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Thixotropic Characterization of Fresh Cement Pastes

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ABSTRACT

The time and shear rate dependence of the flow of a cement paste has been theoretical and experimentally studied. Thixotropic behavior has been observed and analyzed using a thixotropy model which assumes shear rate and structural state dependence of both structure build-up and break-down processes. Before the appearance of hydration effects, a good agreement between the structural rebuilt-up at rest with the resting time has been found.

INTRODUCTION

Fresh cement pastes are highly concentrated suspension with a complex rheological behavior. As the basic component of a concrete, it mainly determines its rheological properties in fresh state, and its mechanical properties in hardened state. Considered as colloidal suspension, the interactions among particles may lead to a composition dependant[1] microstructure formation in the suspension at rest. Depending on how the structure responds to an applied shear, one can observe different types of macroscopic flow behaviour[2-4]. In general, the rheological properties of cement pastes are dependent on both, the shear (rate or stress) and time. This means that a complete rheological characterization of this material must consider both steady and transitory studies[5].

Thixotropic fluids are characterized by a variable viscosity which reversibly decreases with time under high shear rates and, because of the reversibility, the viscosity increases in time at low shear rates. There are several reviews about the theoretical literature on this time dependent material property[6-8]. They are based on three different approaches: a continuum mechanics approach, a microstructural and a structural kinetics one. Due to the wide range and the complex nature of the microstructures that can be found in thixotropic systems, the structural kinetics approach might be more suited for a general thixotropy model than the others[9].

In a valuable contribution to the description of thixotropy from the structural kinetics point of view, Cheng and Evans[10] proposed a general mathematical form of the equation of state of a thixotropic material. This consists in a constitutive equation, which links the shear stress (τ) to the shear rate ($\dot{\gamma}$) by means of a viscosity function which depends on the shear rate and a structural parameter (λ) related to the flocculation level inside the material, and a kinetic or evolution equation, which expresses the time evolution of the microstructure.

Very recently, Coussot´s et al. version[11] of Cheng and Evans approach has been applied to the rheology study of fresh cement pastes[5]. An experimental method that combines steady and transient measurements to determine the four model parameters was proposed. Despite the good agreement between model predictions and experimental data corresponding to both steady and transitory experiments, the model fails when compared with the experimental starting apparent viscosity. The time dependency predicted by the model is due to a critical assumption: "*the structuration at rest is independent of the state of structuration itself*".

In this work, we will use a simplified version of a structural kinetics model for thixotropy. *The dependence of the structuration at rest with the state of structuration of the material* is taken into account. Moreover, *the shear rate dependence of the build-up process during shear* is also explicitly considered. The model has been checked with experimental data obtained with a fresh cement paste.

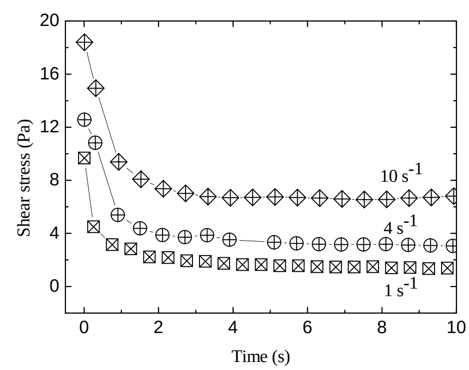

Figure 1. Typical experimental results for the variation of the shear stress with time. HAC80 cement paste. Step-up from rest.

THEORETICAL BACKGROUND

A cement paste is a concentrated suspension which essentially consists of water and cement particles. Moreover, different liquid and/or solid additives may be added to get desired properties in the material. In the resulting dispersion a continuous solid network is formed at rest, due to the connection, favored by thermal diffusion, between the solid particles. This structure is macroscopically manifested by the necessity to apply a minimum or yield stress to observe the flow of the sample. In other words, the material behaves solid-like under relatively small applied stresses and liquid-like when the yield stress is exceeded. Other effect due to the existence of the solid network is the time dependence of the break-down structure when a shear is applied to the material[12]. When this time evolution of the structure is reversible, the phenomenon is named thixotropy. Accompanying the breaking up of the links between particles, the build-up of the solid structure due to the formation of links between particles is also given. It is assumed that at the lower shear the build-up process dominates on the break-down, being the opposite at the higher shear[13].

