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Relationship between the late-age hydration and strength development of cement-slag mortars

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The relationship between the late-age hydration and strength development of cement-slag mortars have been investigated by measuring the compressive strengths and the non-evaporable water contents. The results show that the late-age strength increases with increasing the slag content. Increasing the fineness of slag makes greater contribution to the late-age strength improvement at high water to binder ratio than that at low water to binder ratio. At lower water to binder ratio, the increasing rates of compressive strength and non-evaporable water content are smaller. There is a linear relationship between the increasing rate of compressive strength and the increasing rate of non-evaporable water contents. The slope is almost the same for all the samples at constant water to binder ratio and decreases with decreasing the water to binder ratio.

Keywords: Cement, Slag, Hydration, Compressive strength, Non-evaporable water content

1 Introduction

Ground granulated blast furnace slag (GGBFS) is widely used as a partial replacement for Portland cement in modern concrete. The use of slag reduces the cost of raw materials, saves the resources and energy, and decreases the CO_2 emission[1,2]. Slag has both latent hydraulic activity and pozzolanic characteristics. Mixing slag with water leads to low hydration rate, but mixing cement with slag increases the activity of slag. The slag can react with $Ca(OH)_2$ that is produced by the hydration of Portland cement. Thus, the hydration of Portland cement and the pozzolanic reaction of slag occur simultaneously and may also influence the reactivity of each other[3]. The overall reactivity of slag is affected by its particle size and glass content[4], and it is also related to the hydration conditions, such as the content of cement, water to binder ratio and curing temperature[5, 6] *et al.* The hydration of composite binder containing slag generates large amount of hydration products, and then enhances the mechanical properties of mortars or concretes.

Han *et al.*[7] found that the addition of slag decreased the compressive strength of mortar and the non-evaporable water content of paste at early age. However, the compressive strength and the non-evaporable water content increased at late age (90 days), exceeding that of the Portland cement when 30% slag was added. Sajedi[8, 9] investigated the curing regime and temperature on the compressive strength of cement-slag mortars. The highest strength was obtained when the OPC-slag mortars were cured in water without heating. Kolani *et al.*[10] studied the non-evaporable water content of slag-blended cement pastes and pointed out that the non-evaporable water contents of samples containing 30%, 50% and 70% of slag show larger values than those of samples of cement replaced by an inert material. For slag-blended cements, hydration reactions of both clinker and slag contributed to the non-evaporable water content. Vejmelkova *et al.*[11] reported that lower amount of $Ca(OH)_2$ was observed in composite binder containing slag. Additional calcium silicate hydrate (C-S-H) formed by the pozzolanic reaction of slag partially filled the pores. In the long term, the reduction of the amount of $Ca(OH)_2$ became moderate[5, 12]. Yang *et al.* [13] investigated the hydration products and strength development of calcium hydroxide-based alkali-activated slag mortars. It was found that the Si/Ca ratio in C-S-H gel increased with the hydration time. The growth and intensity of C-S-H gel were consistent with higher strength development.

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It is obvious that fine ground granulated blast furnace slag (FGGBFS) reacts faster than coarse slag particles due to the increased specific surface area. The apparent rate of hydration and the pozzolanic reaction also increase. Meanwhile, the increasing rate of compressive strength of mortar or concrete improves. Sengul *et al.*[14] investigated the compressive strength of concretes containing 50% finely ground fly ash or 50% finely ground slag with water to binder ratio of 0.60 and 0.38. It was found that the compressive strengths of the concretes with fly ash or slag were lower than that of Portland cement concrete at high water to binder ratio, but the reduction of strength was less at low water to binder ratio and the compressive strength of concrete with 50% slag was higher than that of Portland cement concrete. Teng *et al.*[15] reported that concrete with 30% ultrafine GGBFS had a higher early strength compared to the control mixes at 3 days and the improvement in the mechanical properties was more obvious for concrete with lower water to binder ratio. Incorporation of ultrafine GGBFS decreased the chloride diffusivity coefficient, reduced the porosity and increased the electrical resistivity measurement of concrete. Binici *et al.*[16] found that finely ground blended cement samples had higher compressive strength and sodium sulfate resistance compared to the coarser blended cement. However, for the same mineral admixture content, the hydration heat of the finer samples was higher than that of the coarser ones. Öner *et al.*[17] pointed out that it was not only the fineness of the cement-slag mix but also the individual components that governed the choice of the mix composition for a desired strength.

