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Effect of Nanoparticle-Additives on the Rheological Properties of Clay-Based Fluids at High Temperature and High Pressure

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Introduction

Recently, the nanoparticle additives are explored as an alternative to the polymer based additives. Inorganic characteristics of the nanoparticles additives are expected to stabilize the drilling fluids even at high temperature and high pressure which are conditions at the bottom of wellbores. In this study, we investigated high temperature and high pressure properties of the bentonite fluids containing iron oxide nanoparticles. We show the role of the nanoparticle additives in stabilizing clay-particle based drilling fluids. A balance between the electrostatic interaction and the van der Waals interaction stabilizes the dispersion of the nanoparticles. The role of nanoparticle additives is attributed to the fact that larger surface area of smaller particles overcomes the driving force for the phase separation such as gravity and packing entropy. In addition, the rheological properties of the bentonite fluids were examined as a function of temperature (20 ~ 200 ^oC) and pressure (1 ~ 100atm). The end part of the paper reports the effect of the new additives on other properties of the drilling fluids such as filter cake formation and fluid loss control. This systematic study will point to a way to synthesizing the new fluid that is suitable for high temperature and high pressure operation.

I1. Experimental procedure

2.1 Sample preparation

Fluid suspensions containing bentonite and iron oxide nanoparticles were prepared using commercially available bentonite and two iron oxide nanoparticles having a different size (3nm and 30nm) with respect to amount of iron oxide particle in the fabricated fluid samples. The suspensions were prepared by adding bentonite and/or iron oxide particles to deionized water then the mixture was agitated using a mechanical stirrer for 30 min with subsequent ultra-sonication for 30 min at room temperature. The prepared fluid suspensions were 5wt% bentonite, 5wt% bentonite with 0.5wt% 30nm-sized iron oxide paritcle, 5wt% bentonite with 5wt% 30nm-size iron oxide particle, 5wt% bentonite with 0.5wt% 3nm-sized iron oxide particle, and 5wt% bentonite with 5wt% 3nm-size iron oxide particle. Raw materials (bentonite, 3nm and 30nm iron oxide nanoparticle) were obtained from Aldrich and Alfa Aesar.

2.2 Rheological measurements

The influence of iron oxide particle on the rheological behavior were investigated with a rate controlled MCR 301 (Anton parr, Germany) installed with Peltier plate served to control the temperature 25 ^oC and high temperature and pressure (HTHP) cell which is possible to probe rheological behavior of fabricated samples at ranging from 25 ^oC to 200 ^oC under 100 bar atmosphere. During the tests under both normal cell device maintained at 25 ^oC and HTHP atmosphere, the shear rate of rotational cone-type geometry increased step by step changed by 4 s^{-1} every 10 s, 1 and 200 s^{-1} and 10 s^{-1} every 10 s, respectively. In order to explore viscoelastic property of fabricated samples small amplitude oscillatory tests were carried out in the operating condition at strain variation of 0.001%~100% at fixed angular frequency, 10 rad/s. Before the measurement, a preshear was performed at shear rate of 50 s^{-1} for 5 minutes.

2.3 Static Fluid Filtration Testing

Static filtration testing was conducted in accordance with API standards using an Ofite 171-00 Static Filter Press with a regulated CO2 pressurization system and standard 2.5-inch diameter filter paper. Adjustments were made to the total filtration time as per Arthur's et al.[2] recommendation to give a more accurate representation of the fluid filtration properties. Operating pressures of 100 pounds per square inch (psi) at atmospheric temperature were used. The mass of the filtrate was recorded per unit time with a sample rate between five to six measurements per second using a Mettler Toledo PL-602S balance, BalanceLink software and a personal computer. The volume was then calculated per the average density of the filtrate collected, allowing volume versus time to be determined.

Filter cake thicknesses were measured using a depth gauge. The filter paper was removed from the pressure vessel with the filter cake intact. Excess water and solution was removed using low- pressure compressed air. The thickness was immediately measured with multiple iterations to provide a large sample population.

2. Results and discussion

2.1 Effect of addition of iron oxide on bentonite suspension

Room temperature viscosity and yield stress of 5wt% bentonite fluids with the different amount of nanoparticle additives are shown in Fig. 1 and Table 1. There were two trends of fluid samples which were clearly observed in here. Firstly, addition of smaller iron oxide (3nm-sized) particles provides bentonite fluid with higher viscous property and yield stress than those of bentonite fluids with 30nm-sized iron oxide particle. It could be associated with dispersion ability of smaller particles to be well-distributed more effectively on the surface of bentonite than the large and sized particles. Oxide nanoparticles embedded in randomly formed pore structure on the surface of clay particle confer link between bentonite particles, which might promote gelation of the bentonite particles [4, 5]. Secondly, increase in concentration of adding iron oxide particle into bentonite fluid results in increasing both viscosity and yield stress. Especially, there was a substantial difference of viscosity and yield stress between 5wt% bentonite with 5wt% iron oxide 3nm-sized particle and other fluid samples. In addition to aforementioned effect of particle size on the gelation of the suspension, drastic increase in viscosity and yield stress observed in here could be also explained by consideration of synergy of homocoagulation of between exceed iron oxide particle and heterocoagulation of iron oxide with bentonite particle in the suspension [6].

