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Rheological Modelling of Cementitious Materials.

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ABSTRACT

The use of structural units and effective volume fraction as a function of shear rate has been incorporated by Quemada[1] in his rheological model for particle suspensions in order to account for inter-particle forces. We have used this rheological model to describe the behaviour of cementitious material suspensions.

INTRODUCTION

The term complex fluids is widely used to describe fluids like concentrated suspensions i.e. fluids that have a shear dependent behaviour. These fluids often show a shear thinning behaviour when exposed to low and moderate shear rates, followed by a shear thickening behaviour at higher shear rates. Concentrated suspensions of cementitious particles often show such a complex behaviour

Most rheological models that describe the behaviour of suspensions of particles in Newtonian fluids, are based on the assumption that suspensions are diluted. Furthermore, the particles to be non-interacting hard spheres, (HS), of even size.

A different model, trying to account for inter particle forces in concentrated suspensions has been suggested by Quemada[1]. To develop this model the concept of structural units (SU) and effective volume fraction, (EVF), has been used.

A SU is an aggregate of smaller particles of various sizes that stick together due to surface forces. The space between the particles in the SUs is filled with the suspending fluid and this fluid becomes a part of the SUs. The result is a reduction of the EVF of the continuous phase and an increase of the EVF of the particles. Under steady shear flow conditions the SUs are considered to have a shear dependent mean radius and to be approximately spherical in shape so that a complex fluid can be considered as a roughly monodisperse suspension of SUs.

The shear thinning behaviour going from low to moderate shear rates, can thus be accounted for by the increase in the EVF of the suspending fluid due to the shear induced reduction of the SUs' size and the consequent release of locked up fluid. The shear thickening behaviour that very often appears when going from moderate to high shear rates is expected to be due to a shear induced flocculation.

EXPERIMENTAL CONDITIONS

Sample preparation

The Class G clinker slurry was prepared by using clinker that forms the basic constituent in the production of Class G cement, as specified by API[2]. The clinker was ground and we used the fraction that passed through a sieve with a mesh opening of 75 micron in dry sieving analysis. A sample of 10 ml was hand mixed with water for 30 seconds and the rheological properties were measured 3 minutes after the clinker's first contact with water. The zeta potential of the clinker has been measured[3] to + 4 mV.

The Class G cement slurry was mixed in accordance with API[2]. However, the prescribed consistometer conditioning time, prior to any measurement, was increased with 10 minutes for our sample. The zeta potential of the Class G cement has been measured[4] to – 6.1 mV.

The micro silica slurry came as a ready prepared sample from Elkem ASA Materials. It is used as a gas migration preventive in well cementing. The zeta potential of the micro silica particles was measured using an AcoustoSizer from Colloidal Dynamics. The measured zeta potential was – 42.7 mV. The particle size distribution measured was rather narrow with a d-50 of 0.24 µm. The measurements were carried out on a slurry having a solid volume fraction of 0.311.

Viscosity measurements

For our rheological measurements we have used a Physica UDS 200 rheometer fitted with a concentric cylinder configuration named Z3 DIN. All samples were measured at a temperature of 25ºC ±0.5.

Rheological model

The Quemada model is based on the Krieger-Dougherty (K-D) equation shown in Eq. 1. The K-D model has been found to be suitable for describing the behaviour of concentrated suspensions of both spherical and non-spherical particles.

$$\eta = \eta_F \left(1 - \frac{\phi}{\phi_m}\right)^{-[\eta]\phi_m} \qquad (1)$$

Here η is the viscosity of the suspension, η_F is the viscosity of the suspending fluid, ϕ is the volume fraction of particles, ϕ_m is the maximum packing fraction and $[\eta]$ is the intrinsic viscosity. The intrinsic viscosity is dimensionless for suspensions, it is the limiting value of the reduced viscosity as the concentration approaches zero.

