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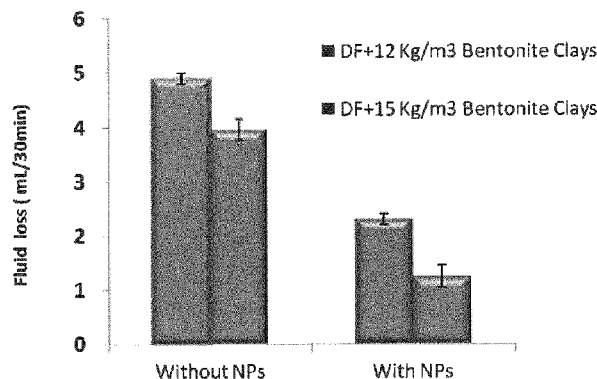
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(54) Title: NOVEL NANOPARTICLE-CONTAINING DRILLING FLUIDS TO MITIGATE FLUID LOSS

Figure 18



(57) Abstract: The present invention is directed to a well fluid, and in particular a drilling fluid having low amounts of nanoparticles which act as fluid loss material for reducing fluid loss in an underground formation. The fluid is a nanoparticle-containing well fluid comprising a base fluid and about 5 wt% or less nanoparticles, for preventing or reducing fluid loss to an underground formation, wherein the well fluid is a drilling fluid, kill fluid, completion fluid, or pre-stimulation fluid. The invention also includes in situ and ex situ methods of forming the nanoparticles.

NOVEL NANOPARTICLE-CONTAINING DRILLING FLUIDS TO MITIGATE FLUID LOSS

Field of the Invention

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The present invention relates to drilling fluids and in particular drilling fluids with nanoparticles for mitigating fluid loss to underground formations.

Background of the Invention

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Hydrocarbons, such as oil and gas, are recovered from underground formations through drilled wells. The success of any well drilling operation depends on many factors and one of the most important is the drilling fluid. Drilling fluids, also called drilling muds, are circulated from the surface through the drill string and introduced to the bottom of the borehole as fluid spray out of drill bit nozzles and subsequently circulated back to the surface via the annulus between the drill string and the well hole. Drilling fluids are formulated to cool down and lubricate the drill bit, remove cuttings from the hole, prevent formation damage, suspend cuttings and weighting materials when circulation is stopped, and cake off the permeable formation by retarding the passage of fluid into the formation.

Drilling operations face great technical challenges with drilling fluid loss being the most notable. Fluid loss is also an issue for other well fluids such as kill fluids, completion fluids and stimulation fluids. Drilling fluid loss is the partial or complete loss of fluid to the formation during drilling. Loss of fluid, in turn, impacts the cost of drilling. Therefore, drilling and other well fluids are typically formulated with loss circulation materials or additives (LCM). The primary function of LCM is to plug the zone of loss in the formation, away from the borehole face so that subsequent operation will not suffer additional fluid losses. LCM form a barrier, such as filter cake, which limits the amount of drilling fluid penetrating the formation and prevents loss. New lost circulation materials have been developed in the past 10 years. However, these lost circulation materials are not sufficiently effective to serve their primary goal of eliminating fluid loss.

It is often impossible to reduce fluid loss with these micro and macro type fluid loss additives due to their physio-chemical and mechanical characteristics. LCM with diameters in the range of 0.1-100 μm may play an important role when the cause of fluid

loss occurs in 0.1 μm -1 mm porous formations. In practice, however, the size of pore openings in formations such as shales that may cause fluid loss is in the range of 10 nm-0.1 μm and these larger micro and macro type fluid loss additives are not effective in reducing fluid loss.

5 Nanoparticles have been used in well fluids for a number of purposes.

U.S. Patent 3,622,513 (1971) is directed to oil-based drilling fluids with improved plastering properties and reduced fluid loss properties at extreme conditions of borehole temperature and pressure. The drilling fluids contain asphaltous material and a weighting agent, usually barium sulfate having a particle size of 100 to 200 μm , which primarily
10 result in the formation of the filter cake to prevent fluid loss to the formation. The drilling fluids also contain a small amount of a secondary weighting material inert to the fluid and having a particle size of less than 3 μm . Preferred inert materials for the secondary weight phase include metal oxides such as iron oxides and titanium oxides. The fluids showed some reduction in fluid loss. However, the compositions required extra additives, such as
15 the asphalt material, which bind to the nanoparticles and acted as a filler or plaster between the particles at high temperature to reduce the fluid loss. The fluid may also contain other lost circulation additives.

U.S. Patent 3,658,701 (1972) is directed to an oil based drilling fluid, including an invert emulsion drilling fluid, employing particular oxides, such as manganese oxide, to
20 reduce fluid loss. The oxide is used with asphalt constituents. The asphaltic materials bind the metal oxide at high temperature and acted as a filler between the particles to reduce the fluid loss. With the addition of MnO_2 , and the asphaltic material, the fluid loss reduction was approximately 66% as compared to the control sample at 300°F with substantially no breakdown of the emulsion. The patent does not disclose the size of the particles. Further,
25 it appears that the asphaltic material is necessary to obtain the fluid loss benefit.

U.S. Patent 6,579,832 (2003) is directed to a method of rapidly adjusting the fluid density of drilling fluids using superparamagnetic nanoparticles. The particles were effective to change the density state of the fluid required to control subsurface pressures, and to preserve and protect the drilled hole until a casing is run and cemented. The
30 nanoparticles were sized between 0.5 and 200 nm and formed into clusters having an average size of between 0.1 and 500 μm . The clusters were formed by incorporating the nanoparticles into a matrix of glass or ceramic. Group VIII metals Cd, Au and their alloys were found to provide an excellent result in adjusting fluid density in a reversible manner.

90% of the supermagnetic nanoparticles from the treated drilling fluid from the downhole location were recovered by a magnetic field at the surface resulting in the adjustment of drilling fluid density within a short period of time and circulation of the magnetic nanoparticles to the surface level for reuse in the drilling fluid. This patent does not
5 however disclose the use of the nanoparticles for reducing fluid loss. The nanoparticles controlled only density of the fluid. The nanoparticles were formed into clusters on a matrix and required an external magnetic field for recovery.

U.S. Patent Application 2009/314549 (2009) considered compounds for reducing the permeability of shale formations using specific nanoparticles in the drilling fluids. By
10 identifying the pore throat radii of shale samples, fine particles were selected that would fit into the pore throats during the drilling process and create a non-permeable shale surface. The drilling mud was a water-based mud with nanoparticles having a size range of 1-500 nm selected from silica, iron, aluminum, titanium or other metal oxides and hydroxides and also composed of a surface active agent. The aqueous well-drilling fluid contained
15 between about 5 to 50 weight percent, based on the weight of the aqueous phase and resulted in a reduction in permeability of the shale, which resulted in drastic reduction of absorbed water and potential for collapse. The minimum concentration required to reduce the fluid penetration was 10 wt% nanoparticles and in some cases, required high concentrations of nanoparticles of 41 wt%.

20 The application of this fluid pertained to nanopore throat reduction rather than reducing overall fluid loss which can occur in macro, micro, and nano type pores. Reducing permeability and plugging the pore throat requires that the fluid particles interact with the pores internally. This blocks the pore channel and can cause formation damage which will reduce or interrupt oil and gas production. Further, permeability
25 reduction took a longer time with a higher amount of silica nanoparticles. It would be more preferable to plug the pore externally and avoid reducing permeability and formation damage.

Aqueous-based drilling fluids generally require a higher concentration of nanoparticles than other types of drilling fluids. They also require additional additives
30 such as surfactants to stabilize the nanoparticles in the fluid system whereas other based fluids, such as invert emulsion drilling fluids, do not need to include other additives to completely disperse the nanoparticles. Nanoparticles that have a hydroxyl group tend to agglomerate faster in aqueous based fluids. This agglomeration causes poor dispersions

and the addition of surfactants reduces this problem. Poor dispersion in turn causes fluid loss even after the addition of the nanoparticles. As well, flocculated or poorly dispersed suspensions form more voluminous sediments. The resulting filter cake is not as dense and impenetrable as compared to that formed from a stable suspension. Therefore, the use of nanoparticles in aqueous based fluids teaches little about its use in non-aqueous-based fluids such as invert emulsions. This publication also did not consider high temperature and high pressure conditions.

A related publication is "Use of Nanoparticles for Maintaining Shale Stability" Sensoy (2009). It also discloses the use of nanoparticles in an aqueous drilling fluid for nanopore throat reduction. It found that the 5 wt% of nanoparticles in the fluid was less effective and the minimum level of nanoparticles was at least 10 wt%. It also tested higher levels of 29 wt% and 41 wt%. The paper concludes that higher amounts of nanoparticles were preferable to achieve the nanopore throat reduction. This paper does not discuss reducing drilling fluid loss to the formation.

U.S. Patent 7,559,369 (2009) is directed to a composition for a well treatment fluid and specifically to a well cement composition and a method of cementing a subterranean formation. The cement composition comprises cement, water and at least one encapsulated nanoparticle selected from the group consisting of particulate nano-silica, nano-alumina, nano-zinc oxide, nano-boron, nano-iron oxide and combinations thereof. The nanoparticles have a particle size in the range of from about 1 nm to about 100 nm and are present in an amount in the range of from about 1% to about 25 wt%. They reduce the cement setting time and increased the mechanical strength of the resulting cement. This patent teaches nothing about the use of nanoparticles as loss circulation materials in drilling fluids and their effect on fluid loss to the formation.

U.S. Patent Application 2011/59871 (2010) relates to a drilling fluid including graphene and chemically converted nanoplatelet graphenes with functional groups. The graphene comprised about 0.001% to about 10 vol% of the drilling fluid. The functionalized chemically-converted graphene sheets were about 1.8 to about 2.2 nm in thickness. Whatman 50 allowed some graphene oxide to pass through the filter. Nanoparticles pass through the filter paper along with the filtrate which may block the interporosity of rock and create formation damage. This may result in permeability impairment and thus lead to a reduction in oil and gas production.

U.S. Patent Application 2009/82230 (2009) relates to an aqueous-based well treatment fluid, including drilling fluids, containing a viscosifying additive. The additive has calcium carbonate nanoparticles with a median particle size of less than or equal to 1 μm . The amount of calcium carbonate nanoparticles used in the drilling fluid was
5 approximately 20 wt%. The nanoparticles used in the well treatment fluid were capable of being suspended in the fluid without the aid of a polymeric viscosifying agent. The addition of the nanoparticles altered the viscosity of the fluid. Nanoparticles suspended in a well treatment fluid even at high temperature as 350°F typically exhibit sag (inadequate suspension properties) no greater than about 8%. The viscosity changes of a fluid with the
10 addition of nanoparticles are well known. However, even with the high amount of nanoparticles added to the fluid formulation, no fluid loss value is reported.

U.S. Patent 2011/162845 discloses a method of servicing a wellbore. It introduces a lost circulation composition into a lost circulation zone to reduce the loss of fluid into the formation. The lost circulation composition comprised Portland cement in an amount
15 of about 10 wt% to about 20 wt% (of the lost circulation composition), nanoparticles and in particular nano-silica in an amount of about 0.5 wt% to about 4 wt% and having a particle size of about 1 to about 100 nm, amorphous silica in an amount of about 5 wt% to about 10 wt%, synthetic clay in an amount of about 0.5 wt% to about 2 wt%, sub-micron sized calcium carbonate in an amount of about 15 wt% to about 50 wt% and water in an
20 amount of about 60 wt% to about 75 wt%. The lost circulation compositions rapidly developed static gel strength and remained pumpable for at least about 1 day. The sample was observed to gel while static but returned to liquid upon application of shear.

Loss circulation additives are formed with a mix of nanocomponents and cement to reduce the setting time for mud cake formation and development of gel strength. However,
25 high amounts of the nanoparticles are required with the cement to develop the mud cake formation and gel strength.

There is therefore a need for an additive for drilling fluids to effectively reduce fluid loss to the formation, form thin filter cakes, prevent formation damage, and without affecting the characteristics of the drilling fluid.
30

SUMMARY OF THE INVENTION

The present invention overcomes at least one disadvantage of the prior art fluids.

In particular, the present invention is directed to well treatment fluids, and in particular drilling fluids, kill fluids, pre-stimulation fluids and completion fluids having nanoparticles. These nanoparticles act as loss circulation material for reducing or preventing fluid loss to the formation. In a preferred aspect, the invention is directed to
5 invert emulsion drilling fluids having nanoparticles as loss circulation material for reducing fluid loss to the formation. The nanoparticles are preferably hydroxide, oxide, sulphate, sulphide, and carbonate nanoparticles. The nanoparticles are present in the fluid in low amounts. As a result, the nanoparticles do not significantly alter the other characteristics of the fluid.

10 In a further aspect of the invention, the present invention is directed to novel *ex situ* and *in situ* methods for preparing the nanoparticle-containing drilling fluids.

