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Roles of Packing Density and Water Film Thickness in Rheology and Strength of Cement Paste

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Abstract

Lowering the water/cementitious materials (W/CM) ratio is the key for the production of high-strength concrete and high-performance concrete, but there is a limit to lowering the W/CM ratio because the water added must be enough to fill the voids between solid particles and form water films coating the solid particles. Hence, an increase in packing density of the cementitious materials would allow a lower W/CM ratio to be adopted. This research aims to evaluate the effects of adding superfine cement (SFC) and condensed silica fume (CSF) on the packing density of cementitious materials, and study the roles of packing density and water film thickness in the rheological properties and compressive strength of cement paste. The results showed that the addition of SFC and/or CSF can significantly increase the packing density and water film thickness, and thereby greatly improve the rheological and strength performances of cement paste.

1. Introduction

It is well known that lowering the water/cementitious materials (W/CM) ratio would improve the strength and durability of concrete (Aitcin 1995, 1998; Bhartkumar *et al.* 2001). In this regard, Neville (1995) remarked that what makes the concrete a high performance one is a very low water/cement ratio. Walraven (2009) pointed out that the use of water/cement ratios so low that all water is used for hydration is a revolutionary step. However, since the water added must be more than enough to fill the voids between the solid particles so that there would be excess water (water in excess of that needed to fill the voids) for lubricating the solid particles to provide workability, there is a lower limit to the W/CM ratio. For this reason, lowering of the W/CM ratio while keeping satisfactory workability is the key to the production of high-performance concrete. This raises the fundamental questions of how low the W/CM ratio can be reduced to and what factors govern this lower limit of W/CM ratio.

In relation to the above questions, Nanthagopalan *et al.* (2008), Wong and Kwan (2008a) and Kwan and Wong (2008a) have conducted packing density measurements and found that the packing density plays an important role in the flowability of cement paste. This is because a higher packing density would lead to a smaller amount of water needed to fill the voids. With the packing density increased by certain means, such as adding ultrafine particles to fill into the voids between cement grains, then for the same amount of water added, there would be more excess water available for lubricating the cement paste or

for the same amount of excess water needed for lubricating the cement paste, the amount of water to be added could be reduced to lower the W/CM ratio. Hence, for given flowability requirement, an increase in packing density should, *prima facie*, allow a lower W/CM ratio to be adopted.

Although seldom verified by packing density measurement, many researchers have advocated the use of supplementary cementitious materials (SCM) to increase the packing density so as to improve the performance of concrete. Feldman and Huang (1985) found that the addition of condensed silica fume (CSF) could densify the cement paste matrix. ACI Committee 363 (1992) mentioned that the addition of CSF would allow the W/CM ratio to be reduced. De Larrard and Sedran (1994) added CSF to increase the packing density and reduced the W/CM ratio to as low as 0.14. Sedran *et al.* (1996) professed that the performance optimization of concrete is mainly a matter of maximising the packing density. Lange *et al.* (1997) showed that blending ordinary cement with a finer slag-based cement could improve the overall performance of mortar through increasing the packing density. Niu *et al.* (2002) suggested that the particle size distribution and range are the main factors governing the packing density. Lee *et al.* (2003) attributed the higher fluidity of a cement paste with a wider particle size range to the higher packing density of the particle system. Yahia *et al.* (2005) pointed out that the addition of fillers could increase the packing density and liberate part of the water entrapped in the voids to improve the flowability. Park *et al.* (2005) showed that fly ash, finely ground slag and CSF could fill into the voids between cement grains and thus increase the packing density. Plank *et al.* (2009) postulated that the addition of particles finer than cement to fill voids would improve packing and reduce water demand. Sakai *et al.* (2009) revealed that the filling and ball bearing effects of CSF would improve the packing and fluidity of cement paste.

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However, the addition of SCM to increase the packing density may have either beneficial or detrimental effects on the flowability/workability. On the use of CSF as SCM, Kohno and Komatsu (1986) and Artelt and Garcia (2008) reported that at a constant high-range water reducing admixture (HRWRA) dosage, the addition of CSF would decrease the flow of mortar. However, Duval and Kadri (1998) found that the addition of CSF up to 10% would reduce the HRWRA demand but further addition of CSF would increase the HRWRA demand. Likewise, Zhang and Han (2000) found that the addition of CSF could decrease the yield stress and viscosity of cement paste. On the use of fly ash or slag, Collins and Sanjayan (1999) reported that the addition of ultrafine fly ash would increase the workability but the addition of ultrafine slag would slightly decrease the workability. However, Gao *et al.* (2001) showed that the addition of superfine slag could improve the workability. Long *et al.* (2002) observed that the addition of ultrafine fly ash or slag could improve the fluidity of cement paste at low water content. Later, Jones *et al.* (2006) found that the addition of ultrafine fly ash would also increase the flow of mortar. On the use of rice husk ash, Cordeiro *et al.* (2009) found that the addition of ultrafine rice husk ash would reduce the yield stress and viscosity only when the HRWRA dosage is increased to allow for the increase in solid surface area whereas Givi *et al.* (2010) showed that partial replacement of cement by a coarser rice husk ash gives better workability than by a finer rice husk ash. On the use of cement with different fineness, Kaufmann *et al.* (2004) found that the rheological properties of cement paste could be improved by blending normal cement with ultrafine cement. Similarly, Zhang *et al.* (2011) blended three cements of different fineness to increase the packing density and thereby produced a high-performance cement.

