Analyzing Effects of Varied Silica Fume Sources within Baseline UHPC

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Abstract:

Silica fume has been used for many years as a fine-grained supplementary cementitious material in ultra-high performance concrete (UHPC) to aid in improving strength and durability. Since silica fume is a waste product, much variability is present among different silica fume sources. This study compared the functionality of eight silica fume products in an otherwise identical cementitious matrix using a standard reference UHPC known as Cor-Tuf Baseline (CTB). The studied silica fumes were obtained from multiple suppliers and geographical locations. Both densified and undensified silica fumes were evaluated. Silica fumes were substituted one for another on a 1:1 basis (by mass) for initial batching. Fresh properties of interest in this study included mixing time and flow percentage. Hardened properties of interest included compressive strength and density. The effects of different mixing actions were studied as well as different high temperature curing conditions. Results of this study indicated that some silica fumes, while similar in composition to others tested, presented many difficulties in producing a UHPC. The state of silica fume densification did not exclusively determine its usefulness in the production of a UHPC. Increased shearing action during mixing was seen as advantageous for increased fluidity and ease of production. The use of a steam generator for high temperature curing was more beneficial in strength development than placing the samples in a high temperature water bath at the same temperature. Two of the eight silica fumes tested were found to be acceptable for CTB production.

Keywords: compressive strength, densification, fresh properties, silica fume, UHPC

1. Introduction

Silica fume is a highly reactive pozzolan due to a high amorphous silicon dioxide (SiO_2) content and an extremely small particle size. Portland cement mixtures when mixed with water form two primary chemical compounds, calcium silicate hydrate (CSH) and calcium hydroxide (CH). Silica fume adds strength to a portland cement mixture by reacting with CH to form additional CSH, which is the primary strength giving phase in portland cement concrete. The very fine particle size of silica fume also improves particle packing in cementitious mixtures leading to decreased interfacial transition zone porosity and increased overall strength gain, durability, and decreased permeability. Due to these properties, silica fume is a common addition to most ultra-high performance concrete (UHPC) mixtures.

Ultra-high performance concrete is a family of materials that typically exhibits high compressive strengths in excess of 150 MPa and high durability due to negligible interconnected porosity. UHPC formulations generally consist of a high cementitious content incorporating oil-well or low-heat portland cement, siliceous fine aggregates, crushed quartz or other micron-sized powder, silica fume, water, high-range water-reducing admixtures (HRWRA) to control rheology, and other components that vary by manufacturer. The high compressive strengths of UHPC lead to brittle behavior similar to ceramics. To overcome this brittle behavior, steel fiber reinforcement is commonly used. The addition of steel fiber reinforcement aids in delocalizing micro- and macro-scale cracking, and leads to improvements in tensile properties and minimized spallation during failure (Scott et al. 2015).

Many UHPC formulations exist, including those commercially available from vendors as well as in-house mixtures. Cor-Tuf Baseline (CTB) is one such UHPC formulation developed by the U.S. Army Engineer Research and Development Center (ERDC) as an in-house laboratory standard reference material with minimal batch-to-batch variation. The general mixture proportion for CTB is described in United States Patent 7,744,690 B2 (Durst et al. 2010), and the development process is described in a 2008 Northwestern University PhD dissertation (O'Neil 2008). CTB has a compressive strength that can range from 193 to 220 MPa on average (Scott et al 2015). The present study analyzed the effects of substituting one silica fume source for another by mass in a standard reference mixture proportion.

2. Materials

American Petroleum Institute (API) class H oil well cement was used as the primary cementitious component in this study. Class H oil well cement was used instead of a more traditional Type I/II Portland cement due to its coarser grinding, typically higher dicalcium silicate (C_2S) content, and lack of tricalcium aluminate (C_3A), which allowed for slower hydration. Two inert constituents were used as fine aggregates in this study. Unground silica was used as the primary fine aggregate in all mixture proportions, and angular ground quartz silica was also used as a fine aggregate for this study. The only admixture used in this study was a high-range water-reducing admixture (HRWRA) to improve the workability of the low water-to-cement ratio mixture. The product used was a polycarboxylate HRWRA. This HRWRA provides a lubricating effect that allows for stiffer mixtures to be more readily placed into molds and forms without dramatically altering the water-to-cement ratio of the mixture. One negative side effect of using a high dosage rate of HRWRA is a retarding effect on the setting time of the material.Steel fibers were used as tensile reinforcement in the composite matrix. 1.2-inch (30-mm) fibers with hooked ends and an aspect ratio (L/d) of 55 were used.

