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Influence of controlled dispersion on rheology of swelling clay suspensions in the presence of coal flotation reagents

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Abstract: Swelling clay minerals, which are innately capable of dispersing into thin flakes in water, can significantly depress coal flotation. Some researchers partially attribute depression to pulp viscosity increments. This study sought to understand the role of swelling clay minerals in fine coal flotation, by investigating the rheological behavior of bentonite suspensions under controlled and uncontrolled dispersion conditions. The effect of collector, frother, and solution pH on rheological properties of the pulp was studied. Findings showed that at a natural pH, Newtonian flow properties were displayed when bentonite was directly added into a swelling suppressed solution containing calcium ions. The same process was repeated under uncontrolled conditions, and the suspensions transferred from Newtonian to non-Newtonian flows with pseudo-plastic characteristics, depending on the solid density. Further, pH value, methyl isobutyl carbinol (MIBC) and kerosene had the potential to alter the rheological behavior of controlled and uncontrolled systems, especially pH value in the uncontrolled system.

Keywords: *swelling clay, rheological properties, controlled dispersion, flotation reagents*

Introduction

Swelling clay minerals, such as bentonite, can significantly depress coal flotation recovery (Arnold and Aplan, 1986; Zhang et al., 2013; Cruz et al., 2015). Some researchers (Arnold and Aplan, 1986; Wang and Peng, 2013; Zhang et al., 2013) have partially attributed this depression to the increased pulp viscosity and natural swelling of the clay. High pulp viscosity can lead to a greater water carry-over, greater entrapment into froth mass and greater attachment to the rough surfaces of the coal surface (Arnold and Aplan, 1986). Additionally, the high pulp viscosity can result in poor gas dispersion, cavern formation, increased turbulence damping and bubble coalescence (Ndlovu et al., 2013).

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The slurry rheology is a complex function of processes that occur at the scale of the suspended particles. These processes include particle volume fractions, particle size distribution and interactions between particles (He et al., 2004; Mueller et al., 2010). As one of the most important factors, the increase in particle volume fraction leads to a remarkable increase in the viscosity. The suspension behavior can change from Newtonian to non-Newtonian flow (He et al., 2004). The suspension rheology of clay minerals indicates the level of inter-particle interactions or aggregation in combination with anisometric particle shape and surface charges. In homoionic sodium montmorillonite suspensions with a pH below 5, electrostatic attraction between the electronegative base face and edge surface (which is charged positively) may cause either an edge-face contact form or a house of cards network. As a result, the suspension shows non-Newtonian natures with a high-yield stress requirement (Brandenburg and Lagaly, 1988). With incremental changes in the pH value, the house of cards network breaks down due to reduction in the positive charge on the edges. The face-face contact may form three-dimensional lamellar structures when the free energy of the system is at its lowest level. This network shows some elasticity in contrast to the more rigid house of cards structure (Rand and Melton, 1977). The edge-edge contact form may occur under conditions of low ionic strength at the pH value of the isoelectric point due to high basal surface repulsion (Morris and Zbik, 2009). As the contact area is small, the network based on edge-edge contacts is not very stable, and no definite yield stress is needed to destroy it (Brandenburg and Lagaly, 1988) .

It has been shown that dry clays exist as stacks of individual clay platelets aligned in a face-face orientation (Lim et al., 2009). In either de-ionized water or low electrolyte concentration solutions, the close-packed structure can break up into thinner lamellas and even into single platelets with a flat sheet-like shape and a high aspect ratio. When this occurs, the subsequent addition of electrolytes cannot rearrange the disordered lamellas into efficient face-face oriented states (Pashley and Quirk, 1984). Therefore, the uncontrolled dispersion approach has been demonstrated to only moderately improve sedimentation and dewaterability of clay-based coal tailings (Ross De Kretser et al., 1997). Tanihara and Nakagawa (1973) and Deason and Onoda (1984) first introduced the controlled dispersion method. It inhibits clay swelling and dispersion using a high salinity solution with specific ions, such as Ca^{2+}. On wetting in the high electrolyte concentration solution, clay breakup is prevented and the large-sized particles remain naturally compacted face-face orientation. Because of the large starting size, great improvements in suspension behavior were observed (Deason and Onoda, 1984). Since controlled and uncontrolled dispersion methods can result in different association forms in individual clay platelets, the rheological properties of the flotation slurry containing swelling clays would inevitably be changed, consequently the efficiency of flotation.

