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INTERACTION OF SILICA FUME WITH CALCIUM HYDROXIDE SOLUTIONS AND HYDRATED CEMENT PASTES

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ABSTRACT

The interactions of silica fume (SF) with calcium hydroxide and with Portland cement have been studied using microscopy-based techniques and x-ray diffraction. Digestion of SF in calcium hydroxide solution for up to 120 days showed it to persist in the form of agglomerates coated with amorphous calcium silicate hydrates. Similar SF microstructures were found in cement pastes hydrated for up to 180 days, including those produced by very high shear mixing. These results show that SF persists in cements long after the principal hydration reactions have ceased. They also demonstrate the difficulty in obtaining satisfactory dispersion of SF in cement, due to the high agglomerate strength of the SF. It is the behavior of these agglomerates, rather than that of the individual SF particles, which controls the pozzolanic activity. *© 1998 Elsevier Science Ltd*

Introduction

Silica fume (SF) is a by-product of the silicon and ferro-silicon industry. It is formed by condensation from the vapor phase of SiO_2. SF occurs as near-perfect spheres with diameters ranging from 20 to 500 nm. Typically, 85% to 95% of the SF is in the form of amorphous silica (1,2), with various impurities present, such as silicon metal and carbon. The addition of SF to cement paste has been shown to give rise to high early strengths, although the mechanisms by which SF operates are unclear. Three principal types of interactions have been suggested:

1. SF particles cause pore blockage in the hydrating cement, which densifies the hydrating gel structure (1,3).
2. Pozzolanic reactions occur between the silica-rich SF particles and the portlandite, which is a by-product of Portland cement hydration (4).
3. SF particles act as nucleation sites for cement hydration, accelerating the process (5).

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This paper describes the microscopic studies we have carried out to investigate the interactions of SF with $Ca(OH)_2$ (portlandite—a hydration product of cement) and with ordinary Portland cement (OPC).

Materials and Techniques

The SF used in this investigation was a commercially available undensified material supplied by Blue Circle Cement Ltd. The amount of amorphous silica in the SF was $\approx$92 wt%, determined by digestion in boiling 0.8 M NaOH (6). The principal undigested impurity residues were silicon metal and amorphous carbon. SF was left in contact with a saturated solution (0.15 wt%) of calcium hydroxide at 20°C for up to 120 days, stored under a nitrogen atmosphere to minimize carbonation. The method and amount of materials used were the same as described by Grutzeck et al. (7). After 7 and 120 days of reaction with the solution, the SF residue was examined both in the as-reacted condition and after repeated washing and centrifuging. Powder specimens for transmission electron microscopy (TEM) investigation were prepared by producing a suspension of the solid in ethanol by very light grinding in a mortar and pestle and passing a holey carbon film on a copper TEM grid through the suspension. A 2.5-nm-thick platinum coating was applied to specimens prior to secondary electron imaging. Where energy-dispersive x-ray analysis (EDXA) was performed, carbon coating was used instead. Examination was carried out optically using a stereo light microscope, and electron-optically using a JEOL 6400 scanning electron microscope (SEM) at 15 kV and a JEOL 2000 FXI (STEM) at 200 kV.

Results

SF Characterization

Viewed optically at 30× magnification, the as-received SF appeared to have a wide range of particle sizes, ranging from below the limit of resolution of the microscope (<10 μm) up to $\approx$0.5 mm (Fig. 1). The higher resolution obtainable in the SEM showed that these "particles" were agglomerates of thousands of individual SF spheres (Fig. 2). These agglomerates tended to break up under intense electron beam irradiation in the SEM, suggesting that electrostatic bonding is responsible for much of the agglomerate strength. The near-perfect sphericity of the SF particles was evident in secondary electron (SE) images (Fig. 3). The SF spheres were quite smooth, with no obvious surface morphology and little apparent fusion between touching spheres.

Digestion in Saturated Calcium Hydroxide Solution (20°C)

Calcium hydroxide is a hydration product of OPC, and it was of interest to examine the degree of interaction with SF. Specimens of SF reacted with $Ca(OH)_2$ for 7 days and subsequently examined in both unwashed and water washed conditions (not shown) were indistinguishable from the as-received SF (Fig. 3), with no indication that the smallest SF particles had reacted preferentially. There was no microscopic evidence for any calcium-silicate-hydrate (CSH) gel formation. EDXA of individual SF particles digested for 7 days

