obtained. Visual compatibility observations with mineral oil such precipitation, phase separation, and foam generation were recorded. A Mastersizer 2000 was used to obtain the particle size distribution and specific surface area of Mn_3O_4 particles. Shear

stress, viscosity, and sagging tendency were evaluated using a Fan 35A viscometer and density variation measurements. The drilling fluids were subjected to heat aging up to 400°F.

Appendix B and Table 14 summarize the dispersants' chemical ingredients, compatibility with oil, and particle settling results in oil solutions. The provided information and results would guide the drilling engineer to select appropriate dispersants. Several dispersants was tested but only a few showed high dispersion capacity of manganese tetraoxide particles. Transparency testing showed that the optimum concentration for dispersants were nearly between 0.2 and 2 wt% based on dispersant S9. Increasing dispersant S9 concentration from 0.25 to 1 wt% lowered the viscosity of the 13.8 lbm/gal drilling fluids. The sagging tendency was lowered with dispersed drilling fluids (16.3 and 20 lbm/gal) and in the presence of clay and cement contaminations with dispersants S1, S2, S3, and S5 in most of the cases (Appendix C). The shear stresses for 13.8, 16.3, 17.5, and 20 lbm/gal drilling fluids were reduced in the presence of dispersants (e.g., S1, S2, S3, S5, S9) at shear rates up to 100 s^{-1}. The use of dispersant S5 for ilmenite and API barite oil-based drilling fluids showed a higher sagging tendency than that of manganese tetraoxide oil-based drilling fluids.

Experimental Studies

The compositions of oil-based drilling fluids used in this study are shown in **Tables 9** to **13** . The oil phase was mineral oil, and the weighting material was manganese tetraoxide (Mn_3O_4). The drilling fluid densities were 15 to 20 lbm/gal. The Mn_3O_4 particles (SG of 4.8) were spherical and have an average particle size of 1 μm in diameter. Drilling fluid additives and contaminants such as cement (Portland cement with 1-5 wt% quartz) and clay were obtained from a local service company. The clay contamination was a mixture of clays and fines (e.g., quartz; cristobalite, illite, mixed layer clay; kaolinite, and chlorite).

Materials	Unit	Amount
Mineral Oil— 0.80 SG @15°C, 2.1 cp @ 40°C	cm^3	220
Organically modified hectorite	g	3
Organically modified clay	g	2
Lime	g	20
HT Primary emulsifier	g	20
HT Secondary emulsifier	g	16.5
Deionized water	cm^3	22.75
Calcium chloride	g	7.3
Organophilic lignite	g	12
HT Secondary emulsifier	g	1.5
Manganese tetraoxide	g	508
Dispersant	g	1.75
* Cement or clay contamination were added at nearly 20 g		

Table 9—Composition of Mn_3O_4 oil-based drilling fluid (16.3 lbm/gal).

Materials	Unit	Amount
Mineral Oil— 0.80 SG @15°C, 2.1 cp @ 40°C	cm^3	195
Viscosifier — organically modified hectorite	g	3
Viscosifier — organically modified clay	g	2
Lime	g	20
HT Primary emulsifier	g	20
HT Secondary emulsifier	g	16.5
Deionized water	cm^3	19.5
Calcium chloride	g	6.4
HT Filtration control - organophilic lignite	g	12
HT Secondary emulsifier	g	1.5
Manganese tetraoxide	g	780
Dispersant	g	3.1
*Cement or clay contamination were added at nearly 27 g		

Table 10—Composition of Mn_3O_4 oil-based drilling fluid (20 lbm/gal).

Materials	Unit	Amount
Mineral oil	cm^3	313.3
Amine-based wetting agent	g	18
Fatty acid-based emulsifier	g	14
Organophilic clay	g	1.6
Lime	g	16
Lignite-based fluid loss agent	g	16.8
Polymeric fluid loss agent	cm^3	7.2
Calcium chloride	g	31
Water	g	104.5
Manganese tetraoxide	g	1106
Dispersant	g	2.4

Table 11—Composition of Mn$_3$O$_4$ oil-based drilling fluids (17.5 lbm/gal).

Materials	Unit	Amount
Mineral oil	cm^3	242.5
Viscosifier — organically modified hectorite	g	3
Viscosifier — organically modified clay	g	2
Lime	g	20
HT Filtration control - organophilic lignite	g	20
HT Secondary emulsifier	cm^3	16.5
Calcium chloride	g	7.9
Water	g	24.5
Manganese tetraoxide	g	373.5
Dispersant	g	1.7 and 6.8

Table 12—Composition of Mn$_3$O$_4$ oil-based drilling fluids (13.8 lbm/gal).

Materials	Unit	Amount	Amount	Amount
Mineral oil	cm^3	313.3	313.3	313.3
Amine-based wetting agent	g	18	16	14
Fatty acid-based emulsifier	g	14	14	14
Organophilic clay	g	1.6	1.6	3
Lime	g	16	16	16
Lignite-based fluid loss agent	g	16.8	16.8	16.8
Polymeric fluid loss agent	cm^3	7.2	7.2	7.2
Dispersant	g	2.4	2.4	2.4
$CaCl_2$	g	31	31	31
Water	g	104.5	104.5	104.5
Mn_3O_4 (weighting agent)	g	1106	-	-
$FeTiO_3$ (weighting agent)	g	-	1186	-
$BaSO_4$ (weighting agent)	g	-	-	1277

Table 13—Oil-based drilling fluids composition with Mn_3O_4, $FeTiO_3$ or $BaSO_4$ as weighting agents (17.5 lbm/gal).

Dispersant concentrations in the drilling fluids were between 0.15 and 1 wt% active ingredients. Dispersants were obtained from several manufacturers and companies worldwide, including: Tetra Technologies, AkzoNobel, Oil Chem Technologies, Flotec, Clariant, Sasol, Trican, BASF, Cargill, Halliburton, Rhodia, Borregaard, Expo Chemical Company, Georgia-Pacific, Stepan, Huntsman Corporation, Ciba Specialty Chemicals, Omnova Solutions, Asahi Kasei Corporation, International Specialty Products, and several other chemical manufacturers. More than 400 companies have been contacted to provide dispersants. The targeted dispersants were non-toxic to aquatic organisms, anionic or non-ionic, and may have the affinity to absorb on the surface of Mn_3O_4 particles. Appendix A shows a list of dispersants, their chemical ingredients, compatibility information, and hazard rating. Compatibility tests were conducted by mixing 1.6 wt% dispersant with mineral oil at 80 rpm for 20 minutes and then allowing the mixture to remain still for 2 hours. Visual observations of compatibility, foam, precipitation, and phase separation were recorded.

Transparency testing and particle size analysis were conducted using visual observation to evaluate particle dispersion and settling velocities. Samples of the drilling fluids were diluted with deionized water until the solution became transparent. Dispersant was then added at concentration 0.1 wt%. Finally, the fluids were analyzed using a Spectrek PC-2200 laser particle analyzer. Transparency measures of dispersant solutions in the presence of Mn_3O_4 particles were studied as a function of concentration and settling time. The following procedure was to prepare 10 g of dispersant solution in a 10 cm^3 graduated cylinder. Then, 2-2.5 g Mn_3O_4 particles were added to the dispersant solution and mixed thoroughly until the solid particles were dispersed in the solution. The liquid level was fixed at 10 cm^3. Volumetric readings of changes in solution transparency due to particle settling were taken as a function of time. Dispersion of solid particles were higher at a lower transparency (Fig. 2). The solution transparency indication was calculated using Eq. 2.

Compatibility tests were conducted by mixing 1.6 wt% dispersant with mineral oil at 80 rpm for 20 minutes and then allowing the mixture to remain still for 2 hours. Visual observations of compatibility, foam, precipitation, and phase separation were recorded.

A Fann 35A viscometer was used for rheological measurements at 120°F. Static heat aging of the drilling fluid samples was done in 500-ml stainless steel aging cells for 16 hours at 400°F. After heat aging, the drilling fluids were mixed for 15 minutes before taking the rheological measurements. The dynamic sag tendency of the drilling fluids was determined using a Fan 35A viscometer and a sag shoe. Dynamic sag values were calculated from the difference in drilling fluid densities before and after 30 minutes of shearing. A 10 cm^3 syringe and a balance were used in density measurements for determining the dynamic sag values in lbm/gal. Static sag was measured after heat aging was applied for 16 hours at 400°F. The aging cells were placed at an angle of 45°. A 10 cm^3 syringe and a balance were used in density measurements, and the sag value was calculated using Eq. 1.

Dispersant Compatibility and Comparison with Water-Based Fluids

The dispersant compatibility in mineral oil solutions and hazard rating information are summarized in Appendix A. Dispersants S1-S32 are compatible with mineral oil showing no precipitations of phase separations. Dispersants

N33-N69 either precipitated or phase separated with mineral oil. Dispersant N60 (based on sulphonated acrylate copolymer) was compatible with the water-based system and showed excellent dispersion capabilities (i.e. Mn_3O_4 particle settling time was 24 hours at 75% transparency). However, it phase separated with mineral oil and showed very low Mn_3O_4 particle settling time of dispersion of manganese tetraoxide particles of nearly 0.01 hours at 75% transparency (**Fig. 33**). A lignosulphonate-based dispersant (N47) was not compatible with mineral oil but was soluble and provided higher particle dispersion in aqueous solutions (Fig. 33). The manganese tetraoxide particle settling times at 75% transparency were 0.03 and 0.73 hours for oil- and aqueous-based solutions, respectively (Dispersant N47). Dispersant N50 was based on a mixture of high molecular mass saturated fatty alcohols, mainly cetyl alcohol and stearyl alcohol with 28 ethylene oxide residues in the alcohol chain. It precipitated with mineral oil and showed poor dispersion with a particle settling time of 0.02 hours at 75% transparency (Fig. 33). Dispersant S2 was compatible with mineral oil and showed excellent dispersion (particle settling of 2.75 hours at 75% transparency). Dispersant S2 was based on alkoxylated fatty acids, and polyethylene glycol ether acetic acid (Fig. 33). Detailed compatibility and dispersants information is summarized in Appendix A.

Fig. 33—Dispersants (from left to right) N60 with oil, N60 with water, N47 with oil, N47 with water, N50 with oil, S2 with oil. Dispersant concentration was 1.6 wt%. Dispersants information in Appendix A.

Dispersant Concentration and Particle Settling of Mn₃O₄ Oil-Based Fluids

The optimum range of dispersant concentration was investigated through a transparency testing of Mn_3O_4/mineral oil solutions at varying dispersant concentration and particle settling times. **Fig. 34** shows that the settling of manganese tetraoxide particles increases with time and dispersant concentration up to 3 wt%. At dispersant concentrations above 3 wt%, particle settling increases with time. Fig. 34 indicated that the optimum dispersant concentration is between 0.2 and 2 wt%. Dispersant S9 was used (based on benzene sulfonic acid). Rheological measurements were performed for 15 lbm/gal oil-based drilling fluids at 0, 0.25, and 1 wt% dispersant concentration. Drilling fluids were first aged at 400°F before measurements were taken. Shear stress was lower with drilling fluids dispersed with 1 wt% rather than with 0.25 wt% dispersant concentrations, especially at a high shear rate. The highest shear stresses were obtained when no dispersant was used (**Fig. 35**).

The dispersion of Mn_3O_4 particles in oil solutions was evaluated from settling times of Mn_3O_4 particles. Particle settling times were between 0.01 and 24 hours for dispersants S1 to S32 (

Table 14). The particle settling times of the remaining dispersants (i.e. N33-N69) were between 0.003 to 0.5 hrs. The chemical ingredients of the dispersant with the highest settling time, S1, include fatty alcohol with 5 ethylene oxide units, polyethylene glycol ether carboxylic acid, and the phosphate functional group. The particle settling of dispersant S2 was 2.75 hours at 75% transparency. It was based on fatty acids with alkoxy groups such as ethylene/propylene oxides, and polyethylene glycol ether acetic acid. Dispersants S3 to S7 were based on ethoxylated fatty alcohols with particle settling times between 0.4 and 0.85 hrs. Dispersant S2 was an anionic based on alkoxylated C12-C14 fatty acid with 5 monomer units of ethylene oxide, 6 units of propylene oxide, and polyethylene glycol ether. Dispersants S3 and S5 were fatty alcohols with approximately 9 and 6.5 moles ethylene oxide units and a minimum amount of glycols. The particle settling was longer with dispersant S3. Dispersants S7, S11, and S13 were another line of ethoxylated alcohols with 12, 6, and 9 ethylene oxides. The particle settling of dispersant S7 was longer than those of both S11 and S13. It is observed that dispersants of the same product line with higher total number of alkoxylated monomer units showed longer particle settling times. The tested dispersants were commercially available, and

the chemical ingredients are summarized in Appendix A based on the released chemical information. It was observed that acrylate and lignosulfonate-based dispersants were more effective with water-based systems, while ethoxylated alcohols were more effective with oil-based systems. The phosphate functional group may attribute to the higher particle settling of dispersant S1.
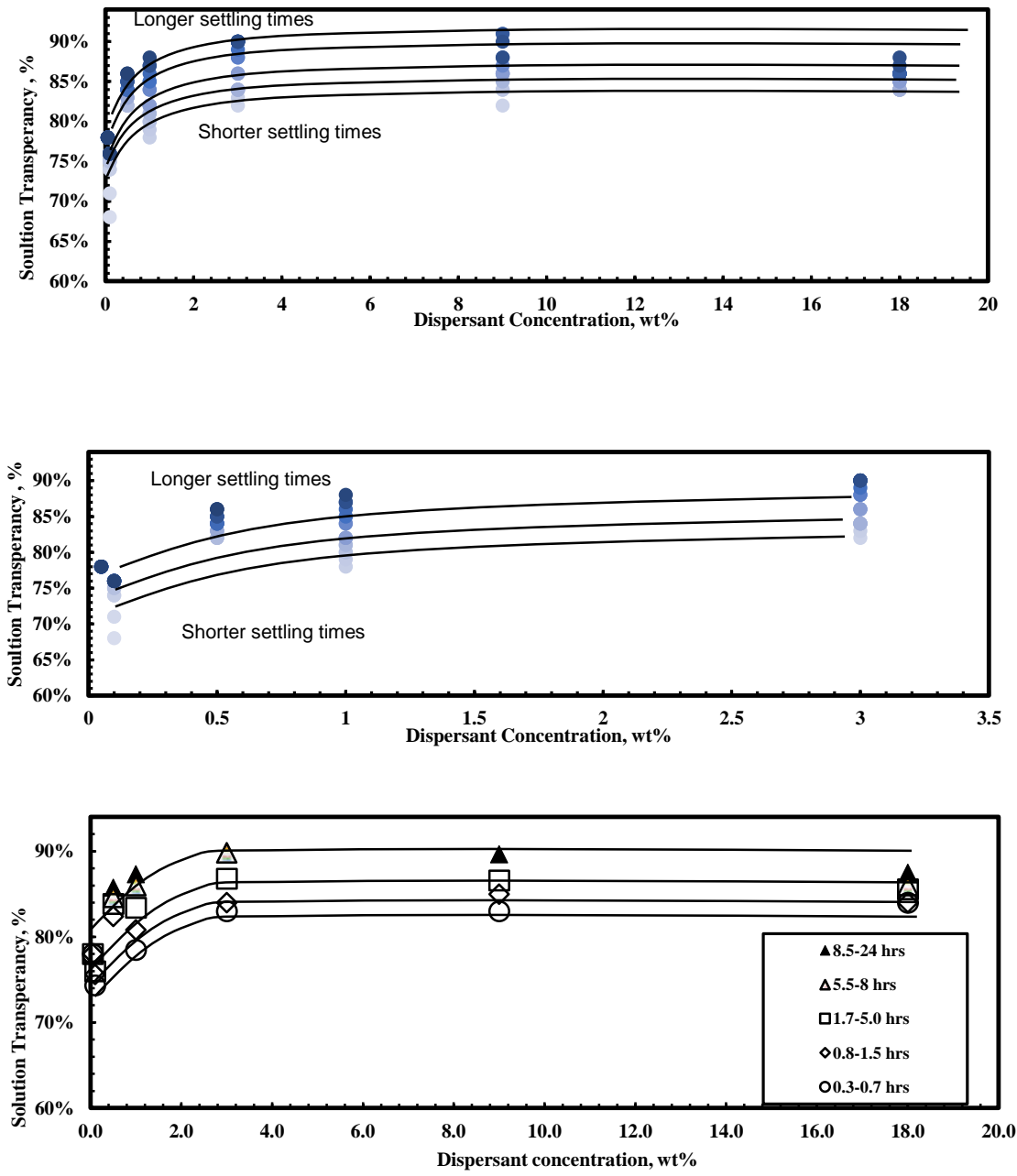
Fig. 34—Solution transparency of manganese tetraoxide/mineral oil solutions with dispersant S9.
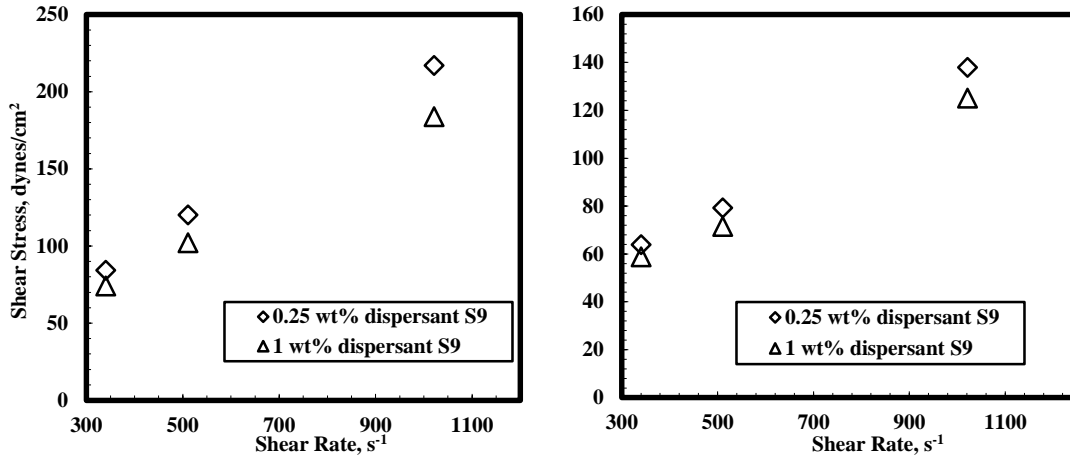
Fig. 35—Shear stress/rate of drilling fluids with composition shown in Table 12 at a) 77 and b) 120°F. Fluids were heat aged at 400°F. Dispersant S9 was used.