Although there are many publications investigating various aspects of composite binder containing slag, there have been few studies on the long term strength development, and none that concern the relationship between the late-age hydration and strength development. The long-term performance of mortar or concrete should be given more attention. In this paper, the compressive strength of mortar and the non-evaporable water content of hardened paste containing 0, 25% or 50% slag were measured, taking into account of the water to binder ratio and the fineness of slag. The relationship between the late-hydration and strength development of cement-slag mortars was discussed.

2 Experimental Procedure

2.1 Materials

Portland cement conforming to Chinese National Standards GB175-2007 and ground granulated blast furnace slag (GGBFS) with two different fineness conforming to Chinese National Standards GB/T118046-2008 were used in this paper. The specific surface areas of Portland cement, GGBFS and finely ground granulated blast furnace slag (FGGBFS) are 356 m^2/kg, 421 m^2/kg and 659 m^2/kg, respectively. The chemical compositions of Portland cement and slags (GGBFS and FGGBFS) are shown in Table 1.

2.2 Mix proportions

The replacing ratios of GGBFS or FGGBFS are 25% and 50% by mass in this paper. The GGBFS and FGGBFS were added separately to the pastes or mortars. Three water to binder ratios for all samples were used: 0.45, 0.35 and 0.25. The sand to binder ratios for all the mortars are 3.0. The mix proportions of pastes and mortars are shown in Table 2.

2.3 Test methods

Mortar bars of 40×40×160 mm^3 were prepared. All the mortars were cured in a fog room at 20℃ and 95% relative humidity (RH). After one day, mortars were demoulded and then still cured in the fog room. At the ages of 28, 90, 360 and 720 days, the compressive strengths of mortars were measured as per Chinese National Standard GB/T17671-1999. One mortar were broken into two segments on the flexural testing machine, and then the two segments were used to measure the compressive strength of mortar. The compressive strength of one sample is the mean value of compressive strengths of three mortars (six segments).

The pastes were prepared for the measurement of the non-evaporable water content (w_{ne}). The pastes were mixed uniformly by a mechanical mixer for 3 min and then cast into polyvinyl chloride tubes. All

Table 1 — Chemical compositions of cement and slags (*wt*.%).

Composition	CaO	SiO_2	Al_2O_3	MgO	Fe_2O_3	SO_3	Na_2O_{eq}	LOI
Cement	62.71	22.33	4.75	1.98	2.78	2.37	0.48	2.03
Slags	39.47	30.14	18.64	8.68	0.75	0.24	0.46	0.54

Note: $Na_2O_{eq}=Na_2O+0.658K_2O$

Table 2 — Mix proportions of pastes and mortars.

Samples		Composition of binder (wt.%)			Water to binder ratio	Sand to binder ratio
Pastes	Mortars	Cement	GGBFS	FGGBFS		
PC0	C0	100	0	0	0.45	3.0
PL1	L1	75	25	0	0.45	3.0
PL2	L2	50	50	0	0.45	3.0
PF1	F1	75	0	25	0.45	3.0
PF2	F2	50	0	50	0.45	3.0
PC00	C00	100	0	0	0.35	3.0
PL11	L11	75	25	0	0.35	3.0
PL22	L22	50	50	0	0.35	3.0
PF11	F11	75	0	25	0.35	3.0
PF22	F22	50	0	50	0.35	3.0
PC000	C000	100	0	0	0.25	3.0
PL111	L111	75	25	0	0.25	3.0
PL222	L222	50	50	0	0.25	3.0
PF111	F111	75	0	25	0.25	3.0
PF222	F222	50	0	50	0.25	3.0

