TPR 2741
2009

Synthesis and rheological properties of cation-exchanged Laponite suspensions

Tran X. Phuoc[a,b,*], Bret H. Howard[a], Minking K. Chyu[a,b]

[a] National Energy Technology Lab, P.O. Box 10940, MS 84-340, Pittsburgh, PA 15236, United States
[b] Department of Mechanical Engineering and Material Science, University of Pittsburgh, 648 Benedum Hall, 37000 O'Hara Street, Pittsburgh, PA 15261, United States

ARTICLE INFO

ABSTRACT

In this paper we report our new approach to synthesize cation-exchanged Laponite suspensions. General observations of the prepared samples indicated that an aqueous suspension of 1 wt.% Laponite retained its free flowing liquid phase characteristics even after aging for several weeks. When bivalent cationic metals (Cu, Co, Ni) were ablated into the suspension, the strong charge of the crystal face was reduced and, on standing, the suspension gelled becoming highly viscous. This sol–gel transition was induced by the formation of a space-filled structure due to both van der Waals and electrostatic bonds between the positively charged rims and negatively charged faces. Rheological properties of such prepared suspensions were measured using a Brookfield DV-II Pro Viscometer with a small sample adapter (SSA 18/13RPY). The yield strengths of $2.2 \, N/m^2$, $3.2 \, N/m^2$, and $1.7 \, N/m^2$ were measured for Ni-, Co-, and Cu-modified Laponite suspensions, respectively. These yield strengths are sufficiently high for suspending weighting materials such as barite which requires the gel strength of about $0.5 \, N/m^2$.

Published by Elsevier B.V.

1. Introduction

In geological drilling, drilling fluids are injected into the drill string, spray out of drill bit nozzles and recirculate up the annulus between the drill string and the well hole to the well surface. These drilling fluids perform various functions such as cooling, lubrication of the drill, removal of cutting debris from the hole, suspending cutting debris and as weighting materials during stoppages of circulation [1]. In order to perform these functions, drilling fluids with high viscosity are desirable. However, if viscosity is too high, friction may impede the circulation of the fluid causing excessive pump pressure, decrease drilling rate, and hamper the removal of solid. Therefore, it is important to design a suitable fluid rheology. Fluids with good pumpability and low viscosity at high shear rates and higher viscosity at low shear rates are advantageous for this application. Commonly, additives such as clays, biopolymers like xanthan gum, cellulose polymers or starch are utilized for such high viscous and shear-thinning fluids.

Disadvantages of these polymeric additives and surfactants include their high cost and their degradation at high temperature leading to changes in the fluid rheological properties [2,3]. Hiller [4] studied the effects of applied pressure up to 500 atm. Annis [5] studied the rheology of aqueous fluids at temperature up to 150 °C and suggested that high temperature caused flocculation of bentonite fluids, resulting in an increase in both the

yield stress and viscosity at low shear rates. He also reported that the time-dependent gel strength was mostly affected by elevated temperatures. Sinha [6] investigated water-based clay suspensions as well as oil-based muds using a falling-bob consistometer and suggested that, compared with oil-based muds and inverted emulsion muds, the equivalent viscosity of water-based muds was not affected to the same extent by the variation of temperature and pressure. He concluded that temperature was the dominating variable in the case of water-based muds. Alderman et al. [7] measured the yield stresses for more complex drilling fluids and reported that the measured yield stresses were weakly dependent on temperature below a critical temperature (T_R) and were essentially independent of pressure. Above T_R the yield stress increased rapidly with increasing temperature. The addition of deflocculants decreased the gel structuring temperature of a mud. The application of high pressure seemed to have practically no effect on the plastic viscosity of a deflocculated mud at low temperatures. However, at high temperature (above T_R) the effect of pressure became significant.

The use of nano-scale particles for improving suspension viscosity at high temperature and high pressure has been investigated. Nano-scale particles display unusual surface morphologies and high surface reactivity due to their large surface area ($500 \, m^2/g$) and high proportion of surface atoms (>40%) versus bulk. When these nanomaterials are added to the clay suspensions they will pseudo-crosslink with the clay disks through charge attraction and surface adsorption. As a result, a sol–gel transition can be induced by the formation of a stronger dynamic network of space-filled structure due to electrostatic bonds between the positively charged rims and negatively charged faces. Mongondry et al. [8]

* Corresponding author at: National Energy Technology Lab, P.O. Box 10940, MS 84-340, Pittsburgh, PA 15236, United States. Tel.: +1 412 386 6024.
E-mail address: tran@netl.doe.gov (T.X. Phuoc).

reported that the aggregation and gelation of aqueous Laponite dispersion depended on the concentration of either pyrophosphate or polyethylene oxide that was added to the suspension. At low concentrations of pyrophosphate, the aggregation of Laponite was only retarded, without significant modification of the structure of the aggregates and gels. At higher concentrations, aggregations and gels broke up. Baird and Walz [9,10] studied the effects of added silica nanoparticles on the structure and rheological properties of aqueous kaolinite suspensions. They showed that, in the absence of additives, kaolinite platelets quickly aggregated and settled. When silica nanoparticles and salt (NaCl) were added together, the suspension began to stabilize. When the concentrations of salt and nanoparticles exceeded a specific lower limit, the suspension underwent a transition to a gel and developed a finite yield stress. Increasing the concentration of nanoparticles or of the added salt substantially increased the measured yield values. Huang and Crews [11] have reported viscosity of viscoelastic-surfactant stimulation (VES) fluids with and without nanoparticles at temperature of 121 °C at a shear rate of 100 1/s. VES fluids are composed of a base fluid and low-molecular weight surfactants that form elongated micelle structures and increase the fluid viscosity. In this study, the base fluid was 4% VES mixed with 1.4 kg/l of $CaCl_2/CaBr_2$ brine nanoparticles. The particle size was 30 nm in diameter. When nanoparticles were added, they crosslinked the VES micelles through charge attraction and surface adsorption to form a much stronger dynamic which stabilized VES micelles and maintained the fluid viscosity stable at 200 cp. Without nanoparticles, the system was not thermally stable and the viscosity of the base fluid reduced from 200 cp to 40 cp in 80 min.

