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Research paper

Shear-thinning behaviour of dense, stabilised suspensions of plate-like particles. Proposed structural model.

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ABSTRACT

A structural model was developed to describe the shear-thinning behaviour of dense, stabilised suspensions of plate-like particles. The model is based on the following main assumptions: the particles are distributed in more or less compact layers, oriented parallel to the flow; the particles are assumed to behave as hard disks, disk thickness being the sum of crystal thickness plus twice the Debye length; when the shear stress increases, the orientation of the plate-like particles in the flow direction also increases, thus increasing layer compactness. In order to test the proposed model, a kaolin was selected and characterised. The kaolin was used to prepare more than 40 aqueous suspensions, modifying the solids volume fraction between $\phi = 0.20$ and $\phi = 0.475$ and the dispersant (sodium silicate) content between $X_s = 0.075$ and $X_s = 0.225$ mg dispersant/m^2 solid. The flow curves of all suspensions were determined in the quasi-steady state. The results confirmed the validity of the model to satisfactorily describe the combined effect of ϕ and X_S on the flow curves in the shear-thinning range.

1. Introduction

Certain technologies used to refine and improve the industrial properties of kaolins (such as modern wet processing) and most practical applications of kaolins (such as the processing of ceramics or paper) need highly concentrated, stable kaolin dispersions with controlled rheological properties. To prepare homogeneous suspensions of kaolin with up to 70% (*w*/*w*) solids, anionic dispersants, mainly involving silicates, polyphosphates, and polyacrylates, are added (Bergaya et al., 2006).

The rheological behaviour of dense suspensions of plate-like particles is very complex, even for well-stabilised dispersions. In fact, it was verified in a previous paper (Amorós et al., 2010) that the flow curves of electrostatically well-stabilised, highly concentrated kaolin dispersions exhibit a shear-thinning segment that is sometimes followed by a shear-thickening segment. Although much theoretical and experimental work has been done, no theory currently appears fully able to predict the evolution of the flow curves with volume fraction in the case of anisotropic particles (Philippe et al., 2013). For colloidal hard spheres, the first and one of the most appropriate ways to calculate the effective hard sphere diameter was the Barker–Henderson model, based on the perturbation theory for fluids, developed in the 1960s (Barker and Henderson, 1967) (Barker and Henderson, 1976). Subsequently, various authors (Russel and Gast, 1986) (Krieger, 1972) (Beenakker, 1984) (De Kruif et al., 1985) have consequently advocated the use of effective approaches to link suspension viscosity and volume fraction. In that context, in previous papers (Amorós et al., 2010) (Amorós et al., 2012), the rheological properties of well-stabilised dispersions of kaolin were interpreted by considering the thickness of the plate-like particle with its ionic double layer as an effective thickness. The effective volume fraction of the dispersions, calculated from the ionic strength of the resulting solutions and the average thickness of the clay mineral particles, described well the combined effect of the solids volume fraction and the dispersant additions on dispersion rheological properties such as plastic viscosity and extrapolated yield stress, both determined by applying the Bingham model, or the storage modulus and the loss (or damping) factor, both determined in a linear viscoelastic regime.

Some authors (Philippe et al., 2013) (Michot et al., 2009) (Paineau et al., 2011) (Bihannic et al., 2010), adapting Quemada's equation (Quemada, 1977) (Quemada, 1998) for hard spheres to the case of disk-like particles (natural swelling clay minerals), were able to rationalise the evolution with size and volume fraction of viscosity, at different shear stresses. In this approach, the effective volume fraction accounts for the fluid volume trapped by the particles through their average motion, which depends on the volume fraction of spheres with excluded volume encompassing the particle, and an orientation parameter, which depends on shear stress. In fact, as shear stress increases, the confinement of the particles along the velocity streamlines also increases, "shrinking" the effective volume of the particles. This interpretation is in agreement with the strong shear-thinning behaviour of dense, well-stabilised suspensions of plate-like particles.

The structural model developed in the present paper is based on an idealised structure in which the particles form more or less compact

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layers, oriented to the flow. The variable selected to characterise the structure of the dispersion is the ratio of the average interlayer distance to the effective thickness of the plate-like particles. This dimensionless variable, which determines the relative viscosity of the suspension, can be related to the effective volume fraction (used in previous papers (Amorós et al., 2010; Amorós et al., 2012)) and layer compactness by geometrical arguments. The effect of shear stress on relative viscosity, in this model, is quantified by the evolution of layer compactness with shear stress. Thus, when the shear stress increases, the plate-like particles become more oriented in the flow direction, increasing layer compactness and the dimensionless interlayer distance.

