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A modified model for the viscosity of ceramic suspensions

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Abstract

The viscosity and shear rate as a function of 2–24% volume concentration of solids was determined for alumina and kaolin slurries. A model of viscosity as a function of volume concentration of a dispersed phase in a matrix and a bidimensional balance of forces acting on a particle in suspension is presented. The theoretical model was compared with experimental data accomplished with a double concentric cylinders rheometer. A good correlation of the proposed model with the measured data could be verified. The forces of mechanical origin that cause restrictions to particle rotation and translation appear to remarkably influence the variation of viscosity.

Keywords: Viscosity; Ceramic slurries; Ceramic suspensions; Volume concentration of solids

1. Introduction

Understanding and controlling the properties of suspensions in wet processing of ceramics is essential for designing equipments, reducing production costs and tailoring products microstructure. Increasing the amount of solids in suspension, which means decreasing viscosity to a certain level, is an objective to be reached, because removal of water through drying is usually a cost intensive process.

Viscosity is a property related to the resistance of a fluid to flow when submitted to a shear stress or a speed gradient. This phenomenon is similar to the attrition that delays the motion of a solid block on a surface. This approach suggests that the viscosity of fluids can be understood as a macroscopic manifestation resulting of intermolecular and/or interparticle attritions inside the system. A larger or smaller attrition can be associated to the attraction and repulsion forces of electromagnetic and/or mechanical origin, like particles rotation and translation. In suspensions of colloidal particles (<1 μm), the attrition caused by interactions of electromagnetic origin becomes more important than for particles of larger diameter, in which the variation of viscosity is affected mainly by attrition originated from mechanical forces.

Models of viscosity as a function of volume concentration of solids have been developed since the first decades of the 20th century. Einstein [1] made hydrodynamic calculations related to suspensions of rigid, identical spherical particles. Experimentally Einstein's model was validated only for dilute suspensions ($<2\%$ volume of solids), where the attrition produced by mechanical forces causes little influence on viscosity. In practice, the particles are generally anisometric and the volume concentration in suspensions of industrial interest is much higher, which makes the influence of the hydrodynamic attrition significant. In this paper a mathematical model to describe the viscosity as a function of the volume concentration of solids in a suspension of ceramic particles, considering the influence of hydrodynamic forces, is presented.

2. Models of suspension viscosity as a function of solids concentration

Concentration is a way of correlating the amount of phases in a multiphase system. Depending on the physical state of the phases, e.g. solid–solid or solid–liquid, different forms of representing concentration are convenient. In a solid–liquid system, the volume fraction of a phase is more usual. In a solid–solid system the Fullman

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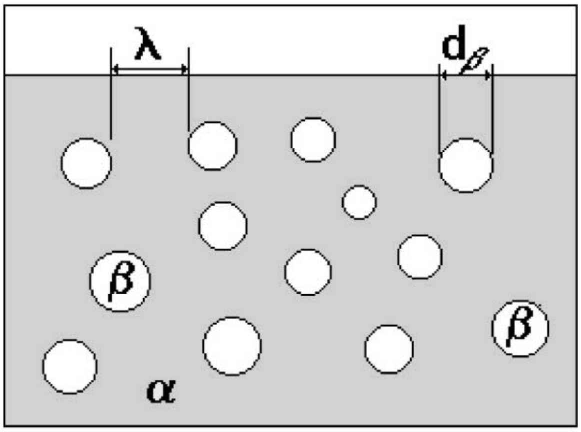


Fig. 1. A typical two-phase system.

model of the mean free path λ [2] can also be used, as shown in Fig. 1, meaning an average distance between two particles of phase β having an average size d_β in a matrix of phase α. In a suspension of solid particles in a liquid medium, the solid dispersed phase corresponds to β and the liquid matrix phase corresponds to α.

The mean free path λ is defined as:

$$\lambda = \frac{2}{3} d_\beta \frac{(1-\phi_\beta)}{\phi_\beta} \tag{1}$$

where ϕ_β is the volume fraction of phase β in the system $\alpha+\beta$, and d_β is the average diameter of phase β.

The viscosity of a suspension η_s is expressed commonly as a relative viscosity η_r, defined as:

$$\eta_r = \frac{\eta_s}{\eta_\alpha} \tag{2}$$

where η_α is the viscosity of the liquid phase α.

Several models of η_r have been developed as a function of ϕ_β. Rutgers [3] had compiled a list of over 100 such equations. Some of the most popular ones are referred to as follows by the respective authors in chronological order:

- Einstein [1]

$$\eta_r = 1 + k_h\phi_\beta \tag{3}$$

where k_h is an apparent hydrodynamic shape factor of the particle that is 2.5 for a very dilute suspension ($\phi_\beta < 2\%$) of noninteracting spheres [4].