During coal flotation, collectors and frothers are commonly added to modify the surface hydrophobicity of particles and the surface tension of the solution, respectively. These flotation reagents may interact with clay particles. Pulp pH can change the interaction form between particles. The interactions and changes in pulp may further change the slurry rheology. This study aims to understand the rheological properties of bentonite suspension under controlled and uncontrolled dispersion conditions in both the absence and presence of collector and frother. Additionally, the pH is tested to determine if it is a factor that affects the rheological behavior of slurry.

Experimental

Materials

The material used in this study was a run-of-mine bentonite, obtained from Anhui, China. The bentonite was received in large lumps. Dry grinding and manually dry sieving were conducted to create a stock sample with a particle size < 1 mm. During this process, a large proportion of rocks and sand in the run-of-mine bentonite was separated. A particle size distribution of the bentonite was measured using a Laser Diffraction Mastersizer with a dilution suspension of 0.1% solids by weight. A certain amount of bentonite was added into tap water to obtain 0.1 wt.% suspension. The suspension was conditioned with dispersant (sodium hexametaphosphate) for 1 min followed by 20 s of ultrasonic dispersion. Then, the particle size distribution was measured. The results are shown in Fig. 1, indicating that 80 wt.% of particles are smaller than 13 μm. A quantitative X-ray diffraction (XRD) analysis shows that the stock bentonite sample contains 71.3 wt.% montmorillonite, 8.9 wt.% quartz, 3.5 wt.% albite and other materials. The cation exchange capacity (CEC) of the dry sample was tested as 74 meq/100g using a methylene blue dye method described by Hang and Brindley (1970).

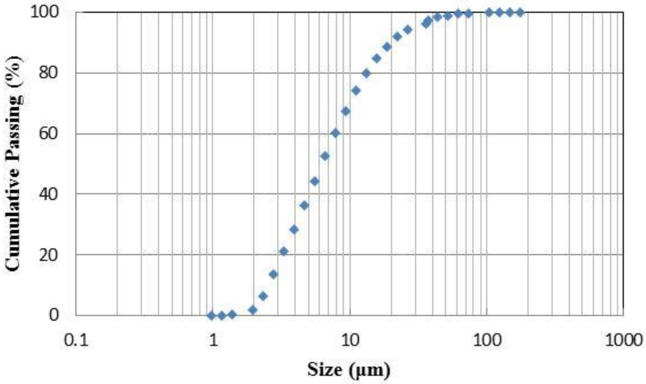

Fig. 1. Particle size distribution of stock bentonite sample

A fine coal sample was obtained from a coal preparation plant, China. The -250 μm particle size fraction with 4.3% ash content was sieved for flotation tests. Analytical grade hydrochloric acid was used to adjust the suspension pH to 7.4 and 5.5. Kerosene and MIBC, industrial grade, were used as a collector and a froth, respectively.

Methods

Preparation of controlled and uncontrolled bentonite suspensions and swelling test

Both controlled and uncontrolled methods were used in this study, as described by Lim et al. (2009). To prepare the controlled dispersion suspension, 50 mM of $CaCl_2$ solution was prepared and, while stirring continuously, a certain amount of stock bentonite was added into the electrolyte solution. A 50 mM of Ca^{2+} concentration far exceeds the maximum amount exchanged with monovalent ions and can effectively inhibit swelling. Then, the mixture was shaken many times, and then left for 24 h for use. In the uncontrolled dispersion method, a certain amount of bentonite was added into the RO-water when stirring, and then it was hand-shaken for 2-3 min followed by leaving for 12 h to fully hydrate and swell. After that, the same amount of $CaCl_2$ as in the controlled system was added into the resulting mixture, then it was efficiently stirred for 5 min. Finally, the sample was again left for 12 h in order to reach chemical equilibrium. The natural pH of both the controlled and uncontrolled suspensions was around 8.6. Suspensions with either natural pH, adjusted pH, conditioned with MIBC or kerosene were subjected to rheology measurements.

Swelling tests were carried out using standard test methods for determining a bentonite swell index (ASTM-D5890) at natural pH under controlled and uncontrolled conditions.

Rheology measurements

Rheological properties were measured using an Ares rheometer with Couette geometry (bob and cup) from TA Instruments Ltd. (U.S.). The suspension was fully mixed and settled for 5 min. Then, the sample of 15 dm^3 was taken from the upper portion with a 20 dm^3 syringe for measurement. The distance between the cup base and bob tip was automatically set at 8.0 mm. The shear rate in this test was between 0.1 and 750 s^{-1}. All tests were performed at ambient temperature (around 25℃）.

