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Rheological modelling of cementitious materials using the Quemada model

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Abstract

In the present study the rheological model proposed by Quemada [D. Qemada, Rheological modelling of complex fluids I. The concept of effective volume fraction revisited, Eur. Phys. J. AP, 1 (1998) 119–127.] has been shown to be able to predict the rheological behaviour of concentrated cementitious suspensions used for well cementing. The concentrated suspensions consisted of mixtures of API Class G oil well cement and manganese tetraoxide weight additives. The input for our modelling was based on measured particle fractions, packing fractions and viscosity curve measurements.

Keywords: Rheological modelling; Cementitious suspensions; Oil well cement

1. Introduction

Rheological modelling of cementitious materials has always been a subject of great importance when working with oil well cementing. The need for predicting the rheological behaviour of the suspensions when experiencing conditions outside the available measuring range for the equipment designed in accordance with API specifications [2,3] has always been present. Cementitious suspensions behave in a non-Newtonian way. They are shear-rate dependent and normally termed as shear-thinning suspensions. Rheological measurements are normally performed in the laboratory within a given range of shear rates. Based on these measured values the models should be able to predict the shear-dependent behaviour of the suspensions outside the measured interval of shear rates. For the present work it was thus essential to use the values obtained within the limited shear-rate range given by API [2,3] for our modelling.

Many models have been introduced for this purpose. The simplest model used is the Bingham model which gives a straight line based on only two measured points. This model predicts a constant plastic viscosity for the suspension, independent of shear rate, and a yield stress, which is the shear stress at zero shear rate. Another simple but also widely used model is the power law model. This model has been found to be able to describe the shear-thinning behaviour of a variety of cementitious suspensions, but in contrast to the Bingham model it does not predict any yield stress. The Herschel–Bulkley model is a third and also widely used model for cementitious suspensions. This model could be said to provide the user with a combination of the two previous mentioned models, since it is able to describe both a power law type shear-thinning behaviour and also a yield stress.

In this paper we have evaluated a model proposed by Quemada [1] in 1998, shown in Eq. (1), and tried to apply data measured in accordance with specifications given by API [2]. This is a model found to be able to describe the behaviour of shear-thinning suspensions [1,4,5]. In addition to measured rheological values the use of this model can also be based on measured values of the solid volume fractions and the particle packing fractions of the suspensions using Eqs. (2), (3) and (4). The latter approach has been the purpose of the present work.

1.1. Rheological modelling

In the rheological model proposed by Quemada [1], he tries to account for the inter-particle forces in concentrated suspensions. Due to these inter-particle forces, the particles

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form aggregates or structural units (SUs). These SUs will lock up some of the suspending fluid resulting in an increase of the effective volume fraction (EVF) of the particles in the suspension finally resulting to an increase in viscosity.

The size and number of these SUs are shear-dependent. When sheared under a constant rate they are expected to become more spherical and even of size, resulting in a nearly monodisperse size distribution. When the shear rate increases the size of the SUs decreases releasing some of the locked up fluid. Thus, the EVF decreases and as a result, the viscosity is reduced.

The forming of SUs is also expected to influence the packing of individual particles. At low shear rates the forming of SUs reduces the limiting maximum packing factor, ϕ_0, because the packing within the SUs themselves is not at a maximum. At higher shear rates, where all the SUs are broken down into primary particles or irreducible aggregates a higher limiting maximum packing, ϕ_∞, will be obtained.

Quemadas model is defined by:

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

Here η_∞ is the limiting steady state viscosity as $\Gamma \to \infty$. Γ is a dimensionless shear variable either expressed in terms of the shear rate, $\Gamma=\dot{\gamma}/\dot{\gamma}_c$ or the shear stress, $\Gamma=\sigma/\sigma_c$, using a characteristic shear rate $\dot{\gamma}_c$ or stress σ_c, respectively. Further, $\dot{\gamma}_c=t_c^{-1}$ where t_c is a characteristic time required for dimensional homogeneity. The exponent p in Eq. (1) should, according to Quemada [1] be less than one and has often been found experimentally to be close to 0.5.

