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New Acid Soluble Drilling Fluids: Analysis of Two Cases

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List of abbreviations and symbols

WBM	Water based mud / drilling fluid
YP	yield point
LSYP	low shear yield point
PV	plastic viscosity
ppb	pounds per barrel
ECD	equivalent circulating density
cp	centipoise
HPHT	high pressure, high temperature
pcf	pounds per cubic foot (lbm/ft3)
rpm	revolution per minute
SG	specific gravity
NPT	Nonproductive time
ROP	Rate ofpenetration
Pf	filtrate alkalinity
Pm	mud alkalinity
CMC	carboxyl-methyl cellulose
PDC	Polycrystalline Diamond
PHPA	encapsulating polymer composite
OBM	Oil based mud

Introduction

Nowadays one of the primary causes of nonproductive time suffered by the worldwide oil industry is a stuck pipe in the wellbore due to differential sticking (Mitchell 2002; Santos 2000). The ability to free stuck pipes, then, becomes essential to optimize both nonproductive time and monetary costs. In case of a stuck pipe incident, if pulling and working the string has failed to free the pipe, spotting fluids are generally used around the stuck part of the string, in an attempt to eliminate the root cause of the sticking. These fluids function by attacking the filter cake and breaking it down, resulting in a reduction of the bond between cake and pipe.

Among spotting fluids, diesel oil has found the most use with a success rate of around 51% (Clark et all, 1992) (Krol, 1981). However, due to environmental concerns, a number of environmentally friendly alternatives have been introduced and have gained more traction over the years (Kercheville 1986), with one such fluid being a mixture of water/brine with polyethylene glycol (Walker 1980; Halliday 1989). Alternatives include spotting fluids comprised of aqueous lower alcohols with a weighting agent (Walker 1985), and two-phase spotting fluids comprised of a mixture calcium chloride brine and commercial spotting fluid. Surfactant-based spotting fluids, used to free drills by means of lubrication, also find use due to their environmentally friendly nature (Toro 2014). A study of literature reveals that due to filter-cake being barite-based, a variety of barite dissolvers, each comprising of different chelating agents, are used as additives (Montgomery 2007). Heat generating spotting fluids, which, due to the exothermic heat generation, loosen the stuck zones downhole are also used (Hilfiger 2017).

These spotting fluids require a lot of time to break down the filter cake. Any spotting fluid pill used in the wellbore requires a minimum of 12 hours of soak time to release the stuck pipe. This involves a lot of rig time, chemicals, crew support, and therefore a lot of money.

Instead of using remedial measures to release the stuck pipe from the wellbore, it was decided to develop a fluid, which would help to prevent the stuck pipe in the first place. It was decided to modify conventional barite based water based muds, especially the high density muds, to make them more stuck-pipe resistant. This work describes the analysis of two cases of the formulation of new drillings muds formulated with a combination of barite and manganese tetroxide: 100pcf and 150pcf, and 120pf and 150pcf respectively. These fluids are more sag resistant and show better rheology as compared to conventional muds formulated with 100% barite. The thin filter-cake obtained for the new high-density drilling muds makes it more resistant to differential sticking as compared to the conventional muds formulated with 100% barite. For high-density fluids, which can be more prone to differential sticking, acid-soluble manganese tetroxide would help in releasing the pipe in case there is a stuck-pipe incident. Aqueous solutions of different organic acids have been shown in this paper to dissolve the manganese tetroxide thereby disrupting the filter-cake formed by these new water based muds. Therefore, instead of using expensive spotting fluids, a viscosified acid pill would be able to release the pipe in case of a stuck- pipe incident.

In more details in the first chapter we will talk about drilling fluid, its functions and properties, such as viscosity, density, gel strength, filtration, sand content, pH determination and etc. In chapter 2 we will discuss classification of all exist kinds of drilling fluids like water-based, oil-based and gas-based drilling fluids. Starting from the third chapter the analysis starts directly. We will introduce you to two exist cases of formulations of drilling fluids based on the combination of two different weighting agents of barite and manganese tetroxide - Mn_3O_4. The concept is to describe the formulation of medium and high-density drilling fluids in two cases with 100 pcf and 150pcf, and 120 pcf and 150 pcf density fluids and analyze their results in terms of such parameters as plastic viscosity, yield point, gel strength and low shear yield point. Moreover, in this chapter we will get known with static aging process of 150pcf and 120pcf at different temperatures, and filter-cake breaking experiments of WBMs using different organic acids are described. In the results chapter we see the comparison of rheological data of 120pcf and 150 pcf WBM formulated with a combination of barite and manganese tetroxide and 100% barite and the results of static aging studies in both cases. Based on the results and graphs that we give in this chapter, we will confirm then the effectivity of combination of barite and manganese tetroxide than the single use of 100% barite only, as they show good sag resistance and minimal free water separation.

1. Theoretical background

Drilling fluid or drilling mud is a critical component in the rotary drilling process. Its primary functions are to remove the drilled cuttings from the borehole whilst drilling and to prevent fluids from flowing from the formations being drilled, into the borehole. Since it is such an integral part of the drilling process, many of the problems encountered during the drilling of a well can be directly, or indirectly, attributed to the drilling fluids and therefore these fluids must be carefully selected and/or designed to fulfil their role in the drilling process. Functions and Properties of a Drilling Fluid

Table 1 - Functions and physical properties of drilling fluid

Function	**Physical/Chemical Property**
Transport cuttings from the Wellbore	Yield Point, Apparent Viscosity, Velocity, Gel Strength
Prevent Formation Fluids Flowing into the Wellbore	Density
Maintain Wellbore Stability	Density, Reactivity with Clay
Cool and Lubricate the Bit	Density, velocity
Transmit Hydraulic Horsepower to Bit	Velocity, Density, Viscosity

The drilling fluid must be selected and or designed so that the physical and chemical properties of the fluid allow these functions to be fulfilled. However, when selecting the fluid, consideration must also be given to:

• the environmental impact of using the fluid

• the cost of the fluid

• the impact of the fluid on production from the pay zone.

1.1.1. Remove cuttings from the Wellbore

The primary function of drilling fluid is to ensure that the rock cuttings generated by the drilllbit are continuously removed from the wellbore. If these cuttings are not removed from the bit face the drilling efficiency will decrease. It these cuttings are not transported up the annulus between the drillstring and wellbore efficiently the drillstring will become stuck in the wellbore. The mud must be designed such that it can:

• carry the cuttings to surface while circulating

• suspend the cuttings while not circulating

• drop the cuttings out of suspension at surface.

The rheological properties of the mud must be carefully engineered to fulfil these requirements. The carrying capacity of the mud depends on the annular velocity, density and viscosity of the mud. The ability to suspend the cuttings depends on the gelling (thixotropic) properties of the mud. This gel forms when circulation is stopped and the mud is static. The drilled solids are removed from the mud at surface by mechanical devices such as shale shakers, desanders and desilters. It is not economically feasible to remove all the drilled solids before recirculating the mud. However, if the drilled solids are not removed the mud may require a lot of chemical treatment and dilution to control the rheological properties of the mud (Al-Yasiri M.S., Al-Sallami W.T., 2015).

1.1.2.Prevent Formation Fluids Flowing into the Wellbore

The hydrostatic pressure exerted by the mud colom must be high enough to prevent an influx of formation fluids into the wellbore. However, the pressure in the wellbore must not be too high or it may cause the formation to fracture and this will result in the loss of expensive mud into the formation. The flow of mud into the formation whilst drilling is known as lost circulation. This is because a certain proportion of the mud is not returning to surface but flowing into the formation.

When drilling through permeable formations (e.g. sand) the mud will seep into the formation. This is not the same as the large losses of fluid which occurs in fractured formations, discussed above. As the fluid seeps into the formation a filter cake will be deposited on the wall of the borehole. Some fluid will however continue to filter through the filter cake into the formation. The mud and the filtrate can damage the productive formations in a number of ways. The loss of mud can result in the deposition of solid particles or hydration of clays in the pore space. The loss of filtrate can also result in the hydration of clays. This will result in a reduction in the permeability of the formation. In addition to damaging the productivity of the formations the filter cake can become so thick it may cause stuck pipe. The ideal filter cake is therefore thin and impermeable.

1.1.3.Maintain Wellbore Stability

Data from adjacent wells will be useful in predicting borehole stability problems that can occur in troublesome formations (eg unstable shales, highly permeable zones, lost circulation, overpressured zones).

Shale instability is one of the most common problems in drilling operations. This instability may be caused by either one or both of the following two mechanisms:

• the pressure differential between the bottomhole pressure in the borehole and the pore pressures in the shales and/or,

• hydration of the clay within the shale by mud filtrate containing water.

The instability caused by the pressure differential between the borehole and the pore pressure can be overcome by increasing the mudweight. The hydration of the clays can only be overcome by using non water-based muds, or partially addressed by treating the mud with chemicals which will reduce the ability of the water in the mud to hydrate the clays in the formation. These muds are known as inhibited muds.

1.1.4.Cool and Lubricate the Bit

The rock cutting process will, in particular with PDC bits, generate a great deal of heat at the bit. Unless the bit is cooled, it will overheat and quickly wear out. The circulation of the drilling fluid will cool the bit down and help lubricate the cutting process.

1.1.5.Transmit Hydraulic Horsepower to Bit

As fluid is circulated through the drillstring, across the bit and up the annulus of the wellbore the power of the mud pumps will be expended in frictional pressure losses. The efficiency of the drilling process can be significantly enhanced if approximately 65% of this power is expended at the bit. The pressure losses in the system are a function of the geometry of the system and the mud properties such as viscosity, yield point and mud weight. The distribution of these pressure losses can be controlled by altering the size of the nozzles in the bit and the flowrate through the system. It is possible that in order to meet all of these requirements, and drill the well as efficiently as possible, more than one type of mud is used (e.g. water-based mud may be used down to the 13 3/8" casing shoe, and then replaced by an oil-based mud to drill the producing formation). Some mud properties are difficult to predict in advance, so the mud programme has to be flexible to allow alterations and adjustments to be made as the hole is being drilled, (e.g. unexpected hole problems may cause the pH to be increased, or the viscosity to be reduced, at a certain point) (Adams, N.J., 1985).

1.2. Field Tests on Drilling Fluids

The properties of drilling mud are regularly measured by the mud engineer. These measurements will be used to determine if the quality of the mud has deteriorated and requires treatment. The properties will be specified by the drilling engineer before the drilling operation commences but these properties may be adjusted if for instance it is found that the drilled cuttings are not being removed efficiently or if losses are experienced.

1.2.1.Mud Density

The density of the drilling mud can be determined with the mud balance. The cup of the balance is completely filled with a sample of the mud and

the lid placed firmly on top (some mud should escape through the hole in the lid). The balance arm is placed on the base and the rider adjusted until the arm is level. The density can be read directly off the graduated scale at the left-hand side of the rider.

1.2.2.Viscosity

Viscosity is a measure of a liquid’s resistance to flow. Two common methods are used on the rig to measure viscosity:

Marsh funnel: The Marsh Funnel is used to make a very quick test of the viscosity of the drilling mud. However, this device only gives an indication of changes in viscosity and cannot be used to quantify the rheological properties of the mud, such as the Yield Point or Plastic Viscosity.

Rotational viscometer: The multi-rate rotational viscometer is used to

quantify the rheological properties of the drilling mud. The assessment is made by shearing a sample of the mud, at a series of prescribed rates and measuring the shear stress on the fluid at these different rates. The essential elements of the device are a plumb bob attached to a torsion spring and deflection gauge and a cylinder which can be rotated at a range of rotary speeds. The plumb bob is suspended inside the cylinder and the whole is immersed in a sample of the drilling mud. When the outer cylinder is rotated the mud between the cylinder and plumb bob is sheared. The deflection of the plumb bob is a measure of the viscosity of the drilling fluid at that particular shear rate ((ACC), 2006).

1.2.3.Gel Strength

The gel strength of the drilling mud can be thought of as the strength of any internal structures which are formed in the mud when it is static. The gel strength of the mud will provide an indication of the pressure required to initiate flow after the mud has been static for some time. The gel strength of the mud also provides an indication of the suspension properties of the mud and hence its ability to suspend cuttings when the mud is stationary. The gel strength can be measured using the multi-rate viscometer.

1.2.4.Filtration

The filter cake building properties of mud can be measured by means of a filter press. The following are measured during this test:

• the rate at which fluid from a mud sample is forced through a filter under specified temperature and pressure.

• the thickness of the solid residue deposited on the filter paper caused by the loss of fluids.

The first of the above reflects the efficiency with which the solids in the mud are creating an impermeable filter cake and the second the thickness of the filter cake that will be created in the wellbore. This type of test does not accurately simulate downhole conditions in that only static filtration is being measured. In the wellbore, filtration is occurring under dynamic conditions with the mud flowing past the wall of the hole.

