Smart Spacer Fluid Modified with Iron Oxide Nanoparticles for Cleaning Bentonite Clay Contamination

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Abstract

The focus of this study was to make the fluids highly sensing to be used for real time monitoring of changes during the installation and entire service life. For optimizing the well cementing, it is important to develop technology to monitor drilling and cementing operation in real time during the well installation to minimize operation delays, failures and ensure safety. In this study, the effects of pressure and magnetic field strength on the electrical resistivity and rheological properties of a sensing smart spacer fluid modified with iron oxide nanoparticles (nanoFe_2O_3) were investigated. The magnetic field strength was varied from 0 T to 0.6 T. The nanoFe_2O_3 contents (particle size of 30 nm) in the spacer fluid were varied up to 1% by the weight of the spacer fluid to enhance the sensing and rheological properties of the spacer fluid. The initial resistivity of the spacer fluid without any nanoFe_2O_3 at 25°C was 0.2 Ωm. Addition of 1% nanoFe_2O_3 increased the electrical resistivity by 3.5%. Adding nanoFe_2O_3 enhanced the piezoresistive behavior of the smart spacer fluid. Increase in the magnetic field strength improved the rheological properties of the spacer. The rheological properties of the spacer fluids were characterized by high strain rate to determine the nonlinear behavior of the shear thinning spacer fluid. The spacer fluid rheology was modelled using Herchel Bulkley model and Vipulanandan model. The electrical resistivity was used as sensing parameter to monitor the percentage of oil cleaning efficiency of the spacer fluid. Based on the new Vipulanandan rheological model, the maximum shear stress tolerance (τ_{max}) for the spacer fluid increased from 49.4 Pa to 65.5 Pa, 33% increase at the temperature of 25°C with 1% addition of nanoFe_2O_3.The cleaning efficiency of the spacer fluid in removing Bentonite drilling fluid contamination was 82.5% without the addition of nanoFe_2O_3. With the addition of nanoFe2O3 the cleaning efficiency increased from 82.5% to 99.4%, 17% increase in the efficiency. The maximum shear stress tolerance (τ_{max}) correlated well with the cleaning efficiency. Also the change in the electrical resistivity of the spacer fluid after cleaning correlated well with the cleaning efficiency and hence can be used for in-situ monitoring of the cleaning operation.

1.Introduction

Real time monitoring the performance of materials used in oil, gas and water vertical wells construction and horizontal direction drilling (HDD) for installing pipelines are gaining importance over time. With the industrialization and growth of population around the world, the demand for oil and gas and installation of various pipelines are increasing around the world. With the increasing pressure, the oil and gas industry is now forced to drill to greater depths reaching about 30,000 ft. The advancements in the field of drilling by integrating vertical drilling with horizontal drilling have enabled oil and gas industry to expand to many inaccessible areas around the world. In the construction of an oil well first, a wellbore is drilled, and a metal casing is placed inside of it. Spacer Fluid is pushed inside through the casing out into the annulus for cleaning the casing of any drilling fluids residue. Spacer fluids have been primarily developed to separate the cement slurry from the drilling fluid because of contamination of the cement affecting the cementing operation and long-term stability of the cemented wells. Also in HDD, the boreholes have to be cleaned during the installation of the pipelines. Effective removal of the drilling fluids and associated residues from the wellbore prior to the completion of wells and installing the pipelines are critical issues to be considered.

The quality of the cementing job strongly depends on the cleaning efficiency of the spacer fluid in removing not only the drilling fluid with the cuttings but also the filter cakes during the drilling operation. Based on the applications, different types of spacer fluids are used with varying material properties such as density, rheology and cleaning efficiency. The cleaning efficiency of spacer fluids currently cannot be obtained in the field and hence needs more reliable methods for real time monitoring. New parameters have to be investigated to quantify the cleaning efficiency and its performance in the field.

Spacer Fluids

The most common types of spacer fluids include water-based spacers and oil based spacer fluids. Selecting the proper spacer fluid is typically important and is dependent on the chemistry of the drilling fluid, its composition and conditions of the drilled holes. Spacer fluids play a crucial role in proper displacement of the drilling mud and removal of the filter cake developed along the drilled holes. Various types of spacer systems are available in the oil and gas industry, but they may not be suitable for changing geological conditions along the drilled holes. Generally, a spacer fluid is composed of the following components. (1) Water/Oil as the base fluid of spacer system; (2) Weighting materials to increase the density of the spacer system; (3) Rheological modification agent or polymers and (4) A proper surfactant Package. Using these components in the spacer fluid makes the spacer density and rheological properties fall in between the density and rheological profile of drilling fluid and cement.