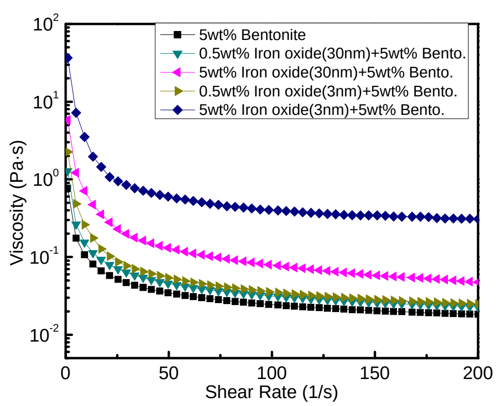

Figure 1. Measured Viscosity of prepared fluid samples as a function of shear rate

As a following exploration to scrutinize detailed particle interaction via analysis of viscoelastic behavior in prepared fluid samples small amplitude oscillatory tests were carried out and illustrated in Fig. 2. The strength of the interparticle interaction and the particle networks in the fluids can be evaluated by monitoring the transition of the fluids from a solid-like status to a liquid-like status [7]. Interpretation of variation of the storage modulus (G') and loss modulus (G") of the fluid systems as a function of shear stress obtained through amplitude oscillatory test is utilized as a appropriate tool for examination of strength of particle association in the fluid.

Table 1. Change of yield stress as a function of content of iron oxide particle in 5wt% bentonite aqueous suspension

Fluids samples	Yield stress (Pa)
5wt% bentonite	1.27
0.5wt% iron oxide (30nm) + 5wt% bentonite	1.80
5wt% iron oxide (30nm) + 5wt% bentonite	7.67
0.5wt% iron oxide (3nm) + 5wt% bentonite	3.33
5wt% iron oxide (3nm) + 5wt% bentonite	36.89

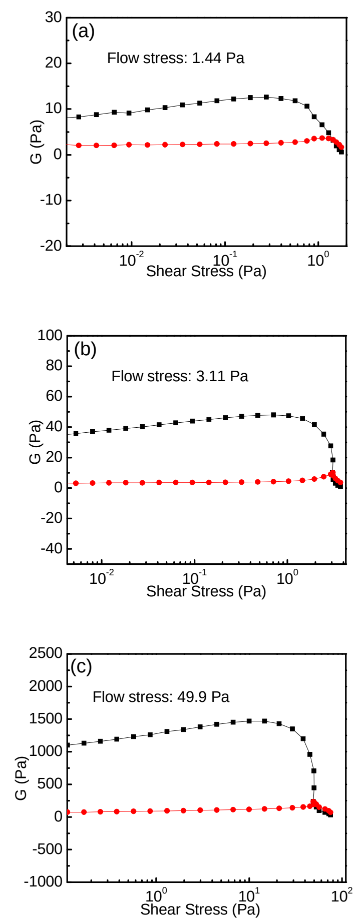

Figure 2. Variation of flow stress as a function of prepared fluid samples; 5wt% bentonite (a), 5wt% bentonite with 0.5wt% iron oxide 3nm-sized particle (b), and 5wt% bentonite with 5wt% iron oxide 3nm-sized particle (c). (black: Storage modulus, G' and red: Loss modulus, G")

Apparent tendency in accordance with aforementioned results in Fig 1 was confirmed that flow stress of samples at which value of strorage and loss modulus are overlapped was increased with increment of particle size and composition of addition of iron oxide into bentonite fluid. Fluid system containing 5wt% bentonite with 5wt% iron oxide 3nm-sized particle possessed the highest strength of particle interaction among the fabricated fluid samples. In a comparison with 5wt% pure bentonite fluid (Fig.2(a)), merely 1.44 Pa applied to pure bentonite system was adequate to lead to transformation of fluid state from gel-like to liquid-like structure while the shear stress necessary for resulting in collapse of solid-like structure in fluid system containing 5wt% bentonite with 5wt% iron oxide 3nm-sized particle to liquid-like was measured approximately 49.9 Pa (Fig.2(c)). Such an immense increase in flow stress shown in this result would be attributed to increase in interaction strength related to synergy effect of both homocoagulation and heterocoagulation between the particles in the suspension.