Dispersant	Settling time, hrs	Dispersant	Settling time, hrs	Dispersant	Settling time, hrs
S1	24.00	S24	0.01	N47	0.03
S2	2.75	S25	0.01	N48	0.02
S3	0.87	S26	0.01	N49	0.02
S4	0.85	S27	0.01	N50	0.02
S5	0.50	S28	0.01	N51	0.02
S6	0.47	S29	0.01	N52	0.01
S7	0.42	S30	0.01	N53	0.01
S8	0.35	S31	0.01	N54	0.01
S9	0.33	S32	0.01	N55	0.01
S10	0.32	N33	0.50	N56	0.01
S11	0.30	N34	0.50	N57	0.01
S12	0.28	N35	0.50	N58	0.01
S13	0.28	N36	0.50	N59	0.01
S14	0.10	N37	0.09	N60	0.01
S15	0.09	N38	0.08	N61	0.01
S16	0.06	N39	0.08	N62	0.01
S17	0.05	N40	0.07	N63	0.01
S18	0.04	N41	0.07	N64	0.01
S19	0.03	N42	0.06	N65	0.01
S20	0.03	N43	0.03	N66	0.004
S21	0.02	N44	0.03	N67	0.004
S22	0.02	N45	0.03	N68	0.004
S23	0.02	N46	0.03	N69	0.003

Table 14—settling times of Mn_3O_4 particles in mineral oil

Sagging Tendency and Comparison with Ilmenite/Barite-Based Drilling Fluids

Sag is a measure of the variation of drilling fluid densities as the weighting material is settling. Appendix C summarizes the dynamic and static sag results for the tested Mn_3O_4 oil-based drilling fluids. At densities of 16.3 lbm/gal (Table 9), the dynamic sag value was 0.08 lbm/gal. The sag values increased with cement and clay contaminated drilling fluids to 0.13 and 0.24 lbm/gal. The dynamic sag values for 20 lbm/gal oil-based drilling fluids (Table 10) decreased from 0.27 lbm/gal to 0.18 and 0.20 for cement and clay contaminated drilling fluids, respectively.

Dispersants S2, S3, and S5 were based on ethoxylated alcohols (Appendix B). Adding the dispersants to both 16.3 and 20 lbm/gal drilling has reduced the sag values. The lowest sag values were 0.04 and 0.11 lbm/gal for drilling fluids with densities 16.3 and 20 lbm/gal, respectively (dispersant S5 was used). A similar trend of results was noticed with cement and clay contaminated 16.3 and 20 lbm/gal oil-based drilling fluids. For example, using dispersant S5, the dynamic sag values were reduced from 0.13 lbm/gal to 0.06 lbm/gal in cement contaminated drilling fluids (16.3 lbm/gal). In clay contaminated drilling fluids (20 lbm/gal), the dynamic sag was reduced from 0.20 to 0.13 lbm/gal when dispersant S5 was used. When both contaminated and non-contaminated drilling fluids were subject to heat aging at 400°F and 16 hrs, only drilling fluids with dispersant S5 showed lower sag values compared to S2 and S3.

The static sag values were also lowered from 0.508 to 0.507 when dispersant S5 was used and increased to 0.509 with drilling fluids dispersed with S3 in 20 lbm/gal drilling fluids subjected to heat aging at 400°F. The combination of anionic and nonionic dispersants (S2 and S5) showed no improvement in the static sag factor results. Three oil-based drilling fluids (17.5 lbm/gal) weighted with manganese tetraoxide, ilmenite, and API barite showed nearly similar viscosity measurements (Fig. 36); however, the sagging tendency was the lowest with manganese tetraoxide drilling fluids, although dispersant S5 was used with the three drilling fluids. The static sag factors were 0.507, 0.511, and 0.528 for manganese tetraoxide, ilmenite, and API barite oil-based drilling fluids (17.5 lbm/gal). Dispersant S5 was probably more effective with Mn_3O_4 oil-based drilling fluids. The type of weighting material used may have also contributed to the sagging tendency.
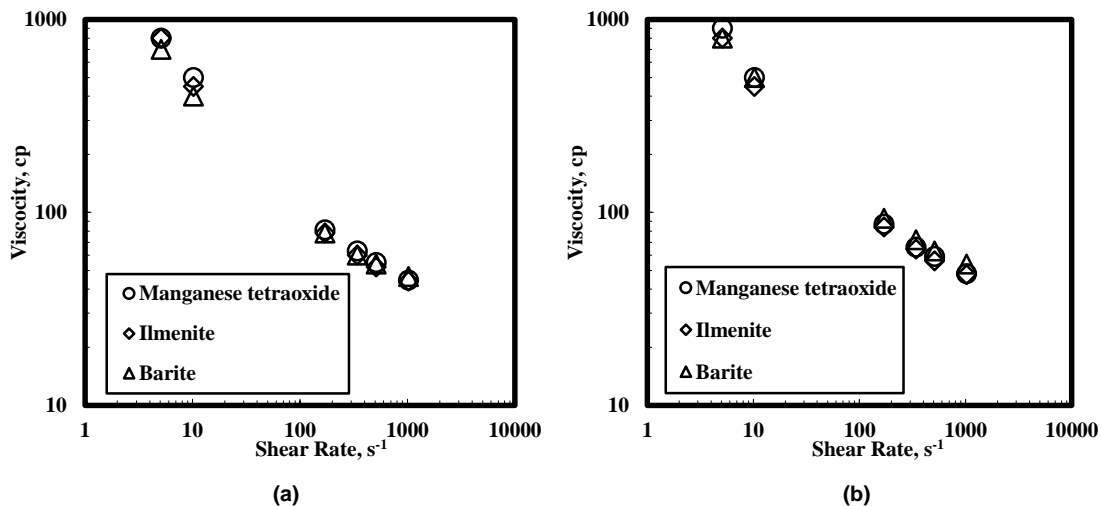
Fig. 36—Viscosity at 120°F of drilling fluids with composition shown Table 13 a) before heat aging and b) after heat aging at 400°F. Dispersant S5 was used.

Rheological Behavior of Mn₃O₄ Oil-Based Drilling Fluids

The use of dispersants with manganese tetraoxide drilling fluids has reduced the shear stresses in most of the examined cases. For example, **Fig. 37** and **Appendix E** show that using dispersants S2, S3, and S5 resulted in lower shear stress for 16.3 and 20 lbm/gal drilling fluids even after the drilling fluids were subjected to heat aging at 400°F. These results agreed with particle settling results and sagging tendency results. Dispersants with the longest particle settling lowered the sagging tendency and rheological properties.

Dispersant S1 was an anionic based on ethoxylated alcohol C16-C18, phosphate, and polyethylene glycol ether carboxylic acid. Dispersant S5 was nonionic fatty alcohols with approximately 6.5 moles of ethylene oxide and minimum amount of glycols. The combination of nonionic and anionic dispersants showed nearly similar rheological behavior (**Fig. 38** and Appendix E). The plastic viscosity and static sag factors were lower with the nonionic dispersant (i.e. S5). The HP/HT fluid loss was lower with the anionic dispersant (S1).

Fig. 39 and Appendix E show that the presence of cement or clay contamination causes a slight increase in the rheological behavior of the drilling fluids (16.3 and 20 lbm/gal). Adding dispersants to the contaminated drilling fluids showed nearly similar or slightly lower viscosities. The sagging tendency

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was lower with dispersed drilling fluids in most of the results (Appendix E and **Figs. 40** and **41**).

Dispersant loading was increased from 7 to 28 g/l oil in the 13.8 lbm/gal manganese tetraoxide drilling fluids, and, as a result, the shear stresses for the drilling fluids were lowered (**Fig. 42** and Appendix E). The rheological behavior of 13.8, 16.3, 17.5, and 20 lbm/gal manages tetraoxide oil-based drilling fluids are summarized in **Fig. 43** and Appendix E. Higher density and higher oil/water ration drilling fluids showed higher shear stresses.
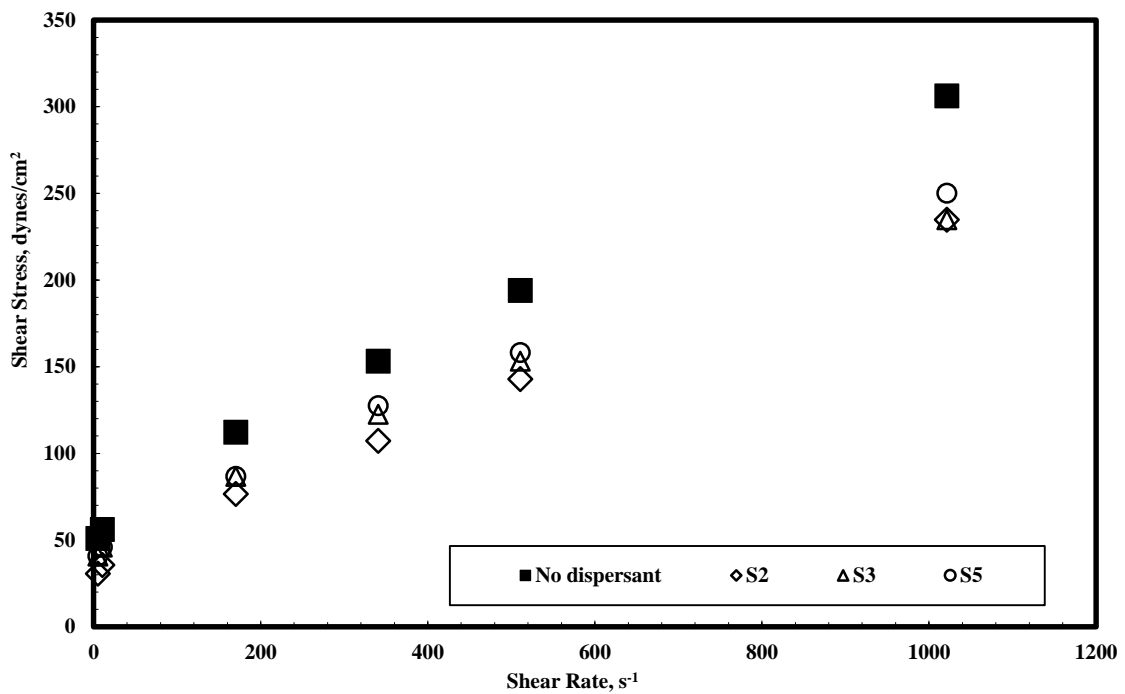
Fig. 37—Shear stresses for non-contaminated 16.3 lbm/gal Mn_3O_4 oil-based drilling fluids before heat aging. Dispersant concentration was 8 g/l oil.
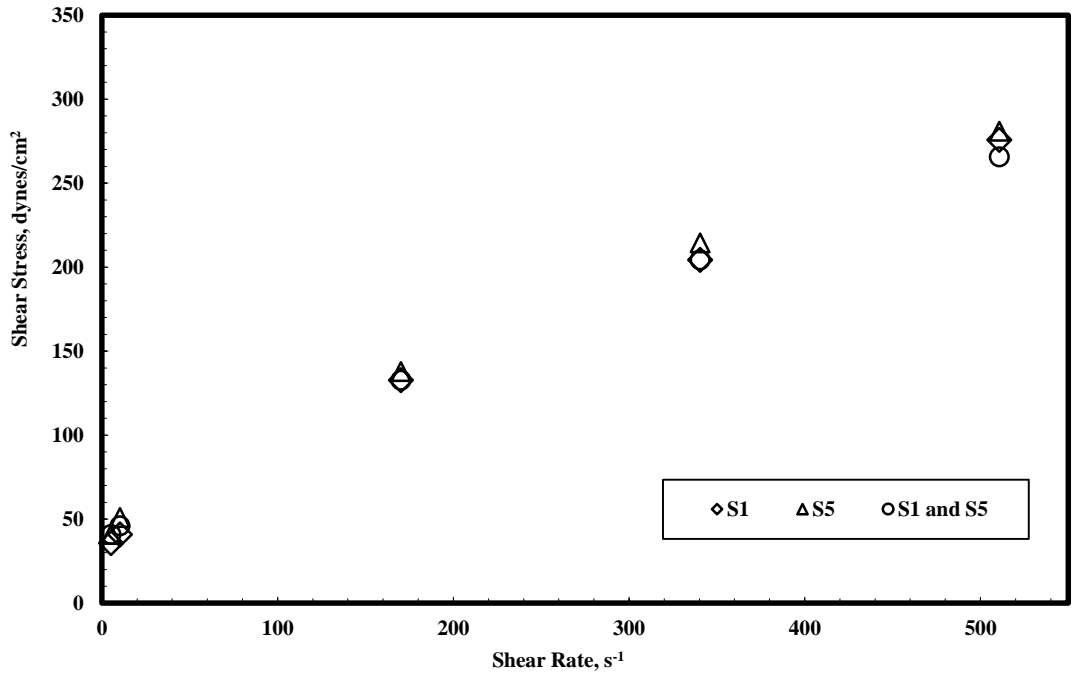
Fig. 38—Shear stress/rate for 17.5 lbm/gal Mn$_3$O$_4$ oil-based drilling fluids before heat aging. Dispersants S2 and S5 were used.
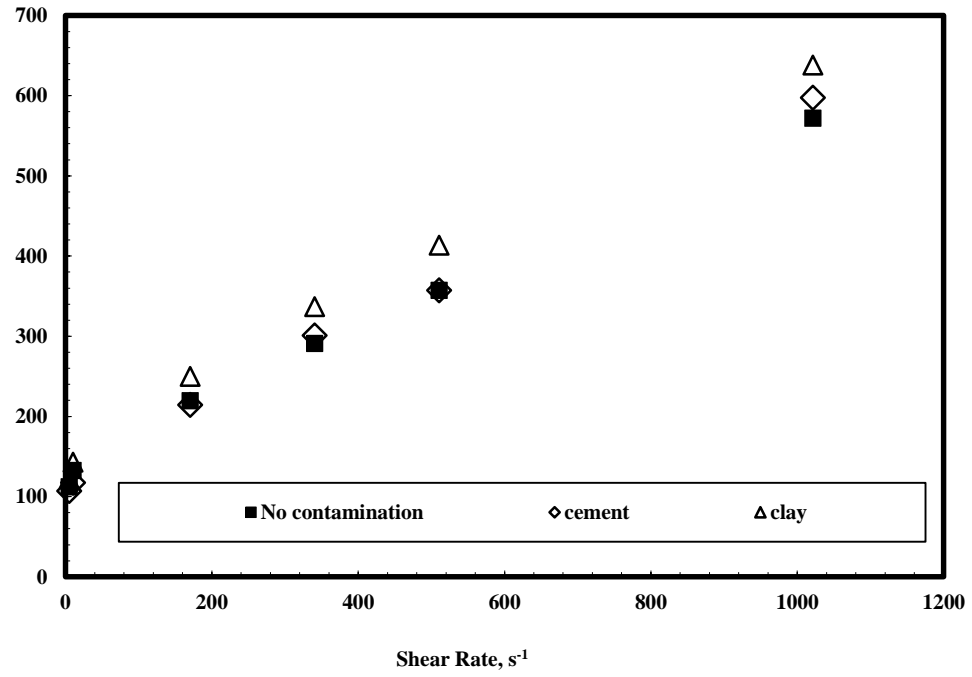
Fig. 39—Shear stress/rate for 17.5 lbm/gal Mn$_3$O$_4$ oil-based drilling fluids after heat aging at 400°F for 16 hrs.
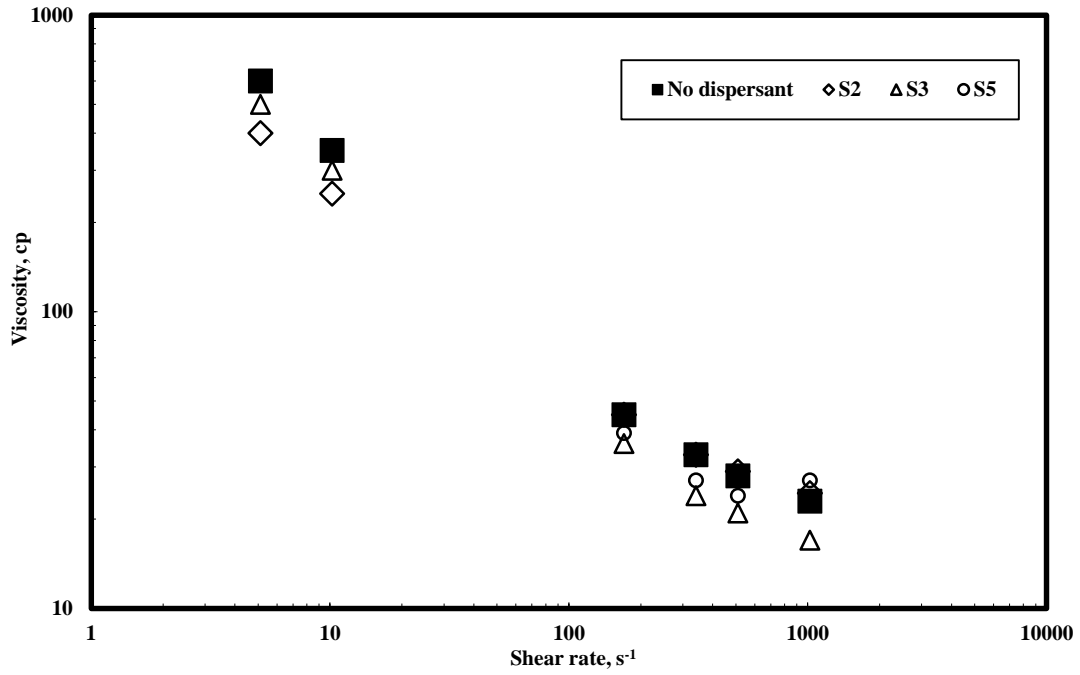
Fig. 40—Viscosities for cement contaminated 20 lbm/gal Mn$_3$O$_4$ oil-based drilling fluids before heat aging. Dispersant concentration was 15 g/l oil.
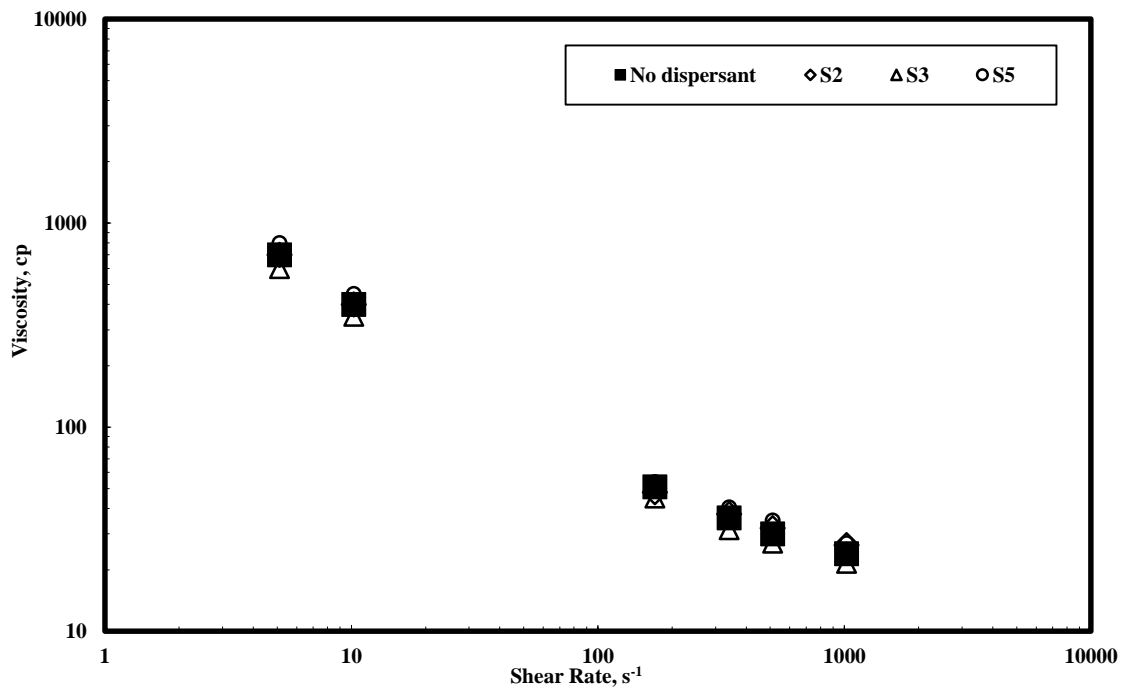
Fig. 41—Viscosities for clay contaminated 20 lbm/gal Mn$_3$O$_4$ oil-based drilling fluids before heat aging. Dispersant concentration was 15 g/l oil.

