

# Understanding the Temporary Water Binding Potential of Very-Fine Grained Materials

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## Abstract

Ultra-high-performance concrete is generally developed through the mixing of multiple fine to very fine powders with limited volumes of water and admixtures leading to increased mixing time and difficulty. Because water content is critical to development of a hydrated microstructure in these low content composites, as well as to facilitate easier and more efficient mixing, water demand at very early ages must be well characterized and understood. Traditional ASTM methods are insufficient for characterizing the water demand of very-fine grained materials like silica fumes used in UHPC due to the difficulty in ascertaining their saturated surface dry conditions. This study considered several alternate approaches to quantify the required water demand for such constituents of a UHPC mixture and discusses the necessity of including these characteristics in proper mixture design. Alternate approaches considered included statistical approximation, atmospheric absorption, vacuum filtration, and dynamic vapor sorption analyses. Advantages and disadvantages of each approach are discussed, and recommendations for preferred protocols and analysis are given.

**Keywords:** Material characterization; water demand; mixing; workability; rheology

## 1. Background

Previous research by the authors has shown how silica fume substitution in ultra-high performance concrete (UHPC) mixtures is not as straightforward as many assume. Depending on the mixture composition, some silica fumes can be successfully incorporated with little adjustment while others prove exceptionally challenging. Even with successful incorporation, production of workable mixtures often proves difficult (Burroughs et al. 2016). Further research has shown the absorption capacity of silica fumes during early ages must be considered in order to predict how difficult it is to incorporate a given silica fume during mixing and thereby forecast expected fluidity (Burroughs et al. 2020). Determining this absorption capacity requires the application of novel techniques, as no standard test method for absorption capacity of very-fine grained materials currently exists. This paper focuses on four different novel techniques for estimating absorption capacity of such materials and provides recommendations for preferred testing protocols for silica fumes and other fine-grained materials used to develop UHPC mixture proportions moving forward.

## 2. Materials

Seven commercially available silica fumes were considered for this analysis. Three products (SF1, SF2, and SF4) were described by the supplier as undensified silica fumes or microsilica, meaning little to no processing was performed on the materials after they were collected as an industrial waste product. The remaining four silica fumes were described as densified, meaning pneumatic pressure was applied to the raw waste stream to intentionally cause agglomerations to occur. The agglomerated form is used to facilitate easier material handling and reduce dust during use. Particle size distributions for each silica fume determined using laser diffraction analysis are shown in Figure 1. Table 1 includes additional characterization data for each silica fume including specific surface area (SSA), specific gravity ( $G_s$ ), loss on ignition (LOI), silica content ( $\text{SiO}_2$ ), and calcium oxide content (CaO). SSA was determined in accordance with ASTM C1069 (ASTM International 2014) using the Brunauer-Emmett-Teller (BET) method and nitrogen gas. Specific gravity was determined in accordance with ASTM C1240 (ASTM International 2015a) with modifications made for SF5. Chemical analysis showed that SF5 contained 19.5% CaO, so kerosene was used for analysis rather than water to prevent any hydraulic reactivity. Each of the other six silica fumes contained less than 2.0% CaO, so hydraulic activity was not expected. LOI was determined in accordance with ASTM C1240 (ASTM International 2015a) by firing each specimen at 750 °C (1382 °F) for 45 minutes and allowing specimen to cool to room temperature in a desiccator prior to weighing.

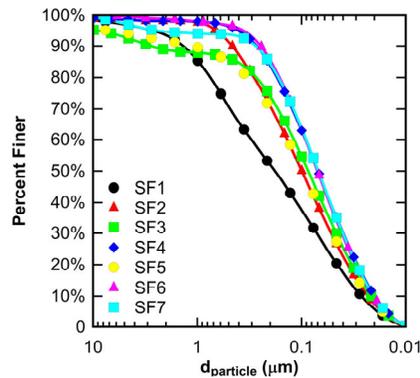


Figure 1. Silica fume particle size distributions ( $1 \mu\text{m} = 3.94 \times 10^{-5} \text{ in.}$ )

Table 1. Silica fume characteristics.

