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A preliminary assessment of the use of an amorphous silica residual as a supplementary cementing material

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Abstract

An amorphous silica (AS) by-product was investigated as a possible supplementary cementing material (SCM). Standard ASTM tests for the SCM as well as specific surface area measurement, electron microscopy, Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), ^{29}Si nuclear magnetic resonance (NMR) spectroscopy, thermal analysis, and cement paste and mortar cube strength studies were conducted. A 10:90 AS:OPC paste (w/cm of 0.4) and mortar cubes (w/cm = 0.50 to 0.60) were prepared. AS is a white amorphous material ($\bar{x}$= 29 ± 9 (1σ) nm) with a surface area of 95,000 m^2/kg, the latter resulting in a high water demand. All of the AS in 10:90 AS:OPC paste reacted by 7 days, consuming more than 50% of the calcium hydroxide. The compressive strength of OPC paste remained unchanged with the addition of AS but that of mortar increased. © 2000 Elsevier Science Inc. All rights reserved.

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1. Introduction

Amorphous silica (AS) is a by-product from the production of Hi-Sil®, a fine-grained silica manufactured by PPG Industries, Lake Charles, LA. Annually, approximately 15,000 tons (wet weight) of the AS residual (filter cake) is landfilled at an approximate cost of US$25/ton. Considering the moisture contained in the filter cake, the annual production of dry AS waste is approximately 4000 tons. A preliminary investigation indicated that AS possessed many physical and chemical properties similar to those of silica fume (SF). This kind of fine-grained silica has been often used to study the effect of grain size on cement hydration rate and in the synthesis of calcium silicate hydrates (C-S-H) [1]. If this by-product AS could be used in Portland cement (OPC) concrete, it can effect considerable cost savings to the manufacturer and also reduce landfill use.

Currently, SF is widely used as a supplementary cementing material (SCM) to enhance the strength and durability of concrete. Concrete containing SF has yielded higher compressive strengths, increased sulfate and acid resistance, and decreased chloride permeability in many applications [1]. As a result, SF–OPC concrete is used extensively in new construction and rehabilitation projects in a variety of loading situations and adverse environments.

As a result of an earlier exploratory investigation, a research project was initiated to determine the viability of AS as an SCM in OPC concrete. This paper discusses the material characterization of AS and the results of OPC:AS paste and mortar studies completed thus far. To assess the relative behavior of SF and AS when used as SCMs, a representative SF was also included in the investigation.

Results of the preliminary investigation suggested that drying of the moist AS filter cake, de-agglomerating it into a powder, and adding the resultant powder to OPC as a slurry with the mixing water was the most efficient means of making workable cement pastes [2]. It was also observed that more than 10% AS was very difficult to mix with OPC at a water/cementitious materials (w/cm) ratio of 0.40 because of the high water demand of this material. In the present study, only 10% AS by weight of cement has been used in cement pastes and mortars. This represents the maximum amount recommended by the Canadian Committee CSA Standard A23.5 for SF in OPC concrete [1]. No superplasticizer

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was used in this stage of the study to keep the number of variables at a minimum.

1.1. Production of AS

The first step in the Hi-Sil® production process is the manufacture of sodium silicate by reacting sodium hydroxide with silica sand in a high-temperature furnace. The sodium silicate is subsequently cooled to room temperature and dissolved in water. Afterwards, the AS is precipitated by reacting the sodium silicate with either carbonic or sulfuric acid. A slurry containing the precipitate is then passed through a filter press where most of the coarser silica is retained.

The filtrate is later sent to a settling tank where an ionic flocculant is added. The flocculated silica is sent to a filter press where a filter cake with up to 74% moisture (on a dry weight basis) is produced. The filter cake is finally disposed of in a landfill.

The color of the filter cake often varies with time over the same day, usually from a very light brown to colorless. The bulk composition of the filter cake is not very different from the actual product itself. However, the filter cake does not meet the stringent quality control criteria necessary for the Hi-Sil® product.

2. Experimental methods

2.1. Sampling and processing of AS

In order to conduct a thorough physical and chemical characterization of the AS, a representative sampling program for the material was conducted. Initially, representative samples were collected from different points and over a 1-week period during normal production activity. It included various samples of the final slurry and filter cake at the beginning and end of the manufacturing process over a period of several months. In addition, grab samples of the filter cake collected over a 2-year period were available.

Small quantities of the above samples were dried in glass vials in an oven at 105°C to remove moisture. Furthermore, in order to make AS crystallize into a stable crystalline form, several grams of a composite AS sample were heated to 900°C and maintained overnight in a muffle furnace.