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Fig. 42—Shear stress/rate of 13.8 lbm/gal Mn₃O₄ oil-based drilling fluids after heat aging at 350°F and 16 hours.

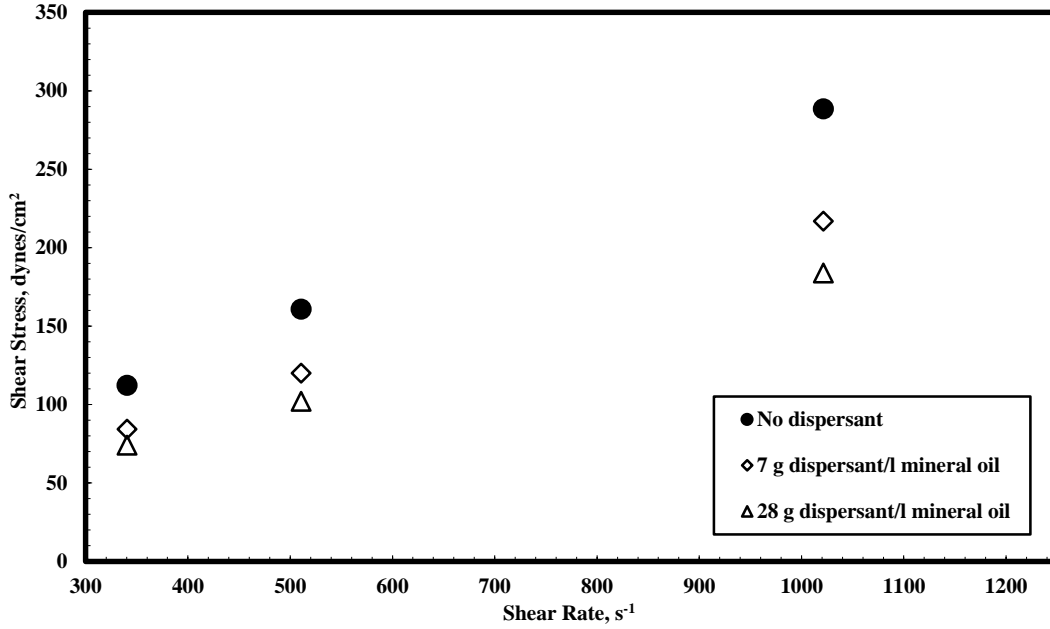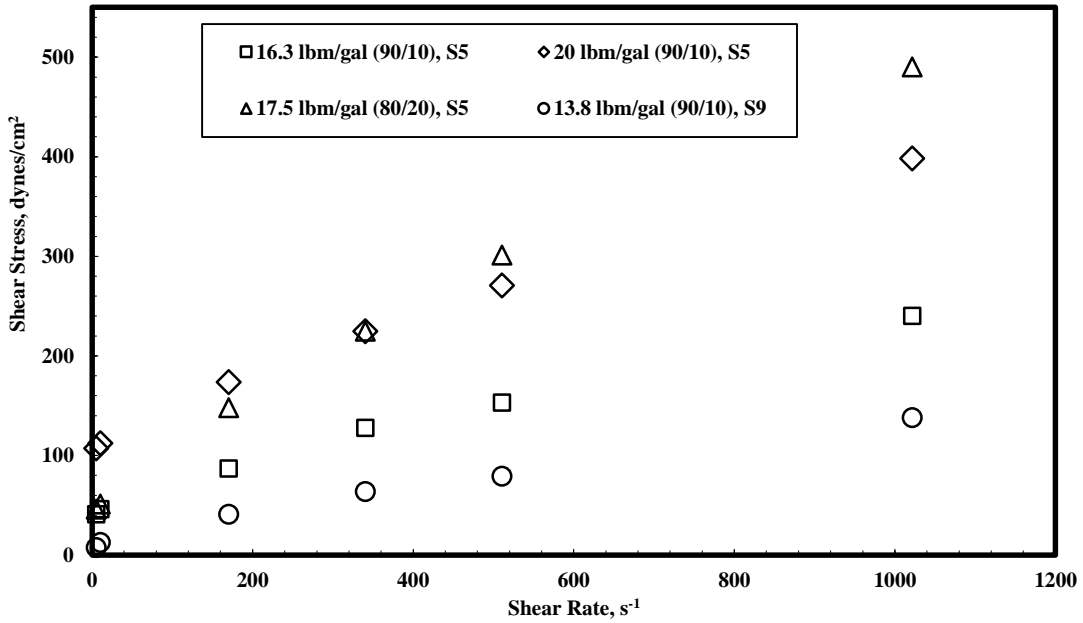Fig. 43—Shear stress/rate for Mn₃O₄ oil-based drilling fluids after heat aging at 400°F and 16 hrs. Oil/water ratios were 90/10 and 80/20. Dispersants S5 and S9 were used.

Conclusions

The dispersion of manganese tetraoxide particles in oil-based drilling fluids (13.8 to 20 lbm/gal) has been studied. Appendix A and Table 7 summarize the dispersants' chemical ingredients, compatibility with oil, and particle settling results in oil solutions. Several dispersants were tested, but only a few showed high dispersion capacity of manganese tetraoxide particles. Transparency testing showed that the optimum concentration for dispersants was between 0.2 and 2 wt%, based on dispersant S9. Increasing dispersant S9, concentration from 0.25 to 1 wt% lowered the viscosity of the 13.8 lbm/gal drilling fluids. Sagging tendency was lowered with dispersed drilling fluids (16.3 and 20 lbm/gal) and in the presence of clay and cement contaminations with dispersants S1, S2, S3, and S5 in most of the cases (Appendix B). The shear stresses for 13.8, 16.3, 17.5, and 20 lbm/gal drilling fluids was reduced in the presence of dispersants (e.g., S1, S2, S3, S5, S9) at shear rates up to 100 s^{-1}. The ilmenite and API barite oil-based drilling fluids showed higher sagging tendency than manganese tetraoxide oil-based drilling fluids in the presence of dispersant S9, although rheological behavior for the three drilling fluids was nearly similar. Based on the experimental results, the following conclusions can be drawn:

1. Alkoxylated fatty alcohols/acids and sulfonic acid-based dispersants showed high potential to disperse Mn_3O_4 oil-based drilling fluids. The number of alkoxylated units and the presence of a phosphate functional group may favor the dispersion with manganese tetraoxide oil-based fluids.

2. Effective dispersants with manganese tetraoxide oil-based drilling fluids may not be suitable for other oil-based drilling fluids (e.g., ilmenite and barite oil-based drilling fluids)

3. Optimum dispersant concentration is between 0.2 and 2 wt%. Dispersant concentration of 1 wt% is recommended as a median concentration.

4. Increasing the dispersant loading (e.g. from 7 to 28 g/l oil) may improve the dispersion of particles and lower the drilling fluid viscosities.

5. Acrylate and lignosulphonate-based dispersants were not effective with manganese tetraoxide oil-based fluids.

CHAPTER V

REMOVAL OF MN3O4-BASED FILTER CAKE USING GLYCOLIC ACID[*]

Overview

The removal of filter cake generated by drilling fluids weighted with Mn_3O_4 particles may require strong acids such as HCl. Organic acids are not efficient with high density drilling fluids (> 100 lbm/ft^3) that contain large amounts of weighting materials such as Mn_3O_4. A filter cake removal treatment with HCl only in a high temperature and corrosive environment cannot be used, especially if HCl concentration is higher than 5 wt%. HCl at concentrations greater than 5 wt% can release chlorine gas, a toxic and corrosive gas. In certain cases, a two-step treatment to degrade polymers and, then use organic acids to dissolve solid particles in the filter cake is recommended. The cleanup of filter cake generated by high density drilling fluids (12.7 lbm/gal) that are based on manganese tetraoxide (Mn_3O_4) particles as a weighting material was investigated using a glycolic acid system.

The reaction of glycolic and HCl acids with manganese tetraoxide particles was investigated using a glass reactor apparatus. The solubility of filter cake was examined using an HP/HT filter press at 250°F.

Glycolic or HCl acids (4 wt%) dissolved 75 wt% of manganese tetroxide particles. The dissolved manganese ions were higher with glycolic acid (i.e. 10,000 mg/l) than that of HCl (8,500 mg/l). The reaction time when using HCl was nearly 5 times faster than the glycolic acid reaction with the manganese tetroxide particle. The Mn_3O_4-based filter removal efficiency was nearly 90 wt% when glycolic acid was used in the single or two-step procedure to dissolve the filter cake. Glycolic acid concentrations were 7 and 10 wt% during the single

and two-step filter cake removal procedures, respectively. The removal efficiencies by flow rate were higher with sandstone core samples (i.e. 125 vol%) than that of limestone core samples (i.e. 100 vol%).

Experimental Procedure

Water-based drilling fluid weighted with manganese tetraoxide was prepared using
Table 3. The density of the drilling fluid was 12.7 lbm/gal. The drilling fluid additives were obtained from a local service company. Indiana limestone and Berea sandstone cores (1 in x 2.5 in) were used. The porosities of Berea and Indiana core samples were nearly 18 and 23 vol%, respectively. The permeabilities were 50 to 60 and 100 md for Berea and Indiana core samples, respectively. Glycolic acid was 70 % by weight. α-amylase enzyme was obtained from a local service company. It can degrade starch present in the filter cake. The enzyme/stabilizer system was reported to be active at temperatures up to 250°F (Samuel et al.).

The reaction of glycolic acid with manganese tetraoxide particles was examined at 190°F under magnetic stirring using a flask, condenser and a hot plate. The weight of manganese tetraoxide particles and glycolic acid solution were 4 and 200 g, respectively. During each experiment, samples were collected at different times and filtered through a 0.2-micron syringe filter. Then the acid concentration was measured through acid/base titration.

Pressurized visual cells were used to assess the compatibility of the cleaning fluid systems at 200°F and 300 psi. The volume of a visual cell was 100 cm^3. The cells were heated electrically by silicone heater plates and pressurized though a nitrogen gas cylinder. A cell jacket was used to maintain temperature.

The filter cake was generated by using HP/HT filter press. The Berea and Indiana core samples were used. The cleaning fluids were soaked with a filter at 250˚F and 300 psi. The filter cake removal efficiency by mass and by flow rate were calculated using Eq. 3 and 4, respectively.

$$Removal\ efficiency\ by\ weight, \% \ = \left(\frac{W_f}{W_i}\right) \times 100 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

$$Removal\ efficiency\ by\ flow\ rate, \% = \left(\frac{t_i}{t_f}\right) \times 100 \dots\dots\dots\dots\dots\dots\dots\ (4)$$

Where W_i and W_f are the weights of the filter cake initially and after the filter cake removal process, respectively. The times required to flow 150 cm^3 of deionized water through the core sample at 60 psi initially and after the filter cake removal process are denoted in Eq. 4 as t_i and t_f, respectively.

Compatibility and Reaction of Mn$_3$O$_4$ Particles

Glycolic acid and enzyme mixtures were not compatible at temperatures of 77, 200, and 300°F because of observed precipitations. The concentrations of the enzyme or glycolic acid were 5 and 10 wt%. A solution of pH below 4 to 5 caused the α-amylase enzyme to lose activity and precipitate. Thus, a mixture of glycolic acid and enzyme cannot be used to dissolve a Mn$_3$O$_4$-based filter cake. Rather, a two-step procedure can be employed, which involves the use of both the enzyme and the acid.

