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Properties of Portland Cement-Silica Fume Pastes

I. Porosity and Surface Properties

by R.F. Feldman and Huang Cheng-yi

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RÉSUMÉ

Détermination de caractéristiques telles que la porosité, la répartition des pores par taille, leur superficie totale et le retrait au séchage pour des mélanges ciment Portland-poussière de silice (0-30 %) après durcissement de 1 à 180 jours avec des rapports $e/(c+ps)$ de 0,25 et 0,45. La porosité a été mesurée au moyen de techniques utilisant l'hélium, le mercure et l'eau. On a constaté que dans les mélanges de pâte, une structure de pores discontinues se forme dès sept jours après le début du durcissement par suite de la réaction du $Ca(OH)_2$ avec la poussière de silice. Les pores ne sont pas aussi gros que ceux des mortiers à cause de l'absence d'effets d'interface. Les porosités totales des mélanges ne peuvent être mesurées qu'au moyen de l'eau, tandis que pour les pâtes de ciment ordinaires, il existe d'autres techniques.

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PROPERTIES OF PORTLAND CEMENT-SILICA FUME PASTES
I. POROSITY AND SURFACE PROPERTIES

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ABSTRACT

Properties such as porosity, pore-size distribution, surface area and drying shrinkage are determined for silica fume-portland cement blends (0-30% silica fume) cured from 1 to 180 days at $w/(c+sf)$ of 0.25 and 0.45. Porosity was measured by helium, mercury and water techniques. It is shown that in paste blends a discontinuous pore structure is formed after as little as seven days of curing due to reaction of $Ca(OH)_2$ with silica fume. The pores are not so large as those in mortars owing to the lack of interface effects. Total porosities of the blends can only be measured by a water technique, whereas for plain cement pastes other techniques are applicable.

Introduction

Studies of portland cement-silica fume mortars show that the sand-matrix interface has a definite effect on pore-size distribution, porosity, and mechanical properties (1-3). Further work has demonstrated that the hydration rate of these mortars, in relation to that of pastes, is affected and that freeze-thaw resistance is improved by the addition of silica fume (2,4). The objective is to gain a basic understanding of the structure of the pastes and clarify these observations. Several surface chemical properties of the system, a portland cement-silica fume blend, during the hydration reaction in paste form were measured.

Experimental

Materials

Normal Type I portland cement and silica fume containing 95.2% SiO_2 , 1.56% carbon, 0.27% K_2O , 0.1% Na_2O (surface area 21 000 m^2/kg) were used. Pastes were prepared at $w/(c+sf)$ (water/cement + silica fume) ratios of 0.25 and 0.45, containing, 0, 10 and 30% silica fume at each water-to-binder ratio and melment superplasticer in amounts of 0, 0.3 and 2.0% by weight of binder, respectively.

Properties

Porosity. Three techniques were used to determine porosity:

- (1) Helium comparison pycnometry - The application of this technique to the hydrated portland cement system has been described (5). Solid volumes of d-dried specimens are measured at various times; using apparent volume measured from the thickness and diameter of the disc samples (with a micrometer), porosity and density are calculated. Seven determinations were carried out on each sample and the average is reported.
- (2) Mercury porosimetry - Pore-size distributions were obtained at various times by intruding mercury into the dried specimens (heated at 100°C for 8-14 h under vacuum) at pressures up to 408 MPa (1). The volume of mercury intruded at the maximum pressure was considered to be the total porosity.
- (3) Porosity, using water as fluid - Damp-dry specimens were placed in desiccators conditioned at 11% RH with salt solutions (5). The weight change from the damp-dry condition to 11% RH was recorded as a percentage of the d-dried volume of the specimen.

Density. This was calculated using values determined for solid volume and weight.

Mercury re-intrusion. Mercury was removed by heating specimens already subjected to mercury porosimetry at 105°C in vacuum for up to two months until weight returned to the approximate original value (6). Re-intrusion was performed on three mixes prepared at a $w/(c+sf)$ of 0.45 and cured for 90 days.

Drying shrinkage. This was measured using a modified Tuckerman optical strain gauge (7,8). Specimens of each mix cured for 90 days were sliced from discs approximately $30 \times 10 \times 1.3$ mm and placed consecutively in desiccators (conditioned by means of saturated salt solutions and magnesium perchlorate) at 58, 42, 11 and 0% RH. The time required to reach equilibrium varied with relative humidity; at 58% RH about one month was required, while at 0% RH four months were required.

