# Influence of amorphous silica on the hydration in ultra-high performance concrete

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## ARTICLE INFO

## ABSTRACT

Amorphous silica particles (silica) are used in ultra-high performance concretes to densify the microstructure and accelerate the clinker hydration. It is still unclear whether silica predominantly increases the surface for the nucleation of C–S–H phases or dissolves and reacts pozzolanically. Furthermore, varying types of silica may have different and time dependent effects on the clinker hydration. The effects of different silica types were compared in this study by calorimetric analysis, scanning and transmission electron microscopy, in situ X-ray diffraction and compressive strength measurements. The silica component was silica fume, pyrogenic silica or silica synthesized by a wet-chemical route (Stoeber particles). Water-to-cement ratios were 0.23. Differences are observed between the silica for short reaction times (up to 3 days). Results indicate that silica fume and pyrogenic silica accelerate alite hydration by increasing the surface for nucleation of C–S–H phases whereas Stoeber particles show no accelerating effect.

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## 1. Introduction

The development of high strength concretes goes back to the 1970s [1], but has regained a keen interest leading to new research efforts for ultra-high performance concretes (UHPCs). UHPC is defined by its high compressive strength, dense structure and low capillary porosity [2]. These properties are obtained via a low water-to-cement ratio (w/c < 0.3 by mass), amorphous silica particles (so-called silica) as supplementary material and an optimal packing of the particles [3]. A commonly used silica component is silica fume which is a by-product of the industrial silicon production with particle sizes in the sub-micrometer range [4–6]. Silica with primary particles smaller than 100 nm (so-called nano silica) is increasingly applied to optimize UHPC for highly challenging practical applications [7]. Still, some problems remain unsolved, mostly because results for so-called ordinary concretes (OC), i.e. for concretes with compressive strength lower than approximately 60 MPa and w/c ratios higher than 0.35 by mass, cannot be transferred to UHPCs in all cases. At least for stoichiometric reasons, the amount of water ($H$)[1] is insufficient in UHPC for a complete

hydration of the clinker minerals (alite $C_3S$, belite $C_2S$, aluminate $C_3A$ and aluminate ferrite $C_4AF$)[1] and less portlandite and water is available for the pozzolanic reaction of silica in comparison to OC.

Two reaction processes should be considered in UHPC containing silica:

- The silica surface works as a nucleation center for the formation of calcium silicate hydrate phases (C–S–H phases, $C_xS_uH_{w+x}$, $C_3S_2H_4$)[1] produced by hydration of (e.g.) alite (Eq. (1)), the so-called seeding effect [8–12].
- Silica ($S$)[1] reacts pozzolanically (Eq. (2)) with portlandite ($CH$)[1] produced by hydration of (e.g.) alite (Eq. (1)) [13–16].

$$2C_3S + 7H \rightarrow C_3S_2H_4 + 3CH \tag{1}$$

$$uS + xCH + wH \rightarrow C_xS_uH_{w+x} \tag{2}$$

Clearly, the two processes do not exclude each other, but there may be a chance to observe different reaction products at comparable reaction times for the two processes.

Undissolved silica particles may generally form a denser microstructure by reducing voids between the other solid concrete components

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[1] $H = H_2O$, $C = CaO$, $S = SiO_2$, $A = Al_2O_3$ and $F = Fe_2O_3$ according to conventional cement chemistry notation

(so-called filler effect) [4,17,18]. The seeding effect is one of the principal mechanisms contributing to the filler effect [10]. Further mechanisms of the filler effect (e.g. increase of particle packing density) were not in the scope of this study, but were partly studied before by Oertel et al. [19].

Previously, we examined the reactivity of varying types of silica (silica fume, pyrogenic silica and silica synthesized by hydrolysis and condensation of alkoxy silanes, so-called Stoeber particles) and further traced the reactions of these silica in pastes with a low w/c ratio within the first hour of hydration [20]. The reactivities of the silica were classified from highest to lowest based on the surface silanol group density, total content of silanol groups and solubility in alkaline suspension: Stoeber particles ≫ pyrogenic silica > silica fume. Our experimental results gave no indication for the seeding effect or the pozzolanic reaction within the first hour of hydration. Instead, it was assumed that silicate ions react with cations ($Na^+$, $K^+$ and $Ca^{2+}$) from the pore solution to alkali silicate oligomers and calcium silicate oligomers. The amount of silicate ions and oligomers depends on the reactivity of the silica.

The aim of this study is to compare the effects of various types of silica on the hydration process in cementitious systems with a low w/c ratio and to correlate the observations with the reactivity of the silica. Thereby, the emphasis was to evaluate the effects of silica in practical relevant paste and mortar formulations. Heat flow calorimetry (up to 7 days) and measurements of the compressive strength (2, 7 and 28 days) are used to examine the overall evolution of the hydration reactions. The content of crystalline phases is detected by in situ X-ray diffraction (XRD, up to 3 days). The microstructure of the pastes is investigated 20 h after mixing by transmission electron microscopy (TEM) and scanning electron microscopy (SEM). Herein, the samples were prepared using cross section polishing (CSP) [21] and focused ion beam technique (FIB) [22] which are both relatively new to the cementitious community. Paste and mortars are formulated with a w/c ratio and a silica content which are typical for UHPC. This combination of exterior and in situ methods helped to draw a clearer picture on the overall hydration of real UHPC systems containing various types of reactive silica.

