AADE 2009NTCE-18-04 : Use of magnetic nanoparticles for smart drilling fluids.

Jung-Kun Lee, Department of Mechanical Engineering and Material Science, University of Pittsburgh, Pittsburgh, PA 1526

Travis Sefzik, Department of Mechanical Engineering and Material Science, University of Pittsburgh, Pittsburgh, PA 1526

You-Hwan Son, Department of Mechanical Engineering and Material Science, University of Pittsburgh, Pittsburgh, PA 1526

Tran X. Phuoc, National Energy Technology Lab, Pittsburgh, PA 15236

Yee Soong, National Energy Technology Lab, Pittsburgh, PA 15236

Donald Martello, National Energy Technology Lab, Pittsburgh, PA 15236

Minking K. Chyu, Department of Mechanical Engineering and Material Science, University of Pittsburgh, Pittsburgh, PA 1526

Abstract

In the present research, we investigate a magnetically controllable drilling fluid that offers an *in-situ* control of the viscosity under a magnetic field as well as significant nanoparticle based lubrication. To this end, the drilling fluids containing the magnetic nanoparticles are prepared and the fundamental roles of the magnetic nanoparticles used in the complex fluids are explored in relationship to the configuration of the magnetic nanoparticles and bentonites, which will allow for designing of the drilling fluids with desired rheology and heat transfer. Two different drilling fluids are exploited. One is based on hybrid particles where the nanoparticles are embedded in the interlayer space of bentonite particles and the other is based on the simple mixture of nanoparticles and bentonite particles. Magnetorheology measurement of the new fluids shows that the viscosity of the fluid can be increased by one order of the magnitude when the magnetic field of 0.7T was applied. In addition, the addition of the nanoparticles turns out to alter the rheology of the base drilling fluids under zero magnetic field. This is attributed to the fact that the nanoparticles modify the interparticle interactions of the bentonite particles within the fluids. Our results suggest that the *in-situ* tunability of the drilling fluids can be enhanced significantly by using the magnetic nanoparticles.

1. Introduction

In-situ control of viscosity of drilling fluids in deep well bores is currently limited, since the rheological response of drilling fluids is determined by the composition of various inorganic and polymer constituents in the drilling fluids. Once the composition of the drilling fluids is carefully balanced in the mud tank, the rheological response of the drilling fluids cannot be easily altered in the well bores [1]. This restricts the drilling fluids' performance because the environment in the well bores continuously varies. For example, the physical and chemical properties of rocks in subterranean wells are not constant, which causes different level of drill-tip vibration and drill-cut sedimentation as the well bores get deeper. In addition, since the drill-cuts are added to the drilling fluids during the drilling, the viscosity of the drilling fluids keep changing in the subterranean wells. Therefore, a gradual tuning of the rheological properties of the drilling fluids is required to maintain the performance of the drilling fluids in response to the consistent change in the drilling ambient. This indicates that the lack of *in-situ* controllability of drilling fluids can be a significant problem which decreases the rate of penetration and the life-time of the drill bits.

In this study, rheology of mixtures between bentonite particles and iron oxide nanoparticles were investigated in both water and oil based fluids. When such a magnetizable fluid is subjected to a magnetic force, the particles are rearranged, interactions between long-range, attractive van der Waals, Coulombic, steric and other forces are rebalanced and, thus, providing a wide range of controllability of the fluid viscosity, density and thermal conductivity [2-4]. Such magnetic nanoparticle based fluids are, therefore, multifunctional in that these magnetic nanoparticles will not simply offer an independent way for rapidly tuning the rheological response but also provide excellent heat transfer.

2. Experiment

Aqueous drilling fluids containing bentonite particles and magnetic nanoparticles were prepared using two commercially available bentonites (pure bentonite and water based bentonite) and three magnetic nanoparticles with different size (3nm, 30nm, and 20μm). For stable dispersion of particles in either water or paraffin oil, we used four different surfactants (Darvan 811, BYK U, BYK

U-80, and BYK 204). Among many different combinations of bentonite, iron oxide, and surfactants are possible, we present only four "model" fluid combinations that provide different rheological behaviors. These are:

- Pure Bentonite dispersed in water.
- Pure bentonite dispersed in water with Darvan 811 surfactant.
- Water-based bentonite dispersed in highly viscous paraffin oil using BYK U-80 in paraffin.
- Water-based bentonite dispersed in slightly viscous paraffin using BYK 204.

In each of four fluid systems, three iron oxide sizes (20 um, 30 nm, and 3 nm) were added.

To make stable fluids, bentonite particles and/or iron oxide particles were added to water or paraffin oil containing a suitable amount of dispersants. Then, the mixtures were stirred using an overhead mixer for 1 hr, followed by ultrasonic agitation for 10 min at room temperature.