Recently, the authors' research team demonstrated that the addition of fine SCM has two distinct effects on the rheology of cement paste (Kwan and Wong 2008b; Wong and Kwan 2008b; Kwan *et al.* 2012). One effect is that the fine SCM particles fill into the voids between cement grains to increase the packing density so that the amount of excess water available for lubrication increases. Another effect is that the addition of fine SCM increases the total surface area of the solid particles and thus for the same amount of excess water, the average thickness of the water films coating the solid particles decreases. This is in agreement with Claisse *et al.* (2001), who showed that the specific surface area has great influence, and Ferraris *et al.* (2001), who pointed out that both the packing density and solid surface area would affect the rheological properties of cement paste. The increase in packing density and the increase in surface area have opposite effects and therefore, depending on their relative magnitudes, their net effect may be positive or negative. To allow for these opposite effects, the authors' research team has proposed to evaluate the net effect of adding SCM in terms of the water film thickness, which is defined as average thickness of the water films coating the solid

particles and may be determined as the excess water to solid surface area ratio (Fung and Kwan 2010; Kwan *et al.* 2010; Li and Kwan 2011).

In this study, two types of SCM, namely, superfine cement (SFC) and condensed silica fume (CSF), were added to ordinary Portland cement (OPC) to form triple-blended cementitious materials so as to evaluate the effects of triple blending on the packing density of cementitious materials, the water film thickness of cement paste formed at different W/CM ratios, and the rheology and strength of cement paste.

2. Materials

Three types of cementitious materials, namely, OPC, SFC and CSF, were used. The OPC was of strength grade 52.5N and obtained locally in Hong Kong, whereas the SFC and CSF were imported from Europe. According to the suppliers, the OPC and CSF had been tested to verify its compliance with BS EN 197-1: 2000 and ASTM C 1240-03, respectively, and the SFC was a slag-based cement containing 80% slag and 20% Portland cement. The solid densities of the OPC, SFC and CSF had been measured in accordance with BS EN 196-6: 2010 as 3112 kg/m³, 2940 kg/m³, 2196 kg/m³, respectively. Their particle size distributions were measured by a laser diffraction particle size analyzer and the results obtained are plotted in Fig. 1. Based on these particle size distributions, the specific surface areas of the OPC, SFC and CSF were calculated as 1.26×10^6 m²/m³, 2.29×10^6 m²/m³ and 13.3×10^6 m²/m³ (equivalent to 407 m²/kg, 780 m²/kg and 6039 m²/kg), respectively.

To disperse the cementitious materials and reduce agglomeration, a widely used third-generation HRWRA was added to all the cement paste samples. It was an aqueous solution with a solid mass content of 20% and a relative density of 1.03. Its molecular structure is characterized by a monomer main chain attached with copolymer side chains and is particularly effective because it can disperse fine particles by both electrostatic repulsion and steric repulsion. As the HRWRA is a surface reactant and it is the dosage of HRWRA per solid surface area of the particles that governs the effectiveness, the HRWRA dosage

Fig. 1 Particle size distributions of OPC, SFC and CSF.

was expressed in terms of the liquid mass of HRWRA per solid surface area of the cementitious materials. Before setting the HRWRA dosage to be used, trial cement paste mixing using different HRWRA dosages was carried out and it was found that the saturation dosage of the HRWRA (the dosage beyond which further addition yields little further increase in flowability) was 26×10^{-6} kg/m² (this corresponds to 1.05% by mass of cement when only OPC is used). Hence, the HRWRA dosage in terms of liquid mass of HRWRA per solid surface area of cementitious materials was set constant as 26×10^{-6} kg/m² for all the cement paste samples. Since SFC and CSF have higher fineness, the HRWRA dosage per mass of cementitious materials was higher at higher SFC and CSF contents.

3. Experimental program

The experimental program consisted of three parts. The first part was to measure the packing densities of cementitious materials in order to study the effects of adding SCM on the packing density. The second part was to measure the flow spread, flow rate, yield stress and apparent viscosity of cement paste samples in order to study the effects of adding SCM on the rheological performance. The third part was to measure the cube strength of cement paste samples in order to study the effects of adding SCM on the strength performance. Based on the results of the first part, the water film thickness of each cement paste sample was calculated. From the water film thickness so obtained and the results in the second and third parts, the roles of packing density and water film thickness in the rheology and strength of cement paste were studied. In all the three parts, the SFC content was varied from 0% to 20% in increments of 10% by volume while the CSF content was varied from 0% to 10% in increments of 5% by volume. In the second and third parts, the W/CM ratio was varied between 0.16 and 0.24 by mass for rheology and strength measurements (some samples with the W/CM ratio by mass reduced to 0.14 were tested to determine the peak strength in each SFC + CSF series, as will be explained later). The SFC and CSF contents were expressed as volumetric percentages because it is the solid volume rather than the mass that is more important in rheological studies whereas the W/CM ratio was expressed as mass ratio for easier interpretation of strength results.