The term χ in Eq. (1) is called a structural index and is defined by:

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

The index χ can be expressed through a relation between the asymptotic constant viscosities, η_∞ and η_0 at high and low shear rates respectively and this relation for obtaining the index χ was used by Hodne and Saasen [4]. χ can also be expressed in terms of the limiting maximum packing, ϕ_0 and ϕ_∞ as $\dot{\gamma} \to 0$ and $\dot{\gamma} \to \infty$ respectively, defined by:

$$\phi_0 = \frac{\phi_m}{1+CS_0} \tag{3}$$

$$\phi_\infty = \frac{\phi_m}{1+CS_\infty} \tag{4}$$

where ϕ_m is the maximum packing fraction, C is a compactness factor and is directly related to the mean compactness φ of the SUs through: $C=\varphi^{-1}-1$. Further, when the SUs are considered as being roughly identical, the mean compactness fraction $\varphi=\phi_A / \phi_{Aeff}$, here ϕ_A is the volume fraction of particles contained in all the SUs and ϕ_{Aeff} is the EVF of the SUs. The factor $S=\phi_A / \phi$ is a structural variable defined as the ratio between the aggregated and the particle volume fraction and S_0 and S_∞ are the limiting values of S at very low and very high shear respectively. Quemada [1] refers to the formation and break down of SUs as relaxation processes with mean relaxation times, t_A and t_D respectively. The number fraction S of aggregated particles is defined as:

$$\frac{dS}{dt} = \kappa_A(S_0-S) - \kappa_D(S-S_\infty) \tag{5}$$

where $\kappa_A=t_A^{-1}$ and $\kappa_D=t_D^{-1}$ are shear-dependent kinetic constants of formation and rupturing of SUs. At a steady state $dS/dt=0$ and $S=S_{eq}$ and Eq. (5) is given by:

$$S_{eq} = \frac{S_0 + S_\infty\theta}{1+\theta} \tag{6}$$

where θ is defined as:

$$\theta = \kappa_D/\kappa_A = f(\Gamma). \tag{7}$$

This solution corresponds to the equilibrium structure the system reaches under constant shear, characterized by the dimensionless shear variable Γ. By the use of dimensional analysis, Quemada [1] have shown that $\theta \propto \sigma$ and that due to the non-linear variation of σ v.s. $\dot{\gamma}$, very often approximated by a power law, a non-linear dependence in θ of $\dot{\gamma}$ is expected. Thus, for concentrated suspensions and for the simplest modelling, Quemada [1] assumes that:

$$\theta(\dot{\gamma}) = \kappa_D/\kappa_A = (t_c\dot{\gamma})^p \tag{8}$$

For a shear-thinning fluid the value of χ should lie in the range: $0 < \chi < 1$ [1].

2. Sample preparation and experimental methods

2.1. Sample compositions

The preparation of the suspensions prior to rheological measurements was done in accordance with API [2,3]. This preparation consists of an initial short period of high speed mixing in a Warring Blender, followed by 20 min of mixing at rather low speed, 150 rpm, in an atmospheric consistometer. The volume of each sample was approximately 600 ml. All samples were mixed using either a Class G cement delivered by Norcem ASA or a mixture of Class G cement and manganese tetraoxide, with the product name Micromax®, delivered by Elkem ASA. Micromax is used as a weighing agent in well cementing.

The Class G cement has been measured to have an almost log normal particle size distribution with a d50 of 12.6 μm, a d16 of 5.44 μm and a d84 of 29.2 μm. This was measured on a suspension having a solid volume fraction of 0.418 and by using an AcoustoSizer from Colloidal Dynamics. The Blaine surface area of the Class G cement is given by the manufacturer to be 320 m^2/kg. The particle size distribution of the Micomax, presented by Elkem ASA [6], is rather narrow with a mean diameter of 0.4 μm. The surface area is presented by Elkem ASA to be 2–4 m^2/g, it was measured by the use of nitrogen

adsorption, BET [7], and the specific density to be within the range of 4.75–4.95. We measured the specific density of the Class G cement and the Micromax to be 3.2 and 4.8 respectively, and these values were used in our calculations. As the suspending fluid we used distilled water; no other additives were used. All samples were prepared at a temperature of 25± 2 °C.

2.2. Chemically bound water

The amount of chemically bound water onto the cement particles was measured in accordance with the procedure given by Justnes [8]. The measurements were carried out after the initial API-mixing of the suspensions, i.e. starting approximately 22 min after the first contact between the cement and water. For these measurements we mixed one volume of suspension with three volumes of 96% ethanol. This mixing was done twice and after each mixing the water and ethanol was removed by filtration through a pre-filter type AP2004700 delivered by Millipore. This filter holds back the cement particles giving a clear and visible filtrate. The filtration was aided by the use of a vacuum pump and the whole process was carried out within 20 min. The samples were then placed in a heating cabinet at a temperature of 110 °C until no further weight reduction was observed. This was normally achieved within 48 h. The samples were then placed in an oven and heated for 48 h at a temperature of 900 °C. The weight reduction during the latter heating process was then registered. The same heating procedure was also used to measure the weight loss on a sample of cement that had not been mixed with water. The loss registered for this latter sample representing the cement used for our experiments was used to correct the total loss registered for the water mixed samples and the net loss was given as the weight of chemically bound water. The net loss registered in our measurements was approximately 0.7% by weight. This is in accordance with an expected approximate value of 0.8% given by Justnes [8].