The effect of iron oxide particles on the rheological behavior with and without external magnetic field was probed using a rheometer (MCR 301, Anton Parr) installed with magneto rheological device. A rotational speed of cone-plate type holders was between 0.1rpm and 100rpm. The external magnetic field ranged from 0T to 0.75T which is far higher than the magnetic field required to saturate the magnetic moment of the iron oxide particles in the fluids.

3. Results and discussion

Figure 1. Fluid behavior models as a function of shear stress and shear rate (left) and equations governing models of fluidic behavior (right).

Figure 1 illustrates Newtonian fluid behavior as well as several non-Newtonian models. Analysis on correlation between shear stress and shear rate in drilling fluids primarily follows the Bingham Plastic model,

$$\tau^{1/2} = \tau_0^{1/2} + (\eta \dot{\gamma})^{1/2} \qquad (1)$$

where τ represents shear stress, τ_0 yield strength, η true viscosity, and γ shear rate [5].

It should also be noted that the similar Bingham-Casson model,

$$\tau^n = \tau_0^n + (\eta \dot{\gamma})^n \qquad (2)$$

is also being investigated due to its robust nature, including the fitted exponent, n, roughly representing the boundary between Newtonian and non-Newtonian behavior [6]. As n increases, fluids shows shear thinning behavior more clearly, which indicates effective rearrangement of gel-networks of particles under shear stress. Using several models in Fig. 1, we characterized the viscoelatic behavior of fluids containing both bentonite particles and magnetic nanoparticles.
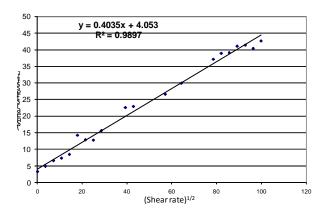

Figure 2. An example of fitting the relation between shear rate and shear stress for bentonite fluid using Bingham plastic model.

From various fluids described in an experimental section, a great body of data has been collected to provide the following trends:

- Increasing particle (both clay and iron oxide) will increase fluid viscosity
- Addition of a surfactant, to act as a dispersion agent, will generally decrease viscosity (with the exception of U-80)
- Including particles of smaller sized particles (*i.e.,* using nano- instead of micro-scale) will increase viscosity
- The application of an external magnetic field will effectively increase the viscosity of an MRF given that an appreciable amount of iron oxide is present in the fluid (iron oxide needs to be at least 5 wt% of continuous phase).

These trends will be further explored below by providing the apparent viscosity at a shear rate of 0.5 and 40 1/s, viscosity and yield from fitting data to the Bingham Plastic fluid model, where each are appropriate. Details of experimental results are as follows.

3-1. Effect of clay concentration (without embedding iron oxide particles)

Addition of increasing concentrations of clay particles will increase the viscosity of fluids, as expected. In tables below (apparent viscosity measured at shear rates of 0.5 and 40 1/s, arbitrarily chosen "low" and "high" shear rates) one will notice that the dominant trend is the tendency for apparent viscosity to decrease as

Bentonite without dispersant> Benonite/D811 > Water-Bentonite/U-80 > Water-Bentonite/204.

Viscosity measured at Shear Rate = 0.5 1/s

Clay	Surfactant	Clay Composition		
		2.5%	5.0%	10%
Pure bentonite		1.127	3.669	192.758
Pure bentonite	5 wt% D811	2.320	3.354	25.329
Water-based bentonite	5 wt% U-80	0.994	0.785	3.023
Water-based bentonite	5 wt% 204	3.324	0.143	0.197

Viscosity measured at Shear Rate = 40 1/s

Clay	Surfactant	Clay Composition		
		2.5%	5.0%	10%
Pure bentonite		0.043	0.193	2.199
Pure bentonite	5 wt% D811	0.042	0.062	0.661
Water-based bentonite	5 wt% U-80	0.265	0.158	0.253
Water-based bentonite	5 wt% 204	0.374	0.118	0.121

Table 1. Change in apparent viscosity as a function of bentonite content in aqueous fluids.

This trend is further justified in the following two charts, representing parameters obtained from fitting shear stress/shear rate data to the Bingham Plastic model. Again, this trend is primarily seen only with the 10wt% clay samples and is most prominent in fitting yield to the model.