2.2. Experimental procedures

The details of experimental procedures for scanning electron microscopy (SEM), energy dispersive X-ray (EDX) microanalysis, Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), and thermal analysis (derivative thermogravimetry (DTG)) are provided elsewhere [3].

Transmission electron microscopy (TEM) specimens were prepared by evaporating to dryness a very dilute suspension of AS on copper grids on which a 2% solution of collodion in amyl acetate was earlier deposited. The copper grids were then coated with carbon. Poly Latex microspheres with 110-nm diameter were used as internal standards (SPI West Chester, PA). Observations were made at 80 keV with a JEOL 100-CX transmission electron microscope. The particle size distribution was measured by image analysis [4]. Aitcin et al. [5] followed a similar procedure for the measurement of the particle size distribution of SF from a variety of sources.

^{29}Si solid-state magic angle spinning nuclear magnetic resonance spectroscopy (MAS-NMR) studies were done on a (9.4 T) Chemagnetics Infinity 400 MHz wide-bore NMR spectrometer. A 5 μs 90° pulse with a relaxation delay of 5 s was used to acquire the spectrum at a resonance frequency of 79.46 MHz. The spectra were obtained using approximately 300 mg of sample in a zirconia rotor spinning at 5 kHz, and were reported relative to external tetramethylsilane. The peak areas for MAS-NMR spectroscopy were determined using Peakfit® [6]. From many determinations, using duplicate and triplicate samples, integrations under peaks were reproducible to within ±4%.

2.3. Cement paste and mortar preparation

Filter cake material was used for cement paste and mortar studies. It was placed in thin layers in a gravity oven at 100 ± 5°C for at least 24 h. The dry material was finely deagglomerated using a ceramic mortar and pestle.

Using this material, standard 50 mm (2 in.) cubes of cement paste and mortar were prepared in accordance with the ASTM C305 and C109 Procedures. The cement used in preparing all specimens was a Type I Portland cement with a Blaine surface area of 3600 m^2/kg. The properties of the SF used in this study are shown in Table 1. Ottawa sand conforming to ASTM-C778 was used for mortar preparation. All cubes were cured for 24 h in a 100% relative humidity room after being molded. They were then stored in a lime bath under ambient laboratory conditions until testing.

Table 1
Average physical properties of AS and SF

Physical property	AS	SF
Color	White	Dark gray
Moisture content (as received)	74.4%	Not applicable
Moisture content (dried)	4.1%	1.5%
Loss on ignition (%)	4.6	4.4
Particle size (nm, 1σ)	29 ± 9	190 ± 40
Specific surface area (m^2/kg) BET	95,000	22,000
Specific gravity	2.08	2.26

For the cement paste and mortar investigation, a 10% replacement of OPC with either AS or SF in paste or mortar was utilized. For the cement paste cubes, a w/cm ratio of 0.40 was used for all mixes. Below this w/cm, AS:OPC mixtures were very difficult to mix. For the mortar study, the reference OPC mortar was made at w/cm = 0.45 with a corresponding flow of 100 ± 5 mm. Below w/cm = 0.50, the mortars containing AS were almost like dry powder. Additional water was needed to prepare workable mixes. Thus, mortar cubes containing AS were made at w/cm = 0.50, 0.55, and 0.60. At w/cm = 0.55, a flow of 104 ± 5 mm was attained for AS:OPC mortar.

The compressive strength of the cement paste and mortar cubes was determined according to the ASTM C109 Procedure. Each cube was loaded to failure and a maximum compressive strength was determined. The loading rate in each test was 0.4 kN/s (100 lb/s).

3. Results

3.1. Characterization of AS

3.1.1. Physical

A composite collection of filter cake residual was used to determine the physical characteristics of AS. The recommended ASTM standards or other approved methods were adhered to in each test. The data for SF were provided by its manufacturer. The test results for AS and the SF are presented in Table 1. The 4.1% moisture content of AS was due to incomplete drying of AS at 100 ± 5°C which failed to extract all the moisture from the interior of the large agglomerates.

3.1.2. Electron microscopy

In the scanning electron microscope, AS was found to be present as agglomerates of individual AS particles. These agglomerates were tens of μm in diameter. Similar to SEM, TEM also showed agglomerates of AS particles. However, the shape and size of the individual particles were more distinct in the transmission electron microscope. The particles had wavy, smooth boundaries. A representative TEM photomicrograph of an AS agglomerate is shown in Fig. 1. The grain density (particles/volume) varies from place to place in the agglomerate. The particles appear to be elongated platelets with an average length:-breadth ratio of 2:1. The thickness of the particles is only several nanometers as they appear transparent under the electron beam (Fig. 1).