During recent years the operators are to explore and produce from increasingly more difficult environments. Fluid displacements in offshore environments require spacer fluids to perform more than one operation effectively at low and high temperatures encountered in the well. In each of these cases there have to be a novel design to adjust for different conditions. Use of nanoparticles in spacer system can provide enhancements in rheological, thermal, mechanical, magnetic and optical profiles. Nanoparticles with noticeable alterations in the optical, magnetic field strength and electrical properties are excellent tools for the development of sensors and the formation of imaging contrast. Since the nanoparticles are extremely small in size, nanoparticles are preferred to be used as their abrasive forces are negligible with less kinetic energy impact.

2. Objectives

The overall objective was to develop and characterize highly sensing smart spacer fluid with nanoFe_2O_3 for in–situ electrical sensing and property modifications under application of different pressures. The specific objectives are as follows:

(1). Design spacer fluid with higher cleaning efficiency (>95%) of oil-based drilling fluid contamination using iron nanoparticles and investigate the effects of magnetic field and temperature on the sensing and rheology property modifications.

(2). Characterize the spacer fluid to identify the critical electrical property for real-time monitoring.

(3). Model the rheological and cleaning efficiency of the spacer fluids using Vipulanandan Models.

3. Materials and Methods

Materials

UH Biosurfactant

The biosurfactant used in this study was produced from waste oil with acclimated bacteria in continuously stirred batch reactor. The critical micelle concentration (CMC) for this biosurfactant is 0.5 g/L and the surface tension reduces to 30 dynes/cm. The biosurfactant is water soluble and based on Fourier Transform Infra Read (FTIR) spectroscopy analyses both carboxyl (COO-) and hydroxide (OH-) groups were identified in the biosurfactant.

Diesel Oil

Diesel oil, representing the oil-based drilling fluid, with a density of 5.6 ppg was used for the cleaning efficiency test. The resistivity of the Oil was greater than 1000 Ωm.

Spacer Fluid Preparation

The spacer fluid was prepared by using water as the base fluid. Rheology modifiers such as Guargum up to 1% and UH biosurfactant up to 0.4% were added. Also up to 3% KCl was added with the weighting agent lead nitrate ($Pb(NO_3)_2$). KCl was first mixed with water and was mixed thoroughly till it completely dissolved. Then rheology modifier Guargum was added followed with the UH Bio-surfactant and mixed until uniform solution is obtained. This uniform mixture was then mixed with the weighting agent to obtain the spacer fluid. Also, Nano Iron was added to the spacer fluid to enhance the performance with pressure, temperature and magnetic field. Also, the fluid was characterized with electrical resistivity and density measurements at each stage of mixing.

Methods of Testing

Density

The density plays a major role in providing the needed hydrostatic pressure in the drilled holes. Density of the spacer fluid with and without Nano Iron was measured immediately after mixing using the standard mud balance cup.

HPHT Testing

The spacer fluid was tested up to of 500 psi pressure. The change in the bulk resistivity of the material with the applied pressures were measured and modelled using the Vipulanandan model.

Rheological Properties

Rheological properties determine the pump ability and cleaning capability of spacer. The rheology tests for smart spacer fluid with different contents of Nanoiron (nanoFe_2O_3) at temperature of 25°C to 75°C and magnetic fields of 0 to 0.6T were tested using a viscometer in the speed range of 0.3 to 600 rpm (shear strain rate of 0.5 s^{-1} to 1024 s^{-1}) and related shear stresses were recorded. The speed accuracy of this device was 0.001 rpm. The temperature of the spacer was controlled to an accuracy of ±2˚C. The viscometer was calibrated using several standard solutions. All the rheological tests were performed after 10 minutes of mixing of the spacer solutions. The viscometer was calibrated using several standard solutions.

Cleaning efficiency test

The cleaning efficiency test was performed on the spacer fluid to quantify the ability of the spacer to clean the diesel oil representing the oil-based drilling fluid. For this test the following procedure was followed. Initially the viscometer cup and the spindle were cleaned and dried.

The dry weight of the spindle was measured (W_1). The viscometer cup was filled with diesel oil and ran the spindle for 10 minutes at 100 rpm. After 10 minutes, the viscometer spindle was weighed again with the contamination (W_2). Then the spacer fluid was placed in the cup and the spindle was rotated again for 10 minutes at 100 rpm. Then the viscometer spindle was weighted again (W_3). Also, the change in the electrical property of the cleaning spacer fluid was measured.

Modeling

Rheological Modeling

The spacer fluid showed non-linear shear thinning behavior with a yield stress. Based on the test results, following conditions have to be satisfied for the model to represent the observed behavior. Hence the conditions are as follows:

$$\tau = \tau_o \text{ when } \dot{\gamma} = 0; \quad \text{and } \dot{\gamma} \rightarrow \infty \Rightarrow \tau = \tau^*. \tag{1}$$

The rheological models used for predicating the shear thinning behavior of spacer fluids are summarized below.