In one embodiment, the invention provides a nanoparticle-containing well fluid comprising a base fluid and about 5 wt% or less nanoparticles. The nanoparticles act as fluid loss agents for reducing or preventing fluid loss to an underground formation.

15 Preferably, the well fluid is drilling fluid, kill fluid, completion fluid, or pre-stimulation fluid.

In a further embodiment, the invention provides a use for the nanoparticle-containing fluid for reducing or preventing fluid loss to an underground formation. Preferably the fluid is a drilling fluid and fluid loss is prevented or reduced during drilling
20 of a well in the formation.

In a further embodiment, the invention provides a method of making the nanoparticle-containing well fluid by forming the nanoparticles *ex situ*, comprising the steps of providing aqueous-based precursor solutions for forming the nanoparticles, mixing the precursor solutions under high shear, and adding the mixed precursor solution
25 to the well fluid, to form the nanoparticle-containing fluid, wherein the nanoparticles act as fluid loss material for reducing fluid loss in an underground formation.

In a further embodiment, the invention provides a method for making a nanoparticle-containing well fluid by forming the nanoparticles *in situ*, comprising the steps of providing aqueous-based precursor solutions for forming the nanoparticles, adding
30 the precursor solutions to the well fluid, and subjecting the fluid to mixing and shear to form the nanoparticle-containing fluid, wherein the nanoparticles act as a fluid loss material for reducing fluid loss in an underground formation.

The features and advantages of the present invention will be apparent to those skilled in the art and are described below in more detail with reference to specific embodiments.

5 BRIEF DESCRIPTION OF THE FIGURES

Embodiments of the invention will be described with reference to the figures, which illustrate aspects of the invention but should not be considering limiting, in which:

Figure 1 is a schematic representation of the *ex situ* scheme of preparing
10 nanoparticles and the nanoparticles-based drilling fluid;

Figure 2 is a schematic representation of the *in situ* scheme of preparing nanoparticles and the nanoparticles-based drilling fluid;

Figure 3 is an X-ray diffractogram pattern of *ex situ* prepared nanoparticles;

Figures 4a)-c) are TEM Photographs and the corresponding particle size
15 distribution for the *ex situ* Fe(OH)₃ nanoparticles;

Figures 5a)-d) show SEM images of mud cake a) without nanoparticles (SE); b) without nanoparticles (BSE); c) *in situ* nanoparticles (SE); and d) *in situ* nanoparticles (BSE);

Figures 6a)-b) shows elements containing mud cake without nanoparticles and b)
20 mud cake with nanoparticles from EDAX data;

Figures 7a)-c) show a nanoparticle-based drilling fluid stability evaluation;

Figures 8a)-b) show the rheology behavior of drilling fluid 90 oil:10 water (v/v), with a) LCM and nanoparticles made by both *ex situ* and *in situ* methods and b) with nanoparticles only, made by both *ex situ* and *in situ* methods;

Figures 9a)-b) show gel strength behavior of drilling fluid 90 oil:10 water (v/v) with a) LCM and nanoparticles made by *ex situ* and *in situ* methods and b) with nanoparticles only made by *ex situ* and *in situ* methods;
25

Figure 10 shows the shelf life of drilling fluid samples using rheology behaviour;

Figure 11 shows the aging effect of drilling fluid samples using gel strength
30 behaviour;

Figure 12 shows mud cake before and after addition of nanoparticles;

Figure 13 shows API fluid loss of different drilling fluid sample without using LCM;

Figure 14 shows the fluid loss reduction of high temperature high pressure drilling fluid filtrates;

Figure 15 shows high temperature high pressure drilling fluid filter cake;

Figure 16 shows the effect of shearing on fluid loss control;

5 Figure 17 shows the quality of unblended and blended drilling muds;

Figure 18 shows the effect of organophilic clays on fluid loss control;

Figure 19 shows nanoparticle-containing drilling fluid stability evaluations for 4 additional nanoparticle-containing drilling fluids; and

10 Figure 20 shows nanoparticle-containing drilling fluid filter cake for 4 additional nanoparticle-containing drilling fluids.

DESCRIPTION OF EMBODIMENTS OF THE INVENTION

The present invention is an economic and effective method of controlling lost
15 circulation. Use of the nanoparticles in the well fluids will prevent or reduce fluid loss to the formation as compared to a fluid without loss circulation materials.

The nanoparticle containing fluids have one or more of the following advantages. The nanoparticle-containing fluids reduce fluid loss into the formation as compared to fluids without the nanoparticles. The nanoparticles form a thin and firm filter cake in the
20 formation. They cause minimal formation damage. They are stable at extremely high temperatures. The nanoparticles are present in the fluids at low concentrations and may be used without other loss circulation materials. The nanoparticles can be formed *ex situ* or *in situ* in the fluid. This results in time and cost savings. Since less fluid is lost to the formation, the cost of the fluid is lower. The nanoparticles result in lower torque and drag,
25 thereby increasing the extended reach of the well. Since a lower concentration of nanoparticles is used, there is less formation damage, no significant changes to the characteristics of the fluid, and an increased productivity index. The nanoparticles may also be effective at reducing fluid loss in both low temperature low pressure environments and high temperature high pressure environments.

30 The base fluid of the present invention can be a well completion fluid and preferably is a drilling fluid, kill fluid, pre-stimulation fluid, or completion fluid. More preferably, it is a drilling fluid and in particular, an invert emulsion drilling fluids. These fluids, and in particular drilling fluids, are well known in the art.

The drilling fluids are preferably invert emulsion fluids. Hydrocarbon based drilling emulsions contain a large amount, i.e. 95%, of hydrocarbon based material (oil) as the continuous phase of the emulsion. The remainder of the emulsion is a minor amount of an aqueous phase as the discontinuous phase of the emulsion. Invert emulsions are a type of water-in-oil emulsions which use hydrocarbon-based materials but which contain smaller amounts of the hydrocarbon-based material in the continuous phase and larger amounts of the aqueous discontinuous phase as compared to other hydrocarbon-based fluids.

The drilling fluids may contain a number of common additives such as weighting agents, emulsifiers, foaming agents, etc. The nanoparticles are selected so that they do not affect the other characteristics of the drilling fluids.

Nanoparticles (NPs) act as a loss circulation material (LCM) by virtue of their size domain, hydrodynamic properties and interaction potential with the formation. The nanoparticles will be selected in accordance with the specific well fluid, the formation, bottomhole pressures and temperatures, and other well and operating parameters.

The nanoparticles are preferably selected from metal hydroxides, e.g. iron hydroxide, metal oxides, e.g. iron oxide, metal carbonates, e.g. calcium carbonate, metal sulfides, e.g. iron sulfide, and metal sulfate, e.g. barium sulfate. More preferably, they are metal hydroxides such as iron hydroxide. In some cases, the specific nanoparticles may form under formation conditions. For example, iron hydroxide may convert to iron oxide under high temperature high pressure conditions. If the selected nanoparticles are sulfide or sulfate nanoparticles, they may act as weighting material in addition to loss circulation material.

It was previously thought that high amounts of nanoparticles, in combination with other LCM and/or asphaltic materials, were required to reduce fluid loss. It has now been surprisingly found that very low levels of nanoparticles in drilling fluid will substantially reduce fluid loss to the formation, even without other LCM being present. The use of the nanoparticles in the fluids results in a fine, thin, impermeable layer of particles forming good quality filter cake at the borehole wall. This filter cake reduces the fluid lost to the formation. The filter cake is formed even with low concentrations of the nanoparticles.

The nanoparticles are present in the base fluid in amounts below about 5 wt%, more preferably below about 4 wt %, more preferably below about 3 wt%, even more preferably below about 1 wt%. Further preferred amounts of the nanoparticles in the fluid

is between about 0.5 wt% and about 1%, preferably between about 0.6 wt% and about 1 wt%, and most preferably in an amount between about 0.74 wt% and about 1 wt%. Because the amount of nanoparticles is low, other additives are generally not required to stabilize the particles although in some water-based drilling fluids, surfactant or polymeric additives may be required. Further, the nanoparticles do not agglomerate in the fluid even after several weeks.

Preferably the nanoparticles have a particle size in the range of 1-300 nm, more preferably 1-120 nm and even more preferably the majority or most of the nanoparticles have a particle size in the range of 1-30 nm. More preferably substantially all of the nanoparticles have a particle size in the range of 1-30 nm.

The particle sizes of the nanoparticles are not limited to these specific ranges. The particle size will vary in accordance with the invert emulsion drilling fluid. The water droplets in the invert emulsion of the drilling fluid provide control over the particle sizes and therefore the nanoparticle sizes can be varied according to the diameter of the water pools in the invert emulsion. Any surfactants in the fluid will also influence the nanoparticle size since the surfactants tightly hold the water pools in the oil phase.

One benefit of using low concentrations of the nanoparticles is that the nanoparticles do not significantly affect other characteristics of the fluid. In particular, after the addition of the nanoparticles, there should be no significant change in the specific gravity, apparent viscosity, pH, or mud weight of the fluid. There will also be no significant change in the rheology of the fluid.

The use of the nanoparticle-containing drilling fluid of the present invention resulted in a significant reduction in fluid loss to the formation. In low pressure low temperature (LPLT) formations, fluid loss could be reduced by as much as 70% when using drilling fluid with LCM with *ex situ* formed nanoparticles and as much as 80% when using drilling fluid with LCM and *in situ* formed nanoparticles as compared to the drilling fluids without LCM or nanoparticles. Prior references used as much as 30 wt% nanoparticles and found the fluid loss reduction to be less than 40%. See Amanullah et al. (2011) and Srivatsa (2010). It is worth noting that prior use of nanoparticles of iron oxide/hydroxide resulted in less than 7% fluid loss reduction. In high pressure high temperature formations, fluid loss using the present invention was reduced by more than 50% with LCM and *ex situ* nanoparticles and as much as 60% with LCM and *in situ* nanoparticles, as compared to the drilling fluid without LCM or nanoparticles.

The nanoparticles in the drilling fluid do not cause significant formation damage. They plug the pores in the formation externally to reduce fluid loss rather than internally, thereby avoiding formation damage. The nanoparticles control the spurt and fluid loss into the formation and therefore control formation damage. They form a thin, non-erodible and impermeable mud-cake. Small particles of high concentrations may bridge across the pore throat. Smaller particles aggregate around larger ones and fill in the smaller spaces and effectively plug the pore spaces.

The use of nanoparticles also can reduce the total solid concentration. The use of the nanoparticles to produce better fluid loss control means that high amounts of clays are not needed in the fluid. It also avoids formation damage which decreases the rate of penetration.

The present invention also includes the use of these nanoparticle-containing fluids as a pre-stimulation treatment fluid. The nanoparticles will generate an almost perfect sealant from the wellbore to the formation. By removing the filter cake in selected sections of the wellbore, stimulation can be performed selectively either by hydraulic fracturing or for acid treatments.

The nanoparticles-containing drilling fluid can be used in a variety of formations. However, it is preferably used in formations with smaller pore sizes, and most preferably in shale formations having pore openings smaller than 100 μm . It is also preferable in naturally fractured formations because it has a bridge-building capability with other fluids.

In a further aspect of the invention, the present invention is directed to a method of making the nanoparticle-containing fluid. The fluid can be made using either an *in situ* or *ex situ* process. The *in situ* process is preferred.

The nanoparticles can be formed and suspended *in situ* in the drilling fluid. This eliminates the need to pre-form the nanoparticles. In this method, precursors of the nanoparticles are prepared, preferably as aqueous solutions. Selecting appropriate precursors is within the common knowledge in this field, according to the desired nanoparticle. The precursor solutions are added to the prepared drilling fluid and mixed. Shear is applied to the drilling fluid to ensure mixing of the nanoparticles precursors and complete formation of the nanoparticles in the drilling fluid.

It is thought that this *in situ* method uses the dispersed water pools of the invert emulsion drilling fluid as nano-reactors to form the nanoparticles. The results that follow

later in this description show that the *in situ*-formed nanoparticles may provide improved fluid loss reduction over fluids having nanoparticles formed *ex situ*.

In the *ex situ* process, the nanoparticles are pre-formed from their precursors. Precursors, preferably in aqueous precursor solutions, are mixed and high shear applied.

5 The formed nanoparticles are then added to the prepared drilling fluid. The fluid and nanoparticles are mixed.

In both processes, whether *in situ* or *ex situ*, mixing and the application of shear is preferably applied prior to storage of the drilling fluid to avoid the formation of fish eyes.

In one example of the *ex situ* method, an invert emulsion drilling fluid having iron
10 (III) hydroxide as the loss circulation material is formed, where the fluid has lower fluid loss in a drilling operation. The fluid is formed by the steps of solubilizing a desired amount of an anhydrous iron (III) chloride powder, adding a stoichiometric amount of sodium hydroxide pellets, mixing the solution preferably at 25°C, recovering the iron (III) hydroxide nanoparticles and forming a bulk aqueous solution of nanoparticles, mixing the
15 nanoparticles solution in the invert emulsion drilling fluid in a slurry to form the nanoparticle-containing drilling fluid. The resultant *ex situ* prepared iron (III) hydroxide nanoparticles were characterized using X-ray powder diffraction (XRD) and transmission electron microscopy (TEM).