1.2.5.Sand Content

A high proportion of sand in the mud can damage the mud pumps and is therefore undesirable. The percentage of sand in the mud is therefore measured regularly using a 200 mesh sieve and a graduated tube. The glass measuring tube is filled with mud up to the scribe line. Water is then added up to the next scribe line. The fluids are mixed by shaking and then poured through the sieve. The sand retained on the sieve should be washed thoroughly to remove and remaining mud. A funnel is fitted to the top of the sieve and the sand is washed into the glass tube by a fine spray of water. After allowing the sand to settle the sand content can be read off directly as a percentage.

1.2.6.Liquid and Solid Content

If pipe sticking is to be avoided, the proportion of solids in the mud should not exceed 10% by volume. A carefully measured sample of mud is heated in a retort until the liquid components are vaporised. The vapours are then condensed, and collected in the measuring glass. The volume of liquids (oil and/or water) is read off directly as a percentage. The volume of solids (suspended and dissolved) is found by subtraction from 100%.

1.2.7.pH Determination

The pH of the mud will influence the reaction of various chemicals and must therefore be closely controlled. The pH test is a measure of the concentration of hydrogen ions in an aqueous solution. This can be done either by pHydrion paper or by a special pH meter. The pH paper will turn different colours depending on the concentration of hydrogen ions. A standard colour chart can be used to read off the pH to the nearest 0.5 of a unit (on a scale of 0 to 14).

With a pH meter the probe is simply placed in the mud sample and the reading taken after the needle stabilises. The meter gives a more accurate result to 0.1 of a unit.

1.2.8. Alkalinity

Although pH gives an indication of alkalinity it has been characteristics of a high pH mud can vary considerably despite constant pH. A further analysis of the mud is usually carried out to assess the alkalinity. The procedure involves taking a small sample, adding phenolphthalein indicator and titrating with acid until the colour changes. The number of ml of acid required per ml of sample is reported as the alkalinity. (Pf = filtrate alkalinity, Pm = mud alkalinity).

1.2.9. Chloride content

The amount of chloride in the mud is a measure of the salt contamination from the formation. The procedure for measuring the quantity of salt in the mud is to take a small sample of filtrate of the mud, adding phenolphthalein and titrating with acid until the colour changes. 25 - 50 ml of distilled water and a small amount of potassium chromate solution is then added. The solution is stirred continuously while silver nitrate is added drop by drop. The end point is reached when the colour changes.

1.2.10. Cation Exchange Capacity

This test gives an approximate measure of the bentonite (sodium montmorillonite) content of the mud. The sodium cation (Na^+) of bentonite is held loosely on the clay structure and is readily exchanged for other ions and certain organic compounds. Methylene blue is an organic dye which will replace the exchangeable cations in montmorillonite and certain other mud additives (eg organic compounds such as CMC, lignite). A small mud sample is put in a flask where it is first treated with hydrogen peroxide to remove most of the organic content. Methylene blue solution

is added in increments of 0.5 ml. After each increment the flask is well shaken, and while the solids are still suspended one drop is placed on filter paper. The end point is reached when the dye appears as a greenish-blue ring around the solids on the filter paper (Annis, R.M., Smith, V.M., 1996).

2. Classification of drilling fluids

The drilling fluids are complex mixtures formed from solids, liquids, chemicals, and sometimes even gases. From the chemical point of view, they can assume aspects of suspension, colloidal dispersion or emulsion, depending on the physical state of the components. The drilling fluids are generally classified under three distinct classes such as water-based drilling fluids, oil-based drilling fluids and synthetic-based drilling fluids. In the proper selection of the drilling fluid, there are some governing agents such as the type of formation encountered, temperature and pressure of the formation, ecological and environmental considerations and cost need to be put into consideration when a proper selection of the drilling fluid. Notwithstanding the efficacy of oil-based fluids, they can give negative impact to environment when the pollutant is discharged and subsequently dispersed to the sea. Their enhanced drilling performance decreases drilling time and provides advantaged safety, human health, and, in some cases, environmental performance above diesel oil fluids. They were developed to provide an environmentally superior alternative to oil-based drilling fluids.

There are several different types of drilling fluids, based on both their composition and use. The three key factors that drive decisions about the type of drilling fluid selected for a specific well are:

- Cost
- Technical performance
- Environmental impact.

Selecting the correct type of fluid for the specific conditions is an important part of successful drilling operations. In geotechnical engineering, drilling fluid is a fluid used to drill boreholes into the earth. In drilling rigs, drilling fluids help to do drill for exploration of oil and natural gas. Liquid drilling fluid is often called drilling mud (Mukherjee, 2013).

2.1. Water-based drilling fluids

Water-based drilling fluids account for 80% of the total drilling operation carried out due to their environment friendly nature and they are highly cost-effective as compared to the synthetic or oil-based drilling fluids. The choice of the drilling fluid depends on the factors (Medhi et al., 2019). These factors are:

- the location and the type of formation which is to be drilled,
- the variation in the pressure and temperature of the wellbore,
- the nature of the formation fluids i.e. strength, porosity and permeability
- factors while making the selection of the drilling fluids are production factors, environmental factors and safety.

The water-based fluids are used to drill approximately 80 % of all wells. These fluids may be fresh water, seawater, brine, saturated brine, or a formate brine. The type of fluid selected depends on anticipated well conditions or on the specific interval of the well being drilled. Some commercial bentonite or attapulgite also may be added to aid in fluid-loss control and to enhance hole-cleaning effectiveness. The water-based fluids fall into two broad categories such as nodispersed and dispersed. (Medhi et al., 2019).

Water itself may be used as a drilling fluid. However, most drilling fluids require some degree of viscosity to suspend the Barites and to carry drilled cuttings up the annulus of the wellbore. The viscosity of water based muds is generated by the addition of clay or polymers. However, the cheapest and most widely used additive for viscosity control is clay. The clay material in water based mud is responsible for two beneficial effects:

• an increase in viscosity which improves the lifting capacity of the mud to carry cuttings to the surface. (This is especially helpful in larger holes where annular velocity is low).

• building a wall cake in permeable zones, thus preventing fluid loss. The clays are not the only solids in a drilling fluid.

There are two types of solids which may be present in a water based mud:

• active solid - these are solids which will react with water and can be controlled by chemical treatment. These may be commercial clays or hydratable clays from the formations being drilled.

• inactive or inert solids - these are solids which do not readily react with water. These may be drill solids such as limestone or sand. Barite is also an inert solid. In order to appreciate how clays play an important part in water based muds some understanding of clay chemistry is necessary.

2.1.1.Clay Chemistry

Clay minerals can be divided into two broad groups.

• Expandable (hydrophilic) clays - these will readily absorb water (e.g. montmorillonite).

• Non-expandable (hydrophobic) clays - these will not readily absorb water (e.g. illite).

Expandable and Non-expandable clays in water the most commonly clay used in drilling fluids is Wyoming Bentonite (sodium montmorillonite). In fresh water the clay layers absorb water, the chemical bonds holding them together are weakened and the stack of layers disintegrates. This process is known as dispersion (i.e. less face-to-face association). Dispersion results in an increase in the number of particles in suspension, which in turn increases the number of suspended particles and causes the fluid to thicken or viscosify. During this process, positively charged cations separate from the clay surface leaving the flat surface of the particles negatively charged while the edges are positively charged. It is likely therefore that some plates will tend to form edge-to-face arrangements. This process is known as flocculation.

2.1.2.Additives to WBM's a.

a) Viscosity control additives

To reduce the viscosity of the mud:

• lower the solids content.

• reduce the number of particles per unit volume.

• neutralize attractive forces between the particles.

The use of screens, desilters and other mechanical devices will reduce viscosity, but chemical additives may also be used. These chemicals produce negatively charged anions in solution and thereby reduce the positive charge on the edge of the clay plates. This reduces the edge-to-face association and therefore reduces viscosity. Such chemicals are called thinners (or dispersants) and include: Phosphates; Lignites; Lignosulphonates; and Tannins.

b) Density control additives

Barite (barium sulphate, $BaSO_4$) is the primary weighting material used in muds. Densities of 9 ppg to 19 ppg can be achieved by mixing water, clay and barite. Other weighting materials are calcium carbonate and galena (lead sulphide). The drill solids from the formation will increase the mud density if they are not separated out.

c) Filtration control additives

Loss of fluid from the mud occurs when the mud comes into contact with a permeable zone. If the pores are large enough the first effect will be a spurt loss, followed by the buildup of solids to form a mud cake. The rate at which fluid is lost is a function of the differential pressure, thickness of filter cake and viscosity of the filtrate. Excessive filtration rates and thick wall cake can lead to problems such as:

- tight spots in the hole
- differential pipe sticking
- formation damage due to filtrate invasion.

Since a filter cake attains its greatest thickness under static conditions the mud is tested under static conditions. Dynamic filtration results in a thinner mud cake due to erosion effects, but the rate of filtration will be higher. The aim is to deposit a thin and impermeable filter cake. Several types of material may be added to the mud to control fluid loss.

- Clays - Bentonite is an effective fluid loss control agent because of its particle size and shape, and also because it hydrates and compresses under pressure. The particle size distribution is such that most particles will be less than 1 micron. Care should be taken not to remove these small particles by using a centrifuge for solids control.

- Starch - these organic chemicals will swell rapidly and seal off the permeable zones effectively.

• CMC - this is an organic colloid (sodium carboxyl-methyl cellulose). The long chain molecules can be polymerized into 3 different grades (high, medium and low viscosity). It is thought that CMC controls filtration by wedging long chain polymers into the formation and plugging the pores. CMC works well in most water-based muds, but less effective in high salt concentrations (>50,000 ppm).

• Polyacrylates (Cypan) - these are long chain polymers which become absorbed onto the edge of clay particles.

• Lignosuphonates - similar in action to starch in reducing fluid loss.

• Polyanoinic cellulose (Drispac) - an organic compound which is used to control fluid loss in high salt concentrations, and is often used in low solids mud. May also be used as a viscosifier.

The water loss allowable in any particular area will largely depend on experience. As the well is being drilled the fluid loss must be adjusted as new formations are penetrated. The surface hole may be drilled with a fluid loss of 20 cc, but across productive formations it will be reduced (down to possibly 5 cc). Control over fluid loss depends on the correct addition of chemicals and keeping the clay solids dispersed. Fluid loss control agents may also act as thinners, or viscosifiers under certain circumstances, and react unfavourably with other chemicals in the mud.

d) pH control additives

Caustic soda NaOH is the major additive used to keep the pH of the mud high. This is desirable to prevent corrosion and hydrogen embrittlement. The pH of most muds lies between 9.5 and 10.5. Caustic potash, KOH and slaked lime, Ca(OH)2 may also be used.

e) Removal of contaminants

Various substances may enter the mud and cause an adverse effect on the quality of the mud and reduce its efficiency. These contaminates must be removed. The main contaminates are listed below:

• Calcium (Ca^{2+}) - may enter from cement, gypsum, lime or saltwater. It reduces the viscosity building properties of bentonite. It is usually removed from fresh water muds by adding soda ash Na_2CO_3, which forms insoluble $CaCO_3$. If calcium is present in the mud the pH will normally be too high.

• Carbon dioxide (CO_2) - present in formations which when entrained in the mud can cause adverse filtration and gelation characteristics. To remove CO_2 calcium hydroxide can be added to precipitate $CaCO_3$.

• Hydrogen sulphide (H_2S) - present in formations. Highly toxic gas which also causes hydrogen embrittlement of steel pipe. Add NaOH to keep pH high and form sodium sulphide. If the pH is allowed to drop the sulphide reverts back to H_2S.

• Oxygen (O_2) - entrained into mud in surface pits, causes corrosion and pitting of steel pipe. Sodium sulphite (Na_2SO_3) is added at surface to remove the Oxygen.

2.1.3.Inhibited Muds

The hydration of clays is severely reduced if the water used to make up the mud contains a high salt concentration. If a shale zone is being drilled with a fresh water mud the clays in the formation will tend to expand and the wellbore becomes unstable (sloughing shale). By using a mud containing salt or calcium there will be less tendency for this problem to occur. An inhibitive mud is defined as one where the ability of active clays to hydrate has been greatly reduced. Another advantage is that the water normally used in hydration is available to carry more solids. Inhibitive muds are principally used to drill shale and clay formations, and are characterized by:

• low viscosity.

• low gel strength.

• greater solids tolerance.

• greater resistance to contaminants.

a) Calcium treated muds.

When Ca^{2+} ions are added to a clay-water mud the mud begins to thicken due to flocculation. At the same time a cation exchange reaction begins whereby Ca^{2+} replaces Na^{2+} on the clay plates. Calcium montmorillonite does not hydrate as extensively as sodium montmorillonite, and the plates begin to aggregate

b) Lignosulphanate treated muds.

An inhibited mud can also be formed by adding large amounts (12 lb/bbl) of lignosulphanate to a clay-water system. Chrome lignosulphanate is commonly used since it is relatively cheap and has a high tolerance for salt and calcium.

c) Saltwater muds.