- Mooney [5]

$$\eta_r = \exp\left[k_h\phi_\beta/(1-k_2\phi_\beta)\right] \tag{4}$$

where k_2 is a constant.

- Krieger and Dougherty [6]

$$\eta_r = 1 - (\phi_\beta/\phi_{\beta cr})^{-k_h\phi_{\beta cr}} \tag{5}$$

where $\phi_{\beta cr}$ is the packing factor at which flow is blocked.

3. Suspension viscosity as a function of mean free path

Rodrigues Neto [7] proposed that the viscosity of suspensions could be written in terms of mean free path λ.

$$\eta_r = a\frac{1}{\lambda^n} \tag{6}$$

where a, n are constants.

This model follows a power law where the constant a represents the viscosity value when λ tends to zero and the exponent n defines the slope of the curve.

When the limit is applied to Eq. (6) with λ tending to infinite, the relative viscosity tends to zero.

$$\lim_{\lambda\to\infty} a\frac{1}{\lambda^n} = 0 \tag{7}$$

In conditions of infinite free mean path, the result should be the unity because only the liquid phase is present and, therefore, the relative viscosity is 1. The model can be written again as:

$$\eta_r = 1 + a\frac{1}{\lambda^n} \tag{8}$$

4. Balance of forces on a particle in suspension

Another approach for the problem of particles in suspension is to consider the forces of the particle–particle and particle–medium interactions. For instance, a bidimensional balance of forces acting on particles in suspension was presented by Hong [8], as shown in Fig. 2.

In this case, each component of force can be expressed as follows:

- F_d is the linear restrictive force, according to the Stokes' law;
- F_{dl} is the force of hydrodynamic thrust;
- F_g is the gravitational force;
- F_p is the force of interaction particle–particle;
- F_{sl} is the force of hydrostatic thrust;
- M_r is the rotational restrictive force;
- v is the linear velocity; and
- ω is the angular velocity.

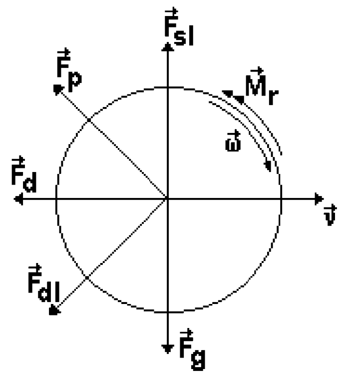


Fig. 2. Bidimensional balance of forces on a particle in suspension (adapted from Hong [8]).

Some assumptions can be made to simplify this balance:

- the particles are large enough (larger than colloidal size), so that the particle–particle interactions F_p can be neglected;
- the forces of hydrostatic F_{sl} and hydrodynamic F_{dl} thrust and the gravitational force F_g can be neglected, in other words, the vertical movement is irrelevant;
- the linear velocity equals the angular velocity on the particles surface; and
- the particles do not adsorb water.

After those considerations only the rotational restrictive M_r and translational F_d forces are considered:

$$M_r = -8\pi\eta_\alpha r_\beta^3\omega \tag{9}$$

$$F_d = -6\pi\eta_\alpha r_\beta v \tag{10}$$

where r_β is the particle radius.

Knowing that:

$$v = \omega r_\beta \tag{11}$$

and combining Eqs. (9) and (10) results:

$$\frac{M_r}{F_d} = \frac{2}{3}d_\beta \tag{12}$$

where d_β is the particle diameter.

5. Materials and methods

The experiments were performed with aqueous slurries of alumina (Alcoa, calcined, 98.45% α-alumina, average size 1.20 μm, 3.65 g/cm^3) and kaolin (Brasil Minas, industrial mineral, 97.78% kaolinite, average size 3.73 μm, 2.48 g/cm^3). No additives were used for dispersing the powders in water. Viscosity was measured in a CSL rheometer of T. A. Instruments with double concentric cylinders geometry at 25 °C.

The suspensions were formulated with solids volume concentrations from 2 to 24%. They were initially electromagnetic stirred for 20 min. An up and down sequence of shear rate from 1000 to 50 and then to 1000 s^{-1} was used to avoid sedimentation, since no dispersing agent was used. Viscosity data were collected in the descending stage.

6. Results and discussion

From Eq. (1) it can be observed that the ratio λ/d_β or $3\lambda/2d_\beta$ is always constant for a given volume fraction, independent of material. In Eq. (8) both constants a and n depend on material characteristics. Dividing λ by the mean particle size d_β and considering that the ratio 2/3 can be inside a, Eq. (8) can be rearranged as

$$\eta_r = 1 + b\left(\frac{2d_\beta}{3\lambda}\right)^n \tag{13}$$

where b is a constant.