In an example of the *in situ* method, the iron (III) hydroxide nanoparticles were
20 prepared within the invert emulsion fluid, starting from FeCl₃ and NaOH precursors. The *in situ* particles were characterized following their collection on the filter cake using scanning electron microscopy (SEM). Preliminary API test results indicated that optimum control of fluid loss has been achieved using the nanoparticle-containing drilling fluid. Moreover, at the level of nanoparticles added, of about 1 wt%, no impact on drilling fluid
25 specific gravity, apparent viscosity and pH was observed.

1. Drilling Fluid Samples

The invert emulsion was supplied by a Calgary based drilling fluid company. One mix of the drilling fluids was test; namely, 90 oil: 10 water (v/v). The compositions of the
30 invert emulsion drilling fluid are shown in Table 1. The LCM, mainly Gilsonite, content of the drilling fluid was fixed at 1.6 wt%. In one example, no LCM was used. The nanoparticles concentration was maintained at 0.74 wt% for the *in situ* and *ex situ* prepared particles.

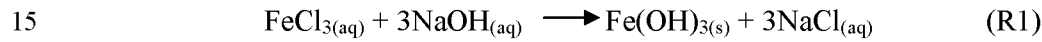
Table 1: Compositions of drilling fluid samples

Oil: water (v/v) = 90:10
Base Oil = Low-aromatic hydrotreated oil
Brine = 30% Calcium Chloride
Organophilic Clays = 15 kg/m ³
Hot Lime = 35 kg/m ³
Primary Emulsifier = 10 L/m ³
Secondary Emulsifier = 5 L/m ³

2. Preparation of Fe(OH)₃ nanoparticles and the nanoparticle-containing drilling fluid

Iron (III) hydroxide nanoparticles were prepared by aqueous reaction between FeCl₃ and NaOH at specified temperature and rate of mixing as per the following reaction. The product Fe(OH)₃ nanoparticles were collected and their identity was confirmed using XRD and their particle size distribution was determined using TEM.

Ex situ preparation: Iron hydroxide nanoparticles were prepared by first solubilizing the specific amount of anhydrous iron (III) chloride powder (laboratory grade, Fisher Scientific Company, catalog # I89-500, Toronto, Canada) in 2 mL deionized water to give final concentration of 2.5 M followed by addition of a stoichiometric amount of NaOH_(s) pellets (Fisher Scientific Company, Toronto, Canada) under 200 rpm of mixing and 25°C. The color of the aqueous solution turned reddish brown signaling the formation of precipitate of Fe(OH)_{3(s)} as per reaction (R1).



The particles were recovered, part was dried for characterization and the rest was mixed with the invert emulsion drilling fluid in a slurry form as shown in Figure 1. The fluids were mixed, and shear applied, to achieve a homogenous mixture using a Hamilton beach mixer.

In situ preparation: This nanoparticle synthesis followed the two microemulsion method for nanoparticle synthesis. 1 mL of 5 M FeCl_{3(aq)} was added to 250 mL of the drilling fluid and in a separate vial 1 mL of 16 M NaOH_(aq) was added to 250 mL of the drilling fluid. The two vials were mixed overnight at 200 rpm and 25 °C as shown in Figure 2.

Two control samples were prepared, one containing the FeCl_{3(aq)} in the drilling fluid and another containing the NaOH_(aq) in the drilling fluid. The samples were left to mix overnight at 200 rpm and 25°C. It is worth noting that no phase separation was

observed in the nanoparticle-containing fluids as well as in the control samples, even for a period of 6 weeks.

3. Characterization methods and techniques

5 Particle characterization: *Ex situ* prepared $\text{Fe}(\text{OH})_3$ nanoparticles were characterized using XRD. The *in situ* prepared nanoparticles were characterized using SEM following their collection on the filter cake. For the *ex situ* prepared particles, the aqueous colloidal suspension was first centrifuged at 5000 rpm to recover the nanoparticles followed by washing several times with deionized water. The particles were
10 left to dry at room temperature for 24 h. The dried particles were ground using a pastel and mantel before been introduced to Ultima III Multipurpose Diffraction System with $\text{Cu K}\alpha$ radiation operating at 40 KV and 44 mA (Rigaku Corp., TX). JADE software was used to identify the structure. The particle size distribution was determined by collecting transmission electron microscopy photographs on a Phillips Tecni TEM (voltage of
15 200KV) equipped with a slow-scan camera. The ground particles were dispersed in methanol and one drop of the methanol dispersion was deposited on a copper grid covered with carbon and left to dry overnight before the TEM images could be collected.

Droplets size measurement of the water-in-oil emulsion: Samples with primary emulsifier were prepared using the same composition of 10 vol% water to 90 vol% oil as
20 the drilling fluid sample except that solids were excluded. The water droplet diameter was measured using Morphologi G3 microscope (Malvern Instruments Inc, USA).

Drilling fluid characterization: The filtration properties of the different drilling fluids were measured according to API 30-min test. Data was collected using a standard FANN filter press (Fann Model 300 LPLT (100psi and 25°C), Fann Instrument Company,
25 USA) and filter paper (Fann Instrument Company, USA). A volume of 500 mL of the drilling fluid was poured into the filter press cup and 100 ± 5 psi of pressure was applied through CO_2 supply cylinder at room temperature of 25° C. The volume of permeate was reported after 2.5 min and 30 min from the graduated cylinder reading. Three replicates were prepared for every sample and the 95% confidence interval is reported in the tables.
30 The smoothness of the final filter cake was reported through visual observation; while the thickness was measured using a digital caliper (0-6" TTC Electronic digital calipers model # T3506, Canada). The iron and calcium content in the filtrate was determined by inductively coupled plasma (ICP) (IRIS Intrepid IIXDL, ThermoInstruments Canada Inc.,

Mississauga, ON, Canada). Iron content of the filtrate is correlated to nanoparticles escaping the filtration process.

The effect of nanoparticles on the characteristics of the drilling fluid was determined as follows: Fann Model 140 mud balance (Fann Instrument Company, USA) was used to measure the mud density in the presence and absence of nanoparticles. Care was taken in order to eliminate any error due to air entrapment. pH measurements were performed using pH paper (0-14) (VWR international, Catalog # 60775-702 Edmonton, Canada). A rotational Fann 35 viscometer (Fann Instrument Company, USA) was used to measure the shear characteristics of the drilling fluid at six different speeds. A volume of approximately 500 mL of the fluid was poured into the viscometer cup, and the mud was sheared at a constant rate in between an inner bob and outer rating sleeve. The system was left to rotate at a certain rpm until reaching the steady state reading for 5 min. The readings were taken at 600, 300, 200, 100, 6 and 3 rpm and noted down. The experiments were conducted at room temperature of 25°C. The dimensions of bob and rotor were chosen such that the dial reading on the viscometer is equivalent to apparent viscosity in centipoise at rotor speed of 300 rpm. The apparent viscosities for all rotor speeds are calculated using equation (E1) below.

$$\text{Apparent/ Effective viscosity, } \mu_a = 300 \left(\frac{\theta}{N} \right) \quad (\text{E1})$$

where N is the rotor speed (rpm) and θ is the viscometer dial reading ($^{\circ}$). The shear rate can be calculated as per equation (E2).

$$\text{Shear rate, sec}^{-1} = 1.7023N \quad (\text{E2})$$

The plastic viscosity and yield point are found using the following equations:

$$\text{Plastic viscosity, } \mu_p = \theta_{600} - \theta_{300} \quad (\text{E3})$$

$$\text{Yield point, } Y_p = \theta_{300} - \mu_p \quad (\text{E4})$$

where μ_p is the plastic viscosity (cP), Y_p is the yield point ($\text{lb}_f/100\text{ft}^2$), and θ_{600} and θ_{300} are the torque readings at 600 rpm and 300 rpm respectively.

Gel strength of the drilling fluid was measured at a lower shear rate after the drilling mud is static for a certain period of time. The 3 rpm reading was used for calculating the gel strength after stirring the drilling fluid at 600 rpm from the Fann viscometer. The first reading is noted after the mud is in a static condition for 10 sec (10 sec gel strength). The second gel strength is noted after 10 minutes (10 min gel strength). Gel strength is usually expressed in the pressure unit $\text{lb}_f/100\text{ft}^2$. The difference between the initial gel strength and the 10 min value was used to define how thick the mud would be during round trips. See ASME Drilling Fluids Processing Handbook (2005).

10 4. Nanoparticles (NPs) characterization

The *ex situ* prepared $\text{Fe}(\text{OH})_{3(s)}$ were identified using X-ray diffraction (XRD) analysis. The particle size distribution of the nanoparticles was determined from the TEM photographs. The details of the particle morphology are described herein.

15 4.1 X-ray diffraction analysis

The X-ray diffraction pattern of the *ex situ* prepared nanoparticles is shown in Figure 3. The XRD pattern shows that there is no evidence of strong distinct peaks which would be expected from a crystalline material. The peak maximum around $2\theta = 35^\circ$ can be attributed to the presence of aggregates dispersed in an amorphous phase. Nevertheless, Streat et al. (2008) also prepared ferric hydroxide using ferric chloride and stoichiometric quantity of sodium hydroxide with deionized water and observed the same XRD pattern. Reaction pH might affect the final nature of the iron oxide material. See Cai et al. (2001). Cai et al. (2001) reported that the reaction pH affects the crystallinity of iron oxide material. At low pH, $\text{pH} \geq 1.5$, the peaks were found narrow and distinct, while at $\text{pH} = 4$ there were two broad and less intense peaks apparent in the diffraction pattern, similar to those shown in Figure 3, indicating poor crystallinity. At higher pH, $\text{pH} \geq 6$, the XRD pattern showed crystalline structure. It is to be noted that amorphous iron (III) hydroxide can transform into $\alpha\text{-Fe}_2\text{O}_3$ and $\beta\text{-FeOOH}$ as well as $\alpha\text{-FeOOH}$ as a result of further transformation. See Nassar and Husein (2007). Energy dispersive X-ray (EDX) associated with the SEM helped identify the *in situ* formed particles as shown in Figures 5 a)-d) and Figures 6a)-b).

4.2 Electron microscopy results

4.2.1. Droplet size

The emulsion samples containing the primary emulsifier, oil and water were characterized using Morphologi G3 microscope. A typical water droplet diameter in the invert emulsion containing many water droplets was 20 μm . Nonetheless, a few smaller water droplets ($>5 \mu\text{m}$) were observed in the emulsion. Similar observations have been reported by Fjelde et al. (2007) for 25/75 and 5/95 water-in-oil emulsions at different temperature, while using primary emulsifiers. The stirring speed may also affect the droplet size distribution. See Fjelde (2007). Kokal (2006) has shown that the water droplets in emulsion can vary in size from less than 1 μm to more than 1000 μm . Typically, in oil based drilling fluids, macroemulsions with droplet sizes in the range of 0.1-100 μm are used. See Bumajdad et al. (2011) and Kokal (2006).

4.2.2. Particle size distribution

Figures 4a-c show the TEM photographs and the corresponding particle size distribution histograms for the *ex situ* prepared $\text{Fe}(\text{OH})_3$ particles. The histograms show a spread in the size distribution with most of the population falling in the range between 1-30 nm. TEM image shows some aggregates, which are believed to form during nanoparticle preparation due to the high mixing. It should be noted that the resultant nanoparticles did not exhibit magnetic properties at room temperature, which precludes magnetic attraction. Nevertheless, the wide size distribution of particles prompted further consideration of the filtration characteristics of LCM-free nanoparticle-containing drilling fluid. The results are detailed below.

4.2.3 SEM Analysis

SEM images of the mud cake without nanoparticles and with nanoparticles are shown in Figures 5 a)-d). The observed morphologies of the two samples have some distinct features. No cracks were visible, except clay surface was covered with $\text{Fe}(\text{OH})_3$ particles by the SEM observation. The mud cake with nanoparticles showed a smooth and clean surface. Mud cake without nanoparticles showed a rough surface and seemed to be deformed and fractured which led to a porous surface causing more fluid loss. It can be observed that the formation of voids and gap of pores were filled with nanoparticles eventually reducing the fluid loss. Thus, it can be inferred that the adsorption reaction of

Fe(OH)₃ nanoparticles on organophilic clays may be attributed to the surface chemical reactivity. Results are in agreement with Lai (2000) who reported that Cu ions were adsorbed on iron oxide coated sand. Addition of Fe(OH)₃ nanoparticles causes a change of elemental constitution through adsorption reaction. The elemental distribution mapping of EDAX for the sample of mud cake without nanoparticles and mud cake with nanoparticles are illustrated in Figures 6a)-b). Results indicated that iron ions could penetrate into the micropores and mesopores of the cakes containing clays. It can be also attributed to a diffusion of the adsorbed metals from the surface into the micropores which are the least accessible sites of adsorption.