2.2 Viscosity of fluid samples under high temperature and high pressure (HTHP)

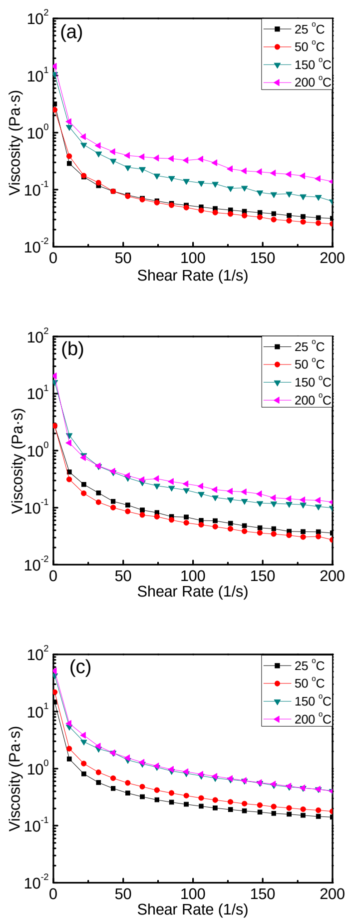

Figure 3. Variation of viscosity of prepared fluid samples; 5wt% bentonite (a), 5wt% bentonite with 0.5wt% iron oxide 3nm-sized particle (b), and 5wt% bentonite with 5wt% iron oxide 3nm-sized particle (c) as a function of temperature under 100bar atmosphere.

In addition to investigation of rheological property at room temperature under atmosphere, we enquired into viscosity variation of as-prepared fluid samples under high pressure environment (100bar) as a function of temperature as seen in Fig 3. Change of viscosity under temperature variation was evidently observed in all sample fluids, although no significant difference between viscosity measured at 25 °C and 50 °C. This result obviously could be supported by previously reported research stating colloidal systems composed of bentonite to be thicken considerably above about 120 °C due to a condition of high salinity in bentonite-based suspension [8]. Fluid sample containing 5wt% bentonite with 5wt% iron oxide 3nm-sized particle holds the higher viscosity measured than that of fabricated-fluid suspensions as ever under HTHP atmosphere as well as the trend clearly seen in aforementioned results indicating increase in viscosity as increasing of iron oxide content in fluid suspensions.

2.3 Fluid Filtration Behavior

Comparing the fluid filtrate volume per unit time provides fluid filtration properties as seen in Figure 1. The 5.0 wt. % bentonite solution had a 30-minute average filtrate of 10.4 milliliters (mL), a 60-minute average filtrate of 14.6 [mL] and a 90-minute average filtrate of 17.1 [mL]. This data was used as the control group. The bentonite solution with 0.5 wt. % 30 [nm] Fe_2O_3 had a 30-, 60- and 90-minute average filtrate of 9.8 [mL], 13.9 [mL] and 15.4 [mL], respectively. These values reflect a 6.14%, 4.94% and 9.67% improvement in fluid filtration loss reduction, respectively. The bentonite solution with 5.0 wt. % 30 [nm] Fe_2O_3 had a 30-, 60- and 90-minute average filtrate of 11.9 [mL], 16.9 [mL] and 20.6 [mL], respectively. These values reflect a 14.5%, 15.8% and 20.8% decline in fluid filtration loss reduction, respectively. The bentonite solution with 0.5 wt. % 3 [nm] Fe2O3 had a 30-, 60- and 90-minute average filtrate of 10.7 [mL], 15.0 [mL] and 18.3 [mL], respectively. These values reflect a 2.3%, 3.1% and 7.2% decline in fluid filtration loss reduction, respectively. Finally, the bentonite solution with 5.0 wt. % 3 [nm] Fe_2O_3 had a 30-, 60- and 90-minute average filtrate of 12.5 [mL], 16.0 [mL] and 17.6 [mL], respectively. These values reflect a 20.3%, 10.0% and 2.8% decline in fluid filtration loss reduction, respectively.