Property	SF1	SF2	SF3	SF4	SF5	SF6	SF7
SSA ( $\text{m}^2/\text{g}$ )	18.1	29.3	22.0	29.4	25.7	24.0	22.8
$G_s$	2.37	2.23	2.30	2.23	2.23	2.26	2.21
LOI (%)	0.9	0.9	2.0	0.9	5.1	2.5	2.0
$\text{SiO}_2$ (%)	92.2	95.9	83.4	97.8	70.0	90.4	94.3
CaO (%)	1.5	0.3	0.9	0.3	19.5	0.6	0.6
Notes: 1 ft = 0.31 m; 1 lb = 453.6 g							

### 3. Methods

Due to the very small average particle size ( $\sim 100$  nm/ $3.94 \times 10^{-6}$  in.) of silica fume, traditional absorption techniques for materials in concrete were not suitable for these materials. ASTM C127 (ASTM International 2015b) is only applicable to coarse aggregates and requires the physical drying of surfaces for testing. The surfaces of silica fume particles can be finer than can be seen with the human eye, so physical drying is not feasible. ASTM C128 (ASTM International 2015c) is applicable for fine aggregates but deemed unsuitable for silica fume. This approach requires a sample to be saturated for 24 hours before drying. During the drying process, silica fume particles tend to agglomerate even further, making it impossible to determine when the material reaches saturated-surface-dry (SSD) conditions. Due to these difficulties, four different approaches were used to estimate the absorption capacity of silica fume: statistical approximation, atmospheric absorption, vacuum filtration, and dynamic vapor sorption. Each is described in detail below.

#### 3.1. Statistical Approximation

The first approach used to estimate the absorption capacity of silica fume was statistical approximation based on particle size distribution, density, and specific surface area. The primary advantage of this approach is the rapidity in which absorption capacity can be estimated as it requires no novel information. With the exception of particle size distribution, density and specific surface area are generally included in the technical data sheet provided with each material. It is recommended to perform these measurements to check the supplier's data where possible, but statistical approximation can be performed either way. The primary drawback is that this approach is purely a mathematical approximation; therefore, no actual measurement of absorption is used. The estimation process is as follows, and an example calculation is shown in Table 2.

1. The volume ( $V_{particle}$ ) and surface area ( $A_{s,particle}$ ) of a representative spherical particle in each size bin ( $d_{particle}$ ) is calculated.
2. Assuming a total unit volume ( $V_{assumed}$ ), the number of particles ( $n_{particles}$ ) in each bin is determined by dividing the bin volume ( $f_{vol}V_{assumed}$ ) by the volume of the representative particle ( $V_{particle}$ ).
3. The total surface area within each bin ( $A_{s,bin}$ ) is determined by multiplying the number of particles ( $n_{particles}$ ) in each bin by the surface area of the representative particle ( $A_{s,particle}$ ).
4. The total surface area for the entire distribution ( $A_{s,total}$ ) is determined by summing the bin surface areas ( $A_{s,bin}$ ).
5. The mass of the distribution ( $m_{distribution}$ ) is determined by dividing the total surface area ( $A_{s,total}$ ) by the specific surface area (SSA).
6. The actual volume ( $V_{total}$ ) is determined by dividing the mass of the distribution ( $m_{distribution}$ ) by the measured density ( $\rho$ ).
7. The percentage of solids in the distribution ( $p_{solids}$ ) is determined by dividing the total volume ( $V_{total}$ ) by the assumed volume ( $V_{assumed}$ ).
8. The porosity ( $\Phi$ ) is determined by subtracting the percentage of solids ( $p_{solids}$ ) from 1.

9. The volume of water required to fill the porosity ( $V_{water}$ ) is determined by multiplying the porosity ( $\Phi$ ) by the total volume ( $V_{total}$ ).
10. The mass of water required to fill the porosity ( $m_{water}$ ) is determined by multiplying the volume of water ( $V_{water}$ ) by the density of water ( $\rho_{water}$ ).
11. The mass absorption capacity ( $a_{SA}$ ) is calculated by dividing the mass of water required to fill the porosity ( $m_{water}$ ) by the mass of the distribution ( $m_{distribution}$ ).

