Non-Asphalitic, Fluid-Loss-Control Agent for High-Temperature Applications in Synthetic-Based Invert Emulsion Drilling Fluids
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Abstract

This paper discusses the design, development and testing of an organo-amine quebracho-based fluid loss agent which is stable to 400°F. This quebracho-based fluid loss agent is compatible with synthetic-based fluids and is environmentally acceptable. The performance advantages of this product include high-temperature stability, low fluid losses, minimal to no side effects and good rheological properties. Traditionally invert emulsion drilling fluids have been used to optimize drilling performance primarily due to the high level of wellbore stability and high penetration rates seen when utilizing these fluids. Invert emulsion fluids require various additives such as emulsifiers, fluid-loss-control (FLC) agents, viscosifier etc. The list of various FLC agents traditionally used include: asphalt, polymers, Gilsonite, and amine-treated lignite. Such materials are not always compatible with the environment and do not degrade easily making it difficult to use in areas where tough environmental regulations are in place.

A new environmentally acceptable FLC agent has been developed utilizing naturally occurring quebracho and fatty acid derived amines. The product is lipophilic and when used in the range of 4 to 8 lb/bbl has been found to give high-temperature, high-pressure fluid losses which are less than 6 mL; the product is stable up to a high temperature of 400°F. The paper includes the laboratory evaluation and field application of this additive in invert emulsion drilling fluids.

Introduction

For oil well drilling operations, two types of drilling fluids, or “muds” are generally utilized, water-based drilling fluids (WBM) and invert emulsion drilling fluids (IEDF). IEDF includes both oil-based drilling fluids (OBM) and synthetic-based drilling fluids (SBM). The pros and cons associated with WBM and OBM are well documented. In general, WBM are considered more health, safety and environmentally (HS&E) friendly and economical. However IEDF are considered the preferred drilling fluids over WBM when drilling water-sensitive shale formations and other difficult wells due to their superior shale inhibition and lubricity properties. IEDF also provide excellent borehole stability, thermal stability, corrosion inhibition, ease in engineering and fluid maintenance, better fluid loss control and excellent filtercake quality.

Fluid loss control (FLC) and filtercake quality of a drilling fluid plays an important role in the wellbore construction process and can influence various important aspects of drilling operations, such as wellbore stability, completion process, formation damage, downhole mud losses, and differential sticking. Ultimately, FLC and filtercake quality become critical parameters for both the drilling operation and after drilling for well productivity. Different additives may be utilized in IEDF formulations in order to minimize the fluid losses to formation and to enhance the filtercake quality. These additives may be either dispersed or solubilized in the oil phase. Various fluid loss additives have been developed and utilized in IEDF during drilling operation. However, the most widely used FLC additives are Gilsonite, amine-treated lignite and synthetic organo-soluble gel resin.

Pros and Cons of Current FLC Additives

Gilsonite. Even though the cost of Gilsonite has increased recently, it is still one of the most economical FLC additives for invert emulsion drilling fluids. Also, Gilsonite is a very versatile FLC additive for different temperatures due to its availability in a wide melting-point range. In spite of its versatility and relatively low cost, there is the issue of potential formation damage which have prompted various papers to be written concerning formation damage and formation damage mechanisms while utilizing Gilsonite. However, formation damage by Gilsonite depends upon the type of formation drilled, fluid formulation and quality of Gilsonite. Gilsonite also has other performance-related issues – once the Gilsonite melts or dissolves, it contributes to high viscosity and gel strengths in the drilling fluid without contributing to fluid loss properties. The biggest drawback of Gilsonite is environmental concerns. It contains aromatic components and therefore cannot be used in SBM for the Gulf of Mexico where aromatic contamination is prohibited due to environmental regulations on disposal of SBM and cuttings generated during drilling operation.

Oil-Soluble Polymeric Resin. Polymeric resin additives are expensive when compared to the cost associated with Gilsonite. Polymeric resin works well as an FLC additive, but when used at higher concentrations, it contributes to high viscosity in various fluid formulations. As a polymeric resin, there is also the potential for formation damage depending upon formation. Overall polymeric resin polymer performs
well as fluid-loss-control additive but cost is the biggest drawback.