The particle size distribution (Fig. 2) was determined by measuring the longer dimension of the individual particles from the transmission electron photomicrographs. A total of 234 particles from several agglomerates were counted following the suggestions of Aitcin et al. [5]. AS had an average particle diameter of 29 ± 9 (1σ) nm. The figure shows that the particle size distribution is normal and the size range is quite narrow. The particle size distribution of the SF used in this study,

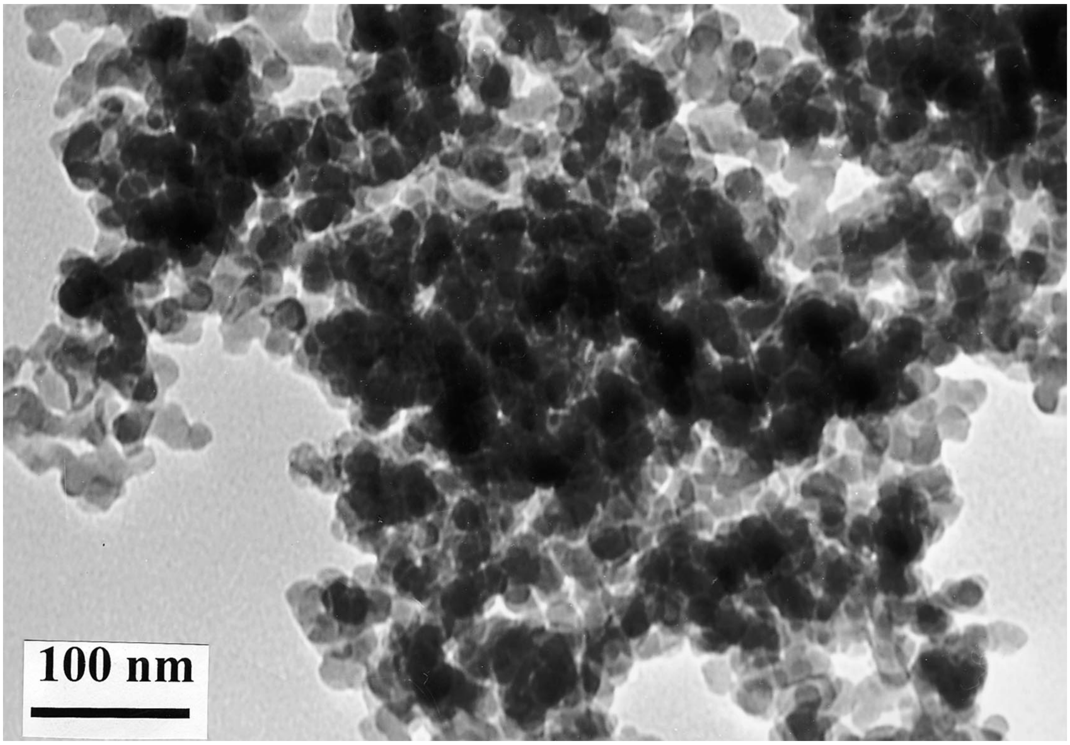

Fig. 1. Transmission electron photomicrograph of AS.

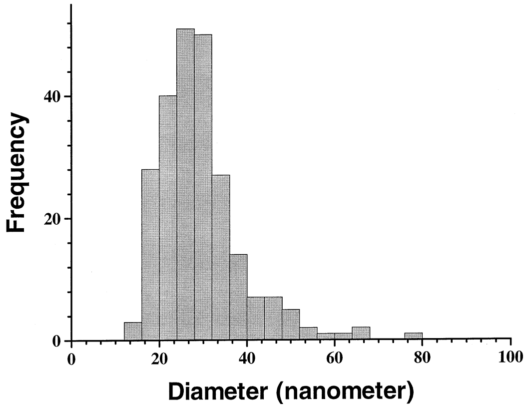

Fig. 2. Particle size distribution of AS. $\bar{x} = 29 \pm 9$ (1σ) nm.