True Viscosity

Clay	Surfactant	Clay Composition		
		2.5%	5.0%	10%
Pure bentonite		0.017	0.039	0.454
Pure bentonite	5 wt% D811	0.003	0.004	0.020
Water-based bentonite	5 wt% U-80	0.198	0.125	0.128
Water-based bentonite	5 wt% 204	0.327	0.107	0.114

Yield Strength

Clay	Surfactant	Clay Composition		
		2.5%	5.0%	10%
Pure bentonite		0.137	2.493	33.462
Pure bentonite	5 wt% D811	1.124	1.150	12.029
Water-based bentonite	5 wt% U-80	0.197	0.075	1.117
Water-based bentonite	5 wt% 204	0.424	0.024	0.008

Table 2. True viscosity and yield strength that were obtained by fitting the relationship of shear stress-shear strain.

We also investigated the effect of dispersing agent on the rheology of bentonite fluids. Although the trend is not seen in every case, the addition of surfactant generally will decrease the viscosity of fluids. The surfactant U-80 appears to be a significant outlier in this trend. Although parameters obtained from fitting data to the Bingham Plastic model are inconclusive at the moment, data from measuring the apparent viscosity at low and high shear rates suggest that the surfactant/apparent viscosity effect will present itself as (no surfactant) > D811 in systems where water is used as a continuous phase and (no surfactant) > U-80 > U > 204 in systems using paraffin as the continuous phase.

Viscosity measured at Shear Rate = 0.5 1/s

Clay	In Water		In Paraffin Oil			
	-	D811	-	U	U-80	204
10 wt% pure bentonite	192.758	25.329	0.555	0.770	1.375	0.248
10 wt% water-based bentonite			11.755	0.832	3.023	0.197
10 wt% Nanoclay bentonite			0.190	1.517	8.351	0.382

Viscosity measured at Shear Rate = 40 1/s

Clay	In Water		In Paraffin Oil			
	-	D811	-	U	U-80	204
10 wt% pure bentonite	2.199	0.661	0.169	0.142	0.193	0.135
10 wt% water-based bentonite			0.171	0.151	0.253	0.121
10 wt% Nanoclay bentonite			0.913	0.200	0.329	0.149

Table 3. Change in apparent viscosity of aqueous and oil-based fluids using different surfactants.

3-2. Effect of iron oxide particle addition on bentonite fluids

Figure 3 shows the effect of varying iron oxide particle concentration and size in each of the clay (at 5wt%)/iron-oxide/surfactant combinations. Addition of increasingly smaller iron oxide particles (down to 3 nm) will provide the most viscous fluid, which can be attributed to the

ability of smaller particles to disperse more effectively than the large, bulk particles. Therefore, larger surface area of smaller particles provides bridges between bentonite particles and promotes the gelation of the bentonite particles [7,8].
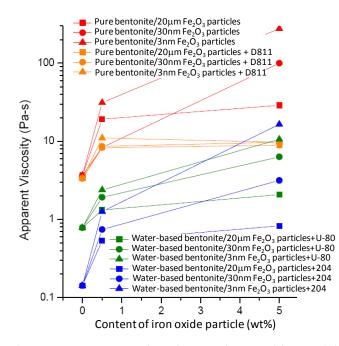

Figure 3. Apparent viscosity vs. iron oxide particle content in fluids using different bentonite and iron oxide particles, and different surfactants.
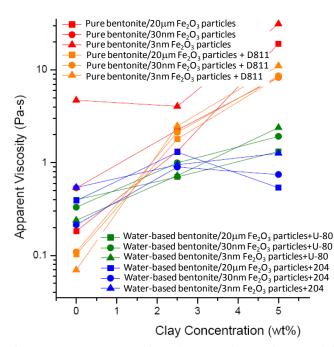

Figure 4. Apparent viscosity vs. bentonite particle content in fluids using different bentonite and iron oxide particles, and different surfactants.

In addition, just as with clay, increasing the iron composition will also act to increase fluid viscosity, as shown in Fig. 4. This correlation between viscosity and

iron content was observed in all fluids, regardless of measuring shear rates. In addition to changing the content of iron oxide nanoparticles, we also explored the change in the visoelastic behavior of bentonite fluids as a function of bentonite content. Similar to samples prepared without iron oxide, the data in the chart below show that the same trend will be seen also with iron oxide present – increasing the concentration of clay will increase the fluid viscosity. Inconsistencies in trends can be accounted for by considering the significant effect of iron oxide concentration (see previous section) and the difficulty in producing a 0.5 wt% fluid, all of which were prepared in 20 grams of continuous phase. Regardless of inconsistencies, the general trend holds that increasing clay concentration will effectively increase the apparent viscosity.