Herschel-Bulkley model (1926)

The Herschel-Bulkley (Eqn.(2)) model defines a fluid with three parameters and can be represented mathematically as

$$\tau = \tau_{o1} + k * (\dot{\gamma})^n \tag{2}$$

where τ , τ_{o1}, $\dot{\gamma}$, k and n represent the shear stress, yield stress, shear strain rate, correction parameter and flow behavior index respectively. For $\tau < \tau_o$ the material remains rigid. The model assumes that below the yield stress (τ_o), the slurry behaves as a rigid solid. The exponent n describes the shear thinning and shear thickening behavior. Slurries are considered as shear thinning when n <1 and shear thickening when n >1.

$$\text{when } \dot{\gamma} \rightarrow \infty \Rightarrow \tau_{max.} = \infty \tag{3}$$

Hence Herschel-Bulkley model doesn't satisfy the upper limit condition for the shear stress limit.

Vipulanandan Rheological model (2014)

The Vipulanandan Rheological Model relationship is as follows.

$$\tau - \tau_{o2} = \frac{\dot{\gamma}}{C + D * \dot{\gamma}}, \tag{4}$$

where τ: shear stress (Pa); τ_{o2}: yield stress (Pa); C $(Pa.\ s)^{-1}$ and D $(Pa)^{-1}$: are model parameters and $\dot{\gamma}$: shear strain rate (s^{-1}).

$$\text{Also when } \dot{\gamma} \rightarrow \infty \Rightarrow \tau_{max} = \frac{1}{D} + \tau_{o2}. \tag{5}$$

Hence this model has a limit on the maximum shear stress; the slurry will produce at relatively high rate of shear strains.

Cleaning Efficiency

The cleaning efficiency of the spacer is calculated using the following formula

$$Cleaning\ efficiency(\%) = \frac{W_3 - W_2}{W_2 - W_1} * 100, \tag{6}$$

where,

W_1 = Weight of the viscometer spindle before the test in gms,

W_2 = Weight of viscometer spindle with the contamination in gms and

W_3 = Weight of the viscometer spindle after the test in gms.

Vipulanandan Cleaning Efficiency models

The relation between maximum shear stress capacity and cleaning efficiency for smart spacer fluid is given as follows:

$$CE(\%) = \frac{\tau_{max}}{E + F * \tau_{max}}, \tag{7}$$

where CE (%) = Cleaning efficiency in percentage, τ_{max} = Maximum Shear Stress capacity of the spacer fluid (Pa) and E and F are the Model parameters.

Piezoresistivity Model

Piezoresistivity of the slurry shall be modeled using the Vipulanandan correlation Model and the relationship is as follows:

$$\frac{\Delta\rho}{\rho_o} = \frac{p}{J + K * p} \tag{8}$$

where $(\Delta\rho/\rho_o)$ is the change in bulk resistivity, p is the pressure applied. Parameters J and K are the model parameters.

4. Results and Discussions

Spacer fluid applications require the materials to be multifunctional. Hence the spacer fluid must be modified or treated to enhance the different properties such as density, rheology, cleaning efficiency, and sensitivity. In this study, the water based spacer fluid was modified with nanoFe_2O_3 for insitu sensing, property modifications and to investigate the effect of magnetic field and temperature on the sensing property.

Material Characterization

It is important to identify the critical electrical property that can be used to monitor the spacer fluids in the field during various applications. The electrical impedance-frequency response using the two probes and alternative current (AC) coupled with the Vipulanandan Impedance Model was used to identify critical electrical property such as inductance, capacitance (permittivity), resistance (resistivity) or a combination for the spacer fluids.

Vipulanandan Impedance Model

Equivalent Circuits

Identification of the most appropriate equivalent circuit to represent the two probe contacts and the electrical properties of the testing material is essential to further understand its properties. In this study, an equivalent circuit to represent the smart spacer fluid was required for better characterization through the analyses of the Impedance Spetroscopy (IS) data. Based on the testing results of the smart space fluids tested in this study, the typical impedance-frequency response and the equivalent electrical circuit are shown in Figure 1, which includes the two contacts and the bulk material (smart space fluid). This is also refereed as CASE 2 in the literatue.