In total, 45 cement paste samples were produced for rheology tests and 49 cement paste samples were produced for strength tests. Their mix proportions are summarized in **Table 1**. Each cement paste sample so produced was assigned an identification code of P-X-Y-Z, in which P denotes paste, X and Y denote the SFC and CSF contents each expressed as a percentage of the total cementitious materials by volume, and Z denotes the W/CM ratio by mass. Each cement paste sample was of 2550 ml size. It was produced by mixing the designed mix proportions of OPC, SFC, CSF and water together, as per **Table 1**, in a standard mixer complying with BS EN 196:

Parts 1-3. To ensure thorough mixing of the cementitious materials with water, a special mixing procedure of adding the cementitious materials in several small increments to the water was adopted. The authors' research team has been using this method of mixing for cement paste containing ultrafine fillers (Wong and Kwan 2008a; Kwan and Wong 2008a) because the conventional method of mixing all the cementitious materials and water in one go would cause difficulties when the ultrafine filler content is high and/or the water content is low due to the apparent dryness of the cement paste formed. The whole sample preparation and testing procedures were carried out in a laboratory maintained at a temperature of 24 ± 2 °C and a relative humidity of 75 ± 5 %.

4. Test methods

4.1 Measurement of packing density and calculation of water film thickness

The wet packing method developed by the authors' research team (Wong and Kwan 2008a; Kwan and Wong 2008a) was used to measure the packing density of the cementitious materials. Since details of the method have been given before, only an outline is presented here. Basically, this method determines the packing density of a given mix of solid particles containing particulate materials denoted by α , β and γ etc as the maximum solid concentration of the solid particles when mixed with water at different water contents. From the bulk density, mix proportions and water content of the water-solid mixture, the solid concentration may be determined as:

$$\phi = \frac{M/V}{\rho_w u_w + \rho_\alpha R_\alpha + \rho_\beta R_\beta + \rho_\gamma R_\gamma} \quad (1)$$

where M/V is the measured bulk density of the water-solid mixture, u_w is the water volume to solid volume ratio of the water-solid mixture, ρ_w is the density of water, ρ_α , ρ_β and ρ_γ are the respective solid densities of α , β and γ , and R_α , R_β and R_γ are the respective volumetric ratios of α , β and γ to the total solid particle content. To measure the maximum solid concentration, six to eight water-solid mixture samples are formed of the solid particles with different water contents ranging from insufficient to more than sufficient to fill the voids between the solid particles. Generally, the solid concentration of the water-solid mixture would first increase as the water content increases and then decrease as the water content becomes more than sufficient to fill the voids and further increases. The maximum solid concentration $\phi_{\max}$, which occurs when the solid particles are tightly packed against each other, is taken as the packing density of the solid particles.

From the packing density, the voids ratio u (voids volume to solid volume ratio) and excess water ratio u_w' (excess water to solid volume ratio) may be evaluated as:

$$u = \frac{1 - \phi_{\max}}{\phi_{\max}} \quad (2)$$

Table 1 Mix proportions, packing density and water film thickness.