In the thixotropic behaviour we found a double dependence of the viscosity of the material: with the shear and the time. In order to study only the time effect, the commonly used method consists in the application of a constant shear rate. The viscosity (or the shear stress) is determined as a function of the time. The typical dependence obtained in step-up experiments is shown in Fig. 1. It has been found that for a given shear rate the viscosity decreases with time until a steady value. When a step-down experiment is made, the viscosity increases with time until a steady value, as can be seen in Fig. 2. The rate at which the viscosity varies is a function of the shear rate.

Cheng and Evans[10] proposed a general framework for the structural kinetics approach used to model thixotropy. Moreover the constitutive equation (Eq. 1), that relates the shear stress with the shear rate by means of a viscosity function, a kinetics equation (Eq. 2), which governs the evolution with time of a structural parameter which characterizes the state of the structure, is also formulated,

$$\tau = \eta(\dot{\gamma}, \lambda)\dot{\gamma} \qquad (1)$$

$$\frac{d\lambda}{dt} = f(\dot{\gamma},\lambda) - g(\dot{\gamma},\lambda) \quad (2)$$

As λ is shear and time dependent, the viscosity is also shear and time dependent. The first-order rate equation expresses that the evolution with time of the structural level is the result of a dynamic balance between the build-up and break-down of the structure. In general, these are both shear and instantaneous structure dependent.

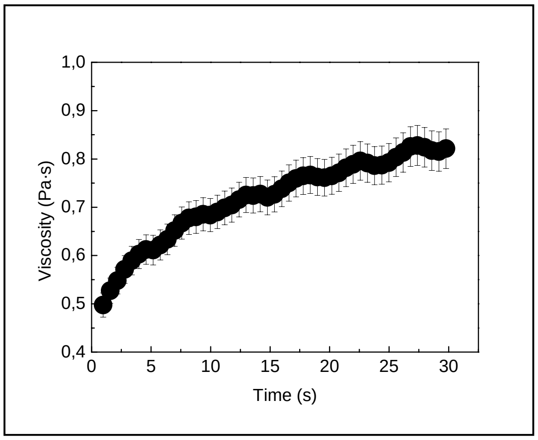

Figure 2. Typical experimental results for the variation of the viscosity with time. HAC80 cement paste. Step-down: $\dot{\gamma}$ =50 to10 s^{-1}.

Several rheological models have been used to characterize the rheology of cement pastes[14]. The basic one is a single Bingham model, which will be used in this study. Therefore, the constitutive equation of the model will be,

$$\tau = \tau_y + \eta_p \dot{\gamma} \quad (3)$$

where τ_y is the yield stress and η_p the plastic viscosity.

As was below established, the second equation of state in a structural kinetics model for thixotropy is the kinetic or rate equation. This expresses the time evolution of a structural parameter, $\lambda \ (0 \le \lambda \le 1)$, that describes the local degree of interconnection of the microstructure. The completely build-up and completely broken down structures are represented by a value for λ of, respectively, *1* and *0*. We will assume that the aggregate breakdown is flow induced by the shear rate, being proportional to this magnitude, while the build-up results from the Brownian motion and the shear rate. This last dependence is frequently ignored[5,16-17], despite the agreement with the experimental data is not enough satisfactory[5]. On the other hand, contrary to the assumption by Roussel[5], it will be accepted that both processes, the breakdown and build-up of the microstructure, will dependant on the actual state of structuration of the material. These considerations result in the following kinetic equation,

$$\frac{d\lambda}{dt} = \begin{cases} \frac{\beta^2}{\dot{\gamma}}(1-\lambda) - \alpha\dot{\gamma}\lambda; & \dot{\gamma} > 0 \\ \beta(1-\lambda); & \dot{\gamma} = 0 \end{cases} \quad (4)$$

where $\beta^2 / \dot{\gamma}$ is the build-up rate, and $\alpha\dot{\gamma}$ is the breakdown rate. It has been supposed that the first one is inversely proportional to the shear rate, while the second one is directly proportional to the same magnitude. In this manner is introduced, in the simpler way, the intuitive fact that a higher shear rate favors the breakdown of the structure, but it is worst for its build-up. Sometimes an exponential dependence on the deformation rate, in the rate of breakdown term is included[17] in order to account for the most usual fact that the shear stress evolution in the shear-rate step-up experiments is faster than that in the step-down cases. The square is necessary to make dimensionally right the equations without the introduction of a third adjustable parameter. As can be also seen, the build-up and breakdown processes, respectively decrease and increase with the existing structure.