Cryovitrification-SEM (Cryo-SEM)

In order to avoid structure alteration caused by sample drying, a Cryo-SEM analysis was performed to test the aggregate structure of the suspended clay platelets. After fully mixing and settling for 5 min, a sample was taken from the upper portion of clay suspension by a large-aperture (>2 mm), and then quickly mounted in a small metal rivet. The sample was then immediately plunged into a Dewar of liquid propane and cooled down in liquid nitrogen, which reduces the temperature at >800 °C/min freezing water without allowing crystallization, i.e. vitrifying. After that, the vitrified sample was transferred under vacuum to the sample preparation chamber equipped with an Oxford Instrument, where the sample was fractured to develop a fresh surface. In order to expose the aggregate structure, a small amount of vitrified water was sublimated off by raising the stage temperature to -90 °C for 9 min, then lowering the temperature back down to -180 °C. The sample was coated with 3 nm gold and palladium, and then subjected to scanning tests by PHILIPS XL30 field emission gun scanning electron microscope.

Flotation test

Batch flotation was carried out by using a 1.0 dm^3 plexiglass flotation cell. A 3 wt.% controlled and uncontrolled bentonite suspensions were prepared at natural pH. First, 63 g coal sample was added in either the controlled or uncontrolled suspension in the flotation cell for 5 min pre-conditioning. Then, kerosene (240 g/Mg) and MIBC (180 g/Mg) were added step by step and the mixing time was 4 min. The impeller speed was kept constant at 950 rpm. In the flotation stage, four froth concentrates were consecutively collected after 1, 2.5, 5 and 10 min, respectively. Flotation concentrates and tailings were then filtered, dried at 80 °C, weighed and combusted at 815°C for 2.5 h to obtain ash contents. The procedure to calculate combustible and ash recovery was described elsewhere (Wang and Peng, 2013).

Results

Effect of solid concentration

The effects of solid concentration on the rheological behavior of the controlled and uncontrolled dispersion system were measured at the natural pH. The results for the measurement are given in Fig. 2. As seen, the increased solid concentration shifts the curves slightly upward. For controlled dispersions, these curves are linear and pass through the origin, which implies that suspensions are Newtonian flows throughout the tested solid concentrations. The slopes of these lines are known as the viscosity and are constant and independent of the shear rate. Both the basic face and edge face of the clay particles are negatively charged at alkaline pH and the inter-particle forces are repulsed (Brandenburg and Lagaly, 1988). As a result, in this study, no aggregates were developed and the particles moved independently under applied stress. However, the uncontrolled dispersions show different rheological natures in the same solid concentration range when compared to the controlled systems. The suspension changes from Newtonian flow to non-Newtonian flow with pseudoplastic properties when the solid concentration increases. For a specific pseudoplastic flow, the viscosity decreases with the increasing shear rate, caused by the fracture of aggregates into smaller units, even into individual particles (He et al., 2004). The process is referred to as rheologically shear-thinning behavior (Cruz et al., 2015). Lagaly (1989) explained that under this phenomenon, clay particles are subjected to increasing geometrical constraints, and they could no longer occupy equilibrium positions, so they must assume an ordered array, which reduces interparticle repulsion as much as possible. As a result, works are required to shift the particles out of these positions and the flow become plastic.

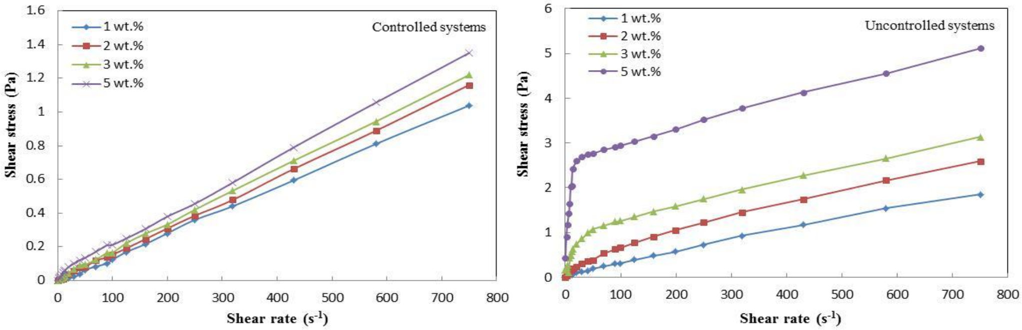

Fig. 2. Rheograms of dispersion systems at different concentrations

To further understand the influence of dispersion methods, apparent viscosity indices of both types of suspensions at a shear rate of 100 s^{-1} were calculated at different solid concentrations. As shown in Fig. 3, controlled dispersion has a significant effect on the rheological properties of suspension. For instance, at the solid concentration of 5 wt.%, the uncontrolled suspension produced an apparent viscosity almost 10 times higher than the controlled suspension.

