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INFLUENCE OF SILICA FUME ON THE MICROSTRUCTURAL

DEVELOPMENT IN CEMENT MORTARS

by Huang Cheng-yi and R.F. Feldman

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RÉSUMÉ

Des mortiers de ciment contenant 0%, 10% et 30% de silice fine ont été préparés avec des rapports eau/ciment + silice fine de 0,45 et 0,60. La résistance à la compression, les teneurs en $Ca(OH)_2$ et en eau non évaporable et la répartition dimensionnelle des pores ont été soumises à un contrôle continu pendant 180 jours. La silice fine réagit avec la plus grande partie du $Ca(OH)_2$ formé lors de l'hydratation en moins de 28 jours et augmente la résistance à la compression du mortier. De plus, elle modifie la répartition dimensionnelle des pores des mortiers en réagissant avec le $Ca(OH)_2$ formé autour des grains de sable et celui dispersé dans la pâte de ciment.



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INFLUENCE OF SILICA FUME ON THE MICROSTRUCTURAL DEVELOPMENT IN CEMENT MORTARS

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ABSTRACT

Cement mortars containing 0, 10 and 30 percent silica fume were prepared at water/cement + silica fume ratios of 0.45 and 0.60. Compressive strength, $Ca(OH)_2$ and non-evaporable water contents and pore-size distribution were monitored up to 180 days. Silica fume reacts with most of the $Ca(OH)_2$ formed during hydration within 28 days and improves the compressive strength of the mortar. In addition it affects the pore-size distribution of mortars by reacting with $Ca(OH)_2$ formed around the sand grains and also with that dispersed throughout the cement paste.

Introduction

Waste materials such as fly ash and blast furnace slag, when mixed with portland cement and hydrated, produce a pore structure more discontinuous and impermeable than that of hydrated portland cement paste (1). Recent work suggests that "condensed silica fume", a byproduct of the ferro-silicon industry, produces a similar effect (2, 3).

Little work has been done on microstructural changes in mortars containing silica fume. Preferential deposition of $Ca(OH)_2$ in the interfacial zone around aggregates has been observed (4). Also, since the difference between the microstructure of hydrated pastes and blends has been related to the $Ca(OH)_2$ component (1), significant differences in the properties of portland cement mortars with and without silica fume can be anticipated. The objective of this work was to follow changes, such as compressive strength, pore structure, $Ca(OH)_2$ and non-evaporable water contents of mortars containing 0 to 30 percent silica fume.

Experimental Materials

Type I portland cement with a $C_{3}A$ content of 11.82% and silica fume containing 95.2% SiO₂, 1.56% carbon, 0.27% K₂O, 0.10% Na₂O, and having a surface area 21,000 m²/kg were used. Ottawa silica sand passing ASTM-ClO9 was used for making mortar at a sand-binder ratio of 2.25. Binder in the mortar contained cement with 0, 10 or 30 percent silica fume. Mixes were prepared at w/(c+s.f.) (water/(cement + silica fume)) of 0.45 and 0.60. Melment admixture was used at a dosage of 0.3 and 2% only in mortars made with w/(c+s.f.) of 0.45 and containing 10 and 30 percent of silica fume, respectively.

Mixing

Cement was mixed with a portion of the water in a Hobart Model N-50 mixer (ASTM C-305). The remaining water was then added while mixing at a slow speed for 2 min; silica fume was then mixed at a low speed for 2 min and at a medium speed for another 2 min. The sand was then added at a slow speed for 2 min and at a medium speed for 3 min.

Properties determined

Compressive strength (51 mm cubes); $Ca(OH)_2$ content (thermal analysis); non-evaporable water (thermogravimetry-weight-loss between 100-1000°C); and pore size distribution (Hg porosimetry to 408 MPa) were determined. The details of these are described in reference 1.

