Effect of swelling clay dispersion type on fine coal flotation

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Abstract: The influence of bentonite dispersion on fine coal flotation was examined to better understand the role of swelling clay in the process of flotation. It was found that the coal flotation recovery was lower with uncontrolled dispersion of bentonite than with controlled dispersion. The detrimental effect was attributed to the increase in slime coating. In the uncontrolled dispersion, the dispersed bentonite platelets formed an extensive card-house structure. The three-dimensional networks increased the slurry viscosity, and caused significant coating of the coal particles, thereby inhibiting particle mobility and bubble-particle attachment. In the controlled dispersion, the bentonite mineral appeared as separate particles with low aspect ratios. The coal particles were partially coated, and the slurry viscosity was lower, resulting in higher flotation recovery. The findings in this study suggested that a practical solution to mitigate the negative impact of swelling clay on flotation would be to maintain high electrolyte levels in the wash water to inhibit clay swelling and dispersion.

Keywords: fine coal flotation, swelling clay, controlled dispersion, CaCl2, slime coating

1. Introduction

Swelling clays such as bentonite have an innate capacity to hydrate and disperse into thin flakes in suspension. Owing to this tendency, they cause several problems in mineral processing operations such as high pumping energy, high water consumption, and difficulties in dewatering (De Kretser et al., 1997; Lim et al., 2009). In the case of mineral flotation, previous studies have demonstrated that the presence of even small amounts of bentonite can reduce both the mineral grade and recovery compared to that of kaolinite, a type of non-swelling clay (Arnold and Aplan, 1986; Xu et al., 2003; Wang et al., 2015). These studies correlated the negative impacts with a few characteristics of the bentonite mineral such as coating of the valuable mineral surfaces by electrostatic attraction, increase in reagent consumption due to clay-rich surfaces, increase in pulp viscosity, and variations in froth stability resulting from clay aggregation (Arnold and Aplan, 1986; Polat et al., 2003; Wang and Peng, 2014). However, none of the previous studies took into account another important feature of bentonite, i.e., swelling and dispersion. Bentonite is a type of anisotropic phyllosilicate comprising silica tetrahedral (T) and octahedral (O) sheets, which form hydrogen bonds in a 2:1 (T-O-T) fashion. In sedimentary form, dry bentonite exists as stacks of this united structure aligned in a face-face orientation. On dispersion in a solution with high electrolyte concentration, especially one containing certain cations such as calcium ions, the closely packed structure can be maintained, and the swelling and dispersing behaviours are suppressed. This is because some calcium cations exchange into the interlayer space and generate an additional attractive force between the layers (Lim et al., 2009). The resultant suspension in this case would contain larger clay particles, and the net number of interactions between the clay particles would be lower. This approach has been termed as controlled dispersion by Tanihara and Nakagawa (1973), and Deason and Onoda (1984), can significantly improve the dewaterability of coal tailings (De Kretser et al., 1997). On the contrary, uncontrolled dispersion occurs when the aqueous ionic strength that initially wets the swelling clay is insufficient to suppress its dispersion into individual platelets. In this case, numerous
platelets with sheet-like particle shapes, and high aspect ratios are randomly oriented and interact in suspension, leading to high network strength and poor dewaterability. Investigations in soil science have demonstrated that spontaneous rearrangement of these disordered clay platelets into an efficient face-face orientation cannot occur without the application of significant external pressure (Pashley and Quirk, 1984), therefore dewaterability of a suspension with dispersed clay platelets can only be moderately improved by the subsequent addition of an electrolyte.

Rheology has been acknowledged as a useful index to characterize particulate suspension. In the case of clay suspension, the rheology data can be used to understand the interaction between clay particles. For example, the card-house structure resulting from the edge-face interaction is predominantly characterized by non-Newtonian flow with development of yield stress. This type of structure results in high viscosity. Face-face association leads to the formation of lamellar-structured aggregates with low yield stress requirement. The presence of clay in ores can dramatically affect pulp rheology. According to Farrokhpay et al. (2016), in the flotation of copper ore, montmorillonite significantly changes the rheology and froth stability, causing both flotation grade and recovery to decline. Other researchers indicated that the increase in yield stress and apparent viscosities reduces the probability of collision between bubbles and particles. This is due to the poor dispersion of the bubbles and the mobility of the particles in flotation cells, resulting in poor flotation performance (Bakker et al., 2009; Shabalala et al., 2011).