the pastes were cured in an environmental chamber of 20±1℃ and 95% RH. At the ages of 28, 90, 360 and 720 days, the pastes were crushed into small pieces and put into acetone to cease further hydration. Then the pastes were ground until the powders all passing through 0.08 mm sieve. The non-evaporable water content of paste was determined as the difference in mass between the hardened paste heated at 105℃ and 1000℃ normalized by the mass after heating at 105℃, and correcting for the loss on ignition of the unhydrated sample. The w_{ne} was calculated according to the following equations:

$$w_{ne} = ((m_{105}-m_{1000})/m_{105}-w_{SL,C})/(1-w_{SL,C}) \quad \ldots(1)$$

$$w_{SL,C}= f_{SL}\bullet w_{SL,I}+ f_{C}\bullet w_{C,I} \quad \ldots(2)$$

where m_{105} and m_{1000} were the masses of the pastes measured after ignition at 105℃ and 1000℃, respectively; f_{SL} and f_{C} were the mass percents of slag and cement in the binder, respectively; $w_{SL,I}$ and $w_{C,I}$ were the loss on ignition of slag and cement, respectively.

3 Results and Discussion

3.1 Compressive strength of mortar at 720 days

The compressive strengths of mortars cured for 720 days at different water to binder ratios are shown in Fig. 1. The samples C0, L1, L2, F1 and F2 present Portland cement mortar, mortar with 25% GGBFS, mortar with 50% GGBFS, mortar with 25% FGGBFS and mortar with 50% FGGBFS, respectively. The samples C0, C00, C000 present mortars with water to binder ratios of 0.45, 0.35 and 0.25, respectively. The way of naming other mortar specimens is same. It can be seen from Fig. 1(a) that the compressive strength of mortar increases with increasing the content of slag. The chemical effect of slag becomes important at late ages. For composite binder containing up to 50% slag, the amount of calcium hydroxide produced by cement hydration is enough to stimulate fully the hydration activity of slag[18]. Slag reacts with calcium hydroxide generating calcium silicate hydrates, which fill the pores and densify the structure of mortar. Moreover, the particle size of slag is finer than that of cement, so slag particles fill the gaps between cement particles, hydration products, paste and sand[19], which increases the compressive strength. From Fig. 1(a), it is clear that the compressive strength of mortar containing FGGBFS is higher than that mortar containing GGBFS at the same replacing ratio. FGGBFS particles react faster than GGBFS particles due to its larger specific surface area, thus its reaction degree is higher at the age of 720 days. FGGBFS presents better particle packing as finer slag particle filling up the pores and sand-cement paste interface. The densification of the interfacial transition zone between hardened paste and sand improves the homogeneity of the mortar and its compressive strength. Therefore, better chemical effect (pozzolanic reaction) and physical effect (filler effect) of FGGBFS lead to higher compressive strength of mortar.

As expected, decreasing water to binder ratio increases the compressive strength of mortar for all

