



## Uncovering the role of micro silica in hydration of ultra-high performance concrete (UHPC)

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### ABSTRACT

This study aims to clarify the role of micro silica in hydration of UHPC. The behavior of two different types of micro silica in UHPC was investigated with regard to their filler effect and pozzolanic reaction by using analytical techniques; XRD, TG, <sup>29</sup>Si and <sup>27</sup>Al NMR spectroscopy, and MIP. The micro silica with high pozzolanic activity led to the higher level of Al-substitution for Si in C-S-H and the denser structure, thus increasing compressive strength, whereas that facilitating filler effect limited the consumption of Ca(OH)<sub>2</sub> even after high temperature curing and led to the higher amount of AFm phase. In the UHPC showing high filler effect, additional hydration of C<sub>3</sub>S and C<sub>2</sub>S occurred at later ages, increasing the fraction of Q<sup>1</sup> site in C-S-H and decreasing the porosity in the pore diameter region below 10 nm. Consequently, a significant increase in the compressive strength of this UHPC was achieved.

### 1. Introduction

Ultra-high performance concrete (UHPC) was recently defined as a cement-based composite with a compressive strength exceeding 150 MPa [1]. UHPC is typically fabricated using cement, water, micro silica, filler and fine aggregate as well as superplasticizer. The most distinctive properties of UHPC are extremely low porosity and high packing density, resulting from particles with widely distributed diameters ranging from 0.1 to 1000 μm and a water-to-cement (w/c) ratio as low as 0.20. The key feature in the material design of UHPC is the use of amorphous silica which can be classified into silica fume, micro silica and nano silica, etc., according to their particle size and physical property. The distinct characteristics of UHPC such as workability and mechanical strength are considerably dependent on physical properties and types of amorphous silica used.

Amorphous silica, which consists solely or mostly of SiO<sub>2</sub>, plays a role in improving the rheology and the mechanical performance of UHPC due to their inherited properties (e.g. high purity, spherical particle with very fine size, high pozzolanic activity [2,49,51] and high specific surface areas) [3]. One of commonly used amorphous silica is silica fume which is a by-product of industrial silicon production and it has particle sizes in the sub-micrometer range. The generally known behavior of amorphous silica in UHPC is twofold as follows. First is

pozzolanic reaction in which the incorporated micro silica reacts with portlandite (Ca(OH)<sub>2</sub>, CH) resulted from the hydration of alite [4,5,50]. Second, the particle size of amorphous silica ranging in sub-micrometers is effective for filling the voids present among cement particles and other constituent materials, termed as filler effect [4].

Cement matrix is significantly densified by the filler effect, since the voids present in the matrix can be filled with undissolved silica particles [6,7]. Another principle of filler effect is that nucleation of calcium silicate hydrate (C-S-H) phases which are formed from alite hydration occurs on the surface of filler materials [2,8]; this effect accelerates cement hydration and is more precisely termed as the seeding effect [9,10,11]. Incorporation of supplementary cementitious materials (SCMs) such as amorphous silica in cement may act as nucleation sites for the growth of C-S-H [17], and similar effect can be anticipated by incorporating other mineral powders (e.g., quartz [13], rutile [14], limestone [15,16], synthetic C-S-H [10,17]). In general, filler effect of amorphous silica is accepted to accelerate the hydration of the clinker phases (especially, C<sub>3</sub>A and C<sub>3</sub>S) at an early age, while pozzolanic reaction of amorphous silica starts at a later stage and is enhanced with pH and temperature [2].

It should be noted that pozzolanic reaction of amorphous silica with CH to form C-S-H gel is limited due to the very low w/c ratio (< 0.25 by mass) of UHPC system, instead the role of amorphous silica

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predominantly facilitates the filler effect [18]. Even though filler effect and pozzolanic reaction were found to be clearly inclusive of each other [5], the filler effect is a more notable phenomenon in UHPC than in other concrete blended with SCMs. The incorporation of a large amount of amorphous silica in UHPC mixture and its low w/c ratio can promote filler effect rather than pozzolanic reaction. Especially during early ages (< 24 h), amorphous silica is anticipated to most dominantly behave as a filler in UHPC, which increases hydration rates by seeding effect [19,20], while pozzolanic reaction is probably negligible due to the relatively low alkalinity of the pore solution at this stage [2].

Some researchers experimentally demonstrated an enhanced hydration degree of cement at early age by incorporating silica fume with small size particles and high surface area, which effectively increases the extent of C-S-H nucleation [11,21,22]. However, the surface area of amorphous silica is not always correlated with the extent of the seeding effect, and its reactivity is also a governing factor. For instance, if one is easily dissolved due to its high reactivity, its filler effect is less likely and the pozzolanic reaction is to be dominant. On the other hand, another one with relatively low reactivity but greater particle size can be more favorable for the filler effect, since undissolved particles can play a role of nucleation seeding. In a previous study, it was found that the reactivity of three types of silica (Pyrogenic silica, silica fume and Stoeber silica) had a close relation with the specific surface area, surface silanol group density, total content of silanol groups and solubility in alkaline suspension [4]. It was revealed that the degree of pozzolanic reaction was higher for Stoeber particles (with higher amount of silanol group) than for the less reactive pyrogenic silica and silica fume (with lower surface silanol group density and lower total amount of silanol groups). In their later study, silica fume and pyrogenic silica was found to accelerate the alite hydration by increasing the surface for nucleation of C-S-H phases whereas Stoeber particles showed no accelerating effect [5].