4.3. Effect of nanoparticles on drilling fluid characterization

Stability of nanoparticle-containing drilling fluid: The assessment of the stability of the nanoparticle-containing drilling fluids was determined by visual observation. Stability relates here to the ‘shelf life’ of nanoparticle-containing drilling fluid. Figures 5a)-c) are photographs of samples representing the initial fluid without nanoparticles and the nanoparticle-containing drilling fluids. The figures show no agglomeration, even when the samples were left for several weeks. The stability is attributed to the fact that the amount of nanoparticles added in formulating the nanoparticle-containing drilling fluid was low, for example, in Figures 7a)-c), only 0.74 wt%. Moreover, steric hindrance arising from the surface active agents surrounding the particles helps stabilize the particles against the van der Waals attractive forces. Consequently, no other additives were required to stabilize the particles.

Several other concentrations, below 0.5 wt%, of iron hydroxide nanoparticles were tested. Further, higher concentrations of greater than 5 wt% were found to lead to particle agglomeration. Another qualitative assessment of the stability of nanoparticle-containing drilling fluid was done by checking its rheology after 1 month which is detailed in the next section.

Rheology behavior of nanoparticle-containing drilling fluid: Drilling fluids with good pumpability exhibit lower viscosity at high shear rate and higher viscosity at lower shear rate. This property of drilling mud is used widely where high viscosities are required during tripping operation and low viscosities required during drilling operation to clean the cuttings from the bottom of the hole. See Srivatsa (2010) and Amanullah et al (2011). The plot of apparent viscosity and shear rate as shown in Figures 8a)-b) resembles the

non-linearity of the curves at low shear rates and approach linearity at high shear rates. The addition of nanoparticles created a slight change in the rheology and supports the theory that nanoparticle behavior is governed by nanoparticle grain boundary and surface area/unit mass. See Amanullah et al. (2011).

5 The addition of small concentrations of nanoparticles is not sufficient to cause significant rheology changes in the system compared to the drilling fluid without LCM and nanoparticles, and the drilling fluid with LCM only. However, the particle size, nature of particle surface, surfactants, pH value and particle interaction forces may play significant roles to alter the viscosity. Most of the nanoparticles are assumed to be in the
10 water pools surrounded by surfactants. Some of the particles, nevertheless, may attach themselves to the clay suspension as a result of electrostatic and van der Waals forces. The results are also highly dependent on the hydroxyl group (-OH) on the surface of the nanoparticles, which causes nanoparticles to be agglomerated in an organic solution. This leads to a higher mass of selective physiosorption of organic clay suspension on the
15 surface of the free nanoparticles which is thought to reduce the fluid viscosity slightly. See Srivastva (2010).

 A comparison of the gel strength of the nanoparticle-containing drilling fluid and the drilling fluid without LCM and nanoparticles, is shown in Figures 9a)-b). During these experiments, special attention to the rheology of the nanoparticle-containing drilling fluid
20 was considered. Measurement was done immediately after the preparation and also after 1 month. Figures 10 and 11 show the time dependent rheological and gel strength behavior of the drilling fluid respectively compare with the nanoparticle-containing drilling fluid. Analyses of the rheological profiles of the drilling fluids shown in the figures indicate no significant changes of the viscous profile of the nanoparticle-containing fluid, even after
25 static aging for 1 month. The 10 second and 10 minute gel strengths shown in the figures also demonstrate the short and long term stability of the nanoparticle-containing fluid to fulfill its functional task during drilling operation.

Drilling fluid density and pH: Mud density is one of the important drilling fluid properties because it balances and controls formation pressure. Moreover, it also helps
30 wellbore stability. The mud density 0.93 g/cm^3 was found almost constant in all the samples of 90:10 (v/v) oil/water types shown in Table 2. The addition of nanoparticles did not increase the mud weight. This provides the advantage of reducing the total solids

concentration in the drilling fluid as and when necessary, which is detailed in the next section.

Table 2: Density measurements of drilling fluid samples

Sample Type	Density (g/cm^3)			
	DF	DF + LCM	DF + LCM + <i>Ex-situ</i> NPs	DF + LCM + <i>In-situ</i> NPs
Oil/Water 90:10 (v/v)	0.93±0.02	0.93±0.02	0.93±0.02	0.93±0.02

5

Table 3 indicates that a pH level 12.5 was also found in all samples, even nanoparticles addition did not change the pH of the drilling fluid samples.

Table 3: pH measurements of drilling fluid samples

Sample Type	pH			
	DF	DF + LCM	DF + LCM + <i>Ex-situ</i> NPs	DF + LCM + <i>In-situ</i> NPs
Oil/Water 90:10 (v/v)	12.5	12.5	12.5	12.5

10

LPLT Filtration property of nanoparticle-containing drilling fluid: Filtration property is dependent upon the amount and physical state of colloidal materials in the mud. When mud containing sufficient colloidal material is used, drilling difficulties are minimized. The spurt loss of the drilling fluid is considered as one of the sources of solid particles and particulates invasion to the formation that can cause serious formation damage. This is due to the formation of an internal mud cake in the vicinity of the wellbore. Consequently, internal pore throat blockage may create a flow barrier to reduce oil and gas flow. Moreover, higher particle flocculation in drilling fluid causes higher mud cake thickness.

15

This highlights the importance of using low concentrations of dispersed nanoparticles in fluid design with virtually no spurt loss, low filtrate volume and good quality filter cake. The ultra dispersed nanoparticles in the present drilling fluid system forms a well dispersed plastering effect on the filter paper and improves the fluid performance. The filtration properties of the drilling fluid are determined by means of the standard filter press. The effectiveness of the nanoparticles in fluid loss prevention can be

20

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- clearly seen from Table 4A. The API fluid loss of the samples indicated a decreasing trend in fluid loss over a period of 30 minutes with around 9% for the drilling fluid with 1.6% w/w LCM, 70% when using fluid with LCM and *ex situ* prepared nanoparticles together, and more than 80% when using fluid with LCM and *in situ* prepared nanoparticles together. The reported literature values for the loss reduction was less than 40% even after addition of 30 wt% of nanoparticles. See Amanullah et al. (2011) and Srivatsa (2010).

Table 4A: API Fluid Loss of Different Drilling Fluid (DF) Samples

Sample Types	Time (min)	LPLT Fluid Loss (mL)			
		DF	DF+1.6% w/w LCM	DF+1.6% w/w LCM+0.74% w/w NPs <i>ex-situ</i>	DF+14% w/w LCM+0.74% w/w NPs <i>in-situ</i>
90:10 (v/v)	7.5	2.0±0.2	1.4±0.2	0.20±0.2	-
Oil:Water	30	3.96±0.2	3.6±0.1	1.10±0.1	0.50±0.2

- Fluid loss results for fluids with other nanoparticles are shown in Tables 4B and 4C below. Table 4B sets out fluid loss results after 30 minutes for both *ex situ* and *in situ* prepared nanoparticles of CaCO₃, Fe(OH)₃, BaSO₄, and FeS, in invert emulsion drilling fluids and compares the results to that achieved with the drilling fluid alone. Table 4B sets out the fluid loss results after 30 minutes for water-based drilling fluids with CaCO₃ and Fe(OH)₃ nanoparticles formed *ex situ* and *in situ*.

Table 4B: LPLT Fluid Loss with Different Nanoparticles for Invert Emulsion DF (95% CI)

Fluid Types	DF	DF+ 4 wt% CaCO ₃ (<i>ex-situ</i>)	DF+4 wt% CaCO ₃ (<i>in-situ</i>)
mL/ 30 min	8.7±2	2.8±0.6 (68%*)	3.9±0.3 (55%*)

Fluid Types	DF	DF+ 0.74 wt% Fe(OH) ₃ (<i>ex-situ</i>)	DF+ 0.74 wt% Fe(OH) ₃ (<i>in-situ</i>)
mL/ 30 min	3.96±0.2	1.25±0.2 (68%*)	0.90±0.2 (77%*)

Fluid Types	DF	DF+3 wt% BaSO ₄ (<i>ex-situ</i>)	DF+3 wt% BaSO ₄ (<i>in-situ</i>)
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mL/ 30 min	10.95±0.3	3.5±0.3 (68%*)	1.6±0.3 (85.3%*)
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Fluid Types	DF	DF+3 wt% FeS (<i>ex-situ</i>)	DF+3 wt% FeS (<i>in-situ</i>)
mL/ 30 min	10.95±0.3	1.15±0.3 (89.5%*)	0.93±0.1 (91.5%*)

* % fluid loss reduction

Table 4C: LPLT Fluid Loss with Different NPs for Water Based Mud (95% CI)

Fluid Types	Water based DF	Water based DF+ 0.60 %w/w Fe(OH) ₃ (<i>ex-situ</i>)	Water based DF+ 0.60 %w/w Fe(OH) ₃ (<i>in-situ</i>)
mL/ 30 min	8.8±0.6	8.0±0.2 (9%*)	6.3±0.2 (28.4%*)

5

Fluid Types	Water based DF	Water based DF+ 3 %w/w CaCO ₃ (<i>ex-situ</i>)	Water based DF+ 3 %w/w CaCO ₃ (<i>in-situ</i>)
mL/ 30 min	9.5±0.2	6.5±0.2 (31.6%*)	6.8±0.2 (28.4%*)

* % fluid loss reduction

Figures 4a-c - LPLT tested at 100 psi; 25°C.

The optimum stability concentration of the nanoparticles was also considered.

- 10 Various nanoparticles were tested in 500 mL samples of invert emulsion drilling fluids. See Figure 18. The optimum stability concentrations varied with different nanoparticles. Generally, the ranges are 0.5% w/w to 5% w/w for Fe(OH)₃, 0.5% w/w to 10% w/w for each of BaSO₄, and FeS, and 0.5% w/w to 20% w/w for CaCO₃. Although generally no additives are needed for stabilization, water-based drilling fluids may require surfactant or
- 15 polymeric additives to stabilize the nanoparticles.

- In order to prevent drilling and completion problems, mud cake quality and build up characteristics are very important. nanoparticles mediated drilling fluid form thin and impermeable filter cake. Figures 12 (a-d) show the mud cake formation before and after addition of nanoparticles. The nanoparticles (Figures 12 c-d) deposit a fine thin layer of
- 20 particles and looks reddish brown which shows that iron (III) hydroxide are deposited on

the cake surface. The filtration properties of a drilling fluid with nanoparticles only consider the wall/cake building ability of the nanoparticles with solid components of drilling fluid are shown in Figure 13. Figure 19 shows the filter cakes formed from the nanoparticles-containing fluids tested in Table 4B and 4C.

5 An interesting discovery was that a wide range of nanoparticles particle size gave lower permeability than that achieved using LCM. A reasonably low fluid loss value and thin mud cake with a thickness of less than 1 mm achieved with the nanoparticle-containing drilling fluid was a significant improvement compared to the drilling fluid with conventional LCM. Properly dispersed nanoparticles having good filtration characteristics
10 give the drilling fluid its distinctive character.

Loss of fluid from the invert emulsion drilling fluid usually results in the loss of oil and chemicals into the formation. The presence of iron and calcium content in the filtrate were determined by inductively coupled plasma (ICP). Results are shown in Table 5. In the total filtrate volume, the nanoparticle-containing fluid reduced the Ca content 500
15 times than the filtrate without nanoparticle-containing fluid. Iron content was found nil in both cases. The results are attributed to the fact that bentonite clays are highly negatively charged and therefore favorably attract iron in the nanoparticles. Therefore, larger surface area of nanoparticles provided bridges between the bentonite particles. During filtration, the bentonite clays and iron aggregates became physically significant preventing the di-
20 valent positively charged Ca content in the filtrate. Moreover, NaCl salts used as a bridging solid are produced during the nano-based fluid formulation which can act as the inhibitor to prevent clay swelling and clay dispersion which in turn lead to the elimination of clay related formation damage mechanism. See Amanullah et al. (2011).

25 Table 5: ICP Test Results of the Collected Filtrate to Determine the Ca and Fe Content

Filtrate Samples	Ca Content (mg)	Fe Content (mg)
Without NPs (in total volumes)	478	Nil
With NPs (in total volumes)	0.87	Nil

The effectiveness of the nanoparticle-containing drilling fluid at high temperature high pressure (500 psi and 177°C) can be seen in Table 6. The fluid loss of the samples indicated a decreasing trend in fluid loss over the 30 minute period with less than 10% for
30 the drilling fluid with 1.6 wt% LCM, about 50% for the drilling fluid with LCM and

0.74 wt% *ex situ*- prepared nanoparticles, and 60% for the drilling fluid with LCM and 0.74 wt% *in situ*-prepared nanoparticles.