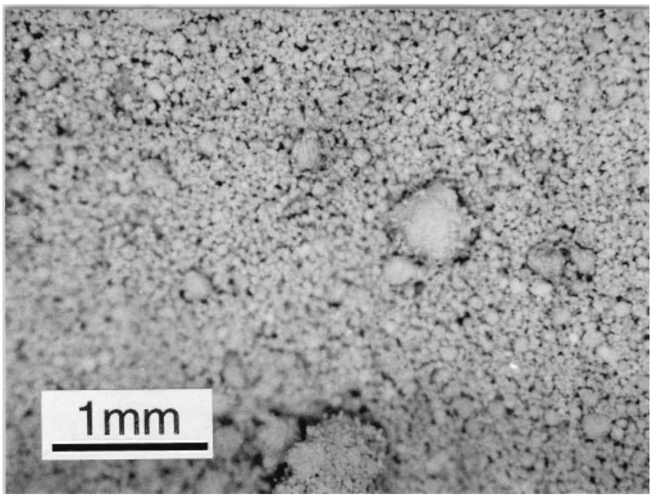

FIG. 1.
Optical micrograph of as-received SF showing agglomeration into spherical particles up to ≈0.5 mm in diameter.

showed x-ray peaks due to silicon only (the analysis system used was unable to detect oxygen), with only a trace of calcium present, suggesting little reaction between the SF and the calcium hydroxide. These observations were supported by x-ray diffraction (XRD) results (Cu Kα radiation) (Fig. 4), which still showed a strong broad peak (centered on 2ø ≈22°) characteristic of amorphous SF, after this reaction period.

STEM examination of SF agglomerates (unwashed) remaining after 120 days digestion

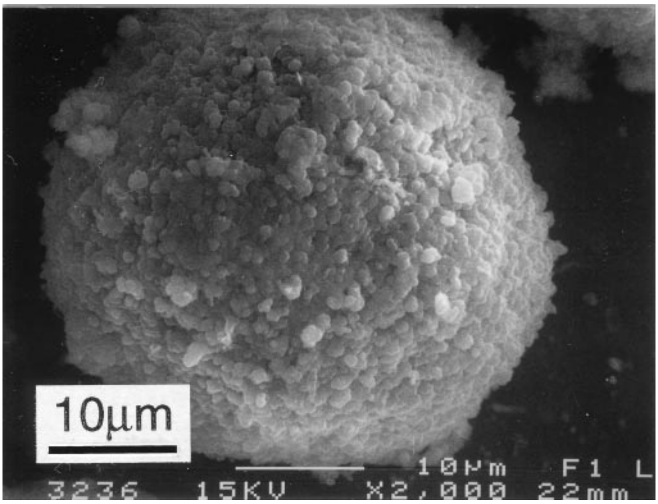

FIG. 2.
SEM image of an SF agglomerate. The large particle is composed of many densely packed individual SF particles.

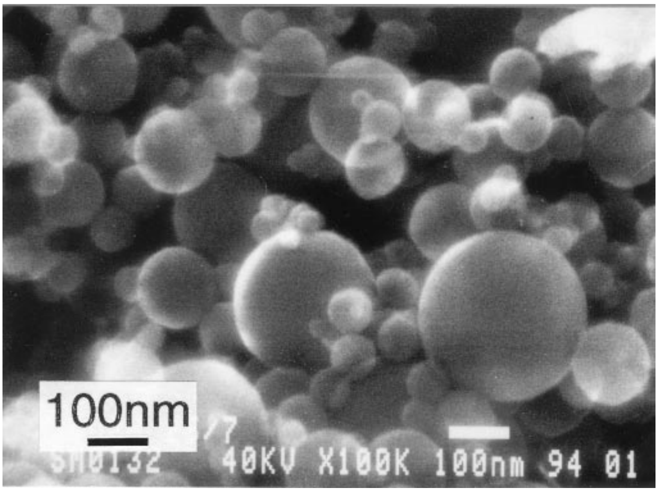

FIG. 3.
STEM SE image of as-received SF spheres, which appear smooth and featureless.

showed SF particles covered in small platelets (Fig. 5), that analyzed as being rich in calcium, suggesting them to be portlandite ($Ca(OH)_2$). EDXA of individual SF spheres showed them to be silicon-rich, with a just a few percent calcium present. This suggested that the SF particles were still intact and were coated with a thin veneer of portlandite and/or CSH.