3-3. Effect of magnetic field on drilling fluids containing bentonite particles and γ-phase iron oxide nanoparticles

Samples containing pure-gamma phase iron oxide were used for magnetic-field experiments. Change in the viscosity under magnetic field is clearly observed. The effect of magnetic field on the viscosity gets pronounced when the concentration of γ-phase iron oxide nanoparticles increases. When 5 wt% of γ-phase iron oxide particles are added, the viscosity increases more than 5 times. More interestingly, it appears as if systems prepared with the surfactant "204" will provide the greatest increase in viscosity when approaching the peak magnetic field (at 0.75 T).

Peak Viscosity Under Magnetic Field (Shear Rate = 0.5 1/s)

Clay	Iron	Surfactant	0.5%	% Increase	5%	% Increase
5wt% Bentonite (Sigma)	Fe2O3 (Pure Gamma)		9.696	116	207.200	207
5wt% Bentonite (Sigma)	Fe2O3 (Pure Gamma)	5 wt% D811	11.310	131	81.900	840
5 wt% Water-based Bentonite	Fe2O3 (Pure Gamma)	5 wt% U-80	4.233	220	48.850	772
5 wt% Water-based Bentonite	Fe2O3 (Pure Gamma)	5 wt% 204	3.618	487	68.270	2162

Peak Viscosity Under Magnetic Field (Shear Rate = 40 1/s)

Clay	Iron	Surfactant	0.5%	% Increase	5%	% Increase
5wt% Bentonite (Sigma)	Fe2O3 (Pure Gamma)		0.225	109	2.886	194
5wt% Bentonite (Sigma)	Fe2O3 (Pure Gamma)	5 wt% D811	0.298	192	2.062	644
5 wt% Water-based Bentonite	Fe2O3 (Pure Gamma)	5 wt% U-80	0.454	122	2.583	387
5 wt% Water-based Bentonite	Fe2O3 (Pure Gamma)	5 wt% 204	0.580	228	2.672	468

Table 4. Change in apparent viscosity as a function of magnetic field in fluids containing different amount of 30nm Fe_2O_3 particles.

As for samples containing a constant 0.5 wt% iron oxide and varying concentrations of clay particles, data is partially inconclusive at the moment, but show that the addition of clay particles decreases the ability of Fe_2O_3

nanoparticle dispersed fluids to be affected by the external magnetic field. This suggests that there is certainly an attractive interaction between the bentonite and iron oxide nanoparticles, which provides the dependence of the magnetic field in addition to stabilizing the bentonite fluids [9,10].

Peak Viscosity Under Magnetic Field (Shear Rate = 0.5 1/s)

Clay	Iron	Surfactant	Clay Composition					
			0%	% Increase	2.5%	% Increase	5%	% Increase
Pure bentonite	0.5 wt% Fe$_2$O$_3$		1.024	191	2.357	105	9.696	116
Pure bentonite	0.5 wt% Fe$_2$O$_3$	5 wt% D811	2.552	2337	3.844	181	11.310	131
Water-based bentonite	0.5 wt% Fe$_2$O$_3$	5 wt% U-80	1.803	545	2.185	220	4.233	220
Water-based bentonite	0.5 wt% Fe$_2$O$_3$	5 wt% 204	0.771	362	2.945	329	3.618	487

Peak Viscosity Under Magnetic Field (Shear Rate = 40 1/s)

Clay	Iron	Surfactant	Clay Composition					
			0%	% Increase	2.5%	% Increase	5%	% Increase
Pure bentonite	0.5 wt% Fe$_2$O$_3$		0.045	2066	0.174	223	0.225	109
Pure bentonite	0.5 wt% Fe$_2$O$_3$	5 wt% D811	0.081	2864	0.111	262	0.298	192
Water-based bentonite	0.5 wt% Fe$_2$O$_3$	5 wt% U-80	0.373	184	0.288	105	0.454	122
Water-based bentonite	0.5 wt% Fe$_2$O$_3$	5 wt% 204	0.281	163	0.454	181	0.580	228

Table 5. Change in apparent viscosity as a function of magnetic field in fluids containing different amount of bentonite particles.

4. Conclusion

We investigate a magnetically controllable drilling fluid that offers an *in-situ* control of the viscosity under a magnetic field as well as significant nanoparticle based lubrication. In fluids containing different bentonite and iron oxide particles, the general trend holds that increasing iron oxide concentration or clay concentration will effectively increase the viscosity, which is more pronounced as the particle size decreases. This particle size dependence is attributed to the fact that larger surface area of smaller particles may promote the gelation of the bentonite particles.

For the first time, the dependence of viscosity on the magnetic field in the fluids containing bentonite-iron oxide particle mixtures was observed. In addition to the rearrangement of magnetic nanoparticles, there is certainly an attractive interaction between the bentonite and iron oxide nanoparticles. This provides the dependence of the magnetic field in addition to stabilizing the bentonite fluids.

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