

## HYDRATION REACTIONS IN PORTLAND CEMENT-SILICA FUME BLENDS

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### ABSTRACT

Early hydration reactions of portland cement-silica fume blends were followed by conduction calorimetry,  $\text{Ca}(\text{OH})_2$  estimation, and later reactions by  $\text{Ca}(\text{OH})_2$  and non-evaporable water contents. Silica fume accelerated both  $\text{C}_3\text{S}$  and  $\text{C}_3\text{A}$  hydration in the first few hours. At longer periods pastes of blends hydrated to a greater extent than mortars, possibly because sand acted as a  $\text{Ca}(\text{OH})_2$  sink in the mortars.

### Introduction

When siliceous by-products such as condensed silica fumes, fly ash and blast furnace slag are mixed with portland cement and hydrated, they produce a pore structure more discontinuous and impermeable than that of hydrated cement paste (1-4).

Microstructural studies show that in mortars containing silica fume part of the change in pore distribution results from silica fume reacting with the  $\text{Ca}(\text{OH})_2$  formed around the sand grains. Silica fume in the mortar also improves the bond between the hydrated cement matrix and the sand, and enhances freeze-thaw resistance (5).

These investigations revealed the importance of the sand-matrix interface affecting the properties of concretes and mortars. An understanding of the role of the sand-cement interface requires a study of the hydration of silica-fume-cement blend. The object of this paper is to follow the hydration characteristics of cement containing 0-30% silica fume and formed at a water/solid ratio of 0.25 or 0.45, and compare some of these results with mortars.

### Experimental

### Materials

Normal Type I portland cement and silica fume from eastern Canada were used. Their chemical composition and some physical properties are given in

Table I. Ottawa silica sand ground to pass 100 mesh sieve and a fly ash were also used in some of the experiments as replacements for cement. 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, with Melment in amounts of 0, 0.3 and 2.0% by weight of binder. Heat evolution for periods less than three days was measured on blends at a  $w/(c+sf)$  of 0.60, using 0, 10, 20 and 30% silica fume.

### Mixing

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

### Properties determined

#### $\text{Ca(OH)}_2$ content

A Differential Scanning Calorimeter (DSC cell), a module of the Du Pont 1090 Thermal Analysis System, was used to obtain thermograms from which the relative areas of the peaks resulting from  $\text{Ca(OH)}_2$  decomposition were determined. In each experiment a 20-mg sample was heated in  $\text{N}_2$  atmosphere at a rate of  $20^\circ\text{C}/\text{min}$ . Measurements were made at a  $w/(c+sf)$  of 0.25 and 0.45 for hydration times of 1, 3, 7, 14, 28, 90 and 180 days, and at a  $w/(c+sf)$  of 0.6 for hydration times of 1.5, 4, 6, 8, 10, 12, 16, 24 and 72 h.

TABLE I

Chemical Composition and some Physical Properties of Cement,  
Silica Fume and Fly Ash

	Portland Cement %	Silica Fume %	Fly Ash %
$\text{SiO}_2$	21.16	95.17	55.6
$\text{Al}_2\text{O}_3$	5.87	0.21	22.7
$\text{Fe}_2\text{O}_3$	2.21	0.13	4.3
$\text{CaO}$	63.07	0.23	13.3
$\text{MgO}$	1.56	0.15	2.4
I.L.	1.36	2.30	0.6
$\text{SO}_3$	3.29	0.12	0.16
$\text{Na}_2\text{O}$	0.09	0.10	
$\text{K}_2\text{O}$	1.08	0.27	
C		1.56	
 $\text{C}_3\text{S}$	43.96		
$\text{C}_2\text{S}$	27.47		
$\text{C}_3\text{A}$	11.82		
$\text{C}_4\text{AF}$	6.72		
 Specific surface area, Blaine ( $\text{m}^2/\text{kg}$ )	332		
 Specific surface area, $\text{N}_2$ adsorption ( $\text{m}^2/\text{g}$ )		21	
 Pozzolanic activity index with portland cement		110%	
with lime		5.8 MPa	

Non-evaporable water content

This was measured at hydration times of 1, 3, 7, 14, 28, 90 and 180 days by determining the loss in weight between 100 and 1000°C using a Thermogravimetric Module of the Du Pont 1090 system.