SF digested in $Ca(OH)_2$ for 120 days and water washed prior to examination clumped

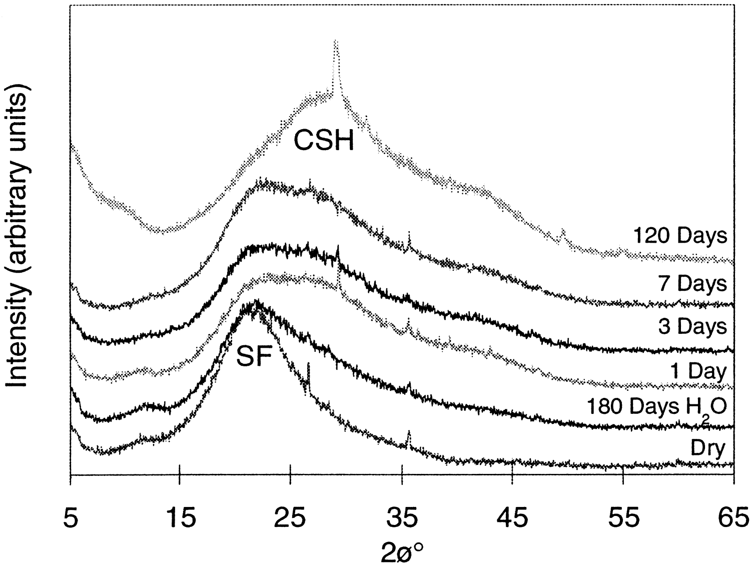

FIG. 4.
XRD of SF after exposure to water and saturated $Ca(OH)_2$ solution. In $Ca(OH)_2$ the SF pattern changes little up to 7 days, but after 120 days extensive CSH formation has occurred.

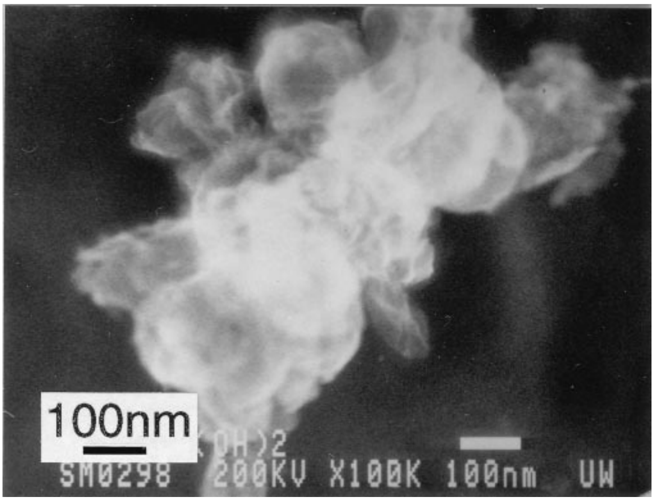

FIG. 5.
SE image of SF agglomerate [unwashed, 120 days, Ca(OH)$_2$ solution] showing SF spheres rich in Si. Ca-rich platelets [probably mainly Ca(OH)$_2$] are present.

together into large agglomerations (Fig. 6), with little evidence of individual SF spheres. Analysis of the outer regions of these agglomerates showed them to be silicon-rich, but with significant amounts of calcium present. The thickness of the agglomerates was too great to permit quantitative EDXA, but it was evident that a CSH reaction product had formed. The differences between the unwashed (Fig. 5) and the washed SF (Fig. 6) suggested that lowering of the pH as a result of dilution during washing caused soluble silicates to precipitate out onto the SF agglomerates. Where one such agglomerate had fractured open, intact SF particles were still present in the interior (Fig. 7A). EDXA showed the particles to be very silicon-rich. These particles showed considerable surface etching as a result of attack by Ca(OH)$_2$ (Fig. 7B).

XRD results (Fig. 4) showed that there was little difference in the XRD patterns of as-received (dry) SF, and SF fully hydrated by storing it in water for 180 days, indicating no tendency to gel formation at neutral pH. SF exposed to saturated calcium hydroxide solution for 1, 3, and 7 days showed no significant decrease in the main broad amorphous SF peak (centered at 2ø ≈22°), although a second weak broad peak (centered at 2ø ≈ 28°) indicated some CSH gel formation. SF stored in calcium hydroxide solution for 120 days was found to have undergone considerable reaction, as the broad CSH peak in the XRD pattern increased at the expense of the SF peak. A shoulder on the CSH peak at 2ø ≈ 22° indicated that SF was still present. The small sharp peak at 2ø = 29.4° is probably due to limited CaCO$_3$ formation in the long-term test.