Additionally, clay minerals can cover the surface of valuable minerals and inhibit bubble-particle attachment. In order to explain the slime coating phenomenon, the zeta potential of fine clays and mineral particles has been measured in numerous investigations (Edwards et al., 1980; Basnayaka et al., 2017). Xu et al. (2003) suggested a method based on zeta potential distribution, individually and collectively, to characterize the slime coating of clay particles on coal. The results can be used to explain the observed depression of coal flotation by montmorillonite.

The objective of this study was to explore the dissimilar effects of controlled and uncontrolled dispersion of bentonite on fine coal flotation in identical solution chemical environments. Pulp rheology and zeta potential distribution were examined to understand how they modified slurry properties and particle interactions, and lead to different flotation behaviours. The results of the present research are expected to outline an operating window for the flotation of clay-rich ores, an endeavour that has been termed as “a mineral processing nightmare”.

2. Materials and methods

2.1. Materials

A coal sample with particle diameter in the range 0.5–6 mm was obtained from the Taixi coal preparation plant in Ningxia Province, China. The coal sample was ground to a size of ~45 μm, and the ash content of the sample was 10.8%.

The swelling clay used in this work was bentonite powder with an 80% passing of 20 μm ($P_{80} = 20 \mu m$) diameter, obtained from Suzhou Clay Group, China. The samples were separated from the as-mined bentonite only through dry preparation techniques, and did not undergo aqueous dispersion. Therefore, the naturally aligned structure was maintained.

Quantitative X-ray diffraction analysis of the bentonite sample showed that the composition of the sample was as follows: 71.3 wt.% montmorillonite, 8.9 wt.% quartz, 3.5 wt.% albite, and the remainder comprising other materials. The cation exchange capacity of the dry sample was determined to be 74 meq/100 g using the methylene blue dye method described by Hang and Brindley (1970). Analytical CaCl$_2$ purchased from Guoyao Group, China, was used to prepare CaCl$_2$ solution.

2.2. Preparation of controlled and uncontrolled bentonite suspensions

Controlled dispersion suspension was prepared by adding 12 g of the bentonite sample to 0.8 dm$^3$ of a 50 mmol/dm$^3$ CaCl$_2$ solution. This matches the calcium ion concentration of the flotation feed in the plant where the coal sample was obtained. The CaCl$_2$ concentration far exceeds the maximum amount exchanged with monovalent ions, and can effectively inhibit swelling (Lim et al., 2009). Based on the
According to the report by Lim et al. (2009), uncontrolled dispersion suspension was prepared by dispersing 12 g of the bentonite sample in 0.8 dm$^3$ of reverse osmosis-water and stirred as in the controlled case. The suspension was left to stand for 12 h to fully hydrate and swell, after which it was remixed for 5 min to well disperse. An amount of CaCl$_2$, equal to that used for controlled dispersion, was then added, and the mixing progressed for another 30 min. The resulting suspension was again left to stand for 12 h to reach chemical equilibrium.

2.3. Flotation tests
A total of 68 g of a coal sample was added to the clay suspension prepared earlier by stirring. The mixture was dispersed for 15 min using an ultrasonic bath machine with a frequency of 20 kHz, and then transferred to a 1 dm$^3$ XFDIII laboratory flotation cell. The final volume of the flotation slurry was regulated to 1 dm$^3$ by adding the required quantity of the 50 mmol/dm$^3$ CaCl$_2$ solution. The solid content in the flotation cell was about 7.4%. Industrial-grade kerosene and methyl isobutyl carbinol (MIBC) were used as a collector and a frother, respectively. The impeller speed, collector dosage, frother dosage, and air flow rate were held constant at 1800 rpm, 160 g/Mg, 240 g/Mg, and 0.04 m$^3$/h, respectively. After conditioning for 5 min, the collector and frother were added to the pulp step by step. The conditioning was performed for another 5 min. During the flotation, four concentrates were collected after cumulative times of 1, 2.5, 5, and 8 min. These concentrates and tailings were filtered, dried at 80 °C, and weighed for the analysis. Approximately 1 g of each dried product was burned in an oven at 815 °C for 2 h. The residual ash was weighed to determine the ash content of and other combustible matter of the samples. The procedure to analyze the ash and combustible content has been described elsewhere (Wang and Peng, 2013). The ash or combustible recovery of the concentrate was calculated as the percentage of ash or combustible content in the flotation feed.