Specific Surface Area

This was measured with N_2 gas as the adsorbate, using a Quantasorb Model QS-7 sorption system.

Results

Mercury Porosimetry

The pore-size distribution curves for the $w/(c+sf) = 0.25$ mixes with 0, 10 and 30% silica fume are presented in Fig. 1(a-c); the symbols used for the specimen types are defined in Table I. Total porosities decrease with time of hydration, values being, respectively, 16.81, 14.43 and 10.08% with 0, 10 and 30% silica fume at 180 days. The curves are essentially concave to the pore-size axis for 0% silica fume (S^L) and become increasingly convex with increasing silica fume content and longer curing times. The threshold pore diameter (diameter at which the slope of the volume-diameter curve increases abruptly) of the curves decreases with increase in silica fume

TABLE I
Nomenclature for Mixes

% silica fume	$w/(c+sf)^*$	
	0.25	0.45
0	S^L	S^H
10	P_{10}^L	P_{10}^H
30	P_{30}^L	P_{30}^H

*Water-to-cement plus silica fume ratio by weight

FIG. 1
Pore-size distribution curves
of cement pastes with
different silica fume contents
($w/(c+sf) = 0.25$), (a) 0%
silica fume, (b) 10% silica
fume, (c) 30% silica fume

content, as was also observed by Sellevold et al. (9). At pore diameter greater than the threshold diameter the pore volume spread between 1 and 180 days increased with silica fume content. With 30% silica fume content, P_{30}^L , specimens hydrated for 28 to 180 days had higher pore volumes, for pores down to about 20 nm, than specimens hydrated for seven days.

The pore-size distribution curves for $w/(c+sf) = 0.45$ mixes are presented in Fig. 2(a-c) for 0, 10 and 30% silica fume. Total porosities of 28.30, 29.80 and 25.3% were observed for 0, 10 and 30% silica fume content. The curves change from concave (to the pore-size axis) for 0% (S^H) to increasingly convex with increased curing time for 10 and 30% silica fume content (P_{10}^H , P_{30}^H). For specimens containing silica fume at maximum intrusion pressure the curves are similar to those for mortars in that the slopes reach maximum values after about 14 days; those without silica fume are relatively constant. Threshold diameters decrease with silica fume content, and spread of pore volume between 1 and 180 days also increases with silica fume content, as for the $w/(c+sf)$ ratio of 0.25. In the range of pore diameters up to 100 nm and above the pore volume for specimen P_{30}^H is largest after 180 days of hydration, over 4% compared with values for short periods of hydration (e.g., 2.5% after 7 days).

Comparison of results for mortars hydrated at a $w/(c+sf) = 0.45$ with and without silica fume reveals great differences (1). Without silica fume the mortar hydrated at 180 days displayed a more gradual threshold, commencing around 300 nm pore diameter, with a pore volume of about 3%; the paste has a value of only about 1% at this pore diameter. Addition of silica fume increases the threshold diameter for mortars, but in pastes there is a decrease. The spread of pore volume in the higher pore range was also much greater for mortar than for paste.

Re-intrusion

Specimens of pastes, S^H , P_{10}^H and P_{30}^H , hydrated for 90 days and used for mercury intrusion experiments were prepared for second intrusion by heating at 105°C for 6-10 weeks in vacuum (2,6). The final weight of the specimens indicated that most of the mercury had been removed. Results are presented in Fig. 3(a-c) for S^H , P_{10}^H and P_{30}^H . Results for specimen S^H show little difference between first and second intrusion, although the threshold pore diameter is slightly larger for the second intrusion. The difference increases with silica fume content, the pore volume becoming greater in the pore diameter range 3×10^1 to 3×10^4 nm for the second intrusion. P_{10}^H becomes concave to the pore diameter axis. In general, a higher proportion of the pore volume is intruded at higher pore sizes.

Comparison of these results with those of equivalent mortars shows that most of the changes between first and second intrusion occur for the mortar blend at around $10^3 - 10^4$ nm; for paste most changes occur gradually over the range 3×10^1 to 3×10^4 nm. Increase in volume in the higher size range is also greater for mortar specimens.

Helium Pycnometry

Porosity measurements by helium pycnometry were taken of all the specimens after they were dried as for mercury intrusion measurements. Porosity values by the two techniques did not differ significantly for specimens fabricated at a $w/(c+sf)$ of 0.25. At a $w/(c+sf)$ of 0.45, however, significant differences did occur (Fig. 4). For specimen S^H the porosity values were very similar, remaining close to the line of equality, but values for P_{10}^H deviated after 7 days and for P_{30}^H after 14 days, the mercury intrusion technique giving higher porosity values.