Results

Compressive strength

Compared to the reference mortar, that with silica fume showed greater strengths at a w/(c+s.f.) of 0.45. The increased strength was observed at curing periods as early as one day. After 14 days curing the strengths were 57, 44 and 40 MPa for 30, 10 and 0 percent silica fume content, respectively. Corresponding strengths after 90 days curing were 77, 54 and 48 MPa. At a w/(c+s.f.) of 0.60, however, no significant increase in strength occurred due to silica fume addition. A comparison of the compressive strengths of mortars and pastes containing 0 to 30 percent silica fume at a w/(c+s.f.) of 0.45 is presented in Figs. 1 and 2. The rate of strength development for cement or mortar containing 0 or 30 percent silica fume is shown in Fig. 1. Each experimental point is the mean value for three specimens; the bars give the maximum and minimum values. With no silica fume, the paste is stronger than mortar throughout, having a strength of 68 MPa, compared to 55 MPa for mortar, at 180 days. The mixes containing 30 percent silica fume show the reverse trend. After seven days curing, the curves representing mortar and paste begin to diverge; the mean strength of mortar after 180 days curing is 82 MPa compared to 74 MPa for paste.



FIG. 1 Compressive strength of cement pastes and mortars containing 0 and 30 percent silica fume (w/(c+s.f.) = 0.45).

The ratio of compressive strengths of mortar to paste containing 0, 10 or 30 percent silica fume is plotted as a function of curing time in Fig. 2. After an initial decrease, this ratio for specimens containing 30 percent silica fume increases to a value of 1.11 after 180 days curing; for specimens containing no silica fume the ratio begins to decline after 7 days curing, to a value of 0.80 after 180 days. Specimens containing 10 percent silica fume do not show as rapid a decline in ratio. The ratio after 180 days curing is 0.90.

Calcium hydroxide and non-evaporable water contents

The change in Ca(OH)₂ content with curing age for mortars with three silica fume contents (0,10,30%) at two w/(c+s.f.) ratios (0.45 and 0.60) is presented in Fig. 3. The nomenclature for the six mixes is shown in this figure. Specimens C^H and C^k (0% silica fume) attain values of 20.3 and 17.3% Ca(OH)₂, respectively, while the 10 percent blends (B^H₁₀ and B^k₁₀) show maximum Ca(OH)₂ contents at around seven days; they decrease to 7.5 and 4.6% after 180 days⁴ curing. Blends B^H₃₀ and B^k₃₀ show decreasing values after one day's curing. B^k₃₀registers zero Ca(OH)₂ after 3 days⁴ curing while B^H₃₀ does so after 14 days.

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FIG. 2 Dependence of ratio of compressive strengths of mortar to paste on age and silica fume content (w/(c+s.f.) = 0.45).



FIG. 3 Ca(OH) $_2$ content versus hydration age for mortars containing silica fume.



FIG. 4 Nonevaporable water versus hydration time for mortars with and without silica fume



FIG. 5

Pore size distribution curves of cement mortar with different silica fume contents (w/(c+s.f.) = 0.45) (a) 0% silica fume (b) 10% silica fume (c) 30% silica fume. 290

The change in non-evaporable water content with time is shown in Fig. 4. The results are plotted as non-evaporable water per ignited weight of cement plus silica fume. C^{H} and C^{A} attained values of approximately 20.2 and 18.9%, respectively, after 180 days' curing. B^{H}_{10} and B^{H}_{30} have values in excess of that of C^{H} at one day and about the same at 3 days, but at 7 days C^{H} has the largest value and at approximately 180 days the values are 20.2, 17.3 and 15.2% for C^{H} , B^{H}_{10} and B^{H}_{30} , respectively. This is probably due to lower combined water associated with calcium silicate hydrate (CSH) produced in the blends than with the total combined water associated with Ca(OH) or the CSH produced in C^{H} . The CSH produced in the blends has a lower CaO/SiO ratio than that produced in normal mortar (3). In addition, the CSH produced in the blends may give off more combined water below 100°C (reference temperature from which it is determined). Similar results were obtained for C^{A} , B^{L}_{10} , B^{A}_{30} ; their values at 3 days were 13.1, 11.8 and 10.9, respectively, and at 180 days were 18.9, 12.4 and 11.8, respectively. The reason for such a decrease in the value for B^{A}_{10} is not known but an amount of unreacted silica fume in B^{A}_{30} is partly responsible for its low value. In addition the values of nonevaporable water content for B^{A}_{10} and B^{A}_{30} do not change much from 3 to 180 days, but large changes in Ca(OH) (for B^{A}_{10}), compressive strength, and pore size distribution and porosity, indicate that a significant reaction is occurring in this period.