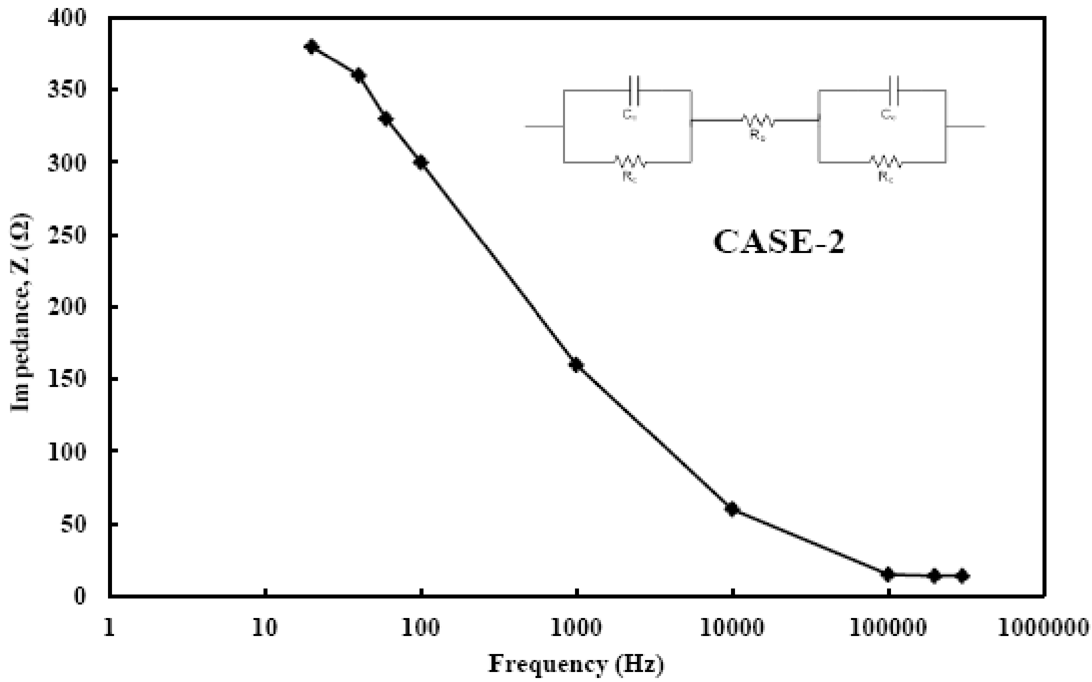

Figure 1 Typical Impedance-frequency Response and the Equivalent Electrical Circuit Representing the Smart Spacer Fluid with the 2- Probe Monitoring.

CASE-2: Special Bulk Material - Resistance Only

The total impedance of the equivalent circuit for CASE-2 (Z_2) is as follows:

$$Z_2(\sigma) = R_b(\sigma) + \frac{2R_c(\sigma)}{1+\omega^2 R_c^2 C_c^2} - j\frac{2\omega R_c^2 C_c(\sigma)}{1+\omega^2 R_c^2 C_c^2}. \qquad (9)$$

$$= R_2 + j\,X_2 \qquad (10)$$

The term R_2 in Eqn. (3) represents the real part of the impedance (Z_{real} of Z_2) and X_2 represents the imaginary part of the impedance (Z_2). When the frequency of the applied signal was very low, $\omega \rightarrow 0$, $Z_2 = R_2 = R_b + 2R_c$, and when it is very high, $\omega \rightarrow \infty$, $Z_2 = R_2 = R_b$ and X_2 will be equal to zero. In CASE-2, if the impedance is measured at very high frequency it will measure the resistance (R_b) in the material and eliminates the effects of the contacts and also it is frequency independent. This becomes another unique advancement in the measurement and also monitoring since the resistance is independent of the very high frequency of measurement.

Also in this study, changing spacer fluid conditions were monitored using the LCR meter at

300 kHz frequency to eliminate the contacts and measure the bulk spacer fluid resistance. Also the measured resistance was correlated to resistivity (material property) which was measured using the conductivity probe and digital resistivity meter.

(a).Conductivity Probe

Commercially available conductivity probe was used to measure the conductivity which is inverse of resistivity. The conductivity measuring range was from 0.1 μS/cm to 100 mS/cm, representing a resistivity of 0.1Ω.m to 10,000 Ω.m.

(b).Digital Resistivity Meter

Digital resistivity meter (used in the oil industry) was used measure the resistivity of the smart spacer fluid directly. The resistivity range for this device was 0.01 Ω -m to 400 Ω -m.

(c). Two Probe Method

In this study high frequency alternative current (AC) measurement was adopted to overcome the interfacial problems and minimize the contact resistances. Electrical resistance (R) was measured using a LCR meter (measures the inductance (L), capacitance (C) and resistance (R)) during all the cleaning tests. This device has a least count of 1 μΩ for electrical resistance and measures the impendence (resistance, capacitance and inductance) in the frequency range of 20 Hz to 300 kHz. Based on the impedance (z) – frequency (f) response it was determined that the smart spacer fluid was a resistive material. Hence the resistance was measured at 300 kHz using the two probe method during the entire testing time.

Density

Spacer Fluid

The density of the spacer fluid was 8.46 ppg. With the addition of 0.5% and 1% nanoFe_2O_3 (based on total weight of the spacer fluid) increased the density to 8.51 and 8.55 ppg. The density was increased by 0.6% with addition of 0.5% nanoFe_2O_3. The density also increased by 1% with the addition of 1% nanoFe_2O_3.

Water Based Drilling Fluid

The water-based drilling fluid is prepared by addition of 8% bentonite by weight of water. The density and resistivity of the drilling fluid was 8.2 ppg and 7 Ω-m.

Piezoresistivity

The smart spacer fluid with and without nanoFe_2O_3 were subjected to pressure up to 500 psi in the high pressure high temperature chamber (HPHT) to investigate the piezoresistive behavior and the model in Equation (8) predicted the results very well.

