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Aggregation and breakage kinetics of fresh cement paste

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ABSTRACT

The influence of shear-induced forces on the microstructure of fresh cement pastes was studied. Aggregation and breakage kinetics of the paste matrix are highly influenced by the shear history. It was found that the kinetics of re-aggregation is relatively slow, and time scale for recovery is longer than the time needed for breakdown. When the aggregation kinetics dominates, network interactions among particles develop and the average floc size increases. When the breakage kinetics dominates, network interactions among particles are broken and are accompanied by a decrease in the average floc size. The results suggest that there is a limiting size to floc growth. Minor additions of clays can significantly impact the structural network development and result in a more flocculated structure. The flocs produced by the clays were highly stable flocs with strong interparticle bonds that were able to oppose floc breakage and floc erosion.

1. Introduction

There is a growing interest in characterizing the stability and rheological properties of concentrated suspensions, such as cement paste. In its fresh state, concrete can be considered a suspension consisting of sand and gravel particles suspended in a paste matrix. Concrete is heterogeneous on many length scales, and thus paste matrix can also be considered a concentrated flocculated[1] suspension. As a result, the macroscopic flow behavior and rheological properties of concrete are highly impacted by the inherent structure of the paste matrix. Similar to other concentrated suspensions, cementitious fluids may display many complex rheological behaviors, including yielding, shear thinning, shear thickening, rheopexy, thixotropy, and dilantancy. When cement paste is sheared, the intrinsic network structure will respond to the shear-induced stresses, and this response is governed by the interactions among the particles. Obtaining a reliable estimate of the interparticle forces in cement is an essential step to understanding the rheological behavior of cementitious suspensions. However, the chemistry of even plain cement in the fresh state is very complex, and this has made it difficult to obtain quantitative relationships between the rheological properties and the interparticle forces of cementitious suspensions.

While rheological measurements provide a quantitative measurement of the mechanical properties of fluids, they are also indirect qualitative probes of fluid structure. As stated by Larson [1], rheometry is often most useful when supplemented by other experimental methods that characterize fluid structure and flow-induced structural changes. Understanding the internal structure of suspensions is not an easy task, especially when the suspension is polydispersed. However in fresh paste cementitious systems, direct measurement and characterization of the agglomerate structure are difficult due to issues such as polydispersity, low-transparency, high solid volume fraction, and hydration. Thus there is a lack of fundamental knowledge about the internal structure of fresh cement paste, which is especially important during processing of concrete (i.e. mixing, transporting, pumping, casting, and finishing). In addition, the initial fresh state microstructure affects the final microstructure, thereby influencing mechanical properties of hydrated paste or concrete [2].

The rheology of concrete is related to the degree of flocculation/coagulation of the paste matrix [3], and the degree of flocculation/coagulation is a function of the interparticle forces. Simply stated, particles will aggregate when attractive forces exceed the repulsive forces (regardless of the origin of the forces). Thus, perhaps the most representative parameter for studying the flocculation process (and indirectly the interparticle forces) is to monitor the change in size of the particle aggregates. Yang et.al [4] conducted sedimentation studies on cement pastes and used the vertical gradient in the particle size distribution of the cement sediments to determine whether the suspensions were dispersed or flocculated/coagulated. While sedimentation studies may be used to qualitatively observe the structure of cement

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[1] In this paper, aggregation, agglomeration and flocculation will be used interchangeably. Aggregation is the general process that describes the formation of particles collecting to form a cluster. Coagulation will be used to reference a specific type of aggregation in which irreversible bonds are formed between the particles. An aggregate/floc/agglomerate is a cohesive mass consisting of two or more primary particles.

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suspensions, they are usually conducted with solid volume concentrations much lower than what would be used in practical mixtures [4–6]. In addition, these measurements are static measurements that do not provide information about the dynamic response of the structure to flow. Granulometric measurements [5,7,8] have also been used to gain insight about the ability of the cement paste microstructure to reform by periodically subjecting the samples to ultrasonic treatment. However, the samples for the complementary sedimentation studies were highly diluted (w/c = 300) and this dilution will affect floc aggregation. Kjeldsen et al. [9] measured the size distribution of magnesium oxide particles in an electrolytic solution simulating that of cement paste. In order to estimate the effects of shear-induced forces the particle size distribution was measured before and after ultrasonic treatment. However, this approach does not provide real-time information about the response of the microstructure while being subjected to ultrasonic forces. Ultrasonic wave methods have recently emerged as a promising technique to examine the fresh state microstructural changes associated with flocculation in cement pastes [10], however with this method the sample is in a state of no flow. To overcome the limitations of the aforementioned tests, a different approach based on measuring particle size with a scanning laser microscope was used by the authors. This method allows for one to monitor the size evolution and distribution of the particles in real-time when subjected to shear [11]. To the authors' knowledge this is the first time that in-situ investigation of the microstructural response (via particle-size measurements) of concentrated cement paste suspensions subjected to shear-induced stresses has occurred, and the results presented in this paper contribute towards addressing questions such as: what is the microstructure of fresh cement paste? How do the different material ingredients influence the rate of aggregation and interparticle strength? How does the microstructure of fresh cement paste respond to shear-induced stresses?