Mix no.	Dosage of each ingredient (kg/m ³)					Packing density	Water film thickness (μm)
	OPC	SFC	CSF	Water	SP		
P-0-0-0.16	2068.4	0.0	0.0	314.3	21.7	0.630	-0.070
P-0-0-0.18	1986.1	0.0	0.0	341.6	20.8		-0.021
P-0-0-0.20	1910.1	0.0	0.0	366.8	20.0		0.028
P-0-0-0.22	1839.6	0.0	0.0	390.2	19.3		0.077
P-0-0-0.24	1774.2	0.0	0.0	411.8	18.6		0.127
P-10-0-0.16	1864.3	195.7	0.0	311.6	23.4	0.646	-0.039
P-10-0-0.18	1790.4	187.9	0.0	338.9	22.5		0.006
P-10-0-0.20	1722.1	180.8	0.0	364.1	21.7		0.051
P-10-0-0.22	1658.8	174.1	0.0	387.5	20.9		0.097
P-10-0-0.24	1600.0	168.0	0.0	409.2	20.1		0.142
P-20-0-0.16	1659.6	392.0	0.0	308.9	25.2	0.659	-0.017
P-20-0-0.18	1594.1	376.5	0.0	336.2	24.2		0.025
P-20-0-0.20	1533.5	362.2	0.0	361.4	23.3		0.067
P-20-0-0.22	1477.3	348.9	0.0	384.8	22.5		0.109
P-20-0-0.24	1425.1	336.6	0.0	406.5	21.7		0.151
P-0-5-0.16	1970.5	0.0	73.2	302.4	32.0	0.663	-0.011
P-0-5-0.18	1892.9	0.0	70.3	329.9	30.7		0.022
P-0-5-0.20	1821.2	0.0	67.6	355.3	29.6		0.054
P-0-5-0.22	1754.7	0.0	65.2	378.8	28.5		0.087
P-0-5-0.24	1692.9	0.0	62.9	400.7	27.5		0.120
P-10-5-0.16	1765.7	196.2	73.3	299.7	33.8	0.685	0.012
P-10-5-0.18	1696.4	188.5	70.4	327.1	32.5		0.043
P-10-5-0.20	1632.4	181.4	67.8	352.5	31.3		0.074
P-10-5-0.22	1573.0	174.8	65.3	376.1	30.1		0.105
P-10-5-0.24	1517.7	168.7	63.0	398.0	29.1		0.136
P-20-5-0.14	1626.4	409.7	76.5	267.1	37.2	0.699	-0.005
P-20-5-0.16	1560.3	393.1	73.4	296.9	35.6		0.024
P-20-5-0.18	1499.3	377.7	70.5	324.4	34.2		0.054
P-20-5-0.20	1442.9	363.5	67.9	349.8	33.0		0.083
P-20-5-0.22	1390.6	350.3	65.4	373.4	31.8		0.112
P-20-5-0.24	1341.9	338.1	63.1	395.3	30.7	0.693	0.141
P-0-10-0.14	1951.1	0.0	153.0	260.4	44.2		-0.010
P-0-10-0.16	1872.0	0.0	146.8	290.4	42.4		0.014
P-0-10-0.18	1799.1	0.0	141.1	318.1	40.8		0.038
P-0-10-0.20	1731.6	0.0	135.8	343.7	39.2		0.063
P-0-10-0.22	1669.0	0.0	130.9	367.4	37.8		0.087
P-0-10-0.24	1610.8	0.0	126.3	389.4	36.5	0.709	0.111
P-10-10-0.14	1736.6	205.1	153.2	257.7	46.1		0.002
P-10-10-0.16	1666.5	196.8	147.0	287.7	44.3		0.025
P-10-10-0.18	1601.8	189.2	141.3	315.3	42.5		0.048
P-10-10-0.20	1541.9	182.1	136.0	340.9	40.9		0.071
P-10-10-0.22	1486.4	175.5	131.1	364.6	39.5		0.095
P-10-10-0.24	1434.7	169.4	126.6	386.7	38.1	0.722	0.118
P-20-10-0.14	1521.5	410.7	153.4	254.9	48.0		0.011
P-20-10-0.16	1460.3	394.2	147.2	284.9	46.1		0.033
P-20-10-0.18	1403.9	378.9	141.5	312.5	44.3		0.055
P-20-10-0.20	1351.6	364.8	136.3	338.1	42.7		0.077
P-20-10-0.22	1303.1	351.7	131.4	361.9	41.1		0.099
P-20-10-0.24	1258.0	339.6	126.8	384.0	39.7		0.122

$$u'_w = u_w - u \quad (3)$$

The excess water ratio u'_w has the physical meaning of being the amount of excess water in the cement paste per solid volume of the cementitious materials. On the other hand, the specific surface area (surface area per solid volume) of the cementitious materials A_{CM} can be calculated as:

$$A_{CM} = A_\alpha R_\alpha + A_\beta R_\beta + A_\gamma R_\gamma \quad (4)$$

in which A_α , A_β and A_γ are respectively the specific surface areas of α , β and γ . With the values of u'_w and A_{CM} so determined above, the water film thickness (WFT) may be calculated as:

$$\text{WFT} = \frac{u'_w}{A_{CM}} \quad (5)$$

As explained before, the WFT has the physical meaning of being the average thickness of water films coating the solid particles.

4.2 Measurement of flow spread and flow rate

The mini slump cone test and Marsh cone test were respectively used to measure the flow spread and flow rate, as suggested by Aitcin (1998). However, there are many different versions of mini slump cone and Marsh cone. In this study, the mini slump cone adopted was the same as that used by Okamura and Ouchi (2003) while the Marsh cone adopted was the same as that specified in BS EN 445: 1997, as in previous studies (Kwan and Wong 2008b; Wong and Kwan 2008b; Kwan *et al.* 2012). **Figure 2** shows the dimensions of the mini slump cone and Marsh cone. To perform the mini slump cone test, the slump cone was placed at the centre of a levelled steel plate, the cement paste was poured slowly into the slump cone until it was full, the slump cone was gently lifted and finally the flow spread was determined as the average diameter of the cement paste patty formed minus the base diameter of the slump cone. To perform the Marsh cone test, the orifice of the Marsh cone was first closed, the cement paste was poured slowly into the Marsh cone until it was full, the orifice was opened to allow the cement paste to flow out, the flow time was recorded and finally the flow rate was determined as the volume of cement paste divided by the flow time.

4.3 Measurement of rheological properties

The rheometer and test method used were the same as those used in previous studies (Wong and Kwan 2008b; Kwan *et al.* 2012). Basically, the rheometer was of the coaxial cylinder type. Its spindle, which rotated at controlled speed, has a diameter of 25.0 mm, while its outer cup, which served also as a container, has an inner diameter of 27.1 mm. To avoid slippage, the surface of the spindle was grooved and the inner surface of the out cup was roughened by gluing onto the surface a thin sheet of sand paper. After deducting the thickness of the sand paper, the effective inner diameter of the outer cup was

Fig. 2 Dimensions of mini slump cone and Marsh cone.