NanoFe_2O_3 = 0%: The resistivity of the spacer fluid decreased nonlinearly with increase in the pressure (Figure 3). At 500 psi pressure the decrease in the resistivity was 0.7%, indicating low piezoresistivity characteristics of the spacer fluid.

NanoFe_2O_3 = 0.5%: The resistivity of the smart spacer fluid with 0.5% nanoFe_2O_3 decreased nonlinearly with increase in the pressure (Figure 3). At 500 psi pressure the decrease in resistivity was 4%, indicating the piezoresistivity characteristics of the smart spacer fluid.

NanoFe_2O_3 = 1%: The resistivity of the smart cement slurry with 1% nanoFe_2O_3 decreased nonlinearly with increase in the pressure (Figure 3). At 500 psi pressure the decrease in resistivity was 8%, indicating the piezoresistivity characteristics of the smart spacer fluid.

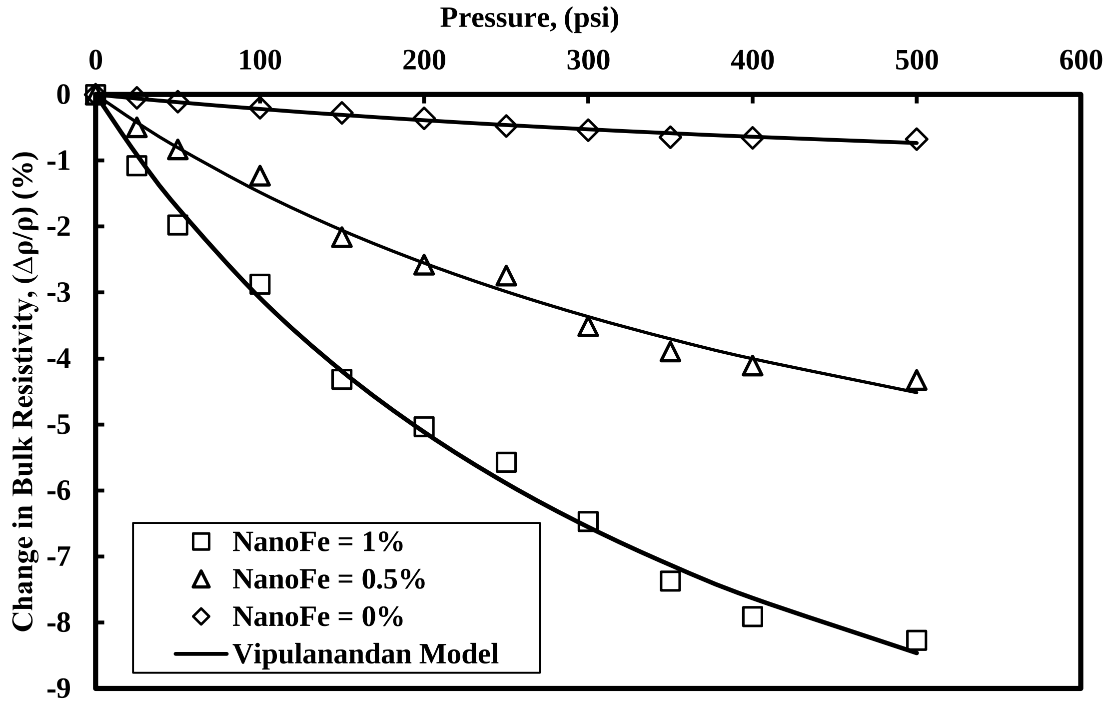

Figure 3 Measured and Predicted Stress-Resistivity Relationship for the Smart Spacer Fluid with different nanoFe_2O_3 contents.

Rheology

Effect of NanoFe_2O_3

Shear stress – shear strain rate relationships were predicted using the Vipulanandan rheological model and compared with the Herschel Bulkley models, as shown in Figure 3.

Herschel-Bulkley model (1926)

The root mean square of error (RMSE) for the Herschel Bulkley model varied between 1.54 to 2.36 Pa. The model parameter k for the spacer fluid at 25 ^oC varied from 4.58 to 8.14 Pa.s^n as summarized. The model parameter n was in the range of 0.29 to 0.33 (Table 1).

Vipulanandan Rheological model (2014)

The shear thinning behavior of the spacer fluid with and without nanoFe_2O_3 was modeled using the Vipulanandan rheological model up to a shear strain rate of 1024 s^{-1} (600 rpm). Increasing the nanoFe_2O_3 content in the spacer fluid increased the yield stress of the spacer fluid. The yield stress of the spacer fluid increased from 3.94 Pa to 6.63 Pa when nano Fe_2O_3 was increased from 0% to 1% at 25 ^oC as shown in figure 3. The τ_{max} for the spacer fluid increased from 49.4 Pa to 65.5 Pa, 33% increase at the temperature of 25 ^oC with 1% addition of nanoFe_2O_3 respectively as summarized. The root mean square of error was in range of 1.39 to 2.13 Pa (Table 1).