**Amine-Treated Lignite.** This is also can be an economical FLC additive, however in the lower cost range it has limited temperature stability. Over all the performance is substandard and therefore lost popularity in the field as a FLC additive. More thermally stable amine-treated lignites are available that can extend the temperature range of filtration control, however these materials are significantly more expensive.

**Other Additives.** Along with the above noted additives, there are various other FLC agents such as oil-soluble surfactants have been developed without big success. There is a need for a new FLC additive which addresses the environmental concern associated with Gilsonite, performance issues associated with amine-treated lignite and high cost associated with polymeric resin.

**Drilling Fluid Filtration Process and Characterization**

The filtration process according to the API RP 13B-2 method is characterized by two separate stages. In the first stage, rapid invasion of the porous formation by drilling fluid and any solids present occurs (Fig. 1). This first stage is very rapid and also known as spurt loss. An internal cake is built in the rock formation near the drilled wellbore surface. However, this invasion of fluid and solids in the rock formation is a big factor in the formation damage mechanism. Once the spurt loss slows down, the external cake starts building and the second stage begins. During the second stage, an external cake is build (Fig. 2) as the fluid (filtrate) continues to invade the formation until the filtercake is sufficient to stop the filtrate flow. This filtrate invasion can cause changes in wettability and formation stability that affect future production.

The thickness of the filter cake can either increase as under static conditions or remain constant as under dynamic conditions. However for IEDF, the formation damage can be related to solids invasion and interaction with surfactants in the filtrate. In IEDF, the filtrate is composed of base oil and oil-soluble products such as emulsifiers, wetting agents, rheology modifiers and fluid-loss-control additives. The filtrate loss to formation must be controlled so it does not create emulsions with reservoir fluids or interact with the formation.

**Development of Amine-Modified Quebracho**

To overcome some of the aforementioned problems, such as environmental concerns, performance limitations, economic disadvantages and formation damage issues, a new amine-modified quebracho-based product (AMQ) has been developed. This AMQ is completely soluble to dispersible in most base fluids. The product is stable to temperatures in excess of 400°F and performs well in a variety of drilling fluid formulations. The product is prepared from readily available naturally occurring quebracho and naturally occurring fatty acid derived fatty amine. AMQ is relatively non-toxic to marine environment and is HS&E friendly. The performance of AMQ with respect to its fluid-loss control properties and formation damage is better than the traditional additives including Gilsonite and amine-treated lignite.

**Chemical Composition**

The non-asphaltic FLC agent is synthesized by reacting naturally occurring quebracho with fatty amine at elevated temperature. The final product is in the form of a fine powder with a reddish brown color. The product is completely soluble to dispersible in most invert emulsion base fluids.

**Environmental Aspects**

As mentioned earlier, this FLC agent is derived from naturally occurring raw materials and therefore it was expected to be non-toxic and HS&E friendly. AMQ was tested for toxicity according to a 10-day Acute Sediment Toxicity Test using *Leptocheirus plumulosus*, developed by work group formed under the Synthetic Based Research Group and approved by US EPA. The toxicity of the test drilling fluid was compared to a reference SBM (C16-C18 internal olefin) with and without the test sample. For compliance the ratio of the reference drilling fluid median lethal concentration (LC50) to the tested drilling fluid LC50 should be <1.0. The test results are given in Fig. 3. The studies showed that formulations containing AMQ (used in the range of 4 to 8 lb/bbl) had ratio less than 1.

![Fig. 3 – Toxicity test results. Pass/Fail ratio with and without AMQ.](image-url)
Aromatics and Polycyclic Aromatic Hydrocarbons

Synthetic base fluids are manufactured from ethylene and therefore contain less than 0.001% aromatics content by weight. Therefore, disposal of these fluids has a relatively low impact to the environment. Although the aromatics may constitute only minor fraction of total hydrocarbon; FLC agents such as Gilsonite, will contaminate the SBM with aromatics, produce sheen and therefore require more costly disposal of the SBM as it cannot be discharged overboard. The newly developed AMQ FLC additive will not contaminate the SBM with aromatic hydrocarbons, will not cause sheen on the surface of water and will have a relatively low impact on the environment.

