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Influence of superplasticizer dosage on the viscosity of cement paste with low water-binder ratio

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HIGHLIGHTS

- Underlying mechanism of SP dosage on viscosity of cement pastes is proposed.
- A high concentration of un-adsorbed SP is found in interstitial solution of the paste.
- Hydroclustering and SP entanglements could be induced in paste with low w/b.

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ABSTRACT

In this paper, the influence and underlying mechanism of superplasticizers (SP) dosage on the viscosity of cement pastes with four water-binder ratio (w/b) were investigated. The results showed that apparent viscosity of the pastes with w/b of 0.24 and 0.32 decreased with SP dosage. Whereas, it is reverse for cement paste with w/b of 0.20 and 0.16. The addition of SP increased the packing density and the water film thickness of pastes with a w/b of 0.32 and 0.24. However, the increase of SP dosage had little effect on the packing density and the water film thickness of pastes with a very low w/b (0.16). For the cement pastes with a very low w/b (e.g., 0.16), the small spaces between the binder particles and the high concentration of the un-adsorbed SP in the interstitial solution may be the primary factors responsible for the increase in viscosity of the pastes.

1. Introduction

High-rise, long-span structures are increasingly used in modern civil infrastructures due to their environmental, economic, and aesthetic advantages. Having sophisticated geometry, appearance, exposure and loading conditions, these structures often require outstanding properties (such as high strength, impermeability, and durability). As a low water-to-binder ratio (w/b) is commonly used to achieve such strength and impermeability [1–3], superplasticiser (SP) is frequently employed to improve the concrete workability. Research has indicated that, if a polycarboxylate ether (PCE)-based plasticizer or superplasticizer is employed, a concrete can maintain good flowability at a w/b as low as 0.16 and achieve a compressive strength higher than 150 MPa [4].

Superplasticizers are generally long-chain polymers or co-polymers with negative charges. When mixed in concrete, they will adsorb on the surface of cement particles and make the cement particles negatively charged. As these negatively charged cement particles repel each other, the water that is trapped in the agglomerated cement particles is therefore released. Resulting from addition of SP, not only the released water improves concrete flowability, but also the particle dispersion (or de-agglomeration) significantly homogenizes the concrete material. Some research has also suggested that SP can further help increase the packing density of solid particles in a cement paste [5].

Although it is well accepted that SP improves concrete flowability, there is no consensus on how SP affects the viscosity of cement paste. Some researchers reported that addition of SP reduced both yield stress and viscosity [6–9], while others [10] demonstrated that the dosage of SP had little/no effect on viscosity of concrete. Banfill [11] found that concrete with the same slump values exhibited different viscosity (stickiness) as different types and amounts of SP were used. Cyr [12] and Anagnostopoulos [13] revealed that viscosity of cement paste was related to its shear-thickening behaviour, which increased with the SP dosage. Roussel [14] believed that the increasing SP dosage would increase the apparent

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viscosity of a cement paste at a high shear rate, and he suggested that the residual difference between polymers in the final macroscopic viscosity come from the pronounced increase in the local viscosity of interstitial fluid between neighbouring particles. These above-mentioned researches imply that the dosage of SP may have a critical effect on the viscosity of a cement paste.

Viscosity of a cement paste is complex, depending upon the particle volume fraction, shape, interaction, spatial arrangement or packing, etc. Having high binder content and very low w/b, high and ultra-high performance concrete (HPC and UHPC) often requires much higher amount of SP than conventional concrete for reaching a given flowability. When the rheology of such HPC and UHPC is studied, a shear-thickening response is likely observed [15–18]. As a result, the rheological behaviour of a cement paste with a low w/b is very complex. The influence and mechanism of SP dosage on viscosity of cement paste with a low w/b has not been fully investigated.

This paper aims at investigating the influence of SP dosage on viscosity of cement pastes made with a low w/b (0.32, 0.24, 0.20 and 0.16). The underlying mechanism is also discussed based on the results from the examination of the viscosity of the interstitial solution containing unabsorbed SP and the thickness of the water films wrapping solid particles in pastes.

2. Experimental program

2.1. Materials

Portland cement (CEM, Chinese Type P·II 52.5), silica fume (SF) and ultra-fine slag (USL) were used as a binder in this study. Their chemical compositions and physical properties are given in Table 1. A polycarboxylate-based superplasticizer (SP) with solid content of 30% and specific density of 1.07 g/cm^3 is adopted as a water reducer. Its chemical structure of the main component is presented in Fig. 1. The side chain length (average number of ethylene oxide units) was 53. The M_w (mass-average molecular weight) and PDI (polydispersity index) of the SP were 58.2×10^3 g/mol and 2.0, respectively. Furthermore, the density of side chains (q:p) was 1:3.25.

2.2. Mix proportions

The mix proportions of the cement pastes used are given in Table 2, where the binder was made with 75% cement, 10% silica fume, and 15% ultra-fine slag for all the mixes. Four w/b ratios (0.32, 0.24, 0.20, and 0.16) were employed. In the study of flow behaviour of paste, good fluidity and stability was necessary for ensuring the accuracy and comparability of results. Based on this, four levels of SP dosage (by the total weight of the binder) were chosen for paste with the same w/b. All the mixes were repeated three times.