Silica fume is used as the primary supplementary cementitious material (SCM) in Cor-Tuf Baseline (CTB). Eight distinct silica fume products were considered in this study. The traditional silica fume used in CTB, SF-1, was used as a reference material in this study. SF-1 was not a traditional silica fume according to ASTM C1240 (ASTM 2015a) as it was produced as a by-product in a zirconium furnace rather than as a by-product of a ferro-silicon alloys furnace. This gave SF-1 a high silica purity and unique properties that were advantageous to UHPC mixtures. Seven additional silica fume materials were also considered. They were labeled SF-2 through SF-8. Both densified and undensified silica fumes were considered. SF-1 was an undensified silica fume, but both types of fume were studied for completeness. SF-3 and SF-7 were the densified fumes studied. All other fumes were undensified.

3. Silica Fume Characterization

Each silica fume source was characterized in its powder state in two ways: (1) particle size distribution was determined through the use of laser diffraction analysis, and (2) bulk chemical analysis was determined through the use of x-ray fluorescence (XRF) spectroscopy.

3.1. Methods and Procedures

Laser diffraction was used to determine particle size distributions by measuring the angular variation in intensity of light scattered as a laser beam passed through a dispersed particulate sample. A narrow beam of monochromatic light from a He-Ne laser, $\lambda = 633$ nm, is passed through the dispersed sample, and the angular distribution of the diffracted light is measured. The angle of the diffracted light increases as particle size decreases. This technique is used to determine particle sizes in nanometer to micrometer range (McCave et al. 1986).

Laser diffraction was performed using a Beckman Coulter LS laser diffraction particle size analysis system. Sample preparation was performed by sonication using a 600W ultrasonic probe for 15 minutes in deionized water. The sonication time was selected after a small study of the effect of sonication time on dispersion that indicated 15 minutes was sufficient to fully disperse the silica fume in deionized water. Following sonication, the dispersed silica fume and deionized water solution were passed into the laser diffraction system using a peristaltic pump. Two consecutive laser diffraction measurements with a length of 60 seconds each were performed. Following the laser diffraction measurements, integrated analysis algorithms were used to generate particle size distributions and associated statistics.

X-ray fluorescence (XRF) spectroscopy is a non-destructive chemical analysis technique utilized to measure the bulk chemical composition of samples. During the analysis, an x-ray beam (source) hits a sample and its atoms interact with the received radiation. The energy causes an electron that is positioned in an inner shell in the atom to be dislodged, making the atom unstable and creating a vacancy. At this point, an electron that is positioned in another orbit inside an outer shell moves to the vacancy in order to make the atom stable, and in the process emits an x-ray at a unique energy value (in keV). This energy is known as the binding energy, which is characteristic of that specific element. The process of emissions of characteristic x-rays is called x-ray fluorescence (XRF). When the source energy changes, the same process described above occurs. During this process the different characteristic x-rays with their corresponding energy values are emitted producing a spectra.

3.2. Characterization Data

Figure 1 shows the particle size distributions for the all silica fume products tested. The solid blue line represents the reference silica fume, SF-1. These test results show that SF-2, SF-4, SF-6, and SF-7 are finer than the reference material, whereas SF-3, SF-5, and SF-8 are coarser. SF-6 and SF-7 are produced at the same location, so their similar particle size distributions were expected.

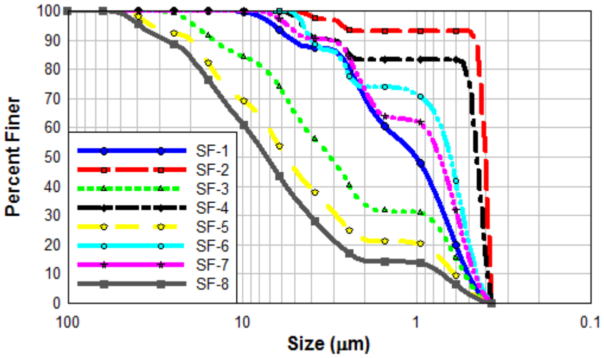

Figure 1. Particle Size Distributions for Silica Fumes.