The solubility of Mn$_3$O$_4$ particles in glycolic acid experiments indicated the effectiveness of glycolic acid to dissolve manganese tetroxide particles. The solubility of Mn$_3$O$_4$ was 75 wt%, and nearly 10,000 mg/l of manganese ions were measured in the reacted acid after 30 min. The concentration of glycolic acid was 4 wt% and the reaction temperature was 190°F (**Fig. 44**).
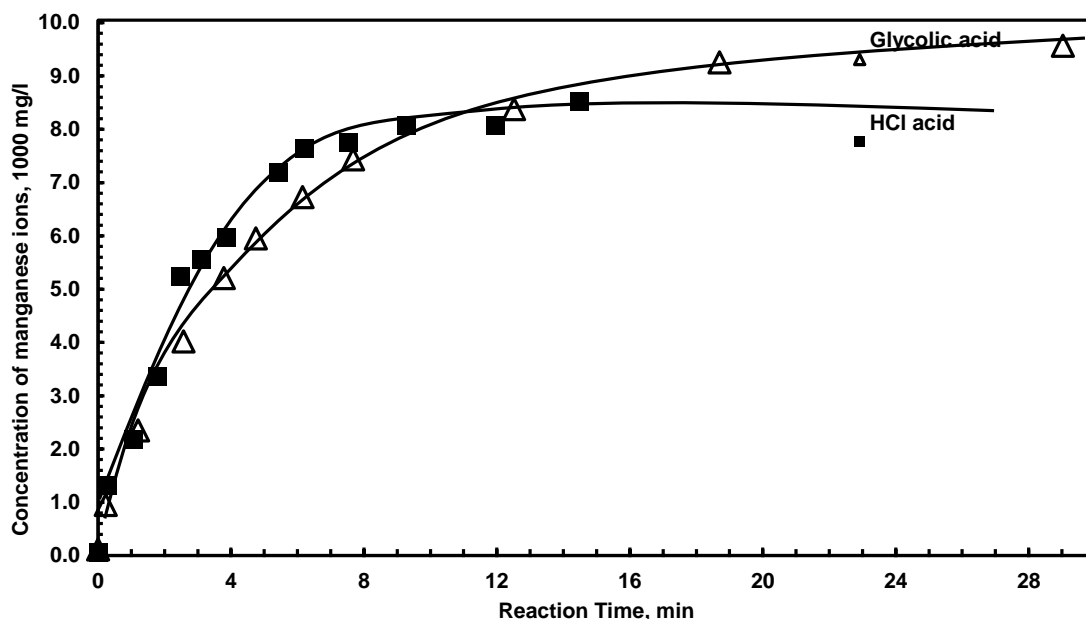
Fig. 44—Manganese ions concentration in 4 wt% acid solutions during the reaction with manganese tetraoxide particles at 190°F.

The pH of the glycolic acid increased from 1.9 to 3.6 when the reaction reached equilibrium after nearly 25 min. The density of the spent acid was 1.015 g/cm^3. The glycolic acid concentration at equilibrium was 1.3 wt%, indicating that nearly 67 wt% of the acid was consumed (**Fig. 45**).

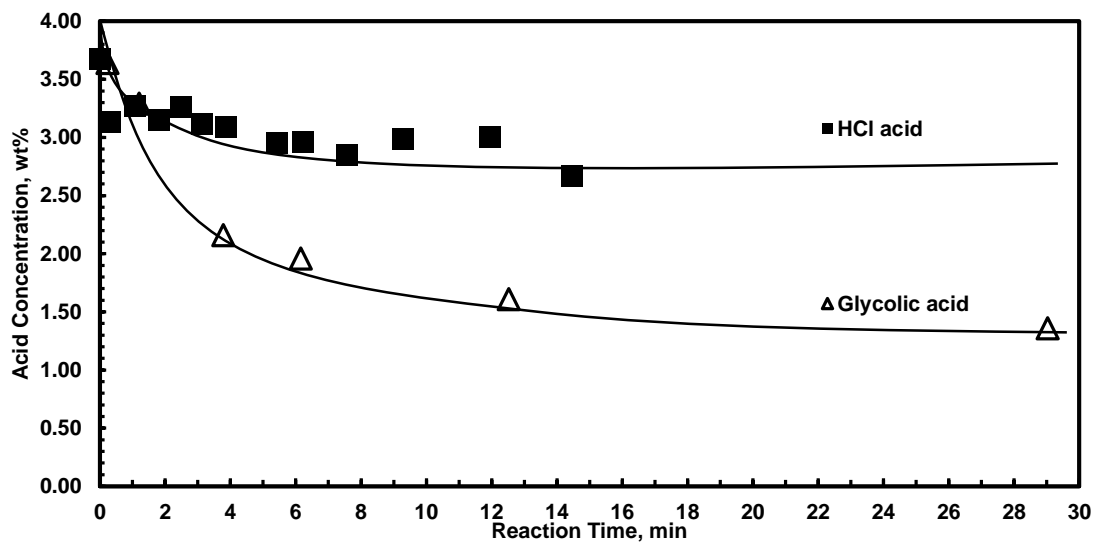**Fig. 45—Acid concentrations during the reaction with manganese tetraoxide particles at 190°F.**

HCl acid at an initial concentration of 4 wt% showed nearly 8500 mg/l of manganese ions slightly lower than the glycolic acid dissolving performance (Fig. 44). This is most likely because the HCl/Mn_3O_4 reaction produced manganese dioxide at low HCl concentrations (Moajil and Nasr-El-Din 2010). A mixture of HCl and glycolic acid at low concentrations would lead to a complete dissolution of manganese tetroxide particles similar to the lactic and HCl acids mixture (Al Moajil and Nasr-El-Din 2014). HCl cannot be used at higher concentrations (e.g. 10 wt%) because of the release of corrosive and poisonous chlorine gas (Moajil and Nasr-El-Din 2010). The consumption of HCl acid was lower than glycolic acid (Fig. 45). This increased the risk of corrosion when flowing back the well if HCl was used rather than glycolic acid.

Dissolution of Mn_3O_4-Based Filter Cake

Two methods were used to dissolve the Mn_3O_4-based filter cake: (1) a two-step procedure that involved α-amylase enzyme and glycolic acid, (2) a single-step procedure that involved HCl and a glycolic acid mixture. Although glycolic acid was effective to dissolve manganese tetraoxide particles, it did not dissolve the filter cake because of the presence of adsorbed polymers. Fig. 5 showed the aggregation of Mn_3O_4 particles in the presence of adsorbed polymers. Starch present in the filter cake adsorbed on the surface of manganese tetraoxide aggregates in the filter cake. Starch in the top layer of the filter cake was identified by an iodine test. Thus, it was required to degrade starch first using α-amylase enzyme prior to glycolic acid. The single-step procedure did not require an enzyme because HCl was strong enough to react with the cake in the presence of biopolymers. The advantages of the two-step procedure were, longer reaction time and avoided use of strong acids such as HCl. The single-step procedure would be less expensive and require lower concentrations of HCl and glycolic acids.

The experiment results of the two-step procedure to dissolve the filter cake showed nearly 88% removal efficiency by weight for Berea and Indiana core samples. The enzyme was first soaked with the filter cake for 20-24 hours at a concentration of 10 wt% to degrade the starch in the filter cake. Then, glycolic acid solution was soaked with the filter cake to dissolve manganese tetroxide particles and complete the filter cake dissolution process. Both 5 and 10 wt% of

glycolic acid solutions showed similar removal efficiencies. Thus, 5 wt% glycolic acid was sufficient to dissolve the filter cake. The obtained removal efficiencies agreed with the solubility results discussed previously. The filter cake removal efficiencies by flow rate were nearly 100 and 125 to 130% for Indiana and Berea core samples, respectively. This showed improvement to the permeability of the sandstone samples while causing no damages to either the limestone or sandstone core samples. The removal efficiencies by flow rate were nearly 125 and 145 % at 5 and 10 wt% glycolic acid, respectively. **Figs. 46** to **49** show pictures of the filter cakes before and after the reaction with the enzyme and glycolic acid. Pictures of cleaning solutions before and after the reaction are shown in

Fig. 50**.**

| (a) | (b) | (c) |

Fig. 46—Two-step procedure to dissolve Mn$_3$O$_4$-based filter cake on Berea core samples at 250°F: (a) before removal, (b) after enzyme reaction, and (c) after glycolic acid reaction. The glycolic acid and enzyme concentrations were 5 and 10 wt%, respectively.

| (a) | (b) | (c) |

Fig. 47—Two-step procedure to dissolve Mn$_3$O$_4$-based filter cake on Indiana core samples at 250°F: filter cake (a) before removal, (b) after enzyme reaction, and (c) after glycolic acid reaction. The glycolic acid and enzyme concentrations were 5 and 10 wt%, respectively.

(a)   **(b)**   **(c)**

Fig. 48—Two-step procedure to dissolve Mn$_3$O$_4$-based filter cake on Indiana core samples at 250°F: filter cake (a) before removal, (b) after enzyme reaction, and (c) after glycolic acid reaction. The enzyme and glycolic acid concentrations were 10 wt%
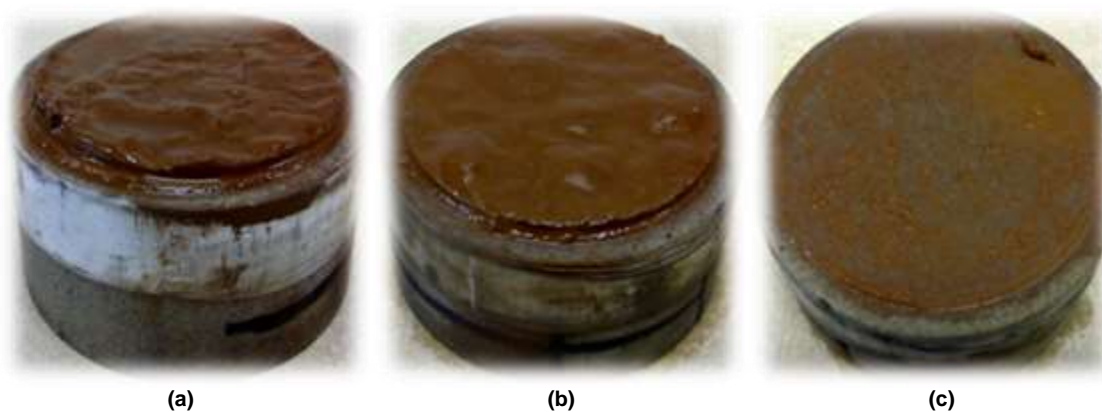

(a)   **(b)**   **(c)**
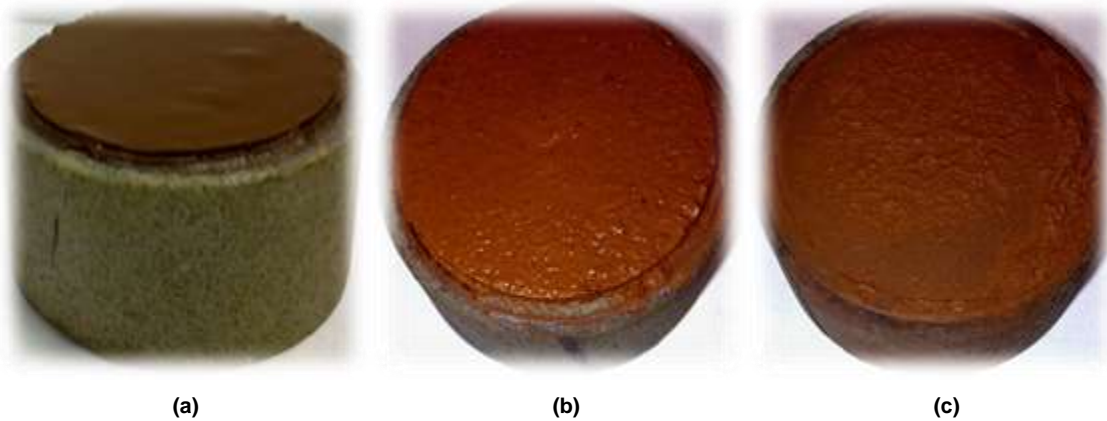
Fig. 49—Two-step procedure to dissolve Mn$_3$O$_4$-based filter cake on Berea core samples at 250°F: filter cake (a) before removal, (b) after enzyme reaction, and (c) after glycolic acid reaction. The enzyme and glycolic acid concentrations were 10 wt%
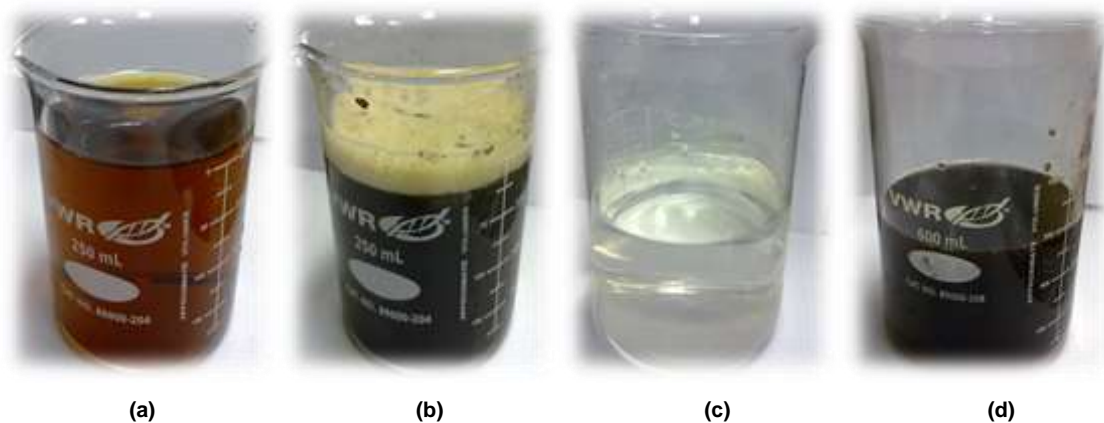
Fig. 50—Cleaning fluids solutions before and after the reaction with filter cake: (a) 10 wt% enzyme solution before reaction (pH of 6), (b) enzyme solution after reaction (pH of 5.7), (c) 10 wt% glycolic acid solution before reaction, and (d) 10 wt% glycolic acid solution after reaction.

The single-step procedure to dissolve the filter cake showed a removal efficiency by weight of nearly 90% for Berea and Indiana core samples. The cleaning solution contained 1 wt% HCl and 7 wt% glycolic acid. The removal efficiency was 50 wt% when the glycolic acid concentration was lowered to 4 wt%. The HCl/glycolic acid mixtures were soaked with filter cake for nearly 20-24 hours AT 250°F. The filter cake removal efficiencies by flow rate were nearly 100 and 120% for Indiana and Berea core samples, respectively. This showed improvement to the permeability of the sandstone samples while causing no damages to either the limestone or sandstone core samples. The cleaning solution contained 1 wt% HCl and 7 wt% glycolic acid. **Figs. 51** and **52** show pictures of the filter cake the HCl/glycolic acid mixture before and after the reaction.

(a)   **(b)**

Fig. 51—Single-step procedure to dissolve Mn$_3$O$_4$-based filter cake at 250°F. Pictures showed filter cake (a) before reaction, (b) after HCl/glycolic acid reaction. The HCl and glycolic acids concentrations were 1 and 7 wt%.
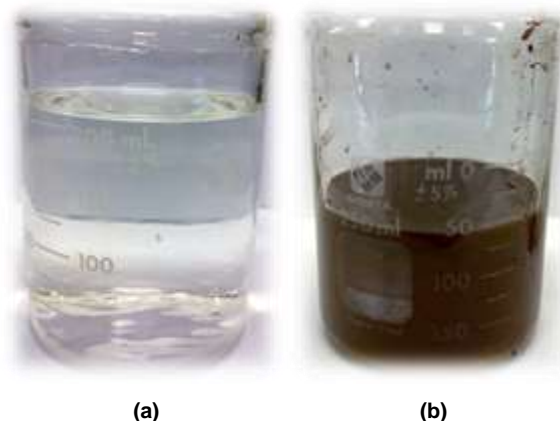
(a)   **(b)**

Fig. 52—Cleaning fluids solutions before and after the reaction with filter cake: (a) 1 wt% HCl/7 wt% glycolic acid mixture before reaction (pH of zero) (b) HCl/glycolic acid mixture after reaction (pH of 2.5).

Reaction Rate Reduction Using Surfactants

Several approaches control the reaction rate of Mn$_3$O$_4$-based filter cake with acid systems. The acid and enzyme concentration and type of cleaning fluid affects the reaction rate. The amount of starch present in the filter cake will slow the reaction rate. Additives such as surfactants can control the reaction rate of manganese tetraoxide-based filter cake if absorbed on the surface of manganese tetraoxide particles. The surfactant should be compatible with aqueous systems and have an affinity to adsorb on manganese tetraoxide particles.