Filler effect is more likely to accelerate the hydration of aluminate phases, which normally gives rise to a second or shoulder peak in a calorimetric curve after the main peak associated with the hydration of alite, rather than that of calcium silicate phases [2,23]. The additions of the fine materials, i.e., corundum and rutile, have much more significant impact on the aluminate reaction than on the silicate reaction, as the hydration of the aluminate phases is often more sensitive to nucleation effects [23]. In other studies [11,24], it was found that the high surface area of amorphous silica has a high capacity to adsorb sulfate ions, and the decreased sulfate concentration accelerates the formation of monosulfate. At the same time, the change in the sulfate concentration also influenced the dissolution and formation of sulfate containing phases [11].

To date, the filler effect and pozzolanic reaction of amorphous silica in UHPC have been investigated in a limited number of studies. In more detail, the influence of the two different behaviors (filler effect and pozzolanic reaction) of micro silica on the hydration and microstructure of UHPC has been poorly understood. In this regard, this paper investigated the role of micro silica in hydration and strength of UHPC. Two types of micro silica with different extent of pozzolanic reactivity and filler effect were considered: one is silica fume and another one is amorphous silica containing a minor quantity of zirconium. The water adsorption/desorption rate, surface area, and particle size of the micro silica were measured, and the correlation of the results with the hydration and strength development of UHPC was discussed. The role of micro silica in UHPC were investigated with regard to their filler effect and pozzolanic reaction by using analytical techniques; X-ray diffraction (XRD), thermogravimetry (TG), nuclear magnetic resonance (NMR) spectroscopy, and mercury intrusion porosimetry (MIP).

**Table 1**

Chemical composition of binder materials used in this study.

(wt%)	OPC		Micro silica-I	Micro silica-II
	XRD Rietveld analysis			
SiO <sub>2</sub>	21.23	C <sub>3</sub> S	59.2	92.0
Al <sub>2</sub> O <sub>3</sub>	5.64	C <sub>2</sub> S	21.9	0.53
Fe <sub>2</sub> O <sub>3</sub>	3.38	C <sub>4</sub> AF	9.2	0.97
CaO	61.4	C <sub>3</sub> A	3.6	0.48
MgO	2.20	Gypsum	2.3	1.18
TiO <sub>2</sub>	0.23	Anhydrite	1.9	–
K <sub>2</sub> O	1.15	Others	1.8	0.70
SO <sub>3</sub>	2.25			0.23
Na <sub>2</sub> O	0.11			0.56
Cl	0.06			0.14
ZnO	0.15			0.17
ZrO <sub>2</sub>	–			–
				4.16

## 2. Experimental procedure

### 2.1. Materials

Ordinary Portland cement (OPC, ASTM C150 Type I) used in this study was provided by Asia Cement Corp., South Korea. Two types of amorphous silica (micro silica-I and -II) were supplied by Elkem Corp., South Korea and S. Corp., China, respectively. Silica powder with diameters of 1–5 μm was used as a fine filler, and micro sand with diameters of 100–800 μm were used as a fine aggregate.

The chemical compositions of these materials are listed in Table 1. Micro silica-I and -II showed very similar chemical compositions in terms of SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub> and CaO, while the micro silica-I contained 1.18% of MgO and the micro silica-II had no MgO. It is noted that only the micro silica-II contained 4.16% of ZrO<sub>2</sub>. The specific gravity of micro silica-I and -II were 2.20 and 2.50, respectively. The mineralogical composition of the anhydrous OPC determined by XRD Rietveld analysis is also listed in Table 1.

The maximum water adsorption/desorption contents of micro silica-I were 56.8 (P/P<sub>0</sub> = 0.9730) and 6.78 cm<sup>3</sup>/g (P/P<sub>0</sub> = 0.0965), respectively, and those of micro silica-II were 10.8 (P/P<sub>0</sub> = 0.9466) and 2.03 cm<sup>3</sup>/g (P/P<sub>0</sub> = 0.0857), as measured using a BELSORP-aqua3 (BEL JAPAN, INC.) instrument. This property may affect the level of slump flow of UHPC by adsorbing some of the mix water in the fresh state. The amount of superplasticizer required to obtain high slump flow of UHPC (> 750 mm) can be varied depend on the type of micro silica with different adsorption content. For instance, micro silica with a higher water adsorption content requires a higher superplasticizer amount to reach similar flow.

The surface area was measured by nitrogen adsorption using a Micromeritics ASAP2420 by degasifying at 300 °C and 1.333 Pa (10 μmHg) for 2 h. The surface areas of micro silica-I and -II were 23.5 and 9.42 m<sup>2</sup>/g, respectively. The micro silica-II used in this study showed the lower surface area than the minimum specific area (15 m<sup>2</sup>/g) for silica fume stated in ASTM C1240.

The particle size distribution of the raw materials was measured using a laser particle-size analyzer (CILAS 1090L, CILAS, FRANCE), and is shown in Fig. 1. The mean particle size of the micro silica-I (0.31 μm) was lower than that of the micro silica-II (0.93 μm).

### 2.2. Mixture proportions and samples preparation

The mixture proportions of UHPC are provided in Table 2. A water-to-binder (cement + micro silica) ratio was 0.187 and a shrinkage reducing agent/cement ratio was 0.01. Superplasticizer-to-cement ratios for UHPC incorporating micro silica-I and -II were 0.023 and 0.062, respectively. The UHPC incorporating the micro silica-II required much

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