In order to test the proposed model, a kaolin was selected and characterised. The kaolin was then used to prepare more than 40 aqueous suspensions, modifying the solids volume fraction between $\phi = 0.20$ and $\phi = 0.475$ and the dispersant (sodium silicate) content between $X_s = 0.075$ and $X_s = 0.225$ mg dispersant/m^2 solid. The flow curves of all suspensions were determined in the quasi-steady state.

2. Development of the structural model to obtain the relationship between the flow curves, ϕ, and X_S, for dense, stabilised dispersions

2.1. Relationship between suspension viscosity (η), ϕ and X_S at constant shear stress (σ)

A structural model was used, based on the following assumptions:

i) At high shear rates, $\dot{\gamma}$, it may be assumed, in a first approach, that the plate-like particles are oriented parallel to the flow, forming compact layers (Fig. 1). For this structure:

$$\frac{h}{e} = \frac{V_{total} - V^p_{layer}}{V^p_{layer}} = \frac{\phi^p_{layer} - \phi}{\phi} \tag{1}$$

where V_{total} and V^p_{layer} are the volumes of the suspension and the particle layer, h is the interlayer distance and ϕ and ϕ^p_{layer} are the solids volume fractions of the suspension and the layer, respectively.

ii) It is assumed that the kaolin particles behave as thin disks, of identical thickness, "e", with diameters that display a wide distribution (Fig. 1), as a result of which the compactness of the ordered layer, $\phi^p_{max} = \phi^p_{layer}$, can reach a value of 0.9 (Qazi et al., 2010). The ratio of the average inter-particle separation, "h", to thickness, "e", or the dimensionless average distance, h*, then becomes:

$$h* = \frac{h}{e} = \frac{\phi^p_{max} - \phi}{\phi}. \tag{2}$$

iii) In view of the pronounced effect of the inter-particle dimensionless average separation distance, h*, on suspension viscosity (analogous to that of ϕ on η) (Amorós et al., 2010) (Quemada, 1998) (Amorós et al., 2002), the following expression was chosen to describe this effect:

$$-\frac{d\ln\eta}{dh^*} = -\frac{d\eta}{\eta dh^*} = B\frac{1}{(h^*)^2} \tag{3}$$

where B is the proportional coefficient.
When infinite dilution is taken as boundary condition, i.e. when

$$\phi \to 0, h^* \to \infty, \eta = \mu \tag{4}$$

where μ is the viscosity of water.
Integrating Eq. (3) with boundary condition (4) yields:

$$\eta_R = \frac{\eta}{\mu} \cdot \exp\left(\frac{B}{h^*}\right). \tag{5}$$

This equation also obeys the divergence condition, i.e. for $h^* = 0, \eta = \infty$.
Substituting Eq. (2) into Eq. (5) then gives:

$$\eta_R = \exp\left(\frac{B \cdot \phi}{\phi^p_{max} - \phi}\right). \tag{6}$$

iv) If it is assumed that the orientation of the particles to the flow is not completely parallel, which is what generally occurs, including at high shear stresses (Philippe et al., 2013) (Bihannic et al., 2010) (Fig. 2), using the same geometric arguments as in i), one obtains:

$$\frac{h}{c} = \frac{\phi_{layer} - \phi}{\phi} \tag{7}$$

where "c" is the layer thickness, which is always greater than "e", the particle thickness, and ϕ_{layer} is its volume fraction, which is always smaller than ϕ^p_{max}, corresponding to the compact layer.
Thus, by geometry, the following is obeyed:

$$\frac{c}{e} = \frac{\phi^p_{max}}{\phi_{layer}} > 1. \tag{8}$$

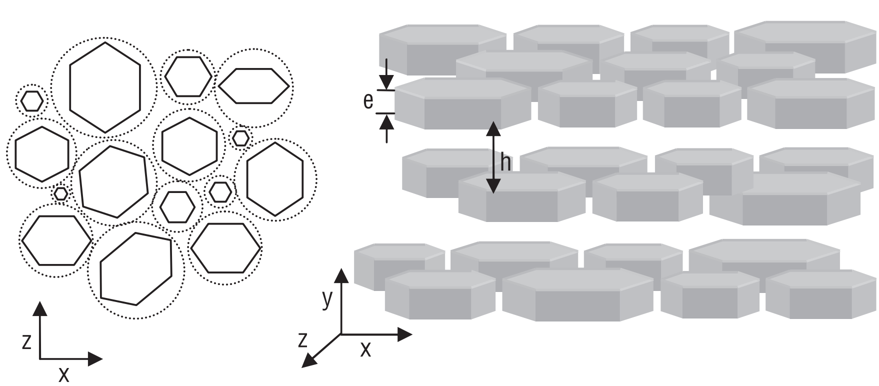

Fig. 1. Idealised structure of the kaolin suspension. Particle layers and particles entirely oriented to the flow. Flow is in the x-direction.