Table 1 Rheological model parameters for the spacer fluids with different nanoFe_2O_3 contents at 25^{o}C.

	Hershel Bulkey Model				Vipulanandan Model				
Model Parameter	**Yield Stress (τ_{01} (Pa))**	**n**	**k**	**RMSE (Pa)**	**Yield Stress (τ_{02} (Pa))**	**A $(Pa.s)^{-1}$**	**B $(Pa)^{-1}$**	**τ_{max} (Pa)**	**RMSE (Pa)**
NanoFe = 0%	**0**	**0.332**	**4.58**	**1.54**	**3.94**	**3.43**	**0.022**	**49.4**	**1.39**
NanoFe= 0.5%	**0**	**0.289**	**7.61**	**2.30**	**5.43**	**1.95**	**0.019**	**58.1**	**1.70**
NanoFe = 1%	**0**	**0.294**	**8.14**	**2.36**	**6.63**	**1.79**	**0.017**	**65.5**	**2.13**

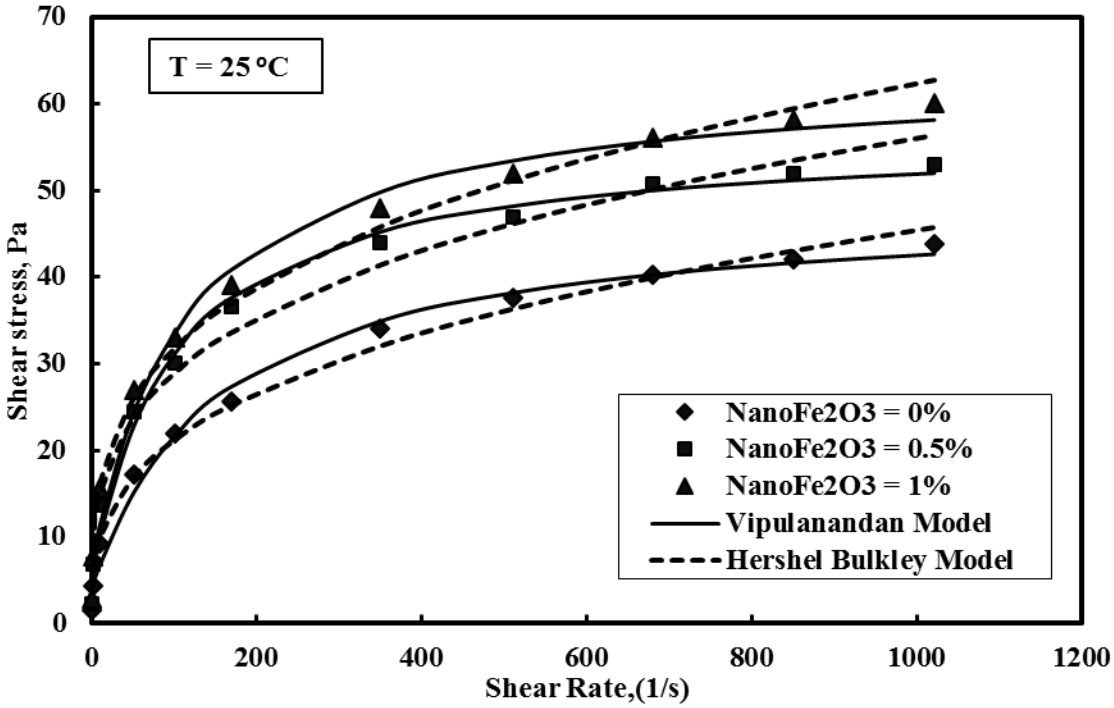

Figure 3 Shear Stress- Shear Strain rate Relationship for Spacer Fluid different nanoFe_2O_3 contents.

Cleaning Efficiency

The cleaning efficiency test to evaluate the smart spacer fluids to effectively clean the bentonite drilling mud contaminated metal cylindrical tube (from the viscometer) was performed as shown in Figure 4. The weight of the metal tube was measured before contamination, after contamination and after cleaning. The cleaning efficiency of the spacer fluid was 82.3% without the addition of nanoFe_2O_3. With the addition of nanoFe_2O_3 the cleaning efficiency increased from 82% to 99%, 20.7% increase in the efficiency as shown in Figure 5.