Pore size distribution

The pore-size distribution for the w/(c+s.f.) of 0.45 and 0.60 is shown in Figs. 5 and 6, respectively. Results for mortar without silica fume are shown in Fig. 5a; the total porosity down to 100 nm pore diameter for the 180 day specimen is about 5.5% of volume, as compared with less than 2.0% for the equivalent cement paste (2). The volume of mercury intruded into the specimen decreases with curing time over the full range of pressure in a progressive manner, except for the three-day specimen, which has a lower than expected porosity above 300 nm diameter. The curves for all samples at high pressures are concave to the pressure axis.

The pore-size distribution curves for specimens $B_{10}^{\&}$ are presented in Fig. 5b. At values below 60 nm, the total intruded volume generally decreases as the curing age increases. After three days the curves at the high pressure end are convex to the pressure axis. This trend is similar to that observed previously for fly ash and slag blends (1), where it was related to the disruption of discontinuous pores by the high pressure intrusion and to the extent of the reaction of the Ca(OH)₂. A plot of the slope of the curves in Figs. 5 and 6 at the maximum intrusion pressure dV/dlogD (%/nm)10 versus age of curing is presented in Fig. 7. There is a large increase in slope with time for those specimens where Ca(OH)₂ content is low or decreasing. At 100 nm the curves in Fig. 5b for all the curing ages, except one day, for mortars with 10 percent silica fume, merge with the same pore volume of about 7.5%, while from 200 nm to 3000 nm, the pore volumes for 90-and 180-day cured specimens are greater than all but the one-day cured specimen.

The distribution curves for specimens B_{30}^{ℓ} are presented in Fig. 5c. The trend is the same as in Fig. 5b in that in the 100 to 3000 nm range the total pore volume is greater in many cases for the specimens cured for longer times. The total pore volume down to a pore size of 300 nm for the 90- and 28-day cured specimens is greater than that for the one-day specimen; the three-day



FIG. 6 Pore size distribution curves of cement mortar with different silica fume contents (w/(c+s.f.) = 0.60) (a) 0% silica fume (b) 10% silica fume (c) 30% silica fume.

specimen has the lowest porosity. At the pore size of 30 nm, the total intruded volume decreases with age of curing and with ages greater than three days, the curves are sharply convex to the pressure axis. The change in slope with time of these curves at maximum pressure (Fig. 7) shows that for B_{30}^{ℓ} and B_{10}^{ℓ} , large changes occur up to 28 days, while for C^{ℓ} the change is slight. This is the period in which the major portion of Ca(OH) 2 is being formed by hydration reactions or being consumed by the reaction with silica fume. Previous work with fly ash and slag (1) revealed that the convex curves were a result of the formation of a discontinuous structure when Ca(OH) 2 reacted with the pozzolan. It was concluded that during the mercury intrusion experiment, rupture of the structure occurred. In this case with silica fume, the pozzolanic reaction and the formation of the discontinuous structure commences only after about three days' curing.

The results for samples made at the w/(c+s.f.) of 0.60 (Fig. 6) show a similar trend as for the w/(c+s.f.) of 0.45. The total volumes down to 100 nm pore diameter for specimens C^{H} , B^{H}_{10} and B^{H}_{30} in Figs. 6a,b,c are approximately 3, 7 and 8 percent, respectively, for the 90-day cured specimens. Total porosity for the whole pore size range for C^{H} (Fig. 6a) decreases generally with curing time in a progressive manner. Specimen B^{H}_{10} (Fig. 6b) displays some merging in the distribution curves and at about 500 nm, samples cured for 14 and 28 days have total porosities that are lower than samples cured for 90 and 180 days. These effects are even more apparent for specimen B^{H}_{30} , where over some ranges three-day cured specimens have lower porosities than those