Inhibitive muds having a salt concentration (NaCl) in excess of 1% by weight are called salt water muds. These are often used in marine areas where fresh water is not readily available. As stated earlier commercial clays (e.g. bentonite) will not readily hydrate in water containing salt concentration (i.e. bentonite behaves like an inert solid). To build viscosity therefore the clay must be prehydrated in fresh water, then treated with deflocculant before increasing salinity. The Ca^{2+} and Mg^{2+}ions can be removed by adding NaOH to form insoluble precipitates which can be removed before building viscosity. After conversion salt water muds are not greatly affected by subsequent contamination. However, the increased salt content may make it more difficult to maintain other mud properties. (Alkalinity is controlled by adding NaOH and filtration by adding bentonite). Corrosion may be a major problem in salt water muds unless alkalinity is controlled.

d) KCL - polymer system.

This mud system was specifically developed to combat the problem of water sensitive, sloughing shales. The potassium chloride concentration must be at least 3 - 5% by weight to prevent swelling of shales containing illite and kaolinite. For shales containing bentonite the KCl concentration must be raised to 10%. Polyacrylamide polymers are used to control the viscosity of the mud and are used in concentrations of around 0.75 lb/bbl. Potassium hydroxide or caustic soda may be used to control the pH at around 10. This system allows good shale stabilisation, hole cleaning and flocculation of drilled solids. The

KCl polymer system is stable up to 300°F. Temperatures above 300°F will cause slow degradation of the polymer.

e)Polyol muds.

Polyol is the generic name for a wide class of chemicals – including glycerol, polyglycerol or glycols such as propylene glycol – that are usually used in conjunction with an encapsulating polymer (PHPA) and an inhibitive brine phase (KCl). These materials are nontoxic and pass the current environmental protocols, including those laid down in Norway, UK, Netherlands, Denmark and USA.

f) Silicate Fluids

Silicate fluids used as a shale hydration suppressor. The Sodium Silicate precipitates a layer of Silicate over the reactive sites on the clay particle and over microfractures in the matrix thus preventing hydration by water migration into the clay.

2.1.4.Brine Drilling Fluid Polymers

Brine Drilling Fluid Polymers are added to brine to viscosity the water and provide some filtration control. Certain polymers (XC or Duovis) are of particular value since they possess low viscosity at high shear rate, and high viscosity at low shear rates. The effect of this is good flow properties in the drillstring (at high shear rate) combined with good lifting properties in the annulus (low shear rates). About 0.5 lb/bbl of XC polymer should be added. Drilled solids must be controlled by dilution and mechanical devices. Good performance is achieved using desanders and desilters.

2.2. Oil-based muds

In many aspects an oil-based fluid can be described as an ideal fluid because the interactions with the formation are minimal. The main advantages of this situation are that the borehole is stable for an extended period of time and the cuttings can come to the surface solids removal equipment in such a size range that a significant proportion can be removed. This reduces the volume of fluid that is used.

The main feature is a continuous low viscosity oil phase. This reduces the reaction with the polar or water wetting formations. The oil phase also contains solids such as the weighting materials and drilled solids. Again, because of the nonpolar nature of the oil, the viscosity effects of the solids are minimal.

Surfactants are used to make the solids oil wet and, more importantly, to emulsify the brine phase which is added to the oil. The emulsifiers are a special group of chemicals characterized by the presence, in the same molecule, of two contrasting groups, one with strong attractive forces for water and the other attracting strongly to oil. To stabilize inverted emulsions an oil soluble surfactant must be used.

The brine phase contains salts to control the activity of the brine preventing it from being drawn from the fluid into the formation. This is a very important factor in formulating an oil-based fluid. It is not just the oil that prevents the water entering the formation, but also the high salinity of the brine phase.

Viscosity control is difficult in oil-based fluids and relies on the use of surfactant treated bentonite. The viscosity mechanism is due to water adsorbed on the clay platelets.

Fluid loss control is very well developed in oil-based fluids and relies on colloidal particles including colloidal sized water droplets and differences in wettability. The fluid loss control may be so well developed that the penetration rate is seriously limited. Therefore, inverted systems can be designed to have high fluid loss characteristics.

Oil-based systems possess properties that are highly desirable and are not obtainable with water-based systems. One of these is the very low level of reaction with the formation, combined with minimal penetration of the fluid phase of the fluid into the formation. This leads to maximum borehole stability over a prolonged time span.

The advantages and related benefits of oil-based fluids may be summarized as follows:

- A maximum level of shale hydration inhibition is realized.
- A properly conditioned oil mud should have no effect on a shale formation. Therefore, gauge hole can be drilled through water-sensitive shales. This

leads to improved cement bonding and reduced cement requirements. Improved log response and better cuttings removal are also beneficially affected.

- The non-polar environment results in consistent fluid properties, low chemical maintenance costs, stability under high temperature conditions, minimal effects on properties from drilled solids, good resistance to salt and gypsum contamination and good protection of drill string against the corrosive gases H_2S and CO_2.
- Formulation for low fluid loss results in low torque, especially in deviated holes, minimized differential sticking problems and low formation damage factors in oil reservoirs.
- Formulation for high fluid loss results in high rates of penetration. The low solids content and reducion in cuttings stickiness when using oil-based fluids also improves penetration rates.
- More competent cuttings at surface increase shale shaker efficiency. Oil-based fluids have a higher drilled solids tolerance, which can reduce dilution requirements.
- Due to their stability and solids tolerance, oil mud can sometimes be used for more than one well.
- Oil-based fluids have application on wells with bottom hole temperatures up to 300°C.
- Low aromatic oil-based fluids result in improved rig conditions, low odour, clean handling on the rig, minimal effects on the marine environment, low viscosity imparting improved rheological properties and high flash point giving extra safety.
- Other advantages include: flexibility with respect to formulation and application, reduced corrosion rates, and reduction in tubular stress fatigue.

The oil-based drilling fluids were developed and introduced in the 1960s to help the drilling problems. They are formulated with diesel, mineral oil, or low-toxicity linear olefins and paraffins. Barite is used to increase system density, and specially treated organophilic bentonite is the primary viscosifier in most oil-based systems. The emulsified water phase also contributes to fluid viscosity. Organophiliclignitic, asphaltic and polymeric materials are added to help control HP/HT (High pressure/High temperature) (Romagnoli R.; 2018).

An oil-based mud is one in which the base fluid from which the mud is made up is oil. Since the 1930's it has been recognized that better productivity is achieved from reservoirs when oil based fluids rather than water based fluids are used to drill through the reservoir. This is largely because the oil does not cause the clays in the reservoir to swell or cause changes in wettability of the formations. Crude oil was first used to drill through the pay zone, but it suffered from several disadvantages (low gel strength, limited viscosity, safety hazard due to low flash point). Modern oil-based muds use low-toxicity base oils and a variety of chemical additives to build good mud properties. The use of oil in the drilling fluid does have several disadvantages:

• higher initial cost.

• more stringent pollution controls required.

• reduced effectiveness of some logging tools (resistivity logs).

• detection of kicks more difficult due to gas solubility in base oil.

However, for some applications oil-based muds are very cost effective. These include:

• to drill and core pay zones.

• to drill troublesome formations (e.g. shale, salt).

• to add lubricity in directional drilling (preventing stuck pipe).

• to reduce corrosion.

• as a completion fluid (during perforating and workovers). There are three types of oil-based muds in common use:

• full oil (water content < 5%).

• invert oil emulsions (water content 5 - 50%).

• Synthetic or Pseudo oil based mud

2.2.1.Full Oil Base Drilling Fluids

Oil Base Drilling Fluids Company (now Hughes Drilling Fluids) was formed by George Miller to manufacture, market, and service the first commercial oil base drilling fluid, Black Magic. On May 1, 1942, Richfield Oil Company (now ARCO) used Black Magic as a completion fluid. Black Magic at that time was composed of air blown asphalt dispersed in a diesel oil which contained naturally occurring naphthenic acid, quick lime, and 5% by volume water. The uses of Black Magic in these early years were as completion fluids for low pressure and/or low permeability sands, coring fluids, and to free stuck pipe. This original system performed well when applied properly. However, it had some obvious drawbacks. Asphalt was the primary viscosifier and fluid loss control additive. It did a good job of both but contributed to very high apparent and plastic viscosities and consequently was detrimental to drilling rates when compared to a water mud of the same density. It was also much more expensive per unit volume than water mud.

2.2.2.Inverts or Invert Emulsion Muds.

Because it did perform many functions well, the industry then set about to improve on it. From this work came the development of what are called the invert emulsion muds. Invert emulsion means that water is emulsified in oil (water-in-oil emulsion). In the earlier years (1940’s), one of the most popular water muds run was oil-in-water. These muds were called oil emulsion systems. Therefore, during the development of invert emulsion systems, the term” inverts” or invert emulsion was used to differentiate the oil system containing some oil.

The control of the water base muds is made possible because of the wide variety of additives available for performing specific functions. At this time in history, development of oil mud additives and the technology of oil muds were pointed in the same direction. The first step dealt with the amount of water emulsified. Inverts were developed to contain and tolerate a much greater water volume than true oil muds. Rheology could then be controlled by altering oil/water ratios. This allowed the system to have adequate weight material suspension and filtration control with lower viscosity and gels. Water contamination became a less acute problem with inverts.

Water contamination was an acute problem causing excessive viscosity and waterwetting of solids, necessitating replacement of the system or at least dilution with new mud. Water contamination of invert emulsions required adjustment of mud properties by the addition of oil and emulsifiers. The principal components in the oil muds could not be added to adjust a single property without affecting most of the other mud properties. Single additives to adjust or control specific mud properties were not available at the time to provide the flexibility and versatility needed for lower cost. The original inverts were composed of the same basic ingredients as the true oil muds. The concentrations of materials differed however. Calcium and magnesium soaps were used along with asphalt in small concentrations. Sodium chloride brine was used as the internal phase. The earliest of these systems, No-Blok (Magcobar) and Kenex (Ken Corp., later IMC) did not have any other additives. Although they were more flexible (rheologically) than the true oil mud, they were not as stable.

2.2.3.Synthetic or pseudo oil based muds.

In recent years the base oil in OBMs has been replaced by synthetic fluids such as esters and ethers. These fluids are generally called **synthetic or pseudo oil based muds.**

2.3. Water in oil emulsions

The water in invert emulsion muds is dispersed as small droplets throughout the oil. Emulsifiers coat the droplets, preventing them from coalescing and making the mud unstable (i.e. larger water droplets will settle out and break down the emulsion). A calcium or magnesium fatty acid soap is often used as an emulsifier in an oil-based mud. The long hydrocarbon chain of the soap molecule tends to be soluble in oil while the ionic portion tends to be soluble in water. When soap is added to a mixture of oil and water the molecule takes up the position shown in Figure 1.

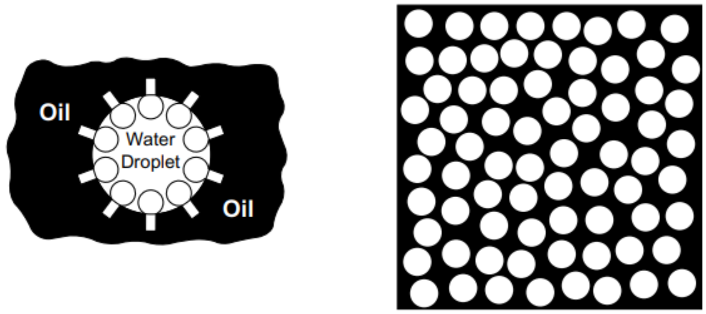

Figure 1 - Water droplets dispered in a continuous oil phase.

This reduces the surface energy of the interface and keeps the water droplets in the emulsion. Other types of emulsifiers can also be used (e.g. naphthenic acid soaps and soaps from tree sap). The effectiveness of an emulsifier depends on the alkalinity and electrolytes present in the water phase and also on the temperature of the mud. To increase the stability, the water droplets should be as small and uniform as possible. This is done by shearing the mud by agitators. When oil is added the stability increases, since the distance between droplets becomes greater. This causes a decrease in viscosity. For good mud properties there must be a balance between oil and water. The water droplets help to:

• support the barite.

• reduce filter loss.

• build viscosity and gel strength.

2.3.1.Wettability control

When a drop of liquid is placed on a solid it will either:

• spread itself over the surface of the solidor

• remain as a stable drop.

The shape that the drop takes up depends on the adhesive forces between the molecules of the solid and liquid phases. The wettability of a given solid surface to a given liquid is defined in terms of the contact angle q. For a solid/liquid interface which exhibits a small contact angle less than 90°, the solid is preferentially wetted by the liquid.

2.3.2. Viscosity control

Excessive viscosity in an oil-based mud may be the result of:

• too much water content - When water is properly emulsified it behaves like a solid. As the water fraction increases so does the viscosity.

• drilled solids - The solids content affects viscosity in oil-based in the same way as water-based muds. The buildup of fine solids (e.g. due to diamond bit drilling) may produce high PV, YP and gel strengths. Finer shaker screens (120 mesh) should be used to reduce this effect. Water wet solids may also cause problems with high YP. It is recommended that pilot tests should be done to assess the implications of adding chemicals to the mud to control viscosity. Emulsifiers and wetting agents may be added to reduce viscosity. Water and special viscosifiers (organically treated bentonite) may be added to the mud to increase viscosity.