Rate of heat evolution

This was determined by a conduction calorimeter (supplied by Technical Physics Department, TNO and TH, Delft, Holland) of sensitivity 16.5 mV/W. Measurements were made at a w/(c+sf) of 0.60 using 0, 10, 20 and 30% silica fume content pastes, a 30% ground silica sand paste, and a 30% fly ash paste. Experiments were continued for 72 h.

Results $\text{Ca}(\text{OH})_2$  content

The amount of  $\text{Ca}(\text{OH})_2$  liberated during the early stages of the cement paste hydration (0-72 h) was determined at a w/s of 0.60 for binders containing 0 and 30% silica fume or 30% ground silica sand. These results are presented in Fig. 1 as the per cent of  $\text{Ca}(\text{OH})_2$  per unit weight of ignited sample. The three curves are very similar up to 8 h, but after this period the  $\text{Ca}(\text{OH})_2$  content is greatest for the cement paste alone, followed by the sand blend and the silica fume blend. This indicates that both ground sand and silica fume accelerate the production of  $\text{Ca}(\text{OH})_2$  from the cement in the first eight hours. Although these blends are only 70% cement, the  $\text{Ca}(\text{OH})_2$  contents are as high as for pure cement. The heat evolution data confirm these results. Beyond eight hours,  $\text{Ca}(\text{OH})_2$  in both sand and silica fume blends decreases greatly relative to the cement. However, based on cement content, the sand blend and the cement have the same  $\text{Ca}(\text{OH})_2$  content, while with the silica fume it is lower.

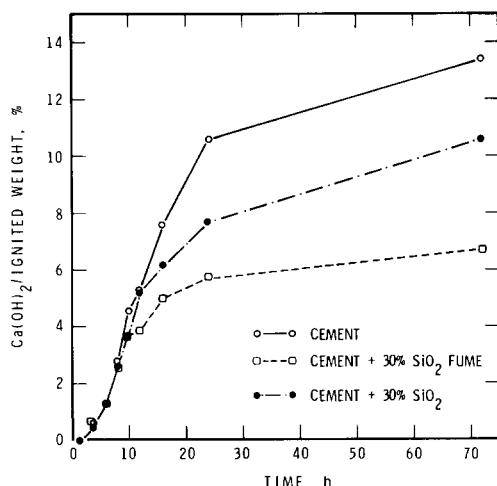


FIG. 1  
Change in  $\text{Ca}(\text{OH})_2$  content at early times for cement and cement blends.

The  $\text{Ca}(\text{OH})_2$  content for the 0, 10 and 30% silica fume blends mixed at a w/(c+sf) of 0.25 and 0.45 and hydrated up to 180 days are presented in Fig. 2, along with the nomenclature for these mixes. At a w/(c+sf) of 0.45, with 0% silica fume ( $\text{Si}^{\text{H}}$ ), there is little increase in  $\text{Ca}(\text{OH})_2$  beyond 14 days; it attains a value of about 16.2% after 180 days hydration. The equivalent value

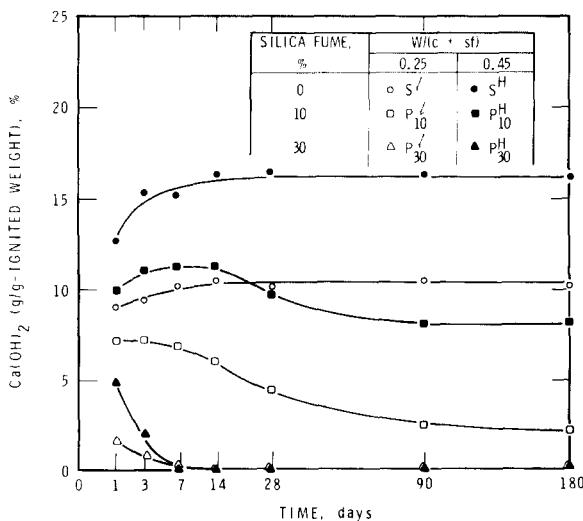


FIG. 2  
Change in  $\text{Ca}(\text{OH})_2$  content to 180 days for various silica fume-cement mixtures

for mortar, presented previously (5), is 17.3%. This value was obtained by determining the  $\text{Ca}(\text{OH})_2$  content thermogravimetrically, using a 1000 mg specimen for greater accuracy; the calculation was based on binder content, omitting the large quantity of sand in the mortar. The paste prepared at a  $w/(c+sf)$  of 0.25 ( $S^H$ ) shows similar results in that little change occurred after 14 days, yielding a value of 10.4% after 180 days.