2.3. Density measurements of suspensions

To enable measurements of the amount of air still remaining in the suspensions two types of instruments were used. One was a DMA 4500 densitometer from Anton Paar. This is an instrument that uses the oscillating u-tube principle for measurement. The accuracy is within ±0.0001 g/cm^3. The density measurements with this instrument were carried out at 25±0.02 °C. The other instrument used was a pressurized fluid density balance from Halliburton having an accuracy of ±0.01 g/cm^3. This is a density balance where the suspension is placed in a cup equipped with a lid that can be fastened to the cup. Using a valve arrangement in the lid, the cup can be pressurized by pumping in an additional volume of the suspension in question. This is carried out using a handheld piston pump, the recommended force [3] applied is 230 N or above which for the pump in question can be calculated to result in a pressure of approximately $18.7 \cdot 10^5$ Pa or higher. The volume of air contained in the suspension is thus compressed to a level where its influence on the measured density can be neglected and the density value obtained, by using this balance, is for the suspension without air. These measurements were carried out in accordance with the recommended practice given by API [2,3] and at a temperature of 25±2 °C.

2.4. Packing measurements

For the packing measurements we used a 50 ml dispensable plastic syringe as shown in Fig. 1. Both the piston and the bottom of the syringe were perforated with approximately 40 holes, each with a diameter of 1.1 mm. Two filters of the pre-filter type AP2004700 delivered by Millipore were fitted inside, one at each end. The syringe was filled with the suspension in question and the water was pressed out, by hand force only, while the syringe was vibrated. The loss of water was registered and the packing obtained could thus be calculated and used as the lower limit for the maximum packing fraction ϕ_m, in our modelling.

2.5. Rheological measurements

For the rheological measurements we used a Physica UDS 200 rheometer fitted with a concentric cylinder configuration, named Z3 DIN, but where we exchanged the original rotating cylinder having a smooth surface with one having a roughened surface. The roughened rotor was made especially for these measurements in order to avoid or minimize slippage. Slippage that was discovered during the early stages of this work when measuring our suspensions at shear rates below 51 s^{-1} and using the rotor having a smooth surface. Slippage has also in retrospect been found to appear at the same shear rate when measuring the same type of suspensions using a Chan 35 rheometer [5]. However, at that time when these measurements referred to [5] were carried out, the appearance of slippage was not identified.

For roughening of the surface a router was used to make 12 grooves evenly spaced and axially placed into the surface of the rotating cylinder. These grooves had a depth of 1.2 mm, a width

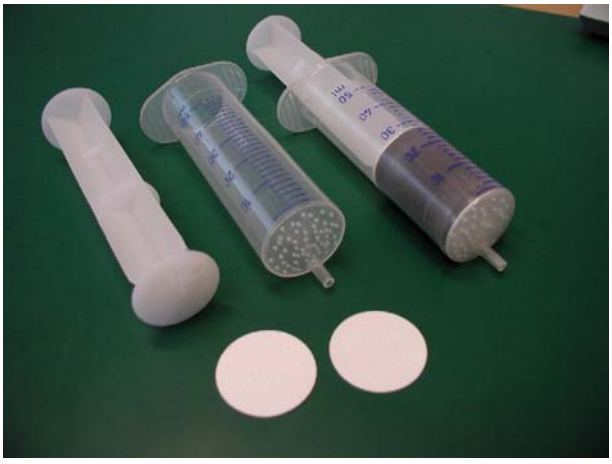

Fig. 1. Equipment used for packing experiments, one unused syringe is shown in a dismantled state the other syringe shown has been used for a packing experiment.

of 3 mm and a length equalling the length of the cylinder. This leaves 12 sections of the initially smooth surface, having a width of approximately 3.5 mm, between the grooves. The sample volume used for rheological measurements was approximately 8 ml and all the samples were measured at a temperature of 25 °C±0.5 °C.

Prior to measurements the samples were sheared continuously for 1 min at a shear rate of 1022 s^{-1}, the measurements were then carried out at consecutively decreasing shear rates of 511 – 340 – 170 – 102 – 51 – 34 –17 – 10.2 – 5.1 – 3.1 – 2 – 1.5 – 0.75 – 0.5 – 0.2 – 0.1 – 0.05 s^{-1}. The first 8 shear rates from 511 and down to 10.2 s^{-1} are in accordance with the recommended values given by API [3], the shear rates from 5.1 and down to 0.05 s^{-1} were added to the sequence in order to obtain an extended range of values at low shear rates. For all shear rates the period of shear lasted for 20 s and all readings used were taken at the end of each period of constant shear.