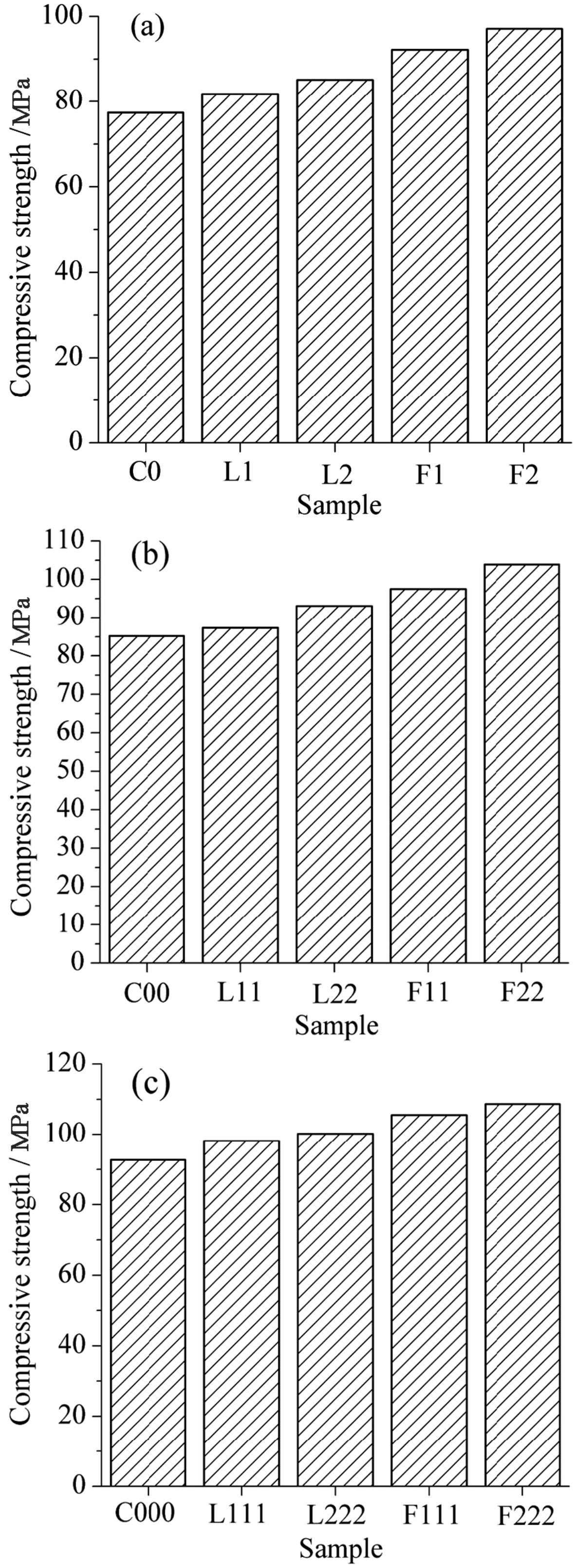

Fig. 1 — The compressive strengths of mortars cured for 720 days (a) Water to binder ratio of 0.45, (b) water to binder ratio of 0.35 and (c) water to binder ratio of 0.25.

samples. As shown in Fig. 1(b) and Fig. 1(c), the compressive strengths of mortars with water to binder ratios of 0.35 and 0.25 show similar regularity to that with water to binder ratio of 0.45. But the gap between compressive strength of Portland cement mortar and that of mortar containing GGBFS or FGGBFS becomes small. The paste with low water to binder ratio is much denser than that with high water to binder ratio. There are fewer pores in hardened paste and the interfacial transition zone between hardened paste and sand improves at low water to binder ratio. Thus, the contributions of pozzolanic reaction and filler effect of slag to the compressive strength become small at low water to binder ratio. Meanwhile, at late ages, the amount of water provided to the hydration of cement and pozzolanic reaction of slag is limited. Note that the gap between compressive strength of mortar containing GGBFS and that of mortar containing the same amount of FGGBFS is also small at low water to binder ratio. For example, the compressive strengths of samples F1 and F2 are 12.71% and 14.10% higher than those of samples L1 and L2, respectively. However, the compressive strengths of samples F111 and F222 are 7.54% and 8.38% higher than those of samples L111 and L222, respectively. It is elucidated that at low water to binder ratio, an increase in fineness of slag makes smaller contribution to the late-age compressive strength improvement. The results obtained in this paper are in agreement with literature [20].

Fig. 2 presents the increasing rate of compressive strength of mortar cured from 28 days to 720 days at different water to binder ratios. As shown in Fig. 2(a), an increase in the content or fineness of slag increases the increasing rate of compressive strength of mortar. It is indicated that the mortar containing slag still has high increasing rate of compressive strength at late ages compared with Portland cement mortar, and then enhances the compressive strength. As explained above, the increased amount of hydration products owing to the pozzolanic reaction of slag and the filler effect owing to the finer slag particles make the strength continue to grow at late ages. The FGGBFS has greater effect on the increment of compressive strength due to its larger specific surface area.