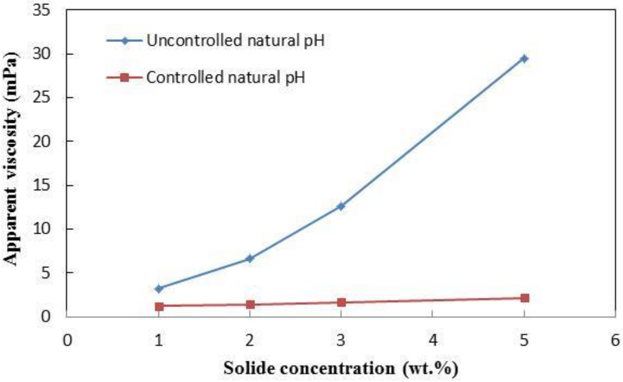

Fig. 3. Apparent viscosity of suspensions as a function of their concentrations at a shear rate of 100 s^{-1}

Effect of collector and frother

The trend of rheological indices as a function of solid concentrations demonstrates that the distinct difference between behaviors of the controlled and uncontrolled systems occurred at solid concentrations of no less than 3 wt.%. Therefore, the solid concentration of samples in the next stage was set at 3 wt.%.

Figure 4 shows rheograms of 3 wt.% suspensions in the absence and presence of MIBC. The addition of 90 g/Mg MIBC to the bentonite suspensions slightly shifts the curve upward with higher shear stress and viscosity. Adding 180 g/Mg and 270 g/Mg MIBC contribute to pesudoplasitc characteristics in the controlled systems. As the dosage increased the pesudoplastic characteristics become more obvious. However, MIBC does not change the pseudoplastic characteristics in the uncontrolled suspensions.

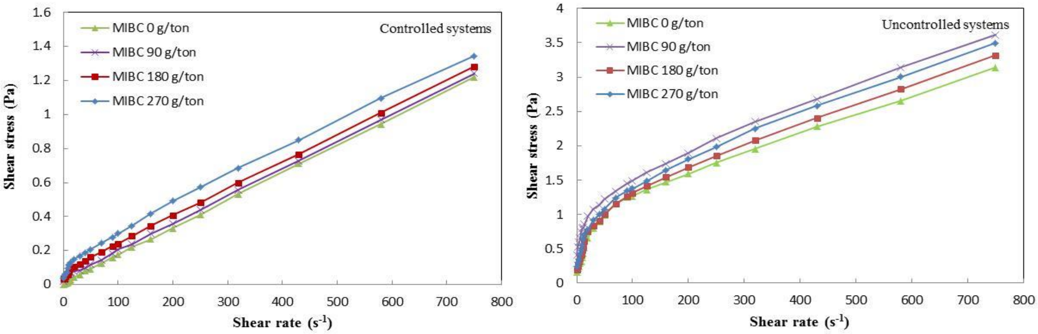

Fig. 4. Rheograms of 3 wt.% dispersion systems
in the absence and presence of MIBC expressed in g/Mg (g/ton)

Previous investigations have shown that some surfactants can alter the rheological behaviors of clay suspensions. Schott (1968) reported that surfactants could enhance the viscosity of compared non-ionic surfactant which could be adsorbed not only at the edges or outermost surfaces of the clay mineral layers but also can penetrate between layers. In our study, the increased viscosity may be attributed to the crosslinks of MIBC between clay particles resulting in structures that are more flow-resistant. Additionally, it is also hypothesized that possible adsorption of MIBC tails on the interlayer space could result in swelling and dispersion of close-packed clay particles in the controlled system. This process may also alter the suspension rheological behavior. Detailed investigations are underway to further study the adsorption, conformation and micellization of MIBC on close packed clay particles.