2.3.3. Filtration control

Only the oil phase in OBM is free to form a filtrate, making an oil-based mud suitable for formations which must not be damaged. The fluid loss is generally very small with oil-based muds. If water is present more emulsifying agent should be added. Excessive filtrate volumes can be cured by adding polymers, lignite etc (Heriot-Watt Institute of Petroleum Engineering, 2005).

2.4. Gas-based drilling fluids

Low density fluids are sometimes called gas-based or reduced pressure drilling fluids. The original purpose of these fluids was either to avoid loss of circulation or reduce the amount of water lost into production zones. Improved rates of penetration and longer bit life soon became well-known secondary benefits. These systems can be classified as follows:

- Gas or Air
- Mist / Foam
- Stiff / Stable Foam

- Aerated Drilling Fluids

Dry gas drilling was first patented in 1866 and is still used in many areas today. When drilling with gas or air, enough volume must be supplied to generate annular velocities in the range of 900 m/min. Care must be taken to avoid the risk of downhole fires and explosions.

The injection into a gas of small amounts of drilling fluid or water containing a foaming surfactant results in a mist or foam drilling fluid. The foaming surfactant mixes with the formation water. This increases carrying capacity, permitting the removal of water from the hole at lower annular velocities.

A stable foam is obtained by mixing: water, soda ash, bentonite, guar gum and a foaming agent. Stiff foam fluids have the consistency of shaving cream. They are used when: an air drilling operation encounters a water flow, for clean out and remedial jobs (Romagnoli. R.; 2018).

Aerated drilling fluids were first used in 1953 and various systems have been used to inject air into the drilling fluid thus reducing hydrostatic head, such as: injecting air into the standpipe or into the annulus, using a dual drill string-one within the other.

3. Methods and Materials

Stuck pipe is one of the big challenges to the worldwide oil industry. It affects to the nonproductive time thus causes great economic losses to the oil industry. Many types of techniques have been developed to solve this problem after they occur. Ideally, the objective should be to avoid the problem of stuck pipe before they occur. The choice of treatment to release a stuck pipe should be cost effective and also quick. Importance of a choice of drilling fluid with correct additives and rheology takes the first place.

New drilling fluids have been developed and designed with a combination of two different weighting agents of barite and manganese tetroxide - Mn3O4. The concept is to describe the formulation of medium and high-density drilling fluids with 100 pcf, 120 pcf and 150 pcf density fluids and to compare their results in terms of such parameters as plastic viscosity, yield point, gel strength and low shear yield point. All these parameters result in the efficiency of drilling fluids, so in better sag resistance, lower ECD (equivalent circulating density), lower fluid cost, filter-cake breaking, consequently, lower total cost. These drilling fluids have been formulated with a combination of barite and manganese tetroxide as weighting materials and hot rolled at 270°F, 250°F and 300°F, respectively. After hot rolling these fluids at the specified temperatures, rheological properties and high temperature and pressure (HTHP) fluid loss were measured. Sag resistance of the drilling fluids was estimated by static aging experiments. The fluids were aged in inclined at 45° and vertical positions (90°). Different breaker fluids were tested on the new drilling fluids so as to calculate the % filter-cake removal efficiency to estimate the filter-cake breaking potential of these manganese tetroxide based drilling fluids. The new fluid when static aged shows superior rheology, thin filter cake and better sag resistance as compared to the fluid formulated with only barite as the weighting agent. Different filter-cake breaker fluids have been shown to partially dissolve the filter cake of drilling fluids formulated with the acid-soluble manganese tetroxide as a weighting agent. So, partial dissolution of filter cake is sufficient to free the pipe in the case of stuck in the wellbore. These new drilling fluids formulated with a combination of barite and manganese tetroxide as a weighting agent shows good rheology, barite-sag resistance over conventional drilling fluids consisting 100% barite.

Lower ECD values due to lower plastic viscosity. Manganese tetroxide has a higher specific gravity of 4.95 as compared to the conventional weighting agent barite that has a specific gravity of 4.2. Drilling fluids, especially the high-density fluids, formulated with 100% barite would have a higher solids loading as compared to fluids formulated with a combination of barite and manganese tetroxide. Higher solid loading in the fluids results in drilling fluids having a higher plastic viscosity (PV) value. The equivalent circulating density (ECD) depends on the plastic viscosity value of the drilling fluid. Higher PVs result in higher ECDs due to the increased pump pressures required to pump the fluid (Nicora 2001). In addition to the influence of PV on the ECD values, PV also affects the rate of penetration (ROP). Higher PVs decreases the rate of penetration (ROP) thereby resulting in slower drilling and subsequently higher drilling costs (Beek 1995). An advantage of having a drilling fluid with a lower PV value is also to maintain a higher YP PV ratio which improves cutting transport through the annulus in the laminar flow region at high YP values (Okrajni 1986). Thus, the use of a weighting agent having a higher density like manganese tetroxide in combination with barite would help to decrease the solids loading as compared to the conventional fluid formulated with 100% barite. This decreased solids loading would result in a lower PV which subsequently would result in a lower equivalent circulating density, higher ROPS, higher YP PV ratio and subsequently faster drilling and lower drilling costs.

Better sag resistance: One of the primary requirements of a good drilling fluid is its ability to withstand settling of its weighting agent while drilling or when the fluid is kept static for a certain period of time. API barite owing to its bigger particle size has been estimated to settle 200 times faster than manganese tetroxide (Steele et al. 2007). This lower settling velocity shown by manganese tetroxide can be expected to result in a greater sag resistance for the fluid formulated with a combination of manganese tetroxide and barite as compared to the conventional fluid formulated with 100% barite.

Lower fluid cost: It is known that manganese tetroxide is relatively more expensive than barite. Thus, the use of manganese tetroxide as the only weighting agent for the fluid will result in increased cost of the fluid. In other words, the use of a combination of barite and manganese tetroxide would not only reduce the fluid cost but also result in greater sag resistance and lower ECDS as compared to a fluid formulated with 100% barite.

Acid solubility of manganese tetroxide leading to filter-cake breaking: Apart from the higher density shown by manganese tetroxide, another feature that sets it apart from barite is its ability to solubilize in any organic or mineral acid. This ability of manganese tetroxide to solubilize in acıd presents an opportunity to formulate a drilling fluid whose filter cake in the wellbore can be easily removed by using either an organic or a mineral acid. Thus in the event of a stuck pipe the partial breaking of the filter-cake formed by a drilling fluid formulated with barite and manganese tetroxide will result in the sticking force being reduced thereby releasıng the stuck pipe in the wellbore (Montgomery et. al., 2007).

In this work we will analyze two cases described by Alabdullatif 2014, Wagle 2015 and Wagle 2016 in different laboratory researches. First, we will describe the formulation of 100pcf and 150pcf drilling fluids with a 60/40 %v/v combination of barite and manganese tetroxide as weighting materials, static aging of 150 pcf WBM at 300°F, the utility of manganese tetroxide based drilling fluids through lab Investigation. Secondly, we will describe the second case of the same formulations of 120pcf and 145pcf water based drilling fluids with no incidences of stuck pipe, static aging of 120 pcf water based drilling fluid at 250°F. And, finally, we will see the results of using different filter-cake breaker fluids for the partial dissolution of manganese tetroxide based filter cake, will compare and evaluate two different cases and prescribe each to the respective conditions.

3.1. Laboratory Experiments: first case

Water based drilling fluids (WBMs) having 60/40% v/v combination of barite and manganese tetroxide (Mn_3O_4) were formulated using commercially available drilling fluid additives viz. bridging agents, viscosifiers, rheology modifiers, disersants, shale inhibitors, filtration control agents, etc. These WBMs were then hot rolled at the desired temperatures for 16 hours after which the filtration and rheology properties of WBMs were measured using standard instruments (Wagle, V. et al 2017b).

In this paper, the laboratory studies on these WBMs have been divided into three sections:

(A) Formulation of 100 pcf and 150 pcf WBMs: 100 pcf and 150 pcf WBMs were formulated having 60/40% v/v combination of barite and manganese tetroxide.

(B) Static aging of 150 pcf WBM at 300°F: 150pcf WBM was static aged at 300°F to determine the barite sag resistance of the fluid. Top water separation was measured and sag factor was calculated to determine the stability of the fluid after static aging at 300°F.

(C) Filter-cake breaking experiments of WBMs using different organic acids: The filter-cake formed during the HTHP fluid loss experiments of 100 pcf WBM were subjected to different organic acid treatments so as to study the extent of filter-cake breaking due to the dissolution of manganese tetroxide by organic acids.

The experimental procedure for this study is shown below.

3.1.1. Formulation of 100 pcf and 150 pcf drilling fluids

100 pcf and 150 pcf WBMs were formulated using a standard multimixer in stainless steel mud cups. The mixing order of products, the concentrations and mixing time for the 100 pcf and 150 pcf WBMs are given in Table 4 and Table 5.

After formulating the 100 pcf and 150 pcf WBMs, the fluids were subjected to hot rolling in high pressure, high temperature (HPHT) stainless steel cells at 270°F and 300°F, respectivly, for 16 hours. The WBMs after hot rolling were subsequently mixed for 5 min using a multimixer and their rheology was measured at 120°F using a rheometer. HTHP fluid loss measurements were performed at 270°F and 300°F, respectively. All the tests were performed according to procedures mentioned in API 13B-1 (Wagle, V. et al 2017b).

The rheology of the fluid was characterized in terms of plastic viscosity (PV), yield point (YP) and low shear yield point (LSYP). The PV, YP and LSYP were calculated using Equations 1, 2, and 3.

$$PV = (600 \text{ rpm reading}) - (300 \text{ rpm reading}) \quad \text{(Equation 1)}$$

YP = (300 rpm reading) – PV (Equation 2)

LSYP = [2×(3 rpm reading)] – (6 rpm reading) (Equation 3)

The gels formed in the fluid were characterized by the 10 sec/10 min gel strength, which represents the highest dial reading at 3 rpm on the viscometer, after keeping the fluid static for an interval of 10 sec/10 min. The gel strengths indicate the suspension ability of the fluid for cut drill solids and barite particles when drilling stops.

3.1.2.Static aging of 150 pcf WBM at 300°F:

The formulated 150 pcf WBM was subsequently placed in HPHT stainless steel cells and static aged in vertical and inclined positions at 300°F by placing the cells at 90° and at 45°, respectively. The 150 pcf WBM was initially hot rolled at 300°F for 16 hours. After hot rolling, the mud was mixed for 5 minutes using a multimixer and then subsequently static aged for 24hours at 300°F.

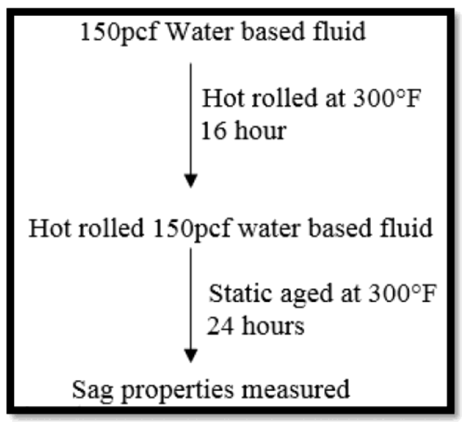

Figure 2 - Static aging procedure for 150 pcf WBM at 300°F (Wagle, V. et al 2017b).

The 150 pcf fluid after static aging was allowed to cool in a water bath. Any top free water separation in the mud was determined by removing the water with the help of a syringe.

Sag factor analysis was done to determine the extent of barite sag in the 150 pcf mud after static aging. For this analysis, 10ml aliquots of the fluid were drawn from the top and bottom portions of the mud placed in the HTHP aging cell by using a 10ml syringe. The specific gravity of the top and bottom portion of the mud was determined by measuring the weights of the drawn mud on an analytical balance.

The sag factor, for the static aged fluids was calculated using the formula (Equation 4).

$$SagFactor = \frac{SG_{bottom}}{SG_{bottom} + SG_{top}} \qquad \text{(Equation 4)}$$

where,

- SG_{bottom} is the density of the static aged drilling fluid at the bottom of the aging cell
- SG_{top} is the density of the static aged drilling fluid at the top of the aging cell

3.1.3. Filter-cake breaking experiments of Manganese tetroxide based drilling fluids

Filter-cake breaking experiments were performed on 100 pcf WBM formulated with 60/40 %v/v barite/ manganese tetroxide. These experiments were conducted in order to study the efficiency of various organic acids to remove the filter cake formed by the 100 pcf WBM formulated with barite and manganese tetroxide. The filter-cake breaking experiments were performed using a HPHT filter press at 270°F. A filter cake was first prepared on a 50µ ceramic disk at 250°F using a 500 ml HPHT cell according to API 13B-1. The organic acids were brought in contact with the filter-cake with a soaking time of 4.5hours at 270°F. The efficiency of the filter-cake breaker fluids in the removal or breaking of the filter cake was then calculated by the following formula (Equation 5) (Wagle, V. et al 2017b).

$$\%\ Filtercake\ Removal\ Efficiency = \frac{(W_1 - W_2)}{W_1} \times 100 \qquad \text{(Equation 5)}$$

where,

- $W1$ = Weight of the filter cake before its treatment with breaker fluid
- $W2$ = Weight of the filter cake after its treatment with breaker fluid

3.2. Laboratory Experiment: second case

A. **Formulation of 120 pcf and 150 pcf water based drilling fluids:** 120 pcf and 150 pcf water based drilling fluids were formulated having 60/40% v/v combination of barite and manganese tetroxide.

