



Amorphous silica in ultra-high performance concrete: First hour of hydration



Tina Oertel^{a,b,*}, Frank Hutter^a, Uta Helbig^c, Gerhard Sextl^{a,d}

^a Fraunhofer-Institute for Silicate Research ISC, Neunerplatz 2, 97082 Würzburg, Germany

^b Chair for Inorganic Chemistry I, Universität Bayreuth, Universitätsstr. 30, 95440 Bayreuth, Germany

^c Chair for Crystallography and X-ray Methods, Technische Hochschule Nürnberg Georg Simon Ohm, Wassertorstraße 10, 90489 Nürnberg, Germany

^d Chair for Chemical Technology of Advanced Materials, Julius Maximilian Universität, Röntgenring 11, 97070 Würzburg, Germany

ARTICLE INFO

Article history:

Received 7 June 2013

Accepted 7 January 2014

Available online xxx

Keywords:

Silica fume (D)

Amorphous material (B)

Hydration (A)

Cement paste (D)

Ultra-high performance concrete

ABSTRACT

Amorphous silica in the sub-micrometer size range is widely used to accelerate cement hydration. Investigations including properties of silica which differ from the specific surface area are rare. In this study, the reactivity of varying types of silica was evaluated based on their specific surface area, surface silanol group density, content of silanol groups and solubility in an alkaline suspension. Pyrogenic silica, silica fume and silica synthesized by hydrolysis and condensation of alkoxy silanes, so-called Stoeber particles, were employed. Influences of the silica within the first hour were further examined in pastes with water/cement ratios of 0.23 using in-situ X-ray diffraction, cryo scanning electron microscopy and pore solution analysis. It was shown that Stoeber particles change the composition of the pore solution. Na^+ , K^+ , Ca^{2+} and silicate ions seem to react to oligomers. The extent of this reaction might be highest for Stoeber particles due to their high reactivity.

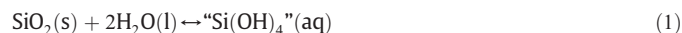
© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

Ultra-high performance concrete (UHPC) was recently defined by Naaman and Wille [1] as a cement-based concrete with a compressive strength at least equal to 150 N/mm^2 . This very dense and durable concrete is achieved by reducing the water/cement ratio (w/c ratio) to less than 0.3 by mass and by adding amorphous silica [2,3]. Silica fume is the most commonly used amorphous silica in cementitious systems. Its beneficial influence on concrete properties has been known since the 1950s but the topic is currently regaining considerable interest with a new focus on silica components with primary particles smaller than 100 nm, so-called nano silica. Those nano silica could further improve UHPC because of their advanced properties (e.g. higher purities, smaller primary particles and higher specific surface areas) [4].

Before the effects of silica in cementitious systems are discussed, the dissolution of silica in highly alkaline solutions needs to be considered. The chemical reactions involved are fundamental to describe the reaction mechanisms of silica components in cementitious systems. In water, the silica surface and monosilicic acid (“ $\text{Si}(\text{OH})_4$ ”, the quotation mark refers to uncertainties about its stability) exhibit a depolymerization–polymerization equilibrium shown in Eq. (1) [5]. “ $\text{Si}(\text{OH})_4$ ” is only stable for low concentrations (less than $2 \cdot 10^{-3} \text{ M}$). Otherwise,

“ $\text{Si}(\text{OH})_4$ ” and silicate ions (e.g. H_3SiO_4^-) condense to polysilicic acids of low molecular weight (so-called oligomeric silicate species, Eq. (2)) [5,6].



Silicate ions (H_3SiO_4^- , $\text{H}_2\text{SiO}_4^{2-}$, HSiO_4^{3-} and SiO_4^{4-}) are formed by deprotonation of “ $\text{Si}(\text{OH})_4$ ” (e.g. H_3SiO_4^- according to Eq. (3)) when the pH is above 9 and by dissolution of silica (e.g. H_3SiO_4^- according to Eq. (4)) when the pH rises above 10.7 [5]. Oligomerization and dissolution of silica proceed simultaneously.