Quemada's model is defined by Eq. 2.

$$\eta = \eta_\infty \left[\frac{1+\Gamma^p}{\chi + \Gamma^p}\right]^2 \qquad (2)$$

Here η_∞ is the limiting steady state viscosity as $\Gamma \to \infty$. Γ is a dimensionless kinetic constant expressed in terms of a shear variable: either $\Gamma = \dot{\gamma}/\dot{\gamma}_c$ for dilute systems or $\Gamma = \sigma/\sigma_c$ for concentrated systems. In this expression we use a characteristic shear rate $\dot{\gamma}_c$ or stress σ_c. The characteristic shear rate, $\dot{\gamma}_c = t_c^{-1}$ where t_c is a characteristic time required for dimensional homogeneity. According to Quemada[1] the exponent p should be less than one and has often been found experimentally to be close to $1/2$.

Quemada's structural index, χ, is defined by Eq. 3. This index represents a relation between the asymptotic constant viscosities at high shear rates and low shear rates and for a shear thinning fluid the value of χ should lie between $0 < \chi < 1$.

$$\chi = \chi(\phi) = \frac{1 - \phi/\phi_0}{1 - \phi/\phi_\infty} \equiv \pm\left(\frac{\eta_\infty}{\eta_0}\right)^{\frac{1}{2}} \qquad (3)$$

The structural index depends on the limiting maximum packing at $\Gamma \to \infty$ and $\Gamma \to 0$, respectively, defined by Eq. 4 and 5:

$$\phi_\infty = \frac{\phi_m}{1 + CS_\infty} \qquad (4)$$

$$\phi_0 = \frac{\phi_m}{1 + CS_0} \qquad (5)$$

where C is a compactness factor and is directly related to φ, the mean compactness of SUs, through, $C = \varphi^{-1} - 1 = (1-\varphi)/\varphi$ which is the fluid fraction divided by the solid fraction. Further, the volume fraction $\varphi = \phi_{Aeff}/\phi_A$ where ϕ_{Aeff} is the EVF of SUs and ϕ_A the volume fraction of particles contained in all the SUs. $S = \phi_A/\phi$ is a structural variable defined as the aggregated fraction and S_0 and S_∞ are the limiting values of S at very low and very high shear respectively.

The packing fractions, ϕ_∞ and ϕ_0, in Eq. 4 and 5 are involved in the corresponding steady state limiting viscosities, η_∞ and η_0 shown in Eq. 6 and 7.

$$\eta_\infty = \eta_F \left(1 - \frac{\phi}{\phi_\infty}\right)^{-2} \tag{6}$$

$$\eta_0 = \eta_F \left(1 - \frac{\phi}{\phi_0}\right)^{-2} \tag{7}$$

For our data fitting we have used a simple spreadsheet and as a measure of the applicability of the model to our data sets, we have used the correlation coefficient R^2

RESULTS AND DISCUSSION

In Fig. 1 we have plotted the viscosity measured on a Class G clinker slurry as a function of shear rate. The measured values are marked as points in the figure. The solid volume fraction of the slurry was 0.419. The slurry show a pseudo plastic or shear thinning behaviour in the measured interval having a viscosity of 35.7 Pas and 55.3 mPas at a shear rate of 1.49 and 1020 s^{-1} respectively.

The line shown in Fig. 1 represents the data calculated by use of the Quemada model. The parameters selected for the model are shown in Table 1.

The calculated curve also indicates that the measured data represents a shear thinning region. In addition it indicates an upper and lower plateau (at low and high shear rates respectively) with regards to the viscosity of the slurry.

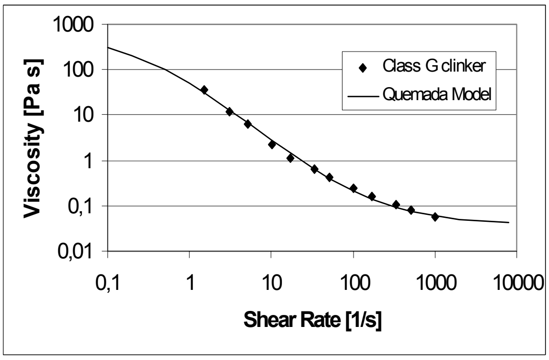

Figure 1. Viscosity as a function of shear rate of a suspension of Class G clinker. The points represents measured values, the drawn line represents model values.