B. **Static aging of 120 pcf water based drilling fluid at 250°F:** 120pcf water based drilling fluid was static aged at 250°F to determine the barite sag resistance of the fluid. Top water separation was measured and sag factor was calculated to determine the stability of the fluid after static aging at 250°F.

C. **Filter-cake breaking experiments of water based drilling fluids using different filter-cake breaker fluids:** The filter-cake formed during the HTHP fluid loss experiments of 120 pcf WBM were subjected to different breaker fluid treatments so as to study the extent of filter-cake breaking due to the dissolution of manganese tetroxide by different breaker fluids. Different breaker fluids viz. glycolic acid, aqueous HCl acid, formic acid precursor and a combination of formic acid precursor and aqueous HCl acid were used in the study.

The experimental procedure for this study is shown below:

3.2.1. Formulation of 120 pcf and 150 pcf water based drilling fluids

120 pcf and 150 pcf water based drilling fluids were formulated using a standard multimixer in stainless steel mud cups. The mixing order of products, the concentrations and mixing time for the 120 pcf and 150 pcf water based drilling fluids are given in Table 2 and Table 3.

Table 2 - Formulation of 120pcf drilling fluid with 60/40 v/v% barite/ manganese tetroxide and 100% barite

Additives	**120pcf fluid with 60/40 v/v % barite/manganese tetroxide**	**120pcf fluid with 100% barite**
Water, bbl	0.71	0.68
Bentonite, ppb	2.0	2.0
Sodium carbonate, ppb	0.3	0.3
Potassium hydroxide, ppb	0.5	0.5
Potassium chloride, ppb	10.0	10.0
Viscosifier, ppb	0.35	0.35
Filtration control agent, ppb	2.0	2.0
Polymeric Filtration control agent, ppb	0.75	0.75
HPHT fluid loss additive, ppb	4.0	4.0
Barite, ppb	224.7	409.6
Manganese tetroxide, ppb	176.5	–
Oxygen scavenger, ppb	0.3	0.3
Chrome-free lignosulfonate, ppb	2.5	2.5

Table 3 - Formulation of the new 150pcf drilling fluid with 60/40 v/v% barite/ manganese tetroxide

Additives	**150pcf fluid with 60/40 v/v % barite/manganese tetroxide**	**150pcf fluid with 100% barite**
Water, bbl	0.53	0.49
Bentonite, ppb	4.00	4.00
Sodium carbonate, ppb	0.30	0.30
Sodium hydroxide, ppb	0.40	0.40
Potassium chloride, ppb	15.00	15.00
Viscosifier, ppb	0.35	0.35
HPHT fluid loss additive, ppb	6.00	6.00
Barite, ppb	345.00	625.00
Manganese tetroxide, ppb	270.00	–
Oxygen scavenger, ppb	0.30	0.30
Chrome-free lignosulfonates, ppb	4.00	4.00
Lubricant, ppb	7.00	7.00

After formulating the 120 pcf and 150 pcf water based drilling fluids, the fluids were subjected to hot rolling in high pressure, high temperature (HPHT) stainless steel cells at 250°F and 300°F, respectivly, for 16 hours. The water based drilling fluids after hot rolling were subsequently mixed for 5 min using a multimixer and their rheology was measured at 120°F using a rheometer. HTHP fluid loss measurements were performed at 250°F and 300°F, respectively. All the tests were performed according to procedures mentioned in API 13B-1 (Wagle, V. et al 2017a).

The rheology of the fluid was characterized in terms of plastic viscosity (PV), yield point (YP) and low shear yield point (LSYP). The PV, YP and LSYP were calculated using Equations 1, 2, and 3 (Wagle, V. et al 2017a).

The gels formed in the fluid were characterized by the 10 sec/10 min gel strength, which represents the highest dial reading at 3 rpm on the viscometer, after keeping the fluid static for an interval of 10 sec/10 min. The gel strengths indicate the suspension ability of the fluid for cut drill solids and barite particles when drilling stops (Wagle, V. et al 2017a).

3.2.2. Static aging of 120 pcf WBM at 250°F:

The formulated 120 pcf water based drilling fluid was subsequently placed in HPHT stainless steel cells and static aged in vertical and inclined positions at 250°F by placing the cells at 90° and at 45°, respectively. The 120 pcf WBM was initially hot rolled at 250°F for 16 hours. After hot rolling, the mud was mixed for 5 minutes using a multimixer and then subsequently static aged for 24hours at 250°F.

The 120 pcf fluid after static aging was allowed to cool in a water bath. Any top free water separation in the mud was determined by removing the water with the help of a syringe.

Sag factor analysis was done to determine the extent of barite sag in the 120 pcf mud after static aging. For this analysis, 10ml aliquots of the fluid were drawn from the top and bottom portions of the mud placed in the HTHP aging cell by using a 10ml syringe. The specific gravity of the top and bottom portion of the mud was determined by measuring the weights of the drawn mud on an analytical balance (Wagle, V. et al 2017a).

The sag factor, for the static aged fluids was calculated using the formula (Equation 4).

3.2.3.Filter-cake breaking experiments of Manganese tetroxide based drilling fluids

Filter-cake breaking experiments were performed on 120 pcf water based drilling fluid formulated with 60/40 %v/v barite/ manganese tetroxide. These experiments were conducted in order to study the efficiency of various breaker fluids to remove the filter cake formed by the 120 pcf water based drilling fluid formulated with barite and manganese tetroxide. The filter-cake breaking experiments were performed using a HPHT filter press at 250°F. A filter cake was first prepared on a 50μ ceramic disk at 250°F using a 500 ml HPHT cell according to API 13B-1. The breaker fluids were brought in contact with the filter-cake with a soaking time of 4.5hours at 270°F. The efficiency of the filter-cake breaker fluids in the removal or breaking of the filter cake was then calculated by the following formula (Equation 5).

4. Results and Discussion

4.1. Laboratory Experiments: first case

4.1.1. Formulation of 100 pcf and 150 pcf fluids with 60/40 %v/v barite/ manganese tetroxide.

100 pcf and 150 pcf WBMs with a 60/40 %v/v barite/ manganese tetroxide combination as weighting agents were formulated and hot rolled at 270°F and 300°F, respectively. The rheological and filtration properties of the fluid were measured after hot rolling at the specified temperatures.

4.1.1.1. Formulation of 100 pcf fluid formulated with 60/40 %v/v barite/manganese tetroxide combination:

100 pcf water based drilling fluid was formulated with 60/40 %v/v barite/manganese tetroxide combination. A number of combinations of barite and manganese tetroxide ranging from 20/80 v/v% to 80/20 v/v% were tried for the 100 pcf WBM. The best results were obtained with 60/40 v/v% barite and manganese tetroxide combination. Good rheology and low HTHP fluid loss were taken into consideration while deciding the best combination for the 100 pcf fluid. Apart from rheology and HTHP fluid loss, economic considerations, which involved a limited use of the expensive manganese tetroxide was also taken into account while choosing 60/40 v/v% of barite and manganese tetroxide as the best combination for the 100 pcf WBM (Wagle, V. et al 2017b).

Table 4 gives the concentration of the additives and their mixing order used to formulate 100 pcf WBM. A combination of 3 ppb of prehydrated bentonite and 1 ppb of viscosifier was used in the formulation to get optimum rheology for the 100 pcf WBM. Since the mud was hot rolled at 270°F, a 3 ppb of high temperature fluid loss additive to achieve the lowest possible HTHP fluid loss for the mud.

The 100 pcf fluid was then subsequently hot rolled at 270°F for a period of 16 hours. The rheology and filtration properties after hot-rolling the 100 pcf fluid at 270°F for 16 hours is shown in Figure 3.

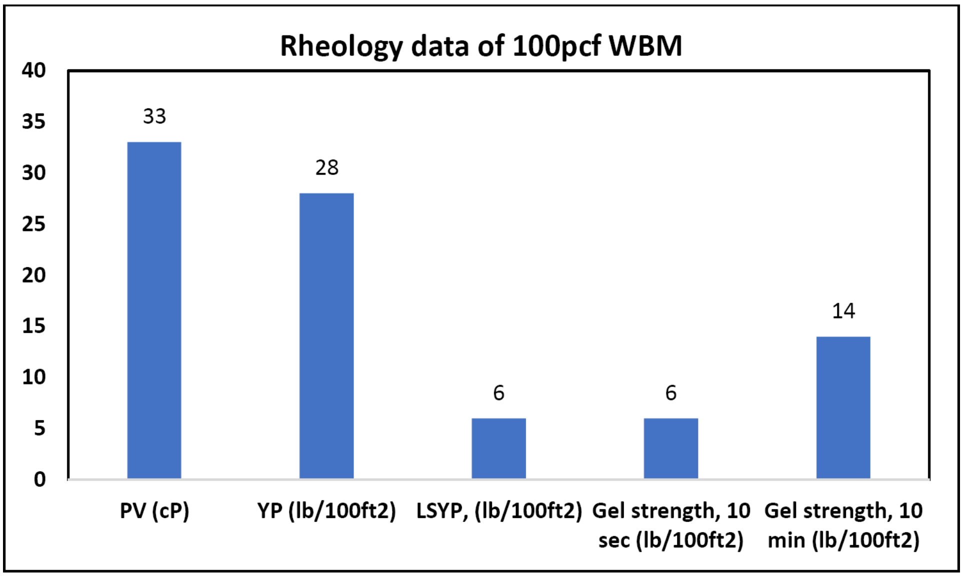

Figure 3 - Rheology data of 100 pcf WBM formulated with barite and manganese tetroxide (Wagle, V. et al 2017b)

Table 4 - Formulation of 100pcf WBM with 60/40 v/v% barite/ manganese tetroxide

Additive	**Concentration**
Water, bbl	0.75
Bentonite, ppb	3.00
Viscosifier, ppb	1.00
Filtration control agent, ppb	4.00
HTHP fluid loss additive, ppb	3.00
NaCl, ppb	58.00
NaOH, ppb	0.50
Bridging agent, ppb	10.00
Lime	0.25
Barite, ppb	121.1
Manganese tetroxide, ppb	95.1
H2S scavenger, ppb	0.35
High temperature stabilizer, ppb	2.00

The combination of barite and manganese tetroxide gave a 100 pcf fluid with a PV of 33 cp and a good YP and LSYP of 28 lb/100ft^2 and 6 lb/100ft^2, respectively. Good YP and LSYP values ensure that the fluid has the desired sag resistance and good cuttings carrying capacity (Miller 2015). 10 sec and 10 min gel strength values were 6 lb/100ft^2 and 14 lb/100ft^2, respectively. The HTHP fluid loss measured at 270°F was only 10 ml. These results showed that the fluid formulated with a combination of barite and manganese tetroxide was stable with good rheology and filtration properties (Wagle, V. et al 2017b).

4.1.1.2. Formulation of 150 pcf water based mud formulated with 60/40 %v/v barite/manganese tetroxide combination

150 pcf water based mud was formulated with a 60/40 %v/v combination of barite and manganese tetroxide. To compare the performance of this 150 pcf WBM, a conventional WBM with 100% barite was also formulated. Both the muds were rolled at 300°F for a period of 16 hours. A comparison was made so as to study the effect of this combination on the rheology and filtration properties of this new 150 pcf WBM. The mixing order of additives for the new 150 pcf fluid and its conventional fluid counterpart is given in Table 5.

Table 5 - Formulation of the new 150 pcf drilling fluid with 60/40 v/v% barite/ manganese tetroxide

Additives	**150 pcf fluid with 60/40 v/v% barite/ manganese tetroxide**	**150 pcf fluid with 100% barite**
Water, bbl	0.53	0.49
Bentonite, ppb	4.00	4.00
Sodium carbonate, ppb	0.30	0.30
Sodium hydroxide, ppb	0.40	0.40
Potassium chloride, ppb	15.00	15.00
Polymer, ppb	0.35	0.35
HPHT fluid loss additive, ppb	6.00	6.00

Barite, ppb	345.00	625.00
Manganese tetroxide, ppb	270.00	–
Oxygen scavenger, ppb	0.30	0.30
Chrome-free lignosulfonates, ppb	4.00	4.00
Lubricant, ppb	7.00	7.00

Figure 4 shows the rheology for both the 150 pcf WBMs after hot-rolling at 300°F for 16 hours. The new 150 pcf WBM formulated with a combination of barite and manganese tetroxide gave a PV of 38 cp whilethe fluid formulated with 100% barite gave a PV of 52 cp. It was anticipated that the fluid formulated with a combination of barite and manganese tetroxide would show lower plastic viscosity than the fluid formulated with 100% barite.