26.6 mm.

The shearing sequence applied to each cement paste sample consisted of two shearing cycles. The first shearing cycle (pre-shearing cycle) was to ensure that each cement paste sample had undergone the same shearing history before measurement. The second shearing cycle (data-logging cycle) was the cycle in which actual measurement was carried out by a data-logger. During each shearing cycle, the shear rate was continuously increased from 0 to 50 s⁻¹ in 75 s and then continuously decreased from 50 to 0 s⁻¹ in another 75 s. There was no equilibrium period during shearing and readings were taken in the second shearing cycle at 1.0 s time intervals. Two shear stress-shear rate curves were obtained, one at increasing shear rate and the other at decreasing shear rate. The curve at decreasing shear rate, which is generally more consistent and repeatable, was used for evaluating the rheological properties of the cement paste sample.

To evaluate the rheological properties of the cement paste sample, a smooth curve based on the Herschel - Bulkley nonlinear rheological model, which best fit the experimental shear stress - shear rate curve, was first obtained by regression analysis. Then, from the best-fit curve so obtained, the shear stress at a shear rate of 0 s⁻¹ and the ratio of shear stress to shear rate at a shear rate of 50 s⁻¹ were taken as the yield stress and the apparent viscosity, respectively.

4.4 Measurement of compressive strength

Six 70.7 mm cubes were made from each cement paste sample. The cubes were each made by placing the cement paste into a cube mould, mounting the mould on a vibration table for compaction and covering the top surface of the mould with a plastic sheet. The cubes were then stored in the laboratory at a temperature of 24 ± 2 °C and a relative humidity of 75 ± 5 %. At 1 day after casting, the moulds were removed and the cubes were water cured in lime saturated water at a temperature of 27 ± 2 °C. Three of the cubes were tested at an age of 7 days while the other three cubes were tested at an age of 28 days.

5. Test results

5.1 Packing density and voids ratio

The packing density results of the cementitious materials containing various amounts of SFC and CSF are tabulated in the seventh column of **Table 1** and plotted against the CSF contents at different SFC contents in **Fig. 3**. It is seen that with no SFC and no CSF added, the cement was measured to have a packing density of 0.630. With only SFC added, the packing density was increased to 0.646 at a SFC content of 10% and to 0.659 at a SFC content of 20%. With only CSF added, the packing density was increased to 0.663 at a CSF content of 5% and to 0.693 at a CSF content of 10%. These results show that the addition of either SFC or CSF to cement could significantly increase the packing density of the cementitious materials. Comparatively, CSF is more effective than SFC in im-

Fig. 3 Variations of (a) packing density and (b) voids ratio with SFC and CSF contents.

Fig. 4 Variation of WFT with W/CM ratio: (a) double blended mixes; (b) triple blended mixes.

proving the packing density. This is probably due to the much higher fineness of CSF, which allows the CSF particles to fill into the voids of the cement grains without loosening the packing of the cement grains.

The packing density results also show that with both SFC and CSF added so that the cementitious materials become triple-blended, the packing density could be further increased. For instance, at a SFC content of 20%, the addition of 5% CSF increased the packing density from 0.659 to 0.699 whereas the addition of 10% CSF increased the packing density to 0.722. Likewise, at a CSF content of 10%, the addition of 10% SFC increased the packing density from 0.693 to 0.709 whereas the addition of 20% SFC increased the packing density to 0.722. Hence, triple blending of cement with both SFC and CSF is more effective than double blending of cement with either SFC or CSF in improving the packing density. This is because the SFC is finer than the cement and the CSF is finer than the SFC. When triple blended together, the SFC particles would fill into the voids between cement grains while the CSF particles would fill into the voids between the SFC particles. Such successive filling of voids by finer particles is the most effective means of improving the packing density.

The voids ratios of the cementitious materials, as cal-

culated by Equation (2), are also plotted against the CSF contents at different SFC contents in **Fig. 3**. From the curves plotted, it is evident that the addition of SFC and/or CSF would effectively reduce the voids ratio of the cementitious materials. Comparing the increases in packing density with the corresponding reductions in voids ratio, it can be seen that although the maximum increase in packing density was only 14.6%, the corresponding maximum reduction in voids ratio was as much as 34.6%. The relatively large reduction in voids ratio would substantially decrease the amount of water needed to fill the voids and increase the amount of excess water available for forming water films.

5.2 Water film thickness

The water film thickness (WFT) of the cement paste samples are tabulated in the last column of **Table 1** and plotted against the W/CM ratios in **Fig. 4**. It should be noted that some of the WFT values are negative. A negative WFT value indicates that the amount of water in the cement paste was not sufficient to fill the voids between the solid particles, leading to the entrapment of air in the cement paste.