Table 6: High Pressure High Temperature (HTHP) Filtration Property of Nanoparticle-
5 Containing Drilling Fluid

Sample Types	Time (min)	HTHP Fluid Loss (mL)			
		DF	DF + 1.6 wt% LCM	DF + 1.6 wt% LCM + 0.74 wt% NPs <i>ex situ</i>	DF + 1.6 wt% LCM + 0.74 wt% NPs <i>in situ</i>
90:10 (v/v) oil:water	7.5	9±0.1	6.2±0.2	2±0.2	---
	30	19±0.1	14.4±0.1	9±0.1	7.5±0.2

Effect of High Shear on Fluid loss Control: Proper shearing influenced the fluid loss numbers. Care must be taken to allow sufficient turbulent shearing action time during the fluid preparation. Shearing device may significantly increase the dispersed phase fraction and dampens coalescence by breaking agglomerated particles. See Amanullah et al. (2011). A Hamilton Beach three blade high speed mixer was used in addition of vigorous agitation of fluid during preparation steps. This inexpensive equipment is used mostly in food processing. High-shear mixers provide rapid micro-mixing and emulsification. Unblended fluid has higher fluid loss than blended fluid as shown in Figure 16. Even nanoparticle-containing unblended fluids were affected due to proper shearing. Therefore, a shearing process needs to be designed to achieve optimum results. These indicate that high shear mixing device is important for innovative nanoparticle-containing drilling formulations. Low degree of mixing can lead to the formation of ‘fish eyes’ causing filtration issues and effects on filter cake. The fish eyes on the unblended mud cake were clearly apparent in Figure 17. It was also noticed that fish eyes were completely minimized after high shear. Therefore the preferred processing order of building the mud and shearing immediately before storage may reduce the frequency of fish eyes as compared to drilling fluid that is stored before shearing.

Effect of Organophilic Clays on Fluid Loss Control: Increasing concentration of organophilic clay particles increased the fluid loss control. Figure 18 shows the effect of varying organophilic clays with iron hydroxide nanoparticles. Increasing 20 wt% clays will increase 20% fluid loss control. Solids content of the drilling fluid is one of the factors that causes formation damage and decreases the rate of penetration (ROP). See Newman et

al. (2009). Solids are added to fulfill the functional tasks of the mud, such as increase viscosity and fluid loss control. The higher the amount of total solid in the drilling fluid; the lower the rate of penetration which in turn increases rig days and reduces productivity index. The addition of increasing clays with nanoparticles reduced the fluid loss which can be attributed to the fact that the larger surface area of nanoparticles provides bridges between clays particles and disperses them more effectively. Due to low concentration (< 1 wt%) of nanoparticles in the fluid formulation with desirable fluid loss property, total solid concentration can be decreased to enhance the rate of penetration. This demonstrates the potential of the novel nanoparticle-containing fluid formulation using a low amount of nanoparticles to produce better fluid loss control than using significantly high amount of clays.

Effect of oil:water ratio on fluid loss control: Filtration behavior of emulsified oil is strongly influenced by oil/water ratio, additive chemistry and concentration. Therefore, it would be expected that oil/water ratio will affect fluid loss. It is of interest to compare effects of water content in drilling fluid on fluid loss control. A series of experiments were undertaken to investigate the effect of oil/water ratios namely 90:10 (v/v) and 80:20 (v/v) mixes. The results are shown in Table 8 and clearly illustrate the decrease in filtrate loss with increasing water content in the emulsion system. Increase in water content from 10 to 20 percent by volume caused the fluid loss to decrease 26% and 25% for drilling fluid control samples and drilling fluid containing gilsonite. Addition of nanoparticles again decreases the fluid loss to 44% and 10% for *ex situ* and *in situ* methods respectively. The reduction of fluid loss was dramatic in case of *ex situ* which suggests that extra water pools are required to disperse them effectively. *In situ* prepared nanoparticles are more readily dispersed in the 10% water content. When the water content increases, water droplets in the invert emulsion system are within the vicinity of each other and associate to create larger water droplets in the system. Since the filter cake is partly formed by the water droplets, an increase in water droplet size will increase the size of the nanoparticles and form a larger molecular size. The frequency of large sized nanoparticles can be higher with the available binding sites with other nanoparticles present in waterpools and clays and establishes the fact that increasing water in the emulsion system forms low permeability filter cake. Thus, using high water content clearly improves the fluid loss control. Increase in water pools increases the available binding sites for the nanoparticles which form more homogeneous systems. High water content reduces the interaction

between the surfactant head groups and colloidal nanoparticles which attributed to the increase in nanoparticles size and thereby enhances particle aggregation during filtration. See Husein and Nassar 2008. An investigation done with different oil/water ratios by Aston et al (2002) found the similar trends. 80:20 oil/water ratio (OWR) compared to the
 5 invert emulsion at 90:10 OWR added value by reducing the base oil content thus adding substantial savings.

Table 7: Effect of Oil/Water Ratio on Fluid Loss Control

Sample Types	Time (min)	LPLT Fluid Loss (mL)			
		DF	DF + 1.6 wt% LCM	DF + 1.6 wt% LCM + 0.74 wt% NPs <i>ex situ</i>	DF + 1.6 wt% LCM + 0.74 wt% NPs <i>in situ</i>
90:10 (v/v) oil:water	7.5	2.0±0.2	1.4±0.2	0.2±0.2	---
	30	3.96±0.2	3.6±0.1	1.10±0.1	0.50±0.2
80:20 oil:water	7.5	1.0±0.2	1.0±0.2	-	-
	30	2.9±0.1	2.7±0.2	0.62±0.1	0.45±0.1

10 Table 8: Performance of *ex situ* vs *in situ* prepared nanoparticles using three different samples of drilling fluid from three different suppliers

	Samples	Density	pH	API LPLT fluid loss/30 min (mL)
		(gm/mL)		
15	Supplier A			
	DF	0.93±0.02	12.5	3.9±0.2
	DF+LCM	0.93±0.02	12.5	3.6±0.1
	DF+LCM+ <i>Ex situ</i> NPs	0.93±0.02	12.5	1.1±0.1
20	Supplier B			
	DF	0.93±0.02	12.5	16.5±0.3
	DF+LCM	0.93±0.01	12.5	12.7±0.4
	DF+LCM+ <i>Ex situ</i> NPs	0.93±0.02	12.5	7.5±0.2
25	Supplier C			
	DF	0.90±0.02	12.5	1.2±0.2
	DF+LCM	0.90±0.02	12.5	1.0±0.1
	DF+LCM+ <i>Ex situ</i> NPs	0.90±0.01	12.5	0.5±0.1

The results in Table 8 show the application of nanoparticles in drilling fluids for preventing fluid loss. Since it is not possible to maintain all of the mud properties at
 30 optimum, it is the industry practice to reach a compromise by keeping one critical property at optimum and the rest at reasonable levels. In most cases, the filtration property of the

mud is maintained at optimum. The incorporation of custom prepared nanoparticles in invert emulsion fluid systems substantially reduced the fluid loss due to the nanoparticles themselves and nano-induced aggregates. However, the use of nanoparticles in the drilling fluid at a right concentration and adoption of a specific preparation method left the fluid with desirable properties of mud density, pH and rheology behavior. The addition of nanoparticles does not change these properties in the base fluid. Formation damage due to filtrate and solids invasion is a major contributor to cost, lost time and lost production. Nanoparticles work in emulsion based fluids, even at extreme high temperatures, providing a thin filter cake that gives maximum formation protection at minimum concentration and cost. Tailor made nanoparticles with specific characteristics will reduce the circulation loss and other technical challenges faced with commercial drilling fluid during oil and gas drilling operation.

The present invention is described with reference to specific examples and embodiments. Those skilled in this field will understand that numerous variations and modifications are possible, without departing from the scope of this invention. Although the invention is described in terms of drilling fluids and in particular invert emulsion drilling fluids, it will be apparent to a person skilled in this field that the invention may apply to other well fluids that suffer from fluid loss to the formation, including completion fluids, kill fluids, and pre-stimulation fluids.

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- Streat, M., Hellgardt, K and Newton, N.L.R., "Hydrous ferric oxide as an adsorbent in water treatment part 1. Preparation and physical characterization", Process Safety and Environmental Protection, 86, pp1-9, (2008)

CLAIMS:

1. A nanoparticle-containing well fluid comprising a base fluid and about 5wt% or less nanoparticles, for preventing or reducing fluid loss to an underground formation,
5 wherein the well fluid is a drilling fluid, kill fluid, completion fluid, or pre-stimulation fluid.
2. The well fluid of claim 1 wherein the well fluid is a drilling fluid.
- 10 3. The well fluid of claim 2 wherein the drilling fluid is an invert emulsion drilling fluid.
4. The fluid of any one of claims 1 to 3 wherein the nanoparticles are present in an amount of less than about 4 wt%.
- 15 5. The fluid of claim 4 wherein the nanoparticles are present in an amount of less than about 3 wt%.
6. The fluid of claim 5 wherein the nanoparticles are present in an amount of less than
20 about 1 wt%.
7. The fluid of claim 6 wherein the nanoparticles are present in an amount of between about 0.1 to about 1 wt%.
- 25 8. The fluid of claim 7 wherein the nanoparticles are present in an amount of between about 0.5 to about 1.0 wt%.
9. The fluid of claim 8 wherein the nanoparticles are present in an amount of between about 0.6 to 1wt%.
- 30 10. The fluid of claim 9 wherein the nanoparticles are present in an amount of between about 0.74 to about 1wt%.

11. The fluid of any one of claims 1 to 10 wherein the nanoparticles have a particle size of between about 1 to about 120 nm.
12. The fluid of claim 11 wherein the nanoparticles have a particle size of between
5 about 1 to about 30 nm.
13. The fluid of claim 11 wherein the majority of the nanoparticles have a particle size in the range of 1-30 nm.
- 10 14. The fluid of claim 11 wherein substantially all of the nanoparticles have a particle size in the range of 1-30 nm.
15. The fluid of any one of claims 1 to 14 wherein the nanoparticles are one or more of metal hydroxide, metal oxide, metal carbonate, metal sulfide, and metal sulfate.
- 15 16. The fluid of claim 15 wherein the nanoparticles are selected from the group consisting of iron hydroxide, iron oxide, calcium carbonate, iron sulfide, barium sulfate, or a mixture thereof.
- 20 17. The fluid of claim 15 wherein the nanoparticles are iron oxide formed from iron hydroxide in high pressure high temperature conditions in the underground formation.
18. The fluid of any one of claims 1 to 16 wherein the nanoparticles are formed *in situ* in the fluid or formed *ex situ* and added to the fluid.
- 25 19. A use of the well fluid defined in any one of claims 1 to 18 for reducing or preventing fluid loss to an underground formation.
20. The use of claim 19 for reducing or preventing fluid loss during drilling of a well
30 into the underground formation.
21. The use of claim 19 or 20 wherein the formation is a high temperature high pressure formation.

22. The use of claim 19 or 20 wherein the formation is a low temperature low pressure formation.
23. The use of any one of claims 19 to 22 wherein the reduction of fluid loss is at least
5 about 50% compared to a well fluid that does not contain loss circulation materials or nanoparticles.
24. The use of claim 23 wherein the reduction of fluid loss is at least about 70% compared to a well fluid that does not contain loss circulation materials or nanoparticles.
- 10 25. The use of any one of claims 19 to 24 wherein the underground formation has pore opening smaller than 100 μm .
26. The use of claim 25 wherein the underground formation is a shale formation.
- 15 27. A method of making the nanoparticle-containing well fluid defined in any one of claims 1 to 17 by forming the nanoparticles *ex situ*, comprising the steps of providing aqueous-based precursor solutions for forming the nanoparticles, mixing the precursor solutions under high shear, and adding the mixed precursor solution to the well fluid, to
20 form the nanoparticle-containing fluid, wherein the nanoparticles act as fluid loss material for reducing fluid loss in an underground formation.
28. A method for making a nanoparticle-containing well fluid defined in any one of claims 1 to 18 by forming the nanoparticles *in situ*, comprising the steps of providing
25 aqueous-based precursor solutions for forming the nanoparticles, adding the precursor solutions to the well fluid, and subjecting the fluid to mixing and shear to form the nanoparticle-containing fluid, wherein the nanoparticles act as a fluid loss material for reducing fluid loss in an underground formation.
- 30 29. The method of claim 28 wherein the fluid is an invert emulsion drilling fluid and the nanoparticles form in the dispersed water pools of the invert emulsion drilling fluid.
30. The method of claim 27 or 28 wherein the nanoparticle is iron (III) hydroxide.