In this work, we use a novel approach to synthesize cation-exchanged Laponite suspensions and probe the effects of various metals on the suspension's structural, thixotropic, and rheological properties. To prepare the samples for this study, we used aqueous Laponite suspensions as the base fluid and, instead of adding nanoparticles to the suspensions, we used laser ablation of an appropriate target material under a liquid to intercalate the suspended Laponite crystals with cationic metal species. Synthesis of cation-exchanged Laponite nanocomposites has been reported by suspending a Laponite sample in an aqueous salt solution containing the appropriate cation and heat to a high temperature [12,13]. Use of the laser ablation technique for this purpose, however, has not been previously demonstrated. The general steps of laser ablation in this application are: a high-power laser beam is focused for an appropriate time onto a solid target submerged in a liquid at the focal point causing the solid to be heated, melted, vaporized, and ionized rapidly. As a result, a plume of highly excited metal atoms is formed and expands violently into the surrounding liquid where these exited atoms interact with each other and with the liquid molecules. Thus, by ablating a metal target submerged in an aqueous Laponite suspension, the ablated material can interact with the suspended Laponite disks resulting in a Laponite-nanohybrid material. Although the technique has been considered as an attractive

technique for the preparation of nanoparticles and nanomaterial fabrications [14–20], use of the technique to synthesize nanohybrids has not been reported before. In the following sections, the characterization and rheological properties of such prepared suspensions will be discussed.

2. Experimental apparatus

The present experimental apparatus, shown in Fig. 1, was described in detail elsewhere [16]. In summary, laser ablation of a metal target (Co, Ni, or Cu) submerged in aqueous Laponite suspensions was carried out using a laser beam generated by a single-mode, Q-switched Nd-Yag laser operating at 1064 nm with a pulse duration of 5.5 ns and 10 Hz repetition rate. The Laponite suspensions were prepared by simply mixing Laponite powder (Laponite RD from Southern Clay Products) with deionized water (DW) and stirring for 24 h using a magnetic stirrer. The laser beam with fluence of 0.265 J/cm^2 was aligned horizontally and it was focused on the metal target using a 75 mm focal-length lens. The laser beam was 10 mm below the liquid surface. All metal samples (25 mm × 25 mm and 1 mm thick) with 99.995% purity were purchased from Alfa Aesar. All metal samples had smooth surfaces and were used as received. The metal weight fraction was determined by measuring the weight of the metal plate before and after ablation using a microbalance (VP64CN, OHAUS Corporation).

The colloidal suspensions obtained were carefully sampled for transmission electron microscopy (TEM), X-ray diffraction (XRD), and rheological property measurements. The TEM observations were performed using a JEOL 200CX at 200 kV. A small drop of each sample was placed on a copper grid and allowed to dry before being examined in the transmission electron microscope. The TEM images were analyzed using the Image-Pro plus and Gatan Digital Micrograph program. XRD characterization was carried out using a PANalytical X'Pert Pro MPD powder diffractometer having a θ–2θ configuration, a Cu X-ray source operated at 45 kV and 40 mA and an X'Celerator detector equipped with a monochromator. Samples for XRD measurement were prepared by evaporating a small amount of the sample suspension on a zero background quartz plate at ambient temperature.

Viscosity measurements were performed using a Brookfield DV-II Pro Viscometer with a small sample adapter (SSA18/13RPY). The adapter consisted of a cylindrical sample holder, a water jacket and spindle. The viscometer drives the spindle immersed into the sample holder containing the test fluid sample. The viscometer can provide a rotational speed that can be controlled to vary from 10 rpm to 200 rpm yielding a shear rate from 13.2 1/s to 264 1/s. Viscosity is determined by measuring the viscous drag of the fluid against the spindle when it rotates. The water jacket is connected to a refrigerated circulating water bath (TC-502, Brookfield) that controls the water temperature from −20 °C to 150 °C. The sample holder can accommodate sample volumes up to 15 ml. The
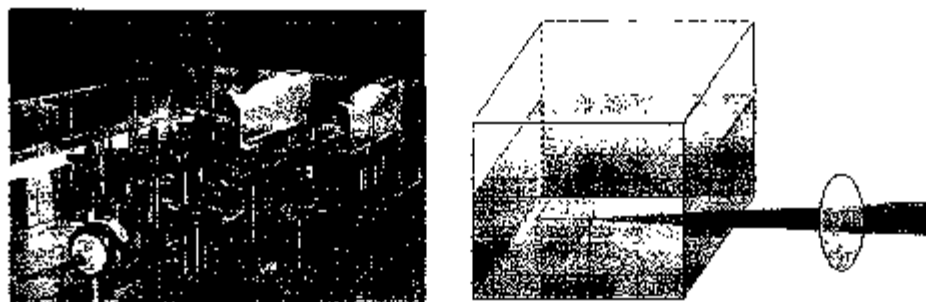

Fig. 1. A sketch of the present laser ablation in liquid technique.

temperature of the sample is monitored by a temperature sensor embedded in the sample holder.