The paste  $P^H_{10}$  attains a  $\text{Ca}(\text{OH})_2$  content of 11.2% after about 10 days and then decreases to 9.7 at 28 days and 8.1 and 8.3% at 90 and 180 days. Thus considerable change still occurs between 28 and 90 days. The equivalent mortar prepared at the same  $w/(c+sf)$  ratio of 0.45 and 10% silica fume attains a maximum of 9.5%  $\text{Ca}(\text{OH})_2$  at about 7 days, declining gradually to 4.6% after 180 days, with most of the decrease taking place between 14 and 28 days. Paste  $P^L_{10}$  declines from a maximum of 7.2% at one day to 2.2% at 180 days.

Pastes  $P^H_{30}$  and  $P^L_{30}$  both have  $\text{Ca}(\text{OH})_2$  levels of zero at 14 days; for  $P^H_{30}$  at three and seven days, however, the levels are 2.0 and 0.4% as compared to 1.5 and 0% at one and three days for the equivalent mortar.

#### Non-evaporable water content

The change per unit weight of ignited sample over time in non-evaporable water content is shown in Fig. 3. The specimens at a  $w/(c+sf)$  of 0.45, made at a higher water content, naturally show the largest gain;  $S^H$  attains 19.2% after 28 days and 20.7% after 180 days. Specimen  $P^H_{10}$  attains 15.1% after 28 days but only 15.5 after 180 days, while  $P^H_{30}$  has the non-evaporable water content of 14.4% after 28 days and 15.3% after 180 days. The non-evaporable water content level attained by  $P^H_{10}$  is low compared to that of  $S^H$ , even if it is calculated on the basis of ignited weight of cement, assuming that the silica fume either does not react or does not contribute to the non-evaporable water; on this basis, however, the value for  $P^H_{30}$  is close to that of  $S^H$ , but for both  $P^H_{10}$  and  $P^H_{30}$  (especially  $P^H_{10}$ ) they are almost constant after 28 days. Results for comparable mortars, determined similarly to those of  $\text{Ca}(\text{OH})_2$  and based on binder content (5), show similar trends; the 30% silica fume content specimen changed from 11.5% at 14 days to 11.9% at 180 days; over the same period, measurements for the 10% silica fume mortar

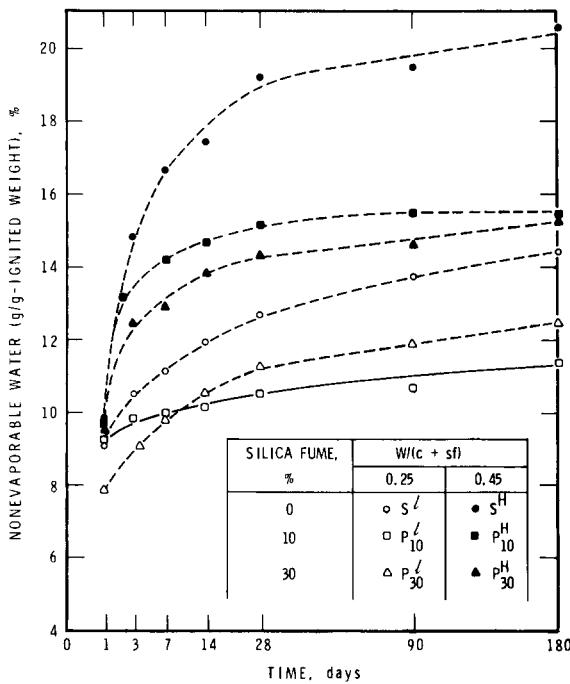


FIG. 3  
Change in non-evaporable water content with time for various silica fume-cement mixtures.

declined from 13.5% at 28 days to 11.9% at 180 days. Similar results are obtained for mortars made at  $w/(c+sf)$  of 0.60. Pastes made at a  $w/(c+sf)$  of 0.6 also have shown much less change in non-evaporable water content between 10 and 90 days with silica fume contents from 8 to 20% (6). Others have found similar effects (7). With various fibres included in pastes, the degree of hydration is 25% lower than the reference paste (8).