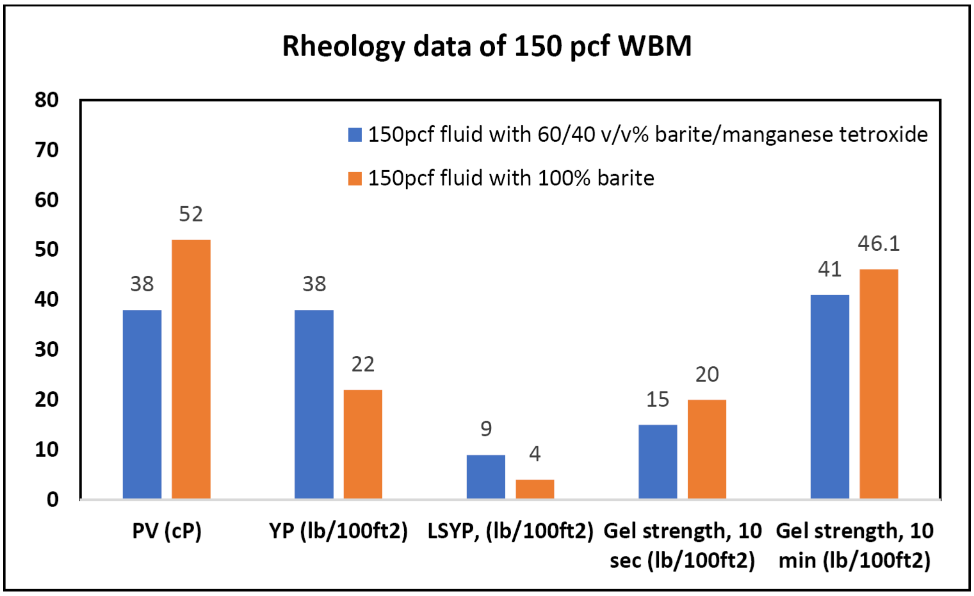

Figure 4 - Comparison of rheology data of 150 pcf WBM formulated with a combination of barite and manganese tetroxide and 100% barite (Wagle, V. et al 2017b)

A high-density150 pcf water based mud requires a large concentration of weighting agent to achieve the desired density. The increased number of solids will lead to a high PV value as well as excessive heat and dehydration. As the volume of solids in the drilling fluid goes up, the particles become more closely packed together and it becomes more difficult for them to move freely. This will result in particle-particle interactions and increase in plastic viscosity. The lower PV shown by the new 150 pcf WBM shows that the use of manganese tetroxide, which has a higher specific gravity of 4.95 than barite helps to decrease the solids loading in the new 150 pcf fluid as compared to the conventional fluid formulated with 100% barite. This decreased solids loading in the new 150 pcf water based mud results in lesser particle-particle interactions thereby resulting in a lower PV value of 38 cp.

A water based mud which has a high plastic viscosity would also show increased equivalent circulating density (ECD) due to increased pump pressures needed to pump the mud into the wellbore (Nicora 2001). Therefore, it is well known that the ECD has to be minimized by minimizing the PV value especially with high density fluids that require high solid loadings (Kulkarni 2014). Apart from higher ECDs, another drawback of water based mud having a high plastic viscosity is that it also decreases the rate of penetration (ROP) (Beck 1995). Therefore, the new 150 pcf WBM with its lower PV would lead to lower ECD and higher ROP as compared to the conventional 150 pcf WBM.

The new 150 pcf WBM shows a YP and LSYP of 38 lb/100 ft^2 and 9 lb/100 ft^2, respectively. The conventional 150 pcf WBM formulated with 100% barite gave a YP and LSYP of 22 lb/100 ft^2 and 4 lb/100 ft^2, respectively. A good LSYP value (≥ 5 lb/100 ft^2) for a fluid signifies that the fluid has good cuttings carry capacity and sag resistance (Wagle 2012; Maghrabi 2015). The new fluid, which has an LSYP of 9 lb/100 ft^2, therefore would show better sag resistance and cuttings carrying capacity than from the conventional fluid, which has an LSYP of only 4 lb/100 ft^2.

4.1.2.Static aging of 60/40 %v/v barite/ manganese tetroxide based fluids.

Inadequate suspension of barite in the drilling fluid is one of the main causes of barite sag when the mud is kept static for certain duration of time in the wellbore. Lost circulation, mud weight fluctuations, stuck pipe, wellbore instability, etc., are some of problems associated with barite sag. To estimate the sag resistance of the newly developed fluid, static sag measurements were performed on 150 pcf water based mud at 300°F. The procedure followed for the static sag measurements has been explained earlier in the Methods and Materials section. A sag factor greater than 0.53 implies that the fluid has potential to sag (Maxey 2007).

4.1.2.1. Sag Performance Test – 90°.

Static sag performance tests were conducted on 150 pcf water based muds by keeping the cell in a vertical position (90°) at 300°F. The sag performance of 150 pcf water based mud formulated with **60/40 %v/v** barite/manganese tetroxide was also compared to the conventional 150 pcf water based mud formulated with 100% barite as the weighting agent. The volume of top free fluid separated from the water based muds after 24 hours of static aging was measured and the sag factor for both the muds was then calculated using Equation 4. The sag factor and volume of top free fluid for both the water based muds is given in Figure 5. The 150 pcf water based mud formulated with a combination of barite and manganese tetroxide gave a top free fluid separation of 15 ml and a sag factor of 0.51 while the conventional fluid with 100% barite as weighting agent gave a top free water separation of 23 ml and sag factor of 0.53. Lower sag factor and free water separation exhibited by the water based mud formulated with a combination of barite and manganese tetroxide showed that it has greater sag resistance as compared with the conventional water based mud formulated with 100% barite (Wagle, V. et al 2017b).

4.1.2.2. Sag Performance Test – Inclined Position (45°).

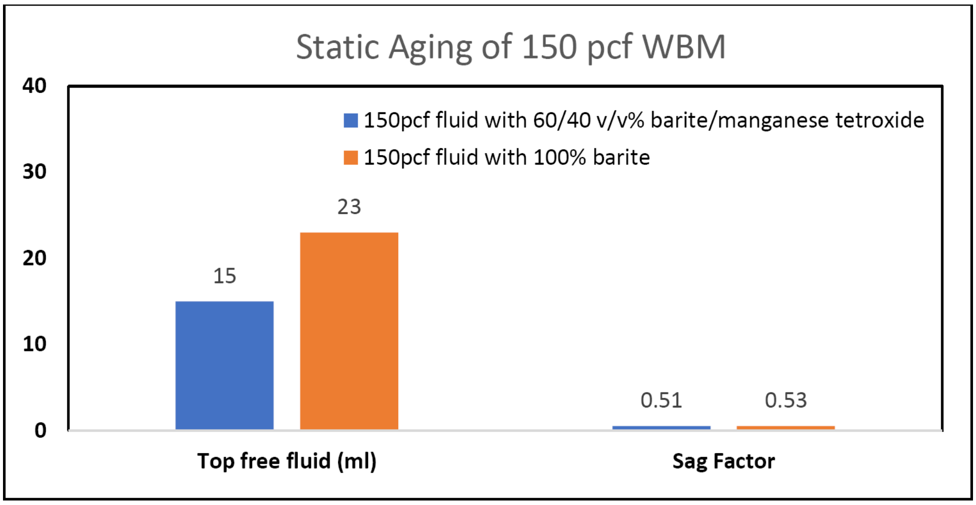

Figure 5 - Static aging studies of 150 pcf WBM (90°) (Wagle, V. et al 2017b)

Barite sag is more likely to occur while drilling deviated wells having an angle greater than 30° (Bern, 1996). To simulate conditions of drilling in deviated wells and to test the sag resistance of barite/manganese tetroxide based water based muds in such wells, 150 pcf water based mud was static aged at 300°F for 24 hours in aging cells held at an angle of 45°. Conventional 150 pcf water based mud with 100% barite as the weighting agent was also formulated and its sag performance was compared with 60/40 v/v% barite/manganese tetroxide based 150 pcf water based mud.

Figure 6 shows the top free fluid and the sag factor for the two 150 pcf static aged water based muds. The conventional fluid with 100% barite gave a top free water separation of 24 ml and sag factor of 0.53 while the 150 pcf fluid formulated with a 60/40 %v/v combination of barite and manganese tetroxide gave a top free fluid separation of 15 ml and sag factor of 0.51. These results therefore show that the 150 pcf water based mud formulated with a combination of barite and manganese tetroxide shows better sag performance as compared to the conventional water based mud formulated with 100% barite when static aged in an inclined position.

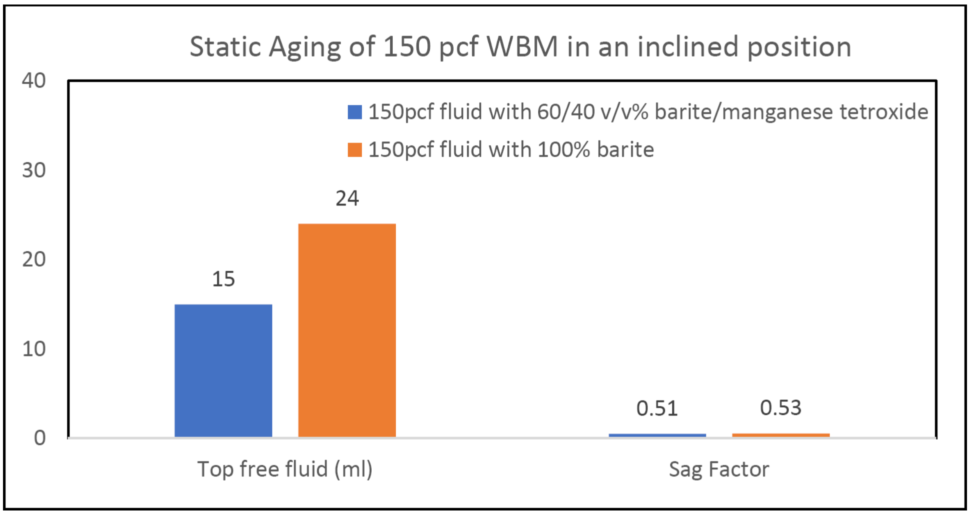

Figure 6 - Static aging studies of 150 pcf WBM in an inclined set up (45°) (Wagle, V. et al 2017b)

4.1.3. Filter-cake breaking experiments with 100 pcf water based mud.

To mitigate any issues arising due to a stuck pipe event, it would be imperative to remove the filter cake formed during drilling with the water based mud formulated with a combination of barite and manganese tetroxide. This breaking of the filter cake will result in the sticking force being reduced thereby releasing the stuck pipe in the wellbore (Montgomery et. al. 2007). Manganese tetroxide is acid soluble while barite does not show any acid solubility. This acid solubility property of manganese tetroxide can be employed to remove the filter cake in the wellbore by using any acid treatment.

In this study, aqueous solutions of cheap organic acids like formic, citric and acetic acids have been used as filter-cake breaker solutions. Filter-cake breaking experiments with 100 pcf fluid formulated with 60/40 v/v% combination of barite and manganese tetroxide were performed at 270°F with aqueous solutions of these organic acids. The filter cake of 100 pcf water based fluid prior to any acid treatment is shown in Figure 7.

Figure 7 - Filter-cake of 100 pcf WBM before any treatment with aqueous organic acid (Wagle, V. et al 2017b)

The strength of these three different aqueous organic acid breaker solutions was kept constant so as to have a fair comparison of the performance of these acids solutions in breaking the 100 pcf fluid filter cake. 15% w/w formic acid, 15% w/w citric acid and 15% w/w acetic acid solutions were therefore used for the study. The results of the tests with these filter-cake breaker fluid solutions are shown in Figure 8, Figure 10 and Figure 9.

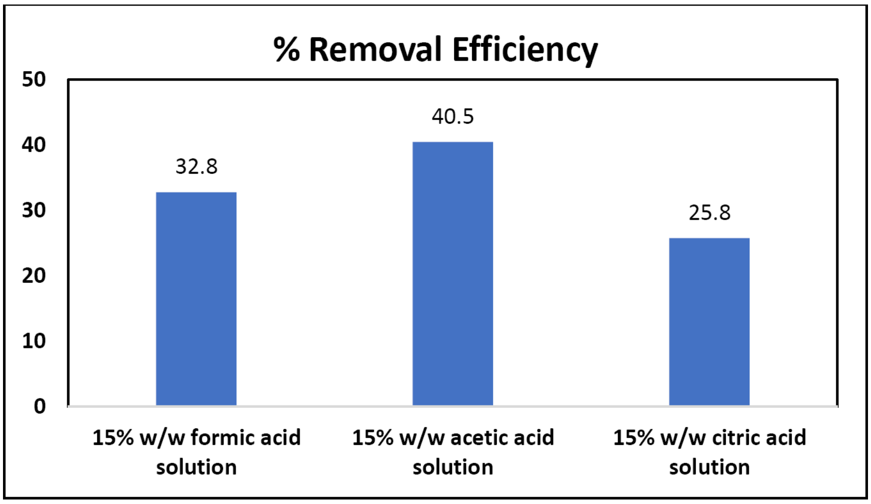

Figure 8 - Filter-cake breaking results of 100 pcf fluid at 270°F (Wagle, V. et al 2017b)

15% w/w formic acid (Figure 10) and 15% w/w citric acid (Figure 9) solutions gave 32.8% and 25.8% filter- cake removal efficiency respectively. The best performance in filter-cake removal was however shown by 15% w/w acetic acid solution (Figure 11) resulting in 40.5% filter-cake removal efficiency. The low filter-cake removal efficiency by using aqueous citric acid solution may be due to the formation of manganese citrate formed due to the reaction of citric acid and manganese tetroxide (Al Moajil 2008).