3. Results and discussions

Laponite is synthetic sodium magnesium silicate clay. The Laponite crystals have a disk shape with a diameter of about 25 nm and a thickness of about 1 nm. When Laponite is dispersed in water the sodium ions are released and the Laponite disks have a strongly negative face charge. The edge charge depends on the acid–base behavior of the Si–OH and Mg–OH amphoteric hydroxyl groups, which are the main species on the edge. Below pH 9, the magnesium ions dissolve in the solution and above pH 10, the dissolution of silica occurs [21]. In salt-free water, these disks are stabilized, separated by a few water layers by electrostatic repulsion between the negatively charged faces [21]. General observations of the prepared samples indicated that an aqueous solution of 1 wt.%. Laponite remained free flowing even after several weeks of aging. Its viscosity was too low to be measurable using the present viscometer.

When Fe was ablated into a Laponite suspension, it remained free flowing, however, when the bivalent metals Cu, Co, or Ni were ablated into Laponite suspensions, the mixture was observed to undergo a transition to a stable gel very quickly. Even a small amount of ablated metal induced gel formation when the mixture was allowed to rest. The gels could easily be reverted to a low viscosity liquid with simple shaking. The gel structure quickly reformed when the mixtures were again allowed to stand.

To determine if Laponite gels can be formed by simply mixing the metal-derived nanoparticles with Laponite suspensions, we first generated an aqueous solution containing only Co, Cu, or Ni nanoparticles by ablating the appropriate metal plate submerged in pure deionized water. The solution was then mixed with 1 wt.% Laponite. We observed that the suspensions prepared this way did not gel but remained stable, free flowing liquids. However, when we irradiated the suspension with an intense pulse laser at 1064 nm for about 30 min, the suspensions underwent a gel formation similar to what we observed when Co, Cu, or Ni metal plate was ablated in the aqueous Laponite suspensions. A possible explanation for this behavior is that the laser irradiation, in addition to generating the nanoparticles through ablation of the target, is also interacting with and modifying the suspended nanoparticles converting them to the actual species that is interacting with the Laponite sol inducing gel formation.

The sol–gel transition observed here can be attributed to the interaction of the cationic metals and/or nanoparticles with the suspended Laponite disks. As a result, the negative charges on Laponite crystal faces are reduced and a sol–gel transition induced by the formation of a space-filled structure due to both van der Waals and electrostatic bonds between the positively charged rims and negatively charged faces [8,9]. XRD and TEM were used to probe for evidence of intercalation or Laponite layer ordering. Fig. 2 shows the typical XRD diffraction patterns measured for unmodified Laponite, Cu-modified and Co-modified Laponite suspensions. All diffraction patterns were similar. No peaks assignable to species other than Laponite were observed. Due to the preparation method used for the XRD samples, the clay crystals are expected to be somewhat oriented enhancing basal reflections. All diffraction patterns including the baseline Laponite (not modified by ablated material) showed a (0 0 1) reflection at around $2\theta = \sim 7^\circ$ corresponding to an interplanar distance of about ~ 1.3 nm. Fig. 2 shows the (0 0 1) reflections for the Co and Cu Laponite samples versus the baseline Laponite. This interplanar value is about 0.4 nm more than the actual Laponite layer thickness of 0.92 nm. The layer separation of about 0.4 nm suggests that on drying and collapsing the gel, the Laponite layer faces are occupied by simple hydrated cationic
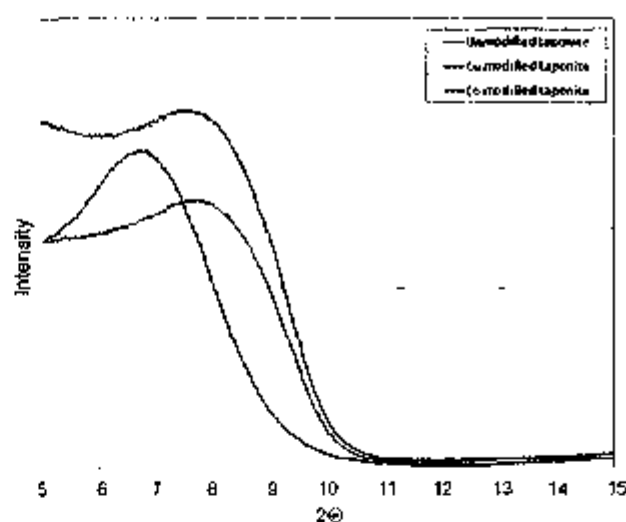

Fig. 2. Typical X-ray diffraction patterns of the cation-exchanged Laponite suspensions.

species not the much larger nanoparticles. The ionic species are likely Ni^{2+}, Co^{2+}, or Cu^{2+}. Closer examination of the (0 0 1) reflections (Fig. 2) shows that the layer separation of the modified Laponites is actually about 0.15 nm less than the baseline unmodified Laponite. This difference is likely due to a higher level of interlayer hydration in the unmodified Laponite. These differences will be examined more closely in future work.

Typical TEM images comparing the Fe and the Ni nanoparticle ablated in Laponite mixtures are shown in Fig. 3. Fe nanoparticles of varying sizes up to about 40 nm in diameter (Fig. 3a) were randomly distributed among the Laponite disks. The TEM image of Ni nanoparticles ablated in the Laponite suspension is presented in Fig. 3b. The Ni particles sizes were from 2 nm to about 10 nm in diameter. Some larger particles of about 20–25 nm were also observed. In general, TEM indicated that both the non-gelling Fe and the gelling Ni nanoparticle-Laponite mixtures had similar morphologies so no direct information on the cause of the differences in behavior is evident. In both cases, the average size of the visible nanoparticles was of the same order of magnitude as the 25 nm Laponite crystal diameters.