**Table 2. Example calculation for statistical approximation of absorption capacity.**

$d_{particle}$ (nm)	$V_{particle}$ (nm <sup>3</sup> )	$A_{s,particle}$ (nm <sup>2</sup> )	$f_{vol}$	$f_{vol}V_{assumed}$ ( $\mu\text{m}^2$ )	$n_{particles}$	$A_{s,bin}$ ( $\mu\text{m}^2$ )
52.6	76100	8680	2.73%	0.027	359	3.12
All Other Diameters			97.27%	0.973	44800	71.88
$V_{assumed}$ ( $\mu\text{m}^3$ )						1
$A_{s,total}$ ( $\mu\text{m}^2$ )						75.0
$SSA$ (m <sup>2</sup> /g)						18.1
$m_{distribution}$ (pg)						4.14
$\rho_{measured}$ (g/cm <sup>3</sup> )						2.36
$V_{total}$ ( $\mu\text{m}^3$ )						1.75
$\rho_{solids}$						0.571
$\Phi_{volumetric}$						0.429
$V_{water}$ ( $\mu\text{m}^3$ )						0.75
$m_{water}$ (pg)						0.75
$a_{SA}$ (%)						18.1
Notes: 1 ft = 0.31 m; 1 lb = 453.6 g						

### 3.2. Atmospheric Absorption

Atmospheric absorption involved suspending specimens of silica fume above a reservoir of distilled water in a sealed container. The reservoir of water below caused the humidity within the chamber and the moisture content of silica fume specimens to change as the sealed system approached equilibrium. Minor fluctuations in laboratory temperature also caused changes in chamber humidity. Mass change of specimens was recorded over a 13-month period to measure the amount of moisture absorbed by the silica fumes. This test setup and the raw data collected are shown in Figure 2. Advantages to this approach include simple test setup and data interpretation. The main disadvantages are the time required for the mass of each specimen to stabilize and the potential underestimation of absorption capacity as the specimens are never exposed to liquid water. As shown in Figure 2, some specimens, such as SF3, had obviously stabilized after 400 days, while others, such as SF4, were still trending upward at least slightly. Some of the apparent noise in the data over the testing period is certainly attributable to changes in humidity in the chamber as a result of having to open the container to weigh each specimen.

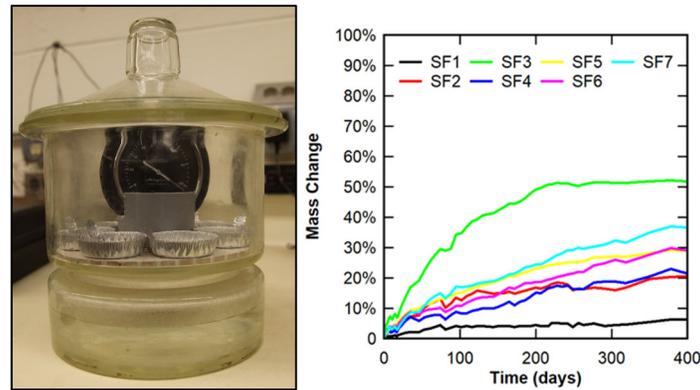


Figure 2. Atmospheric absorption setup (left) and raw data (right).

### 3.3. Vacuum Filtration

The vacuum filtration technique involved filtering solutions of silica fume and distilled water mixed in prescribed ways through a fine filter ( $0.22 \mu\text{m}/8.7 \times 10^{-6} \text{ in.}$ ) under vacuum until no additional water was readily removed. While some very fine particles of silica fume were able to pass through the filter, the vast majority of particles remained agglomerated on the filter. The moisture content of the material remaining on the filter was then determined after drying overnight in a  $105^\circ\text{C}$  ( $221^\circ\text{F}$ ) oven. Suspensions of silica fume and distilled water were combined using three approaches: as-received, after shear mixing, and after sonication. The as-received specimens were prepared by simply pouring distilled water into a beaker containing silica fume and allowing the turbulence created to blend the materials. Other specimens were mixed using a paddle mixer for five minutes at different rates (100, 200, and 500 RPM) to see what effect shear rate had on the measurements. Lastly, additional specimens were prepared by sonicating silica fume in distilled water for 10 minutes using a 700 W ultrasonication probe. The vacuum filtration setup is shown in **Error! Reference source not found.** Advantages to this approach included rapidity of testing (less than 24 hours) and physical inundation of each specimen with excess liquid water. The main drawback to this approach was the difficulty in determining when SSD condition was reached. Visual examination of the specimen could not be used as a determining factor for SSD because exposed surfaces always reached approximate SSD condition well before internal surfaces. For consistency of measurement, the vacuum filtration test continued until at least 60 seconds elapsed between successive water droplets descended from the test specimen.