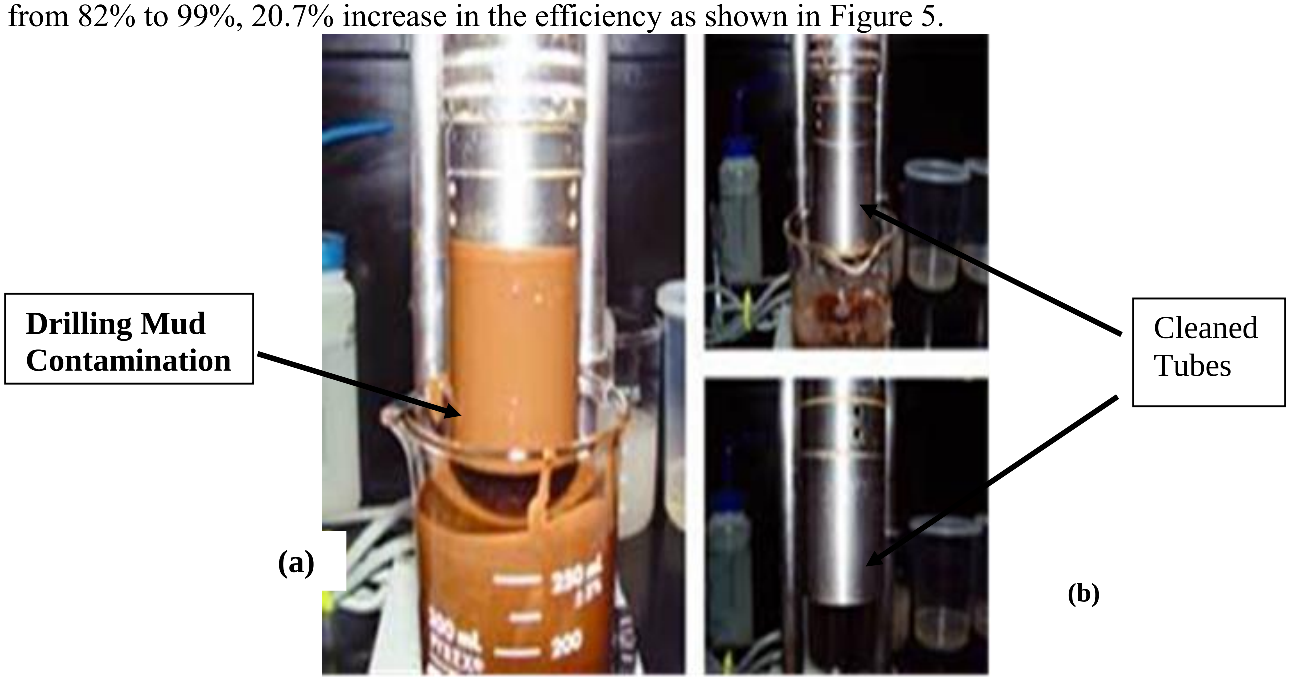

Figure 4 Cleaning Efficiency Test using Viscometer (a) Drilling Mud Contaminated Cylinder and (b) After Cleaning with the Spacer Fluid

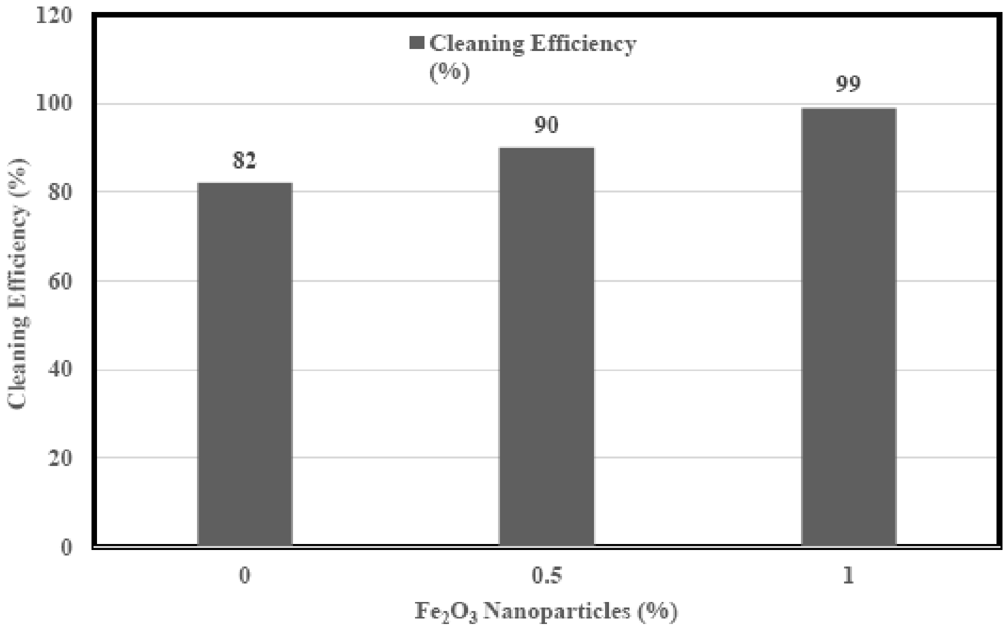

Figure 5 Cleaning efficiency of Spacer Fluid with Varying NanoFe_2O_3 Contents.