The specimens at  $w/(c+sf)$  of 0.25 show similar trends to those observed for the higher ratio, although changes between 28 and 180 days are greater. At one day, non-evaporable water content for  $S^L$  and  $P^L_{10}$  are similar, while it is much lower for  $P^L_{30}$ , presumably due to the larger dose of Melment and low water content (9).  $S^H$ ,  $P^H_{10}$  and  $P^H_{30}$  are, however, all very similar after one day.

#### Rate of heat evolution

The effect of silica fume content on the rate of heat evolution of cement at a  $w/(c+sf)$  of 0.60 is shown in Fig. 4. There are three peaks evident, especially with 10, 20 and 30% silica fume mixes. The results are plotted on the basis of the cement content for comparison; there is considerable increase in the rate of heat evolution and the occurrence of the peaks is accelerated, the greater the silica fume content. However, there is little effect on the dormant period which occurs at about 1.75 h, an observation reported previously (10).

The total heat evolved at various times from the start of the hydration reaction is plotted in Figs. 5 and 6; the dependence of heat evolution on silica fume content is clearly shown. If these results are plotted against

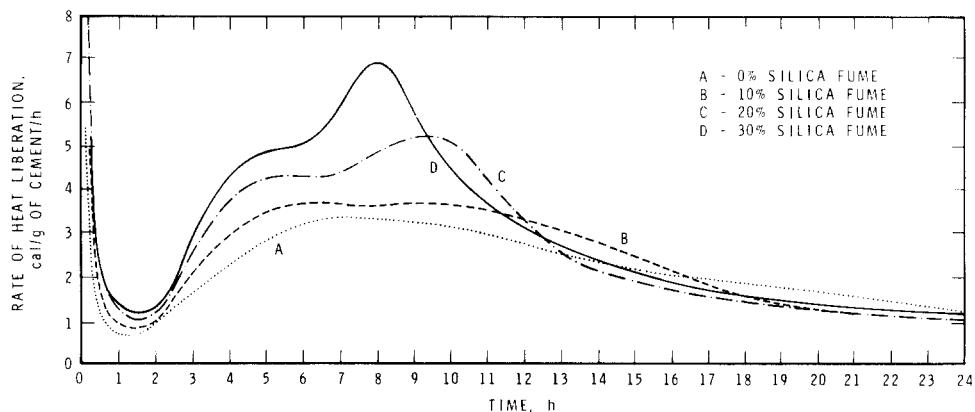


FIG. 4

Change in rate of heat evolution of cement-silica fume pastes with time.

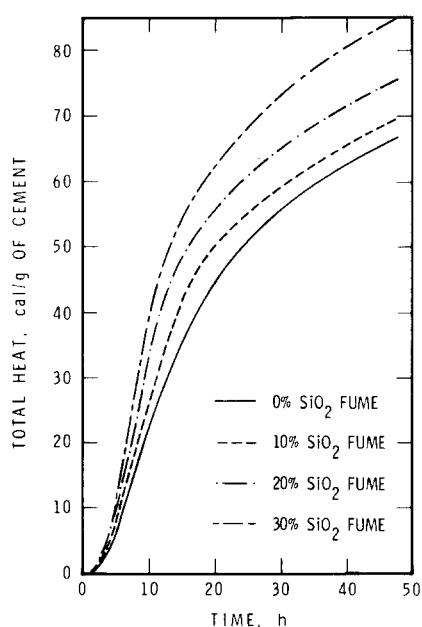


FIG. 5

Total heat evolved by cement-silica fume blends during hydration with time.

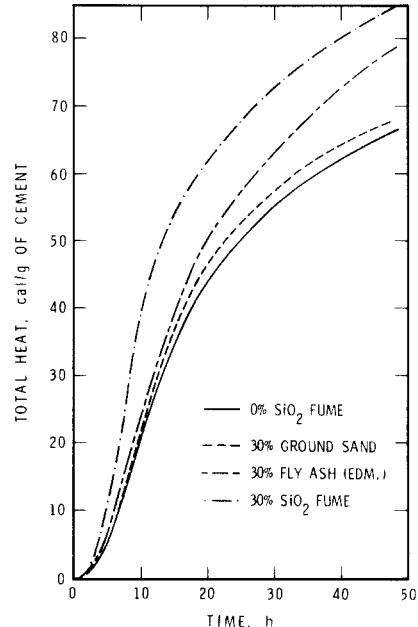


FIG. 6

Total heat evolved by various cement blends during hydration with time.

