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The rheological properties of ternary binders containing Portland cement, limestone, and metakaolin or fly ash

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ABSTRACT

The influence of limestone particle size and the type and extent of (partial) cement replacement on the yield stress and plastic viscosity of ternary pastes are studied. Interpretations based on Bingham model indicate: (i) for binary/ternary blends containing coarse limestone, the yield stress and plastic viscosity remain unchanged or decrease with increasing cement replacement, (ii) in ternary blends, plastic viscosity increases with the fine limestone content, and (iii) the yield stress in ternary blends containing fly ash is dependent on the limestone content and fineness whereas in blends containing metakaolin, the yield stress reduces with an increase in limestone content, irrespective of the limestone particle size. These are attributed to: particle packing, water demand, and the interparticle spacing and contacts which are quantified using microstructural simulations. The yield stress and plastic viscosity show strong direct correlations to the specific surface area and inverse correlations to the water film thickness.

1. Introduction and background

An increasing emphasis on the sustainability of cement-based materials has resulted in the enhanced use of materials such as limestone, to replace a portion of the cement in the binder. Limestone is an abundant natural material, is relatively inexpensive, and its use helps mitigate the environmental impacts associated with the production of Portland cement. ASTM C 595-12 has recently specified a Type IL cement that can include up to 15% of limestone powder as a cement replacement material [1] — an increase from the 5% level previously allowed in the U.S.

Several studies have shown the beneficial effects of limestone additions on both the fresh and hardened properties of cementing systems [1–5]. The positive effects on the hardened properties are attributed to a combination of enhancing hydration through the filler effect, improved particle packing and the formation of carboaluminate phases [6,7]. However, limestone powders, based on their particle characteristics and interactions with other solids in the binder, can influence the fresh (rheological) properties of the paste fraction. Recent studies have demonstrated strategies to formulate ternary blends containing limestone and an aluminous cement replacement material such as metakaolin or fly ash without inducing any reductions in the mechanical properties of these mixtures, as compared to pure OPC formulations [2,8,9]. Thus, this work builds on prior efforts to determine if the benefits realized in hardened properties, may also be applicable to the fresh properties of these mixtures.

Several studies have evaluated the rheological properties of cementitious mixtures containing a variety of cement replacement materials [10–14]. The rheological parameters (yield stress and plastic viscosity, based on a Bingham or Herschel–Buckley representation) have been noted to be strongly dependent on the water-to-powder mass ratio, type/dosage of cement replacement materials used, and the particle size distributions of the solids [10–14].

This paper investigates the rheological properties of ternary blends containing limestone and metakaolin or fly ash, with special emphasis on quantifying the influence of: (i) limestone particle size and dosage, and (ii) fly ash or metakaolin additions for pastes proportioned at a fixed water-to-solid ratio (by volume). Experimental assessments of rheological properties are integrated with computational packing studies to elucidate the influences of particle number density, specific surface area, and water film thickness. Overall, the results provide a clear understanding of the effects of cement replacement by limestone in combination with fly ash or metakaolin on the fresh properties, thus enabling new strategies to proportion binder formulations which show comparable or superior properties to traditional OPC formulations [2].

2. Experimental program

2.1. Materials and mixtures

The materials used include: a commercially available Type I/II ordinary Portland cement (OPC) conforming to ASTM C150 [15], a Class F

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fly ash and metakaolin conforming to ASTM C618 [16], and a nominally pure limestone powder (purity > 95% $CaCO_3$, by mass) of three different median particle sizes denoted as 0.7 μm, 3 μm, and 15 μm, conforming to ASTM C568 [17]. Fig. 1 shows the particle size distributions (PSD) of the limestone, metakaolin and fly ash, as measured using laser diffraction, along with their median particle sizes.

The compositions of the Portland cement and the cement replacement materials are presented in Table 1. Binary blends were prepared wherein: OPC was replaced by limestone of different particle sizes at levels ranging from 0 to 40%, by fly ash from 0 to 10% and by metakaolin from 0 to 10%; all by volume. Ternary blends containing limestone powder and fly ash or metakaolin were also prepared. Table 2 shows the proportions of the different mixtures evaluated. All pastes were proportioned at a fixed volumetric water-to-solid ratio, $(w/s)_v = 1.26$ and/or 1.42, corresponding to a mass based water-to-solid ratio $(w/s)_m = 0.40$ and/or 0.45 so that the influences of the OPC replacement materials and their particle size distributions on the rheological properties could be consistently compared.

Table 1
Composition and specific surface areas (m^2/kg) of the materials used in this study as determined using X-ray fluorescence (XRF) and the Blaine's air permeability apparatus per ASTM C205-11.

Phase (%)	OPC	Class F fly ash	Metakaolin
SiO_2	21.06	58.4	51.7
Al_2O_3	3.86	23.8	43.2
Fe_2O_3	3.55	4.19	0.5
CaO	63.75	7.32	–
MgO	1.83	1.11	–
SO_3	2.93	0.44	–
Na_2O	0.12	1.43	–
K_2O	0.48	1.02	–
LOI	1.99	0.5	0.16
SSA (m^2/kg)	470	218	3255

Limestone powder contains 95–97% $CaCO_3$ as per the manufacturer. The Blaine specific surface areas are 4970 m^2/kg, 2400 m^2/kg, and 613 m^2/kg for the limestone powders having median particle sizes of 0.7 μm, 3 μm, and 15 μm respectively.