By applying the above mentioned procedure, the rheology of three different suspensions was measured. One was a neat Class G cement suspension having a specific density of 1.91, a W/C ratio of 0.44 by weight and a solid volume fraction of 0.41. This is close to the water cement ratios used in tail cements, tail cements being the last cement suspension pumped down in the well during a primary cementing operation. In the second suspension we investigated the effect of partly replacing the cement with Micromax. In this suspension the solid volume fraction was kept constant at 0.41 and the cement was partly replaced by 11.4% by volume of Micromax. This resulted in a suspension with a specific density of 1.98 and a W/C ratio of 0.49. In the third suspension we investigated the effect of adding Micromax to the cement suspension. In this suspension the W/C ratio was kept constant at 0.44 and the suspension was added 10.3% by volume of Micromax. This gave a suspension with a specific density of 2.03 and a solid volume fraction of 0.44.

2.6. Practical rheological modelling

For our data analysis we used Visual Basic integrated in a spreadsheet in Excel. The iterations in our spreadsheet were performed using the Solver Function, which is based on the non-linear optimized Generalized Reduced Gradient, GRG2 [9]. As a measure of the applicability of the model to our data sets we used the correlation coefficient R^2, equal to the squared Pearson function R in Excel.

For our modelling we used six variable parameters: the exponent of the shear stress ratio p, the characteristic time t_c, the volume fraction ϕ, the maximum packing fraction ϕ_m and the volume fraction of particles contained in all the SUs, ϕ_{A0} and $\phi_{A\infty}$ as the shear rate $\rightarrow 0$ and $\rightarrow \infty$ respectively.

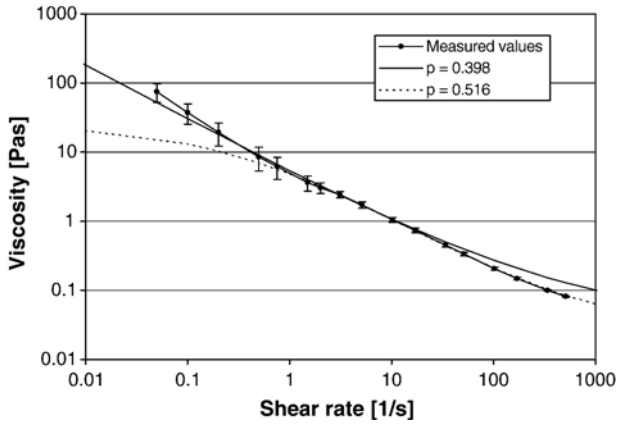

Fig. 2. Measured and modelled data for a neat Class G cement suspension having a specific density of 1.91, a solid volume fraction of 0.41 and a W/C ratio of 0.44 by weight.

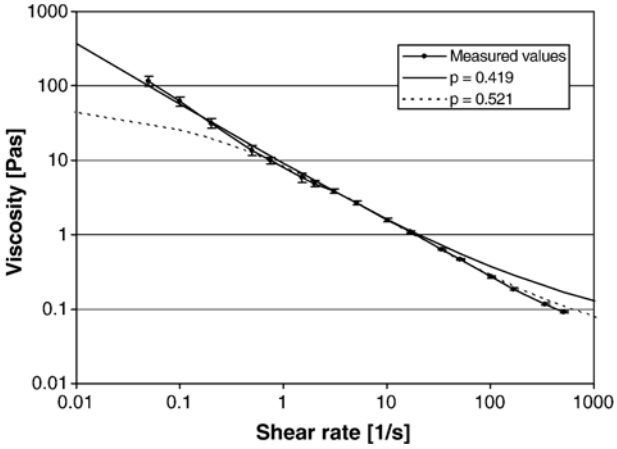

Fig. 3. Measured and modelled data for a Class G cement suspension where 11.4% by volume of the cement is replaced with Micromax, having a specific density of 1.98, a total solid volume fraction of 0.41 and a W/C ratio of 0.49 by weight.

3. Results and discussion

3.1. Rheology

The rheology of the three suspensions presented under "Rheological measurements" subsection was measured. In Figs. 2, 3 and 4 the viscosity of the three suspensions is shown as a function of shear rate. The measured values are marked as points and each point represents the average of three measurements carried out on three different suspensions. The standard deviation for each measured point has also been marked. In the figures we have also drawn the curves representing the "best fit" found in our modelling.