The effect of kerosene on the rheological behavior of bentonite suspensions was also investigated. As seen from Fig. 5, kerosene, similarly to MIBC, can slightly increase the rheological properties and promote controlled suspension transfer from Newtonian to non-Newtonian flow. Firth and Nicol (1981) as well as Arnold and Aplan (1986) believed that the bentonite particles could attach strongly to the oil droplets in the coal flotation system. In this study, the change of flow type and increasing viscosity may be attributed to aggregation of bentonite particles induced by kerosene.

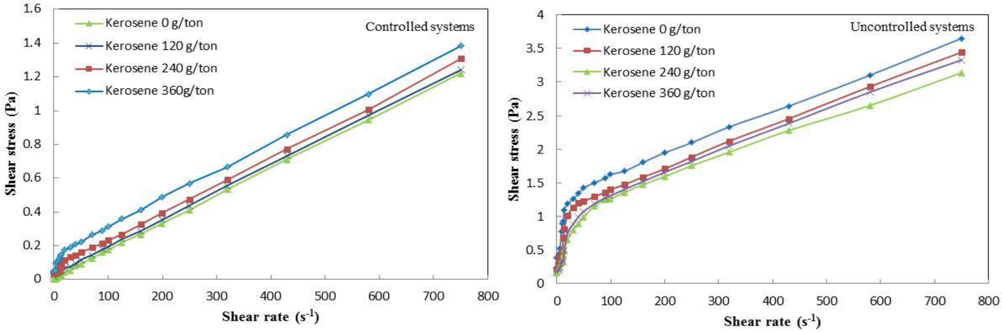

Fig. 5. Rheograms of 3 wt.% dispersion systems
in the absence and presence of kerosene expressed in g/Mg (g/ton)

Effect of solution pH

Figure 6 shows the effects of solution pH on the dispersion rheology. When dispersion is uncontrolled, the shear stress markedly decreases when the pH decreases from 8.6 to 7.4, and then slightly increases at pH 5.5. This change trend is consistent with that reported by Brandenburg and Lagaly (1988), who investigated the rheological behavior of dispersions of 4 wt.% sodium bentonite (sourced from Wyoming) in NaCl solutions at different pH levels.

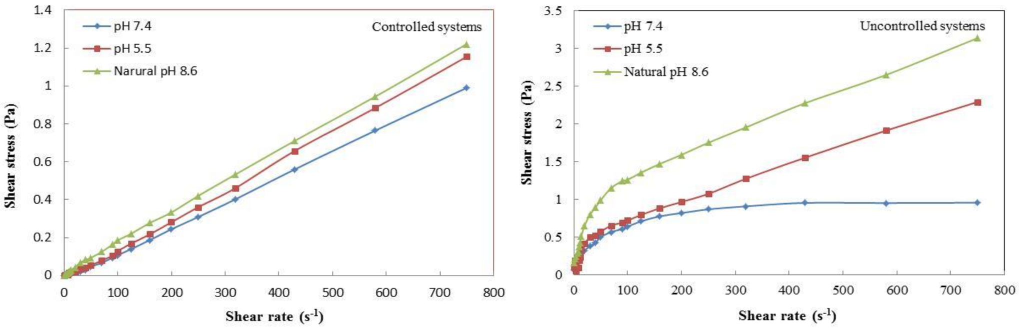

Fig. 6. Rheograms of 3 wt.% dispersion systems at different pH values

Discussion

The difference in suspension rheology between two dispersion methods may arise from the changes in the number of units available to build gel structures and the number of surfaces for particle interactions.

The results of free swell tests under controlled and uncontrolled dispersion conditions are presented in Fig. 7. It is evident that bentonite clay exhibited high swelling in uncontrolled solution when compared with that in controlled dispersion.

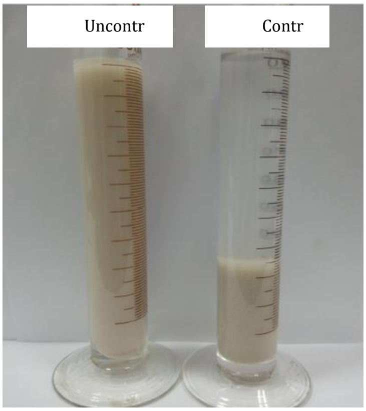

Fig.7. Photograph of free swell test results under controlled
and uncontrolled dispersion conditions

