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Determination of characteristic rheological parameters in Portland cement pastes

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HIGHLIGHTS

- In rheological studies, the stimulus type may yield different shear strength values depending on the measurement scheme used.
- Similar behaviour: ≈50% decline in shear stress after 30″ of rotation and further loss when the stimulus was repeated.
- Clearly different behaviour: higher shear strength in PC2 paste, greater bond recovery in PC1 paste.
- The explanation lies in the very different $N_2Oeq.$ (%) contents in the liquid phase of the two PC pastes.

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ABSTRACT

The standard use of admixtures in Portland cements (with and without mineral additions)-based concrete manufacture today has made the physical–chemical interaction among the various components a highly topical issue.

One way to analyse the resulting effects is discussed in this paper, which substantiates the importance of a careful selection of the parameters used to evaluate the rheological behaviour of plain fresh pastes of Portland cements. To this end, the pastes studied in this research contained no mineral additions.

The initial analysis explored the variations in rheometer response depending on angular velocity and phase duration. Ramp direction, number of angular velocities and the size of the inter-velocity steps were also studied. Lastly, the importance of allowing the cement paste sample to rest during the measurement sequence was also analysed.

These trials were conducted on two types of Portland cements with completely different mineralogical compositions. They were repeated every 20 min prior to the initial setting time, more exactly up to the first nadir on their heat of hydration release curves, determined in earlier conduction calorimetry studies.

The results showed that parameter selection in designing a scheme to evaluate the rheological behaviour of fresh Portland cement pastes had a substantial effect on the response obtained. That response was also highly dependent upon the degree and type of hydroxy-induced alkalinity in the liquid phase of the pastes, in turn a result of the mineralogical and chemical composition of the PCs, in particular their N_2O and K_2O (%) contents, which therefore proved to play a prominent role in rheological behaviour.

1. Introduction

A number of papers [1–3] have been published on the variations in the technological properties of Portland cement blended with active mineral additions. One of the properties that varies significantly once hydration begins is rheology, with the change of state in the material, in whose measurement and analysis a series of different methodologies are called into play [4–7].

The rheological behaviour of pastes, mortars and concretes continues to be a subject of analysis in light of the large number of factors involved in cement blending, mixing and hydration (such as type of cement, type and proportions of mineral additions and presence or otherwise of admixtures). Very generally, rheology describes the deformation of a "body" subjected to loading. The "body" in this case refers to solid and liquid materials. Ideal solids deform elastically, whereby the energy required in the deformation is recovered when the load is removed. Ideal fluids, by contrast, deform irreversibly because they flow. The energy required for deformation is dissipated in the fluid as heat and cannot be recovered by merely removing the load involved. Real bodies behave neither like ideal solids nor ideal fluids, and may

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be irreversibly deformed under the effect of sufficiently large forces. The vast majority of liquids exhibit behaviour somewhere in between fluids and solids: they are viscoelastic bodies. Solids may be subjected to perpendicular and tangential stress, whereas fluids can be subjected to tangential (shear) stress only.

Fluid viscosity, represented as η, is defined as its resistance to flow when subjected to shear stress. Newton was the first to formulate a law for viscosity, known as his friction law, according to which for ideal liquids:

$$\tau = \eta \cdot \gamma$$

where τ is shear stress, η is viscosity and γ is strain or the shear rate. The correlation between shear stress, τ, and strain, γ, is defined as the liquid's fluid behaviour. This correlation, known as a flow curve, is plotted in Fig. 1.

For ideal liquids, the flow curve is a straight line: the quotient of all the $\tau - \gamma$ pairs on that line is a constant. In other words, viscosity, η, is unaffected by changes in shear rate. All liquids for which this relationship holds are called "Newtonian" and all others "non-Newtonian" fluids. Cement paste fluid behaviour cannot be described by a flow curve such as in Fig. 1. Rather, since these pastes tend to form flocs, a certain minimum shear stress needs to be applied before they begin to flow. In this case the flow equation can be expressed as shown below.

$$\tau = \tau_0 + \mu \cdot \gamma$$

This equation describes the so-called Bingham model, where τ is shear stress; τ_0, threshold shear stress; μ, plastic viscosity; and γ shear rate or strain. Plastic viscosity is an indication of the number and size of the flocs, while threshold shear stress is a measure of the strength and number of interactions severed when stress is applied.