All the three suspensions showed an increased viscosity with decreasing shear rates, within the measured interval. The increase in viscosity values measured at low shear rates is expected to be due to a build up of structure or SUs as the Quemada model predicts because of cross linking of particles. Whether the slight deviation from a straight line, occurring for all our suspension, but which can be seen to be most profound for the suspensions drawn in Figs. 2 and 3, starting at the shear rate of 2 s^{-1} and ending approximately at a shear rate of 0.5 s^{-1}, is due to slippage could not be said based on the development of the measured viscosity during the 20 s periods at constant shear. However, based on comparisons with our early measurements when using a rotor with a smooth surface and where slippage

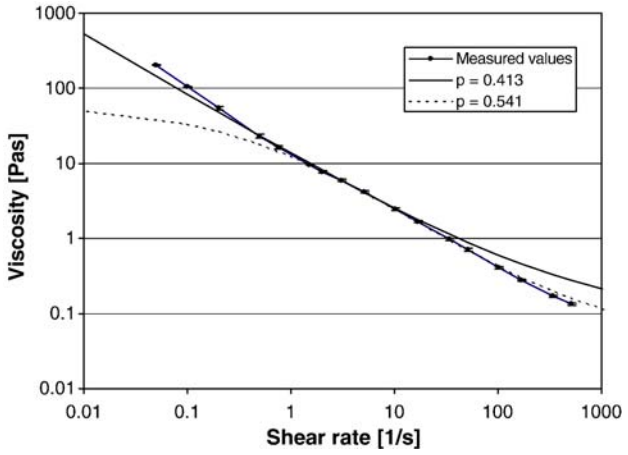

Fig. 4. Measured and modelled data for a Class G cement suspension where 10.3% by volume of Micromax is added, having a specific density of 2.03, a total solid volume fraction of 0.44 and a W/C ratio of 0.44 by weight.

was identified to occur, it could be said to be an indication. Here it should also be mentioned that Guillot [10] reports that the decreasing and increasing viscosity values measured as a function of decreasing shear rates could be caused by sedimentation. However, no sign of sedimentation was found when inspecting the measuring cup afterwards.

The viscosity measured for the neat Class G suspension, shown in Fig. 2, was the lowest throughout the measured interval. It increased from 81 mPa s at a shear rate of 511 s^{-1} to 75 Pa s at a shear rate of 0.05 s^{-1}. The suspension containing Micromax, having a specific density of 2.03 and a solid volume fraction of 0.44, showed the highest values throughout the measured interval. The measured values obtained for this suspension are shown in Fig. 4. The viscosity of the suspension increased from 133 mPa s at a shear rate of 511 s^{-1} to 205 Pa s at a shear rate of 0.05 s^{-1}.

In Fig. 3 the measured viscosity values for the suspension with a specific density of 1.98 and where the solid volume fraction was kept the same as that of the neat Class G suspension are shown. The measured values for this suspension were intermediate to those of the other two suspensions. For this suspension the measured viscosity increased from 89 mPa s at a shear rate of 511 s^{-1} up to 116 Pa s at a shear rate of 0.05 s^{-1}.

The standard deviation for the various average measured viscosity values plotted in Figs. 2, 3 and 4 was calculated for all three suspensions. For the neat Class G suspension shown in Fig. 2 the standard deviation was found to gradually increase from less then ±2.5% at the shear rate of 511 s^{-1} to approximately ±10.5% at the shear rate of 3.1 s^{-1} and further to approximately ±38% at a shear rate of 0.5 s^{-1} before gradually decreasing to approximately ±30% at the lowest shear rate of 0.05 s^{-1}. This increase in the standard deviation coincides with the recommendations given by API [3] saying that repeatability of data taken at shear rates at and below 10.2 s^{-1} is often poor and at the discretion of the operator may be omitted from the test.

For the second suspension shown in Fig. 3, where 10.4% of the volume of cement was replaced by Micromax but where the solid volume was kept the same as that of the neat suspension, the standard deviation was also found to gradually increase with decreasing shear rates. From approximately ±3% at a shear rate of 511 s^{-1} to within ±16% at the lowest shear rates. For the third suspension also containing Micromax but where the solid volume was increased from that of the two suspensions mentioned above, the standard deviation was found to vary but to be rather low, less than ±5.4%, within the measured range of shear rates. This is shown in Fig. 4.

When using the model proposed by Quemada, one of our aims was to evaluate if good predictions could be made for the rheological behaviour of our suspensions at low shear rates based on comparisons between values predicted by the model and measured values obtained within the shear-rate range given by API [2]. This standard gives that measurements should be carried out in a consecutive falling order, after an initial shearing of the sample for one minute at a shear rate of 511 s^{-1}, in steps of constant shear rates lasting 20 s, down to a shear rate of 5.1 or 3.1 s^{-1}, the latter being dependent on type of rheometer used for measurements. However, when using the Physica 200 rheometer and monitoring the development of the viscosity we found that the initial shearing for one minute was insufficient to give stable readings towards the end of that period. Only, after shearing the sample for one minute at a shear rate of 1022 s^{-1} did we obtain stable readings at 511 s^{-1}. The observed instabilities were found to relate to variations in the density of the suspensions. Based on density measurements of the suspensions we found that they still contained air after the initial API preparation of continuous mixing, lasting for approximately 22 min. The air content and its influence on the viscosity will be addressed in future work.