the total weight of the blend, an increase in total heat evolved over the cement without silica fume addition would still be recorded up to 20 h of hydration for all three additions. This result is contrary to earlier ones

(10) which were obtained at a  $w/(c+sf)$  of 0.5 and 20°C, in contrast to the present work which was performed at a  $w/(c+sf)$  of 0.60 and 25°C. Further heat evolution measurements presented in Fig. 6 compare various additions replacing 30% cement. The ground silica sand has only a very slight effect, but the fly ash has a considerably greater effect. Whether this is due to acceleration of the cement hydration or early pozzolanic reaction is not known. However, during the first 12 h, the silica fume, even at 10% addition, causes the largest acceleration of the cement hydration reaction.

#### Discussion

1. The effect of an amorphous silica (Aerosil, with a surface area of 200  $\text{m}^2/\text{g}$ ) on the hydration of  $\text{C}_3\text{S}$  and cement has been reported previously (10). It was found that the  $\text{Ca}^{++}$  and  $\text{OH}^-$  ion concentration is greatly reduced within the first 10 minutes. The hydration of  $\text{C}_3\text{S}$  is accelerated because a retarding hydrate layer that forms on the surface of the  $\text{C}_3\text{S}$  grain at early times is converted more rapidly in the lower  $\text{Ca}^{++}$  and  $\text{OH}^-$  solution to a second, less retarding layer. In addition, it was suggested that in cement the retarding coating of ettringite on  $\text{C}_3\text{A}$  was not formed as efficiently, also because of the lower  $\text{Ca}^{++}$  concentration in the early periods. It appears that large amounts of silica fume, although not possessing as large a surface area as Aerosil, impose similar effects on  $\text{C}_3\text{S}$  in the cement hydration. Before eight hours hydration, larger quantities of  $\text{Ca}(\text{OH})_2$  relative to the cement alone were present, probably due to the nucleating influence of the silica fume surface. After eight hours, the  $\text{Ca}(\text{OH})_2$  content is lower than would be produced by normal cement hydration, and it is probable that at this point  $\text{Ca}^{++}$  ions have reacted with the silica fume. Heat evolution results would indicate this, since ground silica sand, which also appears to accelerate the cement hydration ( $\text{Ca}(\text{OH})_2$  content results) gives a relatively low heat evolution curve. Silica fume, from its effect on peak 3 of Fig. 4, also affects the hydration rate of  $\text{C}_3\text{A}$ .
2. The rates of hydration in mortars and pastes containing silica fumes are somewhat different. Hydration proceeds faster in pastes with silica fume, regarding both  $\text{Ca}(\text{OH})_2$  and non-evaporable water contents; the hydration reactions in mortars containing silica fume terminate earlier with regard to the above two parameters. In an earlier paper (5), it was shown that the sand-paste interface in mortars affected pore structure and strength. The interface around various types of inclusions is normally lime-rich, and in the presence of silica fume, it is influenced during the reaction. Reduction of  $\text{Ca}(\text{OH})_2$  content during the reaction also greatly reduces the permeability of these bodies, even with regard to the mobility of ions such as  $\text{Cl}^-$  and  $\text{OH}^-$  (1). Large quantities of sand in mortars appear to act as a sink for crystallized  $\text{Ca}(\text{OH})_2$ . If, at early periods of hydration (within 14 days), sand particles limit the amount of  $\text{Ca}(\text{OH})_2$  that is deposited in the paste matrix, the paste itself may become less permeable and access to cement grains by  $\text{H}_2\text{O}$  may be reduced; this may result in limited hydration relative to mixes without sand.

#### Conclusions

1. Silica fume accelerates hydration reactions in portland cement by providing nucleation sites for  $\text{Ca}(\text{OH})_2$  within minutes after reaction commences, and also by reacting with  $\text{Ca}^{++}$  ions. Reduced  $\text{Ca}^{++}$  ion affects the nature of hydration products.
2. The degree of hydration of pastes and mortars of silica fume-cement blends differs, possibly due to the presence of sand in the mortar, which acts as

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a sink for well crystallized  $\text{Ca}(\text{OH})_2$  and lowers the permeability of the paste phase of the mortar.

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