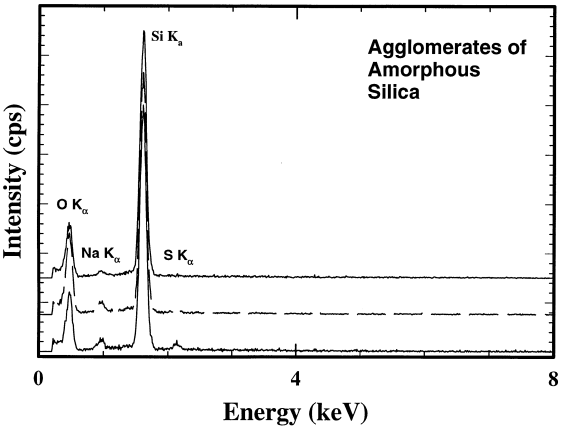

Fig. 3. EDXRA analyses.

measured from scanning electron photomicrographs, was 190 ± 40 (1σ) nm.

3.1.3. Specific surface area

The specific surface area of AS and SF, as determined by the BET method, are shown in Table 1. The determination was done by a commercial testing laboratory. The specific surface area of AS was more than four times that of the SF used in this study.

3.1.4. Bulk chemical analysis

The bulk chemical analyses, shown in Table 2, were determined by inductively coupled plasma-mass spectrometry on samples of filter cake material collected over a period of 1 year. The SF analysis was obtained from its manufacturer. Generally, amounts less than 5% of elements and compounds other than SiO_2 were present in the AS. The presence of certain elements was dependent on the use of either carbonic or sulfuric acid in the production process. For example, the amount of Na_2O was highly variable, ranging over an order of magnitude (Table 2).

3.1.5. EDX microanalysis

EDX microanalyses of dry AS agglomerates are shown in Fig. 3. The principal element is Si. The amounts of Na and S vary from agglomerate to agglomerate, but are less than 0.5% each.

Table 2
Bulk chemical analysis of SCMs used in this study

Oxide (%)	SF	AS
SiO_2	93.83	95–98
Al_2O_3	0.32	0.12
CaO	0.81	0.06–0.21
Fe_2O_3	0.18	0.06–0.3
MgO	0.33	0.02–0.04
Na_2O	0.08	0.65–4.49
K_2O	0.69	0.006–0.06
SO_4	Not determined	1.34
P_2O_5	0.10	Not determined

3.1.6. FT-IR

Fig. 4 shows the FT-IR patterns of AS, crystallized AS, SF, and quartz. The band at 623 cm^{-1} is typical of cristobalite, which distinguishes it from other forms of crystalline silica [7]. This band is very weak in AS, but becomes sharper and stronger when AS is heated to 900°C. The broader 802 cm^{-1} band in AS shifts to 789 cm^{-1} when heated. One of the characteristic bands of tridymite (another polymorph of silica), which distinguishes it from other crystalline silicas, is at 790 cm^{-1}. The FT-IR pattern then suggests that cristobalite and tridymite were both forming when AS is heated to 900°C. The weak cristobalite band, seen in AS, is absent in SF (Fig. 4).

3.1.7. XRD

Fig. 5 shows the XRD patterns of AS, crystallized AS, and SF. The AS pattern has no peaks but a broad hump over the range 15° to 50° 2θ (centered at 24.47° 2θ, corresponding *d* spacing is 0.363 nm). There is also a minor hump around 45° 2θ (centered at 43.00° 2θ, corresponding *d* spacing being 0.210 nm). The absence of peaks in the AS XRD pattern confirms that it is amorphous. When AS was heated to 900°C, the broad hump in the pattern completely disappeared. None of the background was left, suggesting all of it crystallized. Peaks of both tridymite (PDF 18-1170, [8]) and cristobalite (PDF 39-1425, [8]) were identified in the pattern. The XRD peak intensities suggest that there is more tridymite than cristobalite. Similar to AS, SF is also completely amorphous but the broad hump is located at a lower value of 2θ (centered at 21.64° 2θ, corresponding *d* spacing is 0.410 nm, which is very close to one of the most intense peaks of tridymite).

3.1.8. MAS-NMR

Fig. 6 shows the ^{29}Si NMR spectrum of AS. The width of the peak confirms that AS is amorphous. The position of the ^{29}Si NMR peak indicates that AS is fully polymerized (Q^4) [9]. The AS spectrum consists of a major peak centered