Figure 8 shows the SEM micrographs of the aggregates from the uncontrolled dispersions under cryogenic conditions at pH 5.5 and 8.6. Figure 8 shows that a large number of individual platelets and thinner lamella are developed. When the pH of the solution is 5.5, high positive charge densities on the particle edges are obtained, which lead to the edge-face contacts shown in Fig. 8a. Brandenburg and Lagaly (1988) suggested that edge-face contacts contributed to clusters with finite sizes based on the flow analysis. However, they did not conduct the SEM measurement to confirm their hypothesis. Figure 8b shows that aggregates are obviously separated and finite in size. Despite the edge-face contact in this dispersion, the presence of Ca^{2+} may cause the development of face-face contacts (Brandenburg, 1988). In Figure 8a, the face-face contacts can also be seen, which build up a band-like structure. However, the band-like structure unions are not strong enough to create a particulate structure throughout the whole system. Therefore, the flow is slightly plastic with lower viscosity than is observed under alkaline conditions. When pH increases, the net charges of the edges become too small to maintain the rigid edge-face network structure and destruction of the card-house structure occurs, leading to a decrease in shear stress. At natural pH 8.6 in uncontrolled suspension, the edges of the clay particles are negatively recharged (Lagaly, 1989). Therefore, it can be predicted that the particles are dispersed separately. However, Brandenburg and Lagaly (1988) proposed that in alkaline solutions, Ca^{2+} ions are likely enriched in contact regions between silicate layers and thin lamellas, forming a layer of gegen ions and attractive electrostatic potential, promoting the face-face contacts. Figure 7c shows that clay particles are mainly associated in a face-face manner, with some face-edge organization. The particulate structure develops into a cellular structure and spans the network throughout the system, which is strong enough to enhance viscosity or consistency and to establish a distinct stress yield. For controlled systems, due to the prevention of swelling and dispersion, clay particles contain a number of platelets in closely packed face-face orientation (shown in Fig. 9a). Further, as shown in a low magnification micrograph in Fig. 9b, the particles appear to be largely separated, while almost no extended network develops. The smaller surface and the net reduction in the overall number of particles interaction determine the Newtonian properties of the clay suspension. To further investigate the effect of controlled dispersion and slurry viscosity on fine coal flotation recovery, flotation tests at natural pH were conducted. Figure 10 shows the combustible recovery and ash recovery as a function of flotation time. The final combustible recovery (86%) under controlled dispersion condition is much higher than that of uncontrolled condition (74%). This is consistent with the reports by Bakker (2009) that the reduction of the pulp viscosity can improve fine particle flotation. Schubert (2008) found that the low viscosity resulted in a reduction in turbulence damping in favor of particle-bubble attachment and detachment, thus enhancing the fine particle flotability. Additionally, a larger numbers of units and surface in uncontrolled system may consume more flotation reagent than that in controlled system. So enough reagent amount for the flotation process may not be available. Detailed studies are underway to investigate the adsorption and its effect on flotation recovery.