Based on the characterization results so far, the mechanism controlling the difference in behavior of iron compared to cobalt, copper, and nickel is not known at this time. However, one possibility is that different cationic species are reducing the strong negative charge of the Laponite crystal faces in the Fe modified suspension versus the other three samples. If the gelling is simply a result of hydrated metal cations in solution resulting from the laser ablation process then the gelling difference could be due to the difference in the strength of interaction of the expected cationic species, Fe^{3+} versus Ni^{2+}, Co^{2+}, or Cu^{2+}, with the Laponite crystal faces. Further work will attempt to clarify this difference in behavior and explain its controlling mechanism.

For suspension rheological properties, we show in Fig. 4 the plastic viscosity, η_∞, for Ni-, Cu-, and Co-exchanged Laponite suspensions. The viscosity of aqueous suspensions containing 1% Laponite without metals was not reported here because it was too low to be measurable by the present viscometer (below 2 cp). The results shown were recorded after the suspensions were sheared at a given shear rate until they reached a steady state, typically about 1 h. The viscosities decreased rapidly with increasing shear rates indicating that the prepared suspensions are excellent shear-thinning fluids. As indicated in the figures, the weight percents of metals were negligibly small compared to that of Laponite and yet
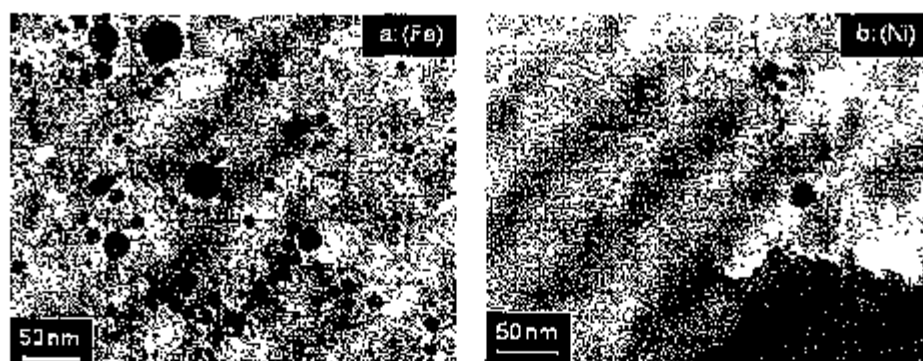
Fig. 3. TEM images of cation-exchanged Laponite nanocrystals ((a) Fe particles, and (b) Ni particles).

the range of the viscosity reported here was several hundred times higher that those obtained for suspensions containing 1 wt.% of only Laponite. For example, at a shear rate of 3.41/s, viscosity of Ni-exchanged Laponite was about 900 cp and it decreased rapidly to about 90 cp as the shear rate increased to 68 1/s. For the same range of shear rates, similar results were also shown for Cu- and Co-exchanged Laponite suspensions. Thus, in addition to shear-thinning behavior, cation-modified Laponite can be thought of as an effective additive for fluid viscosity enhancement.

The corresponding shear stresses, in terms of $\tau^{1/2}$ versus $\gamma^{1/2}$, are shown in Fig. 5. The results indicated that the shear stresses measured for Ni- and Cu-exchanged Laponite suspensions exhibited a linear increase with $\gamma^{1/2}$ while the shear stress of Co-exchanged Laponite suspensions did not. For this case, the dependence of the stress on the shear rate was observed to occur only at low and high shear rate values. For the range of the shear rate from 10 1/s to about 34 1/s, it became independent of the shear rate.

A least square curve fit to our present is shown as the solid lines in Fig. 5. Depending on the metal used, the intercepts, of the curves were 22.11 cp/s (2.2 N/m²) for Ni-exchanged Laponite and 17.20 cp/s (1.7 N/m²) for Cu-exchanged Laponite suspensions. Since the intercepts represent the shear stresses when the shear rate is zero, these values can be thought of as the yield strengths of the prepared cation-modified Laponite suspensions. These yield strengths are sufficiently high for suspending weighting materials such as barite which requires the gel strength of about 0.5 N/m². Thus, cation-modified Laponite nanohybrids can be considered to have potential as gel forming agents.

Many studies have been made to relate the yield stress of a suspension system to the particle–particle van der Waals and the electrostatic interaction potentials [22–24]. Sakairi et al. [22] studied the effects of salt concentration on the yield stress of Na-montmorillonite suspensions. They assumed that at the point of yielding, the yield stress is equivalent to the strength of electrostatic repulsion and developed an equation showing the dependence of the yield stress on the ionic strength and volume fraction. Similarly, in a study of the yield stress of Laponite suspensions, Laxton and Berg [23] related the electrostatic repulsion portion to the zeta potentials of the Laponite face and edge. Thus, we can attribute our results reported in Figs. 4 and 5 to the interactions between the Laponite positively charged edges and the negatively charged faces.