Comparing the curves for cement paste samples containing only cement and SFC, it can be seen that within

the range of W/CM ratio between 0.16 and 0.24, the addition of SFC always increased the WFT. Comparing the curves for cement paste samples containing only cement and CSF, it can also be seen that within the range of W/CM ratio between 0.16 and 0.22, the addition of CSF increased the WFT but at a W/CM ratio of 0.24, the addition of CSF decreased the WFT. Hence, the addition of a SCM to fill into the voids between cement grains in order to increase the packing density does not always increase the WFT. Whether the WFT would be increased or decreased is dependent on the W/CM ratio. At low W/CM ratio, when the proportional increase in the amount of excess water is larger than the proportional increase in the solid surface area, the WFT would be increased. At high W/CM ratio, when the proportional increase in the amount of excess water is smaller than the proportional increase in the solid surface area, the WFT would be decreased. Overall, SFC is more effective in increasing the WFT than CSF at W/CM ratio > 0.20 whereas CSF is more effective in increasing the WFT than SFC at W/CM ratio < 0.20 .

Comparing the curves for cement paste samples containing cement, SFC and CSF, it is obvious that after adding 5% CSF, the effect of adding SFC would become relatively small and after adding 10% CSF, the effect of adding SFC would become even smaller. Nevertheless, with up to 20% SFC and 10% CSF added, the WFT would be increased at W/CM ratio ≤ 0.22 but decreased at W/CM ratio = 0.24. Hence, triple blending with both SFC and CSF added is more effective in increasing the WFT at low W/CM ratio than at high W/CM ratio. Particularly, the addition of 20% SFC and 10% CSF would, at a W/CM ratio of 0.16, dramatically increase the WFT from $-0.070 \mu\text{m}$ to $0.033 \mu\text{m}$ and therefore allow the W/CM ratio to be lowered to 0.16. In order to find out how low the W/CM ratio could be lowered to, the W/CM ratios of some cement paste samples were lowered to 0.14 to evaluate the effect on the WFT. The results, tabulated in **Table 1**, reveal that with 10% or 20% SFC and 10% CSF added, the W/CM ratio may be lowered to 0.14 without causing the WFT to become negative.

5.3 Flow spread and flow rate

The flow spread results are plotted against the W/CM ratio and WFT in **Fig. 5**. From the scattering of the flow spread-W/CM ratio curves, it is evident that the W/CM ratio is not the key factor governing the flow spread of cement paste, although generally the flow spread increases with the W/CM ratio. Comparing the flow spread-W/CM ratio curves, it can be seen that the addition of SFC and/or CSF has larger effect on the flow spread at low W/CM ratio than at high W/CM ratio. For instance, the addition of 20% SFC and 10% CSF greatly increased the flow spread from absolute 0 to 146.8 mm at W/CM ratio = 0.16 but caused very little change in the flow spread at W/CM ratio = 0.24. Although the flow spread-W/CM ratio curves are quite scattered, the flow spread-WFT curves are so close to each other that only one best-fit curve derived by regression analysis is plotted in the figure. The correlation of the flow spread to the WFT yielded an R^2 value of 0.963. This high R^2 value indicates that the WFT is the key factor governing the flow spread of cement paste. The addition of SFC and/or CSF exerted their effects mainly through the WFT. In other words, it was the change in WFT due to the addition of SFC and/or CSF that caused the change in flow spread.

The flow rate results are presented in **Fig. 6** in the form of flow rate-W/CM ratio and flow rate-WFT curves. As before, the scattering of the flow rate-W/CM ratio curves indicates that the W/CM ratio is not the key factor governing the flow rate, albeit the flow rate generally increases with the W/CM ratio. Comparing the flow rate-W/CM ratio curves, it can be seen that the addition of SFC and/or CSF could significantly increase the flow rate only at low W/CM ratio. At W/CM ratio = 0.16, the addition of 20% SFC and 10% CSF greatly increased the flow rate from absolute 0 to 2.6 ml/s. However, at W/CM ratio = 0.24, the addition of the same amounts of SFC and CSF did not affect the flow rate much. Unlike the flow rate-W/CM ratio curves, the flow rate-WFT curves are very close to each other. This allows a single best-fit curve to be established by regression analysis, as plotted in the figure. The correlation of the flow rate to the WFT yielded an R^2 value of 0.948. This high R^2 value indicates

(a)

(b)

Fig. 5 Flow spread versus (a) W/CM ratio, and (b) WFT.

Fig. 6 Flow rate versus (a) W/CM ratio, and (b) WFT.

that the WFT is the key factor governing the flow rate of cement paste. It was the change in WFT due to the addition of SFC and/or CSF that caused the change in flow rate.

5.4 Yield stress and apparent viscosity

While the samples P-0-0-0.16, P-10-0-0.16, P-20-0-0.16, P-0-5-0.16 and P-0-0-0.18 were tested for their rheological properties using the rheometer, the torque required to shear the cement paste had exceeded the capacity of the rheometer and thus for these samples, the yield stress and apparent viscosity were not obtained. For these samples, the yield stress and apparent viscosity may be considered to be very large and outside the ranges of the yield stress and apparent viscosity presented herein.