FIG. 2
Pore-size distribution curves of cement pastes with different silica fume contents ($w/(c+sf) = 0.45$), (a) 0% silica fume, (b) 10% silica fume, (c) 30% silica fume

Porosity, Water as Fluid

The ratio of the weight of water lost between damp-dry and 11% RH (percentage of volume at d-dried condition) and the porosity determined by helium pycnometry for all preparations (vol/vol percent) are presented as a function of curing time in Fig. 5. At day one most of the points fall between ratios of 0.86 and 0.93, and at three days, between 0.93 and 1.02; after three days, ratios for P_{10}^L and P_{30}^L increase rapidly, but S^L and S^H are scattered near 1.10. From 14 to 180 days, ratios for P_{10}^L , P_{30}^L and P_{30}^H are in excess of 1.50, that for P_{10}^H near 1.45 and those for S^L and S^H near 1.10. Following three days of curing it is clear that under these experimental conditions most blends no longer absorb helium in all of their pores.

Results generally indicate that both helium pycnometry and mercury porosimetry give relatively accurate porosity results for plain paste at w/c above 0.40 (5,10). Those using water as fluid are, however, faced with two problems: (1) selection of the right fluid density as hydration proceeds and the size of the pores diminishes; (2) the fact that decomposition of hydrates occurs during drying of specimens from 100 to 11% RH. The results presented in Fig. 5 for plain pastes are used as a calibration of those for plain pastes measured by water. It is assumed that the same correlation would apply to blended pastes. Thus, all results obtained with water as fluid for one-day curing were divided by 0.90, those for three and seven days by 1.00, and those for 14 days and over by 1.10 to obtain the porosity of the blends.

A plot of adjusted porosities determined by water for all the specimens cured from 1 to 180 days versus porosity determined by mercury porosimetry are presented in Fig. 6. Points for specimens S^L , S^H and P_{10}^H are scattered fairly closely round the line of equality, but points for P_{10}^L , P_{30}^L and P_{30}^H deviate widely, displaying higher values by the water technique, especially after longer curing periods. It is clear that mercury intrusion does not measure the correct porosity under these conditions. Previous workers have also indicated that evaporable water contents are significantly higher than mercury intrusion volumes (9).

Density Values

Densities calculated from the adjusted water porosities for all the specimens as a function of curing time are presented in Fig. 7. Values for the blends do not change significantly beyond 28 days. P_{30}^H and P_{10}^H have values of approximately 2.05 and 2.14 g/mL, respectively, after 180 days curing; S^L and S^H have values of 2.40 and 2.22 g/mL, respectively. Values for the plain pastes by helium pycnometry are 2.39 and 2.24 g/mL, respectively, and those by mercury porosimetry are 2.35 and 2.23 g/mL, respectively. There is thus good correspondence. Values for the blends by helium pycnometry and Hg porosimetry are much lower: 1.78 and 2.00 g/mL for P_{10}^H and P_{30}^H , respectively, for He; and, for Hg, 1.83 g/mL for P_{30}^H and 2.10 g/mL for P_{10}^H .

Drying Shrinkage

The results for shrinkage as a function of decreasing relative humidity are presented in Fig. 8 for all the specimens. For mixes with a w/(c+sf) of 0.25 no significant difference is observed for P_{10}^L and S^L , but P_{30}^L shows slightly larger values. Shrinkage for specimens S^L , P_{10}^H and P_{30}^H is larger the greater the silica fume content, especially in the 100 → 42% RH range; shrinkage in the 11 → 0% RH range does not show this same order of increase. A large component of shrinkage in the 100 → 42% RH range is usually irreversible, and it appears that 30% addition of silica fume at a w/(c+sf) of 0.45 increases this form of shrinkage significantly.