At present, we do not fully understand why different rheological and thixotrpic properties are obtained when using copper, cobalt and nickel. However, we expect that Laponite crystals dispersed in water will have a strongly negative face charge and weakly positive edge charge. In salt-free water, these crystals are stabilized, separated by a few water layers by electrostatic repulsion between the negatively charged faces. In order to create a sol–gel transition, the negative charges on the face must be reduced so that a space-filled structure due to electrostatic bonds between the positively charged rims and the negatively charged faces can be induced. In the present work, such a charge reduction was obtained by interacting Cu, Co, or Ni with the faces of the Laponite disk. Fig. 6 shows the TEM images of Cu, Ni, and Co ablated in deionized water stabilized by 0.1 wt.% PVP revealing that the ablated particles are different in sizes and shapes. Co particles were spherical with diameter ranging from 10 nm to 15 nm. Ni particles were much smaller with particle diameters ranging from about 2 nm to 5 nm. Cu particles had a
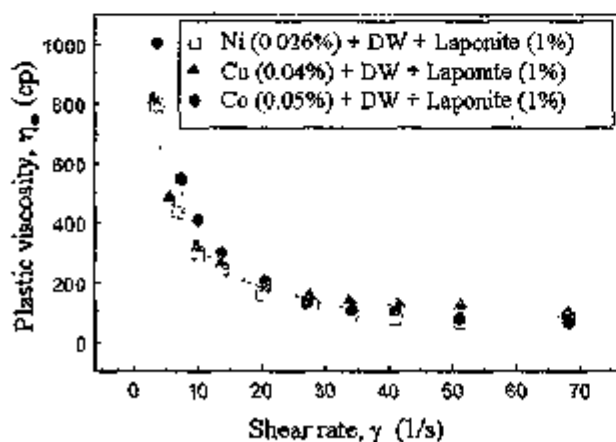
Fig. 4. Plastic viscosity of cation-exchanged Laponite suspension as a function of the shear rate (measured at 25 °C).
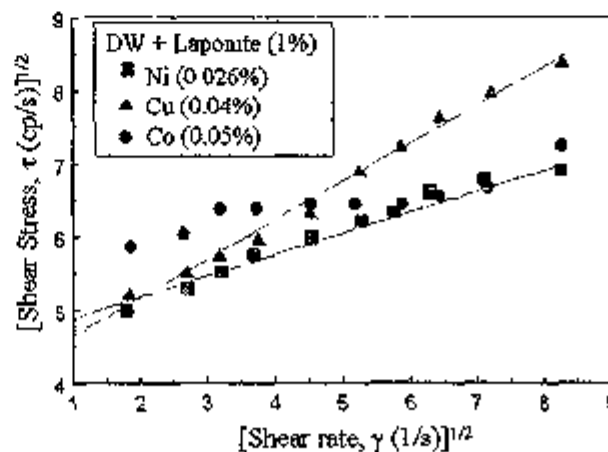

Fig. 5. Shear stress versus shear rate measured for various cation-exchanged Laponite suspension (measured at 25 °C).
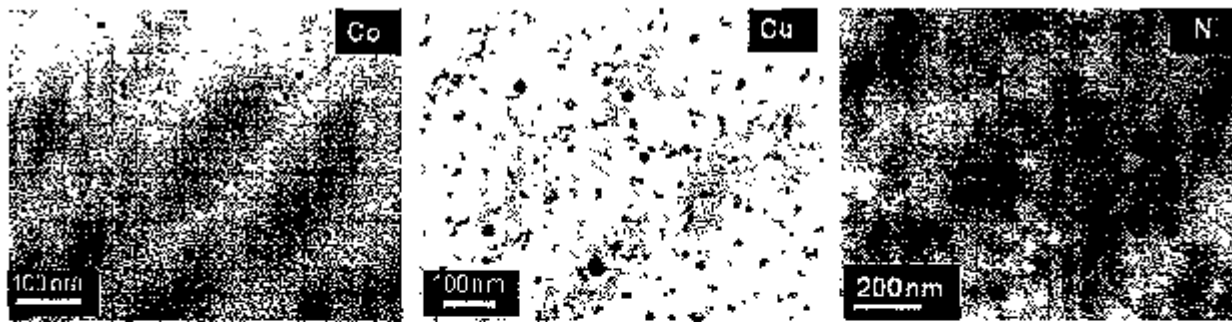
Fig. 6. TEM images of Cu, Co, and Ni nanoparticles ablated in deionized water stabilized by PVP (0.1 wt %).

needle shape with lengths ranging from 20 nm to 30 nm and diameters ranging from 5 nm to 10 nm. Some larger particles of 30 nm in size were also presented. These differences might alter the charge reduction and could be the reason why different rheological and thixotropic behaviors are obtained when using copper, cobalt and nickel.

To examine the thixotropy of the prepared cation-modified Laponite suspensions we simply observed the suspension behavior in terms of its changing rheological properties with shearing time. It is known that rheological properties of a thixotropic material depend not only on its initial strength but also on the shear rate and the shearing time, therefore, the measured values of these properties will depend on how the sample is loaded into a viscometer and how long it is left at rest before shearing [25,26]. Thus, to obtain similar initial conditions for all measurements we first shook the samples to liquefy the suspension so that it could be loaded into the viscometer sample holder using a pipette. We sheared the test sample with a high and constant shear rate until its viscosity was steady out at a constant value. We then suddenly decreased the viscometer shear rate and observed the suspension buildup via its changing viscosity (shear stress) as a function of time. To observe the suspension breakup, we first sheared the sample with a low shear rate (for all experiments here we used 3.4 1/s) until its viscosity steady out then we suddenly increased the shear rate and observed the changing viscosity (or stress) as a function of time. Typical results on the rheological properties of Ni-exchanged Laponite suspensions measured during gel breakup and buildup are shown in Fig. 7. It is clear that for a given shear rate the suspensions reached a steady state condition quickly after shearing for about 5–10 min. Such fast breakup and buildup behavior are critical in many applications. One of such applications is for oil and gas drilling. During drilling, circulation might have to stop and start many times for various reasons. In a deep well, drill bits break more often, for example, and changing the bit often requires many hours. One of the most important requirements of any good drilling fluid

is its ability to suspend cuttings and weight materials when circulation is stopped. If the solids are not kept in suspension during this time, their settling will result in deposition of solids on the bit which can become stuck. In order for the fluid to have an adequate suspending ability it must develop high gel strength quickly when the fluid is not in motion. Conventional drilling fluids with high gel strength usually require high energy to initiate circulation, generating pressure surges in the annulus while the flow is being reestablished. Although Ni-exchanged Laponite suspensions have great gel strength at rest, the structure can be quickly broken. Therefore, they can be transformed into a low viscosity fluid that does not induce significant friction losses during circulation and, yet, can quickly develop high gel strength after the pump is turned off, preventing solids from settling.