When measuring the density of the suspensions after one minute of constant shear at a shear rate of 1022 s^{-1} in the rheometer we found that this shearing removed most of the air. We therefore assumed that the lack of stability found when the suspension was sheared for one minute at 511 s^{-1} was due to insufficient removal of air and we therefore changed the initial period of shear using this higher shear rate.

In the 2005 edition of recommended practice from API [3] the sequence of shear rates has been changed from the early version [2], now the recommendation given is to start at a shear rate of 10.2 s^{-1}, increasing in steps to a shear rate of 511 s^{-1} before decreasing through the same steps to a shear rate of 10.2 s^{-1}. The duration of each period at constant shear rate has been reduced from 20 to 10 s. The values to be reported are the average of the measured values at increasing and decreasing shear. Further, the recommended initial period of constant shear, lasting for one minute, prior to any measurements has been removed. These changes in the recommended practice, we find, does not improve the removal of air prior to the rheological measurements. However, also here, more work is needed before any conclusions can be drawn with certainty.

Continuing, we were able to obtain stable readings using our roughened cylinder down to a shear rate of 0.05 s^{-1}. At lower shear rates our rheometer was found not to be able to maintain a stable shear rate during the measuring period of 20 s and thus these results have been omitted.

Based on this we found that we would use the shear rates from 511 down to 3.1 s^{-1} as basis for our comparison between model values and measured values. These shear rates being in accordance with the shear rates given in the previous version of the API [2].

3.2. Modelling

Using the parameters with limiting values as listed in Table 1 for modelling of our suspensions we found two optimal solutions for each set of data. The values resulting in optimal solutions are listed in Table 2. Further, these optimal solutions were found to describe two distinct types of curves as shown in Figs. 2, 3 and 4. One type is seen to indicate a lower and an upper plateau of the viscosity with respect to shear rate, going through a shear-thinning region in between. For short this will be denoted as an s-type of curve, and in the figures they are drawn using a dotted line. The other type also indicates an upper plateau but here no lower plateau is indicated. Instead a shear-thinning region towards lower shear rates is indicated. For short this will be denoted as a j-type of curve, and in the figures they are drawn as solid lines. The j-type of curves can also be said to indicate the existence of a yield stress while the s-type of curves could be found to predict the non-existence of a yield stress. Based on a review written by Banfill in 2003 [10] where he reports that hitherto all models reported used for cement pastes indicate the existence of a yield stress, the Quemada models' prediction of the non-existence of a yield stress is found to be somewhat interesting.

From Figs. 2, 3 and 4 it can be seen when comparing the curves given by the model with measured values, that the j-type of curves are found to give the best prediction of the rheological behaviour of the suspensions for the lowest shear rates and thus, indicate the existence of a yield stress. For the highest shear rates the s-type of the curves is found to give the best prediction of the rheological behaviour of our suspensions.

The two different types of curves have also been found in some earlier work [4,5], where a somewhat different approach was used when applying the Quemada model on various suspensions, containing cementitious materials. However, the presence of two optimal solutions for each suspension was not discovered. It is expected that this lack of discovery were due to the use of a somewhat simpler type of modelling tool.

The curves in Figs. 2, 3 and 4 represent the best fit of each type for their respective suspension and their respective exponent p is used as a legend. The variable p, the exponent in Eq. (1), should according to Quemada [1] be <1 and has often been found to be close to 0.5. As can be seen from Table 1, in our modelling the exponent was allowed to vary within the range of $0.01 \le p \le 0.99$.

The exponent p was found to be the most influential factor in our modelling. For the j-type of curves indicating a shear-thinning behaviour of the suspensions for low shear rates, the exponent was always less than 0.5, and for our three suspensions it was found to lie in the range of $0.398 \le p \le 0.419$. For the s-type of curves indicating an upper and lower plateau the exponent p was always higher than 0.5 and for our three suspensions it was found to lie in the range of $0.516 \le p \le 0.541$.