FIG. 3 Pore-size distribution curves of cement paste with different silica fume contents, first and second intrusion ($w/(c+sf) = 0.45$, 90 days curing), (a) 0% silica fume, (b) 10% silica fume, (c) 30% silica fume

FIG. 4 Comparison of porosities determined by helium pycnometry and mercury porosimetry on specimens made at $w/(c+sf)$ of 0.45

FIG. 5 Ratio of pore volumes - unadjusted value by water technique divided by value by helium pycnometry versus time

FIG. 6 Porosity determined by mercury porosimetry versus adjusted porosity values determined by water technique

FIG. 7 Density of blends versus time of curing using adjusted porosity values by water technique

FIG. 8 Dependence of shrinkage of cement blend pastes cured for 90 days on relative humidity

Specific Surface Area

The values of surface area by N_2 adsorption, using the method of drying described above, show very low areas and very little change with curing time. At a $w/(c+sf)$ of 0.45 all values vary from about 22 to 20 m^2/g during curing from 7 to 180 days. At a $w/(c+sf)$ of 0.25 specimen S^L shows a constant value of 10 m^2/g from 7 to 180 days of curing, while for P_{10}^L and P_{30}^L the values vary from about 9 to 7 m^2/g .

Discussion

Changes in pore distribution curves as a result of silica fume additions occur in paste blends to a lesser extent than in mortar blends (1). For mortars, such features as variations in the large pore-size range were generally attributed to formation of discontinuous pores, due partially to the removal of lime accumulated at the sand-paste interface and partially to reaction of lime with silica fume within the matrix. Other features such as increases in pore volume between 7 and 180 days of curing in certain pore-size ranges also occur in both mortar and paste blends, but again to a lesser extent in pastes. Calcium hydroxide is formed in paste in a variety of crystal sizes, but it is probable that crystals, or accumulations of crystals, are found to a larger extent around inclusions such as sand grains. In the absence of inclusions, as in paste blends, it is reasonable to assume that the occurrence of a large volume of trapped pores of this pore-size range is unlikely. Consequently, the threshold values of pore size for mercury intrusion in paste blends and mortar blends are quite different. In paste blends the threshold value decreases with silica fume addition, while in the mortar blends it increases and becomes less abrupt.

The difference between intrusion and re-intrusion curves displayed by mortar blends on the one hand and paste blends on the other may also be explained by the very specific role the interface of the inclusion has to play in accumulating calcium hydroxide. The size-range of the relatively isolated pores responsible for the intrusion/re-intrusion curve hysteresis is controlled by the calcium hydroxide at the sand-grain interface; when sand grains are not present, both volume and average size of isolated pores decrease.

Previous work (10) has shown that helium pycnometry and mercury porosimetry give similar porosities for pastes above w/c of 0.40, and that densities obtained from these results are consistent with those of known CSH material. More recent work (11) has also indicated that in fly-ash and slag blends mercury intrusion gives higher porosities than helium pycnometry or methanol saturation owing to the presence of isolated pores into which mercury enters as a result of partial breaking of the structure. This occurs, as well, for silica fume blends at curing times as early as seven days.

The technique of measuring porosity, however, by recording the weight of water loss between the damp-dry condition and 11% RH and of calibrating this technique with plain pastes and helium pycnometry, has shown that mercury does not reach all the pores of specimens P_{10}^L , P_{30}^L , and P_{30}^H , although it appears to reach most of the pores of S^L , S_{10}^H , and P_{10}^H . Calibration of this technique (drying to 11% RH) incorporates the density values of water in different-sized pores and gets round the problem of including the water from decomposing hydrates as pore water during drying below 11% RH. The density obtained in this case is, however, that of the dried material. Values thus obtained for both plain pastes and blends are reasonable.

The increase in drying shrinkage by addition of 30% silica fume may be partially related to the fact that no calcium hydroxide is present to restrain

the material during drying, and that there is a greater amount of CSH per volume of material in P_{30}^H than in P_{10}^H or S^H . There is only 10% difference in shrinkage between 0 and 11% RH for P_{10}^H and P_{30}^H , however, compared to over 30% difference between 100 and 42% RH. The difference appears to be due to the irreversible shrinkage effect, which may be caused by a difference in ionic charges on the C-S-H product (8); this may be caused by reduction of $[Ca^{++}]$ in the pore solution brought on by complete depletion of $Ca(OH)_2$ in the material.

Conclusions

1. Relatively discontinuous pores are formed in pastes of silica fume blends after only seven days of curing. They are related to the consumption of calcium hydroxide crystals by reaction with silica fume.
2. The discontinuous pores are not so numerous or so large as those in mortars of the same w/(c+sf) and silica fume content owing to lack of inclusions such as sand that provide interfaces where larger formations of calcium hydroxide form.
3. Total porosities are not measured for the paste blends by helium or mercury intrusion, but may be measured by weight loss of water to 11% RH.
4. Drying shrinkage is increased significantly in the presence of large amounts of silica fume.
5. Surface areas measured by N_2 adsorption show little change between 7 and 180 days of curing, and silica fume has little influence.

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