Research Article

Mechanism Underlying Bonding Water Film Effect on Rheological Parameters

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From experiments on bonding water of different slurries and the analysis of flow curves, the bilinear fluid model has been improved. The results showed that the rheological parameters correspond to physical processes at different stages of shear strain. As shear rate increases, slurries evolve from high-viscosity Bingham fluids to low-viscosity Bingham fluids. Specific surface area determines the number of edge-to-face arrangements; mineral composition influences the binding strength of each edge-to-face arrangement; and the volume fraction of particles regulates the distance between clay particles and number of edge-to-face arrangements.

1. Introduction

The rheological behavior of slurries has been the focus of attention in many engineering applications such as hydraulic dredging [1], well drilling [2], slurry shield tunneling [3], and paper industry [4]. The physical state of a clay may change with increasing water content: from a solid to a semirigid plastic, then to a gel, and finally to a suspension. Water in slurries is classified as being either adsorption water, capillary water, or free water depending on its distance from the surfaces of clay particles [5]. The rheological behavior of a clay-water system is determined by the forces that control the spatial arrangement and dynamics of clay particles with bonding water. These forces which mainly related to the particle hydration slow down the dynamics of water molecules within the force field of the clays. Thus, the forces increase the viscosity of slurry and modify its rheological behavior. But the effects of bonding water on the rheology of slurry are not yet well understood.

The non-Newtonian rheological characteristics of slurries depend on the particle size distribution [6] and the number and lifetime of the particle bindings [7] and are obviously related to volume fraction of particles in slurries [8]. A previous study pointed out that a slurry with more clay minerals has higher yield strength [9] because of the relationship between moisture and friction of the minerals [10]. Moreover,

the thickness of bonding water films positively relates to cation exchange capacity (CEC) [11].

The Bingham model is usually used to describe slurries of high water content [12]. When water content decreases, slurries become fluids displaying power-law fluid with yield stress [13] and can be described by the Herschel-Bulkley model [14]. In ranges of lower shear stress, edge-to-face arrangement of clay mineral lamellae causes elasticity [15, 16]. Viscoelastic behavior certainly occurs, but it liquefies in the upper stress range. So some researchers believe slurry can be described by a complex model combining the Bingham model at low strain rate and the Herschel-Bulkley model at high strain rate [17]. Also, it can be described by a bilinear fluid model combining the description of a pseudo-Newtonian fluid at low strain rate and a Bingham fluid at high strain rate [18–20]. Actually, slurries under shearing produce a fast layer that transfers momentum to an adjoining layer of slower speed, with the value of yield stress reflecting the rate of flux of momentum [7]. However, the variation of microcell resisting shear force with macroscopic model parameters is still unclear.

This study on slurries improves the bilinear fluid model providing a better fit to actual flow curves and better analysis of effects of specific surface area (SSA), mineral composition, and volume fraction of particles (ϕ_c) on rheological properties. The correspondence between rheological parameters

FIGURE 1: Particle size distribution curve of slurries.

TABLE 1: Physical properties of slurries.

Slurry type	Specific gravity	Liquid limit (%)	Plastic limit (%)	Clay fractions ^a (%)	SSA (m ² /g)	CEC (mEq/100 g)
Sed	2.68	56	29%	26.3%	37.2	41.3
Sed ⁽⁺⁾	2.68	68	37%	56.4%	79.5	89.1
Sed ⁽⁻⁾	2.68	47	24%	15.2%	17.4	18.3
K	2.65	39	23%	29.7%	31.9	6.7
Bent	2.75	162	51%	26.2%	552.7	93.4

^a<5 μm.

and microscopic physical processes when slurries undergo shearing is also discussed.

2. Materials and Methods

2.1. Preparation of Slurries. Five groups of slurries were used in experiments: original sediment (Group Sed, from Taihu Lake, Jiangsu province, China), sediment with added clay fractions (Group Sed⁽⁺⁾), sediment with reduced clay fractions (Group Sed⁽⁻⁾), kaolin with distilled water (Group K, from Hebei province, China), and bentonite with distilled water (Group Bent, from Jiangsu province, China). The 4.5% organic matter in Group Sed was extracted using H₂O₂ in pretreatment, and Group Sed was divided into Group Sed⁽⁺⁾ and Group Sed⁽⁻⁾ using the hydrostatic settlement method. The particle size distribution for each group was measured with Mastersizer 2000 laser particle characterization system (Malvern Instruments Ltd., Malvern, UK) using pure ethyl alcohol as dispersion medium. Distribution results for Group Sed, Group K, and Group Bent were similar when particle size is less than 10 μm (Figure 1). The physical properties of clay

TABLE 2: Mineral composition analysis.