In addition to the difference between Newtonian and non-Newtonian fluids, the latter may exhibit *dilatant* or *thixotropic* behaviour, as illustrated in Fig. 1 [8,9].

A material's rheology is measured with rheometers or viscometers. A rheometer is a device that measures the viscoelastic properties of solids, semi-solids and fluids, whereas a viscometer is a more sensitive instrument that cannot accommodate large particles.

The two main types of viscometers are:

(a) native stress-controlled viscometers, in which the shear stress is user-defined to find the respective shear rate (or strain)
(b) native strain- (or shear rate)-controlled viscometers, in which the strain is user-defined to find the respective shear stress [10].

With the ultimate aim of researching the effect of active and non active (*fillers*) mineral additions on pure Portland cement rheology, the impact of the variables involved on the findings was analysed in this first stage. After establishing a measuring scheme, the variations in paste rheological behaviour were determined from initial hydration up to the first nadir on the calorimetric curve. The trials were conducted on two pure Portland cements with very different potential mineralogical compositions, whose behaviour in conduction calorimetry and response to sulphate attack had been studied in prior research [11–22]. Finally, this rheological study of PCs is much involved with segregation phenomena and workability of their respective concretes and mortars and, as a consequence, with their durability.

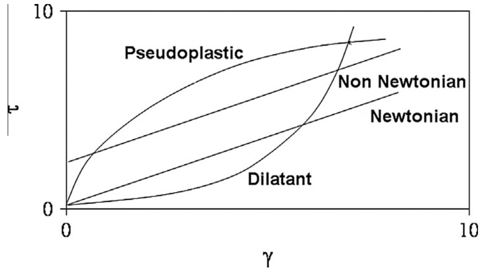

Fig. 1. Fluid types.

2. Materials and methodology

To ascertain the differences in the response depending on the variations in the rheological trial parameters, pastes were prepared with ordinary type CEM I Portland cement [23] (whose mineralogical composition and other physical parameters, midway between PC1 and PC2, were as follows: 58.5% C_3S; 7.5% C_2S; 7.5% C_3A; and 11.5% C_4AF; density 3.06 and BSS 325), distilled water and a water-cement ratio of 0.5. The paste was mixed manually for 2 min in a porcelain crucible and poured into the viscometer annulus.

The rheological measurements were taken with a Haake Roto Visco 1 rotational viscometer fitted with a Z38 DIN 53018 rotor spindle, a Z43 DIN 53018 graduated flask, a temperature control unit for coaxial cylindrical systems and a DC 30-B3 circulation thermostat [10].

The measurement schemes analysed, designed by combining angular velocity, stage duration and velocity step size (in rad/s), are shown in Fig. 2.

Based on the results obtained in the preceding stage, a measurement scheme was designed and trials were conducted every 20 min (up to the time of the respective first nadir on the calorimetric curve [11–16] (Fig. 3)) on two pure Portland cement pastes whose mineralogical composition was diametrically opposed. This compositional difference explained the difference in test time [11–16]: 120 min in paste PC1 and only 100 min in paste PC2, because 100 min is very near to 97 min 12 s $\approx$ 97 min, which was really the age of the 1st nadir for PC2. The physical–chemical characteristics of the two Portland cements are given in Table 1, along with their potential mineralogical composition, density and Blaine specific surface (BSS).

The two Portland cements exhibited similar fineness (Tabla 1 y Fig. 4), and the difference in their density could be partially attributed to their mineralogical composition. The water demand to prepare a standard consistency paste [24] was higher in PC1 than in PC2, a finding related to the capacity to form new hydrated compounds that required more chemically combined water. Setting times [24], in turn, were shorter in PC1 (Initial Setting Time: 200 min) than PC 2 pastes (IST: 270 min) [11–22]. This was also

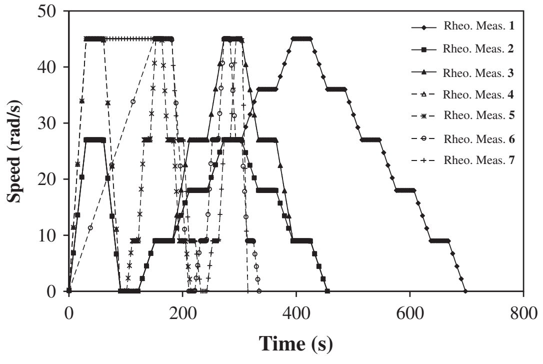

Fig. 2. Rheological measurement schemes.