31. The method of claim 28 or 29 wherein the aqueous-based precursor solutions comprise an aqueous based solution containing $\text{FeCl}_{3(\text{aq})}$ and an aqueous based solution containing $\text{NaOH}_{(\text{aq})}$.
- 5 32. The method of claim 28 or 29 wherein the aqueous-based solutions comprise an aqueous based solution containing $\text{Ca}(\text{NO})_3$ and an aqueous based solution containing Na_2CO_3 .
- 10 33. The method of claim 28 or 29 wherein the aqueous-based solutions comprise an aqueous based solution containing BaCl_2 and an aqueous based solution containing Na_2SO_4 .
34. The method of claim 28 or 29 wherein the aqueous-based solutions comprise an aqueous based solution containing Na_2S and an aqueous based solution containing FeCl_2 .

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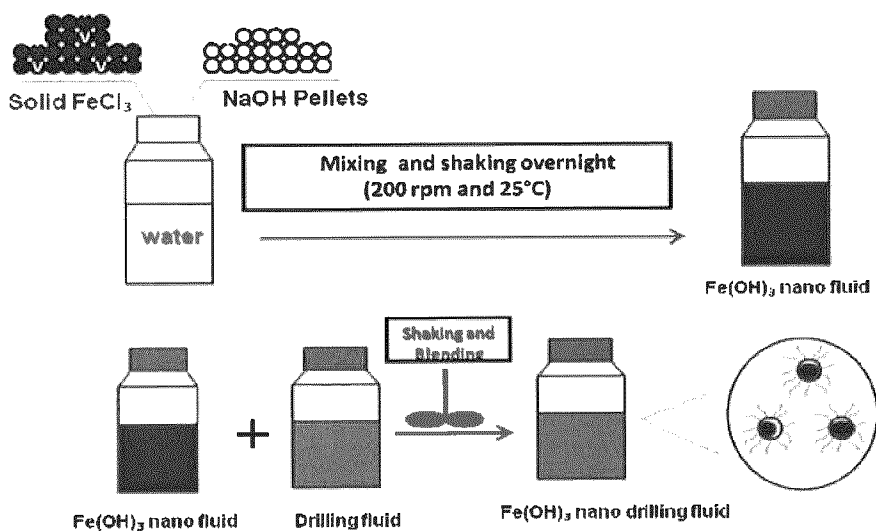


Figure 1

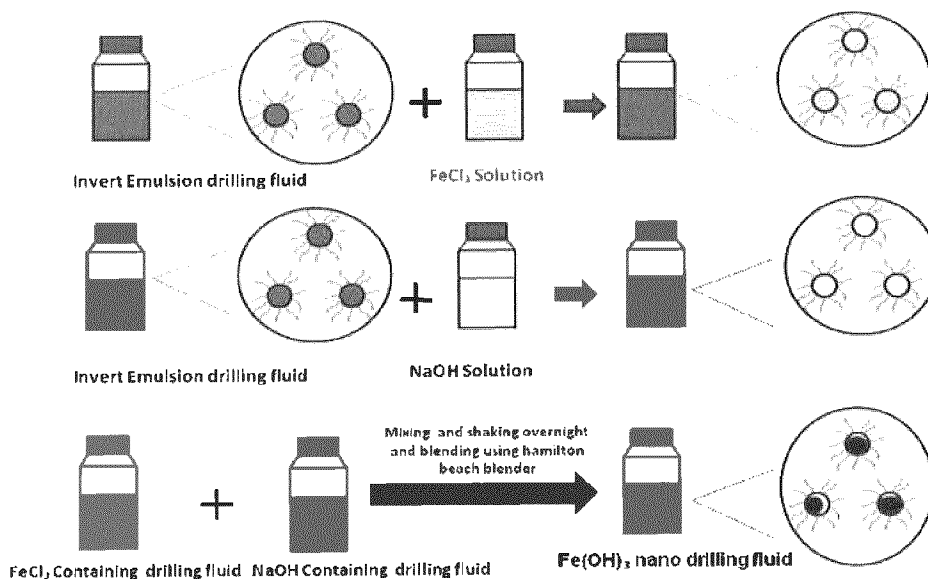


Figure 2

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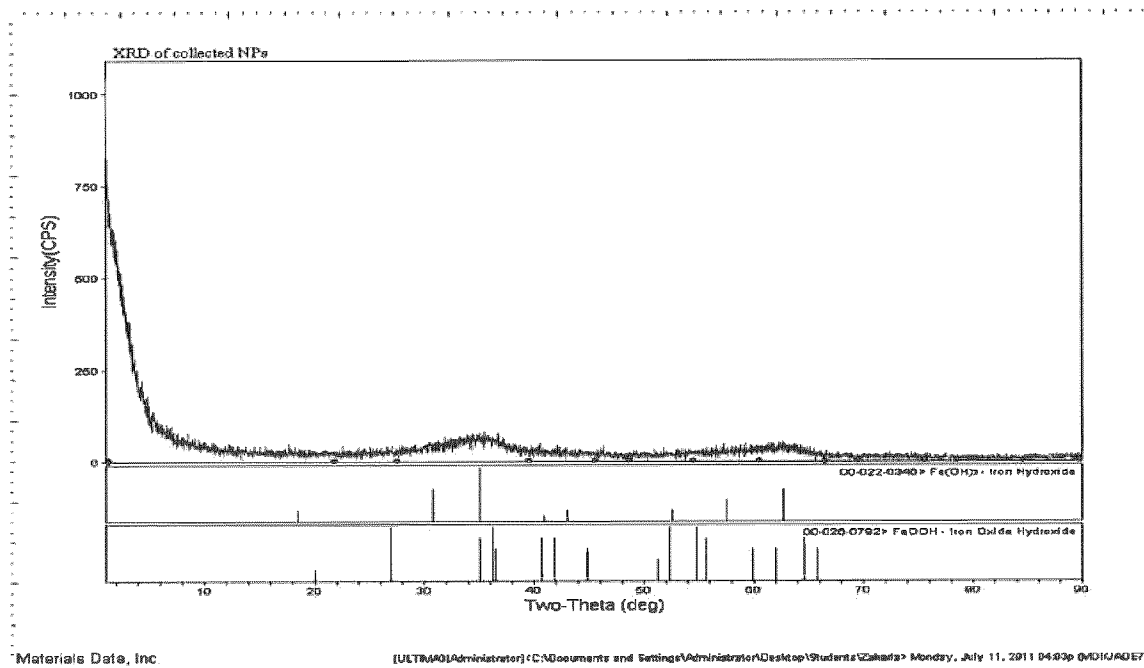


Figure 3



Figure 4a)

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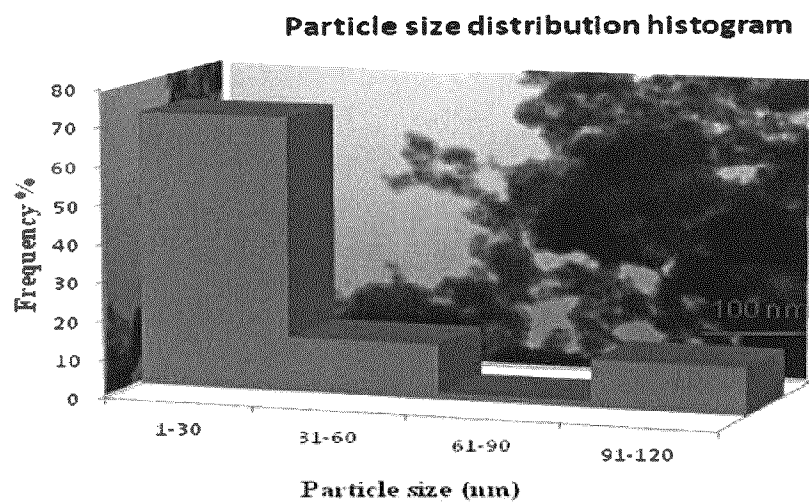


Figure 4b)

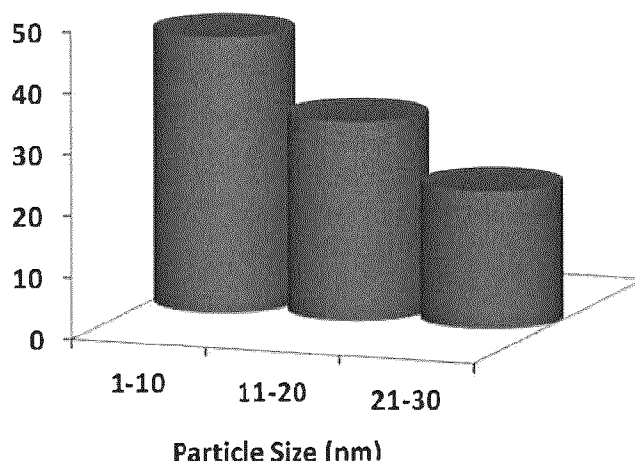


Figure 4c)

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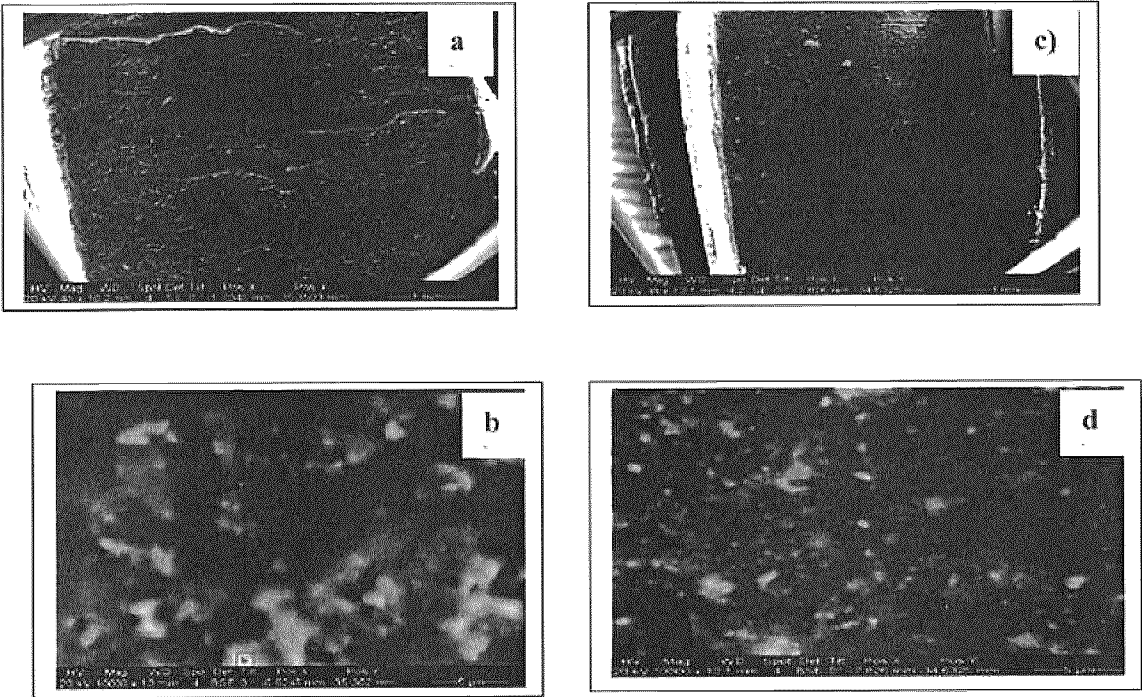


Figure 5

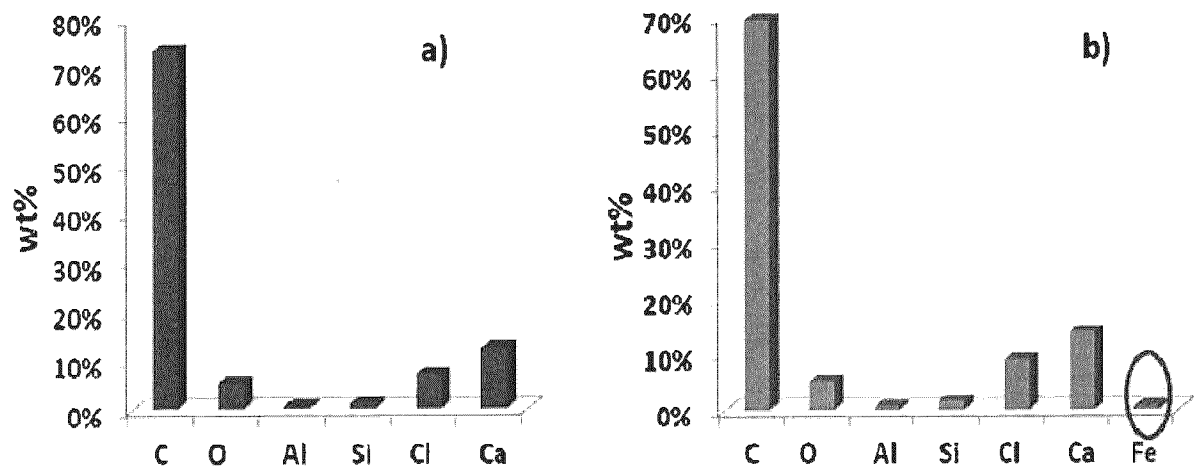
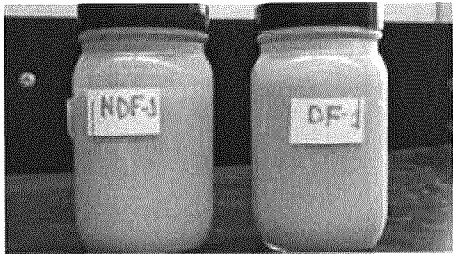