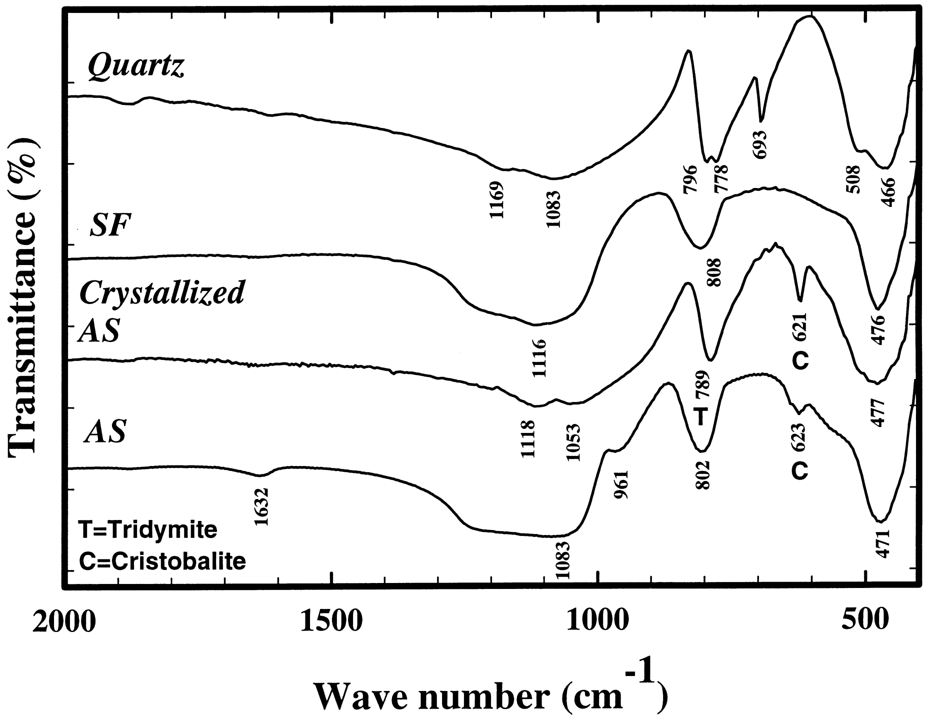

Fig. 4. FT-IR spectra.

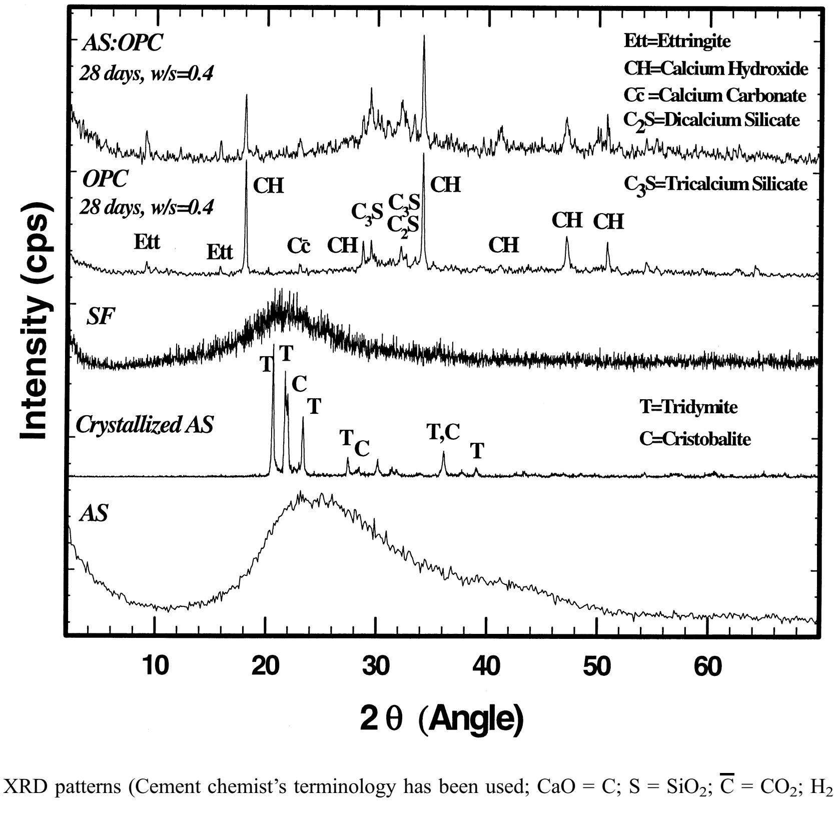

Fig. 5. XRD patterns (Cement chemist's terminology has been used; CaO = C; S = SiO_2; $\overline{C}$ = CO_2; H_2O = H).