Figure 3. Vacuum filtration test setup.

### 3.4. Dynamic Vapor Sorption

Dynamic vapor sorption (DVS) is an approach that measures the change in mass of materials over time when exposed to sweeps of relative humidity (RH) at a constant temperature. For this study, silica fume specimens were exposed to an adsorption sweep from 5% to 95% RH in 5% RH increments at  $23^\circ\text{C}$  and a desorption sweep from 95% to 5% RH in 5% RH increments at

23°C. The raw data were then fit to the Double Log Polynomial (DLP) model, as shown in Equation 1. An example plot of adsorption and desorption sweeps with DLP fits is shown in Figure 4. Absorption capacity was calculated as the average of the extrapolated DLP fits at 100% RH for both the adsorption and desorption sweeps. The expected moisture content at 100% RH had to be extrapolated due to equipment constraints. Advantages of the DVS approach include high fidelity data and control over moisture conditions. Furthermore, DVS can be performed on a material in a reasonable amount of time, with the average test taking less than a week. Depending on the model of analyzer used, multiple specimens can even be analyzed in parallel, significantly reducing the time needed to study multiple silica fumes or estimate variability within a single source. The main disadvantage is the requirement for specialized equipment with such equipment typically only found in an academic type environment.

$$m = \beta_3[\ln(-\ln(RH))]^3 + \beta_2[\ln(-\ln(RH))]^2 + \beta_1[\ln(-\ln(RH))] + \beta_0 \quad (1)$$

Where,

$m$  = moisture content

$RH$  = relative humidity

$\beta_i$  = model coefficients

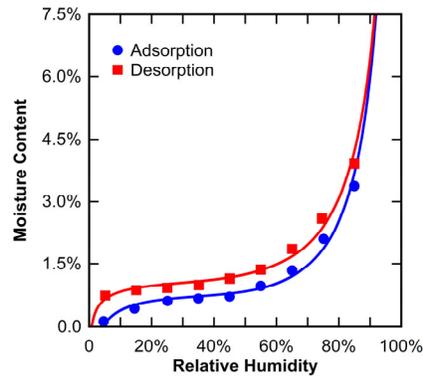


Figure 4. Example DVS plot with DLP fits.

#### 4. Results and Discussion

Tabulated results for each of the four test protocols is given in Table 3. Statistical approximation shows the least variability across the seven silica fumes, whereas DVS shows the greatest differences between silica fumes. Approaches that showed greater delineation between the seven silica fumes are more desirable in classifying these materials. When comparing the different mixing styles for vacuum filtration, the general trend shows a noticeable reduction in residual moisture for the sonicated samples. This is most likely a result of less water being held in the void space contained in agglomerations of particles. As such, the sonicated specimens provide the most realistic results for the vacuum filtration approach. Without sonication, the vacuum filtration approach most likely overestimates absorption capacity, especially for undensified silica fumes. Results for densified silica fumes are more realistic. Across the other three techniques, SF1

showed the least absorption/water-binding potential, and SF3 showed the greatest. Densified silica fumes tended to temporarily bind more water than undensified fumes, most likely due to the presence of void space within the intentionally agglomerated clusters.