Thus, several surfactants were examined for their thermal stability and compatibility. Because the surface charge on the Mn$_3$O$_4$ particles is positive at low pH environments (pH < 5), the anionic surfactants will absorb on the surface

of the Mn_3O_4 particles (Morimoto and Kittaka 1974; Kittaka et al. 1987). Three commercially available anionic surfactants were selected. Surfactant A was based on sulfonic acid. Surfactant B was based on a maleic acid copolymer. Surfactant C was based on an ethoxylated alkylphenol. It contained 12 ethylene oxide units and a phosphate functional group. All surfactants were compatible with aqueous systems in the presence of salts (i.e. $CaCl_2$ and NaCl) at 5 and 10 wt% salt concentrations. **Fig. 53** showed that all of the three surfactants slowed the reaction of lactic acid with manganese tetraoxide particles. The concentrations of lactic acid and surfactant were 4 wt% and 0.3 wt%, respectively. The solution pH values before and after reactions were 2.0 (± 0.5) and 4.0 (± 0.5), respectively. The solution was prepared in deionized water where the Mn_3O_4 amount was 4 g in a 200 g solution. The anionic surfactant most likely adsorbed on the surface of manganese tetraoxide particles and provided a barrier between the lactic acid and the manganese tetraoxide particles that slowed the reaction rate. Surfactant C showed the slowest reaction rate followed by surfactant B, and surfactant A showed the fastest reaction rate. The use of surfactants during the cleaning of the filter cake that is based on manganese tetraoxide will slow the reaction of the cleaning fluid with the filter cake. As a result, a uniform removal of the filter cake would be achieved.
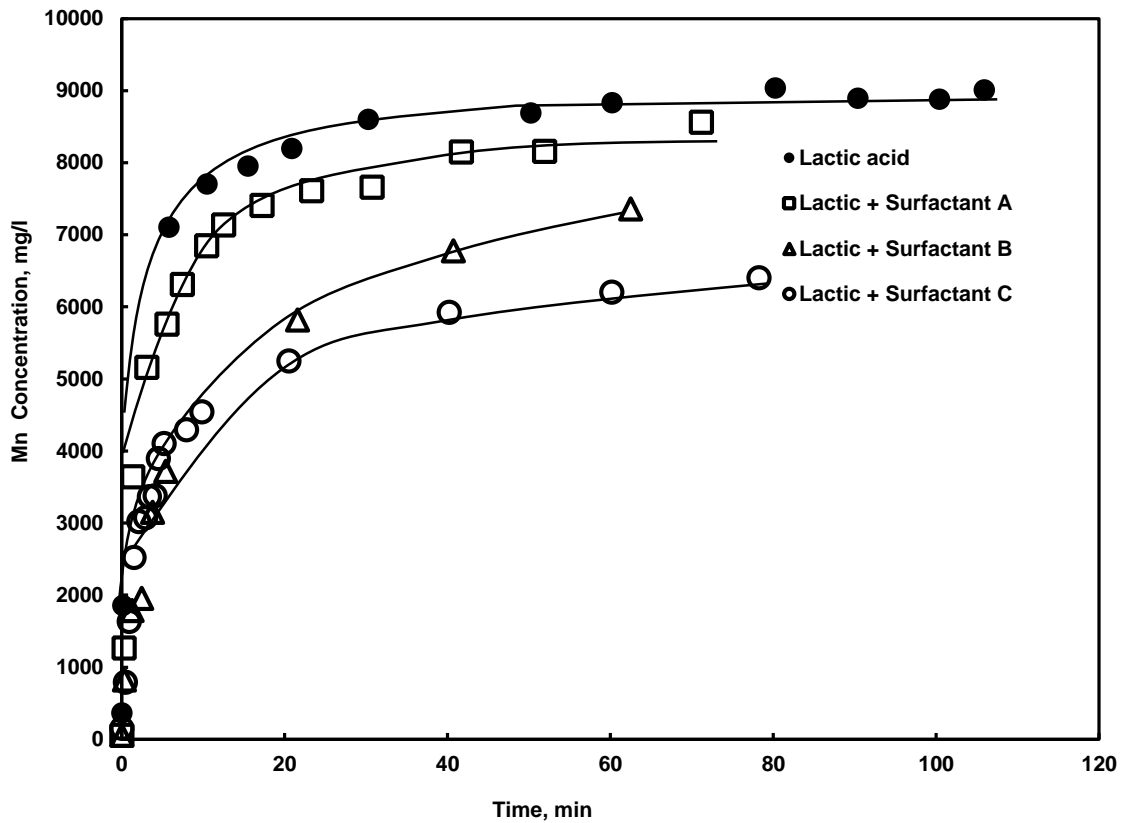
Fig. 53—Effect of surfactants on the reaction of lactic acid with manganese tetraoxide particles, 4 wt% lactic acid and 0.3 wt% surfactant, 190°F

Conclusions

The dissolution of filter cake generated by 12.7 lbm/gal manganese tetraoxide water-based drilling fluids was investigated using an enzyme and glycolic and HCl acids. A mixture of α-amylase enzyme and glycolic acid was not compatible because of the lower pH of the solution. Glycolic or HCl acids (4 wt%) dissolved 75 wt% of manganese tetroxide particles. The dissolved manganese ions were higher with glycolic acid (i.e. 10,000 mg/l) than that of HCl (8,500 mg/l). The reaction time when using HCl was nearly 5 times faster than the time of glycolic acid reaction with manganese tetroxide particle. About 68 wt% of glycolic acid was consumed (i.e. utilized to dissolve Mn_3O_4 particles), while only 25 wt% of HCl acid was consumed. The Mn_3O_4-based filter removal efficiency was nearly 90 wt% when glycolic acid was used in the single or two-step procedure to dissolve the filter cake. Glycolic acid concentrations were 7 and 10 wt% during

the single and two-step filter cake removal procedures, respectively. HCl and α-amylase enzyme were used at a concentration of 10 wt%. The removal efficiencies by flow rate were higher with sandstone core samples (i.e. 125 vol%) than those of limestone core samples (i.e. 100 vol%). Based on the obtained results the following conclusions can be drawn:

1. Glycolic acid can be used to dissolve Mn_3O_4-based filter cake by following either the single or two-step filter cake removal procedures.

2. Glycolic acid system is more effective with sandstone formation.

3. The suggested glycolic acid concentrations are 7 and 10 wt% by using the single and two-step procedures, respectively.

4. The reaction rate of manganese tetraoxide particles can be controlled using surfactants A, B, or C. They were based on sulfonic acid, maleic acid copolymer, and ethoxylated phosphate ester.

CHAPTER VI

CONCLUSIONS

The dispersion of manganese tetraoxide particles in water and oil-based drilling fluids (12.7 to 20 lbm/gal), applicable for high temperature drilling, has been studied. More than 50 commercially available chemicals were examined. Appendix A and B summarize the dispersants chemical ingredients, compatibility with water/oil, and hazard information. The provided information and results would guide the drilling engineer to select appropriate dispersants.

Linear and varying structures of manganese tetraoxide aggregates has been identified in the filter cake micro structure. A list of examined dispersants were sorted in Appendices A and B by particle settling times. Laser particle analysis showed that aggregation of particles was reduced in the presence of dispersant B15. Dispersants A01 and B15 reduced the sag factor and fluid loss for the water-based drilling fluids in the presence of cement contamination. Dispersants A01 and B15 are based on anionic lignosulfonate and acrylate copolymers, respectively. Dispersant A01 showed the longest particle settling time in $CaCl_2$ solutions. Several dispersants precipitated and showed shorter particle settling times in 5 and 10 wt% $CaCl_2$ solutions. Dispersant solutions with NaCl had varying interactions with compatibility and particle settling. The settling times of manganese tetraoxide particles were lower, higher, or did not change for several dispersants solutions.

Zeta potential measurements showed a region of dispersion stability at a pH of 6 to 11 for lignosulfonate and sulfonic acid-based dispersants (i.e. B17 and C31). Zeta potential and particle settling tests indicated that dispersion with acrylic/sulfonic copolymer (B18) is more effective than acrylic/sulfonic copolymer dispersant (B18). Zeta potential values increased with temperature in C31 dispersant solution (i.e. 77 and 120°F). Zeta potential and transparency experiments showed that the optimum dispersant concentration was below 1 wt% and nearly 0.5 wt%. TGA analysis showed that the dispersants A01, B15, and C25 were thermally stable between 300 and 500°F. SEM images of filter cake showed that aggregation of particles was reduced when dispersant A01 was used in clay contaminated drilling fluid. In most cases, the rheological behavior of the contaminated and non-contaminated drilling fluids (17.5 and 20 lbm/gal)

before/after heat aging at 400°F was improved in the presence of dispersants (e.g. A01 and B15). Cement, clay, or rock salt were used as contaminants. The sagging tendencies of contaminated and non-contaminated drilling fluids were improved in the presence of dispersants. For example, the sag factor was reduced from 0.55 to 0.51 in clay and rock salt contaminated drilling fluids when dispersant A01 was used.

Several dispersants were tested, but only a few showed high dispersion capacity of manganese tetraoxide particles in oil-based systems. Transparency testing showed that the optimum concentration for dispersants was nearly between 0.2 and 2 wt% based on dispersant S9. Increasing dispersant S9 concentration from 0.25 to 1 wt% lowered the viscosity of the 13.8 lbm/gal drilling fluids. Sagging tendency was lowered with dispersed drilling fluids (16.3 and 20 lbm/gal) and in the presence of clay and cement contaminations with dispersants S1, S2, S3, and S5 in most of the cases (Appendix B). The shear stresses for 13.8, 16.3, 17.5, and 20 lbm/gal drilling fluids were reduced in the presence of dispersants (e.g., S1, S2, S3, S5, S9) at shear rates up to 100 s^{-1}. The ilmenite and API barite oil-based drilling fluids showed a higher sagging tendency than that of manganese tetraoxide oil-based drilling fluids although the rheological behavior for the three drilling fluids were nearly similar in the presence of dispersant S9.

The dissolution of filter cake generated by 12.7 lbm/gal manganese tetraoxide water-based drilling fluids was investigated using an enzyme, glycolic and HCl acids. A mixture of α-amylase enzyme and glycolic acid was not compatible because of the lower pH of the solution. Glycolic or HCl acids (4 wt%) dissolved nearly 75 wt% of manganese tetroxide particles. The dissolved manganese ions were higher with glycolic acid (i.e. 10,000 mg/l) than that of HCl (8,500 mg/l). The reaction time when using HCl was nearly 5 times faster than the time of the glycolic acid reaction with manganese tetroxide particles. About 68 wt% of glycolic acid was consumed (i.e. utilized to dissolve Mn_3O_4 particles), while only 25 wt% of HCl acid was consumed. The Mn_3O_4-based filter removal efficiency was nearly 90 wt% when glycolic acid was used in the single or two-step procedure to dissolve the filter cake. Glycolic acid concentrations were 7 and 10 wt% during the single and two-step filter cake removal procedures, respectively. HCl and α-amylase enzyme were used at a concentration of 10 wt%. The removal efficiencies by flow rate were higher with

the sandstone core samples (i.e. 125 vol%) than that of the limestone core samples (i.e. 100 vol%).

Based on the obtained results for the dispersion and filter cake removal studies, the following conclusions can be drawn:

1. Several types of dispersants can be recommended for manganese tetraoxide water-based drilling fluids such as:
    a. Sulphonated copolymers of acrylic and maleic acids,
    b. Calcium/iron lignosulfonates,
    c. Nonylphenol ethoxylated fatty alcohols/acid/esters containing phosphate or sulfate functional groups.

2. Alkoxylated fatty alcohols/acids and sulfonic acids-based dispersants showed high potential to disperse Mn_3O_4 oil-based drilling fluids. The number of alkoxylated units and presence of phosphate functional group may change the dispersion capacity.

3. Acrylate and lignosulphonate-based dispersants were not effective with manganese tetraoxide oil-based fluid.

4. Mono- and Divalent salts may reduce the dispersion of manganese tetraoxide. Thus, testing dispersants in the presence of divalent salts is important to ensure the effectiveness of the dispersion process.

5. The presence of dispersants in manganese tetraoxide drilling lowered the sagging tendency and rheological behavior of the drilling fluid in most examined cases.

6. The quality of manganese tetraoxide particles (i.e. narrow PDS range) can minimize the particles aggregation caused by the particle size.

7. Particle settling and zeta potential measurement are important initial steps to compare the effectiveness of dispersants.

8. The optimum dispersant concentration was found below 1 wt% and nearly 0.5 wt% for water-based fluids.

9. The effectiveness of anionic lignosulfonates can be higher than that of nonionic lignosulfonates with water-based fluids.

10. Effective dispersants with manganese tetraoxide oil-based drilling fluids may not be suitable for other oil-based drilling fluids (e.g. ilmenite and barite oil-based drilling fluids)

11. Increasing the dispersant loading (e.g. from 7 to 28 g/l oil) may improve the dispersion capacity for oil-based systems.

12. The Optimum dispersant concentration was between 0.2 and 2 wt%. A dispersant concentration of 1 wt% is recommended as a median concentration.
13. Glycolic acid can be used to dissolve Mn_3O_4-based filter cake by following either the single or two-step filter cake removal procedures.
14. Glycolic acid system can be more effective with sandstone formation.
15. The suggested glycolic acid concentrations are 7 and 10 wt% by using the single and two-step procedures, respectively.
16. The reaction rate of manganese tetraoxide particles can be controlled using surfactants A, B or C. They were based on sulfonic acid, maleic acid copolymer, and ethoxylated phosphate ester.

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APPENDIX A

DISPERSANTS INFORMATION AND DATA FOR WATER-BASED FLUIDS

No.	Chemical ingredient	Origin	HFR	Other
A01	Biopolymer sulphonated acrylate and malic copolymer (anionic)	Liquid	100	Yellow, little foam
A02	Tristyrylphenol ethoxylate phosphate ester	Viscous liquid	110	Clear, little foam
A03	Propylene glycol, tristylphenol phosphate ester, potassium salt	Liquid	110	Clear, little foam
A04	Tristyrylphenyl ether phosphate, TEA salt		110	Clear, little foam
A05	Ethoxylated alcohol sodium laureth sulfate, fatty alcohol(c12-14), poly ethylene glycol, ethersulphate sodium salt	Liquid		Clear, foam
A06	Alkyl benzene sulphonic acid, sodium salt	Liquid		Clear, foam
A07	Nonylphenol ethoxylate phosphate ester (10 EO), phosphate (97 wt%)	Liquid	210	Clear, foam
A08	Nonylphenol ethoxylate phosphate ester (6 EO), phosphoric acid (<3 wt%)	Liquid	210	Cloudy white, foam
A09	Nonylphenol ethoxylate phosphate ester (12 EO), phosphate (97 wt%)	Liquid	210	Clear, foam
A10	Tridecyl alcohol phosphate ester (3 EO) phosphoric acid (<3 wt%)	Liquid	310	Clear, foam
A11	Tridecyl alcohol phosphate ester (6 EO) nonylphenol ethoxylate phosphate (97 wt%)	Liquid	310	Cloudy white, foam
A12	Phosphoric acid	Liquid	210	Clear, foam
A13	Poly(methylvinylether/maleic acid) copolymer	Powder		
A14	2-butenedioic acid-polymer with methoxyethene 2513-40-6	Powder		
B13	Tridecyl alcohol phosphate ester (12 eo),phosphoric acid	Liquid	210	Clear, foam
B14	Sodium laureth sulfate 26-28 % (alcohols, c12-14, ethoxylated, sulfated, sodium salts)	Liquid gel		Clear, foam
B15	Calcium lignosulfonate (anionic)	Solid powder		Dark, no foam
B16	Iron lignosulfonate salt (anionic)	Solid		Dark, no foam
B17	Iron lignosulfonate salt (anionic)	Solid		Dark, little foam
B18	Anionic acrylic copolymer	Liquid	110	
B19	Ethoxylated alcohol (5 EO), phosphate, c16-c18, polyalkylene glycol ether carboxylic acids	Liquid		Cloudy white, no foam
B20	Polyethylene glycol ether acetic acid, alkoxylated fatty acids	Liquid		Cloudy white, foam

No.	Chemical ingredient	Origin	HFR	Other
B21	Oxoalcohol, polyethylene glycol, poly propylene glycol, acetic acid (alcohols, c12-14, ethoxylated, sodium salts)	Liquid	1N0	Yellow, foam
B22	Dinonylphenol, ethoxylated, carboxymethylated	Liquid		Cloudy white, foam
B23	Lignosulfonate blend polyelectrolyte polymers of sulfonated lignin - nonionic	Powder		Dark, foam
B24	Sodium c13-17 alkane sulfonate	Liquid		Yellow, foam
B25	Ferrochrome lignosulfonate			
C25	Lignosulfonate blend polyelectrolyte polymers of sulfonated lignin- anionic	Powder	110	Black, foam
C26	Lignosulfonate blend polyelectrolyte polymers of sulfonated lignin -nonionic	Powder	110	Black, foam
C27	Sodium polyacrylate	Liquid	100	Clear
C28	Anionic / lignosulfonate blend polyelectrolyte polymers of sulfonated lignin	Powder	110	Black, foam
C29	Acrylate polymer	Liquid	100	Clear
C30	Polyether-carboxylate polymer	Solid-powder	1N0	Clear
C31	Dodecyl benzene sulfonic acid	Liquid	310	
C32	Proprietary (0.48 g/cm^3, ph. (1% water = 10)	Solid-powder	230	
C33	Sodium alkylbenzenesulphonate	Powder		Clear, foam
C34	Ethoxylated nonylphenol $C_{15}H_{23}$ O-(C_2H_4O)n pH of 10.5 to 12	Liquid	210	
C35	Sodium butyl naphthalene sulfonate	Solid	210	
C36	Sulfonated synthetic polymer	Solid-powder	1N0	
C37	Ethoxylated alcohol (alcohols, c6-c12, ethoxylated)	Liquid	210	Cloudy white, foam
C38	Ethylene glycol, polyethylene glycol, terephthalic acid copolymer			Cloudy white, foam
C39	Ethoxylated alcohol, trideceth-9 (isotridecanol, ethoxylated)	Liquid	210	Clear, foam
C40	Sodium diisopropyl naphthalene sulfonate	Solid	310	Light yellow, foam
C41	Ethylene glycol, polyethylene glycol, terephthalic acid copolymer	Granules		
C42	Ethoxylated alcohol	Liquid	210	Cloudy white, foam
C43	Laurylamine,ethoxylated	Liquid		Clear
C44	Ethoxylated alcohol (isotridecanol, ethoxylated)	Cloudy liquid	210	Cloudy white, foam
C45	Ethoxylated alcohol (alcohols, c10-c16, ethoxylated)	Liquid	210	Clear, foam
C46	Ethoxylated polyoxypropylene, HO(C_3H_{40})m (C_2H_4O)0(C_3H_6)nH	Liquid	110	