The yield stress results are plotted against the W/CM ratio and WFT in Fig. 7. Comparing the yield stress-W/CM ratio curves, it can be seen that within the range of W/CM ratio covered, the addition of SFC and CSF has significant effect on the yield stress. However, at the same W/CM ratio, the addition of SFC and/or CSF could increase or decrease the yield stress. Such effect of adding SFC and/or CSF on the yield stress appears to be fairly complicated. In this regard, the effect of adding SFC

and/or CSF is better revealed by the yield stress-WFT curves. Although the yield stress-WFT curves are quite scattered, an obvious trend that at the same WFT, the yield stress was generally higher when the packing density of the cementitious materials was higher could be observed. To study this trend, the yield stress was correlated to both the WFT and the packing density by multi-variable regression analysis. The equation so obtained for the yield stress in terms of both the WFT and the packing density is presented in the figure. Several best-fit curves at constant packing density are plotted in the figure alongside the data points. The correlation of the yield stress to both the WFT and the packing density yielded an R^2 value of 0.902. This high R^2 value indicates that the yield stress is governed by both the WFT and the packing density.

The variations of the apparent viscosity with the W/CM ratio and WFT are presented in Fig. 8. From the apparent viscosity-W/CM ratio curves, it is evident that the addition of SFC and CSF has significant effect on the apparent viscosity within the whole range of W/CM ratio covered. However, at the same W/CM ratio, the addition of SFC and/or CSF could increase or decrease the apparent viscosity and therefore has no definite beneficial

Fig. 7 Yield stress versus (a) W/CM ratio, and (b) WFT.

Fig. 8 Apparent viscosity versus (a) W/C/M ratio, and (b) WFT.

or adverse effect on the apparent viscosity. The effect of adding SFC and/or CSF is better revealed by the apparent viscosity-WFT curves. Although these curves are rather scattered, an obvious trend that at the same WFT, the apparent viscosity was generally higher when the packing density of the cementitious materials was higher could be observed. To study this trend, the apparent viscosity was correlated to both the WFT and the packing density by multi-variable regression analysis. The equation so obtained for the apparent viscosity is presented in the figure and several best-fit curves at constant packing density are plotted alongside the data points. The correlation of the apparent viscosity to both the WFT and the packing density yielded an R^2 value of 0.937, which is high enough for drawing the conclusion that the apparent viscosity is governed by both the WFT and the packing density.

From the above analysis, it is evident that at the same WFT, the yield stress and apparent viscosity are higher when the packing density of the cementitious materials is higher. The probable reasons are: (1) at a higher packing density, the particles are more tightly packed against each other, thereby causing the cement paste to require a larger shear stress to undergo shear deformation; (2) at a higher packing density, the amount of finer particles filled into the voids between larger particles is larger and as a result the amount and size of water pores in the cement paste are smaller, thus rendering the flow of water inside the paste and the shear deformation of the paste more difficult; and (3) the larger amount of finer particles filled into the voids between larger particles would increase the number of contact points between particles for transmitting cohesive forces between particles and thus render the paste more cohesive and reluctant to flow.

5.5 Cube strength

The 7-day and 28-day cube strength results are presented in **Figs. 9** and **10**, respectively. Each cube strength result presented is the average of the three cubes tested at the same time. The variations of the 7-day and 28-day cube strengths with the W/C/M ratio reveal that regardless of age, the cube strength increased as the W/C/M ratio de-

creased and then turned to decrease as the W/C/M ratio further decreased to lower than a certain optimum value. With no SFC and CSF added, the maximum 7-day and 28-day cube strengths achieved were 127.5 and 140.8 MPa, respectively. With 20% SFC added, the maximum 7-day and 28-day were 142.7 and 151.5 MPa, respectively. With 10% CSF added, the maximum 7-day and 28-day were 147.0 and 173.2 MPa, respectively. With 20% SFC and 10% CSF added, the maximum 7-day and 28-day were 155.2 and 184.0 MPa, respectively. It should however be noted that the higher strengths with SFC and/or CSF added were achieved at lower W/C/M ratios. In conclusion, with SFC and/or CSF added and the W/C/M ratio lowered at the same time to take advantage of the increase in packing density, the 7-day and 28-day strengths of the cement paste could be increased by about 20% and 30%, respectively.

On the other hand, the variations of the 7-day and 28-day cube strengths with the WFT reveal that regardless of age, the maximum cube strength generally occurred at an optimum WFT of around 0.02 to 0.05 μm . When the WFT was larger than the optimum, the cube strength decreased as the WFT increased because of the corresponding increase in W/C/M ratio with the WFT. When the WFT was smaller than the optimum, some of the voids were incompletely filled with the mixing water, thus resulting in entrapment of air in the cement paste and reduction of the cube strength as the WFT decreased. Hence, while the optimum W/C/M ratio for maximum strength varies with the SFC and CSF contents, the optimum WFT for maximum strength is more or less constant. Both the optimum W/C/M ratio and optimum WFT for maximum strength are governed by the need to ensure complete filling of the voids with water. As the optimum WFT is rather low, the authors have the feeling that if the WFT is really set so low in the mix design of paste/mortar/concrete, then due to unavoidable non-uniform mixing in actual production, which could cause incomplete filling of the voids with water, the strength could fluctuate with a large standard deviation. To ensure good quality control, it is better to set a higher WFT than the optimum.