It can be seen from Fig. 2(b) and Fig. 2(c) that the increasing rate of compressive strength of all samples decreases with decreasing the water to binder ratio. At the age of 28 days, the compressive strength is considerably high due to the dense microstructure of mortar at low water to binder ratio. The compressive

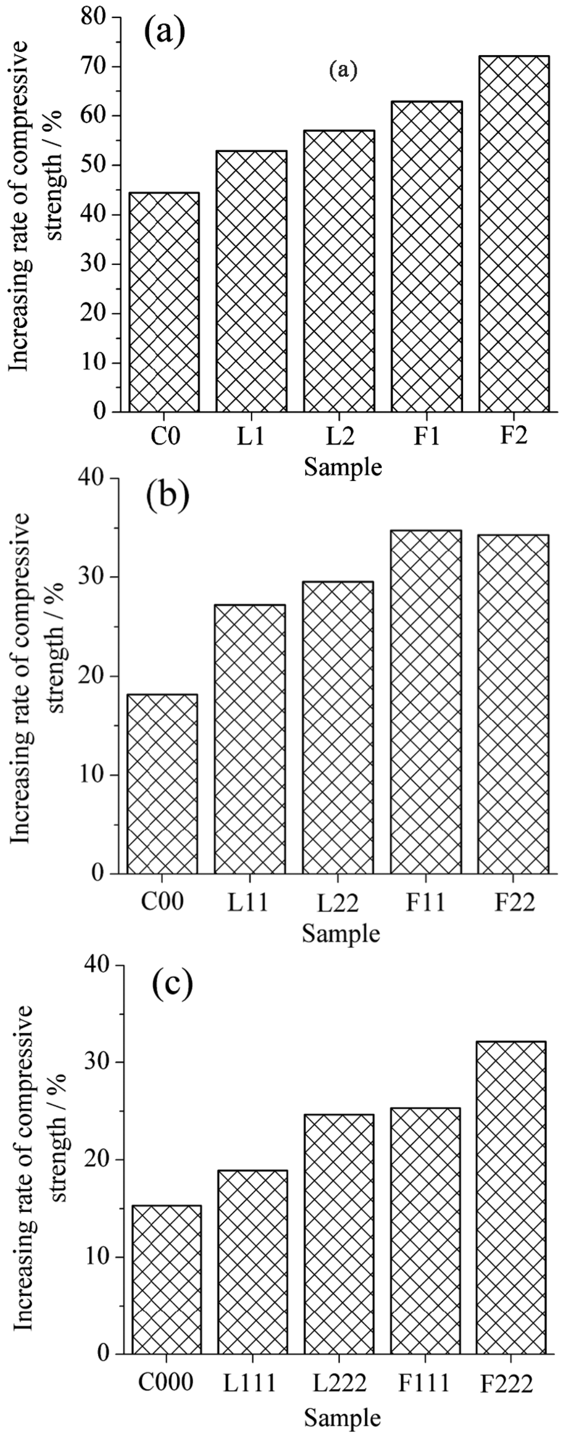

Fig. 2 — The increasing rate of compressive strength of mortar cured from 28 days to 720 days (a) Water to binder ratio of 0.45, (b) water to binder ratio of 0.35 and (c) water to binder ratio of 0.25.

strengths of samples C000, L111, L222, F111 and F222 are 80.4, 82.5, 80.4, 84.2 and 82.2 MPa, respectively, at 28 days. Thus, the growing space of strength is small at late ages. For mortar with high water to binder ratio, the microstructure of mortar is loose and certain amount of water still provides for the further reaction. The hydration products fill the space, which previous fill up with water. Thus the increasing rate of compressive strength is high at late ages. From Fig. 2(b) and Fig. 2(c), note that the gap between the increasing rate of compressive strength of Portland cement mortar and that of mortar containing GGBFS or FGGBFS is small, as well as the gap between the increasing rate of compressive strength of mortar containing GGBFS and that of mortar containing FGGBFS. It is elucidated that at low water to binder ratio, the contribution of slag and its fineness to the late-age strength grow is small. The results are consistent with the compressive strengths of mortars at the age of 720 days (Fig. 1(b) and Fig. 1(c)).