The characteristic time, t_c, as defined by Quemada [1] to be the time needed for obtaining a suspension of almost mono-disperse SUs and being the inverse of the characteristic shear rate $\dot{\gamma}_c$, was for our modelling purpose limited to the applied range of shear rates from 511 down to 3.1 s^{-1}, this gives a range of t_c from 1.96 ms to 322.58 ms respectively. The optimal value obtained for t_c, resulting in the best fit of the model, was found to be equal to the lower limiting value of 1.96 ms for all the j-type of curves and for two of the s-type of curves. This latter was for the two suspensions containing Micromax. For the neat Class G suspension the value of t_c, resulting in an optimal s-type of curve, was found to be 2.25 ms. This gives that all the characteristic shear rates, $\dot{\gamma}_c$, used in our modelling for obtaining optimal solutions were found to lie in the range of shear rates from approximately 444 to 511 s^{-1}.

In an attempt to evaluate how sensitive our model was to changes in the characteristic time we used the upper limiting value of t_c, 322.58 ms, equalling a shear rate of 3.1 s^{-1}, together with the optimal values obtained for the exponents p, shown in Table 2, as constants. The other parameters were allowed to vary within the limiting ranges as given in Table 1. Thus, we modelled six new curves, one for each value of p. The result of this change of t_c to a higher value was that all the curves of the s-type, having an exponent $p>0.5$, changed to j-type of curves. For the j-type of curves, having an exponent $p<0.5$, no change in curve shape was observed. Therefore, the model under given circumstances is rather sensitive to the value used for t_c.

Table 1
Parameters and limiting values used when modelling a neat Class G cement suspension and two suspensions also containing Micromax

Suspension:	Neat Class G, SG=1.91	Cement added Micromax, SG=1.98	Cement added Micromax, SG=2.03
Parameters:	Limitations used	Limitations used	Limitations used
Exponent, p	$0.01 \le p \le 0.99$	$0.01 \le p \le 0.99$	$0.01 \le p \le 0.99$
Characteristic time, t_c	$0.00196 \le t_c \le 0.32258$	$0.00196 \le t_c \le 0.32258$	$0.00196 \le t_c \le 0.32258$
Solid volume fraction, ϕ	$0.42 \le \phi \le 0.43$; $\phi<\phi_0<\phi_\infty$	$0.42 \le \phi \le 0.43$; $\phi<\phi_0<\phi_\infty$	$0.45 \le \phi \le 0.46$; $\phi<\phi_0<\phi_\infty$
Max packing fraction, ϕ_m	$0.69 \le \phi_m \le 0.74$	$0.71 \le \phi_m \le 0.74$	$0.71 \le \phi_m \le 0.74$
Volume fraction of particles contained in all the SUs when the shear rate $\to 0$, ϕ_{A0}	$\phi_{A0} \le \phi$	$\phi_{A0} \le \phi$	$\phi_{A0} \le \phi$
Volume fraction of particles contained in all the SUs when the shear rate $\to 0$, $\phi_{A\infty}$	$\phi_{A\infty} \le \phi_{A0}$	$\phi_{A\infty} \le \phi_{A0}$	$\phi_{A\infty} \le \phi_{A0}$

As basis for the values used for the solid volume fraction ϕ, in our modelling we used the calculated fractions based on the densities found for the particles as mentioned under "Sample preparation and experimental methods" section. To obtain the lower limiting values they were corrected for the amount of dissolved ions reducing the volume fraction and for the amount of water chemically bound to the particles increasing the volume fraction. These corrections were based on values measured after approximately 22 min of hydration, this is the time needed for the recommended API sample preparation prior to rheological measurements [2,3]. The reduction of the solid volume fraction due to dissolved ions was based on density measurements of the cement filtrate and it was found to be approximately 0.9% by volume. The solid volume increase due to chemically bound water was found to be approximately 2.4% by volume, giving a net solid volume increase of approximately 1.5%. For the Micromax particles our measurements did not show any dissolved ions or chemically reacted water, thus the corrections of the lower limiting solid volume fractions used for our modelling was only based on the respective content of cement particles.

For the upper limiting volume fractions used in our modelling we adjusted the lower limiting value for the amount of air found in our suspensions after the API-mixing and prior to the viscosity measurements. This air is expected to adhere to the particles and thus it was found to result in an increased solid volume fraction of approximately 2%.

Furthermore, for the solid volume fraction, ϕ, the limits given by Quemada [1] for pseudo-plastic fluids, $\phi<\phi_0<\phi_\infty$, were used, with ϕ_0 and ϕ_∞ being the maximum packing fractions as the shear rate $\rightarrow 0$ and $\rightarrow\infty$ respectively. These limits reflect the effect of shear on the maximum obtainable packing and that the forming of SUs when shear rates are reduced also reduces the obtainable maximum packing. Also it sets an upper limit for the solid volume fraction of the suspension in question.

When modelling, the solid volume fractions ϕ, resulting in the optimal solutions were always the given limiting values. For the neat Class G suspension the limiting upper values were used for both curves. For the suspension containing Micromax having a specific density of 1.98, both the upper and the lower limiting values were used, one for each type of curve, and for the suspension containing Micromax having a specific density of 2.03, the lower limiting values were used for both curves.