Figure 6a)

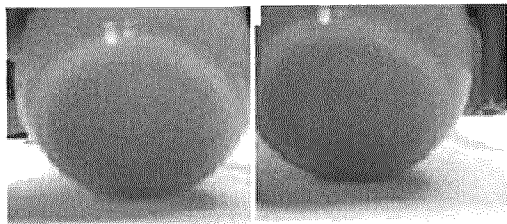
Figure 6b)



a)



b) nano based fluid initial fluid



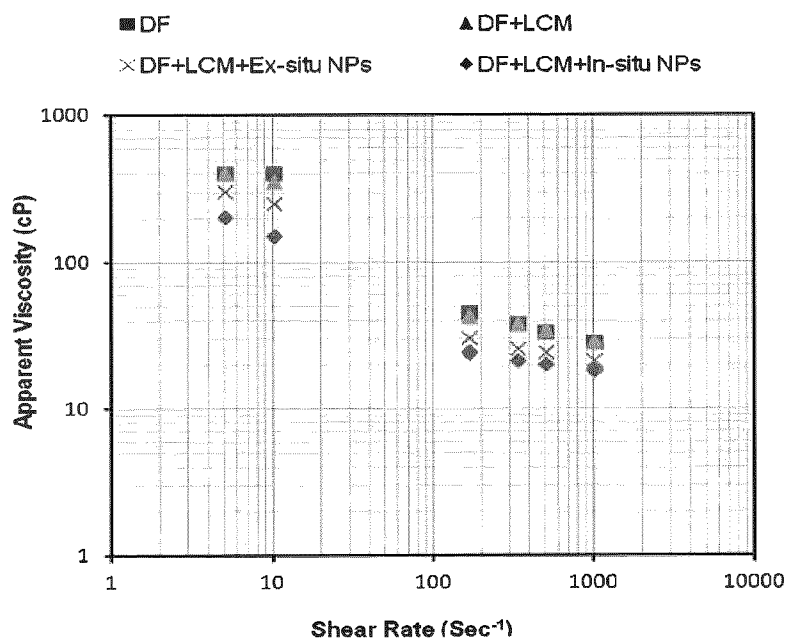
c)

 nano based fluid initial fluid

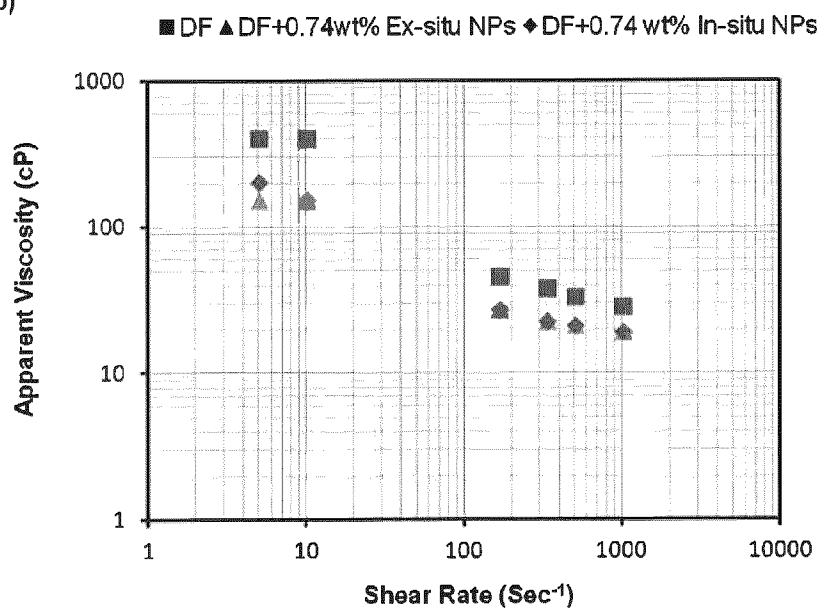
Figures 7a)-c)

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8a)



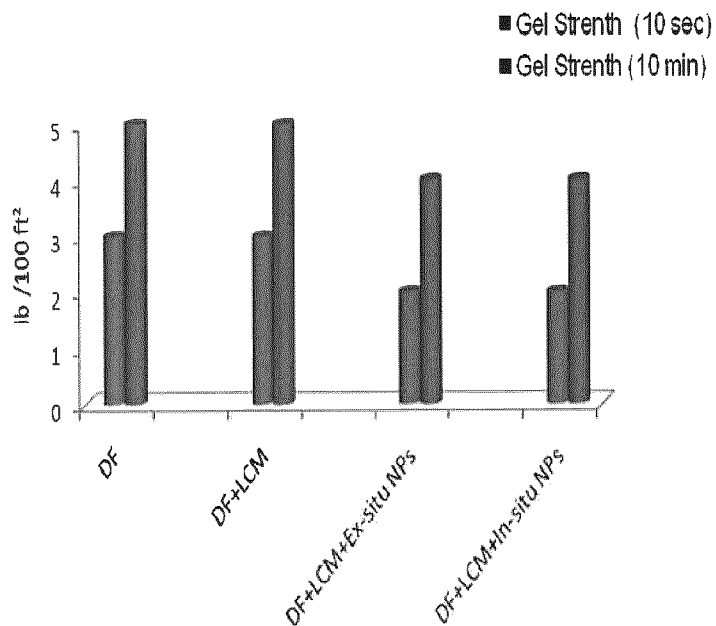
8b)



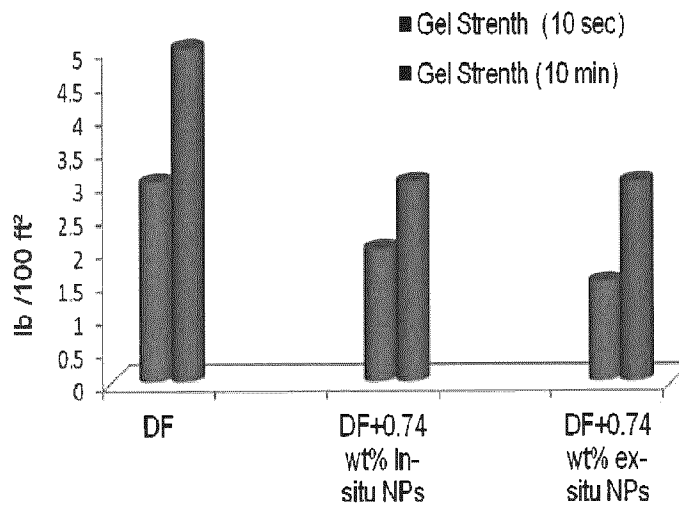
Figures 8a) and 8b)

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9a)



9b)



Figures 9a) and 9b)

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■ DF after preparation ◆ DF after 1 month ▲ DF+NPs after preparation × DF+NPs after 1 month

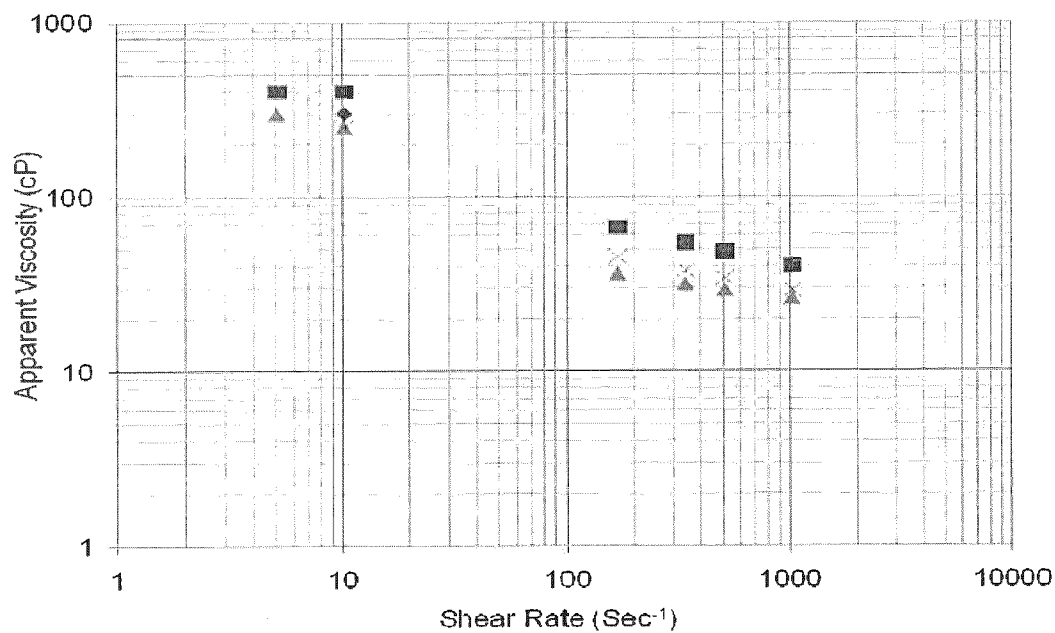


Figure 10

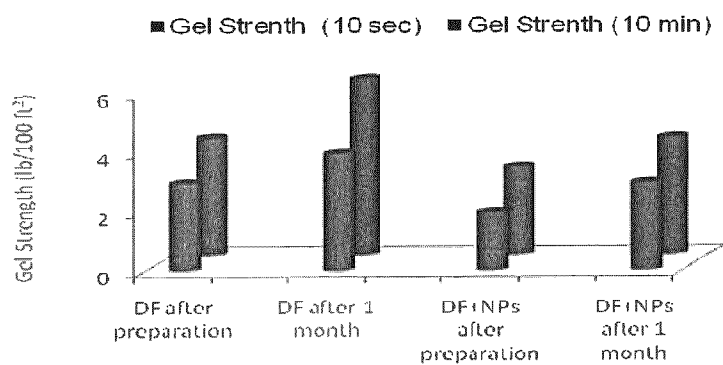


Figure 11

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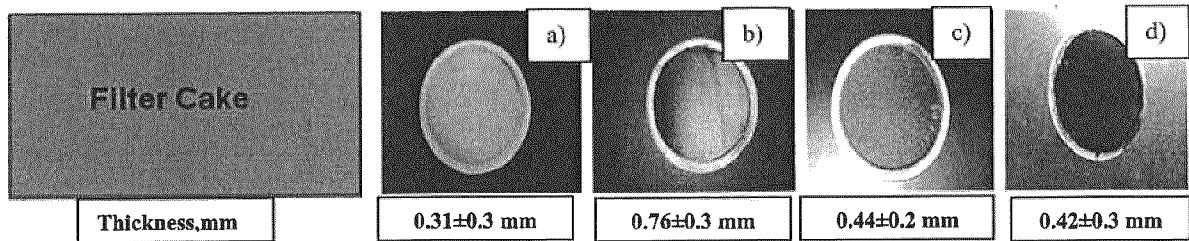


Figure 12

Samples Types	Time (min)	LPHT Fluid Loss (mL)		
		DF	DF +0.74wt% NPs <i>ex-situ</i>	DF +0.74wt% NPs <i>in-situ</i>
90:10 (v/v) Oil: Water	7.5	2 ± 0.2	0.15 ± 0.1	-
	30	3.96 ± 0.2	1.25 ± 0.2	0.9 ± 0.2

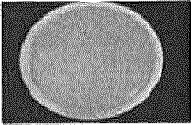
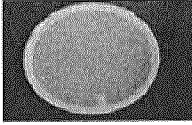
Mud Cake			
	DF	DF+0.74% w/w NPs Ex-situ	DF+0.74 %w/w NPs In-situ
Thickness,mm	0.31 ± 0.3 mm	0.38 ± 0.1 mm	0.35 ± 0.1 mm