Behaviour of SF in Cement Pastes

Fracture surfaces, ground paste, and acid-insoluble residues of a low C$_3$A Portland cement paste (20 wt% SF, water to binder ratio of 0.5, no superplasticiser) were examined after 180

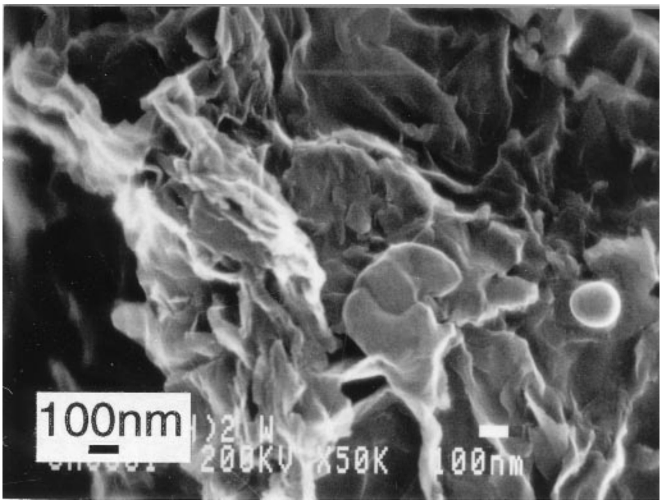

FIG. 6.
SE image of large agglomeration of SF [washed, 120 days, $Ca(OH)_2$ solution]. No SF particles are evident in the large mass of CSH that has formed.

days of hydration. The fracture surface showed few general features that could be attributed to SF. However, in some regions, clusters of particles with the shape and size of SF spheres were found (Fig. 8). It was not possible to carry out meaningful EDXA on these features in this imaging mode. If these particles were SF, then there was strong evidence to suggest that it was heterogeneously distributed throughout the paste. Examination of ground paste after 180 days of hydration showed spherical features of the appropriate size for SF particles (Fig. 9). EDXA of such a feature (arrowed) showed a high silicon to calcium ratio (3Si :1Ca), whereas the angular particles nearby were much poorer in silicon (0.5Si : 1Ca).

It was impossible to eliminate the effects of adherent and adjacent particles of CSH from the imaging and analysis of the SF particles in these specimens. To remove the cementitious material, acid digestion was carried out on hydrated pastes using dilute nitric acid, with repeated centrifuging and washing. Acid digestion of SF alone showed no observable reaction. The acid-insoluble residue extracted from the paste consisted almost entirely of SF (Fig. 10A), which was agglomerated in a manner similar to that seen in the hydrated pastes examined in bulk (Fig. 8). The SF morphology was still fairly spherical, although there was some surface roughening and individual SF particles appeared fused together, possibly by remnants of the glue-like CSH phase. EDXA of several different particles detected only silicon.

From high-resolution imaging (Fig. 10B), it was apparent that the surviving SF had undergone partial reaction, and that the particle surfaces were quite heavily etched, in a manner very similar to that observed for SF in calcium hydroxide solution (Fig. 7B). It was clear that there was considerable, albeit slow, interaction between SF and the cement paste. Some SF persisted long after the principal cement hydration reactions had stopped (180 days after mixing), showing evidence of surface attack. Similar results were obtained for pastes containing 5% and 20% SF. Although it was not possible to recover quantitatively all the SF from acid-digested pastes, it was apparent that some of the SF originally added to the paste