Slurry type	Illite	Kaolin	Montmorillonite	Quartz
Sed	61.4%	13.2%	4.8%	20.6%
K	2.5%	90.1%	1.2%	6.2%
Bent	2.8%	1.7%	95.3%	0.2%

particles in slurries are listed in Table 1. Results of analysis for the mineral composition from X-ray diffractometry are listed in Table 2.

2.2. Instrumentation and Methods. The measurements of the flow curves of the slurry groups were obtained by using a rotational rheometer (NXS-11B, Chengdu Instrument Factory, Chengdu, China) which was equipped with a concentric cylinder geometry [21]. The rheometer has 5 test systems for testing various slurries (Table 3) and 15 grades of rotation speed in the range of 5.6~360 r/min. The measuring ranges of the rheometer and shear stress are 2.8~1.78 × 10⁷ mPa·s and 27.67~21,970 Pa, respectively. The rheometer has 5 test

FIGURE 2: The variation of typical flow curves with water content. (a) Plot of log shear stress versus log shear rate. (b) Plot of log apparent viscosity versus log shear rate.

TABLE 3: Test systems of NXS-11B type rotational rheometer.

Test system	A	B	C	D	E
Diameter of inner bob (cm)	4	4	2	2	2
Diameter of outer cup (cm)	3.846	3.177	1.460	0.862	0.432
Height of inner bob (cm)	7	5	3	1.5	0.7
Specimen volume (mL)	20	60	9	10	12

systems for testing various slurries (Table 3). All the measurements were carried out at a constant temperature of 25°C.

To measure the adsorption water content, the following procedure was used: add some dry clay powders with mass m_s into a volumetric flask with enough distilled water. When the clay reaches adsorption saturation, the water volume would shrink ΔV . The mass ratio of absorption water and dry clay can be calculated from

$$w_b = \frac{\Delta V \rho_b \rho_f}{m_s (\rho_b - \rho_f)}, \quad (1)$$

with the density of distilled water being $\rho_f = 1.0 \text{ g/m}^3$. The average density of adsorption water in typical clay is $\rho_b = 1.4 \text{ g/m}^3$ [22].

3. Results

3.1. Rheological Behaviors of Slurries. The flow curves of five groups of slurries are obtained through the controlled shear rate test. Take Group Sed⁽⁺⁾ as an example; typical curves plotted in a log-log scale are shown in Figure 2. The results showed that all flow curves of the slurries had a similar

FIGURE 3: Determination of dynamic yield stress, Bingham yield stress, plastic viscosity of low shear rate region, and plastic viscosity of high shear rate region for the Group Sed⁽⁺⁾ sample at a water content of 113.5%.

tendency that at high water content they were close to indicating ideal Bingham fluids; and at low water content, the flow curves exhibit both pseudoplastic (shear-thinning) and viscoplastic (presence of a yield stress) behavior.

Values for the rheological parameters are deduced from the flow curves. To illustrate, we take the data for Group Sed⁽⁺⁾ at water content of 113.5% as an example (Figure 3).

FIGURE 4: Schematic diagram of improved bilinear fluid model.

To describe precisely the physical meaning of the rheological parameters, the bilinear fluid model was improved as follows:

$$\tau = \begin{cases} \tau_0 + \eta_l \dot{\gamma} & (\dot{\gamma} \leq \dot{\gamma}_c) \\ \tau_c + \eta_h \dot{\gamma} & (\dot{\gamma} > \dot{\gamma}_c) \end{cases}. \quad (2)$$

There are some rheological parameters: τ_0 is the dynamic yield stress, which is explained as the extrapolated stress from the low shear rate region. At stresses below this yield stress, the slurry behaves like a solid. τ_c is the intersection of the linear part of high shear rate region on the rheogram and the vertical coordinates (as shown in Figure 3), which can be called the Bingham yield stress [19]. η_l and η_h are the plastic viscosities (PV) which correspond to the gradient of the linear part of the rheogram in low shear rate region and high shear rate region, respectively. $\dot{\gamma}_c$ is the shear rate in the transition region (at this shear rate $\tau = \tau_{ya}$, which can be defined as the apparent yield stress [19]). Usually, τ_{ya} is a little higher than τ_c on the rheogram. For convenience sake, τ_{ya} is approximately equal to τ_c .