No.	Chemical ingredient	Origin	H	F	R	Other
C47	Ethoxylated alcohol	Liquid	2	1	0	Yellow, foam
C48	Ethoxylated alcohol (alcohols, c10-c16, ethoxylated)	Liquid	2	1	0	Clear, foam
C49	Ethoxylated alcohol (alcohols, c10-c16, ethoxylated)	Liquid	2	1	0	Clear, foam
C50	Ethoxylated alcohol (isotridecanol, ethoxylated)	Liquid	2	1	0	Clear, foam
C51	1-hexanol, hexy alcohol	Liquid	2	2	0	Clear, phase separation
C52	Organic acid	Liquid	1	1	0	Cloudy yellow
C53	Linear primary alcohol mixture (1-decanol, 1-octanol, 1-hexanol)	Liquid	2	2	0	Clear, phase separation
C54	Alcohols, c20-c28, ethoxylated	Solid	1	1	0	Clear, foam, ppt, ps
C55	Ethoxylated alcohol (alcohols, c6-c12, ethoxylated)	Liquid	2	1	0	Clear, foam, ps
C56	Polyether-carboxylate polymer	Solid-powder				Not compatible
C57	Sulphonated organic polymer	Solid-powder	1	1	0	Not compatible
C58	Sulfonated synthetic polymer	Solid-powder	1	1	0	Not compatible

No.	Chemical ingredient	Company	Origin	HFR	Other
S1	Ethoxylated alcohol (5 EO), phosphate, c16-c18, polyalkylene glycol ether carboxylic acids		Liquid		Clear, foam
S2	(isononanol, ethoxylated, propoxylated, carboxymethylated) fatty alcohol(c12-14), poly ethylene glycol, ether, acetic acid		Liquid		Clear, foam
S3	Ethoxylated alcohol (alcohols, c10-c16, ethoxylated), biodegradable, OCNS group D equivalent, non-bioaccumulative		Liquid	210	
S4	Ethoxylated alcohol (alcohols, c10-c16, ethoxylated)		Liquid	210	
S5	Ethoxylated alcohol (alcohols, c10-c16, ethoxylated), biodegradable, OCNS group D equivalent, non-bioaccumulative		Liquid	210	
S6	Ethoxylated alcohol		Solid	110	Cloudy white, foam
S7	Ethoxylated alcohol (isotridecanol, ethoxylated)		Liquid	210	
S8	Dinonylphenol,ethoxylated,carboxymethylated		Liquid		Cloudy clear
S9	Dodecylbenzene sulfonic acid, partly biodegradable, OCNS group b		Liquid	310	
S10	(alcohols, c12-14, ethoxylated, sodium salts) oxoalcohol, polyethylene glycol, poly propylene glycol, ether acetic acid		Liquid	110	Clear, foam
S11	Ethoxylated alcohol (isotridecanol, ethoxylated)		Cloudy liquid	210	Clear
S12	Sodium c13-17 alkane sulfonate		Liquid		Yellow ppt
S13	Ethoxylated alcohol, trideceth-9 (isotridecanol, ethoxylated)		Liquid	210	Ppt
S14	Ethoxylated alcohol		Liquid	210	Ps
S15	Tridecyl alcohol phosphate ester (6eo) nonylphenol ethoxylate phosphate (97 wt%)		Liquid	310	Ps
S16	Laurylamine,ethoxylated		Liquid		Dark
S17	Tridecyl alcohol phosphate ester (3eo) phosphoric acid (<3 wt%)		Liquid	310	Clear
S18	Linear primary alcohol mixture (1-decanol, 1-octanol, 1-hexanol)		Liquid	220	Clear, foam
S19	Ethoxylated alcohol (alcohols, c6-c12, ethoxylated)		Liquid	210	
S20	Ethoxylated alcohol (alcohols, c6-c12, ethoxylated)		Liquid	210	
S21	1-hexanol, hexy alcohol		Liquid	220	
S22	Aqueous solution of florinated polyether co polymer		Liquid	110	Clear

No.	Chemical ingredient	Company	Origin	HFR	Other
S23	Nonylphenol ethoxylate phosphate ester (10 EO) nonylphenol ethoxylate phosphate (97 wt%)		Liquid	210	Cloudy
S24	Nonylphenol ethoxylate phosphate ester (12 EO) nonylphenol ethoxylate phosphate (97 wt%)		Liquid	210	Cloudy white
S25	Polyether glycol monotridecyl ether phosphate,phosphoric acid		Liquid	210	Cloudy
S26	Sodium polyacrylate		Liquid	100	Clear
S27	Nonylphenol ethoxylate phosphate ester (6 EO) phosphoric acid (<3 wt%)		Liquid	210	Cloudy white
S28	Phosphoric acid		Liquid	210	Cloudy white
S29	Ethoxylated alcohol		Liquid	210	Cloudy white, foam
S30	Propylene glycol,tristylphenol phosphate ester,potassium salt		Liquid	110	Clear
S31	Tristyrylphenyl ether phosphate, phosphoric acid		Viscous liquid	110	Clear
S32	Acrylate polymer		Liquid	100	Clear
N33	Ethoxylated polyoxypropylene, $HO(C_3H_4O)m\ (C_2H_4O)0(C_3H_6)nH$		Liquid	110	Brown
N34	Ethoxylated nonylphenol $C_{15}H_{23}\ O$-$(C_2H_4O)n$ pH of 10.5 to 12		Liquid	210	Clear, foam
N35	Sodium butyl naphthalene sulfonate		Solid	210	
N36	Sodium diisopropyl naphthalene sulfonate		Solid	310	Clear
N37	Sodium laureth sulfate 26-28 % [alcohols, c12-14, ethoxylated, sulfated, sodium salts]		Liquid gel		Clear, foam, ps, ppt
N38	Iron lignosulfonate salt		Solid		Grey ppt
N39	Dodecylbenzene sulfonic acid,1-methoxy-2-propanol		Liquid	320	Clear, ppt
N41	Acrylic acid copolymer		Liquid	100	Clear, ppt
N42	Sodium alkylbenzenesulphonate		Powder		Cloudy, foam, ps, ppt
N43	Iron lignosulfonate salt		Solid		Grey ppt
N44	Anaionic calcium lignosulfonate		Solid powder		Brown ppt
N45	Diethylene glycol monobutyl ether		Liquid	210	Clear, ps, ppt
N46	Anionic acrylic copolymer		Liquid	110	Ps
N47	Anionic / lignosulfonate blend polyelectrolyte polymers of sulfonated lignin		Powder	110	Clear, ppt
N48	Isotridecanol, ethoxylated		Solid	110	Cloudy, foam, ps, ppt
N49	Alcohols, c20-c28, ethoxylated				Clear, ps, ppt
N50	Ethoxylated alcohol, cetearth-28		Solid	110	Clear, ps, ppt

No.	Chemical ingredient	Company	Origin	HFR	Other
N51	Aqueous solution of florinated polyether co polymer		Liquid	1 1 0	Clear, ps
N52	Alkyl benzene sulphonic acid sodium salt		Liquid		Cloudy , foam, ps, ppt
N53	Alcohols, c20-c28, ethoxylated		Solid	1 1 0	Cloudy , foam, ps, ppt
N54	Nonionic / lignosulfonate blend polyelectrolyte polymers of sulfonated lignin		Powder	1 1 0	Clear, ppt
N55	Ethoxylated alcohol		Solid	2 1 0	Cloudy, ps, ppt
N56	Poly(methylvinylether/maleic acid) copolymer		Powder		Cloudy white, ps, ppt
N57	Blend of fully biodegradable, surfactants, organic acids and plant extracts				Clear, ps
N58	Ethoxylated sulfated alcohol sodium laureth sulfate, fatty alcohol(c12-14), poly ethylene glycol, ethersulphate sodium salt		Liquid		Clear, ps, ppt
N59	Anionic / lignosulfonate blend polyelectrolyte polymers of sulfonated lignin		Powder	1 1 0	Brown, ppt
N60	Presence of acrylic acid and malic acid (anionic)		Liquid	1 0 0	Clear, ps
N61	Nonionic / lignosulfonate blend polyelectrolyte polymers of sulfonated lignin		Powder		Brown, ps, ppt
N63	Polyether-carboxylate polymer		Solid-powder	1 1 0	
N64	Dodecylbenzene sulfonic acid, 1-methoxy-2-propanol		Liquid	3 2 0	Clear, ps
N65	Polyether-carboxylate polymer		Solid-powder		
N66	Organic acid		Liquid	1 1 0	
N67	Sulfonated synthetic polymer		Solid-powder	1 1 0	
N68	Sulfonated synthetic polymer		Solid-powder	1 1 0	
N69	Sulphonated organic polymer		Solid-powder	1 1 0	

APPENDIX C

DYNAMIC AND STATIC SAG OF OIL-BASED DRILLING FLUIDS

Density, lbm/gal	Weighting Material	Oil/Water ratio	Dispersant	Contamination	Heat Aging/Rolling	Dynamic or Static Sag	Unit
16.3	Mn_3O_4	90/10	-	-	-	0.08	lbm/gal
16.3	Mn_3O_4	90/10	S3	-	-	0.07	lbm/gal
16.3	Mn_3O_4	90/10	S2	-	-	0.06	lbm/gal
16.3	Mn_3O_4	90/10	S5	-	-	0.04	lbm/gal
20	Mn_3O_4	90/10	-	-	-	0.27	lbm/gal
20	Mn_3O_4	90/10	S3	-	-	0.15	lbm/gal
20	Mn_3O_4	90/10	S5	-	-	0.11	lbm/gal
16.3	Mn_3O_4	90/10	-	Cement	-	0.13	lbm/gal
16.3	Mn_3O_4	90/10	S2	Cement	-	0.13	lbm/gal
16.3	Mn_3O_4	90/10	S5	Cement	-	0.06	lbm/gal
16.3	Mn_3O_4	90/10	S3	Cement	-	0.04	lbm/gal
16.3	Mn_3O_4	90/10	-	Clay	-	0.24	lbm/gal
16.3	Mn_3O_4	90/10	S5	Clay	-	0.03	lbm/gal
16.3	Mn_3O_4	90/10	S3	Clay	-	0.03	lbm/gal
16.3	Mn_3O_4	90/10	S2	Clay	-	0.02	lbm/gal
20	Mn_3O_4	90/10	-	Cement	-	0.18	lbm/gal
20	Mn_3O_4	90/10	S5	Cement	-	0.14	lbm/gal
20	Mn_3O_4	90/10	-	Clay	-	0.20	lbm/gal
20	Mn_3O_4	90/10	S5	Clay	-	0.13	lbm/gal
16.3	Mn_3O_4	90/10		-	400.00	0.11	lbm/gal
16.3	Mn_3O_4	90/10	S2	-	400.00	0.15	lbm/gal
16.3	Mn_3O_4	90/10	S3	-	400.00	0.15	lbm/gal
16.3	Mn_3O_4	90/10	S5	-	400.00	0.07	lbm/gal
20	Mn_3O_4	90/10	-	-	400.00	0.25	lbm/gal
20	Mn_3O_4	90/10	S3	-	400.00	0.27	lbm/gal
20	Mn_3O_4	90/10	S5	-	400.00	0.14	lbm/gal
16.3	Mn_3O_4	90/10		Cement	400.00	0.09	lbm/gal
16.3	Mn_3O_4	90/10	S2	Cement	400.00	0.23	lbm/gal

Density, lbm/gal	Weighting Material	Oil/Water ratio	Dispersant	Contamination	Heat Aging/Rolling	Dynamic or Static Sag	Unit
16.3	Mn_3O_4	90/10	S3	Cement	400.00	0.10	lbm/gal
16.3	Mn_3O_4	90/10	S5	Cement	400.00	0.07	lbm/gal
16.3	Mn_3O_4	90/10		Clay	400.00	0.21	lbm/gal
16.3	Mn_3O_4	90/10	S3	Clay	400.00	0.25	lbm/gal
16.3	Mn_3O_4	90/10	S2	Clay	400.00	0.20	lbm/gal
16.3	Mn_3O_4	90/10	S5	Clay	400.00	0.16.3	lbm/gal
20	Mn_3O_4	90/10	-	Cement	400.00	0.34	lbm/gal
20	Mn_3O_4	90/10	S5	Cement	400.00	0.13	lbm/gal
20	Mn_3O_4	90/10	-	Clay	400.00	0.19	lbm/gal
20	Mn_3O_4	90/10	S5	Clay	400.00	0.11	lbm/gal
20	Mn_3O_4	90/10	-	-	400.00	0.508	Static
20	Mn_3O_4	90/10	S3	-	400.00	0.509	Static
20	Mn_3O_4	90/10	S5	-	400.00	0.507	Static
20	Mn_3O_4	90/10	-	Cement	400.00	0.503	Static
20	Mn_3O_4	90/10	S5	Cement	400.00	0.503	Static
20	Mn_3O_4	90/10	-	Clay	400.00	0.502	Static
20	Mn_3O_4	90/10	S5	Clay	400.00	0.503	Static
17.5	Mn_3O_4	80/20	S1/S5	-	400.00	0.507	Static
17.5	Mn_3O_4	80/20	S5	-	400.00	0.507	Static
17.5	Mn_3O_4	80/20	S1	-	400.00	0.505	Static
17.5	API $BaSO_4$	80/20	S5	-	400.00	0.528	Static
17.5	$FeTiO_3$	80/20	S5	-	400.00	0.511	Static
17.5	Mn_3O_4	80/20	S5	-	400.00	0.507	Static

APPENDIX D

SHEAR STRESSES FOR MN3O4 WATER-BASED DRILLING

FLUIDS

(a)

(b)

Shear stresses for 17.5 lbm/gal water-based drilling fluid contaminated with cement: a) before heat aging, b) after heat aging at 400°F for 16 hrs. Dispersant concentration was 8 g/l water.

(a)

(b)

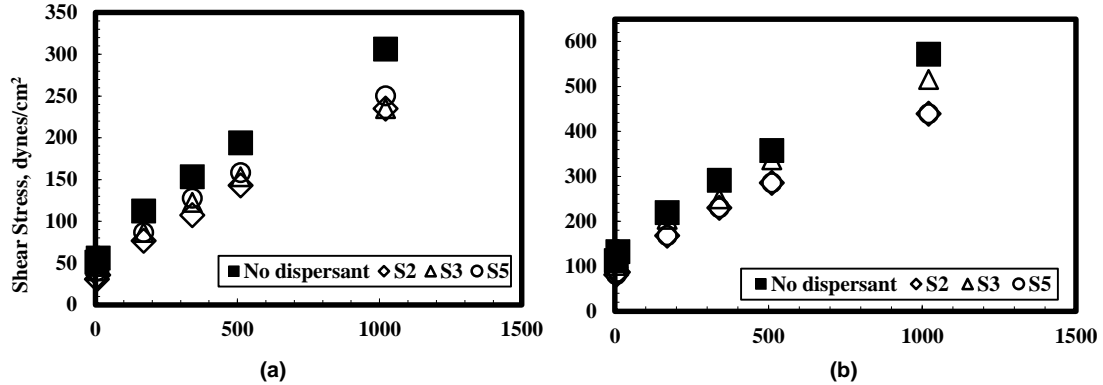**Shear stresses for 20 lbm/gal water-based drilling fluid contaminated with cement: a) before heat aging, b) after heat aging at 400°F for 16 hrs. Dispersant concentration was 15 g/l water.**

(a)

(b)

Shear stresses for 17.5 lbm/gal water-based drilling fluid contaminated with cement and rock salt: a) before heat aging, b) after heat aging at 400°F for 16 hrs. Dispersant concentration was 8 g/l water.

Shear stresses for 20 lbm/gal water-based drilling fluid contaminated with cement and rock salt: a) before heat aging, b) after heat aging at 400°F for 16 hrs. Dispersant concentration was 15 g/l water.