Figure 10 - Filter-cake of 100 pcf WBM after treatment with a combination of 15% w/w formic acid (Wagle, V. et al 2017b)

Figure 9 - Filter-cake of 100 pcf fluid after treatment with a combination of 15% w/w citric acid (Wagle, V. et al 2017b)

Figure 11 - Filter-cake of 100 pcf fluid after treatment with a combination of 15% w/w acetic acid (Wagle, V. et al 2017b)

Partial removal of filter-cake would be needed to release a stuck pipe in a wellbore. Partial removal of the filter-cake would decrease the sticking force and release the stuck-pipe. 15% w/w formic acid and 15% w/w acetic acid breaker solutions with 32.8% and 40.5% filter-cake removal efficiency, respectively, can therefore be expected to decrease the sticking force and thereby release the stuck pipe in the wellbore.

4.2. Laboratory Experiments: second case

4.2.1. Formulation of 120 pcf and 150 pcf fluids with 60/40 %v/v barite/ manganese tetroxide

Two drilling fluids, one medium mud weight viz. 120pcf and the other with a high mud weight viz. 150pcf were formulated with a 60/40 %v/v barite/ manganese tetroxide combination as weighting agents. These two fluids were hot rolled at 250°F and 300°F, respectively. After hot rolling these fluids at the specified temperature, their rheological and filtration properties were measured.

4.2.1.1. Formulation of 120pcf fluid.

The new 120pcf drilling fluid was formulated with a ratio of 60/40 %v/v barite/ manganese tetroxide as weighting agents. The additives used to formulate the 120pcf fluid are given in Table 2. The 120pcf fluid was hot rolled at 250°F for 16 hours. The performance of the 120pcf fluid formulated with a combination of barite and managanese tetroxide was also compared with a 120pcf fluid formulated with 100% barite. To make a fair comparison of the performance of these two fluids, all the additives, their concentrations and mixing time were kept the same. The rheology of both the fluids after hot-rolling at 250°F for 16 hours is shown in Figure 12.

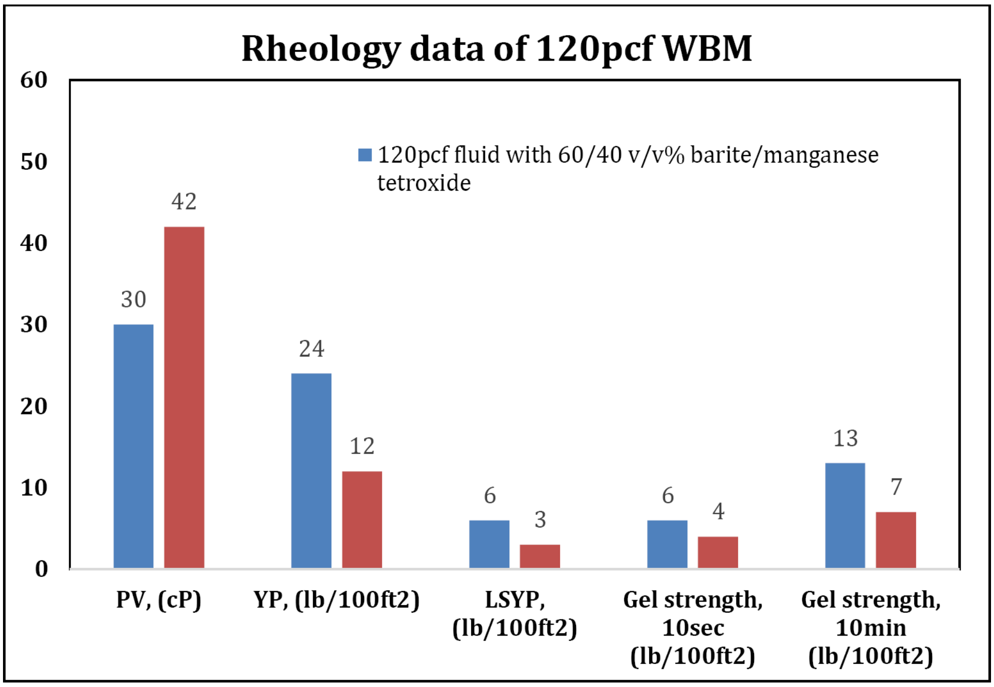

Figure 12 - Rheological properties of 120pcf fluids with 60/40 v/v (Wagle, V. et al 2017a)

The 120pcf fluid formulated with a combination of barite and manganese tetroxide gave a PV of 30cp and a good YP and LSYP of 24 lb/100ft^2 and 6 lb/100ft^2 respectively. The addition of 2ppb of bentonite and 0.75ppb of viscosifier in the 120pcf fluid resulted in good and optimum YP and LSYP values thereby ensuring that the fluid would have the desired sag resistance and good cuttings carrying capacity. The 120pcf fluid gave a 10sec and 10min gel strength of 6 lb/100ft^2 and 13 lb/100ft^2 respectively. The solid loading in a high density mud like 120pcf fluid being high, a chrome-free lignosulfonate deflocculant with a concentration of 2.5ppb was also added to the fluid. The addition of the chrome-free lignosulfonate dispersant helped in avoiding higher PV and gel strength values for the 120pcf fluid. A HPHT fluid loss additive with a concentration of 4ppb was added to the fluid for better fluid loss control. Therefore, the HTHP fluid loss measured at 250°F after a 30min period was only 10ml. These results showed that the 120pcf fluid formulated with a combination of barite and manganese tetroxide was stable with good rheology and filtration properties (Wagle, V. et al 2017a).

The 120pcf fluid formulated with 100% barite gave a PV of 42cp, YP of 12 lb/100ft^2 and LSYP of 3 lb/100ft^2 respectively. A comparison of the rheological properties of both the 120pcf fluids show that the fluid formulated with 100% barite has a higher PV and lower YP and LSYP as compared to the fluid formulated with a combination of barite and manganese tetroxide. A good LSYP value (≥ 5 lb/100ft^2) for a fluid signifies that the fluid has good cuttings carry capacity and sag resistance (Wagle, 2012 and Maghrabi 2015). The new fluid which has a LSYP of 6 lb/100ft^2 thus would show good sag resistance and cuttings carrying capacity than the conventional fluid which has LSYP of only 3 lb/100ft^2.

A 120 pcf water based mud requires a large concentration of weighting agent to achieve the desired density. The increased number of solids will lead to a high PV value as well as excessive heat and dehydration. As the volume of solids in the drilling fluid goes up, the particles become more closely packed together and it becomes more difficult for them to move freely. This will result in particle-particle interactions and increase in plastic viscosity. The lower PV shown by the new 120 pcf WBM shows that the use of manganese tetroxide, which has a higher specific gravity of 4.95 than barite helps to decrease the solids loading in the new 120 pcf fluid as compared to the conventional fluid formulated with 100% barite. This decreased solids loading in the new 120 pcf water based mud results in lesser particle-particle interactions thereby resulting in a lower PV value of 30 cp. A water based mud which has a high plastic viscosity would also show increased equivalent circulating density (ECD) due to increased pump pressures needed to pump the mud into the wellbore (Nicora 2001). Therefore, it is well known that the ECD has to be minimized by minimizing the PV value especially with high density fluids that require high solid loadings (Kulkarni 2014). Apart from higher ECDs, another drawback of water based mud having a high plastic viscosity is that it also decreases the rate of penetration (ROP) (Beck 1995). Therefore, the new 120 pcf WBM with its lower PV would lead to lower ECD and higher ROP as compared to the conventional 120 pcf WBM (Wagle, V. et al 2017a).

The new and the conventional 120pcf fluid gave a HTHP fluid loss of 10ml and 12ml respectively. These results show that the performance of the new 120pcf fluid formulated with a combination of barite and manganese tetroxide is better than the conventional 120pcf fluid formulated with 100%barite.

4.2.1.2. Formulation of 150pcf fluid.

Like the 120pcf fluid, a comparison of performance in terms of rheology and filtration properties of the new 150pcf fluid formulated with a ratio of 60/40 v/v% barite/ manganese tetroxide as weighting agent was made with a conventional fluid formulated with 100% barite. The additives, their concentrations and time of mixing were kept the same for both the fluids to have a fair comparison of their rheology and filtration properties after hot rolling. The additives and the order of addition for the both the 150pcf fluids are given in Table 3. Both the fluids were hot rolled at 300°F for a period of 16 hours after which the rheology and filtration properties were measured.

Figure 13 shows the rheology for both the 150 pcf WBMs after hot-rolling at 300°F for 16 hours. The new 150 pcf WBM formulated with a combination of barite and manganese tetroxide gave a PV of 38 cp while the fluid formulated with 100% barite gave a PV of 52 cp. Similar to the 120pcf fluid, it was anticipated that the 150pcf fluid formulated with a combination of barite and manganese tetroxide would show lower plastic viscosity than the fluid formulated with 100% barite. The new 150 pcf WBM showed a YP and LSYP of 38 lb/100 ft^2 and 9 lb/100 ft^2, respectively. The conventional 150 pcf WBM formulated with 100% barite gave a YP and LSYP of 22 lb/100 ft^2 and 4 lb/100 ft^2, respectively. The new and the conventional 150pcf fluid gave a HTHP fluid loss of 18ml and 20ml respectively. These results show that the new 150pcf fluid formulated with a combination of barite and manganese tetroxide is much better than the conventional 150pcf fluid in terms of rheology and filtration properties.

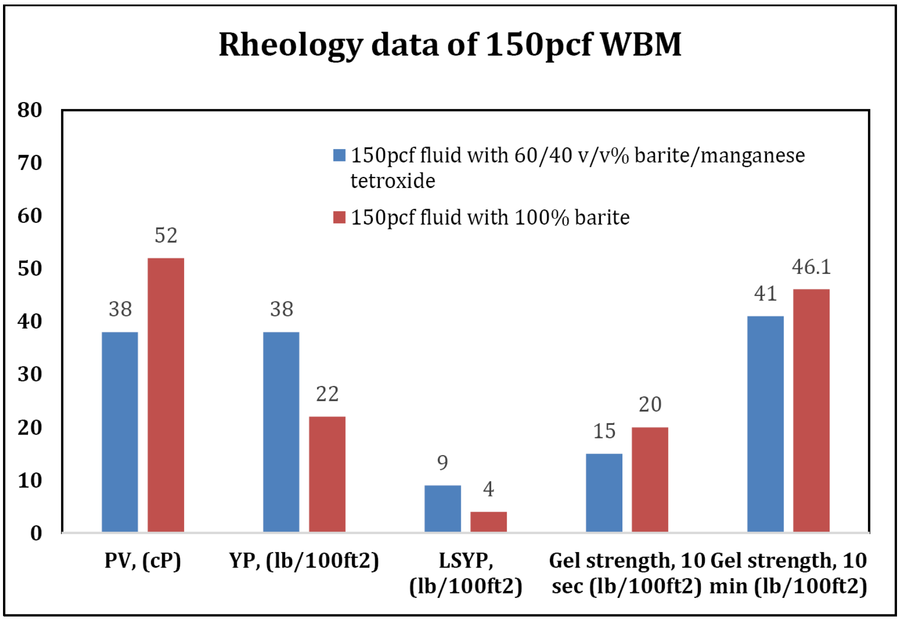

Figure 13 - Rheological properties of 150pcf fluids with 60/40 v/v (Wagle, V. et al 2017a)

4.2.2.Static aging of 120pcf formulated with 60/40 v/v% barite/ manganese tetroxide based fluids

A drilling fluid in the absence of good rheology is more likely to suffer issues associated with barite sag. This is due to inadequate suspension of solids in the fluid when it is kept static in the wellbore. Barite sag can cause problems such as mud weight fluctuations, lost circulation, stuck pipe, wellbore instability etc. To determine the sag resistance of these fluids the following procedure was followed in the laboratory.

Figure 14 shows the testing method employed for the static aging studies of the 120pcf fluid. Two different 120pcf fluids were formulated viz. one with 60/40 v/v% barite and manganese tetroxide and the other with 100% barite as weighting agents. These two 120pcf fluids were formulated and subsequently hot rolled at 250°F 16hrs for a time period of 16 hours. These fluids were then static aged at 250°F for a time period of 24hrs in aging cells. Both the fluids were static aged by keeping the aging cells in vertical (90°) and inclined position (45°). After static aging, the fluids in the cell were first inspected for any water separation and then subsequently the top free water separation was measured in ml. Sag factor was calculated as shown in Equation 4. A fluid that shows a sag factor value greater than 0.53 has the potential to sag (Maxey 2007).

