Concentration effects in the rheology of cement pastes: Krieger-Dougherty revisited

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ABSTRACT

Cement pastes are concentrated suspensions of granular particles in water and their rheology strongly affects the behaviour of all concretes and other cementitious materials. While the rheology of cement pastes has been extensively studied over the last 60 years, leading to the general conclusion that cement particle shape, size and concentration are key variables, the overwhelming majority of the results to date have been expressed in terms of the effect of water/cement ratio on the measured rheological parameters. While this has been helpful in making empirical progress, a more fundamental approach requires that the concentration be expressed in volumetric terms. A suitable relationship is the Krieger-Dougherty equation:

$$\eta(\phi) = \eta_s\left(1 - \phi/\phi_m\right)^{-[\eta]\phi_m}$$

Here $\eta(\phi)$ *is the viscosity at solid volume fraction* ϕ *of a suspension of particles whose maximum packing fraction is* ϕ_m *when dispersed in a medium of viscosity* η_s. $[\eta]$ *is referred to as the intrinsic viscosity and varies according to the shape of the particles, from 2.5 for spheres up to very high numbers for fibres of high aspect ratio. While originally formulated for viscosity the Krieger-Dougherty equation can be used for other rheological parameters such as yield stress. From the relationship between* $\eta(\phi)$ *and* ϕ *curve fitting enables the values of* ϕ_m *and* $[\eta]$ *to be estimated for a liquid medium of viscosity* η_s.

This paper uses a comprehensive series of datasets relating rheology and concentration, which have been collected from the literature over the past 60 years. Each dataset has been converted from the original water/cement ratio form to volume concentration and then fitted to the logarithmic transformation of the Krieger-Dougherty equation by linear regression. The logarithmic form makes it possible to use a linear fit, whereas the untransformed equation diverges to infinity at the maximum packing fraction which makes it difficult to assess the best fit of the data.

The paper draws conclusions on the appropriate values of the suspension parameters (maximum packing fraction and intrinsic viscosity) for the different datasets and discusses the implications of the findings in the light of what we know about the properties of cement. It considers the validity of the equation for modelling the rheology of cement pastes and other cementitious materials.

ORIGINALITY:

The originality of this paper lies in the fact that no-one has attempted a widely applicable correlation between cement paste rheology and concentration which exploits the rich array of data that has been collected since research on cement paste rheology started. A graphical survey was carried out in Tattersall and Banfill's book in 1983 but is purely empirical showing the range of measured rheological parameters obtained at a range of water/cement ratios. A few individual papers have attempted to fit their own data to the Krieger-Dougherty equation but the fit has mostly been made 'by eye'. The logarithmic transformation of the equation has been used by Hendrickx et al but no attempt at a wider comparison was made.

CHIEF CONTRIBUTIONS:

An ability to model the rheology of cementitious materials depends on the veracity of the relationship between rheology and concentration. At the time of writing there is no generally applicable relationship for this and this paper offers the possibility of deriving such a relationship. This is a novel contribution.

KEYWORDS: *Cement paste, rheology, concentration, plastic viscosity, yield stress*

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1. INTRODUCTION

An ability to model and predict the flow behaviour of fresh cement based materials is important to optimise their performance in use. Flow of concrete into formwork, pumping, compaction by vibration, injection of grout, oilwell cementing and application of mortar by hand are all situations where rheology is a controlling factor. Increasing use of computer-based modelling and simulation requires good quality data on the rheology of the materials concerned, all of which is governed by the rheology of cement paste, the universal constituent of all cement based materials.

The rheology of cement pastes is generally well explained by the Bingham model, although many other equations of flow, all involving a yield stress, have been used to characterise the experimental data obtained (Banfill, 2006). Tattersall and Banfill (1983) presented an empirical graphical compilation of data showing the inverse exponential relationship between water/cement ratio *WC* and the yield stress τ_0 and plastic viscosity μ of cement pastes, which has been widely used by others, and takes the form

$$\tau_0 = A_1 e^{-B_1 WC} \qquad \text{and} \qquad \mu = A_2 e^{-B_2 WC} \tag{1}$$

where A_1, A_2, B_1 and B_2 are constants. However, water/cement ratio is an inconvenient concept for fundamental studies, all of which use solid concentration as the controlled variable (Buscall et al, 1987, Zhou et al, 1999). A widely employed relationship in studies of suspension rheology is that of Krieger and Dougherty (1959), the use of which for cement pastes was investigated by Struble and Sun (1995):

