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Modelling the yield stress of ternary cement–slag–fly ash pastes based on particle size distribution

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ABSTRACT

Mineral admixtures are blended with Portland cement to improve strength and durability, and/or to reduce the cost and environmental footprint of concrete mixes. Some mineral admixtures such as fly ash have also been reported to enhance workability of blended cements. This study shows that the key parameter controlling the yield stress of ternary Portland cement–blast furnace slag–fly ash pastes, in the absence of an added rheology-modifying admixture, is the width of the particle size distribution (PSD) at a given water/solid mass ratio. A small addition of fly ash has a significant effect on workability because of its broad PSD, and any other precursors with a similar PSD could possibly have a comparable effect. A model to predict the yield stress is therefore derived based on the Rosin–Rammler PSD width parameter, *n*, and the water/solid mass ratio, which provides a good description of the experimental yield stress data. It is believed that a broader PSD provides a higher packing density of particles which reduces the volume of water volume required to fill the voids. The excess water is then used to disperse particles and reduces inter-particle forces, hence yield stress. Therefore, at a given water/solid ratio, PSD width is able to be used as a sole parameter to correlate the yield stress of such concentrated suspensions. Also, a very low yield stress can be approached if the PSD is broad enough, in the absence of any rheology-modifying admixtures.

1. Introduction

A variety of mineral admixtures, in particular ground granulated blast furnace slag, coal fly ash, calcined clays, silica fume and finely ground limestone, are now commonly used as blending agents to enhance various properties of Portland cement based concretes, including strength, durability, cost, and CO_2 emissions. Organic admixtures such as polycarboxylate ether (PCE) superplasticisers are widely used to optimise concrete workability by reducing yield stress [1]. However, some mineral admixtures can also provide plasticising effects, enhancing paste and concrete workability. If used appropriately, mineral admixtures can be highly cost-effective and offer lower environmental impact than chemical superplasticisers due to their origin as industrial by-products, and they can also provide advantages in terms of concrete strength and durability properties [2–4]. For instance, ultra-fine fly ash was found to increase the workability of cement paste without addition of water reducer admixtures [5], as well as acting as a pozzolan. Cement blends with fly ash (FA) and silica fume (SF) (cement + FA, cement + SF, and cement + FA + SF) have shown improved workability at certain mixture proportions [6–8]. However, in some instances, silica fume has also been reported to reduce the workability of blended cements [5,9], depending on its particle size distribution (PSD) and dosage.

Cement–fly ash blends generally show higher flowability than Portland cement paste. Some reasons that are assumed in the literature to be responsible for this effect were summarised by Lee et al. [8] as follows: (a) the lower density of fly ash compared to cement causes a higher particle volume at constant mass ratio, so the paste volume of a concrete mixture increases; (b) fly ash reduces flocculation of the cement particles by a dilution effect; (c) reduced growth of hydrate products at early age due to the slower reaction of the fly ash, particularly at high replacement levels; (d) the 'ball bearing effect' induced by the spherical shape of fly ash particles that facilitates the movement of neighbouring particles. Also, increasing the density of particle packing by filling of smaller particles into the voids between larger particles, and the lower surface area/volume ratio of spherical particles compared to angular cement or slag grains, will result in lower water uptake in voids and on surfaces, and hence the excess water is made available to facilitate flow [5,6]. However, the relative influences of each of these effects remain to some extent to be determined.

The design of concrete often involves a balance between early-age and later-age properties, and beside fly ash which provides higher fluidity in Portland cement blends, one mineral admixture which provides

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Table 1
Chemical composition of the GGBFS, OPC, and FA used, as determined by XRF. LOI is loss on ignition at 1000 °C, water demand is described in Section 2.3, and density was measured according to ASTM C188-09.

Oxide component	GGBFS (wt.%)	OPC (wt.%)	Fly ash (wt.%)
SiO_2	33.4	20.3	48.8
TiO_2	0.6	0.0	1.7
Al_2O_3	15.5	4.5	28.5
Fe_2O_3	0.5	4.6	12.5
MnO	0.3	0.0	0.0
MgO	6.1	1.2	0.3
CaO	41.6	62.9	4.4
Na_2O	0.0	0.3	0.3
K_2O	0.3	0.3	0.4
SO_3	2.4	2.6	0.3
LOI	−0.4	3.3	2.7
Density (g/cm^3)	2.85	3.22	2.19
Water demand (wt.% of solid)	30.0	28.0	23.0

particularly appealing properties in the hardened state is blast furnace slag [10,11]. Ternary mixtures of Portland cement, fly ash and blast furnace slag have been studied for properties such as compressive strength [12–14] and durability [2], and are standardised in the European Union (EN 197-1 [15]) in categories including CEM II/(A,B)-M and CEM V/(A, B), and in the ASTM regime (ASTM C595 [16]) as type IT.