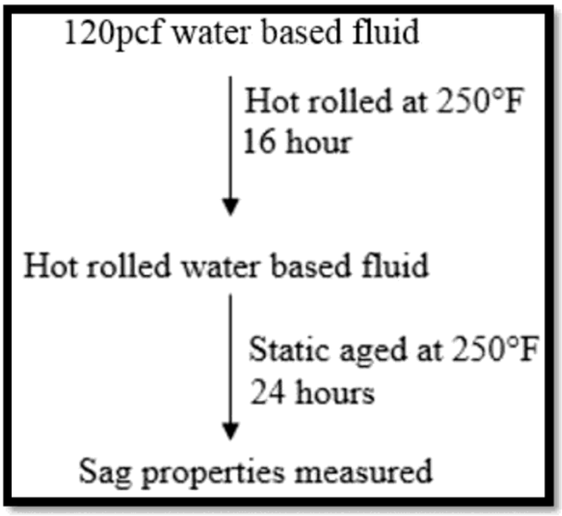

Figure 14 - Static aging studies of 120pcf water based fluids formulated with 60/40 v/v% of barite/manganese tetroxide (Wagle, V. et al 2017a)

4.2.2.1. Sag Performance Test – 90°.

Static aging tests were perfomed on medium density 120pcf fluids at 250°F for a period of 24 hours. The additives used to formulate the fluids in this study, their mixing order, and mixing time are given in Table 2. After 24 hours of static aging, the sag factor and the volume of top free fluid separated from the drilling fluid was measured and is given in Table 6. 120pcf fluid formulated with 60/40 v/v% barite/manganese tetroxide when static aged at 250°F gave a sag factor of 0.51 and top free fluid separation of 1ml.

Table 6 - Sag factor and water separation for 120pcf fluid (90°)

	120pcf fluid with 60/40 v/v% barite/manganese tetroxide	**120pcf fluid with 100% barite**
Static aging temperature	250°F	250°F
Top free fluid	1ml	10ml
Sag Factor	0.51	0.53

The sag performance of 60/40 **v/v%** barite/ manganese tetroxide based 120pcf fluid was also compared to the conventional 120pcf fluid formulated with 100% barite as the weighting agent. The conventional fluid with 100%

barite gave a sag factor of 0.53 and a top free water separation of 10 ml whereas the 120pcf fluid formulated with a combination of barite and manganese tetroxide gave a sag factor of 0.51 and a top free fluid separation of 1ml. These static aging studies showed that the medium density 120pcf fluid formulated with a combination of barite and manganese tetroxide showed better sag resistance as compared with conventional 120pcf fluid formulated with only barite as weighting agent.

4.2.2.2. Sag Performance Test – Inclined Position (45°).

To simulate the conditions of drilling in deviated wells, the new 120pcf fluid formulated with 60/40 v/v% barite/ manganese tetroxide was also static aged along with its 100% barite counterpart at 250°F for 24 hours in aging cells held at an angle of 45°. The inclined setup is shown in Figure 15. This was done to test and compare the sag-performance of 60/40 v/v% barite/ manganese tetroxide and 100% barite based fluids while drilling deviated wells.

Figure 15 - Inclined setup at 45° (Wagle, V. et al 2017a)

The top free separated fluid and sag factor of the two static aged fluids are given in Table 4. The 120pcf fluids formulated with 60/40 v/v% barite/manganese tetroxide and 100% barite gave a sag factor of 0.51 and 0.53 respectively. Also, the 120pcf fluids formulated with 60/40 v/v% barite/manganese tetroxide and 100% barite gave a top free fluid separation of 2ml and 12.5ml respectively. Lower sag factor and top free water separation obtained for the fluid formulated with a combination of barite and manganese tetroxide demonstrates that it shows better sag performance in inclined static condition as compared to the conventional drilling fluid formulated with 100% barite. This also implies that the performance of the formulated fluid with a combination of barite and manganese tetroxide while drilling deviated wellbores would be much better as compared to the conventional drilling fluid formulated with 100% barite.

Table 7 - Sag factor and water separation for 120pcf fluid drilling fluids static aged in an inclined set up (45°)

	120pcf fluid with 60/40 v/v% barite/manganese tetroxide	**120pcf fluid with 100% barite**
Static aging temperature	250°F	250°F
Top free water	2ml	12.5ml
Sag Factor	0.51	0.53

4.2.3. Filter-cake breaking of 120pcf 60/40 v/v% barite/ manganese tetroxide based drilling fluids

In the case of a stuck pipe event due to differential sticking, it becomes imperative to release the stuck pipe as soon as possible to reduce the non-productive time and resume drilling operations. Therefore, in the case of a stuck pipe event while drilling with the 60/40 v/v% barite/ manganese tetroxide based drilling fluid, it was very important to evaluate the efficacy of different breaker fluids in breaking its filter-cake and thereby releasing the stuck pipe (Wagle, V. et al 2017a).

120pcf fluid (Table 2) with 60/40 v/v% barite/ manganese tetroxide was first formulated and hot rolled at 250°F respectively. A filter cake of 120pcf fluid as shown in Figure 16 was first prepared on a 50µ ceramic disk at 250°F using a 500 ml HPHT cell.

Figure 16 - Filter-cake of 120pcf fluid before any acid/acid percursor treatment (Wagle, V. et al 2017a)

Four different different filter-cake breaker fluids viz. glycolic acid, HCl acid, formic acid precursor and a combination of formic acid precursor with 1% HCl acid were used in the experiments. The filter-cake of the 120pcf fluid as shown in Figure 16 was then contacted with the filter-cake breaker fluids for a time period of 4.5 hours at 250°F. Figure 17 shows the % removal efficiency for the four filter-cake breaker fluids used in the experiments.

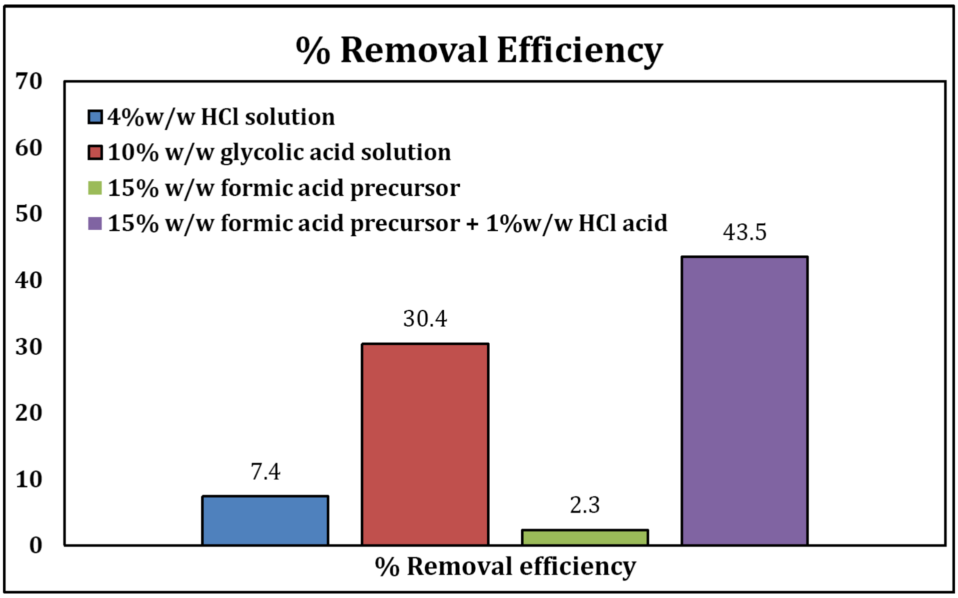

Figure 17 - Removal efficiency of different filter-cake breaker fluids at 250°F (Wagle, V. et al 2017a)

4%w/w aqueous HCl solution was initially used as a breaker fluid to remove the filter-cake. The use of HCl solution in a concentration greater than 5%w/w was avoided in these experiments. This was due to the fact that HCl in a higher concentration reacts with manganese tetroxide to release chlorine gas (Vernon, 1891; De Beni, 1975 and Depourdeaux, 1975).

Equation 6 shows the release of chlorine gas when manganese tetroxide is treated with a higher concentration of aqueous HCl solution.

$$Mn_3O_4 + 8HCl \rightleftharpoons 3MnCl_2 + Cl_2 + 4H_2O \qquad \text{(Equation 6)}$$

However, owing to the low concentration of aqueous HCl used as a breaker fluid, 4%w/w HCl solution resulted in only 7.4% breakage of the filter-cake (Figure 18). This showed that at 250°F, the filter-cake removal efficiency of HCl acid having a concentration below 5%w/w would not be sufficiently high to release stuck- pipe.

Figure 18 - Filter-cake of 120pcf fluid after treatment with 4%w/w HCl (Wagle, V. et al 2017a)

The filter-cake of 120pcf drilling fluid was also treated with aqueous organic acid based breaker fluid viz. 10%w/w glycolic acid solution. A 30.4% removal efficiency was obtained after 4.5hours of contact time with aqueous glycolic acid (Figure 19). This shows that the filter-cake when contacted with 10%w/w aqueous solution of glycolic acid can thus be expected to partly remove the filter-cake thereby decreasing the sticking force. The decrease in the sticking force would ensure the release of the stuck pipe in the wellbore.

Figure 19 - Filter-cake of 120pcf fluid after treatment with 10%w/w glycolic acid (Wagle, V. et al 2017a)

The filter-cake of 120pcf drilling fluid was also treated with 15%w/w aqueous formic acid precursor solution. 4.5 hours of treatment time with the acid precursor solution resulted in just 2.3% breakage of the filter-cake (Figure 20). This was expected since the formic acid precursor hydrolyzes into formic acid very slowly at 250°F. Thus, the low amount of formic acid generated even after 4.5 hours of contact of the breaker fluid with the filter-cake resulted in very low filter-cake removal efficiency.

Figure 20 - Filter-cake of 120pcf fluid after treatment with 15%w/w formic acid precursor (Wagle, V. et al 2017a)

Thus to fasten the hydrolysis rate of the formic acid precursor solution at 250°F and to increase the concentration of formic acid, a combination of 15%w/w acid precursor and 1%w/w HCl acid was used as the breaker fluid (Figure 21). HCl is relatively cheaper as compared to other mineral or organic acids and hence was chosen to act as a catalyst to increase the rate of hydrolysis of the formic acid precursor. This increase in the rate of hydrolysis of the precursor results in a faster release of the formic acid required to break the filter-cake. This combination of HCl acid and formic acid precursor resulted in 43.5% breakage of the filter- cake after 4.5 hours.

This higher removal efficiency therefore showed that the use of low concentration of HCl acid along with the formic acid precursor increases the filter-cake removal efficiency.

Figure 21 - Filter-cake of 120pcf fluid after treatment with a combination of 15%w/w formic acid precursor and 1% w/w HCl (Wagle, V. et al 2017a)

Conclusion

Drilling fluids were formulated with a combination of barite and manganese tetroxide as weighting agents with good rheology and filtration properties. These fluids showed better rheological properties than fluids formulated with 100% barite as weighting agent.

In the first case static aging tests performed on 150 pcf drilling fluids showed that high-density water based muds formulated with a 60/40 %v/v combination of barite and manganese tetroxide show better sag resistance in comparison with conventional fluids formulated with 100% barite. And this 150pcf drilling fluid when static aged in inclined position and formulated with a 60/40 %v/v combination of barite and manganese tetroxide as weighting agents showed good sag resistance and minimal free water separation, while for 100 pcf fluid, treatment with 15% w/w acetic acid and 15% w/w formic acid resulted in good filter-cake removal efficiency of 40.5% and 32.8%, respectively.

In the second case 120 pcf drilling fluid when formulated with a 60/40 %v/v combination of barite and manganese tetroxide again showed better sag resistance in comparison with conventional fluids formulated with 100% barite. And 120 pcf drilling fluid formulated with a 60/40 %v/v combination of barite and manganese tetroxide as weighting agents when static aged in inclined position showed good sag resistance and minimal free water separation, as in the first case. For 120 pcf fluid, treatment with 10%w/w glycolic acid and a combination of 15%w/w formic acid precursor and 1% w/w HCl resulted in good filter-cake removal efficiency.

This means that acid treatment involving aqueous solutions of relatively cheap organic acids like formic acid, acetic acid and citric acid can be used to release stuck pipe in the wellbore. And, overall, the use of weighting agent having the higher density like manganese tetroxide in combination with barite decreases the solids loading as compared to the conventional fluid formulated with 100% barite. These decreased solids result in a lower plastic viscosity which results in a lower equivalent circulating density, higher rates of penetrations, faster drilling, and lower drilling costs, respectively.

In addition to all of the above, also one of the reasons why water based drilling fluid containing a combination of manganese tetroxide and barite as weighting agents is the best choice in comparison with fluid formulated with 100% barite, is that this fluid has the lower cost. It is known that manganese tetroxide is relatively more expensive than barite. Thus, the use of manganese tetroxide as the only weighting agent for the fluid will result in increased cost of the fluid. In other words, the use of a combination of barite and manganese tetroxide would not only reduce the fluid cost but also result in greater sag resistance and lower circulating densities as compared to a fluid formulated with 100% barite. All these factors prove the effectiveness of the method analysed in this work in both practical cases which plays one of the most important factors in fluid choosing during drilling operations.

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