The increasing rates of non-evaporable water contents of pastes cured from 28 days to 720 days at different water to binder ratios are shown in Fig. 3. The samples P0, PL1, PL2, PF1 and PF2 present Portland cement paste, paste with 25% GGBFS, paste with 50% GGBFS, paste with 25% FGGBFS and paste with 50% FGGBFS, respectively. The samples P0, P00, P000 present pastes with water to binder ratios of 0.45, 0.35 and 0.25, respectively. The way of naming other paste specimens is same. The non-evaporable water content of hardened paste represents the quantity of hydration products[7]. The pozzolanic reaction of slag also generates C-S-H gel, which is similar to the hydration products of Portland cement but with low Ca/Si ratio[21]. Thus, the non-evaporable water content can be used to evaluate the hydration degree of composite binder containing different content of slag. It can be seen from Fig. 3a that the increasing rate of non-evaporable water content of Portland cement paste is lower than that of paste containing GGBFS or FGGBFS. The hydration activity of slag is fully stimulated at the age of 720 days. Large amount of hydrates produced by pozzolanic reaction of slag contributes to the non-evaporable water content. What's more, the reaction of slag consumes $Ca(OH)_2$, which further promotes the hydration of cement, and then increases the non-evaporable water content. Therefore, high increasing rate of non-evaporable water content results in a high increasing rate of compressive strength (Fig. 2a). It should be noted that the increasing rate of non-evaporable water content of hardened paste containing FGGBFS is lower than that of hardened paste containing GGBFS, which presents adverse regularity as the increasing rate of compressive

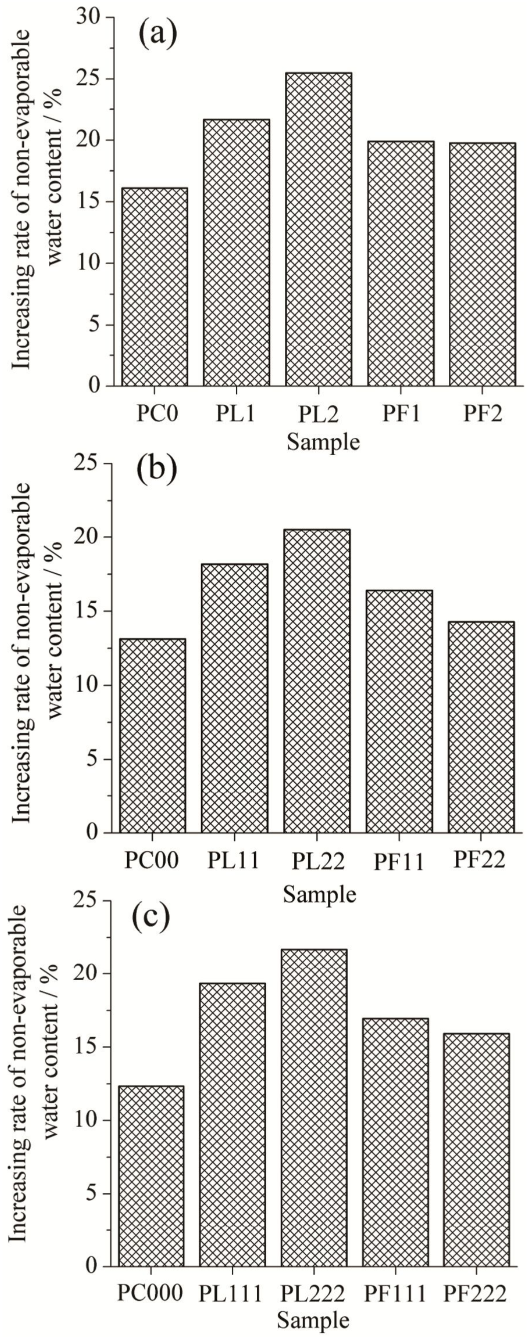

Fig. 3 — The increasing rate of non-evaporable water content of paste cured from 28 days to 720 days (a) Water to binder ratio of 0.45, (b) water to binder ratio of 0.35 and (c) water to binder ratio of 0.25.