2.2. Rheological experiments

All powders were dry blended prior to wet mixing. Mixing was performed in accordance with ASTM C1738 [18] using a high shear mixer. The mixing sequence used was as follows: (i) the mixer was run at 4000 rpm for approximately 30 s while the blended powders and water are added, (ii) the mixer was run at 12,000 rpm for 30 s, (iii) the mixing container was scraped and the paste allowed to rest, while covered for 2 min, (iv) the contents were mixed at 12,000 rpm again for 90 s, and (v) a final round of hand mixing was carried out to verify the homogeneity of the paste. Around 5 mL of paste was then discharged on to the rheometer using a disposable syringe. The time elapsed from water addition to the beginning of the rheological assessment was approximately 5 min.

The fresh properties of fresh pastes were evaluated using a rotational rheometer (TA Instruments AR2000 EX) in a parallel plate configuration, provided with Peltier elements located within the bottom plate which were conditioned to 25 ± 0.5 °C. To reduce slip on the plates, a serrated upper plate was used while the Peltier plate was covered with 150 grit adhesive backed, resin coated sandpaper (mean surface roughness of 16.89 μm). The upper plate used had a diameter of 50 mm, and the gap was set to 2 mm based on a series of trial mixtures that achieved consistent results over the range of fluidities considered [19]. The rheological procedure consisted of a ramp up pre-shear phase from 5-to-100/s lasting around 90 s to homogenize the paste, followed by a ramp up from 5-to-100/s, and followed immediately by a ramp down from 100-to-5/s. A step up, or step down shear rate of 10/s was implemented, as shown in Fig. 2(a). Shear stress and shear rate data were extracted using TA Instruments' TRIOS software package. With the exception of the pre-shear range, at each step, data is acquired every second, until a steady state is achieved — as defined by three consecutive torque measurements within 5% of each other, at which time the experiment advances to the next shear rate. The time at each shear step is typically 5 s.

A non-Newtonian relationship between the shear stress and shear rate as shown in Fig. 2(b) was used to interpret the measurements. As such, the shear stress–shear rate datasets for the descending (down ramp) curve were fitted using a least squares function corresponding to the Bingham model as shown in Eq. (1) [20]. The Bingham model is commonly used for the rheological characterization of cement pastes [10–12,19,21] and a good linear fit (R^2 values > 0.95) between the

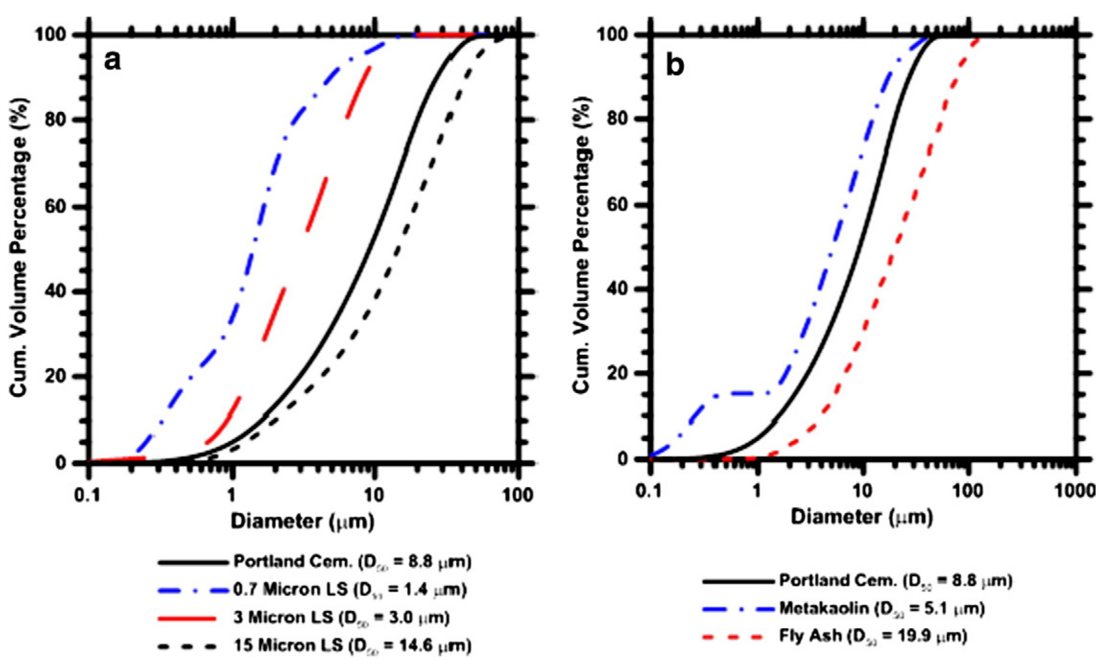

Fig. 1. The particle size distributions (PSDs) of: (a) the OPC and limestone powders, and (b) the OPC, fly ash, and metakaolin powders.