2. Experimental program

2.1. Mix proportions and materials

Two cements and a class F fly ash (FA) were used. Cement replacement was conducted on a mass basis. The physical, mechanical, and chemical properties of the cements are given in Table 1 and the chemical properties of the fly ash are given in Table 2. The particle size distributions of the cements and fly ash are shown in Fig. 1. The

Table 1
Physical, chemical, and mechanical properties of cements.

	Cement	
Oxide analysis	A	B
CaO (%)	62.0	63.7
SiO_2 (%)	18.7	20.4
Al_2O_3 (%)	5.7	4.1
Fe_2O_3 (%)	2.5	2.4
SO_3 (%)	4.3	2.3
MgO (%)	2.4	3.9
MgO (%)	0.85	0.26
Equivalent alkali (%)		1.3
Free lime (f-CaO) (%)	1.94	1.5
Specific surface (m^2/kg)	388	365
Compound		
C_3S (%)	56	67
C_2S (%)	11	14*
C_3A (%)	11	7
C_4AF (%)	8	7*
Initial set	120	101
Fineness, 45 μm (% pass)	91.6	93
Blaine specific surface (m^2/kg)	388	365
3 day f'c (psi/MPa)	3440/23.7	3272/22.6
28 day f'c (psi/MPa)	5920/40.8	6729/46.4
Air content (mortar) (%)	8	6

* Calculated using Bogue calculation.

Table 2
Chemical properties of fly ash.

Oxide	Fly ash
Al_2O_3 (%)	17.86
CaO (%)	12.50
Fe_2O_3 (%)	7.49
K_2O (%)	1.24
MgO (%)	3.72
Na_2O (%)	0.17
P_2O_5 (%)	0.10
SiO_2 (%)	54.35
SO_3 (%)	0.53
TiO_2 (%)	1.15
LOI (750 °C) (%)	0.06

superplasticizer (SP) was a carboxylated polymer in aqueous solution (specific gravity = 1.04). A liquid water-soluble cellulose-based viscosity modified agent (VMA) with a specific gravity of 1.002 and solids content of 0.7% was employed in some of the mixtures. The manufacturer's recommended dosage for the VMA ranged from 130 to 910 mL/100 kg of cementitious materials. Based on these recommendations, two dosages were used in this study: a medium dosage of 400 mL/100 kg of cementitious materials and a high dosage of 800 mL/100 of cementitious materials. Two clays and silica fume were also used in some mixtures. The silica fume was in a dry, densified powered form. The first clay was metakaolinite in pulverized powder form. Metakaolinite is composed of pozzolonic amorphous alumino silicates formed by controlled calcination of kaolinite. The chemical formula for kaolinite is $Al_2Si_2O_5(OH)_4$ and the general formula for metakaolinite is $Al_2Si_2O_7$. The second clay was sepiolite in slurry form. Sepiolite is a hydrated magnesium silicate serpentine mineral commonly found in Spain and it is used as a rheological aid for some cement products [12]. The chemical formula for sepiolite is $Mg_4Si_6O_{15} \cdot 6(H_2O)$. Both clays were incorporated into the mixtures at a dosage of 1.5% solids content based on the mass of cement. The water content for the sepiolite mix was adjusted to take into account the water in the sepiolite slurry. The mix compositions are shown in Table 3.

2.2. In-situ particle size measurement using Focused Beam Reflectance Measurement (FBRM)

The FBRM method is a particle size analysis measurement technique that provides information about particle chord length distribution in real-time. While there are various techniques for determining particle size, few can be applied in situ or used for materials with high solid volume concentrations [13]. The significant advantage of the FBRM

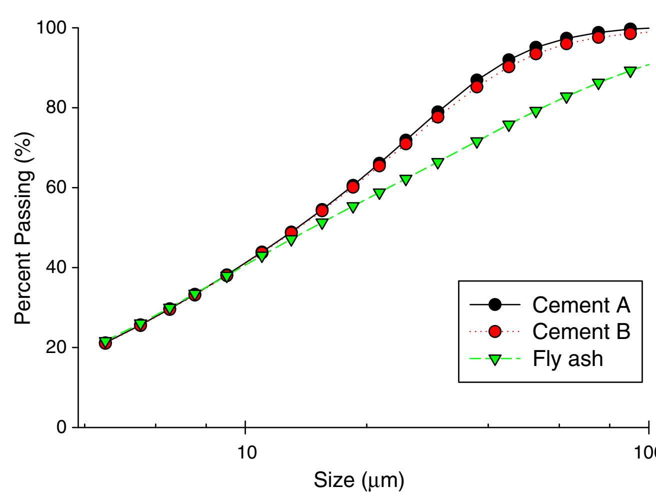

Fig. 1. Volume size particle size distribution of cements and fly ash (determined by laser diffraction).