2.4. Rheology measurements and froth stability
A VT500 rotational viscotester from HAAKE instruments was used for pulp rheology measurements. A total of 9 cm$^3$ of slurry was extracted from the prepared clay or clay/coal mixture while the suspension was being mixed. The sample was immediately transferred to the cup of the viscometer. A rheogram was produced in 30 s to reduce the influence of particle settling. The measurements were conducted at ambient temperature (25 °C), and the shear rate for the rheogram was between 1/s and 350/s.

The effect of bentonite dispersion on froth stability was investigated in a specially designed column that had previously been used by Xing et al. (2017) to assess the effects of the compound collector and blending frother on the froth stability. The column is 400 mm high and 50 mm in diameter. The air was introduced through a porous ceramic plate at the bottom of the column. The air flow is regulated by means of an air rotameter and air compressor. The air flow rate was maintained at 0.04 m$^3$/h. In each case, 200 cm$^3$ of flotation pulp was transferred to the column which had been conditioned with collector and frother. The froth height was recorded as a function of time since the air was introduced into the column (time $t=0$) until the maximum steady-state froth height was attained. At this point, the air supply was turned off, and froth decay was measured. The half-life of the froth, which refers to the time needed for the froth to collapse to half of its maximum height, was recorded.

2.5. Zeta potential distribution measurements
Zeta potential distribution measurements for the samples were carried out using ZetaPALS (Brookhaven, USA). The suspension prepared was sufficiently dispersed, and 20 cm$^3$ of the dispersed suspension was then transferred into a centrifugal tube by a pipette. After the suspension had settled for 10 min, a quantity of 1 cm$^3$ was extracted from the upper portion to measure the zeta potential distribution of the samples. Each measurement was repeated 10 times. The natural pH of the suspension was 7.8.
2.6. Cryogenic scanning electron microscopy (cryo-SEM) analysis

A sample of a few µdm³ of the flotation concentrates was extracted in a small metal rivet. The sample was immediately plunged into liquid nitrogen of the cryo-vitrification unit to freeze the water without allowing crystallization. The vitrified samples were then transferred to the liquid nitrogen-cooled specimen stage of a HITACHI S-4300 field emission scanning electron microscope equipped with energy dispersive X-ray spectroscopy (EDS). The frozen sample was fractured in vacuum. The sample temperature was raised from -180 °C to -100 °C for 10 min to sublime the vitrified water, and then reduced to -180 °C. Finally, the sample was coated with golden plasma before SEM imaging and EDS analysis.

3. Results and discussion

3.1. Flotation

Fig. 1 shows the combustible recovery and ash recovery as a function of flotation time. In the absence of bentonite, a maximum combustible recovery was about 97%. However, a significant decrease in the combustible recovery was observed in the presence of bentonite, both in controlled and uncontrolled dispersion. This was consistent with the results from previous studies, which showed that montmorillonite clay decreased coal flotation recovery significantly (Arnold and Aplan, 1986; Xu et al., 2003). Xu et al. (2003) reasoned that montmorillonite had a stronger affinity to coal, leading to a severe slime coating on the coal surface. This coating can hinder air bubble-coal attachment, and cause a significant reduction in coal flotation recovery.

Fig. 1. Combustible recovery and ash recovery as a function of flotation time

It is interesting to note that although the coal was floated in identical solution chemical environments, the controlled and uncontrolled dispersion suspensions showed obviously different flotation behaviours. Controlled suspension exhibited a faster flotation kinetics than uncontrolled suspension. Under the current flotation condition, a flotation time of 5 min resulted in a 74% and 65% combustible recoveries for the controlled and uncontrolled suspensions, respectively. The combustible recovery was 93% at the completion of 8 min of flotation in the case of controlled suspension. However, it decreased dramatically to 71% in the uncontrolled suspension. Ash recovery in both the cases, however, stayed at nearly the same level i.e., 16%.