$$\eta(\phi) = \eta_s \left(1 - \phi / \phi_m \right)^{-[\eta]\phi_m} \tag{2}$$

Here $\eta(\phi)$ is the viscosity at solid volume fraction ϕ of a suspension of particles whose maximum packing fraction is ϕ_m when dispersed in a medium of viscosity η_s. $[\eta]$ is referred to as the intrinsic viscosity and varies according to the shape of the particles, from 2.5 for spheres up to very high numbers for fibres of high aspect ratio.While formulated for the viscosity of Newtonian liquids, it can be applied to Bingham materials to predict the variation of yield stress and plastic viscosity. However, defining the parameters of the equation from experimental data is uncertain because predicted yield stress and plastic viscosity diverge to infinity as the volume fraction approaches the maximum packing fraction. A possible solution lies in the use of the logarithmic form of the equation, as was done for mortars by Hendrickx et al (2009).

This paper applies the logarithmically transformed equation to a number of experimental datasets, most of which have been published in the literature, and investigates the possibility of deriving generally applicable values of the material constants in order to facilitate their use in the modelling of cement paste rheology.

2. THEORY

The solid concentration in a cement paste is defined by the volume fraction ϕ and is related to the water/cement ratio by mass as follows

$$\phi = \frac{\rho_w}{\rho_c} \Bigg/ \left(WC + \frac{\rho_w}{\rho_c} \right) \tag{3}$$

where ρ_w and ρ_c are the density of water and cement respectively. In this paper the density of cement is taken as 3150 kg/m^3, so equation 3 becomes

$$\phi = 0.3175/(WC + 0.3175) \qquad (4)$$

The logarithmic form of the Krieger-Dougherty relation (equation 2) is

$$\ln\eta(\phi) = \ln(\eta_s) - \phi_m[\eta]\ln(1-\phi/\phi_m) \qquad (5)$$

From this a graph of $\ln\eta$ against $\ln(1-\phi/\phi_m)$ should be a straight line with intercept $\ln(\eta_s)$ and slope $-\phi_m[\eta]$. Since the liquid medium in a cement paste is water, by definition $\eta_s = 0.001$ Pa.s and therefore $\ln(\eta_s) = -6.91$. This also applies to the plastic viscosity of a Bingham material so from a set of volume fraction – plastic viscosity data it is simply necessary to choose by inspection a value of ϕ_m such that the intercept of the graph, obtained by extrapolating the experimental points, is -6.91. The value of $[\mu]$ is then obtained from the slope of the line.

In principle, the same process can be used for yield stress but the fact that the yield stress of the liquid medium is zero makes extrapolation impossible. In practice using the same value of ϕ_m as for plastic viscosity will give a value of $(\tau_0)_s$ that is zero within experimental error. Since $[\mu]$ and $[\tau_0]$ are constants that reflect the geometrical features of the particles in the suspension their values should be similar.

3. PROCEDURE

35 datasets from 14 reference sources, reporting the effect of water/cement ratio (or in a few cases volume fraction) on measured yield stress and plastic viscosity were used. The criteria for inclusion in the study are (i) there are at least four points, i.e. four different water/cement ratios, (ii) there are values for both yield stress and plastic viscosity at each water/cement ratio, (iii) the material is Portland cement alone, i.e no limestone, flyash, slag etc, to ensure that the assumed density of 3150 kg/m^3 is valid, and (iv) the pastes are of cement and water only with no admixtures present. Many sources do not report the mixing method used and some do not mention the type of rheometer used for the tests, matters that have been criticised previously (Tattersall and Banfill, 1983). In most cases the values of yield stress and plastic viscosity were obtained by reading graphs and some datasets had to be disregarded because the graphs are just too small to be readable.

After conversion of water/cement ratio to volume fraction using equation (4) the value of ϕ_m was varied until the best fit straight line through the graph of $\ln\mu$ against $\ln(1-\phi/\phi_m)$ by linear regression gave an intercept of –6.91. $[\mu]$ was obtained from the slope of the graph. The same value of ϕ_m was used for the graph of $\ln\tau_0$ against $\ln(1-\phi/\phi_m)$ in order to obtain the values of $(\tau_0)_s$ and $[\tau_0]$. All statistical calculations used the appropriate functions in Excel®.