**Table 3. Estimated absorption capacity by various techniques.**

Silica Fume	$a_{SA}$ (%)	$a_{AA}$ (%)	$a_{VF,AR}$ (%)	$a_{VF,100 RPM}$ (%)	$a_{VF,200 RPM}$ (%)	$a_{VF,500 RPM}$ (%)	$a_{VF,Sonicated}$ (%)	$a_{DVS}$ (%)
SF1	18.1	6.4	121.9	115.9	95.2	94.5	38.6	11.2
SF2	14.8	20.6	198.2	159.5	149.2	147.3	64.6	77.9
SF3	22.5	52.2	63.5	58.7	57.5	59.7	38.7	123.9
SF4	20.5	23.0	192.4	168.9	145.6	152.3	64.1	55.3
SF5	18.5	29.2	67.3	68.1	57.7	57.6	68.9	39.6
SF6	24.0	29.9	73.0	53.4	51.3	67.7	47.0	72.7
SF7	26.2	36.9	60.3	47.3	46.6	56.7	32.0	68.4

Regardless of the technique used, the biggest takeaway from this study is that silica fume particles do absorb or temporarily bind water to some degree. Both the atmospheric absorption and DVS techniques showed a roughly tenfold increase between low absorption and high absorption silica fumes. As these two techniques were the most experimentally rigorous approaches used, there is strong suggestion that such ranges in silica fume absorption capacity exist. Based on testing difficulty, control, and confidence in data, it is recommended that DVS be used to analyze the potential absorption capacity of very-fine grained materials. The least reliable method is vacuum filtration due to the inherent difficulty to determine approximate SSD conditions with this approach.

Characterization data such as this is incredibly useful when choosing materials for use in a UHPC. Figure 5 shows the associated water demand for mixing each of the seven silica fumes tested. The statistic shown on the y-axis ( $t_{coating}$ ) is calculated using the Water Thickness Model developed by the authors and published elsewhere considering a 1:1 mass ratio of silica fume to water (Burroughs et al. 2020). Greater positive amplitudes represent excess water coating each particle in suspension and thus less water demand. An amplitude of zero indicates that the silica fume has reached SSD conditions, and negative amplitudes indicate additional water is needed to bring that material to SSD. Calculations were performed using the DVS estimates of absorption capacity. As shown, SF1 was clearly the silica fume that could most readily be expected to incorporate into a UHPC, having more than double the excess water than seen with any other silica fume. On the opposite end of the spectrum, SF3 would not reach SSD in these conditions, making its usefulness for UHPC production very low. Statistics such as this could be used to grade silica fumes (and other very-fine grained materials) for use in mixing UHPC. Other factors such as pozzolanic reactivity certainly must also be considered when choosing materials for use in UHPC; however, reactivity is irrelevant to consider if a material cannot be successfully incorporated into a matrix to process a placeable UHPC.

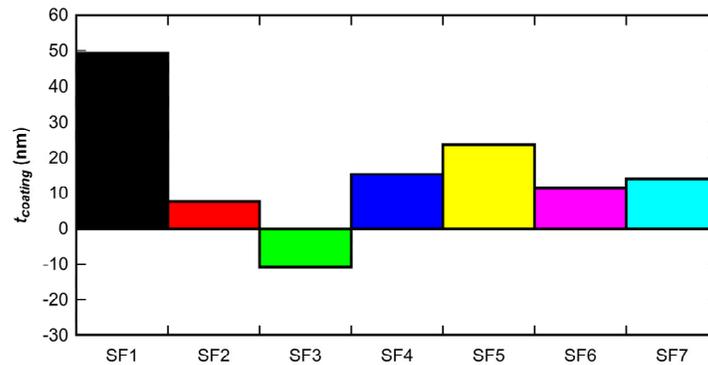


Figure 5. Water demand for mixing of each silica fume. (1 nm =  $3.94 \times 10^{-8}$  in.).

## 5. Conclusions

Very fine-grained materials such as silica fume have the potential to absorb or temporarily bind water during the mixing process of concrete. Due to the increased volumes of such materials being used in the production of UHPC, it is critical that this material property be analyzed and understood before incorporation in a mixture proportion. Of the four different approaches used in this study, dynamic vapor sorption is recommended as the most appropriate way to determine this absorption capacity, as this approach gives high fidelity results in a reasonable amount of time (typically less than one week). The absorption capacity measured using these approaches can be used in conjunction with models previously published in the literature to grade very-fine grained materials with respect to their use in successfully mixing UHPC.

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