Most researchers in this area have used the time derivative $d\lambda/dt$ to describe the structure strength of a thixotropic material, where λ is the material structure which is equal to 1 when the system structure is completely built and zero when its structure is completely broken-down. The most general description of $d\lambda/dt$ due to shearing is the sum of the breakdown term which is proportional to the product of the current level of structure and the shear rate, $\propto \lambda \dot{\gamma}^a$, and the buildup term which depends on the driving force for the buildup, $\propto (1-\lambda)^b$. From this simple theory, many models to predict properties of thixotropic materials have been developed. For a non-Newtonian fluid, the upper viscosity limit, $\lambda = 1$ corresponds to η_0 and the lower viscosity limit, $\lambda = 0$ corresponds to η_∞. The following equation can be used to describe the response of the viscosity to a step-wise change from one limit to another [27]

$$\eta = \eta_\infty - (\eta_\infty - \eta_0)e^{-(\beta t)^r} \tag{1}$$

where η_0 is the viscosity at the commencement of shearing, η_∞ is the plastic viscosity, r is a dimensionless constant, β is a time constant, and t is the shearing time. As discussed by Barnes [27], this equation describes the functional dependency of the viscosity
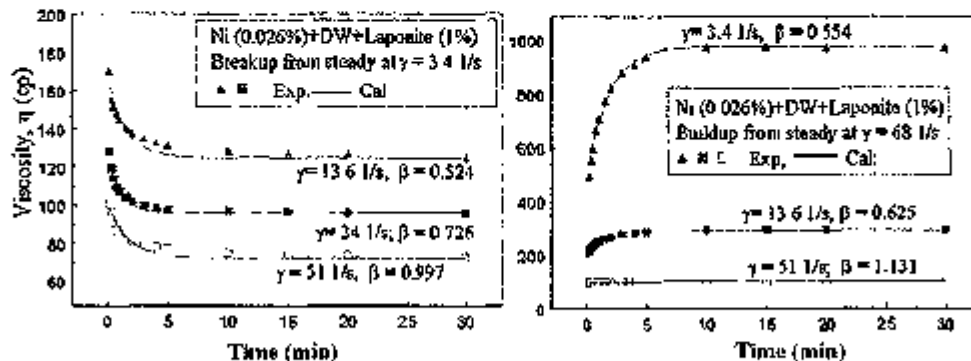

Fig. 7. Viscosities of Ni-exchanged Laponite suspensions during gel buildup and breakup (measured at 25 °C).
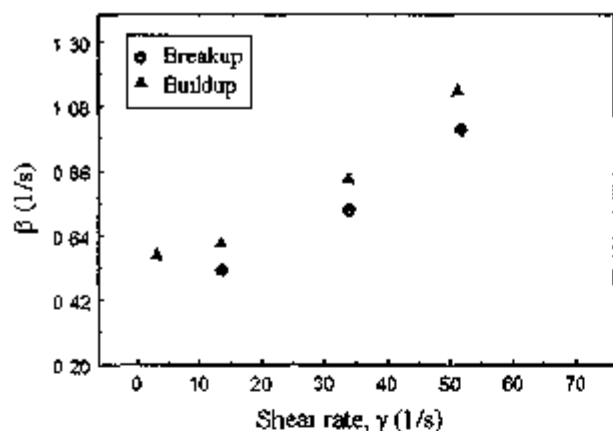
Fig. 8. The time constant β in Eq. (1) as a function of the shear rate

on the shear rate and the shearing time. It can cope with buildup and breakdown in step-up or step-down tests with values of β and r depending on both the shear rate and the direction. The values of r also vary with the condition of the test and the particular system being tested and they decrease linearly with the log of the shear rate, typically from 0.7 to 0.9 at $10^{-2}\,s^{-1}$ [27].

To check the validity of Eq. (1), we fit our measured properties for Ni-exchanged Laponite suspension during buildup and breakup. For simplicity we used $r = $ unity and conducted a least square fit of our measured values to the above equation. It was found that an expression of this type described our experimental results very well. As shown in Fig. 8, the time constant β was found to depend on both the shear rate and the direction as discussed by Barnes [27]. β increased with the shear rate and, for a given shear rate, its values in the buildup direction were higher than those in the breakdown direction.

