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RÉSUMÉ

Des mortiers ayant un rapport sable/liant (ciment et condensat de silice) de 2,25 ont été réalisés en remplaçant 0%, 10% et 30% de ciment par du condensat de silice dans des mortiers à rapports eau/ciment + condensat de silice de 0,45 et 0,60. La résistance à la compression, la répartition dimensionnelle des pores, la porosité, la teneur en hydroxyde de calcium et le degré d'hydratation ont été mesurés en fonction du temps (jusqu'à 180 jours). La durabilité des mortiers a été évaluée a) en mesurant la résistance des mortiers non aérés et durcis pendant 28 jours, à des cycles de gel et de dégel et b) en exposant des échantillons à une solution concentrée de sels renfermant des chlorures.

Un changement significatif s'est produit dans la structure des pores des mélanges après 7 jours environ : elle était relativement irrégulière. Une amélioration de la résistance à l'action du gel a été obtenue dans le cas des échantillons durcis pendant 28 jours et préparés avec un rapport eau/ciment + condensat de silice de 0,60, le ciment étant remplacé à 10%, puis à 30%, par du condensat de silice. La résistance à la solution saline s'est considérablement améliorée après 7 jours dans le cas des échantillons préparés avec un rapport eau/ciment + condensat de silice de 0,45 et contenant 30% de condensat de silice. Après 28 jours, des échantillons contenant 10% de condensat de silice, préparés avec un rapport eau/ciment + condensat de silice de 0,45 résistaient également à l'attaque des solutions salines.

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Summary

A finely divided silica by-product of the ferro-silicon industry, condensed silica fume, has been found to react relatively rapidly with hydrating cement to produce a dense impermeable body.

Mortars with a sand-binder (cement and silica fume) ratio of 2.25 were made by replacing 0, 10 and 30% cement with silica fume at w/c + sf of 0.45 and 0.60. Compressive strength, pore size distribution, porosity, calcium hydroxide content, and degree of hydration were measured as a function of time (up to 180 days). Durability of mortars was assessed by (a) measuring the resistance of non air-entrained mortars, cured for 28 days, to freezing and thawing cycles, and (b) exposing specimens to a concentrated solution of salts containing chlorides.

Significant change occurred in the pore structure of the blends after about 7 days; it was relatively discontinuous. Improvement in resistance to frost action resulted for specimens cured for 28 days and prepared at a w/c + sf of 0.60, with 10 and 30% silica fume replacement. Resistance to the salt solution improved greatly after 7 days for specimens made at w/c + sf of 0.45 and containing 30% silica fume. After 28 days specimens containing 10% silica fume prepared at w/c + sf of 0.45 were also resistant to attack by salt solutions.

1. Introduction

Blast furnace slag and fly-ashes used with portland cement are known to produce impermeable bodies with discontinuous pore structure (1,2). Relatively long periods of curing are necessary, however, before the desirable microstructure is well formed. If condensed silica fume (sf), a by-product of the ferro-silicon industry, is added to hydrating cement it reacts rapidly to produce a dense impermeable body (3-5), but the mechanism leading to the formation of the modified microstructure and information with regard to its durability is still incomplete (6-8). Mortars covering a

large range of silica fume contents (0-30%) and a practical w/c + sf range of 0.45-0.60 have now been assessed for durability to frost action and salt attack. Attempts have also been made to correlate the results with various microstructural, mechanical, and chemical properties of the specimens.

2. Experimental

Materials. Type I portland cement with a C_3A content of 11.82% and silica fume containing 95.2% SiO_2, 1.56% carbon, 0.27% K_2O, 0.10% Na_2O (surface area 21 000 m^2/kg) were used. Ottawa silica sand passing ASTM-C109 was used for mortar with sand-binder ratio of 2.25. Cement in the mortar contained either 10 or 30% silica fume. Mixes were prepared at w/c + sf of 0.45 and 0.60.