Test Strategy

Mud Formulations and Test Methods. Standard methods as outlined in API RP RB 13B-2 were used to test laboratory test fluids and evaluate their conventional drilling fluid properties such as plastic viscosity (PV), yield point (YP), 10-minute and 10-second gel strengths, electrical stability (ES), and high-temperature, high-pressure fluid loss (HTHP FL).

Mud Formulations. To demonstrate the effectiveness and versatility of the AMQ as a FLC agent, the AMQ was tested in a variety of fluid formulations. These fluid formulations included variations in 1) base oils, 2) oil/water ratio, 3) mud weights, and 4) temperatures. These formulations cover a wide range of field applications. The components that were used to formulate the muds include viscosifier (1-2 lb/bbl), lime (2-4 lb/bbl), emulsifier (10-12 lb/bbl), and wetting agent (2-4 lb/bbl).

Performance of AMQ

Effect of Base Fluids. To demonstrate the effectiveness and compatibility of AMQ as a FLC agent in various base fluids, formulations containing 8 lb/bbl of the product were prepared according to standard OBM mixing procedure. The fluids used were low-toxicity mineral oil (LTMO), synthetic fluid (Synthetic B), IO16-18 (olefins) and diesel. These fluids were hot rolled at 250°F for 16 hours. After heat aging, the rheological properties of the test fluids were measured with using a Fann 35 rheometer at 120°F. The HTHP filtration tests were conducted using high-pressure cells at 250°F with 500-psi differential pressure. Figure 4 shows the rheological properties and Figure 5 shows the HTHP fluid loss properties of the heat aged fluids. The fluid loss studies show that the AMQ is compatible with all the base fluids that were tested with good rheological properties and fluid loss control.

Impact of Oil/Water Ratio. To find the effects of oil/water (O/W) ratios on fluid loss properties of AMQ, 12-lb/gal fluids with O/W ratios of 90:10, 80:20, and 70:30 were prepared. The base fluid used was IO16-18 and the IEDF treated with 8 lb/bbl of AMQ for this test series. These fluids were heat aged at 250°F for 16 hours while rolling. After heat aging the rheological properties were measured according to API methods at 120°F. The rheological properties and HTHP fluid losses of these fluids are shown in
Effect of Mud Weights. To determine the effect of mud weight on FLC properties, the fluid formulations for 10, 12, 14 and 16-lb/gal drilling fluids containing 8 lb/bbl of AMQ were prepared and evaluated. For 10- and 12-lb/gal fluids, 80:20 O/W ratios were used; in 14- and 16-lb/gal fluids, 90:10 O/W ratios were used.

These muds were heat aged at 250°F for 16 hours, and after heat aging the rheological properties was measured at 120°F. The results are given in Figure 8. The HTHP fluid loss of the heat aged fluids was measured at 250°F and is shown in Figure 9. The results showed that variations in mud weights had minimal effect on fluid loss with AMQ as a fluid loss control agent.

Temperature Stability of AMQ. Thermal stability of a drilling fluid and drilling fluid additives is considered to be an important aspect of drilling fluid. Most of the drilling fluid formulations are stable in the range of 250 to 300°F. However once temperatures exceed 300°F, then thermal stability of the fluid formulation and additives becomes an issue.

To demonstrate the temperature stability of AMQ FLC additive, two different fluid formulations, with mud weights of 15 and 16 lb/gal and O/W ratios of 80:20 and 85:15 respectively were utilized. One IEDF uses a low-toxicity mineral oil as the base fluid (LT MOBM) and the other an IODE-16-18 as the base fluid.