## 2. Experimental procedures

### 2.1. Materials

The following types of silica were used which are identical to previous studies [19,20]: silica fume (Silicoll P®, Sika GmbH, Germany, undensified powder, mean particle size of 283 nm), pyrogenic silica (AEROSIL® OX 50, Evonik Industries, Germany, powder, mean particle size of 197 nm) and Stoeber particles (prepared at Fraunhofer–Institute ISC based on the Stoeber process [23], mean particle size of 242 nm, aqueous suspension 50 wt%). Details on their properties (morphology, specific surface area, $SiO_2$ content, surface silanol group densities, content of silanol groups and solubilities in alkaline suspension) and the synthesis of Stoeber particles were given by Oertel et al. [19,20]. In detail, the specific surface area is almost similar for silica fume (20 $m^2/g$) and Stoeber particles (17 $m^2/g$), whereas it is twice as high for pyrogenic silica (38 $m^2/g$).

Silica fume and pyrogenic silica are formed in high temperature processes [5,24], whereas Stoeber particles are synthesized at ambient temperatures.

Pastes were prepared as described by Oertel et al. [19,20] using silica, Portland cement (CEM I 52.5R HS/NA, Holcim Sulfo 5, Holcim AG, Germany, content[2] of clinker minerals in wt%: $C_3S$ 64.6, $C_2S$ 12.8, $C_3A$ 0.2, $C_4AF$ 16.6), superplasticizer (polycarboxylate ether, SikaViscoCrete®–2810, Sika GmbH, Germany, water content of 60 wt% considered in the calculation of the w/c ratio) and de-ionized water.

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[2] Provided by the supplier.

Mortars were composed of silica, Portland cement, superplasticizer, de-ionized water, quartz powder (W12: 0.3–110 μm, Quarzwerke Frechen, Germany) and quartz sand (F32: 0.125–0.5 mm, Quarzwerke Frechen, Germany). They were mixed under similar conditions but with an intensive mixer (Eirich EL1, rotation speed: 1000 rpm).

The formulations of the pastes and mortars were based on UHPC formulated by Fröhlich and Schmidt [25] with a w/c ratio of 0.23 by mass (Table 1). Furthermore, samples without any addition of silica were prepared.

### 2.2. Characterization methods

Mortars were used for the compressive strength measurements and pastes for all other characterization methods.

Heat flow calorimetry was measured using a cement calorimeter MC CAL® (isothermal conditions, 20 °C, step size 60 s). The pastes (mass: 8.54 g for pastes without silica, 10 g for pastes containing silica) were mixed outside the calorimeter in a vibrating mixer (adjusted mixing procedure: 0.5 min without particles, 1 min containing silica fume or Stoeber particles, 7 min containing pyrogenic silica). A second sample (control sample) was measured for each paste and showed values similar to the first sample.

Paste samples for SEM (Carl Zeiss Supra 25 microscope) and TEM (JEOL JEM 2011 microscope, 200 kV, approximately −180 °C, in annular dark field mode) analyses were stored at 20 °C ± 1 °C in small plastic vessels properly sealed to avoid evaporation of water. The hydration process of the samples was stopped after 20 h by solvent replacement using isopropyl alcohol. Samples were further rinsed with acetone, dried at 40 °C and stored in argon until samples were prepared using CSP (JEOL SM–09010) and FIB (FEI Quanta 200 3D). The benefits of those methods are that they only deteriorate the material to a minimum extent and further allow the preparation of translucent lamellae being necessary for TEM analyses. The samples were stored in nitrogen during preparation to avoid carbonation. Energy dispersive X-ray spectroscopy (EDX) was conducted without a standard. The interaction area of the electron beam is reduced remarkably due to the thin lamella allowing EDX line scans with high resolution.

In situ XRD analyses were recorded with a PANalytical X'Pert Pro diffractometer using Cu Kα1/2 radiation. Fluorescence was suppressed by a secondary nickel filter. Details of the parameter configuration are listed in Table 2. Samples were transferred to the holder immediately after mixing; the surface was smoothed and also sealed with a Kapton® polyimide film to prevent evaporation of water. Measurements were taken with an X'Celerator detector (counting time 21 s) 10 min, 1 h, 2 h, 4 h, 5 h, 10 h, 20 h, 30 h, 40 h, 50 h 60 h and 72 h after mixing. A qualitative analysis for the first hour of hydration was previously given in [20].

A Philips PW 1710 diffractometer (Cu Kα, equipped with a secondary monochromator) was used for subsequent XRD measurements (step size 0.02°, counting time 2 s). Samples were prepared on a sapphire single crystal.

A ToniZEM device was used to measure compressive strengths of mortars after 2, 7 and 28 days. Thirty specimens (die: 2 × 2 × 2 cm$^3$)

**Table 1**
Composition of pastes and mortars based on the UHPC formulation M3Q [25] with w/c = 0.23 by mass.

| Material | Density [g/cm$^3$] | Paste: content per volume [kg/m$^3$] | Mortar: content per volume [kg/m$^3$] |
|---|---|---|---|
| Water | 1.0 | 175.0 | 175.0 |
| Portland cement | 3.0 | 825.0 | 825.0 |
| Silica | 2.2 | 175.0 | 175.0 |
| Superplasticizer | 1.1 | 27.5 | 27.5 |
| Quartz sand | 2.7 | – | 975 |
| Quartz powder | 2.7 | – | 200 |

The water content of the superplasticizer (60 wt%) is considered in the w/c ratio.