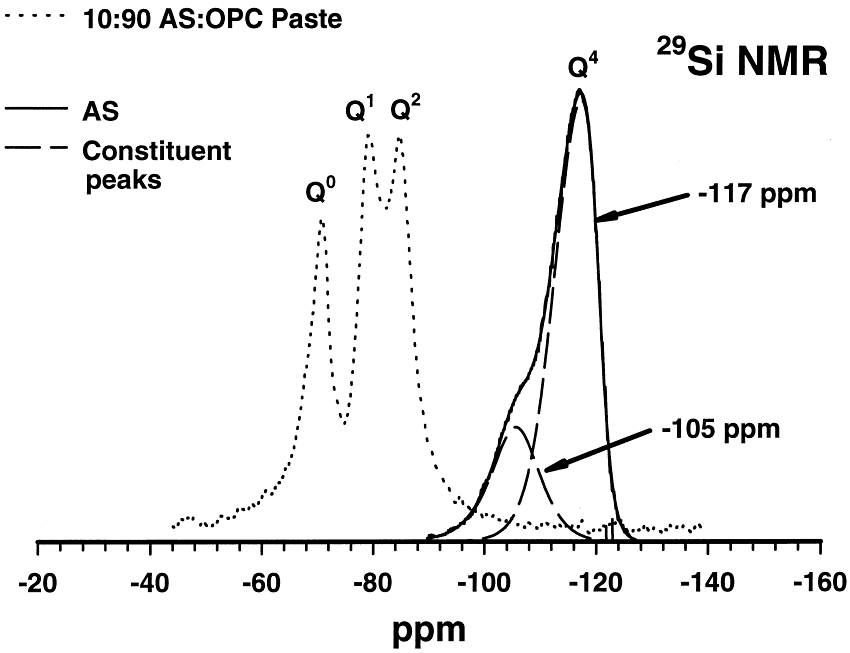

Fig. 6. MAS-NMR spectra.

at −117 ppm and a minor peak at −105 ppm. The ratio between these populations is 83:17. The MAS-NMR peak for cristobalite is at −105 ppm [10].

3.2. AS:OPC paste

3.2.1. Thermal analysis

DTG studies of the 10:90 AS:OPC pastes showed that the addition of AS did not affect the presence of ettringite and calcium hydroxide, the usual crystalline phases in hydrated OPC. However, the amount of calcium hydroxide was reduced by more than 50%. Fig. 7 shows that for OPC only, the calcium hydroxide content increases from 7 to 14 days, but after that remains constant, within experimental error.

3.2.2. XRD

The XRD patterns of 10:90 AS:OPC paste is shown in Fig. 5. No new crystalline phase due to the addition of AS is present.

3.2.3. Nuclear magnetic resonance spectroscopy

Fig. 6 shows the MAS-NMR pattern of a 7-day old 10:90 AS:OPC paste. The spectrum of the AS:OPC paste

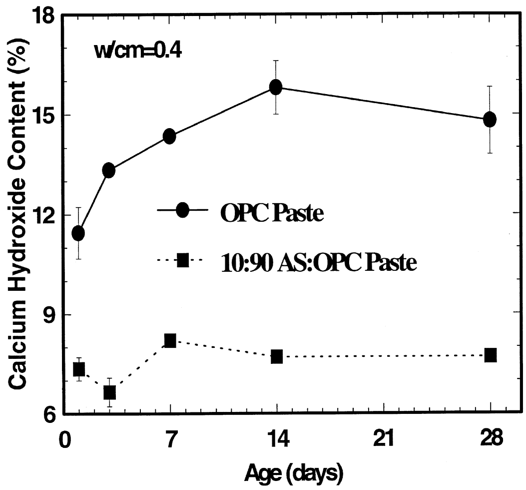

Fig. 7. Variation in CH content in AS cement paste with age.

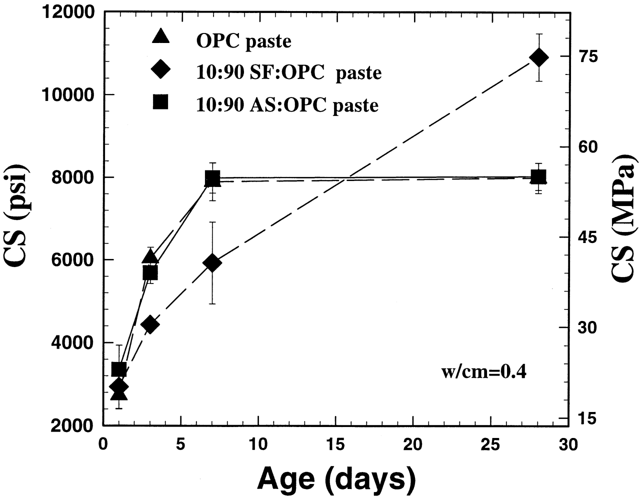

Fig. 8. Compressive strengths of AS cement pastes with age.

