Construction and Building Materials 79 (2015) 65–72

Contents lists available at ScienceDirect

Construction and Building Materials

journal homepage: www.elsevier.com/locate/conbuildmat

Rheological evaluations of interground and blended cement–limestone suspensions

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HIGHLIGHTS

- Rheological effects of limestone in cementitious suspensions brought out.
- Reduction in yield stress with limestone addition; no changes in plastic viscosity.
- Lower apparent yield stress when limestone is interground than blended.
- Viscoelastic storage modulus and apparent yield stress well related.

ARTICLE INFO

Article history:
Received 4 August 2014
Received in revised form 22 October 2014
Accepted 24 December 2014
Available online 21 January 2015

Keywords:
Rheology
Cement
Limestone
Interground
Fly ash

ABSTRACT

This paper reports a comparative study of the rheological properties of suspensions composed using ordinary portland cement (OPC), interground with, and blended with limestone. Two different interground portland limestone cements (PLCs) and three blended limestone cements were examined. The blended mixtures were prepared using the same limestone content (by replacement) as the interground mixture, and blended to match the particle size distribution (PSD) of the plain OPC and interground PLCs. This methodology was used to separate the influence of packing and surface area from the influence of the limestone incorporation technique (i.e., intergrinding or blending). The results indicate that the inclusion of limestone decreases the yield stress due to reduced van der Waals forces between limestone-to-OPC particles, as compared to OPC-to-OPC particle interactions. The plastic viscosity is noted to be independent of the limestone replacement level, and dependent solely on the volumetric solid loading and PSD of the solids in the suspension. Intergrinding of limestone is shown to have beneficial effects on the yield stress compared to PSD-matched OPC–limestone blends, due to coarser OPC fraction in the interground PLC as compared to the blended mixture. Finally, via oscillatory shear experiments, the use of a stress plateau identification technique is demonstrated to be an accurate means to identify the yield stress in cementitious suspensions all suspensions.

1. Introduction

There continues to be interest in the use of fine limestone as a partial replacement for ordinary portland cement (OPC) in concrete. This is due to benefits linked to: low environmental impact, improved particle packing and filler effects resulting from provision of additional surface for reactions, and reactions with the aluminate phase(s) [1–8]. There are two main strategies for replacing OPC with limestone: (i) intergrinding the limestone with the clinker in a ball mill (interground portland limestone cement, IPLC), to which the PLCs available in the market fall into, and (ii) mechanical mixing or blending of the OPC with limestone (blended portland limestone cement, BPLC). As limestone is a softer material than the clinker, intergrinding results in limestone particles that are finer than the OPC particles [9,10], while blending can be tailored to produce a system where the particle size distributions (PSDs) of the limestone is similar, finer, or coarser than OPC. Several studies [11–14] have investigated the influence of limestone on the rheological performance of cement suspensions. These studies have investigated the influences of: fineness, superplasticizers, and limestone content on rheology. However, in these studies limestone replacement was carried out by intergrinding or using limestone that is coarser or finer than the OPC. Thus the influence of limestone in these systems is difficult to discern as it is

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http://dx.doi.org/10.1016/j.conbuildmat.2014.12.054
0950-0618/

confounded with the effects of changes in particle surface area and particle packing.

The study presented in this paper separates the effects of changes in particle surface area and particle packing to explore the effects of limestone incorporation technique: blending versus intergrinding limestone, on paste rheology. BPLC suspensions are prepared with limestone which is PSD-matched to OPC to minimize or eliminate the above-mentioned confounding effects. Rheological characterization of cementitious suspensions is commonly carried out using strain/stress growth experiments from which parameters such as the apparent yield stress and plastic viscosity are extracted. The apparent yield stress is indicated by a non-zero stress at a zero strain rate and the plastic viscosity is a measure of the increase in strain rate required for a unit increase in stress. This work applies a new stress plateau identification technique presented in [15,16] to determine the apparent yield stress, and extract the plastic viscosity from the linear portion of the shear rate-shear stress response. In an effort to facilitate discussions on the material response, which is the focus of the paper, a brief review of the factors that influence the rheological response of particulate suspensions, apparent yield stress in particular, follows.

1.1. Apparent yield stress and its determinants in particulate suspensions

The plastic viscosity of a suspension is strongly influenced by the solid loading and particle separation, as it is a measure of resistance to flow once it has commenced. The apparent yield stress, on the other hand, is primarily influenced by particle effects, such as jamming, particle spacing, surface area and roughness [14,17,18], and interparticle forces (van der Waals and electrostatic repulsive forces) [19,20]. The interaction potential between particles in a colloidal suspension is governed by DLVO theory, which combines the effects of van der Waals and electrostatic forces [21,22]. Though cementitious suspensions have larger particles than would generally be considered colloidal, DLVO theory is likely still applicable as the influence of Brownian motion is minimal due to the relative size of the particles present in the suspension. Electrostatic repulsive forces originate from the adsorbed ions in the diffuse portion of the electric double layer (EDL) [21]. The EDL constitutes an inner stern layer of tightly held ions that carry a charge that is opposite to that on the particle surface and the more weakly held ions in the diffuse outer layer having the same charge as the particle surface.