2.3. Experimental procedures

2.3.1. Mix protocols

The mixing protocol, as well as the early hydration and adsorption of SP, had a very strong influence on the rheological behaviour of the paste. In this work, we aimed to focus on the influence of SP dosage on viscosity of cement pastes at early stage (5–10 min after adding water). Therefore, a mixing protocol was set for all the paste. The sample preparations were conducted at temperature of 20 ± 2 °C. For a given mix, 300 g of binder was firstly placed into a Hobart mixer. The corresponding water with SP was then added. The sample was mixed at a low speed (140 ± 5 rpm) for 2 min and then at a high speed (285 ± 5 rpm) for another 1.5 min.

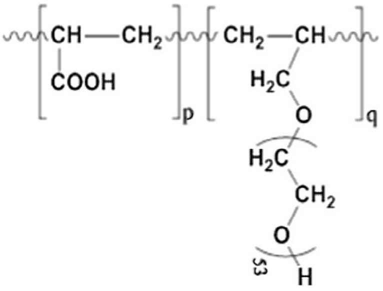

Fig. 1. Chemical structure of main component of the SP.

Furthermore, considering that the role of early hydration on rheological behaviour of the paste was very complex, all the tests such as rheology and adsorption were carried out immediately after mixing, and testing time was fixed almost the same to avoid discussing the effects of hydration.

2.3.2. Flow measurement

The flow spread value was measured by using a mini cone according to the standard method GB/T8077-2000 (height = 60 mm, top diameter = 35 mm, and bottom diameter = 60 mm) [19]. Immediately after the mixing, the cement paste was poured into the cone on a glass plate, and then the cone was vertically lifted. The flow spread value of the tested paste was determined by the average of two perpendicularly crossing diameters of the spread paste.

2.3.3. Apparent viscosity measurement for cement pastes

The apparent viscosity, defined as the ratio of shear stress and shear rate, was measured using a Brookfield R/S SST2000 rheometer with Spindle CC25 (Fig. 2a). The shearing procedure [20] used for the rheology tests of cement pastes was shown in Fig. 3. Based on the fact that the shear rate during concrete pouring was about 10 s^{-1} to 20 s^{-1} [21], the maximum shear rate for the pastes presented in this paper was set to 25 s^{-1}. After placing the paste into the rheometer, the sample was left to equilibrate for 30 s and then sheared at a constant rate of 25 s^{-1} for 1 min (referred to "pre-shear", for reducing the sedimentation). After the "pre-shear", the spindle was stopped for 1 min. In this period the sample was gently stirred to mitigate the formation of preferential shear planes due to particle orientation. The sample was then subjected to a controlled rate for the hysteresis loop test, in which the shear rate was first increased from 0 to 25 s^{-1} within 1 min and then immediately decelerated back to 0 s^{-1} within another 1 min. The apparent viscosity of the tested paste was computed based on the down curve of the hysteresis loop.

2.3.4. Viscosity measurement for superplasticizer solutions

In order to examine the effects of superplasticizer on viscosity of cement paste in detail, different amounts of SP were added into simulated cement paste pore solutions, and the viscosity of the superplasticizer solutions was measured. Two synthetic solutions as cement filtrates were used. One was saturated calcium hydroxide solution (synthetic solution 1), and another was prepared from 1.72 g/L $CaSO_4 \cdot 2H_2O$, 6.959 g/L Na_2SO_4, 4.757 g/L K_2SO_4 and 7.12 g/L KOH [22] (synthetic solution 2). The viscosity of the solutions was measured using the Brookfield R/S SST2000 rheometer with Spindle CC45 (Fig. 2b) and with the sharing procedure as shown in Fig. 4. The average viscosity acquired from step 2 was applied to characterize the viscosity of solution.

2.3.5. Superplasticizer adsorption measurement

In order to assess the interaction of SP and cementitious materials, adsorption of SP on the surface of cementitious materials was quantified using a Total Organic Carbon (TOC) apparatus (Multi N/C 3100). Immediately after the mixing, the pastes were first centrifuged at a speed of 10,000 rpm for 5 min so as to extract the interstitial fluid, and this acquired liquid phase was then acidified using 1 mol/l HCl to remove inorganic carbon (carbonates). The obtained mixture was diluted with deionized water to 10 times of the original interstitial fluid, followed by analyzing

Table 1
Chemical compositions and physical properties of cementitious materials.

Cementitious materials	Chemical compositions (%)									Specific gravity (g/cm^3)	Surface area* (m^2/kg)
	CaO	SiO_2	Al_2O_3	MgO	Fe_2O_3	TiO_2	SO_3	K_2O	Na_2O		
Cement	63.80	19.41	4.33	1.29	2.91	0.26	3.89	0.68	1.29	3.12	382
Silica fume	0.10	98.1	0.15	0.14	0.08	0.20	0.51	0.12	0.17	2.84	21000
Ultra-fine slag	34.53	29.86	18.11	11.26	0.54	0.83	3.13	0.35	0.49	2.09	810

* Blaine surface area for cement and ultra-fine slag, BET surface area for silica fume.