4. RESULTS

Figure 1 is an example of a set of data (Ish-Shalom and Greenberg, 1962), from which $\phi_m = 0.562$. The lines calculated by linear regression and their respective equations are marked on the graph, from which the plastic viscosity line, with its high value of R^2 suggesting a good fit to the data, has an intercept of –6.91. The intercept of the yield stress line is –1.98, corresponding to $(\tau_0)_s = 0.14$ Pa. This can be considered to be zero within experimental error because the data for yield stress was obtained by extrapolating each flow curve to zero shear rate and controlled shear rate rheometers cannot, by definition, be exact at zero shear rate. The points in the yield stress data set have wider confidence intervals and this is reflected in the lower R^2 value and the error in the intercept. Clearly, since $\ln 0 = -\infty$ the actual value for an infinitely dilute suspension is almost meaningless. Finally, for this set of data, $[\mu] = 4.25$ and $[\tau_0] = 3.53$. These are slightly lower than but still consistent with the parameters reported by Struble and Sun (1995), which were in the ranges $\phi_m = 0.64 - 0.80$ and $[\eta] = 4.5 - 6.8$.

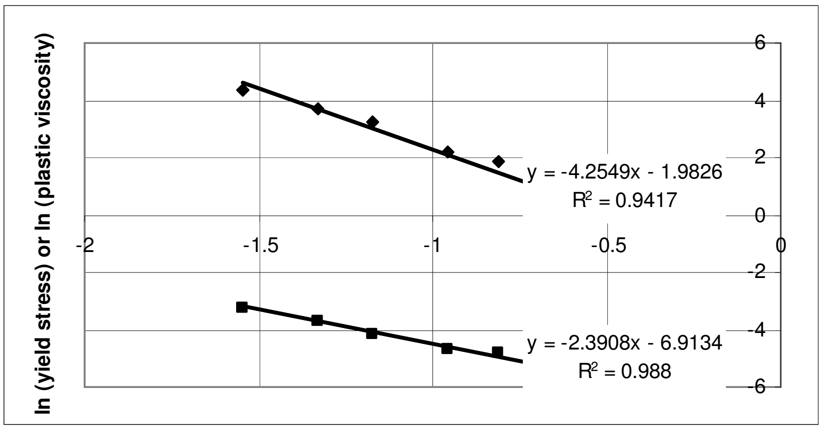

Figure 1: $\ln \mu$ (lower line) and $\ln \tau_0$ (upper line) plotted against $\ln(1-\phi/\phi_m)$. Data of Ish-Shalom and Greenberg, 1962.

In choosing the value of ϕ_m to give the best fit straight line through the graph of $\ln \mu$ against $\ln(1-\phi/\phi_m)$ by maximising R^2 it was found that in 6 of the 35 datasets it was impossible to choose a rational value. In these cases the best fit value of ϕ_m either exceeded 1.0 or fell below the highest value of ϕ in the dataset, both of which are impossible by definition. These datasets were therefore excluded from further consideration. Of the remaining 29 datasets, it was possible to adjust the value of ϕ_m to achieve a best fit line that achieved an intercept of –6.91 in only 21 cases. It was felt inappropriate to artificially fix the value of the intercept at –6.91 in the remaining 8 cases as this would have biased the conclusions. Thus, in 21 datasets it was possible to follow the procedure outlined in section 3. The outcome of this exercise is summarised in Table 1.

Table 1: Values of ϕ_m to achieve $\ln(\eta_s) = -6.91$

Individual values of ϕ_m	**Mean**	**Median value**
0.4, 0.477, 0.5, 0.51, 0.52, 0.521, 0.53, 0.561, 0.562, 0.562, 0.585, 0.59, 0.59, 0.615, 0.645, 0.748, 0.775, 0.784, 0.79, 0.93, 0.988	0.63	0.585

For the 29 cases where it was possible to choose a rational value of ϕ_m to give a best fit straight line even with a different intercept from –6.91, the values are given in Table 2.

Table 2: Values of ϕ_m to achieve best fit of ln μ against $\ln(1-\phi/\phi_m)$

Individual values of ϕ_m	**Mean**	**Median value**
0.42, 0.45, 0.45, 0.46, 0.46, 0.47, 0.47, 0.48, 0.495, 0.5, 0.5, 0.52, 0.52, 0.52, 0.52, 0.53, 0.53, 0.53, 0.54, 0.565, 0.58, 0.59, 0.62, 0.65, 0.65, 0.65, 0.65, 0.9, 0.988	0.54	0.52

In both Tables 1 and 2 the mean is higher than the median value, suggesting that the two values above 0.9 are skewing the distribution. When these are removed the means fall from 0.63 to 0.59 and 0.54 to 0.51 respectively, similar to the medians. Thus the most suitable general value of ϕ_m to achieve the twin objectives of a good fit to the measured data and an intercept near to –6.91 is $\phi_m = 0.55$.