Table 1 summarizes the chemical testing results for the nine different silica fumes considered. The four oxide contents represent the components that make up the majority of the silica fume. The "Balance" column is the remaining percentage of the chemical composition that does not fall into one of the main four oxide categories. Loss on ignition, or LOI, is the percentage of mass loss when the silica fume is heated to high temperature. LOI gives an indication of the amount of carbon present in a silica fume.

Table 1. Chemical composition of silica fumes.

Silica Fume	SiO_2	CaO	MgO	Na_2O	Balance	LOI
SF-1	97.30	0.00	0.06	0.00	2.64	1.35
SF-2	95.04	0.01	0.38	1.78	2.79	1.39
SF-3	93.26	0.00	0.21	1.24	5.29	3.93
SF-4	74.95	17.90	2.89	0.52	3.74	0.89
SF-5	97.21	0.00	0.15	0.16	2.48	1.61
SF-6	96.06	0.00	0.14	0.12	2.68	2.73
SF-7	93.65	0.10	0.37	0.23	5.65	4.47
SF-8	97.42	1.27	0.09	0.01	1.21	0.93

With the exception of the SF-4 fume, Table 1 shows that silicon dioxide makes up at least 93% of all silica fumes tested. The SF-4 fume was only 75% silicon dioxide and had a much higher percentage of calcium oxide than the other fumes.

4. UHPC Evaluation

4.1. Methods and Procedures

4.1.1. Mixture Proportioning

The standard baseline reference mass mixture proportion for CTB (MP-1) used in this study is given in Table 2 below. Each of the eight studied silica fumes was incorporated into the CTB mixture proportion using the mixing methods and curing processes described in Section 4.1.2 and Section 4.1.4.

Table 2. Mixture proportions.

Material	MP-1 – pcy (kg/m^3)	MP-2 – pcy (kg/m^3)	MP-3 – pcy (kg/m^3)
Cement	1350 (804)	1400 (829)	1360 (805)
Unground Silica	1310 (778)	1350 (802)	1310 (779)
Ground Silica	375 (223)	387 (230)	376 (223)
Silica Fume	527 (313)	408 (242)	528 (313)
HRWRA	23.2 (13.7)	23.9 (14.2)	23.2 (13.8)
Water	282 (167)	291 (173)	274 (163)
Steel Fibers	420 (249)	433 (257)	421 (250)

4.1.2. Mixing Procedures

Three different mixers that had different mixing actions were used in this study. Bench-scale planetary style mixing was completed using a 12-qt (11.3-L) Hobart Legacy® Countertop mixer fitted with a flat beater and bowl-scraper attachment. This mixer was used for all preliminary batching and down selection of potential silica fume sources. Steel fibers were not included in bench-scale mixtures. The standard batch volume for bench-scale mixing was 0.075 ft^3 (0.002 m^3). This volume represented the final wet out volume of concrete. The dry powders used took up considerably more volume prior the addition of water, so batch size was limited by the amount of dry powder that could be successfully mixed in the mixer.

All bench-scale mixing was performed with an attachment speed of 33 RPM. For control, all bench-scale mixing was performed in a constant temperature room set at 65°F (18°C). All dry materials were added at one time and dry blended for five minutes. All liquids were then added and mixed until the mixture “broke over”. “Break over” is defined in Section 4.1.3. After each mixture broke over, five additional minutes of mixing was conducted to ensure thorough mixing. ASTM standard 2-in (50-mm) cubes were cast for compressive strength testing using the materials mixed with the bench-scale mixer.

High shear mixing was used as a robust mixing technique for larger scale batching. High shear mixing was performed using an Eirich high shear mixer. The standard batch size used was 2.0 ft^3 (0.056 m^3). Steel fibers were included in each batch, and 4 in. x 8 in. (100 mm x 200 mm) cylinders and 4 in. x 4 in. x 15 in. (100 mm x 100 mm x 375 mm) beams were cast for compressive strength and flexural strength testing, respectively. Traditional rotating drum mixing was performed as a worst-case-scenario mixing technique. Batches that are successfully mixed using this technique are assumed to be mixable in any concrete mixer. A Gilson rotating drum mixer was used in this study. Steel fibers were included in these batches, and 4 in. x 8 in. (100 mm x 200 mm) cylinders were cast for compressive strength testing. The standard batch size was 1.5 ft^3 (0.042 m^3).