Fig. 9 shows the effects of the various metals on the viscosities of the modified Laponite suspensions. Measurements were conducted over a 2-h period where a shear rate of 56 1/s was used during the first hour which was suddenly decreased to 5.6 1/s for the second hour. The results observed for the shear rate of 56 1/s indicated that the viscosities of all suspensions behaved similarly, that is, they all decreased quickly and steady out after about 10 min of shearing. For the shear rate of 5.6 1/s, however, the measured viscosities of Cu and Co-exchanged Laponite suspensions exhibited a mixed thixotropic behavior while a positive thixotropic behavior was observed for the suspension modified with Ni.
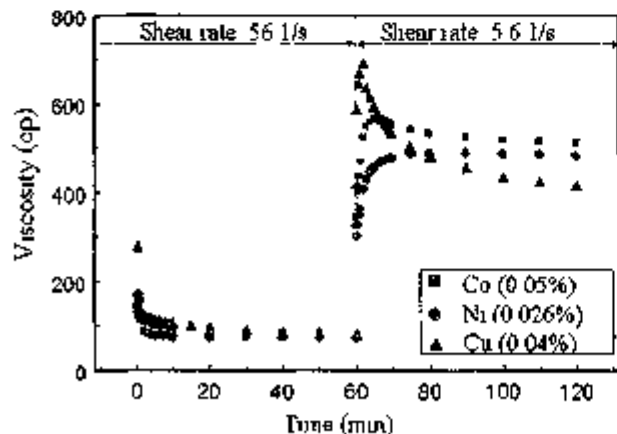

Fig. 9. Viscosities of cation-exchanged Laponite suspensions: effects of different metals (DW + 1% Laponite by weight, 25 °C).
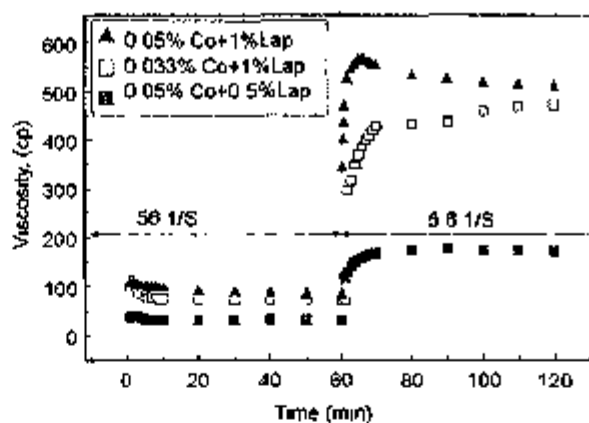

Fig. 10. Effect of concentrations of Co nanoparticles and Laponite of the viscosity of Co-exchanged Laponite suspensions (measured at 25 °C)
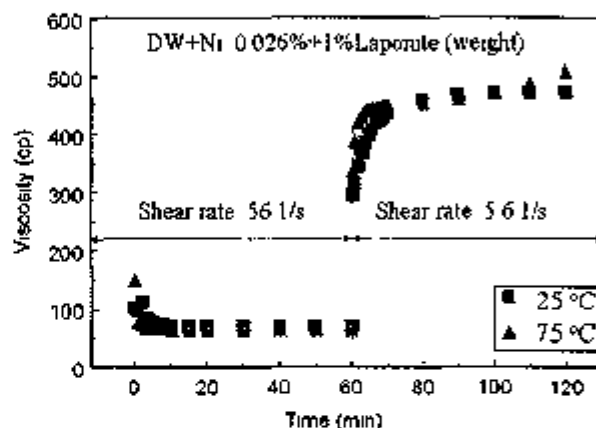

Fig. 11. Effect of temperature on the viscosity of Ni-exchanged Laponite suspensions

Fig. 10 shows the effects of the concentrations of Laponite and Co on suspension viscosities. For example, the viscosities of the suspension containing 0.05% Co and 0.5% Laponite were stable at 27 cp and 170 cp when it was sheared at 56 1/s and 5.6 1/s, respectively. For the same Co concentration and shear rates, the viscosities increased to 84 cp and 512 cp when Laponite concentration was increased to 1%. For the same Laponite concentration, an increase in Co concentration from 0.033% to 0.05% resulted in changes in the viscosities of the suspensions from 70 cp to 82 cp and from 470 cp to 512 cp when they were sheared at 56 1/s and 5.6 1/s, respectively. The ability of cation-modified Laponite nanohybrids to stabilize viscosity of Laponite suspensions at elevated temperature was also demonstrated, Fig. 11. The viscosities of Ni-exchanged Laponite suspensions measured at 25 °C and 75 °C and found to be nearly identical.

4. Conclusions

We have conducted a preliminary study on the use of laser-generated nanoparticles for maintaining rheological properties of Laponite suspensions at high temperature. To do so, we prepared cation-modified Laponite suspensions and examined the effects of four metals, Fe, Ni, Co, and Cu, on the suspension structural, thixotropic, and rheological properties. To prepare the samples we used laser ablation of a metal target in liquid in the presence of aqueous Laponite and found that the technique can be used to successfully produce cation-modified Laponite crystals. Although

the weight percent of the nanoparticles was negligibly small compared to that of Laponite, aqueous suspensions of these modified Laponite crystals were highly viscous with excellent shear-thinning and thixotropic behavior. The fluid gelled quickly with significantly high gel strength when it was at rest nevertheless its structure was broken easily and it transformed into a low viscosity fluid quickly on shearing. Despite the fact that the laser-generated nanoparticle-Laponite mixtures were found to have promising shear-thinning and thixotropic behaviors, the exact mechanism for the behavior was not identified by the characterization done so far. Nanoparticles and/or hydrated metal ions could be playing a role in the observed behaviors. In addition, the specific species comprising the nanoparticles generated by the laser technique used in this study are not yet known. Answering these questions will be the goal of future investigations.

Given the enormous amount of material that is needed for drilling operations, use of the laser-ablation technique to synthesize materials for drilling application appears economically unpractical at present. However, the development of a better understanding of these systems is expected to lead to alternative, more economical synthetic routs to these materials.