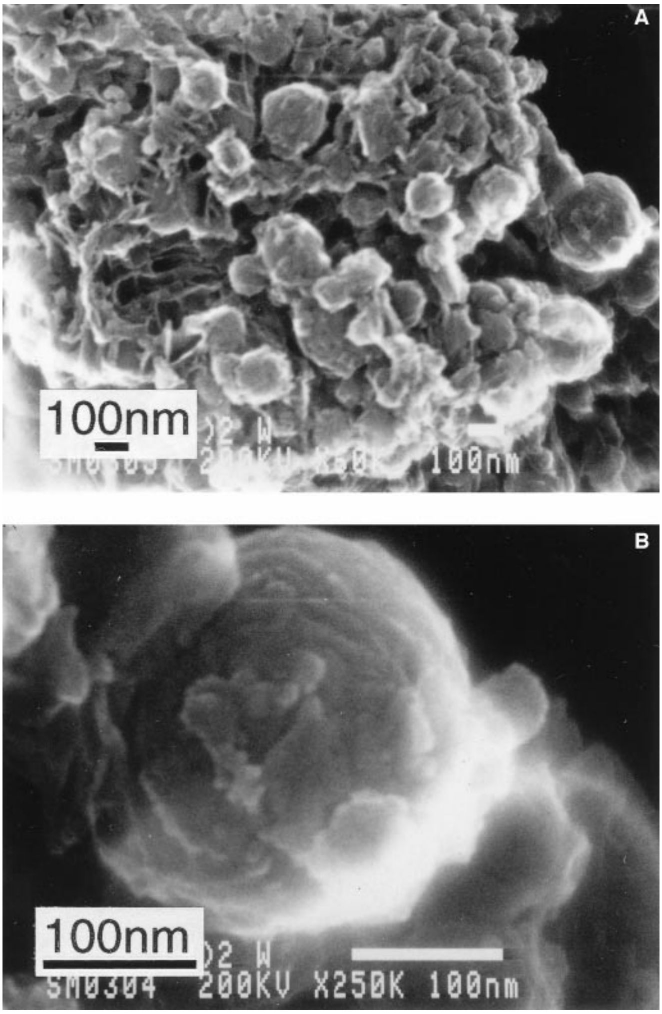

FIG. 7.
(*A*) As in Figure 6, but across a fractured agglomerate. CSH is present on the outer surface (*left*) and intact SF is present within the core of the agglomerate (*right*). (*B*) Detail of (*A*) showing an Si-rich SF particle with a spherical morphology and a highly etched surface.

remained at 180 days. The fact that SF also persisted in the paste containing only 5% SF suggested that the failure of SF to react completely was not a consequence of the paste becoming saturated with silicon-containing species.

Agglomeration of SF in Paste

Examination of small fragments of paste suggested that SF remained agglomerated within the cement paste (Fig. 8). To study this effect more fully, a series of SF-containing pastes were

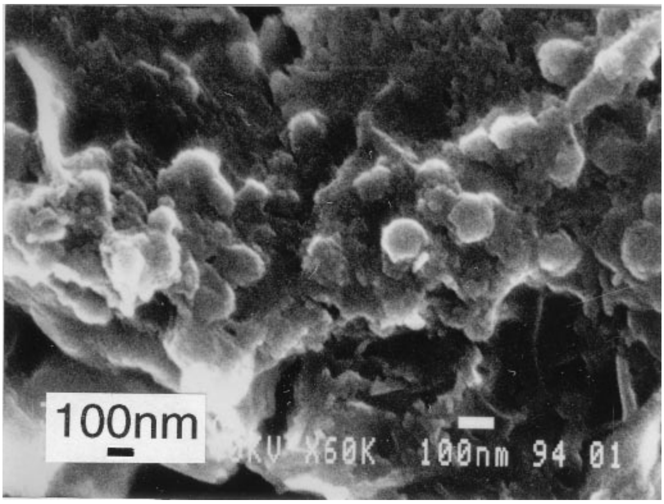

FIG. 8.
SE image of cement paste fracture surface (20% SF, 180 days hydration) showing a cluster of SF-like features, suggesting poor SF dispersion.

made with various additions using two types of mixing technique: normal hand mixing, and higher shear mixing in a mortar and pestle. Examination of polished sections of hydrated pastes (Portland cement, 20% SF, water to binder ratio of 0.5, with and without superplasticiser, hydrated for 7 days) showed that, when compared with equivalent reference material made by the usual hand mixing technique (Fig. 11A), higher shear mixing resulted in a reduction of the maximum agglomerate size by a factor of ≈2 (Fig. 11B). However, despite

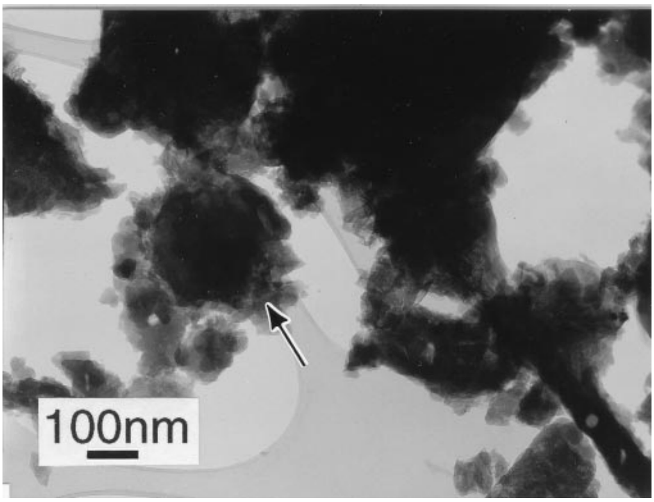

FIG. 9.
TEM bright-field image of ground-up cement paste (20% SF, 180 days of hydration). Among the angular CSH particles, rounded SF particles rich in Si (*arrow*) are present.