Rheology of a concrete at early age is an important parameter, especially when aiming for the production of self-compacting concretes which need very high fluidity [2,4,17,18]. The majority of published characterisation studies focus mainly on the use of spread flow and slump tests. These tests are simple and widely deployed methods used to monitor mortar and concrete workability and flow behaviour. They are able to calculate yield stress using fundamental rheological principles with moderate to high accuracy [19]. Conversely, laboratory analysis of rheology by means of rheometers is often conducted using paste specimens, and rheological parameters are determined from flow (shear stress–shear rate) curves. Although these two categories of rheological measurements have some differences in their method of application, both provide good indication of yield stress changes. Reducing yield stress as close to zero as possible will increase the workability, provide better ability to fill voids, and enable surface self-levelling.

Rheological changes of blended cement with slag, fly ash, silica fume [9], and also limestone [20] have been studied, aiming at flow enhancement for self-compacting concrete. They observed yield stress and apparent viscosity reduction at certain mixture proportions. Although the cement–fly ash system always results in lower yields stress and viscosity compared to Portland cement, there are contradictory observations when other mineral admixtures are used, e.g. when Portland cement is blended with different PSD of silica fume, either an increase or decrease in yield stress and viscosity is obtained. A different rheological behaviour is also observed for slag at different proportions blended with Portland cement with/without the presence of other precursors [9,20]. Therefore it seems that physical properties related to the mixture PSD determine the rheological behaviour of the pastes. Lee et al. [8] analysed a range of different fly ashes with a range of PSD blended with Portland cement, and found that a wider PSD, as characterised by the Rosin–Rammler equation, correlated with higher fluidity. However, they used plasticising admixtures in their system that affect the packing of particles and inter-particle forces, hence the rheological behaviour, so that the relationship between PSD and fluidity might be affected. Also, their method of monitoring fluidity using apparent viscosity highly depends on shear rate; Portland cement pastes are known to be shear sensitive [21] and shear thinning behaviour has also been observed in concentrated fly ash suspensions [22].

The current study aims to generalise the description of rheological behaviour of cement blended with mineral admixtures and without rheology-modifying admixtures, for application to any mix proportion of Portland cement, blast furnace slag and fly ash. This study presents ternary yield stress diagrams for this system from direct measurement using vane geometry for 30 mixtures at each of three water/solid ratios. A model is developed which relates the paste yield stress to the width parameter of the Rosin–Rammler PSD and the water/solid mass ratio (w/s). It is suggested that this model could be generalised to most concentrated suspensions having a mono-modal PSD, such as blended cementitious binders.

2. Experimental

2.1. Materials

Ground granulated blast furnace slag (GGBFS) and FA, with chemical compositions as displayed in Table 1, were provided by Zeobond Pty Ltd, Australia. Ordinary Portland cement (OPC) with chemical composition shown in Table 1, Type GP according to Australian Standard AS3972 [23], was obtained from a local retailer. Particle density was measured according to ASTM C188-09 [24] as shown in Table 1. The volume average PSD of the main precursors was analysed by laser diffraction in water using a Malvern Mastersizer instrument. The PSD for the other blends of the three main precursors is calculated based on the mix proportions from Table 2 and the particle size distribution of each main precursor. An arithmetic mean over the range of all particle sizes was calculated in order to create PSD curves for each binary or ternary mixture. A total of 30 different mixtures were studied, including pure OPC, GGBFS, and FA, and 27 different binary and ternary mixtures of these three precursors as shown in Table 2. The sample codes are shown as xO–yS–zF, where O represents OPC, S is slag, F is fly ash, and the values x, y, and z denote the proportion of each constituent from a total of 8 units (i.e., $x + y + z = 8$). The mix denoted as O = S = F has equal mass of each precursor. The samples were formulated by mixing of the dry components then adding the water while hand mixing to combine

Table 2
The precursor proportions of the binary and ternary mixtures.

Sample code	OPC (wt.%)	GGBFS (wt.%)	Fly ash (wt.%)	*n* value
O0–S1–F7	0	12.5	87.5	0.720
O0–S2–F6	0	25.0	75.0	0.746
O0–S4–F4	0	50.0	50.0	0.803
O0–S6–F2	0	75.0	250	0.869
O1–S1–F6	12.5	12.5	75.0	0.751
O1–S2–F5	12.5	25.0	62.5	0.779
O1–S3–F4	12.5	37.5	50	0.802
O1–S3.5–F3.5	12.5	43.75	43.75	0.819
O1–S4–F3	12.5	50	37.5	0.836
O1–S5–F2	12.5	62.5	25	0.875
O2–S0–F6	25	0	75	0.749
O2–S1–F5	25	12.5	62.5	0.776
O2–S2–F4	25	25	50	0.806
O2–S3–F3	25	37.5	37.5	0.834
O2–S4–F2	25.0	50.0	25.0	0.868
O2–S5–F1	25.0	62.5	12.5	0.918
O2–S6–F0	25.0	75.0	0	1.149
O3–S2–F3	37.5	25.0	37.5	0.833
O3–S2.5–F2.5	37.5	31.25	31.25	0.851
O3–S3–F2	37.5	37.5	25.0	0.870
O = S = F	33.3	33.3	33.3	0.846
O4–S0–F4	50	0	50	0.801
O4–S2–F2	50	25	25	0.870
O4–S4–F0	50	50	0	1.030
O5–S1–F2	62.5	12.5	25	0.869
O5–S2–F1	62.5	25	12.5	0.917
O6–S1–F1	75	12.5	12.5	0.916