Cleaning Efficiency and Maximum Shear Stress

The maximum shear stress (τ_{max}) of the smart spacer fluid indicated the better cleaning ability of spacer fluid with 1% nanoFe_2O_3 as shown in Figure 6. The τ_{max} increased from 49.4 to 65.5 Pa, a 32.5% increase with the addition of 1% nanoFe_2O_3 the cleaning efficiency increased from 82 to 99%. The relation between maximum shear stress and cleaning efficiency for the smart spacer fluids was modelled using Vipulanandan Cleaning Efficiency model in Eqn. (7). The model parameters E and F were 0.49 Pa/percent and 0.0025 /percent respectively for the cleaning efficiency model. The R^2 and RMSE for the model are 0.99 and 1.53%. The main reason for the increased efficiency was having better rheological properties which produced higher shear stresses for cleaning and also high surface to volume ratio of the nanoparticles. The maximum shear stress required to generate 100% cleaning efficiency was about 67 Pa.

5. Conclusions

In this study smart spacer fluid samples were tested for material characterization, rheological, cleaning efficiency and piezoresistivity behavior. Also the effects of the magnetic field strengths, temperatures and bentonite contamination on the electrical resistivity and rheological properties of nanoFe_2O_3 modified spacer fluid were investigated. Based on the experimental study and analytical modeling following conclusions are advanced:

1. Based on the material characterization, resistivity was proved to be the sensing electrical property of the smart space fluid.
2. The electrical resistivity of the spacer fluid decreased with increasing temperature and it was a good sensing parameter for real-time monitoring to predict the rheological properties of spacer fluid in the field.

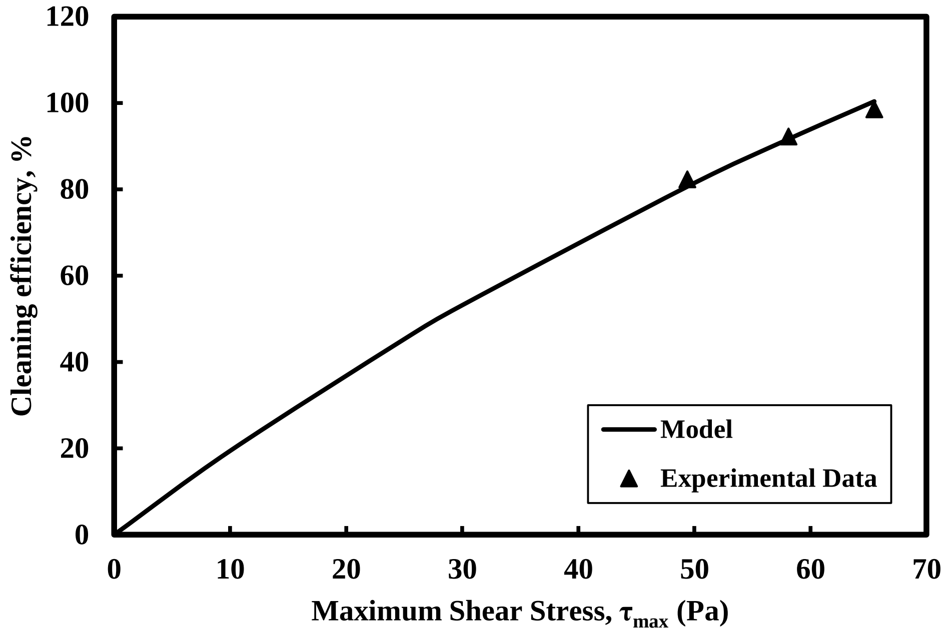

Figure 6 Relation Between Maximum Shear Stress and Cleaning Efficiency of the Spacer Fluid.

3. The addition of nanoFe_2O_3 up to 1% modified the yield stress, shear thinning behavior, and ultimate shear stress limit of the spacer fluid and Vipulanandan Rheological Model predicted the experimental results very well based on the root mean square error (RMSE). The amounts of changes in the properties were influenced by the temperature, nanoFe_2O_3 content, and magnetic field strength and have been quantified using the Vipulanandan Correlation Model.
4. The smart spacer fluid with nanoFe_2O_3 showed better rheological properties compared to spacer fluid without nanoFe_2O_3. The ultimate shear stress, a new rheological property quantified by the Vipulanandan Rheological Model of the spacer fluid correlated well with the cleaning efficiency.

6. Acknowledgement

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7. References

Carney, L. (1974). “Cement Spacer Fluid.” Journal of Petroleum technology, Society of Petroleum Engineers, Vol. 26, pp 856-859.

Vipulanandan, C. and Mohammed, A. (2014). “Hyperbolic rheological model with shear stress limit for acrylamide polymer modified bentonite drilling muds.” Journal of Petroleum Science and Engineering, Vol. 122, pp. 38–47.

Vipulanandan, C. and Prashanth, P. (2013). “Impedance spectroscopy characterization of a piezoresistive structural polymer composite bulk sensor.” Journal of Testing and Evaluation, Vol. 41, pp. 898-904.