3.2. Slurry rheology and froth stability

The rheological behaviours of the individual bentonite suspensions prepared via controlled and uncontrolled dispersion were investigated first. Fig. 2 shows the rheograms of two dispersions, and the relationship between shear stress and shear rate was indicated. Under conditions of controlled dispersion, the suspension behaved as a Newtonian fluid with the shear stress versus shear rate curve being linear and passing through the origin. The slope of the line, known as the viscosity, was constant and independent of the shear rate. The phenomenon implied that no aggregates were developed, and
that bentonite particles moved independently under the stress applied. However, under conditions of uncontrolled dispersion, the bentonite suspension exhibits non-Newtonian behaviour with pseudo plastic characteristics. The viscosity of this flow type decreases with increase in shear rate. It appears that bentonite forms aggregates in suspensions. Under shear force, the large clay aggregates are separated into smaller units and, under very high shear forces, into individual particles. Such a process rheologically manifests itself as shear-thinning behaviour (Cruz et al., 2015). Since the solid concentration in the two suspensions is the same, the difference in flow type could be related to the bentonite particle shape. Upon uncontrolled dispersion in solution, bentonite particles appear as thinner sheets with high aspect ratio. It is known that thinner particles can produce a higher degree of texture than can thicker compact particles of equivalent Stokes diameter, resulting in higher shear stress (He et al., 2004).

Fig. 2. Shear stress of controlled and uncontrolled suspensions as a function of shear rate

Fig. 3. Froth height as a function of time since the introduction of air

Fig. 2 also exhibits the rheograms of the controlled and uncontrolled flotation slurries containing coal and bentonite mineral. Compared to the Newtonian behaviour of the individual controlled bentonite suspension, the controlled flotation slurry displays distinct pseudo plastic characteristics and higher shear stress requirement. According to literature, the fluid change can be attributed to not only the increase in solid concentration but also the interaction between the coal and clay particles, which is examined below. Uncontrolled flotation pulps exhibit non-Newtonian behaviour like the individual uncontrolled bentonite suspension does, and reveal higher viscosity. Although its solid concentration is equal to that of the controlled flotation slurry, the uncontrolled flotation slurry produces significantly higher shear stress. For instance, at a shear rate of 100/s, its shear stress is 1.73 Pa, which is 0.83 Pa higher than that (0.90 Pa) of the controlled flotation slurry.

Fig. 3 shows the effect of bentonite dispersion type on froth stability and froth height as a function of time since the introduction of air. In the same processes, the average half-life of the froth in controlled and uncontrolled slurries was measured as 8.4 s and 9.3 s, respectively. These results are consistent with
the findings of previous researchers that froth stability is related to slurry viscosity; the higher the slurry viscosity, the more stable the froth is (Farrokhpay, 2012). However, the slight enhancement in froth stability may have no significant impact on flotation behaviours.

3.3 Zeta potential distribution

The zeta potential distributions of coal, bentonite suspensions created by the two different dispersion methods, and their mixtures with coal are compared in Fig. 4. The peaks of these curves for the individual uncontrolled and controlled bentonite suspensions were located at -26.5 mV and -13.6 mV, respectively. The peak of individual coal suspension was located at -0.17 mV.

For the uncontrolled bentonite-coal mixture, the distribution was a bimodal curve similar to that of the individual uncontrolled bentonite suspension, and the peak values measured were also extremely close in the two cases. The corresponding distribution peak for the coal suspension alone disappeared in the curve. According to reports by Xu et al. (2003), the results indicate that all the coal particles are almost fully covered by the bentonite particles, which accounts for the observed depression of coal flotation as shown in Fig. 1. For the controlled bentonite-coal mixture, the peaks were located somewhere between those of the controlled bentonite suspension and coal suspension alone. This implies that some of the bentonite particles partially coated the coal particles while some others remained as individual particles in the suspension of the mixture.