These fluid formulations were heat aged at temperatures ranging from 300 to 400°F, for 16 hours. After each heat aging cycle, the rheological properties were measured at 120°F. The HTHP fluid loss was conducted with high pressure cells at 300°F with 500-psi differential pressure. The results for the 15 lb/gal mud are given in Figures 10 and 11. Figure 12 gives the rheology and HTHP fluid loss for 16 lb/gal drilling fluid aged at 375°F.
The results show that the AMQ material is thermally stable and produces adequate fluid loss control up to 400°F. In a further series of experiments, the AFQ material was tested in a synthetic drilling fluid formulation designed for extreme temperature application. In combination with a secondary filtration control additive, good filtration control was achieved after 24-hr static aging at 485°F and 575°F, showing the high thermal stability of the material.

The results show that newly developed non-asphaltic fluid-loss-control agent can be used to replace Gilsonite and other polymeric FLC agents which are currently used in high-temperature applications in SBM and other IEDF. The newly developed AMQ fluid-loss-control additive is stable to temperatures up to 400°F and offers a significant improvement in thermal stability when compared with other drilling fluid additives. The following experiments show the comparison of performance of AMQ with other fluid loss additives.

**Comparison of FLC Agents.** The performance of AMQ as a fluid-loss-control agent in high temperature applications, was compared with amine-treated lignite (AML), using formulation with mud weight of 12 lb/gal and O/W ratio of 80:20. These formulations containing 10-lb/bbl fluid loss additive were heat aged at 300°F for 16 hours. After heat aging, rheology was measured at 120°F and HTHP fluid losses measured at 300°F with 500-psi differential pressure. The results are shown in Figure 13.

**Table 1 – 14.2-lb/gal IEDF Formulation for FLC Comparison of AMQ and Polymeric Agent**

<table>
<thead>
<tr>
<th></th>
<th>Polymeric FLC Agent</th>
<th>AMQ</th>
</tr>
</thead>
<tbody>
<tr>
<td>IO16-18</td>
<td>209</td>
<td>204</td>
</tr>
<tr>
<td>Viscosifier</td>
<td>0.75</td>
<td>0.75</td>
</tr>
<tr>
<td>Lime</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>Emulsifier</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td>Wetting agent</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>CaCl2</td>
<td>6.77</td>
<td>6.73</td>
</tr>
<tr>
<td>Water</td>
<td>21</td>
<td>21</td>
</tr>
<tr>
<td>AMQ</td>
<td>9</td>
<td></td>
</tr>
<tr>
<td>Commercial Polymer FLC Agent</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>Barite (micronized)</td>
<td>317</td>
<td>312</td>
</tr>
<tr>
<td>Calcium carbonate</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>Rev. Dust</td>
<td>25</td>
<td>25</td>
</tr>
<tr>
<td>O/W ratio</td>
<td>90/10</td>
<td>90/10</td>
</tr>
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</table>

**Table 2 – Return Permeability Test on Sandstone (T = 400°F, Overbalanced pressure = 725 psi)**

<table>
<thead>
<tr>
<th>Drilling Fluid</th>
<th>Initial Permeability (mD)</th>
<th>Return Permeability after wellbore end trimmed (mD)</th>
<th>% Return Permeability</th>
</tr>
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<tbody>
<tr>
<td>OBM – Gilsonite</td>
<td>104</td>
<td>44.4</td>
<td>43</td>
</tr>
<tr>
<td>OBM-AMQ</td>
<td>25.2</td>
<td>19</td>
<td>74</td>
</tr>
</tbody>
</table>

**Fig. 13 – Rheological properties and HTHP fluid loss test at 300°F of mud containing either AMQ or AML.**

For the comparison of AMQ against a polymeric FLC additive, 14.2-lb/gal fluid formulations in Table 1 were utilized. This fluid formulation had O/W ratio of 90:10 and micronized barite was used as weighting agent. These fluids were heat aged at 350°F for 16 hours. After heat aging the rheology were measured at 120°F and the HTHP fluid loss was measured at 300°F at 500-psi differential pressure. The results are given in Figure 14. The comparison of the performance of AMQ against commercially available fluid loss additives showed that AMQ performed significantly better in high-temperature applications.