As seen from the fluid filtration loss data in Figure 4, there is no correspondence between the concentration and size of nanoparticles to the fluid filtration properties. Only the 0.5 wt. % 30 [nm] Fe_2O_3 bentonite solution exhibited decreased fluid filtrate loss in comparison to the 5.0 wt. % bentonite solution. This suggests that a critical net charge within the solution was achieved near this concentration. Near this critical concentration, the net repulsive and attractive forces were in a ratio such that the clay platelets aligned more frequently in face-to-face than face-to-edge configurations, reducing the penetrable surface area of the filter cake formation. As the concentration of 30 [nm] Fe_2O_3 increased from 0.5 wt.% to 5.0 wt.% in the bentonite solution samples, the fluid filtrate loss increased 18.0%, 17.9% and 25.2% for the 30-, 60- and 90-minute average respectively. As the concentration of 3 [nm] Fe_2O_3 increased from 0.5 wt.% to 5.0 wt.% in the bentonite solution samples, the fluid filtrate loss increased 14.9% and 6.3% for the 30- and 60- minute averages respectively, but decreased 4.3% for the 90-minute average. It is interesting to note that the 5.0 wt. % 3 [nm] Fe2O3 solutions exhibited a reduced-slope linear fluid filtrate loss rate as time approached the 60-minute mark. This behavior possibly coincides with an observed relatively dense and non-deformable lower filter cake with a very large airy upper filter cake, in comparison to all other samples, as seen in Figure (#). It is possible that compaction of the 3 [nm] particles created an impermeable filter cake, which, if time were allowed to continue, would produce a fluid filtration behavior in which the filtrate volume line would intersect that of the bentonite solution control and thus yield a lower filtrate volume rate.

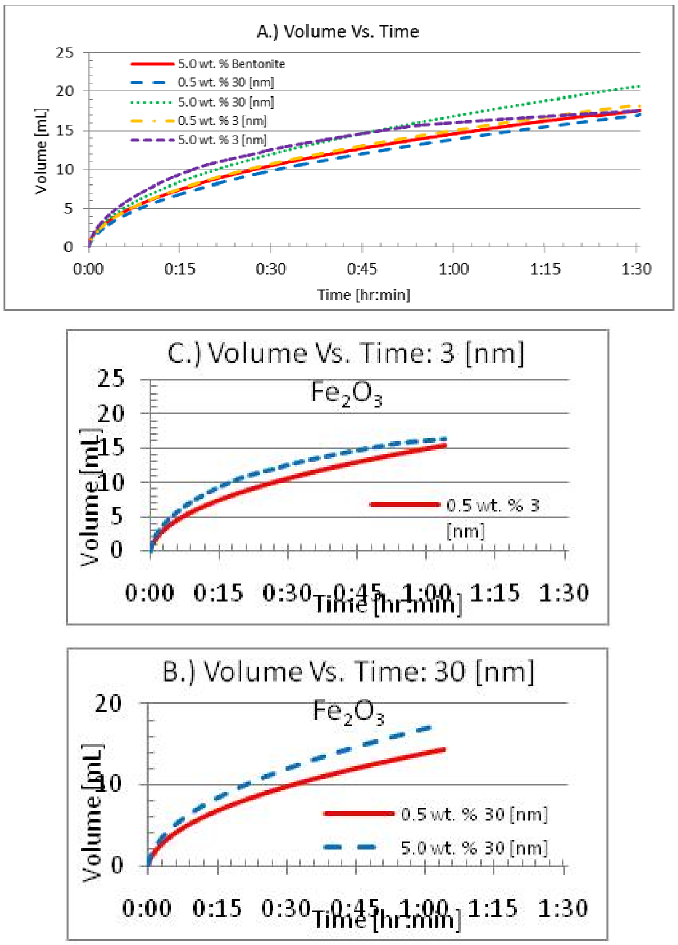

Figure 4. Volume Fluid Filtrate vs. Time: A.) All samples B.) 30 [nm] Fe_2O_3 samples C.) 3 [nm] Fe_2O_3 samples

3. Conclusions

We investigated rheological and filtration behaviors of bentonite fluids containing iron oxide nanoparticle with different size at ambient condition as well as harsh circumstance (high temperature and high pressure). The experiment results show that increase in content of addition of iron oxide particle into bentonite suspension resulted in increasing viscosity, yield stress, and strength of particle interaction obtained through probed flow stress. In addition to concentration of iron oxide particle in suspension, addition of smaller size nanoparticle was found as an effective factor to improve viscosity of fluid system. Two concepts would be considered to explain such a considerable elevation of rheological property of fabricated fluid systems. First, oxide nanoparticles embedded in randomly dispersed pore structure on the surface of clay particle confer links between bentonite particles, which might promote gelation of the bentonite particles. Second, synergy originated by both homocoagulation of between exceeds iron oxide particle and heterocoagulation of iron oxide with bentonite particle in the suspension may play a important role in such a improvement. The viscosity measure of fabricated fluid suspensions under HTHP environment indicated change of viscosity under temperature variation was evidently observed in all sample fluids due to thicker particle associated with increased salinity in the colloidal system as well as increase in viscosity as increasing of iron oxide content in fluid suspensions which is more pronounced as the particle size decreases.

4. References

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