For the maximum packing fraction ϕ_m, we used as the lower limiting values, the highest packing values we were able to obtain in our packing experiments as described under "Packing measurements" subsection. As the upper limiting values we used 0.74, which is the theoretical maximum packing fraction for face centred packing of mono-disperse spheres [1,11], it also reflects the shear-dependent development of the SUs as described under "Rheological modelling" subsection.

The values used in the model for obtaining optimal solutions for the maximum packing fractions ϕ_m, were the lower limiting values of 0.71 for all the suspensions containing Micromax. For the neat Class G suspension and for the j-type of curve the value used for ϕ_m was 0.726 and for the s-type of curve it was 0.728.

The last two variables ϕ_{A0} and $\phi_{A\infty}$, being the volume fractions contained in all the SUs when the shear rate tends to zero and infinity respectively, were limited to be less or equal to the volume fraction ϕ and further $\phi_{A\infty}$ was limited to be less or equal to ϕ_{A0}.

The values for ϕ_{A0} and $\phi_{A\infty}$ used in the model for obtaining optimal solutions are shown in Table 2. They indicate a build up of SUs when the shear rate is reduced. The model gives the volume fraction of particles contained in the SUs to increase from an average of approximately 0.1 when $\dot{\gamma}\rightarrow\infty$ to an average of approximately 0.2 as $\dot{\gamma}\rightarrow 0$. This build up of SUs, when the shear rate decreases, is in accordance with Quemada's model [1]. However, we have not been able to verify this increase of SUs directly through measurements.

The correlation coefficients R^2, listed in Table 2, were used to indicate if a good agreement between data generated by the model and our measured values could be found. The data compared were the values obtained from the model and the measured values for the 10 shear rates in the interval from 511 s^{-1} down to 3.1 s^{-1}. The correlation coefficients obtained showed a good agreement between the different sets of data. For one of our optimal modelling solutions the correlation coefficient was found to be above 0.9997, for two the correlation coefficients were above 0.9998 and for the remaining three the optimal correlation coefficients were above 0.9999.

In Table 2 we have also included the values given by the model for the limiting viscosities, η_0 and η_∞ as the shear rate $\dot{\gamma}\rightarrow 0$ and $\dot{\gamma}\rightarrow\infty$ respectively. All the values obtained for η_∞ could be said to indicate an upper plateau for the viscosities with

Table 2
Optimal parameters found when modelling our suspensions

Parameters	Neat Class G SG=1.91		Cement+Micromax, SG=1.98		Cement+Micromax, SG=2.03	
p	0.398	0.516	0.419	0.521	0.413	0.541
t_c	0.00196	0.00225	0.00196	0.00196	0.00196	0.00196
ϕ	0.43	0.43	0.43	0.42	0.45	0.45
ϕ_m	0.726	0.728	0.71	0.71	0.71	0.71
ϕ_{A0}	0.223	0.221	0.211	0.208	0.213	0.210
$\phi_{A\infty}$	0.113	0.097	0.118	0.101	0.133	0.111
R^2	0.999869	0.999905	0.999953	0.999899	0.999736	0.999940
η_0	2.4 MPa s	26.3 Pa s	2.4 MPa s	59.2 Pa s	2.7 MPa s	61.6 Pa s
η_∞	32.3 mPa s	24.2 mPa s	42.6 mPa s	28.7 mPa s	68.9 mPa s	42.1 mPa s

The two optimal solutions found for each of the three suspensions are given. Included are also the limiting viscosity values as given by the model.

regard to high shear rates. For the s-type of curves, all having an exponent $p \geq 0.516$, and where a lower plateau for the viscosity is indicated, as can be seen in Figs. 2, 3 and 4, the values given for η_0 are found to be to low when compared with the measured values. This is also found to be true for the values given for η_0, for the j-type of curves all having an exponent $p \leq 0.419$. However, the latter curves are found to better reflect the true development of the viscosity for our suspensions as $\dot{\gamma} \rightarrow 0$.

4. Conclusions

A series of experiments have been conducted to see if the model proposed by Quemada [1] could be used for predicting the rheological behaviour of selected cementitious suspension when measurements are performed in accordance with API procedures [2]. By applying a range of measured viscosity values and values obtained for particle fractions and maximum packing fractions, we found that the model could be used for this purpose. However, as the model within the given set of restrictions were found to predict two optimal solutions for each of our suspensions, one found to coincide best with data at lower shear rates, and one found to coincide best with data at higher shear rates, care should be taken as to which solution to choose when studying phenomena at either higher or lower shear rates.

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