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FIG. 7 Dependence of slope of pore size distribution curve (at maximum intrusion pressure) on age and silica fume content.

cured for longer periods; the 180-day cured specimen has as high a porosity as the one-day specimen at 2000 nm. These effects are usually accompanied by abrupt jumps in the distribution curves. Both specimens B_{10}^{H} and B_{30}^{H} have an increasing slope at the maximum intrusion after about three days of curing. This effect, plotted in Fig. 7, is similar to that for B_{10}^{L} or B_{30}^{L} .

Discussion

The strength of a composite material is not only dependent on the relative proportions of components (for example in mortar, the proportion of cement paste and sand) but also on the strength of the bond between the components. Although silica sand is denser and stronger than cement paste, the strength of mortar is lower than that of paste (Figs. 1 and 2) owing partly to a weak sand-cement bond. The addition of silica fume to the mortar appears to improve that bond. A preferential deposition of $Ca(OH)_2$ in the interfacial zone (less than 50 microns) around aggregates in concrete and fibres in paste has been observed (4-6). It has also been observed in this work for the mortars, as shown in Fig. 8. The strength of mortar without silica fume decreases significantly in comparison to the paste after 14 days, when large quantities of $Ca(OH)_2$ have been formed (Figs. 2 and 3). At this period large quantities of $Ca(OH)_2$ in specimens B_{30}^{ℓ} , B_{30}^{ℓ} , B_{10}^{ℓ} and B_{10}^{ℓ} have reacted with silica fume. After 28 days the strength development curves of B_{30}^{ℓ} and paste with 30 percent silica fume diverge, B_{30}^{ℓ} becoming stronger. This is probably due to a better bond being formed between the sand grains by the new CSH formed from the reaction of $Ca(OH)_2$ with silica fume. Although no $Ca(OH)_2$ appears after three days in B_{30}^{ℓ} (Fig. 3), the Ca(OH)₂ that is continuously being formed is completely reacted with silica fume to give better bonding characteristics.

The development of pore structure leads to similar conclusions (Figs. 5 and 6). The pore structure developed between 3 and 14 days shows lower values of pore volume than those cured for longer periods, for size range 100-1000 nm. This may be the result of the lime concentrated around the sand grain forming an initial structure; a subsequent structure resulting from new



FIG. 8

Scanning electron micrograph showing large Ca(OH) $_2$ formation near sand particle in mortar (w/(c+s.f.) = 0.60 after 7 days' curing).

CSH formation by reaction between the silica fume and this lime may dominate the pore structure in the 100-1000 nm range. The abrupt increases in intruded volume suggest that in this region of mercury pressure, rupture of the pore structure may occur. Such a rupture takes place at higher pressures for hydrated fly ash and slag blends, and this probably occurs with the silica fume blends at both intermediate and high pressures (1,7). These abrupt increases in intruded volume at intermediate pressures have not been observed for cement pastes containing silica fumes (2), in contrast to the mortars.

mortars. The progressive manner in which the pore distribution changes with time for specimens C^{ℓ} and C^{H} (Figs. 5a and 6a) supports the idea that the lime that is formed preferentially around the sand grain is converted by reaction with nearby silica fume to CSH with a relatively discontinuous pore structure.

Conclusions

1. Silica fume reacts with most Ca(OH) 2 produced in hydrated cement-silica
fume mortars within 28 days.
2. The addition of silica fume to mortars results in an improved bond between
the hydrated cement matrix and the sand.
3. Ca(OH) ₂ seems to form preferentially around the sand grain in
mortars.
4. Cement mortars have higher pore volumes in the 100-4000 nm pore diameter
range than equivalent cement pastes cured under similar conditions.
5. Silica fume affects the pore distribution of mortars by reacting with the
Ca(OH) 2 formed around the sand grains as well as with the Ca(OH) dispersed
throughout the cement paste.

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