If only the first Eq. (4) was accepted for all $\dot{\gamma}$-values, a conflict would be found in the limit $\dot{\gamma} = 0$. Certainly, the structure would increase with time with an infinite rate! We have solved this undesirable prediction by assuming that in rest ($\dot{\gamma} = 0$), the build-up of the structure is due to Brownian motion (β) and only depends on the existing structure.

The model equations complete incorporating a λ-dependence in the constitutive equation (Eq. 3). We will assume the yield stress vary proportionally to the initial structure, while the plastic viscosity vary with the n-power of the instantaneous structure. Therefore,

$$\tau_y = \lambda_o \tau_{yo} \tag{5}$$

$$\eta_p = \lambda^n \eta_{po} \tag{6}$$

where τ_{yo} is the yield stress and η_{po} the plastic viscosity corresponding to the completely build-up structure. Therefore, the structural kinetics model here used for the characterization of the thixotropic behavior of fresh cement pastes, is defined with the kinetic equation (Eq. 4) and the following constitutive equation,

$$\tau = \left(\lambda_o \tau_{yo} + \lambda^n \eta_{po} \dot{\gamma}\right) \tag{7}$$

EXPERIMENTAL

The rheological tests were carried out by using a high-accuracy rheometer Gemini150 (Malvern). This rheometer is capable to work in the CS and CR modes. Standard serrated plate-plate geometry was used (diameter = 40 mm) after calibration (the manufacturer recommends 4% tolerance). The sample was maintained at 25 ^{0}C with a Peltier plate.

The formulation of the cement paste here studied is shown in Table 1. The cement is a commercially manufactured Portland cement I 42.5 R/SR, and the additives are also commercially distributed.

In order to be sure all samples of the cement paste are studied starting from identical initial conditions, a pre-shear of 100 s^{-1} during 30 s was applied, and the coincidence of the corresponding steady shear stress value was taken as the demonstration of that fact. The relatively high shear rate applied during the pre-shear was intended to cause structural breakdown of the cement paste sample and create uniform conditions before testing.

Table 1. Composition of the cement paste.

Component	HAC80 (kg/m^3)
Cement	1000
Microsilica	100
Lignosulfonate	5
Acrylic	30
Water	365

RESULTS AND DISCUSION

The steady state behaviour has been determined by means of a decreasing flow curve. After the pre-shear, the sample is sheared following a decreasing ramp, but only when a stationary stress value is measured at each shear rate, the rheometer steps-down to the following shear rate.

For a constant shear rate value, the following condition is accomplished when the steady state is reached,

$$\frac{d\lambda}{dt} = 0 \tag{8}$$

This means that the build-up and breakdown structure rates are in a dynamic equilibrium when a certain structural level is reached. Imposing the condition (8) in the first Eq. (4), the structure parameter value corresponding to the steady state (λ_{ss}) is obtained,

$$\lambda_{ss} = \frac{1}{1 + \delta\dot{\gamma}^2} \tag{9}$$

where $\delta = \alpha / \beta^2$. As can be seen, the model predicts that the higher the breakdown rate ($\alpha\dot{\gamma}$) compared to the build-up rate ($\beta^2/\dot{\gamma}$), the lower the steady state structure parameter. It is interesting to note that only in the limits $\dot{\gamma} \to 0$ and $\dot{\gamma} \to \infty$, the values $\lambda = 1$ and $\lambda = 0$ are, respectively, obtained.

Substituting Eq. 9 in Eq. 7, the steady flow curve will be obtained,

$$\tau_{ss} = \lambda_o \tau_{yo} + \frac{\eta_{po}}{\left(1 + \delta \dot{\gamma}^2\right)^n} \dot{\gamma} \qquad (11)$$

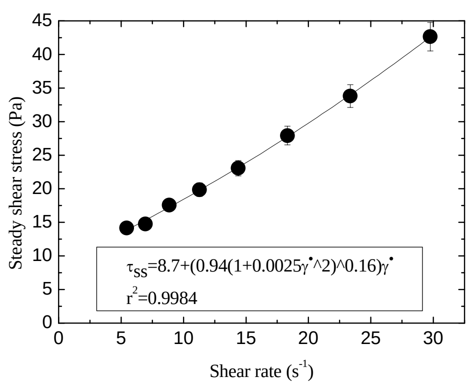

Figure 3. Steady flow curve.