The hydration of the Portland cement clinker minerals^{1,2} (alite C_3S , belite C_2S , aluminate C_3A and aluminate ferrite C_4AF) is a complex reaction and its sub-processes are still under investigation [7]. The main processes, however, are well known [7–11]. Generally, alite hydrates and forms portlandite¹ (CH) and calcium silicate hydrate phases¹ (C–S–H

¹ Abbreviations are according to the conventional cement chemistry notation: C = CaO, S = SiO_2 , A = Al_2O_3 , F = Fe_2O_3 , H = H_2O and S = SO_3 .

² Alite, belite, aluminate and aluminate ferrite contain impurities. Therefore their chemical composition is slightly different than the composition of the pure minerals C_3S , C_2S , C_3A and C_4AF .

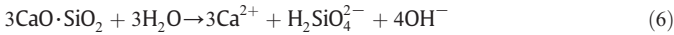
* Corresponding author. Tel.: +49 911 5880 1247; fax: +49 911 5880 5177.

E-mail addresses: tina.oertel@isc.fraunhofer.de (T. Oertel), uta.helbig@th-nuernberg.de (U. Helbig).

phases, $C_3S_2H_4$, $C_xS_uH_{w+x}$). This chemical reaction is approximately represented by Eq. (5) [10,12].



Thereby, alite ($C_3S = 3CaO \cdot SiO_2$) dissolves congruently (Eq. (6)) in the first seconds after mixing with water to ionic species [7].



Besides alite, the aluminate phase determines early processes. It reacts with calcium sulfate¹ (CSH_2) to ettringite¹ ($C_6AS_3H_{32}$, Eq. (7)) [9,10] which is formed to a certain amount quickly after the addition of water [13–15].



The effects of silica in cementitious systems were most often studied for so-called ordinary concretes (OC), i.e. for concretes with compressive strengths lower than approx. 60 N/mm² and w/c ratios higher than 0.35 by mass [16–21]. The beneficial contribution of silica in those concretes is twofold. On the one hand, C–S–H phases are formed in the pozzolanic reaction with portlandite (Eq. (8)) which results from the hydration of alite (Eq. (5)).



On the other hand, silica particles fill voids between particles of cement and other components because they are significantly smaller (so-called filler effect) [8]. The prerequisite for an optimal effect is the dispersion to primary particles [22]. The filler effect supports the formation of a denser microstructure because the gaps between the particles are minimized which have to be bridged by hydration products [23]. Furthermore, C–S–H phases from alite hydration nucleate on the silica surface [18,24]. This process is also attributed to the filler effect but is more precisely called the seeding effect.

It is commonly observed and accepted that the addition of silica accelerates the cement hydration [16–20,25–28], but the exact mechanism is not yet known and different models are proposed. The acceleration is generally attributed to the seeding effect because the hydration proceeds faster in the presence of nucleation sites for C–S–H phases [29]. Some others conclude that silica cannot dissolve because the concentration of silicate ions would increase and subsequently suppress the hydration of alite [16]. On the contrary, other authors [17,25,26,30] postulate that silica dissolves rapidly in the pore solution of concrete (Eq. (4)) prior to the pozzolanic reaction (Eq. (8)). They propose that the pozzolanic reaction reduces the concentrations of Ca^{2+} and OH^- ions and therefore the dissolution of alite would be accelerated [17,25,26,30].

The discussion is further complicated because differing properties of different types of silica may affect the reaction mechanism. The specific surface area was identified as the most important factor [16,17,26,27,30]. Some authors further assume that the content of $\equiv Si-OH$ groups (so-called silanol groups) is also of crucial importance [16,25,31]. The silanol group density depends on the conditions during the synthesis of the silica. Although silanol groups form during the synthesis at high temperatures (e.g. the flame hydrolysis of $SiCl_4$), a considerable amount of those groups condenses to $\equiv Si-O-Si-$ bonds (so-called siloxane bonds) and aggregates of individual particles are formed when silanol groups of adjacent particles condense [5,32]. Otherwise, a considerably higher amount of silanol groups remains after the hydrolysis and condensation of alkoxy silanes at ambient temperatures (e.g. using the Stoeber process [33]) [34]. In detail, a certain amount of surface ethoxy groups ($\equiv Si-O-C_2H_5$) does not condense throughout the Stoeber process. They are subsequently replaced by silanol groups in an aqueous medium [34,35]. One might expect that the silanol group density has an influence on the silica reactivity because silanol groups adsorb ions, water and other polar molecules [36]. If a surface consists mostly of

siloxane bonds, it is considered to be hydrophobic because of the lower concentration of adsorption sites [36].