Figure 13

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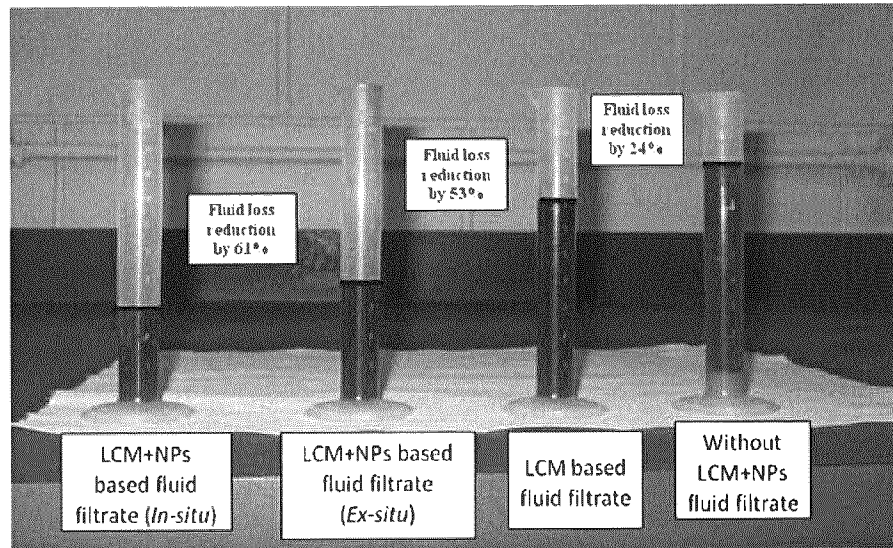


Figure 14

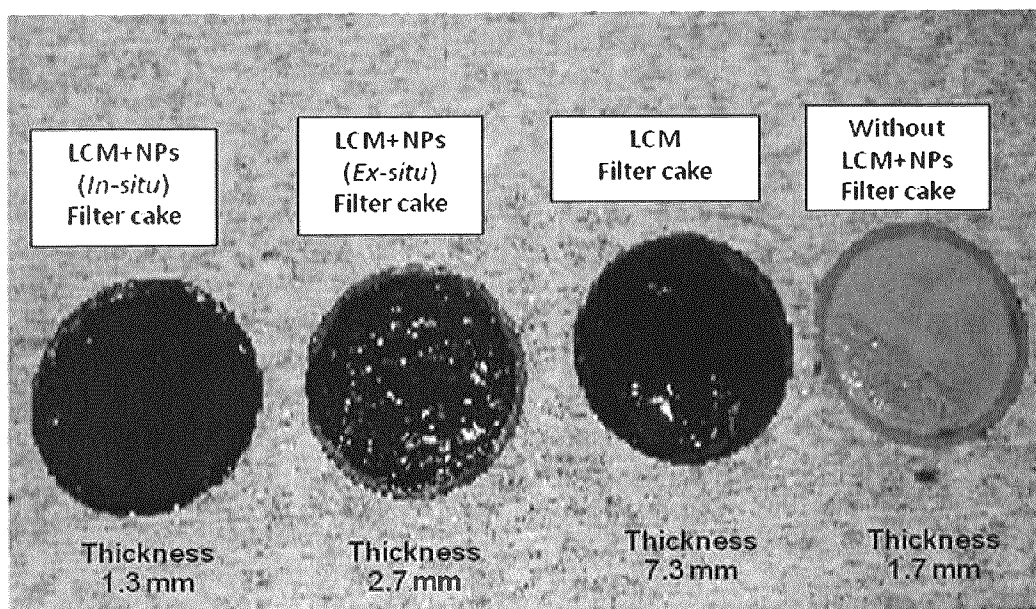


Figure 15

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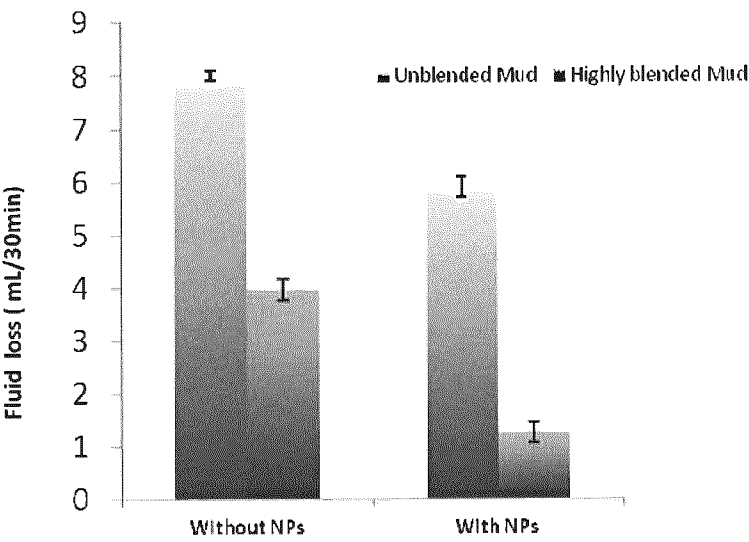


Figure 16

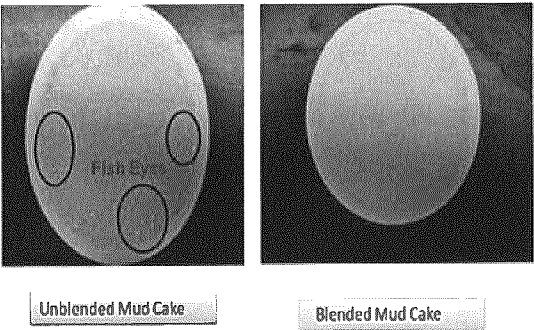


Figure 17

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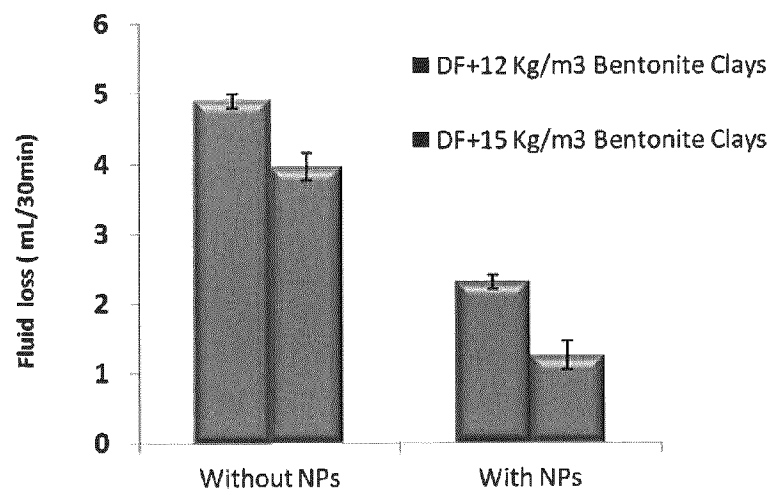


Figure 18

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FeS NPs	BaSO4 NPs	CaCO3 NPs	Fe(OH)3 NPs
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Figure 19

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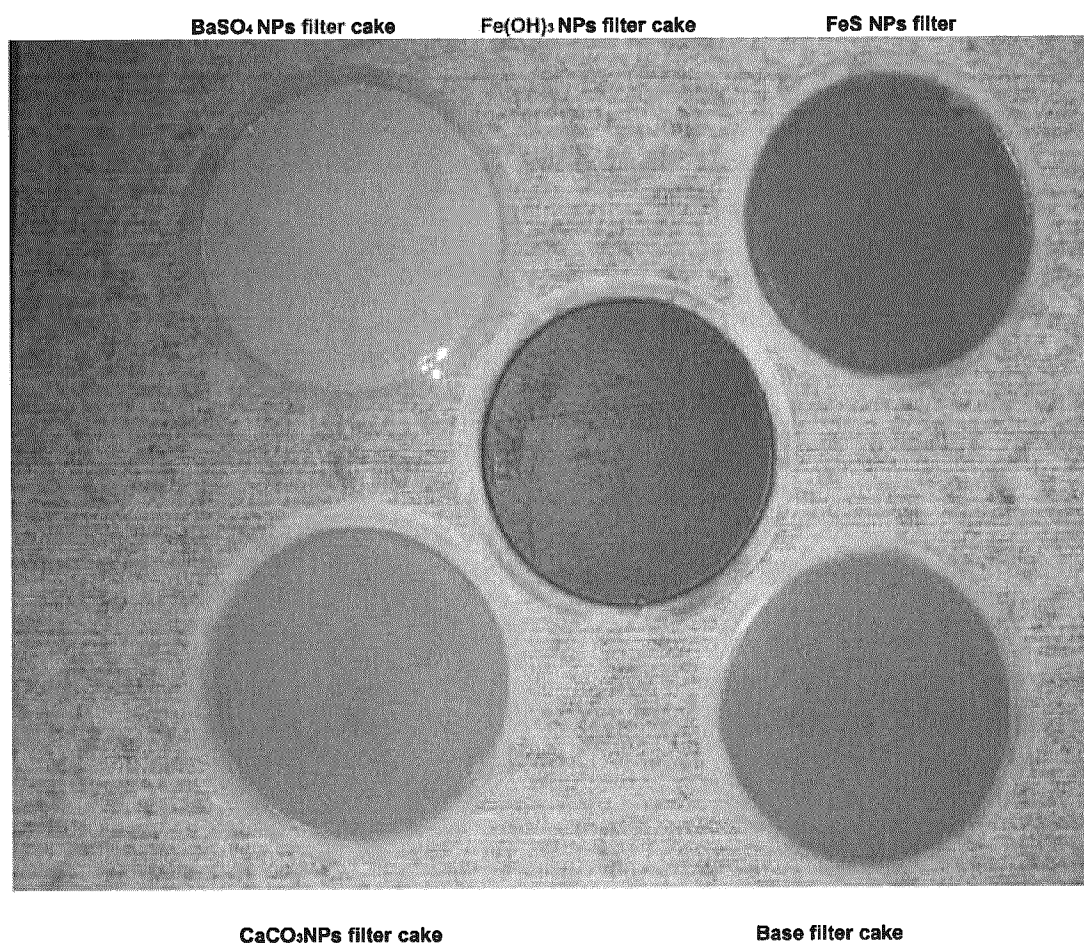


Figure 20

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CA2012/050075

A. CLASSIFICATION OF SUBJECT MATTER

IPC: **C09K 8/03** (2006.01) , **C09K 8/36** (2006.01) , **C09K 8/42** (2006.01) , **E21B 21/00** (2006.01) , **E21B 33/13** (2006.01)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC: **C09K 8/03** (2006.01) , **C09K 8/36** (2006.01) , **C09K 8/42** (2006.01) , **E21B 21/00** (2006.01) , **E21B 33/13** (2006.01)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

IPC: **C09K 8/*** (2006.01) , **E21B** (2006.01)
Canadian Patent Database, Epoque, Google Scholar

Electronic database(s) consulted during the international search (name of database(s) and, where practicable, search terms used)

Canadian Patent Database, Epoque, Google Scholar

key words: fluid loss control agent, FLCA, lost circulation material, lcm, lost circulation agent, nanoparticle

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CA2485777 13-05-2005 (13-May-2005) Couillet, Isabelle et al. ([0011] - [0012]; [0022] - [0025]) -----	1, 2, 4 - 17, 18 - 28 and 30 - 34
X	Sensoy, Taner Use of Nanoparticles for Maintaining Shale Stability, Master's Thesis presented at The University of Texas at Austin May 2009 -----	1, 2, 11 - 16, 18 - 27, 30, and 34
X	Aston, M. et al. Towards Zero Loss Oil Based Muds. <i>Presented at the SPE Annual Technical Conference and Exposition San Antonio, Texas, USA 29-09-2002 (29-September 2006)</i> Society of Petroleum Engineers, SPE 77446 -----	1 - 10, 18 - 20, and 23 - 24
X	Amanullah, Md. et al. Preliminary Test Results of Nano-based Drilling Fluids for Oil and Gas Field Application. <i>Presented at the SPE/IADC Drilling Conference and Exposition Amsterdam, The Netherlands 01-03-2011 (01-March-2011)</i> Society of Petroleum Engineers SPE/IADC139534 -----	1, 2, 4 - 14, 18 - 20, 23, and 24
X	Nashaat, Nassar and Hussein, Maen Preparation of Iron Oxide Nanoparticles from FeCl3 solid Powder Using Microemulsions 20-04-2006 (20-April-2006) <i>Physica Status Solidi (a)</i> volume 203, Number 6, Wiley Interscience. pages	X - 27 - 34

[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier application or patent but published on or after the international filing date	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&" document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

July 16, 2012 (04-07-2012)

Date of mailing of the international search report

16 July 2012 (16-07-2012)

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Authorized officer

Scott Curda (819) 994-1685

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CA2012/050075

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	Srivatsa, Jayanth et al. An experimental Investigation on the use of Nanoparticles as Fluid Loss Control Additives in a Surfactant - Polymer Based Drilling Fluid. <i>International Petroleum Technology Conference, Bangkok, Thailand 07-02-2011 (07-February-2011)</i> IPTC14952	1 - 34

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/CA2012/050075

Patent Document Cited in Search Report Date	Publication Date	Patent Family Member(s)	Publication
CA2485777A1	13 May 2005 (13-05-2005)	CA2485777A1 CA2485777C RU2004133166A RU2359112C2 US2005107265A1 US7081439B2	13 May 2005 (13-05-2005) 13 January 2009 (13-01-2009) 20 April 2006 (20-04-2006) 20 June 2009 (20-06-2009) 19 May 2005 (19-05-2005) 25 July 2006 (25-07-2006)