From the steady flow curve, three constants of the model (τ_y, η_{po} and *n*) and the ratio of the others (δ) can be obtained. In Fig. 3 the experimental steady shear stress of HAC80 cement paste is plotted in terms of the shear rate. Fitting Eq. (11) to these experimental data, the following constant values are obtained,

$$\begin{aligned} \tau_y &= (8.7 \pm 0.2) Pa \\ \eta_{po} &= (0.94 \pm 0.01) Pa{\cdot}s \\ \delta &= (2.5 \pm 0.3) 10^{-3} s^2 \\ n &= -(0.16 \pm 0.01) \end{aligned} \qquad (12)$$

To obtain the parameters α and β, transient experiments were made. From the first Eq. 4, the time evolution of the structural parameter λ, for a constant applied shear rate and for an initial lambda value equal to λ_i, can be obtained,

$$\lambda(t) = \lambda_{ss} + [\lambda_i - \lambda_{ss}] \exp\left(- \frac{\beta^2}{\dot{\gamma}\lambda_{ss}} t \right) \qquad (13)$$

where Eq. 9 has been used. As can be seen, the structural parameter evolves from the initial (λ_i) to the steady (λ_{ss}) value at a rate $\beta^2 / \dot{\gamma}\lambda_{ss}$ which increases with the shear rate, according to the general experimental observation. Substituting Eq. 13 in Eq. 7, the time evolution of the shear stress corresponding to a transitory step essay, can be obtained.

From the second Eq. 4, the evolution of the structural state with the rest time can be obtained,

$$\lambda_r = 1 + (\lambda_{ssi} - 1) \exp(-\beta t_r) \qquad (14)$$

where t_r is the rest time after a equilibrium structure λ_{ssi} has been previously reached. This result predicts that the structure tends to the limit value $\lambda = 1$ when the rest time infinitely increases.

Substituting Eq. 13 in Eq. 7, the time dependence of the shear stress can be obtained and, from this, the initial shear stress just when a shear rate is applied after the rest period can be deduced,

$$\tau_o = \tau_y + \eta_{po} \dot{\gamma} \lambda_r^n \qquad (15)$$

The experimental results on three different step-up essays corresponding to samples which previously were rested during 75 s, are shown in Fig. 1. Using Eq. 12 after substituting Eq. 14 in Eq. 15, the mean β value is obtained. The results for this parameter and the last one of the model, α, are,

$$\beta = (2.3 \pm 0.2) \cdot 10^{-2}\ s^{-1}$$
$$\alpha = (1.3 \pm 0.2) \cdot 10^{-6} \quad (16)$$

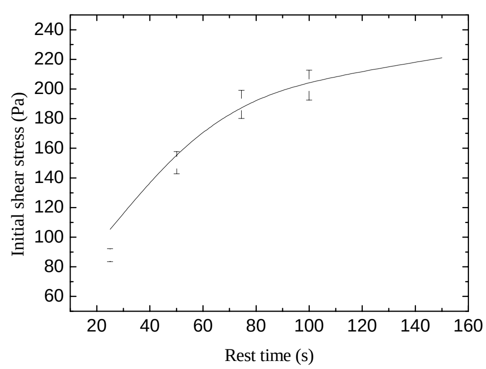

Figure 4. Experimental and theoretical prediction of the initial shear stresses corresponding to step-up essays from rest to $\dot{\gamma} = 1 s^{-1}$ after different rest times.

To check the validity of the model, the experimental initial shear stress of several samples of HAC80 cement paste have been compared with the theoretical prediction. These samples were rested during different time intervals after the pre-shear. After this, a shear rate ($\dot{\gamma} = 1 s^{-1}$) was applied and the initial shear stress value was recorded. The structural parameter that results after the rest time is obtained with Eq. 14. This magnitude, identified with λ_o in Eq. 7 is used to obtain the initial shear stress just when the step-up starts. The yield stress corresponding to the completely structured sample, τ_{yo}, was before obtained as the quotient,

$$\tau_{yo} = \frac{\tau_y}{\lambda_o} = \frac{8.7}{0.0385} \approx 227\,Pa \quad (17)$$

where $\lambda_o = 0.0385$ is the steady structural parameter value corresponding to the pre-shear. The theoretical prediction so obtained has been plotted with the experimental results in Fig. 4. As can be seen the agreement is very satisfactory for the rest times we could study. The model predicts an increase in the structure formation with the rest time, but at extremely larger rest times, a maximum structure is formed. We could not observe this saturation due to the appearance of hydration effects in the samples. It would be desirable to design some experimental test which permits us obtain information of the behaviour of fresh pastes at these large rest times. The use of different paste formulations could possibly solve this limitation of the test.

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