Substituting Eq. (12) in (13):

$$\eta_r = 1 + b\left(\frac{M_r}{F_d\lambda}\right)^n \tag{14}$$

The proposed model shows how the relative viscosity can be associated to mechanical rotational and translational forces of particles in suspension.

Starting from the model of the free mean path of Fullman it is possible to find relationships with measurable properties. The model that describes the viscosity of suspensions as a function of volume fraction of solids can be then written as:

$$\eta_r = 1 + b\left(\frac{\phi_\beta}{1-\phi_\beta}\right)^n \tag{15}$$

This model was used in this work to predict the rheological behaviour of alumina and kaolin suspensions. The model fitted the experimental results satisfactorily in the tested ranges, as shown in Fig. 3. The coefficients b and n were calculated by least squares regression. When compared with other models, Fig. 4, the proposed model appears to show a better correlation for both alumina (R=0.9989) and kaolin (R=0.9926).

From the regression fit of the curves, the constant n for alumina and kaolin was 2.8, very close to 3. According to Rodrigues Neto [7], such value can be associated to the cubic aspect of the particles.

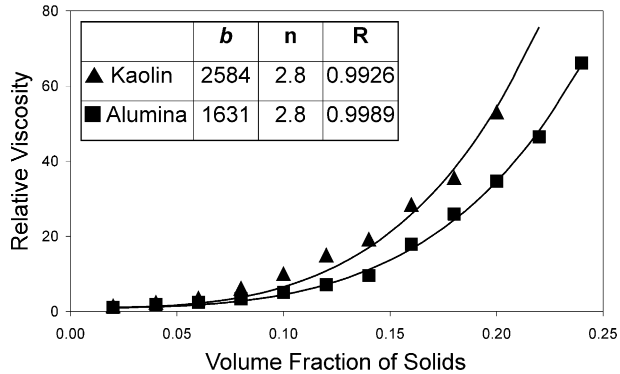
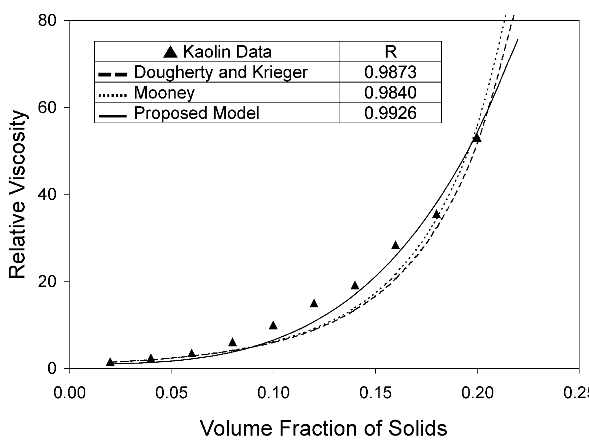
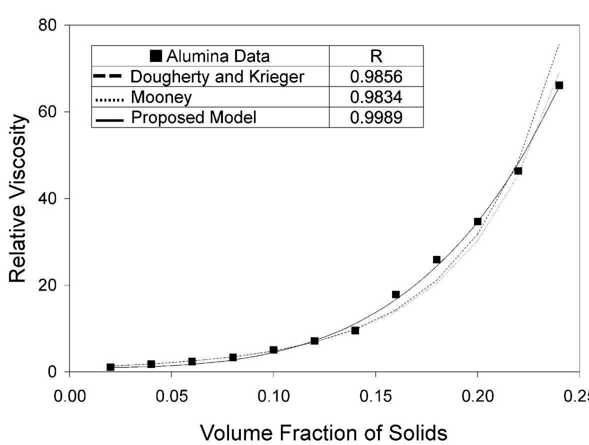


Fig. 3. Viscosity experimental data for alumina and kaolin suspensions compared to the proposed model.



(a)



(b)

Fig. 4. Models of viscosity compared for (a) kaolin and (b) alumina suspensions.