Properties determined. Compressive strength (51 mm-cubes); $Ca(OH)_2$ content (thermal analysis) (9); non-evaporable water (thermogravimetry); pore size distribution (Hg porosimetry to 408 MPa); resistance to salt solution (27.5% $CaCl_2$, 3.9 $MgCl_2$, 1.8% NaCl, 0.1% $NaHCO_3$ - pH of 6.3) (10); freeze-thaw resistance (freeze in air - thaw in water, -18°C to +5°C, two cycles in 24 h, ASTM-C666B).

3. Results

Compressive strength. Results and nomenclature for specimens are presented in Fig. 1 and Table I. Large increases in strength were obtained with silica fume additions at w/c + sf of 0.45 for both early and late curing periods. At w/c + sf of 0.60, however, the strength at 180 days was the same for 30% replacement and the reference; the 10% replacement resulted in lower strength.

Calcium hydroxide and non-evaporable water content. The quantity of calcium hydroxide present after 180 days of curing is tabulated in Table I. The reference cement contains 17.32 and 20.35% ignited weight for w/c of 0.45 and 0.60, respectively. The specimens with silica fume had greatly reduced calcium hydroxide content owing to pozzolanic reaction. The non-evaporable water content was larger in specimens without silica fume: 20.2, 17.3 and 15.2 at 0, 10 and 30% silica fume, respectively, after 180 days of curing at w/c + sf of 0.60. This probably reflects the difference in the amount of hydrate water for the CSH product and $Ca(OH)_2$.

Pore size distribution. Pore size distributions in mortars of cement are quite different from those of neat cement pastes. A comparison of the

results for mortars (Fig. 2) $C^{\ell}(90)$ and $C^{H}(90)$ with those for pastes (11) reveals that total pore volume for pores greater than 90 nm (in specimens $C^{\ell}(90)$ and $C^{H}(90)$) are about 6% mL/mL; the porosity of neat cement paste is only about 2% porosity. Pore volumes for mortars with 30% silica fume ($B^{\ell}_{30}(90)$ and $B^{H}_{30}(90)$, Fig. 2) are about 8 and 10%, respectively. Permeability data did not indicate that mortars would have such large increases in large pores nor that the addition of pozzolana would result in further increase (1,11). Experiments (2) to investigate the application of Hg porosimetric techniques to blended cements (involving removal of Hg from intruded specimens by distillation followed by re-intrusion) revealed that the microstructure of hydrated blends, in contrast with that of cement paste, consists of relatively large, discontinuous pores, and that narrow walls separating the pores can be broken during Hg intrusion. Hence, the actual pore size distribution value will be quite different from that measured on first intrusion.

The results of repeated intrusion experiments for mortar without silica fume are shown in Fig. 2. Both specimens, $C^{\ell}(90R)$ and 30% silica fume $B^{\ell}_{30}(90R)$, show differences from first intrusion, but the effect is large for the blend $B^{\ell}_{30}(90R)$. The first intrusion curve for these mortar blends shows abrupt increases in intruded volume at about 4000 nm, and repeated intrusion ($B^{\ell}_{30}(90R)$) indicates that a large number of pores with new entrances at about 10 000 nm have been created. Previous work (12) related the difference in the microstructure of hydrates, pastes, and blends to the $Ca(OH)_2$ content. In mortars, a preferential deposition of $Ca(OH)_2$ in the interfacial zone around aggregates has been observed (13). This phenomenon, with subsequent reaction between $Ca(OH)_2$ and silica fume, may explain the results of the Hg intrusion measurements.

Freeze-thaw resistance. The freeze-thaw resistance results for mortars cured for 28 days are presented in Fig. 3. None of these specimens was air-entrained; samples $C^{\ell}(28)$ and $B^{\ell}_{10}(28)$ showed no sign of deterioration after 600 cycles. Specimen $B^{\ell}_{30}(28)$ failed, however, after 190 cycles, although it had the highest compressive strength at 28 days (68 MPa, see Fig. 1). Previous work had indicated that concrete at a w/c of 0.4 and silica fume content of 20-30% exhibits excessive expansion (6). The samples cured at w/c + sf of 0.60 displayed different behaviour; specimen $C^{H}(28)$ broke after 128 cycles, but specimen $B^{H}_{10}(28)$ showed little sign of deterioration after 600 cycles; sample $B^{H}_{30}(28)$, while showing 0.02% expansion at 250 cycles, was

still intact after 580 cycles. These results indicate a significant improvement in durability with addition of silica fume, confirming previous indications (8,14).