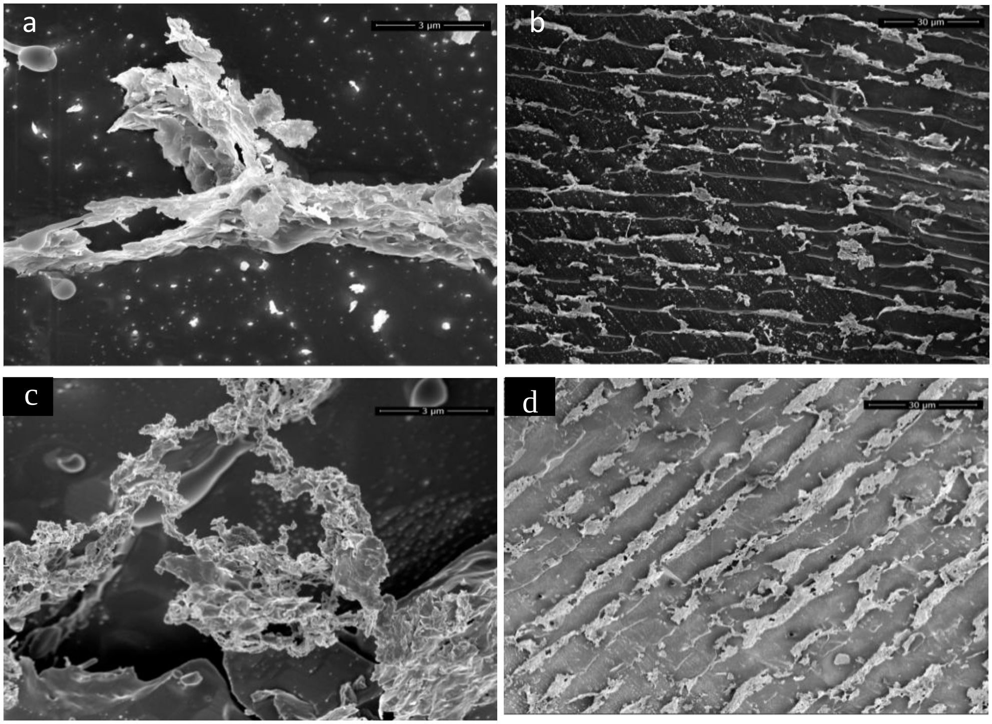

Fig. 8. Cryo-SEM micrographs of aggregates from uncontrolled dispersions
at pH 5.5 (a and b) and 8.6 (c and d)

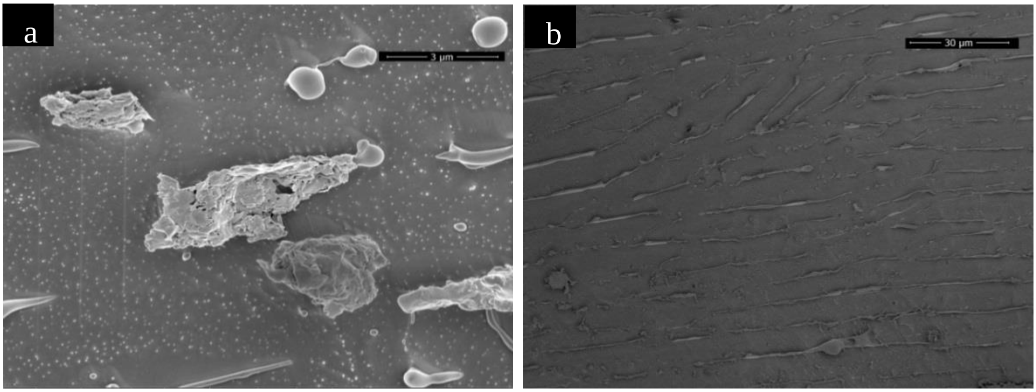

Fig. 9. Cryo-SEM micrographs of aggregates from controlled dispersion at natural pH

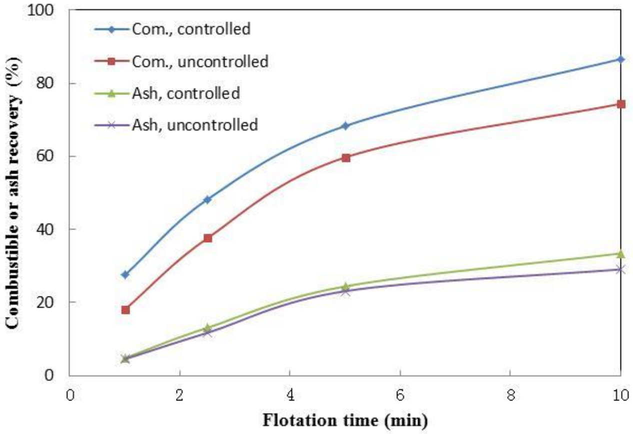

Fig. 10. Combustible recovery and ash recovery as a function of flotation time from coal flotation with uncontrolled and controlled bentonite

Conclusion

When tested at solid concentrations (from 1 wt.% to 5 wt.%), controlled dispersion bentonite suspensions followed Newtonian flows. However, in the same solid concentration range, uncontrolled systems transferred from Newtonian to non-Newtonian flow.

The collector kerosene and the frother MIBC were able to slightly increase the viscosity of suspensions, and depending on the dosage, impart non-Newtonian characteristics on the controlled suspensions.

The pH of the solution can alter the rheological properties based on the aggregate structure of the bentonite particles. For uncontrolled suspensions that were at medium acidity, the numerous platelets and lamellas built separate and finite aggregates with edge-face and face-face contacts, which contributed to the lower viscosity. In an alkaline medium, the higher viscosity resulted from the formation of a band-like structure throughout the whole system with associated platelets and lamellas in the face-face contact. In contrast, the platelets remained the close-packed face-face contact and particles were with the smaller aspect ratio. The change of suspension viscosity was smaller than in the uncontrolled system.

Acknowledgements

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