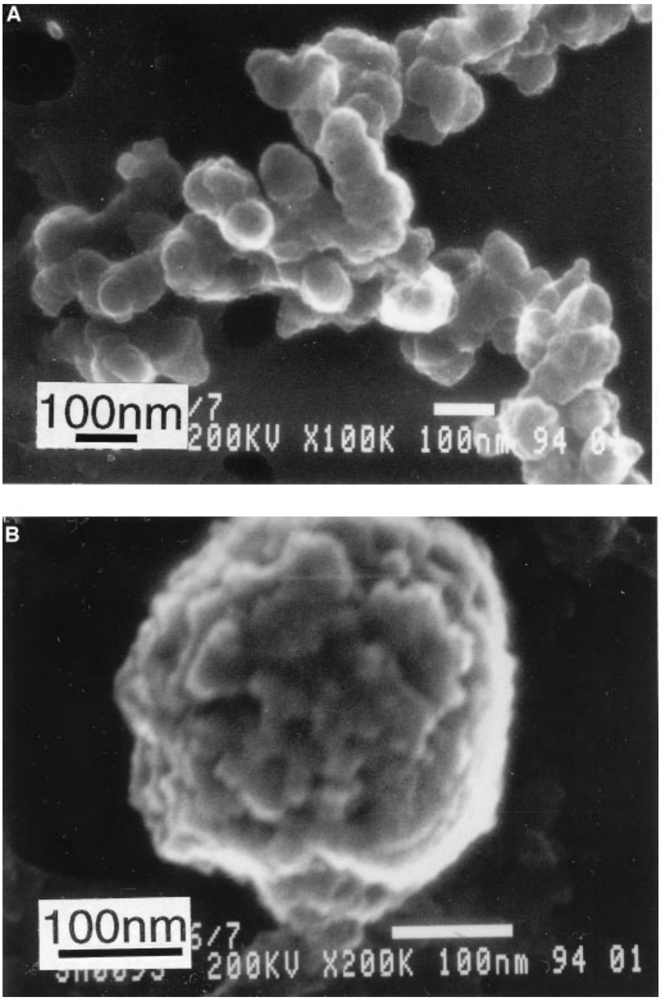

FIG. 10.
(*A*) SE image of acid-insoluble residue from digestion of cement paste (20% SF, 180 days of hydration). The residue is agglomerated SF. (*B*) Detail of (*A*) showing the surface of a heavily etched SF particle.

the very high shear forces involved in mortar and pestle mixing, large agglomerates of SF were found to be present within the pastes (superplasticiser was found to have minimal effect on the size of the SF agglomerates). Individual SF particles were evident within these agglomerates (Fig. 12), and EDXA of the agglomerate cores showed them to be very rich in silicon, suggesting minimal SF/cement reaction. The composition of the cores of SF agglomerates in pastes did show a change from extremely silicon-rich at 7 days, to a ratio of $\approx$ 2.5Si : 1Ca at 180 days. This suggested that a slow reaction was taking place, with SF in the cores of agglomerates being slowly converted to CSH. However, the composition at 180 days was still very silicon-rich relative to the more typical composition of CSH (0.6Si : 1Ca), suggesting the reaction to be still incomplete.

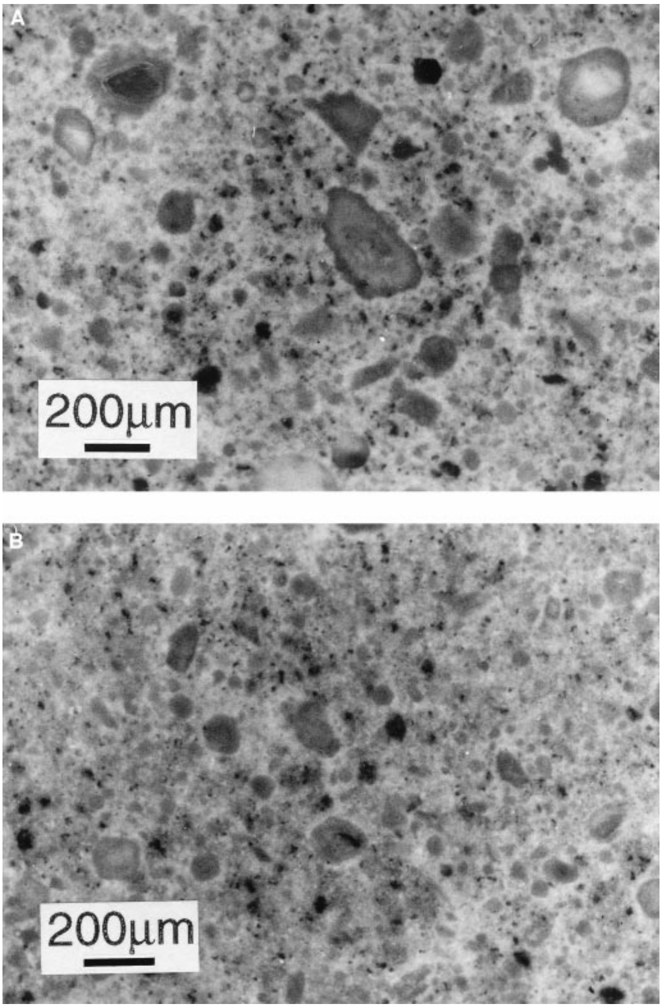

FIG. 11.
(*A*) Optical micrograph of paste (20% SF + superplasticiser, 7 days of hydration, normal hand mixing) showing SF agglomerates up to 250 μm in diameter. (*B*) As for (*A*), but mixed by grinding in a mortar and pestle (very high shear), showing a reduction in SF agglomerate size.