Viscoplasticity material can be described by an appropriate mathematical model, and the basic components used to describe the viscoplastic properties are friction elements and Newton sticky pots. According to the proposed model in (2), a mechanical model is represented schematically in Figure 4. The model consists of two friction elements and two Newton sticky pots. At stresses below the dynamic yield stress, the friction element τ_0 remains rigid and $\dot{\gamma} = 0 \text{ s}^{-1}$. As soon as the strain energy exceeds the level required by the von Mises criterion [23], the elastic stress in the friction element attains the yield value and the friction element τ_0 breaks allowing deformation of Newton sticky pot η_l . Consequently, the slurry predicts a Bingham fluid behavior of high viscosity at low shear rate ($0 < \dot{\gamma} \leq \dot{\gamma}_c$). As the shear rate exceeds $\dot{\gamma}_c$, the friction element τ_c breaks and the whole system predicts a Bingham fluid behavior of low viscosity at high shear rate ($\dot{\gamma} > \dot{\gamma}_c$) due to the Newton sticky pot η_h .

In general, as water content decreased, all flow curves of slurries evolved along a pathway describing a Newton fluid, a Bingham fluid, and then a power-law fluid with yield

FIGURE 5: Sectioning of fluid type by the ratio of plastic viscosities in the improved bilinear fluid model.

TABLE 4: Adsorption water-dry clay mass ratio.

Slurry type	Bound water-dry clay mass ratio
Sed	0.1156
Sed ⁽⁺⁾	0.2565
Sed ⁽⁻⁾	0.0513
K	0.0132
Bent	0.2143

stress. This trend could be described using a ratio of plastic viscosities (PV):

$$I_{PV} = \frac{\eta_l}{\eta_h}. \quad (3)$$

To evaluate the shear-thinning behavior, the relationship between I_{PV} and ϕ_c is plotted in Figure 5. If $I_{PV} = 5$ and $I_{PV} = 15$ are taken as the lower and upper limits, respectively, for Bingham fluids, the I_{PV} distribution for Group Sed, Group Sed⁽⁺⁾, and Group Sed⁽⁻⁾ evolves along the same pathway with increasing ϕ_c . However, the I_{PV} distribution of Group Bent retains the character of a power-law fluid with yield stress, whereas Group K retains Bingham fluid characteristics even at high ϕ_c .

3.2. Adsorption Water Content. The adsorption water-dry clay mass ratio w_b of all groups is listed in Table 4. Obviously, slurry groups with high value of SSA and CEC have larger w_b .

4. Discussion

4.1. Relationship between SSA and Rheological Behaviors. In comparing Group Sed, Group Sed⁽⁺⁾, and Group Sed⁽⁻⁾, which are of similar mineral composition but different SSA, their bilinear rheological parameters were found to be entirely different (Figure 6).

FIGURE 6: Bilinear rheological parameters of Group Sed, Group Sed⁽⁺⁾, and Group Sed⁽⁻⁾.

Supposing the adsorption water was evenly distributed over the clay particle surface, the thickness of the adsorption water film δ_b is then obtained from

$$\delta_b = \frac{w_b m_s}{\rho_b m_s \text{SSA}} = \frac{w_b}{\rho_b \text{SSA}}. \quad (4)$$

With the existing data, the thickness ratio of the adsorption water film for each of the three groups is $\delta_b(\text{Sed}) : \delta_b(\text{Sed}^{(+)}) : \delta_b(\text{Sed}^{(-)}) = 1 : 1.04 : 0.95$. This implies that the same mineral composition leads to the same charge density on the particle surface and consequently the same thickness of bonding water, irrespective of SSA. Therefore, the bonding strength of every edge-to-face arrangement was almost the same in slurries at similar ϕ_c . Nevertheless, slurries with higher SSA had more edge-to-face arrangements, leading to differences in macroscopic rheological parameters among the groups. Moreover, all τ_0 and τ_c , as well as all η_l and η_h , were close when $\phi_c = 0.15$. That implies that slurry viscosity derives mainly from hydration forces from capillary

water because of greater distances between particles and less edge-to-face arrangements. In this situation, SSA had little influence on rheological behavior. However, such an influence would be more obvious if ϕ_c increased.

4.2. Relationship between Mineral Composition and Rheological Behavior. Comparing Group Sed, Group K, and Group Bent, which have very similar particle size distributions but different mineral compositions, their bilinear rheological parameters were also found to be entirely different (Figure 7).