The constant b can be divided in two contributions. One, related to electromagnetic aspects, could vary depending on interaction between phases, composition and properties of the liquid phase and also additives. The other contribution, related with mechanical-geometrical aspects, must have been responsible for the differences of viscosities of the tested materials. SEM micrographs

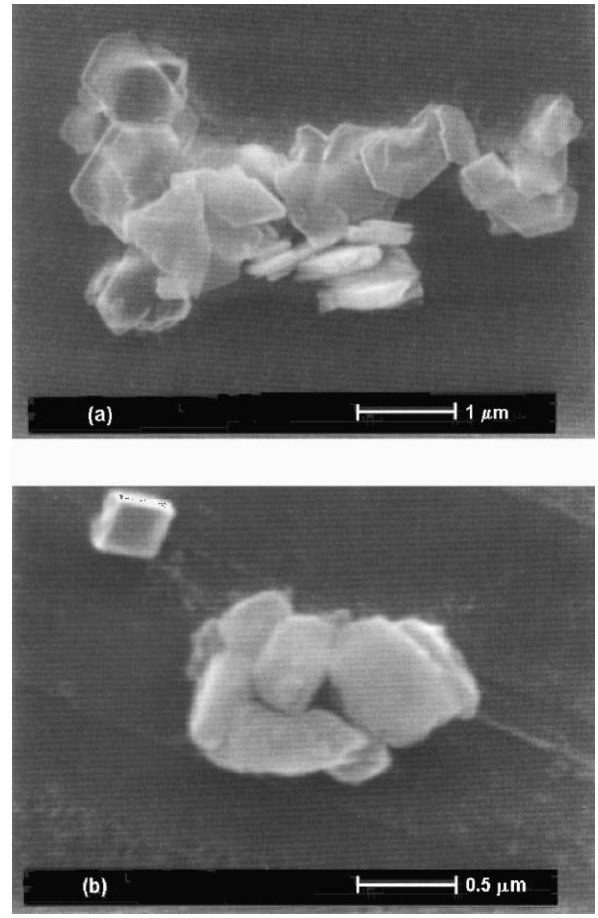


Fig. 5. SEM micrographs of the ceramic powders: (a) kaolin, (b) alumina.

(Fig. 5) show kaolin particles to be much more irregular than the alumina particles.

A first approach for the constant b, obtained by dimensional analysis, can be:

$$b = K\frac{A_s \rho_\beta d_\beta}{\psi_a} \tag{16}$$

where K is a constant; A_s is the specific surface area; ρ_β is the density of the particle; ψ_a is the apparent sphericity.

The constant K includes the electromagnetic contributions and a possible mechanical-geometrical contribution still not considered, as for instance the moment of inertia. The other variables represent mechanical-geometrical properties.

Finally, the apparent sphericity ψ_a deserves a special attention, because it can take into account the variation of the viscosity with the shear rate. This approach suggests that as the shear rate increases the particles will be rotating faster and their appearance will tend to resemble a sphere ($\psi_a = 1$). In this point, viscosity will be the lowest for a certain volume concentration of solids, Fig. 6, as observed also by Liu and Chou [9]. Besides,

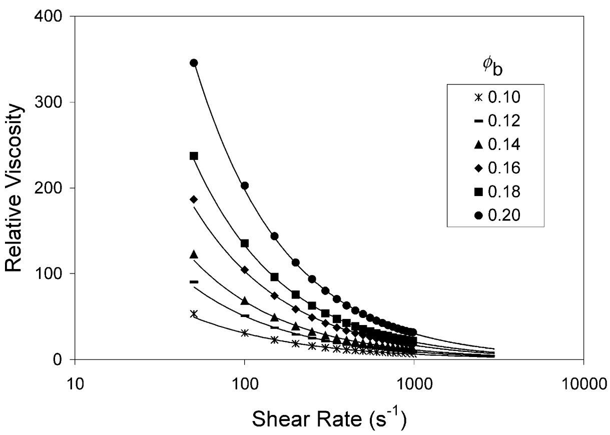


Fig. 6. Relative viscosity of alumina suspension as a function of shear rate for different volume concentration of solids ϕ_β.

the tendency of the flow curves in the range of concentrations analyzed is to reach a limit value of relative apparent viscosity for higher shear rates.

7. Conclusions

Viscosity is a property that represents macroscopically the attritions inside a fluid. These attrition forces are a consequence from electromagnetic and mechanical interactions. Mechanical aspects influence suspension viscosity as a function of solids concentration remarkably. It is possible to represent the viscous effects with measurable properties, for instance, the volume fraction of solids.

Starting from the Fullman model of the free mean path and from a bidimensional balance of forces acting on a particle in suspension, a model that describes the viscosity of suspensions as a function of volume fraction of solids was obtained. The results attest that the assumptions made are suitable for the materials and methods employed in this investigation.

For suspensions of industrial interest, usually more concentrated, it is convenient to study more thoroughly the constant K, which is probably associated with electromagnetic effects. The influence of additives also should be included in the model, mainly if the objective is to increase the concentration of solids. The validity of the model presented for the constant b needs to be further analyzed.

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