Acknowledgements

References

[1] G.V. Chilingarian, P. Vorabutr, Drilling and Drilling Fluids, Elsevier, 1983.
[2] W. Gusler, M. Pless, J. Maxey, P. Grover, J. Perez, J. Moon, T. Baaz, A new extreme HPHT viscometer for new drilling fluid challenge, SPE Drilling and Completion 81 (June) (2007).
[3] D.J. Oakley, K. Morton, A. Eunson, A. Gilmour, D. Pritchard, A. Valentine, Innovative drilling fluid design and rigorous pre-wall planning enable success in extreme HTHP well, in: 2000 IADC/SPE Asia Pacific drilling technology, 11–13 September, Malaysia, 2000 (IADC/SPE62729).
[4] K.H. Hiller, Rheological measurements on clay suspensions and drilling fluids at high pressure and high temperature, J. Petrol. Technol. 15 (1963) 779–790.
[5] M.R. Annis, High temperature flow properties of water-base drilling fluids, J. Petrol. Technol. 19 (1967) 1074–1080.
[6] B.K. Sinha, A new technique to determine the equivalent viscosity of drilling fluids under high pressure and temperature, SPE J. 10 (1970) 33–40.
[7] H.J. Alderman, A. Gavignet, D. Guillot, G.C Maitland, High temperature and high pressure rheology of water-based muds, SPE Paper 18035, 1988 SPE Meeting, Houston, Texas.
[8] P. Mongondry, T. Nicolai, Jea-Francois Tassin, Influence of pyrophosphate or polyethylene oxide on the aggregation and gelation of aqueous laponite dispersions, J. Colloid Interface Sci. 275 (2004) 191–196.
[9] J.C. Baird, J.Y. Walz, The effects of added nanoparticles on aqueous kaolinite suspensions I. Structural effects, J. Colloid Interface Sci. 297 (2006) 161–169.
[10] J.C. Baird, J.Y. Walz, The effects of added nanoparticles on aqueous kaolinite suspensions, II. Rheological effects, J. Colloid Interface Sci. 306 (2007) 411–420.
[11] T. Huang, J.B. Crews, Nanotechnology applications in viscoelastic surfactant stimulation fluids, SPE 107728 (2007).
[12] J. Norris, R.F. Giese, P.M. Costanzo, C.J. Van Oss, The surface energies of cation-substituted Laponite, Clay Minerals 28 (1993) 1–11.
[13] N. Negrete-Herrera, J.L. Putaux, A. Bourgeat-Lami, Synthesis of polymer/Laponite nanocomposite latex particles via emulsion polymerization using silylated and cation-exchanged Laponite clay platelets, Prog. Solid-State Chem. 34 (2006) 121–137.
[14] G.W. Yang, Laser ablation in liquids: application to the synthesis of nanocrystals, Prog. Mater. Sci. 52 (2007) 647–698.
[15] J. Zhang, C.Q. Lan, Nickel and cobalt nanoparticles produced by laser ablation of solids in organic solution, Mater. Lett. 62 (2008) 1521–1524.
[16] T.X. Phuoc, Y. Soong, M.K. Chyu, Synthesis of Ag-deionized water nanofluids using multi-beam laser ablation in liquids, Opt. Lasers Eng. 45 (2007) 1099–1106.
[17] M. Saito, K. Yasukawa, T. Umeda, Y. Aoi, Copper nanoparticles fabricated by laser ablation in polysiloxane, Opt. Mater. 30 (2008) 1201–1204.
[18] T. Tsuji, D.-H. Thang, Y. Okazaki, M. Nakanishi, Y. Tsuboi, M. Tsuji, Preparation of silver nanoparticles by laser ablation in polyvinylpyrrolidone solutions, Appl. Surf. Sci. 254 (2008) 5224–5230.
[19] Tae-Bong Hur, T.X. Phuoc, M.K. Chyu, Synthesis of Mg–Al and Zn–Al layered double hydroxide nanocrystals using laser ablation in water, Opt. Lasers Eng. 47 (2009) 695–700.
[20] T.X. Phuoc, B.H. Howard, D.V. Martello, Y. Soong, M.K. Chyu, Synthesis of Mg(OH)₂, MgO, and Mg nanoparticles using laser ablation of magnesium in water and solvents, Opt. Lasers Eng. 46 (2008) 829–834.
[21] J. Fripiat, J. Cases, M. Francois, M. Letellier, Thermodynamic and microdynamic behavior of water in clay suspensions and gels, J. Colloid Interface Sci. 89 (1982) 378–400.
[22] N. Sakairi, M. Kobayashi, Y. Adachi, Effects of salt concentration on the yield stress of sodium montmorillonite suspensions, J. Colloid Interface Sci. 283 (2005) 245–250.
[23] P.B. Laxton, J.C. Berg, Relating clay yield stress to colloidal parameters, J. Colloidal Interface Sci. 296 (2006) 749–755.
[24] R.G. Larson, The Structure and Rheology of Complex Fluids, Oxford University Press, New York, 1999.
[25] S.P. Li, W.G. Hou, J.F. Hu, D.Q. Li, Influence of shear rate on thixotropic suspensions, J. Dispersion Sci. Technol. 24 (2003) 709–714.
[26] S.P. Li, W.G. Hou, D.J. Sun, P.Z. Guo, C.X. Jia, The thixotropic properties of hydrotalcite-like montmorillonite suspensions, Langmuir 19 (2003) 3172–3177.
[27] H.A. Barnes, Thixotropy—a review, J. Non-Newtonian Fluid Mech. 70 (1997) 1–33.