It is now possible to apply $\phi_m = 0.55$ to every one of the 35 datasets to obtain an overall relationship. Figure 2 includes 161 data points, including both those from datasets for which it was impossible to find a rational value of ϕ_m and those with an intercept significantly different from –6.91. The best fit straight lines are plotted, and presented with their respective equations obtained by linear regression. The value of R^2 is higher for the ln μ graph than for ln τ_0 which is consistent with the smaller spread in the data, but both are highly significant correlations. In view of the difficulty in assigning an appropriate value of the intercept in the ln τ_0 graph no attempt is made to force the line to an intercept. On the other hand, for the ln μ graph the free linear regression gave an intercept of –6.4 (R^2 = 0.7), which is not significantly different from –6.91. Using the standard error on the slope to give the 90% confidence interval, from the ln μ graph the slope is –3.31±0.21 and intrinsic viscosity [μ] = 6.0±0.4 and from the ln τ_0 graph the slope is –1.75±0.24 and intrinsic yield stress [τ_0] = 3.1±0.4. Finally, a prediction interval can be defined from these data. According to Chatfield (1975) there is a probability (1-α) that a future observation of y at a point x_0 will lie between

$$\hat{a}_0 + \hat{a}_1 x_0 \pm t_{\alpha/2,n-2}\, s_{y:x} \sqrt{\left[1 + \frac{1}{n} + \frac{(x_0 - \bar{x})^2}{\sum_{i=1}^{n}(x_i - \bar{x})^2}\right]} \tag{6}$$

Setting $y = \ln\mu$, $x = \ln(1-\phi/\phi_m)$, $x_0 = -1.5$, $\hat{a}_0 = -6.91$, $\hat{a}_1 = -3.31$ and $t_{\alpha/2,n-2} = 1.655$ at α = 90%, $\bar{x}$ is the mean and x_i is the ith value of x, with n = 161 and $s_{y:x}$ is the standard error, gives the prediction interval at $\ln(1-\phi/\phi_m) = -1.5$ as 1.945±1.356. The dashed lines on Figure 2 represent this prediction interval and, as expected, about 12 points out of 161 lie outside these limits. Repeating the same process for the yield stress line gives the prediction interval at $\ln(1-\phi/\phi_m) = -1.5$ as 2.873±1.563. The dashed lines on Figure 2 show that about 20 points lie outside these limits.

These relationships can now be summarised as a pair of formulae, expected to be able to predict yield stress and plastic viscosity of cement pastes at solid volume fraction ϕ with 90% confidence:

$$\ln \tau_0 = 0.24 - (1.75 \pm 1.2) \ln(1 - \phi/0.55) \quad (7)$$

$$\ln \mu = -6.91 - (3.3 \pm 1.0) \ln(1 - \phi/0.55) \quad (8)$$

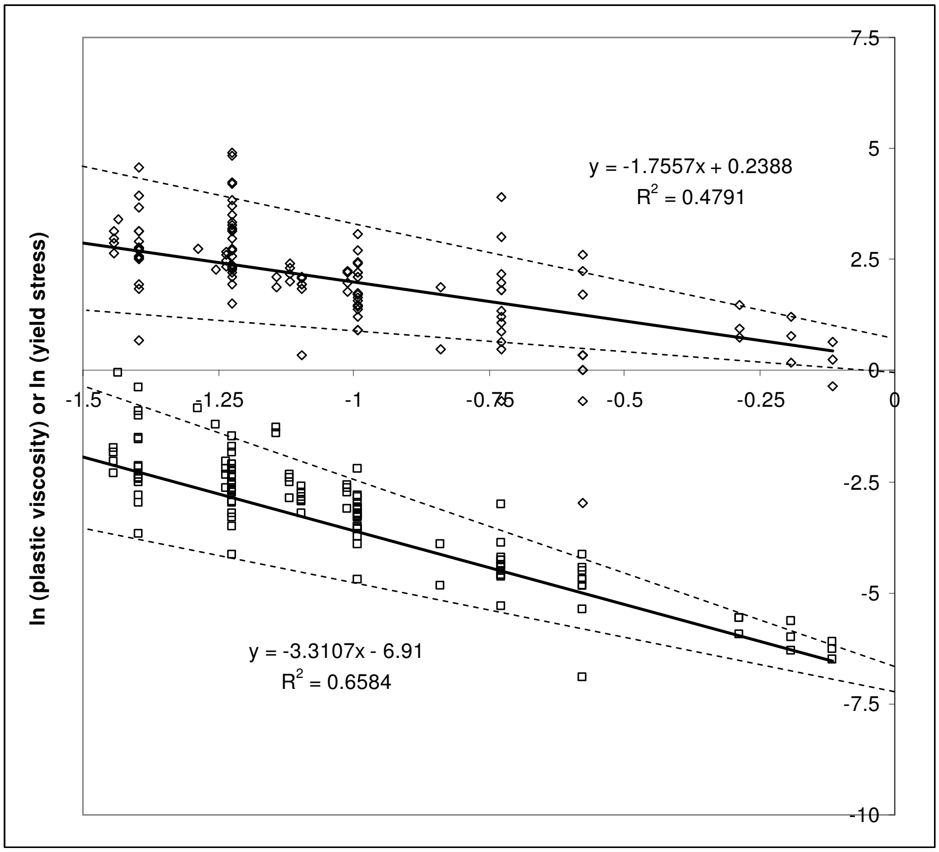

Figure 2: ln μ (lower line) and ln τ_0 (upper line) plotted against $\ln(1-\phi/\phi_m)$ for 161 points

4. DISCUSSION

ϕ_m in equation 2 is typically between 0.6 and 0.7 for mono-sized spherical particles and decreases for asymmetrical particles and flocculated dispersions because they cannot pack together so closely. Polydispersity enables closer packing, with higher ϕ_m. Additionally ϕ_m increases with shear rate, e.g. from 0.63 to 0.71 over a 10^5 fold range of shear rate (Barnes et al, 1989). Struble and Sun (1995) gave 0.64 for a single flocculated cement paste, at high shear rate: their 7 values for dispersed cement were higher (up to 0.80). Therefore the value of 0.55 obtained from here seems reasonable for undispersed cement pastes at low shear rates. [μ] is 2.5 for spheres, 3 to 5 for angular particles and higher still for rods or fibres (Barnes et al, 1989). The observed value of 6 is consistent with the kind of irregular flocculated structure likely to be found in a cement paste. The observed value of the intrinsic yield stress [τ_0] of 3.1 is lower but this is again reasonable because yield stress is more strongly affected by interparticle interactions and thus the state of flocculation in the paste than the plastic viscosity. Struble and Sun (1995) reported values of 4.5 to 6.8, of which one (6.3) was for a flocculated paste.

The validity of equations 7 and 8 may be checked by using them to predict the yield stress and plastic viscosity of plain cement pastes from other datasets, see Table 3. Only two of the ten measured values fall outside the prediction interval, and one of those is only marginal. This shows that the prediction equations are satisfactory, but the prediction intervals are wide, covering a 6- to 40-fold range. This reflects the experimental differences in paste preparation, test methods and materials (Banfill, 2006). It would be interesting to extend the analysis to dispersed cement pastes containing superplasticisers.

Table 3: Comparison between measured yield stress (Pa) and plastic viscosity (Pa.s) and the 90% prediction interval for equations 7 and 8.

Reference	ϕ	**Lower** τ_0	**Mean** τ_0	**Upper** τ_0	**Measured** τ_0	**Lower** μ	**Mean** μ	**Upper** μ	**Measured** μ
Nehdi and Rahman 2004	0.443	2.0	13	83	12	0.043	0.21	1.6	1.28
Nehdi and Rahman 2004	0.388	1.6	6.3	26	7	0.017	0.057	0.25	0.34
Rudzinski 1984	0.346	1.4	4.3	13	10	0.01	0.026	0.088	0.045
Rudzinski 1984	0.328	1.3	3.7	10	8	0.008	0.02	0.06	0.03
Puertas et al 2005	0.443	2.0	13	83	38	0.043	0.21	1.6	0.8
Grzeszczyk 1997	0.388	1.6	6.3	26	13	0.017	0.057	0.25	0.26

5. CONCLUSIONS

The logarithmic form of the Krieger-Dougherty equation has been fitted to 161 measured values of yield stress and plastic viscosity of cement pastes, taken from 14 reference sources. Prediction equations for these two parameters have been derived and are able to predict the properties of cement pastes that were not part of the original datasets.

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