In the present work, the use of different cements (high and low C_3A) did not influence the agglomeration, nor did the use of superplasticiser. This clearly indicates that the SF used here was not readily dispersed in laboratory pastes; therefore, its full dispersion in typical industrially produced mortars and concretes seems unlikely. Furthermore, pastes using supplementary cementitious materials, such as fly ash and milled blast furnace slag, instead of SF to replace Portland cement did not show the agglomeration observed for SF, indicating that the agglomeration phenomenon is unique to SF.

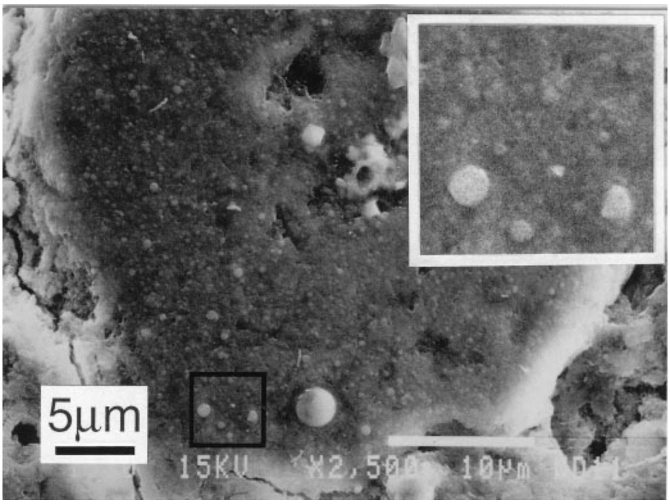

FIG. 12.
SE image of SF agglomerate shown in Figure 11B. Spherical SF is absent around the periphery due to conversion to CSH, but unreacted SF particles (inset width = 5 µm) can be seen within the agglomerate.

Discussion

Characterisation of SF both optically and using electron microscopy highlighted the tendency of the material to form agglomerates (Figs. 1 and 2). Comparison of the amorphous silica content and the general nature of the impurities occurring in the present SF suggested it to be very similar to a large number of SFs described in the literature (1,2,5,8,9). The degree of SF agglomeration was found to be quite considerable (Fig. 2). Agglomeration is influenced by many factors, particularly the mechanical handling. Agitation is used to densify SF, and although the material used here was nondensified, agglomeration was still pronounced. It is not clear how much influence minor impurities and moisture content influence SF agglomeration behaviour. What is clear from the literature is that persistent agglomeration of SF is a widely reported phenomenon.

Characterisation of the reaction of SF with an excess of calcium hydroxide solution using both XRD (Fig. 4) and electron microscopy (Figs. 5–7) showed that the reaction was quite slow. Unreacted SF was recovered even after 120 days of reaction. From a purely chemical viewpoint, considering the reactivity of amorphous silica, combined with the very large surface area of SF, a high reactivity with calcium hydroxide might be expected. Rapid formation of CSH gel in as little as 5 minutes has been reported (7,10). The present microscopy and XRD results suggested limited reaction of SF after 7 days of digestion in calcium hydroxide solution (Fig. 4). However, considerable reaction had occurred in the 120-day exposure test. Microscopy showed that SF was only present inside large masses of CSH (Fig. 7A). This suggests that the SF agglomerates may become coated with a layer of CSH, which subsequently retards reaction of calcium hydroxide with SF remaining inside the coated agglomerate. Superficial reaction of individual SF spheres was noted, in the form of surface etching (Fig. 7B). The discrepancy between the apparently sluggish SF/calcium hydroxide reaction seen here, and the much more rapid reactions reported elsewhere (7,10), may be the result of differences in the degree of SF agglomeration and agglomerate strength rather than some innate chemical differences between the SF used in the respective studies.