**Formation Damage Issues.** To demonstrate the advantage of AMQ in reducing potential for formation damage, studies on return permeability were conducted on the high-permeability sandstone and Berea core samples. The return permeability test results on sandstone are shown in Table 2 and on Berea core samples are shown in Table 3.

**Fig. 14 – Rheological properties and HTHP fluid loss test at 300°F of mud containing either AMQ or polymeric FLC Agent.**
Table 3 – Return Permeability Test on Berea Core
(T = 248°F, Overbalanced pressure = 500 psi)

<table>
<thead>
<tr>
<th>Drilling Fluid</th>
<th>Initial Permeability (mD)</th>
<th>Volume of filtration, (mL/% pore volume)</th>
<th>Return Permeability (mD/% Return)</th>
<th>Flow initiation pressure (psi)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10-lb/gal mud with AMQ</td>
<td>73.7</td>
<td>2.61 / 20.6</td>
<td>74.0 / 100.4</td>
<td>22.36</td>
</tr>
<tr>
<td>15-lb/gal mud with AMQ</td>
<td>71.4</td>
<td>1.43 / 11.3</td>
<td>76.0 / 106.5</td>
<td>19.52</td>
</tr>
</tbody>
</table>

The return permeability tests in sandstone (Table 2) showed that with a return permeability of 74% in this series, the AMQ is significantly less damaging than the Gilsonite.

In the second series of tests, two return permeability tests were conducted to evaluate the effects of density on the permeability of Berea core samples using a 10-lb/gal and 15-lb/gal IEDF containing AMQ. The results of these tests in Table 3 indicated that both of the fluids are non-damaging to Berea core under the test conditions indicated with return permeability of near 100%. This can be related to the quality of the filter cake formed and the minimal amount of fluid invasion that occurred.

Field Application Studies

Several studies have been completed using AMQ with a wide range of fluid formulations and aging temperatures to assess the potential use in specific field applications. Following are the typical such formulations developed for field applications and their performance in laboratory settings.

Egypt

The study involved comparing AMQ with a commercial polymeric FLC additive. The field required 17.2-lb/gal fluid formulations with 85:15 O/W ratios. The fluid formulation is given in Table 4. The fluids were heat aged at 370°F for 16 hours. After the heat aging period, the rheologies were measured at 150°F and HTHP fluid loss at 350°F at a differential pressure of 500 psi. The results in Figure 15 show that the fluid formulation containing AMQ is stable to high temperature and perform better than the commercial polymeric FLC additive.

Deep Gas Well

The objective for this field application was to develop a 19-lb/gal fluid formulation, which is stable to 450°F using low toxic mineral oil as the base fluid. The application of this fluid was in deep gas well which had bottomhole temperatures in excess of 450°F. The formulation developed for this application was a 19-lb/gal drilling fluid with O/W ratio of 95/15. This fluid was hot rolled at 450°F for 16 hours and after hot rolling the fluid properties were measured at 150°F. The rheology and HTHP fluid losses are given in Figure 16. The results showed that the fluid formulation containing AMQ was stable to 450°F with excellent fluid loss control.

North Sea Well

The objective for this field application was to maintain a low filtration loss through the production interval and utilize a filtration control additive that did not contribute to formation damage. Bottomhole temperature (BHT) was measured at 275°F and the HTHP filtration loss was measured both on conventional filter paper and on a 5-micron aloxite disc. The filtration behavior of the field fluid can be seen in Figure 17. Plotted against depth and shown for both the 12¾-in. and 8½-in. intervals. The results show that filtration behavior was readily controlled with the AMQ material.
Conclusions

A non-asphaltic amine-treated quebracho-based (AMQ) fluid-loss-control agent for high-temperature applications has been developed and tested in both the laboratory and the field. The AMQ shows beneficial properties of fluid loss control, minimal formation damage potential and acceptable environmental impact when compared with other commercially available fluid loss additives. The product is stable to temperatures greater than 550°F and performs well in variety of the drilling fluid formulations as a fluid-loss-control agent.

References