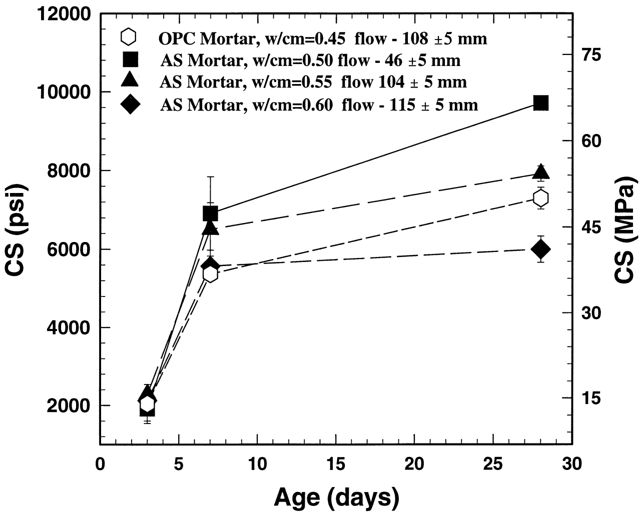

Fig. 9. Compressive strengths of AS mortar with age.

shows the complete absence of the AS peak by 7 days. The amount of Q^2 is higher than that usually found in 7-day old OPC pastes.

3.3. Compressive strength

3.3.1. AS:OPC paste

Fig. 8 shows the strengths of hardened OPC paste, with and without AS or SF, over time. The addition of SF to OPC yielded lower strength up to 7 days but much higher strength than the OPC paste by 28 days. Based on visual observations during and after testing, the cubes containing the SCMs exhibited a slightly more brittle behavior under loading than the corresponding OPC cubes.

3.3.2. Mortar

Fig. 9 shows the variation in the compressive strength of AS:OPC mortars at various w/cm ratios over time. A reference OPC mortar was also included for comparison at a w/cm = 0.45. The recorded flow values for each mix are also shown. All mixes were easily molded. The maximum compressive strength of 67 MPa was reached at w/cm = 0.50. The drop in strength at w/cm = 0.60 was quite significant in comparison with the other AS:OPC mortars.

4. Discussion

4.1. Comparison of AS and SF

AS has an average particle diameter of 29 ± 9 (1σ) nm. In comparison, the SF being used in the study has an average diameter of 190 ± 40 (1σ) nm. Aitcin et al. [5] found that particle diameter of SF from various sources ranged from 180 to 260 nm. Svenkerud et al. [11] reported a mean particle size of 150 nm for an SF. SF particles are perfectly spherical [1], as expected for a condensation process. In contrast, AS, a precipitate from the reaction between a sodium silicate solution and an acid, shows a wide range of shapes. The shape can generally be described as a flattened ellipsoid with axes of different lengths. The smaller diameter, and flattened shape, combine to produce the very high specific surface area of AS. The specific surface area of the silica products from PPG Industries ranges from 18,000 to 250,000 m^2/kg (http:/www.ppg.com/silicas.html). The by-product is a composite of all the silica products. A value of 95,000 m^2/kg is thus, a reasonable one for the filter cake.

AS crystallizes to tridymite and cristobalite, which are metastable phases and have complex chemistry [12]. Intimate intergrowth of these two phases at the molecular level is also common. This crystallization behavior of AS is unlike SF, which crystallizes only into cristobalite (Fig. 4) [1]. Both cristobalite and tridymite are crystallized artificially from silicic acid or AS glass in the presence of alkali oxides, which act as accelerators [7]. The sodium in AS probably serves the same purpose in this instance. Both tridymite and cristobalite have more open crystal structures than quartz and the incorporation of other ions such as sodium is more common. The stable crystalline form is an indicator of volume and structural property changes that can potentially occur in AS with time.

The results of the XRD, NMR and FT-IR studies all verify that AS is amorphous. Both the NMR and FT-IR results indicate that there are two structurally distinct populations of silica in AS. Among silica polymorphs, the peak ^{29}Si NMR shift empirically correlates with the secant of the mean Si–O–Si bond [9]. The higher the mean angle, the more negative is the shift. Thus, in AS, the silica population with -117 ppm shift has a higher mean Si–O–Si bond angle than the silica population with -105 ppm shift. The former may also be more reactive than the latter. The ^{29}Si NMR spectrum of SF shows a wider variation depending on the source, but usually has a peak around -110 ppm [13,14].