Shear stresses for 17 lbm/gal water-based drilling fluid contaminated with cement or rock salt: a) before heat aging, b) after heat aging at 400°F for 16 hrs. Dispersant concentration was 8 g/l water.
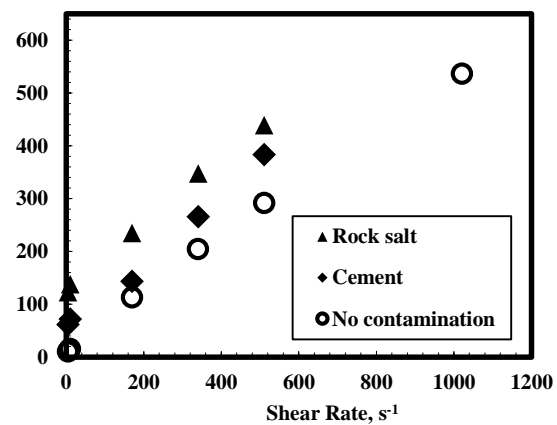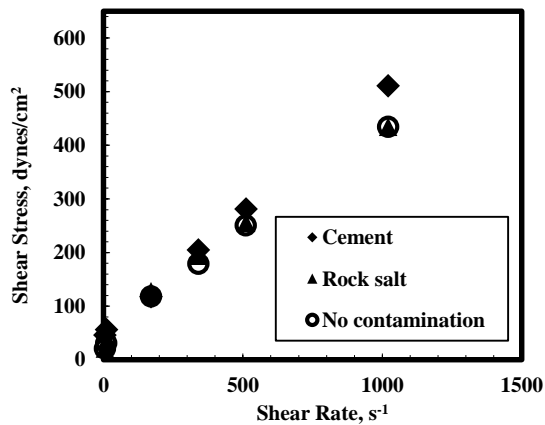
Shear stresses for 20 lbm/gal water-based drilling fluid contaminated with cement or rock salt: a) before heat aging, b) after heat aging at 400°F for 16 hrs. Dispersant concentration was 15 g/l water.
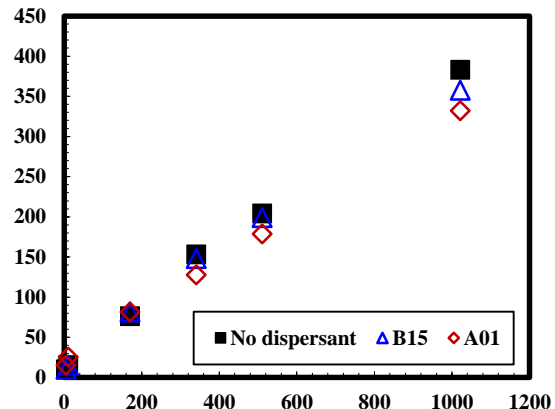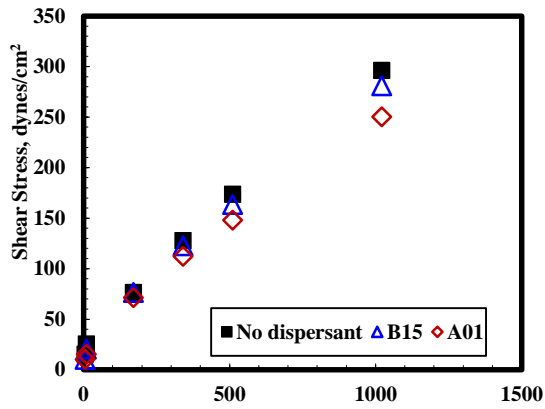
Shear stresses for 17.5 lbm/gal non-contaminated water-based drilling fluids: a) before heat aging, b) after heat aging at 400°F for 16 hrs. Dispersant concentration was 8 g/l water.
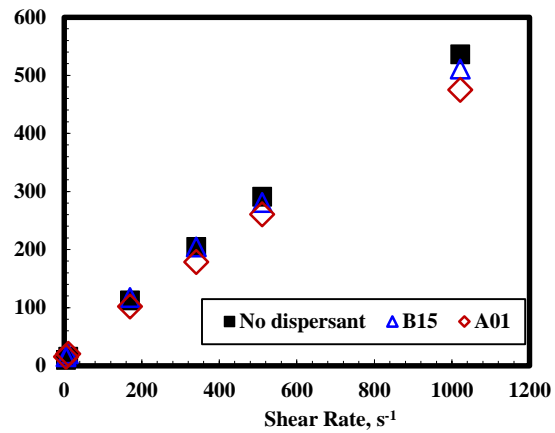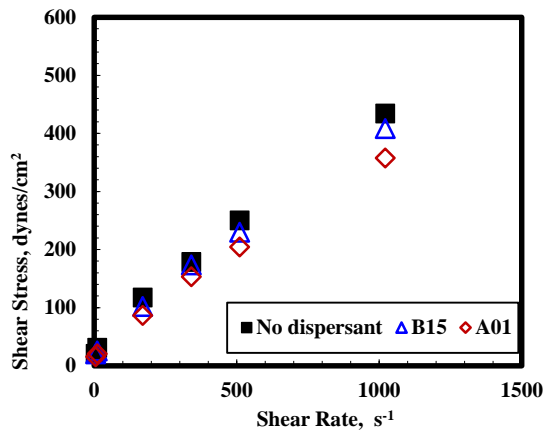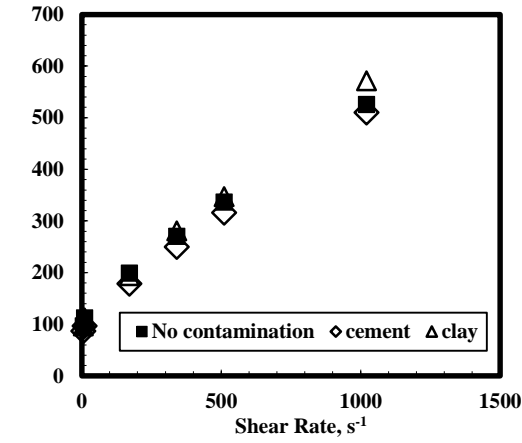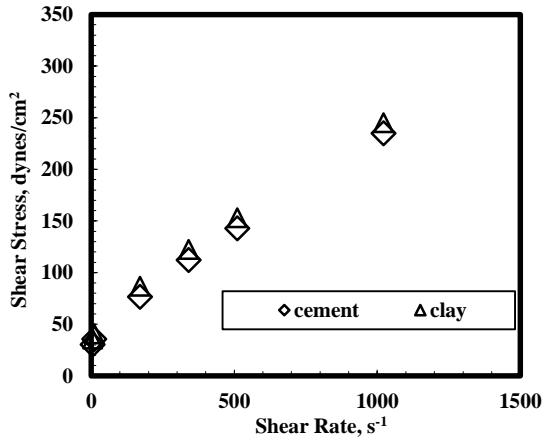

Shear stresses for 20 lbm/gal non-contaminated water-based drilling fluids: a) before heat aging, b) after heat aging at 400°F for 16 hrs. Dispersant concentration was 15 g/l water.
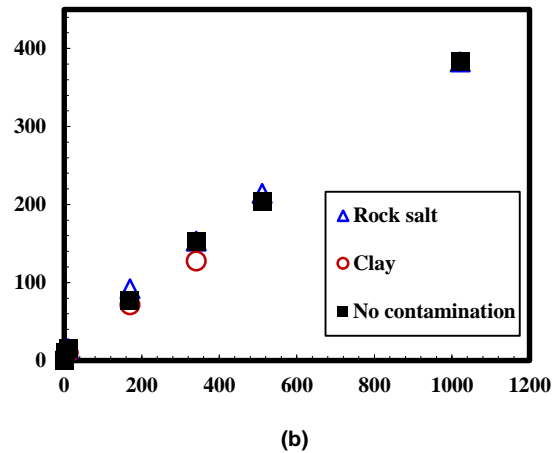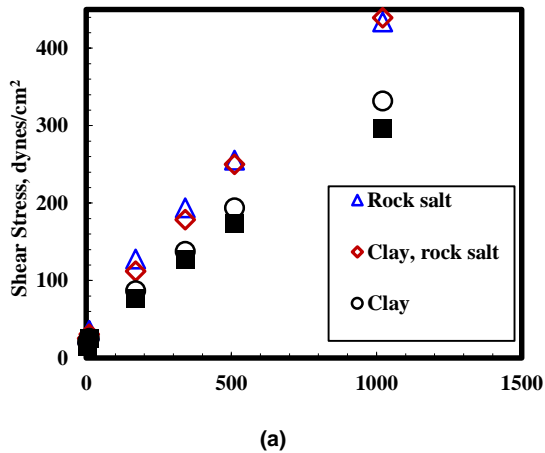
**Shear stresses for 17.5 lbm/gal contaminated water-based drilling fluids: a) before heat aging, b) after heat aging at 400°F for 16 hrs.**
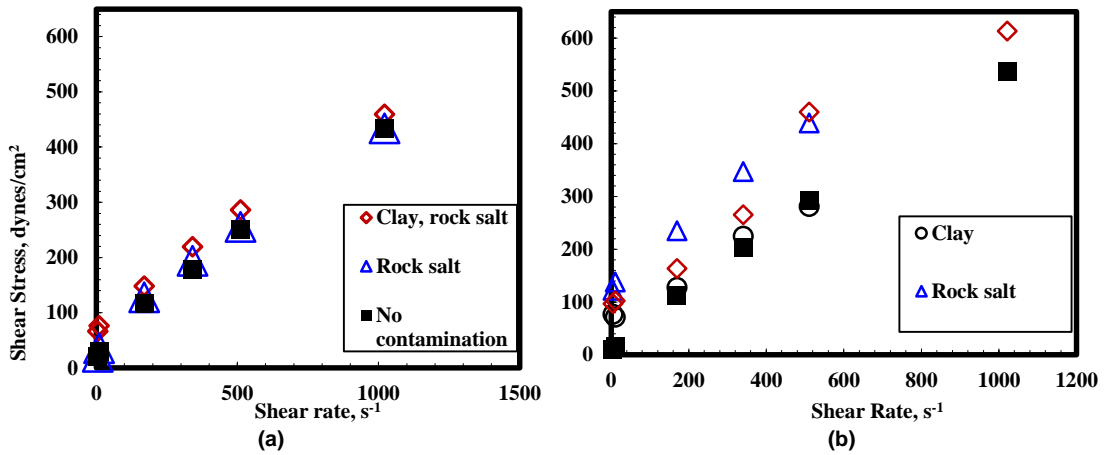
Shear stresses for 20 lbm/gal contaminated water-based drilling fluids: a) before heat aging, b) after heat aging at 400°F for 16 hrs.
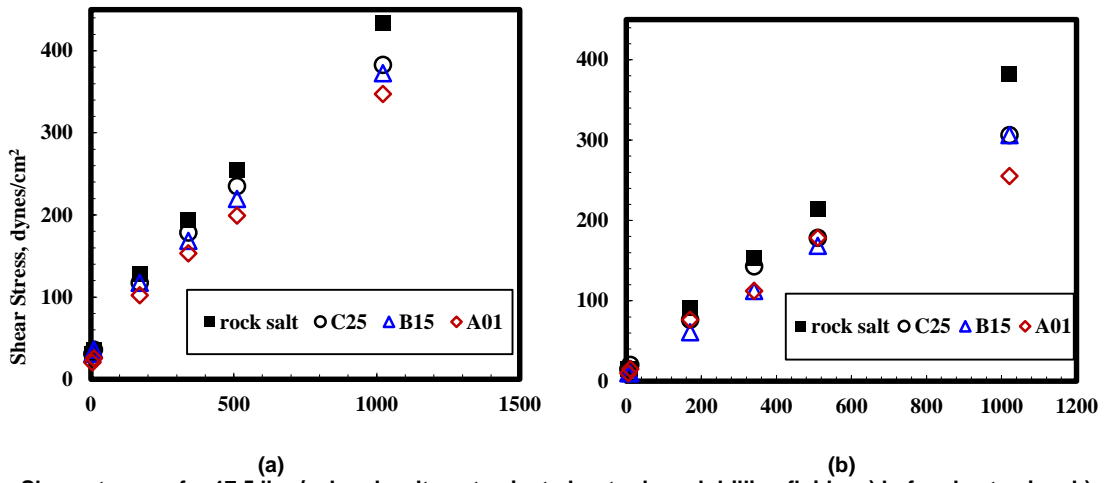
Shear stresses for 17.5 lbm/gal rock salt contaminated water-based drilling fluids: a) before heat aging, b) after heat aging at 400°F for 16 hrs. Dispersant concentration was 8 g/l water.
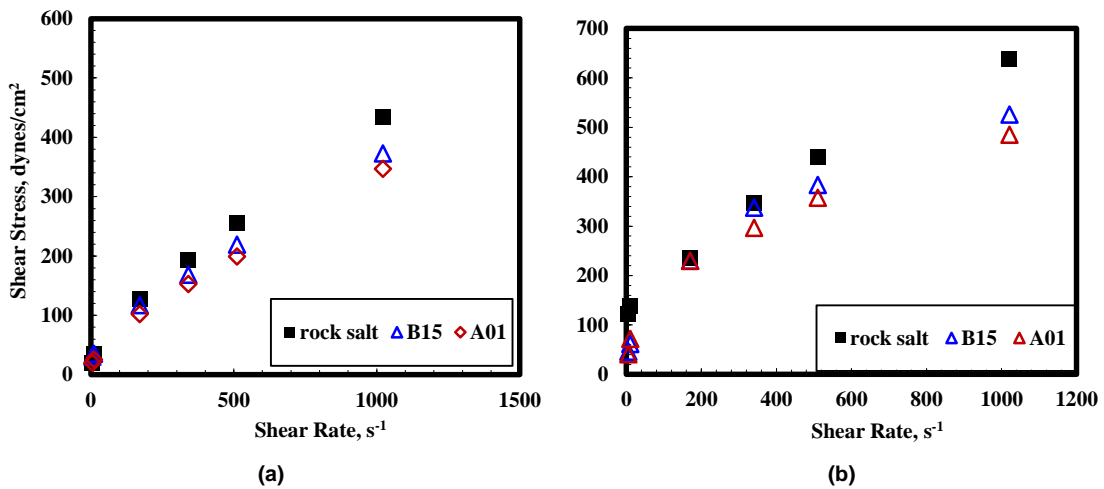
Shear stresses for 20 lbm/gal rock salt contaminated water-based drilling fluids: a) before heat aging, b) after heat aging at 400°F for 16 hrs. Dispersant concentration was 15 g/l water.

(a)   (b)
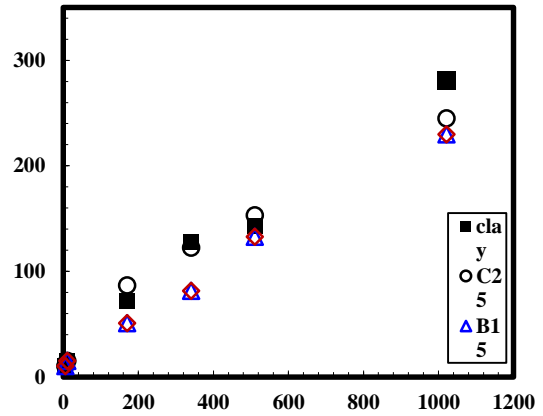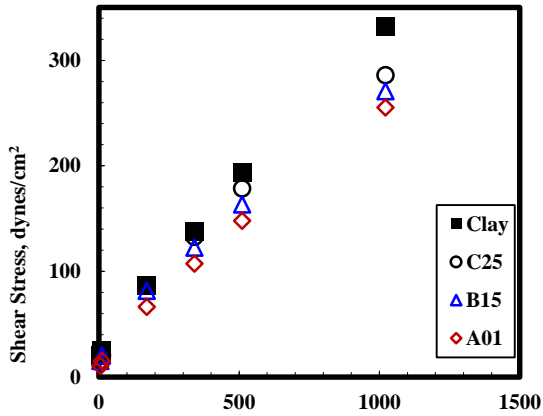
Shear stresses for clay and rock salt contaminated 17.5 lbm/gal water-based drilling fluids: a) before heat aging, b) after heat aging at 400°F for 16 hrs. Dispersant concentration was 8 g/l water.

(a)   (b)
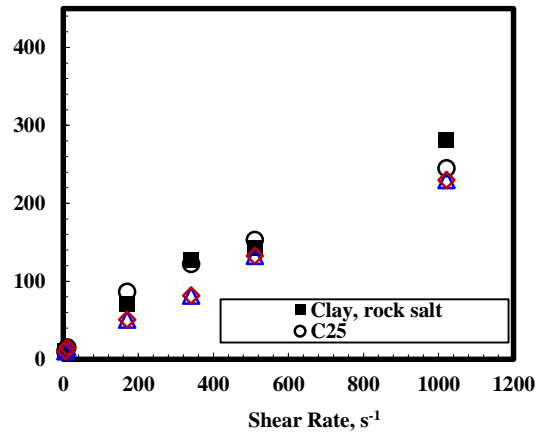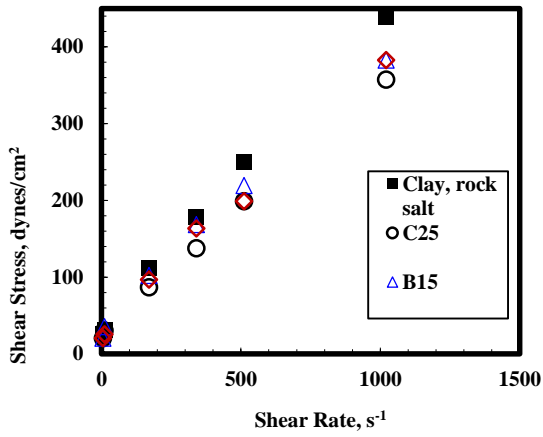
Shear stresses for clay and rock salt contaminated 20 lbm/gal water-based drilling fluids: a) before heat aging, b) after heat aging at 400°F for 16 hrs. Dispersant concentration was 15 g/l water.