Microscopy of ground cement pastes suggested that unreacted SF persisted even after 180 days. Li et al. (8) have shown that only 75% of SF was consumed in a cement paste after 90 days of hydration. Our cement pastes showed extensive formation of angular particles with a composition characteristic of CSH (Fig. 9) (1,11), in addition to the presence of rounded particles very rich in silicon. The composition and morphology of these rounded particles suggested them to be SF, and nitric acid digestion of SF-containing cement paste liberated a significant amount of unreacted SF. This SF (Fig. 10B) showed similar surface etching to that noted for SF reacted with calcium hydroxide (Fig. 7B). This etched topography is consistent with a reaction impeded by the development of a surface layer of CSH.

Microscopy of fracture surfaces and polished sections of SF-containing cement pastes confirmed the presence of undispersed SF agglomerates (Figs. 11 and 12). Very high shear mixing was shown to result in a reduction of SF agglomerate size, but not its complete dispersion (Fig. 11). Chemical analysis across SF agglomerates confirmed that the outer surface had a composition characteristic of CSH, whereas the core of the agglomerate was silicon-rich. Ours is by no means the first study to report SF agglomerates in fully hydrated cements. Bonen and Diamond (11) found what they termed “large silica particles” in an SF-containing cement after 365 days of hydration. Analysis profiles across their “particles” showed increasing silicon and decreasing calcium on moving towards the centre of the particles. The outer composition was typical of CSH, whereas the interior was silicon-rich, in some instances containing only silicon. Lagerblad and Utkin (3) noted that SF was difficult to disperse and found SF agglomerates up to 0.5mm in diameter in hydrated pastes. Their work showed that mixing sequence, mixing duration, and aggregate grading all influenced SF dispersion. Only 4 of 14 of their experimental mixes produced pastes containing $<10\%$ undispersed SF. This highlights the difficulties associated with SF dispersion.

Measurements of pozzolanic reactions in SF-containing cements have shown that reactions can persist up to 550 days (12). The rate of such reactions decreases with time, in some instances in a near-parabolic manner (13). Such kinetics would be expected of a diffusion controlled reaction. Wild et al. (13) attribute the persistence of SF to be due to the development of a diffusion inhibiting layer of CSH reaction product around SF particles. It is apparent from the present work that the large SF agglomerate size and the formation of envelopes of CSH on these agglomerates enables SF to persist in cement pastes for very long periods. Conventional thinking on silica fume suggests very rapid initial reaction in cement pastes from considerations of the shape, size, and surface area of individual SF particles. However, this work demonstrates that the behaviour of SF is dominated not by its particulate properties but by its agglomerate structure.

The variable pozzolanic reactivity reported for SF (4) probably is not directly related to differences in bulk SF compositions, because most SFs appear to contain roughly similar amounts of amorphous silica. Rather, it may be a reflection of differences in SF agglomerate strength, with strongly agglomerated SF being less reactive, due to surface area considerations. SF agglomerate strength probably is influenced by both the presence of impurity films, which may coat the surface of individual SF spheres and influence their agglomeration behaviour, and by the physical handling following manufacture.

The rapid formation of a gel when SF contacts solutions containing low levels of calcium hydroxide solution has been reported (7,10) and has been used to explain the high water demand of cement pastes containing SF. Our studies (based on XRD and STEM) failed to find evidence for rapid gel formation. An alternative explanation for the high water demand considers the stability of SF agglomerates, both in solution and in pastes. Such agglomerates are likely to have a huge internal surface area relative to their volume and a very high capillarity owing to the small size of the interstices between the SF spheres. The agglomerates would therefore abstract large amounts of water from the paste as it was being mixed, contributing to its stiffening. Bonen and Khayat (1) found that, after storage in water, SF subsequently had a free water content of 40%, whereas freshly produced (dry) SF had a free water content of $<1\%$.

Conclusions

1. The SF used in this study exhibited a strong tendency to form agglomerates up to several hundreds of micrometers in diameter, which were not readily dispersed in solution or in cement pastes, even by high shear mixing.
2. In pastes hydrated for up to 180 days, and in saturated $Ca(OH)_2$ solutions reacted for up to 120 days, imaging and EDXA showed that partially reacted SF persisted within the agglomerates, whereas the peripheral regions reacted to form CSH. The outer layer of CSH appeared to impede further reaction of the SF with $Ca(OH)_2$ in both solution and paste.
3. Conventional thinking on the pozzolanic behaviour of SF in cement has focused on the size and shape of SF particles (microspheres). However, the high agglomerate strength and the difficulty in dispersing the SF in cement cannot be overlooked. The surprisingly slow pozzolanic reaction of this SF in cement paste can be understood by considering the behaviour of SF agglomerates, rather than of individual SF particles. This agglomerate structure also may contribute to the increased water demand.

Acknowledgments

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