Fig. 9 7-day cube strength versus (a) W/CM ratio, and (b) WFT.

Fig. 10 28-day cube strength versus (a) W/CM ratio, and (b) WFT.

5.6 Concurrent strength-flowability performance

The effects of SFC and CSF on the concurrent strength-flowability performance of cement paste are illustrated by plotting the 28-day cube strengths against the flow spread and flow rate values in **Fig. 11**. Each strength-flowability performance curve is a plot of the strength and flowability that can be concurrently achieved by a cement paste having certain SFC and CSF contents. Comparing the performance curves for different SFC and CSF contents, it is evident that the performance curve is always shifted upwards and to the right as the SFC or CSF content increases. Since shifting of the curve upwards would lead to a higher strength at the same flowability and shifting of the curve to the right would lead to a higher flowability at the same strength, this indicates that the addition of SFC and/or CSF can increase the strength at the same flowability, increase the flowability at the same strength, or increase both the strength and flowability at the same time. Relatively, the addition of both SFC and CSF gives the best overall performance, especially at high strength level.

6. Roles of packing density and water film thickness

Based on the above analysis of experimental results, we advocate that the key factors governing the rheology and strength of cement paste are the packing density and water film thickness. The packing density is dependent on the particle size distribution and range of the cementitious materials and the addition of SCM finer than cement to fill into the voids between cement grains could increase the packing density. Triple blending of cement with two SCMs of different sizes so that the voids could be filled successively by finer and even finer particles is more effective than just double blending in increasing the packing density. Since the water added must be more than sufficient to fill the voids between the cementitious materials, an increase in packing density would allow the W/CM ratio to be lowered to increase the strength and decrease the porosity of the concrete.

However, the solid surface area of the blended cementitious materials needs also to be considered. The addition of an ultrafine SCM would increase the packing density and the solid surface area at the same time and thus depending on the W/CM ratio, could increase or decrease the water film thickness. In fact, as demon-

Fig. 11 Concurrent 28-day cube strength and flowability performance: (a) strength-flow spread performance; (b) strength-flow rate performance.

strated by the experimental results of this study, the addition of CSF, which is extremely fine, would increase the water film thickness only at fairly low W/CM ratio because of the very large increase in solid surface area, whereas the addition of SFC, which is coarse than CSF but finer than cement, would increase the water film thickness over a much wider range of W/CM ratio because of only modest increase in solid surface area. The water film thickness affects not only the rheology but also the strength of cement paste. There is an optimum water film thickness for maximum strength, which is more or less constant regardless of the mix composition of the cementitious materials. However, this optimum water film thickness should really be taken as the minimum value of water film thickness to be adopted for the mix design of concrete in actual production because an excessively low water film thickness could lead to large fluctuation in strength due to possible incomplete filling of the voids with water.

7. Conclusions

An experimental study on the effects of triple blending ordinary cement with SFC and CSF at various W/CM ratios on the packing density, rheology and strength of cement paste has been carried out. The test results demonstrated that the addition of up to 20% SFC and up to 10% CSF can effectively increase the packing density of the cementitious materials and relatively, the ultrafine CSF is more effective. However, despite significant increase in the packing density, the water film thickness of the cement paste formed may be increased or decreased, depending on the corresponding increase in solid surface area and the W/CM ratio. Because of only modest increase in solid surface area, the addition of SFC would increase the water film thickness within the whole range of W/CM ratio between 0.16 and 0.24. However, because of very large increase in solid surface area, the addition of CSF would increase the water film thickness only at W/CM ratio lower than or equal to 0.22 and decrease the water film thickness at W/CM ratio equal to 0.24.

Correlating the flow spread and flow rate to the water film thickness, it was found that the flowability of cement paste is governed solely by the water film thickness. Correlating the yield stress and apparent viscosity to both the packing density and water film thickness, it was also found that the rheological properties are governed by both the packing density and water film thickness. Very high R^2 values of at least 0.902 were achieved in the above correlations. Furthermore, from the variations of the cube strengths with the W/CM ratio and water film thickness, it was seen that while the optimum W/CM ratio for maximum strength varied with the SFC and CSF contents, the optimum water film thickness for maximum strength remained a very small but positive value regardless of the SFC and CSF contents. However, the optimum water film thickness of around 0.02 to 0.05 μm should be taken as the minimum value of water film thickness to be adopted for the mix design of concrete in actual production in order to avoid large fluctuation in strength due to incomplete filling of voids with water. Therefore, to answer the questions raised at the beginning, the W/CM ratio can only be lowered until the resulting water film thickness is just equal to the above optimum value and the factors governing the lower limit of W/CM ratio are the packing density and solid surface area.

Finally, the concurrent strength-flowability performance results of the cement paste samples revealed that the addition of SFC and CSF to increase the packing density of the cementitious materials can increase the strength at the same flowability, increase the flowability at the same strength, or increase both the strength and flowability at the same time. This opens up the possibility of improving the performance of cement by triple blending cement with SCMs of suitable fineness to increase the packing density without excessive increase in solid surface area.

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