Resistance to salt solution exposure. The salt solution used in this work simulated that of groundwater from a potash mine. Specimens cured for 7 and 28 days were exposed to the solution and tested periodically in flexure. Of those cured for 7 days, $B^{\ell}_{30}(7)$ showed no ill effects after 325 days, while $C^{\ell}(7)$ and $B^{\ell}_{10}(7)$ showed significant signs of deterioration. All specimens cured at w/c + sf of 0.60 deteriorated rapidly, the larger the silica fume content the greater the deterioration; at 7 days at a w/c + sf of 0.60 not enough reaction between silica fume and $Ca(OH)_2$ has occurred to produce a significant reduction in permeability.

Results for specimens cured at 28 days are presented in Fig. 4. At both w/c + sf ratios, resistance improved with amount of silica fume. Specimens without silica fume (C^{H}, C^{ℓ}) were both relatively non-resistant. No apparent deterioration has occurred for specimens B^{ℓ}_{10}, $B^{\ell}_{30}(28)$; but although there was improvement in durability (with silica fume addition) specimens B^{H}_{10}, $B^{H}_{30}(28)$ showed a significant decrease in stiffness with exposure. Mercury intrusion experiments on specimens exposed to salt solutions are shown in Fig. 5. Specimen $B^{\ell}_{30}(28)$-c showed no decrease in stiffness and no apparent change in pore size distribution, except for a slight reduction in porosity. Specimen $C^{H}(28)$-c, which contained no silica fume, failed rapidly and displayed a large increase in pore volume, mainly in the pore size range 2×10^4 and 1×10^3 nm. This was probably the result of crack spaces created by leaching of $Ca(OH)_2$.

4. Discussion

The addition of condensed silica fume to mortars can greatly increase their strength and resistance to salt solutions, provided they are not prepared at excessively high w/c + sf ratios (i.e. >0.45 in this work). The rapid deterioration of mortar specimen $B^{\ell}_{30}(28)$ with freeze-thaw cycling (although it possessed the highest strength and salt solution resistance) is probably related to its low permeability and large amount of silica fume content (30%). The silica fume is in excess of that needed for complete reaction of $Ca(OH_2$ (5); at a w/c + sf ratio of 0.45 the results indicate a large amount of evaporable water. The greater permeability of specimen $B^{H}_{30}(28)$ (w/c + sf of 0.60) ensures greater frost resistance. Specimen

$B^{H}_{10}(28)$, with less silica fume (10%), displayed very little sign of deterioration. The large pores with narrow necks, simulating air-entrainment, may be responsible for the better frost resistance of some of the preparations.

5. Conclusions

1. Silica fumes react rapidly with $Ca(OH)_2$ produced during cement hydration.
2. In the cement-silica fume system a microstructure is formed that has large pores separated by narrow necks, resulting in the formation of an impermeable body.
3. Silica fume additions can result in improved strength at moderate w/c + sf.
4. Resistance to salt solution corrosion is improved by addition of silica fume, even after only 7 days of curing.
5. Frost resistance of mortars, even those cured at w/c + sf of 0.60 (without air-entrainment), can be improved with silica fume addition.