4.1.3. Fresh Properties

Mixing time was measured as the elapsed time from the addition of water until the batch "broke over". Breaking over was defined as the time at which the material wet out enough to become a fluid. The time was measured using a stopwatch and recorded to the nearest quarter minute due to the subjective nature of determining break over. Mixing time was recorded for bench-scale batches only.

Workability was measured in accordance with ASTM C1437 (ASTM 2013b). This test method determined the flow of a material as a percentage of spread from an initial cone diameter. The flow cone is filled halfway with mortar and tamped 20 times prior to adding the remaining volume. The tamping process is repeated on the second layer, and the excess mortar is struck off the top of the mold with a straight edge. The flow cone is removed, and the flow table is dropped 25 times in 15 seconds. The resulting diameter of the mortar is measured with special calipers at four defined points. The sum of these four diameters represents the percentage increase in the diameter of the flow cone. Workability was only measured for bench-scale batches.

4.1.4. Curing Regimes

The standard curing method for cast samples was seven days at a room temperature (23°C), 100% humidity environment, followed by six days in a high temperature 195°F (90°C), 100% humidity environment. The room temperature curing was performed in the ERDC's Moist Curing Room. High temperature curing was performed either by submerging the samples in a hot water bath or by using a steam generator to saturate the samples with steam underneath an insulated cover. All samples cast using the bench-scale planetary mixer were cured using the hot water bath. Samples from the high shear mixer were cured using the steam generator. Samples made using the traditional rotating drum mixer were cured using both high temperature apparatuses, and the technique used is noted in the results.

4.1.5. Hardened Properties

The density of each mixture was determined using hydrostatic weighing, which compares the mass of the sample "in air" to the mass of the sample submerged in water. This procedure was performed in accordance with ASTM C39 (ASTM 2015b).

The compressive strength, designated by f_c', of each mixture proportion was measured in accordance with ASTM C39 (ASTM 2015b) for cylindrical samples and ASTM C109 (ASTM 2013a) for cubic samples. A Tinius Olsen Universal Testing Machine (UTM) capable of applying 440-kips (1,950 kN) of force was used to test cubic samples, and a 1,000-kip (4,450 kN) SATEC load frame was used to test cylindrical samples. Each load frame was connected to a data collection system that recorded load and displacement data. Data of interest for each sample was the peak load obtained. Compressive strength was calculated as the peak load divided by the cross-sectional area of the sample. All compressive strength tests were performed at 14 days, which was one day after the end of standard curing.

Flexural strength, designated by f_b, of fiber reinforced samples was measured in accordance with ASTM C78 (ASTM 2015c). The standard sample geometry was a 4 in. x 4 in. x 15 in. (100 mm x 100 mm x 375 mm) flex beam. The simply supported span length was 12 in. (300 mm), and the flexural load was applied at third points [4 in. and 8 in. (100 mm and 200 mm)]. Load versus position data were recorded with the peak load being the data of interest.

4.2. Results and Discussion

4.2.1. Bench-scale Planetary Mixing

The results for mixtures using bench-scale planetary mixing are shown in Table 3. Only three of the eight tested silica fumes successfully mixed and produced a UHPC similar to CTB, one of those being the reference silica fume. SF-2 was an undensified silica fume, and SF-7 was a densified product. All other tested silica fumes were allowed to mix for at least one hour without breaking over. Even after four times the allowed mixing time, these materials were unsuitable for the production of CTB. Both other silica fumes mixed much quicker than the reference and exhibited higher fluidity. The increased fluidity of SF-7 suggests that the densified silica fume was not breaking apart as expected, so the silica fume had less surface area for reaction. The density results were similar for all three silica fume sources, and SF-7 samples tested at a higher compressive strength than the other two materials.

Table 3. Bench-scale planetary mixing results.