The thickness ratio of the adsorption water for each of three groups is $\delta_{bw}(\text{Sed}) : \delta_{bw}(\text{K}) : \delta_{bw}(\text{Bent}) = 1 : 0.13 : 2$. The specific surface area can be very large. The primary surface area of montmorillonite, that is, the surface area exclusive of interlayer zones, ranges from 50 to 120 m²/g [24]. Thus, the SSA for Group Bent was weighted by a hypothetical factor 1/16 to account for the large difference between internal and external surface areas. The same particle size distribution implies an equal number of edge-to-face arrangements,

FIGURE 7: Bilinear rheological parameters for Group Sed, Group K, and Group Bent.

whereas thickness differences in adsorption water reflected differences in charge density over the mineral surfaces. The surface charge density is obtained from

$$\sigma = \frac{\text{CEC}}{\text{SSA}} F, \quad (5)$$

where F is Faraday's constant, C/mol.

The charge density was positively related to CEC, and the fractional ratio for the three groups of $\sigma(\text{Sed}):\sigma(\text{K}):\sigma(\text{Bent}) = 1:0.18:2.43$ was close to the thickness ratio of adsorption water film. With higher charge density, the particle can adsorb more hydration cations. This leads to thicker bonding water films and higher bonding strength in edge-to-face arrangements. Therefore, surface charge density had a decisive influence on rheological parameters. However, for slurries at low ϕ_c , the rheological parameters were similar in value as described earlier.

4.3. Internal Mechanism of Rheological Behaviors. The rheological properties of clay minerals depend on the particle structure. The clay mineral lamellae generally carry negative charges on their faces and positive charges on their edges [25]; thus the card-houses structure can be formed. The edge-to-face arrangements are the major binding elements in clay-water systems (Figure 8). The high viscosities are due to the existence of flocs which contain immobilized suspending fluids in their structures, and the effective particle volume fraction is increased. When slurries undergo shearing, the impulse is passed from fast to slow flocs due to differences in speed between adjacent layers. In this process, there are three stages depending on shear rate.

Stage I. If shear rate is extremely low, the shear force imparted is less than the bonding strength of the edge-to-face arrangements. The floc would not distort and the macroscopic shear strength equaled the dynamic yield stress τ_0 . This indicated

FIGURE 8: Various stages of edge-to-face arrangements under shearing.

that the slurries possessed a very strong solid-like behavior rather than a liquid-like behavior.

Stage II. If the shear rate is low and less than $\dot{\gamma}_c$, the shear stress is greater than τ_0 . The floc begins to distort, and a short distance appeared in the edge-to-face arrangement. However, the particles are still subjected to surface charge attraction. The internal friction of slurries mainly comes from hydration of the adsorption water, leading to a higher viscous coefficient η_l . Once the shear rate reaches $\dot{\gamma}_c$, the effect of adsorption water maximizes and subsequently the macroscopic shear strength equals τ_c .

Stage III. If the shear rate exceeds $\dot{\gamma}_c$, the effect of adsorption water gradually weakens. The internal friction of slurries mainly stems from hydration of the capillary water, leading to a lower coefficient of viscosity η_h .

Moreover, shear rate and volume fraction of particles are primarily important, because these rheological parameters reflect not only the strength of edge-to-face arrangements but also the number of such arrangements. In slurries with low ϕ_c , large separations between flocs led to less efficient edge-to-face arrangements. As a result, all macroscopic rheological parameters are low in value.

5. Conclusions

The improved bilinear fluid model describes more precisely the rheological curves of slurries. If the shear rate is around zero, the edge-to-face arrangement mainly produces binding forces among particles which then is seen as a dynamic yield stress τ_0 at the macroscopic scale. The separation in edge-to-face arrangements is stretched with increasing shear rate, and slurries appear as Bingham fluids characterized by high coefficients of viscosity η_l as a consequence of hydration of high-density adsorption water. Once the shear rate exceeds $\dot{\gamma}_c$, the separation in edge-to-face arrangements weakens binding from adsorption water. Capillary water and free water dictate the behavior of slurries which appear as Bingham fluids characterized by yield point τ_c and low coefficient of viscosity η_h .

Slurry groups of the same mineral composition but different SSA had different rheological parameters. The primary reason is the difference in number of edge-to-face arrangements, although the thickness of bonding water and the binding strength of each arrangement were similar. Slurry groups with the same SSA but different mineral compositions had different rheological parameters. This is because the surface charge densities of different minerals are not equal, leading to difference in binding strength of edge-to-face

arrangements. Clay minerals with higher surface charge densities have thicker bonding water films. Volume fraction of particles can affect the spacing between particles and the number of edge-to-face arrangements. If $\phi_c < 0.15$, the effect of hydration on particles could be ignored; thus the rheological parameters of all slurry groups were close.

Competing Interests

The authors declare that they have no competing interests.

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