Two mechanisms were proposed so far to describe the acceleration of the cement hydration when the amount of silanol groups is increased. On the one hand, Björnström et al. [16] suggest that silicate ions from the dissolution of alite (Eq. (6)) preferentially react with those groups. On the other hand, Mostafa and Brown [31] and Qing et al. [25] assume that silanol groups react with portlandite to C–S–H phases (Eq. (8)). Besides [16,25,31], there are only a few studies which distinguished between different types of silica (e.g. silica from flame hydrolysis or silica prepared by the Stoeber process) and their particular influence on cement hydration.

The described observations were mostly made on OC, but it is of interest to investigate how well the results may be transferred to UHPC. In the literature described so far, only Qing et al. [25] and Korpa et al. [26,28] used w/c ratios less than 0.3 by mass which are suitable for UHPC. The major difference between both cementitious systems is that the clinker minerals fully hydrate in OC (approximately a w/c ratio of 0.38 by mass is necessary [8]), whereas the amount of water is insufficient for a complete hydration in UHPC. Subsequently, less portlandite is available in UHPC for the pozzolanic reaction of silica in comparison to OC.

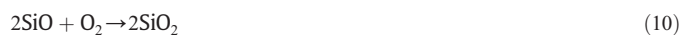
The aim of this study is to further investigate if certain silica properties have an influence on the early hydration of UHPC and if there is a prevalent reaction mechanism. Three different silica components are used: conventional silica fume, commercial pyrogenic silica and Stoeber particles synthesized by hydrolyzing alkoxy silanes. They are characterized for their specific surface areas, silanol group densities and solubilities in alkaline suspension. Based on the results, their hypothetical reactivities in a cementitious environment are evaluated. Further effects are investigated directly in the mixtures of cement, silica and water (so-called pastes) with very low w/c ratios (suitable for UHPC) by in-situ X-ray diffraction (XRD), cryo scanning electron microscopy (cryo SEM) and pore solution analysis.

2. Experimental procedures

2.1. Materials

The following types of silica were used: silica fume (Silicoll P®, undensified, Sika GmbH, Germany), pyrogenic silica (AEROSIL® OX 50, Evonik Industries, Germany) and Stoeber particles (prepared at Fraunhofer-Institute ISC).

Silica fume and pyrogenic silica are formed in high temperature processes: pyrogenic silica in a flame hydrolysis reaction of silicon tetrachloride at about 1800 °C (Eq. (9)) [37,38] and silica fume as a by-product of the industrial silicon production through oxidization of gaseous SiO at temperatures above 2000 °C (Eq. (10)) [8,38,39].



The suspension of Stoeber particles was synthesized by hydrolysis and condensation of tetraethyl orthosilicate ($Si(OC_2H_5)_4$) to amorphous silica particles in an ethanolic (C_2H_5OH) solution with ammonia (NH_3) catalysis (Eq. (11)) [33]. 6750.0 g of C_2H_5OH (CSC Jäckle Chemie GmbH, Germany), 337.5 g of aqueous NH_3 solution (25%, Sigma-Aldrich Chemie GmbH, Germany), 337.5 g of $Si(OC_2H_5)_4$ (98%, Sigma-Aldrich Chemie GmbH, Germany) and 281.3 g of de-ionized water were mixed in a round-bottom flask and rested for 24 h at room temperature. The mean particle size of 242 nm was adjusted by the relative concentrations of precursors ($Si(OC_2H_5)_4$, H_2O) and catalyst (NH_3). After synthesis, C_2H_5OH and NH_3 were stepwise exchanged with de-ionized water by rotary evaporation. This exchange is sufficient to replace surface ethoxy groups with silanol groups [35] and to remove adsorbed NH_4^+ ions from the silica surface (confirmed by infrared spectroscopy

Download English Version:

<https://daneshyari.com/en/article/7885600>

Download Persian Version:

<https://daneshyari.com/article/7885600>

[Daneshyari.com](https://daneshyari.com)