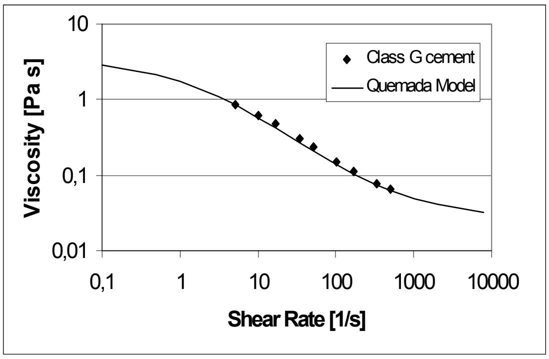

Figure 2. Viscosity as a function of shear rate of a suspension of Class G cement. The points represents measured values, the drawn line represents model values.

The viscosity of a Class G cement slurry is shown in Fig. 2. The measured values are marked as points. The solid volume fraction of the slurry was 0.408. The slurry shows a shear thinning behaviour in the measured interval. The measured viscosity is reduced from 847 mPas at a shear rate of 5.1 s^{-1} to 64.9 mPas at a shear rate of 511 s^{-1}.

The line shown in Fig. 2 represents the data calculated by use of the Quemada model with selected parameters shown in Table 1. Again the calculated curve confirms the shear thinning region of the measured values and indicates an upper and lower plateau.

In Fig. 3 the viscosity of a slurry containing micro silica, or silica fume, having a solid volume fraction of 0.311 is shown. The measured viscosities are again shown as points and the calculated values are shown as a line.

The slurry shows a shear thinning behaviour within the measured region with a measured viscosity of 233 mPas at a shear rate of 5.1 s^{-1} to 21.7 mPas at a shear rate of 1022 s^{-1}.

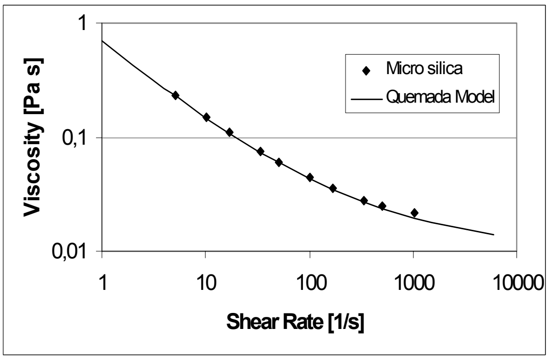

Figure 3. Viscosity as a function of shear rate of a suspension of micro silica. The points represents measured values, the drawn line represents model values.

The calculated curve confirms the existence of a shear thinning region, indicating that the shear thinning region continues down to very low shear rates. Only for the very high shear rates the existence of a plateau is indicated although we have not measured it directly

All the three different slurries containing cementitious materials have different solid content and different particle size distributions. Still they all seem to fit to the Quemada model.

In both the Class G clinker slurry and the Class G cement slurry the particles are expected to be in a flocculated state[5] due to their rather low zeta potentials. The lower plateau followed by a shear thinning region may be interpreted as a break up of flocks or SUs and an increase of the EVF of the continuous phase. The upper plateau indicated may further be interpreted as a region where SUs are broken down to the single particle level due to high shear forces.

Table 1. Selected parameters for the Quemada model calculations.

	Class G clinker	Class G cement	Micro silica
η_0	600 Pas	3.5 Pas	120 Pas
η_∞	40 mPas	26 mPas	10 mPas
t_c	7 ms	4.2 ms	8 ms
p	0.78	0.58	0.43
R^2	0.9945	0.9938	0.9999

The micro silica particles show a somewhat different behaviour at lower shear rates as no plateau is indicated. This could be due to the fact that the micro silica particles have a rather high zeta potential which prevents them from forming flocks to the same degree as the clinker and cement does.

CONCLUSIONS

We have found that the rheological model suggested by Quemada[1] can be used to describe the rheological behaviour of various types of cementitious materials blended with water, like a clinker slurry, a Class G oil well cement slurry or a micro silica slurry.

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