Property/Batch	SF-1	SF-2	SF-7
Time – min	14:45	6:15	9:15
Flow – %	57.6	60.6	82.1
ρ – lb/ft^3 (kg/m^3)	148.1 (2372)	145.9 (2337)	149.2 (2390)
f_c' – ksi (MPa)	27.0 (186)	26.8 (185)	29.7 (205)

4.2.2. High-shear Mixing

The results for mixtures using high-shear mixing are shown in Table 4. Here, only the two non-reference silica fumes that were successful in producing CTB using bench-scale planetary mixing were tested. One key difference in these samples was the presence of steel fiber reinforcement. Once again, the two mixtures had similar densities, and SF-7 samples tested with a slightly higher compressive strength. For both materials, the measured flexural strength was approximately 14% of the measured compressive strength. The results here are very similar for both silica fume sources, which suggests that both densified and undensified silica fumes perform similary with appropriate mixing techniques and adequate batch sizes.

Table 4. High-shear mixing results.

Property/Batch	SF-2	SF-7
ρ – lb/ft^3 (kg/m^3)	158.1 (2533)	159.9 (2561)
f_c' – ksi (MPa)	28.0 (193)	28.9 (199)
f_b– ksi (MPa)	3.98 (27.4)	4.18 (28.8)

4.2.3. Traditional Rotating Drum Mixing

The results for mixtures made using traditional rotating drum mixing are shown in Table 5. Traditional rotating drum mixing is a much less energy intensive mixing process, so the mixtures had more difficulties in mixing. In order to ease some of these difficulties, the mixture proportions for these batches were changed slightly. Preliminary workability testing of drum-mixed SF-2 CTB showed decreased fluidity when compared with traditional CTB. To counter this, 25% of the original silica fume content was removed, which allowed for easier mixing and similar fresh properties. This mixture proportion is shown in Table 2 as MP-2. Drum-mixed SF-7 CTB actually exhibited excess fluidity when compared to reference materials. To balance this, 3% of the mix water was withheld from the batch. This mixture proportion is shown in Table 2 as MP-3. The labels A and B in Table 5 for SF-7 indicate different methods of high temperature curing. SF-7A samples were cured by submerging samples in a hot water bath set to 195°F (90°C). SF-7B samples were cured under a steam blanket using a steam generator set to the sample temperature. The samples for SF-7A and SF-7B were cast out of the same batch of fresh CTB, with only the different high temperature curing applied. As with high-shear mixing, the samples tested were fiber reinforced. Similar densities were observed for both silica fume sources, but the removal of 25% of silica fume for SF-2 caused a significant reduction in compressive strength. The decrease in silica fume also caused a small reduction in density when compared to SF-7 samples. The reduction in strength was to be expected because less silica fume was available to fill small voids in the matrix and for secondary pozzolanic reaction. For the SF-7 samples, the steam generator samples were marginally stronger than the hot water bath samples. While only a small increase, these results suggest that the use of a steam generator is more effective than the use of a hot water bath. Certainly, the use of a steam generator is more practical as sample size increases.

Table 5. Traditional rotating drum mixing results.

Property/Batch	SF-2	SF-7A	SF-7B
ρ – lb/ft^3 (kg/m^3)	160.6 (2573)	162.4 (2601)	162.4 (2601)
f_c' – ksi (MPa)	23.6 (163)	26.4 (182)	27.3 (188)

5. Conclusions

The present study used three different mixing techniques to study eight distinct silica fume sources. The findings of this study suggest the following conclusions:

- When used in small batches, the agglomerations in densified silica fumes may not adequately break apart. This can lead to higher than expected fluidity and segregation of fibers.
- When using larger batches and high intensity mixing, there was no significant differences in hardened properties observed between UHPC made with densified or undensified silica fumes. However, with low intensity mixing such as a traditional rotating drum, the agglomerations in densified sililca fumes may still not adequately disperse. The resulting increased fluidity led to different adjustments to the baseline mixture proportion than with undensified silica fume.
- The use of a steam generator and steam blanket for high temperature curing of UHPC was more effective than the use of a hot water bath set at the same temperature.
- Results suggest that silica fumes with an apparent $d_{50} \leq 1$ μm are best suited for the production of suitable UHPC. Selection of silica fume should be based on performance in matrix.

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