Electrostatic repulsive effects are proportional to: $\exp[-\kappa(r-2a)]$ [23,24], where r is the distance from the center of the particle, κ is the Debye length, and a is the particle diameter. Van der Waals forces, on the other hand have been shown to be proportional to $1/r^2$, and thus do not decay as rapidly (with distance) as the electrostatic repulsive force. Further, it is noted that van der Waals forces between the same materials are always attractive, while between two different materials they may be repulsive. Above a certain particle concentration, termed the coagulation limit, the effect of the van der Waals attractive forces dominate over the electrostatic repulsive forces, and it has been shown that cementitious suspensions are often above this limit [24,25]. Though portland cement grains are polycrystalline, the occurrence of coagulation in portland cement suspensions combined with the likelihood that electrostatic effects are repulsive due to similar surface charges on cement grains indicate that the net van der Waals effect is attractive. Thus, above the coagulation limit, as limestone replaces portland cement in the suspension, the contacts between OPC particles are decreased, and the influence of limestone–cement and limestone–limestone contacts become more prevalent, and interparticle attractive forces would be expected to decrease along with the apparent yield stress.

2. Experimental program

2.1. Materials

Two as-manufactured IPLCs were used in this study, one conforming to ASTM C1157 [26] and the other to ASTM C595 [27] with the former being the finer of the two. The control OPC used in this study was a Type I/II OPC, conforming to ASTM C150 [28], and was the parent OPC used to generate the three different BPLC mixtures. Limestone of four different median particle sizes (0.7, 3, 10, and 15 μm) was blended with the pure OPC to form the BPLC mixtures. Each of the BPLC mixture has a particle size distribution that matches either that of the OPC, the ASTM C1157 PLC or ASTM C595 PLC. The purity of the limestone used is greater than 95% $CaCO_3$. In the figures and discussions in this paper, the ASTM designation (for example, C 595) is used for the interground and the corresponding blended systems. For the size matched BPLC mixtures, the notation '=' is used in the figures to refer to the distribution that the blend is matched to, i.e., OPC + LS = OPC refers to the OPC–limestone blend which matches the particle size distribution of OPC. The oxide compositions and physical characteristics of these materials are presented in Table 1.

The particle size distributions (PSDs) of the OPC and the as-obtained IPLCs, determined using dynamic light scattering, are shown in Fig. 1(a) and (b), respectively. BPLCs were prepared to match the PSDs of the two IPLCs and the parent OPC, using the same replacement level of OPC by limestone as in the IPLCs (11.1% by mass; 12.7% by volume, as provided by the supplier). Thus, three blended cement mixtures were created. A least-squares fitting and error minimization procedure was adopted to obtain the quantities of limestone of each size required to match the PSD curves of the OPC or IPLCs. The differential PSDs of these blended systems as compared to the OPC and the corresponding IPLC systems are presented in Fig. 1(c). The best possible matches were made by blending chosen amounts of OPC and the four limestone particle sizes such that the limestone volume fraction in the blend is 12.7%, by minimizing the least squares error. It is notable that the blended mixtures were able to reasonably match the size distribution of the OPCs or the IPLCs except for the case of the C1157 IPLC. The C1157 IPLC is notably finer than the blend. However, Fig. 1(c) shows that the finer fraction in the C1157 IPLC and the corresponding BPLC mixture are very similar. Since the limestone is ground finer than the clinker in the intergrinding process, it is important to match the finer fraction appropriately to ensure comparability, which has been accomplished here.

2.2. Experimental procedure

The suspensions were prepared at a constant volumetric water-to-solids ratio (w/s = 1.42), which corresponds to a mass based w/s = 0.45 for OPC suspensions, and a slightly higher mass-based w/s for blends of limestone due to the lower specific gravity of this material. A constant volumetric ratio was used as the flow behavior of concentrated suspensions is influenced by the volume fraction of solids [29,30]. The specimens were mixed in accordance with ASTM C1738 [31], using a low shear rate of 5000 RPM for initial mixing, followed by a 30 s mixing period at a high shear rate of 12,000 RPM, a two minute covered rest period, and finally a 90 s mixing at the high shear rate.

Two different rheological experiments were conducted: one, a typical shear rate ramp study similar to the one developed in [16], using the parallel plate configuration, and two, a stress growth, low-amplitude oscillatory shear study using a concentric cylinder geometry. The typical shear rate ramp study allows for the determination of yield stress and plastic viscosity of the suspensions while the stress growth study provides the viscoelastic parameters of the suspension. Both studies were carried out using a TA Instruments AR 2000EX dynamic shear rheometer, with all rheological parameters (stress, strain rate, storage modulus, and loss modulus) being extracted using the TA Instruments Trios software package. The shear rate ramp study was conducted using a 50 mm parallel plate configuration with the Peltier plate conditioned to a surface temperature of 25 ± 0.1 °C. The upper surface of the plate geometry was serrated to a depth of 1 mm and the lower surface of contacting plate (i.e., Peltier cover plate) was serrated to a depth of 0.15 mm to

Table 1
Chemical composition and physical characteristics of the materials.

Material	SiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	CaO (%)	MgO (%)	SO_3 (%)	D_{50} (μm)
OPC (ASTM C150)	19.60	4.09	3.39	63.21	3.37	3.17	12.4
IPLC (ASTM C595)	18.57	3.80	2.99	63.87	2.93	3.15	11.3
IPLC (ASTM C1157)	18.57	3.84	3.11	63.59	3.38	3.23	8.3