VISCOSITIES AND SHEAR STRESSES FOR MN3O4 OIL-BASED

DRILLING FLUIDS

(a)   **(b)**

Shear stresses for non-contaminated 16.3 lbm/gal oil-based drilling fluids: a) before heat aging, b) after heat aging at 400°F for 16 hrs. Dispersant concentration was 8 g/l oil.
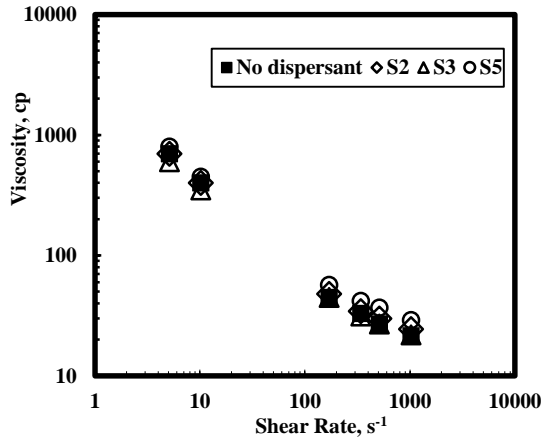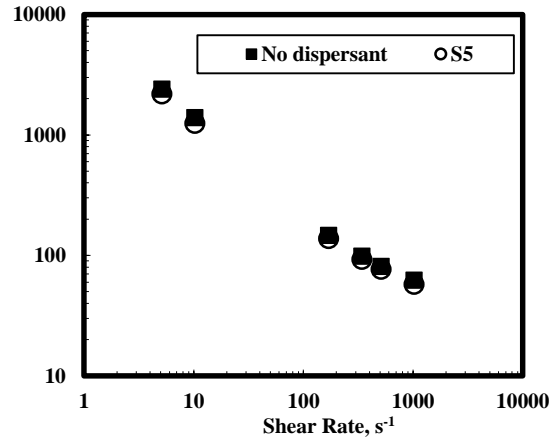

(a)   **(b)**
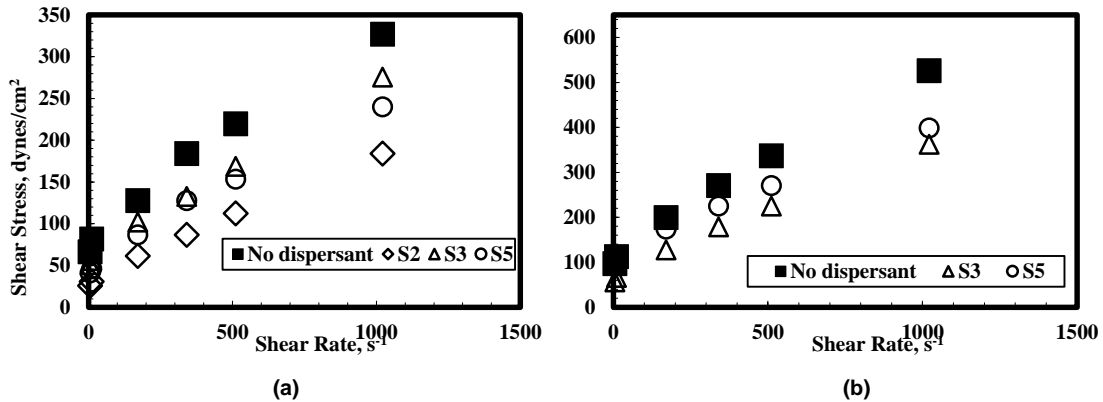
Shear stresses for non-contaminated 20 lbm/gal oil-based drilling fluids: a) before heat aging, b) after heat aging at 400°F for 16 hrs. Dispersant concentration was 15 g/l oil.
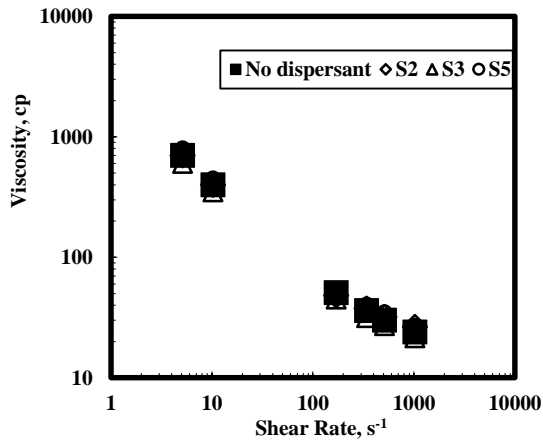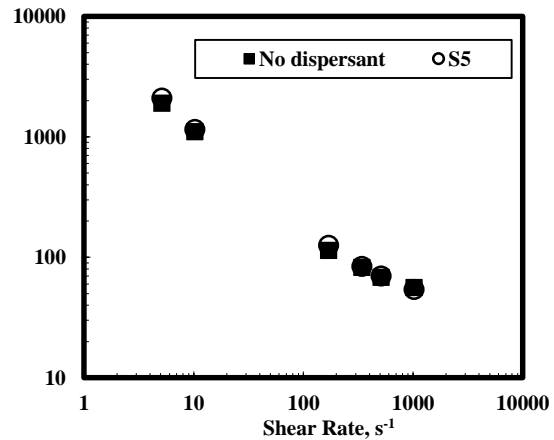

(a)   **(b)**
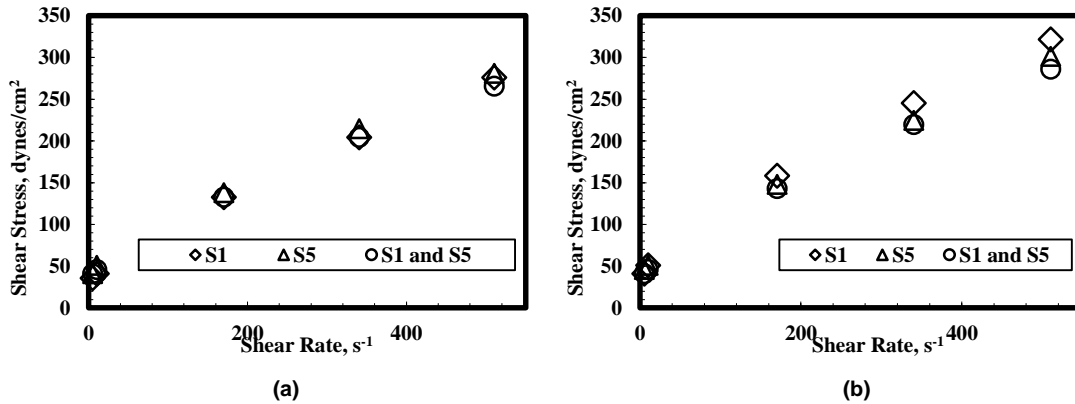
Shear stresses for non-contaminated 17.5 lbm/gal oil-based drilling fluids: a) before heat aging, b) after heat aging at 400°F for 16 hrs.
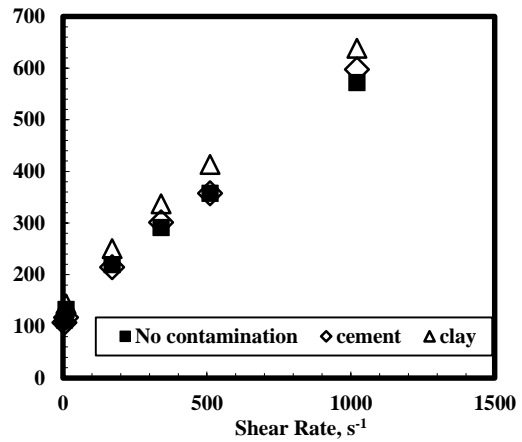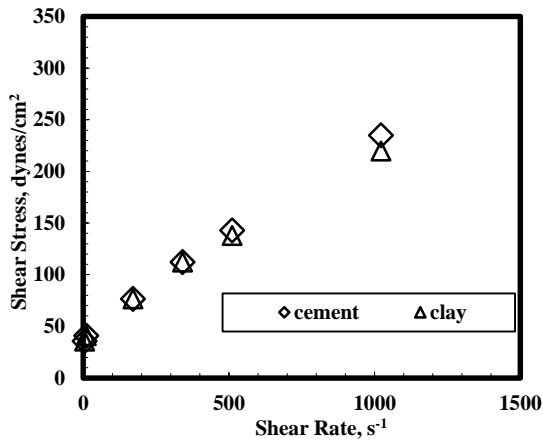
Shear stresses for -contaminated 16.3 lbm/gal oil-based drilling fluids: a) before heat aging, b) after heat aging at 400°F for 16 hrs.

Shear stresses for -contaminated 20 lbm/gal oil-based drilling fluids: a) before heat aging, b) after heat aging at 400°F for 16 hrs.
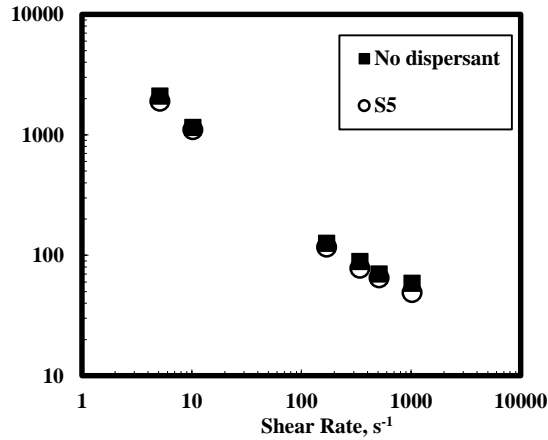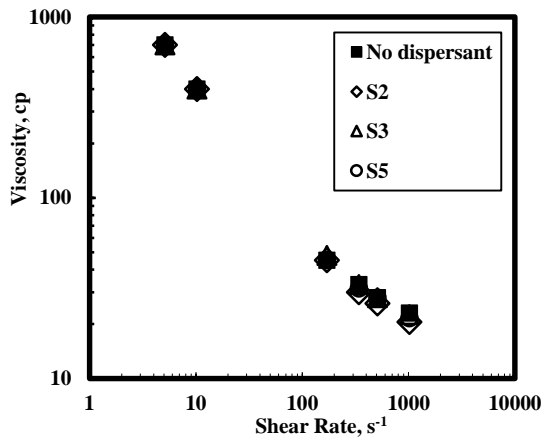
Viscosities for cement contaminated 16.3 lbm/gal oil-based drilling fluids: a) before heat aging, b) after heat aging at 400°F for 16 hrs. Dispersant concentration was 8 g/l oil.
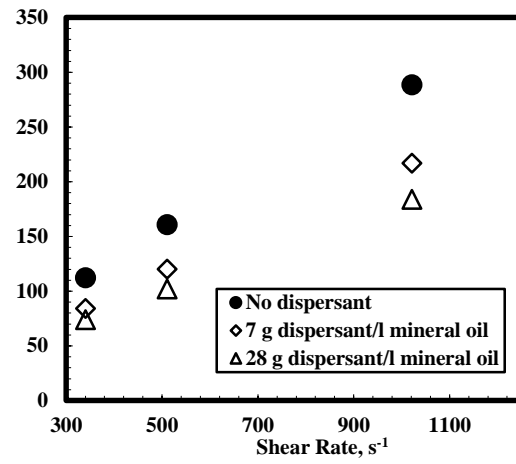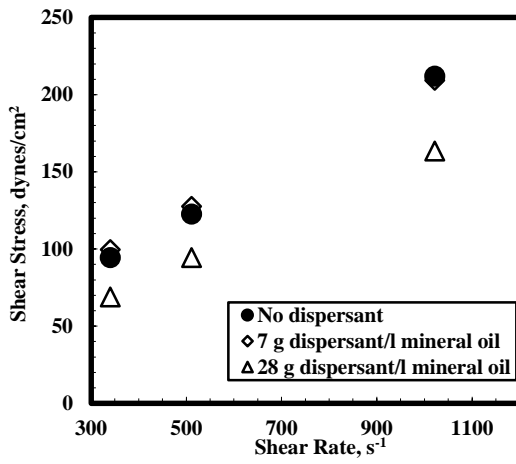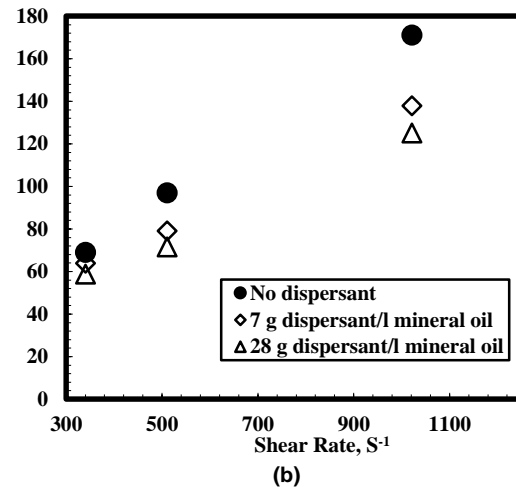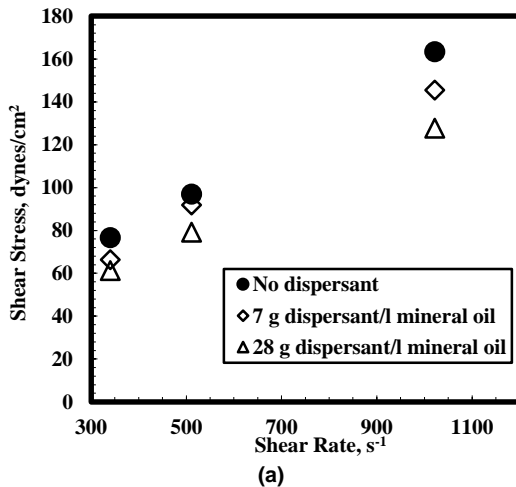
(a)   **(b)**
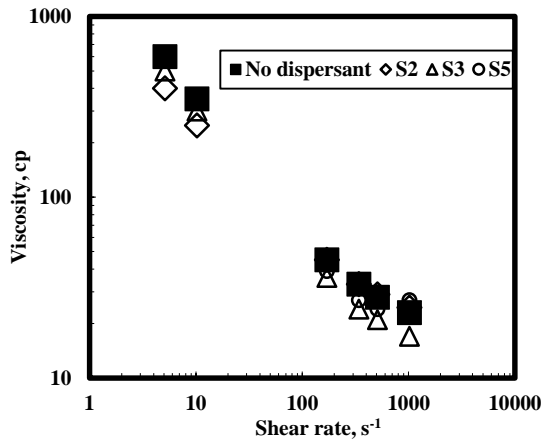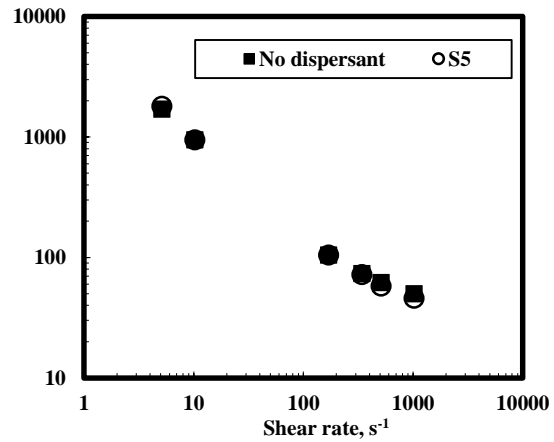
Viscosities for cement contaminated 20 lbm/gal oil-based drilling fluids: a) before heat aging, b) after heat aging at 400°F for 16 hrs. Dispersant concentration was 15 g/l oil.


(a)   **(b)**

Viscosities for clay contaminated 16.3 lbm/gal oil-based drilling fluids: a) before heat aging, b) after heat aging at 400°F for 16 hrs. Dispersant concentration was 8 g/l oil.


(a)   **(b)**

Viscosities for clay contaminated 20 lbm/gal oil-based drilling fluids: a) before heat aging, b) after heat aging at 400°F for 16 hrs. Dispersant concentration was 15 g/l oil.

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Shear stresses for non-contaminated 13.8 lbm/gal oil-based drilling fluids: a) before heat aging, b) after heat aging at 350°F for 16 hrs. Viscometer reading was at 77°F

Shear stresses for non-contaminated 13.8 lbm/gal oil-based drilling fluids: a) before heat aging, b) after heat aging at 350°F for 16 hrs. Viscometer reading was at 120°F
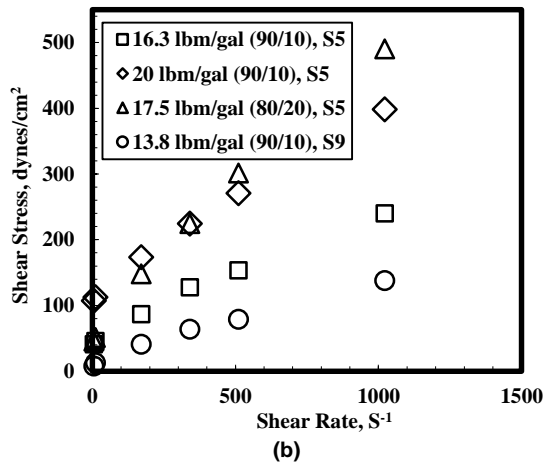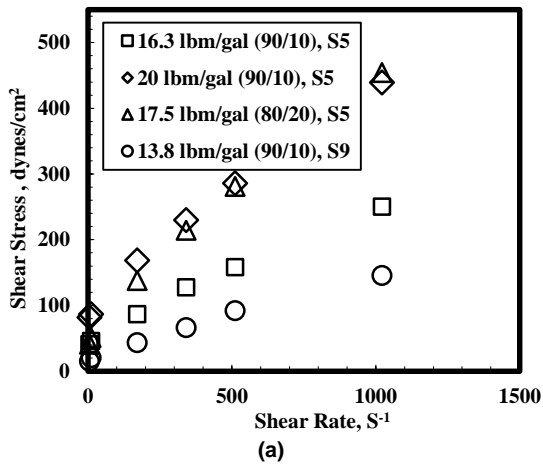
Shear stresses for oil-based drilling fluids: a) before heat aging, b) after heat aging at 400°F for 16 hrs.

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