![Fig. 4. Zeta potential distribution of controlled and uncontrolled dispersions of bentonite alone and in mixture with coal in the presence of 0.5 mmol/dm³ CaCl₂ at pH 7.8](image)
3.4 Cryo-SEM image analysis

Fig. 5 shows the representative cryo-SEM images of the concentrates from the flotations of controlled and uncontrolled slurries. The particles chosen for EDS analysis are indicated by the arrows in Fig. 5. Fig. 6 shows that the results of the two analyses are the same. As shown in Figs. 5 a1 and 5 a2, some small separated particles are coated on the surface of large coal particles. The EDS analysis of these particles detected Si and Al signals clearly, which confirmed that these small particles are bentonite minerals. In this case, the bentonite mineral appears as particles containing closely packed platelets associating in the face-face manner. However, in Figs. 5 b1 and 5 b2, it can be seen that many coal particles were coated with an extensive three-dimensional porous structure. The results of the EDS analysis confirmed that these were also clay minerals. The extensive porous structures resulted from the bentonite platelets associating in the edge-edge and edge-face manners. The covered surface of the coal particles in uncontrolled concentrates was evidently larger than that in controlled concentrates.

Fig. 5. SEM images of concentrates from controlled slurry flotation (a1, a2) and uncontrolled slurry flotation (b1, b2)

Fig. 6. EDS analysis of particles indicated by arrows in Fig. 5

In the controlled slurry, bentonite minerals appear as separated particles with a lower aspect ratio i.e., ratio of particle diameter to thickness. These particles have an overall negatively charged surface. Meanwhile, the coal surfaces also exhibit a negative charge. Theoretically, the electrostatic forces between the coal and bentonite particles are repulsive, and hence slime coating was not expected to
occur. However, the coating of bentonite particles on coal was evidently identified by the zeta potential distribution measurements and cryo-SEM analysis. For the slime coating of clay on coal, Oats et al. (2010) calculated the interaction force between coal and clay using the DLVO theory, and suggested that van der Waals attraction, and not the double-layer force, was the driving force. In the uncontrolled slurry, bentonite mineral had dispersed into numerous thin flakes, even into individual platelets with higher aspect ratio and greater negative charge. These units interact in edge-face and edge-edge manners and form voluminous, three-dimensional card-house structures. Obviously, the interaction force between coal and clay cannot be calculated using the DLVO theory in this case. By integrating all the information gathered in this study, we can deduce that the three-dimensional aggregates coated on the coal surface are strong sufficiently to undergo flotation, and are subsequently recovered into the concentrate. Obviously, the extent of coating on the surface of the coal particles by the three-dimensional structure far exceeds that by the separated bentonite particles in the controlled slurry. This could account for the lower combustible recovery in uncontrolled flotation. On the other hand, the three-dimensional aggregates enhance the rheology of the flotation slurry. Patra et al. (2012) identified that pulp rheology had a strong effect on the selective separation of Ni minerals from the fibrous minerals entangled in the flotation slurry, leading to the formation of large networks with a simultaneous increase in pulp viscosity and the subsequent poor flotation of Ni minerals. According to previous investigations, the higher viscosity resulting from the three-dimensional structure of bentonite inhibited the mobility of the coal particles and mineralized bubbles in the pulp phase, and also impeded particle-bubble attachment, which subsequently caused combustible recovery to decline.

The practical application of controlled dispersion would entail high overall salinity levels and calcium ions in the wash water. Through control of solution chemistry of the process water that swelling clays first encounter whether in coal processing plant or the mine, the clay particles will remain closely packed in a face-face association.

4 Conclusions

The current study found that dispersion type of swelling clay has a significant effect on fine coal flotation. Uncontrolled dispersion of swelling clay results in significant reduction of combustible recovery compared with controlled dispersion because the resultant high slurry viscosity can reduce the mobility of bubbles and coal and, thereby, the frequency of bubble-coal collisions. Additionally, the decrease in combustible recovery is also attributed to the severe slime coating of the extensive three-dimensional clay structure on coal. The extent of coating far exceeds that by the separated bentonite particles in the controlled slurry. The separated bentonite particles with low aspect ratios in controlled dispersion lead to a lower slurry viscosity and partially slime coating, consequently a higher combustible recovery.

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References