strength (Fig. 2a). It is due to the fact that FGGBFS particles are much finer than GGBFS particles, and finer slag particles lead to high hydration degree at the age of 28 days. Kocaba *et al.*[22] used the BSE-EDS method to study the reaction degree of slag in hardened paste with 40% of GGBFS at water to binder ratio of 0.4 and found that 30-55% reacted at 28 days. Lumley *et al.*[23] also found that 30-55% of GGBFS reacted at 28 days in the case of water to binder ratio of 0.4-0.6 and at 20℃ using the selective dissolution method. Thus, the reaction degree of FGGBFS in hardened paste is much high at 28 days. Meanwhile, greater water requirement is needed for FGGBFS due to its larger specific surface area, but the water provided for reaction is limited at 720 days. Therefore, the increasing rate of non-evaporable water content of paste containing FGGBFS at late ages is low.

The change rules shown in Fig. 3b and Fig. 3c are similar to that shown in Fig. 3a. But the increasing rate of non-evaporable water content decreases with decreasing the water to binder ratio. The amount of water in paste with high water to binder ratio is larger than that in paste with low water to binder ratio at late ages. Due to the continuous hydration of cement and the reaction of slag, the increment of hydration products increases the non-evaporable water content. But for paste with low water to binder ratio, the reaction degree of slag is relatively low[24], which results in small amount of hydration products. The increasing rate of non-evaporable water content of sample PF22 is even lower than that of sample PF11 at low water to binder ratio (Fig. 3b and Fig. 3c). It is due to that the reaction of large amount of FGGBFS needs much more water. It is also indicated that the low water to binder ratio has great impact on the pozzolanic reaction of FGGBFS at late ages. From Fig. 2 and Fig. 3, it is clear that the filler effect of FGGBFS plays an important role in increasing the compressive strength at late ages, especially in sample with low water to binder ratio.

3.2 The relationship between compressive strength and non-evaporable water content

Figure 4 gives the relationship between the increasing rate of compressive strength and increasing rate of non-evaporable water content of samples cured from 28 days to 90, 360 and 720 days at different water to binder ratios. There is a linear relationship between the increasing rate of compressive strength and the increasing rate of non-evaporable water content for all samples. The quantity of hydration products presented by the non-evaporable water content is the main factor influencing the strength, but the strength is also affected by the pore structure, the cohesion of the compositions in the mix[25], the interface between the paste and aggregate. The slope of the linear fitting line is almost same for all samples

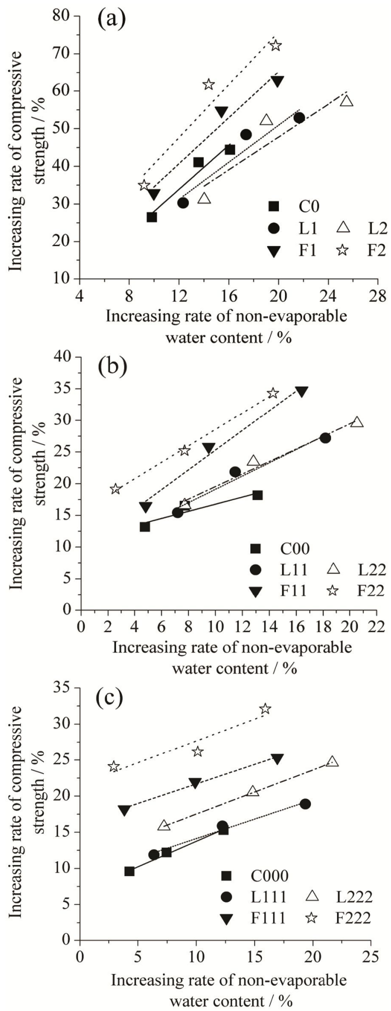

Fig. 4 — The relationship between increasing rate of compressive strength and increasing rate of non-evaporable water content at different water to binder ratios (a) Water to binder ratio of 0.45, (b) water to binder ratio of 0.35 and (c) water to binder ratio of 0.25.

with the same water to binder ratio. Moreover, the slope decreases with decreasing the water to binder ratio due to the lower increasing rates of compressive strength and non-evaporable water content of sample with low water to binder ratio. For FGGBFS, the greater contribution to the late-age compressive strength and the relatively smaller contribution to the non-evaporable water content result in the linear fitting line is high.