4.2. Pozzolanic behavior of AS

Consumption of calcium hydroxide in AS:OPC paste starts within the first day of curing. By 7 days, more than half of the calcium hydroxide that would have been produced in the absence of AS, is consumed. The calcium hydroxide content in AS:OPC paste fluctuated for the first 7 days due to the competing reactions between production by calcium silicate hydration and consumption by AS. Very little pozzolanic reaction was occurring in older pastes. Yogendran et al. [15] and Zhang and Gjorv [16] observed similar trends in SF:OPC pastes. The complete absence of such a hump in the AS:OPC XRD pattern suggests that the AS has reacted. If AS were present as a mechanical mixture in the AS:OPC paste, then the AS hump should have been present in its XRD pattern centered at 24.47° 2θ, with the intensity reduced directly in proportion to its concentration.

The AS ^{29}Si MAS-NMR peak was absent in the 10:90 AS:OPC paste by 7 days. The nature of the C-S-H in this paste was also different. It appears to be more polymerized (more Q^2) than is normal in OPC paste of this age, a common observation for cements with pozzolans [17]. Dobson et al. [18] studied the hydration reaction of C_3S in the presence of a reactive silica by MAS-NMR. The reactive silica had a specific surface area of 19,000 m^2/kg and was 85% to 96% amorphous. The C-S-H produced had a C/S ratio of 1.5 in the presence of the reactive silica and 1.8 for the C_3S alone. Young [13] and Adulaijan et al. [14] showed that when SF is reacted with C_3S or OPC, the C-S-H is more polymerized than observed in the absence of SF.

4.3. OPC paste and mortar with AS

OPC mortar has significantly lower strength than OPC paste. The addition of SF to OPC mortar, however, has produced strengths even higher than that of cement pastes [19]. This increase can be explained either by improved bonding between aggregate and paste or increased strength of the paste itself [19–22].

Similar to SF, the addition of AS to OPC paste and mortar had a positive effect on compressive strength. The 28 day strengths of 10:90 AS:OPC paste was similar to the control OPC paste. The strength of AS:OPC mortar at w/cm = 0.55 was higher than that of both OPC paste and mortar. At the same w/cm ratio, the initial higher strength of AS-containing paste relative to SF-containing paste is presumably due to the acceleratory affect of the finer grain size of AS compared to SF [1]. Bonen and Diamond [23] found undispersed agglomerates of SF in SF:OPC pastes, but these had high amounts of calcium at the periphery and Na in the center, suggesting that they had reacted. The Ca/Si mole ratio of these agglomerates at the periphery was similar to that of the cement matrix. Some researchers [23,24] have expressed concern that in high alkali cement, these SF agglomerates can form expansive silica gel.

White specks were commonly seen in the AS:OPC pastes with the naked eye and AS agglomerates were observed in AS:OPC mortar with the SEM. Grinding by ceramic mortar and pestle was not efficient enough for complete de-agglomeration of AS. It is expected that a better grinding process will reduce this problem. Though these specks suggested insufficient mixing, MAS-NMR and XRD evidence indicated that this material had reacted completely.

The agglomerates found in AS:OPC pastes have the potential to form expansive alkali silica gel, since the Na_2O content of AS is high in comparison to SF. Ten percent replacement of cement by AS contributes, at the most, only 0.5% of the total Na_2O. However, EDX and bulk analyses suggested that the sodium distribution is not homogeneous in AS and locally, it may be high. Duchesne and Berube [25] noted that the hydrates in SCM-enhanced concrete had lower C/S ratios compared to control Portland cement concrete and could contain more alkalies, provided they are available. AS may act similarly. More studies will be conducted to examine the effect of alkalies in concrete containing AS.

No detailed experimentation has yet been undertaken to understand the mechanical and chemical effect of partial substitution of Portland cement by AS. Substitution of AS in cement paste reduced bleeding compared to Portland cement alone or even with 10% SF replacement. The pozzolanic reactivity of AS is very similar to that of SF, if not more rapid. Thus, the mechanical and chemical effects of Portland cement substitution should be very similar to those of SF [26].

5. Conclusion

AS is a white, amorphous SCM with a very small average particle diameter ($\bar{x}$ = 29 ± 9 (1σ) nm) and extremely high specific surface area (95,000 m^2/kg). The research conducted to date indicates that AS has physical and chemical properties similar to those of SF. In addition, its behavior in cement paste and mortar cubes, indicates the likelihood that it will perform in a manner similar to SF when incorporated into OPC concrete. Future studies will address the behavior of fresh and hardened concrete containing this material.

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