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Table I. Nomenclature and Properties of Mortar Specimens

Silica fume (%)	w/c + sf (0.45)	S	$Ca(OH)_2$ (%)	Melment (%)	w/c + sf (0.60)	S	$Ca(OH)_2$ (%)	Melment (%)
0	$C^{\ell}(180)$	54	17.32	0	$C^{H}(180)$	45	20.35	0
10	$B^{\ell}_{10}(180)$	56	4.55	0.3	$B^{H}_{10}(180)$	39	7.45	0
30	$B^{\ell}_{30}(180)$	82	0	2.0	$B^{H}_{30}(180)$	45	0	0

(180) - days of curing; S - compressive strength (MPa); C - cement mortar; B - blended mortar

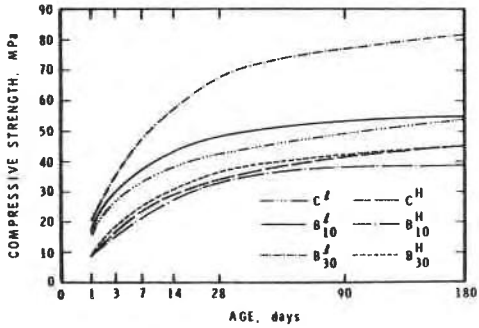

Figure 1. Compressive strength vs hydration time of mortars with and without silica fume

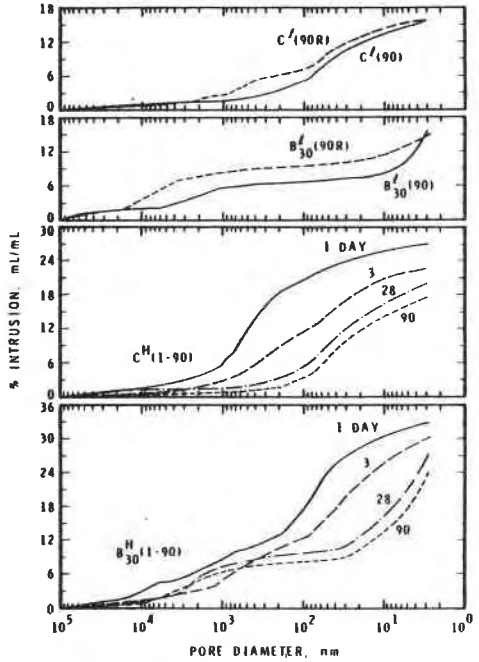

Figure 2. Pore size distribution of mortars with and without silica fume

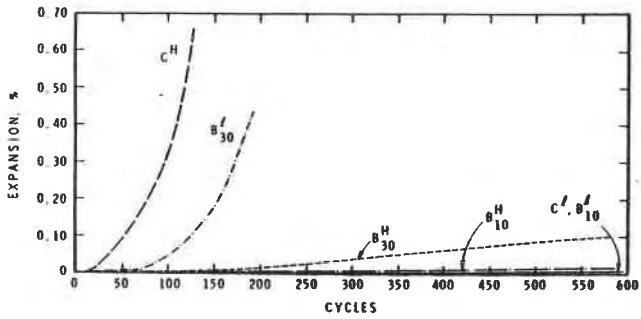

Figure 3. Linear expansion vs cycles of freeze-thaw for mortars

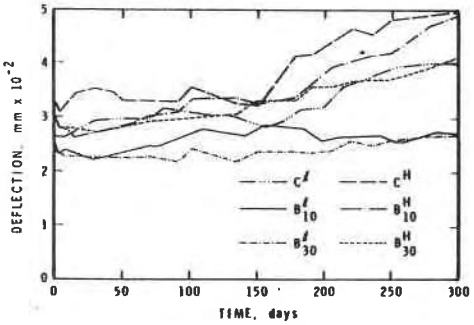

Figure 4. Flexural deflection of mortar specimens vs time of exposure to salt solution (28 days cured)

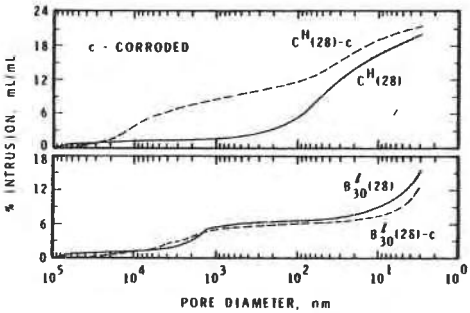

Figure 5. Pore size distribution of mortars before and after exposure to salt solution