The relationship between the increasing rate of compressive strength and the increasing rate of non-evaporable water content for different samples are shown in Fig. 5. Large slope of the linear fitting line is observed for all samples with high water to binder ratio, which is indicated that the compressive strength and non-evaporable water content progressively

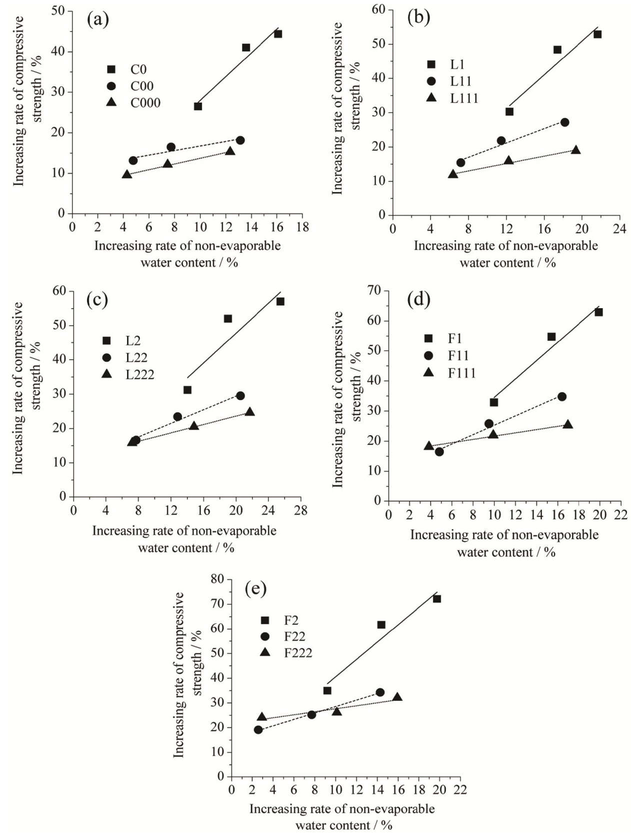

Fig. 5 — The relationship between increasing rate of compressive strength and increasing rate of non-evaporable water content for different samples. (a) Portland cement, (b) 25% GGBFS, (c) 50% GGBFS, (d) 25% FGGBFS and (e) 50% FGGBFS.

increase with increasing the curing ages. But at low water to binder ratio, the compressive strength is relatively high at the age of 28 days due to the dense microstructure of hardened paste and interfacial transition zone. The non-evaporable water content slowly increases due to the lack of water content at late ages. Thus, the slope of linear fitting line of sample with low water to binder ratio is small.

4 Conclusions

(i) The compressive strength of mortar cured for 720 days increases with increasing the content of slag. FGGBFS makes much more contributions to the late-age compressive strength than GGBFS due to its larger surface area. Increasing the fineness of slag has greater effect on the late-age strength improvement at high water to binder ratio than that at low water to binder ratio.

(ii) An increase in the content or fineness of slag increases the increasing rate of compressive strength of mortar. At low water to binder ratio, the contribution of slag and its fineness to the late-age strength grow is relatively small.

(iii) The increasing rate of non-evaporable water content of hardened paste containing slag is higher than that of Portland cement paste. Increasing the fineness of slag decreases the increasing rate of non-evaporable water content. At low water to binder ratio, the increasing rate of non-evaporable water content is relatively low.

(iv) There is a linear relationship between the increasing rate of compressive strength and the increasing rate of non-evaporable water content. The slope of the linear fitting line is almost same for all samples at constant water to binder ratio. The slope decreases with decreasing water to binder ratio.

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